DIAZINE-BRIDGED COORDINATION POLYMERS OF COPPER AND NICKEL
SYNTHESIS AND THERMAL, SPECTRAL,
STRUCTURAL AND MAGNETIC PROPERTIES

by
TOM OTIENO
B.Sc. (Hons.), The University of Nairobi, 1986
M.Sc., The University of British Columbia, 1989

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

in
THE FACULTY OF GRADUATE STUDIES
(Department of Chemistry)

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
January 1993
© Tom Otieno, 1993
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

(Signature)

Department of Chemistry

The University of British Columbia
Vancouver, Canada

Date January 10/93

DE-6 (2/88)
ABSTRACT

A large number of coordination compounds of copper(I), copper(II) and nickel(II) have been prepared and characterized by thermal, spectroscopic and X-ray diffraction methods as well as by elemental analysis and magnetic susceptibility measurements. The neutral ligands used in the study were pyrazine (1,4-diazine), pyridazine (1,2-diazine), methylpyrazine, 2,5-dimethylpyrazine, pyridine and 4,4'-bipyridine. Anionic ligands of a range of coordinating abilities were employed. These include cyanate, nitrate, methanesulfonate, hexafluoroarsenate, hexafluorophosphate, chloride and thiocyanate anions. Polymeric and mononuclear compounds were isolated. The polymeric materials were found to be of three basic structural types: one-dimensional extended chains, two-dimensional square lattices or infinite three-dimensional lattices. These include the novel copper(I) complexes, [Cu2(2,5-me2pyz)3][PF6]2 and [Cu(2,5-me2pyz)2][PF6], which have graphite-related and diamond-related cationic lattices, respectively. Cu(mepy)2(NCO)2, a two-dimensional polymer, represents the first compound containing methylpyrazine to be structurally characterized by single crystal X-ray diffraction.

Magneto-structural correlations were made for all the compounds. Whenever possible the magnetic susceptibility data of the complexes were analyzed by theoretical models. The trimeric compound, [Cu(pdz)2(NO3)2]3, was found to exhibit the largest antiferromagnetic exchange coupling, with a J value of -139 cm⁻¹. The copper ions in another pyridazine complex, Cu(pdz)(NCO)2, were also found to be strongly coupled antiferromagnetically, with a J value of -44 cm⁻¹. Five nickel compounds, Ni(py)2(NCS)2, Ni(py)Cl2, Ni(pyz)Cl2, Ni(pyz)(NCO)2 and Ni(pyz)(NCS)2, exhibited metamagnetic behaviour. All the other copper(II) and nickel(II) complexes studied were found to be magnetically dilute or to involve only weakly antiferromagnetically coupled metal centres.
TABLE OF CONTENTS

ABSTRACT ........................................................................................................ ii
TABLE OF CONTENTS .................................................................................... iii
LIST OF TABLES ............................................................................................... x
LIST OF FIGURES ............................................................................................ xiii
LIST OF ABBREVIATIONS AND SYMBOLS ................................................. xvii
ACKNOWLEDGEMENTS ................................................................................. xxii
DEDICATION .................................................................................................... xxiii

CHAPTER 1 INTRODUCTION ........................................................................... 1
1.1 Background ................................................................................................. 1
  1.1.1 General .................................................................................................. 1
  1.1.2 Pyrazine ................................................................................................ 2
  1.1.3 Methylpyrazine ..................................................................................... 8
  1.1.4 Pyridazine ............................................................................................. 10
1.2 Objective and scope of the thesis ............................................................... 13
1.3 Organization of the thesis .......................................................................... 16
1.4 Theoretical aspects of physical methods of characterization .................... 16
  1.4.1 Elemental analysis .............................................................................. 18
  1.4.2 Differential scanning calorimetry ...................................................... 18
  1.4.3 Infrared spectroscopy .......................................................................... 19
  1.4.4 Electronic spectroscopy ..................................................................... 20
  1.4.5 Electron spin resonance spectroscopy ............................................. 20
  1.4.6 Powder X-ray diffraction ................................................................. 23
  1.4.7 Single crystal X-ray diffraction ......................................................... 25
  1.4.8 Magnetic susceptibility measurements ......................................... 26
CHAPTER 2 RESULTS AND DISCUSSION: COPPER(II) COMPLEXES

2.1 Complexes of copper(II) cyanate

2.1.1 Introduction

2.1.2 The crystal structure of Cu(mepyz)$_2$(NCO)$_2$

2.1.3 Thermal properties

2.1.4 Infrared spectra

2.1.5 Powder X-ray diffraction patterns

2.1.6 Electronic spectra

2.1.7 Electron spin resonance spectra

2.1.8 Magnetic properties

2.2 Complexes of copper(II) nitrate

2.2.1 Introduction

2.2.2 Synthesis

2.2.3 The crystal structure of [Cu(pdz)$_4$(NO$_3$)]$[NO_3]$

2.2.4 The crystal structure of Cu(pdz)$_3$(NO$_3$)$_2$

2.2.5 The crystal structure of [Cu(pdz)$_2$(NO$_3$)$_3$]

2.2.6 Infrared spectra

2.2.7 Electronic spectra

2.2.8 Electron spin resonance spectra

2.2.9 Magnetic properties

2.2.10 Powder X-ray diffraction patterns

2.3 Complexes of copper(II) sulfonates

2.3.1 Introduction

2.3.2 Infrared and electronic spectra

2.3.3 Electron spin resonance spectra

2.3.4 Magnetic properties
2.4 Complexes of copper(II) hexafluorophosphate and hexafluoroarsenate

2.4.1 Introduction ................................................................. 120
2.4.2 Thermal properties ......................................................... 122
2.4.3 Infrared spectra ............................................................... 124
2.4.4 Electronic spectra ............................................................. 131
2.4.5 Electron spin resonance spectra ......................................... 132
2.4.6 Magnetic properties .......................................................... 135

2.5 Summary and conclusions ..................................................... 136

CHAPTER 3 RESULTS AND DISCUSSION: NICKEL(II) COMPLEXES

3.1 Complexes of nickel(II) cyanate ........................................... 139
3.1.1 Introduction ................................................................. 139
3.1.2 Thermal properties .......................................................... 139
3.1.3 Infrared spectra ............................................................. 142
3.1.4 Electronic spectra ........................................................... 147
3.1.5 Magnetic properties ........................................................ 151

3.2 Complexes of nickel(II) chloride .......................................... 162
3.2.1 Introduction ................................................................. 162
3.2.2 Thermal properties .......................................................... 163
3.2.3 Infrared spectra ............................................................. 166
3.2.4 Electronic spectra ........................................................... 169
3.2.5 Magnetic properties ........................................................ 174

3.3 Complexes of nickel(II) thiocyanate .................................... 183
3.3.1 Introduction ................................................................. 183
3.3.2 Thermal properties .......................................................... 184
3.3.3 Infrared spectra ............................................................. 188
3.3.4 Powder X-ray diffraction patterns ...................................... 196
3.3.5 Electronic spectra ......................................................... 201
3.3.5 Magnetic properties .................................................. 205
3.4 Summary and conclusions ............................................. 213

CHAPTER 4  RESULTS AND DISCUSSION: COPPER(I) COMPLEXES ...... 215
4.1 Complexes of copper(I) trifluoromethanesulfonate ................. 215
   4.1.1 Introduction ...................................................... 215
   4.1.2 The crystal structure of Cu(2,5-me2pyz)2(CF3SO3) ........... 216
   4.1.3 Thermal properties ............................................. 223
   4.1.4 Infrared spectra ............................................... 225
   4.1.5 Electronic spectra ............................................. 228
   4.1.6 Magnetic properties .......................................... 229
4.2 Complexes of copper(I) hexafluorophosphate ........................ 230
   5.2.2 Synthesis ........................................................ 231
   5.2.3 The crystal structure of [Cu2(2,5-me2pyz)3][PF6]2 .......... 232
   5.2.4 The crystal structure of Cu(2,5-me2pyz)2[PF6] .............. 237
   5.2.5 The infrared spectrum of [Cu2(2,5-me2pyz)3][PF6]2 ......... 242
5.3 Summary and conclusions ............................................. 243

CHAPTER 5  EXPERIMENTAL ...................................................... 245
5.1 Introduction ............................................................ 245
5.2 Synthetic methods .................................................... 246
   5.2.1 Complexes of copper(II)- and nickel(II)- cyanates ........... 246
      5.2.1.1 Bis(pyridine)copper(II) cyanate, Cu(py)2(NCO)2 .......... 247
      5.2.1.2 Poly-dicyanato-N-bis(μ-methylpyrazine)copper(II),
              Cu(mepyz)2(NCO)2 ........................................ 248
      5.2.1.3 Mono(methylpyrazine)copper(II) cyanate, Cu(mepyz)(NCO)2 249
      5.2.1.4 Mono(pyrazine)copper(II) cyanate, Cu(pyz)(NCO)2 ... 249
5.2.1.5 Mono(pyridazine)copper(II) cyanate, Cu(pdz)(NCO)₂ ............ 250
5.2.1.6 Tetrakis(pyridine)nickel(II) cyanate, Ni(py)₄(NCO)₂ .................. 250
5.2.1.7 Bis(pyridazine)nickel(II) cyanate, Ni(pdz)₂(NCO)₂ .................... 251
5.2.1.8 Bis(pyrazine)nickel(II) cyanate hemihydrate,
   Ni(pyz)₂(NCO)₂·½H₂O ..................................................... 251
5.2.1.9 Mono(pyrazine)nickel(II) cyanate, Ni(pyz)(NCO)₂ .................... 251
5.2.1.10 Attempted syntheses .................................................. 252

5.2.2 Complexes of copper(II) nitrate ........................................... 253
5.2.2.1 Tetrakis(pyridazine)copper(II) nitrate, Cu(pdz)₄(NO₃)₂ .......... 254
5.2.2.2 Nitrato(tetrakis(pyridazine)copper(II) nitrate,
   [Cu(pdz)₄(NO₃)] [NO₃] ..................................................... 254
5.2.2.3 Nitrato(nitrato-O,O')tris(pyridazine)copper(II),
   Cu(pdz)₃(NO₃)₂ .................................................................. 255
5.2.2.4 Bis[μ-nitrato-O-dinitratobis(a-μ-pyridazine)pyridazinecopper(II)]-
   copper(II), [Cu(pdz)₂(NO₃)₂]₃ ............................................. 256

5.2.3 Complexes of copper(II) sulfonates ....................................... 257
5.2.3.1 Tetrakis(pyridazine)copper(II) methanesulfonate,
   Cu(pdz)₄(CH₃SO₃)₂ .......................................................... 257
5.2.3.2 Attempted syntheses ..................................................... 258

5.2.4 Complexes of copper(II) hexafluoroarsenate, copper(II)
   hexafluorophosphate and copper(I) hexafluorophosphate ............ 259
5.2.4.1 Tetrakis(pyrazine)copper(II) hexafluoroarsenate,
   Cu(pyz)₄(AsF₆)₂ ................................................................ 260
5.2.4.2 Tetrakis(methylpyrazine)copper(II) hexafluoroarsenate,
   Cu(mepy)₄(AsF₆)₂ ................................................................ 261
5.2.4.3 Tetrakis(4,4'-bipyridine)copper(II) hexafluoroarsenate,
   Cu(4,4'-bipy)₄(AsF₆)₂ ....................................................... 261
5.2.4.4 Tetrakis(pyrazine)copper(II) hexafluorophosphate,
Cu(pyz)$_4$(PF$_6$)$_2$ ................................................................. 261
5.2.4.5 Tetrakis(methylpyrazine)copper(II) hexafluorophosphate,
Cu(mepyz)$_4$(PF$_6$)$_2$ ................................................................. 261
5.2.4.6 Poly-bis(μ-2,5-dimethylpyrazine)copper(I) hexafluorophosphate,
[Cu(2,5-me$_2$pyz)$_2$][PF$_6$] and poly-tris(μ-2,5-dimethylpyrazine)-
dicopper(I) hexafluorophosphate, [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ .... 262
5.2.4.7 Attempted syntheses .......................................................... 263
5.2.5 Complexes of nickel(II) chloride ........................................... 265
5.2.5.1 Tetrakis(pyridine)nickel(II) chloride, Ni(py)$_4$Cl$_2$ .............. 266
5.2.5.2 Mono(pyridine)nickel(II) chloride, Ni(py)Cl$_2$ ..................... 266
5.2.5.3 Bis(pyrazine)nickel(II) chloride, Ni(pyz)$_2$Cl$_2$ .................. 267
5.2.5.4 Mono(pyrazine)nickel(II) chloride, Ni(pyz)Cl$_2$ ................. 267
5.2.5.5 Attempted synthesis .......................................................... 268
5.2.6 Complexes of nickel(II) thiocyanate ..................................... 269
5.2.6.1 Tetrakis(pyridine)nickel(II) thiocyanate, Ni(py)$_4$(NCS)$_2$ ...... 270
5.2.6.2 Bis(pyridine)nickel(II) thiocyanate, Ni(py)$_2$(NCS)$_2$ .......... 270
5.2.6.3 Tris(pyridazine)nickel(II) thiocyanate, Ni(pdz)$_3$(NCS)$_2$ ...... 271
5.2.6.4 Bis(pyridazine)nickel(II) thiocyanate, Ni(pdz)$_2$(NCS)$_2$ ...... 271
5.2.6.5 Bis(pyrazine)nickel(II) thiocyanate, Ni(pyz)$_2$(NCS)$_2$ ........ 271
5.2.6.6 Mono(pyrazine)nickel(II) thiocyanate, Ni(pyz)(NCS)$_2$ ........ 272
5.2.7 Copper(I) trifluoromethanesulfonate and its complexes ............ 272
5.2.7.1 Copper(I) trifluoromethanesulfonate, Cu(CF$_3$SO$_3$) .......... 273
5.2.7.2 Poly-(trifluoromethanesulfonato-Ο)μ-pyrazine(pyrazine)copper(I),
Cu(pyz)$_2$(CF$_3$SO$_3$) .............................................................. 274
5.2.7.3 Mono(pyrazine)copper(I) trifluoromethanesulfonate,
Cu(pyz)(CF$_3$SO$_3$) ................................................................. 274
5.2.7.4 Poly-(trifluoromethanesulfonato-\(O\))\(\mu\)-2,5-dimethylpyrazine-
(2,5-dimethylpyrazine)copper(I), Cu(2,5-me\(_2\)pyz)\(_2\)(CF\(_3\)SO\(_3\))... 275

5.2.7.5 Mono(2,5-dimethylpyrazine)copper(I) trifluoromethanesulfonate,
Cu(2,5-me\(_2\)pyz)(CF\(_3\)SO\(_3\)) .................................................. 275

5.2.7.6 Attempted syntheses .................................................. 276

5.3. Physical experimental methods ........................................... 277

5.3.1 Elemental analysis ...................................................... 277

5.3.2 Thermal analysis ....................................................... 277

5.3.3 Infrared spectroscopy .................................................. 278

5.3.4 Electronic spectroscopy ................................................ 278

5.3.5 Electron spin resonance spectroscopy ............................... 279

5.3.6 Powder X-ray diffraction ............................................. 280

5.3.7 Single crystal X-ray diffraction ..................................... 280

5.3.8 Magnetic susceptibility measurements ............................... 280

CHAPTER 6 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK ... 283

6.1 Conclusions ................................................................. 283

6.2 Suggestions for further work ............................................. 286

REFERENCES ........................................................................... 289

APPENDIXES

I  Single crystal X-ray diffraction data ..................................... 303

II  Infrared spectral data ....................................................... 336

III Powder X-ray diffraction data .......................................... 347

IV  Magnetic data for copper(II) complexes ............................. 353

V  Magnetic data for nickel(II) complexes ............................... 358
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Crystal data for Cu(mepy)₂(NCO)₂. .......................................................... 39</td>
</tr>
<tr>
<td>2-2</td>
<td>Selected bonding parameters for Cu(mepy)₂(NCO)₂ .............................................. 40</td>
</tr>
<tr>
<td>2-3</td>
<td>Cyanate ion band energies and assignments for copper(II) complexes .............. 46</td>
</tr>
<tr>
<td>2-4</td>
<td>Most coordination sensitive infrared absorption bands of methylpyrazine ......... 50</td>
</tr>
<tr>
<td>2-5</td>
<td>Electronic spectral data for compounds of copper(II) cyanate ...................... 54</td>
</tr>
<tr>
<td>2-6</td>
<td>Esr spectral data for compounds of copper(II) cyanate .................................. 57</td>
</tr>
<tr>
<td>2-7</td>
<td>Magnetic parameters for compounds of copper(II) cyanate ........................... 66</td>
</tr>
<tr>
<td>2-8</td>
<td>Crystal data, nitrate group dimensions and copper-ligand bond lengths for [Cu(pdz)₄(NO₃)][NO₃] ......................................................... 75</td>
</tr>
<tr>
<td>2-9</td>
<td>Internal bonding parameters for pyridazine. ................................................. 80</td>
</tr>
<tr>
<td>2-10</td>
<td>Crystal data for Cu(pdz)₃(NO₃)₂. ................................................................. 82</td>
</tr>
<tr>
<td>2-11</td>
<td>Selected bond lengths (Å) and bond angles (°) for Cu(pdz)₃(NO₃)₂ .................... 83</td>
</tr>
<tr>
<td>2-12</td>
<td>Crystal data for [Cu(pdz)₂(NO₃)₂]₃. ............................................................. 87</td>
</tr>
<tr>
<td>2-13</td>
<td>Internal bonding parameters for the nitrate ions in [Cu(pdz)₂(NO₃)₂]₃ .............. 87</td>
</tr>
<tr>
<td>2-14</td>
<td>Some bonding parameters for [Cu(pdz)₂(NO₃)₂]₃ .............................................. 88</td>
</tr>
<tr>
<td>2-15</td>
<td>Nitrate ion band energies and assignments for Cu(pdz)₄(NO₃)₂ complexes .......... 97</td>
</tr>
<tr>
<td>2-16</td>
<td>Electronic spectral data for compounds of copper(II) nitrate ..................... 100</td>
</tr>
<tr>
<td>2-17</td>
<td>Esr spectral data for compounds of copper(II) nitrate ................................. 102</td>
</tr>
<tr>
<td>2-18</td>
<td>Magnetic parameters for [Cu(pdz)₂(NO₃)₂]₃ .................................................. 106</td>
</tr>
<tr>
<td>2-19</td>
<td>Esr spectral data for compounds of copper(II) sulfonates ............................ 119</td>
</tr>
<tr>
<td>2-20</td>
<td>Band energies and assignments for the hexafluoroarsenate and hexafluorophosphate and hexafluoroarsenate anions ................................................................. 126</td>
</tr>
<tr>
<td>2-21</td>
<td>Electronic spectral data for compounds of copper(II) hexafluoroarsenate and hexafluorophosphate ................................................................. 131</td>
</tr>
</tbody>
</table>
3-1 Thermal parameters for complexes of nickel(II) cyanate ...................... 140
3-2 Cyanate ion band energies and assignments for nickel(II) complexes ........ 145
3-3 Electronic spectral band energies and assignments for complexes of nickel(II)
cyanate, O_h symmetry ...................................................... 148
3-4 Ligand field parameters for complexes of nickel(II) cyanate, O_h symmetry .. 148
3-5 Magnetic parameters for complexes of nickel(II) cyanate ....................... 154
3-6 Thermal parameters for complexes of nickel(II) chloride ....................... 164
3-7 Electronic spectral band energies and assignments for complexes of
nickel(II) chloride, O_h symmetry ........................................... 170
3-8 Electronic spectral band energies and assignments, and ligand field parameters
for nickel(II) complexes, D_{4h} symmetry ................................ 172
3-9 Magnetic parameters for complexes of nickel(II) chloride ....................... 175
3-10 Thermal parameters for complexes of nickel(II) thiocyanate ................... 186
3-11 Thiocyanate ion band energies and assignments for nickel(II) complexes .... 192
3-12 Selected powder X-ray diffraction data for some M(py)_2(NCS)_2 complexes .. 198
3-13 Electronic spectral band energies and assignments for complexes of nickel(II)
thiocyanate, O_h symmetry ................................................... 203
3-14 Ligand field parameters for complexes of nickel(II) thiocyanate,
O_h symmetry ................................................................. 204
3-15 Electronic spectral band energies and assignments for Ni(py)_2(NCS)_2,
D_{4h} symmetry ................................................................. 204
3-16 Magnetic parameters for complexes of nickel(II) thiocyanate ................ 207
3-17 Selected magnetic properties of metamagnetic nickel(II) complexes .......... 214
4-1 Crystal data for Cu(2,5-me_2pyz)_2(CF_3SO_3) ................................... 219
4-2 Selected bonding parameters for Cu(2,5-me_2pyz)_2(CF_3SO_3) and
Cu(pyz)_2(CF_3SO_3) ............................................................. 219
4-3 Internal bonding parameters for 2,5-dimethylpyrazine, L, in CuL(CF₃SO₃) and NiLBr₂. ................................................................. 221

4-4 Magnetic susceptibility data for Cu(2,5-me₂pyz)₂(CF₃SO₃) .......................... 230

4-5 Crystal data for [Cu₂(2,5-me₂pyz)₃][PF₆]₂. .................................................. 235

4-6 Crystal data and selected bonding parameters for [Cu(2,5-me₂pyz)₂][PF₆] … 242

6-1 Summary of structural and magnetic properties of the compounds investigated in this work ......................................................... 285
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Structures of neutral ligands used in this study</td>
<td>15</td>
</tr>
<tr>
<td>1-2</td>
<td>Diffraction of X-rays by two successive planes</td>
<td>24</td>
</tr>
<tr>
<td>1-3</td>
<td>Plots of magnetic susceptibility as a function of temperature for different types of magnetic materials</td>
<td>31</td>
</tr>
<tr>
<td>1-4</td>
<td>Plots of magnetic moment as a function of temperature for different types of magnetic materials</td>
<td>31</td>
</tr>
<tr>
<td>2-1</td>
<td>Atom numbering scheme for Cu(mepyz)$_2$(NCO)$_2$</td>
<td>37</td>
</tr>
<tr>
<td>2-2</td>
<td>Stereoviews of (a) the geometry about the copper atoms and (b) the extended two-dimensional polymeric structure of Cu(mepyz)$_2$(NCO)$_2$</td>
<td>38</td>
</tr>
<tr>
<td>2-3</td>
<td>DSC curves for (a) Cu(mepyz)$_2$(NCO)$_2$ and (b) Cu(mepyz)(NCO)$_2$</td>
<td>43</td>
</tr>
<tr>
<td>2-4</td>
<td>Proposed structures for Cu(pyz)(NCO)$_2$ (R = H) and Cu(mepyz)(NCO)$_2$ (R = CH$_3$)</td>
<td>51</td>
</tr>
<tr>
<td>2-5</td>
<td>Proposed structure for Cu(pdz)(NCO)$_2$</td>
<td>51</td>
</tr>
<tr>
<td>2-6</td>
<td>Powder X-ray diffraction patterns for ML(NCO)$_2$ complexes</td>
<td>53</td>
</tr>
<tr>
<td>2-7</td>
<td>Electronic spectra of copper(II) cyanate complexes</td>
<td>55</td>
</tr>
<tr>
<td>2-8</td>
<td>Esr spectra of copper(II) cyanate complexes</td>
<td>59</td>
</tr>
<tr>
<td>2-9</td>
<td>Magnetic susceptibility versus temperature plots for Cu(pyz)(NCO)$_2$</td>
<td>64</td>
</tr>
<tr>
<td>2-10</td>
<td>Magnetic susceptibility versus temperature plots for Cu(mepyz)(NCO)$_2$</td>
<td>65</td>
</tr>
<tr>
<td>2-11</td>
<td>Magnetic moment versus temperature plots for Cu(py)$_2$(NCO)$_2$ and Cu(pdz)(NCO)$_2$</td>
<td>69</td>
</tr>
<tr>
<td>2-12</td>
<td>Magnetic susceptibility versus temperature plots for Cu(pdz)(NCO)$_2$</td>
<td>70</td>
</tr>
<tr>
<td>2-13</td>
<td>Atom labelling scheme for [Cu(pdz)$_4$(NO$_3$)]$_2$[NO$_3$]</td>
<td>76</td>
</tr>
<tr>
<td>2-14</td>
<td>Stereoviews of (a) the geometry about copper and (b) the unit cell packing diagram in Cu(pdz)$_4$(NO$_3$)[NO$_3$]</td>
<td>77</td>
</tr>
<tr>
<td>Page</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>2-15</td>
<td>Atom labelling scheme for Cu(pdz)$_3$(NO$_3$)$_2$</td>
<td></td>
</tr>
<tr>
<td>2-16</td>
<td>Stereoview of the stereochemistry of copper in Cu(pdz)$_3$(NO$_3$)$_2$</td>
<td></td>
</tr>
<tr>
<td>2-17</td>
<td>Atom labelling scheme for [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$</td>
<td></td>
</tr>
<tr>
<td>2-18</td>
<td>Stereoviews of (a) the molecular structure and (b) the crystal packing diagram of [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$</td>
<td></td>
</tr>
<tr>
<td>2-19</td>
<td>Infrared spectra of pyridazine complexes of copper(II) nitrate</td>
<td></td>
</tr>
<tr>
<td>2-20</td>
<td>Esr spectra of pyridazine complexes of copper(II) nitrate</td>
<td></td>
</tr>
<tr>
<td>2-21</td>
<td>Plots of reciprocal susceptibility versus temperature for [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$</td>
<td></td>
</tr>
<tr>
<td>2-22</td>
<td>Powder X-ray diffraction patterns for (a) Cu(pdz)$_3$(NO$_3$)$_2$, (b) [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$ and (c) Cu(pdz)$_4$(NO$_3$)$_2$</td>
<td></td>
</tr>
<tr>
<td>2-23</td>
<td>Esr spectra of (a) Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$, (b) Cu(pyz)(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$ and (c) Cu(pyz)(CH$_3$SO$_3$)$_2$</td>
<td></td>
</tr>
<tr>
<td>2-24</td>
<td>DSC curves for (a) Cu(pyz)$_4$(AsF$_6$)$_2$, (b) Cu(mepy)$_4$(AsF$_6$)$_2$ and (c) Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$</td>
<td></td>
</tr>
<tr>
<td>2-25</td>
<td>Infrared spectrum of Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$</td>
<td></td>
</tr>
<tr>
<td>2-26</td>
<td>Infrared spectra of the isomers of Cu(pyz)$_4$(PF$_6$)$_2$</td>
<td></td>
</tr>
<tr>
<td>2-27</td>
<td>Esr spectrum of Cu(pyz)$_4$(AsF$_6$)$_2$</td>
<td></td>
</tr>
<tr>
<td>2-28</td>
<td>Esr spectra of (a) Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$ and (b) Cu(pyz)$_4$(PF$_6$)$_2$</td>
<td></td>
</tr>
<tr>
<td>3-1</td>
<td>DSC curve for Ni(py)$_4$(NCO)$_2$</td>
<td></td>
</tr>
<tr>
<td>3-2</td>
<td>Infrared spectra of (a) Ni(pyz)(NCO)$_2$ and (b) Ni(pyz)$_2$(NCO)$_2$·1/2H$_2$O</td>
<td></td>
</tr>
<tr>
<td>3-3</td>
<td>Proposed structures for Ni(pyz)X$_2$ complexes</td>
<td></td>
</tr>
<tr>
<td>3-4</td>
<td>Proposed structures for Ni(pyz)$_2$X$_2$ complexes</td>
<td></td>
</tr>
<tr>
<td>3-5</td>
<td>Proposed structure for Ni(pdz)$_2$(NCO)$_2$</td>
<td></td>
</tr>
<tr>
<td>3-6</td>
<td>Effects of octahedral and tetragonally elongated ligand fields on the triplet terms of the nickel(II) ion</td>
<td></td>
</tr>
<tr>
<td>3-7</td>
<td>Electronic spectrum of Ni(py)$_4$(NCO)$_2$</td>
<td></td>
</tr>
</tbody>
</table>
3-8 Magnetic susceptibility versus temperature plots for
Ni(pyz)2(NCO)2.1/2H2O ................................................................. 155
3-9 Magnetic susceptibility versus temperature plots for Ni(pdz)2(NCO)2 ........ 156
3-10 Magnetic susceptibility versus temperature plot for Ni(pyz)(NCO)2 .......... 160
3-11 Magnetic moment versus temperature plots for Ni(py)4(NCO)2 and
Ni(pyz)(NCO)2 ................................................................................ 160
3-12 Selected magnetization isotherms for Ni(pyz)(NCO)2 ......................... 161
3-13 DSC curves for (a) Ni(py)4Cl2 and (b) Ni(py)Cl2 ............................ 165
3-14 Proposed structure for Ni(py)Cl2 .................................................. 168
3-15 Electronic spectrum of Ni(py)4Cl2 .................................................. 173
3-16 Magnetic moment versus temperature plots for Ni(py)Cl2, Ni(pyz)Cl2
and Ni(py)4Cl2 ................................................................................ 176
3-17 Magnetic susceptibility versus temperature plot for Ni(py)4Cl2 .......... 176
3-18 Magnetic susceptibility versus temperature plots for Ni(pyz)2Cl2 .......... 177
3-19 (a) Magnetic susceptibility versus temperature plot and
(b) selected magnetization isotherms for Ni(pyz)Cl2 ............................ 181
3-20 (a) Magnetic susceptibility versus temperature plots and
(b) selected magnetization isotherms for Ni(py)Cl2 ............................ 182
3-21 DSC curves for (a) Ni(pdz)3(NCS)2 and (b) Ni(pdz)2(NCS)2 ............ 187
3-22 Infrared spectrum of Ni(pdz)2(NCS)2 .............................................. 194
3-23 Proposed structure for Ni(py)2(NCS)2 ............................................. 194
3-24 Powder X-ray diffraction patterns for (a) Ni(py)2(NCS)2,
(b) Ni(pyz)(NCS)2 and (c) Ni(pyz)(NCO)2 ........................................... 199
3-25 Powder X-ray diffraction patterns for (a) Ni(pdz)2(NCS)2,
(b) Ni(pdz)3(NCS)2 and (c) [Cu(pdz)2(NO3)2]3 .................................... 200
3-26 Magnetic susceptibility versus temperature plot for Ni(pdz)3(NCS)2 .... 206
3-27 Magnetic susceptibility versus temperature plots for Ni(pyz)2(NCS)2 .... 209
3-28 (a) Magnetic susceptibility versus temperature plots and  
(b) selected magnetization isotherms for Ni(py)$_2$(NCS)$_2$ .......................... 210
3-29 Magnetic moment versus temperature plots for Ni(py)$_2$(NCS)$_2$,  
Ni(pyz)(NCS)$_2$ and Ni(py)$_4$(NCS)$_2$ ................................................. 211
3-30 (a) Magnetic susceptibility versus temperature plots and  
(b) selected magnetization isotherms for Ni(pyz)(NCS)$_2$......................... 212
4-1 Atom labelling scheme for Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) ...................... 217
4-2 Stereoscopic views of (a) the unit cell packing and (b) the coordination  
about copper in Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) ........................................ 218
4-3 Infrared spectra of (a) 2,5-me$_2$pyz, (b) Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) and  
(c) Cu(me$_2$pyz)(CF$_3$SO$_3$) .......................................................................... 227
4-4 Atom labelling scheme for [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ .................. 234
4-5 Stereoview of the geometry about copper in [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ ...... 235
4-6 Stereoscopic view of the unit cell packing diagram for  
[Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ ........................................................................ 236
4-7 Stereoview of a schematic representation of the graphite-like  
structure of [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ ...................................................... 236
4-8 Atom labelling scheme for [Cu(2,5-me$_2$pyz)$_2$][PF$_6$] ......................... 239
4-9 Stereoview of the geometry about the copper ions in  
[Cu(2,5-me$_2$pyz)$_2$][PF$_6$] ............................................................................. 240
4-10 Stereoview of the crystal packing diagram for [Cu(2,5-me$_2$pyz)$_2$][PF$_6$] ...... 240
4-11 Stereoview of a schematic representation of the diamond-like  
structure of [Cu(2,5-me$_2$pyz)$_2$][PF$_6$] ......................................................... 241
4-12 Stereoview of the alternate orientations of the PF$_6^-$ anions in  
[Cu(2,5-me$_2$pyz)$_2$][PF$_6$] ............................................................................. 241
**LIST OF ABBREVIATIONS AND SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>angle</td>
</tr>
<tr>
<td>A</td>
<td>electron-nuclear hyperfine coupling constant</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>AF</td>
<td>antiferromagnetic</td>
</tr>
<tr>
<td>Anal.</td>
<td>analysis</td>
</tr>
<tr>
<td>arb.</td>
<td>arbitrary</td>
</tr>
<tr>
<td>axial (esr spectrum)</td>
<td>spectrum indicative of axial symmetry</td>
</tr>
<tr>
<td>B</td>
<td>inter-electronic repulsion (Racah) parameter</td>
</tr>
<tr>
<td>B</td>
<td>magnetic induction</td>
</tr>
<tr>
<td>β</td>
<td>angle, nephelauxetic parameter or electron Bohr magneton</td>
</tr>
<tr>
<td>βN</td>
<td>nuclear Bohr magneton</td>
</tr>
<tr>
<td>4,4'-bipy</td>
<td>4,4'-bipyridine</td>
</tr>
<tr>
<td>B.M.</td>
<td>electron Bohr magneton</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>calcd.</td>
<td>calculated</td>
</tr>
<tr>
<td>cm(^{-1})</td>
<td>wavenumber(s)</td>
</tr>
<tr>
<td>d</td>
<td>crystal interplanar spacing</td>
</tr>
<tr>
<td>D</td>
<td>dimensional or axial zero-field splitting parameter</td>
</tr>
<tr>
<td>dabco</td>
<td>1,4-diazabicyclo[2.2.2]octane</td>
</tr>
<tr>
<td>deg or °</td>
<td>degree(s)</td>
</tr>
<tr>
<td>°C</td>
<td>degree(s) Celsius</td>
</tr>
<tr>
<td>δ</td>
<td>bendig vibrational mode</td>
</tr>
<tr>
<td>ΔH</td>
<td>change in enthalpy</td>
</tr>
<tr>
<td>DIL</td>
<td>magnetically dilute</td>
</tr>
<tr>
<td>DM</td>
<td>diamagnetic</td>
</tr>
</tbody>
</table>
2,2-dmp  2,2-dimethoxypropane
DPPH  2,2'-diphenyl-1-picrylhydrazyl
Dq  octahedral ligand field parameter
Dqxy  equatorial plane ligand field parameter
Ds and Dt  tetragonal parameters
DSC  differential scanning calorimetry
eqn(s).  equation(s)
esr  electron spin resonance
η  hapticity
EtOH  ethanol
F  fit quality factor
Fig(s).  figure(s)
γ  angle or nuclear magnetogyric ratio
g  gram(s) or acceleration due to gravity
g  Landé splitting factor
G  Gauss
GHz  gigaHertz
h  hour(s) or Planck's constant
H or H  magnetic field
He  metamagnetic transition field (critical field)
H  Hamiltonian
hfac  1,1,1,5,5,5-hexafluoropentane-2,4-dionate
I  total nuclear spin
isotropic (esr spectrum)  spectrum indicative of cubic symmetry
I.U.P.A.C.  International Union of Pure and Applied Chemistry
J  exchange coupling constant
k  Boltzmann's constant
### Conversion Factors and Units

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>kHz</td>
<td>kiloHertz</td>
</tr>
<tr>
<td>$\chi$</td>
<td>magnetic susceptibility</td>
</tr>
<tr>
<td>$\chi_g$</td>
<td>gram magnetic susceptibility</td>
</tr>
<tr>
<td>$\chi_m$</td>
<td>molar magnetic susceptibility</td>
</tr>
<tr>
<td>kJ</td>
<td>kilojoule(s)</td>
</tr>
<tr>
<td>M</td>
<td>magnetization</td>
</tr>
<tr>
<td>m</td>
<td>medium or mass</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>mepyiz</td>
<td>methylpyrazine</td>
</tr>
<tr>
<td>2,5-me$_2$pyz</td>
<td>2,5-dimethylpyrazine</td>
</tr>
<tr>
<td>mg</td>
<td>milligram(s)</td>
</tr>
<tr>
<td>min</td>
<td>minute(s)</td>
</tr>
<tr>
<td>mL</td>
<td>millilitre(s)</td>
</tr>
<tr>
<td>MM</td>
<td>exhibits metamagnetic behaviour</td>
</tr>
<tr>
<td>mmol</td>
<td>millimole(s)</td>
</tr>
<tr>
<td>mol</td>
<td>mole(s)</td>
</tr>
<tr>
<td>$m_s$</td>
<td>spin quantum number</td>
</tr>
<tr>
<td>$\mu$</td>
<td>bridging</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>effective magnetic moment</td>
</tr>
<tr>
<td>MW</td>
<td>molecular weight</td>
</tr>
<tr>
<td>N</td>
<td>Avogadro's number</td>
</tr>
<tr>
<td>nm</td>
<td>nanometre(s)</td>
</tr>
<tr>
<td>NIR</td>
<td>near-infrared</td>
</tr>
<tr>
<td>$\nu$</td>
<td>electronic transition, stretching vibrational mode or frequency</td>
</tr>
<tr>
<td>obs.</td>
<td>observed</td>
</tr>
</tbody>
</table>
Oe  Oersted(s)
Ω  ohm(s)
%P  percent paramagnetic impurity
π  3.142, bonding orbital or bonding type
π*  antibonding orbital
pyz  pyrazine
pdz  pyridazine
py  pyridine
ref(s).  reference(s)
ρ  density
rhombic (esr spectrum)  spectrum indicative of rhombic symmetry
s  strong
S  total electron spin
sh  shoulder
σ  standard deviation or bonding type
sp  split
SQUID  superconducting quantum interference device
T  temperature
TGA  thermogravimetric analysis
θ  diffraction angle or Weiss constant
terpy  2,2':6',2''-terpyridine
TIP  temperature independent paramagnetism
triflate  trifluoromethanesulfonate
UV  ultraviolet
ν  very
Vis  visible
VSM  vibrating sample magnetometer
w  weak
xs  excess
ZFS  zero-field splitting
\approx  approximately
\parallel  parallel
\perp  perpendicular
>  greater than
>>  much greater than
<  less than
<<  much less than
ACKNOWLEDGEMENTS

I would like to express my sincerest thanks to my research supervisor, Dr. R.C. Thompson, for his guidance during the course of this work. I also wish to thank the members of my guidance committee, Drs. F. Aubke, G. Patey and A. Storr for their constructive remarks during the final preparation of this thesis.

Many thanks go to Dr. S.J. Rettig for the crystal structure determinations, Mr. P. Borda for his microanalytical services, and Drs. F.G. Herring and P.S. Phillips for their assistance in obtaining some of the esr spectra. My gratitude is also extended to the staff of the electronic, mechanical and glassblowing shops for their technical assistance. I would also like to thank Dr. C. Orvig for the use of his UV-Vis spectrophotometer, Drs. W. Hardy and J. Carolan of the Physics Department for the use of their SQUID magnetometer, and Dr. R. Parsons, also of the Physics Department, for the use of his powder X-ray diffractometer.

Finally, I wish to thank my colleagues, both present and past, Drs. J.-L. Du and M. Ehlert and Mr. S. Xia for their invaluable help in various aspects of this work.
DEDICATION

To my mother, Mrs. Hilda R.A. Odhuno
CHAPTER 1

INTRODUCTION

1.1 Background

1.1.1 General

There has been considerable research activity involving inorganic polymers in recent years (1-6). A major impetus for this activity has been the search for new advanced industrial materials. The research into these materials has been directed towards a wide range of properties such as thermal, electrical, photochemical, mechanical and biomedical. For any new product to be competitive, it should overcome the problems associated with those materials it seeks to replace while at the same time retaining their beneficial qualities. Thus complexes in which metal centres are bridged by organic ligands offer a promise of systems which combine the useful properties of metals (e.g. strength, electrical conductivity, high thermal stability) with those of organic polymers (e.g. lightness, flexibility, ease of fabrication). The metal centres may be bound to the bridging ligands through heteroatoms of the ligands (coordination polymers) or through metal-carbon bonds (organometallic polymers).

Purely academic interest has been an equally important driving force behind the increased research in the field of inorganic polymers in recent years. Such studies have been undertaken with the purpose of increasing our understanding of the factors that govern the chemical and physical properties of these materials, as well as the fundamental theories of such properties. The need for continued basic research in the field of inorganic polymers was perhaps best expressed by Ray (6), "... a better understanding of the principles underlying structure-property relationships in inorganic materials will not only result in a more effective utilization of materials we have
available at the present time, but will also lead to the discovery of new materials with improved properties. Because research of this nature necessarily takes a long time to be fruitful, we cannot afford to wait until the crisis point in the supply of organic materials arrives; this research must be intensified and extended now if the results are to be available in time."

Magnetochemistry- the measurement and analysis of the response of a material to the presence of a magnetic field- is an area where fundamental research activity has continued to grow. This is evidenced by the large number of articles that continue to be published on the subject, selected examples of which are references 7-28. A substantial amount of work in this area has been aimed toward an understanding of the structural and chemical features which govern the sign and magnitude of exchange coupling constants. Polymeric materials have also been prepared and probed in order to determine the factors which govern magnetic dimensionalities. In addition, magnetochemical studies have been undertaken in order to test the validity of existing theoretical models. Diazine-bridged coordination polymers are among those materials that have been widely investigated by magnetic susceptibility measurements. The three diazines, pyrazine, methylpyrazine and pyridazine (see Fig. 1-1), were the major potentially bridging neutral ligands used in the work described in this thesis and a review of the research that has been reported on metal complexes incorporating these ligands is presented below. Greater emphasis is laid on structural and magnetic studies as these are of greatest relevance to the work presented here.

1.1.2 Pyrazine

The pK values for the acid dissociation of the monoprotonated (pK₁) and diprotonated (pK₂) pyrazine are +0.65 and -5.78, respectively (29), indicating that pyrazine acts as a weak base towards the proton. Due to the particularly low basicity of the second nitrogen atom, pyrazine would be expected to utilize only one of its
nitrogen atoms in bonding to metal ions. However, in the early sixties, spectroscopic and magnetic studies on transition metal-pyrazine complexes indicated that both ring nitrogen atoms could be bonded to metal atoms to give polynuclear complexes (30-34). This has since been confirmed by many single crystal X-ray diffraction studies (35-52). Ironically, monodentate pyrazine coordination has been confirmed by X-ray crystallography in only five compounds (44, 53-56). The ability of pyrazine to accept electrons from metal ions into antibonding $\pi$-orbitals of one nitrogen atom, with the concomitant enhancement of the basicity of the second nitrogen atom, has been suggested as a probable explanation for the ligand's ability to coordinate through both its nitrogen atoms (30, 32, 57).

Pyrazine-bridged metal complexes that have been characterized by single crystal X-ray diffraction studies can be classified into several categories including dimers (35-39), chains (35, 40-44) and sheets (45-48). There are also cases where dinuclear metal species are bridged by pyrazine ligands to form tetranuclear (43) or polymeric chain (49-51) compounds. In the case of Cu(pyz)X$_2$ (X is Cl or Br), the copper atoms are bridged by pyrazine ligands in one dimension and halogen atoms in another, resulting in sheet structures (52). Details pertaining to the structures of individual complexes that are of relevance to the present work will be discussed in appropriate sections.

A significant part of the early work on transition metal complexes of pyrazine was concerned with structural diagnosis. Of particular interest was the mode of pyrazine ligand coordination. In this regard, Lever et al. (31, 33) observed that complexes of the type M(pyz)$_2$X$_2$ (M is Co or Ni and X is Cl, Br or I), but not those of the type M(pyz)X$_2$, exhibited an infrared absorption band around 980 cm$^{-1}$. They proposed that the presence of this band is characteristic of monodentate pyrazine coordination. Stidham and Chandler (58) extended this idea further, proposing that the intensity of the band could be used as a measure of polymer chain length. They suggested that the absence of a band in the 950-1000 cm$^{-1}$ region is indicative of
pyrazine-bridged polymers of long chain lengths, a weak band indicates a shorter chain length polymer and a stronger band indicates monodentate pyrazine coordination. They thus proposed short chain lengths for some pyrazine complexes of zinc, cadmium and mercury halides and long ones for others. However, contrary to expectations based on those structures, they observed that in general there was no correlation between chain length and solubility or thermal stability. Dorrity and Orrell (59) also concurred with Lever et al. on the use of the pyrazine band around 980 cm$^{-1}$ as a means of distinguishing between monodentate and bidentate pyrazine ligands. The former suggested additional criteria based on far-infrared spectral data. However, they based their conclusion on the erroneous belief (see next paragraph) that the ML$_2$X$_2$ complexes contained monodentate pyrazine ligands.

Working with the complexes Sn(pyz)$_2$X$_4$ and Sn(pyz)X$_4$ [X is Cl, Br or I], Goldstein et al. (60) demonstrated that the mode of pyrazine coordination could be unequivocally assigned from vibrational spectral data by the invocation of the mutual exclusion principle. They also undertook more detailed analyses of the mid-infrared and Raman as well as the far-infrared spectra of the M(pyz)$_2$X$_2$ complexes (45, 61, 62). From these studies they concluded that both the mid- and far-infrared criteria for determining the denticity of pyrazine proposed by Lever et al. (31, 33) and Dorrity and Orrell (59), respectively, were wrong. This conclusion has since been supported by single crystal diffraction studies on Co(pyz)$_2$Cl$_2$, Cu(pyz)$_2$(ClO$_4$)$_2$, Cu(pyz)$_2$(CH$_3$SO$_3$)$_2$ and Fe(pyz)$_2$(NCS)$_2$ (45-48). All of these complexes have sheet structures in which pyrazine ligands are bidentate bridging and the anions are monodentate terminal. This is the same structure Godstein et al. (61) proposed for M(pyz)$_2$X$_2$ (M is Co or Ni and X is Cl, Br or I). In contrast, Lever et al. (31, 33) proposed a structure in which the halogen atoms are bridging and the pyrazine ligands are terminal.
We recently pointed out that when Raman data are not available, the band that occurs at 417 cm\(^{-1}\) in the infrared spectrum of uncoordinated pyrazine \(63\) may be a useful indicator of the denticity of pyrazine \(44\). The band generally shifts to about 450 cm\(^{-1}\) in the case of monodentate coordination and to 470 cm\(^{-1}\) or higher for bidentate coordination. However, as noted in ref. \(44\), an exception to this criterion has been observed in \(\text{Cu(pyz)}_2\text{(CH}_3\text{SO}_3)_2\) \(47\). Hence, like most empirical criteria of this type, care must be taken in its application. It would appear that in the absence of single crystal X-ray data, a combination of Raman and infrared spectral data provides the most reliable means of elucidating the mode of pyrazine coordination.

Pyrazine-bridged coordination polymers are of interest to magnetochemists because of the potential for magnetic exchange interactions between metal ions being propagated via the bridging pyrazine system. Magnetic susceptibility measurements taken to liquid helium temperature revealed no substantial magnetic interaction through pyrazine in \(\text{Co(pyz)}_2\text{X}_2\) (\(X\) is Cl or Br), \(\text{Fe(pyz)}_2\text{X}_2\) (\(X\) is Cl, Br, I, ClO\(_4\) or CH\(_3\)SO\(_3\)), \(\text{Fe(pyz)}_2\text{(CF}_3\text{SO}_3)_2\cdot\text{CH}_3\text{OH}, \text{Fe(pyz)Cl}_2, \text{Fe(pyz)(p-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2.2\text{CH}_3\text{OH, M(pyz)(p-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2\) (\(M\) is Fe or Ni), or \(\text{Ni(pyz)}_3(\text{CH}_3\text{SO}_3)_2.2\text{CH}_3\text{OH\)} \(17, 64-66\). In addition, conclusive evidence of exchange coupling was not found in \(\text{Ni(pyz)}_2\text{X}_2\) (\(X\) is Cl, Br or I) on measurements made in the temperature range 330-90 K \(61\) and, in the case of \(\text{Ni(pyz)}_2\text{Cl}_2\), down to 4.4 K in the present work. Significant antiferromagnetic coupling was, however, detected in \(\text{Fe(pyz)(CF}_3\text{SO}_3)_2, \text{Ni(pyz)}_2(\text{NO}_3)_2, \text{Fe(pyz)}_2(\text{NCS})_2\) and \(\text{Fe(pyz)(NCO)}_2\), each of which exhibits a maximum in a plot of magnetic susceptibility versus temperature \(48, 65-67\).

In contrast to the cobalt(II), nickel(II) and iron(II) complexes, magnetic exchange has been found to be more common in pyrazine-bridged copper(II) polymers. \(\text{Cu(pyz)}_2(\text{ClO}_4)_2, \text{Cu(pyz)}_2(\text{CH}_3\text{SO}_3)_2, \text{Cu(pyz)(CH}_3\text{SO}_3)_2, \text{Cu(pyz)(p-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2, \text{Cu(pyz)}_3(\text{NO}_3)_2, \text{Cu(pyz)(CF}_3\text{SO}_3)_2, \text{Cu(pyz)(NO}_3)_2, \text{and [Cu(terpy)(pyz)]}[\text{ClO}_4]_2,\) where terpy is \(2,2':6',2''\)-terpyridine, all show maxima in their susceptibility versus
temperature plots (46, 47, 66, 68-73). This is conclusive evidence that the copper(II) ions in all of these complexes are coupled antiferromagnetically. With the exception of Fe(pyz)(NCO)$_2$, which exhibits a maximum at 38 K in its susceptibility versus temperature plot, the susceptibility maxima for all of the antiferromagnetically coupled complexes discussed above lie in the range 3-12 K.

The shortest separation between adjacent copper ions is 6.712(1) Å in Cu(pyz)(NO$_3$)$_2$ (41) and 6.9134(2) Å in Cu(pyz)$_2$(CH$_3$SO$_3$)$_2$ (47). Such long distances preclude direct magnetic exchange interactions between the metal ions. In order to investigate the mechanism of exchange in pyrazine-bridged copper(II) complexes, Richardson and Hatfield (15) investigated the series of complexes CuL(NO$_3$)$_2$, where L is pyrazine, chloropyrazine, methylpyrazine, 2,5- and 2,6-dimethylpyrazine, and phenazine. They showed that the variation of the antiferromagnetic coupling correlates neither with the $\sigma$-basicity nor with steric factors but with the energy of the $\pi \rightarrow \pi^*$ transition of the ligands. These results indicate the presence of an exchange mechanism involving the pyrazine $\pi$-system.

The unpaired electron of a copper(II) ion in a tetragonally elongated ligand environment is predominantly in the $d_{x^2-y^2}$ orbital (74). If, as remarked above, the exchange interaction involves the ligand $\pi$-system, then overlap between this orbital and the pyrazine $\pi$-system is essential for the propagation of magnetic exchange through pyrazine bridges. The most effective overlap occurs when there is a non-zero dihedral angle between the plane of the pyrazine and the xy copper plane. In Cu(pyz)(NO$_3$)$_2$ the pyrazine rings are canted at an angle of 48° out of the copper xy plane (41). In the two-dimensional sheet polymer Cu(pyz)$_2$(ClO$_4$)$_2$, the pyrazine rings are canted at an angle of 66.1° to the CuN$_4$ plane (46). One set of pyrazine rings in Cu(pyz)$_2$(CH$_3$SO$_3$)$_2$, the set believed to afford the primary route for magnetic exchange interactions in the complex, is canted out of the xy plane by 28.5° (47). All three complexes exhibit maxima in their susceptibility versus temperature curves, indicating
that the metal ions are antiferromagnetically coupled. In contrast, Cu(pyz)(hfac)$_2$
(where hfac is 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) shows no evidence of
magnetic exchange down to 1.8 K (16). This compound has a linear structure resulting
from pyrazine bridging in the axial (i.e. z axis) direction between the Cu(hfac)$_2$ units
(35). The absence of exchange interaction has been attributed to the fact that the plane
of the pyrazine bridge lies in the xz plane of the Cu(hfac)$_2$. In such an orientation,
there is no effective $\pi$-orbital overlap between the pyrazine $\pi$-system and the copper
d$_{x^2-y^2}$ orbital. We note that Coronado and Drillon (73) observed magnetic exchange in
[Cu(terpy)(pyz)]$[\text{ClO}_4]_2$ in which, they suggested, the pyrazine ligands are bridging in
axial positions. The structure of this compound has, however, not been confirmed by a
single crystal X-ray diffraction study.

Further evidence for the importance of a $\pi$ pathway in the propagation of
magnetic exchange has been provided by the magnetic properties of vanadyl complexes
of the type [VO(hfac)$_2$L]$_2$ (75). When L is pyrazine or methylpyrazine a maximum is
observed in the susceptibility versus temperature curve, but when L is dabco (dabco is
1,4-diazabicyclo[2.2.2]octane and affords only a $\sigma$-type pathway) there is no evidence
of magnetic exchange interactions. The absence of magnetic exchange in the latter
complex was attributed to the lack of a $\pi$-system in dabco.

Based on theoretical expectations that pyrazine and dabco bridges would be
effective in supporting antiferromagnetic interactions with a $\sigma$-type exchange pathway,
Hendrickson et al. (75) prepared the dinuclear copper(II) complexes
[Cu$_2$(tren)$_2$L](\text{ClO}_4)_4$ where tren is 2,2',2''-triaminotriethylamine and L is pyz or
dabco. These complexes have a trigonal bipyramidal geometry around the copper(II)
ions. The unpaired electrons are located in the d$_{z^2}$ orbitals which are directed at the
nitrogen lone-pair orbitals of pyrazine or dabco, leading to a $\sigma$-type interaction.
Antiferromagnetic exchange was observed in the pyrazine, but not the dabco, complex.
These results were interpreted by Hendrickson et al. (75) to indicate that the $\pi$-system
in the pyrazine ring is indirectly responsible for the observed exchange in the pyrazine complex.

1.1.3 Methylpyrazine

The pK values for the acid dissociation of the monoprotonated (pK₁) and diprotonated (pK₂) methylpyrazine are +1.45 and -5.25, respectively (29). Hence, like pyrazine, methylpyrazine is a weak base which would be expected to preferentially coordinate to metal ions in a monodentate fashion. Complexes in which the ligand is thought to be monodentate, as well as those in which it is thought to be bidentate, have been reported in the literature. However, in no case has the structure been unequivocally established by X-ray crystallography. Lever et al. (31, 33) proposed that the presence of a band of medium intensity near 1250 cm⁻¹ in the infrared spectra of metal methylpyrazine complexes indicates that the ligand is coordinated through only one of its nitrogen atoms. Conversely, the absence of this band indicates bidentate ligation. Ahuja et al. (76-80) used this empirical criterion in the characterization of complexes of methylpyrazine with HgX₂ (X is Cl, Br, CN or NCS), CdX₂ (X is Cl, Br, I, NCS, NO₃ or CH₃COO), ZnX₂ (X is Cl, I or NO₃), ZnSO₄, AgNO₃, UO₂X₂ (X is Cl or NO₃) and UO₂SO₄. They also used an additional criterion based on the intensity of the band near 1250 cm⁻¹. The absence of this band was taken as indicative of methylpyrazine-bridged polymers of long chain length. Bands of weak and medium intensities in this spectral region were taken to be indicative of methylpyrazine-bridged polymers of short chain length and monodentate methylpyrazine coordination, respectively. The basis for the criterion utilizing the intensity of the band around 1250 cm⁻¹ was a similar criterion proposed by Stidham and Chandler (58) for pyrazine (section 1.1.2). However, Goldstein et al. (45, 61) have demonstrated that the use of
the presence or absence of a band at 980 cm\(^{-1}\) in the spectra of metal pyrazine complexes, or the intensity of such a band, as a criterion for determining the denticity of pyrazine is unreliable. Because of the close structural similarity between pyrazine and methylpyrazine, the use of similar criteria based on the band observed around 1250 cm\(^{-1}\) to determine the denticity of methylpyrazine is also probably unreliable. Methylpyrazine, unlike the unsubstituted ligand, has no centre of symmetry and therefore the mutual exclusion of infrared and Raman bands cannot be used to infer its denticity. We therefore examined more closely the infrared spectra of some methylpyrazine-metal complexes for structural correlations (66). We noted that the free ligand bands at 410, 472 and 1021 cm\(^{-1}\) were the most coordination sensitive, invariably shifting to higher energies on coordination. The three bands were observed to shift by 16-22, 33-36 and 10-25 cm\(^{-1}\), respectively, for monodentate coordination. The corresponding shifts observed for bidentate coordination were 34-56, 52-59 and 37-43 cm\(^{-1}\). It was pointed out in reference 66 that there was a need to study a larger number of complexes in order to confirm the validity, or otherwise, of these correlations. In this regard, the need for structural determinations by X-ray crystallography was stressed. We report in Chapter 2 the first single crystal X-ray diffraction study on any compound containing methylpyrazine and, in the light of this, review the infrared structural correlations mentioned above.

Literature reports on low temperature magnetic susceptibility studies on methylpyrazine-bridged transition metal polymers are rare. Magnetic studies on Ni(mepyz)(NO\(_3\))\(_2\) in the temperature range 2.5-82 K, while suggesting that the nickel ions may be coupled antiferromagnetically, revealed no clear evidence of magnetic concentration (66). Cu(mepyz)Br\(_2\), Cu(mepyz)Cl\(_2\), Cu(mepyz)(CF\(_3\)SO\(_3\))\(_2\) and Cu(mepyz)(NO\(_3\))\(_2\) exhibit maxima in their susceptibility versus temperature plots at 28, 19, 7 and 5.5 K, respectively (15, 66, 81). The structures of these compounds are unknown. However, a linear chain structure in which copper(II) ions are bridged by
methylpyrazine and octahedral coordination around each copper ion is completed by two chelating nitrate groups has been proposed for Cu(mepyza)(NO₃)₂ (15). Such a structure has been confirmed for the pyrazine analogue, Cu(pyza)(NO₃)₂, by X-ray crystallography (41). For the other three complexes listed above, extended polymeric sheet structures in which metal ions are bridged by methylpyrazine in one dimension and by the anionic ligands in another have been proposed (66, 81). This kind of structure was recently observed in Cu(pyza)Cl₂ and Cu(pyza)Br₂ by single crystal X-ray diffraction methods (52). Richardson and Hatfield (15) and Hendrickson et al. (75) have demonstrated that the magnetic interactions in pyrazine- and substituted pyrazine-bridged metal complexes proceed via the π-system of the ligands. Hence methylpyrazine is considered to transmit much of the exchange interactions observed in Cu(mepyza)X₂ (X is Cl, Br or CF₃SO₃).

1.1.4 Pyridazine

Like pyrazine and its monomethyl-substituted derivative, pyridazine can bind to metal centres through either one or both of its nitrogen atoms. However, while the former are expected to form linear bridges, pyridazine bridges are expected to be bent. This difference is a consequence of the different relative positions of the donor nitrogen atoms in the ligands; para in pyrazine and ortho in pyridazine. The tendency of pyrazine and pyridazine to bridge metal centres differently is well demonstrated by the adducts they form with [(CH₃)₂ClSn]₂CH₂ (43). While pyridazine is able to bridge the tin centres of the dinuclear unit, pyrazine cannot, and instead, it bridges adjacent dinuclear units to form a tetranuclear species.

Monodentate pyridazine coordination has been confirmed by X-ray crystallography in only one compound, Fe(pdz)(CO)₄ (82). The presence of bidentate
bridging pyridazine ligands has been established by single crystal X-ray diffraction studies in a relatively larger number of complexes. These include the dinuclear complexes [Cu$_2$L(µ-pdz)$_2$][ClO$_4$]$_2$, where L is a 20-membered N$_4$ macrocycle (83), [{Rh(C$_5$Me$_5$)}$_2$(µ-Cl)$_2$(µ-pdz)][ClO$_4$]$_2$ (84), [{Mo(O(X))$_2$(µ-O)(µ-S)(µ-pdz)]}, where X is diisopropyl phosphorodithioate, S$_2$P(Opr')$_2$ (85), Fe$_2$(µ-pdz)(µ-CO)(CO)$_6$ (86), [{(CH$_3$)$_2$ClSn}$_2$(µ-CH$_2$)(µ-pdz)] (43), [{(CH$_3$)$_2$ClSn}$_2$(µ-CH$_2$)(µ-pdz)] (43), the trinuclear complex, Ru$_3$(µ-pdz)(µ-CO)$_3$(CO)$_7$ (87) and the polymeric complexes, Cu(µ-pdz)(µ-CN) (88) and Cu(µ-pdz)Cl$_2$ (89).

Ferraro et al. (90, 91) observed that upon complexation, several pyridazine ring vibrations shift toward higher energies from those observed in the uncomplexed ligand and that the ring vibration around 1290 cm$^{-1}$ diminishes in intensity in complexes. While such features may be used to distinguish between free and coordinated pyridazine molecules, no satisfactory infrared criterion that may be used to distinguish between mono- and bi-dentate pyridazine ligands is currently available. It has been suggested that the appearance of a strong peak at 1430 cm$^{-1}$ attributable to a pyridazine mode is indicative of a bridging pyridazine ligand (92). However, there have not been sufficient studies incorporating both infrared spectroscopy and single crystal X-ray diffraction to support this. In fact, evidence to be presented in this thesis indicates that the proposal mentioned above is not a good indicator of the denticity of pyridazine.

Polymeric pyridazine-bridged metal complexes have attracted very little attention from synthetic, structural and magnetochemical points of view. Since Reimann and Gordon (93) reported the synthesis of Cu(pdz)Cl$_2$ in 1965, synthetic work appears to be limited to the monovalent copper complex, Cu(pdz)(CN) (88), the 1:1 and 1:2 pyridazine complexes of bivalent (mainly first row transition) metal halides and sulphates (90, 91, 94, 95) and the tetravalent tin complexes, Sn(pdz)X$_4$ (X is Cl, Br or I) (96). Most of these complexes were not obtained in crystalline form suitable for single crystal X-ray diffraction studies. As a consequence, secondary methods were
used to elucidate their structures. The Sn(pdz)X4 complexes were postulated to have trans-octahedral structures with bridging pyridazine and terminal halide ligands (96). Six coordinate polymeric complexes of the type M(pdz)X2 can have chain structures with bridging pyridazine and terminal X or vice versa. Polymeric pyridazine complexes of this stoichiometry that have been reported in the literature include Zn(pdz)X2 (X is Cl or Br), Ni(pdz)X2 (X is Br or SO4) and Fe(pdz)(SO4)2 (91, 95). No definite structural assignments were made for these complexes. Chain structures in which six coordinate metal ions are triply-bridged by pyridazine molecules and halide anions were proposed for the M(pdz)X2 complexes (90, 93, 94, 95, 97). While this may be the case for some of the complexes, a recent X-ray structure determination on Cu(pdz)Cl2 showed that it does not hold true for all complexes of this stoichiometry. The structure of the latter consists of zigzag chains of pyridazine-bridged copper(II) ions (89). The chloride ions are not bridging as previously suggested, making the copper ions four coordinate. The only other pyridazine-bridged coordination polymer to be characterized by X-ray crystallography is Cu(pdz)(CN) (88). Its structure consists of infinite chains of CuCN. The chains are doubly bridged by pyridazine ligands, resulting in a 2-dimensional polymeric structure.

Cu(pdz)Cl2 and Cu(pdz)Br2 seem to be the only pyridazine-bridged coordination polymers to be investigated by low temperature magnetic studies. The temperature dependence of the magnetic susceptibility of Cu(pdz)Cl2 was first reported by Hyde et al. (98). Their study covered the temperature range 110 to 369 K. Emori et al. (99) extended the investigation of this complex and its bromo analogue down to 4.2 K. The susceptibility versus temperature curve for Cu(pdz)Cl2 exhibits a broad maximum at about 60 K, indicative of antiferromagnetic coupling, and a paramagnetic behaviour below 20 K. The susceptibility curve for Cu(pdz)Br2 exhibits two maxima, at 12 and
55 K. These were attributed to inter- and intra-chain antiferromagnetic interactions, respectively.

1.2 Objective and scope of the thesis

Several general observations may be drawn from the material presented in sections 1.1.2 to 1.1.4. These observations, which contributed significantly to the definition and execution of the objective of this work with regard to the kind of complexes studied, are enumerated below. (i) Of the three diazines reviewed, pyrazine complexes are the most widely studied and fairly well characterized. (ii) In general, relatively fewer structural and magnetic studies on methylpyrazine-bridged coordination polymers have been reported. In particular, it is noteworthy that there is no report of any X-ray structure determination on a compound (mono- or poly-nuclear) containing this ligand. Magnetically, methylpyrazine appears to be comparable to pyrazine in its ability to facilitate magnetic exchange. (iii) Although only limited structural and magnetochemical studies have been reported for pyridazine-bridged coordination polymers, this ligand appears to mediate magnetic exchange much more efficiently than pyrazine or methylpyrazine. (iv) The most fruitful magneto-structural studies in diazine-bridged coordination polymers have involved copper(II).

The objective of this work was to prepare and probe magneto-structural correlations in pyrazine-, methylpyrazine- and pyridazine-bridged coordination polymers of divalent copper and nickel. While, for the most part, new polymers were targeted, the study included known compounds which, in our view, held promise of exciting magnetic properties. It was also necessary to study mononuclear species which could then serve as model compounds in the study of the polymeric materials. Towards this end, pyridine was commonly used because it is structurally similar to the
diazines but, unlike the latter, it does not have a second donor atom that can readily lead to bridge formation.

In the course of this work two additional ligands were incorporated in the study with the view of investigating the effects of increased steric constraints and longer separation between paramagnetic centres. These were 2,5-dimethylpyrazine and 4,4'-bipyridine. A study of some copper(I) complexes was also undertaken. In a previous study (44) a pyrazine-copper(I) complex was readily isolated in crystalline form suitable for a single crystal X-ray diffraction study and related compounds were sought in the present work. While not of interest from the perspective of magnetic properties, useful correlations between structure and vibrational spectra can be obtained from such compounds. These correlations can then be applied in the characterization of divalent metal polymers not obtained in crystalline form suitable for single crystal X-ray diffraction studies. The structures of the neutral ligands used in this study are shown in Fig. 1-1.
Fig. 1-1. Structures of the neutral ligands used in this study. Alternative names are given in square brackets and abbreviations used in this thesis are given in parentheses.
1.3 Organization of the thesis

Background information on the type of compounds investigated in this work, together with the objective and scope of this thesis, has been presented in the preceding sections. In the rest of this chapter, basic principles of the physical methods of characterization employed in this work are described. Results and discussions are presented according to the central metal ion involved. Chapter 2 deals with copper(II) complexes, Chapter 3 with nickel(II) complexes and Chapter 4 with copper(I) complexes. Each of these chapters is divided into sections, each dealing with complexes pertaining to a particular anionic ligand. Each section begins with a brief overview of previous work pertinent to the present study. Reasons for choosing a particular class of complexes for study in this work are given. Any special requirements for storage and handling of samples are also addressed in the introduction to each section. The results are then presented and discussed. Each of these chapters ends with a summary and conclusion section. Here, results from the various sections, with emphasis on magneto-structural correlations, are summarized and conclusions presented. Synthetic methods and experimental details of the physical methods of characterization are described in Chapter 5. General conclusions about this work as a whole and suggestions for possible, related, further work are presented in Chapter 6. Several appendixes are included after the main body of the thesis. The appendixes contain data which, although useful, would distract attention from the main results of this work if incorporated in the main body of the thesis.

1.4 Theoretical aspects of physical methods of characterization

Several different physical methods of characterization were used in this study. The degree to which each method is routinely used by chemists, and hence their
familiarity with it, varies considerably. While some techniques such as infrared and electronic spectroscopies are commonly used in many laboratories, others like differential scanning calorimetry and variable temperature magnetic susceptibility measurements are more specialized and not readily available. Moreover, the depth of information obtainable from many techniques is, to a large extent, dependent on the nature of the problem at hand. This section, therefore, aims to introduce the fundamental concepts used in the remainder of the thesis and to outline the nature of the information sought from each technique in the present work. Magnetism is discussed in greater detail than the other subjects since it forms the core of the present work. In addition, to most chemists, it is probably the least familiar of the techniques employed here. Moreover, there are many different phenomena in magnetochemistry leading to an abundance of terms, symbols and units. Sometimes the same term is used to describe different quantities. For instance, the term magnetic moment is commonly associated with the effective magnetic moment (as discussed in section 1.4.8) or the spin only magnetic moment. However, it is not uncommon to find the same term used to denote magnetization, particularly in discussions relating to metamagnetism. Such is the diversity of the field of magnetism that it is impossible to find a single text that covers all the concepts and terminology needed, even in a study of modest size such as this one. Hence, some of these are introduced in section 1.4.8. Others will be introduced where needed.

As stated above, the objective of this section was to simply introduce the concepts and terminology used in the remainder of the thesis. For more comprehensive accounts of the subjects the following references may be consulted; elemental analysis (100), differential scanning calorimetry (101), infrared spectroscopy (102, 103), electronic spectroscopy (103, 104), electron spin resonance spectroscopy (103, 105, 106), powder X-ray diffraction (101, 107), single crystal X-ray diffraction (101, 103, 108) and magnetic susceptibility measurements (109-113).
1.4.1 Elemental analysis

The information provided by elemental analysis include empirical formula (and hence stoichiometry) and purity of samples. Only carbon, hydrogen and nitrogen analysis was performed in this work. The analyzer employed operates on a gas chromatographic system. Accurately weighed samples are introduced into a combustion tube at about 1000 °C to coincide with oxygen enrichment of the helium carrier gas. The oxygen facilitates the complete combustion of the sample. The carbon is converted quantitatively to carbon dioxide, the hydrogen to water and the nitrogen to oxides of nitrogen. A secondary reaction tube removes excess oxygen and reduces the nitrogen oxides to nitrogen. The water, carbon dioxide and nitrogen are then separated chromatographically and detected by a thermal conductivity detector. Areas under the peaks in the chromatogram are integrated electronically. The percentage carbon, hydrogen and nitrogen present in the unknown sample is then determined from the area under the carbon dioxide, water and nitrogen peaks, respectively.

1.4.2 Differential scanning calorimetry

In differential scanning calorimetry (DSC) a sample and an inert reference material are simultaneously subjected to a programmed change in temperature. When a thermal event occurs in the sample, extra heat is automatically transferred to the reference (for an exothermic event) or to the sample (for an endothermic event) in order to keep the temperatures of the sample and reference the same. The extra heat (power) is measured and presented as a function of the temperature.

DSC studies on compounds prepared in this work were undertaken in order to determine temperatures at which thermal events, if any, occur, the enthalpy change associated with such events, and the range of thermal stabilities of the compounds.
Thermogravimetric analyses (TGA) were also performed with the objective of using the data in the identification of the origins of the thermal events observed in the DSC curves. It was also anticipated that the combined DSC and TGA studies would yield information regarding the feasibility of obtaining new complexes, with lower ligand to metal ratios than the starting material, by thermolysis.

1.4.3 Infrared spectroscopy

In infrared spectroscopy, the energy absorbed when a molecule moves from one vibrational energy state to another is measured. The energy involved in these transitions normally occur in the infrared region of the electromagnetic spectrum. The vibrational energy states of a molecule are characterized by the motions (i.e. directions, frequencies and amplitudes) of its constituent atoms. The vibrations of linear and nonlinear molecules can be resolved into $3n-5$ and $3n-6$ normal modes, respectively, where $n$ is the number of atoms in the molecule. Group theory can be used to classify these modes to the various species in the point group of the molecule and to indicate the degeneracy and activity of the vibrations. These characteristics are dependent on the point group of the molecule. Consequently, different modes of coordination of a polydentate molecule resulting in symmetry changes may give rise to different spectral characteristics. Hence, in addition to indicating the presence of particular functional groups in a compound, infrared spectroscopy may provide useful information pertaining to the coordination modes of polydentate ligands in the compound. Numerous examples in this thesis will illustrate the application of the principles outlined above and the complications that may arise in the process.
1.4.4 Electronic spectroscopy

In molecular electronic spectroscopy, the energy absorbed when an electron of the molecule undergoes a transition from one electronic state to another is measured. The electronic states are characterized by the way electrons are distributed in them. Energies involved in electronic transitions generally occur in the ultraviolet, visible or near-infrared regions of the electromagnetic spectrum.

The five d-orbitals of free transition metal ions are degenerate. The degeneracy may be lifted when the metal ions are complexed. Different geometrical arrangements of ligands around the metal ions cause the d-orbitals to be split differently in terms of magnitude and energy sequence. Such differences are reflected in the electronic spectra of the complexes in the form of the number of bands, their energies and their molar absorptivities. Hence careful interpretation of electronic spectra of transition metal complexes can yield useful stereochemical information. In the present work, the technique was found to be particularly useful in the characterization of nickel(II) complexes. Only limited structural information can be obtained from powder spectra of copper(II) complexes. Nonetheless, even if only to the extent that they are characteristic of copper(II) species, such spectra are still important. Accurate sample concentration cannot be obtained for solid mulls. Hence molar absorptivities were not determined in this work.

1.4.5 Electron spin resonance spectroscopy

The spin moment of an unpaired electron can interact with an applied magnetic field to give different spin states (m_s) whose energies (E) are given by:

\[ E = g\beta H m_s \]  \hspace{1cm} [1-1]

where \( g \) is the Landé splitting factor, \( \beta \) is the electron Bohr magneton and \( H \) is the
magnitude of the applied magnetic field. The different spin states are characterized by the orientations of the electron spin moments in an applied magnetic field. In electron spin resonance spectroscopy, the energy absorbed when an electron spin moment undergoes a transition from one spin state to another is measured. The energies involved are normally in the microwave region of the electromagnetic spectrum.

For a free electron $m_s = \pm \frac{1}{2}$ and thus only one peak would be observed in its esr spectrum. From equation 1-1 the energy difference ($\Delta E = h\nu$) between the two spin states of a free electron is given by:

$$h\nu = g\beta H$$

where $h$ is Planck’s constant and $\nu$ the frequency of radiation in Hertz. If the electron is within close proximity of an atom with a non-zero nuclear spin, I, then an interaction between the electron spin and nuclear spin, which splits the esr signal into $2I+1$ hyperfine components, occurs. The hyperfine structure can therefore be used to determine the extent of electron delocalization in a compound containing atoms with non-zero nuclear moments. The interaction of an electron spin with an applied magnetic field and a nuclear moment can be represented by a spin Hamiltonian. For metal ions in environments of axial and rhombic symmetries, the Hamiltonians are given by equations 1-3 and 1-4, respectively.

$$H = \beta [g_{||} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A_{||} S_z I_z + A_{\perp} (S_x I_x + S_y I_y)$$

[1-3]

and

$$H = \beta (g_x H_x S_z + g_z H_x S_x + g_y H_y S_y) + A_z S_z I_z + A_x S_x I_x + A_y S_y I_y)$$

[1-4]

where $S$ and $I$ are the total electronic and nuclear spins, respectively. $A$ is the hyperfine coupling constant. Its magnitude is a measure of the strength of the nuclear and electron spin interactions. The subscripts $||$ and $\perp$ indicate parallel and perpendicular components of a given parameter, respectively, relative to the direction of the applied magnetic field whereas $x$, $y$ and $z$ indicate the component of a given
parameter along the x, y and z axes, respectively. For an isotropically tumbling sample, equations 1-3 and 1-4 transform to:

$$\mathbf{H} = g\beta \mathbf{H} \cdot \mathbf{S} + A \mathbf{S} \cdot \mathbf{I}$$  \hspace{1cm} [1-5].$$

Paramagnetic transition metal complexes do not always exhibit esr signals. The reasons for this lies in the efficiency of the relaxation mechanism and zero-field splitting (ZFS) effects. The width of an esr resonance line is inversely related to the relaxation time. Consequently, a short relaxation time results in a broadening of the line width. In some instances the resonance line may be broadened to such an extent that the signal cannot be distinguished from the background.

The degeneracy of the spin states of the ground term may be lifted in the absence of an applied magnetic field by, for example, magnetic dipole-dipole interaction between unpaired electrons or the presence of low symmetry ligand fields. This phenomenon is known as zero-field splitting. At the microwave frequencies of 9.5 GHz (X-band) and 35 GHz (Q-band) commonly used in esr experiments, transitions can occur only if the spin states are separated by less than $1.5 \text{ cm}^{-1}$. Thus if the magnitude of the ZFS is large, no esr signal can be observed.

In this work, the major experimental parameter of interest in the esr studies on the copper(II) compounds was the Landé splitting factor, $g$. The $g$-values are useful in the theoretical analysis of magnetic data. They can also be used in conjunction with other data to deduce the geometry and ground state of transition metal complexes. Both these applications will be demonstrated by several examples in Chapter 2.

---

1 Analysis of the magnetic data of the nickel complexes investigated in this study showed that all but three of them exhibit large zero-field splittings and, hence, they were not examined by esr spectroscopy. No esr signal was observed for the three that showed no ZFS effects; presumably they have short relaxation times even at liquid nitrogen temperature.
1.4.6 Powder X-ray diffraction

A lattice array of atoms can be regarded as an infinite stack of parallel, equally spaced planes. For two (or more) planes, the path length from incoming wavefront, to plane, to scattered wavefront is longer in the case of the lower plane (Fig. 1-2). The condition for the planes to scatter in phase so that the reflected beams interfere constructively, known as Bragg's law, is:

\[ n\lambda = 2d \sin\theta \]  

where \( n \) is an integer, \( \lambda \) is the wavelength of the X-radiation used, \( d \) is an interplanar spacing of the lattice and \( \theta \) is the glancing angle the incident radiation makes with the scattering plane of atoms. It can be seen from Fig. 1-2 that the scattering by atoms in a plane is tantamount to reflection by the plane, and that the reflection occurs in a direction making an angle \( 2\theta \) with the direct X-ray beam. The utility of powder X-ray diffraction is based on three facts: (i) \( \theta \) can only have certain discrete values, (ii) the set of positions of all X-ray reflections from a crystal (expressed in terms of \( 2\theta \) or \( d \)) depends only on the dimensional characteristics of its lattice (i.e. unit cell parameters) and does not depend on the arrangement of its atoms, (iii) the set of intensities of reflections depends entirely on the atomic number and arrangement of various atoms in the unit cell.

Some applications of the powder method are now considered. First, the powder diffraction pattern (locations and relative intensities of reflections) produced by a crystalline substance is characteristic of that substance. Thus, if standard diagrams are available, the powder method can be used as a means of identification of unknown compounds. Secondly, mathematical relationships between the interplanar \( d \) spacings of a substance and its unit cell dimensions are available (107). Hence the powder method provides a way of investigating, within limits, the crystallography of a compound. Thirdly, since the peak positions of all X-ray reflections from a crystal
Fig. 1-2. Diffraction of X-rays by two successive planes.
depend only on the unit cell parameters and not on the arrangement of its atoms, two
crystals having the same type and dimensions of unit cell give the same X-ray diagram
with regard to location of reflections, even if they have completely unrelated chemical
compositions. Thus the powder method can be used to determine if a pure compound
whose structure is unknown, is isomorphous with one whose structure is known. It is
the third application which was of interest in the present work.

1.4.7 Single crystal X-ray diffraction

The techniques discussed above may be used to indirectly deduce structures of
inorganic complexes. However, the most powerful method available for the direct
determination of structures of such complexes is single crystal X-ray crystallography.
The technique allows precise composition and atomic arrangement of a compound to be
determined. Thus the unit cell and its dimensions, atomic coordinates, bond lengths
and bond angles can all be obtained.

The basic principles that govern the diffraction of X-rays by single crystals are
the same as those discussed in section 1.4.6 for diffraction by powder samples.
However, in the powder method the sample consists of randomly oriented
microcrystallites. This makes it difficult to assign a particular reflection to a given
plane. Consequently less structural information may be obtained from the powder
method than from single-crystal X-ray diffraction analysis.
1.4.8 Magnetic susceptibility measurements

Magnetic susceptibility is the quantitative measure of the response of a material to an applied magnetic field. The fundamental mathematical expression for this property, Van Vleck's susceptibility equation, is:

\[
\chi = N \sum_i \frac{((E_i^{(1)})/kT) - 2E_i^{(2)}\exp(-E_i^{(0)}/kT)}{\sum_i \exp(-E_i^{(0)}/kT)}
\]  

[1-7]

where \( \chi \) is the susceptibility, \( N \) is Avogadro's number, \( E_i^{(0)} \) is the energy of the \( i \)th level of the system under consideration in the absence of any magnetic field, \( E_i^{(1)} \) is the first order Zeeman effect coefficient, \( E_i^{(2)} \) is the second order Zeeman effect coefficient, \( k \) is Boltzmann's constant and \( T \) is the temperature. Thus the use of this equation requires the knowledge of the energy levels of a system. A restriction in the use of Van Vleck's equation is that any splitting of the energy levels of the ground state due to the first order Zeeman effect must be small in comparison to the thermal energy i.e. \( g\beta H \ll kT \). Thus the equation may not apply at very low temperatures or very high applied fields.

For experimental purposes, several expressions for the calculation of magnetic susceptibility are available, depending on the experimental method employed in data collection. The apparatus commonly used in the determination of magnetic susceptibilities are broadly of two kinds employing force methods or induction methods. The former relies on the fact that when a material is placed in an inhomogeneous magnetic field it experiences a force. The induction methods, on the other hand, are based on the principle that a magnetic material inserted in an induction detection coil induces a voltage change in the coil. Two instruments based on the induction principle, a vibrating sample magnetometer (VSM) and a superconducting
quantum interference device (SQUID) magnetometer, and one based on the principle of the force methods, a Gouy balance, were used in the present study. The principles underlying the operation of these instruments are now briefly described.

If a body is placed in a magnetic field, \( \mathbf{H} \), it becomes magnetized, i.e. magnetic dipoles in the body align along a common direction and a net magnetic moment forms in the body. The magnetization of the body results in an induced magnetic field within the body. This field, known as the magnetic induction, \( \mathbf{B} \), may be expressed as:

\[
\mathbf{B} = \mathbf{H} + 4\pi \mathbf{M}
\]

[1-8]

where \( \mathbf{M} \) is the magnetization. The ratio \( \mathbf{B}/\mathbf{H} \) is the magnetic permeability of the substance and can be expressed as:

\[
\frac{\mathbf{B}}{\mathbf{H}} = 1 + 4\pi \frac{\mathbf{M}}{\mathbf{H}}
\]

[1-9]

where \( \mathbf{M}/\mathbf{H} \) is the magnetic susceptibility. The susceptibility is normally expressed per unit mass, \( \chi_g \), or per mole, \( \chi_m \), defined as follows:

\[
\chi_g = \frac{\mathbf{M}}{m\mathbf{H}},
\]

[1-10]

\[
\chi_m = \chi_g \times MW
\]

[1-11]

where \( m \) is the mass of the sample and \( MW \) its molecular weight.

In the VSM, the sample is placed in a homogeneous magnetic field and the magnetization is measured directly. The sample is mounted on a rod, about 1 metre long. The problem of accurately measuring a small magnetic field (\( \mathbf{M} \)) in the presence of a large field (\( \mathbf{H} \), applied) is overcome by vibrating the sample at a specific frequency (82 Hz, in this work). This results in an oscillating signal whose strength is proportional to the magnetization. The signal, which is detected as a voltage change in the sample coils, is processed electronically and digitally displayed as the magnetization. The molar magnetic susceptibility is then calculated according to equation 1-11.

The SQUID magnetometer also measures magnetization directly. A loop of superconducting wire is placed around the magnetized sample. The circuit of the loop
is completed with a second loop, of the same superconducting wire, a few centimetres away. This second loop enters the SQUID. The SQUID is a device that can be used as part of an arrangement capable of measuring minute magnetic fields. Both the loops and the SQUID are kept at a temperature of about 4 K so that they are in their superconducting states. The sample, together with its surrounding helium atmosphere, is contained within a tube which is thermally insulated from the detection system so that its temperature can be varied independently. Moving the sample induces a signal in the surrounding loop. Since the double-loop circuit is superconducting, and hence, of zero resistance, no damping or loss of the original signal occurs. Therefore, there appears within the loop inside the SQUID a field which is directly related to the magnetization of the sample. The signal is processed electronically and output as the magnetization. The molar magnetic susceptibility is then calculated according to equation 1-11.

In the Gouy method, a sample is investigated in the form of a long, thin cylindrical rod suspended from a sensitive balance between the poles of a magnet, such that the bottom of the sample is in the region where the magnetic field is strongest and the top is in the region of negligible magnetic field. The sample is usually in the form of a finely ground powder, uniformly packed into a glass tube. The force exerted on a sample in an inhomogeneous field is equal to the product of the magnetic moment and the field gradient. Thus,

$$\partial F = I \partial v (\partial H/\partial l)$$  \[1-12\]

where $\partial F$ is the force, $I$ is the magnetic moment per unit volume and $\partial H/\partial l$ is the field gradient on an element of volume $\partial v$. The following expression for $\chi_g$ may be derived from equation 1-12.

$$\chi_g = (\Delta m/m) \beta$$  \[1-13\]

where $m$ is the mass of the sample and $\Delta m$ is the apparent change in the mass in a magnetic field. The calibration constant, $\beta$, is given by $2gL/H_i^2$ where $g$ is the
acceleration due to gravity, $L$ is the height of the sample and $H_1$ is the difference between the magnetic field strengths at the top and bottom of the sample. The force exerted on the sample is thus measured in terms of the apparent change in mass in the magnetic field and the gram susceptibility calculated according to equation 1-13.

Having defined magnetic susceptibility and described the principles underlying the methods with which it was determined in this work, other concepts and terminology used in the remainder of this thesis are now introduced. Materials may be classified as diamagnetic or paramagnetic depending on their behaviour in a magnetic field. A diamagnetic material is one in which the magnetization, as defined in equation 1-8, is negative. Diamagnetic susceptibilities are generally small, negative, and independent of both field strength and temperature. A paramagnetic material is one in which the magnetization is positive. Paramagnetism is exhibited by substances containing unpaired electrons. If electron spins on the atoms of a substance are randomly oriented, the material is said to be paramagnetic. Materials in which the spins interact to align parallel and antiparallel are said to be ferromagnetically coupled and antiferromagnetically coupled, respectively. In a ferromagnetically coupled material, therefore, the spins reinforce each other and relatively large susceptibilities are observed. In an antiferromagnetically coupled material the spins tend to cancel each other, leading to relatively lower susceptibilities. If the electron spins orient themselves locally relative to one another, short range order is said to occur. This includes magnetic exchange coupling in isolated clusters, chains, or planes of magnetic ions. An extended and cooperative ordering of the spins throughout the lattice is known as long range order. Long range order effects are not commonly observed under ordinary conditions because the thermal energy of the electrons tend to oppose the cooperative ordering of the spins. The susceptibility of each kind of magnetic material has a characteristic temperature dependency. These are illustrated in Fig. 1-3 for diamagnetic, paramagnetic, ferromagnetic and antiferromagnetic materials.
The magnetic properties of materials are also commonly expressed in terms of the effective magnetic moment, \( \mu_{\text{eff}} \), which is related to the magnetic susceptibility by the expression:

\[
\mu_{\text{eff}} = \left( \frac{3k}{N\beta^2} \right)^{1/2} \left( \chi_m T \right)^{1/2}
\]  \[1-14\]

where \( k \) is Boltzmann's constant, \( N \) is Avogadro's number, \( \beta \) is the Bohr magneton, \( \chi_m \) is the molar magnetic susceptibility and \( T \) is the temperature. Upon substituting in numerical values for the constants equation 1-14 becomes:

\[
\mu_{\text{eff}} = 2.828 \left( \chi_m T \right)^{1/2}. \]  \[1-15\]

Since the magnetic moment is derived from the magnetic susceptibility, \( \mu_{\text{eff}} \) of each kind of magnetic material necessarily has a characteristic temperature dependency. The exception, of course, is diamagnetic substances. \( \mu_{\text{eff}} \) cannot be determined for such substances because of the negative sign of diamagnetic susceptibilities. Typical temperature variations of \( \mu_{\text{eff}} \) for ferromagnetic, antiferromagnetic and paramagnetic materials are illustrated in Fig. 1-4.

Transition metal compounds in which there are no spin interactions between the paramagnetic centres are said to be magnetically dilute. When such interactions exist, the compounds are said to be magnetically concentrated. Magnetic ordering can occur via several mechanisms. The spin of a paramagnetic centre may be regarded as a dipole. The local magnetic field associated with such a dipole can influence the orientations of neighbouring dipoles. This kind of interaction is known as dipolar coupling. If the orbitals that contain the unpaired electrons on neighbouring paramagnetic centres overlap directly, the resultant spin interaction is said to occur via direct exchange. If, on the other hand, the magnetic centres are linked by intervening diamagnetic ligands, and the latter mediate the magnetic exchange, the mechanism is referred to as superexchange.
Fig. 1-3. Plots of magnetic susceptibility as a function of temperature for different types of magnetic materials. (A) Ferromagnetic; (B) paramagnetic; (C) antiferromagnetic; (D) diamagnetic.

Fig. 1-4. Plots of magnetic moment as a function of temperature for different types of magnetic materials. (A) Ferromagnetic; (B) paramagnetic; (C) antiferromagnetic.
Magnetic interactions between paramagnetic centres, with total spin \( S_i \) and \( S_j \), may be represented by the spin Hamiltonian:

\[
H = -2J \sum_{i \neq j} [a S_{iz} S_{jz} + b (S_{ix} S_{jx} + S_{iy} S_{jy})]
\]  [1-16]

where \( J \) is the exchange or coupling constant. It is given in energy units and its magnitude is a measure of the strength of the interaction. \( J \) is positive for ferromagnetic coupling and negative for antiferromagnetic coupling. \( a \) and \( b \) are parallel and perpendicular anisotropy parameters, respectively, and can vary independently between the values of zero and one. In the limiting case when \( a = b = 1 \), the Heisenberg model for magnetic exchange is obtained. If \( a = 1 \) and \( b = 0 \), the Ising model for magnetic exchange is obtained whereas the limit in which \( a = 0 \) and \( b = 1 \) gives the X-Y model for magnetic exchange. The exchange is isotropic in the Heisenberg model, that is, all three components of the spin vectors couple equally. In the Ising and X-Y models the exchange is anisotropic. Only the \( S_z \) components of the spin vectors couple in the former while only the \( S_x \) and \( S_y \) components of the spin vectors couple in the latter.

Traditionally magnetic susceptibility measurements on transition metal complexes have been used for structural elucidation through the correlation of the magnitude of the effective magnetic moment with stereochemistry. The magnitude of the magnetic moment can also be related to the number of unpaired electrons in a compound and, hence, the oxidation state of the central metal. Most such studies involve room temperature measurements only. In the work described in this thesis, our main interest was in magneto-structural correlations, particularly in exchange coupled systems. Hence, susceptibility measurement was not usually used as a tool for structural elucidation. Efforts were made to establish the structures of the compounds as much as possible by other techniques. The magnetic properties of the compounds were then explained on the basis of the already established structures.
We end this section with a comment on units used in magnetochemistry. Two main classes of units are available; c.g.s. system of electromagnetic units (cgs-emu) and International System of Units (SI). The former system, in its unrationalized form remains the most common among magnetochemists. This probably arises from the fact that most existing information on magnetic susceptibilities is in this system of units. Moreover, there is no simple multiple of ten for the conversion between the cgs-emu and SI systems. This results from the fact that SI units are rationalized (to ensure that factors of $2\pi$ and $4\pi$ do not appear in electromagnetic formulas). Hence, conversion from cgs-emu to SI magnetic units involves factors which include $4\pi$ since the permeability of free space is $4\pi \times 10^{-7} \text{ kg m s}^{-2} \text{ A}^{-2}$ in SI, but is one and dimensionless in the cgs-emu system. In order to simplify comparison of the material presented here with the existing literature the unrationalized cgs-system is retained in this thesis. This policy is, in fact, followed by all major chemistry journals. A discussion on the conversion of magnetic units between the two systems may be found in references 114 and 115.
2.1 Complexes of copper(II) cyanate

2.1.1 Introduction

Earlier studies on the magnetic properties of pyridine and pyrazine complexes of iron(II) cyanate revealed ferromagnetic exchange in Fe(py)₂(NCO)₂ (116) and antiferromagnetic exchange in Fe(pyz)(NCO)₂ (67). While the molecular structure of neither compound has been determined by single crystal X-ray diffraction methods, spectroscopic studies support polymeric structures for both compounds in which metal ions are linked in chains by double >NCO bridges. In Fe(pyz)(NCO)₂ the chains are cross-linked by bridging pyrazine ligands while in Fe(py)₂(NCO)₂ the fifth and sixth coordination sites on iron are occupied by pyridine molecules, leaving the chains in this compound effectively isolated. The ferromagnetism observed for Fe(py)₂(NCO)₂ was explained by the presence of orthogonal orbital overlap involving the single nitrogen atoms of the bridging cyanate groups (116). The observation of antiferromagnetic coupling in Fe(pyz)(NCO)₂ prompted the suggestion of an exchange mechanism for this compound in which ferromagnetic intrachain interactions via the bridging cyanate groups is combined with antiferromagnetic interchain interactions via the bridging pyrazine ligands resulting in net, strong, antiferromagnetism (67). Such interesting magnetic properties prompted us to investigate related complexes of other metal cyanates and in this section we present the results of our studies on the copper
complexes Cu(py)$_2$(NCO)$_2$, Cu(mepyz)$_2$(NCO)$_2$, Cu(mepyz)(NCO)$_2$, Cu(pyz)(NCO)$_2$ and Cu(pdz)(NCO)$_2$. Their syntheses are described in section 5.2.1.

Cu(py)$_2$(NCO)$_2$ was prepared previously by others (117-119) and is known to exist in two forms, α and β. The compound prepared in the current work is the β-form. Its structure has been determined by X-ray crystallography (118). The copper ions are linked into an infinite three-dimensional lattice by end-to-end bridging cyanate groups. Each copper ion has a distorted CuN$_4$O$_2$ chromophore composed of two nitrogen atoms from pyridine ligands, two nitrogen atoms from cyanate anions, and two oxygen atoms from a different set of cyanate anions. The "tetragonal" axes of adjacent copper(II) chromophores are approximately orthogonal. Cu(mepyz)$_2$(NCO)$_2$ has been shown by single crystal X-ray diffraction, in the present work, to have a polymeric sheet structure in which methylpyrazine ligands are bridging and the cyanate ions are terminal, N-bonded. Polymeric sheet structures for Cu(pyz)(NCO)$_2$ and Cu(mepyz)(NCO)$_2$, and a chain structure for Cu(pdz)(NCO)$_2$, involving bridging neutral ligands and cyanate ions are proposed on indirect evidence to be presented in this section. All the compounds are sufficiently air-stable that manipulations could be carried out in the atmosphere. Samples were, however, stored in a desiccator over Drierite (anhydrous calcium sulphate).

2.1.2 The crystal structure of Cu(mepyz)$_2$(NCO)$_2$

The atom numbering scheme for Cu(mepyz)$_2$(NCO)$_2$ is shown in Fig. 2-1 while stereoviews showing the coordination geometry about copper and the extended two-dimensional polymeric structure are depicted in Fig. 2-2. The crystallographic data

---

1 When this work was already completed a publication appeared in which two forms of Cu(py)$_2$(NCO)$_2$ were reported (119). Our infrared and esr spectra are consistent with that of the isomer designated β in that report.
and selected bonding parameters for this compound are given in Tables 2-1 and 2-2, respectively. A complete set of its structural parameters is presented in Appendix I-1.

The structure of Cu(mepyz)$_2$(NCO)$_2$ is made up of parallel sheets each consisting of an infinite square array of copper ions bridged by bidentate methylpyrazine ligands. Coordination number six for each copper ion is completed by trans-cyanato-N groups. The sheets are disposed such that the copper ions in one sheet lie vertically above and below the centres of the squares formed by the copper ions of adjacent sheets. This type of structure has been observed in the bis(pyrazine)complexes Fe(pyz)$_2$(NCS)$_2$ (48), Cu(pyz)$_2$(CH$_3$SO$_3$)$_2$ (47), Cu(pyz)$_2$(ClO$_4$)$_2$ (46) and Co(pyz)$_2$Cl$_2$ (45). As a consequence of steric constraints imposed by the methyl substituent, however, Cu(mepyz)$_2$(NCO)$_2$ possesses some unique structural features not observed in the other sheet polymers, namely: (i) the methylpyrazine bridges are unsymmetrical, i.e. Cu···mepyz—Cu; (ii) the Cu-mepyz-Cu chains are slightly bent in a zigzag manner, the turning point being, by extrapolation, at the centre of the methylpyrazine rings; (iii) the molecular axes of adjacent copper ions are misaligned by about 75°, the dihedral angle between the square planes about Cu(1) and Cu(2), and (iv) planes of alternate methylpyrazine ligands along any Cu-mepyz-Cu chain are tilted away from the plane of the copper ions in opposite directions by between 30° and 50°. The dihedral angle between the planes of any two trans-methylpyrazine groups is about 80°.

Each copper ion in Cu(mepyz)$_2$(NCO)$_2$ is coordinated to by four methylpyrazine ligands; two through the nitrogen atoms meta to the methyl substituent and two through the ortho ones. The two remaining coordination sites are occupied by nitrogen atoms of the cyanate groups. The complex has an elongated rhombic-octahedral CuN$_2$N$_2$'N$_2''$ chromophore. The mean Cu-N bond length involving the cyanate groups is 1.935(4) Å while that involving the sterically unhindered methylpyrazine nitrogen atoms is 2.076(4) Å. The sterically hindered nitrogen atoms from the remaining methylpyrazine
Fig. 2-1. Atom numbering scheme for Cu(mepy)$\textsubscript{2}$(NCO)$_2$. 
Fig. 2-2. Stereoviews of (a) the geometry about the copper atoms and (b) the extended two-dimensional polymeric structure of Cu(mepy)_2(NCO)_2. In (a) 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.
groups are considerably further from the copper(II) ion (mean Cu-N distance = 2.707(4) Å). The Cu-N(mepyz) distances may be compared to those in Cu(pyz)$_2$(CH$_3$SO$_3$)$_2$ which has strongly bound, equatorially coordinated, and weakly bound, axially coordinated, pyrazine ligands with Cu-N distances of 2.058(2) Å and 2.692(2) Å respectively (47). Significant deviations from linearity (trans N-Cu-N angles, 173.1-178.6°) and orthogonality (cis N-Cu-N angles, 85.0-96.0°) are observed in the bond angles of the coordination polyhedron of copper(II). This is a further consequence of the steric influence of the methyl groups. Ideal angles were observed in Cu(pyz)$_2$(ClO$_4$)$_2$ (46) and, with only two exceptions, in Cu(pyz)$_2$(CH$_3$SO$_3$)$_2$ (47).

Table 2-1. Crystal data* for Cu(mepyz)$_2$(NCO)$_2$.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Monoclinic</th>
<th>Z</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>$P2_1/c$ (#14)</td>
<td>V, Å$^3$</td>
<td>2805.4(8)</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>10.480(2)</td>
<td>$\rho_{\text{calc}}$, g cm$^{-3}$</td>
<td>1.590</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>10.720(2)</td>
<td>$F(000)$</td>
<td>1368</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>25.027(1)</td>
<td>$R$</td>
<td>0.056</td>
</tr>
<tr>
<td>$\beta$, deg</td>
<td>93.849(9)</td>
<td>$R_w$</td>
<td>0.066</td>
</tr>
</tbody>
</table>

* Standard deviations in the last digit are given in parentheses.
Table 2-2. Selected bonding parameters for Cu(mepy2)(NCO)2

<table>
<thead>
<tr>
<th>Distances (Å)</th>
<th>Angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordination sphere of the copper ion</td>
<td></td>
</tr>
<tr>
<td>Cu(1)-N(1)</td>
<td>2.080(4)</td>
</tr>
<tr>
<td>Cu(1)-N(3)</td>
<td>2.067(4)</td>
</tr>
<tr>
<td>Cu(1)-N(5)</td>
<td>1.927(4)</td>
</tr>
<tr>
<td>Cu(1)-N(6)</td>
<td>1.939(4)</td>
</tr>
<tr>
<td>Cu(1)-N(8)\textsuperscript{1}</td>
<td>2.672(4)</td>
</tr>
<tr>
<td>Cu(1)-N(10)</td>
<td>2.734(4)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>NCO</td>
<td></td>
</tr>
<tr>
<td>O(1)-C(11)</td>
<td>1.190(6)</td>
</tr>
<tr>
<td>O(2)-C(12)</td>
<td>1.186(6)</td>
</tr>
<tr>
<td>N(5)-C(11)</td>
<td>1.167(6)</td>
</tr>
<tr>
<td>N(6)-C(12)</td>
<td>1.147(6)</td>
</tr>
<tr>
<td>mepyz\textsuperscript{b}</td>
<td></td>
</tr>
<tr>
<td>N-CH</td>
<td>1.335(6)</td>
</tr>
<tr>
<td>N-CCH3</td>
<td>1.338(6)</td>
</tr>
<tr>
<td>C-CH</td>
<td>1.370(7)</td>
</tr>
<tr>
<td>C-CCH3</td>
<td>1.394(6)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Estimated standard deviations in the least significant figure are given in parentheses.

\textsuperscript{b} Mean values. Pertinent data pertaining to the Cu(2) chromophore were included in calculation of mean values presented in the table and text.

\textsuperscript{1} The superscript refers to symmetry operation \(x-1, y-1, z\).
Even greater deviation from linearity is observed in the Cu-N-C angles of the copper-cyanate fragments which lie in the range 159.5-158.0°. The N-C-O angle, on the other hand does not depart significantly from linearity, having a mean value of 177.7(7)°. The mean N-C and C-O bond lengths of the NCO group are 1.154(6) Å and 1.193(6) Å, respectively. Comparable structural features have been observed in other transition metal complexes containing the NCO group (118, 120-122). For instance, in Cu(py)$_2$(NCO)$_2$ the angles Cu-N-C and N-C-O and the distances N-C and C-O are 151.83(61)°, 177.08(86)°, 1.152 (10) Å and 1.182(9) Å, respectively (118).

The methylpyrazine molecules in Cu(mepy)$_2$(NCO)$_2$ are all planar within experimental error. This is the first complex containing this ligand whose structure has been determined by X-ray crystallography. There are, therefore, no literature values with which the internal bonding parameters reported here for methylpyrazine can be directly compared. However, the parameters are found to be comparable to those of 2,5-dimethylpyrazine molecules in Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$), [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ and [Cu(2,5-me$_2$pyz)$_2$][PF$_6$] discussed in Chapter 4 as well as to those of the unsubstituted pyrazine in its complexes (see, for example, refs. 45-48). The findings of the present study provide some insight to a problem that has intrigued us for some time. The nitrogen atom ortho to the methyl substituent is expected to be more basic and should preferentially coordinate to metal centres when the ligand is terminally bonded. However, the higher basicity is countered by steric considerations. The long Cu-N distance involving the ortho nitrogen atom in Cu(mepy)$_2$(NCO)$_2$ suggest that steric influence may be the more important factor.
2.1.3 Thermal properties

Cu(mepyz)$_2$(NCO)$_2$ exhibits an endothermic peak at 145 °C in its DSC thermogram and this is followed immediately by a series of three exothermic events at about 160, 190 and 290 °C (Fig. 2-3a). The loss of the first molecule of mepyz from this complex is apparently accompanied by complex exothermic decomposition processes, a conclusion supported by the thermogram for Cu(mepyz)(NCO)$_2$ (Fig. 2-3b) which is the same as that for the bis(mepyz) complex except that the initial endothermic event is missing. Cu(pyz)(NCO)$_2$ and Cu(pdz)(NCO)$_2$ show no events prior to exothermic decomposition at 140 °C and 115 °C, respectively. A blue compound of composition Cu(py)$_2$(NCO)$_2$ was earlier reported to decompose at 113 °C (117). The blue colour suggests that it is the $\beta$ isomer that was investigated in the earlier work. Our study on this compound reveals no thermal events in the DSC thermogram up to 135 °C at which temperature exothermic decomposition begins. No details were given in the previous study on how decomposition temperatures were determined.
Fig. 2-3. DSC curves for (a) Cu(mepyz)$_2$(NCO)$_2$ and (b) Cu(mepyz)(NCO)$_2$. 
2.1.4 Infrared spectra

The cyanate anion may coordinate to a metal centre via the nitrogen atom (cyanato-\(N\), OCN\(^-\)) or via the oxygen atom (cyanato-\(O\), NCO\(^-\)). It can also bridge two metal ions and, in principle, three modes of bridging are possible. These are -NCO-, >NCO and >OCN. Because of this ability to coordinate to metal ions in several different ways, a considerable amount of research has been directed at establishing the mode of cyanate ion coordination in a variety of complexes.

Only a few cyanato-\(O\) transition metal complexes have been reported in the literature (123, 124). However in none of these has O-bonding been established unequivocally by single crystal X-ray diffraction. In contrast, many cyanato-\(N\) transition metal complexes have been reported (67, 125-129). Complexes in which the presence of N-bonded cyanate groups has been unambiguously demonstrated by X-ray crystallography include (\(\pi\)-C\(_5\)H\(_5\))Mo(CO)(PPh\(_3\))\(_2\)(NCO) (121) and (\(\pi\)-C\(_5\)H\(_5\))Cr(NO)\(_2\)(NCO) (120) and, in the present work, Cu(mepyz)\(_2\)(NCO)\(_2\). The end-to-end cyanate bridging has been observed by single crystal X-ray studies in the dimeric nickel(II) complex, \([\text{Ni}_2(\text{tren})_2(\text{NCO})_2][\text{BPh}_4]_2\) (130) (where tren is 2,2',2''-triaminotriethylamine) and the polymeric copper(II) complex, Cu(py)\(_2\)(NCO)\(_2\) (118). Whereas the single oxygen atom bridging copper mode has not been observed in any complex by X-ray crystallography, the single nitrogen atom bridging has been observed in AgNCO (122).

When single crystals suitable for diffraction studies are unavailable, useful information on the mode of coordination of the cyanate ion may be obtained from an examination of infrared spectra (125, 127, 131, 132). The three normal modes of vibration of the linear NCO\(^-\) anion are: antisymmetric stretching \(\nu_{CN} (\nu_1)\), bending \(\delta_{\text{NCO}} (\nu_2)\) and pseudosymmetric stretching \(\nu_{\text{CO}} (\nu_3)\). The stretching modes are appreciably mixed in cyanate complexes. In the spectrum of the free ion (as KNCO,
\[ \nu_{\text{CN}} \text{ occurs at } 2165 \text{ cm}^{-1}, \delta_{\text{NCO}} \text{ at } 628 \text{ and } 637 \text{ cm}^{-1} \text{ (the splitting has been attributed to solid state effects (133)) and a doublet, due to Fermi resonance between } \nu_{\text{CO}} \text{ and the first overtone of } \delta_{\text{NCO}}, \text{ is observed at } 1302 \text{ and } 1207 \text{ cm}^{-1}. \] The unperturbed \( \nu_{\text{CO}} \) is calculated to occur at 1254 cm\(^{-1}\). Upon coordination the following changes in the free ion spectrum have been observed: (i) \( \nu_{\text{CN}} \) shifts to higher energies and is either broad or shows some splitting, (ii) \( \nu_{\text{CO}} \) shifts to lower energies, relative to the calculated free ion value, when the anion is O-bonded and to higher energies when N-bonded, (iii) \( \delta_{\text{NCO}} \) is split by at most a few wavenumbers when the cyanate ion is terminal while it typically shows a splitting of 30 to 50 cm\(^{-1}\) when the ion is bridging, and (iv) \( \nu_{\text{CO}} \) tend to have a lower intensity in bridged than in non-bridged complexes. No infrared criterion is currently available for distinguishing between the various possible modes of cyanate ion bridging.

Cyanate band energies for the copper(II) complexes studied in this work, with assignments, are listed in Table 2-3. The \( \nu_{\text{CN}} \) band is shifted to energies above 2165 cm\(^{-1}\) in all complexes. The \( \nu_{\text{CO}} \) mode is also observed at higher energies than the free ion value in the spectra of the five complexes. This is indicative of N-bonding rather than O-bonding in all the complexes. This observation is consistent with the structure of Cu(mepyz)\(_2\)(NCO)\(_2\) as determined by X-ray crystallography. The structure of Cu(py)\(_2\)(NCO)\(_2\), however, involves end-to-end bridging cyanate groups (118) but we note that the Cu-O bond length of 2.607(5) Å is considerably larger than the sum of the ionic radius of a six coordinate Cu\(^{2+}\) cation (0.87 Å) and a two coordinate O\(^{2-}\) anion (1.21 Å) (134), indicating that the Cu-O linkage in Cu(py)\(_2\)(NCO)\(_2\) is very weak. It appears that infrared spectroscopy is insufficiently sensitive to discern the weak Cu-O interactions.\(^2\) The splitting of \( \delta_{\text{NCO}} \) ranges from 12 to 33 cm\(^{-1}\) in the copper complexes

\(^2\) Although we have been able to rationalize the infrared spectrum of Cu(py)\(_2\)(NCO)\(_2\) on the basis of its known structure, these results indicate that the assignment of the cyanate ion as N- or O- bonded based on the position of the \( \nu_{\text{CO}} \) band is not always unequivocal.
giving a less clear indication of terminal versus bridging cyanate than is possible with related nickel(II) complexes (see section 3.1.3). Intermediate $\delta_{\text{NCO}}$ splitting values may result from the tendency of copper to form distorted coordination geometries with the consequent presence of unsymmetrically bridging anionic ligands of the type $\text{--NCO--}$ or $\text{> NCO}$. The structure of Cu(py)$_2$(NCO)$_2$ is known to involve very unsymmetrically bridging M--NCO···M anions and for this complex the splitting of $\delta_{\text{NCO}}$ is 12 cm$^{-1}$.

Table 2-3. Cyanate ion band energies and assignments for copper(II) complexes.$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Energies and assignments</th>
<th>$\Delta\delta_{\text{NCO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v_{\text{CN}}$</td>
<td>$\delta_{\text{NCO}}$</td>
</tr>
<tr>
<td>Cu(py)$_2$(NCO)$_2$</td>
<td>2 148sh</td>
<td>614s</td>
</tr>
<tr>
<td></td>
<td>2 204vs,br</td>
<td>626s</td>
</tr>
<tr>
<td>Cu(mepyz)$_2$(NCO)$_2$</td>
<td>2 167sh</td>
<td>614s</td>
</tr>
<tr>
<td></td>
<td>2 221vs,br</td>
<td>628m</td>
</tr>
<tr>
<td>Cu(mepyz)(NCO)$_2$</td>
<td>2 180vs,br</td>
<td>613s,br</td>
</tr>
<tr>
<td>Cu(pyz)(NCO)$_2$</td>
<td>2 155sh</td>
<td>615s</td>
</tr>
<tr>
<td></td>
<td>2 253vs,br</td>
<td>632s</td>
</tr>
<tr>
<td>Cu(pdz)(NCO)$_2$</td>
<td>2 143w</td>
<td>615s</td>
</tr>
<tr>
<td></td>
<td>2 223vs,br</td>
<td>638m</td>
</tr>
</tbody>
</table>

$^a$ All values are in cm$^{-1}$. w = weak, m = medium, s = strong, v = very, sh = shoulder, br = broad.

$^b$ Magnitude of splitting of $\delta_{\text{NCO}}$.

Infrared absorption bands due to the internal vibrations of the neutral ligand molecules were also identified in the spectra of the complexes under discussion and these are listed in Appendixes II-1, II-2, II-3, and II-4 for pyridine, pyrazine, methylpyrazine, and pyridazine respectively. From studies of infrared spectra of many transition metal complexes of pyridine, it has been noted that, upon coordination, there
are considerable energy shifts in the positions of the 8a (1583 cm\(^{-1}\)), 6a (605 cm\(^{-1}\)) and 16b (405 cm\(^{-1}\)) bands of the free base (135) and that these shifts, together with the presence of a weak band between 1235 and 1250 cm\(^{-1}\), may be used to distinguish coordinated pyridine from the free base (136-138). Cu(py)\(_2\)(NCO)\(_2\) shows only those bands expected for coordinated pyridine as expected from its known structure.

Previous studies on transition metal pyrazine complexes have established that while most pyrazine bands exhibit shifts to higher energies on coordination, the most sensitive is the band at 417 cm\(^{-1}\) in the spectrum of the free ligand (47, 64, 65, 67). Recently it was pointed out that shifts in this band to about 450 cm\(^{-1}\) usually indicate monodentate coordination, whereas, shifts to 470 cm\(^{-1}\) or higher suggest bidentate coordination (44). In Cu(py)z(NCO)\(_2\) this band is at 494 cm\(^{-1}\) consistent with bidentate, bridging, pyrazine coordination. Supporting this is the observation that while complexes containing monodentate pyrazine typically exhibit bands at energies near 1230, 920 and 750 cm\(^{-1}\) (60), no such bands are observed in the spectrum of this complex.

We previously noted that bands exhibited by free methylpyrazine at 410, 472 and 1021 cm\(^{-1}\) are the most coordination sensitive, shifting significantly to higher energies upon coordination (66). We suggested that for a series of related complexes, the extent to which these bands shift may be used to distinguish between terminal and bridging methylpyrazine coordination. With additional data now available only the shifts in the positions of the 410 and 472 cm\(^{-1}\) free ligand bands are considered diagnostic for the mode of methylpyrazine coordination. Data from the previous and present studies are presented in Table 2-4 from which it can be concluded that for terminal methylpyrazine the 410 cm\(^{-1}\) band shifts to between 425 and 440 cm\(^{-1}\), and the 472 cm\(^{-1}\) band to between 500 and 510 cm\(^{-1}\). For bridging bidentate coordination, the bands occur above 440 and 520 cm\(^{-1}\), respectively. Based on these observations it is concluded that methylpyrazine ligands are bidentate bridging in Cu(mepy)z(NCO)\(_2\).
Based on the same observations it would be concluded that methylpyrazine molecules are terminally bonded in Cu(mepyz)$_2$(NCO)$_2$, yet it has been shown by a single crystal X-ray structure determination that the ligands are bridging. This apparent inconsistency arises from the unsymmetrical nature of the methylpyrazine bridges in Cu(mepyz)$_2$(NCO)$_2$ (vide supra). One nitrogen atom of each methylpyrazine ligand is bonded strongly to a copper ion (mean Cu-N bond length = 2.076(4) Å) while the other is only weakly coordinated (mean Cu-N bond length = 2.707(4) Å). Hence, within the sensitivity limits of infrared spectroscopy, the ligands appear as terminally bonded. A similar situation was observed in the infrared spectrum of Cu(pyz)$_2$(CH$_3$SO$_3$)$_2$ (47). This compound contains two types of bridging pyrazine molecules. One type is involved in relatively strong interactions with copper and the other is involved in very weak coordination to the metal. The latter gives rise to a band at an energy expected for monodentate pyrazine. Thus, the tendency of copper(II) to form distorted coordination geometries should always be borne in mind when applying empirical criteria to its complexes. While such criteria are useful for regular geometries, structural distortions may greatly compromise their utility.

The structural information deduced from the infrared spectra of these complexes is now summarized. The spectrum of Cu(pyz)(NCO)$_2$ indicates that the pyrazine ligands are bridging and the cyanate groups are N-bonded in this compound. A comparison of the powder X-ray diffraction patterns (see below) of this compound and its nickel analogue, whose structure has been more conclusively elucidated (see section 3.1.3), shows the two compounds to be isomorphous thus supporting the structure for the copper compound as depicted in Fig. 2-4. The unsymmetrical nature of the bridging cyanate ligands is suggested by the relatively small splitting of the $\delta_{\text{NCO}}$ band in the infrared spectrum. Unsymmetrical cyanate bridging would also result in a distorted octahedral environment about the metal as is typically observed for six-coordinate copper(II) compounds. It seems possible that Cu(mepyz)(NCO)$_2$ has a
structure similar to that of the pyrazine analogue with possibly more symmetrically bridging cyanate groups as indicated by the greater splitting of the $\delta_{\text{NCO}}$ band. Support for the $>\text{NCO}$ bridging mode in both Cu(pyz)(NCO)$_2$ and Cu(mepyz)(NCO)$_2$ is also provided by their esr spectra (vide infra).

The structure of Cu(py)$_2$(NCO)$_2$, as determined by X-ray crystallography (118), has already been described in the preceding sections. Consistent with the structure the pyridine bands in the infrared spectrum show the shifts expected upon coordination and no evidence of uncoordinated base. The fact that the infrared spectrum suggests that the cyanate groups are terminal N-bonded is a consequence of the rather long Cu-O bond distances in the complex.

The infrared spectrum of Cu(mepyz)$_2$(NCO)$_2$ show that the cyanate groups are terminal N-bonded, consistent with the structure of the compound as determined by a single crystal X-ray diffraction study. In contradiction to the X-ray structure analysis, however, the infrared spectral data suggest that methylpyrazine ligands in Cu(mepyz)$_2$(NCO)$_2$ are terminal monodentate. This inconsistency is reconciled by the observation that one N-atom of each methylpyrazine ligand interacts only very weakly with the metal ions.

No satisfactory infrared criterion for distinguishing between mono- and bi-dentate pyridazine ligands is currently available. It has been suggested that the appearance of a strong peak at 1 430 cm$^{-1}$ attributable to a pyridazine mode is indicative of bridging pyridazine ligand (92). However, there have not been sufficient studies incorporating both infrared spectroscopy and single crystal X-ray diffraction to support this. Free pyridazine exhibits a very strong band at 1 415 cm$^{-1}$ (139). Each of the 9 pyridazine complexes studied in the present work exhibits a corresponding band of medium or strong intensity in the range 1 402-1 425 cm$^{-1}$ (Appendix II-4). No correlation between the denticity of pyridazine and the shift in the position of the 1 415 cm$^{-1}$ free pyridazine band is observed. Specifically none of the complexes show
a strong band at 1 430 cm$^{-1}$. This includes [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$ in which the presence of bridging pyridazine has been confirmed by X-ray crystallography. However, pyridazine coordination in Cu(pdz)(NCO)$_2$ is indicated by the fact that most bands assigned to this ligand are shifted from the free ligand values (139). The splitting of the $\delta_{\text{NCO}}$ cyanate band at 23 cm$^{-1}$ is well above that normally observed for terminal cyanate bonding. The structure we propose for this compound (Fig. 2-5) incorporates the "bent" bridge bonding expected for pyridazine and unsymmetrical cyanate bridging.

Table 2-4. Most coordination sensitive infrared absorption bands of methylpyrazine.$^a$

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mepy$b$</td>
<td>410</td>
<td>472</td>
</tr>
<tr>
<td>Cu(mepy)$_4$(NO$_3$)$_2$b</td>
<td>426</td>
<td>508</td>
</tr>
<tr>
<td>Ni(mepy)$_4$(NO$_3$)$_2$.H$_2$O$b$</td>
<td>432</td>
<td>502</td>
</tr>
<tr>
<td>Cu(mepy)$_4$(CF$_3$SO$_3$)$_2$b</td>
<td>431</td>
<td>505</td>
</tr>
<tr>
<td>Cu(mepy)$_4$(AsF$_6$)$_2$</td>
<td>436</td>
<td>507</td>
</tr>
<tr>
<td>Cu(mepy)$_4$(PF$_6$)$_2$</td>
<td>430</td>
<td>506</td>
</tr>
<tr>
<td>Cu(mepy)$_2$(NCO)$_2$c</td>
<td>436</td>
<td>507</td>
</tr>
<tr>
<td>Cu(mepy)(NO$_3$)$_2$b</td>
<td>444</td>
<td>530</td>
</tr>
<tr>
<td>Ni(mepy)(NO$_3$)$_2$b</td>
<td>444</td>
<td>524</td>
</tr>
<tr>
<td>Cu(mepy)(CF$_3$SO$_3$)$_2$b</td>
<td>466</td>
<td>d</td>
</tr>
<tr>
<td>Cu(mepy)(NCO)$_2$</td>
<td>439</td>
<td>522</td>
</tr>
<tr>
<td></td>
<td>448</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All values are in cm$^{-1}$. $^b$ Data from reference 66. $^c$ See text. $^d$ Obscured by anion band.
Fig. 2-4. Proposed structures for Cu(py2)(NCO)₂ (R = H) and Cu(mepy2)(NCO)₂ (R = CH₃). M = Cu, X = >NCO; the dotted lines illustrate the unsymmetrical nature of the >NCO bridges.

Fig. 2-5. Proposed structure for Cu(pdz)(NCO)₂. M = Cu, X = >NCO; the dotted lines illustrate the unsymmetrical nature of the >NCO bridges.
2.1.5 Powder X-ray diffraction patterns

The mode of cyanate anion coordination in CuL(NCO)\(_2\) (L is pyz, mepyz or pdz) could not be fully established by infrared spectroscopy (section 2.1.4). The modes of coordination of all the ligands in the related nickel compound, Ni(pyz)(NCO)\(_2\), have been ascertained (section 3.1.3). A structure involving chains of nickel ions doubly-bridged by \(>\) NCO anions and cross-linked by bridging pyrazine ligands was proposed for the nickel compound. It was therefore of interest to determine if the nickel and copper compounds are isomorphous.

The powder X-ray diffraction patterns for the four ML(NCO)\(_2\) complexes are shown in Fig. 2-6. The positions of the observed reflections, the observed interplanar spacings and the relative reflection intensities are listed in Appendix III. The powder patterns for Cu(pyz)(NCO)\(_2\) and Ni(pyz)(NCO)\(_2\) are sufficiently similar for one to conclude that the two compounds are isomorphous. This is more evident when one considers the locations of the reflections. Since the chemical compositions of the two compounds are very similar, and with nickel having only one less electron than copper, we conclude that the ligands in the two complexes are bound in a similar fashion.

The other two complexes of the type ML(NCO)\(_2\), Cu(mepyz)(NCO)\(_2\) and Cu(pdz)(NCO)\(_2\), have powder diffraction patterns distinctly different from each other and from those shown by the two M(pyz)(NCO)\(_2\) complexes, the lack of isomorphism here being not too surprising in view of the differing chemical nature of the neutral ligands.
Fig. 2-6. Powder X-ray diffraction patterns for ML(NCO)₂ complexes.
(a) Cu(pyz)(NCO)₂; (b) Ni(pyz)(NCO)₂; (c) Cu(mepy)(NCO)₂; (d) Cu(pdz)(NCO)₂.
2.1.6 Electronic spectra

Each of the copper(II) cyanate complexes exhibits a broad electronic absorption band in the 500-900 nm range (Fig. 2-7). With the exception of the spectrum of Cu(pdz)(NCO)$_2$, a shoulder is observed on the main band. Positions of band maxima are listed in Table 2-5. Such spectra do not provide unambiguous stereochemical information; however, they are typical for tetragonally distorted octahedral copper(II) compounds (140, 141). Distorted octahedral geometries have, in fact, been confirmed for Cu(mepyz)$_2$(NCO)$_2$ (this work) and Cu(py)$_2$(NCO)$_2$ (118) by X-ray structural studies. Although the copper ions in these two compounds are in strictly rhombic octahedral ligand environments, four of the Cu-ligand bonds are approximately equal and considerably shorter than the remaining two, resulting in approximately (4+2) type of coordination.

Table 2-5. Electronic spectral data for compounds of copper(II) cyanate.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption maximum</th>
<th>Shoulder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nm</td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>Cu(mepyz)$_2$(NCO)$_2$</td>
<td>748</td>
<td>13 400</td>
</tr>
<tr>
<td>Cu(pdz)(NCO)$_2$</td>
<td>641</td>
<td>15 600</td>
</tr>
<tr>
<td>Cu(mepyz)(NCO)$_2$</td>
<td>619</td>
<td>16 200</td>
</tr>
<tr>
<td>Cu(py)$_2$(NCO)$_2$</td>
<td>603</td>
<td>16 600</td>
</tr>
<tr>
<td>Cu(py)$_2$(NCO)$_2$</td>
<td>602</td>
<td>16 600</td>
</tr>
</tbody>
</table>

*a* Shoulder not observed but band is very broad and asymmetric.
2.1.7 Electron spin resonance spectra

Most of the esr spectra presented in this chapter exhibit broad line widths. We therefore begin by discussing probable causes for this line broadening. One possible factor is spin-lattice relaxation. Consider an electron whose spin is aligned against an applied field. Its spin can be oriented with the field as a result of a fluctuating field
caused by a magnetic nucleus (any atom with non-zero nuclear moment or another electron) passing by it. As the electron spin goes to the more stable orientation (i.e. relaxes) it gives up its excess energy, as translational or rotational energy, to the passing magnetic nucleus. Since the magnitude of the local fluctuating field varies, the energy of each spin state is spread over a range of energies, hence signal broadening. Another probable cause of the broad line widths is magnetic exchange interactions. Magnetic exchange between adjacent dipoles slightly alters the total field at the ions and the energy levels are shifted, resulting in a distribution of energies. Even a small amount of magnetic exchange is sufficient to influence the esr signal. Thus even complexes which are considered magnetically dilute from magnetic susceptibility measurements may show magnetic exchange effects in their esr spectra. Field inhomogeneity also broadens peaks since, in a bulk sample, electrons in different parts of the sample experience different field strengths resulting in a distribution of frequencies. Peak broadening may also result from unresolved hyperfine splitting.

The $g$ values obtained for the complexes are presented in Table 2-6. Cu(pyz)(NCO)$_2$ and Cu(mepy)(NCO)$_2$ exhibit normal axial spectra ($g_{||} > g_{\perp} > 2.04$), indicative of a $d_{x^2-y^2}$ ground state$^3$ for the Cu$^{2+}$ ion (142). The esr spectra of these two compounds are represented by that of Cu(pyz)(NCO)$_2$ in Fig. 2-8a. The stronger peak is assigned to $g_{\perp}$ because in a sample containing randomly oriented axially symmetric crystallites, there are more possible orientations that have the axially symmetric axis perpendicular to the direction of the applied magnetic field than those that have the axis and the field parallel. The esr spectra of these two compounds are consistent with the proposed $>\text{NCO}$, rather than $-\text{NCO}-$, bridging. The latter form of bridging would produce misaligned tetragonal axes, resulting in either reversed or isotropic spectra (119).

$^3$ A $d_{x^2}$ ground state of the Cu$^{2+}$ ion is characterized by a reversed axial spectrum ($g_{\perp} > g_{||}$) with $g_{||}$ less than 2.03, i.e. $g_{\perp} > g_{||} < 2.03$ (142).
Cu(mepyz)$_2$(NCO)$_2$ has a rhombic esr spectrum (Fig. 2-8b). As established by X-ray crystallography, the copper ions in Cu(mepyz)$_2$(NCO)$_2$ have an elongated rhombic-octahedral geometry. For such a complex, a rhombic spectrum in which the lowest $g > 2.04$ is consistent with a $d_{x^2-y^2}$ ground state for the Cu$^{2+}$ ion (142).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$g_1^b$</th>
<th>$g_2^b$</th>
<th>$g_3$</th>
<th>$g_0^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(pyz)(NCO)$_2$</td>
<td>2.288</td>
<td>2.077</td>
<td></td>
<td>2.147</td>
</tr>
<tr>
<td>Cu(mepyz)$_2$(NCO)$_2$</td>
<td>2.212</td>
<td>2.150</td>
<td>2.057</td>
<td>2.140</td>
</tr>
<tr>
<td>Cu(mepyz)(NCO)$_2$</td>
<td>2.280</td>
<td>2.079</td>
<td></td>
<td>2.146</td>
</tr>
<tr>
<td>Cu(pdz)(NCO)$_2$</td>
<td></td>
<td></td>
<td></td>
<td>2.094</td>
</tr>
<tr>
<td>Cu(py)$_2$(NCO)$_2$</td>
<td></td>
<td></td>
<td></td>
<td>2.180</td>
</tr>
</tbody>
</table>

- Data collected at $\approx$ 90 K. Error in $g$ values, $\pm$ 0.003.
- When only two $g$ values are observed $g_1 = g_{||}$ and $g_2 = g_{\perp}$.
- $g_0$ = isotropic $g$ value. For orthorhombic and axial systems $g_0 = (g_1 + g_2 + g_3)/3$ and $g_0 = (g_{||} + 2g_{\perp})/3$, respectively.

Cu(py)$_2$(NCO)$_2$ exhibits a reversed near isotropic esr spectrum (Fig. 2-8c). This compound has been found to exist in two forms, $\alpha$ and $\beta$, both of which have been characterized by esr spectroscopy (119). The esr spectrum reported here confirms the conclusion based on the infrared spectrum discussed earlier, that the compound prepared in the present work is the $\beta$ isomer. A reversed esr spectrum for a six coordinate copper(II) complex may indicate (142, 143) (i) a tetragonally compressed copper(II) chromophore ($d_{z^2}$ ground state) or (ii) misalignment of the local molecular axes of the separate copper(II) chromophores ($d_{x^2-y^2}$ ground state) in the unit cell. With misaligned axes exchange broadening occurs, resulting in a near isotropic signal. When there is total misalignment, i.e. the angle between corresponding axes is 90°, a
reversed axial spectrum is observed. The two cases above may be distinguished by the observation (142, 143) that in (i) \( g_{||} < 2.03 \) and in (ii) \( g_{||} > 2.03 \). Thus the reversal of the esr spectrum of \( \text{Cu(py)}_2(\text{NCO})_2 \) \( (g_{||} \approx 2.05) \) is attributed to case (ii). Since for this compound \( g_{||} \) is close to 2.03 and not well resolved, the use of this criterion in itself is clearly not satisfactory. However, it is known for a fact from a single crystal structural study that the tetragonal axes of adjacent copper ions in \( \text{Cu(py)}_2(\text{NCO})_2 \) are approximately orthogonal (118).

\( \text{Cu(pdz)}(\text{NCO})_2 \) exhibits a single broad asymmetric signal (Fig. 2-8d). For a six coordinate copper(II) complex such a spectrum is suggestive of the \( \text{Cu}^{2+} \) ion in (142) (i) a regular octahedral stereochemistry undergoing a dynamic or pseudo-rotational type of Jahn-Teller distortion, (ii) a lower symmetry than octahedral but undergoing free rotation or (iii) a complex containing grossly misaligned tetragonal axes. The polymeric nature of \( \text{Cu(pdz)}(\text{NCO})_2 \) renders (i) and (ii) unlikely whereas case (iii) is consistent with the proposed structure for this compound (Fig. 2-5). \( \text{Cu(pdz)}(\text{NCO})_2 \) has been shown by magnetic susceptibility studies (vide infra) to be strongly antiferromagnetically coupled. This factor most probably accounts for its very broad esr signal.

None of copper(II) cyanate complexes exhibit electron spin-nuclear spin hyperfine splitting in their esr spectra despite the fact that they contain atoms with non-zero nuclear moments (Cu, \( 3/2 \); N, 1; H, 1/2). It is, therefore, not possible to determine the extent to which the copper(II) d electron is delocalized into the ligand orbitals. The non observance of any hyperfine splitting of the esr signal is, however, not surprising in view of the broad nature of the spectral band widths and the fact that such splittings are generally small in copper(II) complexes. For example, in the compounds \( \text{CuL}_4\text{A}_2 \) (where \( \text{L} \) is pyridine, 3-methylpyridine or 4-methylpyridine and \( \text{A} \) is \( \text{PF}_6, \text{AsF}_6, \text{ClO}_4, \text{BF}_4, \text{FSO}_3 \) or \( \text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3 \)) \( \text{A}_{\perp} \) was found to be of the order of only 20 G and \( \text{A}_{||} \) of the order of 190 G (141).
Fig. 2-8. Esr spectra of copper(II) cyanate complexes. (a) Cu(pyz)(NCO)$_2$; (b) Cu(mepy)$_2$(NCO)$_2$; (c) Cu(py)$_2$(NCO)$_2$; (d) Cu(pdz)(NCO)$_2$. dA/dH = first derivative of absorption curve.
2.1.8 Magnetic properties

Magnetic susceptibility and moment data for the copper(II) cyanate complexes are given in Appendix IV. Cu(py)$_2$(NCO)$_2$ and Cu(mepy$_z$)$_2$(NCO)$_2$ exhibit temperature independent magnetic moments of 1.81 and 1.84 B.M. respectively over the temperature range 82 to 2.4 K. This behaviour is typical of magnetically dilute copper(II) complexes (144). The absence of significant magnetic exchange coupling in these two compounds is a consequence of the fact that the bridging entities in both complexes are unsymmetrical. The asymmetry indicates that the orbitals of the bridging units do not overlap with the orbitals of the two metal centres, which they bridge, to the same extent. In such cases, poor overlap with the orbitals of either of the metal ions adversely affects the ability of the bridging unit to facilitate magnetic exchange. In Cu(py)$_2$(NCO)$_2$, the Cu-N and Cu-O bonds lengths involving the bridging cyanate groups are 1.946(6) Å and 2.607(5) Å, respectively. In Cu(mepy$_z$)$_2$(NCO)$_2$, the mean Cu-N bond length involving the bridging methylpyrazine molecules is 2.076(4) Å for the nitrogen atom meta to the methyl substituent and 2.707(4) Å for the ortho nitrogen atom. As a result of the long (>2.6 Å) copper-ligand bond lengths in the bridging groups, the separation between copper ions in both compounds is too large for magnetic interactions to take place. In Cu(mepy$_z$)$_2$(NCO)$_2$, for example, the distance between two copper ions bridged by methylpyrazine is 7.486(2) Å. The magnetic properties of Cu(mepy$_z$)$_2$(NCO)$_2$ may also be rationalized as follows. The esr spectrum of this compound is consistent with the unpaired electron of each copper ion residing in the d$_{x^2-y^2}$ orbital (vide supra). The geometry around each copper ion may be viewed as a tetragonally elongated octahedron. The "tetragonal axes" of all the copper chromophores lie in the same plane. However the axes on adjacent chromophores are inclined to one another such that a methylpyrazine bridge between two copper centres interacts with a magnetic orbital (d$_{x^2-y^2}$) of one
copper ion and a non-magnetic orbital (d_{z^2}) of the second copper ion. Thus there is no continuous path for magnetic exchange between the copper ions in this compound.

Cu(pyz)(NCO)\textsubscript{2} and Cu(mepy)_2(NCO)\textsubscript{2} exhibit temperature dependent magnetic moments ranging from 1.79 and 1.71 B.M., respectively, at 81 K down to 1.16 and 1.10 B.M. at about 2.3 K. The copper ions in both compounds are clearly antiferromagnetically coupled. The exchange coupling is, however, relatively weak in view of the fact that no susceptibility maximum is observed over the temperature range studied. From spectroscopic and powder X-ray diffraction studies (vide supra) Cu(pyz)(NCO)\textsubscript{2} and Cu(mepy)(NCO)\textsubscript{2} were assigned structures as depicted in Fig. 2-4 in which copper(II) ions are linked by unsymmetrically bridging cyanate anions to form chains. The chains are then cross-linked into sheets by the neutral ligands. Possible pathways for the exchange are via the bridging neutral ligands and/or the anionic ligands. Accordingly we examined fits of the susceptibilities to both the one- and two-dimensional isotropic Heisenberg models described below.

The variation of magnetic susceptibility with temperature in linear chains of antiferromagnetically coupled copper(II) ions may be described by the Heisenberg model of isotropic exchange coupling (20). Bonner and Fisher (145) carried out calculations on short chains and rings (2 to 11 paramagnetic centres) for S = 1/2 spins and extrapolated their results to the limit of an infinite chain. They presented their results graphically. Since an exact expression for the magnetic susceptibility of an infinite chain has not been derived, Hall (146) developed a polynomial which describes the results of Bonner and Fisher (145) very well. The polynomial is referred to as the Heisenberg one-dimensional model in this thesis and is represented by the expression (20):

\[
\chi_m = \frac{Ng^2\beta^2}{kT} \left( \frac{0.250 + 0.14995x^{-1} + 0.30094x^{-2}}{1 + 1.9862x^{-1} + 0.68854x^{-2} + 6.0626x^{-3}} \right) \quad [2-1]
\]
where \( N \) is Avogadro's number, \( g \) is the Landé splitting factor, \( \beta \) is the electron Bohr magneton, \( k \) is Boltzmann's constant, \( x = kT/|J| \), \( T \) is the temperature, \( \chi_m \) is the molar magnetic susceptibility and \( J \) is the exchange coupling constant.

The two-dimensional model used in this work was developed by Lines (147) following the work of Rushbrooke and Wood (148). The latter derived expressions for the magnetic susceptibility and inverse magnetic susceptibility, in ascending powers of the reciprocal temperature, for the isotropic Heisenberg model of any spin and any lattice. They determined the first six coefficients of the series expansion for ferromagnetic systems and suggested the procedure that could be adopted in the treatment of antiferromagnetic systems (148). Following this, Lines (147) developed an expression for an antiferromagnetic two-dimensional square lattice. The expression, henceforth referred to as Lines (two-dimensional) model, is:

\[
\frac{Ng^2\beta^2}{\chi_mJ} = 3\theta + \sum_{n=1}^{\infty} \frac{C_n}{\theta^{n-1}} \quad [2-2]
\]

where \( \theta = kT/JS(S+1) \), \( S \) is the spin of the interacting metal ions, and \( N \) \( g \) \( \beta \), \( J \), \( k \) and \( \chi_m \) are as defined above. The coefficients, \( C_n \), have been determined for values of \( n \) up to 6. For \( S = 1/2 \) these coefficients are (147): \( C_1 \), 4; \( C_2 \), 2.667; \( C_3 \), 1.185; \( C_4 \), 0.149; \( C_5 \), -0.191; \( C_6 \), 0.001. As has already been pointed out by other authors (149), the \( J \) obtained from equation 2-2 is equal to \( 2J \) as reported by Rushbrooke and Wood. The \( J \) in all other models used in this thesis are defined in the same way as that of Rushbrooke and Wood. Hence, for the sake of consistency, the \( J \) values obtained by the use of equation 2-2 and reported in this thesis have been divided by 2.

Occasionally it becomes necessary to correct for the effects of structural paramagnetic impurities on the observed magnetic susceptibilities. In such cases a Curie law term, as represented by equation 2-3 is incorporated into the relevant model and the susceptibility data analyzed according to equation 2-4.
\[ \chi_{\text{para}} = \frac{N g^2 \beta^2 S(S+1)}{3kT}. \]  \[\text{[2-3]}\]

\[ \chi_{\text{cald}} = (1-P)\chi_m + P\chi_{\text{para}}. \]  \[\text{[2-4]}\]

In equation 2-3, \( S \) is the spin of the magnetic ion. All the other terms are as defined above. The term \( P \), in equation 2-4, when multiplied by 100 is termed the percent paramagnetic impurity (\( \%P \)).

The magnetic susceptibilities of Cu(pyz)(NCO)\(_2\) and Cu(mepyz)(NCO)\(_2\) were analyzed by the two models discussed above. Selected best fits are shown in Figs. 2-9 and 2-10 for Cu(pyz)(NCO)\(_2\) and Cu(mepyz)(NCO)\(_2\), respectively. The best fit parameters are given in Table 2-7. The best fit was considered to be that set of fitting parameters which gave the minimum value of the function \( F \), defined as follows.

\[ F = \left( \frac{1}{NT} \sum_{i}^{NT} \left( \frac{\chi_{\text{cald}}^{i} - \chi_{\text{obs}}^{i}}{\chi_{\text{obs}}^{i}} \right)^2 \right)^{1/2}. \]  \[\text{[2-5]}\]

where \( NT \) is the number of data points, and \( \chi_{\text{obs}}^{i} \) and \( \chi_{\text{cald}}^{i} \) are the observed and calculated susceptibilities respectively. The value of the fitting function, \( F \), also provides a measure of the quality of fit. Initially both \( J \) and \( g \) were treated as adjustable parameters. The two models gave good fits for both Cu(pyz)(NCO)\(_2\) and Cu(mepyz)(NCO)\(_2\) although, as judged by the value of \( F \), better agreement between theory and experiment is given by the one-dimensional model. In view of this, and the fact that >NCO bridging ligands have been shown to provide pathways for ferromagnetic rather than antiferromagnetic exchange (116) we conclude that the weak exchange observed in these compounds is transmitted along the chains formed by the
Fig. 2-9. Magnetic susceptibility versus temperature plots for Cu(pyz)(NCO)$_2$.
(a) Linear chain model, solid line generated from $J = -1.15$ cm$^{-1}$, $g = 2.12$; (b) Lines two-dimensional model, solid line generated from $J = -0.70$ cm$^{-1}$, $g = 2.12$. 
Fig. 2-10. Magnetic susceptibility versus temperature plots for Cu(mepyz)(NCO)$_2$.
(a) Linear chain model, solid line generated from $J = -1.17$ cm$^{-1}$, $g = 2.02$;
(b) Linear chain model, solid line generated from $J = -1.43$ cm$^{-1}$ ($g$ fixed at the esr determined value of 2.15).
Table 2-7. Magnetic parameters\(^a\) for compounds of copper(II) cyanate.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(-J (\text{cm}^{-1}))</th>
<th>(g)</th>
<th>(%P)</th>
<th>(F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cu(pyz)(NCO)}_2)(^b)</td>
<td>1.15</td>
<td>2.12</td>
<td>0</td>
<td>0.0105</td>
</tr>
<tr>
<td></td>
<td>1.22</td>
<td>2.15</td>
<td>0</td>
<td>0.0253</td>
</tr>
<tr>
<td>(\text{Cu(mepy)(NCO)}_2)(^b)</td>
<td>1.17</td>
<td>2.02</td>
<td>0</td>
<td>0.0135</td>
</tr>
<tr>
<td></td>
<td>1.43</td>
<td>2.15</td>
<td>0</td>
<td>0.0968</td>
</tr>
<tr>
<td>(\text{Cu(pdz)(NCO)}_2)(^c)</td>
<td>38.0</td>
<td>2.09</td>
<td>0</td>
<td>0.1631</td>
</tr>
<tr>
<td></td>
<td>44.0</td>
<td>2.09</td>
<td>3.02</td>
<td>0.0420</td>
</tr>
</tbody>
</table>

\(^{a}\) Estimated error limits: \(g\), \(\pm 0.02\); \(\%P\), negligible; \(-J\), \(\pm 0.04\ \text{cm}^{-1}\) for \(\text{Cu(pyz)(NCO)}_2\) and \(\text{Cu(mepy)(NCO)}_2\) and \(\pm 1.5\) for \(\text{Cu(pdz)(NCO)}_2\).

\(^{b}\) \(J\) and \(g\) varied. \(\%P\) set at zero.

\(^{c}\) Only \(J\) varied. \(\%P\) set set at zero and \(g\) set to \(g_0\) determined by esr.

\(^{d}\) \(J\) and \(\%P\) varied. \(g\) set to \(g_0\) determined by esr.

...bridging neutral ligands. The apparent lack of contribution to the exchange from the bridging NCO\(^-\) anions may be a consequence of the unsymmetrical bridge bonding. It is interesting to note that the magnitude of the exchange is the same whether the bridge is pyrazine or methylpyrazine. The equivalency of these ligands' abilities to mediate magnetic exchange has been observed previously by Richardson and Hatfield (15) who observed similar exchange coupling constants for the chain compounds \(\text{Cu(pyz)(NO}_3)_2\) (-\(J = 3.7\ \text{cm}^{-1}\)) and \(\text{Cu(mepy)(NO}_3)_2\) (-\(J = 3.1\ \text{cm}^{-1}\)). In addition we note that the magnitude of the exchange in such systems does appear to be a function of the nature of...
the other ligands involved. The magnitude of the exchange is about three times greater in Cu(pyz)(CF3SO3)2 (\(-J = 3.78 \text{ cm}^{-1}\)) than in Cu(pyz)(NCO)2 and Cu(mepyz)(NCO)2. The former compound is also considered to have a structure of the type shown in Fig. 2-4 and a similar exchange pathway involving bridging pyrazine groups (68). Presumably the more weakly basic triflate anion interacts only weakly with the copper. This would lead to stronger bonds between copper and pyrazine and hence stronger exchange.

The \(g\) value obtained from the theoretical analysis of the magnetic susceptibility data of Cu(pyz)(NCO)2 is comparable to the isotropic value, \(g_o\), calculated from the esr spectral data. In the case of Cu(mepyz)(NCO)2, the theoretical \(g\) value is significantly lower than the experimental one. Hence the magnetic susceptibility data were also modelled with \(J\) as the only variable parameter and with \(g\) set equal to the esr \(g_o\) value. The resulting fits were of poorer quality than those obtained when both \(J\) and \(g\) were varied. Attempts were then made to account for the possible influence of paramagnetic impurities on the magnetic susceptibility data of both Cu(pyz)(NCO)2 and Cu(mepyz)(NCO)2. The \(g\) values were set equal to the \(g_o\) values determined by esr and only \(J\) and \(P\) were varied. We were, however, unable to obtain good agreement between theory and experiment. Thus although good fits were obtained for the two compounds under discussion when only \(J\) and \(g\) were varied, the reason for the rather low \(g\) value (in comparison to the esr derived \(g_o\)) obtained for Cu(mepyz)(NCO)2 is not clear.

Cu(pdz)(NCO)2 has a strongly temperature dependent magnetic moment, ranging from 1.63 B.M. at 300 K to 0.43 B.M. at 5 K. This is depicted in Fig. 2-11, along with the corresponding data for the magnetically dilute complex Cu(py)2(NCO)2, for comparison. The strong temperature dependence of the magnetic moment of Cu(pdz)(NCO)2 indicates the presence of relatively strong antiferromagnetic coupling.
This is confirmed by the plot of magnetic susceptibility versus temperature which exhibits a broad maximum around 65 K (Fig. 2-12). An increase in susceptibility at the lowest temperatures of the type seen here is often observed in strongly antiferromagnetically coupled copper(II) complexes and has been accounted for by the presence of small amounts of paramagnetic structural impurities (150). We proposed for Cu(pdz)(NCO)$_2$ a chain structure in which copper ions are triply bridged by pyridazine ligands and unsymmetrical cyanate ions (section 2.1.4., Fig. 2-5). Hence its susceptibility data were analyzed according to the one-dimensional isotropic Heisenberg model for $S = 1/2$ (eqn. 2-1). Experiment and theory are compared in Fig. 2-12 and the best fit values of the magnetic parameters are given in Table 2-7. A good fit was obtained by treating $J$ and $P$ as the adjustable parameters, with $g$ set equal to the value obtained experimentally by esr spectroscopy.

In view of the structure proposed for Cu(pdz)(NCO)$_2$, bridging $>$NCO- or pyridazine ligands may provide the pathway for exchange. Considering the unsymmetrical nature of the $>$NCO- bridges and the fact that these ligands would be expected to transmit ferromagnetic rather than antiferromagnetic exchange (116), we conclude that the cyanate ligands are not responsible for the magnetic exchange observed in Cu(pdz)(NCO)$_2$. Furthermore, the esr spectrum of this compound (vide supra) is consistent with a structure containing misaligned tetragonal axes such as that proposed for this compound (dotted lines in Fig. 2-5). As observed for Cu(mepyz)$_2$(NCO)$_2$ above, such misaligned axes may lead to a situation where the bridging unit occupying an axial coordination site interacts with a magnetic orbital of one copper ion and a non-magnetic orbital of the second copper ion. Hence, according to the structure proposed for Cu(pdz)(NCO)$_2$, the cyanate groups would not be expected to facilitate magnetic exchange. Thus, pyridazine ligands are considered to provide the primary exchange pathway in Cu(pdz)(NCO)$_2$. This conclusion is supported by the observation that the magnitude of exchange in the cyanate compound
(-J = 44.0 cm\(^{-1}\)) is comparable to that reported for Cu(pdz)Cl\(_2\) (-J = 35.8 cm\(^{-1}\)) and Cu(pdz)Br\(_2\) (-J = 31.7 cm\(^{-1}\)) (99). The latter complexes are chain polymers involving just pyridazine bridges (89).

Many exchange coupled pyrazine-bridged complexes of copper(II) have been studied and the largest value of J so far obtained for these is -16.8 cm\(^{-1}\) in Cu(py disproportionator)Br\(_2\) (17). Pyridazine, which provides a shorter, two-atom bridge, would appear to provide a more facile pathway for magnetic exchange in copper(II) systems than does pyrazine. Support for this conclusion comes from the observation that pyrazolyl, a 5-membered heterocyclic ligand which also offers a two N-atom bridge, has been found to propagate magnetic exchange with very high efficiency (27, 151, 152). Strong antiferromagnetic exchange with \(|J|\) values in the range 81 to 105 cm\(^{-1}\) has been observed in a number of copper pyrazolate polymers (151, 152).

![Fig. 2-11. Magnetic moment versus temperature plots for Cu(py)\(_2\)(NCO)\(_2\) and Cu(pdz)(NCO)\(_2\).](image-url)
Fig. 2-12. Magnetic susceptibility versus temperature plots for Cu(pdz)(NCO)$_2$.
(a) Linear chain model, solid line generated from $J = -38.0$ cm$^{-1}$ ($\%P$ set equal to zero); (b) Linear chain model, solid line generated from $J = -44.0$ cm$^{-1}$, $\%P = 3.02$.
In both cases $g$ was set equal to the esr determined value of 2.09.
2.2 Complexes of copper(II) nitrate

2.2.1 Introduction

Cu(pyz)(NO₃)₂ is a linear polymer in which copper(II) ions are bridged by pyrazine ligands (41). A distorted octahedral configuration about each copper centre is completed by two unsymmetrically chelating nitrate groups. Shortly after the structure of this compound was determined in 1970 it was demonstrated that, despite the long separation between the copper ions (6.712 Å) along the chain, there is significant antiferromagnetic coupling between them (69-72). The susceptibility data of Cu(pyz)(NO₃)₂ exhibits a maximum at about 7 K. Antiferromagnetic coupling has since been observed in complexes with substituted pyrazine bridges which are assumed to be isostructural (i.e. CuL(NO₃)₂ where L is Clpyz, mepyz, 2,5- and 2,6-me₂pyz and phenazine) (15) as well as in Cu(pyz)₃(NO₃)₂ (66). The latter compound has also been proposed to have a structure consisting of linear -Cu-pyz-Cu- chains but with six-coordination about copper ions achieved through monodentate pyrazine and nitrate groups. These studies clearly demonstrated that pyrazine type ligands are capable of transmitting magnetic exchange between copper(II) centres. Hence, as part of our search for and study of magnetic exchange effects in transition metal complexes, we decided to investigate complexes formed between copper(II) nitrate and pyridazine. We present in this section results of our studies on [Cu(pdz)₂(NO₃)₂]₃, Cu(pdz)₃(NO₃)₂, [Cu(pdz)₄(NO₃)]₂[NO₃] and Cu(pdz)₄(NO₃)₂. Their syntheses are described in section 5.2.2. We refer to [Cu(pdz)₄(NO₃)]₂[NO₃] and Cu(pdz)₄(NO₃)₂ as the blue and violet forms of Cu(pdz)₄(NO₃)₂ respectively. The structures of [Cu(pdz)₂(NO₃)₂]₃, Cu(pdz)₃(NO₃)₂ and [Cu(pdz)₄(NO₃)]₂[NO₃] were determined by single crystal X-ray diffraction studies in the present work. A mononuclear structure for Cu(pdz)₄(NO₃)₂
involving six-coordinate copper is proposed on the basis of indirect evidence to be presented in this chapter.

\([\text{Cu}(\text{pdz})_2(\text{NO}_3)_2]_3\) is air-stable and was manipulated in the atmosphere but samples were stored in a desiccator. The tetrakis(pyridazine) complexes are unstable and readily darken, whether stored in an inert atmosphere or in air. These complexes were generally handled in an inert atmosphere although no such precautions were taken with the single crystal used in the X-ray analysis of \([\text{Cu}(\text{pdz})_4(\text{NO}_3)]\text{[NO}_3]\). \(\text{Cu}(\text{pdz})_3(\text{NO}_3)_2\) is also unstable and changes colour from bright (royal) blue to greenish blue on standing. For any one of the above unstable compounds the time taken for the colour changes to be observed vary from preparation to preparation, ranging from a few days to several months. We attribute the colour changes, and therefore presumably structural rearrangements, to the release of free pyridazine. This ligand is known to discolor when illuminated (63).

We also report in this section electron spin resonance spectral studies on the related pyrazine and methylpyrazine compounds, \(\text{Cu}(\text{pyz})_3(\text{NO}_3)_2\), \(\text{Cu}(\text{pyz})(\text{NO}_3)_2\), \(\text{Cu}(\text{mepy}z)_4(\text{NO}_3)_2\) and \(\text{Cu}(\text{mepy}z)(\text{NO}_3)_2\). These compounds have already been characterized by the other physical methods used in this study (66).

2.2.2 Synthesis

Pyridazine reacts with ethanolic solutions of copper(II) nitrate trihydrate to give a series of complexes. Synthetic details are presented in section 5.2.2.; however, we find the reactions remarkable and deserving of further comment here. When the ratio of pyridazine to copper is between 1 and 1.5 \([\text{Cu}(\text{pdz})_2(\text{NO}_3)_2]_3\) is obtained. The most remarkable aspect of the reactions of pyridazine and copper(II) nitrate is the observation that under conditions where the ligand to metal ratio is approximately equal
to 4.0 one or the other of three products, never a mixture, is obtained. The three complexes are (i) a blue crystalline material characterized by single crystal X-ray diffraction to be a five-coordinate complex, \([\text{Cu(pdz)}_4(\text{NO}_3)]\)[\text{NO}_3], (ii) a violet powder indirectly characterized as \(\text{trans-Cu(pdz)}_4(\text{NO}_3)_2\), and (iii) a blue crystalline material characterized by single crystal X-ray diffraction to be a six-coordinate complex, \(\text{Cu(pdz)}_3(\text{NO}_3)_2\).

Each of the products was obtained more than once and it is now reasonably well established that while \(\text{Cu(pdz)}_3(\text{NO}_3)_2\) is sometimes obtained when the ligand to metal ratio is near 4.0, it is the only product when the ligand to metal ratio is between 2 and 3. Similarly while \(\text{Cu(pdz)}_4(\text{NO}_3)_2\) is sometimes obtained when the ligand to metal ratio is near 4, a ratio of about 6:1 always yields the violet \(\text{Cu(pdz)}_4(\text{NO}_3)_2\). The precise conditions required for the reproducible synthesis of \([\text{Cu(pdz)}_4(\text{NO}_3)]\)[\text{NO}_3] remain uncertain. However, unlike \(\text{Cu(pdz)}_4(\text{NO}_3)_2\) and \(\text{Cu(pdz)}_3(\text{NO}_3)_2\), it was only obtained when the ligand to metal ratio was slightly greater than 4.0. The possibility that \([\text{Cu(pdz)}_4(\text{NO}_3)]\)[\text{NO}_3] may be an intermediate in the formation of \(\text{Cu(pdz)}_4(\text{NO}_3)_2\) is not supported by observations. If this were so, then crystals of the former returned to the solvent should eventually convert to the latter. This, however, has not been observed. It seems that \([\text{Cu(pdz)}_4(\text{NO}_3)]\)[\text{NO}_3] and \(\text{Cu(pdz)}_4(\text{NO}_3)_2\) are products of two different pathways; however, it is puzzling that mixtures of the two are never observed. A possible explanation for the isolation of any one of the three products from the same concentration of the reagents, without obtaining a mixture, is as follows. Under conditions where the ligand to metal ratio is slightly greater than 4.0 the principle species in equilibrium in ethanol are:

\[
\text{Cu(pdz)}_4(\text{NO}_3)_2 \rightleftharpoons [\text{Cu(pdz)}_4(\text{NO}_3)]^+ + \text{NO}_3^-.
\]  

[2-6]

The neutral species is only slightly soluble in the solvent but readily forms supersaturated solutions, i.e. needs seeding to precipitate. As the \(\text{Cu(NO}_3)_2\) solution is
added to pyridazine, the solubility of $[\text{Cu}(\text{pdz})_4(\text{NO}_3)]^{+}[\text{NO}_3]^-$ is eventually exceeded (as long as Cu(pdz)$_4$(NO$_3$)$_2$ has not precipitated) and the product crystallizes. In the case when the ligand to metal ratio is 4 or slightly less, then Cu(pdz)$_3$(NO$_3$)$_2$ is also in equilibrium with the species shown in equation 2-6. In this case one may get either the tris- or tetrakis(pyridazine) complexes, with the latter generated only if the effective ligand to metal ratio is greater than 4.

It was observed that rapid precipitation generally occurred on mixing pyridazine and copper(II) nitrate trihydrate in approximately 4:1 or 3:1 mole ratios in ethanol. In some experiments, however, immediate precipitation was not observed. In these, X-ray quality crystals of $[\text{Cu}(\text{pdz})_4(\text{NO}_3)][\text{NO}_3]$ and Cu(pdz)$_3$(NO$_3$)$_2$ formed from the 4:1 and 3:1 mixtures, respectively. Perhaps, as alluded to above, saturated solutions are formed under the experimental conditions used. The time of seeding would then determine the rate of precipitation.

2.2.3 The crystal structure of $[\text{Cu}(\text{pdz})_4(\text{NO}_3)][\text{NO}_3]$

The crystallographic data for $[\text{Cu}(\text{pdz})_4(\text{NO}_3)][\text{NO}_3]$ together with the dimensions of the nitrate groups and copper-ligand bond lengths are given in Table 2-8. A more detailed compilation of its structural data can be found in Appendix I-2. The atom numbering scheme is illustrated in Fig. 2-13 while a stereoview of the geometry around the copper ion is shown in Fig. 2-14a.

A five-coordinate metal complex can have two regular geometries, square pyramidal or trigonal bipyramidal. Compounds with these regular geometries as well as those exhibiting a wide range of intermediate geometries are known (134). $[\text{Cu}(\text{pdz})_4(\text{NO}_3)][\text{NO}_3]$ falls into the latter category. Its structure may be regarded as a grossly distorted trigonal bipyramid in which two monodentate pyridazine ligands and
Table 2-8. Crystal data, nitrate group dimensions and copper-ligand bond lengths for [Cu(pdz)$_4$(NO$_3$)][NO$_3$].

<table>
<thead>
<tr>
<th>Crystal data</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/c$ (#14)</td>
<td></td>
</tr>
<tr>
<td>$a$, Å</td>
<td>10.6425(9)</td>
<td></td>
</tr>
<tr>
<td>$b$, Å</td>
<td>16.442(1)</td>
<td></td>
</tr>
<tr>
<td>$c$, Å</td>
<td>11.9930(6)</td>
<td></td>
</tr>
<tr>
<td>$\beta$, deg</td>
<td>98.225(6)</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>$V$, Å$^3$</td>
<td>2076.9(2)</td>
<td></td>
</tr>
<tr>
<td>$\rho_{\text{calcd}}$, g cm$^{-3}$</td>
<td>1.624</td>
<td></td>
</tr>
<tr>
<td>$F(000)$</td>
<td>1036</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>0.034</td>
<td></td>
</tr>
<tr>
<td>$R_w$</td>
<td>0.040</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-O(1)</td>
<td>2.217(2)</td>
<td>O(1)$^b$-N(9)</td>
</tr>
<tr>
<td>Cu(1)-N(1)</td>
<td>2.014(2)</td>
<td>O(2)-N(9)</td>
</tr>
<tr>
<td>Cu(1)-N(3)</td>
<td>2.021(2)</td>
<td>O(3)-N(9)</td>
</tr>
<tr>
<td>Cu(1)-N(5)</td>
<td>2.029(2)</td>
<td>O(4)-N(10)$^c$</td>
</tr>
<tr>
<td>Cu(1)-N(7)</td>
<td>2.018(2)</td>
<td>O(5)-N(10)$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(6)-N(10)$^c$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles (deg)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-N(9)-O(2)</td>
<td>119.9(2)</td>
<td>O(4)-N(10)-O(5)$^c$</td>
</tr>
<tr>
<td>O(1)-N(9)-O(3)</td>
<td>119.0(2)</td>
<td>O(4)-N(10)-O(6)$^c$</td>
</tr>
<tr>
<td>O(2)-N(9)-O(3)</td>
<td>122.4(3)</td>
<td>O(5)-N(10)-O(6)$^c$</td>
</tr>
</tbody>
</table>

$^a$ Standard deviations in the last digit are given in parentheses.

$^b$ Coordinated to copper ion.

$^c$ Involving ionic nitrate group.
Fig. 2-13. Atom labelling scheme for [Cu(pdz)$_4$(NO$_3$)][NO$_3$].
Fig. 2-14. Stereoviews of (a) the geometry about copper and (b) the unit cell packing diagram in Cu(pdz)$_4$(NO$_3$)$_2$[NO$_3$]. In (a) 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.
one monodentate nitrate ion define the equatorial plane. The angles in this plane subtended by the donor atoms of the ligands at the copper centre are: \( O(1)-Cu(1)-N(1) = 99.54(7)° \), \( O(1)-Cu(1)-N(3) = 109.68(8)° \) and \( N(1)-Cu(1)-N(3) = 150.46(8)° \). The two remaining pyridazine ligands, also monodentate, occupy the axial positions \( (N(5)-Cu(1)-N(7) = 176.10(8)°) \). The six \( L_\alpha-Cu-L_i \) \( (L_\alpha \) and \( L_i \) represent donor atoms of the axial and in-plane ligands respectively) angles all lie in the range 88-95°. In a regular trigonal bipyramidal geometry, these angles are 90°. Alternatively, \([Cu(pdz)_4(NO_3)][NO_3]\) may be viewed as having a distorted square pyramidal structure in which the "square" plane is defined by the four donor nitrogen atoms from the pyridazine ligands while the oxygen atom from the nitrate group occupies the apical position. The angles subtended by the \textit{trans} in-plane ligands at the copper centre, \( N(1)-Cu(1)-N(3) \) and \( N(5)-Cu(1)-N(7) \), are 150.46(8)° and 176.10(8)°, respectively, instead of 180°. Further angular distortions are observed in the angles \( L_\alpha-Cu-L_i \) which lie in the range 88-110° and \( L_i-Cu-L_i \) which lie in the range 88-93°. These angles are 90° in a regular square pyramidal geometry. Since \([Cu(pdz)_4(NO_3)][NO_3]\) possess none of the symmetry elements characteristic of either regular trigonal bipyramidal or square pyramidal geometry, the geometrical arrangement of the ligands around the copper ion is best described simply as irregular.

The free nitrate ion has a symmetrical planar structure with all O-N-O angles equal to 120° and N-O bond lengths equal to 1.245(2) Å (153). In a previous study on a number of copper(II) and nickel(II) complexes containing monodentate terminal nitrate groups (154) it was found that the N-O bond involving the coordinated oxygen atom is longer (1.26-1.32 Å), and those involving the other two oxygen atoms are shorter (1.21-1.24 Å), than the N-O bonds of the free nitrate ion. It was also observed that the O-N-O bond angle opposite the coordinated oxygen atom is generally greater, and the other two less, than 120°. Thus the internal bonding parameters of the coordinated nitrate group in \([Cu(pdz)_4(NO_3)][NO_3]\) (Table 2-8) are in good agreement
with those reported in the literature. The N-O bond distances of the non-coordinated NO$_3^-$ ion are all approximately equal (average = 1.214 Å) and compare favourably with values previously reported for transition metal complexes containing ionic nitrate groups (155). For instance, the average N-O$_{\text{nitrato}}$ distance in [Cu(2,2'-bipy)$_2$NO$_2$]$^+$/[NO$_3$]$^-$ is 1.21 Å (155).

All the pyridazine rings in [Cu(pdz)$_4$(NO$_3$)][NO$_3$] are planar within experimental error. Their internal bonding parameters are comparable to those that have been observed in other complexes. For example, in Table 2-9, selected bonding parameters are compared to those observed in Fe(pdz)(CO)$_4$ (82) and [(CH$_3$)$_2$SnCl]$_2$(CH$_2$)(pdz) (43). The former contains terminal, and the latter bridging, pyridazine ligands.

There is extensive hydrogen-bonding (H-bonding) in [Cu(pdz)$_4$(NO$_3$)][NO$_3$]. A stereoview of the unit cell packing diagram, which also illustrates the H-bonding, is shown in Fig. 2-14b. The coordinated nitrate group is involved in two intramolecular H-bonds. The first one is between the copper-bonded oxygen atom and an adjacent pyridazine ligand and the other between one of the non-coordinated oxygen atoms and a different pyridazine ligand but of the same molecule. All three oxygen atoms of the non-coordinated nitrate ion are also H-bonded, but each to a pyridazine ligand bonded to a different copper ion thereby linking the various molecular units into a three-dimensional network.
Table 2-9. Internal bonding parameters for pyridazine.a

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><a href="NO%E2%82%83">Cu(pdz)₄(NO₃)</a>ᵇ</td>
</tr>
<tr>
<td>N(1)-N(2)</td>
<td>1.339(3)</td>
</tr>
<tr>
<td>N(1)-C(1)</td>
<td>1.320(3)</td>
</tr>
<tr>
<td>N(2)-C(4)</td>
<td>1.320(3)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.390(4)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.348(4)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.376(4)</td>
</tr>
</tbody>
</table>

|                  | Fe(pdz)(CO)₄ᶜ |
| N(1)-N(2)       | 1.331(7)       | N(1)-C(8)-C(7) 123.7(7) |
| N(1)-C(8)       | 1.317(8)       | C(8)-C(7)-C(6) 117.7(7) |
| N(2)-C(5)       | 1.332(9)       | C(7)-C(6)-C(5) 117.0(7) |
| C(7)-C(8)       | 1.375(9)       | N(2)-C(5)-C(6) 125.3(7) |
| C(6)-C(7)       | 1.328(10)      | N(2)-N(1)-C(8) 119.0(5) |
| C(5)-C(6)       | 1.349(11)      | N(1)-N(2)-C(5) 117.3(6) |

|                  | [(CH₃)₂SnCl]₂(CH₂)(pdz)ᵈ |
| N(1)-N(2)       | 1.317(8)       | N(1)-C(1)-C(2) 124.9(8) |
| N(1)-C(1)       | 1.322(10)      | C(1)-C(2)-C(3) 116.0(8) |
| N(2)-C(4)       | 1.322(10)      | C(2)-C(3)-C(4) 117.9(9) |
| C(1)-C(2)       | 1.360(13)      | N(2)-C(4)-C(3) 124.5(8) |
| C(2)-C(3)       | 1.338(15)      | N(2)-N(1)-C(1) 119.1(6) |
| C(3)-C(4)       | 1.362(13)      | N(1)-N(2)-C(4) 117.5(6) |

---

a Standard deviations in the last digit are given in parentheses.
b This work; terminal pyridazine ligand.
c Data from ref. 82; terminal pyridazine ligand.
d Data from ref. 43; bridging pyridazine ligand.
2.2.4 The crystal structure of Cu(pdz)$_3$(NO$_3$)$_2$

The crystal data for Cu(pdz)$_3$(NO$_3$)$_2$ are given in Table 2-10 and selected bond lengths and bond angles are listed in Table 2-11. The structure of Cu(pdz)$_3$(NO$_3$)$_2$ with atomic labelling is depicted in Fig. 2-15. A stereoview of the stereochemistry of the copper ion is shown in Fig. 2-16. The copper ion is coordinated to by three terminal pyridazine ligands, one monodentate nitrate group (which is disordered) and one asymmetrically chelating nitrate group resulting in a distorted octahedral stereochemistry. The geometry about the copper ion may be described as a (1+4+1) type, the square plane being defined by the three donor nitrogen atoms of the pyridazine ligands and O(4) of the bidentate nitrate group. The Cu-O bond length involving the second oxygen atom of the bidentate nitrate group is 2.624(3) Å. Although this bond length is considerably longer than the other two Cu-O bond lengths in this compound, it is less than the sum of the van der Waals radii of copper and oxygens atoms, which is 2.90 Å (134), indicating that there is significant copper-oxygen interaction. The distortion of the copper(II) chromophore in Cu(pdz)$_3$(NO$_3$)$_2$ is also reflected in the significant deviations of the L-Cu-L bond angles (L represents the donor atoms of the pyridazine and nitrate groups) from ideal values. The cis and trans L-Cu-L bond angles lie in the ranges 53-110° and 149-178°, respectively.

As mentioned in the last section, it was previously (154) observed that the N-O bond length involving the coordinated oxygen atom of monodentate nitrate groups is generally longer (1.26-1.32 Å) and those involving the other two oxygen atoms are usually shorter (1.21-1.24 Å) than the value of 1.245(2) Å for the N-O bond lengths of the free nitrate ion. It was also observed that the O-N-O bond angle opposite the coordinated oxygen atom is generally greater, and the other two less, than 120°. Similar variations were observed in the N-O bond lengths and O-N-O bond angles of unsymmetrical bidentate nitrate groups. The dimensions of the chelating
nitrate group in Cu(pdz)$_3$(NO$_3$)$_2$ show the expected trends and are comparable to those listed in reference 154 for this type of nitrate group. For the monodentate nitrate group in Cu(pdz)$_3$(NO$_3$)$_2$, however, all three N-O bond lengths are equal, within experimental error, to the free ion value. In addition, only one of the O-N-O bond angles involving this nitrate group is greater than 120°; the other two are equal to this value within experimental error. These unexpected dimensions may be attributed to the fact that the monodentate nitrate group in Cu(pdz)$_3$(NO$_3$)$_2$ is disordered.

All the pyridazine rings in Cu(pdz)$_3$(NO$_3$)$_2$ are planar within experimental error and their bonding parameters (Table 2-11) are comparable to those observed in other complexes (see, for example, Table 2-9).

Studies on several pyridine complexes analogous to Cu(pdz)$_3$(NO$_3$)$_2$ have been reported by several workers. These include M(py)$_3$(NO$_3$)$_2$, where M is Co, Ni, Cu, Zn or Cd (156-161). However, with the exception of the zinc complex, their molecular geometries have not been determined unequivocally. It has been shown by single crystal X-ray diffraction that Zn(py)$_3$(NO$_3$)$_2$ has a seven-coordinate mononuclear structure in which all the pyridine molecules are coordianted and the nitrate groups are bidentate chelating (157).

Table 2-10. Crystal data$^a$ for Cu(pdz)$_3$(NO$_3$)$_2$.

| Crystal system  | Monoclinic   | Z   | 4
| Space group     | $P2_1/c$ (#14) | $V$, Å$^3$ | 1706.2(3)
| $a$, Å          | 8.390(1)      | $\rho_{calc}$, g cm$^{-3}$ | 1.665
| $b$, Å          | 15.585(1)     | $F(000)$   | 868
| $c$, Å          | 13.058(1)     | $R$        | 0.036
| $\beta$, deg    | 92.22(1)      | $R_w$      | 0.038

$^a$ Standard deviations in the last digit are given in parentheses.
Table 2-11. Selected bond lengths (Å) and bond angles (°) for Cu(pdz)$_3$(NO$_3$)$_2$.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>Polyhedron around the copper ion</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-O(1)</td>
<td>2.258(2)</td>
<td>Cu(1)-N(1)</td>
<td>2.025(2)</td>
</tr>
<tr>
<td>Cu(1)-O(4)</td>
<td>2.007(2)</td>
<td>Cu(1)-N(3)</td>
<td>2.042(2)</td>
</tr>
<tr>
<td>Cu(1)-O(5)</td>
<td>2.624(3)</td>
<td>Cu(1)-N(5)</td>
<td>1.984(2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Bidentate NO$_3$</th>
<th></th>
<th>Monodentate NO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(4)$^b$-N(8)</td>
<td>1.283(3)</td>
<td>O(1)$^b$-N(7)</td>
<td>1.243(3)</td>
</tr>
<tr>
<td>O(5)$^b$-N(8)</td>
<td>1.228(4)</td>
<td>O(2)-N(7)</td>
<td>1.24(1)</td>
</tr>
<tr>
<td>O(6)-N(8)</td>
<td>1.208(4)</td>
<td>O(3)-N(7)</td>
<td>1.22(2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Pyridazine</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-N(2)</td>
<td>1.338(3)</td>
<td>C(1)-C(2)</td>
<td>1.388(4)</td>
</tr>
<tr>
<td>N(1)-C(1)</td>
<td>1.311(3)</td>
<td>C(2)-C(3)</td>
<td>1.351(4)</td>
</tr>
<tr>
<td>N(2)-C(4)</td>
<td>1.324(4)</td>
<td>C(3)-C(4)</td>
<td>1.370(4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Polyhedron around the copper ion</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-Cu(1)-O(5)</td>
<td>149.10(9)</td>
<td>O(4)-Cu(1)-N(1)</td>
<td>90.42(8)</td>
</tr>
<tr>
<td>O(4)-Cu(1)-N(5)</td>
<td>162.83(9)</td>
<td>O(4)-Cu(1)-N(3)</td>
<td>88.55(8)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(3)</td>
<td>178.2(1)</td>
<td>O(5)-Cu(1)-N(1)</td>
<td>90.70(8)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-O(4)</td>
<td>95.78(8)</td>
<td>O(5)-Cu(1)-N(3)</td>
<td>87.52(8)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(1)</td>
<td>88.71(8)</td>
<td>O(5)-Cu(1)-N(5)</td>
<td>109.6(1)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(3)</td>
<td>92.71(8)</td>
<td>N(1)-Cu(1)-N(5)</td>
<td>92.08(9)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(5)</td>
<td>101.25(9)</td>
<td>N(3)-Cu(1)-N(5)</td>
<td>88.48(9)</td>
</tr>
<tr>
<td>O(4)-Cu(1)-O(5)</td>
<td>53.33(8)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Bidentate NO$_3$</th>
<th></th>
<th>Monodentate NO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(4)-N(8)-O(5)</td>
<td>117.8(3)</td>
<td>O(1)-N(7)-O(2)</td>
<td>116.8(5)</td>
</tr>
<tr>
<td>O(4)-N(8)-O(6)</td>
<td>118.4(3)</td>
<td>O(1)-N(7)-O(3)</td>
<td>121(1)</td>
</tr>
<tr>
<td>O(5)-N(8)-O(6)</td>
<td>123.8(3)</td>
<td>O(2)-N(7)-O(3)</td>
<td>120(1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Pyridazine</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(1)-C(2)</td>
<td>123.0(3)</td>
<td>N(2)-C(4)-C(3)</td>
<td>125.4(3)</td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)</td>
<td>117.8(3)</td>
<td>N(2)-N(1)-C(1)</td>
<td>120.1(2)</td>
</tr>
<tr>
<td>C(2)-C(3)-C(4)</td>
<td>116.3(3)</td>
<td>N(1)-N(2)-C(4)</td>
<td>117.4(2)</td>
</tr>
</tbody>
</table>

---

\(^a\) Standard deviations in the last digit are given in parentheses.

\(^b\) Coordinated to copper ion.
Fig. 2-15. Atom labelling scheme for Cu(pdz)$_3$(NO$_3$)$_2$. Alternative positions for disordered O atoms are indicated by the letters A and B.
Fig. 2-16. Stereoview of the stereochemistry of copper in Cu(pdz)_3(NO_3)_2. 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.
2.2.5 The crystal structure of $[\text{Cu(pdz)}_2(\text{NO}_3)_2]_3$

The crystallographic data for $[\text{Cu(pdz)}_2(\text{NO}_3)_2]_3$ are given in Table 2-12 whereas selected bonding parameters are presented in Tables 2-13 and 2-14. In Fig. 2-17 is shown the atom labelling scheme. Stereoviews of the molecular structure and the packing diagram are shown in Fig. 2-18.

$[\text{Cu(pdz)}_2(\text{NO}_3)_2]_3$ has a centrosymmetric linear trinuclear structure. The copper ions are linked by two bidentate bridging pyridazine groups and one monodentate bridging nitrate group. The central copper ion is thus surrounded by four pyridazine and two nitrate groups. Octahedral coordination around each of the terminal copper ions is completed by one terminal pyridazine ligand and two terminal nitrate groups.

$[\text{Cu(pdz)}_2(\text{NO}_3)_2]_3$ contains three distinct types of nitrate groups characterized by the mode or strength of coordination to the metal. These are monodentate bridging, strongly coordinated terminal, and weakly coordinated terminal. Our literature search indicates that cases in which a single oxygen atom of the nitrate group bridges two metals are rare, but not unknown (24, 162, 163). In $[\text{Cu(py)}_2(\text{NO}_3)_2]_2.\text{py}$ (162) each copper ion is directly coordinated to by asymmetric chelating nitrate groups and two pyridine moieties. Dimerization is effected through interaction between the copper ion of one monomer and a copper-bonded oxygen atom of the other. $[\text{Cu(py)}_2(\text{NO}_3)_2]_2.\text{py}$ is therefore an example of a compound in which a single oxygen atom of the nitrate group bridges two metal centres. However, bridging nitrate groups in the pyridine complex are simultaneously chelating. Purely single-oxygen atom bridging nitrate groups of the type seen in $[\text{Cu(pdz)}_2(\text{NO}_3)_2]_3$ have previously been observed in $\text{Cu}_2(\text{C}_8\text{H}_6\text{N}_4)(\text{NO}_3)_4$ where $\text{C}_8\text{H}_6\text{N}_4$ is 2,2'-bipyrimidine (163) and $\text{Cu}_2(\text{PAP6Me})(\text{OH})(\text{NO}_3)_3].\frac{1}{2}\text{H}_2\text{O}$ where PAP6Me is 1,4-bis((6-methylpyrid-2-yl)amino)phthalazine (24). However, while the Cu-O-Cu bridges are essentially
Table 2-12. Crystal data\textsuperscript{a} for [Cu(pdz)\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}]\textsubscript{3}.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Monoclinic</th>
<th>(Z)</th>
<th>(V, \text{\AA}^3)</th>
<th>(\rho_{\text{calc}}, \text{g cm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>(P2_1/n) (#14)</td>
<td></td>
<td>1814.1(5)</td>
<td>1.910</td>
</tr>
<tr>
<td>(a, \text{\AA})</td>
<td>8.938(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b, \text{\AA})</td>
<td>13.6677(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c, \text{\AA})</td>
<td>14.933(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\beta, \text{deg})</td>
<td>96.03(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Standard deviations in the last digit are given in parentheses.

Table 2-13. Internal bonding parameters for the nitrate ions in [Cu(pdz)\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}]\textsubscript{3}.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Bond lengths (\text{\AA})</th>
<th>Bond angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>monodentate bridging</td>
<td></td>
</tr>
<tr>
<td>O(1)\textsuperscript{b}-N(7)</td>
<td>1.291(3)</td>
</tr>
<tr>
<td>O(2)-N(7)</td>
<td>1.229(3)</td>
</tr>
<tr>
<td>O(3)-N(7)</td>
<td>1.222(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>strongly coordinated terminal</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(4)\textsuperscript{b}-N(8)</td>
</tr>
<tr>
<td>O(5)-N(8)</td>
</tr>
<tr>
<td>O(6)-N(8)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>weakly coordinated terminal</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(7)\textsuperscript{b}-N(9)</td>
</tr>
<tr>
<td>O(8)-N(9)</td>
</tr>
<tr>
<td>O(9)-N(9)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Standard deviations in the last digit are given in parentheses.
\textsuperscript{b} Coordinated to copper ion.
Table 2-14. Some bonding parameters for [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$.\(^a\)

<table>
<thead>
<tr>
<th>CuL(_n) (bond lengths, Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-O(1)(^b)</td>
<td>2.243(2)</td>
</tr>
<tr>
<td>Cu(1)-N(1)(^b)</td>
<td>2.052(2)</td>
</tr>
<tr>
<td>Cu(1)-N(3)(^b)</td>
<td>2.074(2)</td>
</tr>
<tr>
<td>Cu(2)-O(1)(^b)</td>
<td>2.255(2)</td>
</tr>
<tr>
<td>Cu(2)-O(4)</td>
<td>1.974(2)</td>
</tr>
<tr>
<td>Cu(2)-O(7)</td>
<td>2.516(7)</td>
</tr>
<tr>
<td>Cu(2)-N(2)(^b)</td>
<td>2.036(2)</td>
</tr>
<tr>
<td>Cu(2)-N(4)(^b)</td>
<td>2.063(2)</td>
</tr>
<tr>
<td>Cu(2)-N(5)</td>
<td>1.993(2)</td>
</tr>
</tbody>
</table>

bridging pyridazine

<table>
<thead>
<tr>
<th>bond lengths (Å)</th>
<th>bond angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-N(2)</td>
<td>1.346(3)</td>
</tr>
<tr>
<td>N(1)-C(1)</td>
<td>1.321(3)</td>
</tr>
<tr>
<td>N(2)-C(4)</td>
<td>1.321(3)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.392(4)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.360(4)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.382(4)</td>
</tr>
</tbody>
</table>

terminal pyridazine

<table>
<thead>
<tr>
<th>bond lengths (Å)</th>
<th>bond angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(5)-N(6)</td>
<td>1.331(3)</td>
</tr>
<tr>
<td>N(5)-C(9)</td>
<td>1.326(3)</td>
</tr>
<tr>
<td>N(6)-C(12)</td>
<td>1.330(4)</td>
</tr>
<tr>
<td>C(9)-C(10)</td>
<td>1.387(4)</td>
</tr>
<tr>
<td>C(10)-C(11)</td>
<td>1.343(5)</td>
</tr>
<tr>
<td>C(11)-C(12)</td>
<td>1.401(5)</td>
</tr>
</tbody>
</table>

\(^a\) Standard deviations in the last digit are given in parentheses.
\(^b\) Involving bridging ligand.
Fig. 2-17. Atom labelling scheme for [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$. Alternative positions for disordered O atoms are indicated by letter A.
Fig. 2-18. Stereoviews of (a) the molecular structure and (b) the crystal packing diagram of \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\). In (a) 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.
symmetrical in \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\), they are asymmetrical in the other three compounds. In \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\), the Cu-Obridging distances are 2.243(2) and 2.255(2) Å. The corresponding distances are 2.042(6) and 2.542(8) Å in the pyridine complex, 1.965(3) and 2.300(2) Å in the bipyrimidine complex, and 2.500(10) and 2.680(10) Å (as well as 2.519(2) and 2.870(2) Å) in the PAP6Me complex.

The dimensions of the strongly coordinated terminal nitrate group, along with those of the monodentate bridging one, are similar to those that have been observed in other complexes containing monodentate nitrate groups (154). The N-O bond lengths involving the coordinated oxygen atoms are the longest and fall within the range 1.26-1.32 Å whereas the terminal N-O bond lengths lie in the range 1.21-1.24 Å. In both cases, again in accordance with previous observations (154), the O-N-O bond angles opposite those of the coordinated oxygen atoms are greater than 120° while the rest are less than this angle.

The third type of the nitrate group in \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\) is characterized by a considerably longer Cu-O bond length, a consequence probably of steric factors. In this nitrate group, which is disordered, the N-O bond length involving the coordinated oxygen atom is not longer than, but rather lies between the other two. One of the terminal N-O bonds, at 1.14(1) Å, is unusually short. The O-N-O bond angle opposite the coordinated oxygen atom is less than 120° in contradiction to what is commonly observed (154). The remaining two O-N-O bond angles usually are less than 120° in terminal monodentate nitrate groups but, in \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\), one of them is 136.3(8)°. These unexpected dimensions are most certainly a consequence of the disorder in this nitrate group. The short N-O bond length observed in this compound is, however, not without precedence. A N-O bond of length 1.14(3) Å involving a non-coordinated oxygen atom has been observed in \(K[\text{Au(NO}_3]_4\) (164).

Both the central and terminal copper ions have elongated tetragonal octahedral geometries. However, the former has a CuN₄O₂ chromophore with a 4+2 type
coordination whereas the latter have CuN3OO'O'' chromophores with (1+4+1) type coordination, one of the Cu-O bond lengths being comparable to the three Cu-N bond lengths. In the chromophores of the terminal copper ions the Cu-N bond involving the terminal pyridazine ligand is slightly shorter than those involving the bridging ones. This is probably an electronic effect. In a bridging pyridazine ligand the electron density of the ring system may be distributed evenly over the molecule. In contrast, an uneven electron density distribution may be expected for a terminal ligand, with greater density on the nitrogen atom bound to the metal ion, resulting in a stronger metal-ligand interaction. Steric considerations may also contribute to the observed difference in the Cu-N bond lengths. It is interesting to note that one of the Cu-O distances involving a terminal nitrate group is shorter, while the other is longer, than those involving the bridging nitrate groups. As mentioned in the preceding paragraph the considerably longer Cu-O bond of 2.516 (7) Å is probably a consequence of steric constraints.

[Cu(pdz)2(NO3)2]3 contains both bidentate bridging and monodentate terminal pyridazine ligands and this is the first X-ray structure determination to be reported on such a compound. All the pyridazine rings are planar within experimental error and their internal bonding parameters (Table 2-14) are comparable to those observed in other complexes (see, for example, Table 2-9). In each pyridazine molecule the C-C bond opposite the N-N bond is the shortest of the three C-C bonds in the ligand.

Both intra- and inter-molecular hydrogen bonding exists in this compound. They involve the hydrogen atoms of the pyridazine and the oxygen atoms of the nitrate groups. These can be seen in the crystal packing diagram in Fig. 2-18b.
2.2.6 Infrared spectra

Group theory predicts four normal modes of vibration for the uncoordinated nitrate ion (D$_{3h}$ symmetry). These are the NO$_3$ symmetric stretching ($v_1$, A$_1'$), the NO$_3$ out-of-plane bending ($v_2$, A$_2''$), the NO$_3$ asymmetric stretching ($v_3$, E') and the NO$_3$ in-plane bending ($v_4$, E'). Although $v_1$ is infrared inactive, it has been observed in the infrared spectra of metal complexes where the nitrate ion is outside the coordination sphere (165). This has been attributed to the deformation of ions in the molecular field of the crystals. The D$_{3h}$ symmetry, and hence the degeneracy of the E modes, is retained when the nitrate group is coordinated in a tridentate fashion. Mono- and bidentate coordination, on the other hand, results in a lowering of symmetry to C$_{2v}$ (or C$_s$) and as a consequence, all bands become infrared active, shifts in band positions occur and the degeneracies of the $v_3$ and $v_4$ bands are lifted. Although the band shifts and splittings for bidentate coordination are similar to those for monodentate coordination, they are larger for the former. Curtis and Curtis (168) suggested that this difference may be used to differentiate between the two modes of nitrato group coordination, provided that the same cation is involved. In particular, they observed in a study of amine complexes of nickel(II) nitrate that the splitting of $v_3$ was in the range 105-125 cm$^{-1}$ for monodentate coordination and 180-235 cm$^{-1}$ for bidentate coordination. It has also been suggested that additional support for structural diagnosis for complexes containing the nitrate group may be obtained from the multiplicity and separation of the combination band ($v_1 + v_4$) around 1750 cm$^{-1}$ (168, 169). Ionic nitrate groups generally give rise to one sharp band, while coordinated nitrate groups give two bands. For a given metal and oxidation state, Lever et al. (169) observed that

---

4 Conventions for numbering vibrations for ionic, monodentate and bidentate nitrate groups are different because of the symmetry change on coordination (166, 167). To facilitate direct comparison of nitrate absorption bands in complexes with those of the ionic species, the designations of the free ion only are used in this study. The additional bands are thus referred to as split components of either $v_3$ or $v_4$ (D$_{3h}$).
the separation between these bands lies in the range 5-26 cm\(^{-1}\) for monodentate nitrate groups and 20-66 cm\(^{-1}\) for bidentate ones. Nuttall and Taylor (170) also suggested that the presence of two M-O stretching frequencies in the far-infrared region of the electromagnetic spectrum is characteristic of bidentate nitrate groups. The general applicability of these three criteria has been questioned (171, 172). Nonetheless, vibrational spectroscopy remains a useful diagnostic tool for the mode of nitrate ion coordination in closely related complexes (102, 168).

An analysis of the spectra of the complexes under discussion in this section demonstrates some of the difficulties encountered in the use of the above criteria. For a start, the M-O stretching vibration criterion could not be used because the spectrophotometer used in this work does not have sufficient sensitivity in the far-infrared spectral region.

Only the spectrum of Cu(pdz)\(_3\)(NO\(_3\))\(_2\) shows two, rather weak, bands in the 1 700-1 750 cm\(^{-1}\) spectral range. The bands are separated by 22 cm\(^{-1}\). As discussed above, a separation of this magnitude is consistent with either monodentate or bidentate nitrate group coordination. A bidentate chelating nitrate group is the unique feature pertaining to the nitrate groups that is found only in the structure of Cu(pdz)\(_3\)(NO\(_3\))\(_2\) and not in those of [Cu(pdz)\(_4\)(NO\(_3\))]\([NO_3]\) and [Cu(pdz)\(_2\)(NO\(_3\))\(_2\)]\(_3\). Hence we attribute the splitting of the combination band in Cu(pdz)\(_3\)(NO\(_3\))\(_2\) to the bidentate, rather than the monodentate, nitrate group. The spectra of the other three complexes exhibit a single weak and broad band around 1 740 cm\(^{-1}\) (see Fig. 2-19) indicating that the splitting of the combination band in these complexes, if any, is small. This would suggest that the nitrate groups in these complexes are weakly bound and monodentate. Consistent with this, [Cu(pdz)\(_4\)(NO\(_3\))]\([NO_3]\) and [Cu(pdz)\(_2\)(NO\(_3\))\(_2\)]\(_3\) were shown by single crystal X-ray diffraction studies to contain only monodentate nitrate groups. In this work, the splitting of the \(v_3\) band was found to be the more informative criterion regarding the
idency of the nitrate group. The analysis of the spectra of the four pyridazine-
copper(II) nitrate complexes based on this criterion is presented below.

The infrared absorption energies arising from the vibrations of the nitrate and
pyridazine molecules in CuLm(NO₃)₂ (n is 2, 3 or 4) are listed in Table 2-15 and
Appendix II-4, respectively. The spectra of the complexes in the 1 200-1 800 cm⁻¹
range are reproduced in Fig. 2-19. The spectra are complex and difficult to interpret.
Both pyridazine and nitrate groups absorb in this region. Furthermore, it is observed
that the three complexes whose structures were determined by X-ray crystallography
contain more than one type of nitrate group. It is therefore difficult to positively assign
all the bands. We rationalize our tentative assignments as follows. Free pyridazine
(139) exhibits strong bands at 1415 and 1283 cm⁻¹. The bands are reproduced, with
shifts of up to 10 cm⁻¹ in the thiocyanate complexes (Appendix II-4). In these latter
complexes, there is no difficulty in identifying the pyridazine bands in the
1 200-1 500 cm⁻¹ range since the thiocyanate group does not have absorptions in this
region. Hence, by analogy, we assign the strong bands in the ranges 1 399-1 425 cm⁻¹
and 1 275-1 296 cm⁻¹ in the pyridazine complexes of copper(II) nitrate to the neutral
ligand. These are labelled L in Fig. 2-19.

Pyridazine is infrared transparent between 1 300 and 1 380 cm⁻¹. Hence all the
strong bands in this region in the spectra of the Cu(pdz)ₙ(NO₃)₂ complexes are assigned
to the v₃ (D₃h) vibration of the nitrate group. These are labelled X in Fig. 2-19. We
also assign the very strong bands around 1 470 cm⁻¹, labelled X' in the figure, to v₃
(D₃h). We have observed that in this spectral region, pyridazine bands in metal
complexes generally occur below 1 460 cm⁻¹ and tend to have weak to medium
absorptions (Appendix II-4). These bands, labelled L' in Fig. 2-19, correspond to the
strong band observed at 1 446 cm⁻¹ in the spectrum of free pyridazine (139).
Fig. 2-19. Infrared spectra of pyridazine complexes of copper(II) nitrate.

* = combination band. For (a) a much stronger spectrum is required for this band, which occurs at 1742 cm\(^{-1}\), to be observable. \(L\) and \(L'\) = pyridazine bands; \(X\) and \(X'\) = nitrate bands; \(H\) = 1,3-hexachlorobutadiene bands.
Table 2-15. Nitrate ion band energies and assignments for Cu(pdz)\(_n\)(NO\(_3\))\(_2\) complexes.\(^a\)

<table>
<thead>
<tr>
<th>Nitrate ion(^b)</th>
<th>(v_3)</th>
<th>(v_1)</th>
<th>(v_2)</th>
<th>(v_4)</th>
<th>(v_1 + v_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cu(pdz)}_4(\text{NO}_3)_2)</td>
<td>1 314s</td>
<td>1 039s</td>
<td>823w-m</td>
<td>717w</td>
<td>1 742w</td>
</tr>
<tr>
<td>[\text{Cu(pdz)}_4(\text{NO}_3)][\text{NO}_3]]</td>
<td>1 311s</td>
<td>1 037s</td>
<td>822m</td>
<td>718m</td>
<td>1 742w</td>
</tr>
<tr>
<td>(\text{Cu(pdz)}_3(\text{NO}_3)_2)</td>
<td>1 301s</td>
<td>1 018s</td>
<td>816s</td>
<td>744s</td>
<td>1 744w, 1722w</td>
</tr>
<tr>
<td>[\text{Cu(pdz)}_2(\text{NO}_3)_2] (_3)</td>
<td>1 286s br</td>
<td>1 025s</td>
<td>810m</td>
<td>722m</td>
<td>1 744vw br</td>
</tr>
</tbody>
</table>

\(^a\) All values are in cm\(^{-1}\). \(v\) = very, \(s\) = strong, \(m\) = medium, \(w\) = weak, \(br\) = broad.
\(^b\) Data and assignment from ref. 166.
\(^c\) There may be an overlap between nitrate bands and the pdz bands at 1 410, 1 406, 1 402 and 1 399 cm\(^{-1}\) in \(\text{Cu(pdz)}_4(\text{NO}_3)_2\), \[\text{Cu(pdz)}_4(\text{NO}_3)\][\text{NO}_3]\], \(\text{Cu(pdz)}_3(\text{NO}_3)_2\) and \[\text{Cu(pdz)}_2(\text{NO}_3)_2\] \(_3\), respectively; see Appendix II-4.

From the known structure of \[\text{Cu(pdz)}_4(\text{NO}_3)\][\text{NO}_3]\] two sets of nitrate bands, corresponding to ionic and monodentate nitrate groups, may be expected. (In fact two sets of bands are observed for both \(v_2\) and \(v_4\)). However, as can be seen from Table 2-8, the terminal N-O bond lengths in the two types of nitrate groups are comparable.\(^5\) Hence any doubling of the components of \(v_3\) arising from the presence of two distinct nitrate groups in \[\text{Cu(pdz)}_4(\text{NO}_3)\][\text{NO}_3]\] may not be sufficiently significant as to be observed. In fact only one splitting of \(v_3\) is observed.

\(^5\) For monodentate nitrate groups, the components of \(v_3\) (\(D_{3h}\)) are primarily NO\(_2\) stretching vibrations involving the terminal N-O bonds (166).
Likewise, for \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\), three sets of nitrate bands are to be expected but are not observed. (Two sets are observed for \(v_1, v_2\) and \(v_4\)). In this case, however, there is a significant difference in the terminal N-O bond lengths of the weakly coordinated nitrate group and those of the other two types of nitrate groups. At least two sets of nitrate bands would therefore be expected. The fact that two sets are not observed for \(v_3\) raises the possibility that there may be overlap between nitrate and pyridazine bands around 1 290 and 1 400 cm\(^{-1}\). This may, in fact, apply to all the four \(\text{Cu(pdz)}_n(\text{NO}_3)_2\) complexes. Another notable feature of the spectrum of \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\) is the large splitting of \(v_3\) (192 cm\(^{-1}\)). This suggests, in contradiction to the known structure, that the complex contains bidentate nitrate groups. We believe that this inconsistency arises from the presence of a very short N-O bond length in the complex. A N-O bond length of 1.14 Å corresponds to a valence bond order of \(\approx 1.9\) (154). This is significantly larger than the valence bond order of 1.5 that would be expected for a terminal N-O bond of a monodentate nitrate group. Thus the double bond character of one of the N-O bonds in the disordered nitrate group accounts for the large splitting of \(v_3\) in \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\).

The infrared spectrum of \(\text{Cu(pdz)}_4(\text{NO}_3)_2\) exhibits no bands assignable to the components \(v_3\) whose separation is greater than 125 cm\(^{-1}\). Even assuming that there is overlap between nitrate bands and the pyridazine bands at 1 290 and 1 410 cm\(^{-1}\) the maximum splitting of \(v_3\) would be 120 cm\(^{-1}\). Thus there is no evidence for bidentate nitrate ion coordination in \(\text{Cu(pdz)}_4(\text{NO}_3)_2\). On the basis of its infrared and electronic (\textit{vide infra}) spectra, we postulate for it a \textit{trans}-tetragonal octahedral structure with monodentate pyridazine and nitrate groups.

From the known structure of \(\text{Cu(pdz)}_3(\text{NO}_3)_2\) at least four nitrate bands corresponding to the split components of \(v_3\) (\(D_{3h}\)) of the monodentate and bidentate nitrate groups may be expected. (As may be expected, two bands are observed for both \(v_1\) and \(v_2\)). Only three bands are assigned to the nitrate group in the region of \(v_3\). This
suggests, as noted above for the other Cu(pdz)$_n$(NO$_3$)$_2$ compounds, a possible overlap between nitrate and pyridazine bands around 1 280 and 1 400 cm$^{-1}$. We also note that the largest separation of the bands assigned to the components of $v_3$ (162 cm$^{-1}$) is consistent with the presence of a bidentate nitrate group in Cu(pdz)$_3$(NO$_3$)$_2$.

2.2.7 Electronic spectra

The electronic spectra of the four compounds Cu(pdz)$_4$(NO$_3$)$_2$, [Cu(pdz)$_4$(NO$_3$)][NO$_3$], Cu(pdz)$_3$(NO$_3$)$_2$ and [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$ each exhibit a single broad band in the visible region. The band maxima are listed in Table 2-16. The absorption maximum for Cu(pdz)$_4$(NO$_3$)$_2$, at 17 500 cm$^{-1}$, is at a significantly higher energy than for the other Cu(pdz)$_n$(NO$_3$)$_2$ complexes. However, its absorption energy compares favourably with those observed for Cu(py)$_4$(RSO$_3$)$_2$; 17 400 cm$^{-1}$ when R is CF$_3$, 16 900 cm$^{-1}$ when R is p-CH$_3$C$_6$H$_4$ and 16 800 cm$^{-1}$ when R is CH$_3$ (47, 68, 173). An elongated tetragonal structure has been proposed for these compounds (47, 173) and confirmed by X-ray crystallography for Cu(py)$_4$(CF$_3$SO$_3$)$_2$ (68). Both the electronic and infrared (vide supra) spectra of Cu(pdz)$_4$(NO$_3$)$_2$ are consistent with such a structure. We note that although [Cu(pdz)$_2$(NO$_3$)$_3$]$_2$ has two kinds of copper(II) chromophores, they are not distinguishable in the electronic spectrum. Only one broad absorption band is seen for this compound.
Table 2-16. Electronic spectral data for compounds of copper(II) nitrate.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nm</td>
</tr>
<tr>
<td>Cu(pdz)₄(NO₃)₂</td>
<td>570</td>
</tr>
<tr>
<td>[Cu(pdz)₄(NO₃)][NO₃]</td>
<td>627</td>
</tr>
<tr>
<td>Cu(pdz)₃(NO₃)₂</td>
<td>648</td>
</tr>
<tr>
<td>[Cu(pdz)₂(NO₃)₂]₃</td>
<td>647</td>
</tr>
</tbody>
</table>

2.2.8 Electron spin resonance spectra

The esr spectral results for compounds of copper(II) nitrate are presented in Table 2-17. The spectra of the Cu(pdz)₄(NO₃)₂ complexes are shown in Fig. 2-20. Cu(pdz)₄(NO₃)₂ exhibits a normal axial esr spectrum in which the lowest $g > 2.04$. This indicates a $d_{x²−y²}$ ground state for the copper(II) ion (142), consistent with an elongated tetragonal octahedral structure as proposed above for this complex. There is evidence of a weak peak ($g \approx 2.11$) of unknown origin in the esr spectrum of Cu(pdz)₄(NO₃)₂.

The esr spectrum of Cu(pdz)₃(NO₃)₂ is also of the normal axial type, although $g_{||}$ is not well resolved. Cu(pdz)₃(NO₃)₂ has a distorted-octahedral structure containing terminal pyridazine and both monodentate and bidentate chelating nitrate groups (see section 2.2.4). Its esr spectrum is consistent with such a structure and a $d_{x²−y²}$ ground state for the Cu²⁺ ion.

For a five coordinate mononuclear copper(II) complex a rhombic spectrum with lowest $g > 2.04$ indicates that the copper(II) ion is in an elongated rhombic symmetry with all the axes aligned parallel. Such a spectrum is consistent with a square pyramidal stereochemistry and a $d_{x²−y²}$ ground state. If the lowest $g < 2.03$, a
Fig. 2-20. Esr spectra of pyridazine complexes of copper(II) nitrate.
(a) Cu(pdz)$_4$(NO$_3$)$_2$; (b) Cu(pdz)$_3$(NO$_3$)$_2$; (c) [Cu(pdz)$_4$(NO$_3$)][NO$_3$];
(d) [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$. dA/dH = first derivative of absorption curve.
Table 2-17. Esr spectral data for compounds of copper(II) nitrate.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>$g_1^b$</th>
<th>$g_2^b$</th>
<th>$g_3$</th>
<th>$g_o^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(pdz)$_4$(NO$_3$)$_2$</td>
<td>2.216</td>
<td>2.065</td>
<td>d</td>
<td>2.115</td>
</tr>
<tr>
<td>[Cu(pdz)$_4$(NO$_3$)][NO$_3$]</td>
<td>2.235</td>
<td>2.080</td>
<td>2.048</td>
<td>2.121</td>
</tr>
<tr>
<td>Cu(pdz)$_3$(NO$_3$)$_2$</td>
<td>$\approx$2.24</td>
<td>2.083</td>
<td></td>
<td>$\approx$2.14</td>
</tr>
<tr>
<td>[Cu(pdz)$_2$(NO$_3$)$_2$]$_3$</td>
<td>2.292</td>
<td>2.060</td>
<td>2.011</td>
<td>2.122</td>
</tr>
<tr>
<td>Cu(pyz)$_3$(NO$_3$)$_2$</td>
<td>2.251</td>
<td>2.058</td>
<td></td>
<td>2.122</td>
</tr>
<tr>
<td>Cu(pyz)(NO$_3$)$_2$</td>
<td>2.261</td>
<td>2.060</td>
<td></td>
<td>2.127</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2.133)</td>
</tr>
<tr>
<td>Cu(mepyz)$_4$(NO$_3$)$_2$</td>
<td>2.243</td>
<td>2.066</td>
<td></td>
<td>2.125</td>
</tr>
<tr>
<td>Cu(mepyz)(NO$_3$)$_2$</td>
<td>2.257</td>
<td>2.070</td>
<td></td>
<td>2.132</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2.145)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Data collected at liquid nitrogen temperature. Error in $g = \pm 0.003$; data in parentheses are from ref. 15.

\textsuperscript{b} When only two $g$ values are observed $g_1 = g_{||}$ and $g_2 = g_{\perp}$.

\textsuperscript{c} $g_o =$ isotropic $g$ value. For orthorhombic and axial systems $g_o = (g_{||} + g_2 + g_3)/3$ and $g_o = (g_{||} + 2g_{\perp})/3$, respectively.

\textsuperscript{d} See text.

Compressed rhombic symmetry with all axes aligned parallel is indicated (142). The latter case is consistent with a trigonal bipyramidal stereochemistry and a d$_{2s}$ ground state. For [Cu(pdz)$_4$(NO$_3$)][NO$_3$] the lowest $g$-value of 2.048±0.003 is borderline between the two cases. Therefore the stereochemistry and ground state cannot be determined unequivocally from its esr spectrum. This is consistent with the structure of the compound which is intermediate between square-pyramidal and trigonal bipyramidal (section 2.2.3).

[Cu(pdz)$_2$(NO$_3$)$_2$]$_3$ has a three $g$ esr spectrum. We interpret it as a rhombic spectrum with each $g$ value corresponding to a component along one of the three molecular axes. It is also possible that the spectrum is a composite of two axial
spectra, arising from the central and terminal copper ions in the complex, in which the parallel components overlap. A more definitive assignment might be made by recording the spectrum of this complex in the P-band (15 GHz) or Q-band (35 GHz) frequency ranges. If the second assignment suggested above is the correct one, then the resolution of the parallel components may be achieved in the higher frequency spectrum. Unfortunately, spectrometers operating at these higher frequencies were not available for this study.

For purposes of comparison we examined the esr spectra of two pyrazine and two methylpyrazine copper(II) nitrate complexes which we had available (66) and the results are given in Table 2-17. All four complexes are considered to have elongated tetragonal-octahedral structures. (This has been shown to be the case for Cu(pyz)(NO₃)₂ by single crystal X-ray diffraction (41)). Consistent with this they all give two g value spectra with g₁₁ >> gₚ > 2.04. The average g-values obtained from the esr spectra of Cu(pyz)(NO₃)₂ and Cu(mepy)(NO₃)₂ have been reported before by Richardson and Hatfield (15). Our results are in excellent agreement with theirs (Table 2-17).

2.2.9 Magnetic properties

In metal clusters in which there is magnetic interaction between m paramagnetic ions, the maximum (μₓₓ/ₐ) and minimum (μₘₐₙ/ₐ) "spin only" magnetic moments per paramagnetic ion are given by (174):

\[ \mu_{\text{max}/A} = \frac{2[S_{\text{max}}(S_{\text{max}}+1)]^{1/2}}{m^{1/2}} \]  \hspace{1cm} [2-7]

\[ \mu_{\text{min}/A} = \frac{2[S_{\text{min}}(S_{\text{min}}+1)]^{1/2}}{m^{1/2}} \]  \hspace{1cm} [2-8]
where \( S_{\text{max}} = \sum_{i=1}^{m} S_i \) and \( S_{\text{min}} \) is the minimum value of \( \sum_{i=1}^{m} (\pm S_i) \).

\( \mu_{\text{max}/A} \) and \( \mu_{\text{min}/A} \) can only be attained in the absence of orbital contribution; the former by ferromagnetic and the latter by strongly antiferromagnetic coupling between the paramagnetic ions. For a copper trimer \( S_{\text{max}} = 3/2, S_{\text{min}} = 1/2 \) and \( m = 3 \). Hence \( \mu_{\text{max}/A} \) and \( \mu_{\text{min}/A} \) are 2.24 and 1.00 B.M. respectively.

The magnetic data for the copper(II) nitrate complexes investigated in this work are given in Appendix IV. The linear trimer, \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\), has a magnetic moment of 1.52 B.M. per copper ion at 345 K. The moment decreases gradually to a value of 1.20 B.M. at 90 K, and then remains constant as the temperature is further lowered to 4.2 K. These data suggest that the copper ions in \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\) are strongly antiferromagnetically coupled, although there is still some population of the spin-quartet state above 90 K.

The magnetic susceptibility of a symmetrical linear copper(II) trimer is given by the expression (175):

\[
\chi_m = \frac{Ng^2B^2}{4kT} \left( \frac{e^{-2J/kT} + e^{-2J'/kT} + 10e^{J/kT}}{e^{-2J/kT} + e^{-2J'/kT} + 2e^{J/kT}} \right)
\]

where \( \chi_m \) refers to the molar magnetic susceptibility per trimer, \( J \) is the exchange coupling constant between the central and terminal copper ions \( (J = J_{12} = J_{23}) \) and \( J' \) is the exchange coupling constant between the terminal copper ions \( (J' = J_{13}) \). All the other terms are as defined in equation 2-1. The reciprocal susceptibility data of \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\) were analyzed by the above expression. The results are presented in Table 2-18 and Fig. 2-21. Initially only \( J \) was allowed to vary, with \( J' \) set equal to zero and \( g \) set equal to the \( g_o \) value of 2.12 calculated from the experimental esr data (section 2.2.8). The resultant fit was of poor quality as judged visually and by the
value of $F$. Both $J$ and $g$ were then allowed to vary, with $J'$ still set equal to zero. This procedure led to an improvement in the quality of the fit but the value of $g$ obtained was unrealistically high. A further improvement in the quality of the fit was obtained when all three parameters, $J$, $J'$ and $g$, were varied ($F = 0.0084$). However, this procedure gave an unrealistically high value of $g$ (2.39) and, in addition, both $J$ and $J'$ were indeterminate ($J = J' = -136 \text{ cm}^{-1}$ with standard deviations of 528 and 1050 for $J$ and $J'$, respectively). The susceptibility data were then analyzed for the possible influence of paramagnetic impurities as outlined in section 2.1.8. In the case of $[\text{Cu(pdz)}_2(\text{NO}_3)_2]_3$, however, the Curie law term represented by equation 2-3 was multiplied by a factor of 3. $J$ and $P$ were treated as the adjustable parameters, with $J'$ and $g$ held at 0 and 2.12, respectively. An excellent agreement between experimental and calculated data was obtained, although we find the percent paramagnetic impurity rather high.

As mentioned in sections 2.2.2. and 5.2.2, the reaction of pyridazine with ethanolic solutions of copper(II) nitrate trihydrate give different products, depending on the ratio of the reagents. Each of the compounds obtained has a characteristic infrared spectrum and in no case was a mixture of products observed. However small amounts of impurities may not be detectable by this method. Powder X-ray diffraction studies (see section 2.2.10) suggest that small amounts of $\text{Cu(pdz)}_4(\text{NO}_3)_2$ and/or $\text{Cu(pdz)}_3(\text{NO}_3)_2$ impurities may be present in the sample of $[\text{Cu(pdz)}_2(\text{NO}_3)_2]_3$ used in the magnetic susceptibility measurements. The results are however not unequivocal. Calculations show that only a maximum of 6% $\text{Cu(pdz)}_3(\text{NO}_3)_2$ (or 4% $\text{Cu(pdz)}_4(\text{NO}_3)_2$) can be tolerated for the observed microanalytical data for $[\text{Cu(pdz)}_2(\text{NO}_3)_2]_3$ to remain valid. Hence we conclude that neither of the former products can account for the observed $\%P$ of 13.5% in $[\text{Cu(pdz)}_2(\text{NO}_3)_2]_3$. It is possible that the paramagnetic impurity observed in $[\text{Cu(pdz)}_2(\text{NO}_3)_2]_3$ arises from another compound of empirical formula $\text{Cu(pdz)}_2(\text{NO}_3)_2$. A possible structure,
developed from that of \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\), is a chain polymer in which all the pyridazine ligands are bridging. Octahedral coordination about the copper ions would then be completed by monodentate nitrate groups. Such a compound cannot be distinguished from \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\) by microanalysis and, if the copper ions in it are not very strongly antiferromagnetically coupled, its contribution to the observed susceptibility would be manifested in the form of paramagnetic impurities. Another possibility is that the paramagnetic impurities observed in the susceptibility data of \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\) arises from the presence of \(\text{Cu(pdz)}_3(\text{NO}_3)_2\) and the yet unobserved complex, \(\text{Cu(pdz)}(\text{NO}_3)_2\). A mixture containing 6.5% of each of these two products would contribute \%P of the order observed in \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\) but not affect the microanalytical data of the latter. One way to test the above hypotheses would be to generate a theoretical powder pattern from the single crystal data of \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\) and to compare it with that obtained experimentally on a powder sample (Fig. 2-22b). Unfortunately, the software (176) that was available to us for the generation of theoretical patterns cannot handle more than 10 unique atoms of one kind, as exists in \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\).

Table 2-18. Magnetic parameters for \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\).\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>-J (cm(^{-1}))</th>
<th>g</th>
<th>%P</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>99</td>
<td>2.12</td>
<td>0</td>
<td>0.1592</td>
</tr>
<tr>
<td>(b)</td>
<td>170</td>
<td>2.40</td>
<td>0</td>
<td>0.0167</td>
</tr>
<tr>
<td>(c)</td>
<td>139</td>
<td>2.12</td>
<td>13.5</td>
<td>0.0087</td>
</tr>
</tbody>
</table>

\(^a\) (a): J varied, \(g\) set at esr determined value and \%P set at zero; (b): J and \(g\) varied, \%P set at zero; (c): J and P varied, \(g\) set at esr determined value. \(J'\) set at zero in all three cases. Error limits: -J, ±5 cm\(^{-1}\); \(g\), ±0.02; \%P, negligible (3\(\sigma\) ≈ 5\(\times\)10\(^{-3}\)).
Fig. 2-21. Plots of reciprocal susceptibility versus temperature for \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\). The solid lines were drawn using the parameters given in Table 2-18. The labels (a), (b) and (c) used in this figure are as defined in Table 2-18.
It is concluded that the bulk sample of "Cu(pdz)2(NO3)2" on which the magnetic measurements was made contained $\approx 87\%$ of the trinuclear species [Cu(pdz)2(NO3)2]. The coupling between neighbouring copper ions in this species is antiferromagnetic and is quite strong with $-J = 139$ cm$^{-1}$. The coupling between the terminal copper ions appears to be negligible. The "impurities" in the sample are likely in the form of structural isomers of this compound in which the copper centres are magnetically isolated and provide a paramagnetic contribution of $\approx 13\%$ to the overall susceptibility.

Trinuclear complexes of copper(II) that have been characterized by both single crystal X-ray diffraction and variable temperature magnetic susceptibility studies include Cu$_3$Cl$_8$(adeH)$_2$.4H$_2$O where ade is adeninium (175, 177), Cu$_3$(C$_{11}$H$_{19}$N$_2$O$_2$)$_2$ (178), [Cu$_3$L$_3$OH][SO$_4$]$_{x}$H$_2$O where L is deprotonated pyridine-2-aldehyde oxime (179), [(Cu(es))$_2$Cu(H$_2$O)$_2$][ClO$_4$]$_2$.H$_2$O, where es is NN'-ethylenebis(salicylaldimine) (180-182) and [Cu$_3$(C$_8$H$_{17}$N$_2$O)$_3$(H$_2$O)$_3$(OH)$_{1/2}$][ClO$_4$]$_{3/2}$[H$_2$O]$_4$ where C$_8$H$_{17}$N$_2$O is 2-propylamino-2-methyl-3-butanone oximate (183, 184). The bridging units in most of these complexes are oxygen atoms derived from a variety of ligands. Cu$_3$Cl$_8$(adeH)$_2$.4H$_2$O is a linear trimer, with both chloride and adeninium bridges (177). Its magnetic moment, per copper ion, decreases from 1.86 B.M. at 295 K to 1.00 B.M. at 8 K (175). These properties are consistent with a transition from a spin quartet ground state at the high temperature region to a spin doublet ground state at the lower temperatures. Cu$_3$(C$_{11}$H$_{19}$N$_2$O$_2$)$_2$, which is also linear, exhibits a nearly temperature independent magnetic moment per copper(II) ion of about 1.09 B.M. in the range 296-35 K, indicating that only the spin-doublet is populated even at room temperature (178). Similar results were obtained for [Cu$_3$L$_3$OH][SO$_4$]$_{x}$H$_2$O in which the copper ions define an equilateral triangle of sides 3.21 Å (179). This compound exhibits a temperature invariant magnetic moment of 1 B.M. per copper ion over the range 401-105 K. The copper ions in [Cu$_3$(C$_8$H$_{17}$N$_2$O)$_3$(H$_2$O)$_3$(OH)$_{1/2}$][ClO$_4$]$_{3/2}$[H$_2$O]$_4$ also sit at the corners of an equilateral triangle (183). This compound exhibits an
average magnetic moment of 1.11 B.M. per copper ion over the temperature range 366-78 K (184). In [{Cu(es)}₂Cu(H₂O)₂][ClO₄]₂H₂O, the copper ions are disposed such that they nearly form an isosceles triangle (Cu-Cu bond lengths 2.950(5), 2.975(5) and 5.798(5) Å; the longest Cu-Cu distance being between the terminal copper ions) (180). The magnetic moment of this compound decreases from 1.69 B.M. at 324 K to 1.34 B.M. at 81 K. It was concluded from analyses of its magnetic properties that interaction between the terminal copper ions is negligible (181, 182).

Trimeric structures have also been proposed for other copper(II) complexes but these (174, 179, 181, 182, 185, 186) have not been confirmed by single crystal X-ray diffraction studies. Of particular bearing to the present work is [Cu(bpdpn)]₂CuCl₂, where H₂bpdpn is N,N'-bis(3'-pyridazinecarboxamide)-1,3-propane (186). A trimeric structure in which only the substituted pyridazines act as bridging ligands was proposed for this compound. Its magnetic moment, per copper ion, was reported for two temperatures only, 1.55 B.M. at 304 K and 1.10 B.M. at 89 K. Although no detailed analysis of the magnetic data was presented, the magnitude of the magnetic moment at the two temperatures is comparable to those obtained for [Cu(pdz)₂(NO₃)₂]₃. This would suggest that the magnetic exchange in the nitrate complex is transmitted primarily via the pyridazine molecules. The ability of pyridazine to mediate magnetic exchange efficiently has also been demonstrated in a number of dinuclear copper(II) complexes in which J values ranging from 65 to 652 cm⁻¹ were observed (24-26). In these complexes, the copper ions are bridged by chloride, bromide or hydroxide anions together with substituted pyridazines. However, the diazines are thought to transmit most of the exchange.

Magnetically dilute copper(II) complexes normally exhibit temperature independent magnetic moments in the range 1.75-2.20 B.M. (144). Freshly prepared samples of Cu(pdz)₄(NO₃)₂, [Cu(pdz)₄(NO₃)]₂[NO₃] and Cu(pdz)₃(NO₃)₂ exhibit magnetic moments which are characteristic of magnetically dilute copper(II)
complexes. This is consistent with the monomeric structures determined by X-ray crystallography for \([\text{Cu(pdz)}_4(\text{NO}_3)]\)[\text{NO}_3]\) and \(\text{Cu(pdz)}_3(\text{NO}_3)_2\) and proposed for \(\text{Cu(pdz)}_4(\text{NO}_3)_2\). Within two weeks of its preparation, however, a sample of \(\text{Cu(pdz)}_4(\text{NO}_3)_2\) was observed to have changed colour from violet to black while the microanalytical data remained unchanged. The magnetic moment was found to have dropped to about 1.2 B.M. while remaining temperature independent. We interpret these observations as follows. The complex undergoes trimerization to \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\). This requires the release of six pyridazine molecules for every trimer formed. The black complex is therefore formulated as \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3.6\text{pdz}\). Pyridazine is a light orange liquid but discolours when irradiated (63). This would account for the observed colour change in \(\text{Cu(pdz)}_4(\text{NO}_3)_2\). This view is supported by the further observation that some samples of \(\text{Cu(pdz)}_4(\text{NO}_3)_2\) left in the open air gave a mixture of green and blue products. Presumably under these conditions any pyridazine released is readily swept away and does not therefore stain the products of the structural rearrangement. These products could not be characterized since they were intimately mixed. Other samples of \(\text{Cu(pdz)}_4(\text{NO}_3)_2\) left exposed to the atmosphere decomposed to give a dark brown gummy material. These observations suggest that the decomposition of \(\text{Cu(pdz)}_4(\text{NO}_3)_2\) is complex and may proceed via different pathways. If, as proposed above, only structural rearrangements occur in samples stored in an inert atmosphere then the microanalytical data is not expected to change. This was found to be the case. The magnetic moment per copper ion calculated on the basis of the above formulation is similar to that observed for a pure sample of \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\), hence the conclusion that \(\text{Cu(pdz)}_4(\text{NO}_3)_2\) trimerizes.

\(\text{Cu(pdz)}_3(\text{NO}_3)_2\) undergoes similar but less dramatic changes on standing; the colour changes from bright blue to greenish blue, the microanalytical data remain the same and the magnetic moment drops from 1.83 to 1.70 B.M. These results suggest that \(\text{Cu(pdz)}_3(\text{NO}_3)_2\) undergoes structural changes of the type proposed for
Cu(pdz)$_4$(NO$_3$)$_2$ to form an oligomeric complex. The colour of [Cu(pdz)$_4$(NO$_3$)]$_2$[NO$_3$] was also observed to change from blue to black on standing. No magnetic studies of the black product were undertaken in this case. However, the colour change suggests that perhaps, like Cu(pdz)$_4$(NO$_3$)$_2$ and Cu(pdz)$_3$(NO$_3$)$_2$, [Cu(pdz)$_4$(NO$_3$)]$_2$[NO$_3$] also undergoes oligomerization.

2.2.10 Powder X-ray diffraction patterns

Theoretical analysis of the magnetic susceptibility data of [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$ indicated the presence of a relatively large amount of structural paramagnetic impurity (vide supra). In an effort to identify the impurity, we obtained powder X-ray patterns for Cu(pdz)$_4$(NO$_3$)$_2$, Cu(pdz)$_3$(NO$_3$)$_2$ and [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$. In the latter case, the powder sample used in the magnetic susceptibility studies, and not the single crystals, was used. The powder X-ray diffraction data are given in Appendix III. The powder patterns are shown in Fig. 2-22. Weak to medium peaks are observed in the powder pattern of [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$ at about the same locations that strong ones are observed in those of Cu(pdz)$_4$(NO$_3$)$_2$ and Cu(pdz)$_3$(NO$_3$)$_2$. This observation suggests that the sample of the former may be contaminated with small amounts of the latter. This is, however, not unequivocal as the weak to medium peaks could be an integral part of the powder pattern of [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$.

---

6 The idea was to first establish unambiguously the powder pattern of a structurally pure sample of [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$. This can be achieved by generating such a pattern from single crystal X-ray diffraction data. As mentioned in section 2.2.9, this could not be done in the present work due to software limitations.
Fig. 2-22. Powder X-ray diffraction patterns for (a) Cu(pdz)$_3$(NO$_3$)$_2$, (b) [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$ and (c) Cu(pdz)$_4$(NO$_3$)$_2$. 
2.3 Complexes of copper(II) sulfonates

2.3.1 Introduction

As part of a general search for and study of magnetic exchange effects in coordination compounds, the synthesis and thermal, spectral, structural and magnetic properties of compounds of divalent transition metal sulfonates have been investigated in our laboratory for several years. The compounds investigated so far include ML₄(RSO₃)₂ where M is Fe, Ni or Cu, L is py, pyz or mepyz, and R is CH₃, CF₃ or p-CH₃C₆H₄ (47, 66, 68, 137, 173), Ni(pyz)₃(CH₃SO₃)₂.CH₃OH (66), M(pyz)₂(CH₃SO₃)₂ where M is Cu or Fe (47, 65), Fe(pyz)₂(CF₃SO₃)₂.CH₃OH (65) and ML(RSO₃)₂ where M is Fe, Ni or Cu, L is pyz or mepyz and R is CH₃, CF₃ or p-CH₃C₆H₄ (65, 66, 68).

A number of the tetrakis(pyridine) complexes have been shown by X-ray crystallography to have mononuclear six coordinate structures with monodentate trans-coordinated sulfonate groups (68, 137). Similar structures have been proposed for the other tetrakis(neutral ligand) complexes (47, 66). All the ML₄(RSO₃)₂ complexes were found to be magnetically dilute.

A chain structure in which nickel ions are bridged by bidentate pyrazine ligands has been proposed for Ni(pyz)₃(CH₃SO₃)₂.CH₃OH (66). Octahedral configuration about the nickel ions is achieved through monodentate coordination by two pyrazine and two methanesulfonate groups. Evidence of weak antiferromagnetic coupling was observed in this compound.

A structure in which metal ions are bridged in a square array by neutral ligands and in which anions occupy trans-axial positions has been observed in Cu(pyz)₂(CH₃SO₃)₂ by single crystal X-ray diffraction (47) and proposed for Fe(pyz)₂(CH₃SO₃)₂ and Fe(pyz)₂(CF₃SO₃)₂.CH₃OH on the basis of spectroscopic evidence (65). The magnetic moments of the iron(II) complexes were found to
decrease significantly with decreasing temperature indicating the presence of weak antiferromagnetic coupling. However, unequivocal evidence for this is lacking as the susceptibility versus temperature plot of neither complex exhibits a maximum down to 4.2 K. Cu(pyz)$_2$(CH$_3$SO$_3$)$_2$, on the other hand, shows conclusive evidence for antiferromagnetic spin-spin interaction. Its susceptibility versus temperature plot shows a maximum at 6.2 K (47).

None of the mono(neutral ligand) complexes have been obtained in crystalline form suitable for single crystal X-ray diffraction studies. They have all been indirectly characterized as having structures consisting of square arrays of metal ions bridged in one dimension by double sulfonate bridges and in the other by neutral ligands (65, 66, 68). No clear evidence for magnetic concentration was obtained from magnetic studies on Fe(pyz)(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$, Fe(pyz)(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$.2CH$_3$OH and Ni(pyz)(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$ (65, 66). In contrast, Cu(pyz)(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$, Cu(pyz)(CF$_3$SO$_3$)$_2$, Cu(mepy)(CF$_3$SO$_3$)$_2$ and Cu(pyz)(CH$_3$SO$_3$)$_2$ are magnetically concentrated, each exhibiting a maximum between 5 and 7 K in its susceptibility versus temperature plot (66, 68).

The most fruitful investigations in the search for magnetic concentration in coordination complexes of divalent metal sulfonates has thus involved copper(II). As an extension of the earlier work, we decided to investigate complexes formed by copper(II) sulfonates with pyridazine and 4,4'-bipyridine. Our synthetic endeavors (section 5.2.3) resulted in the isolation of only Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$. We report in this section its spectral and magnetic properties. We also report electron spin resonance spectral studies on Cu(pyz)(CH$_3$SO$_3$)$_2$, Cu(pyz)(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$, Cu(pyz)$_4$(CF$_3$SO$_3$)$_2$, Cu(mepy)$_4$(CF$_3$SO$_3$)$_2$ and Cu(mepy)(CF$_3$SO$_3$)$_2$. These five compounds have been previously characterized by the other techniques used in this study (66). Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$ is deliquescent and the other compounds are hygroscopic. Hence samples were stored and manipulated in a nitrogen atmosphere glove box. Even then
Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$ is still unstable, changing colour from blue to grey within two weeks of its preparation.

2.3.2 Infrared and electronic spectra

The local symmetry around the sulfur atom in a free uncoordinated sulfonate anion, RSO$_3^-$, is C$_{3v}$. Six normal modes of vibration are predicted by group theory. These are the SO$_3$ symmetric stretching ($v_1$, A$_1$), the SC stretching ($v_2$, A$_1$), SO$_3$ symmetric deformation ($v_3$, A$_1$), SO$_3$ antisymmetric stretching ($v_4$, E), SO$_3$ antisymmetric deformation ($v_5$, E) and SO$_3$ rocking ($v_6$, E). All six vibrations are infrared active. However, the $v_6$ band has not been identified in the spectra of complexes containing the sulfonate group (47, 66, 68, 137, 187, 188) except for Co(FSO$_3$)$_2$ and Cu(FSO$_3$)$_2$ in which the band was observed around 420 cm$^{-1}$ (187). Perturbation of the sulfonate group, for example by coordination to metal ions in a mono- or bi-dentate fashion, leads to a lowering of the symmetry below C$_{3v}$. This, in turn, results in the removal of the degeneracy of the E modes. The degree of splitting of the $v_4$ band has been shown to be a good indicator of the mode of anion coordination when closely related complexes are involved (65, 68, 137, 189). For example, $v_4$ is split by 43 and 101 cm$^{-1}$ in Cu(py)$_4$(CF$_3$SO$_3$)$_2$ and Cu(pyz)(CF$_3$SO$_3$)$_2$ respectively (68). A single crystal X-ray diffraction study showed that the former contains monodentate triflate groups whereas bidentate anion coordination was proposed for the latter (68).

The infrared spectrum of Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$ was assigned on the basis that the absorption bands originate from two constituent parts: pyridazine and methanesulfonate groups. The neutral ligand bands are listed in Appendix II-4. Assuming C$_{3v}$ symmetry for the CSO$_3$ fragment of the methanesulfonate anion in Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$ the following assignments, consistent with those given in reference 47, may be made:
$v_4$ (E) | $v_1$ (A$_1$) | $v_2$ (A$_1$) | $v_3$ (A$_1$) and $v_5$ (E)  
---|---|---|---
1178s asy, 1187s, 1210s, 1237s | 1042s | n.o | 532s, 541m, 562s.

All band positions are in cm$^{-1}$. $v_6$ is not observed while $v_2$, expected in the 780 cm$^{-1}$ region, is obscured by pyridazine bands. Pyridazine also absorbs near 1178 cm$^{-1}$ and this may account for the asymmetry of one component of $v_4$. The lowering of the symmetry of the CSO$_3$ moiety in Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$ below $C_{3v}$ is clearly indicated by the splitting of $v_4$. The SO$_3$ deformation region of the spectrum provides further evidence of symmetry reduction. Only two bands ($v_3$ and $v_5$) are expected in $C_{3v}$ symmetry. In Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$, three bands are observed in this region indicating that the doubly degenerate mode, $v_5$, is split. This, in turn, suggests a lowering of the symmetry of the CSO$_3$ moiety below $C_{3v}$. The magnitude of splitting of $v_4$ of 41 cm$^{-1}$ in this complex is to be compared with the value of 49 cm$^{-1}$ observed in Cu(py)$_4$(CH$_3$SO$_3$)$_2$ (47). This suggests that, as was proposed for the pyridine complex, Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$ contains monodentate sulfonate groups. As discussed in section 2.1.4, no satisfactory infrared criterion for distinguishing between terminal and bridging pyridazine ligands has been established. However, we note that all the pyridazine bands in the spectrum of Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$ are shifted from the free ligand values (Appendix II-4) indicating that the ligands are coordinated to the metal ion. Hence we propose a trans-octahedral structure for Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$. A similar structure has been proposed for Cu(py)$_4$(CH$_3$SO$_3$)$_2$ (47) and established by X-ray crystallography for Cu(py)$_4$(CF$_3$SO$_3$)$_2$ and Fe(py)$_4$(RSO$_3$)$_2$ where R is CH$_3$, CF$_3$ and p-CH$_3$C$_6$H$_4$ (68, 137).

In support of the above structural assignment, the electronic spectrum of Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$ exhibits a single broad band which maximizes at 17 400 cm$^{-1}$. This value compares favourably with those reported (47, 68) for Cu(py)$_4$(CH$_3$SO$_3$)$_2$ (16 800 cm$^{-1}$) and Cu(py)$_4$(CF$_3$SO$_3$)$_2$ (17 400 cm$^{-1}$) and is consistent with all three
complexes having tetragonally elongated CuN$_4$O$_2$ chromophores. As mentioned in the preceding paragraph, such a structure has been confirmed for the triflate complex by single crystal X-ray diffraction (68).

2.3.3 Electron spin resonance spectra

In addition to Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$, we also examined the esr spectra of three pyrazine and two methylpyrazine copper(II) sulfonate complexes we had available (66). The results are presented in Table 2-19 and representative spectra are shown in Fig. 2-23. Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$, Cu(pyz)$_4$(CF$_3$SO$_3$)$_2$ and Cu(mepyz)$_4$(CF$_3$SO$_3$)$_2$ are all considered to have distorted octahedral CuN$_4$O$_2$ chromophores. All three compounds exhibit single $g$ spectra, represented by that of Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$ in Fig. 2-23a. This suggests that the distortions in these complexes are not sufficiently large for $g$ to be resolved into either axial or rhombic components.

Cu(pyz)(CH$_3$SO$_3$)$_2$, Cu(pyz)(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$ and Cu(mepyz)(CF$_3$SO$_3$)$_2$ are all considered to have pseudo-octahedrally coordinated copper(II) centres with CuN$_2$O$_4$ chromophores (66). Cu(mepyz)(CF$_3$SO$_3$)$_2$ exhibits a normal axial spectrum with lowest $g > 2.04$. This suggests (i) an elongated tetragonal-octahedral stereochemistry or (ii) a rhombic octahedral stereochemistry, with the "tetragonal" axes aligned, but in which the in-plane rhombic component is small and therefore the two planar components are not resolved (142). Either stereochemistry is consistent with the proposed CuN$_2$O$_4$ chromophore for this compound and a $d_{x^2-y^2}$ ground state. Cu(pyz)(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$ and Cu(pyz)(CH$_3$SO$_3$)$_2$ (Figs. 2-23 b and c, respectively) have rhombic esr spectra although the planar components are not well resolved, especially in the former compound. For a six-coordinate copper(II) complex, a rhombic spectrum in which lowest $g > 2.04$ is indicative of an elongated rhombic-octahedral geometry and a $d_{x^2-y^2}$
Fig. 2-23. ESR spectra of (a) Cu(pdz)₄(CH₃SO₃)₂, (b) Cu(pyz)(p-CH₃C₆H₄SO₃)₂ and (c) Cu(pyz)(CH₃SO₃)₂. $dA/dH$ = first derivative of absorption curve.
ground state for the copper(II) ion (142). The esr spectrum of Cu(pyz)(CH₃SO₃)₂ also shows evidence for weak and very weak shoulders, of unknown origins, with g values of ≈ 2.18 and ≈ 2.28, respectively.

Table 2-19. Esr spectral data for compounds of copper(II) sulfonates.a

<table>
<thead>
<tr>
<th>Compound</th>
<th>g₁ᵇ</th>
<th>g₂ᵇ</th>
<th>g₃</th>
<th>g₀ᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(pdz)₄(CH₃SO₃)₂</td>
<td></td>
<td></td>
<td></td>
<td>2.064</td>
</tr>
<tr>
<td>Cu(pyz)(CH₃SO₃)₂ᵈ</td>
<td>2.352</td>
<td>2.095</td>
<td>2.049</td>
<td>2.165</td>
</tr>
<tr>
<td>Cu(pyz)(p-CH₃C₆H₄SO₃)₂</td>
<td>2.343</td>
<td>≈ 2.09</td>
<td>2.056</td>
<td>≈ 2.16</td>
</tr>
<tr>
<td>Cu(pyz)₄(CF₃SO₃)₂</td>
<td></td>
<td></td>
<td></td>
<td>2.070</td>
</tr>
<tr>
<td>Cu(mepyz)₄(CF₃SO₃)₂</td>
<td></td>
<td></td>
<td></td>
<td>2.069</td>
</tr>
<tr>
<td>Cu(mepyz)(CF₃SO₃)₂</td>
<td>2.278</td>
<td>2.078</td>
<td></td>
<td>2.145</td>
</tr>
</tbody>
</table>

aData collected at liquid nitrogen temperature. Error in g = ±0.003.

ᵇ When only two g values are observed g₁ = g₁ || and g₂ = g₂ .

c g₀ = isotropic g value. For orthorhombic and axial systems g₀ = (g₁ + g₂ + g₃)/3 and g₀ = (g₁ || + 2g₂) /3 respectively.

d See text for further comment.

2.3.4 Magnetic properties

The magnetic data for Cu(pdz)₄(CH₃SO₃)₂ are presented in Appendix IV. The proposed structure for this compound does not contain bridging ligands. It is therefore expected to be magnetically dilute. This is, in fact, found to be the case. A freshly prepared sample of Cu(pdz)₄(CH₃SO₃)₂ exhibits a temperature invariant magnetic moment of 1.79 B.M. over the range 82-4.4 K. This value is within the range of 1.75-2.20 B.M. commonly observed for magnetically dilute copper(II) complexes (144).
The colour of Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$ gradually changes from blue to grey over a period of a few weeks, even when stored in an inert atmosphere. After about six weeks from the date of preparation its magnetic moment was found to have dropped to about 1.72 B.M. while the microanalytical data and infrared spectrum remained unchanged. These characteristics are reminiscent of those of Cu(pdz)$_3$(NO$_3$)$_2$ and, though less dramatic, Cu(pdz)$_4$(NO$_3$)$_2$ as discussed in section 2.2. As with the copper(II) nitrate complexes, these observations suggest that, perhaps, Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$ undergoes structural rearrangements to yield exchange coupled oligomeric complexes. However, unlike in Cu(pdz)$_4$(NO$_3$)$_2$, such exchange must be very weak or the oligomers must be present in small concentrations. This would account for the fact that only a small, but significant, drop in the magnetic moment of Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$ is observed.

2.4 Complexes of copper(II) hexafluorophosphate and hexafluoroarsenate

2.4.1 Introduction

Pyrazine has long been known to form linear bridges between metal ions generating oligomeric species (35-39) or polymeric arrays (35, 40-52). All crystal structure determinations that have been reported on the polymeric materials have revealed one of two basic structural types: (i) one-dimensional extended chain or (ii) two-dimensional square lattice. As mentioned in Chapter 1 our main interest in such materials has been in the correlation of magnetic properties with structure; hence the possibility of generating new structural types has been of primary concern to us. The counter anions present in the materials studied to date typically constitute the ancillary ligands binding to metal centres in monodentate (44-48) bidentate chelating (35, 41, 42) or bridging (52) modes. We reasoned that by utilizing non-coordinating anions as
the counter ions in the synthesis of pyrazine complexes it should be possible to obtain materials in which the metal ions are bonded only to bridging pyrazine ligands, thus generating new polymeric cationic lattices. Any such compounds with three-dimensional frameworks would fall into the class of "scaffolding-like materials" described by Hoskins and Robson (190). Such materials would not only have potential utility in the areas of ion-exchange and catalysis as outlined in the previous work (190) but, where transition metal ions with paramagnetic ground states are incorporated into the structure, would also be of considerable interest to chemists and physicists studying magnetic exchange effects in extended systems (7, 8).

We thus embarked on the investigation of complexes of copper(II) employing pyrazine-type ligands as the potentially bridging ligands and hexafluorophosphate and hexafluoroarsenate as counter anions. These anions are commonly used to precipitate cationic species because of their very weak ligating abilities (191-197); hence they were selected for this study. Complexes with the desired structural features involving cationic arrays and containing copper in the +2 oxidation state have not been isolated in this work; however, two such complexes containing copper in the +1 state have. These compounds were isolated in crystalline form suitable for single crystal X-ray diffraction studies, the results of which are described in Chapter 4.

We also prepared a number of copper(II) compounds which have been indirectly characterized as being mononuclear. These are Cu(py2)4(AsF6)2, Cu(mepy)4(AsF6)2, Cu(4,4'-bipy)4(AsF6)2, Cu(py2)4(PF6)2 and Cu(mepy)4(PF6)2. Their syntheses are described in section 5.2.4. All the complexes are hygroscopic and manipulations were carried out in a nitrogen atmosphere glove box. Preliminary synthetic and infrared spectral studies were previously carried out on some of these complexes in this laboratory (198). Evidence to be presented in this chapter indicates that the complex of composition Cu(py2)4(PF6)2 prepared in the present work and that prepared previously are different isomers.
2.4.2 Thermal properties

The DSC curves for Cu(pyz)$_4$(AsF$_6$)$_2$, Cu(mepy)_4(AsF$_6$)$_2$, and Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$ are shown in Fig. 2-24. That of the pyrazine complex exhibits endothermic events at 239, 318 and 385 °C. The first event ($\Delta H = 148$ kJ mol$^{-1}$) is accompanied by a weight loss of 22% which is consistent with the loss of two molecules of pyrazine (expected weight loss = 21%). If the two remaining molecules of pyrazine are lost in one step a total weight loss of 42% would be expected at the end of the second event. However, the observed total weight loss at the end of this event is 58% indicating that at these temperatures further decomposition has set in. The event at 385 °C must therefore be part of this decomposition process. This conclusion is supported by the observation that a sample of Cu(pyz)$_4$(AsF$_6$)$_2$ heated to the end of the 318 °C event, cooled to room temperature and then again heated, to 450 °C, did not exhibit the event at 385 °C. These results indicate that once the sample is heated to the end of the second event, decomposition proceeds to completion even if heating is stopped.

For Cu(mepy)$_4$(AsF$_6$)$_2$, the DSC curve reveals the onset of an endothermic event at about 145 °C. The event peaks at 162 °C. The region immediately above this temperature shows evidence for both exothermic and endothermic events (Fig. 2-24b). This, together with the irregular profile of the rest of the thermogram, suggests that any neutral ligand dissociation from Cu(mepy)$_4$(AsF$_6$)$_2$ is accompanied by further decomposition processes.

Two events involving relatively low enthalpy changes are observed in the DSC curve of Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$. The first, at 129 °C with $\Delta H$ of 15 kJ mol$^{-1}$, is exothermic and the second, at 207 °C with $\Delta H$ of 36 kJ mol$^{-1}$, is endothermic. Complete sample decomposition begins at about 285 °C. Unfortunately, due to equipment breakdown, no further experiments could be performed to ascertain the origin
Fig. 2-24. DSC curves for (a) Cu(py2)4(AsF6)2, (b) Cu(mepy2)4(AsF6)2 and (c) Cu(4,4'-bipy)4(AsF6)2.
of the events at 129 and 207 °C. We can, therefore, only speculate on their possible causes. A simple, stepwise loss of ligand is deemed unlikely in view of the exothermic nature of the first event. The events may reflect phase changes in the compound. They may also be an indication that the thermal decomposition of the sample actually begins at about 120 °C.

The hexafluorophosphate anion is more readily hydrolyzed than the hexafluoroarsenate anion (199) and hence, in order to protect the fragile DSC sensor from possible corrosion by hydrofluoric acid, the hexafluorophosphate complexes were not studied by the DSC method.

2.4.3 Infrared spectra

Group theory predicts six fundamental vibrations \( (v_1, A_{1g}; v_2, E_g; v_3, T_{1u}; v_4, T_{1u}; v_5, T_{2g}; v_6, T_{2u}) \) for the \( \text{EF}_6 \) (\( E = \text{As, P} \)) moiety in octahedral symmetry. Only the \( T_{1u} \) vibrations are infrared active. When the \( \text{EF}_6 \) moieties are formally coordinated through one fluorine atom to a metal centre, the anion symmetry can be no higher than \( C_{4v} \). As a result, the \( v_1 \) mode becomes infrared active (\( A_1 \) symmetry), \( v_2 \) splits into transitions of \( A_1 \) (ir active) and \( B_1 \) (ir inactive) symmetry, \( v_3 \) and \( v_4 \) both split into infrared active transitions of \( A_1 \) and \( E \) symmetry, \( v_5 \) splits into transitions of \( B_2 \) (ir inactive) and \( E \) (ir active) symmetry, \( v_6 \) splits into transitions of \( B_1 \) (ir inactive) and \( E \) (ir active) symmetry. The infrared active \( E \) modes derived from \( v_5 \) and \( v_6 \) (\( O_h \)) are expected to be at low energies and, perhaps, because of this or interference from other ligand vibrations, they were not observed in earlier work on complexes related to those under consideration here (141). Based on the features outlined above, together with experimental observations, empirical infrared criteria for distinguishing between non-coordinated and coordinated \( \text{AsF}_6^- \) and \( \text{PF}_6^- \) anions have been proposed (141, 193).
Non-coordinated anions are characterized by a very strong \( v_3 \) band which may be split by up to 25 cm\(^{-1} \), strong and unsplit \( v_4 \) band, and weak or absent \( v_1 \) and \( v_2 \) bands. The appearance of the formally forbidden \( v_1 \) and \( v_2 \) vibrations in octahedral symmetry in complexes where the anions are formally non-coordinated may be attributed to reduction of anion site symmetry below \( O_h \), or distortion of the anions through relatively weak interactions with neutral ligand molecules (193). More strongly coordinated \( EF_6^- \) moieties, on the other hand, show greater splitting of degenerate modes and greater intensities of bands formally forbidden in \( O_h \) symmetry.

Absorption bands due to the internal vibrations of pyrazine, methylpyrazine and 4,4'-bipyridine are given in Appendixes II-2, II-3 and II-5, respectively. Bands due to the \( AsF_6^- \) and \( PF_6^- \) moieties with assignments (according to reference 200) are given in Table 2-20. The infrared spectra of \( Cu(4,4'-bipy)_4(AsF_6)_2 \) and \( Cu(mepy)_4(AsF_6)_2 \) exhibit very similar anion bands; that of the former is shown in Fig. 2-25. Each shows strong anion bands assigned to \( v_1 \) and \( v_4 \), a strong broad band assigned to \( \nu_3 \) and a weak band assigned to \( \nu_2 \). \( Cu(mepy)_4(AsF_6)_2 \) shows an additional medium band also assigned to \( \nu_2 \). These spectral characteristics are very similar to those observed in the spectra of the related \( CuL_4(AsF_6)_2 \) (\( L \) is py, 3-mepy or 4-mepy) complexes (141) and suggest that the anions in \( Cu(mepy)_4(AsF_6)_2 \) and \( Cu(4,4'-bipy)_4(AsF_6)_2 \) are coordinated to the metal centres.

In the case of \( Cu(py)_4(AsF_6)_2 \), the anion bands exhibit some significant differences from those of the other \( CuL_4(AsF_6)_2 \) complexes: \( \nu_2 \) is not observed, \( \nu_3 \) is resolved into two components and \( \nu_4 \), though not well resolved, is split. The reason for these differences is not clear. However, the intensity of \( \nu_1 \) (medium to strong) and the splitting of the \( \nu_3 \) and \( \nu_4 \) bands indicate significant anion distortion from \( O_h \) symmetry. Hence the infrared spectrum of \( Cu(py)_4(AsF_6)_2 \) is consistent with appreciable metal-anion interaction in this complex.
Table 2-20. Band energies and assignments for the hexafluorophosphate and hexafluoroarsenate anions.\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v_3)</th>
<th>(v_1)</th>
<th>(v_2)</th>
<th>(v_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(pyz)(_4)(AsF(_6))(_2)</td>
<td>697 vs, as</td>
<td>657 m-s</td>
<td>n.o.</td>
<td>398 vs, sp</td>
</tr>
<tr>
<td></td>
<td>729 s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(mepygz)(_4)(AsF(_6))(_2)</td>
<td>710 s, br</td>
<td>671 s</td>
<td>551 m</td>
<td>402 s</td>
</tr>
<tr>
<td>Cu(4,4'-bipy)(_4)(AsF(_6))(_2)</td>
<td>707 vs, br</td>
<td>675 s</td>
<td>561 w</td>
<td>406 s</td>
</tr>
<tr>
<td>Cu(pyz)(_4)(PF(_6))(_2)</td>
<td>839 vs, br</td>
<td>751 w(^b)</td>
<td>d</td>
<td>565 s</td>
</tr>
<tr>
<td>Cu(mepygz)(_4)(PF(_6))(_2)</td>
<td>859 vs, br</td>
<td>c</td>
<td>d</td>
<td>563 s</td>
</tr>
</tbody>
</table>

\(^a\) All values are in cm\(^{-1}\). Assignments made, assuming \(O_h\) symmetry, according to ref. 200. \(v\) = very, \(s\) = strong, \(m\) = medium, \(w\) = weak, \(a\) = asymmetric, \(sp\) = split, n.o. = not observed.

\(^b\) Pyrazine also has a weak band in this region.
\(^c\) Obscured by neutral ligand band.
\(^d\) Not observed. May be obscured by \(v_4\).

---

Fig. 2-25. Infrared spectrum of Cu(4,4'-bipy)\(_4\)(AsF\(_6\))\(_2\).
The assignment of the PF$_6^-$ anions in Cu(pyz)$_4$(PF$_6$)$_2$ and Cu(mepy)$_4$(PF$_6$)$_2$ as coordinated or non-coordinated is less straightforward than the assignment of the AsF$_6^-$ anions in the complexes considered above. In the former, the neutral ligands have absorption bands in the region where the $v_1$ ($O_h$) band of the PF$_6^-$ anion is expected to occur. Furthermore, the infrared active component of the $v_2$ band is expected in a region where it may be obscured by the $v_4$ vibration (141). The assignment of the PF$_6^-$ anions as coordinated may, however, be made by comparing the electronic spectra of the hexafluorophosphate and hexafluoroarsenate complexes (section 2.4.4). The latter contain coordinated AsF$_6^-$ anions. Hence the observation that the degree of tetragonal distortion in Cu(pyz)$_4$(AsF$_6$)$_2$ and Cu(mepy)$_4$(AsF$_6$)$_2$ is greater than in Cu(pyz)$_4$(PF$_6$)$_2$ and Cu(mepy)$_4$(PF$_6$)$_2$, respectively, suggests that the PF$_6^-$ anions in the hexafluorophosphate complexes are coordinated to the copper ions.

Nearly all the infrared absorption bands of free 4,4'-bipyridine (201) are reproduced in the spectrum of Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$, albeit with some minor shifts and splittings (Appendix II-5). The band shifts indicate that the 4,4'-bipyridine ligands are coordinated to the copper ions. The small splittings observed may result from different environments for the 4,4'-bipy groups arising from different orientations of the ligands, due to steric constraints, about the N-N axes. The splittings may also arise from interactions of some of the 4,4'-bipy molecules with the AsF$_6^-$ moieties. The band shifts and splittings of the magnitude observed here have been observed in spectra of pyridine (137) and pyrazine (47) metal complexes that have been structurally characterized by single crystal X-ray diffraction. We propose for Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$ an elongated tetragonal-octahedral structure containing monodentate 4,4'-bipyridine and hexafluoroarsenate ligands. Similar structures were previously proposed for the related complexes, CuL$_4$(AsF$_6$)$_2$, where L is pyridine or 3- or 4-methylpyridine (141).
It was noted in section 2.1.4 that for terminal methylpyrazine coordination, the band at 410 cm\(^{-1}\) in the infrared spectrum of the free base shifts to between 425 and 440 cm\(^{-1}\) and that at 472 cm\(^{-1}\) shifts to between 500 and 510 cm\(^{-1}\). For bridging bidentate coordination, corresponding bands occur above 440 and 520 cm\(^{-1}\), respectively. The corresponding bands are observed at 430 and 506 cm\(^{-1}\) in the spectrum of Cu(mepy)\(_4\)(AsF\(_6\))\(_2\) and at 427 and 508 cm\(^{-1}\) in the spectrum of Cu(mepy)\(_4\)(PF\(_6\))\(_2\). These results indicate that both compounds contain monodentate methylpyrazine groups. The structure most consistent with the infrared and electronic (vide infra) spectra of Cu(mepy)\(_4\)(AsF\(_6\))\(_2\) and Cu(mepy)\(_4\)(PF\(_6\))\(_2\) is an elongated tetragonal-octahedral one involving monodentate coordination of both the neutral and anionic ligands.

Previous studies on pyrazine complexes have established that while most pyrazine bands exhibit shifts to higher energies on coordination, the most sensitive is the band at 417 cm\(^{-1}\) in the spectrum of the free ligand (47, 64, 65, 67). Recently it was pointed out that shifts in this band to about 450 cm\(^{-1}\) usually indicate monodentate coordination, whereas, shifts to 470 cm\(^{-1}\) or higher suggest bidentate coordination (44). In Cu(pyz)\(_4\)(PF\(_6\))\(_2\) this band occurs at 463 cm\(^{-1}\). Cu(pyz)\(_4\)(AsF\(_6\))\(_2\) exhibits two corresponding bands of medium intensity at 457 and 463 cm\(^{-1}\). Such small band splittings have been observed in other pyrazine metal complexes (66) and, as with the case of 4,4'-bipyridine discussed above, may arise from interactions of the pyrazine molecules with the anionic ligands or from different environments for the pyrazine groups. The position of the diagnostic pyrazine bands in the spectra of Cu(pyz)\(_4\)(PF\(_6\))\(_2\) and Cu(pyz)\(_4\)(AsF\(_6\))\(_2\) do not allow unambiguous assignment of the denticity of pyrazine as they occur between the ranges expected for monodentate and bidentate modes of pyrazine coordination. Presumably, because of the weak ligating abilities of the AsF\(_6^-\) and PF\(_6^-\) anions, the copper(II) ions in Cu(pyz)\(_4\)(AsF\(_6\))\(_2\) and Cu(pyz)\(_4\)(PF\(_6\))\(_2\) interact more strongly with the pyrazine ligands and, as a consequence, the 417 cm\(^{-1}\) free
pyrazine band shifts to higher energies than normally observed for monodentate coordinated pyrazine ligands. From the stoichiometry, the electronic spectrum (vide infra) and the observation from infrared spectral data that all ligands in Cu(pyz)$_4$(AsF$_6$)$_2$ are coordinated to the copper ion, we propose for this compound an elongated tetragonal-octahedral structure with monodentate neutral ligands and coordinated anions. A similar structure is proposed for Cu(pyz)$_4$(PF$_6$)$_2$.

The sample of Cu(pyz)$_4$(PF$_6$)$_2$ used in the present study was prepared by the reaction of Cu(ClO$_4$)$_2$.6H$_2$O, NH$_4$PF$_6$ and pyrazine and its infrared spectrum is shown in Fig. 2-26a. We were unable to obtain an analytically pure sample when KPF$_6$ was used instead of NH$_4$PF$_6$, despite several attempts. The infrared spectrum of the impure product is shown in Fig. 2-26b. The spectrum is identical to that reported in an earlier investigation of Cu(pyz)$_4$(PF$_6$)$_2$ (198). In the earlier study an analytically pure sample of Cu(pyz)$_4$(PF$_6$)$_2$ was prepared by the reaction of AgPF$_6$, anhydrous CuCl$_2$ and pyrazine in methanol. We therefore conclude that Cu(pyz)$_4$(PF$_6$)$_2$ can be isolated in at least two isomeric forms, depending on the starting materials and solvent used.

In summary Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$, Cu(pyz)$_4$(AsF$_6$)$_2$, Cu(mepyz)$_4$(AsF$_6$)$_2$, Cu(pyz)$_4$(PF$_6$)$_2$ and Cu(mepyz)$_4$(PF$_6$)$_2$ are concluded to be mononuclear species with elongated tetragonal-octahedral structures containing monodentate neutral and anionic ligands.
Fig. 2-26. Infrared spectra of the isomers of Cu(pyz)₄(PF₆)₂. (a) PF₆⁻ groups obtained from NH₄PF₆; (b) PF₆⁻ groups obtained from KPF₆.
2.4.4 Electronic spectra

The electronic spectra of the five CuL₄A₂ complexes, where L is pyz, mepyz or 4,4'-bipy and A is AsF₆ or PF₆, all exhibit one broad band in the visible region of the electromagnetic spectrum. The energies of the band maxima are listed in Table 2-21. The relatively high energies at which the band maxima occur are consistent with the elongated tetragonal CuN₄F₂ chromophores (141, 202) proposed for these compounds (see section 2.4.3). The energies of the band maxima observed for the compounds prepared in the present work are comparable to those observed for their pyridine and methyl-substituted pyridine analogues (141). The absorption maxima for the pyridine complexes, for which elongated trans-octahedral structures have been proposed, lie in the range 18 700-19 600 cm⁻¹ (141).

Table 2-21. Electronic spectral data for compounds of copper(II)-hexafluoroarsenate and hexafluorophosphate.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nm</td>
</tr>
<tr>
<td>Cu(mepyz)₄(AsF₆)₂</td>
<td>530</td>
</tr>
<tr>
<td>Cu(4,4'-bipy)₄(AsF₆)₂</td>
<td>530</td>
</tr>
<tr>
<td>Cu(mepyz)₄(PF₆)₂</td>
<td>534</td>
</tr>
<tr>
<td>Cu(pyz)₄(AsF₆)₂</td>
<td>547</td>
</tr>
<tr>
<td>Cu(pyz)₄(PF₆)₂</td>
<td>570</td>
</tr>
</tbody>
</table>
2.4.5 Electron spin resonance spectra

Cu(pyz)$_4$(AsF$_6$)$_2$, Cu(mepy)$_4$(AsF$_6$)$_2$ and Cu(mepy)$_4$(PF$_6$)$_2$ exhibit single peaks in their esr spectra at ~90 K. The $g$ values for the complexes are 2.063, 2.060 and 2.059, respectively. A representative spectrum, that of Cu(pyz)$_4$(AsF$_6$)$_2$, is shown in Fig. 2-27. Six-coordinate copper(II) complexes tend to have tetragonally distorted octahedral structures. This, coupled with the presence of four identical neutral ligands and two, generally, weakly coordinating anionic ligands, should lead to elongated tetragonal-octahedral geometries for the copper ions in the complexes under consideration here. With the ligand fields to which the copper ions are subjected being less than cubic, the $g$ values cannot be isotropic. This is supported by the fact that the single peak in each spectrum is assymmetric about the dA/dH = 0 axis. Presumably the resolution of $g$ into axial components is not observed in the spectra of these compounds as a result of exchange broadening.

Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$ has an esr spectrum (Fig. 2-28a) with four $g$ values (2.233, 2.176, 2.085, 2.056). This spectrum is much like those reported earlier for the the complexes CuL$_4$A$_2$, where L is pyridine, 3-methylpyridine or 4-methylpyridine and A is AsF$_6$ or PF$_6$ (141). In the latter case, the observed spectral features were ascribed to copper nuclear hyperfine interactions. Two components of $g_{||}$ are well resolved while the other two are obscured by the $g$ perpendicular peak. The non-resolution of $g_\perp$ in the spectra of these complexes was attributed to the superimposition of nitrogen hyperfine coupling and to a relatively smaller perpendicular copper hyperfine coupling constant, $A_\perp$, compared to the parallel copper hyperfine coupling constant, $A_{||}$. Like in the earlier study, we conclude that the observed features in the esr spectrum of Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$ arise from copper nuclear hyperfine interaction. $g_{||}$ for this compound is estimated to be 2.149 and $A_{||}$ is estimated to be $76.2 \times 10^{-4}$ cm$^{-1}$. The esr spectrum of Cu(pyz)$_4$(PF$_6$)$_2$ (Fig. 2-28b) also show evidence for copper nuclear
hyperfine interaction. Two of the four components (g at 2.268 and ≈2.19, the latter being weaker) of \(g_{\parallel}\) are observed. As with the CuL4A2 complexes reported earlier (141), and discussed above, the splitting of the \(g_\perp\) peak is not observed in the spectrum of Cu(pyz)4(PF6)2. The single peak observed in the \(g_\perp\) region has a g value of 2.063. \(g_{\parallel}\) for Cu(pyz)4(PF6)2 is estimated to be 2.149 and \(A_{\parallel}\) is estimated to be \(102 \times 10^{-4}\) cm\(^{-1}\).

\[dA/dH = \text{first derivative of absorption curve.}\]
Fig. 2-28. ESR spectra of (a) Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$ and (b) Cu(pyz)$_4$(PF$_6$)$_2$.

dA/dH = first derivative of absorption curve.
2.4.6 Magnetic properties

The magnetic data for the copper(II) hexafluoroarsenate and hexafluorophosphate complexes are presented in Appendix IV. The magnetic moments of Cu(py2)4(AsF6)2, Cu(mepy2)4(AsF6)2 and Cu(mepy2)(PF6)2 are temperature-independent and their magnitudes fall within the range (1.75-2.20 B.M.) expected for magnetically dilute copper(II) systems (144). These results are consistent with the conclusion drawn from spectroscopic studies (vide supra) that these compounds exist as mononuclear species.

The magnetic moment of Cu(4,4'-bipy)2(AsF6)2 decreases from 1.81 B.M. at 82.1 K to 1.70 B.M. at 4.3 K. That of Cu(py2)(PF6)2 drops from 1.92 B.M. at 81.7 K to 1.62 B.M. at 4.4 K. The small, but significant, decrease in the magnetic moments of these compounds indicates that there is very weak antiferromagnetic coupling between the copper(II) ions. Since the structures proposed for these compounds contain no bridging entities, the antiferromagnetic interactions must be intermolecular.

Magnetic properties similar to those observed in Cu(4,4'-bipy)2(AsF6)2 and Cu(py2)(PF6)2 have been observed in [Cu(dien)(4,4'-bipy)(H2O)][ClO4]2 where dien is diethylenetriamine (203). This compound has been shown by X-ray crystallography to be mononuclear with a structure consisting of [Cu(dien)(4,4'-bipy)(H2O)]2+ cations and non-coordinated perchlorate anions. Only one nitrogen atom of the 4,4'-bipy is bonded to the copper(II) ion. The oxygen atom of the water molecule in one cationic unit is hydrogen bonded to the non-coordinated nitrogen atom of a 4,4'-bipy group of a neighbouring unit. The magnetic moment of [Cu(dien)(4,4'-bipy)(H2O)][ClO4]2 decreases from 1.88 B.M. at 50.6 K to 1.70 B.M. at 4.2 K indicating the existence of an antiferromagnetic interaction between the copper(II) ions (203). It was suggested in reference 203 that the magnetic exchange in this compound goes through space and is
between nearest neighbouring copper ions, which are 6.8 Å apart. We propose a similar exchange mechanism in Cu(4,4'-bipy)₄(AsF₆)₂ and Cu(pyz)₄(PF₆)₂. A pathway involving a hydrogen bond between the non-coordinated nitrogen atom of the neutral ligand in one molecule and a H-atom of a neutral ligand (or a F atom of an anionic ligand) in a neighbouring molecule would be too long.

2.5 Summary and conclusions

The correlations between the magnetic properties and structures of all the compounds discussed in this chapter are summarized in this section. [Cu(pdz)₄(NO₃)] [NO₃] and Cu(pdz)₃(NO₃)₂ were shown by single crystal X-ray diffraction studies to be mononuclear species involving five- and six-coordinate copper(II) ions, respectively. Based on indirect evidence Cu(pdz)₄(NO₃)₂, Cu(pdz)₄(CH₃SO₃)₂, Cu(pyz)₄(AsF₆)₂, Cu(mepy)₄(AsF₆)₂, Cu(4,4'-bipy)₄(AsF₆)₂, Cu(pyz)₄(PF₆)₂ and Cu(mepy)₄(PF₆)₂ are concluded to be mononuclear species with elongated tetragonal-octahedral structures incorporating monodentate neutral and anionic ligands. These complexes, with two exceptions, are magnetically dilute, as is usually observed for complexes in which there are no bridging units between paramagnetic centres. Cu(4,4'-bipy)₄(AsF₆)₂ and Cu(pyz)₄(PF₆)₂ show evidence of weak antiferromagnetic interactions between the copper(II) ions. A through-space mechanism has been proposed for these interactions.

The structure of Cu(mepy)₂(NCO)₂, as determined by X-ray crystallography, is made up of parallel sheets each consisting of an infinite square array of copper ions bridged by bidentate methylpyrazine ligands. Coordination number of six about the copper ions is completed by trans N-bonded cyanate groups. Despite the presence of bridging units, the compound is magnetically dilute. This may be attributed to the
unsymmetrical nature of the methylpyrazine bridges, manifested in the form of one short and one relatively long Cu-N bond length. In addition, each methylpyrazine bridge in Cu(mepysh)\(_2\)(NCO)\(_2\) interacts with a magnetic orbital of one copper ion and a non-magnetic orbital of the second copper ion. Consequently, there is no continuous path for magnetic exchange between the copper ions. The bridging cyanate groups in Cu(py)\(_2\)(NCO)\(_2\) are also unsymmetrical (118) and consequently, like its methylpyrazine analogue, this compound is magnetically dilute. \([\text{Cu(pdz)}\(_2\)(\text{NO}_3)\(_2\)]\) was shown by X-ray crystallography to have a centrosymmetric linear trinuclear structure. The copper ions are linked by two bidentate bridging pyridazine groups and one monodentate bridging nitrate group. Neighbouring copper ions in the compound are strongly coupled antiferromagnetically, |J| being 139 cm\(^{-1}\). The coupling between the terminal copper ions appears to be negligible. The pyridazine bridges are considered to provide the primary pathway through which the observed magnetic exchange is mediated.

The structures proposed for Cu(py)(NCO)\(_2\) and Cu(mepysh)(NCO)\(_2\) involve chains of copper ions doubly-bridged unsymmetrically by >NCO anions and cross-linked into sheets by bridging neutral ligands. Both compounds exhibit very weak antiferromagnetic coupling (-J \approx 1 cm\(^{-1}\)), transmitted via the neutral ligands. >NCO bridging groups have been shown (116) to provide pathways for ferromagnetic exchange and their apparent lack of contribution to the exchange in these complexes may be a consequence of the unsymmetrical nature of the bridges.

The antiferromagnetic exchange coupling in Cu(pdz)(NCO)\(_2\) is much stronger (-J = 44.0 cm\(^{-1}\)) than in its pyrazine or methylpyrazine analogues. The proposed structure for this compound consists of linear chains of copper ions triply-bridged by the >NCO and pyridazine ligands. As with the complexes discussed in the preceding paragraph the neutral ligand is considered to propagate the magnetic exchange in this compound. It would seem that pyridazine affords a more efficient pathway for
magnetic exchange between copper(II) ions than either pyrazine or methylpyrazine.

The weakly coordinating anions, AsF$_6^-$ and PF$_6^-$, were employed in this study with the hope of generating novel polymeric cationic lattices incorporating transition metal ions with paramagnetic ground states. However, only cationic lattices containing metal ions with diamagnetic ground states were obtained. Possible reasons for this are examined in section 4.3.
3.1 Complexes of nickel(II) cyanate

3.1.1 Introduction

As was discussed in section 2.1.1, Fe(py)₂(NCO)₂ and Fe(pyz)(NCO)₂ exhibit interesting magnetic properties (67, 116) and, in order to examine more fully the nature of low-dimensional magnetic exchange effects in cyanate complexes, we decided to extend the work to include other metals and diazine ligands. In this section the results of our studies on the nickel(II) complexes Ni(py)₄(NCO)₂, Ni(pyz)₂(NCO)₂·½H₂O, Ni(pdz)₂(NCO)₂ and Ni(pyz)(NCO)₂ are presented. Some studies on Ni(py)₄(NCO)₂ were reported earlier (117) while the synthesis and characterization of the other three complexes are reported here for the first time. Details of their preparations are given in section 5.2.1. Except for Ni(pdz)₂(NCO)₂ which is hygroscopic, the compounds are sufficiently air-stable that manipulations could be carried out in the atmosphere. Samples were, however, stored in a desiccator over Drierite. Ni(pdz)₂(NCO)₂ was handled in an inert atmosphere glove box.

3.1.2 Thermal properties

The thermal parameters for complexes of nickel(II) cyanate are given in Table 3-1. Ni(py)₄(NCO)₂ was previously reported to undergo decomposition at
107 °C (117). The compound prepared in this work exhibits three closely spaced endothermic events at 90, 163 and 192 °C in its thermogram (Fig. 3-1). Weight loss over the three events corresponds to the loss of three pyridine ligands. Exothermic decomposition begins at 265 °C for this complex. No details were given in the previous study (117) on how decomposition temperatures were determined.

Table 3-1. Thermal parameters* for complexes of nickel(II) cyanate.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. °C</th>
<th>ΔHb kJ mol⁻¹</th>
<th>Weight lossb %</th>
<th>Number and type of species lost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(pyz)₄(NCO)₂</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>163</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>192</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(pyz)₂(NCO)₂.½H₂O</td>
<td>222</td>
<td>52</td>
<td>29</td>
<td>1 pyz+ ½H₂O</td>
</tr>
<tr>
<td></td>
<td>320c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(pdz)₂(NCO)₂</td>
<td>255</td>
<td>77</td>
<td>26</td>
<td>1 pdz</td>
</tr>
<tr>
<td></td>
<td>310c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(pyz)(NCO)₂</td>
<td>320c</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a Estimated error limits: peak temp. ±5 °C, ΔH ±5%, weight loss ±5%.

*b Was determined only when well defined thermal events were observed.

c Onset of decomposition.

The DSC thermograms of Ni(pyz)₂(NCO)₂.½H₂O and Ni(pdz)₂(NCO)₂ show endothermic events at 222 °C and 255 °C, respectively, which weight loss measurements indicate are due to the formation of the corresponding NiL(NCO)₂ complexes. Further heating leads to exothermic decomposition beginning at 320 °C and 310 °C, respectively. Consistent with the above, the independently synthesized sample of Ni(pyz)(NCO)₂ exhibits only thermal decomposition beginning at 320 °C.
The DSC results for the pyridazine complex suggested the possibility of synthesizing the mono(pdz) complex in bulk by thermolysis; however repeated attempts to do so failed to yield analytically pure samples. The use of controlled amounts of reagents also failed to yield pure samples of Ni(pdz)(NCO)₂. The latter synthetic route was successfully employed in the preparation of Ni(py)(NCO)₂.

Fig. 3-1. DSC curve for Ni(py)₄(NCO)₂.
3.1.3 Infrared spectra

Absorption bands due to internal vibrations of pyridine, pyrazine and pyridazine ligands are given in Appendices II-1, II-2 and II-4, respectively, while those due to the cyanate groups are given in Table 3-2. Infrared spectra of Ni(pyz)_2(NCO)_2·½H_2O and Ni(pyz)(NCO)_2 are presented in Fig. 3-2 and are representative for this class of complexes. Infrared criteria for distinguishing between these ligands when free and when coordinated, and between the various possible modes of coordination of the pyrazine and cyanate groups were discussed in detail in section 2.1.4. An analysis of the infrared spectra of the nickel(II) cyanate complexes on the basis of that discussion leads to the following conclusions: (i) the cyanate anions are bridging in Ni(pyz)(NCO)_2 and terminal N-bonded in Ni(py)_4(NCO)_2, Ni(pyz)_2(NCO)_2·½H_2O and Ni(pdz)_2(NCO)_2, (ii) the tetrakis(pyridine) complex shows only bands expected for coordinated pyridine and (iii) the pyrazine ligands are bridging in its two complexes studied here. The above analysis, coupled with electronic spectral results (vide infra), leads to the following structural assignments.

For Ni(pyz)(NCO)_2, we propose the structure shown in Fig. 3-3a which involves chains of nickel ions double-bridged by >NCO anions and cross-linked by bidentate pyrazine ligands. This is the structure proposed previously for the analogous iron compound, Fe(pyz)(NCO)_2 (67).

The structure we propose for Ni(pyz)_2(NCO)_2·½H_2O is shown in Fig. 3-4a and is the same as that previously proposed for Fe(pyz)_2(NCS)_2 on the basis of spectroscopic evidence (67) and subsequently confirmed by a single crystal X-ray diffraction study (48). In this structure, bridging pyrazine ligands form a two-dimensional square array with the nickel ions. Terminal N-bonded cyanate anions complete the pseudo-octahedral configuration around each nickel ion. The position of
the half mole of water in the nickel structure cannot be determined from our study but we assume it is lattice water, possibly hydrogen-bonded to the cyanate ligands.

Primarily on the basis of infrared evidence, Ni(py)$_4$(NCO)$_2$ was previously assigned a distorted octahedral structure with trans-coordinated N-bonded cyanate ligands (117). Our spectral data are consistent with this assignment. Moreover, in the present study, a single crystal X-ray diffraction study of the compound revealed disorder, with cyanate and pyridine ligands randomly occupying coordination sites. Although the data could not be refined well enough to yield reasonable bonding parameters the refinement was sufficient to confirm the mononuclear nature and near regular octahedral structure of the compound.

No infrared criterion for distinguishing between terminal and bridging pyridazine has been established to date. However, in the case of Ni(pdz)$_2$(NCO)$_2$, the observations of (i) an electronic spectrum supporting pseudooctahedral stereochemistry (see below) and (ii) an infrared spectrum indicating monodentate cyanate ligands require the pyridazine ligands to be bidentate in this compound. It is unlikely that a 3-membered ring chelate complex is formed; hence, a structure with bridging pyridazine ligands is indicated. A structure like that proposed for the bis(pyrazine) complex is considered unlikely for pyridazine complexes. While pyrazine is capable of forming linear bridges as in Fig. 3-4, pyridazine bridges would be "bent" (recall the structure of [Cu(pdz)$_2$(NO$_3$)$_2$)$_3$, section 2.2.5). The structure we propose for Ni(pdz)$_2$(NCO)$_2$ is shown in Fig. 3-5 where chains of nickel ions are double-pyridazine bridged. Terminal N-bonded cyanate groups occupy the fifth and sixth coordination sites on the nickel ions.
Fig. 3-2. Infrared spectra of (a) Ni(pyz)(NCO)$_2$ and (b) Ni(pyz)$_2$(NCO)$_2$.½H$_2$O.
Table 3-2. Cyanate ion band energies and assignments for nickel(II) complexes.*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Energies and assignments</th>
<th>ΔδNCO&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ν&lt;sub&gt;CN&lt;/sub&gt;</td>
<td>δ&lt;sub&gt;NCO&lt;/sub&gt;</td>
</tr>
<tr>
<td>Ni(py)&lt;sub&gt;4&lt;/sub&gt;(NCO)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2 158sh</td>
<td>617s</td>
</tr>
<tr>
<td></td>
<td>2 210vs,br</td>
<td></td>
</tr>
<tr>
<td>Ni(py)z)&lt;sub&gt;2&lt;/sub&gt;(NCO)&lt;sub&gt;2&lt;/sub&gt;·½H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 218vs,br</td>
<td>621s</td>
</tr>
<tr>
<td>Ni(pdz)&lt;sub&gt;2&lt;/sub&gt;(NCO)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2 131sh</td>
<td>613s</td>
</tr>
<tr>
<td></td>
<td>2 185</td>
<td>621s</td>
</tr>
<tr>
<td></td>
<td>2 205 vs,sp</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 227</td>
<td></td>
</tr>
<tr>
<td>Ni(pyz)(NCO)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2 108sh</td>
<td>621s</td>
</tr>
<tr>
<td></td>
<td>2 218vs,br</td>
<td></td>
</tr>
</tbody>
</table>

* All values are in cm<sup>-1</sup>. w = weak, m = medium, s = strong, v = very, br = broad, sp = split.

<sup>b</sup> Magnitude of splitting of δ<sub>NCO</sub>.

---

Fig. 3-3. Proposed structures for Ni(pyz)<sub>2</sub>X<sub>2</sub> complexes. (a) M = Ni, X = >NCO; (b) M = Ni, X = Cl; (c) M = Ni, X = —NCS—.
Fig. 3-4. Proposed structures for Ni(pyz)_2X_2 complexes. (a) M = Ni, X = —NCO; (b) M = Ni, X = Cl; (c) M = Ni, X = —NCS.

Fig. 3-5. Proposed structure for Ni(pdz)_2(NCO)_2. M = Ni, X = —NCO.
3.1.4 Electronic spectra

The effects of octahedral and tetragonally elongated octahedral ligand fields on the triplet terms of the nickel(II) ion are shown in Fig. 3-6. Three spin allowed transitions are expected in an octahedral nickel(II) complex. These are from the $^3A_{2g}(F)$ ground state to the $^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ excited states and their energies are designated $v_1$, $v_2$ and $v_3$ respectively. In descending to $D_{4h}$ symmetry, each of the three orbitally degenerate $T$ states is split into two components giving rise to, in theory, a total of six spin-allowed transitions. In practice all six bands are rarely seen. Absorption bands in room temperature solid state electronic spectra are generally broad because they contain a number of component vibrational transitions. Poor resolution of components of bands split as a result of spin-orbit coupling effects may also give rise to broad bands. Greater resolution may be achieved in low temperature studies, as has been the case in mull spectra of Ni(py)$_4$X$_2$ (X is Cl or Br) complexes at liquid nitrogen temperature (204). Another reason why all the expected bands are sometimes not observed, in both $O_h$ and $D_{4h}$ symmetries, is that the highest energy band may be obscured by charge transfer or internal ligand bands.

The electronic spectra of the nickel(II) cyanate complexes are given in Table 3-3. A representative spectrum, that of Ni(py)$_4$(NCO)$_2$, is shown in Fig. 3-7. The solid state electronic spectrum of this compound is in good agreement (Table 3-3) with its solution spectrum reported by Nelson and Shepherd (205). Since no splitting of any of the spectral bands is observed for any of the nickel(II) cyanate complexes, any tetragonal distortion arising from the presence of two different types of ligands, the neutral ligand and the cyanate ion, must be small. This is consistent with the single crystal X-ray diffraction data of Ni(py)$_4$(NCO)$_2$ discussed in the preceding section. Thus the spectral bands for these complexes are assigned assuming $O_h$ local symmetry. Although all the bands are expected to be weak because they are Laporte forbidden, the
band assigned to the $^3A_{2g}(F) \rightarrow ^1E_g(D)$ transition is considerably weaker than the rest (Fig. 3-7) because it is also spin forbidden.

Table 3-3. Electronic spectral band energies and assignments for complexes of nickel(II) cyanate, $O_h$ symmetry.\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^3T_{2g}(F)$ ($v_1$)</th>
<th>$^1E_g(D)$ ($v_2$)</th>
<th>$^3T_{1g}(F)$ ($v_3$)</th>
<th>$^3T_{1g}(P)$ ($v_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(py)$_4$(NCO)$_2$</td>
<td>10 100 (990)</td>
<td>13 100 (762)</td>
<td>16 000 (603)</td>
<td>27 000 (370)</td>
</tr>
<tr>
<td>Ni(pdz)$_2$(NCO)$_2$</td>
<td>10 400 (958)</td>
<td>12 900 (777)</td>
<td>16 800 (596)</td>
<td>26 500 (377)</td>
</tr>
<tr>
<td>Ni(pyz)$_2$(NCO)$_2$,½H$_2$O</td>
<td>10 700 (933)</td>
<td>13 100 (762)</td>
<td>17 400 (575)</td>
<td>27 000 (370)</td>
</tr>
<tr>
<td>Ni(pyz)(NCO)$_2$</td>
<td>9 700 (1 033)</td>
<td>12 800 (783)</td>
<td>15 600 (640)</td>
<td>25 300 (396 sh)</td>
</tr>
<tr>
<td>Ni(py)$_4$(NCO)$_2$(^b)</td>
<td>10 050, $\approx$ 13 000sh, 16 610, 26 810</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Transitions are from the $^3A_{2g}$ state; sh = shoulder, estimated uncertainty in absorption maxima is $\pm$ 200 cm$^{-1}$.

\(^b\) Solution spectrum in chloroform at ambient temperature; data from ref. 205.

Table 3-4. Ligand field parameters for complexes of nickel(II) cyanate, $O_h$ symmetry.\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dq (cm$^{-1}$)</th>
<th>B (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(py)$_4$(NCO)$_2$</td>
<td>1 010</td>
<td>820</td>
</tr>
<tr>
<td>Ni(pdz)$_2$(NCO)$_2$</td>
<td>1 040</td>
<td>807</td>
</tr>
<tr>
<td>Ni(pyz)$_2$(NCO)$_2$,½H$_2$O</td>
<td>1 070</td>
<td>820</td>
</tr>
<tr>
<td>Ni(pyz)(NCO)$_2$</td>
<td>970</td>
<td>787</td>
</tr>
</tbody>
</table>

\(^a\) Error limits: Dq $\pm$ 20 cm$^{-1}$, B $\pm$ 14 cm$^{-1}$. 
Fig. 3-6. Effects of octahedral and tetragonally elongated ligand fields on the triplet terms of nickel(II) ion.

Fig. 3-7. Electronic spectrum of Ni(py)$_4$(NCO)$_2$. N = Nujol bands; * = charge transfer or internal ligand bands.
The ligand field parameter, Dq, and the inter-electronic repulsion (Racah) parameter, B, may be derived from the electronic spectra of octahedral nickel(II) complexes. The former may be used to establish a spectrochemical series of ligands if a large number of closely related complexes are available whereas, the latter may be used to derive the nephelauxetic parameter, \( \beta \) (\( \beta = (B_{\text{complex}}/B_{\text{free ion}}) \)). "Metal electron clouds" are more diffuse in complexes than in free ions leading to reduced repulsions between d-electrons. Consequently B in complexes is expected to be lower than in free ions. The more diffuse the electron clouds are (i.e. the stronger the covalent bond) the smaller is \( B_{\text{complex}} \) and hence \( \beta \). Thus \( \beta \) measures the degree of covalency of a complex. The smaller the \( \beta \) value, the more covalent the M-L bonding is.

Dou (206) has derived equations that may be used to calculate Dq and B for d\(^8\) octahedral systems, depending on the spectral bands observed. When all three bands are observed, then,

\[
Dq = \nu_1/10
\]  
and  
\[
B = (\nu_3 + \nu_2 - 3\nu_1)/15.
\]

Results of our calculations using these equations are presented in Table 3-4. Error limits for the parameters given in Table 3-4, and similar parameters elsewhere in this thesis, were estimated from the uncertainty in the transition energies used in evaluating the parameters.

According to their proposed structures, Ni(py)\(_4\)(NCO)\(_2\), Ni(pdz)\(_2\)(NCO)\(_2\) and Ni(pyz)\(_2\)(NCO)\(_2\)·\(1/2\)H\(_2\)O have NiN\(_4\)N\(_2\)' chromophores whereas Ni(pyz)(NCO)\(_2\) has a NiN\(_2\)N\(_4\)' chromophore. Since in all four cases the ligand field is provided by nitrogen atoms, the Dq values of the complexes are comparable. The slight differences may be accounted for by factors such as the differences in basicity and modes of coordination of the ligands. In particular, a single nitrogen atom bridging two metal centres may be
expected to provide a lower ligand field than if it were coordinated to one metal only. This may explain the somewhat lower Dq value for Ni(pyz)(NCO)$_2$. The B values are, as expected, lower than the value of 1080 cm$^{-1}$ for the free Ni$^{2+}$ ion (207) and are of similar magnitude indicating a comparable degree of covalency in the Ni-ligand bonds for the four complexes.

3.1.5 Magnetic properties

The magnetic data for all the nickel(II) complexes studied in this work are given in Appendix V. Nickel(II) complexes which are spin-free, octahedral and magnetically dilute are expected to exhibit temperature independent magnetic moments in the range 2.9 to 3.3 B.M. over a wide range of temperature (208) with, possibly, some temperature dependence at very low temperatures due to the effects of zero field splitting (ZFS). In nickel(II) complexes ZFS effects typically give a splitting of the triplet levels (D/k) of the order of a few Kelvin (21). The mononuclear complex, Ni(py)$_4$(NCO)$_2$, has a temperature independent moment of 3.01 B.M. over the range 82-4.2 K; it exhibits no evidence of significant magnetic exchange or measurable zero field splitting down to 4.2 K.

The magnetic moment of Ni(pyz)$_2$(NCO)$_2$·½H$_2$O is 3.06 B.M. at 82 K, remains fairly constant down to ≈30 K, then decreases significantly to 2.53 B.M. at 4.4 K. Such magnetic behaviour may result from the effects of ZFS or weak antiferromagnetism (AF) or both (21). Accordingly we attempted to fit the susceptibility data to the ZFS model for S = 1 and, in view of the sheet structure proposed for this compound, to Lines two-dimensional Heisenberg model (147) for S = 1. The latter model was discussed in detail in section 2.1.8 in regard to copper(II) complexes. The model may be applied to S = 1 systems by substituting the following
coefficients (147) for \( C_n \) in equation 2-2. \( C_1, 4; C_2, 1.834; C_3, 0.445; C_4, 0.224; C_5, 0.132; C_6, 0.019. \) Carlin (209) has derived the following expressions for the ZFS model from Van Vleck's equation:\(^8\)

\[
\begin{align*}
\chi_{||} &= C(2e^{-x})/(1+2e^{-x}) \\
\chi_\perp &= C(2/x)(1-e^{-x})/(1+2e^{-x}) \\
\chi_m &= (\chi_{||} + 2\chi_\perp)/3
\end{align*}
\]

\[3-3\]

where \( \chi_{||} \) and \( \chi_\perp \) are the parallel and perpendicular magnetic susceptibilities, respectively, \( x = D/kT \), \( C = Ng^2\beta^2/kT \) (\( g \) is \( g_{||} \) and \( g_\perp \) for \( \chi_{||} \) and \( \chi_\perp \), respectively) and \( \chi_m \), which is the quantity obtained when powdered samples are used, is the molar (powder) magnetic susceptibility. \( D \) is the axial zero-field splitting parameter. \( N, \beta, k \) and \( T \) are as defined in equation 2-1.

Susceptibilities were fit to theory employing the variable parameters \( D \) and \( g \) for the ZFS model and \( J \) and \( g \) for Lines model. The function, \( F \), minimized in the fitting program is defined in equation 2-5. Values of \( F \) corresponding to the best fit between theory and experiment together with the corresponding magnetic parameters are given in Table 3-5. While a reasonable fit could be obtained for the magnetic susceptibility of \( \text{Ni(pyz)}_2(\text{NCO})_2\cdot\frac{1}{2}\text{H}_2\text{O} \) employing the ZFS model (Fig. 3-8), a significantly improved fit (as judged visually and by the value of \( F \)) was obtained with the AF model. We conclude that ZFS alone cannot account for the magnetic behaviour of this compound and that there is small but significant antiferromagnetic exchange between metal centres propagated by bridging pyrazine groups. The absolute value of \( J \) reported here should be viewed as an upper limit since the AF analysis which determined \( J \) ignores the effects of ZFS. While the analysis of the magnetic properties

\[8 \text{ The expressions for } \chi_\perp \text{ for a } S=1 \text{ system given by the same author (112) and by O'Connor (21) are incorrect.} \]
of Ni(py)$_4$(NCO)$_2$ described above suggest that ZFS may be quite small in these complexes it is not necessarily negligible.

The magnetic properties of Ni(pdz)$_2$(NCO)$_2$ are very similar to those of the bis(pyrazine) complex. The magnetic moment is 2.92 B.M. at 82 K and remains fairly constant down to ≈30 K below which temperature it decreases significantly to a value of 2.29 B.M. at 4.3 K. We examined fits of the magnetic susceptibility of Ni(pdz)$_2$(NCO)$_2$ to the ZFS model as well as to two antiferromagnetic Heisenberg models for $S = 1$ linear chains. The first of the two AF chain models is a result of the work of Weng (210), who extended the work of Bonner and Fisher (145) on exchange coupled chains of $S = 1/2$ (see section 2.1.8) to include $S = 1, 3/2, 2, 5/2$ and 3 ions. Hiller et al. (211) developed a polynomial which describes Weng's numerical results. The polynomial, henceforth referred to as the Weng model, is (211):

$$
\chi_m = \frac{N g^2 \beta^2}{kT} \left[ \frac{A + Bx^2}{1 + Cx + Dx^3} \right]
$$

where $x = |J|/kT$ and the coefficients are $A = 0.6667$, $B = 2.5823$, $C = 3.6035$ and $D = 39.558$ for chains with spins $S = 1$. The other parameters are as defined in equation 2-1.

It has been shown by Fisher (212) that the susceptibility of a linear chain of $N$ spins with nearest-neighbour isotropic Heisenberg coupling can be calculated explicitly in the limit of infinite spin. Wagner and Friedberg (213) scaled Fisher's results to give agreement at high temperatures with the susceptibility series expansion of Rushbrooke and Wood (148) (see section 2.1.8) resulting in an expression that may be written as:

$$
\chi_m = \frac{N g^2 \beta^2 S(S+1)}{3kT} \left[ \frac{1+u(K)}{1-u(K)} \right]
$$

where $u(K) = \coth K - 1/K$ and $K = 2JS(S+1)/kT$ and $S$ is the spin of the magnetic ion. The other parameters are as defined in equation 2-1. In Wagner and Friedberg's paper, the expression represented by equation 3-5 is divided by two since only half of the
paramagnetic ions in the system they were considering were coupled in long chains. The above expression is referred to as the Wagner-Friedberg (W-F) model in this section and elsewhere in this thesis. The model can be used for any spin by substituting in the appropriate value for \( S \) in equation 3-5. It is applicable to both ferromagnetic and antiferromagnetic systems. The fundamental difference between the Weng and the W-F chain models is that while the former was primarily developed by an extrapolation scheme the development of the latter was based on a series expansion.

Table 3-5. Magnetic parameters for complexes of nickel(II) cyanate.\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Model(^b)</th>
<th>( D ) (cm(^{-1}))</th>
<th>(-J) (cm(^{-1}))</th>
<th>( g )</th>
<th>( F )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(pyz)(_2)(NCO)(_2).(1/2)H(_2)O</td>
<td>ZFS</td>
<td>8.0</td>
<td>-</td>
<td>2.13</td>
<td>0.0251</td>
</tr>
<tr>
<td></td>
<td>W-F</td>
<td>-</td>
<td>0.46</td>
<td>2.18</td>
<td>0.0066</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>-</td>
<td>0.42</td>
<td>2.19</td>
<td>0.0065</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>-</td>
<td>0.24</td>
<td>2.18</td>
<td>0.0052</td>
</tr>
<tr>
<td>Ni(pdz)(_2)(NCO)(_2)</td>
<td>ZFS</td>
<td>9.5</td>
<td>-</td>
<td>2.03</td>
<td>0.0409</td>
</tr>
<tr>
<td></td>
<td>W-F</td>
<td>-</td>
<td>0.61</td>
<td>2.09</td>
<td>0.0111</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>-</td>
<td>0.56</td>
<td>2.10</td>
<td>0.0083</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>-</td>
<td>0.32</td>
<td>2.09</td>
<td>0.0097</td>
</tr>
</tbody>
</table>

\(^a\) Estimated error limits: \( D \pm 1.3 \text{ cm}^{-1}, J \pm 0.03 \text{ cm}^{-1}, g \pm 0.02.\)

\(^b\) ZFS = zero-field splitting, W-F = Wagner-Friedberg, W = Weng, L = Lines.
Fig. 3-8. Magnetic susceptibility versus temperature plots for Ni(pyz)$_2$(NCO)$_2$.1/2$H_2$O. The solid lines were drawn using the parameters given in Table 3-5.
Fig. 3-9. Magnetic susceptibility versus temperature plots for Ni(pdz)$_2$(NCO)$_2$. The solid lines were drawn using the parameters given in Table 3-5.
The best fit magnetic parameters applying the three models to the data for Ni(pdz)$_2$(NCO)$_2$ are given in Table 3-5. The fits to the AF models are very good and better than to the ZFS model as judged visually (Fig. 3-9) and by the values of F. We conclude, as above, that the nickel ions are antiferromagnetically coupled, albeit very weakly, by the bridging ligands. We assume the exchange is one-dimensional in this compound based on the proposed bridging structure. It should be noted, however, that this cannot be tested by experiment since the fit of the susceptibility data, for example, to the Lines two-dimensional model is just as good as those we obtained for the linear chain models. Similarly, while we assumed above that the exchange in Ni(pyz)$_2$(NCO)$_2$.1/2$H$_2$O is two-dimensional based on its proposed structure, equally acceptable fits of the magnetic data to the linear chain models can be obtained for this compound. In the case of these two compounds the magnitude of the exchange is too small to enable one to determine the dimensionality of exchange based solely on fitting to available models. This situation has been encountered previously in the analysis of the data for Cu(pyz)$_2$(CH$_3$SO$_3$)$_2$ (47).

The magnetic properties of Ni(pyz)(NCO)$_2$ are unique. The magnetic susceptibility, which shows no field dependence between 2 549 Oe and 9 225 Oe down to 4.2 K, passes through a maximum at 9.8 K (Fig. 3-10) and is therefore indicative of relatively strong antiferromagnetic exchange. That the exchange coupling in this compound is not simply antiferromagnetic, however, is evidenced from an examination of the magnetic moment data. In Fig. 3-11 the magnetic moment versus temperature plot for Ni(pyz)(NCO)$_2$ is compared to that for the magnetically dilute Ni(py)$_4$(NCO)$_2$. At 80 K the moment of the pyrazine complex is higher than expected for magnetically dilute nickel(II) (rather than lower as would be expected for simple antiferromagnetic coupling), it rises to even higher values as the temperature is lowered (indicative of ferromagnetic exchange) until it reaches a maximum at 13.6 K and then decreases to a value at 4.2 K which is far below the value expected for magnetically dilute nickel(II).
We interpret these results as follows. The nickel ions are coupled ferromagnetically in chains via the bridging cyanate groups. These chains are coupled antiferromagnetically via the pyrazine ligands. This is much the same situation as proposed previously for Fe(pyz)(NCO)$_2$ (67). The difference here is that the antiferromagnetic coupling between ferromagnetic chains is weaker in the nickel complex than in Fe(pyz)(NCO)$_2$ and is seen to take effect only at low temperatures whereas for the iron complex the much stronger antiferromagnetic coupling is manifest at higher temperatures giving rise to a net antiferromagnetic behaviour at all the temperatures studied. In Ni(pyz)(NCO)$_2$ it would appear that neither of the exchange mechanisms dominates leading to intrachain ferromagnetic and interchain antiferromagnetic coupling of the same order of magnitude. Unfortunately, to our knowledge, no theoretical models are presently available for the detailed analysis of such systems.

Magnetic behaviour of the type described here in which magnetic centres are coupled ferromagnetically in chains which are in turn coupled antiferromagnetically is exhibited in a number of linear chain metamagnetic materials such as NiL$_2$X$_2$ (X is Cl or Br and L is pyrazole or pyridine) (214) and M(py)$_2$Cl$_2$ (M is Co, Fe or Ni) and Fe(py)$_2$(NCS)$_2$ (215, 216). A metamagnet$^9$ is a material which at low temperatures undergoes a field-induced first-order phase transition from a state with a low magnetization and low susceptibility (i.e. an antiferromagnet) to a state with relatively high magnetization and high susceptibility (i.e. a ferromagnet) (217). In order to determine whether Ni(pyz)(NCO)$_2$ is also a metamagnet, we examined the field-dependence of its magnetization at low temperatures. The results are shown in Fig. 3-12 for selected temperatures. Metamagnetic transitions are clearly observed.

$^9$ Two important requirements for a material to be a metamagnet are that there should be a strong anisotropy and competing interactions (217). The former prevents the occurrence of a spin-flop phase while the latter ensures that the low temperature phase transition is first-order for $T>0$. In a two-sublattice system, these requirements are met by having a ferromagnetic sublattice spin-spin interaction together with an antiferromagnetic inter-sublattice interaction.
below 10 K. The isotherms become increasingly sigmoidal as the temperature is reduced. However, even at the lowest temperature (2 K) and highest field (50 kOe) employed the magnetization has not reached its saturation value, being only 9.499 cm$^3$ G mol$^{-1}$. The theoretical saturation magnetization, $M_{\text{sat}}$, calculated according to equation 3-6 (112) is 11.170 cm$^3$ G mol$^{-1}$. A value of two for $g$ was assumed in the calculation.

$$M_{\text{sat}} = N g \beta S$$  \[3-6\]

where $N$ is Avogadro's number, $g$ is the Landé splitting factor, $\beta$ is the electron Bohr magneton and $S$ is the total spin of the paramagnetic ion.

The metamagnetic transitions in Ni(pyrazine)(NCO)$_2$ are not as sharp as those observed in, for example, single-crystal samples of FeCl$_2$ (218). This is because in powdered samples as used in the present study, a random orientation of molecular axes is expected and hence all crystal directions contribute to the net magnetization. The metamagnetic transition at 2 K is, however, sufficiently well defined to allow the determination of the transition field in Ni(pyrazine)(NCO)$_2$ to be 8 kOe. The transition field is defined as the extrapolation of the linear portion of the magnetization (M) vs. field curve to the M = 0 axis (215).

Another noteworthy feature of the magnetization isotherms is the slight increase in the transition field with decreasing temperature. This property distinguishes metamagnetic phase transitions from spin-flop ones. These latter transitions also involve a reversal of local spin direction from antiparallel to parallel. However, instead of a simple reversal, the transition occurs via a rotation of spin direction and, unlike metamagnetic transitions, is observed in isotropic or only weakly anisotropic magnetic materials (112, 217). The distinguishing feature between these two types of transitions in the magnetization isotherms is that, with decreasing temperature, the transition field increases for a metamagnetic phase transition but decreases for a spin-flop transition (215).
Fig. 3-10. Magnetic susceptibility versus temperature plot for Ni(pyz)(NCO)$_2$.

Fig. 3-11. Magnetic moment versus temperature plots for Ni(py)$_4$(NCO)$_2$ and Ni(pyz)(NCO)$_2$. 
Fig. 3-12. Selected magnetization isotherms for Ni(pyrazine)(NCO)$_2$. 
3.2 Complexes of nickel(II) chloride

3.2.1 Introduction

The compounds discussed in this section are Ni(pyz)$_2$Cl$_2$, Ni(pyz)Cl$_2$, Ni(py)$_4$Cl$_2$ and Ni(py)Cl$_2$. Details of their syntheses are given in section 5.2.5. The two NiLCl$_2$ compounds are sufficiently air-stable that manipulations could be carried out in the atmosphere but samples were stored in a desiccator over Drierite. Ni(py)$_4$Cl$_2$ and Ni(pyz)$_2$Cl$_2$ are hygroscopic and were handled in a nitrogen atmosphere glove box. The four compounds have been previously characterized by a variety of physical methods. The previous results that are relevant to the present study will be compared with our own in the appropriate sections. Our decision to reinvestigate these compounds stemmed from a magnetochemical interest. A recent study of Ni(pyz)$_2$(NO$_3$)$_2$ demonstrated that pyrazine bridges are capable of transmitting magnetic exchange between nickel(II) centres (66). The antiferromagnetic exchange in this compound is very weak and is only observable at low temperatures. Hence it was of interest to investigate the cryogenic magnetic properties of the structurally similar Ni(pyz)$_2$Cl$_2$ which was previously concluded to be magnetically dilute on the basis of magnetic susceptibility measurements over the temperature range 330-90 K (61). We extended the study to include the related polymeric complexes, Ni(pyz)Cl$_2$ and Ni(py)Cl$_2$ and the monomeric complex, Ni(py)$_4$Cl$_2$. A mention of the low temperature magnetic properties of Ni(pyz)Cl$_2$ was made in a compilation of abstracts of papers presented at a chemical conference (219) but details of the properties do not appear to have been published. High temperature (300-90 K) magnetic susceptibility studies lead to the conclusion that the nickel ions in Ni(py)Cl$_2$ are ferromagnetically coupled (220). Some interesting aspects of the magnetic properties of these polymeric compounds that were not observed in the high temperature studies previously reported are revealed in
the detailed cryomagnetic studies presented here. The structure of Ni(py)$_4$Cl$_2$ has been determined by single crystal X-ray diffraction studies (221), and this mononuclear complex was included in this investigation so that its magnetic properties could be used as a reference with which the properties of the polymers could be compared. It is a six coordinate complex with a trans pseudotetragonal geometry. Deviations from tetragonal symmetry are small, the trans N-Ni-N angle being 178.97(21)° whereas the cis N-Ni-N and Cl-Ni-N angles all lie in the range 89.49-90.51°. The Ni-Cl and Ni-N bond distances are 2.437(2) Å and 2.133(4) Å, respectively.

3.2.2 Thermal properties

The thermal parameters for these complexes are presented in Table 3-6. The thermal dissociation of Ni(py)$_4$Cl$_2$ has been a subject of investigation by several researchers. Two different schemes for this process have been reported. In both schemes the first step involves the dissociation of two pyridine ligands to yield Ni(py)$_2$Cl$_2$ and the second step involves the loss of an additional pyridine ligand to form Ni(py)Cl$_2$. It is in the third step which involves the loss of the remaining pyridine ligand to give NiCl$_2$ that the two schemes differ. In scheme A this process takes place in one step. In scheme B, on the other hand, the process takes place in two steps which involves the formation of an intermediate species of composition Ni(py)$_{2/3}$Cl$_2$. Earlier reports by Brown (222), Majumdar (223), and Beech (224) and their coworkers suggested that the dissociation proceeds via scheme A. A later report by Liptay et al. (225), however, indicated that scheme B is followed. Allan et al. (226) and Wendlandt and Ali (227) while supporting scheme A nevertheless indicated that there was evidence for the existence of a complex of empirical formula Ni(py)$_{2/3}$Cl$_2$. Our data (Table 3-6) and the DSC curve of Ni(py)$_4$Cl$_2$ (Fig. 3-13a) clearly indicate that the dissociation of
this complex follows scheme B, in agreement with the work of Liptay et al. (225). This is further supported by our studies on an independently synthesized sample of Ni(py)Cl₂ which show that the single pyridine ligand is evolved in two steps (Fig. 3-13b) through the intermediate species Ni(py)₂/₃Cl₂, in agreement with the findings of Murgulescu et al. (228, 229).

Table 3-6. Thermal parameters* for complexes of nickel(II) chloride.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. °C</th>
<th>ΔHᵇ kJ mol⁻¹</th>
<th>Weight lossᵇ %</th>
<th>Number and type of species lost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(py)₄Cl₂</td>
<td>149</td>
<td>35</td>
<td>35</td>
<td>2 py</td>
</tr>
<tr>
<td></td>
<td>195</td>
<td>53</td>
<td>53</td>
<td>3 py</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>59</td>
<td>59</td>
<td>3½ py</td>
</tr>
<tr>
<td></td>
<td>345</td>
<td>71</td>
<td>71</td>
<td>4 py</td>
</tr>
<tr>
<td></td>
<td>370ᵇ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(py)Cl₂</td>
<td>284</td>
<td>13</td>
<td>14</td>
<td>⅓ py</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>38</td>
<td>40</td>
<td>1 py</td>
</tr>
<tr>
<td>Ni(pyz)₂Cl₂</td>
<td>270</td>
<td>73</td>
<td>28</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>469</td>
<td>d</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Ni(pyz)Cl₂</td>
<td>474</td>
<td>d</td>
<td>38</td>
<td>39</td>
</tr>
</tbody>
</table>

* Estimated error limits: peak temp. ±5 °C, ΔH ±5%, weight loss ±5%. ᵇ Was determined only when well defined thermal events were observed. ᶜ Onset of decomposition. ᵈ ΔH strongly dependent on lower limit of integration.

The DSC curve for Ni(py)₄Cl₂ exhibits four endothermic events which occur in two pairs. Whereas the pairs are separated by almost 100 °C, the events within each pair overlap. This implies that the species formed after the process taking place in the first event in each pair (i.e. Ni(py)₂Cl₂ and Ni(py)₂/₃Cl₂) are relatively unstable and may not be easy to isolate by thermolysis. This hypothesis is, in fact, supported by
Fig. 3-13. DSC curves for (a) Ni(py)$_4$Cl$_2$ and (b) Ni(py)Cl$_2$. 
experimental evidence. Whereas Ni(py)Cl₂ can be obtained by thermolysis of either Ni(py)₄Cl₂ (230) or Ni(py)₂Cl₂ (220), the synthesis of Ni(py)₂Cl₂ requires that it be precipitated directly from solution using controlled amounts of reagents (220, 230). Therefore, we believe that it is the instability of Ni(py)₂/₃Cl₂ which made its detection difficult in the earlier studies of the thermal decomposition of Ni(py)₄Cl₂.

Two well separated endothermic events (270 and 469 °C), each corresponding to the loss of one pyrazine ligand, are observed in the DSC curve for Ni(pyz)₂Cl₂. Our results are in good agreement with those of Beech and Mortimer (231). These results suggested the possibility of obtaining Ni(pyz)Cl₂ on a preparative scale by the thermolysis of the bis(pyrazine) complex. This was achieved and, consistent with above conclusions, the DSC curve of the independently prepared sample of Ni(pyz)Cl₂ exhibits only one endothermic event at 474 °C.

3.2.3 Infrared spectra

Infrared criteria for distinguishing between free and coordinated pyridine molecules and between monodentate terminal and bidentate bridging pyrazine molecules were discussed in detail in section 2.1.4. Pyridine and pyrazine bands in the infrared spectra of the complexes under discussion in this section are presented in Appendixes II-1 and II-2, respectively. The spectra of Ni(py)₄Cl₂ and Ni(py)Cl₂ show only bands expected for coordinated pyridine ligands. This is consistent with the single crystal X-ray diffraction study of Ni(py)₄Cl₂ which showed that all ligands are coordinated to give a six-coordinate mononuclear structure in which the chloride ions are in trans positions (221).

The electronic spectrum of Ni(py)Cl₂ indicates that the nickel ions are octahedrally coordinated (vide infra), and as discussed in the preceding paragraph, the
mid-infrared spectrum shows that the pyridine molecules are all coordinated. Goldstein and Hughes (232) have assigned metal-ligand vibrational modes, $v_{M-X}$ and $v_{M-N}$, for a series of $M(py)X_2$ complexes, including Ni(py)Cl$_2$. The structure most consistent with the spectroscopic properties of these complexes which they proposed is shown in Fig. 3-14. It consists of double-strand halide-bridged polymeric chains in which each metal ion is surrounded by one pyridine ligand, two bicoordinate halide ions and three tricoordinate halide ions.

The infrared spectrum of Ni(pyz)Cl$_2$ exhibits a strong pyrazine band at 492 cm$^{-1}$, indicating that the pyrazine groups in the complex are bridging. This conclusion is supported by the fact that for the analogous Co(pyz)X$_2$ ($X$ is Cl, Br or I) no coincidences occur of infrared and Raman bands due to internal modes of the pyrazine ligands (233), indicating the presence of a centre of symmetry. Goldstein and Unsworth (233) found the far-infrared spectrum of Ni(pyz)Cl$_2$ to be consistent with the presence of [NiX$_2$] chains. In view of the fact that the electronic spectrum of this compound supports an octahedral ligand geometry around the nickel ion, they proposed for it a structure such as that shown in Fig. 3-3b. In this structure, chains of nickel ions, doubly-bridged by chloride ions, are cross-linked by bidentate bridging pyrazine molecules.

Lever et al. (31, 33) proposed in the early 1960's that the presence of an infrared absorption band around 980 cm$^{-1}$ is characteristic of monodentate pyrazine ligands. On the strength of this criterion they proposed that the structure of complexes of the type $M(py)_2X_2$ ($M$ is Co or Ni and $X$ is Cl, Br or I) consists of chains of metal ions doubly-bridged by halide ions, with octahedral configuration about the metal centres being achieved through two monodentate pyrazine molecules. On the basis of a more detailed analysis of the mid-infrared and Raman as well as the far-infrared spectra of these complexes Goldstein et al. (45, 61), on the other hand, proposed a sheet structure in which the pyrazine ligands are bridging and the halide ions are terminal.
The infrared spectrum of Ni(py)₂Cl₂ recorded in the present study shows a strong pyrazine band at 496 cm⁻¹ and provides further evidence that the pyrazine groups are bridging in this compound and is consistent with the sheet structure proposed by the latter workers. The proposal by Goldstein et al. has since received support from structural determinations of the bis(pyrazine) complexes Co(py)₂Cl₂, Cu(py)₂(ClO₄)₂, Cu(py)₂(CH₃SO₃)₂ and Fe(py)₂(NCS)₂ (45-48), all of which are sheet polymers, by X-ray crystallography.

Fig. 3-14. Proposed structure for Ni(py)Cl₂ (after Goldstein and Hughes (232)).
3.2.4 Electronic spectra

The electronic spectral data for Ni(py)Cl₂ and Ni(py)Cl₂ are given in Table 3-7. The spectra are readily assigned assuming octahedral symmetry about the nickel ions. The spectra of these two compounds have been reported before (222, 230, 233) and our data compares well with the literature values (Table 3-7). We note, however, that for Ni(py)Cl₂ u₁ was not observed in the previous studies. This band occurs below 10 000 cm⁻¹ in the spectrum of this compound reported here. The spectral range over which the spectra were recorded in the previous studies was not reported.

For both Ni(py)Cl₂ and Ni(py)Cl₂ the parameters Dq and B were calculated according to equations 3-1 and 3-2 respectively. The results obtained were: Dq = 900 ± 20 cm⁻¹ and B = 853 ± 14 cm⁻¹ for Ni(py)Cl₂; Dq = 810 ± 20 cm⁻¹ and B = 753 ± 14 cm⁻¹ for Ni(py)Cl₂. The lower Dq values for these complexes in comparison to those of nickel(II) cyanate (Table 3-4) and nickel(II) thiocyanate (Table 3-14) complexes is a reflection of the predominantly chloride ligand environment in Ni(py)Cl₂ and Ni(py)Cl₂. Chlorine is lower than nitrogen in the spectrochemical series.

The intermediate position of the spectral bands of Ni(py)Cl₂ relative to those of Ni(py)₂Cl₄ and NiCl₂, which are considered to have NiN₂Cl₄ and NiCl₆ chromophores, respectively, has been interpreted by Brown et al. (222) as indicating a NiNCl₅ chromophore for the mono(pyridine) complex.
Table 3-7. Electronic spectral band energies and assignments for complexes of nickel(II) chloride, $O_h$ symmetry.$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^3T_2g(F)$ ($v_1$)</th>
<th>$^1E_g(D)$</th>
<th>$^3T_1g(F)$ ($v_2$)</th>
<th>$^3T_1g(P)$ ($v_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(pyz)Cl$_2$</td>
<td>9 000 (1 110)</td>
<td>n.o.</td>
<td>14 500 (688)</td>
<td>25 300 (396 sh)</td>
</tr>
<tr>
<td>Ni(py)Cl$_2$</td>
<td>8 100 (1 240)</td>
<td>11 800 (850 sh)</td>
<td>13 200 (756)</td>
<td>22 400 (446)</td>
</tr>
<tr>
<td>Ni(py)Cl$_2$$^b$</td>
<td>12 100, 13 300, 20 800, 23 800</td>
<td>≈11 800 sh, 12 240, 12 990, 22 520</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(pyz)Cl$_2$$^b$</td>
<td>7 410, 8 770, 14 300, 27 000 sh</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Transitions are from the $^3A_{2g}$ state; sh = shoulder, n.o. = not observed. Estimated uncertainty in absorption maxima is ± 200 cm$^{-1}$. All literature data were obtained by the diffuse reflectance technique at ambient temperatures.

$^b$ Data from ref. 222. $^c$ Data from ref. 230. $^d$ Data from ref. 233.

The electronic spectrum of Ni(py)$_4$Cl$_2$ is shown in Fig. 3-15 and its spectral data are given in Table 3-8. The splitting of $v_1$ ($O_h$ symmetry) shows that the nickel ion is in a lower than $O_h$ symmetry (see Fig. 3-6). Although it is known from an X-ray crystallographic study that this compound has a six coordinate pseudotetragonal structure, the deviation from tetragonal symmetry is small (221). Hence we assumed $D_{4h}$ symmetry in assigning the spectral bands. The spectrum of this compound has been reported before (Table 3-8). The spectral band positions from the present study are in excellent agreement with those reported by Bostrup and Jorgensen (234). The spectrum reported by Rowley and Drago (204), on the other hand, exhibits several additional bands. Greater resolution was achieved in the latter study by recording the spectrum at liquid nitrogen temperature.
Lever et al. (34) previously reported the electronic spectrum of Ni(pyz)₂Cl₂, recorded over a limited range, and assigned the bands assuming O₈ symmetry. The spectrum reported here is similar to that of Ni(py)₄Cl₂, indicating a tetragonal octahedral NiN₄Cl₂ chromophore.

Assuming a ³B₁g ground state the transition energies in a tetragonal nickel(II) complex, considering configurational interaction between states of the same spin and symmetry, are given by the following equations (104).

\[
³B₂g = 10Dq_{xy}
\]

\[
\begin{align*}
³A₂g_{a, b} & : 10Dq_{xy} - 4Ds - 5Dt + 12B - E & = 0 \\
6B & : 20Dq_{xy} + 2Ds - 15Dt + 3B - E
\end{align*}
\]

\[
\begin{align*}
³E₉_{a, b, c} & : 10Dq_{xy} - (35/4)Dt - E & = 0 \\
(+/\sqrt{3/4})(4Ds + 5Dt) & : 10Dq_{xy} + 2Ds - (25/4)Dt + 12B - E & = 0 \\
0 & : 20Dq_{xy} - Ds - 10Dt + 3B - E
\end{align*}
\]

Dq_{xy} is the equatorial plane ligand field parameter, Ds and Dt are tetragonal parameters. The splitting of the ³T₂g (O₈) state is proportional to Dt. Since the splitting is a direct consequence of the tetragonal field, Dt is a direct measure of the degree of tetragonality (i.e. the difference between the equatorial and axial ligand fields). Thus this parameter is useful in determining the relative degree of tetragonal distortion in a series of complexes.
Table 3-8. Electronic spectral band energies and assignments, and ligand field parameters for complexes of nickel(II) chloride, $D_{4h}$ symmetry.\(^a\)

| $^3B_{1g}$ & Ni(py)$_4$Cl$_2$ & Ni(pyz)$_2$Cl$_2$ |
|---|---|---|
| $^3E_g$ & 8 800 (1132) & 9 500 (1053) |
| $^3B_{2g}$ & 10 700 (933) & 10 900 (920) |
| $^1B_{2g}$ & 12 600 (792) & 12 500 (801) |
| $^3A_{2g}, ^3E_g$ & 15 900 (629) & 16 700 (600) |
| $^3A_{2g}, ^3E_g$ & 25 600 (390) & b |
| $D_{q_{xy}}$ & 1 070 & 1 090 |
| $D_t$ & 201 |
| $D_s$ & 422 |
| $B$ & 806 |

**Literature values**

| Ni(py)$_4$Cl$_2$\(^c\) & 8 500, 10 900, 15 900, 25 700 |
| Ni(py)$_4$Cl$_2$\(^d\) & 9 042, 11 730, 12 620, 12 804, 14 930, 16 818, 21 768, 26 759 |
| Ni(pyz)$_2$Cl$_2$\(^e\) & 10 500, 12 200, 16 150 |

\(^a\) Assignments according to reference 204. All values are in cm$^{-1}$; the corresponding values for absorption maxima in nm are given in parentheses. Estimated error limits: $D_{q_{xy}} \pm 20$ cm$^{-1}$, $D_t \pm 57$ cm$^{-1}$, $D_s \pm 5$ cm$^{-1}$, $B \pm 16$ cm$^{-1}$.

\(^b\) Obscured by a more intense (charge transfer or internal ligand) band.

\(^c\) Data from ref. 234; diffuse reflectance technique at ambient temperature.

\(^d\) Data from ref. 204; absorption spectrum recorded at liquid nitrogen temperature as a mull of stopcock grease.

\(^e\) Data from ref. 34; diffuse reflectance technique at ambient temperature.
A computer program which solves the three by three secular determinant, given \( D_{q_{xy}} \) and the transition energies to the three \(^3E\) states has been written by F.G. Herring and J. Mayo of this Department and was used to calculate the tetragonal parameters for \( \text{Ni(py)_4Cl}_2 \) presented in Table 3-8. \( D_{q_{xy}} \) values were obtained using the relationship \( E(^3B_{2g}) = 10D_{q_{xy}} \). Since the \(^3T_{1g}\) terms do not show the expected splitting, we assumed that their \( A_2 \) and \( E \) components are equal to each other and to the observed band energy. We note, however, that Lever (104) has pointed out that this procedure is not entirely satisfactory since the components may, in reality, differ by significant amounts. \( D_t \) values for \( \text{Ni(py)_4(AsF}_6)_2, \text{Ni(py)_4(BF}_4)_2 \) and \( \text{Ni(py)_4(ClO}_4)_2 \) lie in the range 500-568 cm\(^{-1}\) (201, 235). These values are considerably higher than that obtained for \( \text{Ni(py)_4Cl}_2 \) and consistent with the higher degree of tetragonality expected for the complexes containing the relatively weakly coordinating \( \text{AsF}_6^- \), \( \text{BF}_4^- \) and \( \text{ClO}_4^- \) anions.

![Fig. 3-15. Electronic spectrum of Ni(py)_4Cl_2. N = Nujol bands; * = charge transfer bands.](image)
3.2.5 Magnetic properties

The magnetic data for the complexes of nickel(II) chloride are presented in Appendix V. A single crystal X-ray diffraction study has shown that Ni(py)_4Cl_2 has a monomeric, six-coordinate pseudotetragonal structure (221) and it is, therefore, expected to have a temperature independent moment that lies between 2.9 and 3.3 B.M., a characteristic of magnetically dilute six-coordinate nickel(II) complexes (208). Its magnetic moment, which is 3.10 B.M. at 82 K, remains fairly constant as the temperature is lowered to about 20 K. Below this temperature there is a significant decrease in the moment, which attains a value of 2.66 B.M. at 4.3 K. This temperature dependence of the magnetic moment of Ni(py)_4Cl_2, which is illustrated in Fig. 3-16 together with those of Ni(pyz)Cl_2 and Ni(py)Cl_2, is attributed to zero-field splitting effects. Its susceptibility data were analyzed by the zero-field splitting model represented by equation 3-3. The best fit is represented by the solid line in Fig. 3-17. The parameters are comparable with those obtained in a previous study of other NiL_4X_2 complexes (Table 3-9).

The magnetic properties of Ni(pyz)_2Cl_2 are very similar to those of Ni(pyz)_2(NCO)_2.1/2H_2O discussed in section 3.1.5. The magnetic moment is 3.03 B.M. at 82 K and remains fairly constant down to \(\approx 30\) K below which temperature it decreases significantly to a value of 2.25 B.M. at 4.4 K. We examined fits of the magnetic susceptibility data of Ni(pyz)_2Cl_2 to the ZFS model (eqn. 3-3) and, in view of the sheet structure proposed for it, to Lines two-dimensional Heisenberg model represented by equation 2-2. The coefficients required in order to apply the model to \(S = 1\) systems are given in section 3.1.5. The best fits to the two models are represented by the solid lines in Fig. 3-18 and the best fit parameters are given in Table 3-9. The fit to Lines model is very good and better than the ZFS model as judged visually and by the value of \(F\). We, therefore, conclude that the nickel ions are
antiferromagnetically coupled by the bridging pyrazine ligands but the coupling is very weak. Acceptable fits of the magnetic data to the linear chain models represented by equations 3-4 and 3-5 were also obtained (Table 3-9). Thus, as was found for Ni(pyz)₂(NCO)₂½H₂O in section 3.1.5, the magnitude of the exchange in Ni(pyz)₂Cl₂ is too small to enable one to determine the dimensionality of the exchange based solely on fitting of the magnetic data to available models.

Table 3-9. Magnetic parameters for complexes of nickel(II) chloride.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Model</th>
<th>D(cm⁻¹)</th>
<th>J(cm⁻¹)</th>
<th>g</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(py)₄Cl₂</td>
<td>ZFS</td>
<td>6.7</td>
<td>-</td>
<td>2.16</td>
<td>0.0143</td>
</tr>
<tr>
<td>Ni(py)₄(CH₃SO₃)₂</td>
<td>ZFS</td>
<td>9.1</td>
<td>-</td>
<td>2.22</td>
<td>0.0168</td>
</tr>
<tr>
<td>Ni(py)₄(p-CH₃C₆H₄SO₃)₂</td>
<td>ZFS</td>
<td>9.0</td>
<td>-</td>
<td>2.11</td>
<td>0.0068</td>
</tr>
<tr>
<td>Ni(mepy)₄(NO₃)₂.H₂O</td>
<td>ZFS</td>
<td>7.2</td>
<td>-</td>
<td>2.18</td>
<td>0.0101</td>
</tr>
<tr>
<td>Ni(pyz)₂Cl₂</td>
<td>ZFS</td>
<td>10.9</td>
<td>-</td>
<td>2.10</td>
<td>0.0352</td>
</tr>
<tr>
<td></td>
<td>W-F</td>
<td>-</td>
<td>0.72</td>
<td>2.17</td>
<td>0.0064</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>-</td>
<td>0.67</td>
<td>2.18</td>
<td>0.0055</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>-</td>
<td>0.38</td>
<td>2.17</td>
<td>0.0066</td>
</tr>
</tbody>
</table>

a Estimated error limits: D ±1.3 cm⁻¹, J±0.03 cm⁻¹, g±0.02.
b ZFS = zero-field splitting, W-F = Wagner-Friedberg, W = Weng, L = Lines.
c Data from ref. 66.
Fig. 3-16. Magnetic moment versus temperature plots for Ni(py)Cl₂, Ni(pyz)Cl₂ and Ni(py)₄Cl₂.

Fig. 3-17. Magnetic susceptibility versus temperature plot for Ni(py)₄Cl₂. The solid line was drawn using the parameters given in Table 3-9.
Fig. 3-18. Magnetic susceptibility versus temperature plots for Ni(pyz)$_2$Cl$_2$. The solid lines were drawn using the parameters given in Table 3-9.
At 82 K the magnetic moment of Ni(pyz)Cl₂ is higher than that of the monomeric and magnetically dilute complex, Ni(py)₄Cl₂ (Fig. 3-16). The moment rises to even higher values as the temperature is lowered, indicating ferromagnetic coupling between the nickel ions. The moment reaches a maximum at 16.6 K and then decreases to a value of 1.47 B.M. at 4.2 K. The magnetic susceptibility shows no field dependence between 7 501 and 9 225 Oe down to 4.2 K. The data obtained at the latter field are presented graphically in Fig. 3-19a. The susceptibility passes through a maximum at 9.8 K, indicating relatively strong antiferromagnetic exchange. We interpret the magnetic properties of Ni(pyz)Cl₂ as indicating that the nickel ions are coupled ferromagnetically in chains via the bridging chloride ions and the chains are coupled antiferromagnetically via the pyrazine ligands. The interchain interactions would seem to be weaker than the intrachain interactions, becoming observable only at low temperatures.

We have proposed that Ni(pyz)Cl₂ and Ni(pyz)(NCO)₂ are isostructural. The variation of the magnetic susceptibility, and consequently magnetic moment, with temperature for the two compounds are very similar. Since it was shown in section 3.1.5 that the cyanate complex exhibits isothermal magnetization curves characteristic of a metamagnet, we examined the low temperature field dependence of the magnetization of Ni(pyz)Cl₂. Selected magnetization isotherms are shown in Fig. 3-19b. These clearly show that Ni(pyz)Cl₂ is also a metamagnet. The metamagnetic transition field at 2 K is 12.8 kOe. The magnetization has not reached the saturation value at the lowest temperature and highest field used.

The temperature dependence of the magnetic moment of Ni(py)Cl₂ is very similar to that of its pyrazine analogue (Fig. 3-16). However, the magnitude of the moment is considerably larger in the pyridine complex, indicating a much stronger intrachain ferromagnetic coupling. This may be due to the fact that in the proposed double-strand chain structure for this compound, each nickel ion has four nearest nickel
ion neighbours. It must be pointed out, however, that although all the nickel ions are symmetrically equivalent the nearest neighbour interactions are not necessarily equal. There are two possible interaction pathways, intrastrand and interstrand (recall Fig. 3-14). The intrastrand interactions take place via one bi- and one tri-coordinate chloride ion whereas the interstrand interactions takes place via two tricoordinate chloride ions. Both types of chloride ion bridges have been shown to support ferromagnetic exchange; bicoordinate chloride ions in Ni(py)$_2$Cl$_2$ (220) and tricoordinate chloride ions in NiCl$_2$ (236). The intra- and inter-strand interactions in Ni(py)Cl$_2$ are both, therefore, considered to be ferromagnetic.

It is noteworthy that there is an increase in the extent of ferromagnetic coupling with increasing number of chloride ion bridges, and hence the number of nearest neighbour nickel centres, in the compounds Ni(py)$_2$Cl$_2$, Ni(py)Cl$_2$ and NiCl$_2$. The proposed structure of the the bis(pyridine) complex consists of single-strand chains in which the nickel ions are bridged by bicoordinate chloride ions. The fifth and sixth coordination sites on the nickel ions are occupied by pyridine ligands (237). Each nickel ion has two nearest neighbour nickel ions. NiCl$_2$, on the hand, has an infinite two-dimensional sheet structure in which all the chloride ions are bridging in a tricoordinate fashion, resulting in each nickel ion having six nearest neighbour nickel ions (238). The proposed double-strand polymeric structure of Ni(py)Cl$_2$ is intermediate between these two; each nickel ion has four nearest neighbour nickel ions. Positive Weiss constants, $\theta$, of 19, 34 and 68 K for Ni(py)$_2$Cl$_2$, Ni(py)Cl$_2$ and NiCl$_2$, respectively, were obtained from plots of reciprocal susceptibility versus temperature at high temperatures (220, 236).

The magnetic susceptibility of Ni(py)Cl$_2$ shows field dependence in the 2 549 to 9 225 Oe range below $\approx$ 20 K. This is illustrated in Fig. 3-20, together with selected magnetization isotherms. That Ni(py)Cl$_2$ is a metamagnet is clearly demonstrated by the latter. The transition field at 2 K is 1.8 kOe. At the highest field employed
(20 kOe) and 2 K, the magnetization is $8.998 \text{ cm}^3 \text{ G mol}^{-1}$, 81% of the theoretical saturation magnetization which is $11.170 \text{ cm}^3 \text{ G mol}^{-1}$. The kind of behavior observed in the susceptibility plot for Ni(py)Cl$_2$ between 5 251 and 9 225 Oe below $\approx 6 \text{ K}$ in which the susceptibility remains constant with decreasing temperature at constant field and decreases with increasing field at a constant temperature is normally a manifestation of magnetic saturation effects. In a saturated system, all spins are aligned with the field and the magnetization becomes independent of both field and temperature. Since $\chi = \frac{M}{H}$, the susceptibility is also temperature independent but bears an inverse relationship to the field. In Ni(py)Cl$_2$ complete saturation has not been achieved under the experimental conditions in which the data in Fig. 3-20 were collected. In fact at $\approx 2.2 \text{ K}$ the system is only 61%, 56%, 43% and 11% saturated at 9 225, 7 501, 5 251 and 2 549 Oe, respectively. Furthermore, as mentioned above, a saturated magnetic system should exhibit magnetic susceptibility which is inversely related to the field. In contrast, low temperature isothermal susceptibility data for Ni(py)Cl$_2$ show a more complex field dependence, exhibiting a maximum which, at 2 K, is at about 5 000 Oe. Thus the magnetic properties of Ni(py)Cl$_2$ cannot be ascribed to simple saturation effects but are consistent with metamagnetic behavior.
Fig. 3-19. (a) Magnetic susceptibility versus temperature plot and (b) selected magnetization isotherms for Ni(pyz)Cl₂.
Fig. 3-20. (a) Magnetic susceptibility versus temperature plots and (b) selected magnetization isotherms for Ni(py)Cl₂.
3.3 Complexes of nickel(II) thiocyanate

3.3.1 Introduction

Probing low temperature magnetic properties of complexes of nickel(II) thiocyanate with pyridine, pyrazine and pyridazine was a logical extension of our work with nickel(II) cyanate and chloride complexes discussed earlier in this chapter. The investigation was also partly prompted by the observation that although most pyrazine bridged iron(II) complexes generally do not exhibit significant magnetic exchange effects (64, 65), Fe(pyz)$_2$(NCS)$_2$ exhibits antiferromagnetic exchange, with a maximum at $\approx 8$ K in its susceptibility data (67). In this section we report the results of our studies on three new compounds, Ni(pdz)$_3$(NCS)$_2$, Ni(pdz)$_2$(NCS)$_2$ and Ni(pyz)(NCS)$_2$, and three known ones, Ni(py)$_4$(NCS)$_2$, Ni(py)$_2$(NCS)$_2$ and Ni(pyz)$_2$(NCS)$_2$. Relevant results from previous studies on the known compounds will be compared with ours in appropriate sections. The syntheses of these compounds are reported in section 5.2.6. The two pyridazine complexes are hygroscopic and were handled in a nitrogen atmosphere glove box. The rest of the compounds are sufficiently air-stable that manipulations could be carried out in the atmosphere but samples were stored in a desiccator over Drierite.

Ni(py)$_4$(NCS)$_2$ has been shown by X-ray crystallography to have a trans-octahedral structure (239). This mononuclear complex was included in the present study so that its magnetic moment data could serve as a baseline from which magnetic interactions in the polymeric complexes could be measured.
3.3.2 Thermal properties

The thermal parameters for complexes of nickel(II) thiocyanate are given in Table 3-10. Duval (240) reported that Ni(py)$_4$(NCS)$_2$ starts to lose one pyridine molecule at 63 °C to give Ni(py)$_3$(NCS)$_2$ and that the interpretation of the rest of its thermogram is difficult. Majumdar et al. (223), on the other hand, found that this compound decomposes to Ni(NCS)$_2$ via Ni(py)$_2$(NCS)$_2$ and Ni(py)(NCS)$_2$. In contrast to both these reports, subsequent studies by Wendlandt (227), Murgulescu (229) and Liptay (241, 242) and their coworkers established that the pyridine ligands in Ni(py)$_4$(NCS)$_2$ are released in two well defined steps. Our results are consistent with those of the latter workers, with two endothermic events occurring at 177 and 260 °C, each corresponding to the loss of two pyridine molecules. Further support for the above conclusions comes from the fact that we were able to isolate Ni(py)$_2$(NCS)$_2$ by thermolysis on a preparative scale and its DSC curve exhibits only one endothermic event, at 260 °C.

The DSC curve for Ni(pdz)$_3$(NCS)$_2$ is shown in Fig. 3-21a. It exhibits endothermic events at 168 and 293 °C accompanied by weight losses of 17 and 18%, respectively. These values are consistent with the loss of one pyridazine ligand during each of the events. Immediately following the event at 293 °C is the onset of another endothermic event which minimizes at about 350 °C and then rises well above the baseline. The total weight loss observed at the end of the third event is 63%. A total weight loss of 58% would be expected for the dissociation of three pyridazine ligands from Ni(pdz)$_3$(NCS)$_2$. The calculated and observed weight loss figures suggest that the event at 350 °C arises primarily from the loss of the third pyridazine ligand from Ni(pdz)$_3$(NCS)$_2$. However, the rise of this event well above the baseline suggests that the loss of the last pyridazine ligand from Ni(pdz)$_3$(NCS)$_2$ is accompanied by other decomposition processes. The above results suggest that whereas a compound of
composition Ni(pdz)₂(NCS)₂ may be accessible by a thermolysis route, Ni(pdz)(NCS)₂ is not. In practice neither Ni(pdz)₂(NCS)₂ nor Ni(pdz)(NCS)₂ was isolated by thermolysis. However, Ni(pdz)₂(NCS)₂ was precipitated directly from solution using controlled amounts of reagents (section 5.2.6.4). A similar approach failed to produce pure samples of Ni(pdz)(NCS)₂.

The ΔH value of 22 kJ mol⁻¹ corresponding to the event at 168 °C in the DSC curve for Ni(pdz)₃(NCS)₂ is rather low when compared, for example, to the value of 77 kJ mol⁻¹ that accompanies the evolution of one pyridazine ligand from Ni(pdz)₂(NCO)₂. From Tables 3-1 and 3-6 and other studies (66) it is found that the loss of one molecule of the related ligand, pyrazine, from polymeric nickel(II) complexes is usually accompanied by ΔH values of at least 52 kJ mol⁻¹. Thus, it may be that one pyridazine molecule in Ni(pdz)₃(NCS)₂ is only weakly coordinated or is present as lattice pyridazine. There is, of course, also the possibility that the process is not just a simple loss of a pyridazine molecule. Exothermic processes may also be present, resulting in a net low ΔH for the endothermic process.

The DSC curve for Ni(pdz)₂(NCS)₂ (Fig. 3-21b) is difficult to interpret. It exhibits two events which minimize at about 270 and 350 °C. By comparing this curve with that of Ni(pdz)₃(NCS)₂, the former event would be expected to correspond to the loss of one pyridazine ligand and the latter to the loss of the remaining ligand and other unknown decomposition processes. However, the two events in Ni(pdz)₂(NCS)₂ are separated by an exothermic one. The origin of this exothermic event is not known.

One endothermic event, which weight loss measurements indicate is due to the formation of Ni(pyz)(NCS)₂, is observed at 251 °C in the DSC curve of Ni(pyz)₂(NCS)₂. Decomposition of the sample begins at about 320 °C. Based on these results, the mono(pyrazine) complex was in fact synthesized by thermolysis of Ni(pyz)₂(NCS)₂ (section 5.2.6.6). The DSC curve of the former was not recorded due
to equipment breakdown; however, based on the thermal studies on Ni(pyz)$_2$(NCS)$_2$, it is not expected to show any thermal event prior to decomposition.

Table 3-10. Thermal parameters$^a$ for complexes of nickel(II) thiocyanate.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. $^\circ$C</th>
<th>$\Delta$H$^b$ kJ mol$^{-1}$</th>
<th>Weight loss$^b$ %</th>
<th>Number and type of species lost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(py)$_4$(NCS)$_2$</td>
<td>177</td>
<td>128</td>
<td>32</td>
<td>2 py</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>154</td>
<td>64</td>
<td>4 py</td>
</tr>
<tr>
<td></td>
<td>315$^c$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(py)$_2$(NCS)$_2$</td>
<td>260</td>
<td>153</td>
<td>47</td>
<td>2 py</td>
</tr>
<tr>
<td></td>
<td>310$^c$</td>
<td></td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>Ni(pdz)$_3$(NCS)$_2$</td>
<td>168</td>
<td>22</td>
<td>19</td>
<td>1 pdz</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>56</td>
<td>39</td>
<td>2 pdz</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td></td>
<td>58</td>
<td>d</td>
</tr>
<tr>
<td>Ni(pdz)$_2$(NCS)$_2$ $^d$</td>
<td>272</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>350</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(pyz)$_2$(NCS)$_2$</td>
<td>251</td>
<td>74</td>
<td>24</td>
<td>1 pyz</td>
</tr>
<tr>
<td></td>
<td>320$^c$</td>
<td></td>
<td>28</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Estimated error limits: peak temp. ±5 $^\circ$C, $\Delta$H ±5%, weight loss ±5%. $^b$ Was determined only when well defined thermal events were observed. $^c$ Onset of decomposition. $^d$ See text.
Fig. 3-21. DSC curves for (a) Ni(pdz)$_3$(NCS)$_2$ and (b) Ni(pdz)$_2$(NCS)$_2$. 
3.3.3 Infrared spectra

Infrared spectral bands due to the internal vibrations of pyridine, pyrazine and pyridazine ligands in the complexes of nickel(II) thiocyanate are presented in Appendixes II-1, II-2 and II-4, respectively, while those due to the thiocyanate groups are given in Table 3-11. The infrared spectrum of Ni(pdz)$_2$(NCS)$_2$ is shown in Fig. 3-22 and is representative of the thiocyanate class of complexes. Infrared spectra of the pyridine complexes have been reported before (243, 244) and our data are in good agreement with the earlier reports, with the following notable exceptions. We observe two bands, corresponding to the 16b free pyridine band (135), at 439 and 445 cm$^{-1}$ for Ni(py)$_4$(NCS)$_2$ and one at 441 cm$^{-1}$ for Ni(py)$_2$(NCS)$_2$. Clark and Williams (243) observed corresponding bands at 429 and 434 cm$^{-1}$, and 429 cm$^{-1}$, respectively. The values we observe for the bending mode of the thiocyanate group for both compounds are also about 10 cm$^{-1}$ higher than the literature values (243, 244).

The ambidentate thiocyanate ligand may coordinate to a metal centre in a monodentate fashion through the nitrogen atom (M-NCS, thiocyanato-N) or through the sulphur atom (M-SCN, thiocyanato-S). It may also bridge metal centres in an end-to-end fashion (-NCS-) or through single atom bridges (\(\text{>NCS}\), \(\text{SCN}\)). This ability to coordinate to metal centres in a variety of ways has generated considerable research activity aimed at establishing the mode of thiocyanate ion coordination in a variety of complexes.

Monodentate N-bonded NCS groups have been observed by X-ray crystallography in, for example, Fe(pyz)$_2$(NCS)$_2$ (48), Fe(py)$_4$(NCS)$_2$ and Fe(py)$_2$(bpym)(NCS)$_2$.\(^14\)py where bpym is 2,2'-bipyridimidine (245), M(py)$_4$(NCS)$_2$ (M is Ni or Co) (239), Ni(NH$_3$)$_4$(NCS)$_2$ (246), Ni(en)$_2$(NCS)$_2$ (247) where en is ethylenediamine, and Pd(P(n-C$_3$H$_7$)$_3$)$_2$(NCS)$_2$ (248). Examples of complexes in which the presence of monodentate S-bonded thiocyanate groups have been unambiguously
demonstrated by single crystal X-ray diffraction studies include cis and trans-
Pt(NH₃)₂(SCN)₂ (249, 250) and trans-Cu(en)₂(SCN)₂ (251). The end-to-end bridging
of the thiocyanate group has been observed in AgNCS (252), M(py)₂(NCS)₂ (M is Co
or Cu) (253) and Cd(etri)₂(NCS)₂, where etu is ethylenethiourea (254). Single N-atom
bridges have been observed in (n-Bu₄N)₃Re₂(NCS)₁₀ (255), Cd₂(NCS)₄(butrz)₃, where
butrz is 4-t-butyl-1,2,4-triazole (256), Ni₃(detrH)₆(NCS)₆·2H₂O, where detrH is
3,5-diethyl-1,2,4-triazole (257) and Co₂L(OEt)(NCS)₃ (258), where L is a
20-membered macrocyclic ligand and whose structure is given in reference (258). The
single S-atom bridge has been observed in Cu₂L(SCN)₂ (259), where L is the same
macrocylic ligand as in the last example. In Ag(NCS)(P(n-C₃H₇)₃) (260, 261) and
Co(NCS)₆Hg₂·C₆H₆ (262) both end-to-end and single S-atom bridges exist, resulting in
tridentate NCS groups.

In the absence of suitable crystals for X-ray diffraction studies, infrared spectra
may yield useful information regarding the mode of coordination of the thiocyanate
ion. To this end several empirical criteria have been established (131). It must be
pointed out that great care must be exercised in applying these criteria since other
factors such as identity of the metal, its oxidation state, its stereochemistry, the nature
of other ligands and steric considerations may also influence infrared spectra.

The three normal modes of vibration of the linear NCS⁻ anion are:
pseudoantisymmetric stretching \(υ_{CN} (υ₁)\), bending \(δ_{NCS} (υ₂)\) and pseudosymmetric
stretching \(υ_{CS} (υ₃)\). In the spectrum of the free ion (solid KNCS (263, 264)) \(υ_{CN}
occurs at 2053 cm⁻¹, \(δ_{NCS}\) at 484 and 470 cm⁻¹ (the splitting has been attributed to site
symmetry of the NCS⁻ ion in the crystal (263, 264)) and \(υ_{CS}\) at 749 cm⁻¹. Upon
coordination the following changes in the free ion spectrum have been observed. (i) In
N-bonded NCS groups \(δ_{NCS}\) occurs near 470 cm⁻¹ whereas S-bonded NCS groups show
several bands of low intensity at lower energies, the most intense one being near
420 cm⁻¹ (125, 265). (ii) \(υ_{CS}\) occurs at higher energies (780-860 cm⁻¹) relative to the
free ion value when the anion is N-bonded and at lower energies (690-720 cm\(^{-1}\)) when it is S-bonded (125, 243, 265, 266). (iii) With the exception of >NCS bridging thiocyanate groups noted below, \(v_{\text{CN}}\) generally increases above the free ion value in the order \(M\)-NCS \(\approx\) \(M\)-SCN < \(M\)-NCS-M\(^{+}\). In numerical terms, \(v_{\text{CN}}\) usually occurs near the free ion value in N-bonded NCS groups, near 2 100 cm\(^{-1}\) for S-bonded ones and well above 2 100 cm\(^{-1}\) when the anion is bridging through both the nitrogen and sulphur atoms. However, because there is some overlap in the cases of N- and S-terminal bonding, the position of \(v_{\text{CN}}\) is mainly useful for distinguishing between terminal and bridging NCS groups (265, 267). The NCS ligand bridging via the nitrogen atom only is characterized by relatively low \(v_{\text{CN}}\), typically near or below 2 000 cm\(^{-1}\) (256-258). No infrared criterion is currently available for identifying NCS ligands that are bridging through the sulphur atom only. The only complex in which the presence of this type of coordination has been demonstrated unambiguously by a single crystal X-ray diffraction study exhibits \(v_{\text{CN}}\) at 2 105 cm\(^{-1}\) (259), the same spectral region as terminal S-bonded thiocyanate groups. (iv) The integrated intensity (area under the absorption peak) of \(v_{\text{CN}}\) is greater than the free ion value for N-bonding and lower for S-bonding (268-271). (v) In the far-infrared region (272), \(v_{\text{M-N}} > v_{\text{M-S}}\). The bonding criteria (iv) and (v) have been presented in very general terms as they are not applicable to data acquired in the present study and are only included here for completeness.

In accordance with the above discussion on infrared bonding criteria for the thiocyanate group, the occurrence of \(v_{\text{CN}}\) at 2 116 cm\(^{-1}\) for Ni(py)\(_2\)(NCS)\(_2\) and at 2 126 cm\(^{-1}\) for Ni(pyz)(NCS)\(_2\) suggest that the NCS ligands are bridging through both N and S atoms in these complexes. \(v_{\text{CN}}\) at 2 086 cm\(^{-1}\) for Ni(py)\(_4\)(NCS)\(_2\) and Ni(pdz)\(_3\)(NCS)\(_2\) and at 2 084 cm\(^{-1}\) for Ni(pyz)\(_2\)(NCS)\(_2\) and Ni(pdz)\(_2\)(NCS)\(_2\) suggest that these complexes contain terminal thiocyanate ligands. Ni(pdz)\(_3\)(NCS)\(_2\) and Ni(pdz)\(_2\)(NCS)\(_2\) show additional \(v_{\text{CN}}\) bands at 1 992 and 1 973 cm\(^{-1}\), respectively,
indicating that these complexes also contain thiocyanate groups bridging through the N-atom only.

In Ni(py)$_4$(NCS)$_2$ and the two pyridazine complexes $\nu_{CS}$ occurs within the range 780-860 cm$^{-1}$ and $\delta_{NCS}$ above 470 cm$^{-1}$ indicating that the NCS ligands in these complexes are N-bonded. It is difficult to unambiguously assign $\nu_{CS}$ and $\delta_{NCS}$ in the pyrazine complexes since the neutral ligand also has absorptions where these anion bands are expected to occur. The tentative assignments were made by comparison of the spectra with those of Ni(py)$_4$(NCS)$_2$ and Ni(py)$_2$(NCS)$_2$. As discussed in the preceding paragraph, the tetrakis(pyridine) complex contains terminal N-bonded NCS groups whereas the bis(pyridine) complex contains end-to-end bridging NCS groups. Both $\nu_{CS}$ and $\delta_{NCS}$ are at slightly higher energies in the former than in the latter. A parallel situation was observed for Fe(py)$_4$(NCS)$_2$ and Fe(py)$_2$(NCS)$_2$ where the small difference was explained in terms of the slightly smaller C-S bond order in the bridging ligands in Fe(py)$_2$(NCS)$_2$ as compared with terminal N-bonded ones in Fe(py)$_4$(NCS)$_2$ (273). Thus the position of $\nu_{CS}$ (802 cm$^{-1}$) and $\delta_{NCS}$ (492 cm$^{-1}$) indicate that Ni(pyz)$_2$(NCS)$_2$ contains terminal, N-bonded thiocyanate ligands. Even if these assignments are incorrect, N-bonding would still be indicated since no bands are observed at $\approx$ 700 and 420 cm$^{-1}$ suggesting that both $\nu_{CS}$ and $\delta_{NCS}$ are raised in energy above the free ion values. We have not used the $\nu_{CS}$ and $\delta_{NCS}$ bonding criteria on Ni(py)$_2$(NCS)$_2$ and Ni(pyz)(NCS)$_2$ because, as Pecile (270) and Turco and Pecile (266) noted, the presence of -NCS- bridges limits the diagnostic value of $\nu_{CS}$. This appears to apply to $\delta_{NCS}$ as well. AgNCS (252) and Co(py)$_2$(NCS)$_2$ (253) contain -NCS-bridges yet the application of $\nu_{CS}$ and $\delta_{NCS}$ criteria to their spectra would suggest S-bonding in the former (274) and N-bonding in the latter (243).

Infrared bonding criteria for pyridine and pyrazine were discussed in detail in section 2.1.4. Ni(py)$_4$(NCS)$_2$ and Ni(py)$_2$(NCS)$_2$ exhibit only those bands expected for
coordinated pyridine. The spectra of Ni(pyz)$_2$(NCS)$_2$ and Ni(pyz)(NCS)$_2$ indicate that the pyrazine ligands in both complexes are bidentate bridging.

Structural assignments for the nickel(II) thiocyanate complexes are now discussed. The assignments are based largely on analysis of the infrared spectra of the complexes and the observation that their electronic spectra (vide infra) support octahedral or pseudo-octahedral coordination.

For Ni(py)$_4$(NCS)$_2$ infrared spectroscopy shows that all the pyridine ligands are coordinated and the NCS groups are terminal and N-bonded. This is consistent with the structure of the compound established by X-ray crystallography: monomeric trans-octahedral (239).

Table 3-11. Thiocyanate ion band energies and assignments for nickel(II) complexes.$^a$

<table>
<thead>
<tr>
<th>KNCS$^b$</th>
<th>$\nu_{CN}$</th>
<th>$\nu_{CS}$</th>
<th>$\delta_{NCS}$</th>
<th>$2\delta_{NCS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(py)$_4$(NCS)$_2$</td>
<td>2 086s</td>
<td>802s</td>
<td>492s</td>
<td>960w-m 970w-m</td>
</tr>
<tr>
<td>Ni(py)$_2$(NCS)$_2$</td>
<td>2 116vs 2 134sh</td>
<td>786m</td>
<td>478m</td>
<td>485m 943w 959vw</td>
</tr>
<tr>
<td>Ni(pyz)$_2$(NCS)$_2$</td>
<td>2 034sh 2 084vs</td>
<td>802s$^e$</td>
<td>492s$^e$</td>
<td>967sh 973m</td>
</tr>
<tr>
<td>Ni(pyz)(NCS)$_2$</td>
<td>2 082msh 2 126vs</td>
<td>787s$^e$</td>
<td>470m$^e$</td>
<td>≈ 960vw,br</td>
</tr>
<tr>
<td>Ni(pdz)$_3$(NCS)$_2$</td>
<td>1 992vs,br 2 086vs,br</td>
<td>801m</td>
<td>489m,br</td>
<td>d</td>
</tr>
<tr>
<td>Ni(pdz)$_2$(NCS)$_2$</td>
<td>1 935sh 1 973vs 2 084vs</td>
<td>799w,sp 490w</td>
<td>805w sp</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All values are in cm$^{-1}$. v = very, s = strong, m = medium, w = weak, sp = split, sh = shoulder.

$^b$ Data and assignments from ref. 264.

$^c$ Neutral ligand also absorbs in this region; see text.

$^d$ Neutral ligand absorbs in this region; see Appendix II-4.
Single crystal X-ray diffraction studies have shown that Co(py)$_2$(NCS)$_2$ has a polymeric structure in which cobalt ions are doubly-bridged by NCS groups in an end-to-end fashion (253). Two pyridine ligands complete the octahedral configuration about each cobalt ion. Powder X-ray diffraction studies (see next section) have shown that the complexes M(py)$_2$(NCS)$_2$, where M is Co, Fe and Ni, are isomorphous. We therefore assign Ni(py)$_2$(NCS)$_2$ a structure (Fig. 3-23) similar to that of the cobalt complex. Our mid-infrared spectral data, which show that Ni(py)$_2$(NCS)$_2$ contains end-to-end bridging thiocyanate groups and coordinated pyridine ligands, are consistent with such a structure. Engelter and Thornton (244) arrived at similar structural conclusions for Ni(py)$_2$(NCS)$_2$. They based their assignment on an observed band-for-band correspondence in the far-infrared spectra of this compound and its cobalt analogue.

Lever et al. (33) previously proposed that Ni(pyz)$_2$(NCS)$_2$ has a six-coordinate structure with terminal pyrazine units and bridging thiocyanate anions. They based their assignment on a mid-infrared criterion that was latter shown by Goldstein et al. (45, 61) to be unreliable (A more detailed discussion on this subject was presented in section 3.2.3). Our infrared spectral data indicate that Ni(pyz)$_2$(NCS)$_2$ contains bidentate bridging pyrazine ligands and terminal N-bonded NCS groups. We propose for it a sheet structure consisting of an infinite square array of nickel(II) ions bridged by bidentate pyrazine groups, with the fifth and sixth coordination sites on the metal occupied by monodentate N-bonded NCS anions in a *trans* configuration (Fig. 3-4c). The structure is the same as that proposed by Goldstein et al. (61) for M(pyz)$_2$X$_2$ (M is Co or Ni and X is Cl, Br or I). Such a structure has since been observed by X-ray crystallography in several bis(pyrazine) complexes (45-48). It is particularly noteworthy that such a structure for Fe(pyz)$_2$(NCS)$_2$ was first proposed on the basis of spectroscopic evidence (67) of the type used in the present study and was subsequently confirmed by X-ray crystallography (48).
Fig. 3-22. Infrared spectrum of Ni(pdz)$_2$(NCS)$_2$.

Fig. 3-23. Proposed structure for Ni(py)$_2$(NCS)$_2$. 
For Ni(pyz)(NCS)\textsubscript{2} infrared data indicate that both pyrazine and thiocyanate groups are bidentate bridging. Hence we propose for it a sheet structure in which chains of nickel ions, doubly-bridged by thiocyanate groups in an end-to-end fashion, are cross-linked by pyrazine ligands (Fig. 3-3c).

Infrared spectra of Ni(pdz)\textsubscript{3}(NCS)\textsubscript{2} and Ni(pdz)\textsubscript{2}(NCS)\textsubscript{2} indicate that the complexes contain both terminal N-bonded and single N-atom bridging thiocyanate groups. Most of the pyridazine absorption bands exhibit energy shifts from the free ion values (Appendix II-4) suggesting that all the pyridazine ligands are coordinated. Electronic spectral studies (vide infra) indicate that the nickel ions in the two complexes are octahedrally coordinated. From these spectroscopic studies it can be inferred that the complexes are polynuclear and that the ligand arrangement around the nickel ions is pseudo-octahedral in each case. Unfortunately, in the absence of single crystal X-ray diffraction studies, no definite structural conclusions can be drawn for these two complexes. Nevertheless, several structures that are consistent with the spectroscopic properties of Ni(pdz)\textsubscript{2}(NCS)\textsubscript{2} and Ni(pdz)\textsubscript{3}(NCS)\textsubscript{2} may be readily conceived. For the bis(pyridazine) complex these include a linear chain structure in which nickel ions are doubly-bridged by pyridazine and >NCS groups; the pseudo-octahedral geometry about each nickel ion being completed by a terminal pyridazine ligand and a terminal thiocyanato-N group. In this structure adjacent nickel ions are bridged by both pyridazine and thiocyanate groups. It is also possible to have double pyridazine bridges alternating with double thiocyanate bridges. This is equivalent to having pyridazine-bridged dimers linked by >NCS groups to form chains. This kind of structure has been observed in Cd\textsubscript{3}(NCS)\textsubscript{4}(butrz)\textsubscript{3}, where butrz is 4-t-butyl-1,2,4-triazole (256). In this compound linear chains of cadmium ions are formed by alternating triple triazole and double >NCS bridges. Six-coordination about each cadmium ion is completed by a terminal thiocyanato-N group. Although Ni(pdz)\textsubscript{2}(NCS)\textsubscript{2} and [Cu(pdz)\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}]\textsubscript{3} are not isomorphous (see below), a trimeric structure such as that of the copper complex
(section 2.2.5) is also possible for Ni(pdz)$_2$(NCS)$_2$. A similar structure has been observed in Ni$_3$(detrH)$_6$(NCS)$_6$.2H$_2$O, where detrH is 3,5-diethyl-1,2,4-triazole (257).

The structure of Ni(pdz)$_3$(NCS)$_2$ may be based on any of those discussed in the preceding paragraph with regard to Ni(pdz)$_2$(NCS)$_2$, with the third pyridazine ligand only weakly associated in the solid state. The possibility that Ni(pdz)$_3$(NCS)$_2$ contains one weakly coordinated, or lattice, pyridazine molecule per mole of complex was suggested by its thermal properties (section 3.3.2). This compound may also have a chain structure in which nickel ions are bridged by a single thiocyanate group. In this case six-coordination about each nickel ion would be achieved through monodentate coordination of three pyridazine ligands and one thiocyanate group.

3.3.4 Powder X-ray diffraction patterns

Detailed powder X-ray diffraction data for Ni(py)$_2$(NCS)$_2$, Ni(pyz)(NCS)$_2$, Ni(pyz)(NCO)$_2$, Ni(pdz)$_3$(NCS)$_2$ and Ni(pdz)$_2$(NCS)$_2$ are presented in Appendix III. The powder X-ray diffraction patterns for the pyridine and pyrazine complexes are shown in Fig. 3.24 while those for the pyridazine complexes are shown in Fig. 3-25. The powder pattern for the copper complex, [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$, is included in Fig. 3-25 for comparison purposes. Selected data for Ni(py)$_2$(NCS)$_2$ are given in Table 3-12 together with data for Co(py)$_2$(NCS)$_2$ and Fe(py)$_2$(NCS)$_2$ (273), for comparison. It can be seen from the table that the three bis(pyridine) complexes are isomorphous and hence Ni(py)$_2$(NCS)$_2$ is assigned a linear chain structure in which nickel ions are doubly-bridged by thiocyanate ions in an end-to-end fashion. The pseudo-octahedral geometry of each nickel ion is completed by pyridine molecules (Fig. 3-23). This is the structure which has been determined for the cobalt complex by
single crystal X-ray diffraction (253). The same structure was proposed for Fe(py)$_2$(NCS)$_2$ on the basis of isomorphism with the cobalt analogue (273).

Although the analogous complexes Ni(pyz)(NCS)$_2$ and Ni(pyz)(NCO)$_2$ differ only in the nature of the pseudohalide they exhibit no isomorphism (Fig. 3-24). This is further evidence in support of the proposal, based on spectroscopic studies, that the pseudohalides bridge differently in the two complexes. In Ni(pyz)(NCS)$_2$ the thiocyanate ions bridge through both nitrogen and sulphur atoms whereas, in Ni(pyz)(NCO)$_2$, the cyanate ions bridge through the nitrogen atom only (Fig. 3-3).

[Cu(pdz)$_2$(NO$_3$)$_2$]$_3$ was shown by single crystal X-ray diffraction to have a centrosymmetric linear trinuclear structure incorporating both bridging and terminal nitrate groups (section 2.2.5). It was also concluded from infrared spectral studies (vide supra) that the analogous nickel complex, Ni(pdz)$_2$(NCS)$_2$, contains both bridging and terminal thiocyanate groups. It was therefore of interest to determine whether the two compounds are isomorphous. They are not (Fig. 3-25). There is also no isomorphism between Ni(pdz)$_2$(NCS)$_2$ and Ni(pdz)$_3$(NCS)$_2$. The very broad nature of the two peaks that constitute the powder pattern of the latter compound suggest that this compound is amorphous. It is noteworthy that the major peaks in the powder pattern of Ni(pdz)$_2$(NCS)$_2$ occur in two well defined regions; the same regions where the two peaks in the powder pattern of Ni(pdz)$_3$(NCS)$_2$ are observed. This may indicate that the two compounds have the same basic structure.
Table 3-12. Selected powder X-ray diffraction data for some M(py)$_2$(NCS)$_2$ complexes.

<table>
<thead>
<tr>
<th>Ni(py)$_2$(NCS)$_2^a$</th>
<th>Co(py)$_2$(NCS)$_2^b$</th>
<th>Fe(py)$_2$(NCS)$_2^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (Å)</td>
<td>I</td>
<td>d (Å)</td>
</tr>
<tr>
<td>7.302</td>
<td>100.0</td>
<td>7.33vs</td>
</tr>
<tr>
<td>5.212</td>
<td>23.1</td>
<td>5.24m</td>
</tr>
<tr>
<td>5.039</td>
<td>29.8</td>
<td>5.11m</td>
</tr>
<tr>
<td>4.227</td>
<td>28.7</td>
<td>4.25m</td>
</tr>
<tr>
<td>4.067</td>
<td>37.6</td>
<td>3.92m</td>
</tr>
<tr>
<td>3.635</td>
<td>33.0</td>
<td>3.65s</td>
</tr>
<tr>
<td>3.352</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td>3.293</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>3.223</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>2.887</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>2.832</td>
<td>12.9</td>
<td>2.84s</td>
</tr>
<tr>
<td>2.745</td>
<td>8.3</td>
<td>2.76w</td>
</tr>
<tr>
<td>2.679</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>2.636</td>
<td>11.7</td>
<td>2.64m</td>
</tr>
<tr>
<td>2.513</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>2.421</td>
<td>11.1</td>
<td>2.43w</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.38w</td>
</tr>
<tr>
<td>2.350</td>
<td>10.8</td>
<td>2.36w</td>
</tr>
<tr>
<td>2.235</td>
<td>7.0</td>
<td>2.25w</td>
</tr>
<tr>
<td>2.145</td>
<td>7.9</td>
<td>2.24w</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.85w</td>
</tr>
<tr>
<td>1.830</td>
<td>6.4</td>
<td>1.84w</td>
</tr>
<tr>
<td>1.794</td>
<td>5.8</td>
<td>1.80w</td>
</tr>
</tbody>
</table>

\(a\) This work; relative intensities, I, are based on 100 for the strongest intensity observed.

\(b\) Data from ref. 273; vs = very strong, m = medium, w = weak.
Fig. 3-24. Powder X-ray diffraction patterns for (a) Ni(py)$_2$(NCS)$_2$, (b) Ni(pyz)(NCS)$_2$ and (c) Ni(pyz)(NCO)$_2$. 
Fig. 3-25. Powder X-ray diffraction patterns for (a) Ni(pdz)$_2$(NCS)$_2$, (b) Ni(pdz)$_3$(NCS)$_2$ and (c) [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$. 
3.3.5 Electronic spectra

The electronic spectral data for the nickel(II) thiocyanate complexes are presented in Table 3-13 except for Ni(py)$_2$(NCS)$_2$ the data for which are given in Table 3-15. For comparison, spectral data for those complexes that have been previously studied are included in Table 3-13. The spectra of Ni(py)$_4$(NCS)$_2$ and Ni(pyz)$_2$(NCS)$_2$ are readily assigned assuming octahedral symmetry. This is consistent with the known structure of the former (239). The spectra of the pyridazine and mono(pyrazine) complexes are also consistent with octahedral symmetry even though they exhibit only two bands. In these complexes the highest energy band, $v_3$, is obscured by a very strong band, which may be attributed to charge transfer or internal ligand transitions. This was confirmed for the pyridazine complexes by computing $v_3$ as follows (207, 275). The value of Dq/B corresponding to the ratio $v_2/v_1$ was obtained from the appropriate energy ratio diagram and then used to obtain the ratio $v_3/B$ from the corresponding Tanabe-Sugano diagram.$^{10}$ Having derived B from $v_1$ and $v_2$ (see below) $v_3$ was calculated. For Ni(pyz)(NCS)$_2$, $v_3$ could not be computed. This is because the ratio $v_2/v_1$ for this compound does not fall within the range covered by the plot of $v_2/v_1$ versus Dq/B in the energy ratio diagram of $A_2$ ground term ions.

The ligand field parameter, Dq, for the complexes assigned a pseudooctahedral stereochemistry was calculated using equation 3-1. For those complexes for which the expected three transitions were observed the Racah parameter, B, was calculated by means of equation 3-2. Where only $v_1$ and $v_2$ were observed the following equation (206) was used to calculate B.

$$B = (v_2-2v_1)(v_2-v_1)/3(5v_2-9v_1).$$  \[3-7\]

$^{10}$ In reference 275 a range of values for Dq/B and the corresponding values of $v_3/B$, $v_2/v_1$, $v_3/v_1$ and $v_3/v_2$ have been tabulated. Hence the ratio $v_3/B$ corresponding to the experimentally determined $v_2/v_1$ may also be read directly from the table.
Since the magnitude of B depends on the equation used, we also employed the equation based on \( v_1 \) and \( v_2 \) only, even when all three bands were observed. This was done in order to compare this parameter for all the complexes on the same basis. The dependence of the value of B on the method of calculation has been noted before by Lever (104) who pointed out that the variation can be much larger than 10%. This possibly arises from the fact that the different equations used lay greater emphasis on different transition energies. The accuracy with which the different energies are determined, and hence the accuracy of B, may vary. For instance, equation 3-7 places too much reliance on \( v_1 \). This band is generally weak and broad in mull spectra. There may, therefore, be a greater uncertainty in determining its position than in determining the positions of the other bands. Hence, in the present work, the B values obtained using equation 3-7 are considered to be less accurate than those calculated using equation 3-2.

The values of Dq and B for the nickel(II) thiocyanate complexes are given in Table 3-14. Except for Ni(pyz)(NCS)\(_2\) the Dq values for the nickel(II) thiocyanate, and nickel(II) cyanate (Table 3-4), complexes are similar suggesting a similar NiN\(_6\) chromophore. Ni(pyz)(NCS)\(_2\) has a significantly lower Dq. This is consistent with, and is itself further evidence for, the proposed structure for this complex (Fig. 3-3c) in which sulphur atoms enter the coordination sphere of the nickel ion through end-to-end NCS bridging, resulting in a NiN\(_4\)S\(_2\) chromophore. Sulphur is lower than nitrogen in the spectrochemical series and affords a smaller contribution to the ligand field.
Table 3-13. Electronic spectral band energies and assignments for complexes of nickel(II) thiocyanate, O_h symmetry.a

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption maxima in cm⁻¹ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>³T₂g(F) (ν₁)</td>
</tr>
<tr>
<td>Ni(py)₄(NCS)₂</td>
<td>10 200 (982)</td>
</tr>
<tr>
<td>Ni(pdz)₃(NCS)₂</td>
<td>10 600 (945)</td>
</tr>
<tr>
<td>Ni(pdz)₂(NCS)₂</td>
<td>10 500 (956)</td>
</tr>
<tr>
<td>Ni(pyz)₂(NCS)₂</td>
<td>10 500 (954)</td>
</tr>
<tr>
<td>Ni(pyz)(NCS)₂</td>
<td>9 300 (1 070)</td>
</tr>
</tbody>
</table>

Ni(py)₄(NCS)₂ᵈ     | 10 450, 12 800sh, 16 900, =22 200sh, 27 200 |
Ni(pyz)₂(NCS)₂ᵉ     | 10 400, 16 650 |

a Transitions are from the ³A₂₉ state: sh = shoulder, n.o. = not observed. Estimated uncertainty in absorption maxima is ± 200 cm⁻¹. All literature data were obtained by the diffuse reflectance technique at ambient temperatures.
b Calculated, see text for details. c Cannot be calculated, see text for details.
d Data from ref. 230. e Data from ref. 34.
Table 3-14. Ligand field parameters for complexes of nickel(II) thiocyanate, O\textsubscript{h} symmetry.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dq</th>
<th>B\textsuperscript{b}</th>
<th>B\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(py)\textsubscript{4}(NCS)\textsubscript{2}</td>
<td>1 020</td>
<td>867</td>
<td>921</td>
</tr>
<tr>
<td>Ni(pdz)\textsubscript{3}(NCS)\textsubscript{2}</td>
<td>1 060</td>
<td></td>
<td>936</td>
</tr>
<tr>
<td>Ni(pdz)\textsubscript{2}(NCS)\textsubscript{2}</td>
<td>1 050</td>
<td></td>
<td>998</td>
</tr>
<tr>
<td>Ni(pyz)\textsubscript{2}(NCS)\textsubscript{2}</td>
<td>1 050</td>
<td>827</td>
<td>998</td>
</tr>
<tr>
<td>Ni(pyz)(NCS)\textsubscript{2}</td>
<td>930</td>
<td></td>
<td>d</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Error limits: Dq $\pm 20 \text{ cm}^{-1}$, B\textsuperscript{column 3} $\pm 14 \text{ cm}^{-1}$, B\textsuperscript{column 4} $\pm 35 \text{ cm}^{-1}$.

The splitting of $v_1$ (O\textsubscript{h} symmetry) clearly indicates a lower symmetry than octahedral in Ni(py)\textsubscript{2}(NCS)\textsubscript{2} and we assigned its spectrum assuming D\textsubscript{4h} symmetry (Table 3-15). The assignments are consistent with those made in reference 204 for related complexes. The transitions to the $^3A\textsubscript{2g}\textsuperscript{b}$ and $^3E\textsubscript{ig}\textsuperscript{c}$ states are obscured by a more intense band. In the absence of the energy of the latter transition tetragonal parameters, such as those derived for Ni(py)\textsubscript{4}Cl\textsubscript{2} (section 3.2.4), cannot be determined for Ni(py)\textsubscript{2}(NCS)\textsubscript{2}.

Table 3-15. Electronic spectral band energies and assignments for Ni(py)\textsubscript{2}(NCS)\textsubscript{2}, D\textsubscript{4h} symmetry.

| $^3B\textsubscript{1g}$ $\rightarrow$ $^3E\textsubscript{g}$ | $^3B\textsubscript{2g}$ | $^1A\textsubscript{1g}$, $^1B\textsubscript{1g}$ | $^3A\textsubscript{2g}$, $^3E\textsubscript{g}$ | $^1B\textsubscript{2g}$ | $^3A\textsubscript{2g}$, $^3E\textsubscript{1g}$ |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| (cm\textsuperscript{-1}) | 8 500 | 11 200 | 13 800 | 16 600 | 20 700sh | n.o. | (nm) | 1 171 | 890 | 726 | 604 | 483sh |

n.o. = not observed. Masked by a more intense (charge transfer or internal ligand) band. sh = shoulder.
3.3.5 Magnetic properties

As mentioned in section 3.1.5, high-spin octahedral and magnetically dilute nickel(II) complexes are expected to exhibit temperature independent magnetic moments in the range 2.9-3.3 B.M. with, possibly, some temperature dependence at very low temperatures due to the effects of zero-field splitting (ZFS). Ni(py)₄(NCS)₂ and Ni(pdz)₂(NCS)₂ exhibit temperature independent magnetic moments of 3.04 and 3.06 B.M., respectively, over the temperature range 82-4.4 K. Thus they show no evidence for significant magnetic exchange or ZFS down to 4.4 K. Of the three analogous compounds Ni(py)₄(NCO)₂ (section 3.1), Ni(py)₄Cl₂ (section 3.2) and Ni(py)₄(NCS)₂, only the nickel(II) chloride complex exhibits ZFS effects. The crystal structures of the latter two are known. Ni(py)₄Cl₂ has a tetragonally elongated octahedral structure (Ni-N: 2.133(4) Å, Ni-Cl: 2.437(2) Å) whereas Ni(py)₄(NCS)₂ has a nearly regular octahedral structure (Ni-NCS: 2.12(3) Å, Ni-Npy: 2.03(6) Å). In tetragonal octahedral nickel(II) complexes, the ground term may be connected by spin-orbit coupling with the split orbital components of the higher $^3T_{2g}$ term (see Fig. 3-6). To second order, this connection changes the energies of the spin states ($m_s = 0, \pm 1$) by different amounts. This partial removal of spin degeneracy in the absence of an applied magnetic field leads to a temperature-dependent magnetic moment, such as observed in Ni(py)₄Cl₂. Thus the magnetic properties of both Ni(py)₄Cl₂ and Ni(py)₄(NCS)₂ are consistent with their known structures. Although the structures of both Ni(py)₄(NCO)₂ and Ni(pdz)₂(NCS)₂ have not been determined by single crystal X-ray diffraction studies, their magnetic properties indicate that the nickel ions in both compounds are in regular or near regular octahedral ligand environments.

The magnetic moment of Ni(pdz)₃(NCS)₂ shows a small temperature dependence, decreasing from 2.96 B.M. at 82 K to 2.78 B.M. at 4.4 K. Its susceptibility data were analyzed using the ZFS model and the best fit is represented by
the solid line in Fig. 3-26. The best fit parameters are given in Table 3-16. The fit is
good but of inferior quality to that obtained for Ni(py)$_4$Cl$_2$ and of comparable quality to
those obtained for the polymeric compounds, NiL$_2$X$_2$, where L is pyz or pdz and X is
NCO, NCS or Cl (Tables 3-5, 3-9, 3-16). This suggests that there could be very weak
antiferromagnetic coupling between nickel ions in Ni(pdz)$_3$(NCS)$_2$. However, since its
structure could not be deduced unambiguously from available information, further
theoretical analysis of its magnetic data was not undertaken.

Fig. 3-26. Magnetic susceptibility versus temperature plot for Ni(pdz)$_3$(NCS)$_2$. The
solid line was drawn using the parameters given in Table 3-16.
Table 3-16. Magnetic parameters for complexes of nickel(II) thiocyanate.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Model\textsuperscript{b}</th>
<th>D (cm\textsuperscript{-1})</th>
<th>(-J (cm\textsuperscript{-1}))</th>
<th>(g)</th>
<th>(F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(pyz\textsubscript{2})(NCS\textsubscript{2})</td>
<td>ZFS</td>
<td>9.2</td>
<td>-</td>
<td>2.02</td>
<td>0.0361</td>
</tr>
<tr>
<td></td>
<td>W-F</td>
<td>-</td>
<td>0.57</td>
<td>2.08</td>
<td>0.0085</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>-</td>
<td>0.53</td>
<td>2.09</td>
<td>0.0053</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>-</td>
<td>0.30</td>
<td>2.08</td>
<td>0.0074</td>
</tr>
<tr>
<td>Ni(pdz\textsubscript{3})(NCS\textsubscript{2})</td>
<td>ZFS</td>
<td>4.2</td>
<td>-</td>
<td>2.05</td>
<td>0.0306</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Estimated error limits: D \(\pm 1.3\) cm\textsuperscript{-1}, \(-J \pm 0.03\) cm\textsuperscript{-1}, \(g \pm 0.02\).

\textsuperscript{b} ZFS = zero-field splitting, W-F = Wagner-Friedberg, W = Weng, L = Lines.

The magnetic properties of Ni(pyz\textsubscript{2})(NCS\textsubscript{2}) are very similar to those of its cyanate and chloride analogues, Ni(pyz\textsubscript{2})(NCO\textsubscript{2})\textsubscript{1/2}H\textsubscript{2}O and Ni(pyz\textsubscript{2})Cl\textsubscript{2}, discussed earlier in this chapter. The magnetic moment is 2.91 at 82 K, remains fairly constant as the temperature is lowered to about 25 K, then decreases significantly to a value of 1.90 B.M. at 2.5 K. Its magnetic susceptibility data were analyzed using the ZFS model and, because of the sheet structure proposed for it, Lines two-dimensional Heisenberg model (Eqn. 2-2, using the coefficients for \(S = 1\) systems given in section 3.1.5). The best fit to the two models are represented by solid lines in Fig. 3-27 and the best fit parameters are given in Table 3-16. Although a good agreement between theory and experiment is obtained with the ZFS model a better agreement, as judged visually and by the value of \(F\), is obtained using Lines model. This indicates that the nickel ions are coupled antiferromagnetically, albeit very weakly, by the bridging pyrazine ligands. Since the two possible pathways for magnetic exchange in Ni(pyz\textsubscript{2})(NCS\textsubscript{2}) need not be equivalent and, indeed, one may dominate, its susceptibility data were also analyzed using the Weng and Wagner-Friedberg linear chain models represented by equations 3-4 and 3-5, respectively. Fits of comparable
quality to the two-dimensional model were obtained (Table 3-16). As was found for
Ni(pyz)$_2$(NCO)$_2$·0.5H$_2$O (section 3.1.5) and Ni(pyz)$_2$Cl$_2$ (section 3.2.5), the magnitude
of the exchange in Ni(pyz)$_2$(NCS)$_2$ is too small to enable one to determine the
dimensionality of the exchange based solely on fitting of the magnetic data to available
models.

Magnetic susceptibility versus temperature plots and selected isothermal
magnetization curves for Ni(py)$_2$(NCS)$_2$ are shown in Fig. 3-28. The latter show that
the compound is a metamagnet with a transition field, at 2 K, of 1 kOe. The
temperature dependence of the magnetic moment of the compound is compared with
that of the magnetically dilute monomeric compound, Ni(py)$_4$(NCS)$_2$, in Fig. 3-29.
The magnetic moment of Ni(py)$_2$(NCS)$_2$, calculated from susceptibility data obtained at
a field of 9 225 Oe, is 3.25 B.M. at 82 K. It then rises with decreasing temperature to
a maximum of 4.20 B.M. at 6.2 K and then decreases to 3.09 B.M. as the temperature
is lowered further to 2.3 K. Both the magnitude and temperature variation of the
moment between 82 and 6 K are indicative of ferromagnetic exchange between the
nickel ions. Between 82 and \( \approx 4 \) K, the susceptibility of this compound is higher than
that of the magnetically dilute Ni(py)$_4$(NCS)$_2$ and also increases more rapidly with
decreasing temperature, features characteristic of ferromagnetic coupling. No field
dependence of the susceptibility is observed in the temperature range 82-4 K for fields
between 2 549 and 9 225 Oe. Below 4 K, however, the susceptibility goes through a
maximum and also shows field dependence (Fig. 3-28). With increasing field the
maximum broadens, shifts to lower temperatures and finally disappears. This kind of
low temperature susceptibility behaviour is expected for a metamagnet. As the field is
progressively increased there is a transition from an antiferromagnetic to a
ferromagnetic phase, hence the progressive increase in susceptibility and the
concomitant disappearance of the maximum. We interpret the magnetic properties of
Ni(py)$_2$(NCS)$_2$ by proposing that the nickel ions along the chain
Fig. 3-27. Magnetic susceptibility versus temperature plots for Ni(pyz)$_2$(NCS)$_2$. The solid lines were drawn using the parameters given in Table 3-16.
Fig. 3-28. (a) Magnetic susceptibility versus temperature plots and (b) selected magnetization isotherms for Ni(py)$_2$(NCS)$_2$. 
are ferromagnetically coupled but there is a weak antiferromagnetic interchain interaction that causes a three-dimensional antiferromagnetic ordering at lower temperatures.

The magnetic properties of Ni(pyz)(NCS)₂ are summarized in Figs. 3-29 and 3-30. These properties are very similar to those of Ni(py)₂(NCS)₂. However, the moments at any given temperature are lower in the pyrazine complex, the drop in susceptibility at low temperatures is more rapid and at 9 225 Oe the maximum in the susceptibility has not disappeared. The metamagnetic transition field at 2 K is 4 kOe. These properties indicate that the interchain interactions are stronger in Ni(pyz)(NCS)₂ than in Ni(py)₂(NCS)₂, a phenomenon that may be explained by the fact that the Ni(NCS)₂ chains are directly linked by pyrazine moieties in the former compound.

The appearance of the field dependence of the magnetic susceptibility of a substance that shows metamagnetic behaviour depends on the sharpness of the transition and, hence, the temperature and field of measurement. This explains the difference in appearance of Figs. 3-20a, 3-28a and 3-30a for the metamagnetic complexes Ni(py)Cl₂, Ni(py)₂(NCS)₂ and Ni(pyz)(NCS)₂, respectively.

![Fig. 3-29. Magnetic moment versus temperature plots for Ni(py)₂(NCS)₂, Ni(pyz)(NCS)₂ and Ni(py)₄(NCS)₂.](image)
Fig. 3-30. (a) Magnetic susceptibility versus temperature plots and (b) selected magnetization isotherms for Ni(pyz)(NCS)$_2$. 
3.4 Summary and conclusions

The correlations between the magnetic properties and structures of all the compounds discussed in this chapter are summarized in this section. Based on previous evidence and further evidence obtained in this work Ni(py)$_4$(NCO)$_2$, Ni(py)$_4$Cl$_2$ and Ni(py)$_4$(NCS)$_2$ are mononuclear. Not surprisingly, perhaps, they give no evidence for magnetic concentration. The complex which shows the largest tetragonal distortion, Ni(py)$_4$Cl$_2$, gives measurable zero-field splitting effects, again as expected. The pyridazine complexes, Ni(pdz)$_3$(NCS)$_2$ and Ni(pdz)$_2$(NCS)$_2$, to which structures could not be unambiguously assigned are also magnetically dilute. The magnetic moment of the former exhibits a small temperature dependence which is attributed to ZFS effects although very weak antiferromagnetic exchange between the nickel ions cannot be ruled out totally. In Ni(pyz)$_2$(NCO)$_2$.1/2$H$_2$O, Ni(pyz)$_2$Cl$_2$ and Ni(pyz)$_2$(NCS)$_2$, where nickel centres are linked by bridging ligands in sheet structures, evidence for weak antiferromagnetic exchange is seen. Similarly, evidence for weak antiferromagnetic exchange is seen for the linear chain pyridazine-bridged polymer, Ni(pdz)$_2$(NCO)$_2$.

Ni(pyz)(NCO)$_2$, Ni(pyz)Cl$_2$ and Ni(pyz)(NCS)$_2$ have structures in which chains of nickel ions bridged by the anionic ligands are cross-linked by pyrazine ligands to give sheet structures. In Ni(py)$_2$(NCS)$_2$, also, chains of nickel ions are bridged by the anionic ligands but in this case the chains are isolated, the fifth and sixth coordination sites on the metals being occupied by pyridine molecules. Ni(py)Cl$_2$ has a unique structure consisting of double-strand chloride-bridged polymeric chain in which each nickel ion is surrounded by one pyridine ligand, two bicoordinate chloride ions and three tricoordinate chloride ions. These five compounds all exhibit intrachain ferromagnetic exchange coupling and interchain antiferromagnetic exchange coupling. They also show metamagnetic transitions at low temperatures. Some of their properties are compared in Table 3-17. The metamagnetic transitions observed here on powdered
samples are not as distinct as the transitions observed previously on single crystal samples of, for example, FeCl₂ (218). Hence the critical field is obtained in the present work by extrapolating the "straight" portion of the s-shaped magnetization isotherms. This roughly corresponds to the field at which the metamagnetic transition begins. From the values of the critical fields in Table 3-17 it can be seen that the interchain interaction in these complexes decrease in the order Ni(pyz)Cl₂ > Ni(pyz)(NCO)₂ > Ni(pyz)(NCS)₂ > Ni(py)Cl₂ > Ni(py)₂(NCS)₂. In Ni(pyz)(NCS)₂ and Ni(py)₂(NCS)₂ the nickel ions along the chains are linked by the same type of -NCS- bridges, hence it may be assumed that the intrachain interactions in the two complexes are equal. The greater interchain interaction in the former complex may then be attributed to the fact that the pyrazine bridges linking the Ni(NCS)₂ chains provide a direct pathway for antiferromagnetic exchange coupling between the chains. The magnetic moment values indicate that the ferromagnetic intrachain interactions are greatest in Ni(py)Cl₂. This may be because each nickel ion in the complex has four nearest neighbour nickel ions with which to interact whereas all the other complexes have only two.

Table 3-17. Selected magnetic properties of metamagnetic nickel(II) complexes.

<table>
<thead>
<tr>
<th></th>
<th>Hc (kOe)</th>
<th>(\mu_{\text{eff}}) (B.M.)³</th>
<th>82 K</th>
<th>(\approx 22) K</th>
<th>(\approx 4) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(pyz)Cl₂</td>
<td>12.8</td>
<td>3.58</td>
<td>3.97</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>Ni(pyz)(NCO)₂</td>
<td>8</td>
<td>3.59</td>
<td>4.53</td>
<td>2.31</td>
<td></td>
</tr>
<tr>
<td>Ni(pyz)(NCS)₂</td>
<td>4</td>
<td>3.17</td>
<td>3.34</td>
<td>3.55</td>
<td></td>
</tr>
<tr>
<td>Ni(py)Cl₂</td>
<td>1.8</td>
<td>4.30</td>
<td>6.98</td>
<td>4.99</td>
<td></td>
</tr>
<tr>
<td>Ni(py)₂(NCS)₂</td>
<td>1</td>
<td>3.25</td>
<td>3.64</td>
<td>3.85</td>
<td></td>
</tr>
</tbody>
</table>

³ Calculated from susceptibility data collected at a field of 9 225 Oe.
4.1 Complexes of copper(I) trifluoromethanesulfonate

4.1.1 Introduction

The first and, until recently, only reported pyrazine-bridged compounds of copper(I) were bimetallic complexes of composition Cu$_2$LX$_2$, where L is pyrazine or a methylpyrazine and X is Cl, Br, I or CN (30, 32). The primary objective of the present study was to investigate magneto-structural correlations in coordination polymers. Complexes without unpaired electrons, like those of copper(I), do not meet this objective. However, our interest in complexes of copper(I) trifluoromethanesulfonate (copper(I) triflate) was generated by the serendipitous isolation of Cu(pyz)$_2$(CF$_3$SO$_3$) from a solution of copper(II) triflate and pyrazine in a 1:2 mole ratio (44). This compound has unique structural features, containing both bridging and terminal pyrazine groups. However, it was obtained contaminated with an additional unidentified product and in low yields. It was, therefore, desirable to develop a synthetic procedure that would lead to a purer product in high yields. Moreover, its isolation from a copper(II) salt without added reducing agent indicated that it must be more stable than the corresponding copper(II) pyrazine complex. Consequently, it was of interest to see if similar copper(I) complexes of other ligands related to pyrazine could be obtained.
The compounds whose characterization is the subject of this section are Cu(pyz)$_2$(CF$_3$SO$_3$), Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$), Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$) and Cu(pyz)(CF$_3$SO$_3$). Their preparations are described in section 5.2.7. They are all hygroscopic and were generally manipulated in an inert atmosphere glove box. However, crystals of Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$), like those of Cu(pyz)$_2$(CF$_3$SO$_3$) (44), remain intact in the atmosphere for long periods of time and no precautions were taken during the structural determination of this compound.

4.1.2 The crystal structure of Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$)

The crystallographic data for Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) are given in Table 4-1 while some selected bonding parameters are given in Tables 4-2 and 4-3. A more detailed compilation of its structural parameters is given in Appendix I-5. In Fig. 4-1 is shown the atom labelling scheme for Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$). Stereoviews of the unit cell packing and the geometry around each copper(I) ion are shown in Fig. 4-2. X-ray structural analysis shows that the structure of Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) is very similar to that of its pyrazine analogue (44). The structure consists of spiral chains of copper ions linked by bidentate bridging 2,5-dimethylpyrazine ligands. Monodentate neutral ligand and triflate groups complete the coordination around each copper to yield a distorted tetrahedral CuN$_3$O chromophore.

The triflate anion in Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) is very similar, in regard to internal bonding parameters, to that in Cu(pyz)$_2$(CF$_3$SO$_3$). The anion adopts a staggered-ethane configuration about the C-S bond; the O-S-O angles are greater than 109° while the C-S-O angles are less than this angle, indicating that repulsions between adjacent oxygen atoms are greater than those between the oxygen atoms and the
Fig. 4-1. Atom labelling scheme for Cu(2,5-me2pyz)2(CF3SO3).
Fig. 4-2. Stereoscopic views of (a) the unit cell packing and (b) the coordination about copper in Cu(2,5-me₂pyz)₂(CF₃SO₃). In (b) 50% probability thermal ellipsoids are shown for the non-hydrogen atoms. Shaded atoms comprise the asymmetric unit.
Table 4-1. Crystal data* for Cu(2,5-me₂pyz)₂(CF₃SO₃).

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Triclinic</th>
<th>γ, deg</th>
<th>80.26(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>P1 (#2)</td>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>a, Å</td>
<td>9.424(4)</td>
<td>V, Å³</td>
<td>863(1)</td>
</tr>
<tr>
<td>b, Å</td>
<td>12.103(4)</td>
<td>ρ, g cm⁻³</td>
<td>1.650</td>
</tr>
<tr>
<td>c, Å</td>
<td>9.113(4)</td>
<td>F(000)</td>
<td>436</td>
</tr>
<tr>
<td>α, deg</td>
<td>110.97(3)</td>
<td>R</td>
<td>0.033</td>
</tr>
<tr>
<td>β, deg</td>
<td>117.20(3)</td>
<td>Rw</td>
<td>0.039</td>
</tr>
</tbody>
</table>

* Standard deviations in the last digit are given in parentheses.

Table 4-2. Selected bonding parameters*⁺,b for Cu(2,5-me₂pyz)₂(CF₃SO₃) and Cu(pyz)₂(CF₃SO₃).

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Cu-O(1)</th>
<th>2.388(2)</th>
<th>2.331(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-N(1)c</td>
<td>2.007(2)</td>
<td>1.971(1)</td>
<td></td>
</tr>
<tr>
<td>Cu-N(2)c</td>
<td>2.005(2)</td>
<td>2.027(2)</td>
<td></td>
</tr>
<tr>
<td>Cu-N(3)</td>
<td>2.033(2)</td>
<td>1.985(2)</td>
<td></td>
</tr>
<tr>
<td>S-O(1)d</td>
<td>1.433(2)</td>
<td>1.440(2)</td>
<td></td>
</tr>
<tr>
<td>S-O(2)</td>
<td>1.421(2)</td>
<td>1.422(3)</td>
<td></td>
</tr>
<tr>
<td>S-O(3)</td>
<td>1.424(2)</td>
<td>1.432(3)</td>
<td></td>
</tr>
<tr>
<td>Mean bond angles (deg)</td>
<td>O-S-O</td>
<td>114.8(1)</td>
<td>114.7(2)</td>
</tr>
<tr>
<td></td>
<td>C-S-O</td>
<td>103.5(1)</td>
<td>103.6(2)</td>
</tr>
<tr>
<td></td>
<td>F-C-S</td>
<td>111.4(2)</td>
<td>111.5(3)</td>
</tr>
<tr>
<td></td>
<td>F-C-F</td>
<td>107.4(3)</td>
<td>107.4(4)</td>
</tr>
</tbody>
</table>

* Standard deviations in the last digit are given in parentheses.
⁺ Data in column 4 are for corresponding parameters in Cu(pyz)₂(CF₃SO₃) (44).
⁺⁺ Involves bridging pyrazine ligand.
⁺⁺⁺ Involves the coordinated oxygen atom.
trifluoromethyl group; the S-O bond involving the coordinated oxygen atom is longer than those involving the non-coordinated ones.

The 2,5-dimethylpyrazine moieties in Cu(2,5-me\textsubscript{2}pyz)\textsubscript{2}(CF\textsubscript{3}SO\textsubscript{3}) are planar within experimental error and the internal bonding parameters for the three moieties attached to a given copper ion are presented in Table 4.3. For comparison, data obtained for Ni(2,5-me\textsubscript{2}pyz)Br\textsubscript{2} (276) are included in this table. Even though the corresponding parameters for all the 2,5-dimethylpyrazines listed in the table are comparable (indicating lack of substantial distortion of all the rings), it is noteworthy that those for the two bridging ligands in Cu(2,5-me\textsubscript{2}pyz)\textsubscript{2}(CF\textsubscript{3}SO\textsubscript{3}) are essentially identical within experimental error. The terminal 2,5-dimethylpyrazine molecule is the least symmetrical.

A detailed comparison of the structures of Cu(pyz)\textsubscript{2}(CF\textsubscript{3}SO\textsubscript{3}) and Cu(2,5-me\textsubscript{2}pyz)\textsubscript{2}(CF\textsubscript{3}SO\textsubscript{3}) reveals some interesting differences however. Attention was drawn previously (44) to the long Cu-O bond in Cu(pyz)\textsubscript{2}(CF\textsubscript{3}SO\textsubscript{3}) and the fact that the triflate-metal interaction is weak in this compound. The Cu-O distance in Cu(2,5-me\textsubscript{2}pyz)\textsubscript{2}(CF\textsubscript{3}SO\textsubscript{3}) is \(\approx 0.06\) Å longer than in Cu(pyz)\textsubscript{2}(CF\textsubscript{3}SO\textsubscript{3}) (Table 4-2), indicating even weaker metal-anion interactions in the former compound. The observation that the S-O bond associated with the bridging oxygen atom is slightly shorter in Cu(2,5-me\textsubscript{2}pyz)\textsubscript{2}(CF\textsubscript{3}SO\textsubscript{3}) than in Cu(pyz)\textsubscript{2}(CF\textsubscript{3}SO\textsubscript{3}) is also consistent with weaker metal-anion interaction in the former. The S-O bond lengths involving the non-coordinated oxygen atoms also reflect a lower perturbation of the triflate group in the 2,5-dimethylpyrazine complex in that they are essentially equal (difference is 0.003 Å). In Cu(pyz)\textsubscript{2}(CF\textsubscript{3}SO\textsubscript{3}), the corresponding bond lengths differ by 0.010 Å.
Table 4-3. Internal bonding parameters for \(2,5\)-dimethylpyrazine, \(L\), in \(\text{CuL(CF}_3\text{SO}_3)\) and \(\text{NiLBr}_2\).

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>CuL(CF(_3)SO(_3))</th>
<th>NiLBr(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bridging(^c)</td>
<td>Terminal</td>
</tr>
<tr>
<td>C-C</td>
<td>1.382(3)</td>
<td>1.385(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.382(4)</td>
</tr>
<tr>
<td>N-CH</td>
<td>1.341(3)</td>
<td>1.336(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.322(4)</td>
</tr>
<tr>
<td>N-CCH(_3)</td>
<td>1.342(3)</td>
<td>1.340(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.331(4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angles (deg)</th>
<th>CuL(CF(_3)SO(_3))</th>
<th>NiLBr(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bridging(^c)</td>
<td>Terminal</td>
</tr>
<tr>
<td>C-N-C</td>
<td>117.0(2)</td>
<td>116.7(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>116.5(3)</td>
</tr>
<tr>
<td>N-C-C</td>
<td>123.3(2)</td>
<td>123.3(2)</td>
</tr>
<tr>
<td></td>
<td>119.6(2)</td>
<td>120.0(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>124.5(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Standard deviations in the last digit are given in parentheses.
\(^b\) Data for \(\text{Ni(2,5-me}_2\text{pyz)Br}_2\) are from reference 276.
\(^c\) N(1) ligand, first column; N(2) ligand, second column.

In \(\text{Cu(pyz)}_2\)(CF\(_3\)SO\(_3\))\, two bridging pyrazine groups, distinguished by different Cu-N bond distances, are present. In contrast, the two Cu-N bridging distances in \(\text{Cu(2,5-me}_2\text{pyz)}_2\)(CF\(_3\)SO\(_3\)) are equal within experimental error although this compound also contains two crystallographically different bridging ligands. The mean bridging Cu-N distance of 2.006 Å in \(\text{Cu(2,5-me}_2\text{pyz)}_2\)(CF\(_3\)SO\(_3\)) is slightly longer than the corresponding value of 1.999 Å in \(\text{Cu(pyz)}_2\)(CF\(_3\)SO\(_3\)), while the terminal Cu-N distance in \(\text{Cu(2,5-me}_2\text{pyz)}_2\)(CF\(_3\)SO\(_3\)) (2.033(2) Å) is significantly longer than that in
Cu(pyz)$_2$(CF$_3$SO$_3$) (1.985(2) Å). It is interesting that on average Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) has longer Cu-O and Cu-N distances than Cu(pyz)$_2$(CF$_3$SO$_3$), a consequence, presumably, of steric effects imposed by the methyl substituents on the pyrazine ligands of the former.

Steric interactions involving the methyl substituents of the dimethylpyrazine ligands in Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) are responsible for the most obvious structural differences between this compound and Cu(pyz)$_2$(CF$_3$SO$_3$). These differences involve bond angles about the copper ion and the relative orientations of the bridging ligands. The N-Cu-N angle involving the bridging pyrazine ligands is substantially larger (126.28(8)°) for the 2,5-me$_2$pyz derivative than for the unsubstituted pyrazine complex (110.6(1)°). In Cu(pyz)$_2$(CF$_3$SO$_3$) the normals to the mean planes of the bridging pyrazine ligands lie roughly in the plane of the copper ions of the polymeric chain, while in Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) one bridging 2,5-dimethylpyrazine ligand is oriented as in Cu(pyz)$_2$(CF$_3$SO$_3$) and the other (that in the centre of the unit cell; see Fig. 4-2) is oriented approximately at a right angle to the first (the normal to the mean plane being approximately orthogonal to the plane of the copper ions). Thus adjacent bridging 2,5-dimethylpyrazine ligands along the polymer backbone in Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) are mutually orthogonal, minimizing steric interactions between methyl groups on neighbouring bridging dimethylpyrazine ligands. The orientation of the terminal dimethylpyrazine ligand in Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) also differs from that of the corresponding pyrazine ligand in Cu(pyz)$_2$(CF$_3$SO$_3$), as a result of the rearrangement of the bridging ligands and the more stringent steric requirements of the dimethylpyrazine ligands in Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$).
4.1.3 Thermal properties

Cu(pyz)$_2$(CF$_3$SO$_3$) prepared as described in the present study exhibits three endothermic events in its DSC thermogram at 80°, 107° and 217 °C. $\Delta$H for the first two events is 24 kJ mol$^{-1}$ each and for the third event, 55 kJ mol$^{-1}$. Weight measurements before and after the first two events show a loss of 6% and measurements for the third event show an additional 15% weight loss. The total loss for the three events agrees well with the 21% loss expected for the dissociation of one mole of pyrazine. The thermal behavior of this material differs from that of the crystalline sample of Cu(pyz)$_2$(CF$_3$SO$_3$) prepared previously (44). In the latter case a single endothermic event occurs at 204° ($\Delta$H = 61 kJ mol$^{-1}$) and weight loss measurements (obs., 22%) confirm the loss of one mole of pyrazine. These results are interpreted as follows. The synthetic procedure described here produces analytically pure samples of composition Cu(pyz)$_2$(CF$_3$SO$_3$). This material, however, consists of a mixture of the extended chain polymer present in the crystalline form of Cu(pyz)$_2$(CF$_3$SO$_3$), plus lower oligomers which lose pyrazine at lower temperatures than the polymer. Both samples show the onset of exothermic decomposition at temperatures immediately above the $\approx$200 °C endothermic event. The presence of the extended chain polymer in the sample of Cu(pyz)$_2$(CF$_3$SO$_3$) prepared here was confirmed by powder X-ray diffraction. A simulated powder X-ray diffraction pattern for Cu(pyz)$_2$(CF$_3$SO$_3$) was generated using the single crystal X-ray diffraction data from ref. 44 and the computer program LAZY PULVERIX (176). All of the observed peaks in the powder sample prepared here can be assigned to the polymer (see Appendix III) and the absence of peaks assignable to other species suggests that the lower oligomers are present in an amorphous phase.

Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) exhibits two closely spaced endothermic events at 182° and 221 °C (total $\Delta$H for the two events = 104 kJ mol$^{-1}$) in its DSC curve. The
combined weight loss of 24% measured for both events compares favourably with the value of 25% expected for the loss of one ligand. The onset of exothermic decomposition is observed at temperatures immediately above the 221 °C endothermic event.

The thermal analysis results for both Cu(pyz)$_2$(CF$_3$SO$_3$) and Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) suggest the possibility of obtaining their mono-ligated analogues on a preparative scale. As described in section 5.2.7 the syntheses of Cu(pyz)(CF$_3$SO$_3$) and Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$) were, in fact, achieved by preparative thermolysis. The DSC thermogram of Cu(pyz)(CF$_3$SO$_3$) shows the onset of exothermic decomposition at 200 °C with no events below this temperature. This indicates that Cu(pyz)(CF$_3$SO$_3$) does not lose neutral ligand prior to decomposition.

The DSC curve for Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$) exhibits a small, reversible, endothermic event at 137 °C ($\Delta H = 4$ kJ mol$^{-1}$) of unknown origin. There is no weight loss associated with the event and it is this fact that first suggested its reversibility. A melting point determination, with a conventional melting point apparatus (Gallenkamp, No.889339), showed that the sample begins to decompose just above 200 °C without melting. This result is in good agreement with the DSC studies which showed that the complex does not dissociate neutral ligand prior to decomposition, the onset of which occurs at about 205 °C. It is noteworthy that Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) and Cu(pyz)$_2$(CF$_3$SO$_3$) have comparable thermal stabilities as do Cu(pyz)(CF$_3$SO$_3$) and Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$), as judged by the temperatures at which they begin to decompose.
4.1.4 Infrared spectra

The bands observed in the infrared spectra of the complexes under discussion here may, for the most part, be readily separated into absorptions that arise either from vibrations of the neutral ligand or the anion. Infrared absorption bands with assignments are given in Appendixes II-2, II-6 and II-7 for pyrazine, 2,5-dimethylpyrazine and the triflate anion, respectively. Assignments in the 1000 to 1300 cm\(^{-1}\) range are tentative since this region contains bands due to SO\(_3\) and CF\(_3\) stretching modes as well as bands due to the neutral ligands.

The infrared spectrum of Cu(pyz)\(_2\)(CF\(_3\)SO\(_3\)) prepared in this work differs only slightly from that of the crystalline form reported earlier (44). The weak band observed previously at 774 cm\(^{-1}\) is absent here and probably arose from an impurity in the earlier sample. In addition, the bands at 1247 and 1279 cm\(^{-1}\), assigned to the antisymmetric SO\(_3\) stretching mode, are now somewhat broadened and therefore show a less distinct splitting. The band broadening may well be due to the presence of lower oligomers in this sample, as suggested above. The remainder of the spectrum agrees within experimental error with that reported previously.

The infrared spectrum of Cu(pyz)(CF\(_3\)SO\(_3\)) is similar to that of its bis(pyrazine) analogue but with the following notable differences. While Cu(pyz)\(_2\)(CF\(_3\)SO\(_3\)) exhibits two bands of medium intensity at 452 and 472 cm\(^{-1}\), assigned to terminal and bridging pyrazine respectively (44), Cu(pyz)(CF\(_3\)SO\(_3\)) exhibits only one band in this region at 473 cm\(^{-1}\), which is assigned to bridging pyrazine. In addition a medium intensity band at 1051 cm\(^{-1}\) in the spectrum of Cu(pyz)\(_2\)(CF\(_3\)SO\(_3\)) is not observed in that of Cu(pyz)(CF\(_3\)SO\(_3\)) and is likely a vibration associated with terminal pyrazine moieties. The triflate anion bands in the spectra of Cu(pyz)\(_2\)(CF\(_3\)SO\(_3\)) and Cu(pyz)(CF\(_3\)SO\(_3\)) are virtually identical and suggests that the mode of anion coordination in the latter compound is the same as that in the former, i.e., monodentate via oxygen. The
splitting of the antisymmetric SO$_3$ stretching vibration (E symmetry in C$_{3v}$) is only slightly greater in Cu(pyz)(CF$_3$SO$_3$) than in Cu(pyz)$_2$(CF$_3$SO$_3$) (41 versus 32 cm$^{-1}$). This implies a similar degree of anion distortion and, hence, a similar degree of metal-anion interaction in the two compounds. The vibrational spectrum of Cu(pyz)(CF$_3$SO$_3$) is, therefore, consistent with a polymeric structure which involves three-coordinate copper(I) ions bridged by pyrazine ligands. The coordination around each copper ion is completed by a monodentate triflate group to produce a CuN$_2$O chromophore.

The infrared spectra of uncoordinated 2,5-dimethylpyrazine and its complexes, Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) and Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$), are shown in Fig. 4-3. It is evident from both the figure and Appendix II-6 that most of the bands in free 2,5-dimethylpyrazine are present in the spectra of the complexes with most bands shifting by a few wavenumbers to higher energies on coordination. In addition, band splitting is generally evident in Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) as a consequence, in part at least, of the presence of both bridging and terminal 2,5-me$_2$pyz ligands in this compound. The band at 419 cm$^{-1}$ in the spectrum of free 2,5-dimethylpyrazine, like that at 417 cm$^{-1}$ in the spectrum of liquid pyrazine (63, 47, 64, 65, 67), appears to be the most coordination sensitive. In the spectrum of Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) the band is replaced by two bands of medium intensity at 430 and 451 cm$^{-1}$. For Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$), on the other hand, only one corresponding band is observed, at 461 cm$^{-1}$. Assigning the higher energy vibrations to bridging ligands would be consistent with the assignments made previously for the pyrazine analogues and would support the assignment of bridging 2,5-me$_2$pyz in Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$). The close correspondence between the spectral bands assigned to triflate vibrations in Cu(pyz)$_2$(CF$_3$SO$_3$) and Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) is consistent with X-ray diffraction studies which, as described in section 4.1.2, reveal very similar internal bonding parameters for the anions in the two compounds. Apart from the fact that
Fig. 4-3. Infrared spectra of (a) 2,5-me$_2$pyz, (b) Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) and (c) Cu(me$_2$pyz)(CF$_3$SO$_3$).
Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$) exhibits a splitting of the antisymmetric SO$_3$ stretching vibration which is greater than that observed in the other three compounds, its anion spectrum is comparable to those of the other compounds and is consistent with monodentate triflate ion coordination. The structure of Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$) is concluded to be polymeric, and similar to that of its pyrazine analogue, Cu(py)z(CF$_3$SO$_3$). It is also notable that for both the pyrazine and 2,5-dimethylpyrazine pairs of complexes the splitting of the infrared band assigned to the antisymmetric SO$_3$ stretching vibration is slightly, but significantly, greater in the three-coordinate than in the corresponding four-coordinate complex. This possibly reflects stronger metal-triflate interactions in the former complexes due to less steric repulsions associated with a CuN$_2$O chromophore compared to a CuN$_3$O chromophore.

4.1.5 Electronic spectra

The copper(I) ion has a filled d shell and, since no d-d transitions are possible, its compounds are colourless except where colour results from the anion or charge-transfer bands. Cu(py)z$_2$(CF$_3$SO$_3$) is orange in colour, while Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$), Cu(py)z(CF$_3$SO$_3$) and Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$) are yellow. Their visible spectra show the presence of a single intense band at 19 000, 21 900, 19 800 and 20 400 cm$^{-1}$, respectively. The spectra are assigned to metal to ligand $\pi^*$ charge transfer transitions. Methyl substituents on the pyrazine ring may be expected to increase the charge density on the ring making it a poorer $\pi$-acceptor (34). This may account for the fact that the charge transfer transition for each of the 2,5-dimethylpyrazine complexes is higher in energy than that of the corresponding pyrazine complex.
4.1.6 Magnetic properties

The copper(I) ion has a $d^{10}$ electron configuration and its complexes are, therefore, diamagnetic. In the present study the diamagnetism of Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) was, in fact, confirmed by magnetic susceptibility studies over the temperature range 4.2 to 80 K. The results are presented in Table 4-4. As expected, the diamagnetic susceptibility is independent of temperature. A check at a field of 7 501 Oe showed, again in accordance with expectation, no field dependence of the susceptibility. The mean observed diamagnetic molar susceptibility for the complex is $-568 \times 10^{-6}$ cm$^3$ mol$^{-1}$ while that calculated as explained in refs. 109 and 277 is $-196 \times 10^{-6}$ cm$^3$ mol$^{-1}$. Two factors may account for the difference between these values. Firstly, the measured signal is very small, of the same order of magnitude as the diamagnetic susceptibility of the sample holder, and hence subject to a large error. Secondly, the various methods for obtaining the diamagnetic contributions of the components of the complex (cation, anion, organic group) are not entirely satisfactory (109, 277). Whereas the errors inherent in these methods are generally insignificant when used to calculate diamagnetic corrections for paramagnetic substances, this is not the case with diamagnetic substances.
Table 4-4. Magnetic susceptibility data for Cu(2,5-me2pyz)2(CF3SO3)

<table>
<thead>
<tr>
<th>T</th>
<th>(\chi_m)</th>
<th>T</th>
<th>(\chi_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.40</td>
<td>-600</td>
<td>40.2</td>
<td>-566</td>
</tr>
<tr>
<td>6.17</td>
<td>-635</td>
<td>48.0</td>
<td>-600</td>
</tr>
<tr>
<td>7.74</td>
<td>-635</td>
<td>54.9</td>
<td>-600</td>
</tr>
<tr>
<td>8.70</td>
<td>-635</td>
<td>60.4</td>
<td>-566</td>
</tr>
<tr>
<td>10.8</td>
<td>-600</td>
<td>65.6</td>
<td>-566</td>
</tr>
<tr>
<td>16.3</td>
<td>-532</td>
<td>70.1</td>
<td>-532</td>
</tr>
<tr>
<td>21.1</td>
<td>-532</td>
<td>74.5</td>
<td>-532</td>
</tr>
<tr>
<td>26.2</td>
<td>-532</td>
<td>78.2</td>
<td>-532</td>
</tr>
<tr>
<td>30.7</td>
<td>-532</td>
<td>81.9</td>
<td>-493</td>
</tr>
</tbody>
</table>

\(a\) Data collected at 9 225 Oe. Temperatures (T) are in K and diamagnetic molar susceptibilities \((\chi_m)\) in \(10^{-6} \text{ cm}^3 \text{ mol}^{-1}\).

4.2 Complexes of copper(I) hexafluorophosphate

4.2.1 Introduction

As discussed in section 2.4.1, an investigation of complexes of copper(II) hexafluorophosphate and hexafluoroarsenate with pyrazine-type ligands was initiated in the hope of generating new cationic polymers. While no complexes with the desired structural features and containing copper in the +2 oxidation state have been isolated, two such complexes which contain copper in the +1 state have been prepared. These are \([\text{Cu}_2(2,5-\text{me}_2\text{pyz})_3][\text{PF}_6]\) and \([\text{Cu}(2,5-\text{me}_2\text{pyz})_2][\text{PF}_6]\). Their syntheses are described in section 5.2.4. The two complexes were isolated in crystalline form suitable for single crystal X-ray diffraction studies, the results of which are reported in this section. The complexes were obtained as a mixture and in low yields. Only
[Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ could be isolated from the mixture in a reasonably pure form in quantities large enough for characterization by infrared spectroscopy. Both compounds are sufficiently air-stable and no special precautions were taken in handling them.

While cationic polymers of copper(I) with chain (278-281), sheet (282, 283) and three-dimensional lattice structures (190, 284, 285) are known they are relatively rare. "Scaffolding-like materials" involving cationic diamond-like frameworks with anions in lattice cavities include the copper(I) systems Cu[4,4',4'',4'''-tetracyanotetraphenylmethane]BF$_4$.xC$_6$H$_5$NO$_2$, described by Hoskins and Robson (190), and [Cu(NC(CH$_2$)$_4$CN)$_2$]NO$_3$, described earlier by Kinoshita et al. (284). The potential of pyrazine and substituted pyrazine ligands to form such lattices is demonstrated here by the structural characterization of [Cu(2,5-me$_2$pyz)$_2$][PF$_6$]. Only one other example of a three-dimensional cationic lattice involving a pyrazine derivative appears to have been reported, the quinoxaline complex, [Cu$_2$(C$_8$N$_6$N$_2$)$_3$(ClO$_4$)](ClO$_4$) (285). In this compound, the copper(I) and quinoxaline entities form a two-dimensional array. Half of the perchlorates act as bridging ligands between the sheets to generate a three-dimensional array while the other half of the perchlorate ions are non-coordinating and occupy lattice cavities.

4.2.2 Synthesis

Details of the preparation of [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ and [Cu(2,5-me$_2$pyz)$_2$][PF$_6$] are presented in section 5.2.4. However, their isolation from a copper(II) salt without added reducing agent warrants further comment. It would seem that the isolation of copper(I) complexes of pyrazine or methyl-substituted pyrazines from copper(II) salts in alcohol without added reducing agent is not
uncommon. Dibromo(tetramethylpyrazine)dicopper(I) was prepared earlier by refluxing copper(II) bromide and the ligand in ethanol (32). Formation of this linear, two coordinate, copper(I) complex rather than a square planar copper(II) derivative was considered to be more sterically favourable. Cu(pyz)$_2$(CF$_3$SO$_3$)$_2$ was initially obtained by the reaction of Cu(CF$_3$SO$_3$)$_2$ with pyrazine in approximate 1:2 mole ratio in methanol (44). In this case the formation of an insoluble polymer was considered to stabilize the copper(I) derivative. Some copper(I) hexafluoroarsenate complexes were also obtained from copper(II) precursors in the present work (section 5.2.4). Attempts to prepare pyrazine complexes of copper(II) hexafluoroarsenate in methanol yielded an orange solid of empirical formula Cu(pyz)$_3$(AsF$_6$). Furthermore, it was found that the reaction of 2,5-dimethylpyrazine, copper(II) perchlorate hexahydrate and potassium hexafluoroarsenate in ethanol yields a yellow product, among others, believed to be a copper(I) complex. None of these hexafluoroarsenate complexes were obtained in crystalline form suitable for single-crystal X-ray diffraction studies. In addition, [Cu$_3$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ and [Cu(2,5-me$_2$pyz)$_2$][PF$_6$] were obtained from an ethanolic solution of [Cu(PF$_6$)$_2$] and 2,5-dimethylpyrazine without added reducing agent, in the present work. It is believed that, in these complexes, the stabilization of the copper(I) derivatives is achieved through the formation of insoluble polymers. The reducing agent is presumably the solvent.

4.2.3 The crystal structure of [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$

The crystal data for [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ are given in Table 4-5. A complete set of its structural parameters is presented in Appendix I-6. The atom labelling scheme for [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ and a stereoview of the geometry about the copper ions are shown in Figs. 4.4 and 4-5, respectively. A comparison of the
structure of this compound with that of Cu(pyz)$_2$(CF$_3$SO$_3$) (44) is useful. The pyrazine-copper(I) triflate complex consists of zig-zag chains of copper(I) ions linked by bidentate bridging pyrazine ligands. The tetrahedron around each copper ion is completed by a nitrogen atom from a monodentate terminal pyrazine ligand and an oxygen atom from a monodentate terminal trifluoromethanesulfonate group. Along the chain, the terminal ligands lie alternately above and below the plane of the bridging pyrazine molecules. The structure of [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ may be viewed as derived from that of the pyrazine complex with the very weakly interacting PF$_6^-$ anion occupying a position similar to that occupied by the triflate group in the latter complex. The position occupied by the terminal pyrazine in Cu(pyz)$_2$(CF$_3$SO$_3$) is now occupied by a bridging 2,5-me$_2$pyz, thereby yielding a two-dimensional lattice. Thus the structure of [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ is made up of parallel puckered layers of the cation [Cu$_2$(2,5-me$_2$pyz)$_3$]$^{2+}$ in which copper(I) ions are linked by 2,5-me$_2$pyz (Fig. 4-6). PF$_6^-$ anions are located between the layers and interact very weakly with the copper(I) ions through one fluorine atom. Although the Cu(1)\cdots F(2) distance of 2.69(1) Å is approximately 0.25 Å less than the estimated sum of the van der Waals radii of copper and fluorine atoms, it is considerably greater than the 1.89 Å, the sum of the ionic radii of the Cu$^+$ and F$^-$ ions (134). Within each layer the copper ions, which are essentially three coordinate, define hexagons. Thus, except for the puckering of the layers, the structure of [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ is akin to that of an intercalated graphite. The graphite-like structure of this compound is illustrated in Fig. 4-7 in which copper ions are represented by circles, 2,5-me$_2$pyz groups are represented by lines and the PF$_6^-$ ions are omitted for clarity. The structure of [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ may also be compared to those of silicates with the basic formula (Si$_2$O$_5^{2-}$)$_n$, in which SiO$_4$ tetrahedra are linked into infinite two-dimensional networks through the sharing of three oxygen atoms per silicon (144). The adjacent anionic sheets are bound together by the cations that lie between them.
Fig. 4-4. Atom labelling scheme for [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$. Alternative positions for disordered F atoms are indicated by letter A.
Table 4-5. Crystal data* for [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Monoclinic</th>
<th>( Z )</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>( P2_1/n ) (#14)</td>
<td>( V, \ \text{Å}^3 )</td>
<td>1380.6(6)</td>
</tr>
<tr>
<td>( a, \ \text{Å} )</td>
<td>7.799(2)</td>
<td>( \rho_c, \ \text{g cm}^{-3} )</td>
<td>1.783</td>
</tr>
<tr>
<td>( b, \ \text{Å} )</td>
<td>15.862(1)</td>
<td>( F(000) )</td>
<td>740</td>
</tr>
<tr>
<td>( c, \ \text{Å} )</td>
<td>11.225(1)</td>
<td>( R )</td>
<td>0.038</td>
</tr>
<tr>
<td>( \beta, \ \text{deg} )</td>
<td>96.11(1)</td>
<td>( R_w )</td>
<td>0.032</td>
</tr>
</tbody>
</table>

* Standard deviations in the last digit are given in parentheses.

Fig. 4-5. Stereoview of the geometry about copper in [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$.

33% probability thermal ellipsoids are shown for the non-hydrogen atoms.
Fig. 4-6. Stereoscopic view of the unit cell packing diagram for 
[Cu₂(2,5-me₂pyz)₃][PF₆]₂.

Fig. 4-7. Stereoview of a schematic representation of the graphite-like structure of 
[Cu₂(2,5-me₂pyz)₃][PF₆]₂. 2,5-me₂pyz groups are represented by lines 
and PF₆⁻ ions are omitted for clarity. Copper centres are represented by circles.
The copper ions are three coordinate with Cu-N bond lengths of 1.987(4), 1.971(4) and 2.085(4) Å. The mean Cu-N bond length of 2.014 Å is the same as that found in Cu(2,5-me2pyz)$_2$(CF$_3$SO$_3$), (2.015 Å), discussed earlier in this chapter. The dimethylpyrazine molecules are all planar within experimental error. Their internal bonding parameters are comparable to those found in Cu(2,5-me2pyz)$_2$(CF$_3$SO$_3$).

The PF$_6^-$ groups in [Cu$_2$(2,5-me2pyz)$_3$][PF$_6$]$_2$ are disordered. The two alternative positions are interconvertible through rotation about the F(1)-P(1)-F(4) axis. The disorder, and possibly steric considerations as well, may account for the large deviations of the internal bonding parameters of this group from ideal values. For a large number of complexes containing the PF$_6^-$ anion, the bonding parameters have been found to lie in the following ranges (191, 192, 286-290): trans F-P-F angles, 170-180°; cis F-P-F angles, 85-95°; P-F bond lengths, 1.45-1.59 Å. In the compound reported here the trans and cis F-P-F angles lies in the ranges 160-178° and 75-106°, respectively. The P-F bond lengths also show a wide distribution with the shortest being 1.39(1) Å and the longest 1.67(2) Å.

4.2.4 The crystal structure of Cu(2,5-me2pyz)$_2$][PF$_6$]

The atom numbering scheme for [Cu(2,5-me2pyz)$_2$][PF$_6$] is shown in Fig. 4-8 and a stereoview of the geometry about the copper ions is shown in Fig. 4-9. The crystal data and selected bonding parameters are given in Table 4-6. A more detailed compilation of its structural parameters is given in Appendix I-7. The compound contains two crystallographically different copper(I) ions; Cu(1) and Cu(2) occupy sites having $S_4$ and $D_2$ symmetries, respectively. Both have angularly distorted CuN$_4$ chromophores which are related by a non-crystallographic $C_2$ axis coincident with the normal to the plane of the bridging 2,5-me2pyz (Fig. 4-9). It can also be seen from
Fig. 4-9 that the 2,5-me2pyz ligands which do not lie in the Cu(1)-Cu(2) axis are inclined upwards about Cu(1) and downwards about Cu(2). This feature is crucial in determining the overall three dimensional structure of Cu(2,5-me2pyz)2[PF6] as it leads to the crosslinking of a given layer with those immediately above and below it. Thus the structure of Cu(2,5-me2pyz)2[PF6] consists of a three dimensional array of copper(I) ions linked by 2,5-me2pyz molecules (Fig. 4-10). PF6− anions are located in cavities within the lattice. There is no conventional covalent bond between the cations and anions. Although the crystal system is tetragonal the bonding is reminiscent of the diamond structure. This is illustrated in Fig. 4-11 in which, for clarity, 2,5-me2pyz and PF6− groups are represented by lines and open circles, respectively. The structure of Cu(2,5-me2pyz)2[PF6] may also be compared to that of the cristobalite form of silicon dioxide. In this compound, the sharing of all four oxygen atoms per SiO4 tetrahedron results in a three-dimensional framework structure (144).

The dimethylpyrazine groups in Cu(2,5-me2pyz)2[PF6] are planar within experimental error and their internal bonding parameters are very similar to those found in Cu(2,5-me2pyz)2(CF3SO3) and [Cu2(2,5-me2pyz)3][PF6]2 (vide supra). The PF6− groups are disordered. A stereoview of the two alternate orientations is shown in Fig. 4-12. The orientations are interconvertible by a rotation about the F(4)-P(1) bond. The trans and cis F-P-F angles lie in the ranges 176-180° and 83-97°, respectively, while the P-F bond lengths lie between 1.51 Å and 1.58 Å. The deviations of the internal bonding parameters of the PF6− anions in this complex from ideal values are significantly less compared to those in [Cu2(2,5-me2pyz)3][PF6]2 and are in good agreement with literature values (191, 192, 286-290).
Fig. 4-8. Atom labelling scheme for [Cu(2,5-me2pyz)2][PF6]. Alternative positions for disordered F atoms are indicated by letter A. Only the unique F atoms are shown. The remainder of the F atoms are generated by a two-fold rotation about an axis passing through F1, P1 and F2.
Fig. 4-9. Stereoview of the geometry about the copper ions in [Cu(2,5-me₂pyz)₂][PF₆]. 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.

Fig. 4-10. Stereoview of the crystal packing diagram for [Cu(2,5-me₂pyz)₂][PF₆]. 20% probability thermal ellipsoids are shown for the non-hydrogen atoms.
Fig. 4-11. Stereoview of a schematic representation of the diamond-like structure of [Cu(2,5-me_2pyz)_2][PF_6]. For clarity, 2,5-me_2pyz and PF_6^- groups are represented by lines and open circles respectively. Copper centres are represented by shaded circles.

Fig. 4-12. Stereoview of the alternate orientations of the PF_6^- anions in [Cu(2,5-me_2pyz)_2][PF_6]. 20% probability thermal ellipsoids are shown for unique atoms.
Table 4-6. Crystal data and selected bonding parameters for \([\text{Cu}(2,5-\text{me}_2\text{pyz})_2][\text{PF}_6]^{a,b}\)

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>tetragonal</th>
<th>V, Å(^3)</th>
<th>1595.1(5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>(P4n2) (#118)</td>
<td>(\rho_\varepsilon) g cm(^{-3})</td>
<td>1.769</td>
</tr>
<tr>
<td>(a), Å</td>
<td>13.209(2)</td>
<td>(F(000))</td>
<td>856</td>
</tr>
<tr>
<td>(c), Å</td>
<td>9.142(2)</td>
<td>(R)</td>
<td>0.034</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
<td>(R_w)</td>
<td>0.033</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-N(1)</td>
<td>2.126(4)</td>
</tr>
<tr>
<td>Cu(2)-N(2)</td>
<td>2.110(4)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Standard deviations in the last digit are given in parentheses.
\(^b\) Superscripts refer to symmetry operations as defined in Appendix I-7.

4.2.5 The infrared spectrum of \([\text{Cu}_2(2,5-\text{me}_2\text{pyz})_3][\text{PF}_6]_2\)

The infrared spectrum of \([\text{Cu}_2(2,5-\text{me}_2\text{pyz})_3][\text{PF}_6]_2\) exhibits bands that can be readily assigned to the \(\text{PF}_6^-\) anions as follows (193): 566s \((v_4)\), 739w \((v_1)\), 833vs, br \((v_3)\) (all values are in cm\(^{-1}\)). This spectrum meets the criteria for non-coordinating \(\text{PF}_6^-\) anions as described in section 2.4.3 and is consistent with the structure of \([\text{Cu}_2(2,5-\text{me}_2\text{pyz})_3][\text{PF}_6]_2\). The bands due to the internal vibrations of the 2,5-\text{me}_2\text{pyz} ligands in this compound are listed in Appendix II-6. They show good correspondence with those observed in \(\text{Cu}(2,5-\text{me}_2\text{pyz})_2(\text{CF}_3\text{SO}_3)\).
4.3 Summary and conclusions

The complexes of copper(I) trifluoromethanesulfonate discussed in this chapter were prepared by design whereas those of copper(I) hexafluorophosphate were obtained serendipitously. Cu(2,5-me₂pyz)₂(CF₃SO₃) has been shown by single crystal X-ray diffraction to be a chain polymer in which the copper ions are bridged by 2,5-me₂pyz ligands. The tetrahedral coordination about each copper ion is completed by one terminal 2,5-me₂pyz ligand and one terminal triflate group. A similar structure was previously (44) observed for Cu(pyz)₂(CF₃SO₃). Primarily through infrared spectroscopy, Cu(2,5-me₂pyz)(CF₃SO₃) and Cu(pyz)(CF₃SO₃) have been assigned polymeric structures involving bidentate bridging neutral ligands and monodentate terminal triflate groups. The copper ions are thus considered to be three coordinate.

The structures of both [Cu₂(2,5-me₂pyz)₃][PF₆]₂ and [Cu(2,5-me₂pyz)₂][PF₆] have been determined by X-ray crystallography. The former is a two-dimensional cationic polymer with a graphite-related lattice. PF₆⁻ ions occupy inter-layer positions and interact weakly with the copper centres. [Cu(2,5-me₂pyz)₂][PF₆] is a three-dimensional cationic polymer with a diamond-like lattice. PF₆⁻ ions are non-coordinating and occupy positions in lattice cavities. These two compounds represent two new structural types for polymeric transition metal complexes containing pyrazine derivatives as bridging ligands.

The weakly coordinating anions, AsF₆⁻ and PF₆⁻, were employed in this study, in conjunction with potentially bridging neutral ligands, in anticipation that they would yield novel cationic polymers. [Cu₅(2,5-me₂pyz)₃][PF₆]₂ and [Cu(2,5-me₂pyz)₂][PF₆] have the desired structural features, i.e., cationic arrays. However, no such complexes with paramagnetic transition metal ions have been obtained. Such species would be suitable for magnetochemical investigations. Complexes of metals in the +2 oxidation state will, of course, require twice as many counter anions per metal (or anions of
twice the charge). Presumably layer lattice structures, as in \([\text{Cu}_2(2,5-\text{me}_2\text{pyz})_3][\text{PF}_6]_2\), can accommodate additional anions between the layers and hence metal(II) complexes with this structure may not be too difficult to obtain once suitable experimental conditions are established. The synthesis of metal(II) complexes with diamond-related structures may present a greater challenge. In this type of structure the number of cavities equals the number of tetrahedral centres (190). Hence in \([\text{Cu}(2,5-\text{me}_2\text{pyz})_2][\text{PF}_6]\) all cavities contain one \(\text{PF}_6^-\) ion. A metal(II) complex with this structure would require cavities large enough to contain two mononegative anions. Alternatively, it may be possible to employ dinegative anions such as \(\text{SiF}_6^{2-}\) or \(\text{SnF}_6^{2-}\) (requiring only one anion per cavity) in assembling such structures.
5.1 Introduction

Details of the preparations of the complexes characterized in this work are given in the first section of this chapter.\footnote{Exceptions are the compounds of copper(II)-sulfonates and -nitrate that had been previously characterized by most of the techniques used in this study and which were characterized only by esr spectroscopy in the present work. Details of their syntheses may be found in reference 66.} Unsuccessful preparations are also summarized. Experimental aspects of the physical methods employed are presented in the second section. The discussion on the preparations is subdivided according to the anionic ligand involved since compounds containing the same anionic ligand were prepared by very similar methods.

All chemicals and solvents were at least reagent grade quality and were used without further purification. Most of the reactions involved the use of hydrated metal salts and the dehydrating agent, 2,2-dimethoxypropane (291), was routinely added to the alcohols used as solvents. This procedure was found to be generally sufficient to avoid unwanted reaction with water. Although the procedures adopted for many of the reactions made it unnecessary to perform the reactions in an inert atmosphere (for example the use of water as solvent or the use of hydrated salts as starting materials), the syntheses were approached with the premise that all the products were hygroscopic. Hence, once precipitates formed, they were isolated and manipulated using standard vacuum-line techniques for the manipulation of air sensitive compounds (292) or in a nitrogen atmosphere dry box (D.L. Herring Corporation Dri-Lab (Model HE-43)) equipped with a dry train (Model HE-93). The air sensitivity, or otherwise, of a particular compound was subsequently confirmed by exposing small amounts of sample
to the atmosphere and monitoring the infrared spectra and/or microanalytical data. Physical transformations such as colour changes were also looked for. New compounds were, in general, prepared at least twice as a check on the reproducibility of the procedures. In all preparations, heating to temperatures below 160 °C was done in an oil bath. For higher temperatures a furnace (Welmet Industries, type FD303A) was used. The calculation of yields was based on the primary reagents since, in most cases, the intermediate species were not isolated. Hence the reported yields are to be considered as a lower limit. In particular, a near 100% conversion would be expected for complexes prepared by ligand dissociation reactions using thermolysis.

Complexes whose structures were determined by single crystal X-ray diffraction methods are named according to I.U.P.A.C. nomenclature in this section. The remaining complexes are named using a less rigorous system based on their empirical formulae. For convenience, empirical formulae rather than the complex names are widely used in this thesis.

5.2 Synthetic methods

5.2.1 Complexes of copper(II)- and nickel(II)- cyanates

The syntheses of divalent copper and nickel cyanate complexes were accomplished by two general methods which differ mainly in the ligand to metal mole ratio employed and the sequence of combining the reagents. These methods, designated I and II, are summarized below.
Method I

(i) \[ 2 \text{KNCO} + \text{MSO}_4 \times \text{H}_2\text{O} \rightarrow \text{[M(NCO)]}_2 + \text{K}_2\text{SO}_4 \]  

(ii) \[ \text{[M(NCO)]}_2 + 4 \text{L} \rightarrow \text{ML}_n \text{(NC0)}_{2(n)} + x_\text{L} \]  
\( n = 1 \text{ or } 2 \)

An aqueous solution (5 mL) of potassium cyanate was added to a hydrated metal sulfate dissolved in water (5 mL). The resulting solution was filtered directly into the ligand (or a 5 mL aqueous solution in the case of pyrazine). The addition of the metal solution to the ligand ensured that an excess of ligand was maintained throughout the reaction. Precipitates formed immediately and the mixtures were stirred for 0.5 or 1 h. The products were isolated by filtration, washed, and dried in vacuo.

Method II

(i) \[ 2 \text{KNCO} + \text{MSO}_4 \times \text{H}_2\text{O} \rightarrow \text{[M(NCO)]}_2 + \text{K}_2\text{SO}_4 \]  

(ii) \[ \text{L} + \text{[M(NCO)]}_2 \rightarrow \text{ML(NCO)}_{2(n)} \]  

This method was similar to Method I. However the ligand (or ligand solution) was added to the filtered potassium cyanate-metal sulfate solution. In addition, a lower ligand to metal mole ratio was used. These variations were adopted to ensure that at no point during the reaction was the ligand in excess. In this way, where complexes of two or more different stoichiometries may form, the one with the lower ligand to metal ratio may be precipitated preferentially.

5.2.1.1 Bis(pyridine)copper(II) cyanate, Cu(py)$_2$(NCO)$_2$

This compound was prepared as described by Burmeister and O’Sullivan (117) with slight modifications. The quantities of the reagents and solvent were scaled down
to one-quarter of those reported (117). The method is similar to that designated II above but with \( \text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O} \) instead of the sulfate, and a 2:1 rather than a 1:1 ligand to metal mole ratio.

Potassium cyanate (1.63 g, 20.1 mmol in 25 mL of \( \text{H}_2\text{O} \)); copper(II) nitrate trihydrate (2.42 g, 10.0 mmol in 25 mL of \( \text{H}_2\text{O} \)); pyridine (1.7 mL, 21.0 mmol ); 25 mL of water was added; stirring time (0.5 h); washing solvents (water, ethanol and diethyl ether); drying time (0.5 h); colour (blue); yield (74%). *Anal. calcd.* for \( \text{CuC}_12\text{H}_{10}\text{N}_4\text{O}_2 \): C 47.14, H 3.30, N 18.32; found: C 47.14, H 3.30, N 18.36.

The mixture obtained on addition of pyridine to the potassium cyanate-copper(II) nitrate solution was very viscous. Hence, 25 mL of water was added in order to facilitate easier stirring. The products obtained with and without added water differed slightly in both their physical appearance and infrared spectra.\(^{12}\) The one obtained without added water had a violet blue colour and was fluffy. The other product was pale blue and appeared more crystalline.

### 5.2.1.2 Poly-dicyanato-\( \mu \)-bis(\( \mu \)-methylpyrazine)copper(II), \( \text{Cu(mepyz)}_2\text{(NCO)}_2 \)

Synthetic Method I followed by recrystallization; potassium cyanate (0.686 g, 8.46 mmol); copper(II) sulfate pentahydrate (1.00 g, 4.01 mmol); methylpyrazine (1.5 mL, 16 mmol); stirring time (0.5 h); washing solvents (water and methanol, both containing a few drops of methylpyrazine); drying time (0.25 h). Methylpyrazine

\(^{12}\) When this work was already completed, Morazzoni *et al.* (119) reported the preparation of two forms of this compound. They designated "a pale violet micaceous product" obtained by a method which is essentially the same as the one described above without added water as \( \alpha \)-Cu(py)_2(NCO)_2. Dissolution of the \( \alpha \) isomer in excess pyridine followed by dilution with water yielded "navy blue crystalline needles" which they called \( \beta \)-Cu(py)_2(NCO)_2. The infrared spectra of the two forms obtained in the present study are consistent with those obtained by Morazzoni *et al.* Only the \( \beta \) isomer was fully characterized in the present study.
(10 mL) was added to the above product and the solution stirred for 2 h and then filtered. The beaker containing the filtrate was covered with parafilm in which pinholes were made, to allow for slow evaporation of the solvent. Blue crystals in the form of thin sheets formed in about one week and were isolated in 24% yield after decanting and washing with diethyl ether. The total yield was increased to 30% by keeping the supernatant liquid for a few more weeks. *Anal. calcd.* for CuC_{12}H_{12}N_{6}O_{2}: C 42.92, H 3.60, N 25.03; found (for first crop): C 42.76, H 3.59, N 25.19.

Crystals of this compound from different preparations were found to be mostly twinned. Nonetheless, after a painstaking search by the crystallographer, a suitable crystal for an X-ray structural determination was found.

### 5.2.1.3 Mono(methylpyrazine)copper(II) cyanate, Cu(mepy)(NCO)$_2$

Synthetic Method II; potassium cyanate (0.683 g, 8.42 mmol); copper(II) sulfate pentahydrate (1.00 g, 4.01 mmol); methylpyrazine (0.39 mL, 4.3 mmol); stirring time (0.5 h); washing solvents (water and methanol, both containing a few drops of methylpyrazine); drying time (0.25 h); colour (blue); yield (71%). *Anal. calcd.* for CuC$_7$H$_6$N$_4$O$_2$: C 34.79, H 2.50, N 23.18; found: C 34.93, H 2.65, N 22.99.

### 5.2.1.4 Mono(pyrazine)copper(II) cyanate, Cu(pyz)(NCO)$_2$

Synthetic Method I; potassium cyanate (0.692 g, 8.53 mmol); copper(II) sulfate pentahydrate (1.01g, 4.05 mmol); pyrazine (1.37 g, 17.1 mmol); stirring time (1 h); washing solvents (water and methanol); drying time (2 h at room temperature, 4.75 h at 80 °C); colour (blue); yield (57%). *Anal. calcd.* for CuC$_6$H$_4$N$_4$O$_2$: C 31.66, H 1.77, N 24.61; found: C 31.48, H 1.80, N 24.75.
5.2.1.5 Mono(pyridazine)copper(II) cyanate, Cu(pdz)(NCO)$_2$

Synthetic Method I; potassium cyanate (0.673 g, 8.30 mmol); copper(II) sulfate pentahydrate (1.00 g, 4.01 mmol); pyridazine (1.0 mL, 14 mmol); stirring time (0.5 h); washing solvents (water, methanol and diethyl ether); drying time (5 h); colour (blue); yield (66%). *Anal. calcd.* for CuC$_6$H$_4$N$_4$O$_2$: C 31.66, H 1.77, N 24.61; found: C 31.53, H 1.82, N 24.44.

5.2.1.6 Tetrakis(pyridine)nickel(II) cyanate, Ni(py)$_4$(NCO)$_2$

The preparation of this compound has been reported before by Nelson and Shepherd (205) and by Burmeister and O'Sullivan (117). We adopted (with some modifications) the method used by the latter since they reported the amounts of reagents used. These were scaled down by a factor of four in the present work. The synthetic method is similar to that designated II above, except that a large excess of pyridine was employed and Ni(NO$_3$)$_2$.6H$_2$O was used instead of the sulfate. The product was recrystallized from a methanol-methylpyrazine mixture.

Potassium cyanate (1.66 g, 20.5 mmol); nickel(II) nitrate hexahydrate (2.95 g, 10.1 mmol); pyridine (3.8 mL, 47.0 mmol); stirring time (0.5 h); washing solvents (ethanol and diethyl ether). The product was air dried. About 1.7 g was dissolved in a mixture of methanol (5 mL) and methylpyrazine (2 mL). The mixture was stirred for 1.5 h, filtered and the filtrate allowed to evaporate slowly. Blue crystals formed in about a week. These were isolated by decantation, washed with diethyl ether and air dried. *Anal. calcd.* for NiC$_{22}$H$_{20}$N$_6$O$_2$: C 57.55, H 4.39, N 18.30; found: C 57.43, H 4.34, N 18.36. The above crystals were found to be disordered. Repeated attempts to obtain X-ray quality crystals were not successful.
5.2.1.7 Bis(pyridazine)nickel(II) cyanate, Ni(pdz)$_2$(NCO)$_2$

Synthetic Method I; potassium cyanate (0.631 g, 7.78 mmol); nickel sulfate hexahydrate (1.02 g, 3.88 mmol); pyridazine (1.0 mL, 14 mmol); stirring time (0.5 h); washing solvents (water, methanol, and diethyl ether); drying time (5 h at room temperature, 4 h at 80 °C); colour (pale green); yield (67%). Anal. calcd. for NiC$_{10}$H$_8$N$_6$O$_6$: C 39.65, H 2.66, N 27.74; found: C 39.65, H 2.88, N 27.96.

5.2.1.8 Bis(pyrazine)nickel(II) cyanate hemihydrate, Ni(pyz)$_2$(NCO)$_2$.1/2$\text{H}_2$O

Synthetic Method I; potassium cyanate (0.628 g, 7.74 mmol); nickel(II) sulfate hexahydrate (1.00 g, 3.80 mmol); pyrazine (1.26 g, 15.7 mmol); stirring time (1 h); washing solvents (water and methanol); drying time (1.5 h at ambient temperatures, 2.5 h at 60 °C); colour (blue); yield (60%). Anal. calcd. for NiC$_{10}$H$_9$N$_6$O$_{2.5}$: C 38.51, H 2.91, N 26.94; found: C 38.72, H 2.90, N 27.03. The presence of water in this compound was confirmed by infrared spectroscopy. The compound exhibits weak broad bands at ≈3 400 cm$^{-1}$ and ≈1 650 cm$^{-1}$ assigned to O-H stretching and H$_2$O bending vibrations, respectively.

Unsuccessful attempts were made to obtain the anhydrous complex. Heating a sample of Ni(pyz)$_2$(NCO)$_2$.1/2$\text{H}_2$O at 90 °C under vacuum for 8 h had no significant effect whereas refluxing with 2,2-dimethoxypropane for 4 h led to some decomposition, as determined by elemental analysis.

5.2.1.9 Mono(pyrazine)nickel(II) cyanate, Ni(pyz)(NCO)$_2$

Synthetic Method II; potassium cyanate (0.655 g, 8.07 mmol); nickel(II) sulfate hexahydrate (1.00 g, 3.80 mmol); pyrazine (0.306 g, 3.82 mmol); stirring time (1 h); washing solvents (water and methanol); drying time (2 h at room temperature, 1 h at
158 °C); colour (pale green: the precipitate formed immediately on mixing the reagents was blue but, upon stirring the mixture, it turned green.); yield (74%). *Anal calcd.* for NiC₆H₄N₄O₂: C 32.34, H 1.81, N 25.14; found: C 32.29, H 1.94, N 24.92.

5.2.1.10 Attempted syntheses

Unsuccessful attempts were made to make other complexes related to those discussed above. These were Ni(pdz)(NCO)₂, Ni(mepy)(NCO)₂ and M(4,4'-bipy)(NCO)₂, where M is Cu or Ni. The thermal properties of Ni(pdz₂)(NCO)₂ (section 3.1.2) suggested the possibility of synthesizing Ni(pdz)(NCO)₂ in bulk by thermolysis; however, repeated attempts to do so failed to yield analytically pure samples. Efforts to precipitate the compound from aqueous solutions containing pyridazine and NiSO₄.6H₂O in a 1:1 mole ratio were also unsuccessful.

Addition of an aqueous mixture of either NiSO₄.6H₂O or Ni(NO₃)₂.6H₂O and KNCO to excess methylpyrazine did not yield any precipitate even on standing for at least two weeks. Addition of ethanol to a freshly prepared aqueous Ni(NO₃)₂.6H₂O-KNCO-methylpyrazine solution yielded a pale green precipitate, indicating that any product formed is only slightly soluble in ethanol and is precipitated out along with KNO₃. Ni(py₄)(NCO)₂ loses some pyridine easily when exposed to the atmosphere for long periods of time. Therefore, a third attempt at the preparation of Ni(mepy)(NCO)₂ involved trying to substitute the pyridine in Ni(py₄)(NCO)₂ with methylpyrazine by the recrystallization of the pyridine complex from methylpyrazine. Instead of the desired substitution product single crystals of the pyridine complex were obtained (section 5.2.1.6).

Efforts to prepare M(4,4'-bipy)(NCO)₂, where M is Cu or Ni, involved the use of various metal to ligand mole ratios. Solid products were obtained but they were
generally non-stoichiometric. Attempts to prepare the nickel complexes were more promising than attempts to prepare the copper complexes. A sample isolated from a mixture containing nickel(II) sulfate and 4,4'-bipyridine in a 1:2 mole ratio when heated at 80 °C analyzed well for Ni(4,4'-bipy)\textsubscript{1.5}(NCO)\textsubscript{2}. \textit{(Anal calcd. for NiC_{17}H_{12}N_{5}O_{2}: C 54.17, H 3.20, N 18.58; found: C 54.43, H 3.40, N 18.30).} A 1:1 mixture resulted in a product whose observed C, H, N values differed from those calculated for Ni(4,4'-bipy)(NCO)\textsubscript{2} by less than 0.9%. The compound is, however, considered impure as the analyses significantly exceed the accepted tolerance level of 0.3%.

Efforts were also made to isolate pure samples of Cu(NCO)\textsubscript{2} and Ni(NCO)\textsubscript{2} from solutions containing these species and K\textsubscript{2}SO\textsubscript{4}. The intention was to react the pure binary salts directly with ligands to eliminate possible K\textsubscript{2}SO\textsubscript{4} impurities in the final products. Thus ethanol was added to an aqueous mixture of MSO\textsubscript{4}.xH\textsubscript{2}O and KNCO. However, the solid filtered off was green (not white as expected for K\textsubscript{2}SO\textsubscript{4}), leaving only faintly coloured filtrates. In fact Logan \textit{et al.} (293) previously reported that solutions of Ni(NCO)\textsubscript{2} and Co(NCO)\textsubscript{2} are unstable and they were unable to obtain pure samples by any precipitation and recrystallization method. It would appear that the same holds true for Cu(NCO)\textsubscript{2}. Logan \textit{et al.} also observed that the anhydrous salts are unstable at temperatures above 90 °C and can only be obtained from dipyridine compounds by careful warming under vacuum.

5.2.2 Complexes of copper(II) nitrate

Pyridazine reacts with ethanolic solutions of copper(II) nitrate trihydrate to give several different complexes. The particular product obtained depends in part on the ligand to metal mole ratio used in the preparation. For instance, when the ratio is
between 1 and 1.5 a complex of empirical formula Cu(pdz)$_2$(NO$_3$)$_2$ is obtained whereas a ratio of between 2 and 3 yields Cu(pdz)$_3$(NO$_3$)$_2$. A violet compound of empirical formula Cu(pdz)$_4$(NO$_3$)$_2$ is obtained when the ligand to metal mole ratio is 6:1. A ratio of 4 may produce Cu(pdz)$_3$(NO$_3$)$_2$ or either of two derivatives of tetrakis(pyridazine); the violet Cu(pdz)$_4$(NO$_3$)$_2$ or the blue [Cu(pdz)$_4$(NO$_3$) ][NO$_3$]. The latter reaction is particularly remarkable because repeated experiments have shown that any one of the three products may be obtained from the same concentration of reagents. Each of the four complexes was isolated at least three times. They all have characteristic infrared spectra and in no case was a mixture of products observed. The synthesis of these compounds clearly requires further comment and this is done in Chapter 2.

5.2.2.1 Tetrakis(pyridazine)copper(II) nitrate, Cu(pdz)$_4$(NO$_3$)$_2$

A solution of copper(II) nitrate trihydrate (0.333 g, 1.38 mmol) dissolved in 10 mL of ethanol containing 10% v/v 2,2-dmp was filtered into a flask containing pyridazine (0.60 mL, 8.26 mmol) and stirred briefly. The violet precipitate which formed was isolated by filtration, washed with a small amount of solvent and dried for 1 h in vacuo. Anal. calcd. for CuC$_{16}$H$_{16}$N$_{10}$O$_6$: C 37.84, H 3.18, N 27.58; found: C 37.77, H 3.16, N 27.61. Yield, 54%. As mentioned above, this compound was sometimes observed to precipitate out of a mixture containing a ligand to metal ratio of 4:1.

5.2.2.2 Nitratotetrakis(pyridazine)copper(II) nitrate, [Cu(pdz)$_4$(NO$_3$)][NO$_3$]

A solution of copper(II) nitrate trihydrate (0.493 g, 2.04 mmol) dissolved in 10 mL of ethanol containing 10% v/v 2,2-dmp was filtered into a flask containing pyridazine (0.60 mL, 8.26 mmol) and stirred briefly. The blue precipitate which formed was isolated by filtration, washed with a small amount of solvent and dried for
1 h in vacuo. Anal. calcd. for CuC₁₆H₁₆N₁₀O₆: C 37.84, H 3.18, N 27.58; found: C 37.83, H 3.23, N 27.70. Yield, 57%. It was observed that addition of a few millilitres of diethylether to the filtrate obtained above resulted in the formation of single crystals on the sides of the beaker in about 5 days. It was confirmed by infrared spectroscopy that the crystals were Cu(pdz)₄(NO₃)₂{NO₃}. Crystals used for X-ray structural analysis were, however, prepared as discussed in the following paragraph.

On one occasion, a repeat of the procedure outlined in the preceding paragraph did not result in an immediate precipitation of a product. However a blue crystalline precipitate formed immediately on application of a vacuum to the reaction mixture for a brief period. The mixture was left sitting for two days and X-ray quality single crystals formed. These were isolated by decantation, washed with anhydrous diethyl ether and dried in a desiccator over drierite for one day. During the latter procedure the crystals were observed to begin to darken.

5.2.2.3 Nitrato(nitrato-Ο,Ο')tris(pyridazine)copper(II), Cu(pdz)₃(NO₃)₂

Pyridazine (0.40 mL, 5.51 mmol) was slowly added to a filtered solution of copper(II) nitrate trihydrate (0.495 g, 2.05 mmol) dissolved in 10 mL of ethanol containing 10% v/v 2,2-dmp. Less than the 3:1 ligand to metal ratio required by the stoichiometry of the complex was used in order to prevent the possible formation of a tetrakis(pyridazine) derivative. For the same reason, the pyridazine was added to the copper(II) solution rather than the reverse order of addition. Initially a precipitate began to form in ball-like chunks (believed to be [Cu(pdz)₂(NO₃)₂]₃, see below) but, as more pyridazine was added the chunks broke into finer particles. The blue precipitate was isolated by filtration, washed with a small amount of solvent and dried for 1.5 h in vacuo. Anal. calcd. for CuC₁₂H₁₂N₈O₆: C 33.69, H 2.83, N 26.19; found: C 33.63, H 2.86, N 26.28. Yield, 73%.
On some occasions, a repeat of the procedure outlined in the preceding paragraph did not result in immediate precipitation of a product. On one such occasion, fibre-like blue crystals formed when the resulting mixture was allowed to sit at ambient temperature for several hours. These were isolated by decantation and dried in a desiccator over Drierite. The product was confirmed to be Cu(pdz)$_3$(NO$_3$)$_2$ by infrared spectroscopy and elemental analysis. Better X-ray quality crystals were obtained when, in another occasion, the reaction vessel was covered with parafilm and kept in a freezer (-5 °C). Blue crystals began to form within a few hours. Some crystals were removed from the reaction vessel after 4 days and dried in a desiccator over drierite. The composition of the sample was established by elemental and single crystal X-ray diffraction analyses.

Cu(pdz)$_3$(NO$_3$)$_2$ was, also, sometimes observed to precipitate out, in powder form, from a mixture containing a ligand to metal mole ratio of 4:1.

5.2.2.4 Bis[μ-nitrato-O-dinitrobatobis(μ-pyridazine)pyridazine)copper(II)], [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$

Pyridazine (0.38 mL, 5.23 mmol) was slowly added to a filtered solution of copper(II) nitrate trihydrate (0.846 g, 3.50 mmol) dissolved in 8 mL of ethanol containing 10% v/v 2,2-dmp. A blue precipitate, in the form of ball-like chunks, formed. Anhydrous diethyl ether (30 mL) was added to the mixture. This broke the precipitate into finer particles. The product was isolated by filtration, washed with diethyl ether and air dried for about 2.5 weeks during which period its colour changed to green. Anal. calcd. for CuC$_8$H$_8$N$_6$O$_6$: C 27.63, H 2.32, N 24.17; found: C 27.44, H 2.37, N 24.15. Yield, 23%.

The initial blue product was hydrated as confirmed by infrared spectroscopy. Drying it in a desiccator over P$_2$O$_5$ or heating at about 50 °C in vacuo both yielded
green products which had low C and N contents. Moreover the product obtained by the latter method of dehydration was found to be deliquescent. Yet a pure and air-stable product was readily obtained by air-drying the sample.

Single crystals for X-ray structural analysis were grown as follows. To a sample of \([\text{Cu(pdz)}_2(\text{NO}_3)_2]_3\) prepared as described above was added 50 mL of acetonitrile. The resulting blue solution was filtered. The beaker containing the filtrate was covered with parafilm in which pinholes were made to allow for slow evaporation of the solvent. Within 5 days green crystals formed on the sides of the 100 mL beaker, midway from the top. Below these was a blue precipitate in form of a fine powder while on the upper parts of the beaker were observed brown smears, presumably free pyridazine. The bulk of the solution was still blue. Because of the possible contamination of the green crystals with other products, bulk studies on this compound were made on powdered samples prepared as outlined above.

5.2.3 Complexes of copper(II) sulfonates

5.2.3.1 Tetrakis(pyridazine)copper(II) methanesulfonate, \(\text{Cu(pdz)}_4(\text{CH}_3\text{SO}_3)_2\)

Copper(II) methanesulfonate was prepared following a documented procedure (187). A solution of this binary salt (0.511 g, 2.01 mmol) in 6 mL of ethanol containing 10 % v/v 2,2-dmp was filtered into a flask containing pyridazine (1.0 mL, 14 mmol) to give a very dark blue solution. After stirring the solution for 1.75 h, 10 mL of anhydrous diethyl ether was added to it and a blue precipitate formed immediately. This was isolated by filtration, washed with diethyl ether, and dried for 1 h in vacuo. \textit{Anal. calcd.} for \(\text{CuC}_{18}\text{H}_{22}\text{N}_8\text{S}_2\text{O}_6\): C 37.66, H 3.86, N 19.52; found: C 37.75, H 3.95, N 19.50. Yield, 65%. 
5.2.3.2 Attempted syntheses

Addition of an ethanolic solution of Cu(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$ (1.30 mmol) to pyridazine (4.13 mmol) gave an intensely coloured blue solution but no immediate precipitation occurred. The solvent was allowed to evaporate slowly under a nitrogen atmosphere, leaving behind a black product. In a subsequent attempt (7.6:1 pdz to Cu mole ratio was used) anhydrous diethylether was added to the blue solution. Upon stirring the mixture for 1.5 h and allowing it to settle, a two layer system formed. A light blue solution at the top formed the bulk of the mixture. The bottom layer consisted of a dark blue oily material. Most of the solvent evaporated within a week leaving behind an intense dark brown solution which, upon evaporation *in vacuo*, gave a black gummy material. This substance was not characterized.

Reaction of ethanolic solutions of 4,4'-bipyridine and Cu(CH$_3$SO$_3$)$_2$ in a 2.2:1 ratio gave a blue precipitate the infrared spectrum of which indicated the presence of water. Drying at 75 °C gave a product of composition Cu(4,4'-bipy)$_2$(CH$_3$SO$_3$)$_2$ (*Anal. calcd.* for CuC$_{22}$H$_{22}$N$_4$S$_2$O$_6$: C 46.68, H 3.92, N 9.90; found: C 46.37, H 4.20, N 9.82). However, the infrared spectrum of the complex indicated the presence of water. Repeated attempts, which included drying at 100 °C, gave products which according to elemental analysis contained as much as 1.5 moles of water.

In the case of 4,4'-bipyridine and Cu(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$, a 3.2:1 ligand to metal mole ratio mixture in ethanol gave a blue product. Microanalysis indicated that the compound had a composition between those expected for bis- and tris-(4,4'-bipy) derivatives. Drying the sample at about 70 °C for 3 h had no significant effect on the composition.
5.2.4 Complexes of copper(II) hexafluoroarsenate, copper(II) hexafluorophosphate and copper(I) hexafluorophosphate

The synthesis of complexes of copper(II) hexafluoroarsenate and hexafluorophosphate may be represented by the reaction scheme shown in eqn. 5-3 where M is K+ or NH4+, E is As or P and L is pyrazine, methylpyrazine or 4,4'-bipyridine.

\[
\begin{align*}
\text{EtOH} & \quad \text{(i) } \text{Cu(ClO}_4\text{)}_2\cdot 6\text{H}_2\text{O} + 2 \text{MEF}_6 & \rightarrow [\text{Cu(EF}_6\text{)}_2] + 2\text{MClO}_4\text{(s)} \\
\text{EtOH} & \quad \text{(ii) } [\text{Cu(EF}_6\text{)}_2] + x\text{L} & \rightarrow \text{CuL}_4(\text{EF}_6\text{)}_{2(x)}
\end{align*}
\]

In a typical reaction in the preparation of the hexafluoroarsenate complexes, 75 mL of ethanol containing 10% v/v 2,2-dmp was added to about 1 g of potassium hexafluoroarsenate. The potassium salt did not fully dissolve. About 0.8 g of copper(II) perchlorate hexahydrate dissolved in 5 mL of the same solvent was added to the KAsF\textsubscript{6} solution and the mixture stirred for 0.25 h. The potassium perchlorate which formed, and unreacted KAsF\textsubscript{6}, were removed by filtration. To remove any remaining ClO\textsubscript{4}\textsuperscript{-} more KAsF\textsubscript{6} (about 0.5 g) was added to the filtrate and the mixture stirred for 1 h. KClO\textsubscript{4} and excess KAsF\textsubscript{6} were again removed by filtration and the volume of the solution reduced to about 10 mL in vacuo and then, once again, it was filtered. The filtrate was added to an excess of ligand or an ethanolic ligand solution. A precipitate formed immediately. The mixture was stirred for about 0.25 h, filtered, and the precipitate washed with a small amount of the solvent and dried, in vacuo, at ambient temperatures unless stated otherwise.

The hexafluorophosphate complexes were prepared using a similar procedure to that outlined in the preceding paragraph but with NH\textsubscript{4}PF\textsubscript{6} or KPF\textsubscript{6} dissolved in a
smaller volume of solvent than used for KAsF₆. The need to reduce the volume of the final [Cu(PF₆)₂] solution was thus dispensed with. This procedure was adopted in order to minimize the time between the preparation of the [Cu(PF₆)₂] solutions and their complexation with the ligands, since the hexafluorophosphate anion is hydrolyzed more readily than the hexafluoroarsenate anion (199).

5.2.4.1 Tetrakis(pyrazine)copper(II) hexafluoroarsenate, Cu(pyz)₄(AsF₆)₂

Reagents and quantities used were KAsF₆ (0.992 g, 4.35 mmol and 0.515 g, 2.26 mmol), Cu(ClO₄)₂.6H₂O (0.796 g, 2.15 mmol), pyrazine (1.10 g, 13.7 mmol dissolved in 4 mL of solvent); drying time (3.5 h); colour (violet); yield (60%); Anal. calcd. for CuC₁₆H₁₆N₈As₂F₁₂: C 25.23, H 2.12, N 14.71; found: C 24.97, H 2.22, N 14.73.

It is interesting to note that with methanol as solvent a precipitate did not form immediately on addition of a [Cu(AsF₆)₂] solution to a pyrazine solution. Instead a bright blue solution formed which, after a few days, yielded a mixture of violet solid and orange crystals. The solid materials were isolated by decantation and then treated with methanol which dissolved only the purple material. The orange material, which lost its crystallinity when dried, was shown by elemental analysis to be a copper(I) complex of empirical formula Cu(pyz)₃(AsF₆).¹³ Anal. Calcd. for CuC₁₂H₁₂N₆AsF₆: C 29.25, H 2.45, N 17.06; found: C 28.85, H 2.45; N 17.09. The infrared spectrum of the material indicated that it contained only terminal pyrazine and non-coordinated AsF₆⁻ groups. Unfortunately the product was isolated in very low yields that further characterization was not possible.

¹³ Isolation of copper(I) complexes from alcoholic solutions of copper(II) salts without added reducing agent is discussed in Chapter 4.
5.2.4.2 Tetrakis(methylpyrazine)copper(II) hexafluoroarsenate, Cu(mepyz)$_4$(AsF$_6$)$_2$

The reagents and quantities used were KAsF$_6$ (0.831 g, 3.64 mmol and 0.695 g, 3.05 mmol), Cu(ClO$_4$)$_2$.6H$_2$O (0.809 g, 2.18 mmol), methylpyrazine (1.5 mL, 16.4 mmol); drying time (3 h); colour (violet); yield (76%); *Anal. calcd.* for Cu$_{20}$H$_{24}$N$_8$As$_2$F$_{12}$: C 29.37, H 2.96, N 13.70; found: C 29.67, H 2.98, N 13.73.

5.2.4.3 Tetrakis(4,4'-bipyridine)copper(II) hexafluoroarsenate, Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$

Reagents and quantities used were KAsF$_6$ (0.994 g, 4.36 mmol and 0.543 g, 2.38 mmol), Cu(ClO$_4$)$_2$.6H$_2$O (0.812 g, 2.19 mmol), 4,4'-bipyridine (2.24 g, 14.3 mmol dissolved in 8 mL of solvent); drying time (3.5 h at room temperature and 5.5 h at 80 °C); colour (violet); yield (65%); *Anal. calcd.* for CuC$_{40}$H$_{32}$N$_8$As$_2$F$_{12}$: C 45.06, H 3.03, N 10.51; found: C 45.22, H 3.07, N 10.48.

5.2.4.4 Tetrakis(pyrazine)copper(II) hexafluorophosphate, Cu(pyz)$_4$(PF$_6$)$_2$

Reagents and quantities used were NH$_4$PF$_6$ (0.856 g, 5.25 mmol in 20 mL of solvent. A second portion of NH$_4$PF$_6$ was not used), Cu(ClO$_4$)$_2$.6H$_2$O (0.805 g, 2.17 mmol), pyrazine (1.44 g, 18.0 mmol dissolved in 5 mL of solvent); drying time (3.5 h); colour (violet); yield (51%); *Anal. calcd.* for CuC$_{16}$H$_{16}$N$_8$P$_2$F$_{12}$: C 28.52, H 2.39, N 16.63; found: C 28.74, H 2.52, N 16.60.

5.2.4.5 Tetrakis(methylpyrazine)copper(II) hexafluorophosphate, Cu(mepyz)$_4$(PF$_6$)$_2$

Reagents and quantities used were KPF$_6$ (0.808 g, 4.39 mmol and 0.508 g, 2.76 mmol in 30 mL of solvent), Cu(ClO$_4$)$_2$.6H$_2$O (0.811 g, 2.19 mmol), methylpyrazine (0.90 mL, 9.8 mmol); drying time (3.5 h); colour (violet);
yield (53%); *Anal. calcd.* for CuC$_{20}$H$_{24}$N$_8$P$_2$F$_{12}$: C 32.91, H 3.31, N 15.35; found: C 32.94, H 3.35, N 15.50.

5.2.4.6 Poly-bis(μ-2,5-dimethylpyrazine)copper(I) hexafluorophosphate, [Cu(2,5-me$_2$pyz)$_2$][PF$_6$] and poly-tris(μ-2,5-dimethylpyrazine)dicopper(I) hexafluorophosphate, [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$

A solution of [Cu(PF$_6$)$_2$] was prepared following the general method described above using KPF$_6$ (0.847 g, 4.60 mmol and 0.430 g, 2.34 mmol in 20 mL of solvent) and Cu(ClO$_4$)$_2$.6H$_2$O (0.858 g, 2.32 mmol dissolved in 5 mL of solvent). 2,5-Dimethylpyrazine (0.50 mL, 4.58 mmol) was added dropwise to the [Cu(PF$_6$)$_2$] solution. The reaction vessel was continuously shaken during the addition. The blue colour of the solution intensified, but no precipitate formed. The solution was pumped on briefly and then transferred to a nitrogen atmosphere glove box. The reaction flask was covered with parafilm in which pinholes were made to allow for slow evaporation of the solvent. Within four days the colour of the solution had changed from blue to green and a yellow crystalline material formed. After another three days a second product in the form of red-orange crystals also began to form. The yellow and red-orange materials were shown by X-ray crystallography to be [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ and [Cu(2,5-me$_2$pyz)$_2$][PF$_6$], respectively. A third product (blue in colour) also precipitated out of the solution, about two weeks after the initial reaction, but not in a form suitable for single crystal X-ray diffraction studies. Neither was it possible to isolate sufficient sample of this material for bulk studies from the mixture of products. However, because of its blue colour, it is believed to be a copper(II) complex.
5.2.4.7 Attempted syntheses

The thermal properties of Cu(pyz)₄(AsF₆)₂ suggest that it is, in principle, possible to prepare Cu(pyz)₂(AsF₆)₂ from the former compound via a thermal route. In practice, however, this was not achieved. Heating a sample of Cu(pyz)₄(AsF₆)₂ at 120 °C did not result in a change of either the colour or infrared spectrum. In contrast, thermolysis at 140 °C led to a colour change from violet to blue and the product exhibited unusually broad pyrazine bands in the 1000-1200 cm⁻¹ region in its infrared spectrum. Another attempt to make the bis(pyrazine) complex involved the isolation of a product from an ethanol solution containing pyrazine and [Cu(AsF₆)₂] in a 2:1 mole ratio. The blue product which was obtained also exhibited very broad, poorly resolved pyrazine bands in the 1000-1200 cm⁻¹ region in its infrared spectrum. C, H, N analysis of this product gave values that lie between those expected for the tris- and tetrakis-(pyrazine) complexes.

A pyridazine-Cu(AsF₆)₂ complex was made by the same procedure used to make Cu(pyz)₄(AsF₆)₂. The violet colour of the product faded, tending towards blue, upon drying. The sample turned black overnight suggesting that, perhaps, it had decomposed. This was in spite of the fact that the sample had been stored in a vial in an inert atmosphere glove box and, as an additional precaution, the cap of the sample vial had been wrapped with parafilm.

A complex of pyridazine and [Cu(PF₆)₂] was made by the same procedure used to make Cu(mepy)₄(PF₆)₂ using a ligand to metal ratio of 4.2:1. The blue precipitate obtained was shown by infrared spectroscopy to be hydrated. The product turned black in less than 5 minutes upon being heated at 85 °C while attempts to dehydrate another sample in a desiccator over P₂O₅ resulted in a colour change from blue to dark green, and then black within one month. In another experiment the product was air dried. Its colour changed from blue to violet. The microanalytical data for this product
corresponded to a complex of composition Cu(pdz)$_{4.5}$(PF$_6$)$_2$ (Anal. Calcd. for CuC$_{18}$H$_{18}$N$_9$P$_2$F$_{12}$: C 30.29, H 2.54, N 17.66; found: C 30.22, H 2.65, N 17.30) as did those of the original blue sample. The use of a lower pyridazine to copper mole ratio (3.5:1) also yielded a blue product which was shown by infrared spectroscopy to be hydrated. However, its microanalytical data did not correspond to any reasonable formulation (found: C 31.13, H 2.85, N 17.15).

Efforts to make Cu(2,5-me$_2$pyz)$_6$(EF$_6$)$_2$, where E is As or P, were not successful. The use of the above general procedures did not yield precipitates immediately upon the mixing of the Cu(EF$_6$)$_2$ solutions with the ligand. The solutions were left to evaporate slowly in a nitrogen-atmosphere dry box. Within a week a mixture of precipitates formed. The mixture from the 2,5-me$_2$pyz-[Cu(AsF$_6$)$_2$] solution comprised of violet and green components, most of the former being on the upper parts of the reaction flask and the latter at the bottom with the bulk of the solution. The solution, together with the green solid, was carefully poured out of the flask, leaving most of the violet solid behind, and filtered. Repeated washing of the collected green solid with the solvent left behind a yellow product in very low yields. Thus the green product may be a mixture of blue or violet copper(II) complexes and a yellow copper(I) complex. In the case of the 2,5-me$_2$pyz-[Cu(PF$_6$)$_2$] mixture, the solid product comprised of violet, yellow and orange-red components.

In an attempt to isolate a copper(II) complex before reduction occurred, a freshly prepared 2,5-me$_2$pyz-[Cu(AsF$_6$)$_2$] mixture was evaporated to dryness in vacuo. The solid residue was a mixture of greenish grey and orange materials, with the former predominant.

Another approach involved the use of stoichiometric ratios of the reagents to avoid formation of the the violet complexes, believed to be Cu(2,5-me$_2$pyz)$_4$(EF$_6$)$_2$. Indeed after about 2 weeks only an orange solid formed from a 1:1 mixture of an ethanolic solution of [Cu(AsF$_6$)$_2$] and 2,5-me$_2$pyz. This was isolated by filtration,
washed with a small amount of solvent and dried for 2 h in vacuo. Its infrared spectrum exhibited bands due to 2,5-me$_2$pyz ligands and non-coordinated AsF$_6^-$ anions. Microanalytical data suggested the composition Cu(2,5-me$_2$pyz)$_{1.7}$(AsF$_6$) (Anal. calcd. for CuC$_{10.2}$H$_{13.6}$N$_{3.4}$AsF$_6$: C 28.08, H 3.14, N 10.91; found: C 28.26, H 3.26, N 10.76). In order to isolate Cu(2,5-me$_2$pyz)$_2$(AsF$_6$) a shorter drying period would be probably required, as was observed in the preparation of the analogous Cu(pyz)$_2$(CF$_3$SO$_3$) (see section 5.2.7.2). The results may also indicate that a longer drying period would be required in order to obtain a complex of empirical formula Cu(2,5-me$_2$pyz)$_{1.5}$(AsF$_6$). A copper(I) hexafluorophosphate compound with such a formulation was isolated and structurally characterized (see below). Although the above microanalytical results are promising the product was isolated in such extremely low yields that further characterization was not possible. The reaction of 2,5-me$_2$pyz and a solution of [Cu(PF$_6$)$_2$] in a 2:1 molar ratio resulted in the isolation of yellow and red-orange products in crystalline forms suitable for single crystal X-ray diffraction studies (section 5.2.4.6). These were characterized as cationic copper(I) polymers and their structures are discussed in section 4.2.

All attempts to make derivatives of Ni(pyz)$_n$(AsF$_6$)$_2$ were unsuccessful. In a typical reaction, a solution of [Ni(AsF$_6$)$_2$] was prepared by a procedure similar to that used in the preparation of [Cu(AsF$_6$)$_2$]. No precipitate formed immediately on mixing ethanolic solutions of [Ni(AsF$_6$)$_2$] and pyrazine. However, a light blue precipitate formed on stirring the mixture overnight. This product was shown to be non-stoichiometric by elemental analysis. Different pyrazine to nickel mole ratios were tried (7:1, 8:1, 16:1). Similar results to those described above were obtained, even when the reaction time was increased to three days. With methanol as the solvent, a mixture of solid products (blue and colourless) was obtained only after most of the solvent had evaporated (5.5 weeks). The blue solid is probably a nickel(II) complex and the colourless one is probably KClO$_4$. 
With methylpyrazine as the ligand, no precipitate was obtained even after the solution was allowed to sit, covered with parafilm, for over two months. With 4,4'-bipyridine, a precipitate was obtained but this was shown by infrared spectroscopy to be hydrated, even after drying at about 80 °C.

5.2.5 Complexes of nickel(II) chloride

5.2.5.1 Tetrakis(pyridine)nickel(II) chloride, Ni(py)$_4$Cl$_2$

This complex was prepared as described by Rowley and Drago (204) except for the drying time which was reduced to 0.25 h. Nickel (II) chloride hexahydrate (1.03 g, 4.33 mmol) was dissolved in 5 mL ethanol containing about 10% v/v 2,2-dmp and then dehydrated by stirring with more 2,2-dmp (8 mL) for 2 h at room temperature. The resulting solution was treated with pyridine (3.0 mL, 37 mmol). The resultant slurry was stirred for an additional 1 h, filtered, and the blue precipitate washed with ether, and dried under vacuum for 0.25 h. Anal. calcd. for NiC$_{20}$H$_{20}$N$_4$Cl$_2$: C 53.86, H 4.52, N 12.56; found: C 53.76; H 4.57; N 12.68. Yield, 83%.

5.2.5.2 Mono(pyridine)nickel(II) chloride, Ni(py)Cl$_2$

A sample prepared as described in section 5.2.5.1, and shown by infrared spectroscopy to be Ni(py)$_4$Cl$_2$, was heated in vacuo at 140 °C for 5 h during which time the colour changed from blue to yellow. Anal. calcd. for NiC$_3$H$_5$NCl$_2$: C 28.77, H 2.41, N 6.71; found: C 28.97, H 2.51, N 6.62. Yield, 81%.
5.2.5.3 Bis(pyrazine)nickel(II) chloride, Ni(pyz)$_2$Cl$_2$

This pale green compound was prepared as described by Lever et al. (33), washed with water and ethanol, and dried in vacuo at room temperature for 1.25 h and then, at 100 °C for 12 h. Anal. calcd. for NiC$_8$H$_8$N$_4$Cl$_2$: C 33.16; H 2.78; N 19.33; found: C 32.96; H 2.90; N 19.6. Yield, 52%.

Lever et al. (33) did not obtain accurate elemental analysis and published only data for Cl (25.2; expected, 24.5) and N (19.3). Other workers have also prepared this compound (59, 61, 231) but only Beech and Mortimer (231) published microanalytical data. Although the calculated and experimental C and H values agreed to within the generally acceptable tolerance level of 0.3%, the values for nitrogen differed by 0.4%.

The details of the synthesis as performed in this work are described below. Nickel(II) chloride hexahydrate (1.00 g, 4.21 mmol) dissolved in 5 mL of ethanol containing 10% v/v 2,2-dmp was filtered into a 5 mL solution of pyrazine (0.692 g, 8.64 mmol) in the same solvent. The resulting slurry was stirred for 0.25 h. The mixture did not filter easily and the solvent was removed in vacuo. The pale green product was purified by dissolution in aqueous ammonia (50 mL) and acidifying this solution with concentrated hydrochloric acid until the product precipitated. The mixture was stored in a refrigerator overnight. Colourless crystals (presumably NH$_4$Cl) formed above the green solid. Most of the former were easily removed by using a spatula. The mixture was then filtered and the green solid washed and dried as described above.

5.2.5.4 Mono(pyrazine)nickel(II) chloride, Ni(pyz)Cl$_2$

A sample prepared as described in section 5.2.5.3, and shown by infrared spectroscopy to be Ni(pyz)$_2$Cl$_2$, was heated at 255-258 °C for 3 h under a stream of
nitrogen gas to give a pale yellow product. *Anal. calcd.* for NiC₄H₄N₂Cl₂: C 22.91, H 1.92, N 13.36; found: C 22.89, H 1.91, N 13.47.

5.2.5.5 Attempted synthesis

Eight different attempts were made to prepare Ni(pdz)Cl₂ but all were unsuccessful. These involved mixing pyridazine and ethanolic solutions of nickel(II) chloride hexahydrate, isolating the resultant precipitate by filtration, washing it with a small amount of the solvent and then drying it. The conditions which were varied included: ligand to metal mole ratio (0.5:1, 0.8:1, 1:1, 2:1), drying time (1.5 to 17.5 h), and drying temperature (ambient to 105 °C). For the 2:1 pdz to Ni mixtures, the nickel solution was added to pyridazine and an excess of the pyridazine was therefore maintained throughout the reaction. For the rest of the mixtures, pyridazine was added to the nickel(II) solutions to ensure that the ligand was not in excess at any time. The products were green or pale yellow, depending on the drying conditions. They all had similar infrared spectra except for evidence of hydration in some cases. This depended on the drying conditions. However most of the products had comparable microanalytical data. For example, a sample prepared from pyridazine and NiCl₂.6H₂O in a 2:1 mole ratio, dried at room temperature for 5 h and then at 105 °C for 6.5 h gave the following results. *Anal. Calcd.* for NiC₄H₄Cl₂: C 22.91, H 1.92, N 13.36; found: C 23.77, H 2.15, N 13.44.

Attempts to purify one of the products obtained above by the method used to purify Ni(pyz)₂Cl₂ did not yield the desired product. A sample dissolved in 50 mL NH₄OH gave a purple solution. On addition of concentrated hydrochloric acid, the colour of the solution changed to blue, then green and finally yellow. At pH ≈ 4, a white precipitate began to form. More HCl was added to increase the amount of the precipitate. The beaker was covered with parafilm and left sitting at ambient
temperatures. Within 2 h yellow crystals formed above the white precipitate. The crystals gave a white powder when dried and ground. The infrared spectrum of the product was the same as that of NH₄Cl.

The preparation of Ni(pdz)Cl₂ has been reported previously by several workers. Child et al. (94) used a 1:1 ligand to metal mole ratio, washed their product with ethanol and ether and then dried it under reduced pressure over silica gel. They reported analyzing for C, H and N but did not publish the results. Allan et al. (95) did not report the ligand to metal ratio they used. They washed their product with an ethanol-ether mixture and then dried it at 80 °C. They published satisfactory Ni and Cl analyses. Ferraro et. al. (90) used a 2:1 ligand to metal mole ratio, washed their product with ethanol, dried it in vacuo over drierite at room temperature and then, at about 100 °C. The hydrogen content of their product (microanalytical data: C 22.60, H 2.77, N. 13.20) was 0.85% higher than the calculated value. Thus, although Ni(pdz)Cl₂ has been characterized by several research groups, no consistent C, H and N analytical data have been published for the compound.

5.2.6 Complexes of nickel(II) thiocyanate

The syntheses of the nickel(II) thiocyanate complexes can be represented by the reaction scheme outlined in eqn. 5-4. Typically, a solution of about 0.7 g of potassium thiocyanate in 25 mL of ethanol containing 10% v/v 2,2-dmmp was added to about 1 g of nickel(II) nitrate hexahydrate dissolved in 5 mL of the same solvent. The resulting mixture was then either filtered (to remove the precipitated potassium nitrate) directly into an excess of ligand (ligand to nickel mole ratio ≈4.3:1) or, if a lower ligand to nickel mole ratio was desired, filtered and the ligand or ligand solution added to the filtrate. The resulting precipitates were isolated by filtration and dried in vacuo. In
some cases, thermolysis of complexes yielded new derivatives with lower ligand to metal ratios (eqn. 5-4(iii)). The specific details pertaining to each complex are discussed below.

\[
\text{EtOH} \\
\text{(i) } \text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} + 2 \text{ KNCS } \rightarrow [\text{Ni(NCS)}_2] + \text{KNO}_3(\text{s}) \quad [5-4] \\
\text{EtOH} \\
\text{(ii) } [\text{Ni(NCS)}_2] + y \text{ L } \rightarrow \text{ML}_n(\text{NCS})_{2(\text{s})} + (y-n) \text{ L} \\
\text{heat} \\
\text{(iii) } \text{ML}_n(\text{NCS})_{2(\text{s})} \rightarrow \text{ML}_{n-x}(\text{NCS})_{2(\text{s})} + x \text{ L}
\]

5.2.6.1 Tetrakis(pyridine)nickel(II) thiocyanate, Ni(py)$_4$(NCS)$_2$

The quantities of reagents used were Ni(NO$_3$)$_2$.6H$_2$O (1.00 g, 3.44 mmol), KNCS (0.693 g, 7.13 mmol) and pyridine (1.2 mL, 15 mmol). The resulting blue precipitate was isolated by filtration, washed with a small amount of solvent containing pyridine, and dried for 0.5 h in vacuo. Anal. calcd. for NiC$_{22}$H$_{20}$N$_6$S$_2$: C 53.79, H 4.10, N 17.11; found: C 53.93, H 4.12, N 17.09. Yield, 50%.

5.2.6.2 Bis(pyridine)nickel(II) thiocyanate, Ni(py)$_2$(NCS)$_2$

A sample prepared as described in section 5.2.6.1, and shown by infrared spectroscopy to be Ni(py)$_4$(NCS)$_2$, was heated in vacuo at 100 °C for 3.25 h to yield Ni(py)$_2$(NCS)$_2$. This compound is pale green in colour. Anal. calcd. for NiC$_{12}$H$_{10}$N$_4$S$_2$: C 43.27, H 3.03, N 16.82; found: C 43.56, H 3.04, N 16.90. Yield, 55%.
5.2.6.3 Tris(pyridazine)nickel(II) thiocyanate, Ni(pdz)$_3$(NCS)$_2$

The quantities of reagents used were Ni(NO$_3$)$_2$.6H$_2$O (0.909 g, 3.13 mmol), KNCS (0.629 g, 6.47 mmol) and pyridazine (1.00 mL, 13.8 mmol). The blue precipitate which formed was isolated by filtration, washed with a small amount of solvent and dried for 1.5 h \textit{in vacuo}. \textit{Anal. calcd.} for NiC$_{14}$H$_{12}$N$_8$S$_2$: C 40.51, H 2.91, N 26.99; found: C 40.56, H 2.97, N 26.82. Yield, 55%.

5.2.6.4 Bis(pyridazine)nickel(II) thiocyanate, Ni(pdz)$_2$(NCS)$_2$

The quantities of reagents used were Ni(NO$_3$)$_2$.6H$_2$O (1.00 g, 3.44 mmol), KNCS (0.702 g, 7.22 mmol) and pyridazine (0.25 mL, 3.44 mmol). In this case the neutral ligand was added, slowly, to the [Ni(NCS)$_2$] solution. The mixture was stirred for 0.25 h and the precipitate isolated by filtration, washed with a small amount of solvent and dried for 1 h \textit{in vacuo}. The compound is pale green in colour. \textit{Anal. calcd.} for NiC$_{10}$H$_8$N$_6$S$_2$: C 35.85, H 2.41, N 25.08; found: C 35.92, H 2.50, N 25.03. Yield, 58%. It is noteworthy that although a 1:1 pyridazine to nickel mole ratio was used, it is the 2:1 complex that precipitated out.

5.2.6.5 Bis(pyrazine)nickel(II) thiocyanate, Ni(pyz)$_2$(NCS)$_2$

The quantities of reagents used were Ni(NO$_3$)$_2$.6H$_2$O (1.00 g, 3.44 mmol), KNCS (0.674 g, 6.94 mmol) and pyrazine (1.10 g, 13.7 mmol in 5 mL of the ethanol/2,2-dmp solvent). The mixture was stirred for 0.25 h and the blue precipitate formed was isolated by filtration, washed a with small amount of solvent and then dried, \textit{in vacuo}, at room temperature and at 90 °C for 3 h and 5 h respectively. \textit{Anal. calcd.} for NiC$_{10}$H$_8$N$_6$S$_2$: C 35.85, H 2.41, N 25.08; found: C 35.83, H 2.58,
N 25.26. Yield, 44%. The preparation of this complex from pyrazine and disodium tetrathiocyanatonickelate(II) was described in an earlier report by Lever et al. (33).

5.2.6.6 Mono(pyrazine)nickel(II) thiocyanate, Ni(pyz)(NCS)₂

A sample prepared and dried at room temperature as outlined in section 5.2.6.5, and then shown by infrared spectroscopy to be Ni(pyz)₂(NCS)₂, was heated at 235 °C for 3 h under a stream of nitrogen gas to give a green product. Anal. Calcd. for NiC₆H₄N₄S₂: C 28.27, H 1.58, N 21.98; found: C 28.00, H 1.64, N 21.93. Yield, 57%.

5.2.7 Copper(I) trifluoromethanesulfonate and its complexes

The copper(I) triflate used in this study contained some copper(I) oxide (see section 5.2.7.1). The syntheses of the complexes CuLₙ(CF₃SO₃), where L is pyz or 2,5-me₂pyz and n is 1 or 2, and their isolation from the Cu₂O can be represented by the scheme shown in eqn. 5-5. The various steps shown in the equation are explained in sections 5.2.7.2 and 5.2.7.3. In calculating yields, it was assumed that the Cu(CF₃SO₃) was pure. Thus the reported values would be higher if the presence of Cu₂O was taken into account.
\[
\text{MeOH} \\
\text{Cu(CF}_3\text{SO}_3) + \text{Cu}_2\text{O} + \text{xs L} \rightarrow \text{CuL}_2(\text{CF}_3\text{SO}_3) + \text{Cu}_2\text{O} + \text{xs L} \quad [5-5]
\]

\[
\downarrow \quad \text{Filter} \\
\quad \text{(retain residue)}
\]

\[
\text{CuL}_2(\text{CF}_3\text{SO}_3) + \text{Cu}_2\text{O}
\]

1) Acetonitrile

\[
\downarrow \quad 2) \text{Filter} \\
\quad \text{(retain filtrate)}
\]

3) Evaporate

\[
\text{CuL}_2(\text{CF}_3\text{SO}_3)
\]

\[
\downarrow \quad \text{Heat}
\]

\[
\text{CuL}(\text{CF}_3\text{SO}_3)
\]

5.2.7.1 Copper(I) trifluoromethanesulfonate, Cu(CF\text{3SO}_3)

The synthesis of Cu(CF\text{3SO}_3) from cuprous oxide and trifluoromethanesulfonic acid anhydride has been reported by Dines (294). A similar method was used in this work, but with the anhydride replaced by CF\text{3SO}_3H which was readily available. To 16.0 g (112 mmol) of red cuprous oxide was added 50 mL of n-octane and 20 mL (226 mmol) of trifluoromethanesulfonic acid. The mixture was refluxed under nitrogen at about 110 °C overnight, filtered, and the precipitate washed with n-octane and dried in vacuo at room temperature for 6 h, then at 135 °C for 6 h. Cu\textsubscript{2}O was identified by infrared spectroscopy in subsequent reactions involving the Cu(CF\text{3SO}_3). This indicated incomplete conversion of copper(I) oxide to copper(I) triflate in the initial reaction, represented by equation 5-6. The presence of Cu\textsubscript{2}O impurity did not adversely affect the reactions of the Cu(CF\text{3SO}_3) with 2,5-dimethylpyrazine or pyrazine.

\[
\text{Cu}_2\text{O} + 2 \text{CF}_3\text{SO}_3\text{H} \overset{\text{octane \ reflux( \approx 15 \ h)}}{\rightarrow} 2 \text{Cu(CF}_3\text{SO}_3) + \text{H}_2\text{O} \quad [5-6]
\]
5.2.7.2 Poly-(trifluoromethanesulfonato-O)µ-pyrazine(pyrazine)copper(I),
Cu(pyz)$_2$(CF$_3$SO$_3$)

To copper(I) triflate (1.07 g, ≈5 mmol) was added 10 mL of methanol containing 10% v/v 2,2-dmp and the resulting slurry stirred for 0.5 h after which time a 5 mL solution of pyrazine (1.63 g, 20.4 mmol) in the same solvent was added and the slurry stirred for an additional 2 h. On filtering the mixture, the residue was found to consist of a mixture of the desired orange complex and cuprous oxide (see section 5.2.7.1). The solid mixture was washed with a small amount of the solvent. The orange complex was then separated from cuprous oxide by treating the mixture with acetonitrile in which only the former is soluble, followed by filtration. The filtrate was evaporated to dryness in vacuo to give an orange powder which was further dried at room temperature, again in vacuo, for about 0.75 h. Prolonged drying led to loss of some pyrazine. Because of the rapidness of the evaporation step, single crystals could not be obtained by this procedure. *Anal. calcd.* for CuC$_9$H$_8$N$_4$F$_3$SO$_3$: C 29.00, H 2.16, N 15.03; found: C 28.73, H 2.22, N 15.23. Yield, 82%.

5.2.7.3 Mono(pyrazine)copper(I) trifluoromethanesulfonate, Cu(pyz)(CF$_3$SO$_3$)

A sample prepared as described in section 5.2.7.2, and shown by infrared spectroscopy to be Cu(pyz)$_2$(CF$_3$SO$_3$), was heated in vacuo at 140 °C for 3.5 h. The colour changed from orange to yellow. *Anal. calcd.* for CuC$_5$H$_5$N$_2$F$_3$SO$_3$: C 20.52, H 1.38, N 9.57; found: C 20.58, H 1.36, N 9.60. Yield, 67%.
5.2.7.4 Poly-(trifluoromethanesulfonato-O)µ-2,5-dimethylpyrazine(2,5-dimethylpyrazine)copper(I), Cu(2,5-me₂pyz)₂(CF₃SO₃)

A slurry of copper(I) triflate (1.09 g, ≈5 mmol) in 10 mL methanol containing about 10% v/v 2,2-dmp was stirred for 0.5 h before 2,5-dimethylpyrazine (3.0 mL, 27 mmol) was added. The resulting slurry was stirred for an additional 2 h. The solid produced was separated by filtration, washed with a small amount of solvent, and then treated with acetonitrile (2 × 5 mL) to separate the insoluble copper(I) oxide from the soluble complex, as was done for the pyrazine complex above. After filtration, the filtrate was allowed to evaporate slowly (by covering the flask with parafilm in which a pinhole was made) in a nitrogen atmosphere glove box, yielding a crystalline yellow product. Anal. calcd. for CuC₁₅H₁₆N₄F₃SO₃: C 36.41, H 3.76, N 13.06; found: C 36.60, H 3.79, N 12.96. Yield, 55%.

5.2.7.5 Mono(2,5-dimethylpyrazine)copper(I) trifluoromethanesulfonate, Cu(2,5-me₂pyz)(CF₃SO₃)

Cu(2,5-me₂pyz)₂(CF₃SO₃) was prepared as described above except that the acetonitrile solution was evaporated rapidly in vacuo, instead of allowing it to evaporate slowly. The resultant yellow solid was dried at ambient temperature for 1.5 h and characterized as the bis(2,5-me₂pyz) complex by infrared spectroscopy. The sample was heated, in vacuo, at 85 °C for 0.5 h and then at 135 °C for a further 6 h to yield the desired product as a yellow powder. Anal. calcd. for CuC₇H₈N₂F₃SO₃: C 26.21, H 2.51, N 8.73; found: C 26.32, H 2.59, N 8.84. Yield, 64%.
5.2.7.6 Attempted syntheses

The general synthetic procedure discussed at the beginning of this section failed to work for some of the ligands tried. In the case of methylpyrazine, the residue obtained at the first filtration stage consisted of brown and pink solids whose infrared spectra closely resembled that of cuprous oxide. The filtrate was deep orange-brown and, upon standing for several days, yielded dark green crystals. C, H, and N analysis showed the green material to be non-stoichiometric and room temperature magnetic susceptibility measurement showed it to be paramagnetic. When washed repeatedly with the solvent, the crystals progressively turned blue but became powdery on drying. With the exception of the presence of a broad band around 3400 cm\(^{-1}\), the infrared spectrum of this material was similar to that of the copper(II) complex, Cu(mepy\(z\)\(_4\))(CF\(_3\)SO\(_3\))\(_2\) (66). The green crystals were believed to be a mixture of copper(I)- and copper(II) triflate complexes.

With pyridine, the residue obtained in the first filtration stage consisted of pink and greenish-blue materials. The filtrate was very dark brown. Some blue precipitate formed immediately and a second filtration was performed. Slow evaporation of the filtrate yielded a black crystalline solid. Characterization of this material was not attempted. The observations made in the reactions between Cu(CF\(_3\)SO\(_3\)) and methylpyrazine or pyridine suggested that in these reactions copper(I) complexes were not stabilized by polymer formation and in solution disproportionation occurred. This indicated the need for symmetrically bridging ligands in order to obtain stable copper(I) polymers such as Cu(pyz)\(_2\)(CF\(_3\)SO\(_3\)) and Cu(2,5-me\(_2\)pyz)\(_2\)(CF\(_3\)SO\(_3\)).
5.3. Physical experimental methods

5.3.1 Elemental analysis

Carbon, hydrogen and nitrogen analyses were performed by Mr. P. Borda in the microanalytical laboratory of this department.

5.3.2 Thermal analysis

Differential scanning calorimetry (DSC) studies were performed using a Mettler DSC-20 cell interfaced with a Mettler TC 10 TA processor. Output was produced on a Print Swiss Matrix printer/plotter. Finely powdered samples of approximately 4 to 14 mg were weighed and sealed into aluminum pans. A small hole punched in the lid allowed for free access to the measuring cell atmosphere, in this case an inert atmosphere of nitrogen gas at a flow rate of 50 mL min\(^{-1}\). The samples were heated from 35 to 450 °C at a rate of 4 °C per minute. The temperature of the Pt sensor was calibrated using the known fusion temperatures of indium, lead and zinc. The heat flow was calibrated by using an exactly known quantity of indium.

The maximum in the DSC curve and the integrated area enclosed by the curve and the baseline yielded respectively, the temperature and enthalpy of a particular event. From a series of calibrations using indium metal the fusion temperature was found to be accurate to ±0.1 K and the integrated area was accurate to ±2 J g\(^{-1}\), representing an error of approximately ±1% in both measurements. However, for broad or overlapping curves the temperature and enthalpy values are considered accurate to ±5 K and ±5% respectively.
Thermogravimetric analyses were performed by weighing samples prior to and following each thermal event. The accuracy of the weight loss figures is approximately ±5%.

5.3.3 Infrared spectroscopy

A Perkin-Elmer Model 598 Spectrophotometer was used to record infrared spectra over the range 200 to 4000 cm\(^{-1}\). Samples were prepared as both Nujol and 1,3-hexachlorobutadiene mulls and sandwiched between KRS-5 plates (58% thallium iodide, 42% thallium bromide, Harshaw Chemical Co.). For moisture sensitive compounds, the plates were sealed with plastic tape. All spectra were calibrated at 907 and 1601 cm\(^{-1}\) with a polystyrene film. Vibrational energies are considered accurate to ±5 cm\(^{-1}\) for broad bands and ±2 cm\(^{-1}\) for sharp bands.

5.3.4 Electronic spectroscopy

Electronic spectra in the 5 000-50 000 cm\(^{-1}\) region of the electromagnetic spectrum were recorded on a Cary 5 UV-Vis-NIR spectrophotometer. Samples were mulled in Nujol and sandwiched between quartz glass plates. A second set of plates containing only Nujol was placed in the reference beam. The spectra of the copper(I) triflate complexes were obtained over the 12 500 to 27 800 cm\(^{-1}\) range employing a Shimadzu UV-Vis 2100 spectrophotometer. Samples were mulled in Nujol and smeared on filter paper then supported in a quartz glass cuvette. A second cuvette containing Nujol soaked filter paper was used as a reference. Electronic transition energies are considered accurate to ±200 cm\(^{-1}\).
5.3.5 Electron spin resonance spectroscopy

Powdered samples for esr studies were packed into quartz glass tubes of ≈3.0 mm internal diameter to a height of about 5-10 mm. The tubes were sealed with greased caps. The spectra were recorded either on a Varian Associates E-3 X-band spectrometer or on a spectrometer designed by Dr. F.G. Herring of this department (295). The former was equipped with a 100 kHz field modulation. The field sweep was calibrated using a gaussmeter and probe made by the staff of the electronic shop of this department, and the calibration checked with 2,2'-diphenyl-1-picrylhydrazyl (DPPH). The X-band frequency (≈9 GHz) was monitored with a HP5245L electronic counter equipped with a HP5255A plug-in. Measurements were performed at liquid nitrogen temperature.

Dr Herring's equipment consisted of an X-band homodyne spectrometer with a Varian 12-in. magnet equipped with a MkII field-dial control. An Ithaco Dynatrac 391A lock-in amplifier was used to obtain phase-sensitive detection at 100 kHz. Data acquisition was carried out using a Qua-Tech 12-bit data-acquisition board (ADM 12-10), together with a Qua-Tech parallel expansion board (PXB-721) incorporated into an IBM XT computer. Data processing software was as described previously (296, 297). The microwave frequency was measured with a HP5246L frequency counter equipped with a HP5255A plug-in. Field calibration was accomplished using a Varian gaussmeter, the output of which was also corrected for the placement of the gaussmeter probe by calibrating against peroxyamine sulfate in aqueous solution. Measurements were performed at about 90 K. Sample temperature was controlled using a Varian E-257 temperature controller and measured using a copper-constantan thermocouple.
5.3.6 Powder X-ray diffraction

Powder diffractograms were recorded in the range $2\theta = 5-60^\circ$ using an automated Rotaflex Ru-200BH rotating anode powder X-ray diffractometer. Samples were prepared by applying a thin layer of compound slurried in n-octane to a glass slide and allowing the slurry to dry.

5.3.7 Single crystal X-ray diffraction

Single crystal X-ray diffraction structural determinations were performed by Dr. S.J. Rettig in the X-ray crystallography laboratory of this department.

5.3.8 Magnetic susceptibility measurements

Three different kinds of apparatus were used for the magnetic susceptibility measurements. Measurements between 4.2-82 K were routinely made on a vibrating sample magnetometer (VSM). Whenever necessary, temperatures down to 2.2 K were achieved by pumping on the liquid helium used as the coolant. The sensitivity of this instrument above 85 K is low and a Gouy magnetic balance was used for measurements between 85 K and 300 K. Temperatures down to the boiling point of liquid nitrogen (77 K) can be achieved with this apparatus. However, measurements below the boiling point of oxygen (90 K) are more difficult to obtain because of the need to keep oxygen from condensing into the dewar or sample chamber. The SQUID magnetometer employed in this work can be used over the temperature range 1.7-400 K. However, the instrument was acquired only recently by the Department of Physics and was used in this work primarily for field dependence measurements. Magnetic field strengths of
up to 55 000 Oe can be obtained with this instrument, compared to a maximum of about 10 000 Oe for the VSM.

The VSM employed in this work was a Princeton Applied Research Model 155 vibrating sample magnetometer (298). A magnetic field strength of 9 225 Oersteds was employed. Checks for field dependence of the magnetic susceptibilities were made using fields of 2 549, 5 251 and 7 501 Oersteds. Magnetic fields were set to an accuracy of ±0.5% and measured by an F.W. Bell Model 620 gaussmeter. Accurately weighed samples of approximately 80 mg, contained in poly-trichlorofluoromethane (Kel-F) capsules, were attached to a Kel-F holder with epoxy resin. Ultrapure nickel metal was used to calibrate the instrument. Temperature measurement was achieved with a chromel versus Au-0.02% Fe thermocouple (299) located in the sample holder immediately above the sample. The thermocouple was calibrated by using the known susceptibility versus temperature behaviour of tetramethylethylenediammonium tetrachlorocuprate(II) (300) and checked with mercury(II) tetrathiocyanatocobaltate(II) (301). The temperatures are estimated to be accurate to ±1% from the scatter in the data points from four separate calibrations. The accuracy of the magnetic susceptibility values as measured by this technique is estimated to be within ±1%.

The Gouy balance used consisted of a Varian 4-inch electromagnet, Model V4084, with 2-inch tapered pole caps (302), in conjunction with a Mettler AE163 semi-micro balance. Current regulation was provided by a Varian Model U 2300 power supply and a model 2301 A current regulator. The apparatus was fitted with a cryostat for temperature control. Temperature was measured using a copper-constantan thermocouple (303) and a Fluke Model 8120 digital voltmeter. The thermocouple was calibrated using the known temperature dependence of the susceptibility of mercury(II) tetrathiocyanatocobaltate(II) (301). The accuracy of temperature measurements is estimated to be ±1 K. Powdered samples (300-600 mg) were packed into a pyrex tube and measured in a magnetic field gradient with a maximum field of 8 kOe. Due to
errors arising from the inhomogeneous packing of samples, absolute magnetic susceptibilities measured by this technique are generally accurate only to $\pm 5\%$. For each compound measurements were repeated on repacked samples. A reproducibility of about $\pm 2\%$, which is well within the above limits, was obtained in each case.

The SQUID magnetometer employed in this work was a Quantum Design MPMS SQUID Magnetometer. The temperature was measured using a Ge resistance thermometer in the range 2-40 K and a Pt resistance thermometer in the range 40-350 K. Temperature measurement was calibrated using an external Pt resistance thermometer and is accurate to within 0.1%. Susceptibility measurements were calibrated using ultrapure Ni, Pd and Bi standards and are accurate to within $\pm 1\%$. Samples of about 30 mg were held in a holder constructed from poly(vinyl chloride) (PVC) plastic.

Only in the cases of measurements on nickel(II) complexes with the SQUID magnetometer were the contribution of the sample holder found to be negligible. All other measurements by the VSM, Gouy and SQUID apparatus were corrected for sample holder contributions.

Molar magnetic susceptibilities were corrected for the diamagnetism of the metal ions and ligands (111, 277). The corrections, in units of $10^{-6}$ cm$^3$ mol$^{-1}$ are: Cu$^{2+}$, 11; Ni$^{2+}$, 11; NCO$^-$, 21; NO$_3^-$, 20; CH$_3$SO$_3^-$, 35; AsF$_6^-$, 72; PF$_6^-$, 67; Cl$^-$, 26; NCS$^-$, 35; pyridine, 49; pyrazine, 45; methylpyrazine, 57; pyridazine, 45; 4,4'-bipyridine, 93. The molar magnetic susceptibilities were also corrected for the temperature independent paramagnetism of $60 \times 10^{-6}$ cm$^3$ mol$^{-1}$ for Cu$^{2+}$ and $200 \times 10^{-6}$ cm$^3$ mol$^{-1}$ for Ni$^{2+}$.
6.1 Conclusions

A large number of compounds have been prepared and characterized by elemental analysis, magnetic susceptibility measurements, and thermal, spectroscopic and X-ray diffraction methods, where appropriate. Structures of compounds isolated in the form of X-ray quality crystals have been determined by single crystal X-ray diffraction. Structures for the remainder of the compounds have been proposed on the basis of indirect evidence provided by the other physical methods of characterization employed in this study, particularly infrared and electronic spectroscopies. The structural and magnetic properties of the compounds are summarized in Table 6-1. Structurally, the compounds fall into several categories. These include mononuclear, trimeric, and chain-, sheet- and three-dimensional polymeric species. The central metal ions in the mononuclear compounds are either five- or six-coordinate. Some of the chain polymers are bent while others are linear. Two types of sheet polymers have been obtained; those in which the metal ions are bridged by neutral ligands in both dimensions and those in which the neutral ligands bridge in one dimension and the anionic ligands bridge in the second dimension. The metal ions in the polymeric materials are three-, four- or six-coordinate. In addition, two other polynuclear complexes, Ni(pdz)$_3$(NCS)$_2$ and Ni(pdz)$_2$(NCS)$_2$, have been isolated but no definite structure can be assigned to either of them on the basis of evidence obtained in this work. [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ and [Cu(2,5-me$_2$pyz)$_2$][PF$_6$], with graphite-related and diamond-related cationic lattices, respectively, represent two new structural types
for polymeric transition metal complexes containing pyrazine derivatives as the bridging ligands.

A variety of magnetic properties have been observed in these complexes. The properties include diamagnetism (Cu¹ complexes), Curie-type paramagnetism (Cu¹Ι and Ni¹Ι complexes), antiferromagnetism (Cu¹Ι and Ni¹Ι complexes) and metamagnetism (Ni¹Ι complexes). The latter arises when both ferromagnetically coupled and antiferromagnetically coupled phases are present in the same compound. Reasonable magneto-structural correlations have been made for all the complexes.

Evidence presented in this thesis suggests that pyridazine is a much more efficient mediator of magnetic exchange between copper(II) centres than either pyrazine or methylpyrazine. The magnetic properties of Cu(pyz)(NCO)₂ and Cu(mepyz)(NCO)₂ suggest that pyrazine and methylpyrazine are equivalent in their abilities to facilitate magnetic exchange. This is in accord with previous observations (15, 66). No polymeric materials involving 4,4'-bipyridine or 2,5-dimethylpyrazine bridges and containing transition metal ions with paramagnetic ground states have been isolated. Hence conclusions regarding the abilities of these ligands to propagate magnetic exchange interactions cannot be drawn on the basis of this work.

The work described in this thesis was undertaken primarily for academic interest. Nonetheless, results such as those presented here do provide a data base from which technologically useful materials with predefined structures and magnetic properties may be made. A discussion on technologically useful magnetic properties as well as the current uses of magnetic materials may be found in the text by Jakubovics (304).
Table 6-1. Summary of the structural and magnetic properties of the compounds investigated in this work.a

<table>
<thead>
<tr>
<th>compound</th>
<th>structure</th>
<th>magnetic behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(pyz)$_2$(CF$_3$SO$_3$)</td>
<td>chain polymer$^b$</td>
<td>DM</td>
</tr>
<tr>
<td>Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$)</td>
<td>chain polymer$^c$</td>
<td>DM</td>
</tr>
<tr>
<td>Cu(pyz)(CF$_3$SO$_3$)</td>
<td>chain polymer</td>
<td>DM</td>
</tr>
<tr>
<td>Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$)</td>
<td>chain polymer</td>
<td>DM</td>
</tr>
<tr>
<td>[Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$</td>
<td>2-D cationic polymer$^c$ (graphite-related lattice)</td>
<td>DM</td>
</tr>
<tr>
<td>[Cu(2,5-me$_2$pyz)$_2$][PF$_6$]</td>
<td>3-D cationic polymer$^c$ (diamond-related lattice)</td>
<td>DM</td>
</tr>
<tr>
<td>Cu(pdz)$_4$(NO$_3$)$_2$</td>
<td>mononuclear</td>
<td>DIL</td>
</tr>
<tr>
<td>[Cu(pdz)$_4$(NO$_3$)][NO$_3$]</td>
<td>mononuclear$^c$</td>
<td>DIL</td>
</tr>
<tr>
<td>Cu(pdz)$_3$(NO$_3$)$_2$</td>
<td>mononuclear$^c$</td>
<td>DIL</td>
</tr>
<tr>
<td>Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$</td>
<td>mononuclear</td>
<td>DIL</td>
</tr>
<tr>
<td>Cu(pyz)$_4$(AsF$_6$)$_2$</td>
<td>mononuclear</td>
<td>DIL</td>
</tr>
<tr>
<td>Cu(mepy)$_4$(AsF$_6$)$_2$</td>
<td>mononuclear</td>
<td>DIL</td>
</tr>
<tr>
<td>Cu(mepy)$_4$(PF$_6$)$_2$</td>
<td>mononuclear</td>
<td>DIL</td>
</tr>
<tr>
<td>Ni(py)$_4$(NCO)$_2$</td>
<td>mononuclear$^d$</td>
<td>DIL</td>
</tr>
<tr>
<td>Ni(py)$_4$Cl$_2$</td>
<td>mononuclear$^e$</td>
<td>DIL</td>
</tr>
<tr>
<td>Ni(py)$_4$(NCS)$_2$</td>
<td>mononuclear$^f$</td>
<td>DIL</td>
</tr>
<tr>
<td>Cu(mepy)$_2$(NCO)$_2$</td>
<td>sheet polymer$^c$</td>
<td>DIL</td>
</tr>
<tr>
<td>Cu(py)$_2$(NCO)$_2$</td>
<td>3-D polymer$^g$</td>
<td>DIL</td>
</tr>
<tr>
<td>Ni(pdz)$_2$(NCS)$_2$</td>
<td>polynuclear</td>
<td>DIL</td>
</tr>
<tr>
<td>Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$</td>
<td>mononuclear</td>
<td>wAF</td>
</tr>
<tr>
<td>Cu(pyz)$_4$(PF$_6$)$_2$</td>
<td>mononuclear</td>
<td>wAF</td>
</tr>
<tr>
<td>[Cu(pdz)$_2$(NO$_3$)$_2$]$_3$</td>
<td>linear trimer$^c$</td>
<td>vsAF</td>
</tr>
<tr>
<td>Cu(pdz)(NCO)$_2$</td>
<td>chain polymer</td>
<td>sAF</td>
</tr>
<tr>
<td>Ni(pdz)$_2$(NCO)$_2$</td>
<td>chain polymer</td>
<td>wAF</td>
</tr>
<tr>
<td>Cu(mepy)$_2$(NCO)$_2$</td>
<td>sheet polymer</td>
<td>wAF</td>
</tr>
</tbody>
</table>
Table 6-1. cont.

<table>
<thead>
<tr>
<th>compound</th>
<th>structure</th>
<th>magnetic behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(pyz)(NCO)₂</td>
<td>sheet polymer</td>
<td>wAF</td>
</tr>
<tr>
<td>Ni(pyz)₂Cl₂</td>
<td>sheet polymer</td>
<td>wAF</td>
</tr>
<tr>
<td>Ni(pyz)₂(NCO)₂·½H₂O</td>
<td>sheet polymer</td>
<td>wAF</td>
</tr>
<tr>
<td>Ni(pyz)₂(NCS)₂</td>
<td>sheet polymer</td>
<td>wAF</td>
</tr>
<tr>
<td>Ni(pdz)₃(NCS)₂</td>
<td>polynuclear</td>
<td>wAF</td>
</tr>
<tr>
<td>Ni(py)₂(NCS)₂</td>
<td>chain polymer</td>
<td>MM</td>
</tr>
<tr>
<td>Ni(py)Cl₂</td>
<td>double-strand</td>
<td>MM</td>
</tr>
<tr>
<td>Ni(pyz)Cl₂</td>
<td>sheet polymer</td>
<td>MM</td>
</tr>
<tr>
<td>Ni(pyz)(NCO)₂</td>
<td>sheet polymer</td>
<td>MM</td>
</tr>
<tr>
<td>Ni(pyz)(NCS)₂</td>
<td>sheet polymer</td>
<td>MM</td>
</tr>
</tbody>
</table>

a DM = diamagnetic, 2-D = two-dimensional, 3-D = three-dimensional, DIL = magnetically dilute, AF = antiferromagnetically coupled, MM = exhibits metamagnetic behaviour, w = weak, s = strong, v = very.
b Structure determined by single crystal X-ray diffraction (ref. 44).
c Structure determined by single crystal X-ray diffraction (this work).
d Structure determined by single crystal X-ray diffraction (this work, preliminary results).
e Structure determined by single crystal X-ray diffraction (ref. 221).
f Structure determined by single crystal X-ray diffraction (ref. 239).
g Structure determined by single crystal X-ray diffraction (ref. 118).

6.2 Suggestions for further work

Some avenues for further research opened by the results presented in this thesis are considered in this section. Whereas the products of the reaction of pyridazine and copper(II) nitrate trihydrate have been well characterized in the present work, some aspects of their syntheses remain perplexing. For instance it is not clear why, under apparently similar reaction conditions, a 3:1 ligand to metal mole ratio sometimes
results in an immediate precipitation of Cu(pdz)$_3$(NO$_3$)$_2$ in powder form whereas in other cases slow precipitation occurs, resulting in X-ray quality crystals being formed. A similar situation obtains in the preparation of [Cu(pdz)$_4$(NO$_3$)][NO$_3$] from a 4:1 ligand to metal mole ratio. As discussed in Chapter 5, the quality of the crystals of Cu(pdz)$_3$(NO$_3$)$_2$ obtained from a reaction mixture stored at -5 °C were found to be better than those obtained at ambient conditions. Hence it may be useful to investigate the effects of temperature on the rate of formation of these compounds. The most remarkable aspect of the reactions of pyridazine and copper(II) nitrate is the observation that under conditions where the ligand to metal mole ratio is ≈ 4.0 in ethanol solution one or the other of three products, never a mixture, is obtained. It was suggested in Chapter 2 that under these conditions Cu(pdz)$_4$(NO$_3$)$_2$, [Cu(pdz)$_4$(NO$_3$)][NO$_3$] and Cu(pdz)$_3$(NO$_3$)$_2$ are in equilibrium and that the product obtained on any given occasion is governed by the difference in the solubilities of these three compounds, and hence their abilities to form saturated solutions. In order to test this hypothesis, it would be necessary to establish conditions under which slow precipitation occurs, as suggested above. Several solutions would then be made and, before precipitation occurs, each would be seeded by a pure sample of either Cu(pdz)$_4$(NO$_3$)$_2$, [Cu(pdz)$_4$(NO$_3$)][NO$_3$] or Cu(pdz)$_3$(NO$_3$)$_2$. If the three compounds exist in each of the solutions, then, only a single pure product, the same species as the seeding agent, should be obtained from each solution. This nucleating technique may also be used to find out if a pure sample of Cu(pdz)$_4$(NO$_3$)$_2$, [Cu(pdz)$_4$(NO$_3$)][NO$_3$] or Cu(pdz)$_3$(NO$_3$)$_2$ gives a mixture of these three compounds when dissolved in ethanol.

The graphite- and diamond-related structures of [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ and [Cu(2,5-me$_2$pyz)$_2$][PF$_6$], respectively, represent two new structural types for polymeric transition metal complexes containing pyrazine derivatives as the bridging ligands. The two compounds were obtained as a mixture from the reaction of the neutral ligand with copper(II) salts. It would be useful to develop a synthetic route to these complexes in
pure form. A possible approach to this task would be to react the ligand and Cu(PF$_6$) (305) in controlled amounts. (The copper(I) triflate complexes described in section 4.1 were prepared by a similar strategy of using copper(I) precursors). Once developed, the same synthetic method could be applied to the synthesis of related copper(I) complexes of pyrazine or other substituted pyrazine ligands. Likewise, related complexes containing the hexafluoroarsenate anion could be prepared by the reaction of pyrazine-type ligands with Cu(AsF$_6$) (305, 306).

Complexes with cationic lattices such as those observed in [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ and [Cu(2,5-me$_2$pyz)$_2$][PF$_6$] but in which the metal ion is in a paramagnetic ground state would be of considerable interest to chemists and physicists studying magnetic exchange effects in extended systems. No such complexes were isolated in the present study. This is probably due to steric factors; the large size of the PF$_6^-$ and AsF$_6^-$ anions employed and the fact that a +2 metal ion requires twice as many anions as a +1 metal ion. It may be worthwhile trying to make such complexes using counter anions, such as BF$_4^-$, which are smaller than PF$_6^-$ or AsF$_6^-$.

The feasibility of preparing such complexes with dinegative anions such as SiF$_6^{2-}$ or SnF$_6^{2-}$ may also be explored.

An investigation of the solid state electrical conductivity of the compounds reported in this thesis may also be undertaken. Very limited studies of this type have been undertaken on diazine-bridged transition metal complexes (307, 308). Such studies, on polycrystalline or pressed pellet samples, have shown that the presence of bridging diazine moieties leads to enhanced electrical conductivity. For example, Schneider and Hanack (307) have observed a 10$^6$-fold increase in conductivity on going from a monomeric pyrazine complex of iron(II) phthalocyanine to a pyrazine-bridged polymeric derivative (conductivity: $2 \times 10^{-12} \rightarrow 2 \times 10^6 \ \Omega^{-1} \ \text{cm}^{-1}$).
REFERENCES


Dalton Trans.* 1980, 2121.

New York, 1982; Vol. 29, p 203.


1988, 66, 348.


1991, 69, 432.


1974, 17.

Dalton Trans.* 1977, 1121.


1983, 252, 231.


(146) Reference 20 and references therein.


(210) Ref. 211 and references therein.


APPENDIX I
SINGLE CRYSTAL X-RAY DIFFRACTION DATA

I-1. Cu(mepyz)₂(NC0)₂⁺⁻³

Bond lengths involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-N(1)</td>
<td>2.080(4)</td>
<td>Cu(2)-N(7)</td>
<td>2.086(4)</td>
</tr>
<tr>
<td>Cu(1)-N(3)</td>
<td>2.067(4)</td>
<td>Cu(2)-N(9)</td>
<td>2.069(4)</td>
</tr>
<tr>
<td>Cu(1)-N(5)</td>
<td>1.927(4)</td>
<td>Cu(2)-N(11)</td>
<td>1.930(4)</td>
</tr>
<tr>
<td>Cu(1)-N(6)</td>
<td>1.939(4)</td>
<td>Cu(2)-N(12)</td>
<td>1.942(4)</td>
</tr>
<tr>
<td>Cu(1)-N(8)</td>
<td>2.672(4)</td>
<td>Cu(2)-N(2)²</td>
<td>2.647(4)</td>
</tr>
<tr>
<td>Cu(1)-N(10)</td>
<td>2.734(4)</td>
<td>Cu(2)-N(4)³</td>
<td>2.773(4)</td>
</tr>
<tr>
<td>O(1)-C(11)</td>
<td>1.190(6)</td>
<td>O(3)-C(23)</td>
<td>1.199(6)</td>
</tr>
<tr>
<td>O(2)-C(12)</td>
<td>1.186(6)</td>
<td>O(4)-C(24)</td>
<td>1.196(7)</td>
</tr>
<tr>
<td>N(1)-C(1)</td>
<td>1.334(6)</td>
<td>N(7)-C(13)</td>
<td>1.326(6)</td>
</tr>
<tr>
<td>N(1)-C(4)</td>
<td>1.346(6)</td>
<td>N(7)-C(16)</td>
<td>1.339(6)</td>
</tr>
<tr>
<td>N(2)-C(2)</td>
<td>1.325(6)</td>
<td>N(8)-C(14)</td>
<td>1.342(6)</td>
</tr>
<tr>
<td>N(2)-C(3)</td>
<td>1.339(6)</td>
<td>N(8)-C(15)</td>
<td>1.334(6)</td>
</tr>
<tr>
<td>N(3)-C(6)</td>
<td>1.329(6)</td>
<td>N(9)-C(18)</td>
<td>1.328(6)</td>
</tr>
<tr>
<td>N(3)-C(9)</td>
<td>1.340(6)</td>
<td>N(9)-C(21)</td>
<td>1.340(6)</td>
</tr>
<tr>
<td>N(4)-C(7)</td>
<td>1.344(6)</td>
<td>N(10)-C(19)</td>
<td>1.342(6)</td>
</tr>
<tr>
<td>N(4)-C(8)</td>
<td>1.324(6)</td>
<td>N(10)-C(20)</td>
<td>1.339(6)</td>
</tr>
<tr>
<td>N(5)-C(11)</td>
<td>1.167(6)</td>
<td>N(11)-C(23)</td>
<td>1.154(6)</td>
</tr>
<tr>
<td>N(6)-C(12)</td>
<td>1.147(6)</td>
<td>N(12)-C(24)</td>
<td>1.146(7)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.394(6)</td>
<td>C(13)-C(14)</td>
<td>1.403(6)</td>
</tr>
<tr>
<td>C(2)-C(5)</td>
<td>1.505(7)</td>
<td>C(14)-C(17)</td>
<td>1.491(6)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.364(7)</td>
<td>C(15)-C(16)</td>
<td>1.371(7)</td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td>1.391(6)</td>
<td>C(18)-C(19)</td>
<td>1.389(6)</td>
</tr>
<tr>
<td>C(7)-C(10)</td>
<td>1.498(6)</td>
<td>C(19)-C(22)</td>
<td>1.495(7)</td>
</tr>
<tr>
<td>C(8)-C(9)</td>
<td>1.378(7)</td>
<td>C(20)-C(21)</td>
<td>1.367(7)</td>
</tr>
</tbody>
</table>

a Unit cell parameters are given in Table 2-1.
b Estimated standard deviations in the least significant figure are given in parentheses.
c Superscripts refer to symmetry operations: (1) x-1, y-1, z; (2) 1+x, y, z;
(3) x, 1+y, z; (4) x-1, y, z; (5) x, y-1, z; (6) 1+x, 1+y, z.
d \( B_{eq} = (8/3)\pi^2\sum U_{ij}a_i^*a_j^*(a_i.a_j) \)
Bond angles involving nonhydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-Cu(1)-N(3)</td>
<td>176.9(2)</td>
<td>N(7)-Cu(2)-N(9)</td>
<td>178.6(1)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(5)</td>
<td>90.2(2)</td>
<td>N(7)-Cu(2)-N(11)</td>
<td>90.3(2)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(6)</td>
<td>89.4(2)</td>
<td>N(7)-Cu(2)-N(12)</td>
<td>89.2(2)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(8)</td>
<td>89.1(1)</td>
<td>N(7)-Cu(2)-N(2)</td>
<td>89.5(1)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(10)</td>
<td>96.0(1)</td>
<td>N(7)-Cu(2)-N(4)</td>
<td>93.7(1)</td>
</tr>
<tr>
<td>N(3)-Cu(1)-N(5)</td>
<td>91.1(2)</td>
<td>N(9)-Cu(2)-N(11)</td>
<td>91.0(2)</td>
</tr>
<tr>
<td>N(3)-Cu(1)-N(6)</td>
<td>89.6(2)</td>
<td>N(9)-Cu(2)-N(12)</td>
<td>89.5(2)</td>
</tr>
<tr>
<td>N(3)-Cu(1)-N(8)</td>
<td>88.0(1)</td>
<td>N(9)-Cu(2)-N(2)</td>
<td>89.7(1)</td>
</tr>
<tr>
<td>N(3)-Cu(1)-N(10)</td>
<td>86.9(1)</td>
<td>N(9)-Cu(2)-N(4)</td>
<td>87.1(1)</td>
</tr>
<tr>
<td>N(5)-Cu(1)-N(6)</td>
<td>173.1(2)</td>
<td>N(11)-Cu(2)-N(12)</td>
<td>175.7(2)</td>
</tr>
<tr>
<td>N(5)-Cu(1)-N(8)</td>
<td>93.7(2)</td>
<td>N(11)-Cu(2)-N(2)</td>
<td>92.8(2)</td>
</tr>
<tr>
<td>N(5)-Cu(1)-N(10)</td>
<td>85.0(2)</td>
<td>N(11)-Cu(2)-N(4)</td>
<td>85.7(2)</td>
</tr>
<tr>
<td>N(6)-Cu(1)-N(8)</td>
<td>93.2(2)</td>
<td>N(12)-Cu(2)-N(2)</td>
<td>91.5(2)</td>
</tr>
<tr>
<td>N(6)-Cu(1)-N(10)</td>
<td>88.2(2)</td>
<td>N(12)-Cu(2)-N(4)</td>
<td>90.0(2)</td>
</tr>
<tr>
<td>N(8)-Cu(1)-N(10)</td>
<td>174.7(1)</td>
<td>N(2)-Cu(2)-N(4)</td>
<td>176.5(1)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-C(1)</td>
<td>122.3(3)</td>
<td>Cu(2)-N(7)-C(13)</td>
<td>122.3(3)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-C(4)</td>
<td>120.6(3)</td>
<td>Cu(2)-N(7)-C(16)</td>
<td>120.4(3)</td>
</tr>
<tr>
<td>C(1)-N(1)-C(4)</td>
<td>117.0(4)</td>
<td>C(13)-N(7)-C(16)</td>
<td>117.1(4)</td>
</tr>
<tr>
<td>C(2)-N(2)-C(3)</td>
<td>115.7(4)</td>
<td>C(14)-N(8)-C(15)</td>
<td>116.0(4)</td>
</tr>
<tr>
<td>C(2)-N(2)-Cu(2)</td>
<td>132.4(3)</td>
<td>C(14)-N(8)-Cu(1)</td>
<td>129.6(3)</td>
</tr>
<tr>
<td>C(3)-N(2)-Cu(2)</td>
<td>111.2(3)</td>
<td>C(15)-N(8)-Cu(1)</td>
<td>113.8(3)</td>
</tr>
<tr>
<td>Cu(1)-N(3)-C(6)</td>
<td>121.8(3)</td>
<td>Cu(2)-N(9)-C(18)</td>
<td>121.9(3)</td>
</tr>
<tr>
<td>Cu(1)-N(3)-C(9)</td>
<td>121.5(3)</td>
<td>Cu(2)-N(9)-C(21)</td>
<td>122.1(3)</td>
</tr>
<tr>
<td>C(6)-N(3)-C(9)</td>
<td>116.6(4)</td>
<td>C(18)-N(9)-C(21)</td>
<td>116.0(4)</td>
</tr>
<tr>
<td>C(7)-N(4)-C(8)</td>
<td>117.2(4)</td>
<td>C(19)-N(10)-C(20)</td>
<td>117.0(4)</td>
</tr>
<tr>
<td>C(8)-N(4)-Cu(2)</td>
<td>110.7(3)</td>
<td>C(19)-N(10)-Cu(1)</td>
<td>133.1(3)</td>
</tr>
<tr>
<td>C(7)-N(4)-Cu(2)</td>
<td>130.5(3)</td>
<td>C(20)-N(10)-Cu(1)</td>
<td>108.3</td>
</tr>
<tr>
<td>Cu(1)-N(5)-C(11)</td>
<td>150.5(4)</td>
<td>Cu(2)-N(11)-C(23)</td>
<td>150.6(4)</td>
</tr>
<tr>
<td>Cu(1)-N(6)-C(12)</td>
<td>158.0(5)</td>
<td>Cu(2)-N(12)-C(24)</td>
<td>149.5(4)</td>
</tr>
<tr>
<td>N(1)-C(1)-C(2)</td>
<td>121.9(4)</td>
<td>N(7)-C(13)-C(14)</td>
<td>122.4(4)</td>
</tr>
<tr>
<td>N(2)-C(2)-C(1)</td>
<td>121.2(4)</td>
<td>N(8)-C(14)-C(13)</td>
<td>120.3(4)</td>
</tr>
<tr>
<td>N(2)-C(2)-C(5)</td>
<td>118.5(4)</td>
<td>N(8)-C(14)-C(17)</td>
<td>119.2(4)</td>
</tr>
<tr>
<td>C(1)-C(2)-C(5)</td>
<td>120.2(4)</td>
<td>C(13)-C(14)-C(17)</td>
<td>120.4(4)</td>
</tr>
<tr>
<td>N(2)-C(3)-C(4)</td>
<td>124.2(5)</td>
<td>N(8)-C(15)-C(16)</td>
<td>123.8(4)</td>
</tr>
<tr>
<td>N(1)-C(4)-C(3)</td>
<td>119.8(4)</td>
<td>N(7)-C(16)-C(15)</td>
<td>120.3(4)</td>
</tr>
<tr>
<td>N(3)-C(6)-C(7)</td>
<td>122.8(4)</td>
<td>N(9)-C(18)-C(19)</td>
<td>123.3(4)</td>
</tr>
<tr>
<td>N(4)-C(7)-C(6)</td>
<td>119.9(4)</td>
<td>N(10)-C(19)-C(18)</td>
<td>119.7(4)</td>
</tr>
<tr>
<td>N(4)-C(7)-C(10)</td>
<td>120.2(4)</td>
<td>N(10)-C(19)-C(22)</td>
<td>119.9(4)</td>
</tr>
<tr>
<td>C(6)-C(7)-C(10)</td>
<td>120.0(4)</td>
<td>C(18)-C(19)-C(22)</td>
<td>120.5(4)</td>
</tr>
<tr>
<td>N(4)-C(8)-C(9)</td>
<td>122.5(4)</td>
<td>N(10)-C(20)-C(21)</td>
<td>122.3(4)</td>
</tr>
<tr>
<td>N(3)-C(9)-C(8)</td>
<td>120.9(4)</td>
<td>N(9)-C(21)-C(20)</td>
<td>121.6(4)</td>
</tr>
<tr>
<td>O(1)-C(11)-N(5)</td>
<td>178.3(6)</td>
<td>O(3)-C(23)-N(11)</td>
<td>178.2(6)</td>
</tr>
<tr>
<td>O(2)-C(12)-N(6)</td>
<td>177.0(7)</td>
<td>O(4)-C(24)-N(12)</td>
<td>177.3(7)</td>
</tr>
</tbody>
</table>
### Bond lengths involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-H(1)</td>
<td>0.980</td>
<td>C(13)-H(13)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(3)-H(2)</td>
<td>0.980</td>
<td>C(15)-H(14)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(4)-H(3)</td>
<td>0.980</td>
<td>C(16)-H(15)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(5)-H(4)</td>
<td>0.980</td>
<td>C(17)-H(16)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(5)-H(5)</td>
<td>0.980</td>
<td>C(17)-H(17)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(6)-H(6)</td>
<td>0.980</td>
<td>C(17)-H(18)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(6)-H(7)</td>
<td>0.980</td>
<td>C(18)-H(19)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(8)-H(8)</td>
<td>0.980</td>
<td>C(19)-H(20)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(9)-H(9)</td>
<td>0.980</td>
<td>C(19)-H(21)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(10)-H(10)</td>
<td>0.980</td>
<td>C(19)-H(22)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(10)-H(11)</td>
<td>0.980</td>
<td>C(19)-H(23)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(10)-H(12)</td>
<td>0.980</td>
<td>C(19)-H(24)</td>
<td>0.980</td>
</tr>
</tbody>
</table>

### Bond angles involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(1)-H(1)</td>
<td>119.04</td>
<td>N(7)-C(13)-H(13)</td>
<td>118.81</td>
</tr>
<tr>
<td>C(2)-C(1)-H(1)</td>
<td>119.02</td>
<td>C(14)-C(13)-H(13)</td>
<td>118.79</td>
</tr>
<tr>
<td>N(2)-C(3)-H(2)</td>
<td>117.88</td>
<td>C(15)-C(15)-H(14)</td>
<td>118.08</td>
</tr>
<tr>
<td>C(4)-C(3)-H(2)</td>
<td>117.90</td>
<td>C(16)-C(15)-H(14)</td>
<td>118.07</td>
</tr>
<tr>
<td>N(1)-C(4)-H(3)</td>
<td>120.08</td>
<td>N(7)-C(16)-H(15)</td>
<td>119.83</td>
</tr>
<tr>
<td>C(3)-C(4)-H(3)</td>
<td>120.09</td>
<td>C(15)-C(16)-H(15)</td>
<td>119.84</td>
</tr>
<tr>
<td>C(2)-C(5)-H(4)</td>
<td>109.44</td>
<td>C(14)-C(17)-H(16)</td>
<td>109.46</td>
</tr>
<tr>
<td>C(2)-C(5)-H(5)</td>
<td>109.47</td>
<td>C(14)-C(17)-H(17)</td>
<td>109.46</td>
</tr>
<tr>
<td>C(2)-C(5)-H(6)</td>
<td>109.46</td>
<td>C(14)-C(17)-H(18)</td>
<td>109.48</td>
</tr>
<tr>
<td>H(4)-C(5)-H(5)</td>
<td>109.47</td>
<td>H(16)-C(17)-H(18)</td>
<td>109.47</td>
</tr>
<tr>
<td>H(4)-C(5)-H(6)</td>
<td>109.47</td>
<td>H(16)-C(17)-H(18)</td>
<td>109.47</td>
</tr>
<tr>
<td>H(5)-C(5)-H(6)</td>
<td>109.51</td>
<td>H(17)-C(17)-H(18)</td>
<td>109.49</td>
</tr>
<tr>
<td>N(3)-C(6)-H(7)</td>
<td>118.61</td>
<td>N(9)-C(18)-H(19)</td>
<td>118.34</td>
</tr>
<tr>
<td>C(7)-C(6)-H(7)</td>
<td>118.62</td>
<td>C(19)-C(18)-H(19)</td>
<td>118.32</td>
</tr>
<tr>
<td>N(4)-C(8)-H(8)</td>
<td>118.75</td>
<td>N(10)-C(20)-H(20)</td>
<td>118.85</td>
</tr>
<tr>
<td>C(9)-C(8)-H(8)</td>
<td>118.74</td>
<td>C(21)-C(20)-H(20)</td>
<td>118.82</td>
</tr>
<tr>
<td>N(3)-C(9)-H(9)</td>
<td>119.54</td>
<td>N(9)-C(21)-H(21)</td>
<td>119.21</td>
</tr>
<tr>
<td>C(8)-C(9)-H(9)</td>
<td>119.52</td>
<td>C(20)-C(21)-H(21)</td>
<td>119.23</td>
</tr>
<tr>
<td>C(7)-C(10)-H(10)</td>
<td>109.46</td>
<td>C(19)-C(22)-H(22)</td>
<td>109.46</td>
</tr>
<tr>
<td>C(7)-C(10)-H(11)</td>
<td>109.45</td>
<td>C(19)-C(22)-H(23)</td>
<td>109.46</td>
</tr>
<tr>
<td>C(7)-C(10)-H(12)</td>
<td>109.45</td>
<td>C(19)-C(22)-H(24)</td>
<td>109.44</td>
</tr>
<tr>
<td>H(10)-C(10)-H(11)</td>
<td>109.48</td>
<td>H(22)-C(22)-H(23)</td>
<td>109.50</td>
</tr>
<tr>
<td>H(10)-C(10)-H(12)</td>
<td>109.50</td>
<td>H(22)-C(22)-H(24)</td>
<td>109.49</td>
</tr>
<tr>
<td>H(11)-C(10)-H(12)</td>
<td>109.47</td>
<td>H(23)-C(22)-H(24)</td>
<td>109.48</td>
</tr>
</tbody>
</table>
Final atomic coordinates (fractional) and $B_{eq}$ (Å$^2$) for non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>0.01986(7)</td>
<td>0.17501(6)</td>
<td>0.14276(3)</td>
<td>3.52(3)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.1038(4)</td>
<td>0.1120(4)</td>
<td>-0.0147(1)</td>
<td>5.1(2)</td>
</tr>
<tr>
<td>O(2)</td>
<td>-0.0172(5)</td>
<td>0.1444(6)</td>
<td>0.3085(2)</td>
<td>9.2(3)</td>
</tr>
<tr>
<td>N(1)</td>
<td>-0.1053(4)</td>
<td>0.3257(3)</td>
<td>0.1406(1)</td>
<td>3.2(2)</td>
</tr>
<tr>
<td>N(2)</td>
<td>-0.2794(4)</td>
<td>0.5227(4)</td>
<td>0.1364(2)</td>
<td>3.7(2)</td>
</tr>
<tr>
<td>N(3)</td>
<td>0.1364(3)</td>
<td>0.0193(3)</td>
<td>0.1463(1)</td>
<td>3.2(1)</td>
</tr>
<tr>
<td>N(4)</td>
<td>0.3030(4)</td>
<td>-0.1824(4)</td>
<td>0.1460(2)</td>
<td>3.6(2)</td>
</tr>
<tr>
<td>N(5)</td>
<td>0.0249(4)</td>
<td>0.1820(4)</td>
<td>0.0660(2)</td>
<td>3.8(2)</td>
</tr>
<tr>
<td>N(6)</td>
<td>0.0313(4)</td>
<td>0.1825(4)</td>
<td>0.2204(2)</td>
<td>4.6(2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>-0.1048(4)</td>
<td>0.4137(4)</td>
<td>0.1029(2)</td>
<td>3.6(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>-0.1922(4)</td>
<td>0.5119(4)</td>
<td>0.1006(2)</td>
<td>3.5(2)</td>
</tr>
<tr>
<td>C(3)</td>
<td>-0.2797(5)</td>
<td>0.4319(5)</td>
<td>0.1731(2)</td>
<td>4.2(2)</td>
</tr>
<tr>
<td>C(4)</td>
<td>-0.1947(5)</td>
<td>0.3355(5)</td>
<td>0.1766(2)</td>
<td>4.0(2)</td>
</tr>
<tr>
<td>C(5)</td>
<td>-0.1886(5)</td>
<td>0.6090(6)</td>
<td>0.0574(2)</td>
<td>5.2(3)</td>
</tr>
<tr>
<td>C(6)</td>
<td>0.1145(4)</td>
<td>-0.0775(4)</td>
<td>0.1138(2)</td>
<td>3.2(2)</td>
</tr>
<tr>
<td>C(7)</td>
<td>0.1955(4)</td>
<td>-0.1802(4)</td>
<td>0.1136(2)</td>
<td>3.4(2)</td>
</tr>
<tr>
<td>C(8)</td>
<td>0.3238(5)</td>
<td>-0.0866(5)</td>
<td>0.1789(2)</td>
<td>3.8(2)</td>
</tr>
<tr>
<td>C(9)</td>
<td>0.2411(5)</td>
<td>0.0133(4)</td>
<td>0.1800(2)</td>
<td>3.6(2)</td>
</tr>
<tr>
<td>C(10)</td>
<td>0.1626(5)</td>
<td>-0.2883(5)</td>
<td>0.0773(2)</td>
<td>4.4(2)</td>
</tr>
<tr>
<td>C(11)</td>
<td>0.0645(5)</td>
<td>0.1460(4)</td>
<td>0.0263(2)</td>
<td>3.5(2)</td>
</tr>
<tr>
<td>C(12)</td>
<td>0.0055(5)</td>
<td>0.1619(5)</td>
<td>0.2633(2)</td>
<td>4.4(2)</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>0.52126(7)</td>
<td>0.67233(6)</td>
<td>0.14248(3)</td>
<td>3.54(3)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.3920(4)</td>
<td>0.6140(4)</td>
<td>-0.0159(1)</td>
<td>5.4(2)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.4509(5)</td>
<td>0.6674(6)</td>
<td>0.3035(2)</td>
<td>9.1(3)</td>
</tr>
<tr>
<td>N(7)</td>
<td>0.6433(4)</td>
<td>0.8260(3)</td>
<td>0.1423(1)</td>
<td>3.3(2)</td>
</tr>
<tr>
<td>N(8)</td>
<td>0.8189(4)</td>
<td>1.0211(4)</td>
<td>0.1392(2)</td>
<td>3.4(2)</td>
</tr>
<tr>
<td>N(9)</td>
<td>0.4027(3)</td>
<td>0.5184(4)</td>
<td>0.1444(1)</td>
<td>3.3(2)</td>
</tr>
<tr>
<td>N(10)</td>
<td>0.2389(4)</td>
<td>0.3138(4)</td>
<td>0.1441(2)</td>
<td>3.5(2)</td>
</tr>
<tr>
<td>N(11)</td>
<td>0.4928(4)</td>
<td>0.6831(4)</td>
<td>0.0656(2)</td>
<td>3.8(2)</td>
</tr>
<tr>
<td>N(12)</td>
<td>0.5400(4)</td>
<td>0.6710(4)</td>
<td>0.2202(2)</td>
<td>4.4(2)</td>
</tr>
<tr>
<td>C(13)</td>
<td>0.6342(4)</td>
<td>0.9116(4)</td>
<td>0.1040(2)</td>
<td>3.5(2)</td>
</tr>
<tr>
<td>C(14)</td>
<td>0.7215(4)</td>
<td>1.0105(4)</td>
<td>0.1018(2)</td>
<td>3.4(2)</td>
</tr>
<tr>
<td>C(15)</td>
<td>0.8271(5)</td>
<td>0.9324(5)</td>
<td>0.1766(2)</td>
<td>3.9(2)</td>
</tr>
<tr>
<td>C(16)</td>
<td>0.7414(5)</td>
<td>0.8364(5)</td>
<td>0.1792(2)</td>
<td>3.7(2)</td>
</tr>
<tr>
<td>C(17)</td>
<td>0.7064(5)</td>
<td>1.1054(5)</td>
<td>0.0583(2)</td>
<td>5.0(3)</td>
</tr>
<tr>
<td>C(18)</td>
<td>0.4173(4)</td>
<td>0.4198(4)</td>
<td>0.1132(2)</td>
<td>3.3(2)</td>
</tr>
<tr>
<td>C(19)</td>
<td>0.3380(4)</td>
<td>0.3159(4)</td>
<td>0.1128(2)</td>
<td>3.5(2)</td>
</tr>
<tr>
<td>C(20)</td>
<td>0.2239(5)</td>
<td>0.4132(5)</td>
<td>0.1754(2)</td>
<td>3.7(2)</td>
</tr>
<tr>
<td>C(21)</td>
<td>0.3046(4)</td>
<td>0.5134(4)</td>
<td>0.1760(2)</td>
<td>3.6(2)</td>
</tr>
<tr>
<td>C(22)</td>
<td>0.3630(5)</td>
<td>0.2062(5)</td>
<td>0.0781(2)</td>
<td>4.6(2)</td>
</tr>
<tr>
<td>C(23)</td>
<td>0.4440(5)</td>
<td>0.6476(4)</td>
<td>0.0258(2)</td>
<td>3.5(2)</td>
</tr>
<tr>
<td>C(24)</td>
<td>0.4942(5)</td>
<td>0.6703(6)</td>
<td>0.2605(2)</td>
<td>4.5(3)</td>
</tr>
</tbody>
</table>
Hydrogen atom coordinates (fractional) and isotropic thermal parameters (Å²).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B&lt;sub&gt;iso&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>-0.0410</td>
<td>0.4093</td>
<td>0.0761</td>
<td>4.3</td>
</tr>
<tr>
<td>H(2)</td>
<td>-0.3453</td>
<td>0.4351</td>
<td>0.1992</td>
<td>5.1</td>
</tr>
<tr>
<td>H(3)</td>
<td>-0.1987</td>
<td>0.2734</td>
<td>0.2052</td>
<td>4.8</td>
</tr>
<tr>
<td>H(4)</td>
<td>-0.1731</td>
<td>0.6912</td>
<td>0.0737</td>
<td>6.2</td>
</tr>
<tr>
<td>H(5)</td>
<td>-0.1196</td>
<td>0.5893</td>
<td>0.0342</td>
<td>6.2</td>
</tr>
<tr>
<td>H(6)</td>
<td>-0.2705</td>
<td>0.6097</td>
<td>0.0361</td>
<td>6.2</td>
</tr>
<tr>
<td>H(7)</td>
<td>0.0382</td>
<td>-0.0764</td>
<td>0.0890</td>
<td>3.9</td>
</tr>
<tr>
<td>H(8)</td>
<td>0.4009</td>
<td>-0.0867</td>
<td>0.2033</td>
<td>4.5</td>
</tr>
<tr>
<td>H(9)</td>
<td>0.2592</td>
<td>0.0808</td>
<td>0.2058</td>
<td>4.3</td>
</tr>
<tr>
<td>H(10)</td>
<td>0.0825</td>
<td>-0.2708</td>
<td>0.0561</td>
<td>5.2</td>
</tr>
<tr>
<td>H(11)</td>
<td>0.2314</td>
<td>-0.3011</td>
<td>0.0532</td>
<td>5.2</td>
</tr>
<tr>
<td>H(12)</td>
<td>0.1525</td>
<td>-0.3636</td>
<td>0.0988</td>
<td>5.2</td>
</tr>
<tr>
<td>H(13)</td>
<td>0.5640</td>
<td>0.9057</td>
<td>0.0763</td>
<td>4.2</td>
</tr>
<tr>
<td>H(14)</td>
<td>0.8985</td>
<td>0.9362</td>
<td>0.2039</td>
<td>4.7</td>
</tr>
<tr>
<td>H(15)</td>
<td>0.7520</td>
<td>0.7749</td>
<td>0.2081</td>
<td>4.4</td>
</tr>
<tr>
<td>H(16)</td>
<td>0.7836</td>
<td>1.1068</td>
<td>0.0383</td>
<td>6.0</td>
</tr>
<tr>
<td>H(17)</td>
<td>0.6324</td>
<td>1.0840</td>
<td>0.0341</td>
<td>6.0</td>
</tr>
<tr>
<td>H(18)</td>
<td>0.6933</td>
<td>1.1878</td>
<td>0.0740</td>
<td>6.0</td>
</tr>
<tr>
<td>H(19)</td>
<td>0.4876</td>
<td>0.4204</td>
<td>0.0893</td>
<td>4.0</td>
</tr>
<tr>
<td>H(20)</td>
<td>0.1524</td>
<td>0.4142</td>
<td>0.1988</td>
<td>4.5</td>
</tr>
<tr>
<td>H(21)</td>
<td>0.2905</td>
<td>0.5833</td>
<td>0.2002</td>
<td>4.3</td>
</tr>
<tr>
<td>H(22)</td>
<td>0.3783</td>
<td>0.1321</td>
<td>0.1006</td>
<td>5.5</td>
</tr>
<tr>
<td>H(23)</td>
<td>0.2886</td>
<td>0.1919</td>
<td>0.0530</td>
<td>5.5</td>
</tr>
<tr>
<td>H(24)</td>
<td>0.4384</td>
<td>0.2228</td>
<td>0.0581</td>
<td>5.5</td>
</tr>
</tbody>
</table>
Anisotropic thermal parameters $\times 10^3$

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>53.9(4)</td>
<td>40.4(4)</td>
<td>39.3(4)</td>
<td>12.2(3)</td>
<td>0.9(3)</td>
<td>-1.1(3)</td>
</tr>
<tr>
<td>O(1)</td>
<td>71(3)</td>
<td>73(3)</td>
<td>51(2)</td>
<td>-5(2)</td>
<td>12(2)</td>
<td>-12(2)</td>
</tr>
<tr>
<td>O(2)</td>
<td>112(4)</td>
<td>175(6)</td>
<td>63(3)</td>
<td>-27(4)</td>
<td>24(3)</td>
<td>24(3)</td>
</tr>
<tr>
<td>N(1)</td>
<td>44(2)</td>
<td>35(2)</td>
<td>44(2)</td>
<td>5(2)</td>
<td>2(2)</td>
<td>1(2)</td>
</tr>
<tr>
<td>N(2)</td>
<td>44(2)</td>
<td>42(2)</td>
<td>54(2)</td>
<td>-2(2)</td>
<td>3(2)</td>
<td>2(2)</td>
</tr>
<tr>
<td>N(3)</td>
<td>44(2)</td>
<td>31(2)</td>
<td>45(2)</td>
<td>7(2)</td>
<td>-1(2)</td>
<td>-1(2)</td>
</tr>
<tr>
<td>N(4)</td>
<td>49(2)</td>
<td>40(2)</td>
<td>48(2)</td>
<td>6(2)</td>
<td>-4(2)</td>
<td>-3(2)</td>
</tr>
<tr>
<td>N(5)</td>
<td>52(2)</td>
<td>50(2)</td>
<td>43(2)</td>
<td>6(2)</td>
<td>3(2)</td>
<td>1(2)</td>
</tr>
<tr>
<td>N(6)</td>
<td>68(3)</td>
<td>63(3)</td>
<td>42(2)</td>
<td>14(2)</td>
<td>4(2)</td>
<td>-2(2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>46(3)</td>
<td>40(2)</td>
<td>50(3)</td>
<td>2(2)</td>
<td>7(2)</td>
<td>-1(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>42(2)</td>
<td>36(2)</td>
<td>55(3)</td>
<td>-3(2)</td>
<td>2(2)</td>
<td>5(2)</td>
</tr>
<tr>
<td>C(3)</td>
<td>51(3)</td>
<td>55(3)</td>
<td>55(3)</td>
<td>11(2)</td>
<td>7(2)</td>
<td>10(2)</td>
</tr>
<tr>
<td>C(4)</td>
<td>56(3)</td>
<td>52(3)</td>
<td>44(3)</td>
<td>12(2)</td>
<td>23(3)</td>
<td>10(2)</td>
</tr>
<tr>
<td>C(5)</td>
<td>54(3)</td>
<td>63(4)</td>
<td>82(4)</td>
<td>7(3)</td>
<td>19(3)</td>
<td>10(2)</td>
</tr>
<tr>
<td>C(6)</td>
<td>41(2)</td>
<td>39(2)</td>
<td>42(2)</td>
<td>2(2)</td>
<td>-2(2)</td>
<td>-1(2)</td>
</tr>
<tr>
<td>C(7)</td>
<td>41(2)</td>
<td>42(2)</td>
<td>44(2)</td>
<td>2(2)</td>
<td>-1(2)</td>
<td>-2(2)</td>
</tr>
<tr>
<td>C(8)</td>
<td>50(3)</td>
<td>45(3)</td>
<td>47(3)</td>
<td>5(2)</td>
<td>-9(2)</td>
<td>-7(2)</td>
</tr>
<tr>
<td>C(9)</td>
<td>47(2)</td>
<td>42(2)</td>
<td>45(2)</td>
<td>3(2)</td>
<td>-5(2)</td>
<td>-4(2)</td>
</tr>
<tr>
<td>C(10)</td>
<td>52(3)</td>
<td>47(3)</td>
<td>65(3)</td>
<td>11(2)</td>
<td>-9(2)</td>
<td>-15(2)</td>
</tr>
<tr>
<td>C(11)</td>
<td>47(3)</td>
<td>39(3)</td>
<td>46(3)</td>
<td>2(2)</td>
<td>-5(2)</td>
<td>-1(2)</td>
</tr>
<tr>
<td>C(12)</td>
<td>54(3)</td>
<td>65(4)</td>
<td>47(3)</td>
<td>-10(3)</td>
<td>0(2)</td>
<td>-1(3)</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>53.5(4)</td>
<td>40.0(4)</td>
<td>40.4(4)</td>
<td>-13.4(3)</td>
<td>-1.3(3)</td>
<td>1.4(3)</td>
</tr>
<tr>
<td>O(3)</td>
<td>75(3)</td>
<td>80(3)</td>
<td>47(2)</td>
<td>6(2)</td>
<td>-9(2)</td>
<td>-14(2)</td>
</tr>
<tr>
<td>O(4)</td>
<td>96(4)</td>
<td>189(6)</td>
<td>64(3)</td>
<td>18(4)</td>
<td>25(3)</td>
<td>-10(4)</td>
</tr>
<tr>
<td>N(7)</td>
<td>46(2)</td>
<td>36(2)</td>
<td>43(2)</td>
<td>-8(2)</td>
<td>-1(2)</td>
<td>2(2)</td>
</tr>
<tr>
<td>N(8)</td>
<td>43(2)</td>
<td>37(2)</td>
<td>49(2)</td>
<td>1(2)</td>
<td>2(2)</td>
<td>1(2)</td>
</tr>
<tr>
<td>N(9)</td>
<td>41(2)</td>
<td>41(2)</td>
<td>45(2)</td>
<td>-10(2)</td>
<td>-1(2)</td>
<td>2(2)</td>
</tr>
<tr>
<td>N(10)</td>
<td>45(2)</td>
<td>40(2)</td>
<td>49(2)</td>
<td>-8(2)</td>
<td>6(2)</td>
<td>0(2)</td>
</tr>
<tr>
<td>N(11)</td>
<td>50(2)</td>
<td>46(2)</td>
<td>47(2)</td>
<td>-1(2)</td>
<td>4(2)</td>
<td>4(2)</td>
</tr>
<tr>
<td>N(12)</td>
<td>60(3)</td>
<td>63(3)</td>
<td>43(2)</td>
<td>-14(2)</td>
<td>-2(2)</td>
<td>4(2)</td>
</tr>
<tr>
<td>C(13)</td>
<td>45(3)</td>
<td>39(2)</td>
<td>47(2)</td>
<td>-1(2)</td>
<td>-3(2)</td>
<td>1(2)</td>
</tr>
<tr>
<td>C(14)</td>
<td>40(2)</td>
<td>41(2)</td>
<td>49(2)</td>
<td>3(2)</td>
<td>6(2)</td>
<td>6(2)</td>
</tr>
<tr>
<td>C(15)</td>
<td>45(3)</td>
<td>51(3)</td>
<td>52(3)</td>
<td>-11(2)</td>
<td>5(2)</td>
<td>4(2)</td>
</tr>
<tr>
<td>C(16)</td>
<td>48(3)</td>
<td>46(3)</td>
<td>46(3)</td>
<td>-5(2)</td>
<td>-4(2)</td>
<td>4(2)</td>
</tr>
<tr>
<td>C(17)</td>
<td>54(3)</td>
<td>54(3)</td>
<td>78(4)</td>
<td>-7(3)</td>
<td>-7(3)</td>
<td>30(3)</td>
</tr>
<tr>
<td>C(18)</td>
<td>42(2)</td>
<td>41(2)</td>
<td>44(2)</td>
<td>-4(2)</td>
<td>1(2)</td>
<td>-1(2)</td>
</tr>
<tr>
<td>C(19)</td>
<td>44(2)</td>
<td>40(2)</td>
<td>49(3)</td>
<td>-2(2)</td>
<td>2(2)</td>
<td>1(2)</td>
</tr>
<tr>
<td>C(20)</td>
<td>46(3)</td>
<td>53(3)</td>
<td>44(2)</td>
<td>-8(2)</td>
<td>7(2)</td>
<td>-2(2)</td>
</tr>
<tr>
<td>C(21)</td>
<td>48(3)</td>
<td>40(3)</td>
<td>49(3)</td>
<td>0(2)</td>
<td>11(2)</td>
<td>-6(2)</td>
</tr>
<tr>
<td>C(22)</td>
<td>55(3)</td>
<td>47(3)</td>
<td>74(4)</td>
<td>-14(2)</td>
<td>17(3)</td>
<td>-17(3)</td>
</tr>
<tr>
<td>C(23)</td>
<td>47(3)</td>
<td>41(2)</td>
<td>45(3)</td>
<td>3(2)</td>
<td>7(2)</td>
<td>6(2)</td>
</tr>
<tr>
<td>C(24)</td>
<td>54(3)</td>
<td>65(4)</td>
<td>49(3)</td>
<td>9(3)</td>
<td>-2(2)</td>
<td>-3(3)</td>
</tr>
</tbody>
</table>
I-2. \[\text{[Cu(pdz)₄(NO₃)] [NO₃]} \]^{a,b,c}

Bond lengths involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-O(1)</td>
<td>2.217(2)</td>
<td>N(5)-C(9)</td>
<td>1.316(3)</td>
</tr>
<tr>
<td>Cu(1)-N(1)</td>
<td>2.014(2)</td>
<td>N(6)-C(12)</td>
<td>1.324(4)</td>
</tr>
<tr>
<td>Cu(1)-N(3)</td>
<td>2.021(2)</td>
<td>N(7)-N(8)</td>
<td>1.339(3)</td>
</tr>
<tr>
<td>Cu(1)-N(5)</td>
<td>2.029(2)</td>
<td>N(7)-C(13)</td>
<td>1.325(3)</td>
</tr>
<tr>
<td>Cu(1)-N(7)</td>
<td>2.018(2)</td>
<td>N(8)-C(16)</td>
<td>1.322(4)</td>
</tr>
<tr>
<td>O(1)-N(9)</td>
<td>1.270(3)</td>
<td>C(1)-C(2)</td>
<td>1.390(4)</td>
</tr>
<tr>
<td>O(2)-N(9)</td>
<td>1.228(3)</td>
<td>C(2)-C(3)</td>
<td>1.348(4)</td>
</tr>
<tr>
<td>O(3)-N(9)</td>
<td>1.231(3)</td>
<td>C(3)-C(4)</td>
<td>1.376(4)</td>
</tr>
<tr>
<td>O(4)-N(10)</td>
<td>1.213(3)</td>
<td>C(5)-C(6)</td>
<td>1.396(4)</td>
</tr>
<tr>
<td>O(5)-N(10)</td>
<td>1.208(3)</td>
<td>C(6)-C(7)</td>
<td>1.350(5)</td>
</tr>
<tr>
<td>O(6)-N(10)</td>
<td>1.221(4)</td>
<td>C(7)-C(8)</td>
<td>1.375(5)</td>
</tr>
<tr>
<td>N(1)-N(2)</td>
<td>1.339(3)</td>
<td>C(9)-C(10)</td>
<td>1.390(4)</td>
</tr>
<tr>
<td>N(1)-C(1)</td>
<td>1.320(3)</td>
<td>C(10)-C(11)</td>
<td>1.344(4)</td>
</tr>
<tr>
<td>N(2)-C(4)</td>
<td>1.320(3)</td>
<td>C(11)-C(12)</td>
<td>1.378(5)</td>
</tr>
<tr>
<td>N(3)-N(4)</td>
<td>1.339(3)</td>
<td>C(13)-C(14)</td>
<td>1.381(4)</td>
</tr>
<tr>
<td>N(3)-C(5)</td>
<td>1.309(3)</td>
<td>C(14)-C(15)</td>
<td>1.356(4)</td>
</tr>
<tr>
<td>N(4)-C(8)</td>
<td>1.319(4)</td>
<td>C(15)-C(16)</td>
<td>1.385(4)</td>
</tr>
<tr>
<td>N(5)-N(6)</td>
<td>1.335(3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Unit cell parameters are given in Table 2-8.
\(^b\) Estimated standard deviations in the least significant figure are given in parentheses.
\(^c\) \(B_{eq} = (8/3) \pi^2 \sum \epsilon U_{ij} a_i^* a_j^* (a_i, a_j)\).
### Bond angles involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-Cu(1)-N(1)</td>
<td>99.54(7)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(3)</td>
<td>109.68(8)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(5)</td>
<td>88.82(7)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(7)</td>
<td>94.47(7)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(3)</td>
<td>150.46(8)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(5)</td>
<td>88.00(8)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(7)</td>
<td>89.39(7)</td>
</tr>
<tr>
<td>N(3)-Cu(1)-N(5)</td>
<td>88.33(8)</td>
</tr>
<tr>
<td>N(3)-Cu(1)-N(7)</td>
<td>92.52(8)</td>
</tr>
<tr>
<td>N(5)-Cu(1)-N(7)</td>
<td>176.10(8)</td>
</tr>
<tr>
<td>Cu(1)-O(1)-N(9)</td>
<td>121.0(1)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-N(2)</td>
<td>113.1(1)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-C(1)</td>
<td>125.4(2)</td>
</tr>
<tr>
<td>N(2)-N(1)-C(1)</td>
<td>121.4(2)</td>
</tr>
<tr>
<td>N(1)-N(2)-C(4)</td>
<td>117.5(2)</td>
</tr>
<tr>
<td>Cu(1)-N(3)-N(4)</td>
<td>109.1(2)</td>
</tr>
<tr>
<td>Cu(1)-N(3)-C(5)</td>
<td>129.2(2)</td>
</tr>
<tr>
<td>N(4)-N(3)-C(5)</td>
<td>121.7(2)</td>
</tr>
<tr>
<td>N(3)-N(4)-C(8)</td>
<td>117.9(3)</td>
</tr>
<tr>
<td>Cu(1)-N(5)-N(6)</td>
<td>113.4(2)</td>
</tr>
<tr>
<td>Cu(1)-N(5)-C(9)</td>
<td>125.7(2)</td>
</tr>
<tr>
<td>N(6)-N(5)-C(9)</td>
<td>120.9(2)</td>
</tr>
<tr>
<td>N(5)-N(6)-C(12)</td>
<td>117.8(2)</td>
</tr>
<tr>
<td>Cu(1)-N(7)-N(8)</td>
<td>113.7(1)</td>
</tr>
<tr>
<td>Cu(1)-N(7)-C(13)</td>
<td>125.9(2)</td>
</tr>
<tr>
<td>N(8)-N(7)-C(13)</td>
<td>120.4(2)</td>
</tr>
<tr>
<td>N(7)-N(8)-C(16)</td>
<td>118.1(2)</td>
</tr>
<tr>
<td>O(1)-N(9)-O(2)</td>
<td>119.9(2)</td>
</tr>
<tr>
<td>O(1)-N(9)-O(3)</td>
<td>119.0(2)</td>
</tr>
<tr>
<td>O(2)-N(9)-O(3)</td>
<td>121.1(2)</td>
</tr>
<tr>
<td>O(4)-N(10)-O(5)</td>
<td>122.4(3)</td>
</tr>
<tr>
<td>O(4)-N(10)-O(6)</td>
<td>116.1(3)</td>
</tr>
<tr>
<td>O(5)-N(10)-O(6)</td>
<td>121.0(3)</td>
</tr>
<tr>
<td>N(1)-C(1)-C(2)</td>
<td>121.4(2)</td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)</td>
<td>117.9(2)</td>
</tr>
<tr>
<td>C(2)-C(3)-C(4)</td>
<td>117.7(3)</td>
</tr>
<tr>
<td>N(2)-C(4)-C(3)</td>
<td>124.0(3)</td>
</tr>
<tr>
<td>N(3)-C(5)-C(6)</td>
<td>121.2(3)</td>
</tr>
<tr>
<td>C(5)-C(6)-C(7)</td>
<td>117.9(3)</td>
</tr>
<tr>
<td>C(6)-C(7)-C(8)</td>
<td>117.8(3)</td>
</tr>
<tr>
<td>N(4)-C(8)-C(7)</td>
<td>123.6(3)</td>
</tr>
<tr>
<td>N(5)-C(9)-C(10)</td>
<td>122.2(3)</td>
</tr>
<tr>
<td>C(9)-C(10)-C(11)</td>
<td>117.4(3)</td>
</tr>
<tr>
<td>C(10)-C(11)-C(12)</td>
<td>117.9(3)</td>
</tr>
<tr>
<td>N(6)-C(12)-C(11)</td>
<td>123.8(3)</td>
</tr>
<tr>
<td>N(7)-C(13)-C(14)</td>
<td>122.5(2)</td>
</tr>
<tr>
<td>C(13)-C(14)-C(15)</td>
<td>117.8(2)</td>
</tr>
<tr>
<td>C(14)-C(15)-C(16)</td>
<td>117.2(3)</td>
</tr>
<tr>
<td>N(8)-C(16)-C(15)</td>
<td>124.0(3)</td>
</tr>
</tbody>
</table>

### Bond lengths involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-H(1)</td>
<td>0.95(3)</td>
</tr>
<tr>
<td>C(2)-H(2)</td>
<td>0.83(3)</td>
</tr>
<tr>
<td>C(3)-H(3)</td>
<td>0.92(3)</td>
</tr>
<tr>
<td>C(4)-H(4)</td>
<td>0.86(3)</td>
</tr>
<tr>
<td>C(5)-H(5)</td>
<td>0.94(3)</td>
</tr>
<tr>
<td>C(6)-H(6)</td>
<td>0.94(4)</td>
</tr>
<tr>
<td>C(7)-H(7)</td>
<td>0.88(4)</td>
</tr>
<tr>
<td>C(8)-H(8)</td>
<td>0.96(4)</td>
</tr>
<tr>
<td>C(9)-H(9)</td>
<td>0.96(3)</td>
</tr>
<tr>
<td>C(10)-H(10)</td>
<td>0.90(3)</td>
</tr>
<tr>
<td>C(11)-H(11)</td>
<td>0.94(3)</td>
</tr>
<tr>
<td>C(12)-H(12)</td>
<td>1.02(4)</td>
</tr>
<tr>
<td>C(13)-H(13)</td>
<td>0.95(3)</td>
</tr>
<tr>
<td>C(14)-H(14)</td>
<td>0.98(3)</td>
</tr>
<tr>
<td>C(15)-H(15)</td>
<td>0.92(3)</td>
</tr>
<tr>
<td>C(16)-H(16)</td>
<td>0.83(3)</td>
</tr>
</tbody>
</table>
Bond angles involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(1)-H(1)</td>
<td>115(2)</td>
</tr>
<tr>
<td>C(2)-C(1)-H(1)</td>
<td>123(2)</td>
</tr>
<tr>
<td>C(1)-C(2)-H(2)</td>
<td>119(2)</td>
</tr>
<tr>
<td>C(3)-C(2)-H(2)</td>
<td>123(2)</td>
</tr>
<tr>
<td>C(2)-C(3)-H(3)</td>
<td>122(2)</td>
</tr>
<tr>
<td>C(4)-C(3)-H(3)</td>
<td>121(2)</td>
</tr>
<tr>
<td>N(2)-C(4)-H(4)</td>
<td>115(2)</td>
</tr>
<tr>
<td>C(3)-C(4)-H(4)</td>
<td>121(2)</td>
</tr>
<tr>
<td>N(3)-C(5)-H(5)</td>
<td>114(2)</td>
</tr>
<tr>
<td>C(6)-C(5)-H(5)</td>
<td>125(2)</td>
</tr>
<tr>
<td>C(5)-C(6)-H(6)</td>
<td>114(2)</td>
</tr>
<tr>
<td>C(7)-C(6)-H(6)</td>
<td>128(2)</td>
</tr>
<tr>
<td>C(6)-C(7)-H(7)</td>
<td>126(3)</td>
</tr>
<tr>
<td>C(8)-C(7)-H(7)</td>
<td>116(3)</td>
</tr>
<tr>
<td>N(4)-C(8)-H(8)</td>
<td>120(2)</td>
</tr>
<tr>
<td>C(7)-C(8)-H(8)</td>
<td>117(2)</td>
</tr>
<tr>
<td>N(5)-C(9)-H(9)</td>
<td>113(2)</td>
</tr>
<tr>
<td>C(10)-C(9)-H(9)</td>
<td>124(2)</td>
</tr>
<tr>
<td>C(9)-C(10)-H(10)</td>
<td>118(2)</td>
</tr>
<tr>
<td>C(11)-C(10)-H(10)</td>
<td>125(2)</td>
</tr>
<tr>
<td>C(10)-C(11)-H(11)</td>
<td>121(2)</td>
</tr>
<tr>
<td>C(12)-C(11)-H(11)</td>
<td>121(2)</td>
</tr>
<tr>
<td>N(6)-C(12)-H(12)</td>
<td>115(2)</td>
</tr>
<tr>
<td>C(11)-C(12)-H(12)</td>
<td>121(2)</td>
</tr>
<tr>
<td>N(7)-C(13)-H(13)</td>
<td>115(2)</td>
</tr>
<tr>
<td>C(14)-C(13)-H(13)</td>
<td>123(2)</td>
</tr>
<tr>
<td>C(13)-C(14)-H(14)</td>
<td>117(2)</td>
</tr>
<tr>
<td>C(15)-C(14)-H(14)</td>
<td>125(2)</td>
</tr>
<tr>
<td>C(16)-C(15)-H(15)</td>
<td>119(2)</td>
</tr>
<tr>
<td>C(15)-C(16)-H(16)</td>
<td>113(2)</td>
</tr>
<tr>
<td>C(1)-H(1)-O(6)</td>
<td></td>
</tr>
<tr>
<td>C(2)-C(3)-H(3)</td>
<td></td>
</tr>
<tr>
<td>C(4)-C(5)-H(5)</td>
<td></td>
</tr>
<tr>
<td>C(6)-C(7)-H(7)</td>
<td></td>
</tr>
<tr>
<td>C(8)-C(9)-H(9)</td>
<td></td>
</tr>
<tr>
<td>C(10)-C(11)-H(11)</td>
<td></td>
</tr>
<tr>
<td>C(12)-H(12)-O(4)</td>
<td></td>
</tr>
<tr>
<td>O(2)-H(5)-O(4)</td>
<td></td>
</tr>
<tr>
<td>C(8)-H(8)-O(4)</td>
<td></td>
</tr>
<tr>
<td>C(9)-H(9)-O(1)</td>
<td></td>
</tr>
<tr>
<td>C(12)-H(12)-O(5)</td>
<td></td>
</tr>
<tr>
<td>O(4)-H(12)-O(5)</td>
<td></td>
</tr>
</tbody>
</table>

Hydrogen atom coordinates (fractional) and isotropic thermal parameters (Å\(^2\)).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B(_{iso})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>0.142(3)</td>
<td>0.470(1)</td>
<td>0.451(2)</td>
<td>3.7(6)</td>
</tr>
<tr>
<td>H(2)</td>
<td>-0.007(3)</td>
<td>0.386(2)</td>
<td>0.515(3)</td>
<td>6.1(8)</td>
</tr>
<tr>
<td>H(3)</td>
<td>-0.162(3)</td>
<td>0.323(2)</td>
<td>0.393(3)</td>
<td>6.2(8)</td>
</tr>
<tr>
<td>H(4)</td>
<td>-0.149(3)</td>
<td>0.347(2)</td>
<td>0.207(3)</td>
<td>6.5(9)</td>
</tr>
<tr>
<td>H(5)</td>
<td>0.402(3)</td>
<td>0.635(2)</td>
<td>0.156(3)</td>
<td>4.7(7)</td>
</tr>
<tr>
<td>H(6)</td>
<td>0.498(4)</td>
<td>0.654(2)</td>
<td>-0.003(3)</td>
<td>7(1)</td>
</tr>
<tr>
<td>H(7)</td>
<td>0.429(4)</td>
<td>0.561(2)</td>
<td>-0.159(3)</td>
<td>9(1)</td>
</tr>
<tr>
<td>H(8)</td>
<td>0.275(3)</td>
<td>0.474(2)</td>
<td>-0.147(3)</td>
<td>7(1)</td>
</tr>
<tr>
<td>H(9)</td>
<td>0.441(3)</td>
<td>0.515(2)</td>
<td>0.376(2)</td>
<td>3.8(6)</td>
</tr>
<tr>
<td>H(10)</td>
<td>0.588(3)</td>
<td>0.413(2)</td>
<td>0.440(3)</td>
<td>5.6(8)</td>
</tr>
<tr>
<td>H(11)</td>
<td>0.567(3)</td>
<td>0.286(2)</td>
<td>0.354(3)</td>
<td>7(1)</td>
</tr>
<tr>
<td>H(12)</td>
<td>0.386(4)</td>
<td>0.263(3)</td>
<td>0.214(4)</td>
<td>10(1)</td>
</tr>
<tr>
<td>H(13)</td>
<td>0.048(2)</td>
<td>0.587(1)</td>
<td>0.007(2)</td>
<td>3.8(6)</td>
</tr>
<tr>
<td>H(14)</td>
<td>-0.121(3)</td>
<td>0.674(2)</td>
<td>-0.057(3)</td>
<td>6.0(8)</td>
</tr>
<tr>
<td>H(15)</td>
<td>-0.211(3)</td>
<td>0.744(2)</td>
<td>0.091(3)</td>
<td>6.4(8)</td>
</tr>
<tr>
<td>H(16)</td>
<td>-0.125(3)</td>
<td>0.712(2)</td>
<td>0.271(3)</td>
<td>5.7(8)</td>
</tr>
</tbody>
</table>
Final atomic coordinates (fractional) and $B_{eq}$ (Å²) for non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>0.19308(3)</td>
<td>0.52656(2)</td>
<td>0.22467(2)</td>
<td>2.86(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.2639(2)</td>
<td>0.6050(1)</td>
<td>0.3706(1)</td>
<td>4.06(7)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.2756(2)</td>
<td>0.7121(1)</td>
<td>0.2681(2)</td>
<td>5.2(1)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.2625(2)</td>
<td>0.7246(1)</td>
<td>0.4437(2)</td>
<td>5.7(1)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.6121(3)</td>
<td>0.6197(2)</td>
<td>0.2697(2)</td>
<td>7.8(1)</td>
</tr>
<tr>
<td>O(5)</td>
<td>0.7076(3)</td>
<td>0.6601(2)</td>
<td>0.4274(2)</td>
<td>8.3(2)</td>
</tr>
<tr>
<td>O(6)</td>
<td>0.7239(4)</td>
<td>0.5390(2)</td>
<td>0.3721(3)</td>
<td>11.3(2)</td>
</tr>
<tr>
<td>N(1)</td>
<td>0.0708(2)</td>
<td>0.4567(1)</td>
<td>0.2956(1)</td>
<td>2.96(7)</td>
</tr>
<tr>
<td>N(2)</td>
<td>-0.0156(2)</td>
<td>0.4201(1)</td>
<td>0.2198(2)</td>
<td>3.79(9)</td>
</tr>
<tr>
<td>N(3)</td>
<td>0.2882(2)</td>
<td>0.5521(1)</td>
<td>0.0947(2)</td>
<td>3.20(7)</td>
</tr>
<tr>
<td>N(4)</td>
<td>0.2472(2)</td>
<td>0.5028(2)</td>
<td>0.0082(2)</td>
<td>4.4(1)</td>
</tr>
<tr>
<td>N(5)</td>
<td>0.3309(2)</td>
<td>0.4448(1)</td>
<td>0.2798(2)</td>
<td>3.15(7)</td>
</tr>
<tr>
<td>N(6)</td>
<td>0.3129(2)</td>
<td>0.3721(1)</td>
<td>0.2305(2)</td>
<td>4.7(1)</td>
</tr>
<tr>
<td>N(7)</td>
<td>0.0485(2)</td>
<td>0.6014(1)</td>
<td>0.1657(1)</td>
<td>3.03(7)</td>
</tr>
<tr>
<td>N(8)</td>
<td>-0.0042(2)</td>
<td>0.6386(1)</td>
<td>0.2469(2)</td>
<td>3.90(9)</td>
</tr>
<tr>
<td>N(9)</td>
<td>0.2679(2)</td>
<td>0.6818(1)</td>
<td>0.3604(2)</td>
<td>3.47(8)</td>
</tr>
<tr>
<td>N(10)</td>
<td>0.6777(3)</td>
<td>0.6069(2)</td>
<td>0.3593(2)</td>
<td>5.3(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.0752(3)</td>
<td>0.4433(2)</td>
<td>0.4046(2)</td>
<td>3.6(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>-0.0115(3)</td>
<td>0.3922(2)</td>
<td>0.4458(2)</td>
<td>4.3(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>-0.0994(3)</td>
<td>0.3552(2)</td>
<td>0.3706(3)</td>
<td>4.5(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>-0.0966(3)</td>
<td>0.3702(2)</td>
<td>0.2581(3)</td>
<td>4.3(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>0.3789(3)</td>
<td>0.6051(2)</td>
<td>0.0892(2)</td>
<td>4.1(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>0.4362(3)</td>
<td>0.6132(2)</td>
<td>-0.0079(3)</td>
<td>5.5(2)</td>
</tr>
<tr>
<td>C(7)</td>
<td>0.3965(4)</td>
<td>0.5636(2)</td>
<td>-0.0956(3)</td>
<td>5.6(2)</td>
</tr>
<tr>
<td>C(8)</td>
<td>0.3012(3)</td>
<td>0.5092(2)</td>
<td>-0.0838(2)</td>
<td>5.2(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>0.4315(3)</td>
<td>0.4592(2)</td>
<td>0.3546(2)</td>
<td>4.0(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>0.5225(3)</td>
<td>0.3999(2)</td>
<td>0.3874(2)</td>
<td>4.7(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>0.5053(3)</td>
<td>0.3265(2)</td>
<td>0.3385(3)</td>
<td>4.8(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>0.3997(3)</td>
<td>0.3153(2)</td>
<td>0.2591(3)</td>
<td>5.3(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>0.0045(3)</td>
<td>0.6147(2)</td>
<td>0.0583(2)</td>
<td>3.6(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>-0.0954(3)</td>
<td>0.6669(2)</td>
<td>0.0245(2)</td>
<td>4.4(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>-0.1476(3)</td>
<td>0.7067(2)</td>
<td>0.1056(3)</td>
<td>4.3(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>-0.0992(3)</td>
<td>0.6894(2)</td>
<td>0.2165(2)</td>
<td>4.3(1)</td>
</tr>
</tbody>
</table>
Anisotropic thermal parameters $\times 10^3$

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>31.9(2)</td>
<td>58(1)</td>
<td>313</td>
<td>4.2(1)</td>
<td>99</td>
<td>0(4)</td>
</tr>
<tr>
<td>O(1)</td>
<td>33.1(8)</td>
<td>51(1)</td>
<td>27(1)</td>
<td>0.5(1)</td>
<td>-3.1(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>O(2)</td>
<td>40.1(2)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>O(3)</td>
<td>41(1)</td>
<td>52(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>O(4)</td>
<td>59(2)</td>
<td>62(2)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>O(5)</td>
<td>59(2)</td>
<td>62(2)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>O(6)</td>
<td>59(2)</td>
<td>62(2)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>N(1)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>N(2)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>N(3)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>N(4)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>N(5)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>N(6)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>N(7)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>N(8)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>N(9)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>N(10)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>40(1)</td>
<td>50(1)</td>
<td>62(2)</td>
<td>0.2(1)</td>
<td>-3.6(2)</td>
<td>2(1)</td>
</tr>
</tbody>
</table>
### Bond lengths involving nonhydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-O(1)</td>
<td>2.258(2)</td>
<td>N(1)-C(1)</td>
<td>1.311(3)</td>
</tr>
<tr>
<td>Cu(1)-O(4)</td>
<td>2.007(2)</td>
<td>N(2)-C(4)</td>
<td>1.324(4)</td>
</tr>
<tr>
<td>Cu(1)-O(5)</td>
<td>2.624(3)</td>
<td>N(3)-N(4)</td>
<td>1.342(3)</td>
</tr>
<tr>
<td>Cu(1)-N(1)</td>
<td>2.025(2)</td>
<td>N(3)-C(5)</td>
<td>1.314(3)</td>
</tr>
<tr>
<td>Cu(1)-N(3)</td>
<td>2.042(2)</td>
<td>N(4)-C(8)</td>
<td>1.315(4)</td>
</tr>
<tr>
<td>Cu(1)-N(5)</td>
<td>1.984(2)</td>
<td>N(5)-N(6)</td>
<td>1.323(3)</td>
</tr>
<tr>
<td>O(1)-N(7)</td>
<td>1.243(3)</td>
<td>N(5)-C(9)</td>
<td>1.311(4)</td>
</tr>
<tr>
<td>O(2)-N(7)</td>
<td>1.24(1)</td>
<td>N(6)-C(12)</td>
<td>1.349(4)</td>
</tr>
<tr>
<td>O(2A)-N(7)</td>
<td>1.25(1)</td>
<td>C(1)-C(2)</td>
<td>1.388(4)</td>
</tr>
<tr>
<td>O(2B)-N(7)</td>
<td>1.30(2)</td>
<td>C(2)-C(3)</td>
<td>1.351(4)</td>
</tr>
<tr>
<td>O(3)-N(7)</td>
<td>1.22(2)</td>
<td>C(3)-C(4)</td>
<td>1.370(4)</td>
</tr>
<tr>
<td>O(3A)-N(7)</td>
<td>1.23(3)</td>
<td>C(5)-C(6)</td>
<td>1.389(4)</td>
</tr>
<tr>
<td>O(3B)-N(7)</td>
<td>1.34(3)</td>
<td>C(6)-C(7)</td>
<td>1.346(4)</td>
</tr>
<tr>
<td>O(4)-N(8)</td>
<td>1.283(3)</td>
<td>C(7)-C(8)</td>
<td>1.381(4)</td>
</tr>
<tr>
<td>O(5)-N(8)</td>
<td>1.228(4)</td>
<td>C(9)-C(10)</td>
<td>1.362(5)</td>
</tr>
<tr>
<td>O(6)-N(8)</td>
<td>1.208(4)</td>
<td>C(10)-C(11)</td>
<td>1.343(6)</td>
</tr>
<tr>
<td>N(1)-N(2)</td>
<td>1.338(3)</td>
<td>C(11)-C(12)</td>
<td>1.360(6)</td>
</tr>
</tbody>
</table>

### Bond lengths involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-H(1)</td>
<td>0.980</td>
<td>C(7)-H(7)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(2)-H(2)</td>
<td>0.980</td>
<td>C(8)-H(8)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(3)-H(3)</td>
<td>0.980</td>
<td>C(9)-H(9)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(4)-H(4)</td>
<td>0.980</td>
<td>C(10)-H(10)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(5)-H(5)</td>
<td>0.980</td>
<td>C(11)-H(11)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(6)-H(6)</td>
<td>0.980</td>
<td>C(12)-H(12)</td>
<td>0.980</td>
</tr>
</tbody>
</table>

---

*a* Unit cell parameters are given in Table 2-10.

*b* Estimated standard deviations in the least significant figure are given in parentheses.

*c* \( B_{eq} = (8/3)\pi^2 \Sigma U_{ij} a_i a_j^* (a_i, a_j) \).
Bond angles involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-Cu(1)-O(4)</td>
<td>95.78(8)</td>
<td>N(5)-N(6)-C(12)</td>
<td>117.6(3)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-O(5)</td>
<td>149.10(9)</td>
<td>O(1)-N(7)-O(2)</td>
<td>116.8(5)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(1)</td>
<td>88.71(8)</td>
<td>O(1)-N(7)-O(2A)</td>
<td>117.8(6)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(3)</td>
<td>92.84(8)</td>
<td>O(1)-N(7)-O(2B)</td>
<td>117.2(8)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(5)</td>
<td>101.25(9)</td>
<td>O(1)-N(7)-O(3)</td>
<td>121(1)</td>
</tr>
<tr>
<td>O(4)-Cu(1)-O(5)</td>
<td>53.33(8)</td>
<td>O(1)-N(7)-O(3A)</td>
<td>121(1)</td>
</tr>
<tr>
<td>O(4)-Cu(1)-N(1)</td>
<td>90.42(8)</td>
<td>O(1)-N(7)-O(3B)</td>
<td>122(1)</td>
</tr>
<tr>
<td>O(4)-Cu(1)-N(3)</td>
<td>88.55(8)</td>
<td>O(2)-N(7)-O(3)</td>
<td>120(1)</td>
</tr>
<tr>
<td>O(4)-Cu(1)-N(5)</td>
<td>162.83(9)</td>
<td>O(2)-N(7)-O(3A)</td>
<td>122(1)</td>
</tr>
<tr>
<td>O(5)-Cu(1)-N(1)</td>
<td>90.70(8)</td>
<td>O(2)-N(7)-O(3B)</td>
<td>117(1)</td>
</tr>
<tr>
<td>O(5)-Cu(1)-N(3)</td>
<td>87.52(8)</td>
<td>O(2A)-N(7)-O(3A)</td>
<td>105(1)</td>
</tr>
<tr>
<td>O(5)-Cu(1)-N(5)</td>
<td>109.6(1)</td>
<td>O(2A)-N(7)-O(3B)</td>
<td>110(1)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(3)</td>
<td>178.2(1)</td>
<td>O(2B)-N(7)-O(3A)</td>
<td>109(1)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(5)</td>
<td>92.08(9)</td>
<td>O(4)-N(8)-O(5)</td>
<td>117.8(3)</td>
</tr>
<tr>
<td>N(3)-Cu(1)-N(5)</td>
<td>88.48(9)</td>
<td>O(4)-N(8)-O(6)</td>
<td>118.4(3)</td>
</tr>
<tr>
<td>Cu(1)-O(1)-N(7)</td>
<td>130.3(2)</td>
<td>O(5)-N(8)-O(6)</td>
<td>123.8(3)</td>
</tr>
<tr>
<td>Cu(1)-O(4)-N(8)</td>
<td>108.2(2)</td>
<td>N(1)-C(1)-C(2)</td>
<td>123.0(3)</td>
</tr>
<tr>
<td>Cu(1)-O(5)-N(8)</td>
<td>80.1(2)</td>
<td>C(1)-C(2)-C(3)</td>
<td>117.8(3)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-N(2)</td>
<td>118.4(2)</td>
<td>C(2)-C(3)-C(4)</td>
<td>116.3(3)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-C(1)</td>
<td>121.3(2)</td>
<td>N(2)-C(4)-C(3)</td>
<td>125.4(3)</td>
</tr>
<tr>
<td>N(2)-N(1)-C(1)</td>
<td>120.1(2)</td>
<td>N(3)-C(5)-C(6)</td>
<td>122.1(3)</td>
</tr>
<tr>
<td>N(1)-N(2)-C(4)</td>
<td>117.4(2)</td>
<td>C(5)-C(6)-C(7)</td>
<td>118.4(3)</td>
</tr>
<tr>
<td>Cu(1)-N(3)-N(4)</td>
<td>116.6(2)</td>
<td>C(6)-C(7)-C(8)</td>
<td>116.6(3)</td>
</tr>
<tr>
<td>Cu(1)-N(3)-C(5)</td>
<td>122.8(2)</td>
<td>N(4)-C(8)-C(7)</td>
<td>124.6(3)</td>
</tr>
<tr>
<td>N(4)-N(3)-C(5)</td>
<td>120.6(2)</td>
<td>N(5)-C(9)-C(10)</td>
<td>120.4(3)</td>
</tr>
<tr>
<td>N(3)-N(4)-C(8)</td>
<td>117.8(2)</td>
<td>C(9)-C(10)-C(11)</td>
<td>119.5(4)</td>
</tr>
<tr>
<td>Cu(1)-N(5)-N(6)</td>
<td>118.4(2)</td>
<td>C(10)-C(11)-C(12)</td>
<td>117.9(4)</td>
</tr>
<tr>
<td>Cu(1)-N(5)-C(9)</td>
<td>118.6(2)</td>
<td>N(6)-C(12)-C(11)</td>
<td>122.2(4)</td>
</tr>
<tr>
<td>N(6)-N(5)-C(9)</td>
<td>122.4(3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Bond angles involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(1)-H(1)</td>
<td>118.5</td>
<td>C(6)-C(7)-H(7)</td>
<td>121.7</td>
</tr>
<tr>
<td>C(2)-C(1)-H(1)</td>
<td>118.5</td>
<td>C(8)-C(7)-H(7)</td>
<td>121.7</td>
</tr>
<tr>
<td>C(1)-C(2)-H(2)</td>
<td>121.1</td>
<td>N(4)-C(8)-H(8)</td>
<td>117.7</td>
</tr>
<tr>
<td>C(3)-C(2)-H(2)</td>
<td>121.1</td>
<td>C(7)-C(8)-H(8)</td>
<td>117.7</td>
</tr>
<tr>
<td>C(2)-C(3)-H(3)</td>
<td>121.9</td>
<td>N(5)-C(9)-H(9)</td>
<td>119.8</td>
</tr>
<tr>
<td>C(4)-C(3)-H(3)</td>
<td>121.9</td>
<td>C(10)-C(9)-H(9)</td>
<td>119.8</td>
</tr>
<tr>
<td>N(2)-C(4)-H(4)</td>
<td>117.3</td>
<td>C(9)-C(10)-H(10)</td>
<td>120.3</td>
</tr>
<tr>
<td>C(3)-C(4)-H(4)</td>
<td>117.3</td>
<td>C(11)-C(10)-H(10)</td>
<td>120.3</td>
</tr>
<tr>
<td>N(3)-C(5)-H(5)</td>
<td>119.0</td>
<td>C(10)-C(11)-H(11)</td>
<td>121.0</td>
</tr>
<tr>
<td>C(6)-C(5)-H(5)</td>
<td>119.0</td>
<td>C(12)-C(11)-H(11)</td>
<td>121.0</td>
</tr>
<tr>
<td>C(5)-C(6)-H(6)</td>
<td>120.8</td>
<td>N(6)-C(12)-H(12)</td>
<td>118.9</td>
</tr>
<tr>
<td>C(7)-C(6)-H(6)</td>
<td>120.8</td>
<td>C(11)-C(12)-H(12)</td>
<td>118.9</td>
</tr>
</tbody>
</table>

Hydrogen atom coordinates (fractional) and $B_{iso}$ (Å²).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>0.5411</td>
<td>0.0718</td>
<td>0.4571</td>
<td>5.5</td>
</tr>
<tr>
<td>H(2)</td>
<td>0.7824</td>
<td>0.0605</td>
<td>0.3708</td>
<td>6.4</td>
</tr>
<tr>
<td>H(3)</td>
<td>0.9298</td>
<td>0.1879</td>
<td>0.3429</td>
<td>6.3</td>
</tr>
<tr>
<td>H(4)</td>
<td>0.8259</td>
<td>0.3164</td>
<td>0.4043</td>
<td>7.1</td>
</tr>
<tr>
<td>H(5)</td>
<td>0.0603</td>
<td>0.0912</td>
<td>0.5979</td>
<td>5.5</td>
</tr>
<tr>
<td>H(6)</td>
<td>-0.1844</td>
<td>0.1028</td>
<td>0.6810</td>
<td>6.5</td>
</tr>
<tr>
<td>H(7)</td>
<td>-0.2581</td>
<td>0.2378</td>
<td>0.7464</td>
<td>6.6</td>
</tr>
<tr>
<td>H(8)</td>
<td>-0.0825</td>
<td>0.3534</td>
<td>0.7242</td>
<td>6.6</td>
</tr>
<tr>
<td>H(9)</td>
<td>0.4518</td>
<td>0.3574</td>
<td>0.6508</td>
<td>5.9</td>
</tr>
<tr>
<td>H(10)</td>
<td>0.4063</td>
<td>0.5056</td>
<td>0.6439</td>
<td>8.9</td>
</tr>
<tr>
<td>H(11)</td>
<td>0.2547</td>
<td>0.5633</td>
<td>0.5061</td>
<td>10.3</td>
</tr>
<tr>
<td>H(12)</td>
<td>0.1541</td>
<td>0.4701</td>
<td>0.3789</td>
<td>9.5</td>
</tr>
</tbody>
</table>
Final atomic coordinates (fractional) and $B_{eq}$ (Å$^2$) for non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{eq}$</th>
<th>occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>0.33519(4)</td>
<td>0.20556(2)</td>
<td>0.54427(3)</td>
<td>3.85(2)</td>
<td></td>
</tr>
<tr>
<td>O(1)</td>
<td>0.2189(2)</td>
<td>0.15704(13)</td>
<td>0.3966(2)</td>
<td>5.0(1)</td>
<td></td>
</tr>
<tr>
<td>O(2)</td>
<td>0.2241(13)</td>
<td>0.0243(7)</td>
<td>0.4291(8)</td>
<td>6.9(5)</td>
<td>0.41</td>
</tr>
<tr>
<td>O(2A)</td>
<td>0.1314(11)</td>
<td>0.0327(7)</td>
<td>0.4328(9)</td>
<td>6.9(5)</td>
<td>0.41</td>
</tr>
<tr>
<td>O(2B)</td>
<td>0.300(2)</td>
<td>0.0257(12)</td>
<td>0.378(2)</td>
<td>7.0(4)</td>
<td>0.18</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.156(2)</td>
<td>0.0668(13)</td>
<td>0.2788(12)</td>
<td>6.6(6)</td>
<td>0.53</td>
</tr>
<tr>
<td>O(3A)</td>
<td>0.108(3)</td>
<td>0.069(2)</td>
<td>0.288(2)</td>
<td>6.8(8)</td>
<td>0.37</td>
</tr>
<tr>
<td>O(3B)</td>
<td>0.279(4)</td>
<td>0.039(2)</td>
<td>0.305(3)</td>
<td>6.5(6)</td>
<td>0.10</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.3683(2)</td>
<td>0.08943(12)</td>
<td>0.6080(2)</td>
<td>4.6(1)</td>
<td></td>
</tr>
<tr>
<td>O(5)</td>
<td>0.4692(3)</td>
<td>0.1726(2)</td>
<td>0.7249(2)</td>
<td>6.9(1)</td>
<td></td>
</tr>
<tr>
<td>O(6)</td>
<td>0.4368(4)</td>
<td>0.0383(2)</td>
<td>0.7553(2)</td>
<td>11.0(2)</td>
<td></td>
</tr>
<tr>
<td>N(1)</td>
<td>0.5493(2)</td>
<td>0.19728(14)</td>
<td>0.4785(2)</td>
<td>3.9(1)</td>
<td></td>
</tr>
<tr>
<td>N(2)</td>
<td>0.6313(3)</td>
<td>0.2696(2)</td>
<td>0.4640(2)</td>
<td>5.4(1)</td>
<td></td>
</tr>
<tr>
<td>N(3)</td>
<td>0.1228(3)</td>
<td>0.21322(14)</td>
<td>0.6149(2)</td>
<td>4.1(1)</td>
<td></td>
</tr>
<tr>
<td>N(4)</td>
<td>0.0826(3)</td>
<td>0.2904(2)</td>
<td>0.6514(2)</td>
<td>5.1(1)</td>
<td></td>
</tr>
<tr>
<td>N(5)</td>
<td>0.3251(3)</td>
<td>0.3315(2)</td>
<td>0.5226(2)</td>
<td>4.1(1)</td>
<td></td>
</tr>
<tr>
<td>N(6)</td>
<td>0.2375(4)</td>
<td>0.3611(2)</td>
<td>0.4440(2)</td>
<td>6.1(1)</td>
<td></td>
</tr>
<tr>
<td>N(7)</td>
<td>0.1866(3)</td>
<td>0.0826(2)</td>
<td>0.3685(2)</td>
<td>4.6(1)</td>
<td></td>
</tr>
<tr>
<td>N(8)</td>
<td>0.4280(3)</td>
<td>0.0999(2)</td>
<td>0.6992(2)</td>
<td>5.7(1)</td>
<td></td>
</tr>
<tr>
<td>C(1)</td>
<td>0.6034(3)</td>
<td>0.1238(2)</td>
<td>0.4454(2)</td>
<td>4.6(1)</td>
<td></td>
</tr>
<tr>
<td>C(2)</td>
<td>0.7449(4)</td>
<td>0.1164(2)</td>
<td>0.3945(3)</td>
<td>5.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(3)</td>
<td>0.8292(4)</td>
<td>0.1887(2)</td>
<td>0.3786(3)</td>
<td>5.2(2)</td>
<td></td>
</tr>
<tr>
<td>C(4)</td>
<td>0.7662(4)</td>
<td>0.2633(2)</td>
<td>0.4152(3)</td>
<td>5.9(2)</td>
<td></td>
</tr>
<tr>
<td>C(5)</td>
<td>0.0283(3)</td>
<td>0.1468(2)</td>
<td>0.6253(2)</td>
<td>4.6(1)</td>
<td></td>
</tr>
<tr>
<td>C(6)</td>
<td>-0.1155(4)</td>
<td>0.1530(2)</td>
<td>0.6740(3)</td>
<td>5.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(7)</td>
<td>-0.1580(4)</td>
<td>0.2299(2)</td>
<td>0.7113(3)</td>
<td>5.5(2)</td>
<td></td>
</tr>
<tr>
<td>C(8)</td>
<td>-0.0533(4)</td>
<td>0.2970(2)</td>
<td>0.6976(3)</td>
<td>5.5(2)</td>
<td></td>
</tr>
<tr>
<td>C(9)</td>
<td>0.3869(4)</td>
<td>0.3819(2)</td>
<td>0.5940(2)</td>
<td>4.9(1)</td>
<td></td>
</tr>
<tr>
<td>C(10)</td>
<td>0.3615(5)</td>
<td>0.4682(3)</td>
<td>0.5898(4)</td>
<td>7.5(2)</td>
<td></td>
</tr>
<tr>
<td>C(11)</td>
<td>0.2746(6)</td>
<td>0.5014(2)</td>
<td>0.5109(4)</td>
<td>8.6(3)</td>
<td></td>
</tr>
<tr>
<td>C(12)</td>
<td>0.2152(5)</td>
<td>0.4466(3)</td>
<td>0.4379(3)</td>
<td>7.9(2)</td>
<td></td>
</tr>
</tbody>
</table>
Anisotropic thermal parameters $\times 10^2$

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>4.55(2)</td>
<td>4.79(2)</td>
<td>5.32(2)</td>
<td>-0.15(2)</td>
<td>0.63(2)</td>
<td>-0.19(2)</td>
</tr>
<tr>
<td>O(1)</td>
<td>7.24(14)</td>
<td>5.95(13)</td>
<td>5.82(12)</td>
<td>-0.86(10)</td>
<td>-0.43(10)</td>
<td>0.9(4)</td>
</tr>
<tr>
<td>O(2)</td>
<td>14.2(10)</td>
<td>5.9(4)</td>
<td>5.8(6)</td>
<td>-0.6(7)</td>
<td>-3.4(7)</td>
<td>0.9(4)</td>
</tr>
<tr>
<td>O(2A)</td>
<td>12.2(8)</td>
<td>6.2(5)</td>
<td>8.0(6)</td>
<td>-2.2(6)</td>
<td>3.5(6)</td>
<td>-0.6(4)</td>
</tr>
<tr>
<td>O(3)</td>
<td>10.6(11)</td>
<td>9.6(9)</td>
<td>4.6(3)</td>
<td>-2.0(7)</td>
<td>-1.2(6)</td>
<td>-0.7(4)</td>
</tr>
<tr>
<td>O(3A)</td>
<td>7.1(9)</td>
<td>9.2(10)</td>
<td>9.2(12)</td>
<td>3.3(8)</td>
<td>-4.0(7)</td>
<td>-3.9(8)</td>
</tr>
<tr>
<td>O(4)</td>
<td>6.00(12)</td>
<td>5.64(12)</td>
<td>5.80(12)</td>
<td>0.03(9)</td>
<td>0.07(9)</td>
<td>0.54(9)</td>
</tr>
<tr>
<td>O(5)</td>
<td>7.5(2)</td>
<td>11.4(2)</td>
<td>7.2(2)</td>
<td>-1.47(15)</td>
<td>0.12(12)</td>
<td>-1.95(15)</td>
</tr>
<tr>
<td>O(6)</td>
<td>16.7(3)</td>
<td>14.3(3)</td>
<td>10.5(2)</td>
<td>-1.7(2)</td>
<td>-3.9(2)</td>
<td>6.5(2)</td>
</tr>
<tr>
<td>N(1)</td>
<td>4.45(11)</td>
<td>4.99(13)</td>
<td>5.49(13)</td>
<td>-0.22(10)</td>
<td>0.47(10)</td>
<td>-0.02(10)</td>
</tr>
<tr>
<td>N(2)</td>
<td>6.4(2)</td>
<td>5.30(14)</td>
<td>9.0(2)</td>
<td>-0.85(12)</td>
<td>2.78(15)</td>
<td>-0.79(13)</td>
</tr>
<tr>
<td>N(3)</td>
<td>4.81(12)</td>
<td>5.43(13)</td>
<td>5.31(13)</td>
<td>-0.10(10)</td>
<td>0.74(10)</td>
<td>-0.54(10)</td>
</tr>
<tr>
<td>N(4)</td>
<td>6.3(2)</td>
<td>5.92(15)</td>
<td>7.4(2)</td>
<td>-0.31(12)</td>
<td>2.13(13)</td>
<td>-1.45(13)</td>
</tr>
<tr>
<td>N(5)</td>
<td>4.93(12)</td>
<td>5.31(13)</td>
<td>5.28(14)</td>
<td>-0.03(10)</td>
<td>0.82(11)</td>
<td>-0.03(10)</td>
</tr>
<tr>
<td>N(6)</td>
<td>8.4(2)</td>
<td>7.0(2)</td>
<td>7.6(2)</td>
<td>0.93(15)</td>
<td>-0.3(2)</td>
<td>0.27(15)</td>
</tr>
<tr>
<td>N(7)</td>
<td>5.44(14)</td>
<td>6.2(2)</td>
<td>6.0(2)</td>
<td>-0.22(12)</td>
<td>0.02(12)</td>
<td>-0.54(13)</td>
</tr>
<tr>
<td>N(8)</td>
<td>5.8(2)</td>
<td>9.1(2)</td>
<td>6.6(2)</td>
<td>-0.20(15)</td>
<td>0.35(13)</td>
<td>1.6(2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>5.3(2)</td>
<td>4.9(2)</td>
<td>7.2(2)</td>
<td>-0.07(13)</td>
<td>0.77(14)</td>
<td>0.28(14)</td>
</tr>
<tr>
<td>C(2)</td>
<td>6.0(2)</td>
<td>6.0(2)</td>
<td>8.5(2)</td>
<td>1.5(2)</td>
<td>1.6(2)</td>
<td>0.4(2)</td>
</tr>
<tr>
<td>C(3)</td>
<td>5.2(2)</td>
<td>6.9(2)</td>
<td>8.0(2)</td>
<td>0.84(14)</td>
<td>1.7(2)</td>
<td>1.2(2)</td>
</tr>
<tr>
<td>C(4)</td>
<td>6.4(2)</td>
<td>6.3(2)</td>
<td>9.9(3)</td>
<td>-0.9(2)</td>
<td>2.9(2)</td>
<td>0.3(2)</td>
</tr>
<tr>
<td>C(5)</td>
<td>5.5(2)</td>
<td>5.6(2)</td>
<td>6.5(2)</td>
<td>-0.64(13)</td>
<td>0.72(14)</td>
<td>-1.07(14)</td>
</tr>
<tr>
<td>C(6)</td>
<td>5.7(2)</td>
<td>7.2(2)</td>
<td>7.9(2)</td>
<td>-1.7(2)</td>
<td>1.5(2)</td>
<td>-1.5(2)</td>
</tr>
<tr>
<td>C(7)</td>
<td>5.2(2)</td>
<td>8.7(2)</td>
<td>7.2(2)</td>
<td>-0.8(2)</td>
<td>1.55(15)</td>
<td>-1.8(2)</td>
</tr>
<tr>
<td>C(8)</td>
<td>6.6(2)</td>
<td>6.8(2)</td>
<td>7.6(2)</td>
<td>0.5(2)</td>
<td>1.8(2)</td>
<td>-1.7(2)</td>
</tr>
<tr>
<td>C(9)</td>
<td>5.9(2)</td>
<td>6.8(2)</td>
<td>5.9(2)</td>
<td>-1.28(15)</td>
<td>0.35(14)</td>
<td>-1.1(2)</td>
</tr>
<tr>
<td>C(10)</td>
<td>9.6(3)</td>
<td>8.9(3)</td>
<td>10.0(3)</td>
<td>-2.7(2)</td>
<td>2.0(2)</td>
<td>-3.7(2)</td>
</tr>
<tr>
<td>C(11)</td>
<td>13.0(4)</td>
<td>5.1(2)</td>
<td>14.8(5)</td>
<td>0.9(2)</td>
<td>2.7(3)</td>
<td>-0.8(3)</td>
</tr>
<tr>
<td>C(12)</td>
<td>11.7(3)</td>
<td>7.4(3)</td>
<td>10.8(3)</td>
<td>2.0(2)</td>
<td>-1.2(3)</td>
<td>2.0(2)</td>
</tr>
</tbody>
</table>
### Bond lengths involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-O(1)</td>
<td>2.243(2)</td>
<td>Cu(1)-N(9)</td>
<td>1.369(6)</td>
</tr>
<tr>
<td>Cu(1)-N(1)</td>
<td>2.052(2)</td>
<td>O(9A)-N(9)</td>
<td>1.420(7)</td>
</tr>
<tr>
<td>Cu(1)-N(3)</td>
<td>2.074(2)</td>
<td>N(1)-N(2)</td>
<td>1.346(3)</td>
</tr>
<tr>
<td>Cu(2)-O(1)</td>
<td>2.255(2)</td>
<td>N(1)-C(1)</td>
<td>1.321(3)</td>
</tr>
<tr>
<td>Cu(2)-O(4)</td>
<td>1.974(2)</td>
<td>N(2)-C(4)</td>
<td>1.321(3)</td>
</tr>
<tr>
<td>Cu(2)-O(7)</td>
<td>2.516(7)</td>
<td>N(3)-N(4)</td>
<td>1.343(3)</td>
</tr>
<tr>
<td>Cu(2)-O(7A)</td>
<td>2.457(9)</td>
<td>N(3)-C(5)</td>
<td>1.326(3)</td>
</tr>
<tr>
<td>Cu(2)-N(2)</td>
<td>2.036(2)</td>
<td>N(4)-C(8)</td>
<td>1.327(3)</td>
</tr>
<tr>
<td>Cu(2)-N(4)</td>
<td>2.063(2)</td>
<td>N(5)-N(6)</td>
<td>1.331(3)</td>
</tr>
<tr>
<td>Cu(2)-N(5)</td>
<td>1.993(2)</td>
<td>N(5)-C(9)</td>
<td>1.326(3)</td>
</tr>
<tr>
<td>O(1)-N(7)</td>
<td>1.291(3)</td>
<td>N(6)-C(12)</td>
<td>1.330(4)</td>
</tr>
<tr>
<td>O(2)-N(7)</td>
<td>1.229(3)</td>
<td>C(1)-C(2)</td>
<td>1.392(4)</td>
</tr>
<tr>
<td>O(3)-N(7)</td>
<td>1.222(3)</td>
<td>C(2)-C(3)</td>
<td>1.360(4)</td>
</tr>
<tr>
<td>O(4)-N(8)</td>
<td>1.302(3)</td>
<td>C(3)-C(4)</td>
<td>1.382(4)</td>
</tr>
<tr>
<td>O(5)-N(8)</td>
<td>1.231(3)</td>
<td>C(5)-C(6)</td>
<td>1.389(4)</td>
</tr>
<tr>
<td>O(6)-N(8)</td>
<td>1.221(3)</td>
<td>C(6)-C(7)</td>
<td>1.369(4)</td>
</tr>
<tr>
<td>O(7)-N(9)</td>
<td>1.175(7)</td>
<td>C(7)-C(8)</td>
<td>1.393(4)</td>
</tr>
<tr>
<td>O(7A)-N(9)</td>
<td>1.214(8)</td>
<td>C(9)-C(10)</td>
<td>1.387(4)</td>
</tr>
<tr>
<td>O(8)-N(9)</td>
<td>1.141(1)</td>
<td>C(10)-C(11)</td>
<td>1.343(5)</td>
</tr>
<tr>
<td>O(8A)-N(9)</td>
<td>1.073(8)</td>
<td>C(11)-C(12)</td>
<td>1.401(5)</td>
</tr>
</tbody>
</table>

### Bond lengths involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-H(1)</td>
<td>0.980</td>
<td>C(7)-H(7)</td>
<td>0.979</td>
</tr>
<tr>
<td>C(2)-H(2)</td>
<td>0.982</td>
<td>C(8)-H(8)</td>
<td>0.980</td>
</tr>
<tr>
<td>C(3)-H(3)</td>
<td>0.981</td>
<td>C(9)-H(9)</td>
<td>0.979</td>
</tr>
<tr>
<td>C(4)-H(4)</td>
<td>0.980</td>
<td>C(10)-H(10)</td>
<td>0.979</td>
</tr>
<tr>
<td>C(5)-H(5)</td>
<td>0.980</td>
<td>C(11)-H(11)</td>
<td>0.982</td>
</tr>
<tr>
<td>C(6)-H(6)</td>
<td>0.979</td>
<td>C(12)-H(12)</td>
<td>0.980</td>
</tr>
</tbody>
</table>

---

*a* Unit cell parameters are given in Table 2-12.

*b* Estimated standard deviations in the least significant figure are given in parentheses.

*c* Asterisk refers to symmetry operations: 1- x, 1-y-1, 1-z

*d* $B_{eq} = (8/3) \pi^2 \sum \hat{U}_{ij} a_i a_j (a_i, a_j)$
### Bond angles involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-Cu(1)-O(1)*</td>
<td>180.0</td>
<td>Cu(2)-N(2)-N(1)</td>
<td>120.0(2)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(1)</td>
<td>87.76(7)</td>
<td>Cu(2)-N(2)-C(4)</td>
<td>120.2(2)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-N(1)*</td>
<td>92.24(7)</td>
<td>N(1)-N(2)-C(4)</td>
<td>119.6(2)</td>
</tr>
<tr>
<td>O(7)-Cu(2)-N(3)</td>
<td>86.12(7)</td>
<td>Cu(1)-N(3)-N(4)</td>
<td>119.6(1)</td>
</tr>
<tr>
<td>O(7)-Cu(2)-N(3)*</td>
<td>93.88(7)</td>
<td>Cu(1)-N(3)-C(5)</td>
<td>120.8(2)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(1)*</td>
<td>180.0</td>
<td>N(4)-N(3)-C(5)</td>
<td>119.5(2)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(3)</td>
<td>89.81(8)</td>
<td>Cu(2)-N(4)-N(3)</td>
<td>119.9(1)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(3)*</td>
<td>90.19(8)</td>
<td>Cu(2)-N(4)-C(8)</td>
<td>120.5(2)</td>
</tr>
<tr>
<td>N(3)-Cu(1)-N(3)*</td>
<td>180.0</td>
<td>N(3)-N(4)-C(8)</td>
<td>119.5(2)</td>
</tr>
<tr>
<td>O(1)-Cu(2)-O(4)</td>
<td>101.29(8)</td>
<td>Cu(2)-N(5)-N(6)</td>
<td>114.3(2)</td>
</tr>
<tr>
<td>O(1)-Cu(2)-O(7)</td>
<td>170.5(1)</td>
<td>Cu(2)-N(5)-C(9)</td>
<td>123.3(2)</td>
</tr>
<tr>
<td>O(1)-Cu(2)-O(7A)</td>
<td>169.6(2)</td>
<td>N(6)-N(5)-C(9)</td>
<td>122.4(2)</td>
</tr>
<tr>
<td>O(1)-Cu(2)-N(2)</td>
<td>88.21(7)</td>
<td>N(5)-N(6)-C(12)</td>
<td>117.2(3)</td>
</tr>
<tr>
<td>O(1)-Cu(2)-N(4)</td>
<td>87.12(7)</td>
<td>O(1)-N(7)-O(2)</td>
<td>118.2(2)</td>
</tr>
<tr>
<td>O(1)-Cu(2)-N(5)</td>
<td>96.74(8)</td>
<td>O(1)-N(7)-O(3)</td>
<td>118.5(2)</td>
</tr>
<tr>
<td>O(4)-Cu(2)-O(7)</td>
<td>88.0(1)</td>
<td>O(2)-N(7)-O(3)</td>
<td>123.2(2)</td>
</tr>
<tr>
<td>O(4)-Cu(2)-O(7A)</td>
<td>78.6(2)</td>
<td>O(4)-N(8)-O(5)</td>
<td>119.7(2)</td>
</tr>
<tr>
<td>O(4)-Cu(2)-N(2)</td>
<td>93.04(8)</td>
<td>O(4)-N(8)-O(6)</td>
<td>116.7(3)</td>
</tr>
<tr>
<td>O(4)-Cu(2)-N(4)</td>
<td>171.47(8)</td>
<td>O(5)-N(8)-O(6)</td>
<td>123.6(3)</td>
</tr>
<tr>
<td>O(4)-Cu(2)-N(5)</td>
<td>88.22(9)</td>
<td>O(7)-N(9)-O(8)</td>
<td>136.3(8)</td>
</tr>
<tr>
<td>O(7)-Cu(2)-N(2)</td>
<td>92.9(2)</td>
<td>O(7)-N(9)-O(9)</td>
<td>112.4(4)</td>
</tr>
<tr>
<td>O(7)-Cu(2)-N(4)</td>
<td>83.5(1)</td>
<td>O(8)-N(9)-O(9)</td>
<td>111.0(7)</td>
</tr>
<tr>
<td>O(7)-Cu(2)-N(5)</td>
<td>81.8(2)</td>
<td>O(7A)-N(9)-O(8A)</td>
<td>141(1)</td>
</tr>
<tr>
<td>O(7A)-Cu(2)-N(2)</td>
<td>81.5(2)</td>
<td>O(7A)-N(9)-O(9A)</td>
<td>105.6(5)</td>
</tr>
<tr>
<td>O(7A)-Cu(2)-N(4)</td>
<td>93.4(2)</td>
<td>O(8A)-N(9)-O(9A)</td>
<td>110.0(8)</td>
</tr>
<tr>
<td>O(7A)-Cu(2)-N(5)</td>
<td>93.6(2)</td>
<td>N(1)-C(1)-C(2)</td>
<td>122.4(2)</td>
</tr>
<tr>
<td>N(2)-Cu(2)-N(4)</td>
<td>88.57(8)</td>
<td>C(1)-C(2)-C(3)</td>
<td>117.6(2)</td>
</tr>
<tr>
<td>N(2)-Cu(2)-N(5)</td>
<td>174.55(8)</td>
<td>C(2)-C(3)-C(4)</td>
<td>117.9(3)</td>
</tr>
<tr>
<td>N(4)-Cu(2)-N(5)</td>
<td>89.41(8)</td>
<td>N(2)-C(4)-C(3)</td>
<td>122.7(2)</td>
</tr>
<tr>
<td>Cu(1)-O(1)-Cu(2)</td>
<td>98.27(6)</td>
<td>N(3)-C(5)-C(6)</td>
<td>123.2(2)</td>
</tr>
<tr>
<td>Cu(1)-O(1)-N(7)</td>
<td>132.9(1)</td>
<td>C(5)-C(6)-C(7)</td>
<td>117.5(2)</td>
</tr>
<tr>
<td>Cu(2)-O(1)-N(7)</td>
<td>127.2(1)</td>
<td>C(6)-C(7)-C(8)</td>
<td>117.3(2)</td>
</tr>
<tr>
<td>Cu(2)-O(4)-N(8)</td>
<td>121.5(2)</td>
<td>N(4)-C(8)-C(7)</td>
<td>123.0(2)</td>
</tr>
<tr>
<td>Cu(2)-O(7)-N(9)</td>
<td>135.3(4)</td>
<td>N(5)-C(9)-C(10)</td>
<td>121.3(3)</td>
</tr>
<tr>
<td>Cu(2)-O(7A)-N(9)</td>
<td>137.6(5)</td>
<td>C(9)-C(10)-C(11)</td>
<td>117.8(3)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-N(2)</td>
<td>120.3(1)</td>
<td>C(10)-C(11)-C(12)</td>
<td>118.1(3)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-C(1)</td>
<td>119.9(2)</td>
<td>N(6)-C(12)-C(11)</td>
<td>123.2(3)</td>
</tr>
<tr>
<td>N(2)-N(1)-C(1)</td>
<td>119.7(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Bond angles involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(1)-H(1)</td>
<td>118.8</td>
<td>C(6)-C(7)-H(7)</td>
<td>121.4</td>
</tr>
<tr>
<td>C(2)-C(1)-H(1)</td>
<td>118.8</td>
<td>C(8)-C(7)-H(7)</td>
<td>121.3</td>
</tr>
<tr>
<td>C(1)-C(2)-H(2)</td>
<td>121.2</td>
<td>N(4)-C(8)-H(8)</td>
<td>118.6</td>
</tr>
<tr>
<td>C(3)-C(2)-H(2)</td>
<td>121.2</td>
<td>C(7)-C(8)-H(8)</td>
<td>118.4</td>
</tr>
<tr>
<td>C(2)-C(3)-H(3)</td>
<td>121.0</td>
<td>N(5)-C(9)-H(9)</td>
<td>119.3</td>
</tr>
<tr>
<td>C(4)-C(3)-H(3)</td>
<td>121.0</td>
<td>C(10)-C(9)-H(9)</td>
<td>119.4</td>
</tr>
<tr>
<td>C(2)-C(4)-H(4)</td>
<td>118.7</td>
<td>C(9)-C(10)-H(10)</td>
<td>121.2</td>
</tr>
<tr>
<td>C(3)-C(4)-H(4)</td>
<td>118.7</td>
<td>C(11)-C(10)-H(10)</td>
<td>121.0</td>
</tr>
<tr>
<td>C(6)-C(5)-H(5)</td>
<td>118.5</td>
<td>C(10)-C(11)-H(11)</td>
<td>121.3</td>
</tr>
<tr>
<td>C(5)-C(6)-H(6)</td>
<td>121.2</td>
<td>C(12)-C(11)-H(11)</td>
<td>120.6</td>
</tr>
<tr>
<td>C(7)-C(6)-H(6)</td>
<td>121.3</td>
<td>N(6)-C(12)-H(12)</td>
<td>118.5</td>
</tr>
</tbody>
</table>

Hydrogen atom coordinates (fractional) and isotropic thermal parameters (Å²).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Biso</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>0.2682</td>
<td>0.6376</td>
<td>0.4182</td>
<td>3.2</td>
</tr>
<tr>
<td>H(2)</td>
<td>0.0187</td>
<td>0.6357</td>
<td>0.3463</td>
<td>3.8</td>
</tr>
<tr>
<td>H(3)</td>
<td>-0.1180</td>
<td>0.4867</td>
<td>0.3450</td>
<td>4.0</td>
</tr>
<tr>
<td>H(4)</td>
<td>0.0033</td>
<td>0.3476</td>
<td>0.4120</td>
<td>3.7</td>
</tr>
<tr>
<td>H(5)</td>
<td>0.5479</td>
<td>0.5391</td>
<td>0.6986</td>
<td>3.4</td>
</tr>
<tr>
<td>H(6)</td>
<td>0.4847</td>
<td>0.4738</td>
<td>0.8362</td>
<td>4.1</td>
</tr>
<tr>
<td>H(7)</td>
<td>0.3396</td>
<td>0.3268</td>
<td>0.8314</td>
<td>4.1</td>
</tr>
<tr>
<td>H(8)</td>
<td>0.2633</td>
<td>0.2573</td>
<td>0.6887</td>
<td>3.8</td>
</tr>
<tr>
<td>H(9)</td>
<td>0.2160</td>
<td>0.0749</td>
<td>0.5114</td>
<td>4.3</td>
</tr>
<tr>
<td>H(10)</td>
<td>0.3239</td>
<td>-0.0672</td>
<td>0.5832</td>
<td>5.4</td>
</tr>
<tr>
<td>H(11)</td>
<td>0.5691</td>
<td>-0.0557</td>
<td>0.6579</td>
<td>5.9</td>
</tr>
<tr>
<td>H(12)</td>
<td>0.6966</td>
<td>0.0960</td>
<td>0.6558</td>
<td>6.0</td>
</tr>
</tbody>
</table>
Final atomic coordinates (fractional) and $B_{eq}$ (Å$^2$) for non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{eq}$</th>
<th>occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>2.17(2)</td>
<td></td>
</tr>
<tr>
<td>Cu(2)</td>
<td>0.30422(4)</td>
<td>0.28631(2)</td>
<td>0.49440(2)</td>
<td>2.56(1)</td>
<td></td>
</tr>
<tr>
<td>O(1)</td>
<td>0.5193(2)</td>
<td>0.3464(1)</td>
<td>0.4497(1)</td>
<td>2.89(7)</td>
<td></td>
</tr>
<tr>
<td>O(2)</td>
<td>0.7112(2)</td>
<td>0.3530(2)</td>
<td>0.3729(2)</td>
<td>4.8(1)</td>
<td></td>
</tr>
<tr>
<td>O(3)</td>
<td>0.5719(2)</td>
<td>0.2393(1)</td>
<td>0.3671(2)</td>
<td>4.08(9)</td>
<td></td>
</tr>
<tr>
<td>O(4)</td>
<td>0.2246(2)</td>
<td>0.2109(1)</td>
<td>0.3871(1)</td>
<td>3.60(8)</td>
<td></td>
</tr>
<tr>
<td>O(5)</td>
<td>0.2851(3)</td>
<td>0.3220(2)</td>
<td>0.2915(1)</td>
<td>4.9(1)</td>
<td></td>
</tr>
<tr>
<td>O(6)</td>
<td>0.2438(3)</td>
<td>0.1723(2)</td>
<td>0.2493(2)</td>
<td>5.8(1)</td>
<td></td>
</tr>
<tr>
<td>O(7)</td>
<td>0.0804(7)</td>
<td>0.2297(5)</td>
<td>0.5695(4)</td>
<td>4.3(3)</td>
<td>0.54</td>
</tr>
<tr>
<td>O(7A)</td>
<td>0.049(1)</td>
<td>0.2476(6)</td>
<td>0.5305(5)</td>
<td>4.8(3)</td>
<td>0.46</td>
</tr>
<tr>
<td>O(8)</td>
<td>-0.049(2)</td>
<td>0.0970(7)</td>
<td>0.566(1)</td>
<td>12.0(7)</td>
<td>0.54</td>
</tr>
<tr>
<td>O(8A)</td>
<td>-0.074(1)</td>
<td>0.1118(8)</td>
<td>0.5205(9)</td>
<td>9.8(7)</td>
<td>0.46</td>
</tr>
<tr>
<td>O(9)</td>
<td>-0.1272(6)</td>
<td>0.2152(4)</td>
<td>0.4882(4)</td>
<td>6.6(3)</td>
<td>0.54</td>
</tr>
<tr>
<td>O(9A)</td>
<td>0.0257(9)</td>
<td>0.1588(5)</td>
<td>0.6431(4)</td>
<td>6.8(3)</td>
<td>0.46</td>
</tr>
<tr>
<td>N(1)</td>
<td>0.2773(2)</td>
<td>0.4963(1)</td>
<td>0.4501(1)</td>
<td>2.34(7)</td>
<td></td>
</tr>
<tr>
<td>N(2)</td>
<td>0.1998(2)</td>
<td>0.4117(1)</td>
<td>0.4485(1)</td>
<td>2.51(8)</td>
<td></td>
</tr>
<tr>
<td>N(3)</td>
<td>0.4460(2)</td>
<td>0.4372(1)</td>
<td>0.6189(1)</td>
<td>2.35(7)</td>
<td></td>
</tr>
<tr>
<td>N(4)</td>
<td>0.3624(2)</td>
<td>0.3554(1)</td>
<td>0.6159(1)</td>
<td>2.46(8)</td>
<td></td>
</tr>
<tr>
<td>N(5)</td>
<td>0.3912(3)</td>
<td>0.1622(1)</td>
<td>0.5472(1)</td>
<td>2.83(8)</td>
<td></td>
</tr>
<tr>
<td>N(6)</td>
<td>0.5308(3)</td>
<td>0.1709(2)</td>
<td>0.5874(2)</td>
<td>3.8(1)</td>
<td></td>
</tr>
<tr>
<td>N(7)</td>
<td>0.6038(2)</td>
<td>0.3061(1)</td>
<td>0.3952(2)</td>
<td>2.94(9)</td>
<td></td>
</tr>
<tr>
<td>N(8)</td>
<td>0.2522(3)</td>
<td>0.2365(2)</td>
<td>0.3065(2)</td>
<td>3.7(1)</td>
<td></td>
</tr>
<tr>
<td>N(9)</td>
<td>-0.0206(3)</td>
<td>0.1760(2)</td>
<td>0.5505(2)</td>
<td>4.9(1)</td>
<td></td>
</tr>
<tr>
<td>C(1)</td>
<td>0.2114(3)</td>
<td>0.5761(2)</td>
<td>0.4150(2)</td>
<td>2.7(1)</td>
<td></td>
</tr>
<tr>
<td>C(2)</td>
<td>0.0644(3)</td>
<td>0.5761(2)</td>
<td>0.3737(2)</td>
<td>3.1(1)</td>
<td></td>
</tr>
<tr>
<td>C(3)</td>
<td>-0.0135(3)</td>
<td>0.4906(2)</td>
<td>0.3726(2)</td>
<td>3.4(1)</td>
<td></td>
</tr>
<tr>
<td>C(4)</td>
<td>0.0588(3)</td>
<td>0.4095(2)</td>
<td>0.4117(2)</td>
<td>3.1(1)</td>
<td></td>
</tr>
<tr>
<td>C(5)</td>
<td>0.4881(3)</td>
<td>0.4789(2)</td>
<td>0.6977(2)</td>
<td>2.8(1)</td>
<td></td>
</tr>
<tr>
<td>C(6)</td>
<td>0.4516(3)</td>
<td>0.4414(2)</td>
<td>0.7791(2)</td>
<td>3.4(1)</td>
<td></td>
</tr>
<tr>
<td>C(7)</td>
<td>0.3680(3)</td>
<td>0.3573(2)</td>
<td>0.7763(2)</td>
<td>3.4(1)</td>
<td></td>
</tr>
<tr>
<td>C(8)</td>
<td>0.3246(3)</td>
<td>0.3169(2)</td>
<td>0.6920(2)</td>
<td>3.2(1)</td>
<td></td>
</tr>
<tr>
<td>C(9)</td>
<td>0.3171(3)</td>
<td>0.0781(2)</td>
<td>0.5437(2)</td>
<td>3.6(1)</td>
<td></td>
</tr>
<tr>
<td>C(10)</td>
<td>0.3797(4)</td>
<td>-0.0055(2)</td>
<td>0.5849(2)</td>
<td>4.4(1)</td>
<td></td>
</tr>
<tr>
<td>C(11)</td>
<td>0.5196(5)</td>
<td>0.0010(2)</td>
<td>0.6273(2)</td>
<td>4.9(2)</td>
<td></td>
</tr>
<tr>
<td>C(12)</td>
<td>0.5936(4)</td>
<td>0.0913(2)</td>
<td>0.6263(2)</td>
<td>5.0(2)</td>
<td></td>
</tr>
<tr>
<td>Atom</td>
<td>U_{11}</td>
<td>U_{22}</td>
<td>U_{33}</td>
<td>U_{12}</td>
<td>U_{13}</td>
</tr>
<tr>
<td>-------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>Cu(1)</td>
<td>2.65(3)</td>
<td>2.39(2)</td>
<td>3.25(2)</td>
<td>-0.14(2)</td>
<td>0.57(2)</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>3.54(2)</td>
<td>2.21(2)</td>
<td>3.99(2)</td>
<td>-0.12(1)</td>
<td>0.45(2)</td>
</tr>
<tr>
<td>O(1)</td>
<td>3.7(1)</td>
<td>2.85(8)</td>
<td>4.7(1)</td>
<td>-0.09(7)</td>
<td>1.47(8)</td>
</tr>
<tr>
<td>O(2)</td>
<td>4.8(1)</td>
<td>4.7(1)</td>
<td>9.4(2)</td>
<td>-0.8(1)</td>
<td>3.6(1)</td>
</tr>
<tr>
<td>O(3)</td>
<td>5.1(1)</td>
<td>3.0(1)</td>
<td>7.7(1)</td>
<td>-0.02(8)</td>
<td>1.7(1)</td>
</tr>
<tr>
<td>O(4)</td>
<td>5.3(1)</td>
<td>3.7(1)</td>
<td>4.6(1)</td>
<td>-0.57(9)</td>
<td>0.10(9)</td>
</tr>
<tr>
<td>O(5)</td>
<td>8.4(2)</td>
<td>5.1(1)</td>
<td>4.9(1)</td>
<td>0.2(1)</td>
<td>0.2(1)</td>
</tr>
<tr>
<td>O(6)</td>
<td>7.8(2)</td>
<td>8.3(2)</td>
<td>6.2(1)</td>
<td>-0.7(1)</td>
<td>0.7(1)</td>
</tr>
<tr>
<td>O(7)</td>
<td>3.5(3)</td>
<td>6.6(4)</td>
<td>6.2(4)</td>
<td>-0.5(3)</td>
<td>0.6(3)</td>
</tr>
<tr>
<td>O(7A)</td>
<td>5.8(5)</td>
<td>5.4(3)</td>
<td>7.4(5)</td>
<td>0.5(3)</td>
<td>2.6(4)</td>
</tr>
<tr>
<td>O(8)</td>
<td>11.2(7)</td>
<td>8.6(6)</td>
<td>26(2)</td>
<td>-7.6(8)</td>
<td>3.1(7)</td>
</tr>
<tr>
<td>O(8A)</td>
<td>10.9(9)</td>
<td>10.5(9)</td>
<td>16(1)</td>
<td>-7.6(8)</td>
<td>3.1(7)</td>
</tr>
<tr>
<td>O(9)</td>
<td>6.7(3)</td>
<td>9.1(4)</td>
<td>8.8(4)</td>
<td>-0.3(3)</td>
<td>-2.1(3)</td>
</tr>
<tr>
<td>O(9A)</td>
<td>12.0(6)</td>
<td>7.2(4)</td>
<td>7.1(4)</td>
<td>-1.0(4)</td>
<td>2.6(4)</td>
</tr>
<tr>
<td>N(1)</td>
<td>3.4(1)</td>
<td>2.22(8)</td>
<td>3.3(1)</td>
<td>-0.11(8)</td>
<td>0.72(8)</td>
</tr>
<tr>
<td>N(2)</td>
<td>2.9(1)</td>
<td>2.5(1)</td>
<td>4.2(1)</td>
<td>-0.09(8)</td>
<td>0.73(9)</td>
</tr>
<tr>
<td>N(3)</td>
<td>3.1(1)</td>
<td>2.43(9)</td>
<td>3.5(1)</td>
<td>0.03(8)</td>
<td>0.60(8)</td>
</tr>
<tr>
<td>N(4)</td>
<td>3.3(1)</td>
<td>2.33(9)</td>
<td>3.8(1)</td>
<td>-0.23(8)</td>
<td>0.81(9)</td>
</tr>
<tr>
<td>N(5)</td>
<td>4.1(1)</td>
<td>2.5(1)</td>
<td>4.2(1)</td>
<td>0.17(9)</td>
<td>0.8(1)</td>
</tr>
<tr>
<td>N(6)</td>
<td>5.6(2)</td>
<td>3.7(1)</td>
<td>5.0(1)</td>
<td>0.5(1)</td>
<td>-0.7(1)</td>
</tr>
<tr>
<td>N(7)</td>
<td>3.7(1)</td>
<td>2.8(1)</td>
<td>4.8(1)</td>
<td>0.17(8)</td>
<td>1.1(1)</td>
</tr>
<tr>
<td>N(8)</td>
<td>4.2(1)</td>
<td>5.3(1)</td>
<td>4.6(1)</td>
<td>0.6(1)</td>
<td>-0.2(1)</td>
</tr>
<tr>
<td>N(9)</td>
<td>5.4(2)</td>
<td>4.2(1)</td>
<td>9.9(2)</td>
<td>0.1(1)</td>
<td>3.8(2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>3.5(1)</td>
<td>2.8(1)</td>
<td>3.9(1)</td>
<td>0.1(1)</td>
<td>0.8(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>3.5(1)</td>
<td>3.8(1)</td>
<td>4.6(1)</td>
<td>0.9(1)</td>
<td>0.6(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>3.3(1)</td>
<td>4.5(1)</td>
<td>4.9(1)</td>
<td>0.4(1)</td>
<td>0.3(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>3.3(1)</td>
<td>3.6(1)</td>
<td>4.9(2)</td>
<td>-0.3(1)</td>
<td>0.7(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>3.6(1)</td>
<td>3.1(1)</td>
<td>4.1(1)</td>
<td>-0.1(1)</td>
<td>0.5(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>5.2(2)</td>
<td>4.2(1)</td>
<td>3.6(1)</td>
<td>0.1(1)</td>
<td>0.8(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>5.0(2)</td>
<td>4.2(1)</td>
<td>4.1(1)</td>
<td>0.1(1)</td>
<td>1.7(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>4.3(2)</td>
<td>3.0(1)</td>
<td>4.9(2)</td>
<td>-0.2(1)</td>
<td>1.7(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>4.8(2)</td>
<td>2.9(1)</td>
<td>6.4(2)</td>
<td>-0.2(1)</td>
<td>2.4(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>7.8(2)</td>
<td>3.1(1)</td>
<td>6.7(2)</td>
<td>0.6(1)</td>
<td>3.6(2)</td>
</tr>
<tr>
<td>C(11)</td>
<td>10.2(3)</td>
<td>4.0(2)</td>
<td>4.5(2)</td>
<td>2.4(2)</td>
<td>1.5(2)</td>
</tr>
<tr>
<td>C(12)</td>
<td>8.1(3)</td>
<td>5.6(2)</td>
<td>4.7(2)</td>
<td>2.5(2)</td>
<td>-1.6(2)</td>
</tr>
</tbody>
</table>
I-5. **Cu(2,5-me<sub>2</sub>pyz)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sup>a,b,c</sup>**

Bond lengths involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O(1)</td>
<td>2.388(2)</td>
<td>N(2)-C(6)</td>
<td>1.340(3)</td>
</tr>
<tr>
<td>Cu-N(1)</td>
<td>2.007(2)</td>
<td>N(3)-C(8)</td>
<td>1.347(3)</td>
</tr>
<tr>
<td>Cu-N(2)</td>
<td>2.005(2)</td>
<td>N(3)-C(11)</td>
<td>1.332(3)</td>
</tr>
<tr>
<td>Cu-N(3)</td>
<td>2.033(2)</td>
<td>N(4)-C(9)</td>
<td>1.322(4)</td>
</tr>
<tr>
<td>S-O(1)</td>
<td>1.433(2)</td>
<td>N(4)-C(10)</td>
<td>1.331(4)</td>
</tr>
<tr>
<td>S-O(2)</td>
<td>1.421(2)</td>
<td>C(2)-C(3)'</td>
<td>1.382(3)</td>
</tr>
<tr>
<td>S-O(3)</td>
<td>1.424(2)</td>
<td>C(3)-C(4)</td>
<td>1.494(3)</td>
</tr>
<tr>
<td>S-C(1)</td>
<td>1.813(3)</td>
<td>C(5)-C(6)&quot;</td>
<td>1.385(3)</td>
</tr>
<tr>
<td>F(1)-C(1)</td>
<td>1.319(4)</td>
<td>C(6)-C(7)</td>
<td>1.490(3)</td>
</tr>
<tr>
<td>F(2)-C(1)</td>
<td>1.325(4)</td>
<td>C(8)-C(9)</td>
<td>1.382(4)</td>
</tr>
<tr>
<td>F(3)-C(1)</td>
<td>1.311(4)</td>
<td>C(8)-C(12)</td>
<td>1.483(4)</td>
</tr>
<tr>
<td>N(1)-C(2)</td>
<td>1.341(3)</td>
<td>C(10)-C(11)</td>
<td>1.381(4)</td>
</tr>
<tr>
<td>N(1)-C(3)</td>
<td>1.342(3)</td>
<td>C(10)-C(13)</td>
<td>1.483(5)</td>
</tr>
<tr>
<td>N(2)-C(5)</td>
<td>1.336(3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bond lengths involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(2)-H(1)</td>
<td>0.96(3)</td>
<td>C(9)-H(9)</td>
<td>0.93(3)</td>
</tr>
<tr>
<td>C(4)-H(2)</td>
<td>0.92(4)</td>
<td>C(11)-H(10)</td>
<td>0.87(3)</td>
</tr>
<tr>
<td>C(4)-H(3)</td>
<td>0.89(4)</td>
<td>C(12)-H(11)</td>
<td>0.98(4)</td>
</tr>
<tr>
<td>C(4)-H(4)</td>
<td>0.82(4)</td>
<td>C(12)-H(12)</td>
<td>0.96(4)</td>
</tr>
<tr>
<td>C(5)-H(5)</td>
<td>0.98(2)</td>
<td>C(12)-H(13)</td>
<td>0.76(4)</td>
</tr>
<tr>
<td>C(7)-H(6)</td>
<td>0.89(3)</td>
<td>C(13)-H(14)</td>
<td>0.77(6)</td>
</tr>
<tr>
<td>C(7)-H(7)</td>
<td>1.01(7)</td>
<td>C(13)-H(13)</td>
<td>0.93(5)</td>
</tr>
<tr>
<td>C(7)-H(8)</td>
<td>0.82(5)</td>
<td>C(13)-H(16)</td>
<td>0.85(6)</td>
</tr>
</tbody>
</table>

---

* Unit cell parameters are given in Table 4-1.
* The symbols ' and " refer to symmetry operations 1-x, -y, -z and 1-x, 1-y, 1-z, respectively.
* Estimated standard deviations in the least significant figure are given in parentheses.
### Bond angles involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-Cu-N(1)</td>
<td>97.35(8)</td>
</tr>
<tr>
<td>O(1)-Cu-N(2)</td>
<td>100.55(8)</td>
</tr>
<tr>
<td>O(1)-Cu-N(3)</td>
<td>93.93(9)</td>
</tr>
<tr>
<td>N(1)-Cu-N(2)</td>
<td>126.28(8)</td>
</tr>
<tr>
<td>N(1)-Cu-N(3)</td>
<td>115.75(8)</td>
</tr>
<tr>
<td>N(2)-Cu-N(3)</td>
<td>112.99(8)</td>
</tr>
<tr>
<td>O(1)-S-O(2)</td>
<td>114.5(1)</td>
</tr>
<tr>
<td>O(1)-S-O(3)</td>
<td>114.2(1)</td>
</tr>
<tr>
<td>O(1)-S-C(1)</td>
<td>102.8(1)</td>
</tr>
<tr>
<td>O(2)-S-O(3)</td>
<td>115.6(2)</td>
</tr>
<tr>
<td>O(2)-S-C(1)</td>
<td>103.9(2)</td>
</tr>
<tr>
<td>O(3)-S-C(1)</td>
<td>103.7(1)</td>
</tr>
<tr>
<td>Cu-O(1)-S</td>
<td>143.1(1)</td>
</tr>
<tr>
<td>Cu-N(1)-C(2)</td>
<td>119.2(1)</td>
</tr>
<tr>
<td>Cu-N(1)-C(3)</td>
<td>123.8(1)</td>
</tr>
<tr>
<td>C(2)-N(1)-C(3)</td>
<td>117.0(2)</td>
</tr>
<tr>
<td>Cu-N(2)-C(5)</td>
<td>118.5(1)</td>
</tr>
<tr>
<td>Cu-N(2)-C(6)</td>
<td>124.7(1)</td>
</tr>
<tr>
<td>C(5)-N(2)-C(6)</td>
<td>116.7(2)</td>
</tr>
<tr>
<td>Cu-N(3)-C(8)</td>
<td>123.2(2)</td>
</tr>
<tr>
<td>Cu-N(3)-C(11)</td>
<td>120.3(2)</td>
</tr>
<tr>
<td>C(8)-N(3)-C(11)</td>
<td>116.5(2)</td>
</tr>
<tr>
<td>C(9)-N(4)-C(10)</td>
<td>116.5(3)</td>
</tr>
<tr>
<td>S-C(1)-F(1)</td>
<td>111.2(2)</td>
</tr>
<tr>
<td>S-C(1)-F(2)</td>
<td>111.5(2)</td>
</tr>
<tr>
<td>S-C(1)-F(3)</td>
<td>111.6(2)</td>
</tr>
<tr>
<td>F(1)-C(1)-F(2)</td>
<td>106.6(3)</td>
</tr>
<tr>
<td>F(1)-C(1)-F(3)</td>
<td>107.0(3)</td>
</tr>
<tr>
<td>F(2)-C(1)-F(3)</td>
<td>108.7(3)</td>
</tr>
<tr>
<td>N(1)-C(2)-C(3)'</td>
<td>123.3(2)</td>
</tr>
<tr>
<td>N(1)-C(3)-C(2)'</td>
<td>119.6(2)</td>
</tr>
<tr>
<td>N(1)-C(3)-C(4)</td>
<td>119.3(2)</td>
</tr>
<tr>
<td>C(2)'-C(3)-C(4)</td>
<td>121.0(2)</td>
</tr>
<tr>
<td>F(1)-C(1)-F(2)</td>
<td>106.6(3)</td>
</tr>
<tr>
<td>F(1)-C(1)-F(3)</td>
<td>107.0(3)</td>
</tr>
<tr>
<td>F(2)-C(1)-F(3)</td>
<td>108.7(3)</td>
</tr>
<tr>
<td>N(1)-C(2)-C(3)'</td>
<td>123.3(2)</td>
</tr>
<tr>
<td>N(1)-C(3)-C(2)'</td>
<td>119.6(2)</td>
</tr>
<tr>
<td>N(1)-C(3)-C(4)</td>
<td>119.3(2)</td>
</tr>
<tr>
<td>C(2)'-C(3)-C(4)</td>
<td>121.0(2)</td>
</tr>
<tr>
<td>O(1)-S-C(1)</td>
<td>102.8(1)</td>
</tr>
<tr>
<td>O(2)-S-O(3)</td>
<td>115.6(2)</td>
</tr>
<tr>
<td>O(2)-S-C(1)</td>
<td>103.9(2)</td>
</tr>
<tr>
<td>O(3)-S-C(1)</td>
<td>103.7(1)</td>
</tr>
<tr>
<td>N(1)-C(2)-H(1)</td>
<td>118(2)</td>
</tr>
<tr>
<td>C(3)'-C(2)-H(1)</td>
<td>118(2)</td>
</tr>
<tr>
<td>C(3)-C(4)-H(2)</td>
<td>110(2)</td>
</tr>
<tr>
<td>C(3)-C(4)-H(3)</td>
<td>113(2)</td>
</tr>
<tr>
<td>C(3)-C(4)-H(4)</td>
<td>109(3)</td>
</tr>
<tr>
<td>H(2)-C(4)-H(3)</td>
<td>103(3)</td>
</tr>
<tr>
<td>H(2)-C(4)-H(4)</td>
<td>111(3)</td>
</tr>
<tr>
<td>H(3)-C(4)-H(4)</td>
<td>109(3)</td>
</tr>
<tr>
<td>N(2)-C(5)-H(5)</td>
<td>119(1)</td>
</tr>
<tr>
<td>C(6)'-C(5)-H(5)</td>
<td>117(1)</td>
</tr>
<tr>
<td>C(6)-C(7)-H(6)</td>
<td>114(2)</td>
</tr>
<tr>
<td>C(6)-C(7)-H(7)</td>
<td>109(4)</td>
</tr>
<tr>
<td>C(6)-C(7)-H(8)</td>
<td>113(3)</td>
</tr>
<tr>
<td>H(6)-C(7)-H(7)</td>
<td>106(4)</td>
</tr>
<tr>
<td>H(6)-C(7)-H(8)</td>
<td>110(4)</td>
</tr>
<tr>
<td>H(7)-C(7)-H(8)</td>
<td>103(4)</td>
</tr>
</tbody>
</table>

### Bond angles involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(2)-H(1)</td>
<td>118(2)</td>
</tr>
<tr>
<td>C(3)'-C(2)-H(1)</td>
<td>118(2)</td>
</tr>
<tr>
<td>C(3)-C(4)-H(2)</td>
<td>110(2)</td>
</tr>
<tr>
<td>C(3)-C(4)-H(3)</td>
<td>113(2)</td>
</tr>
<tr>
<td>C(3)-C(4)-H(4)</td>
<td>109(3)</td>
</tr>
<tr>
<td>H(2)-C(4)-H(3)</td>
<td>103(3)</td>
</tr>
<tr>
<td>H(2)-C(4)-H(4)</td>
<td>111(3)</td>
</tr>
<tr>
<td>H(3)-C(4)-H(4)</td>
<td>109(3)</td>
</tr>
<tr>
<td>N(2)-C(5)-H(5)</td>
<td>119(1)</td>
</tr>
<tr>
<td>C(6)'-C(5)-H(5)</td>
<td>117(1)</td>
</tr>
<tr>
<td>C(6)-C(7)-H(6)</td>
<td>114(2)</td>
</tr>
<tr>
<td>C(6)-C(7)-H(7)</td>
<td>109(4)</td>
</tr>
<tr>
<td>C(6)-C(7)-H(8)</td>
<td>113(3)</td>
</tr>
<tr>
<td>H(6)-C(7)-H(7)</td>
<td>106(4)</td>
</tr>
<tr>
<td>H(6)-C(7)-H(8)</td>
<td>110(4)</td>
</tr>
<tr>
<td>H(7)-C(7)-H(8)</td>
<td>103(4)</td>
</tr>
<tr>
<td>N(4)-C(9)-H(9)</td>
<td>117(2)</td>
</tr>
<tr>
<td>C(8)-C(9)-H(9)</td>
<td>119(2)</td>
</tr>
<tr>
<td>N(3)-C(11)-H(10)</td>
<td>116(2)</td>
</tr>
<tr>
<td>C(10)-C(11)-H(10)</td>
<td>120(2)</td>
</tr>
<tr>
<td>C(8)-C(12)-H(11)</td>
<td>111(2)</td>
</tr>
<tr>
<td>C(8)-C(12)-H(12)</td>
<td>112(2)</td>
</tr>
<tr>
<td>C(8)-C(12)-H(13)</td>
<td>102(3)</td>
</tr>
<tr>
<td>H(11)-C(12)-H(12)</td>
<td>99(3)</td>
</tr>
<tr>
<td>H(11)-C(12)-H(13)</td>
<td>117(4)</td>
</tr>
<tr>
<td>H(12)-C(12)-H(13)</td>
<td>116(4)</td>
</tr>
<tr>
<td>C(10)-C(13)-H(14)</td>
<td>117(4)</td>
</tr>
<tr>
<td>C(10)-C(13)-H(15)</td>
<td>109(3)</td>
</tr>
<tr>
<td>C(10)-C(13)-H(16)</td>
<td>107(4)</td>
</tr>
<tr>
<td>H(14)-C(13)-H(15)</td>
<td>97(5)</td>
</tr>
<tr>
<td>H(14)-C(13)-H(16)</td>
<td>98(5)</td>
</tr>
<tr>
<td>H(15)-C(13)-H(16)</td>
<td>130(5)</td>
</tr>
</tbody>
</table>
Final atomic coordinates (fractional) and equivalent isotropic thermal parameters (Å²) for non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.32664(3)</td>
<td>0.25447(2)</td>
<td>0.15988(3)</td>
<td>3.06(1)</td>
</tr>
<tr>
<td>S</td>
<td>0.14852(7)</td>
<td>0.20881(5)</td>
<td>0.41331(8)</td>
<td>3.46(2)</td>
</tr>
<tr>
<td>F(1)</td>
<td>-0.0747(3)</td>
<td>0.1201(2)</td>
<td>0.4295(4)</td>
<td>8.4(1)</td>
</tr>
<tr>
<td>F(2)</td>
<td>-0.1222(3)</td>
<td>0.1087(2)</td>
<td>0.1735(3)</td>
<td>8.2(1)</td>
</tr>
<tr>
<td>F(3)</td>
<td>0.0495(3)</td>
<td>-0.0067(2)</td>
<td>0.3004(4)</td>
<td>8.5(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.2020(2)</td>
<td>0.1774(2)</td>
<td>0.2794(3)</td>
<td>4.83(8)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.2617(3)</td>
<td>0.1872(2)</td>
<td>0.5696(3)</td>
<td>5.8(1)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.0672(3)</td>
<td>0.3196(2)</td>
<td>0.4351(3)</td>
<td>5.80(9)</td>
</tr>
<tr>
<td>N(1)</td>
<td>0.4310(2)</td>
<td>0.1035(1)</td>
<td>0.0706(2)</td>
<td>2.53(5)</td>
</tr>
<tr>
<td>N(2)</td>
<td>0.4374(2)</td>
<td>0.3957(1)</td>
<td>0.3634(2)</td>
<td>2.46(5)</td>
</tr>
<tr>
<td>N(3)</td>
<td>0.1164(2)</td>
<td>0.2962(2)</td>
<td>-0.0188(2)</td>
<td>3.24(6)</td>
</tr>
<tr>
<td>N(4)</td>
<td>-0.1786(3)</td>
<td>0.3542(3)</td>
<td>-0.2518(3)</td>
<td>5.4(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>-0.0070(4)</td>
<td>0.1017(3)</td>
<td>0.3239(5)</td>
<td>5.1(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.4058(3)</td>
<td>0.0653(2)</td>
<td>-0.0967(3)</td>
<td>2.72(7)</td>
</tr>
<tr>
<td>C(3)</td>
<td>0.5268(3)</td>
<td>0.0371(2)</td>
<td>0.1695(3)</td>
<td>2.62(6)</td>
</tr>
<tr>
<td>C(4)</td>
<td>0.5616(4)</td>
<td>0.0766(3)</td>
<td>0.3578(3)</td>
<td>3.7(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>0.3649(3)</td>
<td>0.4566(2)</td>
<td>0.4650(3)</td>
<td>2.59(6)</td>
</tr>
<tr>
<td>C(6)</td>
<td>0.5754(2)</td>
<td>0.4394(2)</td>
<td>0.3993(3)</td>
<td>2.51(6)</td>
</tr>
<tr>
<td>C(7)</td>
<td>0.6648(4)</td>
<td>0.3736(3)</td>
<td>0.2946(4)</td>
<td>4.2(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>0.1064(3)</td>
<td>0.3642(2)</td>
<td>-0.1123(3)</td>
<td>3.74(9)</td>
</tr>
<tr>
<td>C(9)</td>
<td>-0.0424(4)</td>
<td>0.3903(3)</td>
<td>-0.2274(4)</td>
<td>5.2(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>-0.1685(3)</td>
<td>0.2876(3)</td>
<td>-0.1586(3)</td>
<td>4.3(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>-0.0209(3)</td>
<td>0.2594(2)</td>
<td>-0.0443(3)</td>
<td>3.79(9)</td>
</tr>
<tr>
<td>C(12)</td>
<td>0.2565(5)</td>
<td>0.4079(3)</td>
<td>-0.0869(5)</td>
<td>4.9(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>-0.3177(5)</td>
<td>0.2453(5)</td>
<td>-0.1800(6)</td>
<td>6.4(2)</td>
</tr>
</tbody>
</table>

Hydrogen atom coordinates (fractional) and isotropic thermal parameters (Å²).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B(iso)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>0.340(4)</td>
<td>0.112(3)</td>
<td>-0.168(4)</td>
<td>4.8(7)</td>
</tr>
<tr>
<td>H(2)</td>
<td>0.470(4)</td>
<td>0.075(3)</td>
<td>0.369(4)</td>
<td>5.0(7)</td>
</tr>
<tr>
<td>H(3)</td>
<td>0.628(4)</td>
<td>0.028(3)</td>
<td>0.414(4)</td>
<td>6.0(8)</td>
</tr>
<tr>
<td>H(4)</td>
<td>0.600(5)</td>
<td>0.144(4)</td>
<td>0.406(5)</td>
<td>6(1)</td>
</tr>
<tr>
<td>H(5)</td>
<td>0.264(3)</td>
<td>0.427(2)</td>
<td>0.444(3)</td>
<td>2.8(5)</td>
</tr>
<tr>
<td>H(6)</td>
<td>0.757(4)</td>
<td>0.408(3)</td>
<td>0.328(4)</td>
<td>4.6(7)</td>
</tr>
<tr>
<td>H(7)</td>
<td>0.694(7)</td>
<td>0.292(6)</td>
<td>0.307(8)</td>
<td>14(2)</td>
</tr>
<tr>
<td>H(8)</td>
<td>0.611(6)</td>
<td>0.360(4)</td>
<td>0.189(7)</td>
<td>10(1)</td>
</tr>
<tr>
<td>H(9)</td>
<td>-0.049(4)</td>
<td>0.438(3)</td>
<td>-0.291(4)</td>
<td>5.6(8)</td>
</tr>
<tr>
<td>H(10)</td>
<td>-0.014(3)</td>
<td>0.213(2)</td>
<td>0.013(4)</td>
<td>3.7(6)</td>
</tr>
<tr>
<td>H(11)</td>
<td>0.330(5)</td>
<td>0.342(4)</td>
<td>-0.104(5)</td>
<td>8(1)</td>
</tr>
<tr>
<td>H(12)</td>
<td>0.320(4)</td>
<td>0.450(3)</td>
<td>0.033(5)</td>
<td>6.3(8)</td>
</tr>
<tr>
<td>H(13)</td>
<td>0.225(5)</td>
<td>0.443(4)</td>
<td>-0.150(6)</td>
<td>8(1)</td>
</tr>
<tr>
<td>H(14)</td>
<td>-0.395(7)</td>
<td>0.254(5)</td>
<td>-0.256(8)</td>
<td>11(2)</td>
</tr>
<tr>
<td>H(15)</td>
<td>-0.318(6)</td>
<td>0.163(4)</td>
<td>-0.221(6)</td>
<td>9(1)</td>
</tr>
<tr>
<td>H(16)</td>
<td>-0.339(6)</td>
<td>0.292(5)</td>
<td>-0.097(8)</td>
<td>12(2)</td>
</tr>
</tbody>
</table>
Anisotropic thermal parameters $\times 10^3$

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>41.2(2)</td>
<td>31.6(1)</td>
<td>35.3(2)</td>
<td>0(1)</td>
<td>15.5(1)</td>
<td>3.4(1)</td>
</tr>
<tr>
<td>S</td>
<td>40.1(3)</td>
<td>46.9(3)</td>
<td>52.6(3)</td>
<td>0.8(2)</td>
<td>23.5(3)</td>
<td>20.5(3)</td>
</tr>
<tr>
<td>F(1)</td>
<td>113(2)</td>
<td>112(2)</td>
<td>146(2)</td>
<td>-23(1)</td>
<td>90(2)</td>
<td>41(2)</td>
</tr>
<tr>
<td>F(2)</td>
<td>67(1)</td>
<td>128(2)</td>
<td>100(2)</td>
<td>-39(1)</td>
<td>7(1)</td>
<td>42(1)</td>
</tr>
<tr>
<td>F(3)</td>
<td>124(2)</td>
<td>47(1)</td>
<td>145(2)</td>
<td>-10(1)</td>
<td>61(2)</td>
<td>18(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>51(1)</td>
<td>87(1)</td>
<td>62(1)</td>
<td>1(1)</td>
<td>32(1)</td>
<td>31(1)</td>
</tr>
<tr>
<td>O(2)</td>
<td>72(1)</td>
<td>88(2)</td>
<td>53(1)</td>
<td>0(1)</td>
<td>17(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td>O(3)</td>
<td>64(1)</td>
<td>50(1)</td>
<td>117(2)</td>
<td>6(1)</td>
<td>49(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td>N(1)</td>
<td>34(1)</td>
<td>29.4(8)</td>
<td>29.0(8)</td>
<td>-1.3(8)</td>
<td>13.4(7)</td>
<td>4.4(7)</td>
</tr>
<tr>
<td>N(2)</td>
<td>30.5(9)</td>
<td>27.5(8)</td>
<td>31.8(8)</td>
<td>-0.6(7)</td>
<td>12.7(7)</td>
<td>6.2(7)</td>
</tr>
<tr>
<td>N(3)</td>
<td>46(1)</td>
<td>38(1)</td>
<td>31.3(9)</td>
<td>1.6(8)</td>
<td>14.2(8)</td>
<td>7.6(8)</td>
</tr>
<tr>
<td>N(4)</td>
<td>54(2)</td>
<td>93(2)</td>
<td>51(1)</td>
<td>17(1)</td>
<td>19(1)</td>
<td>31(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>66(2)</td>
<td>56(2)</td>
<td>82(2)</td>
<td>-9(1)</td>
<td>38(2)</td>
<td>23(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>38(1)</td>
<td>32(1)</td>
<td>31(1)</td>
<td>1.4(9)</td>
<td>14(1)</td>
<td>9.7(8)</td>
</tr>
<tr>
<td>C(3)</td>
<td>35(1)</td>
<td>34(1)</td>
<td>29(1)</td>
<td>-2.5(8)</td>
<td>14.3(8)</td>
<td>6.0(8)</td>
</tr>
<tr>
<td>C(4)</td>
<td>55(2)</td>
<td>51(2)</td>
<td>32(1)</td>
<td>12(1)</td>
<td>22(1)</td>
<td>12(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>28(1)</td>
<td>32(1)</td>
<td>38(1)</td>
<td>-1.3(8)</td>
<td>14.7(9)</td>
<td>9.2(8)</td>
</tr>
<tr>
<td>C(6)</td>
<td>31(1)</td>
<td>32(1)</td>
<td>32(1)</td>
<td>1.4(8)</td>
<td>15.6(8)</td>
<td>8.9(8)</td>
</tr>
<tr>
<td>C(7)</td>
<td>47(2)</td>
<td>54(2)</td>
<td>57(2)</td>
<td>-4(1)</td>
<td>35(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>56(2)</td>
<td>47(1)</td>
<td>37(1)</td>
<td>4(1)</td>
<td>21(1)</td>
<td>12(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>73(2)</td>
<td>79(2)</td>
<td>54(2)</td>
<td>18(2)</td>
<td>26(2)</td>
<td>39(2)</td>
</tr>
<tr>
<td>C(10)</td>
<td>46(1)</td>
<td>68(2)</td>
<td>36(1)</td>
<td>3(1)</td>
<td>16(1)</td>
<td>7(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>47(1)</td>
<td>54(1)</td>
<td>37(1)</td>
<td>-5(1)</td>
<td>13(1)</td>
<td>14(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>71(2)</td>
<td>66(2)</td>
<td>58(2)</td>
<td>-4(2)</td>
<td>29(2)</td>
<td>25(2)</td>
</tr>
<tr>
<td>C(13)</td>
<td>47(2)</td>
<td>123(4)</td>
<td>54(2)</td>
<td>-12(2)</td>
<td>14(2)</td>
<td>13(2)</td>
</tr>
</tbody>
</table>
I-6. [Cu$_2$(2,5-me$_2$pyz)]$_2$[PF$_6$]$_2$\textsuperscript{a,b,c,d}

Bond lengths involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-F(2)</td>
<td>2.69(1)</td>
<td>P(1)-F(6A)</td>
<td>1.67(2)</td>
</tr>
<tr>
<td>Cu(1)-F(2A)</td>
<td>2.73(3)</td>
<td>N(1)-C(1)</td>
<td>1.344(5)</td>
</tr>
<tr>
<td>Cu(1)-N(1)</td>
<td>1.987(4)</td>
<td>N(1)-C(4)</td>
<td>1.340(5)</td>
</tr>
<tr>
<td>Cu(1)-N(2)'</td>
<td>1.971(4)</td>
<td>N(2)-C(2)</td>
<td>1.333(6)</td>
</tr>
<tr>
<td>Cu(1)-N(3)</td>
<td>2.085(4)</td>
<td>N(2)-C(3)</td>
<td>1.343(5)</td>
</tr>
<tr>
<td>P(1)-F(1)</td>
<td>1.559(4)</td>
<td>N(3)-C(7)</td>
<td>1.347(6)</td>
</tr>
<tr>
<td>P(1)-F(2)</td>
<td>1.51(1)</td>
<td>N(3)-C(8)</td>
<td>1.320(6)</td>
</tr>
<tr>
<td>P(1)-F(2A)</td>
<td>1.55(2)</td>
<td>C(1)-C(2)</td>
<td>1.385(6)</td>
</tr>
<tr>
<td>P(1)-F(3)</td>
<td>1.57(1)</td>
<td>C(1)-C(5)</td>
<td>1.508(7)</td>
</tr>
<tr>
<td>P(1)-F(3A)</td>
<td>1.39(1)</td>
<td>C(3)-C(4)</td>
<td>1.384(6)</td>
</tr>
<tr>
<td>P(1)-F(4)</td>
<td>1.558(4)</td>
<td>C(3)-C(6)</td>
<td>1.490(6)</td>
</tr>
<tr>
<td>P(1)-F(5)</td>
<td>1.604(9)</td>
<td>C(7)-C(8)&quot;</td>
<td>1.381(6)</td>
</tr>
<tr>
<td>P(1)-F(5A)</td>
<td>1.56(1)</td>
<td>C(7)-C(9)</td>
<td>1.496(7)</td>
</tr>
<tr>
<td>P(1)-F(6)</td>
<td>1.503(8)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bond lengths involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(2)-H(1)</td>
<td>0.98</td>
<td>C(6)-H(7)</td>
<td>0.98</td>
</tr>
<tr>
<td>C(4)-H(2)</td>
<td>0.98</td>
<td>C(6)-H(8)</td>
<td>0.98</td>
</tr>
<tr>
<td>C(5)-H(3)</td>
<td>0.98</td>
<td>C(8)-H(9)</td>
<td>0.98</td>
</tr>
<tr>
<td>C(5)-H(4)</td>
<td>0.98</td>
<td>C(9)-H(10)</td>
<td>0.98</td>
</tr>
<tr>
<td>C(5)-H(5)</td>
<td>0.98</td>
<td>C(9)-H(11)</td>
<td>0.98</td>
</tr>
<tr>
<td>C(6)-H(6)</td>
<td>0.98</td>
<td>C(9)-H(12)</td>
<td>0.98</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Unit cell parameters are given in Table 4-5.
\textsuperscript{b} The symbols ', " and * refer to symmetry operations \(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z\); \(-x, -y, 1-z\); and \(x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}\) respectively.
\textsuperscript{c} Estimated standard deviations in the least significant figure are given in parentheses.
\textsuperscript{d} \(B_{eq} = (8/3)\pi^2\Sigma\Sigma U_{ij}a_i^*a_j^*(a_i.a_j)\).
Bond angles involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-Cu(1)-N(2)'</td>
<td>144.5(2)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(3)</td>
<td>107.6(2)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-F(2)</td>
<td>82.6(3)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-F(2A)</td>
<td>93.8(5)</td>
</tr>
<tr>
<td>N(2)'-Cu(1)-N(3)</td>
<td>107.8(1)</td>
</tr>
<tr>
<td>N(2)'-Cu(1)-F(2)</td>
<td>99.6(4)</td>
</tr>
<tr>
<td>N(2)'-Cu(1)-F(2A)</td>
<td>80.8(6)</td>
</tr>
<tr>
<td>N(3)-Cu(1)-F(2)</td>
<td>92.3(3)</td>
</tr>
<tr>
<td>N(3)-Cu(1)-F(2A)</td>
<td>104.6(8)</td>
</tr>
<tr>
<td>F(1)-P(1)-F(2)</td>
<td>89.3(5)</td>
</tr>
<tr>
<td>F(1)-P(1)-F(2A)</td>
<td>94(1)</td>
</tr>
<tr>
<td>F(1)-P(1)-F(3)</td>
<td>86.9(6)</td>
</tr>
<tr>
<td>F(1)-P(1)-F(3A)</td>
<td>86.3(8)</td>
</tr>
<tr>
<td>F(1)-P(1)-F(4)</td>
<td>178.2(3)</td>
</tr>
<tr>
<td>F(1)-P(1)-F(5)</td>
<td>95.7(4)</td>
</tr>
<tr>
<td>F(1)-P(1)-F(5A)</td>
<td>75.6(6)</td>
</tr>
<tr>
<td>F(1)-P(1)-F(6)</td>
<td>97.7(5)</td>
</tr>
<tr>
<td>F(1)-P(1)-F(6A)</td>
<td>81.4(7)</td>
</tr>
<tr>
<td>F(2)-P(1)-F(3)</td>
<td>90.8(6)</td>
</tr>
<tr>
<td>F(2)-P(1)-F(4)</td>
<td>90.0(5)</td>
</tr>
<tr>
<td>F(2)-P(1)-F(5)</td>
<td>174.6(6)</td>
</tr>
<tr>
<td>F(2)-P(1)-F(6)</td>
<td>92.7(6)</td>
</tr>
<tr>
<td>F(2A)-P(1)-F(3A)</td>
<td>98(1)</td>
</tr>
<tr>
<td>F(2A)-P(1)-F(4)</td>
<td>84(1)</td>
</tr>
<tr>
<td>F(2A)-P(1)-F(5A)</td>
<td>163(1)</td>
</tr>
<tr>
<td>F(2A)-P(1)-F(6A)</td>
<td>83(1)</td>
</tr>
<tr>
<td>F(3)-P(1)-F(4)</td>
<td>91.5(6)</td>
</tr>
<tr>
<td>F(3)-P(1)-F(5)</td>
<td>87.7(5)</td>
</tr>
<tr>
<td>F(3)-P(1)-F(6)</td>
<td>174.3(6)</td>
</tr>
<tr>
<td>F(3A)-P(1)-F(4)</td>
<td>92.9(8)</td>
</tr>
<tr>
<td>F(3A)-P(1)-F(5A)</td>
<td>96(1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(3A)-P(1)-F(6A)</td>
<td>168(1)</td>
</tr>
<tr>
<td>F(4)-P(1)-F(5)</td>
<td>84.9(4)</td>
</tr>
<tr>
<td>F(4)-P(1)-F(5A)</td>
<td>106.1(6)</td>
</tr>
<tr>
<td>F(4)-P(1)-F(6)</td>
<td>84.0(5)</td>
</tr>
<tr>
<td>F(4)-P(1)-F(6A)</td>
<td>99.3(7)</td>
</tr>
<tr>
<td>F(5)-P(1)-F(6)</td>
<td>88.4(5)</td>
</tr>
<tr>
<td>F(5A)-P(1)-F(6A)</td>
<td>82(1)</td>
</tr>
<tr>
<td>P(1)-F(2)-Cu(1)</td>
<td>155(1)</td>
</tr>
<tr>
<td>P(1)-F(2A)-Cu(1)</td>
<td>147(2)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-C(1)</td>
<td>125.7(3)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-C(4)</td>
<td>117.1(3)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-C(2)</td>
<td>117.0(4)</td>
</tr>
<tr>
<td>Cu(1)-N(2)-C(2)</td>
<td>119.9(3)</td>
</tr>
<tr>
<td>Cu(1)-N(2)-C(3)</td>
<td>122.7(3)</td>
</tr>
<tr>
<td>C(2)-N(2)-C(3)</td>
<td>116.8(4)</td>
</tr>
<tr>
<td>Cu(1)-N(3)-C(7)</td>
<td>124.7(3)</td>
</tr>
<tr>
<td>Cu(1)-N(3)-C(8)</td>
<td>118.2(4)</td>
</tr>
<tr>
<td>C(7)-N(3)-C(8)</td>
<td>116.9(4)</td>
</tr>
<tr>
<td>N(1)-C(1)-C(2)</td>
<td>119.4(4)</td>
</tr>
<tr>
<td>N(1)-C(1)-C(5)</td>
<td>118.7(4)</td>
</tr>
<tr>
<td>C(2)-C(1)-C(5)</td>
<td>121.8(5)</td>
</tr>
<tr>
<td>N(2)-C(2)-C(1)</td>
<td>123.7(5)</td>
</tr>
<tr>
<td>N(2)-C(3)-C(4)</td>
<td>119.9(4)</td>
</tr>
<tr>
<td>C(4)-C(3)-C(6)</td>
<td>118.9(4)</td>
</tr>
<tr>
<td>N(1)-C(4)-C(3)</td>
<td>123.1(4)</td>
</tr>
<tr>
<td>N(3)-C(7)-C(8)</td>
<td>119.1(5)</td>
</tr>
<tr>
<td>N(3)-C(7)-C(9)</td>
<td>119.1(5)</td>
</tr>
<tr>
<td>C(8)-C(7)-C(9)</td>
<td>121.8(5)</td>
</tr>
<tr>
<td>N(3)-C(8)-C(7)</td>
<td>123.9(4)</td>
</tr>
</tbody>
</table>
### Bond angles involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(2)-C(2)-H(1)</td>
<td>118.1</td>
</tr>
<tr>
<td>C(1)-C(2)-H(1)</td>
<td>118.2</td>
</tr>
<tr>
<td>N(1)-C(4)-H(2)</td>
<td>118.5</td>
</tr>
<tr>
<td>C(3)-C(4)-H(2)</td>
<td>118.4</td>
</tr>
<tr>
<td>C(1)-C(5)-H(3)</td>
<td>109.5</td>
</tr>
<tr>
<td>C(1)-C(5)-H(4)</td>
<td>109.5</td>
</tr>
<tr>
<td>C(1)-C(5)-H(5)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(3)-C(5)-H(4)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(3)-C(5)-H(5)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(4)-C(5)-H(5)</td>
<td>109.4</td>
</tr>
<tr>
<td>C(3)-C(6)-H(6)</td>
<td>109.5</td>
</tr>
<tr>
<td>C(3)-C(6)-H(7)</td>
<td>109.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(3)-C(6)-H(8)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(6)-C(6)-H(7)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(6)-C(6)-H(8)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(7)-C(6)-H(8)</td>
<td>109.5</td>
</tr>
<tr>
<td>N(3)-C(8)-H(9)</td>
<td>118.1</td>
</tr>
<tr>
<td>C(7)-C(8)-H(9)</td>
<td>118.0</td>
</tr>
<tr>
<td>C(7)-C(9)-H(10)</td>
<td>109.5</td>
</tr>
<tr>
<td>C(7)-C(9)-H(11)</td>
<td>109.5</td>
</tr>
<tr>
<td>C(7)-C(9)-H(12)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(10)-C(9)-H(11)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(10)-C(9)-H(12)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(11)-C(9)-H(12)</td>
<td>109.5</td>
</tr>
</tbody>
</table>

### Hydrogen atom coordinates (fractional) and isotropic thermal parameters (Å²).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Biso</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>-0.1362</td>
<td>0.3572</td>
<td>0.2999</td>
<td>3.8</td>
</tr>
<tr>
<td>H(2)</td>
<td>0.2234</td>
<td>0.1273</td>
<td>0.3171</td>
<td>3.3</td>
</tr>
<tr>
<td>H(3)</td>
<td>-0.0363</td>
<td>0.3226</td>
<td>0.5711</td>
<td>6.2</td>
</tr>
<tr>
<td>H(4)</td>
<td>0.1582</td>
<td>0.3504</td>
<td>0.5583</td>
<td>6.2</td>
</tr>
<tr>
<td>H(5)</td>
<td>0.0011</td>
<td>0.4031</td>
<td>0.4920</td>
<td>6.2</td>
</tr>
<tr>
<td>H(6)</td>
<td>0.0823</td>
<td>0.1792</td>
<td>0.0324</td>
<td>5.5</td>
</tr>
<tr>
<td>H(7)</td>
<td>-0.0534</td>
<td>0.1146</td>
<td>0.0790</td>
<td>5.5</td>
</tr>
<tr>
<td>H(8)</td>
<td>0.1488</td>
<td>0.1009</td>
<td>0.1146</td>
<td>5.5</td>
</tr>
<tr>
<td>H(9)</td>
<td>0.2740</td>
<td>0.0183</td>
<td>0.6119</td>
<td>3.8</td>
</tr>
<tr>
<td>H(10)</td>
<td>0.7052</td>
<td>0.1245</td>
<td>0.3270</td>
<td>5.6</td>
</tr>
<tr>
<td>H(11)</td>
<td>0.7076</td>
<td>0.1758</td>
<td>0.4500</td>
<td>5.6</td>
</tr>
<tr>
<td>H(12)</td>
<td>0.5409</td>
<td>0.1790</td>
<td>0.3537</td>
<td>5.6</td>
</tr>
</tbody>
</table>
Final atomic coordinates (fractional) and $B_{eq}$ (Å$^2$) for non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{eq}$</th>
<th>occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>0.32309(8)</td>
<td>0.19576(4)</td>
<td>0.55033(5)</td>
<td>3.28(3)</td>
<td></td>
</tr>
<tr>
<td>P(1)</td>
<td>-0.0642(2)</td>
<td>0.0972(1)</td>
<td>0.7295(2)</td>
<td>4.13(8)</td>
<td></td>
</tr>
<tr>
<td>F(1)</td>
<td>-0.2144(5)</td>
<td>0.1512(3)</td>
<td>0.6665(4)</td>
<td>10.2(3)</td>
<td></td>
</tr>
<tr>
<td>F(2)</td>
<td>0.047(2)</td>
<td>0.1230(8)</td>
<td>0.633(1)</td>
<td>8.3(8)</td>
<td>0.65</td>
</tr>
<tr>
<td>F(2A)</td>
<td>0.078(3)</td>
<td>0.159(2)</td>
<td>0.699(3)</td>
<td>12.2(2)</td>
<td>0.35</td>
</tr>
<tr>
<td>F(3)</td>
<td>-0.009(2)</td>
<td>0.1781(6)</td>
<td>0.804(1)</td>
<td>10.7(8)</td>
<td>0.65</td>
</tr>
<tr>
<td>F(3A)</td>
<td>-0.101(3)</td>
<td>0.135(2)</td>
<td>0.835(1)</td>
<td>11.2(2)</td>
<td>0.35</td>
</tr>
<tr>
<td>F(4)</td>
<td>0.0891(5)</td>
<td>0.0459(3)</td>
<td>0.7935(4)</td>
<td>10.2(3)</td>
<td></td>
</tr>
<tr>
<td>F(5)</td>
<td>-0.166(1)</td>
<td>0.0675(8)</td>
<td>0.839(1)</td>
<td>9.6(6)</td>
<td>0.65</td>
</tr>
<tr>
<td>F(5A)</td>
<td>-0.223(2)</td>
<td>0.037(1)</td>
<td>0.719(2)</td>
<td>8(1)</td>
<td>0.35</td>
</tr>
<tr>
<td>F(6)</td>
<td>-0.112(2)</td>
<td>0.0148(5)</td>
<td>0.669(1)</td>
<td>10.5(7)</td>
<td>0.65</td>
</tr>
<tr>
<td>F(6A)</td>
<td>-0.053(3)</td>
<td>0.065(2)</td>
<td>0.589(2)</td>
<td>12(1)</td>
<td>0.35</td>
</tr>
<tr>
<td>N(1)</td>
<td>0.1512(5)</td>
<td>0.2250(2)</td>
<td>0.4130(3)</td>
<td>2.6(2)</td>
<td></td>
</tr>
<tr>
<td>N(2)</td>
<td>-0.0566(5)</td>
<td>0.2628(2)</td>
<td>0.2024(3)</td>
<td>2.8(2)</td>
<td></td>
</tr>
<tr>
<td>N(3)</td>
<td>0.4295(5)</td>
<td>0.0793(2)</td>
<td>0.5132(3)</td>
<td>2.8(2)</td>
<td></td>
</tr>
<tr>
<td>C(1)</td>
<td>0.0427(6)</td>
<td>0.2910(3)</td>
<td>0.4080(4)</td>
<td>2.9(2)</td>
<td></td>
</tr>
<tr>
<td>C(2)</td>
<td>-0.0587(6)</td>
<td>0.3085(3)</td>
<td>0.3020(4)</td>
<td>3.2(2)</td>
<td></td>
</tr>
<tr>
<td>C(3)</td>
<td>0.0487(6)</td>
<td>0.1956(3)</td>
<td>0.2085(5)</td>
<td>2.7(2)</td>
<td></td>
</tr>
<tr>
<td>C(4)</td>
<td>0.1496(6)</td>
<td>0.1774(3)</td>
<td>0.3143(4)</td>
<td>2.8(2)</td>
<td></td>
</tr>
<tr>
<td>C(5)</td>
<td>0.0413(8)</td>
<td>0.3466(4)</td>
<td>0.5169(5)</td>
<td>5.2(3)</td>
<td></td>
</tr>
<tr>
<td>C(6)</td>
<td>0.0574(7)</td>
<td>0.1431(4)</td>
<td>0.0993(4)</td>
<td>4.6(3)</td>
<td></td>
</tr>
<tr>
<td>C(7)</td>
<td>0.5625(7)</td>
<td>0.0684(3)</td>
<td>0.4474(4)</td>
<td>3.1(2)</td>
<td></td>
</tr>
<tr>
<td>C(8)</td>
<td>0.3708(6)</td>
<td>0.0115(3)</td>
<td>0.5637(4)</td>
<td>3.1(2)</td>
<td></td>
</tr>
<tr>
<td>C(9)</td>
<td>0.6353(7)</td>
<td>0.1434(3)</td>
<td>0.3895(5)</td>
<td>4.7(3)</td>
<td></td>
</tr>
</tbody>
</table>
### Anisotropic thermal parameters $\times 10^3$

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>4.51(4)</td>
<td>4.25(4)</td>
<td>3.34(3)</td>
<td>0.47(4)</td>
<td>-1.25(3)</td>
<td>-0.44(4)</td>
</tr>
<tr>
<td>P(1)</td>
<td>4.4(1)</td>
<td>5.0(1)</td>
<td>6.4(1)</td>
<td>-0.1(1)</td>
<td>0.81(9)</td>
<td>-1.0(1)</td>
</tr>
<tr>
<td>F(1)</td>
<td>8.7(3)</td>
<td>15.9(4)</td>
<td>13.8(4)</td>
<td>4.6(3)</td>
<td>-0.9(3)</td>
<td>-0.2(3)</td>
</tr>
<tr>
<td>F(2)</td>
<td>9(1)</td>
<td>12(1)</td>
<td>11(1)</td>
<td>2.3(8)</td>
<td>5.2(8)</td>
<td>5.1(7)</td>
</tr>
<tr>
<td>F(2A)</td>
<td>6(1)</td>
<td>22(3)</td>
<td>19(3)</td>
<td>-7(2)</td>
<td>-2(2)</td>
<td>5(2)</td>
</tr>
<tr>
<td>F(3)</td>
<td>22(2)</td>
<td>6.6(6)</td>
<td>12(1)</td>
<td>-3.0(7)</td>
<td>0.5(8)</td>
<td>-3.4(6)</td>
</tr>
<tr>
<td>F(3A)</td>
<td>16(3)</td>
<td>21(3)</td>
<td>3(1)</td>
<td>4(2)</td>
<td>0(1)</td>
<td>-6(2)</td>
</tr>
<tr>
<td>F(4)</td>
<td>9.0(3)</td>
<td>14.5(4)</td>
<td>15.1(4)</td>
<td>3.5(3)</td>
<td>1.1(3)</td>
<td>6.6(3)</td>
</tr>
<tr>
<td>F(5)</td>
<td>12.0(8)</td>
<td>13.2(8)</td>
<td>13(1)</td>
<td>0.4(7)</td>
<td>6.8(7)</td>
<td>2.9(8)</td>
</tr>
<tr>
<td>F(5A)</td>
<td>7(1)</td>
<td>9(1)</td>
<td>14(2)</td>
<td>-2.1(8)</td>
<td>0(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>F(6)</td>
<td>23(1)</td>
<td>7.0(6)</td>
<td>10.3(7)</td>
<td>-4.8(8)</td>
<td>1.1(8)</td>
<td>-3.6(5)</td>
</tr>
<tr>
<td>F(6A)</td>
<td>9(1)</td>
<td>29(3)</td>
<td>9(1)</td>
<td>6(2)</td>
<td>0(1)</td>
<td>-6(2)</td>
</tr>
<tr>
<td>N(1)</td>
<td>3.4(2)</td>
<td>3.7(3)</td>
<td>2.8(2)</td>
<td>0.2(2)</td>
<td>-0.6(2)</td>
<td>0.2(2)</td>
</tr>
<tr>
<td>N(2)</td>
<td>3.6(2)</td>
<td>3.5(3)</td>
<td>3.3(2)</td>
<td>-0.4(2)</td>
<td>-0.7(2)</td>
<td>0.6(2)</td>
</tr>
<tr>
<td>N(3)</td>
<td>3.7(3)</td>
<td>3.4(3)</td>
<td>3.5(2)</td>
<td>0.2(2)</td>
<td>-0.3(2)</td>
<td>0.1(2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>3.5(3)</td>
<td>3.8(3)</td>
<td>3.5(3)</td>
<td>0.3(3)</td>
<td>0.2(2)</td>
<td>0.1(3)</td>
</tr>
<tr>
<td>C(2)</td>
<td>3.4(3)</td>
<td>3.6(3)</td>
<td>4.8(3)</td>
<td>0.3(3)</td>
<td>-0.7(2)</td>
<td>0.7(3)</td>
</tr>
<tr>
<td>C(3)</td>
<td>3.6(3)</td>
<td>3.3(3)</td>
<td>3.3(3)</td>
<td>-0.7(3)</td>
<td>-0.5(2)</td>
<td>0.1(3)</td>
</tr>
<tr>
<td>C(4)</td>
<td>4.1(3)</td>
<td>2.6(3)</td>
<td>3.6(3)</td>
<td>0.4(2)</td>
<td>-0.9(2)</td>
<td>0.2(2)</td>
</tr>
<tr>
<td>C(5)</td>
<td>7.4(4)</td>
<td>7.5(4)</td>
<td>4.5(3)</td>
<td>3.2(4)</td>
<td>-0.9(3)</td>
<td>-1.9(3)</td>
</tr>
<tr>
<td>C(6)</td>
<td>6.9(4)</td>
<td>6.4(4)</td>
<td>3.7(3)</td>
<td>0.9(3)</td>
<td>-1.3(3)</td>
<td>-1.1(3)</td>
</tr>
<tr>
<td>C(7)</td>
<td>4.1(3)</td>
<td>4.1(4)</td>
<td>3.5(3)</td>
<td>-0.2(3)</td>
<td>-0.3(3)</td>
<td>0.5(3)</td>
</tr>
<tr>
<td>C(8)</td>
<td>3.3(3)</td>
<td>4.3(3)</td>
<td>4.4(3)</td>
<td>0.7(3)</td>
<td>0.6(3)</td>
<td>-0.3(3)</td>
</tr>
<tr>
<td>C(9)</td>
<td>6.9(4)</td>
<td>4.2(4)</td>
<td>7.0(4)</td>
<td>0.0(3)</td>
<td>2.3(3)</td>
<td>0.8(3)</td>
</tr>
</tbody>
</table>
I-7. [Cu(2,5-me₂pyz)₂][PF₆]^{+b}\textsuperscript{c}\textsuperscript{d}

Bond lengths involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-N(1)</td>
<td>2.126(4)</td>
<td>N(1)-C(1)</td>
<td>1.347(7)</td>
</tr>
<tr>
<td>Cu(2)-N(2)</td>
<td>2.110(4)</td>
<td>N(1)-C(4)</td>
<td>1.323(6)</td>
</tr>
<tr>
<td>P(1)-F(1)</td>
<td>1.53(1)</td>
<td>N(2)-C(2)</td>
<td>1.334(7)</td>
</tr>
<tr>
<td>P(1)-F(1A)</td>
<td>1.56(2)</td>
<td>N(2)-C(3)</td>
<td>1.335(6)</td>
</tr>
<tr>
<td>P(1)-F(2)</td>
<td>1.57(1)</td>
<td>C(1)-C(2)</td>
<td>1.386(7)</td>
</tr>
<tr>
<td>P(1)-F(2A)</td>
<td>1.51(1)</td>
<td>C(1)-C(5)</td>
<td>1.485(8)</td>
</tr>
<tr>
<td>P(1)-F(3)</td>
<td>1.526(8)</td>
<td>C(3)-C(4)</td>
<td>1.382(7)</td>
</tr>
<tr>
<td>P(1)-F(4)</td>
<td>1.583(4)</td>
<td>C(3)-C(6)</td>
<td>1.48(1)</td>
</tr>
</tbody>
</table>

Bond lengths involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(2)-H(1)</td>
<td>0.98</td>
<td>C(5)-H(5)</td>
<td>0.98</td>
</tr>
<tr>
<td>C(4)-H(2)</td>
<td>0.98</td>
<td>C(6)-H(6)</td>
<td>0.98</td>
</tr>
<tr>
<td>C(5)-H(3)</td>
<td>0.98</td>
<td>C(6)-H(7)</td>
<td>0.98</td>
</tr>
<tr>
<td>C(5)-H(4)</td>
<td>0.98</td>
<td>C(6)-H(8)</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Bond angles involving hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(2)-C(2)-H(1)</td>
<td>118.0</td>
<td>H(3)-C(5)-H(5)</td>
<td>109.5</td>
</tr>
<tr>
<td>C(1)-C(2)-H(1)</td>
<td>118.1</td>
<td>H(4)-C(5)-H(5)</td>
<td>109.5</td>
</tr>
<tr>
<td>N(1)-C(4)-H(2)</td>
<td>117.7</td>
<td>C(3)-C(6)-H(6)</td>
<td>109.5</td>
</tr>
<tr>
<td>C(3)-C(4)-H(2)</td>
<td>117.6</td>
<td>C(3)-C(6)-H(7)</td>
<td>109.5</td>
</tr>
<tr>
<td>C(1)-C(5)-H(3)</td>
<td>109.5</td>
<td>C(3)-C(6)-H(8)</td>
<td>109.4</td>
</tr>
<tr>
<td>C(1)-C(5)-H(4)</td>
<td>109.5</td>
<td>H(6)-C(6)-H(7)</td>
<td>109.5</td>
</tr>
<tr>
<td>C(1)-C(5)-H(5)</td>
<td>109.5</td>
<td>H(6)-C(6)-H(8)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(3)-C(5)-H(4)</td>
<td>109.5</td>
<td>H(7)-C(6)-H(8)</td>
<td>109.5</td>
</tr>
</tbody>
</table>

\( a \) Unit cell parameters are given in Table 4-6.
\( b \) Superscripts refer to symmetry the operations: (1) -x, -y, z; (2) -y, x, -z;
(3) \( \frac{1}{2} \)-y, \( \frac{1}{2} \)-x, \( \frac{1}{2} \)-z; (4) \( \frac{1}{2} \)+y, x-\( \frac{1}{2} \), \( \frac{1}{2} \)-z; (5) 1-x, -y, z; (6) \( \frac{1}{2} \)-y, \( \frac{1}{2} \)-x, 3/2-z;
(7) \( y \), -x, -z.
\( c \) Estimated standard deviations in the least significant figure are given in parentheses.
\( d \) \( B_{eq} = (8/3) \pi \Sigma U_{ij} \alpha_i \alpha_j (a_i \cdot a_j) \).
Bond angles involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-Cu(1)-N(1)³</td>
<td>125.7(2)</td>
</tr>
<tr>
<td>N(1)-Cu(1)-N(1)⁴</td>
<td>102.0(1)</td>
</tr>
<tr>
<td>N(2)-Cu(2)-N(2)⁵</td>
<td>95.0(2)</td>
</tr>
<tr>
<td>N(2)-Cu(2)-N(2)⁶</td>
<td>97.0(2)</td>
</tr>
<tr>
<td>N(2)-Cu(2)-N(2)⁷</td>
<td>142.2(2)</td>
</tr>
<tr>
<td>F(1)-P(1)-F(2)</td>
<td>180.0</td>
</tr>
<tr>
<td>F(1)-P(1)-F(3)</td>
<td>92.1(6)</td>
</tr>
<tr>
<td>F(1)-P(1)-F(4)</td>
<td>89.0(2)</td>
</tr>
<tr>
<td>F(1A)-P(1)-F(1A)⁶</td>
<td>83(2)</td>
</tr>
<tr>
<td>F(1A)-P(1)-F(2A)⁶</td>
<td>176(1)</td>
</tr>
<tr>
<td>F(1A)-P(1)-F(2A)⁶</td>
<td>93(1)</td>
</tr>
<tr>
<td>F(1A)-P(1)-F(4)</td>
<td>95(1)</td>
</tr>
<tr>
<td>F(1A)-P(1)-F(4)⁶</td>
<td>84(1)</td>
</tr>
<tr>
<td>F(2)-P(1)-F(3)</td>
<td>87.9(6)</td>
</tr>
<tr>
<td>F(2)-P(1)-F(4)</td>
<td>91.0(2)</td>
</tr>
<tr>
<td>F(2A)-P(1)-F(2A)⁶</td>
<td>91(2)</td>
</tr>
<tr>
<td>F(2A)-P(1)-F(4)</td>
<td>85(1)</td>
</tr>
<tr>
<td>F(2A)-P(1)-F(4)⁶</td>
<td>97(1)</td>
</tr>
</tbody>
</table>

Bond angles involving non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(3)-P(1)-F(3)⁶</td>
<td>176(1)</td>
</tr>
<tr>
<td>F(3)-P(1)-F(4)</td>
<td>83.0(7)</td>
</tr>
<tr>
<td>F(3)-P(1)-F(4)⁶</td>
<td>97.1(7)</td>
</tr>
<tr>
<td>F(4)-P(1)-F(4)⁶</td>
<td>178.0(4)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-C(1)</td>
<td>130.2(4)</td>
</tr>
<tr>
<td>Cu(1)-N(1)-C(4)</td>
<td>112.7(3)</td>
</tr>
<tr>
<td>C(1)-N(1)-C(4)</td>
<td>116.1(4)</td>
</tr>
<tr>
<td>Cu(2)-N(2)-C(2)</td>
<td>118.7(4)</td>
</tr>
<tr>
<td>Cu(2)-N(2)-C(3)</td>
<td>124.4(4)</td>
</tr>
<tr>
<td>C(2)-N(2)-C(3)</td>
<td>116.5(5)</td>
</tr>
<tr>
<td>N(1)-C(1)-C(2)</td>
<td>119.3(5)</td>
</tr>
<tr>
<td>N(1)-C(1)-C(5)</td>
<td>120.6(5)</td>
</tr>
<tr>
<td>C(2)-C(1)-C(5)</td>
<td>120.0(5)</td>
</tr>
<tr>
<td>N(2)-C(2)-C(1)</td>
<td>123.9(6)</td>
</tr>
<tr>
<td>N(2)-C(3)-C(4)</td>
<td>119.4(5)</td>
</tr>
<tr>
<td>N(2)-C(3)-C(6)</td>
<td>119.7(5)</td>
</tr>
<tr>
<td>C(4)-C(3)-C(6)</td>
<td>120.9(5)</td>
</tr>
<tr>
<td>N(1)-C(4)-C(3)</td>
<td>124.7(5)</td>
</tr>
</tbody>
</table>

Final atomic coordinates (fractional) and \( B_{eq} (\text{Å}^2) \) for non-hydrogen atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( B_{eq} )</th>
<th>( \text{occ.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.43(4)</td>
<td>0.25</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>1/2</td>
<td>0</td>
<td>1/4</td>
<td>2.57(3)</td>
<td>0.25</td>
</tr>
<tr>
<td>P(1)</td>
<td>0.3113(1)</td>
<td>0.1887</td>
<td>3/4</td>
<td>3.82(5)</td>
<td>0.50</td>
</tr>
<tr>
<td>F(1)</td>
<td>0.2294(8)</td>
<td>0.2706</td>
<td>3/4</td>
<td>12(1)</td>
<td>0.30</td>
</tr>
<tr>
<td>F(1A)</td>
<td>0.197(1)</td>
<td>0.199(2)</td>
<td>0.712(3)</td>
<td>11(1)</td>
<td>0.40</td>
</tr>
<tr>
<td>F(2)</td>
<td>0.3956(7)</td>
<td>0.1044</td>
<td>3/4</td>
<td>10.5(8)</td>
<td>0.30</td>
</tr>
<tr>
<td>F(2A)</td>
<td>0.422(1)</td>
<td>0.186(2)</td>
<td>0.790(3)</td>
<td>12(2)</td>
<td>0.40</td>
</tr>
<tr>
<td>F(3)</td>
<td>0.2329(9)</td>
<td>0.104(1)</td>
<td>0.737(2)</td>
<td>11.1(8)</td>
<td>0.60</td>
</tr>
<tr>
<td>F(4)</td>
<td>0.2930(4)</td>
<td>0.1734(4)</td>
<td>0.9197(5)</td>
<td>8.5(3)</td>
<td></td>
</tr>
<tr>
<td>N(1)</td>
<td>0.1432(3)</td>
<td>-0.0040(4)</td>
<td>0.1060(5)</td>
<td>2.3(2)</td>
<td></td>
</tr>
<tr>
<td>N(2)</td>
<td>0.3489(3)</td>
<td>0.0015(3)</td>
<td>0.1753(5)</td>
<td>2.3(2)</td>
<td></td>
</tr>
<tr>
<td>C(1)</td>
<td>0.1759(4)</td>
<td>0.0451(4)</td>
<td>0.2262(6)</td>
<td>2.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(2)</td>
<td>0.2786(3)</td>
<td>0.0464(3)</td>
<td>0.2576(9)</td>
<td>2.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(3)</td>
<td>0.3156(4)</td>
<td>-0.0496(4)</td>
<td>0.0588(5)</td>
<td>2.3(2)</td>
<td></td>
</tr>
<tr>
<td>C(4)</td>
<td>0.2134(4)</td>
<td>-0.0500(4)</td>
<td>0.0271(6)</td>
<td>2.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(5)</td>
<td>0.1029(4)</td>
<td>0.0946(5)</td>
<td>0.3269(5)</td>
<td>3.3(2)</td>
<td></td>
</tr>
<tr>
<td>C(6)</td>
<td>0.3882(5)</td>
<td>-0.1055(6)</td>
<td>-0.0334(5)</td>
<td>3.5(3)</td>
<td></td>
</tr>
</tbody>
</table>
Hydrogen atom coordinates (fractional) and $B_{iso}$ ($\text{Å}^2$).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>0.3009</td>
<td>0.0824</td>
<td>0.3457</td>
<td>2.9</td>
</tr>
<tr>
<td>H(2)</td>
<td>0.1912</td>
<td>-0.0872</td>
<td>-0.0600</td>
<td>2.9</td>
</tr>
<tr>
<td>H(3)</td>
<td>0.0743</td>
<td>0.0439</td>
<td>0.3934</td>
<td>4.0</td>
</tr>
<tr>
<td>H(4)</td>
<td>0.0483</td>
<td>0.1258</td>
<td>0.2699</td>
<td>4.0</td>
</tr>
<tr>
<td>H(5)</td>
<td>0.1379</td>
<td>0.1469</td>
<td>0.3838</td>
<td>4.0</td>
</tr>
<tr>
<td>H(6)</td>
<td>0.3512</td>
<td>-0.1511</td>
<td>-0.0990</td>
<td>4.2</td>
</tr>
<tr>
<td>H(7)</td>
<td>0.4337</td>
<td>-0.1452</td>
<td>0.0290</td>
<td>4.2</td>
</tr>
<tr>
<td>H(8)</td>
<td>0.4279</td>
<td>-0.0574</td>
<td>-0.0915</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Anisotropic thermal parameters $\times 10^2$

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>2.85(5)</td>
<td>2.85</td>
<td>7.3(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>2.66(5)</td>
<td>2.66</td>
<td>4.46(8)</td>
<td>0.06(6)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P(1)</td>
<td>4.30(7)</td>
<td>4.30</td>
<td>5.9(1)</td>
<td>0.16(8)</td>
<td>0.8(1)</td>
<td>0.8</td>
</tr>
<tr>
<td>F(1)</td>
<td>17(2)</td>
<td>17</td>
<td>11(2)</td>
<td>13(2)</td>
<td>8(2)</td>
<td>8</td>
</tr>
<tr>
<td>F(1A)</td>
<td>4.7(6)</td>
<td>27(3)</td>
<td>8(1)</td>
<td>2(2)</td>
<td>-0.4(7)</td>
<td>-2(2)</td>
</tr>
<tr>
<td>F(2)</td>
<td>10(1)</td>
<td>10</td>
<td>19(2)</td>
<td>7(1)</td>
<td>-1(2)</td>
<td>-1</td>
</tr>
<tr>
<td>F(2A)</td>
<td>3.5(6)</td>
<td>24(3)</td>
<td>18(3)</td>
<td>1(2)</td>
<td>-3(1)</td>
<td>6(3)</td>
</tr>
<tr>
<td>F(3)</td>
<td>11(1)</td>
<td>13(1)</td>
<td>18(1)</td>
<td>-9.0(7)</td>
<td>-1(1)</td>
<td>4(1)</td>
</tr>
<tr>
<td>F(4)</td>
<td>14.6(5)</td>
<td>11.2(5)</td>
<td>6.4(3)</td>
<td>0.9(4)</td>
<td>1.7(3)</td>
<td>3.1(3)</td>
</tr>
<tr>
<td>N(1)</td>
<td>2.3(2)</td>
<td>2.8(2)</td>
<td>3.7(2)</td>
<td>0.0(2)</td>
<td>-0.4(2)</td>
<td>0.0(2)</td>
</tr>
<tr>
<td>N(2)</td>
<td>2.8(2)</td>
<td>2.8(2)</td>
<td>3.3(2)</td>
<td>-0.1(2)</td>
<td>-0.2(2)</td>
<td>-0.2(2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>3.0(3)</td>
<td>2.7(2)</td>
<td>3.4(3)</td>
<td>-0.1(2)</td>
<td>0.2(3)</td>
<td>0.1(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>3.4(2)</td>
<td>2.9(2)</td>
<td>3.0(2)</td>
<td>-0.2(2)</td>
<td>0.0(3)</td>
<td>-0.4(3)</td>
</tr>
<tr>
<td>C(3)</td>
<td>2.8(3)</td>
<td>2.9(2)</td>
<td>3.0(2)</td>
<td>-0.1(2)</td>
<td>-0.6(2)</td>
<td>0.1(2)</td>
</tr>
<tr>
<td>C(4)</td>
<td>2.3(2)</td>
<td>3.4(3)</td>
<td>3.6(3)</td>
<td>0.2(2)</td>
<td>-0.3(2)</td>
<td>-0.1(2)</td>
</tr>
<tr>
<td>C(5)</td>
<td>3.5(3)</td>
<td>4.7(3)</td>
<td>4.6(3)</td>
<td>0.5(2)</td>
<td>0.8(3)</td>
<td>-0.9(3)</td>
</tr>
<tr>
<td>C(6)</td>
<td>3.9(4)</td>
<td>5.3(4)</td>
<td>4.1(3)</td>
<td>0.0(2)</td>
<td>-0.2(3)</td>
<td>-1.1(3)</td>
</tr>
</tbody>
</table>
This appendix contains mainly those bands that are attributed to the internal vibrations of the neutral ligands. Bands assigned to the vibrations of the anionic ligands have been used considerably in the results and discussion sections and are, with the exception of those pertaining to the trifluoromethanesulfonate anion, given in appropriate sections within the main text. Bands that cannot be readily assigned to the vibrations of any of the components of the complexes are listed in this appendix.
II-1 Pyridine

<table>
<thead>
<tr>
<th>py (liquid)b</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>405s</td>
<td>B₂ 16b</td>
<td>438m</td>
<td>433m</td>
<td>439s, sp</td>
<td>441m</td>
</tr>
<tr>
<td></td>
<td>605s</td>
<td>A₁ 6a</td>
<td>630m</td>
<td>641m</td>
<td>630s</td>
<td>633s</td>
</tr>
<tr>
<td></td>
<td>652m</td>
<td>B₁ 6b</td>
<td>n.o.</td>
<td>653w</td>
<td>657m</td>
<td>653vw</td>
</tr>
<tr>
<td></td>
<td>700s</td>
<td>B₂ 11</td>
<td>698s</td>
<td>690s</td>
<td>702s, sp</td>
<td>697vs</td>
</tr>
<tr>
<td></td>
<td>749s</td>
<td>B₂ 4</td>
<td>760s</td>
<td>750s</td>
<td>761s, sp</td>
<td>758vs</td>
</tr>
<tr>
<td></td>
<td>992s</td>
<td>A₁ 1</td>
<td>1010s</td>
<td>1018m</td>
<td>998sh</td>
<td>1006s</td>
</tr>
<tr>
<td></td>
<td>1030s</td>
<td>A₁ 12</td>
<td>1038s</td>
<td>1046m</td>
<td>1037s</td>
<td>1041sh</td>
</tr>
<tr>
<td></td>
<td>1068m</td>
<td>A₁ 18a</td>
<td>1074s</td>
<td>1078s</td>
<td>1064s</td>
<td>1072s</td>
</tr>
<tr>
<td></td>
<td>1148w</td>
<td>B₁ 15</td>
<td>1150m</td>
<td>1157m</td>
<td>1145m</td>
<td>1150m</td>
</tr>
<tr>
<td></td>
<td>1218s</td>
<td>A₁ 9a</td>
<td>1212s</td>
<td>1221m</td>
<td>1211s</td>
<td>1214s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1219m</td>
<td></td>
<td>1215sh</td>
<td>1235vw</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1234vw</td>
<td></td>
<td>1232w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1439s</td>
<td>B₁ 19b</td>
<td>1444vs</td>
<td>1447s</td>
<td>1439s</td>
<td>1443vs</td>
</tr>
<tr>
<td></td>
<td>1482s</td>
<td>A₁ 19a</td>
<td>1483s</td>
<td>1490m</td>
<td>1479s</td>
<td>1487s</td>
</tr>
<tr>
<td></td>
<td>1572s</td>
<td>B₁ 8b</td>
<td>1571vw</td>
<td>n.o.</td>
<td>1571m</td>
<td>1572w</td>
</tr>
<tr>
<td></td>
<td>1583s</td>
<td>B₁ 8a</td>
<td>1601s</td>
<td>1607s</td>
<td>1597s</td>
<td>1602s</td>
</tr>
<tr>
<td>I + 6b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>3036s</td>
<td>A₁ 20a</td>
<td>3025w</td>
<td>3028vw</td>
<td>3042sh</td>
<td>3047vw</td>
<td>3050sh</td>
</tr>
<tr>
<td>3054s</td>
<td>A₁ 2</td>
<td>3045w</td>
<td>3046sh</td>
<td>3064w</td>
<td>3065vw</td>
<td>3064wm</td>
</tr>
<tr>
<td>3083s</td>
<td>B₁ 20b</td>
<td>3099w</td>
<td>3100vw</td>
<td>3092sh</td>
<td>3079vw</td>
<td>3100sh</td>
</tr>
</tbody>
</table>

a All values are in cm⁻¹. v = very, s = strong, m = medium, w = weak, s = shoulder, sp = split, n.o. = not observed. b Data and assignment from ref. 135. 1 = Ni(py)₄Cl₂, 2 = Ni(py)Cl₂, 3 = Ni(py)₄(NCS)₂, 4 = Ni(py)₂(NCS)₂, 5 = Ni(py)₄(NCO)₂, 6 = Cu(py)₂(NCO)₂.
## II-2 Pyrazine

<table>
<thead>
<tr>
<th>Pyrazine (liquid)</th>
<th>3066, 2973</th>
<th>1490s</th>
<th>1418vs</th>
<th>1342m</th>
<th>1148vs</th>
<th>1110m</th>
<th>1067vs, 1022m</th>
<th>950c</th>
<th>804vs</th>
<th>417m</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1u</td>
<td>B1u</td>
<td>B3u</td>
<td>B3u</td>
<td>B3u</td>
<td>B1u</td>
<td>B1u</td>
<td>B1u, B1u</td>
<td>14a</td>
<td>14b</td>
<td>15</td>
</tr>
<tr>
<td>13</td>
<td>19a</td>
<td>19b</td>
<td>14</td>
<td>15</td>
<td>18a, 12</td>
<td>17a</td>
<td>11</td>
<td>11b</td>
<td>11b</td>
<td>16b</td>
</tr>
</tbody>
</table>

| Ni(pyz)2Cl2 | 3113w, 3101w, | 1486w | 1414s | 1389m | 1157m | 1113s, sp | 1117sh | 1062vs | 991w, sp | 819s | 496s |
| Ni(pyz)Cl2   | 3124w, 3064vw | 1484m | 1420s | n.o.  | 1172m | 1118s   |        | 1062s  | n.o.     | 792s | 492s |
| Ni(pyz)2(NCS)2 | 3060w, 3122w | 1490w | 1415s | n.o.  | 1163s | 1120sh  | 1126s  | 1092w, 1057s | n.o. | 812d | 481sd |
| Ni(pyz)(NCS)2 | 3126w, 3062w, | 1490w | 1421s | n.o.  | 1160s | 1124s  | 1130s  | 1092m, 1059s | 960vw, br | 790sd | 470sd |
| Ni(pyz)(NCO)2 | 3121vw, 3059vw | 1487vw | 1419s | 1379w | 1163s | 1126s  | 1094w, 1059s | 985w | 811s | 486s |
| Ni(pyz)(NCO)2 | 3120w       | 1490vw | 1420s | n.o.  | 1173m | 1115s  | 1066s  | n.o.    | 808s     | 491s |     |
| Cu(pyz)(NCO)2 | 3129w, 3073vw | n.o.  | 1421s | n.o.  | 1175m | 1115s  | 1068s  | n.o.    | 808s     | 494s |     |

*continued on the next page*
<table>
<thead>
<tr>
<th>Pyrazine (liquid)$^b$</th>
<th>1490s</th>
<th>1418vs</th>
<th>1342m</th>
<th>1148vs</th>
<th>1110m</th>
<th>1067vs, 1022m</th>
<th>950$^c$</th>
<th>804vs</th>
<th>417m</th>
</tr>
</thead>
<tbody>
<tr>
<td>3066, 2973</td>
<td>B1u</td>
<td>B3u</td>
<td>B3u</td>
<td>B3u</td>
<td>B1u</td>
<td>B1u, B1u</td>
<td>B2u</td>
<td>B2u</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>19a</td>
<td>19b</td>
<td>14</td>
<td>15</td>
<td>18a, 12</td>
<td>17a</td>
<td>11</td>
<td>16b</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cu(pyz)$_2$(CF$_3$SO$_3$)</th>
<th>1490v</th>
<th>1415s</th>
<th>n.o.</th>
<th>n.o.</th>
<th>1120m</th>
<th>1085w, 1050m</th>
<th>n.o.</th>
<th>804sh</th>
<th>450s</th>
</tr>
</thead>
<tbody>
<tr>
<td>3050w, 2946vw</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3104w, 2996vw</td>
<td>1422sh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3120w, 3026vw</td>
<td>1433s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cu(pyz)$_2$(CF$_3$SO$_3$)</th>
<th>1490vw</th>
<th>1425s</th>
<th>n.o.</th>
<th>1153sh</th>
<th>1119sh</th>
<th>1089vw, 1070vw</th>
<th>800w</th>
<th>461vw</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3060w, 2856vw</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3104w, 2998vw</td>
<td>1438s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3128w, 3024vw</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cu(pyz)$_4$(AsF$_6$)$_2$</th>
<th>n.o.</th>
<th>1422s</th>
<th>1352vww</th>
<th>1155ms</th>
<th>1122s</th>
<th>1088w, 1058s</th>
<th>976vw</th>
<th>813s</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3100w, 2998vw</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>457m, sp</td>
<td></td>
</tr>
<tr>
<td>3114w, 3042vw</td>
<td>1371w, br</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>463</td>
<td></td>
</tr>
<tr>
<td>3134w, 3062vw</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cu(pyz)$_4$(PF$_6$)$_2$</th>
<th>n.o.</th>
<th>1421vs</th>
<th>n.o.</th>
<th>1155s</th>
<th>1122vs</th>
<th>1085sh, 1056vs, br</th>
<th>981w</th>
<th>814s</th>
<th>463s</th>
</tr>
</thead>
<tbody>
<tr>
<td>3100w, 3000vw</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3116w, 3082w</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3138w</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All values are in cm$^{-1}$. v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad, n.o. = not observed.

$^b$ Data and assignment from the work of Lord et al. (63). Other weak or very weak bands observed at 597, 700, 752, 789, 823, 1006, 1032, 1048, 1125, 1623, 1745, 1175 and 1875 cm$^{-1}$ and medium ones at 1178, 1935 and 1985 cm$^{-1}$.

$^c$ Calculated (63) for non-planar H-bend.

$^d$ Anion also absorbs in this region.
**II-3 Methylpyrazina**

<table>
<thead>
<tr>
<th>Mepyza (liquid)b</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>410s</td>
<td>439m sp</td>
<td>436s</td>
<td>430m</td>
<td>427m</td>
</tr>
<tr>
<td>472w</td>
<td>522m</td>
<td>507s</td>
<td>506m</td>
<td>508w</td>
</tr>
<tr>
<td>641w</td>
<td>n.o.</td>
<td>636s</td>
<td>630w</td>
<td>630sh</td>
</tr>
<tr>
<td>752m</td>
<td>743m</td>
<td>744m, 748m</td>
<td>742m</td>
<td>741s</td>
</tr>
<tr>
<td>831s</td>
<td>839m</td>
<td>830m, 839m, 847m</td>
<td>839s, 842sh</td>
<td>c</td>
</tr>
<tr>
<td>979w</td>
<td>990w</td>
<td>n.o.</td>
<td>982w, br</td>
<td>972vw, br</td>
</tr>
<tr>
<td>1021s</td>
<td>1030m, 1038sh</td>
<td>1030s</td>
<td>1028m, 1038sh</td>
<td>1029s, 1040sh</td>
</tr>
<tr>
<td>1058s</td>
<td>1087s</td>
<td>1080s</td>
<td>1081s</td>
<td>1083s</td>
</tr>
<tr>
<td>1156s</td>
<td>1164s</td>
<td>1161s</td>
<td>1162s</td>
<td>1165s</td>
</tr>
<tr>
<td>1176m</td>
<td>n.o.</td>
<td>1178w</td>
<td>1179m</td>
<td>1181s</td>
</tr>
<tr>
<td>1252m</td>
<td>1258vw</td>
<td>1258w</td>
<td>1259w</td>
<td>1260w</td>
</tr>
<tr>
<td>1306s</td>
<td>1301m</td>
<td>1297w, 1307w</td>
<td>1306m</td>
<td>1310m</td>
</tr>
<tr>
<td>1402s</td>
<td>1392m</td>
<td>1393s, 1408w-m</td>
<td>1386w-m, 1405m</td>
<td>1410s</td>
</tr>
<tr>
<td>1457m</td>
<td>1445m br</td>
<td>1449m br</td>
<td>1450m, br</td>
<td>1445s</td>
</tr>
<tr>
<td>1478s</td>
<td>n.o.</td>
<td>1480m</td>
<td>1484m</td>
<td>1477m</td>
</tr>
<tr>
<td>1527w</td>
<td>1523w</td>
<td>1526w</td>
<td>1522m</td>
<td>1523w</td>
</tr>
<tr>
<td>1581m</td>
<td>n.o.</td>
<td>1601w</td>
<td>1601m</td>
<td>1602w</td>
</tr>
<tr>
<td>2920w</td>
<td>2943vw</td>
<td>2940w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2995w</td>
<td>2987vw</td>
<td>2988vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3045w</td>
<td>3118w</td>
<td>3039vw, 3071w</td>
<td>3046vw, 3084vw</td>
<td>3108w, br</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3110w</td>
</tr>
</tbody>
</table>

a All values are in cm\(^{-1}\). v = very, s = strong, m = medium, w = weak, sh = shoulder, n.o. = not observed
b Data from reference 66. A weak band also observed at 358 cm\(^{-1}\) in the spectrum of the free ligand.
c Obscurred by anion band.

1 = Cu(mepyza)(NCO)\(_2\), 2 = Cu(mepyza)\(_2\)(NCO)\(_2\), 3 = Cu(mepyza)\(_4\)(AsF\(_6\))\(_2\), 4 = Cu(mepyza)\(_4\)(PF\(_6\))\(_2\).
### Pyridazine

<table>
<thead>
<tr>
<th>Compound</th>
<th>Frequencies</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridazine (liquid)</td>
<td>1570s, 1563vs</td>
<td>A1, B1</td>
</tr>
<tr>
<td>Ni(pdz)$_2$(NCO)$_2$</td>
<td>1582s, 1577m</td>
<td>A1, B1</td>
</tr>
<tr>
<td>Cu(pdz)(NCO)$_2$</td>
<td>1585m</td>
<td>1454w</td>
</tr>
<tr>
<td>Cu(pdz)$_4$(NO$_3$)$_2$</td>
<td>1576s, 1560sh</td>
<td>1452m, 1458sh</td>
</tr>
<tr>
<td>[Cu(pdz)$_4$(NO$_3$) ][NO$_3$]</td>
<td>1569s</td>
<td>1449s, 1406s</td>
</tr>
<tr>
<td>Cu(pdz)$_3$(NO$_3$)$_2$</td>
<td>1573s</td>
<td>1450sh, 1402s</td>
</tr>
<tr>
<td>[Cu(pdz)$_2$(NO$_3$)$_2$]$_3$</td>
<td>1583s, 1579sh</td>
<td>d, 1399s</td>
</tr>
<tr>
<td>Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$</td>
<td>1580sh, 1574m</td>
<td>1451sh, 1425m</td>
</tr>
<tr>
<td>Ni(pdz)$_3$(NCS)$_2$</td>
<td>1580s, 1563sh</td>
<td>1450m, 1415s</td>
</tr>
<tr>
<td>Ni(pdz)$_2$(NCS)$_2$</td>
<td>1579s sp, 1572m</td>
<td>1444s, 1417s</td>
</tr>
</tbody>
</table>

---

*a* All values in are cm$^{-1}$. v = very, s = strong, m = medium, w = weak, sh = shoulder, s = split, n.o. = not observed, asy = asymmetric. *b* Data and assignment from the work of Stidham and Tucci (139). Other weak or very weak bands observed at 623, 687, 1131, 1383, 1703, 1843, 2069, 2124, 2218, 2312, 2354, 2603, 2727, 2862, 3723 and 3811 cm$^{-1}$. *c* Raman band. Infrared inactive in non-coordinated pyridazine. *d* Bands in this region in the complexes obscured by anion vibrations. *e* Anion also absorbs in this region.

*Continued on the next page*
## II-4 cont.

<table>
<thead>
<tr>
<th>Pyridazine (liquid)b</th>
<th>1061s</th>
<th>1049w sh</th>
<th>963vs</th>
<th>760vs br</th>
<th>753c</th>
<th>664m</th>
<th>629w</th>
<th>410c</th>
<th>369s</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1</td>
<td>11</td>
<td>4</td>
<td>6b</td>
<td>6a</td>
<td>16a</td>
<td>16b</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ni(pdz)2(NCO)2</th>
<th>1071s</th>
<th>1066s</th>
<th>975m</th>
<th>773s</th>
<th>750m</th>
<th>675m</th>
<th>n.o.</th>
<th>427s</th>
<th>382w</th>
</tr>
</thead>
<tbody>
<tr>
<td>1079s</td>
<td>995s</td>
<td>790s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cu(pdz)(NCO)2</th>
<th>1074m</th>
<th>1064vw</th>
<th>1005s</th>
<th>770s</th>
<th>n.o.</th>
<th>685w</th>
<th>d</th>
<th>426s</th>
<th>384s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(pdz)4(NO3)2</td>
<td>1074m</td>
<td>1066m</td>
<td>978s</td>
<td>778vs</td>
<td>d</td>
<td>680s</td>
<td>645m</td>
<td>419s</td>
<td>394m</td>
</tr>
<tr>
<td>1084s</td>
<td>984sh</td>
<td>789sh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[Cu(pdz)4(NO3)]2[NO3]</th>
<th>1069sh</th>
<th>1060s</th>
<th>968s</th>
<th>765s</th>
<th>d</th>
<th>679s</th>
<th>642w</th>
<th>421s</th>
<th>389m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>998w</td>
<td>773s</td>
<td>792s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cu(pdz)3(NO3)2</th>
<th>1069s</th>
<th>1059s</th>
<th>974s</th>
<th>769s</th>
<th>d</th>
<th>678s</th>
<th>644m</th>
<th>421s</th>
<th>387s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1088m</td>
<td>987sh</td>
<td>787s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[Cu(pdz)2(NO3)2]3</th>
<th>1074sh</th>
<th>1059w</th>
<th>975s</th>
<th>778s</th>
<th>d</th>
<th>674m sp</th>
<th>641w</th>
<th>424sh</th>
<th>395vw</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1000s</td>
<td>790s</td>
<td></td>
<td></td>
<td>679</td>
<td></td>
<td>432m</td>
<td>441m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cu(pdz)4(CH3SO3)2</th>
<th>1078w</th>
<th>d</th>
<th>976m</th>
<th>771se</th>
<th>749w-m</th>
<th>680m</th>
<th>644w</th>
<th>422m</th>
<th>390w-m</th>
</tr>
</thead>
<tbody>
<tr>
<td>1084m</td>
<td>780se</td>
<td>795me</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ni(pdz)3(NCS)2</th>
<th>1071s</th>
<th>1060sh</th>
<th>975se</th>
<th>769s br</th>
<th>749s</th>
<th>677s</th>
<th>640w</th>
<th>422s br</th>
<th>390m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>999se</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ni(pdz)2(NCS)2</th>
<th>1070sp</th>
<th>1061w</th>
<th>976me</th>
<th>762me</th>
<th>748m</th>
<th>678s</th>
<th>641w</th>
<th>421s</th>
<th>385w</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>996se</td>
<td>778se</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
II-5  4,4'-Bipyridine\textsuperscript{a}

<table>
<thead>
<tr>
<th>4,4'-Bipy (solid)\textsuperscript{b}</th>
<th>Cu(4,4'-Bipy)\textsubscript{4}(AsF\textsubscript{6})\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>374s</td>
<td>c</td>
</tr>
<tr>
<td>494w</td>
<td>496w</td>
</tr>
<tr>
<td>569w</td>
<td>586w</td>
</tr>
<tr>
<td>605s</td>
<td>610m-s, 629m-s</td>
</tr>
<tr>
<td>735s</td>
<td>735sh</td>
</tr>
<tr>
<td>748w</td>
<td>n.o.</td>
</tr>
<tr>
<td>808vs</td>
<td>804s, 811s, 820s</td>
</tr>
<tr>
<td>852w</td>
<td>859w</td>
</tr>
<tr>
<td>965w</td>
<td>n.o.</td>
</tr>
<tr>
<td>982w</td>
<td>n.o.</td>
</tr>
<tr>
<td>994s</td>
<td>990w</td>
</tr>
<tr>
<td>1042w</td>
<td>1038vw, 1046vw</td>
</tr>
<tr>
<td>1078s</td>
<td>1068m, 1077m</td>
</tr>
<tr>
<td>1102w</td>
<td>n.o.</td>
</tr>
<tr>
<td>1131w</td>
<td>n.o.</td>
</tr>
<tr>
<td>1222s</td>
<td>1223m</td>
</tr>
<tr>
<td>1412vs</td>
<td>1409s, 1425s</td>
</tr>
<tr>
<td>1492s</td>
<td>1486w</td>
</tr>
<tr>
<td>1540s</td>
<td>1536m</td>
</tr>
<tr>
<td>1600vs</td>
<td>1593s, 1615s</td>
</tr>
<tr>
<td>3050s</td>
<td>3040wbr, 3126wbr</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All values are in cm\textsuperscript{-1}. \textit{v} = very, \textit{s} = strong, \textit{m} = medium, \textit{w} = weak, \textit{br} = broad, n.o. = not observed. \textsuperscript{b} Data from reference 201. \textsuperscript{c} obscured by anion band.
II-6 2,5-Dimethylpyrazine.\(^a\)

<table>
<thead>
<tr>
<th>2,5-Me(_2)pyz (liquid)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3005(\text{w})</td>
<td>2927(\text{w})</td>
<td>1531(\text{vw})</td>
<td>1449(\text{m br})</td>
<td>1328(\text{s})</td>
<td>1165(\text{m}) (^b)</td>
<td>1037(\text{s})</td>
<td>963(\text{w})</td>
</tr>
<tr>
<td></td>
<td>3085(\text{w})</td>
<td>2965(\text{w})</td>
<td></td>
<td>1488(\text{s})</td>
<td>1380(\text{m})</td>
<td>1255(\text{w}) (^b)</td>
<td>1062(\text{w}) (^\text{sh})</td>
<td></td>
</tr>
</tbody>
</table>

Cu(2,5-me\(_2\)pyz)\(_2\)(CF\(_3\)SO\(_3\))

|                          | 3039\(\text{w}\) \(^\text{sh}\) | 2927\(\text{w}\) |          | 1448\(\text{m br}\) | 1333\(\text{m}\) |          | 1056\(\text{m}\) | 973\(\text{w}\) | 885\(\text{vw}\) |          | 430\(\text{m}\) |
|                          | 3049\(\text{w}\) | 2973\(\text{vw}\) |          | 1494\(\text{s}\) | 1378\(\text{m}\) |          | 1068\(\text{vw}\) | 984\(\text{vw}\) | 900\(\text{vw}\) |          | 451\(\text{m}\) |
|                          | 3079\(\text{w}\) \(^\text{sh}\) | 3001\(\text{vw}\) |          | 1504\(\text{m sh}\) | 1392\(\text{w}\) \(^\text{sh}\) |          | 1075\(\text{w}\) |          | 913\(\text{vw}\) |          |          |
|                          | 3111\(\text{w}\) |          |          |          |          |          |          |          |          |          |          |
|                          | 3115\(\text{w}\) |          |          |          |          |          |          |          |          |          |          |

Cu(2,5-me\(_2\)pyz)(CF\(_3\)SO\(_3\))

|                          | 3068\(\text{vw}\) | 2936\(\text{vw}\) |          | 1443\(\text{w br}\) | 1322\(\text{vw}\) |          | 1048\(\text{w}\) | 975\(\text{w}\) | 894\(\text{w}\) |          | 461\(\text{m}\) |
|                          | 3142\(\text{vw}\) | 2998\(\text{vw}\) |          | 1502\(\text{m}\) | 1341\(\text{w}\) |          | 1089\(\text{w}\) |          |          |          |          |
|                          |          |          |          |          |          |          |          |          |          |          | 1390\(\text{w}\) |

[Cu\(_2\)(2,5-me\(_2\)pyz)\(_3\)][PF\(_6\)]\(_2\)

|                          | 3052\(\text{vw}\) | 2924\(\text{vw}\) |          | 1439\(\text{s}\) | 1336\(\text{m}\) | 1158\(\text{m}\) | 1039\(\text{w-m}\) | 972\(\text{w}\) | 895\(\text{sh}\) |          | 433\(\text{m}\) |
|                          | 3126\(\text{vw}\) | 2964\(\text{vw}\) |          | 1493\(\text{m}\) | 1387\(\text{m}\) | 1227\(\text{vw}\) | 1058\(\text{m}\) |          |          |          | 1077\(\text{w}\) |

\(^a\) All values are in cm\(^{-1}\). v = very, s = strong, m = medium, w = weak, sh = shoulder.

\(^b\) Bands in this region in the complexes obscured by anion vibrations; see footnotes d and e, Appendix II-7.

\(^c\) Not observed in complexes; possibly obscured by anion vibrations.
II-7 Trifluoromethanesulfonate.

<table>
<thead>
<tr>
<th>$\nu_{\text{as}}$ SO$_3$</th>
<th>$\nu$ CF$_3$</th>
<th>$\nu_{\text{as}}$ CF$_3$</th>
<th>$\nu$ CS</th>
<th>$\delta_{\text{as}}$ SO$_3$</th>
<th>$\delta_{\text{as}}$ CS</th>
<th>$\delta_{\text{as}}$ SO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>A$_1$</td>
<td>A$_1$</td>
<td>A$_1$</td>
<td>A$_1$</td>
<td>A$_1$</td>
<td>A$_1$</td>
</tr>
</tbody>
</table>

Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$)

1243s  1224s  1152s  1029s  762m  643s  584m  526s
1264sh$_d$  1163s,sh
1281s  1175s$_c$

Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$)

1234s,sh  1219s  1151s  1028s  759w  636s  584w  529m
1240s  1165s$_e$
1254sh$_d$
1272sh
1291s

Cu(py$z$)$_2$(CF$_3$SO$_3$)

1247s  1218s, sh  1156vs, br  1028vs  759w  639vs  583w  526m
1264vs,sh  1224s  1161s, sh
1275vs

Cu(py$z$)(CF$_3$SO$_3$)

1237s  1227s  1168s  1028s  764w  636s  588w  526m
1278s

---

$^a$ All values are in cm$^{-1}$; $^b$ s = strong, m = medium, w = weak, s = shoulder; $^c$ assignments CS$_3$ part and SCF$_3$ part, C$_3v$ symmetry) from ref. 44. $^d$ 2,5-me$_2$pyz absorbs in this region (1255w, in liquid) and possibly accounts for the shoulders at 1264 and 1254 cm$^{-1}$ in Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) and Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$), respectively; $^e$ 2,5-me$_2$pyz absorbs in this region (1165w, in liquid) and possibly accounts for the shoulders at 1175 and 1165 cm$^{-1}$ in Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$) and Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$), respectively.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Wavenumbers (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(py)$_2$(NCO)$_2$</td>
<td>3513w, 1214m, 949w, 882w, 383s</td>
</tr>
<tr>
<td>Cu(mepy)$_2$(NCO)$_2$</td>
<td>3537w, 398w, 385w</td>
</tr>
<tr>
<td>Cu(mepy)$_2$(NCO)$_2$</td>
<td>3520m br, 1051m, 405m, 399w, 381w</td>
</tr>
<tr>
<td>Cu(pyz)(NCO)$_2$</td>
<td>3535w, 383m br</td>
</tr>
<tr>
<td>Cu(pdz)(NCO)$_2$</td>
<td>3531w, 1247w, 1096w, 376s, 365w</td>
</tr>
<tr>
<td>Ni(py)$_4$(NCO)$_2$</td>
<td>3504w, 3401w, 888w</td>
</tr>
<tr>
<td>Ni(py)$_2$(NCO)$_2$·½H$_2$O</td>
<td>3511w, 2645w, 2549w, 1218w, 325m</td>
</tr>
<tr>
<td>Ni(pdz)$_2$(NCO)$_2$</td>
<td>3501w, 3477w, 1206w, 366w</td>
</tr>
<tr>
<td>Ni(pyz)(NCO)$_2$</td>
<td>3506w, 3440w, 1303w</td>
</tr>
<tr>
<td>Cu(pdz)$_4$(NO$_3$)$_2$</td>
<td>1208w, 942w, 278w</td>
</tr>
<tr>
<td>[Cu(pdz)$_4$(NO$_3$)$_2$][NO$_3$]</td>
<td>1203m</td>
</tr>
<tr>
<td>Cu(pdz)$_3$(NO$_3$)$_2$</td>
<td>1208s, 313s</td>
</tr>
<tr>
<td>[Cu(pdz)$_2$(NO$_3$)$_2$]$_3$</td>
<td>3476w br$^b$, 661w</td>
</tr>
<tr>
<td>Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$</td>
<td>2926w, 1344w, 1331w, 1303m, 1299s, 966w, 359w, 350w, 340w</td>
</tr>
<tr>
<td>Cu(4,4'-bipy)$_4$(AsF$_6$)$_2$</td>
<td>1322w, 1019w, 653m, 529w</td>
</tr>
<tr>
<td>Cu(pyz)$_4$(AsF$_6$)$_2$</td>
<td>1600w, 1232w, 1018w, 917w, 749w, 368w</td>
</tr>
<tr>
<td>Cu(mepy)$_4$(AsF$_6$)$_2$</td>
<td>1133m, 926w, 620w, 499w, 378w</td>
</tr>
<tr>
<td>Cu(pyz)$_4$(PF$_6$)$_2$</td>
<td>1600w, 1230w, 1209w, 1103s, 1020m, 939w, 933w, 920w, 870m, 630sh</td>
</tr>
<tr>
<td>Cu(mepy)$_4$(PF$_6$)$_2$</td>
<td>1134w, 922w, 623w, 542wm</td>
</tr>
<tr>
<td>[Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$</td>
<td>3604w, 1702w br, 937w</td>
</tr>
<tr>
<td>Ni(py)$_4$Cl$_2$</td>
<td>3003w, 1389w, 1355w, 1001w, 982m, 945w, 877w</td>
</tr>
<tr>
<td>Ni(py)$_4$(NCS)$_2$</td>
<td>2876w, 2476w, 1637w, 1356w, 951w, 899w, 883w, 410w, 288sw $^c$</td>
</tr>
<tr>
<td>Ni(py)$_2$(NCS)$_2$</td>
<td>3003w, 2897w, 1643w, 1386w, 1357w, 874w, 288m $^c$</td>
</tr>
<tr>
<td>Ni(pyz)$_2$(NCS)$_2$</td>
<td>3400w, br$^b$, 451w, 299m$^d$</td>
</tr>
<tr>
<td>Ni(pyz)(NCS)$_2$</td>
<td>286$^d$</td>
</tr>
<tr>
<td>Ni(pdz)$_3$(NCS)$_2$</td>
<td>2890w, 548w, br</td>
</tr>
<tr>
<td>Ni(pdz)$_2$(NCS)$_2$</td>
<td>1842w, 1712w, 1703w, 1687w, 1225w, 936w, 862w, 555w</td>
</tr>
<tr>
<td>Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$)</td>
<td>1595wvw</td>
</tr>
</tbody>
</table>

$^a$ All values are in cm$^{-1}$. v = very, s = strong, m = medium, w = weak, br = broad.

$^b$ Suggest that sample may have contained some water. In such an event microanalytical data indicate that the water was significantly less than 1 mole per mole of complex.

$^c$ Previously assigned to $\nu_{M-N}$ (NCS) by metal and ligand isotopic substitution (244).

$^d$ May be $\nu_{M-N}$ (NCS); see footnote c above.
APPENDIX III

X-RAY POWDER DIFFRACTION DATA

<table>
<thead>
<tr>
<th>2θ</th>
<th>d</th>
<th>I</th>
<th>2θ</th>
<th>d</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.44</td>
<td>11.9</td>
<td>11.4</td>
<td>11.46</td>
<td>7.715</td>
<td>100.0</td>
</tr>
<tr>
<td>8.08</td>
<td>10.9</td>
<td>35.7</td>
<td>14.90</td>
<td>5.941</td>
<td>28.6</td>
</tr>
<tr>
<td>11.14</td>
<td>7.936</td>
<td>6.9</td>
<td>17.18</td>
<td>5.157</td>
<td>44.5</td>
</tr>
<tr>
<td>12.38</td>
<td>7.144</td>
<td>100.0</td>
<td>23.18</td>
<td>3.834</td>
<td>25.7</td>
</tr>
<tr>
<td>12.88</td>
<td>6.868</td>
<td>23.6</td>
<td>23.84</td>
<td>3.729</td>
<td>18.4</td>
</tr>
<tr>
<td>14.04</td>
<td>6.303</td>
<td>20.7</td>
<td>26.18</td>
<td>3.401</td>
<td>12.1</td>
</tr>
<tr>
<td>14.52</td>
<td>6.096</td>
<td>11.8</td>
<td>26.74</td>
<td>3.331</td>
<td>12.1</td>
</tr>
<tr>
<td>15.16</td>
<td>5.840</td>
<td>23.8</td>
<td>29.78</td>
<td>2.998</td>
<td>11.5</td>
</tr>
<tr>
<td>15.94</td>
<td>5.556</td>
<td>6.5</td>
<td>31.30</td>
<td>2.856</td>
<td>6.4</td>
</tr>
<tr>
<td>16.96</td>
<td>5.224</td>
<td>19.4</td>
<td>32.48</td>
<td>2.754</td>
<td>11.6</td>
</tr>
<tr>
<td>17.86</td>
<td>4.962</td>
<td>11.8</td>
<td>34.36</td>
<td>2.608</td>
<td>8.4</td>
</tr>
<tr>
<td>19.58</td>
<td>4.530</td>
<td>5.8</td>
<td>35.80</td>
<td>2.506</td>
<td>7.5</td>
</tr>
<tr>
<td>20.86</td>
<td>4.255</td>
<td>19.7</td>
<td>36.56</td>
<td>2.456</td>
<td>4.6</td>
</tr>
<tr>
<td>23.30</td>
<td>3.815</td>
<td>17.5</td>
<td>37.80</td>
<td>2.378</td>
<td>10.2</td>
</tr>
<tr>
<td>24.52</td>
<td>3.628</td>
<td>7.7</td>
<td>38.26</td>
<td>2.351</td>
<td>5.6</td>
</tr>
<tr>
<td>25.62</td>
<td>3.474</td>
<td>40.2</td>
<td>38.56</td>
<td>2.333</td>
<td>5.3</td>
</tr>
<tr>
<td>26.90</td>
<td>3.312</td>
<td>32.0</td>
<td>39.84</td>
<td>2.261</td>
<td>4.7</td>
</tr>
<tr>
<td>28.16</td>
<td>3.166</td>
<td>7.0</td>
<td>40.72</td>
<td>2.214</td>
<td>5.7</td>
</tr>
<tr>
<td>31.18</td>
<td>2.866</td>
<td>7.0</td>
<td>44.34</td>
<td>2.041</td>
<td>7.8</td>
</tr>
<tr>
<td>32.04</td>
<td>2.791</td>
<td>7.6</td>
<td>47.00</td>
<td>1.932</td>
<td>8.7</td>
</tr>
<tr>
<td>33.10</td>
<td>2.704</td>
<td>9.0</td>
<td>47.64</td>
<td>1.907</td>
<td>3.2</td>
</tr>
<tr>
<td>37.36</td>
<td>2.405</td>
<td>5.6</td>
<td>48.38</td>
<td>1.880</td>
<td>4.0</td>
</tr>
<tr>
<td>38.80</td>
<td>2.319</td>
<td>8.0</td>
<td>52.40</td>
<td>1.745</td>
<td>3.0</td>
</tr>
<tr>
<td>39.38</td>
<td>2.286</td>
<td>6.0</td>
<td>54.02</td>
<td>1.696</td>
<td>3.6</td>
</tr>
<tr>
<td>41.04</td>
<td>2.198</td>
<td>4.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The locations of the reflections, 2θ, and the interplanar spacings, d, are in degrees and angstroms, respectively. The relative intensities, I, are based on 100 for the strongest intensity observed.
3. Ni(pyz)(NCO)$_2$

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>$d$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.78</td>
<td>7.506</td>
<td>100.0</td>
</tr>
<tr>
<td>13.96</td>
<td>6.339</td>
<td>54.7</td>
</tr>
<tr>
<td>23.68</td>
<td>3.754</td>
<td>23.3</td>
</tr>
<tr>
<td>25.48</td>
<td>3.493</td>
<td>64.5</td>
</tr>
<tr>
<td>27.26</td>
<td>3.269</td>
<td>7.7</td>
</tr>
<tr>
<td>29.36</td>
<td>3.039</td>
<td>20.8</td>
</tr>
<tr>
<td>32.44</td>
<td>2.758</td>
<td>12.8</td>
</tr>
<tr>
<td>35.02</td>
<td>2.560</td>
<td>7.5</td>
</tr>
<tr>
<td>39.08</td>
<td>2.303</td>
<td>29.1</td>
</tr>
</tbody>
</table>

4. Cu(pyz)(NCO)$_2$

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>$d$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.26</td>
<td>7.852</td>
<td>100.0</td>
</tr>
<tr>
<td>13.50</td>
<td>6.554</td>
<td>25.9</td>
</tr>
<tr>
<td>23.34</td>
<td>3.808</td>
<td>11.7</td>
</tr>
<tr>
<td>25.18</td>
<td>3.534</td>
<td>14.2</td>
</tr>
<tr>
<td>27.58</td>
<td>3.232</td>
<td>13.2</td>
</tr>
<tr>
<td>27.90</td>
<td>3.195</td>
<td>16.1</td>
</tr>
<tr>
<td>32.22</td>
<td>2.776</td>
<td>6.4</td>
</tr>
<tr>
<td>33.28</td>
<td>2.690</td>
<td>6.9</td>
</tr>
<tr>
<td>38.06</td>
<td>2.362</td>
<td>3.7</td>
</tr>
<tr>
<td>39.04</td>
<td>2.305</td>
<td>5.8</td>
</tr>
<tr>
<td>41.86</td>
<td>2.156</td>
<td>2.9</td>
</tr>
<tr>
<td>44.12</td>
<td>2.051</td>
<td>3.5</td>
</tr>
</tbody>
</table>

5. [Cu(pdz)$_2$(NO$_3$)$_2$]$_3$

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>$d$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.09</td>
<td>12.5</td>
<td>10.5</td>
</tr>
<tr>
<td>8.77</td>
<td>10.1</td>
<td>55.4</td>
</tr>
<tr>
<td>10.07</td>
<td>8.776</td>
<td>10.9</td>
</tr>
<tr>
<td>11.02</td>
<td>8.026</td>
<td>45.4</td>
</tr>
<tr>
<td>11.34</td>
<td>7.796</td>
<td>17.1</td>
</tr>
<tr>
<td>11.88</td>
<td>7.442</td>
<td>100.0</td>
</tr>
<tr>
<td>12.78</td>
<td>6.923</td>
<td>43.6</td>
</tr>
<tr>
<td>13.73</td>
<td>6.446</td>
<td>45.8</td>
</tr>
<tr>
<td>14.67</td>
<td>6.032</td>
<td>9.1</td>
</tr>
<tr>
<td>15.04</td>
<td>5.888</td>
<td>9.7</td>
</tr>
<tr>
<td>15.46</td>
<td>5.727</td>
<td>14.8</td>
</tr>
<tr>
<td>16.09</td>
<td>5.506</td>
<td>10.8</td>
</tr>
<tr>
<td>16.32</td>
<td>5.428</td>
<td>12.1</td>
</tr>
<tr>
<td>17.07</td>
<td>5.189</td>
<td>10.2</td>
</tr>
<tr>
<td>17.75</td>
<td>4.993</td>
<td>11.8</td>
</tr>
<tr>
<td>18.35</td>
<td>4.830</td>
<td>11.2</td>
</tr>
<tr>
<td>21.00</td>
<td>4.227</td>
<td>15.4</td>
</tr>
<tr>
<td>21.20</td>
<td>4.189</td>
<td>15.8</td>
</tr>
<tr>
<td>21.91</td>
<td>4.054</td>
<td>14.9</td>
</tr>
<tr>
<td>22.14</td>
<td>4.012</td>
<td>31.3</td>
</tr>
<tr>
<td>22.39</td>
<td>3.968</td>
<td>21.9</td>
</tr>
<tr>
<td>22.99</td>
<td>3.866</td>
<td>30.7</td>
</tr>
<tr>
<td>23.49</td>
<td>3.784</td>
<td>19.3</td>
</tr>
<tr>
<td>23.84</td>
<td>3.729</td>
<td>29.3</td>
</tr>
<tr>
<td>24.37</td>
<td>3.649</td>
<td>17.8</td>
</tr>
<tr>
<td>24.79</td>
<td>3.589</td>
<td>16.1</td>
</tr>
<tr>
<td>25.82</td>
<td>3.448</td>
<td>33.0</td>
</tr>
</tbody>
</table>

---

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>$d$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.21</td>
<td>3.397</td>
<td>17.1</td>
</tr>
<tr>
<td>27.33</td>
<td>3.261</td>
<td>12.5</td>
</tr>
<tr>
<td>27.74</td>
<td>3.213</td>
<td>11.4</td>
</tr>
<tr>
<td>28.19</td>
<td>3.163</td>
<td>20.3</td>
</tr>
<tr>
<td>28.70</td>
<td>3.109</td>
<td>15.2</td>
</tr>
<tr>
<td>29.09</td>
<td>3.068</td>
<td>11.7</td>
</tr>
<tr>
<td>29.65</td>
<td>3.011</td>
<td>15.4</td>
</tr>
<tr>
<td>30.04</td>
<td>2.973</td>
<td>16.9</td>
</tr>
<tr>
<td>30.36</td>
<td>2.942</td>
<td>15.4</td>
</tr>
<tr>
<td>30.80</td>
<td>2.901</td>
<td>15.4</td>
</tr>
<tr>
<td>31.40</td>
<td>2.847</td>
<td>13.0</td>
</tr>
<tr>
<td>31.86</td>
<td>2.806</td>
<td>11.9</td>
</tr>
<tr>
<td>32.86</td>
<td>2.723</td>
<td>17.2</td>
</tr>
<tr>
<td>33.43</td>
<td>2.679</td>
<td>11.8</td>
</tr>
<tr>
<td>34.30</td>
<td>2.613</td>
<td>10.4</td>
</tr>
<tr>
<td>35.65</td>
<td>2.517</td>
<td>11.0</td>
</tr>
<tr>
<td>36.09</td>
<td>2.487</td>
<td>13.5</td>
</tr>
<tr>
<td>37.28</td>
<td>2.410</td>
<td>10.6</td>
</tr>
<tr>
<td>37.83</td>
<td>2.377</td>
<td>9.2</td>
</tr>
<tr>
<td>40.60</td>
<td>2.220</td>
<td>9.2</td>
</tr>
<tr>
<td>41.15</td>
<td>2.192</td>
<td>11.1</td>
</tr>
<tr>
<td>41.56</td>
<td>2.171</td>
<td>10.5</td>
</tr>
<tr>
<td>42.90</td>
<td>2.106</td>
<td>9.1</td>
</tr>
<tr>
<td>45.05</td>
<td>2.011</td>
<td>10.2</td>
</tr>
<tr>
<td>45.75</td>
<td>1.982</td>
<td>8.9</td>
</tr>
<tr>
<td>47.35</td>
<td>1.919</td>
<td>7.9</td>
</tr>
</tbody>
</table>
### 6. Cu(pdz)$_3$(NO$_3$)$_2$

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>$d$</th>
<th>I</th>
<th>$2\theta$</th>
<th>$d$</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.79</td>
<td>10.0</td>
<td>51.9</td>
<td>25.40</td>
<td>3.504</td>
<td>20.6</td>
</tr>
<tr>
<td>10.12</td>
<td>8.731</td>
<td>11.5</td>
<td>26.02</td>
<td>3.422</td>
<td>47.4</td>
</tr>
<tr>
<td>11.30</td>
<td>7.824</td>
<td>67.8</td>
<td>27.91</td>
<td>3.194</td>
<td>14.1</td>
</tr>
<tr>
<td>11.95</td>
<td>7.399</td>
<td>11.1</td>
<td>28.47</td>
<td>3.133</td>
<td>18.8</td>
</tr>
<tr>
<td>12.28</td>
<td>7.205</td>
<td>14.2</td>
<td>28.88</td>
<td>3.089</td>
<td>14.0</td>
</tr>
<tr>
<td>12.71</td>
<td>6.962</td>
<td>37.2</td>
<td>29.48</td>
<td>3.027</td>
<td>14.4</td>
</tr>
<tr>
<td>13.52</td>
<td>6.543</td>
<td>100.0</td>
<td>30.27</td>
<td>2.951</td>
<td>14.8</td>
</tr>
<tr>
<td>13.92</td>
<td>6.357</td>
<td>52.6</td>
<td>30.97</td>
<td>2.885</td>
<td>13.3</td>
</tr>
<tr>
<td>14.66</td>
<td>6.040</td>
<td>23.9</td>
<td>32.43</td>
<td>2.759</td>
<td>15.2</td>
</tr>
<tr>
<td>15.48</td>
<td>5.718</td>
<td>11.8</td>
<td>32.84</td>
<td>2.725</td>
<td>11.4</td>
</tr>
<tr>
<td>17.08</td>
<td>5.186</td>
<td>26.3</td>
<td>34.48</td>
<td>2.599</td>
<td>14.2</td>
</tr>
<tr>
<td>17.68</td>
<td>5.012</td>
<td>22.7</td>
<td>35.39</td>
<td>2.534</td>
<td>12.3</td>
</tr>
<tr>
<td>18.34</td>
<td>4.834</td>
<td>51.7</td>
<td>36.20</td>
<td>2.480</td>
<td>12.6</td>
</tr>
<tr>
<td>20.06</td>
<td>4.422</td>
<td>15.9</td>
<td>36.85</td>
<td>2.438</td>
<td>9.4</td>
</tr>
<tr>
<td>21.08</td>
<td>4.211</td>
<td>52.3</td>
<td>37.50</td>
<td>2.396</td>
<td>11.8</td>
</tr>
<tr>
<td>21.87</td>
<td>4.060</td>
<td>25.6</td>
<td>37.97</td>
<td>2.368</td>
<td>14.5</td>
</tr>
<tr>
<td>22.69</td>
<td>3.915</td>
<td>16.6</td>
<td>38.62</td>
<td>2.330</td>
<td>11.6</td>
</tr>
<tr>
<td>23.33</td>
<td>3.809</td>
<td>53.9</td>
<td>39.33</td>
<td>2.289</td>
<td>9.2</td>
</tr>
<tr>
<td>23.80</td>
<td>3.736</td>
<td>15.7</td>
<td>41.55</td>
<td>2.172</td>
<td>10.1</td>
</tr>
<tr>
<td>24.06</td>
<td>3.696</td>
<td>16.7</td>
<td>45.23</td>
<td>2.003</td>
<td>9.6</td>
</tr>
<tr>
<td>24.75</td>
<td>3.595</td>
<td>60.4</td>
<td>47.77</td>
<td>1.903</td>
<td>8.0</td>
</tr>
</tbody>
</table>

### 7. Cu(pdz)$_4$(NO$_3$)$_2$

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>$d$</th>
<th>I</th>
<th>$2\theta$</th>
<th>$d$</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.14</td>
<td>8.714</td>
<td>100.0</td>
<td>28.88</td>
<td>3.089</td>
<td>13.2</td>
</tr>
<tr>
<td>11.71</td>
<td>7.550</td>
<td>6.8</td>
<td>29.38</td>
<td>3.038</td>
<td>11.7</td>
</tr>
<tr>
<td>12.10</td>
<td>7.306</td>
<td>27.6</td>
<td>29.86</td>
<td>2.990</td>
<td>17.0</td>
</tr>
<tr>
<td>12.55</td>
<td>7.050</td>
<td>98.6</td>
<td>30.10</td>
<td>2.966</td>
<td>21.1</td>
</tr>
<tr>
<td>13.19</td>
<td>6.709</td>
<td>14.9</td>
<td>30.43</td>
<td>2.935</td>
<td>23.2</td>
</tr>
<tr>
<td>15.16</td>
<td>5.840</td>
<td>9.0</td>
<td>31.04</td>
<td>2.879</td>
<td>17.5</td>
</tr>
<tr>
<td>17.46</td>
<td>5.076</td>
<td>61.6</td>
<td>31.31</td>
<td>2.855</td>
<td>12.9</td>
</tr>
<tr>
<td>18.22</td>
<td>4.866</td>
<td>33.6</td>
<td>31.90</td>
<td>2.803</td>
<td>12.1</td>
</tr>
<tr>
<td>18.74</td>
<td>4.730</td>
<td>25.5</td>
<td>32.10</td>
<td>2.786</td>
<td>11.2</td>
</tr>
<tr>
<td>18.99</td>
<td>4.669</td>
<td>16.4</td>
<td>32.35</td>
<td>2.765</td>
<td>10.2</td>
</tr>
<tr>
<td>20.09</td>
<td>4.416</td>
<td>49.4</td>
<td>33.23</td>
<td>2.694</td>
<td>9.3</td>
</tr>
<tr>
<td>20.36</td>
<td>4.360</td>
<td>90.8</td>
<td>34.37</td>
<td>2.607</td>
<td>13.8</td>
</tr>
<tr>
<td>21.12</td>
<td>4.204</td>
<td>19.5</td>
<td>35.80</td>
<td>2.506</td>
<td>12.0</td>
</tr>
<tr>
<td>21.50</td>
<td>4.129</td>
<td>20.3</td>
<td>36.69</td>
<td>2.447</td>
<td>11.9</td>
</tr>
<tr>
<td>22.18</td>
<td>4.005</td>
<td>49.7</td>
<td>37.28</td>
<td>2.410</td>
<td>13.4</td>
</tr>
<tr>
<td>23.77</td>
<td>3.740</td>
<td>40.1</td>
<td>37.61</td>
<td>2.390</td>
<td>11.8</td>
</tr>
<tr>
<td>24.51</td>
<td>3.629</td>
<td>26.3</td>
<td>39.22</td>
<td>2.295</td>
<td>8.2</td>
</tr>
<tr>
<td>25.28</td>
<td>3.520</td>
<td>12.4</td>
<td>39.59</td>
<td>2.275</td>
<td>8.8</td>
</tr>
<tr>
<td>25.84</td>
<td>3.445</td>
<td>13.8</td>
<td>40.53</td>
<td>2.224</td>
<td>10.2</td>
</tr>
<tr>
<td>26.55</td>
<td>3.355</td>
<td>23.8</td>
<td>42.16</td>
<td>2.142</td>
<td>11.5</td>
</tr>
<tr>
<td>27.46</td>
<td>3.246</td>
<td>44.9</td>
<td>46.82</td>
<td>1.939</td>
<td>8.0</td>
</tr>
<tr>
<td>28.07</td>
<td>3.176</td>
<td>14.2</td>
<td>52.35</td>
<td>1.746</td>
<td>8.0</td>
</tr>
<tr>
<td>28.45</td>
<td>3.135</td>
<td>10.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
8. Ni(pyz)(NCS)$_2$

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>$d$</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.91</td>
<td>5.937</td>
<td>98.7</td>
</tr>
<tr>
<td>16.01</td>
<td>5.532</td>
<td>46.9</td>
</tr>
<tr>
<td>16.38</td>
<td>5.407</td>
<td>45.2</td>
</tr>
<tr>
<td>19.75</td>
<td>4.492</td>
<td>90.1</td>
</tr>
<tr>
<td>20.58</td>
<td>4.313</td>
<td>20.8</td>
</tr>
<tr>
<td>23.78</td>
<td>3.739</td>
<td>18.1</td>
</tr>
<tr>
<td>25.27</td>
<td>3.522</td>
<td>100.0</td>
</tr>
<tr>
<td>25.86</td>
<td>3.442</td>
<td>52.0</td>
</tr>
<tr>
<td>27.28</td>
<td>3.267</td>
<td>25.4</td>
</tr>
<tr>
<td>27.79</td>
<td>3.208</td>
<td>18.4</td>
</tr>
<tr>
<td>28.51</td>
<td>3.128</td>
<td>16.1</td>
</tr>
<tr>
<td>32.28</td>
<td>2.771</td>
<td>23.9</td>
</tr>
<tr>
<td>32.85</td>
<td>2.724</td>
<td>15.7</td>
</tr>
<tr>
<td>35.24</td>
<td>2.545</td>
<td>47.8</td>
</tr>
<tr>
<td>36.50</td>
<td>2.460</td>
<td>17.9</td>
</tr>
<tr>
<td>37.99</td>
<td>2.367</td>
<td>37.3</td>
</tr>
<tr>
<td>38.45</td>
<td>2.340</td>
<td>17.5</td>
</tr>
<tr>
<td>39.23</td>
<td>2.295</td>
<td>40.9</td>
</tr>
<tr>
<td>40.29</td>
<td>2.237</td>
<td>22.2</td>
</tr>
<tr>
<td>40.78</td>
<td>2.211</td>
<td>15.9</td>
</tr>
<tr>
<td>41.91</td>
<td>2.154</td>
<td>18.6</td>
</tr>
<tr>
<td>42.89</td>
<td>2.107</td>
<td>14.1</td>
</tr>
<tr>
<td>46.56</td>
<td>1.949</td>
<td>10.8</td>
</tr>
<tr>
<td>48.02</td>
<td>1.893</td>
<td>15.4</td>
</tr>
<tr>
<td>49.52</td>
<td>1.839</td>
<td>11.7</td>
</tr>
<tr>
<td>50.57</td>
<td>1.803</td>
<td>15.0</td>
</tr>
<tr>
<td>51.32</td>
<td>1.779</td>
<td>20.9</td>
</tr>
<tr>
<td>51.92</td>
<td>1.760</td>
<td>13.1</td>
</tr>
<tr>
<td>53.29</td>
<td>1.718</td>
<td>12.5</td>
</tr>
<tr>
<td>57.27</td>
<td>1.607</td>
<td>13.2</td>
</tr>
<tr>
<td>58.44</td>
<td>1.578</td>
<td>12.2</td>
</tr>
</tbody>
</table>

9. Ni(py)$_2$(NCS)$_2$

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>$d$</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.11</td>
<td>7.302</td>
<td>100.0</td>
</tr>
<tr>
<td>17.00</td>
<td>5.212</td>
<td>23.1</td>
</tr>
<tr>
<td>17.59</td>
<td>5.039</td>
<td>29.8</td>
</tr>
<tr>
<td>21.00</td>
<td>4.227</td>
<td>28.7</td>
</tr>
<tr>
<td>21.83</td>
<td>4.067</td>
<td>37.6</td>
</tr>
<tr>
<td>24.47</td>
<td>3.635</td>
<td>33.0</td>
</tr>
<tr>
<td>26.57</td>
<td>3.352</td>
<td>12.7</td>
</tr>
<tr>
<td>27.06</td>
<td>3.293</td>
<td>8.4</td>
</tr>
<tr>
<td>27.66</td>
<td>3.223</td>
<td>10.6</td>
</tr>
<tr>
<td>30.95</td>
<td>2.887</td>
<td>8.8</td>
</tr>
<tr>
<td>31.56</td>
<td>2.832</td>
<td>12.9</td>
</tr>
<tr>
<td>32.60</td>
<td>2.745</td>
<td>8.3</td>
</tr>
<tr>
<td>33.42</td>
<td>2.679</td>
<td>8.2</td>
</tr>
<tr>
<td>33.98</td>
<td>2.636</td>
<td>11.7</td>
</tr>
<tr>
<td>35.70</td>
<td>2.513</td>
<td>6.8</td>
</tr>
<tr>
<td>37.11</td>
<td>2.421</td>
<td>11.1</td>
</tr>
<tr>
<td>38.28</td>
<td>2.350</td>
<td>10.8</td>
</tr>
<tr>
<td>40.32</td>
<td>2.235</td>
<td>7.0</td>
</tr>
<tr>
<td>42.09</td>
<td>2.145</td>
<td>7.9</td>
</tr>
<tr>
<td>49.80</td>
<td>1.830</td>
<td>6.4</td>
</tr>
<tr>
<td>50.85</td>
<td>1.794</td>
<td>5.8</td>
</tr>
</tbody>
</table>

10. Ni(pdz)$_3$(NCS)$_2$

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>$d$</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.93</td>
<td>11.1</td>
<td>67.7</td>
</tr>
<tr>
<td>9.76</td>
<td>9.06</td>
<td>59.7</td>
</tr>
<tr>
<td>11.78</td>
<td>7.505</td>
<td>73.1</td>
</tr>
<tr>
<td>12.14</td>
<td>7.285</td>
<td>100.0</td>
</tr>
<tr>
<td>12.64</td>
<td>7.000</td>
<td>22.1</td>
</tr>
<tr>
<td>13.63</td>
<td>6.490</td>
<td>13.3</td>
</tr>
<tr>
<td>14.73</td>
<td>6.010</td>
<td>20.2</td>
</tr>
<tr>
<td>16.01</td>
<td>5.533</td>
<td>10.8</td>
</tr>
<tr>
<td>18.94</td>
<td>4.683</td>
<td>25.4</td>
</tr>
<tr>
<td>20.78</td>
<td>4.271</td>
<td>34.5</td>
</tr>
<tr>
<td>22.68</td>
<td>3.918</td>
<td>42.7</td>
</tr>
<tr>
<td>23.68</td>
<td>3.755</td>
<td>36.5</td>
</tr>
<tr>
<td>24.19</td>
<td>3.676</td>
<td>39.4</td>
</tr>
<tr>
<td>25.78</td>
<td>3.453</td>
<td>40.7</td>
</tr>
<tr>
<td>26.70</td>
<td>3.336</td>
<td>34.9</td>
</tr>
<tr>
<td>27.82</td>
<td>3.204</td>
<td>27.5</td>
</tr>
<tr>
<td>29.90</td>
<td>2.986</td>
<td>17.8</td>
</tr>
<tr>
<td>30.93</td>
<td>2.889</td>
<td>16.2</td>
</tr>
<tr>
<td>34.27</td>
<td>2.615</td>
<td>15.6</td>
</tr>
<tr>
<td>35.58</td>
<td>2.521</td>
<td>15.2</td>
</tr>
<tr>
<td>37.43</td>
<td>2.401</td>
<td>14.7</td>
</tr>
<tr>
<td>38.73</td>
<td>2.323</td>
<td>15.1</td>
</tr>
<tr>
<td>41.07</td>
<td>2.196</td>
<td>14.8</td>
</tr>
<tr>
<td>42.63</td>
<td>2.119</td>
<td>13.0</td>
</tr>
<tr>
<td>46.90</td>
<td>1.936</td>
<td>12.3</td>
</tr>
</tbody>
</table>

11. Ni(pdz)$_2$(NCS)$_2$

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>$d$</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.05</td>
<td>8.799</td>
<td>100.0</td>
</tr>
<tr>
<td>22.64</td>
<td>3.924</td>
<td>82.7</td>
</tr>
</tbody>
</table>
12. **Cu(pyz)$_2$(CF$_3$SO$_3$)**

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>$d$</th>
<th>$I \times 10^{-1}$</th>
<th>$2\theta$</th>
<th>$d$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.65</td>
<td>7.599</td>
<td>29.9</td>
<td>11.76</td>
<td>7.519</td>
<td>13.5</td>
</tr>
<tr>
<td>11.81</td>
<td>7.492</td>
<td>9.7</td>
<td>13.95</td>
<td>6.348</td>
<td>53.7</td>
</tr>
<tr>
<td>14.75</td>
<td>6.007</td>
<td>71.2</td>
<td>14.86</td>
<td>5.957</td>
<td>16.4</td>
</tr>
<tr>
<td>15.10</td>
<td>5.869</td>
<td>25.1</td>
<td>15.27</td>
<td>5.803</td>
<td>16.2</td>
</tr>
<tr>
<td>15.72</td>
<td>5.440</td>
<td>64.9</td>
<td>16.36</td>
<td>5.414</td>
<td>25.1</td>
</tr>
<tr>
<td>19.59</td>
<td>4.531</td>
<td>68.5</td>
<td>19.62</td>
<td>4.524</td>
<td>14.0</td>
</tr>
<tr>
<td>19.72</td>
<td>4.502</td>
<td>33.6</td>
<td>19.74</td>
<td>4.494</td>
<td>21.8</td>
</tr>
<tr>
<td>20.51</td>
<td>4.330</td>
<td>15.7</td>
<td>20.74</td>
<td>4.284</td>
<td>7.8</td>
</tr>
<tr>
<td>20.88</td>
<td>4.255</td>
<td>23.3</td>
<td>20.90</td>
<td>4.250</td>
<td>30.6</td>
</tr>
<tr>
<td>21.52</td>
<td>4.129</td>
<td>100.0</td>
<td>21.80</td>
<td>4.078</td>
<td>13.2</td>
</tr>
<tr>
<td>21.84</td>
<td>4.070</td>
<td>16.9</td>
<td>22.90</td>
<td>3.883</td>
<td>47.1</td>
</tr>
<tr>
<td>23.18</td>
<td>3.838</td>
<td>7.8</td>
<td>23.75</td>
<td>3.746</td>
<td>18.3</td>
</tr>
<tr>
<td>24.46</td>
<td>3.640</td>
<td>6.0</td>
<td>24.87</td>
<td>3.581</td>
<td>6.1</td>
</tr>
<tr>
<td>25.77</td>
<td>3.457</td>
<td>5.4</td>
<td>25.80</td>
<td>3.450</td>
<td>20.5</td>
</tr>
<tr>
<td>27.16</td>
<td>3.283</td>
<td>4.2</td>
<td>27.35</td>
<td>3.261</td>
<td>13.2</td>
</tr>
<tr>
<td>27.86</td>
<td>3.203</td>
<td>16.5</td>
<td>27.96</td>
<td>3.192</td>
<td>6.4</td>
</tr>
<tr>
<td>28.11</td>
<td>3.174</td>
<td>24.0</td>
<td>28.14</td>
<td>3.169</td>
<td>22.9</td>
</tr>
<tr>
<td>29.29</td>
<td>3.050</td>
<td>8.1</td>
<td>29.74</td>
<td>3.004</td>
<td>23.6</td>
</tr>
<tr>
<td>30.46</td>
<td>2.934</td>
<td>20.2</td>
<td>30.50</td>
<td>2.929</td>
<td>15.7</td>
</tr>
<tr>
<td>31.01</td>
<td>2.883</td>
<td>4.4</td>
<td>31.17</td>
<td>2.870</td>
<td>10.2</td>
</tr>
<tr>
<td>31.97</td>
<td>2.799</td>
<td>3.2</td>
<td>31.96</td>
<td>2.798</td>
<td>15.0</td>
</tr>
<tr>
<td>32.21</td>
<td>2.779</td>
<td>4.1</td>
<td>33.36</td>
<td>2.686</td>
<td>11.0</td>
</tr>
<tr>
<td>33.56</td>
<td>2.671</td>
<td>7.1</td>
<td>33.75</td>
<td>2.655</td>
<td>10.7</td>
</tr>
<tr>
<td>34.06</td>
<td>2.632</td>
<td>8.8</td>
<td>34.82</td>
<td>2.576</td>
<td>3.7</td>
</tr>
<tr>
<td>34.83</td>
<td>2.576</td>
<td>8.8</td>
<td>34.86</td>
<td>2.572</td>
<td>18.3</td>
</tr>
<tr>
<td>35.45</td>
<td>2.532</td>
<td>7.3</td>
<td>35.45</td>
<td>2.532</td>
<td>7.3</td>
</tr>
</tbody>
</table>

---

*The simulated powder X-ray diffraction pattern for Cu(pyz)$_2$(CF$_3$SO$_3$) was generated using the single crystal X-ray diffraction data from reference 44 and the computer program LAZY PULVERIX (176).*
Cu(pyz)$_2$(CF$_3$SO$_3$) cont.

<table>
<thead>
<tr>
<th>2θ</th>
<th>d</th>
<th>I×10$^{-1}$</th>
<th>2θ</th>
<th>d</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.56</td>
<td>2.524</td>
<td>5.0</td>
<td>36.00</td>
<td>2.493</td>
<td>19.7</td>
</tr>
<tr>
<td>35.78</td>
<td>2.509</td>
<td>8.5</td>
<td>36.43</td>
<td>2.466</td>
<td>3.0</td>
</tr>
<tr>
<td>35.96</td>
<td>2.497</td>
<td>6.8</td>
<td>36.91</td>
<td>2.435</td>
<td>4.3</td>
</tr>
<tr>
<td>36.04</td>
<td>2.492</td>
<td>4.8</td>
<td>37.42</td>
<td>2.403</td>
<td>9.4</td>
</tr>
<tr>
<td>36.19</td>
<td>2.482</td>
<td>3.1</td>
<td>37.59</td>
<td>2.393</td>
<td>3.2</td>
</tr>
<tr>
<td>36.43</td>
<td>2.466</td>
<td>3.0</td>
<td>38.51</td>
<td>2.378</td>
<td>4.7</td>
</tr>
<tr>
<td>36.91</td>
<td>2.435</td>
<td>4.3</td>
<td>39.07</td>
<td>2.305</td>
<td>3.3</td>
</tr>
<tr>
<td>37.42</td>
<td>2.403</td>
<td>9.4</td>
<td>39.79</td>
<td>2.266</td>
<td>5.2</td>
</tr>
<tr>
<td>40.06</td>
<td>2.251</td>
<td>5.4</td>
<td>40.41</td>
<td>2.232</td>
<td>3.9</td>
</tr>
<tr>
<td>40.48</td>
<td>2.229</td>
<td>10.7</td>
<td>40.54</td>
<td>2.223</td>
<td>18.5</td>
</tr>
<tr>
<td>41.79</td>
<td>2.162</td>
<td>9.7</td>
<td>42.01</td>
<td>2.151</td>
<td>7.8</td>
</tr>
<tr>
<td>42.01</td>
<td>2.151</td>
<td>7.8</td>
<td>42.39</td>
<td>2.132</td>
<td>4.9</td>
</tr>
<tr>
<td>42.47</td>
<td>2.129</td>
<td>5.0</td>
<td>42.54</td>
<td>2.125</td>
<td>4.6</td>
</tr>
<tr>
<td>42.57</td>
<td>2.124</td>
<td>6.0</td>
<td>42.58</td>
<td>2.123</td>
<td>11.7</td>
</tr>
<tr>
<td>42.73</td>
<td>2.116</td>
<td>6.5</td>
<td>42.70</td>
<td>2.116</td>
<td>20.8</td>
</tr>
<tr>
<td>43.35</td>
<td>2.087</td>
<td>3.0</td>
<td>43.81</td>
<td>2.066</td>
<td>3.0</td>
</tr>
<tr>
<td>44.52</td>
<td>2.035</td>
<td>5.2</td>
<td>44.83</td>
<td>2.022</td>
<td>4.1</td>
</tr>
<tr>
<td>45.12</td>
<td>2.009</td>
<td>3.3</td>
<td>45.27</td>
<td>2.003</td>
<td>3.1</td>
</tr>
<tr>
<td>45.28</td>
<td>2.003</td>
<td>5.1</td>
<td>46.80</td>
<td>1.941</td>
<td>5.1</td>
</tr>
<tr>
<td>46.93</td>
<td>1.936</td>
<td>4.7</td>
<td>46.97</td>
<td>1.934</td>
<td>3.3</td>
</tr>
<tr>
<td>47.73</td>
<td>1.906</td>
<td>3.3</td>
<td>47.95</td>
<td>1.897</td>
<td>4.9</td>
</tr>
<tr>
<td>48.14</td>
<td>1.890</td>
<td>9.2</td>
<td>48.20</td>
<td>1.887</td>
<td>18.0</td>
</tr>
<tr>
<td>49.06</td>
<td>1.857</td>
<td>3.3</td>
<td>49.89</td>
<td>1.828</td>
<td>4.4</td>
</tr>
<tr>
<td>50.03</td>
<td>1.823</td>
<td>4.3</td>
<td>50.31</td>
<td>1.814</td>
<td>6.9</td>
</tr>
<tr>
<td>50.62</td>
<td>1.803</td>
<td>3.8</td>
<td>51.07</td>
<td>1.788</td>
<td>3.2</td>
</tr>
<tr>
<td>54.29</td>
<td>1.690</td>
<td>3.2</td>
<td>55.90</td>
<td>1.645</td>
<td>4.6</td>
</tr>
<tr>
<td>56.75</td>
<td>1.622</td>
<td>4.8</td>
<td>58.71</td>
<td>1.573</td>
<td>3.5</td>
</tr>
<tr>
<td>62.05</td>
<td>1.496</td>
<td>3.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX IV
MAGNETIC DATA FOR COPPER(II) COMPLEXES

Temperatures (T) are in K, molar susceptibilities corrected for diamagnetism of all atoms and temperature independent paramagnetism of Cu$^{2+}$ ion ($\chi_m^c$) in $10^{-3}$ cm$^3$ mol$^{-1}$ and magnetic moments ($\mu_{\text{eff}}$) in Bohr Magnetons (B.M.) and were calculated according to expression (a) for $[\text{Cu(pdz)}_2(\text{NO}_3)_2]_2$ and (b) for all other complexes. Except where stated otherwise, all susceptibility measurements were made on a vibrating sample magnetometer at a field of 9 225 Oe.

(a) $\mu_{\text{eff}} = 2.828 \left[ (\chi_m^c/3)T \right]^{1/2}$.

(b) $\mu_{\text{eff}} = 2.828 \left[ \chi_m^c T \right]^{1/2}$.
1. Cu(mepyz)$_2$(NCO)$_2$  
2. Cu(mepyz)(NCO)$_2$  
3. Cu(pyz)(NCO)$_2$

<table>
<thead>
<tr>
<th>T</th>
<th>$c$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>T</th>
<th>$c$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>T</th>
<th>$c$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.40</td>
<td>176</td>
<td>1.84</td>
<td>2.20</td>
<td>68.5</td>
<td>1.10</td>
<td>2.30</td>
<td>73.2</td>
<td>1.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.60</td>
<td>167</td>
<td>1.86</td>
<td>2.60</td>
<td>65.4</td>
<td>1.17</td>
<td>2.98</td>
<td>71.1</td>
<td>1.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.70</td>
<td>156</td>
<td>1.84</td>
<td>2.79</td>
<td>63.8</td>
<td>1.19</td>
<td>3.29</td>
<td>69.5</td>
<td>1.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.08</td>
<td>137</td>
<td>1.84</td>
<td>3.20</td>
<td>61.3</td>
<td>1.25</td>
<td>3.72</td>
<td>66.4</td>
<td>1.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.38</td>
<td>125</td>
<td>1.84</td>
<td>3.64</td>
<td>59.6</td>
<td>1.32</td>
<td>4.07</td>
<td>63.9</td>
<td>1.44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.72</td>
<td>114</td>
<td>1.84</td>
<td>4.18</td>
<td>56.8</td>
<td>1.38</td>
<td>4.32</td>
<td>62.6</td>
<td>1.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.07</td>
<td>103</td>
<td>1.83</td>
<td>4.32</td>
<td>56.8</td>
<td>1.40</td>
<td>4.50</td>
<td>61.1</td>
<td>1.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.32</td>
<td>99.8</td>
<td>1.86</td>
<td>4.66</td>
<td>54.1</td>
<td>1.42</td>
<td>5.05</td>
<td>57.6</td>
<td>1.53</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.82</td>
<td>90.3</td>
<td>1.87</td>
<td>5.09</td>
<td>51.9</td>
<td>1.45</td>
<td>5.54</td>
<td>54.5</td>
<td>1.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.24</td>
<td>80.8</td>
<td>1.84</td>
<td>5.76</td>
<td>48.3</td>
<td>1.49</td>
<td>6.24</td>
<td>51.1</td>
<td>1.60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.24</td>
<td>70.0</td>
<td>1.87</td>
<td>6.30</td>
<td>45.3</td>
<td>1.51</td>
<td>10.6</td>
<td>33.1</td>
<td>1.68</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.91</td>
<td>61.8</td>
<td>1.85</td>
<td>10.8</td>
<td>29.5</td>
<td>1.60</td>
<td>16.2</td>
<td>23.0</td>
<td>1.73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.2</td>
<td>37.9</td>
<td>1.84</td>
<td>16.2</td>
<td>20.9</td>
<td>1.65</td>
<td>21.3</td>
<td>18.0</td>
<td>1.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.3</td>
<td>31.5</td>
<td>1.83</td>
<td>21.2</td>
<td>16.4</td>
<td>1.67</td>
<td>25.9</td>
<td>14.9</td>
<td>1.76</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.9</td>
<td>23.6</td>
<td>1.84</td>
<td>26.5</td>
<td>13.4</td>
<td>1.69</td>
<td>30.5</td>
<td>12.9</td>
<td>1.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.9</td>
<td>19.4</td>
<td>1.84</td>
<td>30.9</td>
<td>11.5</td>
<td>1.69</td>
<td>40.5</td>
<td>9.78</td>
<td>1.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.3</td>
<td>16.1</td>
<td>1.84</td>
<td>40.3</td>
<td>8.84</td>
<td>1.69</td>
<td>48.1</td>
<td>8.28</td>
<td>1.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.6</td>
<td>13.8</td>
<td>1.84</td>
<td>47.8</td>
<td>7.51</td>
<td>1.69</td>
<td>55.0</td>
<td>7.38</td>
<td>1.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.1</td>
<td>10.4</td>
<td>1.83</td>
<td>54.8</td>
<td>6.62</td>
<td>1.70</td>
<td>60.6</td>
<td>6.66</td>
<td>1.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47.6</td>
<td>8.83</td>
<td>1.83</td>
<td>60.4</td>
<td>6.07</td>
<td>1.71</td>
<td>65.8</td>
<td>6.16</td>
<td>1.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>54.7</td>
<td>7.73</td>
<td>1.84</td>
<td>65.7</td>
<td>5.57</td>
<td>1.71</td>
<td>70.4</td>
<td>5.72</td>
<td>1.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.3</td>
<td>6.99</td>
<td>1.84</td>
<td>69.9</td>
<td>5.26</td>
<td>1.71</td>
<td>74.3</td>
<td>5.41</td>
<td>1.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65.5</td>
<td>6.44</td>
<td>1.84</td>
<td>74.2</td>
<td>4.96</td>
<td>1.72</td>
<td>81.3</td>
<td>4.94</td>
<td>1.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70.0</td>
<td>6.01</td>
<td>1.83</td>
<td>81.9</td>
<td>4.49</td>
<td>1.71</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>74.1</td>
<td>5.64</td>
<td>1.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>81.8</td>
<td>5.09</td>
<td>1.82</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>( \mu_{\text{eff}} )</td>
<td>( \chi_m )</td>
<td>T</td>
<td>( \mu_{\text{eff}} )</td>
<td>( \chi_m )</td>
<td>T</td>
<td>( \mu_{\text{eff}} )</td>
<td>( \chi_m )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>----------------</td>
<td>----------</td>
<td>-----</td>
<td>----------------</td>
<td>----------</td>
<td>-----</td>
<td>----------------</td>
<td>----------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.50</td>
<td>164</td>
<td>1.81</td>
<td>5.00</td>
<td>4.54</td>
<td>0.43</td>
<td>4.20</td>
<td>126</td>
<td>1.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.70</td>
<td>154</td>
<td>1.82</td>
<td>8.00</td>
<td>3.08</td>
<td>0.44</td>
<td>6.78</td>
<td>76.7</td>
<td>1.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.08</td>
<td>137</td>
<td>1.84</td>
<td>10.0</td>
<td>2.59</td>
<td>0.46</td>
<td>10.0</td>
<td>53.3</td>
<td>1.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.28</td>
<td>124</td>
<td>1.80</td>
<td>12.0</td>
<td>2.28</td>
<td>0.47</td>
<td>20.0</td>
<td>26.8</td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.63</td>
<td>111</td>
<td>1.80</td>
<td>14.0</td>
<td>2.10</td>
<td>0.48</td>
<td>30.0</td>
<td>17.9</td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.07</td>
<td>102</td>
<td>1.82</td>
<td>16.0</td>
<td>2.00</td>
<td>0.51</td>
<td>40.0</td>
<td>13.4</td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.47</td>
<td>94.8</td>
<td>1.84</td>
<td>18.0</td>
<td>1.94</td>
<td>0.53</td>
<td>50.0</td>
<td>10.7</td>
<td>1.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.66</td>
<td>89.6</td>
<td>1.83</td>
<td>20.0</td>
<td>1.91</td>
<td>0.55</td>
<td>60.0</td>
<td>8.98</td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.17</td>
<td>79.5</td>
<td>1.81</td>
<td>22.0</td>
<td>1.91</td>
<td>0.58</td>
<td>70.0</td>
<td>7.73</td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.61</td>
<td>73.5</td>
<td>1.82</td>
<td>30.0</td>
<td>1.94</td>
<td>0.68</td>
<td>80.0</td>
<td>6.79</td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.98</td>
<td>59.4</td>
<td>1.82</td>
<td>40.0</td>
<td>2.00</td>
<td>0.80</td>
<td>90.0</td>
<td>6.04</td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.20</td>
<td>44.8</td>
<td>1.82</td>
<td>50.0</td>
<td>2.04</td>
<td>0.90</td>
<td>100</td>
<td>5.47</td>
<td>1.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.2</td>
<td>36.2</td>
<td>1.80</td>
<td>60.0</td>
<td>2.05</td>
<td>0.99</td>
<td>110</td>
<td>5.01</td>
<td>1.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.6</td>
<td>24.5</td>
<td>1.80</td>
<td>63.0</td>
<td>2.05</td>
<td>1.02</td>
<td>120</td>
<td>4.64</td>
<td>1.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.4</td>
<td>19.0</td>
<td>1.80</td>
<td>66.0</td>
<td>2.05</td>
<td>1.04</td>
<td>130</td>
<td>4.34</td>
<td>1.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.5</td>
<td>15.5</td>
<td>1.81</td>
<td>68.0</td>
<td>2.05</td>
<td>1.06</td>
<td>140</td>
<td>4.10</td>
<td>1.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.2</td>
<td>13.1</td>
<td>1.81</td>
<td>70.0</td>
<td>2.05</td>
<td>1.07</td>
<td>150</td>
<td>3.89</td>
<td>1.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.5</td>
<td>10.0</td>
<td>1.80</td>
<td>72.0</td>
<td>2.04</td>
<td>1.08</td>
<td>160</td>
<td>3.72</td>
<td>1.26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48.0</td>
<td>8.47</td>
<td>1.80</td>
<td>74.0</td>
<td>2.04</td>
<td>1.10</td>
<td>170</td>
<td>3.57</td>
<td>1.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>55.0</td>
<td>7.46</td>
<td>1.81</td>
<td>76.0</td>
<td>2.03</td>
<td>1.11</td>
<td>180</td>
<td>3.45</td>
<td>1.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.6</td>
<td>6.80</td>
<td>1.82</td>
<td>78.0</td>
<td>2.03</td>
<td>1.13</td>
<td>190</td>
<td>3.34</td>
<td>1.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65.5</td>
<td>6.28</td>
<td>1.81</td>
<td>80.0</td>
<td>2.02</td>
<td>1.14</td>
<td>200</td>
<td>3.25</td>
<td>1.32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70.2</td>
<td>5.88</td>
<td>1.82</td>
<td>82.0</td>
<td>2.02</td>
<td>1.15</td>
<td>210</td>
<td>3.15</td>
<td>1.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>74.4</td>
<td>5.53</td>
<td>1.81</td>
<td>84.0</td>
<td>2.01</td>
<td>1.16</td>
<td>220</td>
<td>3.09</td>
<td>1.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>81.4</td>
<td>5.05</td>
<td>1.81</td>
<td>86.0</td>
<td>2.00</td>
<td>1.17</td>
<td>230</td>
<td>3.03</td>
<td>1.36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>86.0</td>
<td>4.56</td>
<td>1.77</td>
<td>90.0</td>
<td>1.99</td>
<td>1.20</td>
<td>240</td>
<td>2.97</td>
<td>1.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>3.87</td>
<td>1.78</td>
<td>95.0</td>
<td>1.96</td>
<td>1.22</td>
<td>250</td>
<td>2.91</td>
<td>1.39</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>128</td>
<td>3.17</td>
<td>1.80</td>
<td>100</td>
<td>1.94</td>
<td>1.25</td>
<td>260</td>
<td>2.85</td>
<td>1.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>153</td>
<td>2.67</td>
<td>1.81</td>
<td>110</td>
<td>1.89</td>
<td>1.29</td>
<td>270</td>
<td>2.79</td>
<td>1.42</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>2.30</td>
<td>1.82</td>
<td>125</td>
<td>1.81</td>
<td>1.35</td>
<td>280</td>
<td>2.74</td>
<td>1.43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>203</td>
<td>2.02</td>
<td>1.81</td>
<td>140</td>
<td>1.73</td>
<td>1.39</td>
<td>290</td>
<td>2.70</td>
<td>1.44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>221</td>
<td>1.86</td>
<td>1.81</td>
<td>155</td>
<td>1.64</td>
<td>1.43</td>
<td>315</td>
<td>2.60</td>
<td>1.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>237</td>
<td>1.73</td>
<td>1.81</td>
<td>170</td>
<td>1.56</td>
<td>1.46</td>
<td>330</td>
<td>2.55</td>
<td>1.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>254</td>
<td>1.61</td>
<td>1.81</td>
<td>185</td>
<td>1.49</td>
<td>1.48</td>
<td>345</td>
<td>2.50</td>
<td>1.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>278</td>
<td>1.49</td>
<td>1.82</td>
<td>200</td>
<td>1.43</td>
<td>1.51</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>292</td>
<td>1.39</td>
<td>1.80</td>
<td>215</td>
<td>1.37</td>
<td>1.53</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

\[\text{\textsuperscript{a}}\) Susceptibilities above 82 K measured using a Gouy balance.

\[\text{\textsuperscript{b}}\) Susceptibilities measured using a SQUID magnetometer \((H = 10000 \text{ Oe})\).
7. $[\text{Cu(pdz)}_4(\text{NO}_3)]\text{[NO}_3\text{]}$  
8a. $\text{Cu(pdz)}_4(\text{NO}_3)_2^a$  
8b. $\text{Cu(pdz)}_4(\text{NO}_3)_2^a$

<table>
<thead>
<tr>
<th>$T$</th>
<th>$c$ $\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$T$</th>
<th>$c$ $\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$T$</th>
<th>$c$ $\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.32</td>
<td>97.1</td>
<td>1.83</td>
<td>4.40</td>
<td>93.1</td>
<td>1.81</td>
<td>4.32</td>
<td>43.3</td>
<td>1.22</td>
</tr>
<tr>
<td>6.50</td>
<td>62.5</td>
<td>1.80</td>
<td>7.94</td>
<td>50.9</td>
<td>1.80</td>
<td>6.91</td>
<td>26.7</td>
<td>1.21</td>
</tr>
<tr>
<td>10.4</td>
<td>39.3</td>
<td>1.81</td>
<td>11.7</td>
<td>34.4</td>
<td>1.79</td>
<td>10.5</td>
<td>17.7</td>
<td>1.22</td>
</tr>
<tr>
<td>16.4</td>
<td>25.1</td>
<td>1.81</td>
<td>16.8</td>
<td>23.6</td>
<td>1.78</td>
<td>16.2</td>
<td>11.5</td>
<td>1.22</td>
</tr>
<tr>
<td>21.8</td>
<td>19.1</td>
<td>1.82</td>
<td>21.8</td>
<td>18.4</td>
<td>1.79</td>
<td>21.9</td>
<td>8.62</td>
<td>1.23</td>
</tr>
<tr>
<td>26.5</td>
<td>15.7</td>
<td>1.82</td>
<td>26.9</td>
<td>14.9</td>
<td>1.79</td>
<td>26.9</td>
<td>6.99</td>
<td>1.23</td>
</tr>
<tr>
<td>31.0</td>
<td>13.5</td>
<td>1.83</td>
<td>31.5</td>
<td>12.7</td>
<td>1.79</td>
<td>31.3</td>
<td>5.91</td>
<td>1.22</td>
</tr>
<tr>
<td>40.8</td>
<td>10.2</td>
<td>1.82</td>
<td>40.8</td>
<td>9.78</td>
<td>1.79</td>
<td>40.7</td>
<td>4.46</td>
<td>1.20</td>
</tr>
<tr>
<td>48.3</td>
<td>8.58</td>
<td>1.82</td>
<td>48.2</td>
<td>8.24</td>
<td>1.78</td>
<td>48.4</td>
<td>3.79</td>
<td>1.21</td>
</tr>
<tr>
<td>55.1</td>
<td>7.64</td>
<td>1.83</td>
<td>55.2</td>
<td>7.24</td>
<td>1.79</td>
<td>55.4</td>
<td>3.37</td>
<td>1.22</td>
</tr>
<tr>
<td>60.7</td>
<td>6.89</td>
<td>1.83</td>
<td>60.7</td>
<td>6.54</td>
<td>1.78</td>
<td>61.0</td>
<td>3.07</td>
<td>1.22</td>
</tr>
<tr>
<td>65.8</td>
<td>6.40</td>
<td>1.84</td>
<td>65.9</td>
<td>6.05</td>
<td>1.79</td>
<td>65.9</td>
<td>2.83</td>
<td>1.22</td>
</tr>
<tr>
<td>70.3</td>
<td>6.00</td>
<td>1.84</td>
<td>70.2</td>
<td>5.60</td>
<td>1.77</td>
<td>70.6</td>
<td>2.65</td>
<td>1.22</td>
</tr>
<tr>
<td>74.3</td>
<td>5.69</td>
<td>1.84</td>
<td>74.3</td>
<td>5.30</td>
<td>1.77</td>
<td>74.5</td>
<td>2.53</td>
<td>1.23</td>
</tr>
<tr>
<td>81.4</td>
<td>5.20</td>
<td>1.84</td>
<td>81.9</td>
<td>4.85</td>
<td>1.78</td>
<td>81.8</td>
<td>2.34</td>
<td>1.24</td>
</tr>
</tbody>
</table>

9. $\text{Cu(pdz)}_3(\text{NO}_3)_2$  
10. $\text{Cu(mepyz)}_4(\text{AsF}_6)_2$  
11. $\text{Cu}(4,4'-\text{bipy})_4(\text{AsF}_6)_2$

<table>
<thead>
<tr>
<th>$T$</th>
<th>$c$ $\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$T$</th>
<th>$c$ $\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$T$</th>
<th>$c$ $\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.32</td>
<td>98.1</td>
<td>1.84</td>
<td>4.47</td>
<td>91.8</td>
<td>1.81</td>
<td>4.32</td>
<td>84.1</td>
<td>1.70</td>
</tr>
<tr>
<td>7.22</td>
<td>57.8</td>
<td>1.83</td>
<td>6.50</td>
<td>62.9</td>
<td>1.81</td>
<td>7.98</td>
<td>46.3</td>
<td>1.72</td>
</tr>
<tr>
<td>10.6</td>
<td>39.2</td>
<td>1.82</td>
<td>10.9</td>
<td>37.1</td>
<td>1.80</td>
<td>11.4</td>
<td>33.5</td>
<td>1.75</td>
</tr>
<tr>
<td>12.8</td>
<td>32.3</td>
<td>1.82</td>
<td>16.5</td>
<td>25.0</td>
<td>1.82</td>
<td>17.2</td>
<td>22.4</td>
<td>1.76</td>
</tr>
<tr>
<td>17.1</td>
<td>24.3</td>
<td>1.82</td>
<td>21.5</td>
<td>19.0</td>
<td>1.81</td>
<td>22.3</td>
<td>17.4</td>
<td>1.76</td>
</tr>
<tr>
<td>21.2</td>
<td>19.6</td>
<td>1.82</td>
<td>26.5</td>
<td>15.5</td>
<td>1.81</td>
<td>27.4</td>
<td>14.4</td>
<td>1.78</td>
</tr>
<tr>
<td>26.5</td>
<td>15.9</td>
<td>1.84</td>
<td>30.8</td>
<td>13.3</td>
<td>1.81</td>
<td>31.6</td>
<td>12.5</td>
<td>1.78</td>
</tr>
<tr>
<td>31.1</td>
<td>13.5</td>
<td>1.83</td>
<td>31.4</td>
<td>12.9</td>
<td>1.80</td>
<td>41.1</td>
<td>9.69</td>
<td>1.78</td>
</tr>
<tr>
<td>40.6</td>
<td>10.2</td>
<td>1.82</td>
<td>40.3</td>
<td>9.95</td>
<td>1.79</td>
<td>48.5</td>
<td>8.28</td>
<td>1.79</td>
</tr>
<tr>
<td>48.4</td>
<td>8.68</td>
<td>1.83</td>
<td>47.8</td>
<td>8.32</td>
<td>1.78</td>
<td>55.5</td>
<td>7.19</td>
<td>1.79</td>
</tr>
<tr>
<td>55.3</td>
<td>7.68</td>
<td>1.84</td>
<td>54.9</td>
<td>7.31</td>
<td>1.79</td>
<td>61.1</td>
<td>6.56</td>
<td>1.79</td>
</tr>
<tr>
<td>61.0</td>
<td>7.03</td>
<td>1.85</td>
<td>60.4</td>
<td>6.61</td>
<td>1.79</td>
<td>66.1</td>
<td>6.10</td>
<td>1.80</td>
</tr>
<tr>
<td>66.1</td>
<td>6.38</td>
<td>1.84</td>
<td>65.6</td>
<td>6.07</td>
<td>1.78</td>
<td>70.7</td>
<td>5.78</td>
<td>1.81</td>
</tr>
<tr>
<td>70.6</td>
<td>5.99</td>
<td>1.84</td>
<td>70.2</td>
<td>5.68</td>
<td>1.79</td>
<td>74.7</td>
<td>5.31</td>
<td>1.78</td>
</tr>
<tr>
<td>74.4</td>
<td>5.68</td>
<td>1.84</td>
<td>74.4</td>
<td>5.37</td>
<td>1.79</td>
<td>82.1</td>
<td>5.00</td>
<td>1.81</td>
</tr>
<tr>
<td>81.9</td>
<td>5.21</td>
<td>1.85</td>
<td>81.8</td>
<td>4.91</td>
<td>1.79</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

$a$ Data for (8a) were collected on a freshly prepared sample (blue in colour) whereas those for (8b) were collected about one month after preparation, by which time the colour of the sample had changed to black.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>$\chi_m$</td>
<td>$\mu_{\text{eff}}$</td>
<td>$T$</td>
</tr>
<tr>
<td>4.40</td>
<td>91.2</td>
<td>1.79</td>
<td>4.04</td>
</tr>
<tr>
<td>6.58</td>
<td>60.0</td>
<td>1.78</td>
<td>5.42</td>
</tr>
<tr>
<td>11.2</td>
<td>34.6</td>
<td>1.76</td>
<td>7.80</td>
</tr>
<tr>
<td>16.8</td>
<td>23.0</td>
<td>1.76</td>
<td>11.1</td>
</tr>
<tr>
<td>21.7</td>
<td>17.7</td>
<td>1.75</td>
<td>16.4</td>
</tr>
<tr>
<td>26.7</td>
<td>14.4</td>
<td>1.75</td>
<td>21.4</td>
</tr>
<tr>
<td>31.0</td>
<td>12.4</td>
<td>1.75</td>
<td>26.5</td>
</tr>
<tr>
<td>40.4</td>
<td>9.25</td>
<td>1.73</td>
<td>31.2</td>
</tr>
<tr>
<td>47.9</td>
<td>7.77</td>
<td>1.73</td>
<td>40.3</td>
</tr>
<tr>
<td>54.9</td>
<td>6.82</td>
<td>1.73</td>
<td>47.8</td>
</tr>
<tr>
<td>60.5</td>
<td>6.29</td>
<td>1.74</td>
<td>54.8</td>
</tr>
<tr>
<td>65.7</td>
<td>5.76</td>
<td>1.74</td>
<td>60.4</td>
</tr>
<tr>
<td>70.2</td>
<td>5.45</td>
<td>1.75</td>
<td>65.6</td>
</tr>
<tr>
<td>74.4</td>
<td>5.13</td>
<td>1.75</td>
<td>70.0</td>
</tr>
<tr>
<td>81.7</td>
<td>4.71</td>
<td>1.75</td>
<td>74.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>15. Cu(pdz)$_4$(CH$_3$SO$_3$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>$\chi_m$</td>
</tr>
<tr>
<td>4.40</td>
<td>92.7</td>
</tr>
<tr>
<td>6.84</td>
<td>56.8</td>
</tr>
<tr>
<td>6.98</td>
<td>56.3</td>
</tr>
<tr>
<td>9.45</td>
<td>41.3</td>
</tr>
<tr>
<td>11.4</td>
<td>34.3</td>
</tr>
<tr>
<td>16.7</td>
<td>23.3</td>
</tr>
<tr>
<td>21.6</td>
<td>18.2</td>
</tr>
<tr>
<td>31.1</td>
<td>12.8</td>
</tr>
<tr>
<td>40.4</td>
<td>9.82</td>
</tr>
<tr>
<td>48.0</td>
<td>8.34</td>
</tr>
<tr>
<td>55.0</td>
<td>7.40</td>
</tr>
<tr>
<td>60.7</td>
<td>6.73</td>
</tr>
<tr>
<td>65.8</td>
<td>6.12</td>
</tr>
<tr>
<td>70.2</td>
<td>5.85</td>
</tr>
<tr>
<td>74.4</td>
<td>5.52</td>
</tr>
<tr>
<td>81.9</td>
<td>4.98</td>
</tr>
</tbody>
</table>
APPENDIX V

MAGNETIC DATA FOR NICKEL(II) COMPLEXES

This appendix is divided into two parts. In part A are presented variable temperature magnetic susceptibility and moment data obtained at fixed magnetic fields using a vibrating sample magnetometer. In cases where field dependence were observed over the temperature range studied, the data at all fields are presented, otherwise only data at 9.225 kOe are presented. Data from isothermal field dependence studies, obtained by a SQUID magnetometer, are tabulated in part B. Applied magnetic field strengths (H) are in kOe, magnetizations (M) in cm$^3$ G mol$^{-1}$, temperatures (T) in K, molar susceptibilities corrected for diamagnetism of all atoms and temperature independent paramagnetism of Ni$^{2+}$ ($\chi_m^c$) in 10$^{-3}$ cm$^3$ mol$^{-1}$ and effective magnetic moments ($\mu_{\text{eff}}$) in B.M. and were calculated according to the expression:

$$\mu_{\text{eff}} = 2.828 \left[\chi_m^c T\right]^{1/2}.$$
Part A: Variable temperature magnetic studies

1. Ni(py)$_4$(NCO)$_2$

<table>
<thead>
<tr>
<th>T</th>
<th>c</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>T</th>
<th>c</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>T</th>
<th>c</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.32</td>
<td>266</td>
<td>3.03</td>
<td></td>
<td>4.32</td>
<td>152</td>
<td>2.29</td>
<td></td>
<td>4.40</td>
<td>182</td>
<td>2.53</td>
<td></td>
</tr>
<tr>
<td>5.99</td>
<td>189</td>
<td>3.01</td>
<td>6.64</td>
<td>114</td>
<td>2.46</td>
<td>8.04</td>
<td>119</td>
<td>2.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.8</td>
<td>105</td>
<td>3.01</td>
<td>11.0</td>
<td>78.4</td>
<td>2.63</td>
<td>11.4</td>
<td>89.7</td>
<td>2.86</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.1</td>
<td>70.2</td>
<td>3.01</td>
<td>16.3</td>
<td>57.0</td>
<td>2.73</td>
<td>16.8</td>
<td>64.0</td>
<td>2.93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.5</td>
<td>52.3</td>
<td>3.00</td>
<td>21.8</td>
<td>44.6</td>
<td>2.79</td>
<td>21.6</td>
<td>50.7</td>
<td>2.96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.5</td>
<td>42.9</td>
<td>3.02</td>
<td>26.7</td>
<td>37.2</td>
<td>2.82</td>
<td>26.7</td>
<td>41.8</td>
<td>2.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.6</td>
<td>36.9</td>
<td>3.01</td>
<td>31.1</td>
<td>32.4</td>
<td>2.84</td>
<td>31.0</td>
<td>36.1</td>
<td>2.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.1</td>
<td>36.5</td>
<td>3.01</td>
<td>40.3</td>
<td>25.3</td>
<td>2.86</td>
<td>40.4</td>
<td>27.9</td>
<td>3.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>28.1</td>
<td>3.00</td>
<td>47.9</td>
<td>21.6</td>
<td>2.88</td>
<td>48.2</td>
<td>23.5</td>
<td>3.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47.6</td>
<td>23.6</td>
<td>3.00</td>
<td>54.9</td>
<td>19.1</td>
<td>2.90</td>
<td>55.3</td>
<td>20.8</td>
<td>3.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>54.7</td>
<td>20.9</td>
<td>3.02</td>
<td>60.6</td>
<td>17.4</td>
<td>2.90</td>
<td>60.8</td>
<td>19.0</td>
<td>3.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.3</td>
<td>18.9</td>
<td>3.02</td>
<td>65.7</td>
<td>16.1</td>
<td>2.91</td>
<td>65.9</td>
<td>17.7</td>
<td>3.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65.5</td>
<td>17.4</td>
<td>3.02</td>
<td>70.1</td>
<td>15.1</td>
<td>2.91</td>
<td>70.1</td>
<td>16.5</td>
<td>3.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>69.9</td>
<td>16.2</td>
<td>3.01</td>
<td>74.4</td>
<td>14.3</td>
<td>2.92</td>
<td>74.5</td>
<td>15.6</td>
<td>3.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>74.1</td>
<td>15.3</td>
<td>3.01</td>
<td>81.8</td>
<td>13.0</td>
<td>2.92</td>
<td>81.8</td>
<td>14.3</td>
<td>3.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>81.5</td>
<td>13.9</td>
<td>3.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Ni(pdz)$_2$(NCO)$_2$

3. Ni(pyz)$_2$(NCO)$_2$.1/2H$_2$O

4. Ni(pyz)(NCO)$_2$

5. Ni(pyz)$_2$Cl$_2$

6. Ni(pyz)Cl$_2$
7. Ni(py)Cl$_2$

<table>
<thead>
<tr>
<th>$T$</th>
<th>$\chi_m^c$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$T$</th>
<th>$\chi_m^c$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$T$</th>
<th>$\chi_m^c$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.20</td>
<td>738</td>
<td>3.60</td>
<td>2.20</td>
<td>918</td>
<td>4.02</td>
<td>2.11</td>
<td>460</td>
<td>2.79</td>
</tr>
<tr>
<td>3.20</td>
<td>738</td>
<td>4.35</td>
<td>2.60</td>
<td>918</td>
<td>4.37</td>
<td>2.40</td>
<td>460</td>
<td>2.97</td>
</tr>
<tr>
<td>3.54</td>
<td>734</td>
<td>4.56</td>
<td>2.98</td>
<td>918</td>
<td>4.68</td>
<td>2.79</td>
<td>461</td>
<td>3.21</td>
</tr>
<tr>
<td>4.10</td>
<td>734</td>
<td>4.91</td>
<td>3.29</td>
<td>918</td>
<td>4.91</td>
<td>3.20</td>
<td>464</td>
<td>3.45</td>
</tr>
<tr>
<td>4.24</td>
<td>734</td>
<td>4.99</td>
<td>3.72</td>
<td>918</td>
<td>5.23</td>
<td>4.07</td>
<td>469</td>
<td>3.91</td>
</tr>
<tr>
<td>4.34</td>
<td>734</td>
<td>5.05</td>
<td>4.26</td>
<td>918</td>
<td>5.59</td>
<td>4.42</td>
<td>473</td>
<td>4.09</td>
</tr>
<tr>
<td>4.58</td>
<td>734</td>
<td>5.19</td>
<td>4.74</td>
<td>918</td>
<td>5.90</td>
<td>4.97</td>
<td>478</td>
<td>4.36</td>
</tr>
<tr>
<td>4.90</td>
<td>734</td>
<td>5.36</td>
<td>5.32</td>
<td>924</td>
<td>6.27</td>
<td>5.61</td>
<td>489</td>
<td>4.68</td>
</tr>
<tr>
<td>5.38</td>
<td>730</td>
<td>5.60</td>
<td>5.91</td>
<td>924</td>
<td>6.61</td>
<td>6.17</td>
<td>501</td>
<td>4.97</td>
</tr>
<tr>
<td>5.83</td>
<td>730</td>
<td>5.83</td>
<td>9.25</td>
<td>886</td>
<td>8.10</td>
<td>6.84</td>
<td>522</td>
<td>5.34</td>
</tr>
<tr>
<td>6.30</td>
<td>727</td>
<td>6.05</td>
<td>11.2</td>
<td>796</td>
<td>8.44</td>
<td>8.04</td>
<td>588</td>
<td>6.15</td>
</tr>
<tr>
<td>7.10</td>
<td>727</td>
<td>6.43</td>
<td>13.4</td>
<td>626</td>
<td>8.19</td>
<td>9.00</td>
<td>670</td>
<td>6.94</td>
</tr>
<tr>
<td>9.51</td>
<td>701</td>
<td>7.30</td>
<td>17.5</td>
<td>414</td>
<td>7.61</td>
<td>10.2</td>
<td>802</td>
<td>8.09</td>
</tr>
<tr>
<td>11.1</td>
<td>654</td>
<td>7.62</td>
<td>21.5</td>
<td>291</td>
<td>7.07</td>
<td>11.2</td>
<td>830</td>
<td>8.62</td>
</tr>
<tr>
<td>13.7</td>
<td>544</td>
<td>7.72</td>
<td>26.8</td>
<td>200</td>
<td>6.55</td>
<td>12.5</td>
<td>725</td>
<td>8.51</td>
</tr>
<tr>
<td>15.7</td>
<td>464</td>
<td>7.63</td>
<td>31.3</td>
<td>151</td>
<td>6.15</td>
<td>13.1</td>
<td>674</td>
<td>8.40</td>
</tr>
<tr>
<td>17.6</td>
<td>391</td>
<td>7.42</td>
<td>40.6</td>
<td>93.3</td>
<td>5.50</td>
<td>15.4</td>
<td>524</td>
<td>8.03</td>
</tr>
<tr>
<td>19.5</td>
<td>334</td>
<td>7.22</td>
<td>47.9</td>
<td>69.4</td>
<td>5.16</td>
<td>17.1</td>
<td>433</td>
<td>7.70</td>
</tr>
<tr>
<td>21.6</td>
<td>282</td>
<td>6.98</td>
<td>54.9</td>
<td>55.2</td>
<td>4.92</td>
<td>19.3</td>
<td>354</td>
<td>7.39</td>
</tr>
<tr>
<td>24.1</td>
<td>236</td>
<td>6.74</td>
<td>60.4</td>
<td>46.6</td>
<td>4.74</td>
<td>21.3</td>
<td>297</td>
<td>7.11</td>
</tr>
<tr>
<td>26.8</td>
<td>198</td>
<td>6.51</td>
<td>65.5</td>
<td>40.6</td>
<td>4.61</td>
<td>26.2</td>
<td>153</td>
<td>5.66</td>
</tr>
<tr>
<td>29.1</td>
<td>170</td>
<td>6.29</td>
<td>70.1</td>
<td>36.3</td>
<td>4.51</td>
<td>30.8</td>
<td>155</td>
<td>6.18</td>
</tr>
<tr>
<td>31.2</td>
<td>151</td>
<td>6.14</td>
<td>74.1</td>
<td>32.9</td>
<td>4.42</td>
<td>40.4</td>
<td>92.6</td>
<td>5.47</td>
</tr>
<tr>
<td>36.3</td>
<td>113</td>
<td>5.73</td>
<td>81.7</td>
<td>28.2</td>
<td>4.29</td>
<td>47.8</td>
<td>68.6</td>
<td>5.12</td>
</tr>
<tr>
<td>40.4</td>
<td>93.3</td>
<td>5.49</td>
<td></td>
<td></td>
<td></td>
<td>54.7</td>
<td>55.0</td>
<td>4.91</td>
</tr>
<tr>
<td>47.9</td>
<td>68.8</td>
<td>5.13</td>
<td></td>
<td></td>
<td></td>
<td>60.3</td>
<td>46.4</td>
<td>4.73</td>
</tr>
<tr>
<td>54.8</td>
<td>55.2</td>
<td>4.92</td>
<td></td>
<td></td>
<td></td>
<td>65.4</td>
<td>40.5</td>
<td>4.60</td>
</tr>
<tr>
<td>60.4</td>
<td>46.8</td>
<td>4.75</td>
<td></td>
<td></td>
<td></td>
<td>69.9</td>
<td>36.1</td>
<td>4.49</td>
</tr>
<tr>
<td>65.5</td>
<td>40.9</td>
<td>4.63</td>
<td></td>
<td></td>
<td></td>
<td>74.1</td>
<td>32.8</td>
<td>4.41</td>
</tr>
<tr>
<td>70.1</td>
<td>36.3</td>
<td>4.51</td>
<td></td>
<td></td>
<td></td>
<td>81.3</td>
<td>28.3</td>
<td>4.29</td>
</tr>
<tr>
<td>74.2</td>
<td>33.0</td>
<td>4.43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>81.7</td>
<td>28.3</td>
<td>4.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**$H = 7.501$**

<table>
<thead>
<tr>
<th>$T$</th>
<th>$\chi_m^c$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$T$</th>
<th>$\chi_m^c$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$T$</th>
<th>$\chi_m^c$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.30</td>
<td>827</td>
<td>3.90</td>
<td>7.10</td>
<td>813</td>
<td>6.79</td>
<td>27.1</td>
<td>193</td>
<td>6.47</td>
</tr>
<tr>
<td>2.60</td>
<td>827</td>
<td>4.15</td>
<td>9.38</td>
<td>786</td>
<td>7.68</td>
<td>31.3</td>
<td>149</td>
<td>6.11</td>
</tr>
<tr>
<td>2.98</td>
<td>827</td>
<td>4.44</td>
<td>11.7</td>
<td>688</td>
<td>8.02</td>
<td>55.0</td>
<td>55.8</td>
<td>4.95</td>
</tr>
<tr>
<td>3.63</td>
<td>827</td>
<td>4.90</td>
<td>13.7</td>
<td>571</td>
<td>7.91</td>
<td>65.8</td>
<td>41.1</td>
<td>4.65</td>
</tr>
<tr>
<td>4.34</td>
<td>822</td>
<td>5.34</td>
<td>17.9</td>
<td>389</td>
<td>7.46</td>
<td>74.5</td>
<td>33.3</td>
<td>4.45</td>
</tr>
<tr>
<td>4.97</td>
<td>822</td>
<td>5.72</td>
<td>22.1</td>
<td>278</td>
<td>7.01</td>
<td>81.8</td>
<td>28.6</td>
<td>4.33</td>
</tr>
<tr>
<td>5.83</td>
<td>818</td>
<td>6.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### 8. Ni(py)$_4$Cl$_2$

<table>
<thead>
<tr>
<th>T</th>
<th>$c$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>T</th>
<th>$c$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.32</td>
<td>205</td>
<td>2.66</td>
<td></td>
<td>4.40</td>
<td>220</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td>7.94</td>
<td>133</td>
<td>2.91</td>
<td></td>
<td>6.72</td>
<td>144</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td>11.4</td>
<td>95.9</td>
<td>2.96</td>
<td></td>
<td>8.96</td>
<td>110</td>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>16.5</td>
<td>68.3</td>
<td>3.00</td>
<td></td>
<td>11.0</td>
<td>89.9</td>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>21.4</td>
<td>53.3</td>
<td>3.02</td>
<td></td>
<td>13.0</td>
<td>76.6</td>
<td>2.82</td>
<td></td>
</tr>
<tr>
<td>26.3</td>
<td>43.7</td>
<td>3.03</td>
<td></td>
<td>17.4</td>
<td>57.7</td>
<td>2.83</td>
<td></td>
</tr>
<tr>
<td>30.8</td>
<td>37.5</td>
<td>3.04</td>
<td></td>
<td>21.1</td>
<td>47.8</td>
<td>2.84</td>
<td></td>
</tr>
<tr>
<td>40.3</td>
<td>28.7</td>
<td>3.04</td>
<td></td>
<td>26.5</td>
<td>38.9</td>
<td>2.87</td>
<td></td>
</tr>
<tr>
<td>48.1</td>
<td>24.2</td>
<td>3.05</td>
<td></td>
<td>31.1</td>
<td>33.3</td>
<td>2.88</td>
<td></td>
</tr>
<tr>
<td>54.9</td>
<td>21.4</td>
<td>3.07</td>
<td></td>
<td>40.6</td>
<td>25.7</td>
<td>2.89</td>
<td></td>
</tr>
<tr>
<td>60.7</td>
<td>19.4</td>
<td>3.07</td>
<td></td>
<td>47.9</td>
<td>22.0</td>
<td>2.90</td>
<td></td>
</tr>
<tr>
<td>65.8</td>
<td>17.9</td>
<td>3.07</td>
<td></td>
<td>54.9</td>
<td>19.5</td>
<td>2.93</td>
<td></td>
</tr>
<tr>
<td>70.2</td>
<td>16.9</td>
<td>3.08</td>
<td></td>
<td>60.5</td>
<td>17.8</td>
<td>2.93</td>
<td></td>
</tr>
<tr>
<td>74.4</td>
<td>16.0</td>
<td>3.09</td>
<td></td>
<td>65.7</td>
<td>16.5</td>
<td>2.94</td>
<td></td>
</tr>
<tr>
<td>81.8</td>
<td>14.7</td>
<td>3.10</td>
<td></td>
<td>70.2</td>
<td>15.4</td>
<td>2.94</td>
<td></td>
</tr>
</tbody>
</table>

### 9. Ni(pdz)$_3$(NCS)$_2$

<table>
<thead>
<tr>
<th>T</th>
<th>$c$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>T</th>
<th>$c$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.40</td>
<td>264</td>
<td>3.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.13</td>
<td>191</td>
<td>3.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.50</td>
<td>138</td>
<td>3.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.7</td>
<td>110</td>
<td>3.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.0</td>
<td>90.5</td>
<td>3.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.2</td>
<td>68.1</td>
<td>3.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.4</td>
<td>54.8</td>
<td>3.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.5</td>
<td>44.4</td>
<td>3.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.2</td>
<td>37.3</td>
<td>3.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.4</td>
<td>28.9</td>
<td>3.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47.6</td>
<td>24.3</td>
<td>3.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 10. Ni(pdz)$_2$(NCS)$_2$

<table>
<thead>
<tr>
<th>T</th>
<th>$c$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>T</th>
<th>$c$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.40</td>
<td>181</td>
<td>1.90</td>
<td></td>
<td>4.40</td>
<td>261</td>
<td>3.03</td>
<td></td>
</tr>
<tr>
<td>5.91</td>
<td>195</td>
<td>3.04</td>
<td></td>
<td>7.10</td>
<td>161</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>11.4</td>
<td>98.7</td>
<td>3.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.8</td>
<td>67.2</td>
<td>3.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.5</td>
<td>52.6</td>
<td>3.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.8</td>
<td>42.5</td>
<td>3.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.5</td>
<td>36.3</td>
<td>3.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.4</td>
<td>28.5</td>
<td>3.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47.9</td>
<td>24.2</td>
<td>3.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>54.6</td>
<td>21.3</td>
<td>3.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 11. Ni(py)$_2$(NCS)$_2$

<table>
<thead>
<tr>
<th>T</th>
<th>$c$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>T</th>
<th>$c$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>181</td>
<td>1.90</td>
<td></td>
<td>4.40</td>
<td>261</td>
<td>3.03</td>
<td></td>
</tr>
<tr>
<td>2.70</td>
<td>179</td>
<td>1.97</td>
<td></td>
<td>5.91</td>
<td>195</td>
<td>3.04</td>
<td></td>
</tr>
<tr>
<td>2.98</td>
<td>174</td>
<td>2.04</td>
<td></td>
<td>7.10</td>
<td>161</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>3.54</td>
<td>165</td>
<td>2.16</td>
<td></td>
<td>11.4</td>
<td>98.7</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>3.89</td>
<td>158</td>
<td>2.22</td>
<td></td>
<td>16.8</td>
<td>67.2</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>4.26</td>
<td>151</td>
<td>2.27</td>
<td></td>
<td>21.5</td>
<td>52.6</td>
<td>3.01</td>
<td></td>
</tr>
<tr>
<td>4.40</td>
<td>152</td>
<td>2.31</td>
<td></td>
<td>26.8</td>
<td>42.5</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>4.82</td>
<td>143</td>
<td>2.35</td>
<td></td>
<td>31.5</td>
<td>36.3</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>5.32</td>
<td>134</td>
<td>2.39</td>
<td></td>
<td>40.4</td>
<td>28.5</td>
<td>3.03</td>
<td></td>
</tr>
<tr>
<td>5.68</td>
<td>128</td>
<td>2.41</td>
<td></td>
<td>47.9</td>
<td>24.2</td>
<td>3.04</td>
<td></td>
</tr>
<tr>
<td>7.07</td>
<td>112</td>
<td>2.52</td>
<td></td>
<td>54.6</td>
<td>21.3</td>
<td>3.05</td>
<td></td>
</tr>
<tr>
<td>11.4</td>
<td>77.3</td>
<td>2.65</td>
<td></td>
<td>60.3</td>
<td>19.4</td>
<td>3.06</td>
<td></td>
</tr>
<tr>
<td>16.8</td>
<td>55.4</td>
<td>2.73</td>
<td></td>
<td>65.6</td>
<td>17.9</td>
<td>3.06</td>
<td></td>
</tr>
<tr>
<td>21.9</td>
<td>44.3</td>
<td>2.79</td>
<td></td>
<td>70.3</td>
<td>16.8</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>26.9</td>
<td>36.9</td>
<td>2.82</td>
<td></td>
<td>74.4</td>
<td>15.8</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>31.1</td>
<td>31.9</td>
<td>2.82</td>
<td></td>
<td>81.8</td>
<td>14.4</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>40.6</td>
<td>25.1</td>
<td>2.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48.0</td>
<td>21.4</td>
<td>2.87</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>54.9</td>
<td>19.0</td>
<td>2.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.5</td>
<td>17.3</td>
<td>2.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65.7</td>
<td>16.0</td>
<td>2.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70.2</td>
<td>15.0</td>
<td>2.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>74.4</td>
<td>14.2</td>
<td>2.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>81.9</td>
<td>12.9</td>
<td>2.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
13. Ni(pyz)(NCS)$_2$

H = 9.225

\begin{tabular}{ccc}
T & $c_{\chi m}$ & $\mu_{\text{eff}}$ \\
2.11 & 423 & 2.67 \\
2.50 & 436 & 2.95 \\
2.70 & 440 & 3.08 \\
3.08 & 432 & 3.26 \\
3.46 & 415 & 3.39 \\
4.07 & 388 & 3.55 \\
4.40 & 373 & 3.62 \\
4.50 & 360 & 3.60 \\
5.05 & 331 & 3.66 \\
5.61 & 296 & 3.64 \\
8.44 & 198 & 3.66 \\
10.6 & 151 & 3.58 \\
16.2 & 89.2 & 3.40 \\
21.5 & 64.8 & 3.34 \\
26.5 & 51.3 & 3.30 \\
31.1 & 43.2 & 3.28 \\
40.8 & 32.0 & 3.23 \\
48.4 & 26.8 & 3.22 \\
55.1 & 23.5 & 3.22 \\
60.7 & 21.1 & 3.20 \\
65.9 & 19.4 & 3.20 \\
70.3 & 18.1 & 3.19 \\
74.6 & 17.0 & 3.18 \\
81.8 & 15.4 & 3.17 \\
\end{tabular}

H = 5.251

\begin{tabular}{ccc}
T & $c_{\chi m}$ & $\mu_{\text{eff}}$ \\
2.20 & 279 & 2.22 \\
2.70 & 340 & 2.71 \\
3.08 & 382 & 3.07 \\
3.46 & 402 & 3.34 \\
3.98 & 384 & 3.50 \\
4.04 & 382 & 3.51 \\
4.58 & 368 & 3.67 \\
5.17 & 331 & 3.70 \\
5.83 & 297 & 3.72 \\
9.14 & 178 & 3.61 \\
11.4 & 138 & 3.55 \\
16.9 & 85.8 & 3.41 \\
22.1 & 63.4 & 3.35 \\
27.1 & 50.3 & 3.30 \\
31.8 & 41.8 & 3.26 \\
40.7 & 31.9 & 3.22 \\
48.2 & 26.6 & 3.20 \\
55.2 & 23.3 & 3.21 \\
60.7 & 20.9 & 3.19 \\
65.8 & 19.2 & 3.18 \\
70.2 & 17.9 & 3.17 \\
74.3 & 16.8 & 3.16 \\
81.5 & 15.2 & 3.15 \\
87.0 & 14.7 & 3.14 \\
\end{tabular}

H = 2.549

\begin{tabular}{ccc}
T & $c_{\chi m}$ & $\mu_{\text{eff}}$ \\
2.20 & 257 & 2.13 \\
2.40 & 280 & 2.32 \\
2.79 & 309 & 2.63 \\
3.20 & 366 & 3.06 \\
3.54 & 385 & 3.30 \\
3.98 & 387 & 3.51 \\
4.24 & 378 & 3.58 \\
4.42 & 371 & 3.62 \\
4.81 & 353 & 3.69 \\
5.09 & 333 & 3.68 \\
5.68 & 306 & 3.73 \\
6.24 & 281 & 3.74 \\
8.44 & 199 & 3.67 \\
10.4 & 153 & 3.57 \\
15.2 & 90.2 & 3.42 \\
16.2 & 90.2 & 3.42 \\
21.4 & 65.4 & 3.35 \\
26.7 & 51.6 & 3.32 \\
31.2 & 43.2 & 3.28 \\
40.9 & 31.7 & 3.22 \\
48.3 & 26.4 & 3.19 \\
55.2 & 23.0 & 3.19 \\
60.7 & 20.8 & 3.18 \\
65.8 & 19.0 & 3.16 \\
70.3 & 17.7 & 3.15 \\
74.4 & 16.5 & 3.13 \\
81.8 & 15.1 & 3.14 \\
\end{tabular}
14. Ni(py)$_2$(NCS)$_2$

<table>
<thead>
<tr>
<th>T</th>
<th>$c$ $\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>T</th>
<th>$c$ $\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>T</th>
<th>$c$ $\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.30</td>
<td>505</td>
<td>3.05</td>
<td>2.30</td>
<td>464</td>
<td>2.92</td>
<td>2.30</td>
<td>415</td>
<td>2.76</td>
</tr>
<tr>
<td>2.60</td>
<td>507</td>
<td>3.25</td>
<td>2.60</td>
<td>473</td>
<td>3.08</td>
<td>2.60</td>
<td>431</td>
<td>2.94</td>
</tr>
<tr>
<td>2.79</td>
<td>507</td>
<td>3.36</td>
<td>2.79</td>
<td>481</td>
<td>3.22</td>
<td>2.79</td>
<td>444</td>
<td>3.10</td>
</tr>
<tr>
<td>2.98</td>
<td>507</td>
<td>3.48</td>
<td>2.98</td>
<td>489</td>
<td>3.47</td>
<td>2.98</td>
<td>464</td>
<td>3.38</td>
</tr>
<tr>
<td>3.46</td>
<td>501</td>
<td>3.72</td>
<td>3.46</td>
<td>488</td>
<td>3.67</td>
<td>3.46</td>
<td>479</td>
<td>3.68</td>
</tr>
<tr>
<td>3.72</td>
<td>490</td>
<td>3.82</td>
<td>3.72</td>
<td>471</td>
<td>3.87</td>
<td>3.72</td>
<td>448</td>
<td>3.91</td>
</tr>
<tr>
<td>4.26</td>
<td>464</td>
<td>3.98</td>
<td>4.26</td>
<td>461</td>
<td>3.99</td>
<td>4.26</td>
<td>454</td>
<td>4.00</td>
</tr>
<tr>
<td>4.40</td>
<td>458</td>
<td>4.01</td>
<td>4.40</td>
<td>443</td>
<td>4.03</td>
<td>4.40</td>
<td>422</td>
<td>4.00</td>
</tr>
<tr>
<td>4.66</td>
<td>441</td>
<td>4.05</td>
<td>4.66</td>
<td>411</td>
<td>4.09</td>
<td>4.66</td>
<td>381</td>
<td>4.11</td>
</tr>
<tr>
<td>5.39</td>
<td>403</td>
<td>4.17</td>
<td>5.39</td>
<td>379</td>
<td>4.10</td>
<td>5.39</td>
<td>355</td>
<td>4.19</td>
</tr>
<tr>
<td>6.64</td>
<td>319</td>
<td>4.12</td>
<td>6.64</td>
<td>346</td>
<td>4.13</td>
<td>6.64</td>
<td>247</td>
<td>4.08</td>
</tr>
<tr>
<td>8.83</td>
<td>230</td>
<td>4.03</td>
<td>8.83</td>
<td>309</td>
<td>4.17</td>
<td>8.83</td>
<td>190</td>
<td>3.99</td>
</tr>
<tr>
<td>10.9</td>
<td>180</td>
<td>3.96</td>
<td>10.9</td>
<td>224</td>
<td>4.06</td>
<td>10.9</td>
<td>150</td>
<td>3.90</td>
</tr>
<tr>
<td>13.3</td>
<td>141</td>
<td>3.87</td>
<td>13.3</td>
<td>176</td>
<td>3.97</td>
<td>13.3</td>
<td>102</td>
<td>3.73</td>
</tr>
<tr>
<td>16.2</td>
<td>109</td>
<td>3.76</td>
<td>16.2</td>
<td>140</td>
<td>3.87</td>
<td>16.2</td>
<td>77.0</td>
<td>3.62</td>
</tr>
<tr>
<td>21.5</td>
<td>76.8</td>
<td>3.63</td>
<td>21.5</td>
<td>99.3</td>
<td>3.72</td>
<td>21.5</td>
<td>60.3</td>
<td>3.55</td>
</tr>
<tr>
<td>26.7</td>
<td>59.0</td>
<td>3.55</td>
<td>26.7</td>
<td>75.4</td>
<td>3.62</td>
<td>26.7</td>
<td>49.5</td>
<td>3.49</td>
</tr>
<tr>
<td>31.2</td>
<td>48.8</td>
<td>3.49</td>
<td>31.2</td>
<td>59.2</td>
<td>3.55</td>
<td>31.2</td>
<td>35.5</td>
<td>3.37</td>
</tr>
<tr>
<td>40.3</td>
<td>35.6</td>
<td>3.39</td>
<td>40.3</td>
<td>48.4</td>
<td>3.48</td>
<td>40.3</td>
<td>29.1</td>
<td>3.33</td>
</tr>
<tr>
<td>47.7</td>
<td>29.1</td>
<td>3.33</td>
<td>47.7</td>
<td>35.7</td>
<td>3.38</td>
<td>47.7</td>
<td>25.2</td>
<td>3.32</td>
</tr>
<tr>
<td>54.7</td>
<td>25.3</td>
<td>3.33</td>
<td>54.7</td>
<td>29.3</td>
<td>3.34</td>
<td>54.7</td>
<td>22.4</td>
<td>3.28</td>
</tr>
<tr>
<td>60.5</td>
<td>22.6</td>
<td>3.31</td>
<td>60.5</td>
<td>25.4</td>
<td>3.33</td>
<td>60.5</td>
<td>20.4</td>
<td>3.27</td>
</tr>
<tr>
<td>65.6</td>
<td>20.6</td>
<td>3.29</td>
<td>65.6</td>
<td>22.6</td>
<td>3.30</td>
<td>65.6</td>
<td>18.8</td>
<td>3.24</td>
</tr>
<tr>
<td>70.1</td>
<td>19.2</td>
<td>3.28</td>
<td>70.1</td>
<td>20.5</td>
<td>3.27</td>
<td>70.1</td>
<td>17.8</td>
<td>3.25</td>
</tr>
<tr>
<td>74.3</td>
<td>17.9</td>
<td>3.26</td>
<td>74.3</td>
<td>19.1</td>
<td>3.26</td>
<td>74.3</td>
<td>15.8</td>
<td>3.21</td>
</tr>
<tr>
<td>81.4</td>
<td>16.0</td>
<td>3.23</td>
<td>81.4</td>
<td>17.8</td>
<td>3.25</td>
<td>81.4</td>
<td>16.0</td>
<td>3.23</td>
</tr>
</tbody>
</table>

| H = 9.225 |

<table>
<thead>
<tr>
<th>T</th>
<th>$c$ $\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>T</th>
<th>$c$ $\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>T</th>
<th>$c$ $\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.30</td>
<td>520</td>
<td>3.09</td>
<td>6.24</td>
<td>353</td>
<td>4.20</td>
<td>40.4</td>
<td>35.6</td>
<td>3.39</td>
</tr>
<tr>
<td>2.60</td>
<td>516</td>
<td>3.28</td>
<td>6.98</td>
<td>301</td>
<td>4.10</td>
<td>47.9</td>
<td>29.2</td>
<td>3.34</td>
</tr>
<tr>
<td>3.20</td>
<td>507</td>
<td>3.60</td>
<td>9.45</td>
<td>216</td>
<td>4.04</td>
<td>54.9</td>
<td>25.2</td>
<td>3.33</td>
</tr>
<tr>
<td>3.46</td>
<td>498</td>
<td>3.71</td>
<td>11.4</td>
<td>170</td>
<td>3.94</td>
<td>60.4</td>
<td>22.6</td>
<td>3.30</td>
</tr>
<tr>
<td>3.89</td>
<td>475</td>
<td>3.84</td>
<td>13.7</td>
<td>138</td>
<td>3.89</td>
<td>65.5</td>
<td>20.7</td>
<td>3.29</td>
</tr>
<tr>
<td>4.12</td>
<td>450</td>
<td>3.85</td>
<td>18.1</td>
<td>95.9</td>
<td>3.73</td>
<td>70.1</td>
<td>19.1</td>
<td>3.27</td>
</tr>
<tr>
<td>4.34</td>
<td>452</td>
<td>3.96</td>
<td>22.2</td>
<td>74.6</td>
<td>3.64</td>
<td>74.2</td>
<td>17.9</td>
<td>3.26</td>
</tr>
<tr>
<td>5.05</td>
<td>417</td>
<td>4.10</td>
<td>27.0</td>
<td>58.3</td>
<td>3.55</td>
<td>81.8</td>
<td>16.1</td>
<td>3.25</td>
</tr>
<tr>
<td>5.68</td>
<td>380</td>
<td>4.15</td>
<td>31.5</td>
<td>47.9</td>
<td>3.47</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
PART B: Isothermal field dependence magnetic studies

1. Ni(pyz)(NCO)₂

<table>
<thead>
<tr>
<th>H (K)</th>
<th>M (emu)</th>
<th>$\chi_m$ (emu K/mol)</th>
<th>$\mu_{eff}$ (emu)</th>
<th>M (emu)</th>
<th>$\chi_m$ (emu K/mol)</th>
<th>$\mu_{eff}$ (emu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>73.44</td>
<td>147</td>
<td>1.53</td>
<td>112.0</td>
<td>224</td>
<td>2.99</td>
</tr>
<tr>
<td>2.0</td>
<td>279.2</td>
<td>140</td>
<td>1.50</td>
<td>364.9</td>
<td>182</td>
<td>2.70</td>
</tr>
<tr>
<td>4.0</td>
<td>571.3</td>
<td>143</td>
<td>1.51</td>
<td>664.4</td>
<td>166</td>
<td>2.58</td>
</tr>
<tr>
<td>6.0</td>
<td>865.4</td>
<td>144</td>
<td>1.52</td>
<td>963.1</td>
<td>160</td>
<td>2.53</td>
</tr>
<tr>
<td>8.0</td>
<td>1152</td>
<td>144</td>
<td>1.52</td>
<td>1286</td>
<td>161</td>
<td>2.54</td>
</tr>
<tr>
<td>10.0</td>
<td>1470</td>
<td>147</td>
<td>1.53</td>
<td>1663</td>
<td>166</td>
<td>2.58</td>
</tr>
<tr>
<td>12.0</td>
<td>1861</td>
<td>155</td>
<td>1.57</td>
<td>2160</td>
<td>180</td>
<td>2.68</td>
</tr>
<tr>
<td>14.0</td>
<td>2557</td>
<td>183</td>
<td>1.71</td>
<td>2943</td>
<td>210</td>
<td>2.90</td>
</tr>
<tr>
<td>16.0</td>
<td>3676</td>
<td>230</td>
<td>1.92</td>
<td>3907</td>
<td>244</td>
<td>3.12</td>
</tr>
<tr>
<td>18.0</td>
<td>4619</td>
<td>257</td>
<td>2.03</td>
<td>4746</td>
<td>264</td>
<td>3.25</td>
</tr>
<tr>
<td>20.0</td>
<td>5381</td>
<td>269</td>
<td>2.07</td>
<td>5441</td>
<td>272</td>
<td>3.30</td>
</tr>
<tr>
<td>22.0</td>
<td>5991</td>
<td>272</td>
<td>2.09</td>
<td>6021</td>
<td>274</td>
<td>3.31</td>
</tr>
<tr>
<td>24.0</td>
<td>6514</td>
<td>271</td>
<td>2.08</td>
<td>6514</td>
<td>271</td>
<td>3.29</td>
</tr>
<tr>
<td>26.0</td>
<td>6963</td>
<td>268</td>
<td>2.07</td>
<td>6944</td>
<td>267</td>
<td>3.27</td>
</tr>
<tr>
<td>28.0</td>
<td>7356</td>
<td>263</td>
<td>2.05</td>
<td>7317</td>
<td>261</td>
<td>3.23</td>
</tr>
<tr>
<td>30.0</td>
<td>7705</td>
<td>257</td>
<td>2.03</td>
<td>7651</td>
<td>255</td>
<td>3.19</td>
</tr>
<tr>
<td>32.0</td>
<td>8015</td>
<td>250</td>
<td>2.00</td>
<td>7957</td>
<td>249</td>
<td>3.15</td>
</tr>
<tr>
<td>34.0</td>
<td>8299</td>
<td>244</td>
<td>1.98</td>
<td>8227</td>
<td>242</td>
<td>3.11</td>
</tr>
<tr>
<td>36.0</td>
<td>8494</td>
<td>236</td>
<td>1.94</td>
<td>8432</td>
<td>234</td>
<td>3.06</td>
</tr>
<tr>
<td>38.0</td>
<td>8703</td>
<td>229</td>
<td>1.91</td>
<td>8625</td>
<td>227</td>
<td>3.01</td>
</tr>
<tr>
<td>40.0</td>
<td>8846</td>
<td>221</td>
<td>1.88</td>
<td>8800</td>
<td>220</td>
<td>2.97</td>
</tr>
<tr>
<td>42.0</td>
<td>9007</td>
<td>214</td>
<td>1.85</td>
<td>8924</td>
<td>212</td>
<td>2.91</td>
</tr>
<tr>
<td>44.0</td>
<td>9149</td>
<td>208</td>
<td>1.82</td>
<td>9057</td>
<td>206</td>
<td>2.87</td>
</tr>
<tr>
<td>46.0</td>
<td>9283</td>
<td>202</td>
<td>1.80</td>
<td>9181</td>
<td>200</td>
<td>2.83</td>
</tr>
<tr>
<td>48.0</td>
<td>9412</td>
<td>196</td>
<td>1.77</td>
<td>9306</td>
<td>194</td>
<td>2.78</td>
</tr>
<tr>
<td>50.0</td>
<td>9499</td>
<td>190</td>
<td>1.74</td>
<td>9403</td>
<td>188</td>
<td>2.74</td>
</tr>
</tbody>
</table>
Ni(pyrazine)(NCO)₂ cont.

<table>
<thead>
<tr>
<th>H (K)</th>
<th>M (cm⁻¹)</th>
<th>χₚ (Å²)</th>
<th>μₑff (µB)</th>
<th>M (cm⁻¹)</th>
<th>χₚ (Å²)</th>
<th>μₑff (µB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>138.3</td>
<td>277</td>
<td>4.21</td>
<td>153.7</td>
<td>307</td>
<td>4.96</td>
</tr>
<tr>
<td>2.0</td>
<td>482.6</td>
<td>241</td>
<td>3.93</td>
<td>556.6</td>
<td>278</td>
<td>4.72</td>
</tr>
<tr>
<td>4.0</td>
<td>912.3</td>
<td>228</td>
<td>3.82</td>
<td>1057</td>
<td>264</td>
<td>4.59</td>
</tr>
<tr>
<td>6.0</td>
<td>1360</td>
<td>227</td>
<td>3.81</td>
<td>1550</td>
<td>258</td>
<td>4.54</td>
</tr>
<tr>
<td>8.0</td>
<td>1849</td>
<td>231</td>
<td>3.84</td>
<td>2043</td>
<td>255</td>
<td>4.52</td>
</tr>
<tr>
<td>10.0</td>
<td>2404</td>
<td>240</td>
<td>3.92</td>
<td>2543</td>
<td>254</td>
<td>4.51</td>
</tr>
<tr>
<td>12.0</td>
<td>3004</td>
<td>250</td>
<td>4.00</td>
<td>3037</td>
<td>253</td>
<td>4.50</td>
</tr>
<tr>
<td>14.0</td>
<td>3627</td>
<td>259</td>
<td>4.07</td>
<td>3526</td>
<td>252</td>
<td>4.49</td>
</tr>
<tr>
<td>16.0</td>
<td>4234</td>
<td>265</td>
<td>4.12</td>
<td>3995</td>
<td>250</td>
<td>4.47</td>
</tr>
<tr>
<td>18.0</td>
<td>4809</td>
<td>267</td>
<td>4.13</td>
<td>4452</td>
<td>247</td>
<td>4.44</td>
</tr>
<tr>
<td>20.0</td>
<td>5337</td>
<td>267</td>
<td>4.13</td>
<td>4883</td>
<td>244</td>
<td>4.42</td>
</tr>
<tr>
<td>22.0</td>
<td>5806</td>
<td>264</td>
<td>4.11</td>
<td>5288</td>
<td>240</td>
<td>4.38</td>
</tr>
<tr>
<td>24.0</td>
<td>6229</td>
<td>259</td>
<td>4.07</td>
<td>5668</td>
<td>236</td>
<td>4.34</td>
</tr>
<tr>
<td>26.0</td>
<td>6609</td>
<td>254</td>
<td>4.03</td>
<td>6023</td>
<td>232</td>
<td>4.31</td>
</tr>
<tr>
<td>28.0</td>
<td>6953</td>
<td>248</td>
<td>3.98</td>
<td>6348</td>
<td>227</td>
<td>4.26</td>
</tr>
<tr>
<td>30.0</td>
<td>7258</td>
<td>242</td>
<td>3.94</td>
<td>6652</td>
<td>222</td>
<td>4.22</td>
</tr>
<tr>
<td>32.0</td>
<td>7538</td>
<td>235</td>
<td>3.88</td>
<td>6926</td>
<td>216</td>
<td>4.16</td>
</tr>
<tr>
<td>34.0</td>
<td>7792</td>
<td>229</td>
<td>3.83</td>
<td>7184</td>
<td>211</td>
<td>4.11</td>
</tr>
<tr>
<td>36.0</td>
<td>8020</td>
<td>223</td>
<td>3.78</td>
<td>7419</td>
<td>206</td>
<td>4.06</td>
</tr>
<tr>
<td>38.0</td>
<td>8229</td>
<td>216</td>
<td>3.72</td>
<td>7640</td>
<td>201</td>
<td>4.01</td>
</tr>
<tr>
<td>40.0</td>
<td>8403</td>
<td>210</td>
<td>3.67</td>
<td>7845</td>
<td>196</td>
<td>3.96</td>
</tr>
<tr>
<td>42.0</td>
<td>8546</td>
<td>203</td>
<td>3.61</td>
<td>8031</td>
<td>191</td>
<td>3.91</td>
</tr>
<tr>
<td>44.0</td>
<td>8683</td>
<td>197</td>
<td>3.55</td>
<td>8216</td>
<td>187</td>
<td>3.87</td>
</tr>
<tr>
<td>46.0</td>
<td>8817</td>
<td>192</td>
<td>3.51</td>
<td>8370</td>
<td>182</td>
<td>3.82</td>
</tr>
<tr>
<td>48.0</td>
<td>8903</td>
<td>185</td>
<td>3.44</td>
<td>8485</td>
<td>177</td>
<td>3.76</td>
</tr>
<tr>
<td>50.0</td>
<td>9004</td>
<td>180</td>
<td>3.39</td>
<td>8609</td>
<td>172</td>
<td>3.71</td>
</tr>
</tbody>
</table>
Ni(pyz)(NCO)\(_2\) cont.

<table>
<thead>
<tr>
<th>H</th>
<th>M</th>
<th>(c)</th>
<th>(\chi_m)</th>
<th>(\mu_{\text{eff}})</th>
<th>M</th>
<th>(c)</th>
<th>(\chi_m)</th>
<th>(\mu_{\text{eff}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>69.91</td>
<td>140</td>
<td>4.73</td>
<td>30.92</td>
<td>61.7</td>
<td>4.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>280.3</td>
<td>140</td>
<td>4.73</td>
<td>124.5</td>
<td>62.1</td>
<td>4.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>553.0</td>
<td>138</td>
<td>4.70</td>
<td>249.0</td>
<td>62.2</td>
<td>4.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>819.4</td>
<td>136</td>
<td>4.66</td>
<td>373.6</td>
<td>62.2</td>
<td>4.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>1082</td>
<td>135</td>
<td>4.65</td>
<td>497.6</td>
<td>62.1</td>
<td>4.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>1342</td>
<td>134</td>
<td>4.63</td>
<td>622.5</td>
<td>62.1</td>
<td>4.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.0</td>
<td>1592</td>
<td>133</td>
<td>4.61</td>
<td>745.9</td>
<td>62.1</td>
<td>4.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.0</td>
<td>1841</td>
<td>131</td>
<td>4.58</td>
<td>867.4</td>
<td>61.8</td>
<td>4.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>2086</td>
<td>130</td>
<td>4.56</td>
<td>990.8</td>
<td>61.8</td>
<td>4.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.0</td>
<td>2327</td>
<td>129</td>
<td>4.54</td>
<td>1113</td>
<td>61.7</td>
<td>4.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>2567</td>
<td>128</td>
<td>4.52</td>
<td>1235</td>
<td>61.7</td>
<td>4.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.0</td>
<td>2802</td>
<td>127</td>
<td>4.51</td>
<td>1356</td>
<td>61.5</td>
<td>4.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.0</td>
<td>3033</td>
<td>126</td>
<td>4.49</td>
<td>1479</td>
<td>61.5</td>
<td>4.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.0</td>
<td>3264</td>
<td>125</td>
<td>4.47</td>
<td>1598</td>
<td>61.4</td>
<td>4.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28.0</td>
<td>3486</td>
<td>124</td>
<td>4.45</td>
<td>1718</td>
<td>61.2</td>
<td>4.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.0</td>
<td>3703</td>
<td>123</td>
<td>4.44</td>
<td>1836</td>
<td>61.1</td>
<td>4.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.0</td>
<td>3915</td>
<td>122</td>
<td>4.42</td>
<td>1954</td>
<td>61.0</td>
<td>4.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.0</td>
<td>4118</td>
<td>121</td>
<td>4.40</td>
<td>2071</td>
<td>60.8</td>
<td>4.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>36.0</td>
<td>4320</td>
<td>120</td>
<td>4.38</td>
<td>2189</td>
<td>60.7</td>
<td>4.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38.0</td>
<td>4518</td>
<td>119</td>
<td>4.36</td>
<td>2304</td>
<td>60.5</td>
<td>4.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>4713</td>
<td>118</td>
<td>4.35</td>
<td>2420</td>
<td>60.4</td>
<td>4.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>42.0</td>
<td>4902</td>
<td>117</td>
<td>4.33</td>
<td>2535</td>
<td>60.3</td>
<td>4.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>44.0</td>
<td>5085</td>
<td>115</td>
<td>4.29</td>
<td>2647</td>
<td>60.1</td>
<td>4.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>46.0</td>
<td>5263</td>
<td>114</td>
<td>4.27</td>
<td>2759</td>
<td>59.9</td>
<td>4.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48.0</td>
<td>5435</td>
<td>113</td>
<td>4.25</td>
<td>2866</td>
<td>59.6</td>
<td>4.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50.0</td>
<td>5603</td>
<td>112</td>
<td>4.23</td>
<td>2977</td>
<td>59.4</td>
<td>4.08</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table: Ni(py)Cl₂

<table>
<thead>
<tr>
<th>H</th>
<th>M</th>
<th>(X_m)</th>
<th>(\mu_{\text{eff}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(10 K)</td>
<td>(X_m)</td>
<td>(\mu_{\text{eff}})</td>
</tr>
<tr>
<td>0.1</td>
<td>17.19</td>
<td>172</td>
<td>1.66</td>
</tr>
<tr>
<td>0.5</td>
<td>84.70</td>
<td>169</td>
<td>1.64</td>
</tr>
<tr>
<td>1.0</td>
<td>170.4</td>
<td>170</td>
<td>1.65</td>
</tr>
<tr>
<td>1.5</td>
<td>364.5</td>
<td>243</td>
<td>1.97</td>
</tr>
<tr>
<td>2.0</td>
<td>713.6</td>
<td>357</td>
<td>2.39</td>
</tr>
<tr>
<td>2.5</td>
<td>1147</td>
<td>459</td>
<td>2.71</td>
</tr>
<tr>
<td>3.0</td>
<td>1711</td>
<td>571</td>
<td>3.02</td>
</tr>
<tr>
<td>3.5</td>
<td>2297</td>
<td>656</td>
<td>3.24</td>
</tr>
<tr>
<td>4.0</td>
<td>3263</td>
<td>816</td>
<td>3.61</td>
</tr>
<tr>
<td>4.5</td>
<td>4121</td>
<td>916</td>
<td>3.83</td>
</tr>
<tr>
<td>5.0</td>
<td>4768</td>
<td>954</td>
<td>3.91</td>
</tr>
<tr>
<td>5.5</td>
<td>5226</td>
<td>950</td>
<td>3.90</td>
</tr>
<tr>
<td>6.0</td>
<td>5637</td>
<td>939</td>
<td>3.88</td>
</tr>
<tr>
<td>6.5</td>
<td>5964</td>
<td>917</td>
<td>3.83</td>
</tr>
<tr>
<td>7.0</td>
<td>6192</td>
<td>884</td>
<td>3.76</td>
</tr>
<tr>
<td>8.0</td>
<td>6656</td>
<td>832</td>
<td>3.65</td>
</tr>
<tr>
<td>9.0</td>
<td>7032</td>
<td>781</td>
<td>3.53</td>
</tr>
<tr>
<td>10.0</td>
<td>7315</td>
<td>731</td>
<td>3.42</td>
</tr>
<tr>
<td>12.5</td>
<td>7848</td>
<td>628</td>
<td>3.17</td>
</tr>
<tr>
<td>15.0</td>
<td>8294</td>
<td>553</td>
<td>2.97</td>
</tr>
<tr>
<td>20.0</td>
<td>8998</td>
<td>450</td>
<td>2.68</td>
</tr>
</tbody>
</table>

### Table: Ni(py)Cl₂ (continued)

<table>
<thead>
<tr>
<th>H</th>
<th>M</th>
<th>(X_m)</th>
<th>(\mu_{\text{eff}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>30.95</td>
<td>309</td>
<td>7.03</td>
</tr>
<tr>
<td>0.5</td>
<td>179.0</td>
<td>358</td>
<td>7.57</td>
</tr>
<tr>
<td>1.0</td>
<td>363.2</td>
<td>363</td>
<td>7.62</td>
</tr>
<tr>
<td>1.5</td>
<td>546.9</td>
<td>365</td>
<td>7.64</td>
</tr>
<tr>
<td>2.0</td>
<td>729.8</td>
<td>365</td>
<td>7.64</td>
</tr>
<tr>
<td>2.5</td>
<td>912.3</td>
<td>365</td>
<td>7.64</td>
</tr>
<tr>
<td>3.0</td>
<td>1094</td>
<td>365</td>
<td>7.64</td>
</tr>
<tr>
<td>3.5</td>
<td>1275</td>
<td>364</td>
<td>7.63</td>
</tr>
<tr>
<td>4.0</td>
<td>1454</td>
<td>363</td>
<td>7.62</td>
</tr>
<tr>
<td>4.5</td>
<td>1629</td>
<td>362</td>
<td>7.61</td>
</tr>
<tr>
<td>5.0</td>
<td>1795</td>
<td>359</td>
<td>7.58</td>
</tr>
<tr>
<td>5.5</td>
<td>1980</td>
<td>360</td>
<td>7.59</td>
</tr>
<tr>
<td>6.0</td>
<td>2140</td>
<td>357</td>
<td>7.56</td>
</tr>
<tr>
<td>6.5</td>
<td>2322</td>
<td>357</td>
<td>7.56</td>
</tr>
<tr>
<td>7.0</td>
<td>2491</td>
<td>356</td>
<td>7.55</td>
</tr>
<tr>
<td>8.0</td>
<td>2816</td>
<td>352</td>
<td>7.50</td>
</tr>
<tr>
<td>9.0</td>
<td>3141</td>
<td>349</td>
<td>7.47</td>
</tr>
<tr>
<td>10.0</td>
<td>3448</td>
<td>345</td>
<td>7.43</td>
</tr>
<tr>
<td>12.5</td>
<td>4162</td>
<td>333</td>
<td>7.30</td>
</tr>
<tr>
<td>15.0</td>
<td>4829</td>
<td>322</td>
<td>7.18</td>
</tr>
<tr>
<td>20.0</td>
<td>5925</td>
<td>296</td>
<td>6.88</td>
</tr>
</tbody>
</table>
3. Ni(py)Cl₂

<table>
<thead>
<tr>
<th>H</th>
<th>2 K</th>
<th>5 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu_{\text{eff}}$</td>
<td>$\mu_{\text{eff}}$</td>
</tr>
<tr>
<td></td>
<td>$\chi_m$</td>
<td>M</td>
</tr>
<tr>
<td>2.5</td>
<td>168.1</td>
<td>67.2</td>
</tr>
<tr>
<td>5.0</td>
<td>331.6</td>
<td>66.2</td>
</tr>
<tr>
<td>7.5</td>
<td>496.2</td>
<td>66.1</td>
</tr>
<tr>
<td>10.0</td>
<td>665.3</td>
<td>66.4</td>
</tr>
<tr>
<td>12.5</td>
<td>838.3</td>
<td>67.0</td>
</tr>
<tr>
<td>15.0</td>
<td>1013</td>
<td>67.4</td>
</tr>
<tr>
<td>17.5</td>
<td>1429</td>
<td>81.6</td>
</tr>
<tr>
<td>20.0</td>
<td>2029</td>
<td>101</td>
</tr>
<tr>
<td>22.5</td>
<td>2598</td>
<td>115</td>
</tr>
<tr>
<td>25.0</td>
<td>3548</td>
<td>142</td>
</tr>
<tr>
<td>27.5</td>
<td>4391</td>
<td>160</td>
</tr>
<tr>
<td>30.0</td>
<td>5083</td>
<td>169</td>
</tr>
<tr>
<td>32.5</td>
<td>5678</td>
<td>175</td>
</tr>
<tr>
<td>35.0</td>
<td>6195</td>
<td>177</td>
</tr>
<tr>
<td>37.5</td>
<td>6643</td>
<td>177</td>
</tr>
<tr>
<td>40.0</td>
<td>7050</td>
<td>176</td>
</tr>
<tr>
<td>42.5</td>
<td>7426</td>
<td>175</td>
</tr>
<tr>
<td>45.0</td>
<td>7748</td>
<td>172</td>
</tr>
<tr>
<td>47.5</td>
<td>8045</td>
<td>169</td>
</tr>
<tr>
<td>50.0</td>
<td>8320</td>
<td>166</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H</th>
<th>8 K</th>
<th>10 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu_{\text{eff}}$</td>
<td>$\mu_{\text{eff}}$</td>
</tr>
<tr>
<td></td>
<td>$\chi_m$</td>
<td>M</td>
</tr>
<tr>
<td>2.5</td>
<td>295.8</td>
<td>118</td>
</tr>
<tr>
<td>5.0</td>
<td>606.3</td>
<td>121</td>
</tr>
<tr>
<td>7.5</td>
<td>947.6</td>
<td>126</td>
</tr>
<tr>
<td>10.0</td>
<td>1351</td>
<td>135</td>
</tr>
<tr>
<td>12.5</td>
<td>1827</td>
<td>146</td>
</tr>
<tr>
<td>15.0</td>
<td>2343</td>
<td>156</td>
</tr>
<tr>
<td>17.5</td>
<td>2878</td>
<td>164</td>
</tr>
<tr>
<td>20.0</td>
<td>3418</td>
<td>171</td>
</tr>
<tr>
<td>22.5</td>
<td>3958</td>
<td>176</td>
</tr>
<tr>
<td>25.0</td>
<td>4498</td>
<td>180</td>
</tr>
<tr>
<td>27.5</td>
<td>5014</td>
<td>182</td>
</tr>
<tr>
<td>30.0</td>
<td>5504</td>
<td>183</td>
</tr>
<tr>
<td>32.5</td>
<td>5960</td>
<td>183</td>
</tr>
<tr>
<td>35.0</td>
<td>6384</td>
<td>182</td>
</tr>
<tr>
<td>37.5</td>
<td>6770</td>
<td>180</td>
</tr>
<tr>
<td>40.0</td>
<td>7119</td>
<td>178</td>
</tr>
<tr>
<td>42.5</td>
<td>7445</td>
<td>175</td>
</tr>
<tr>
<td>45.0</td>
<td>7740</td>
<td>172</td>
</tr>
<tr>
<td>47.5</td>
<td>8007</td>
<td>168</td>
</tr>
<tr>
<td>50.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>M</td>
<td>$\chi_m$</td>
</tr>
<tr>
<td>----</td>
<td>------</td>
<td>----------</td>
</tr>
<tr>
<td>2.5</td>
<td>247.9</td>
<td>99.1</td>
</tr>
<tr>
<td>5.0</td>
<td>496.0</td>
<td>99.1</td>
</tr>
<tr>
<td>7.5</td>
<td>744.6</td>
<td>99.2</td>
</tr>
<tr>
<td>10.0</td>
<td>991.6</td>
<td>99.1</td>
</tr>
<tr>
<td>12.5</td>
<td>1239</td>
<td>99.1</td>
</tr>
<tr>
<td>15.0</td>
<td>1484</td>
<td>98.9</td>
</tr>
<tr>
<td>17.5</td>
<td>1729</td>
<td>98.7</td>
</tr>
<tr>
<td>20.0</td>
<td>1971</td>
<td>98.5</td>
</tr>
<tr>
<td>22.5</td>
<td>2208</td>
<td>98.0</td>
</tr>
<tr>
<td>25.0</td>
<td>2450</td>
<td>97.9</td>
</tr>
<tr>
<td>27.5</td>
<td>2686</td>
<td>97.6</td>
</tr>
<tr>
<td>30.0</td>
<td>2919</td>
<td>97.2</td>
</tr>
<tr>
<td>32.5</td>
<td>3148</td>
<td>96.8</td>
</tr>
<tr>
<td>35.0</td>
<td>3378</td>
<td>96.4</td>
</tr>
<tr>
<td>37.5</td>
<td>3602</td>
<td>96.0</td>
</tr>
<tr>
<td>40.0</td>
<td>3821</td>
<td>95.4</td>
</tr>
<tr>
<td>42.5</td>
<td>4040</td>
<td>95.0</td>
</tr>
<tr>
<td>45.0</td>
<td>4253</td>
<td>94.4</td>
</tr>
<tr>
<td>47.5</td>
<td>4461</td>
<td>93.8</td>
</tr>
<tr>
<td>50.0</td>
<td>4666</td>
<td>93.2</td>
</tr>
</tbody>
</table>
4. Ni(py)$_2$(NCS)$_2$

<table>
<thead>
<tr>
<th>H</th>
<th>M</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>M</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>39.08</td>
<td>391</td>
<td>2.50</td>
<td>47.95</td>
<td>479</td>
<td>3.39</td>
</tr>
<tr>
<td>0.5</td>
<td>195.1</td>
<td>390</td>
<td>2.50</td>
<td>237.0</td>
<td>474</td>
<td>3.37</td>
</tr>
<tr>
<td>1.0</td>
<td>387.7</td>
<td>388</td>
<td>2.49</td>
<td>471.9</td>
<td>472</td>
<td>3.37</td>
</tr>
<tr>
<td>1.5</td>
<td>582.0</td>
<td>388</td>
<td>2.49</td>
<td>707.0</td>
<td>471</td>
<td>3.36</td>
</tr>
<tr>
<td>2.0</td>
<td>785.7</td>
<td>393</td>
<td>2.51</td>
<td>949.7</td>
<td>475</td>
<td>3.38</td>
</tr>
<tr>
<td>2.5</td>
<td>999.4</td>
<td>400</td>
<td>2.53</td>
<td>1197</td>
<td>479</td>
<td>3.39</td>
</tr>
<tr>
<td>3.0</td>
<td>1225</td>
<td>408</td>
<td>2.55</td>
<td>1450</td>
<td>483</td>
<td>3.40</td>
</tr>
<tr>
<td>3.5</td>
<td>1467</td>
<td>419</td>
<td>2.59</td>
<td>1714</td>
<td>490</td>
<td>3.43</td>
</tr>
<tr>
<td>4.0</td>
<td>1727</td>
<td>432</td>
<td>2.63</td>
<td>1985</td>
<td>496</td>
<td>3.45</td>
</tr>
<tr>
<td>4.5</td>
<td>2005</td>
<td>446</td>
<td>2.67</td>
<td>2260</td>
<td>502</td>
<td>3.47</td>
</tr>
<tr>
<td>5.0</td>
<td>2303</td>
<td>461</td>
<td>2.72</td>
<td>2553</td>
<td>511</td>
<td>3.50</td>
</tr>
<tr>
<td>5.5</td>
<td>2616</td>
<td>476</td>
<td>2.76</td>
<td>2838</td>
<td>516</td>
<td>3.52</td>
</tr>
<tr>
<td>6.0</td>
<td>2946</td>
<td>491</td>
<td>2.80</td>
<td>3125</td>
<td>521</td>
<td>3.54</td>
</tr>
<tr>
<td>6.5</td>
<td>3285</td>
<td>505</td>
<td>2.84</td>
<td>3417</td>
<td>526</td>
<td>3.55</td>
</tr>
<tr>
<td>7.0</td>
<td>3620</td>
<td>517</td>
<td>2.88</td>
<td>3704</td>
<td>529</td>
<td>3.56</td>
</tr>
<tr>
<td>7.5</td>
<td>3955</td>
<td>527</td>
<td>2.90</td>
<td>3986</td>
<td>531</td>
<td>3.57</td>
</tr>
<tr>
<td>8.0</td>
<td>4281</td>
<td>535</td>
<td>2.93</td>
<td>4263</td>
<td>533</td>
<td>3.58</td>
</tr>
<tr>
<td>8.5</td>
<td>4599</td>
<td>541</td>
<td>2.94</td>
<td>4535</td>
<td>534</td>
<td>3.58</td>
</tr>
<tr>
<td>9.0</td>
<td>4900</td>
<td>544</td>
<td>2.95</td>
<td>4797</td>
<td>533</td>
<td>3.58</td>
</tr>
<tr>
<td>9.5</td>
<td>5192</td>
<td>547</td>
<td>2.96</td>
<td>5049</td>
<td>531</td>
<td>3.57</td>
</tr>
<tr>
<td>10.0</td>
<td>5467</td>
<td>547</td>
<td>2.96</td>
<td>5290</td>
<td>529</td>
<td>3.56</td>
</tr>
<tr>
<td>10.5</td>
<td>5734</td>
<td>546</td>
<td>2.96</td>
<td>5530</td>
<td>527</td>
<td>3.56</td>
</tr>
<tr>
<td>11.0</td>
<td>5980</td>
<td>544</td>
<td>2.95</td>
<td>5753</td>
<td>523</td>
<td>3.54</td>
</tr>
<tr>
<td>11.5</td>
<td>6224</td>
<td>541</td>
<td>2.94</td>
<td>5969</td>
<td>519</td>
<td>3.53</td>
</tr>
<tr>
<td>12.5</td>
<td>6653</td>
<td>532</td>
<td>2.92</td>
<td>6364</td>
<td>509</td>
<td>3.49</td>
</tr>
<tr>
<td>15.0</td>
<td>7529</td>
<td>502</td>
<td>2.83</td>
<td>7187</td>
<td>479</td>
<td>3.39</td>
</tr>
<tr>
<td>17.5</td>
<td>8176</td>
<td>467</td>
<td>2.73</td>
<td>7824</td>
<td>447</td>
<td>3.27</td>
</tr>
<tr>
<td>20.0</td>
<td>8661</td>
<td>433</td>
<td>2.63</td>
<td>8318</td>
<td>416</td>
<td>3.16</td>
</tr>
<tr>
<td>25.0</td>
<td>9329</td>
<td>373</td>
<td>2.44</td>
<td>8818</td>
<td>353</td>
<td>3.02</td>
</tr>
<tr>
<td>30.0</td>
<td>9789</td>
<td>326</td>
<td>2.28</td>
<td>9551</td>
<td>318</td>
<td>2.76</td>
</tr>
</tbody>
</table>
Ni(py)$_2$(NCS)$_2$ cont.

<table>
<thead>
<tr>
<th>H</th>
<th>M</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>M</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>49.97</td>
<td>500</td>
<td>4.00</td>
<td>45.44</td>
<td>454</td>
<td>4.26</td>
</tr>
<tr>
<td>0.5</td>
<td>251.7</td>
<td>503</td>
<td>4.01</td>
<td>225.5</td>
<td>451</td>
<td>4.25</td>
</tr>
<tr>
<td>1.0</td>
<td>502.6</td>
<td>503</td>
<td>4.01</td>
<td>450.9</td>
<td>451</td>
<td>4.25</td>
</tr>
<tr>
<td>1.5</td>
<td>750.1</td>
<td>500</td>
<td>4.00</td>
<td>671.9</td>
<td>448</td>
<td>4.23</td>
</tr>
<tr>
<td>2.0</td>
<td>999.9</td>
<td>500</td>
<td>4.00</td>
<td>896.0</td>
<td>448</td>
<td>4.23</td>
</tr>
<tr>
<td>2.5</td>
<td>1248</td>
<td>499</td>
<td>4.00</td>
<td>1115</td>
<td>446</td>
<td>4.22</td>
</tr>
<tr>
<td>3.0</td>
<td>1494</td>
<td>498</td>
<td>3.99</td>
<td>1334</td>
<td>445</td>
<td>4.22</td>
</tr>
<tr>
<td>3.5</td>
<td>1743</td>
<td>498</td>
<td>3.99</td>
<td>1556</td>
<td>445</td>
<td>4.22</td>
</tr>
<tr>
<td>4.0</td>
<td>1990</td>
<td>498</td>
<td>3.99</td>
<td>1772</td>
<td>443</td>
<td>4.21</td>
</tr>
<tr>
<td>4.5</td>
<td>2236</td>
<td>497</td>
<td>3.99</td>
<td>1990</td>
<td>442</td>
<td>4.20</td>
</tr>
<tr>
<td>5.0</td>
<td>2490</td>
<td>498</td>
<td>3.99</td>
<td>2205</td>
<td>441</td>
<td>4.20</td>
</tr>
<tr>
<td>5.5</td>
<td>2735</td>
<td>497</td>
<td>3.99</td>
<td>2420</td>
<td>440</td>
<td>4.19</td>
</tr>
<tr>
<td>6.0</td>
<td>2978</td>
<td>496</td>
<td>3.98</td>
<td>2631</td>
<td>438</td>
<td>4.19</td>
</tr>
<tr>
<td>6.5</td>
<td>3222</td>
<td>496</td>
<td>3.98</td>
<td>2842</td>
<td>437</td>
<td>4.18</td>
</tr>
<tr>
<td>7.0</td>
<td>3462</td>
<td>495</td>
<td>3.98</td>
<td>3049</td>
<td>435</td>
<td>4.17</td>
</tr>
<tr>
<td>7.5</td>
<td>3697</td>
<td>493</td>
<td>3.97</td>
<td>3253</td>
<td>434</td>
<td>4.17</td>
</tr>
<tr>
<td>8.0</td>
<td>3930</td>
<td>491</td>
<td>3.96</td>
<td>3457</td>
<td>432</td>
<td>4.16</td>
</tr>
<tr>
<td>8.5</td>
<td>4160</td>
<td>489</td>
<td>3.96</td>
<td>3662</td>
<td>431</td>
<td>4.15</td>
</tr>
<tr>
<td>9.0</td>
<td>4383</td>
<td>487</td>
<td>3.95</td>
<td>3856</td>
<td>428</td>
<td>4.14</td>
</tr>
<tr>
<td>9.5</td>
<td>4602</td>
<td>484</td>
<td>3.93</td>
<td>4043</td>
<td>426</td>
<td>4.13</td>
</tr>
<tr>
<td>10.0</td>
<td>4823</td>
<td>482</td>
<td>3.93</td>
<td>4242</td>
<td>424</td>
<td>4.12</td>
</tr>
<tr>
<td>10.5</td>
<td>5029</td>
<td>479</td>
<td>3.91</td>
<td>4424</td>
<td>421</td>
<td>4.11</td>
</tr>
<tr>
<td>11.0</td>
<td>5229</td>
<td>475</td>
<td>3.90</td>
<td>4608</td>
<td>419</td>
<td>4.09</td>
</tr>
<tr>
<td>11.5</td>
<td>5412</td>
<td>471</td>
<td>3.88</td>
<td>4787</td>
<td>416</td>
<td>4.08</td>
</tr>
<tr>
<td>12.5</td>
<td>5788</td>
<td>463</td>
<td>3.85</td>
<td>5133</td>
<td>411</td>
<td>4.05</td>
</tr>
<tr>
<td>15.0</td>
<td>6590</td>
<td>439</td>
<td>3.75</td>
<td>5883</td>
<td>392</td>
<td>3.96</td>
</tr>
<tr>
<td>17.5</td>
<td>7262</td>
<td>415</td>
<td>3.64</td>
<td>6568</td>
<td>375</td>
<td>3.88</td>
</tr>
<tr>
<td>20.0</td>
<td>7801</td>
<td>390</td>
<td>3.53</td>
<td>7140</td>
<td>357</td>
<td>3.78</td>
</tr>
<tr>
<td>25.0</td>
<td>8622</td>
<td>345</td>
<td>3.32</td>
<td>8058</td>
<td>322</td>
<td>3.59</td>
</tr>
<tr>
<td>30.0</td>
<td>9203</td>
<td>307</td>
<td>3.13</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Ni(py)$_2$(NCS)$_2$ cont.

<table>
<thead>
<tr>
<th>H</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 K</td>
<td></td>
<td></td>
<td>10 K</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>28.95</td>
<td>290</td>
<td>4.30</td>
<td>22.61</td>
</tr>
<tr>
<td>0.5</td>
<td>145.1</td>
<td>290</td>
<td>4.31</td>
<td>111.2</td>
</tr>
<tr>
<td>1.0</td>
<td>289.2</td>
<td>289</td>
<td>4.30</td>
<td>222.0</td>
</tr>
<tr>
<td>1.5</td>
<td>431.7</td>
<td>288</td>
<td>4.29</td>
<td>331.5</td>
</tr>
<tr>
<td>2.0</td>
<td>574.8</td>
<td>287</td>
<td>4.29</td>
<td>441.5</td>
</tr>
<tr>
<td>2.5</td>
<td>717.7</td>
<td>287</td>
<td>4.29</td>
<td>550.8</td>
</tr>
<tr>
<td>3.0</td>
<td>858.6</td>
<td>286</td>
<td>4.28</td>
<td>659.1</td>
</tr>
<tr>
<td>3.5</td>
<td>1001</td>
<td>286</td>
<td>4.28</td>
<td>768.7</td>
</tr>
<tr>
<td>4.0</td>
<td>1140</td>
<td>285</td>
<td>4.27</td>
<td>876.4</td>
</tr>
<tr>
<td>4.5</td>
<td>1281</td>
<td>285</td>
<td>4.27</td>
<td>985.5</td>
</tr>
<tr>
<td>5.0</td>
<td>1425</td>
<td>285</td>
<td>4.27</td>
<td>1096</td>
</tr>
<tr>
<td>5.5</td>
<td>1565</td>
<td>285</td>
<td>4.27</td>
<td>1204</td>
</tr>
<tr>
<td>6.0</td>
<td>1703</td>
<td>284</td>
<td>4.26</td>
<td>1310</td>
</tr>
<tr>
<td>6.5</td>
<td>1841</td>
<td>283</td>
<td>4.26</td>
<td>1418</td>
</tr>
<tr>
<td>7.0</td>
<td>1979</td>
<td>283</td>
<td>4.26</td>
<td>1526</td>
</tr>
<tr>
<td>7.5</td>
<td>2114</td>
<td>282</td>
<td>4.25</td>
<td>1632</td>
</tr>
<tr>
<td>8.0</td>
<td>2246</td>
<td>281</td>
<td>4.24</td>
<td>1739</td>
</tr>
<tr>
<td>8.5</td>
<td>2383</td>
<td>280</td>
<td>4.23</td>
<td>1846</td>
</tr>
<tr>
<td>9.0</td>
<td>2516</td>
<td>280</td>
<td>4.23</td>
<td>1952</td>
</tr>
<tr>
<td>9.5</td>
<td>2648</td>
<td>279</td>
<td>4.23</td>
<td>2055</td>
</tr>
<tr>
<td>10.0</td>
<td>2789</td>
<td>279</td>
<td>4.22</td>
<td>2162</td>
</tr>
<tr>
<td>10.5</td>
<td>2917</td>
<td>278</td>
<td>4.22</td>
<td>2264</td>
</tr>
<tr>
<td>11.0</td>
<td>3048</td>
<td>277</td>
<td>4.21</td>
<td>2369</td>
</tr>
<tr>
<td>11.5</td>
<td>3177</td>
<td>276</td>
<td>4.20</td>
<td>2472</td>
</tr>
<tr>
<td>12.5</td>
<td>3431</td>
<td>274</td>
<td>4.19</td>
<td>2679</td>
</tr>
<tr>
<td>15.0</td>
<td>4036</td>
<td>269</td>
<td>4.15</td>
<td>3172</td>
</tr>
<tr>
<td>17.5</td>
<td>4610</td>
<td>263</td>
<td>4.10</td>
<td>3657</td>
</tr>
<tr>
<td>20.0</td>
<td>5148</td>
<td>257</td>
<td>4.06</td>
<td>4116</td>
</tr>
<tr>
<td>25.0</td>
<td>6098</td>
<td>244</td>
<td>3.95</td>
<td>4987</td>
</tr>
<tr>
<td>30.0</td>
<td>6897</td>
<td>230</td>
<td>3.84</td>
<td>5734</td>
</tr>
</tbody>
</table>
5. Ni(pyz)(NCS)$_2$

<table>
<thead>
<tr>
<th>H</th>
<th>M</th>
<th>$c_{M}$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>M</th>
<th>$c_{M}$</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>25.33</td>
<td>253</td>
<td>2.01</td>
<td>31.76</td>
<td>317</td>
<td>2.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>244.6</td>
<td>245</td>
<td>1.98</td>
<td>324.9</td>
<td>325</td>
<td>2.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>490.7</td>
<td>245</td>
<td>1.98</td>
<td>660.4</td>
<td>330</td>
<td>2.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>747.4</td>
<td>249</td>
<td>2.00</td>
<td>1020</td>
<td>340</td>
<td>2.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>1020</td>
<td>255</td>
<td>2.02</td>
<td>1425</td>
<td>356</td>
<td>2.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>1320</td>
<td>264</td>
<td>2.05</td>
<td>1876</td>
<td>375</td>
<td>3.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>1669</td>
<td>278</td>
<td>2.11</td>
<td>2378</td>
<td>396</td>
<td>3.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>2116</td>
<td>302</td>
<td>2.20</td>
<td>2909</td>
<td>415</td>
<td>3.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>2874</td>
<td>359</td>
<td>2.40</td>
<td>3455</td>
<td>432</td>
<td>3.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.0</td>
<td>3702</td>
<td>411</td>
<td>2.56</td>
<td>3996</td>
<td>444</td>
<td>3.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>4459</td>
<td>446</td>
<td>2.67</td>
<td>4529</td>
<td>453</td>
<td>3.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.0</td>
<td>5104</td>
<td>464</td>
<td>2.72</td>
<td>5014</td>
<td>456</td>
<td>3.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.0</td>
<td>5673</td>
<td>473</td>
<td>2.75</td>
<td>5468</td>
<td>456</td>
<td>3.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.0</td>
<td>6173</td>
<td>475</td>
<td>2.76</td>
<td>5888</td>
<td>453</td>
<td>3.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.0</td>
<td>6615</td>
<td>472</td>
<td>2.75</td>
<td>6257</td>
<td>447</td>
<td>3.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.0</td>
<td>6999</td>
<td>467</td>
<td>2.73</td>
<td>6597</td>
<td>440</td>
<td>3.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>7332</td>
<td>458</td>
<td>2.71</td>
<td>6908</td>
<td>432</td>
<td>3.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.0</td>
<td>7593</td>
<td>447</td>
<td>2.67</td>
<td>7184</td>
<td>423</td>
<td>3.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.0</td>
<td>7868</td>
<td>437</td>
<td>2.64</td>
<td>7447</td>
<td>414</td>
<td>3.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.0</td>
<td>8101</td>
<td>426</td>
<td>2.61</td>
<td>7673</td>
<td>404</td>
<td>3.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>8307</td>
<td>415</td>
<td>2.58</td>
<td>7885</td>
<td>394</td>
<td>3.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.0</td>
<td>8495</td>
<td>404</td>
<td>2.54</td>
<td>8082</td>
<td>385</td>
<td>3.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.0</td>
<td>8663</td>
<td>394</td>
<td>2.51</td>
<td>8264</td>
<td>376</td>
<td>3.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.0</td>
<td>8816</td>
<td>383</td>
<td>2.48</td>
<td>8434</td>
<td>367</td>
<td>2.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.0</td>
<td>8957</td>
<td>373</td>
<td>2.44</td>
<td>8590</td>
<td>358</td>
<td>2.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>9097</td>
<td>364</td>
<td>2.41</td>
<td>8745</td>
<td>350</td>
<td>2.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.0</td>
<td>9222</td>
<td>355</td>
<td>2.38</td>
<td>8880</td>
<td>341</td>
<td>2.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27.0</td>
<td>9339</td>
<td>346</td>
<td>2.35</td>
<td>9007</td>
<td>334</td>
<td>2.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28.0</td>
<td>9447</td>
<td>337</td>
<td>2.32</td>
<td>9130</td>
<td>326</td>
<td>2.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29.0</td>
<td>9553</td>
<td>329</td>
<td>2.29</td>
<td>9257</td>
<td>319</td>
<td>2.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.0</td>
<td>9654</td>
<td>322</td>
<td>2.27</td>
<td>9364</td>
<td>312</td>
<td>2.74</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Ni(pyz)(NCS)$_2$ cont.

<table>
<thead>
<tr>
<th>H</th>
<th>4 K</th>
<th>5 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>$\chi^c_m$</td>
</tr>
<tr>
<td>0.1</td>
<td>38.32</td>
<td>383</td>
</tr>
<tr>
<td>1.0</td>
<td>394.6</td>
<td>395</td>
</tr>
<tr>
<td>2.0</td>
<td>790.5</td>
<td>395</td>
</tr>
<tr>
<td>3.0</td>
<td>1191</td>
<td>397</td>
</tr>
<tr>
<td>4.0</td>
<td>1595</td>
<td>399</td>
</tr>
<tr>
<td>5.0</td>
<td>2002</td>
<td>400</td>
</tr>
<tr>
<td>6.0</td>
<td>2410</td>
<td>402</td>
</tr>
<tr>
<td>7.0</td>
<td>2825</td>
<td>404</td>
</tr>
<tr>
<td>8.0</td>
<td>3223</td>
<td>403</td>
</tr>
<tr>
<td>9.0</td>
<td>3628</td>
<td>403</td>
</tr>
<tr>
<td>10.0</td>
<td>4030</td>
<td>403</td>
</tr>
<tr>
<td>11.0</td>
<td>4416</td>
<td>401</td>
</tr>
<tr>
<td>12.0</td>
<td>4784</td>
<td>399</td>
</tr>
<tr>
<td>13.0</td>
<td>5143</td>
<td>396</td>
</tr>
<tr>
<td>14.0</td>
<td>5479</td>
<td>391</td>
</tr>
<tr>
<td>15.0</td>
<td>5801</td>
<td>387</td>
</tr>
<tr>
<td>16.0</td>
<td>6102</td>
<td>381</td>
</tr>
<tr>
<td>17.0</td>
<td>6381</td>
<td>375</td>
</tr>
<tr>
<td>18.0</td>
<td>6649</td>
<td>369</td>
</tr>
<tr>
<td>19.0</td>
<td>6897</td>
<td>363</td>
</tr>
<tr>
<td>20.0</td>
<td>7129</td>
<td>356</td>
</tr>
<tr>
<td>21.0</td>
<td>7345</td>
<td>350</td>
</tr>
<tr>
<td>22.0</td>
<td>7554</td>
<td>343</td>
</tr>
<tr>
<td>23.0</td>
<td>7744</td>
<td>337</td>
</tr>
<tr>
<td>24.0</td>
<td>7922</td>
<td>330</td>
</tr>
<tr>
<td>25.0</td>
<td>8098</td>
<td>324</td>
</tr>
<tr>
<td>26.0</td>
<td>8252</td>
<td>317</td>
</tr>
<tr>
<td>27.0</td>
<td>8403</td>
<td>311</td>
</tr>
<tr>
<td>28.0</td>
<td>8544</td>
<td>305</td>
</tr>
<tr>
<td>29.0</td>
<td>8678</td>
<td>299</td>
</tr>
<tr>
<td>30.0</td>
<td>8805</td>
<td>293</td>
</tr>
</tbody>
</table>
Ni(pyz)(NCS)$_2$ cont.

<table>
<thead>
<tr>
<th>H</th>
<th>M</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>M</th>
<th>$\chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>21.59</td>
<td>216</td>
<td>3.72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>220.8</td>
<td>221</td>
<td>3.76</td>
<td>16.66</td>
<td>167</td>
<td>3.65</td>
</tr>
<tr>
<td>2.0</td>
<td>440.7</td>
<td>220</td>
<td>3.75</td>
<td>339.1</td>
<td>169</td>
<td>3.68</td>
</tr>
<tr>
<td>3.0</td>
<td>659.6</td>
<td>220</td>
<td>3.75</td>
<td>507.6</td>
<td>169</td>
<td>3.68</td>
</tr>
<tr>
<td>4.0</td>
<td>879.0</td>
<td>220</td>
<td>3.75</td>
<td>676.7</td>
<td>169</td>
<td>3.68</td>
</tr>
<tr>
<td>5.0</td>
<td>1095</td>
<td>219</td>
<td>3.74</td>
<td>845.0</td>
<td>169</td>
<td>3.68</td>
</tr>
<tr>
<td>6.0</td>
<td>1314</td>
<td>219</td>
<td>3.74</td>
<td>1012</td>
<td>169</td>
<td>3.68</td>
</tr>
<tr>
<td>7.0</td>
<td>1530</td>
<td>219</td>
<td>3.74</td>
<td>1181</td>
<td>169</td>
<td>3.68</td>
</tr>
<tr>
<td>8.0</td>
<td>1746</td>
<td>218</td>
<td>3.73</td>
<td>1347</td>
<td>168</td>
<td>3.67</td>
</tr>
<tr>
<td>9.0</td>
<td>1954</td>
<td>217</td>
<td>3.73</td>
<td>1513</td>
<td>168</td>
<td>3.67</td>
</tr>
<tr>
<td>10.0</td>
<td>2171</td>
<td>217</td>
<td>3.73</td>
<td>1681</td>
<td>168</td>
<td>3.67</td>
</tr>
<tr>
<td>11.0</td>
<td>2380</td>
<td>216</td>
<td>3.72</td>
<td>1842</td>
<td>167</td>
<td>3.65</td>
</tr>
<tr>
<td>12.0</td>
<td>2588</td>
<td>216</td>
<td>3.72</td>
<td>2007</td>
<td>167</td>
<td>3.65</td>
</tr>
<tr>
<td>13.0</td>
<td>2793</td>
<td>215</td>
<td>3.71</td>
<td>2168</td>
<td>167</td>
<td>3.65</td>
</tr>
<tr>
<td>14.0</td>
<td>2996</td>
<td>214</td>
<td>3.70</td>
<td>2330</td>
<td>166</td>
<td>3.64</td>
</tr>
<tr>
<td>15.0</td>
<td>3197</td>
<td>213</td>
<td>3.69</td>
<td>2490</td>
<td>166</td>
<td>3.64</td>
</tr>
<tr>
<td>16.0</td>
<td>3395</td>
<td>212</td>
<td>3.68</td>
<td>2648</td>
<td>165</td>
<td>3.63</td>
</tr>
<tr>
<td>17.0</td>
<td>3588</td>
<td>211</td>
<td>3.67</td>
<td>2805</td>
<td>165</td>
<td>3.63</td>
</tr>
<tr>
<td>18.0</td>
<td>3779</td>
<td>210</td>
<td>3.66</td>
<td>2962</td>
<td>164</td>
<td>3.62</td>
</tr>
<tr>
<td>19.0</td>
<td>3969</td>
<td>209</td>
<td>3.66</td>
<td>3117</td>
<td>164</td>
<td>3.62</td>
</tr>
<tr>
<td>20.0</td>
<td>4159</td>
<td>208</td>
<td>3.65</td>
<td>3270</td>
<td>163</td>
<td>3.61</td>
</tr>
<tr>
<td>21.0</td>
<td>4340</td>
<td>207</td>
<td>3.64</td>
<td>3422</td>
<td>163</td>
<td>3.61</td>
</tr>
<tr>
<td>22.0</td>
<td>4521</td>
<td>205</td>
<td>3.62</td>
<td>3572</td>
<td>162</td>
<td>3.60</td>
</tr>
<tr>
<td>23.0</td>
<td>4687</td>
<td>204</td>
<td>3.61</td>
<td>3720</td>
<td>162</td>
<td>3.60</td>
</tr>
<tr>
<td>24.0</td>
<td>4868</td>
<td>203</td>
<td>3.60</td>
<td>3866</td>
<td>161</td>
<td>3.59</td>
</tr>
<tr>
<td>25.0</td>
<td>5042</td>
<td>202</td>
<td>3.59</td>
<td>4017</td>
<td>161</td>
<td>3.59</td>
</tr>
<tr>
<td>26.0</td>
<td>5207</td>
<td>200</td>
<td>3.58</td>
<td>4157</td>
<td>160</td>
<td>3.58</td>
</tr>
<tr>
<td>27.0</td>
<td>5371</td>
<td>199</td>
<td>3.57</td>
<td>4300</td>
<td>159</td>
<td>3.57</td>
</tr>
<tr>
<td>28.0</td>
<td>5526</td>
<td>197</td>
<td>3.55</td>
<td>4437</td>
<td>158</td>
<td>3.55</td>
</tr>
<tr>
<td>29.0</td>
<td>5682</td>
<td>196</td>
<td>3.54</td>
<td>4575</td>
<td>158</td>
<td>3.55</td>
</tr>
<tr>
<td>30.0</td>
<td>5832</td>
<td>194</td>
<td>3.52</td>
<td>4701</td>
<td>157</td>
<td>3.54</td>
</tr>
</tbody>
</table>