GOLD(II) FLUOROSULFATE DERIVATIVES AND
NEW GOLD(I) AND PLATINUM(II) CARBONYL COMPLEXES

by

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B.Sc. (Hons.), The University of British Columbia, 1990

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Department of Chemistry

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

September 1993
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Department of Chemistry
The University of British Columbia
Vancouver, Canada

Date 15 Oct 1993
Controlled pyrolysis of solid Au(SO$_3$F)$_3$ at gradually increasing temperatures up to 145°C produced Au$^{2+}$ ions as lattice defects. The Au$^{2+}$ ion was also generated in HSO$_3$F via reduction of Au(SO$_3$F)$_3$(solv) by gold metal. Both types of materials obtained were studied by electron resonance spectroscopy, where spectra indicative of high axial symmetry are obtained. The similar $g_{iso}$ values indicate that the same species is present in a similar, near square planar environment both in the solid and in the frozen solution. In solution, the Au$^{2+}$ ion is unstable, and disproportionates to give a diamagnetic, mixed valency compound of the composition Au$^1$Au$^{III}$(SO$_3$F)$_4$. The orange solid was isolated and studied by vibrational spectroscopy. Dissolution of Au$^1$Au$^{III}$(SO$_3$F)$_4$ in HSO$_3$F produced an ESR active species in a highly unsymmetrical environment, postulated to be [Au(SO$_3$F)$_4$]$^{2-}$, on account of partly resolved hyperfine splitting to four fluorines. These results have allowed the identification of Au$^{2+}$ (d$^9$) for the first time.

Reductive carbonylation of Au(SO$_3$F)$_3$ in HSO$_3$F, followed by solvolysis of the product, Au(CO)SO$_3$F, in SbF$_5$ in the presence of CO produced [Au(CO)$_2$][Sb$_2$F$_{11}$], the first example of a linear binary carbonyl cation in a thermally stable isolable compound. The white solid was characterized by vibrational spectroscopy and NMR ($^{19}$F, $^{13}$C) studies. [Au(CO)$_2$][Sb$_2$F$_{11}$] has a very high average C-O stretching frequency of 2235.5 cm$^{-1}$, suggesting that CO is behaving primarily as a $\sigma$ donor, and $\pi$-backbonding is greatly reduced. The Au-C bond is consequently weak, and reaction of a donor solvent such as acetonitrile with [Au(CO)$_2$][Sb$_2$F$_{11}$] displaced CO. Slow solvent evaporation gave crystals of [Au(NCCH$_3$)$_2$][SbF$_6$], which were suitable for a single crystal X-ray diffraction study.

[Au(NCCH$_3$)$_2$][SbF$_6$] has completely linear N-Au-N units, and the anion is octahedral.
Reductive carbonylation of Pt(SO$_3$F)$_4$ in HSO$_3$F produced [Pt(CO)$_4$][Pt(SO$_3$F)$_6$], which could be further reduced to cis-Pt(CO)$_2$(SO$_3$F)$_2$ with CO by heating. Solvolysis of cis-Pt(CO)$_2$(SO$_3$F)$_2$ in SbF$_5$ in the presence of CO yielded [Pt(CO)$_4$][Sb$_2$F$_{11}$]$_2$.

[Pt(CO)$_4$][Pt(SO$_3$F)$_6$] and [Pt(CO)$_4$][Sb$_2$F$_{11}$]$_2$ contain the hitherto unknown square planar [Pt(CO)$_4$]$^{2+}$ cation. The platinum carbonyl complexes were studied by vibrational spectroscopy, and were found to have very high C-O stretching frequencies. The average C-O stretching frequency for [Pt(CO)$_4$][Sb$_2$F$_{11}$]$_2$ is 2261 cm$^{-1}$, and is the highest value so far reported. It was concluded that $\pi$-backbonding was essentially absent in all the carbonyl complexes obtained here.
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<thead>
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<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$\nu$</td>
<td>stretching vibration in cm$^{-1}$ (vibrational spectra)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>deformation mode in cm$^{-1}$ (vibrational spectra); chemical shift in ppm (NMR)</td>
</tr>
<tr>
<td>def</td>
<td>deformation (vibrational spectra)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>rocking mode (vibrational spectra)</td>
</tr>
<tr>
<td>$\Delta \nu$</td>
<td>Raman shift (cm$^{-1}$)</td>
</tr>
<tr>
<td>IR</td>
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<tr>
<td>Ra</td>
<td>Raman</td>
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<tr>
<td>int.</td>
<td>intensity</td>
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<tr>
<td>sym</td>
<td>symmetrical</td>
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<td>as, asym</td>
<td>asymmetrical</td>
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<tr>
<td>s</td>
<td>strong</td>
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<td>m</td>
<td>medium</td>
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<tr>
<td>w</td>
<td>weak</td>
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<td>shoulder</td>
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<tr>
<td>b</td>
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<tr>
<td>t</td>
<td>terminal</td>
</tr>
<tr>
<td>br</td>
<td>bridging</td>
</tr>
<tr>
<td>av., ave</td>
<td>average</td>
</tr>
<tr>
<td>$k, f_r$</td>
<td>force constant (N·m$^{-1}$)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>reduced mass</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>effective magnetic moment (Bohr Magnetons)</td>
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<tr>
<td>$\chi_M^{\text{corr}}$</td>
<td>corrected molar magnetic susceptibility</td>
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c speed of light ($3.0 \times 10^8 \text{ m} \cdot \text{s}^{-1}$)

J coupling constant in Hz (NMR)

$\lambda_{\text{max}}$ maximum intensity absorption in nm (uv-visible spectra)

Anal. calc. analysis calculated (%)

Ref. reference(s)

h hour(s)

(solv) solvated

(s) solid

conj. conjugate
ACKNOWLEDGEMENTS

I would like to express my appreciation and gratitude to Dr. F. Aubke, who has provided me with encouragement, guidance and advice throughout my years of study. Thanks also go to all the members, past and present, of our research group, for their interesting discussions, and many valuable suggestions. In particular, I would like to thank Changqing Wang for allowing me to include some of his unpublished results in this thesis. Our collaborators at the University of Hannover, Germany, are thanked for carrying out the NMR studies and for obtaining some vibrational spectra. Drs. F.G Herring and P.S. Phillips are thanked for their help in obtaining and interpreting the ESR spectra. Thanks go to the technicians, the microanalysis, mechanical engineering, electrical engineering and glassblowing shops for all their assistance. The crystallographers are also thanked for the help they have given me. Financial support by the North Atlantic Treaty Organization (NATO) and by the Natural Science and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.
CHAPTER 1. GENERAL INTRODUCTION

The work discussed in this thesis involves the synthesis and characterization of gold and platinum complexes. First, a brief overview of the relevant chemistry of the two metals will be presented, followed by a discussion of metal carbonyl complexes and the bonding that occurs. Second, a description of the physical methods used to characterize the complexes synthesized in this thesis is provided. The solvent systems used will be briefly discussed, along with some definitions of acid and base behaviour. A few statements outlining the objectives pursued in this work are also provided.

1.1 Gold

Gold has been treasured since ancient times as a sign of wealth, and even now it is used as a monetary standard. This soft, yellow metal is the most ductile and malleable of all the metals. The uses of gold by jewelers and dentists are well known, as are its uses in the electronics and the fine china industries.

Gold occurs in nature as the metal, either in the form of flakes or nuggets, or in veins in quartz or iron pyrite [1]. It is called a noble metal because of its resistance to chemical attack. Other noble metals include rhodium, palladium, iridium, and platinum. Gold is the only metal that is not attacked by sulfur or oxygen at any temperature. The free atom has the electronic configuration [Xe]4f^{14}5d^{10}6s^{1} and belongs to group 11.

Listed below are some of the physical properties of gold [2].

\[
\begin{align*}
\text{Au} & \quad \text{atomic number: 79} \\
\text{atomic weight: 196.97 g\cdot mol}^{-1} \\
\text{melting point: 1064.43°C} \\
\text{boiling point: 2807°C} \\
\text{density (20°C): 19.32 g\cdot cm}^{-3} \\
\text{natural abundance (^{197}\text{Au}): 100%}
\end{align*}
\]
nuclear spin: 3/2

crystal structure: face-centered cubic

The known oxidation states of gold are -1, 0, +1, +2, +3, and +5. Most gold chemistry involves complexes of Au(I) and Au(III).

Gold is capable of gaining an electron and filling its 6s shell, behaviour that has caused it to be called a pseudohalogen. Compounds of the form MAu (M = alkali metal) with the metal in the -1 oxidation state exist, and this has been confirmed in the case of CsAu by electrical conductivity measurements [3]. With the exception of the halogens, gold has the highest electron affinity among the elements [4] (Table 1-1).

Table 1-1. Electron Affinities of the Halogens and Gold

<table>
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<th>Element</th>
<th>Electron Affinity (kJmol(^{-1}))</th>
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<tr>
<td>F</td>
<td>327.9</td>
</tr>
<tr>
<td>Cl</td>
<td>348.8</td>
</tr>
<tr>
<td>Br</td>
<td>324.6</td>
</tr>
<tr>
<td>I</td>
<td>295.3</td>
</tr>
<tr>
<td>At</td>
<td>270</td>
</tr>
<tr>
<td>Au</td>
<td>222.7</td>
</tr>
</tbody>
</table>

Gold(I) complexes have been shown to preferentially exhibit two-fold, linear coordination, e.g. [NC-Au-CN]\(^+\), and σ effects reportedly dominate bonding, even in the presence of π-acid ligands (e.g. CO) [5]. The +2 oxidation state is very rare, and found for only a few compounds (see Chapter 3); of the known Au(II) species, little information regarding the structure is available. All Au(III) complexes reported so far have been found to be low-spin and diamagnetic. Most of these complexes are square planar, although five- and six-coordinate species are also known [6]. No evidence for the +4 oxidation state has yet been found, and the +5 oxidation state exists only in AuF\(_5\) and [AuF\(_6\)]\(^-\) [7].
There is a vast area of research involving the chemistry of gold clusters and organometallic compounds, but the work described in this thesis will involve mono and dinuclear species only.

1.2 Platinum

Platinum has not had as glorious a history as gold. It was discovered in 1735 in South America and given the name *platina del Pinto*, Spanish for "little silver of the Pinto River" [8]. The pure metal is silvery-white, and is also very malleable and ductile. In 1741, platinum was introduced in Europe and over the next 90 years, scientists discovered the ease with which Pt(II) formed complexes with donor atoms (e.g. N, CN⁻, P, S) [5]. The realisation that the divalent metal had square planar geometry introduced the idea of cis- and trans- isomerism. With the elucidation of the trans effect in Pt(II) compounds in the early 20th century, chemists were able to synthesize any Pt(II) complex they wished [8]. The organometallic chemistry of platinum was developing simultaneously, with the preparation of Zeise's salt, K[Pt(C₂H₄)Cl₃]·H₂O, first reported in 1830. Even though the organometallic chemistry of platinum will not be discussed in this thesis, the applications of these compounds in both homogeneous and heterogeneous catalysis in chemistry are of great importance and continuing interest. There is a great deal of cluster chemistry involving platinum, but this topic will also not be addressed in this thesis.

Platinum is usually found in cupronickel ores, but occasionally occurs as the native ore [8]. This group 10 metal has the electron configuration [Xe]4f¹⁴5d⁹6s¹. Some of its physical properties are listed below [2]:

- **Pt**
  - atomic number: 78
  - atomic weight: 195.09 g·mol⁻¹
  - melting point: 1772°C
  - boiling point: 3828±100°C
  - density (20°C): 21.45gcm⁻³
NMR active nucleus: $^{195}$Pt
natural abundance: 33.8%
nuclear spin: 1/2
crystal structure: face-centered cubic

The known oxidation states are 0, +1, +2, +4, +5, and +6. Complexes of platinum in the zero oxidation state are usually coordination complexes with neutral donor ligands, e.g. Pt(PPh$_3$)$_3$ [5]. The +1 oxidation state is rare, with only two compounds reported: Pt$_3$Cl$_3$ [9], and Pt$_3$(SnCl$_3$)$_2$(C$_8$H$_{12}$)$_3$ [10]. The diamagnetic +2 oxidation state is the most common and such complexes preferentially exhibit square planar coordination. There are reports of five-coordinate complexes of Pt(II) with $\pi$-acceptor ligands [11]. There are a limited number of platinum compounds in the +3 oxidation state [12]. Pt(III) is expected to show paramagnetic behaviour (d$^7$). Complexes such as [Pt(NH$_3$)$_2$X$_3$] (X=Cl, Br, I) and [Pt(NH$_3$)$_4$X]$^{2+}$, where platinum has the formal charge of +3, have been shown to be mixed valency compounds of Pt(II) and Pt(IV) [8].

The +4 oxidation state for platium is quite common. The metal has an octahedral coordination sphere, and all Pt(IV) complexes are diamagnetic.

Platinum forms a variety of fluoride compounds in both the +5 and +6 oxidation states. PtF$_5$, PtOF$_3$, and a number of [PtF$_6$]$^+$ salts are known, e.g. M[PtF$_6$] (M=alkali metal), O$_2^+$[PtF$_6$]$^-$. The known structures of the Pt(V) compounds exhibit octahedral symmetry, and are paramagnetic [8]. The only known Pt(VI) compound is the hexafluoride, PtF$_6$. It is also believed to have octahedral symmetry, but this is deduced from its infrared spectrum, since no molecular structure is available [13]. Platinum has never been found in an oxidation state higher than +6.
1.3 Carbonyl Compounds

Carbonyl complexes are found for almost all d-block transition metals. There are thousands of organometallic carbonyl complexes reported, but only a handful of binary transition metal carbonyls are known.

When free carbon monoxide coordinates to a transition metal center, the C-O stretching frequency can either decrease or increase. This allows the division of carbonyl compounds into classical and non-classical transition metal carbonyl complexes. The following discussion centers on the bonding characteristics of terminally bound CO in these two types of complexes.

1.3.1 Classical Transition Metal Carbonyl Complexes

Classical transition metal carbonyl complexes typically involve metals from the d series in the periodic table, and they are characterized by a decrease in the C-O stretching frequency upon coordination of carbon monoxide to the metal. This is caused by \( \sigma \) donation of electron density from the carbon 5\( \sigma \) orbital to a metal orbital of appropriate symmetry, and back donation of electron density from a filled d\( \pi \) orbital on the metal to a p\( \pi \) orbital on the carbon monoxide molecule. The second effect is commonly called \( \pi \)-backbonding. Carbon monoxide becomes a better \( \sigma \)-donor due to the increase of electron density in its p\( \pi \) orbital, and a better \( \pi \)-acceptor due to the decrease of electron density in the 5\( \sigma \) orbital [4][5]. This gives CO the ability to stabilize metals in neutral or low oxidation states. The two phenomena reinforce each other, and are collectively referred to as synergic bonding (Figure 1-1).

The stronger metal-carbon bond and weaker carbon-oxygen bond cause the C-O stretching frequency to decrease from 2143 cm\(^{-1}\) [14] for uncoordinated gaseous carbon monoxide to the range of 2100 cm\(^{-1}\) to 1850 cm\(^{-1}\) [4] for terminally-bound CO.
Figure 1-1. Bonding in Classical Transition Metal Carbonyls.

The easiest method for monitoring the change in \( \nu_{\text{CO}} \) is by infrared spectroscopy, which gives a qualitative measure of the strength of the C-O bond. The greater the decrease in CO stretching frequency, the weaker the C-O bond. A more accurate measure of C-O bond strength is through the use of force constants, since vibrational coupling of \( \nu_{\text{CO}} \) to other vibrations of comparable energy and symmetry, different metal centers and different counterions may affect the C-O stretching frequency. The values of the force constants obtained allow quantitative comparisons of C-O bond strengths among various carbonyl compounds. Force constants can be calculated using either the method of Cotton and Kraihanzel [15] or Jones [16].

The use of \(^{13}\text{C} \) NMR to study labelled samples allows the comparison of chemical shifts of the compounds described in this thesis to those of related species. It also permits (to a limited degree) the study of the behaviour of these species in solution, and the possibility of exchange processes taking place. The typical range of \(^{13}\text{C} \) chemical shifts for classical transition metal carbonyls is 189-220 ppm relative to TMS [17].

Preparation of classical transition metal carbonyl complexes often requires forcing conditions. Binary transition metal carbonyls are most commonly produced by reducing metal salts in an organic solvent with CO under 200-300 atm pressure and at temperatures ranging from 120-300°C. Direct reaction of metal with CO is possible for nickel and iron, but is feasible only for finely divided nickel, which reacts at room temperature; the
reaction of iron with CO requires high temperatures and pressures [5]. Transition metal complexes can be prepared from binary metal carbonyls by using donor ligands (e.g. PR$_3$, NR$_3$; R = alkyl group) to displace a CO molecule. The stoichiometry of these complexes can be predicted using the effective atomic number rule (EAN), which is obeyed by all monomeric, binary metal carbonyl complexes, except [V(CO)$_6$], which has 17 valence electrons [18].

The most common geometries found for both neutral and charged, monomeric binary metal carbonyl species are

(i) octahedral, e.g. Cr(CO)$_6$, [Mn(CO)$_6$]$^+$;
(ii) trigonal bipyramidal, e.g. Fe(CO)$_5$, [Mn(CO)$_5$]$^-$; and
(iii) tetrahedral, e.g. Ni(CO)$_4$, [Fe(CO)$_4$]$^{2-}$.

1.3.2 Non-Classical Transition Metal Carbonyl Complexes

Non-classical transition metal carbonyl complexes usually involve the noble metals. Unlike classical metal carbonyls, the C-O stretching frequency is found in the range 2153-2200 cm$^{-1}$, greater than that of free CO, and it has been postulated that the increase in $\nu$CO is due to decreased $\pi$-backbonding [19]. Again, vibrational and $^{13}$C NMR spectroscopy are useful techniques for deducing the structures of these compounds.

Prior to the work started by this research group, there was no evidence for either linear or square planar binary metal carbonyls. It was thought that Pd, Pt, and Au did not form binary metal carbonyls [5], but matrix isolation experiments have produced Pd(CO)$_n$ and Pt(CO)$_n$ ($n=1$-4) [20], as well as Au(CO)$_n$ ($n=1,2$) [21]. All of these species are thermally unstable. Noble metal carbonyl halides are quite common, the first being three platinum species which were reported in 1870 [22].

The methods of synthesizing non-classical metal carbonyl complexes require less forcing conditions than those required in the preparation of classical transition metal
carbonyl complexes. For example, the preparation of Au(CO)Cl \[23][24\] involves heating gold(III) chloride from 50°C to 120°C in a stream of carbon monoxide.

There is a class of transition metal carbonyl complexes which should be briefly mentioned. These are the carbonylate anions, sometimes called "super-reduced" metal carbonyls. They are prepared by reacting the neutral binary metal carbonyl with strong reducing agents such as aqueous or alcoholic alkali hydroxides, amines, or sodium amalgam. These complexes show extensive \(\pi\)-backbonding, and the C-O stretching frequencies are well below 2143 cm\(^{-1}\) [5].

1.4 Vibrational Spectroscopy

Vibrational spectroscopy is used to provide information about the structure and bonding of functional groups within a molecule. Infrared spectroscopy is based on absorptions caused by irradiation that induce a change in the dipole moment of a molecule, while Raman spectroscopy is based on scattering of the exciting light, causing changes in the polarizability of the molecule. Structural information about a molecule can be obtained by examining the vibrational spectra. For example, the cis- and trans-isomers of ML\(_2\)CO\(_2\) (M = metal, L = ligand) can be easily distinguished by infrared spectroscopy. cis-ML\(_2\)(CO)\(_2\) has two infrared active modes, while trans-ML\(_2\)(CO)\(_2\) only has one (Figure 1-2).

![Diagram of cis- and trans-ML\(_2\)(CO)\(_2\)](image)

Figure 1-2. Infrared Active Modes of cis- and trans-ML\(_2\)(CO)\(_2\)
Since the fluorosulfate and fluoroantimonate anions are of interest to us, a brief overview of their characteristic vibrations will be given.

The $\text{SO}_3\text{F}^-$ anion has $C_{3v}$ symmetry (Figure 1-3). Upon coordination of one or two oxygen atoms to a metal center, the symmetry can be reduced to $C_s$ or $C_1$ (Figure 1-4).

![Figure 1-3. The $\text{SO}_3\text{F}^-$ Anion](image)

![Figure 1-4. Reduced Symmetry of $\text{SO}_3\text{F}^-$](image)

All of the $\text{SO}_3\text{F}^-$ stretching vibrations are both infrared and Raman active. The two most common coordination modes of the $\text{SO}_3\text{F}^-$ group, monodentate and bidentate, can be easily determined by examining the vibrational spectra and identifying the characteristic vibrations. Figure 1-5 shows the expected vibrational band positions for various coordination modes of fluorosulfate groups [25]. The shaded areas show the positions of the diagnostic bands.
<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Bonding or Coordination Mode</th>
<th>Frequency Range (cm(^{-1}))</th>
<th>Stretching Band</th>
<th>Deformation Band</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_{3v})</td>
<td>COVALENT TRIDENTATE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\nu_{\text{as}}) (S-O)</td>
<td></td>
<td>(\nu_{\text{asym}}) (S-O)</td>
<td>(\nu) (S-F)</td>
</tr>
<tr>
<td></td>
<td>(\delta_{\text{asym}}) (S(_{3}))</td>
<td></td>
<td>(\delta_{\text{sym}}) (S(_{3}))</td>
<td>(\gamma) (S(_{3}))</td>
</tr>
<tr>
<td></td>
<td>PURELY IONIC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\nu_{\text{as}}) (S-O)</td>
<td></td>
<td>(\nu_{\text{asym}}) (S-O)</td>
<td>(\nu) (S-F)</td>
</tr>
<tr>
<td></td>
<td>(\delta_{\text{asym}}) (S(_{3}))</td>
<td></td>
<td>(\delta_{\text{sym}}) (S(_{3}))</td>
<td>(\gamma) (S(_{3}))</td>
</tr>
<tr>
<td>C(_{5})</td>
<td>IONIC PERTURBED</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\nu_{\text{as}}) (S(_{2}))</td>
<td></td>
<td>(\nu_{\text{asym}}) (S(_{2}))</td>
<td>(\nu) (S-F)</td>
</tr>
<tr>
<td></td>
<td>(\delta_{\text{asym}}) (S(_{3}))</td>
<td></td>
<td>(\delta_{\text{sym}}) (S(_{3}))</td>
<td>(\gamma) (S(_{3}))</td>
</tr>
<tr>
<td></td>
<td>COVALENT MONODENTATE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\nu_{\text{as}}) (S(_{2}))</td>
<td></td>
<td>(\nu_{\text{asym}}) (S(_{2}))</td>
<td>(\nu) (S-F)</td>
</tr>
<tr>
<td></td>
<td>(\delta_{\text{asym}}) (S(_{3}))</td>
<td></td>
<td>(\delta_{\text{sym}}) (S(_{3}))</td>
<td>(\gamma) (S(_{3}))</td>
</tr>
<tr>
<td></td>
<td>COVALENT BIDENTATE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\nu (S-O))</td>
<td></td>
<td>(\nu_{\text{as}}) (S(_{2}))</td>
<td>(\nu) (S-F)</td>
</tr>
<tr>
<td></td>
<td>(\nu_{\text{asym}}) (S(_{2}))</td>
<td></td>
<td>(\delta_{\text{asym}}) (S(_{3}))</td>
<td>(\gamma) (S(_{3}))</td>
</tr>
</tbody>
</table>

Figure 1-5. Vibrational Band Positions for Various Coordination Modes of the Fluorosulfate Group [25]
The $[\text{Sb}_2\text{F}_{11}]^-$ anion has been shown to have $D_{4h}$ symmetry from single crystal X-ray diffraction studies [26][27]. The Sb-F$_{\text{ax}}$ ($F_{\text{ax}}$ = axial fluorine atom) vibrations are found at ca. 700 cm$^{-1}$, and the Sb-F$_{4\text{eq}}$ ($F_{4\text{eq}}$ = four equatorial fluorine atoms) stretches are found between 600 cm$^{-1}$ and 680 cm$^{-1}$ [28].

If there is some uncertainty in assigning a vibration to a peak, then isotopic substitution is used. The stretching frequency of the peak(s) in question should shift. This will occur because vibrational frequencies depend upon the mass of the atoms involved ($\nu$(in cm$^{-1}$) = $1/2\pi c\sqrt{k/\mu}$), and changing the mass of one of the atoms will change the value of the reduced mass.

1.5 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is a technique commonly used to deduce the structure of molecules. NMR can also be used to study reactions in situ, and identify intermediate species or exchange processes between two or more moieties in the sample. Isotopic labelling of carbon and oxygen in carbon monoxide permits a comparison of $^{13}\text{C}$ resonances to related metal carbonyls, and also allows us to determine if exchange processes are occurring. If the species observed in the course of the reaction are identified, we may be able to propose possible mechanisms for the formation of the product.

The NMR studies described here were carried out at the University of Hannover, Germany.

1.6 Electron Spin Resonance Spectroscopy [29][30]

Electron spin resonance (ESR) spectroscopy is the best method available to us for the study of free radicals. The technique measures the first order Zeeman effect. A molecule with an unpaired electron in a magnetic field has two energy levels for the electron spin, given by

$$E = g\mu_B B_0 m_s \quad (1)$$

where
E is the energy level,
\( \mu_B \) is the Bohr Magneton,
\( B_0 \) is the applied magnetic field,
\( m_s \) is the electron spin,
g is the g-factor

For a free electron, the g value is 2.0023. In isotropic systems (e.g. gases, homogeneous liquids, solutions of low viscosity, crystalline solids with tetrahedral or octahedral symmetry), the g values can be considered as scalar quantities, since the sample orientation is independent of direction. In anisotropic systems such as unstable species generated \textit{in situ}, matrix isolated complexes, solids, or frozen solutions, the g values are direction dependent, and must be considered as symmetric tensors. The tensor can be diagonalized to give three g values: \( g_{xx} \), \( g_{yy} \), and \( g_{zz} \). The g values of isotropic samples are all equal. In anisotropic systems, the three g values may differ, and are averaged to give \( g_{iso} \). The magnitude of \( g_{iso} \) shows whether the unpaired electron is based in transition metal or ligand orbitals.

If there is a nucleus with \( I = n/2 \) \((n = \text{integer} > 0)\) near the unpaired electron, the two will interact, and equation (1) must be modified by adding a hyperfine coupling term:

\[
E = g\mu_B B_0 m_s + A m_s m_I \tag{2}
\]

where

- \( A \) is the hyperfine coupling constant
- \( m_I \) is the nuclear spin quantum number.

The coupling patterns observed in these systems are directly analogous to those obtained in NMR. The treatment of the A values is also analogous to that of the g values: in isotropic systems, the A terms are equal and treated as scalar quantities; in systems with lower symmetry, the A values must be treated as symmetric tensors which can be diagonalized to give \( A_{xx} \), \( A_{yy} \), and \( A_{zz} \). All three values can be averaged to give \( A_{iso} \).

The number represented by \( A_{iso} \) is a measure of the line separation in the multiplet pattern caused by the interacting nuclei, and has units of MHz. Its magnitude is dependent on the spin density at the nucleus in question, and can indicate the extent to which the unpaired electron is delocalized.
1.7 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is also called Electron Spectroscopy for Chemical Analysis (ESCA). It is a technique which can be used to study the chemical composition of solid surfaces, and in this work, it is used to determine the oxidation state of an element in a compound. Each element has a unique spectrum; in a compound, the peaks observed approximately comprise the sum of the spectra of the individual elements [31]. A spectrum is obtained by irradiating the surface of the sample with X-rays (at one energy level) in a vacuum chamber. The electrons emitted from the core levels of the atoms in the compound are sorted according to energy level, and the spectrum is a plot of the number of electrons emitted for a given energy interval against the electrons' kinetic energy. The X-ray sources most commonly used are the Mg $\kappa_\alpha$ (1253.6 eV) and the Al $\kappa_\alpha$ (1486.6 eV). The X-rays, or photons, eject electrons from the surface atoms via the photoelectric effect. The kinetic energy of the emitted electron is given by

$$K.E. = h\nu - BE - \phi_s$$  \hspace{1cm} (3),

where

- $h\nu$ is the energy of the photons
- $BE$ is the binding energy
- $\phi_s$ is the spectrometer work function

The binding energy is defined as the energy separation between the ionized core level and the Fermi level.

After emission of a photoelectron, the ion left is very energetic, and relaxes by emitting a second electron known as the Auger electron (Figure 1-6).

Figure 1-6. Emission of (a) a photoelectron, and (b) an Auger electron [31]
It can be seen that photoionization produces two electrons per atom: a photoelectron and an Auger electron. Detection of the electrons is achieved by using an electron spectrometer set to a given "pass energy", where only electrons within the range of the pass energy will be detected. Applying a variable electrostatic field allows scanning for different electron energies.

1.8 Definitions of Acidity, Basicity, and Superacids

Since the work in this thesis involves the use of highly acidic media in order to carry out the reactions, it is appropriate to quickly review acid-base chemistry and to clarify some definitions.

1.8.1 Acid-Base Definitions

The three most commonly used definitions of acids and bases are those of Arrhenius, Bronsted-Lowry, and Lewis [32]. The Arrhenius definition appeared between 1880 and 1890 and states that in aqueous solution, an acid causes an increase in the concentration of hydrogen ion, $H^+$, and a base causes an increase in the concentration of the hydroxide ion, $OH^-$. However, in the absence of water, this definition was invalid. In 1923, two chemists, J. N. Bronsted and T.M. Lowry, proposed a more general definition for acids and bases: acids acted as proton donors and bases acted as proton acceptors (equation (4)).

$$H_2O + H_2O \rightarrow H_3O^+ + OH^- \quad (4)$$

This explanation could only be applied to protonic substances. G.N. Lewis, in the same year, proposed that acids were electron pair acceptors and bases were electron pair donors.

There is also the solvent system definition, where an acid is a solute capable of increasing the relative concentration of the characteristic cation of the pure solvent, and the
base is a solute capable of increasing the relative concentration of the characteristic anion of the pure solvent. For example, if a solvent autoionizes according to

\[ 2A_2B \rightleftharpoons A_3B^+ + AB^- \quad (5), \]

then an acid in this system would increase the relative concentration of \( A_3B^+ \) and a base would increase the relative concentration of \( AB^- \). The cation is also called the acidium ion and the anion is called the base ion.

1.8.2 Superacids

There are several definitions of superacids, a term first coined in 1927 by Conant and Hall [33]. Gillespie’s definition [34] is valid primarily for Bronsted and conjugate acids and states that a superacid is any acid that is stronger than 100% sulfuric acid. Superacid strength is measured using the Hammett acidity function, \( H_0 \) [35]. Olah et al. defined a Lewis superacid as any acid that is stronger than anhydrous \( \text{AlCl}_3 \); however, they encountered difficulties in determining a scale of acid strengths [32].

The superacid systems discussed in this thesis are Bronsted-Lewis conjugate superacids. These are prepared by the addition of a strong Lewis acid to a strong Bronsted acid. The Lewis acid will shift the equilibrium by complexing and effectively removing the base ion, e.g.

\[ 2 \text{HSO}_3\text{F} + \text{SbF}_5 \rightleftharpoons \text{H}_2\text{SO}_3\text{F}^+ + \text{SbF}_5(\text{SO}_3\text{F})^- \quad (7) \]

The addition of the Lewis acid greatly increases the acidity of the system.

1.8.2a Fluorosulfuric Acid

Fluorosulfuric acid is the solvent of choice for most of the reactions described in this thesis. It is prepared by insertion of \( \text{SO}_3 \) into HF [36]. With its wide liquid range (-88.98 to 162.7°C), reactions can be carried out at different temperatures. Under anhydrous conditions, \( \text{HSO}_3\text{F} \) is unreactive towards glass, permitting easy storage and
handling. It is easily purified by double distillation under an atmospheric pressure of N₂, thereby removing H₂SO₄ and HF, the two main impurities, that are formed when the acid comes into contact with moisture, i.e.

\[ \text{HSO}_3\text{F} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_4 + \text{HF} \] (8)

Fluorosulfuric acid is commercially available. Its low viscosity allows easy manipulation in glass reactors. HSO₃F often has traces of SO₃ and HF present, due to the decomposition of HSO₃F:

\[ \text{HSO}_3\text{F} \rightleftharpoons \text{SO}_3 + \text{HF} \] (9)

and these impurities are difficult to remove. Some physical properties of HSO₃F are listed below [37].

- Boiling point: 162.7 °C
- Melting point: -88.98 °C
- Density (25°C): 1.726 g·ml⁻¹
- Viscosity (25°C): 1.56 cP
- Specific conductance (25°C): 1.084x10⁻⁴ Ω⁻¹cm⁻¹

The high conductivity of fluorosulfuric acid is postulated as being due to the "proton jump" or Grothius mechanism, and ionic molar conductivities at infinite dilution and at 25°C are H₂SO₃F⁺: 185; SO₃F⁻: 135 [40]. Both the infrared and Raman spectra of HSO₃F are known [38][39].

HSO₃F is thought to be one of the strongest simple protonic acids known [40]. Its acidity, as measured on the Hammett acidity scale, is \(H₀ = -15.1\). The acidity of HSO₃F can be greatly increased by the addition of SbF₅ or by the addition of SO₃ and SbF₅ [32]. Unfortunately, the resulting Bronsted-Lewis conjugate superacid systems contain many species in solution, and is not suitable as a solvent if we want to identify moieties generated in situ.
Fluorosulfuric acid is also used in solvolysis reactions with alkali metal halides to form the alkali metal fluoro sulfate, which is then used to prepare the corresponding salts of high valent fluorosulfates [41], e.g.

\[ \text{CsCl} + \text{HSO}_3\text{F} \rightarrow \text{CsSO}_3\text{F} + \text{HCl} \]  

followed by

\[ \text{CsSO}_3\text{F} + \text{Au(SO}_3\text{F})_3 \rightarrow \text{Cs[Au(SO}_3\text{F})_4] } \]  

The synthetic reactions described herein start with gold tris(fluorosulfate), \( \text{Au(SO}_3\text{F})_3 \), or platinum tetrakis(fluorosulfate), \( \text{Pt(SO}_3\text{F})_4 \), in fluorosulfuric acid. These two compounds have been found to behave as Lewis acids in \( \text{HSO}_3\text{F} \) [42][43] by removing the \( \text{SO}_3\text{F}^- \) anion according to

\[ \text{Au(SO}_3\text{F})_3 + 2 \text{HSO}_3\text{F} \rightleftharpoons \text{H}_2\text{SO}_3\text{F}^+ + [\text{Au(SO}_3\text{F})_4]^-. \]  

\[ \text{Pt(SO}_3\text{F})_4 + 4 \text{HSO}_3\text{F} \rightleftharpoons 2 \text{H}_2\text{SO}_3\text{F}^+ + [\text{Pt(SO}_3\text{F})_6]^{2-}. \]  

while the cesium salts of these two compounds behave as bases in \( \text{HSO}_3\text{F} \), e.g. for \( \text{Cs[Au(SO}_3\text{F})_4] } \):

\[ \text{HSO}_3\text{F} \]  

\[ \text{Cs[Au(SO}_3\text{F})_4] } \rightarrow [\text{Au(SO}_3\text{F})_4]^+ + \text{Cs}^+ \]  

\[ [\text{Au(SO}_3\text{F})_4]^+ \rightleftharpoons \text{Au(SO}_3\text{F})_3(\text{solv}) + \text{SO}_3\text{F}^- \]  

1.8.2b Antimony Pentafluoride

Antimony pentafluoride, \( \text{SbF}_5 \), is the strongest Lewis acid known, and is prepared by direct fluorination of the metal or the metal trichloride [32]. It is polymeric, with cis-bridged fluorines, and because of a high degree of association, \( \text{SbF}_5 \) is much more viscous than \( \text{HSO}_3\text{F} \).

It is usually less desirable to use \( \text{SbF}_5 \) as a solvent because its high viscosity makes it difficult to remove. Some physical properties of \( \text{SbF}_5 \) are listed below.

\[ \begin{array}{c|c|c}
\text{SbF}_5 & \text{boiling point} & 142.7°C \\
& \text{melting point} & 7°C \\
\end{array} \]
density @15°C 3.145 g·ml⁻¹
viscosity @20°C 460 cP

Antimony pentafluoride can undergo adduct formation (equation 17) or complex anion formation (equation 18) with a suitable Lewis base [32], e.g.

\[
\begin{align*}
\text{SbF}_5 + \text{SO}_2 & \rightarrow \text{OSO} \rightarrow \text{SbF}_5 \\
\text{SbF}_5 + \text{F}^- & \rightarrow [\text{SbF}_6]^-
\end{align*}
\]

(17) (18)

If SbF₅ is present in excess, the complex anion can give rise to polyanions [32], i.e.

\[
[\text{SbF}_6]^− + \text{excess SbF}_5 \rightarrow [\text{Sb}_2\text{F}_{11}]^−, [\text{Sb}_3\text{F}_{16}]^−, \text{etc.}
\]

(19)

SbF₅ can also solvolyze metal fluorosulfates to give the corresponding metal fluoroantimonates [44], e.g.

\[
\text{Ni(\text{SO}_3\text{F})_2} + 6 \text{SbF}_5 \rightarrow \text{Ni(\text{SbF}_6)_2} + 2 \text{Sb}_2\text{F}_9\text{SO}_3\text{F}
\]

(20)

Compared to the fluorosulfate group, the vibrational bands of the fluoroantimonates appear in a narrow region (< 800 cm⁻¹) and are not as intense [32], so there is less chance of overlapping fluoroantiminate bands with other vibrations of interest.

1.9 Bis(fluorosulfuryl) Peroxide

Bis(fluorosulfuryl) peroxide, S₂O₆F₂, was first prepared in 1956 by the AgF₂ catalyzed reaction of fluorine gas and sulfur trioxide [45]. It can be synthesized in the laboratory in large quantities, and is easily handled under vacuum in glass reactors. Impurities such as SO₃ can be removed from S₂O₆F₂ quickly and efficiently by washing the peroxide with H₂SO₄ in a separatory funnel. Other impurities, e.g. bis(fluorosulfuryl) oxide, S₂O₅F₂, can be removed by cooling S₂O₆F₂ to -78°C and pumping in vacuo [46]. S₂O₅F₂ is also a byproduct formed by the reduction of S₂O₆F₂.

The combination of bis(fluorosulfuryl) peroxide and fluorosulfuric acid is excellent for the clean oxidation of metals to form the corresponding fluorosulfates [47] according to
\[ M + \frac{n}{2} S_2O_6F_2 \rightarrow M(SO_3F)_n \ (M=Ag, \ Pd, \ Ir, \ Pt, \ Sn, \ Au; \ n=1-4) \ \ (21) \]

HSO$_3$F and excess \( S_2O_6F_2 \) are easily removed from the reaction mixture \textit{in vacuo}. The fluorosulfate radical, SO$_3F^-$, is easily obtained due to the low dissociation energy (ca. 23 kcal·mol$^{-1}$) \[48\] of \( S_2O_6F_2 \). Heating \( S_2O_6F_2 \) to 60°C results in the formation of a brown vapour, which is attributed to the SO$_3F$ radical \[49\] (equation (22)).

\[ S_2O_6F_2 \rightarrow 2 \ SO_3F^- \ \ (22) \]

One minor drawback is the exothermic reaction of the peroxide with readily oxidizable materials, e.g. organic compounds, so caution is necessary to ensure that \( S_2O_6F_2 \) does not come into contact with them.

\textbf{1.10 The Scope of This Work}

The work described in this thesis investigates two topics: the unusual magnetic behaviour of Au(SO$_3$F)$_3$, and the use of the superacid system Au(SO$_3$F)$_3$/HSO$_3$F to generate and stabilize gold carbonyl cations.

Au(SO$_3$F)$_3$ showed different magnetic properties depending upon the method of preparation. Oxidation of gold metal by BrSO$_3$F and pyrolysis of the intermediate produced a slightly paramagnetic product \[50\], while oxidation of the metal powder by \( S_2O_6F_2 \) in HSO$_3$F yielded the expected diamagnetic product \[51\]. This unusual magnetic behaviour required closer scrutiny. We wanted to investigate the source of the paramagnetism by controlled heating of a diamagnetic sample of Au(SO$_3$F)$_3$. ESR was used to study any paramagnetic species that may be produced.

Earlier work in our laboratory suggested that a paramagnetic species was also generated by the reduction of Au(SO$_3$F)$_3$ using gold powder in HSO$_3$F, and a more detailed study of this system was also undertaken.

The initial purpose of using the superacid system Au(SO$_3$F)$_3$/HSO$_3$F to protonate CO was to find evidence of the formyl cation, HCO$^+$, detected in interstellar clouds and as short-lived intermediates in hydrocarbon combustion reactions. HCO$^+$ has also been
generated in tubes containing H₂ and CO by electrical discharge, and its microwave spectrum has been recorded [52]. The reaction of CO with the Au(SO₃F)₃/HSO₃F superacid did not provide any evidence of HCO⁺, but instead, the Au(SO₃F)₃ was reduced from the +3 to the +1 oxidation state, and Au(CO)SO₃F was isolated [53]. This outcome was not entirely surprising since CO is commonly used as a reducing agent in the preparation of metal carbonyl complexes (vide supra). What was surprising, however, was evidence of the hitherto unknown linear cation [Au(CO)₂]⁺ as a reaction intermediate [53]. The product, Au(CO)SO₃F, also had an extremely high C-O stretching frequency (ave. 2195 cm⁻¹), and solution studies of the intermediate indicated that the C-O stretching frequency of [Au(CO)₂]⁺ was even higher [53]. However, Au-C vibrations were obscured by fluorosulfate vibrations. In order to clarify the assignment of Au-C vibrations, the use of a more weakly basic anion, e.g. [SbF₆]⁻ or [Sb₂F₁₁]⁻, was recommended. Both of these anions have been found to be among the weakest nucleophiles [54]. One of the goals of this thesis was to try to isolate the [Au(CO)₂]⁺ cation as the fluoroantimonate salt.

Once the study of the reaction between CO and the Au(SO₃F)₃/HSO₃F system is completed, the action of CO upon the Pt(SO₃F)₄/HSO₃F superacid system will be studied to see whether analogous complexes will be formed under similar reaction conditions.

The complete assignment of bands in the vibrational spectra of [Au(CO)₂]⁺, detected only in solution so far, and [Pt(CO)₄]²⁺, which is unknown, may be difficult because there is nothing with which to compare them. However, carbon monoxide and the cyanide anion are isoelectronic, and [Au(CN)₂]⁻ [55][56] and [Pt(CN)₄]²⁻ [16] are known. If the analogous CO complexes can be isolated, they should be isostructural with the CN⁻ compounds, and their vibrational spectra should show similar patterns. Transition metal cyano complexes are usually neutral or anionic, and are often made using basic solvents, e.g. NH₃. Carbonyl complexes are mostly neutral or cationic, and it seems reasonable to use acidic solvents, e.g. H₂SO₄. In both cases the metal is in a low oxidation state (vide supra). The cyanide ligand is not as good a π-electron acceptor as carbon monoxide [57]
due to its negative charge, but it is still capable of undergoing synergic bonding. It should be noted that transition metal cyano complexes, with the negatively charged ligand and the postively charged metal, do not need synergic bonding to explain their stability [57].
References


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22. P. Schützenberger, Compt. Rend. (1870) 70, 1134.
CHAPTER 2. EXPERIMENTAL

2.1 Chemicals

Gold powder (-20 mesh, 99.95% purity) and platinum powder (0.5-1.2 μm) were obtained from the Ventron Corporation (Alfa Inorganics). Fluorosulfuric acid, HSO₃F (technical grade), was obtained from Orange County Chemicals and purified by double distillation under N₂ [1]. Bis(fluorosulfuryl)peroxide, S₂O₆F₂, was prepared by fluorination of SO₃ using AgF₂ as a catalyst [2]. Antimony pentafluoride, SbF₅, was obtained from Ozark-Mahoning and purified first by distillation under N₂ and then by pumping in vacuo at 0°C. Carbon monoxide (C.P. grade, 99.5% purity) was obtained from Linde Gases and dried by passing it through a trap at -196°C. Sulfur dioxide, SO₂, (99.5% purity) was obtained from Matheson Gases and dried by storing over P₄O₁₀. Acetonitrile was obtained from MCB (spectroquality) and also dried by storing over P₄O₁₀. Gold tris(fluorosulfate), Au(SO₃F)₃, platinum tetrakis(fluorosulfate), Pt(SO₃F)₄, cesium fluorosulfate, CsSO₃F, cesium tetrakis(fluorosulfato)aurate(III), Cs[Au(SO₃F)₄], cesium pentakis(fluorosulfato)platinate(IV), Cs[Pt(SO₃F)₅], and cesium hexakis(fluorosulfato)platinate(IV), Cs[Pt(SO₃F)₆], were prepared as described by Lee and Aubke [3][4].

2.2 Apparatus

Volatile materials and gases were measured in a vacuum line of known volume. A Setra 280E pressure transducer with digital output was used to measure the pressure. Standard vacuum line techniques were used to manipulate air and moisture sensitive samples. Synthetic reactions were carried out inside Pyrex round-bottom flasks (50 or 100 mL) fitted with 4 mm Kontes stopcocks and B10 ground glass cones (Figure 2-1).
Figure 2-1. Reactor Used for Synthesis

Filtrations were carried out using an apparatus similar to that described by Shriver [5] (Figure 2-2).

Figure 2-2. Filtration Apparatus
Teflon-coated stir bars were used for mixing the reactants. Since all products were hygroscopic, they were manipulated and stored inside a Vacuum Atmosphere Corp. Dri-Lab, model DL-001-S-G, filled with dry nitrogen and equipped with an HE 493 Dri-Train.

2.3 Instrumentation

2.3.1 Vibrational Spectra

Infrared spectra were recorded on three instruments: a Perkin-Elmer 598 grating spectrometer, a Bomem MB 102 Fourier-Transform infrared spectrometer (FTIR), and a Bomem DA3 Series FTIR. Solid samples were finely ground and pressed as thin films between AgBr or AgCl windows (Harshaw Chemicals). Liquid samples were pipetted onto silicon windows and pressed to form a thin film. Gaseous samples were contained in a 10 cm cell fitted with AgBr windows and a 4 mm Kontes Teflon stopcock. The reported frequencies are accurate to ± 1 cm⁻¹ for spectra of solid samples. The accuracy of the wavenumbers for [Au(CO)₂]⁺(solv) are estimated at approximately ± 0.5 cm⁻¹, and all values are reproducible. Fourier Transform (FT) Raman spectra were obtained courtesy of Dr. H. Homborg and Prof. W. Preetz, University of Kiel, Germany. NMR, Raman and additional FTIR spectra were obtained courtesy of Prof. H. Willner, J. Schaebs, and M. Bodenbinder, University of Hannover, Germany.

2.3.2 Electron Spin Resonance Spectra

ESR spectra were obtained by Drs. F.G. Herring and P.S. Phillips, and F. Mistry all from this department. The samples were cooled to 103 K and kept at that temperature using a Varian E-257 temperature controller. The ESR spectra were run on an X-band homodyne spectrometer with a Varian 12-inch 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 were acquired 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. The relevant data-processing software was as described previously [6][7][8]. 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 collected by the IBM computer. The absolute field was corrected for the placement of the gaussmeter probe by calibrating against peroxyamine sulfate in aqueous solution and was in error by about 0.01 G. The precision of the data is typically about 0.02 G for 2 K points over a 100-G sweep which, together with the ca. 10-kHz error in the microwave frequency, corresponds to an error of ca. 0.00002 in the g values quoted. Liquid samples were contained, under vacuum, in 5 mm ESR tubes fitted with rotationally symmetric Young valves (Young, London). Solid samples were loaded into 2 mm o.d. glass capillary tubes and sealed under dry N₂.

2.3.2a Simulations

The spin Hamiltonian parameters for the observed centers were determined using a program called QPOW, which was obtained from the Illinois ESR Research Center (NIH resources Grant No. RR01811) and used on a 386 PC. The goodness of the fit was established by computer subtraction of the observed and simulated spectra in digital form to obtain a linear residual to within 2% of the total spectrum.

2.3.3 X-ray Crystallographic Data

X-ray data were collected and analyzed by Drs. J. Trotter and R. Jones. Intensity measurements were made on a Rigaku AFC6S diffractometer using graphite monochromatized Mo Kα radiation. Samples were mounted in 0.5 mm o.d. quartz capillaries and sealed under N₂.
2.3.4 **UV-Visible Spectra**

Two types of uv-visible spectrophotometers were used. One was the Varian-Cary 5 UV-VIS-NIR double beam spectrophotometer with a mercury sulfide detector. The second was the HP Vectra System UV/VIS spectrophotometer, a single-beam instrument with an 8452A diode array detector. Spectra were acquired and manipulated on these machines using the associated software. Samples were contained in either a standard 1 x 1 x 2 cm quartz cuvette with a ground glass joint and cap or a 1 mm path length quartz cuvette attached to a tube with a B14 cone and a 4 mm Kontes stopcock (Figure 2-3).

![Figure 2-3. Cuvettes Used for UV-Visible Spectrophotometer Measurements.](image)

2.3.5 **X-ray Photoelectron Spectra**

X-ray photoelectron spectra were acquired using a Leybold MAX 200 spectrometer operating at ultra high vacuum. Unmonochromatized Mg $K_{\alpha}$ radiation at 10 kV and 20 mA was used as the excitation source. The C1s core level was measured at a pass energy of 96 eV. The Au 4f$_{7/2}$ binding energy at 83.8 eV was used as the reference. The peaks were identified by comparison to published data [9] and analyzed by Dr. P. Wong of this department. Samples were mounted on a 1 cm$^2$ x 4 mm-thick piece of aluminum, then attached to the holder under an atmosphere of N$_2$. 
2.4 Microanalysis

Microanalyses were done by Mr. P. Borda of this department and Beller Laboratories, Göttingen, Germany. Samples for melting point measurements were sealed in 2 mm o.d. glass capillaries under N₂. A typical sample size was about 1 mg. Melting points were obtained on a Gallenkamp #889339.
References

CHAPTER 3. SYNTHESIS AND CHARACTERIZATION OF Au$^{2+}$ IN THE SOLID STATE AND IN SOLUTION

3.1 Introduction

Gold tris(fluorosulfate), Au(SO$_3$F)$_3$, was first reported in 1972 [1], and is used as the starting material for all the gold compounds described in this thesis. It was prepared by the reaction of gold metal with an excess of bromine(I) fluorosulfate, and after removal of all volatiles and excess BrSO$_3$F, an intermediate was isolated and determined to be Au(SO$_3$F)$_3$·2BrSO$_3$F by weight. Heating the intermediate to 100°C produced Au(SO$_3$F)$_3$ as an orange-yellow solid. Later work by Lee showed that the intermediate was in fact Br$_3$[Au(SO$_3$F)$_4$] [2], and that Au(SO$_3$F)$_3$ prepared using this method was weakly paramagnetic, with $\mu_{\text{eff}}^{295} = 0.54$ BM [3]. The spin-only value of $\mu_{\text{eff}}^{295}$ for a gold center with one unpaired electron was calculated to be 1.73 BM. A more efficient and direct route to Au(SO$_3$F)$_3$ was also introduced by Lee—the direct oxidation of gold metal by bis(fluorosulfuryl) peroxide, S$_2$O$_6$F$_2$, in fluorosulfuric acid at ambient temperatures. The product was isolated by removing the volatile substances and solvent in vacuo [4].

Gold tris(fluorosulfate) produced by this method was diamagnetic, with $\chi_M = -146 \times 10^{-6}$ cm$^3$ mol$^{-1}$ [4]. This was consistent with a square planar and diamagnetic gold(III) center having the electron configuration [Xe]4f$^1$5d$^8$ [5]. Therefore, it seemed worthwhile to investigate the source of the weak paramagnetism found in samples of Au(SO$_3$F)$_3$ produced via the intermediate.

One explanation for the observed paramagnetism initially considered was temperature-independent paramagnetism due to 2nd order Zeeman splitting, but a magnetic study by Lee using the Gouy method to determine the magnetic behaviour of Au(SO$_3$F)$_3$ [3] showed that a sample of Au(SO$_3$F)$_3$ prepared using BrSO$_3$F followed the Curie-Weiss Law from 295 K to 100 K. Temperature independent paramagnetism which appears in one
sample of Au(SO₃F)₃ and not in another would indicate the existence of two different forms of Au(SO₃F)₃. This was unlikely, since the appearance, melting point, microanalysis, and vibrational spectra of samples prepared using the two methods were identical.

Another explanation was the presence of Br²⁺, which has a ²Π₅/₂ ground state, possibly produced by the pyrolysis of Br³⁺ in the diamagnetic intermediate Br₃[Au(SO₃F)₄], but the Au(SO₃F)₃ made via this intermediate contained no detectable bromine [1]. The Br²⁺ cation gives a well resolved resonance Raman spectrum with a characteristic band at 360 cm⁻¹. Lee did not observe this peak in samples of weakly paramagnetic Au(SO₃F)₃ [3], thus precluding the presence of Br²⁺.

The last remaining explanation for the paramagnetism is the possibility of Au²⁺, generated by the reductive elimination of SO₃F radicals from Au(SO₃F)₃ during the pyrolysis step. Loss of SO₃F radicals due to heating is rather uncommon; so far, only three binary fluorosulfates are known to do this. Silver bis(fluorosulfate), Ag(SO₃F)₂, reductively eliminates SO₃F⁻ at 215°C [6], as does the mixed-valency palladium compound PdᴵᴵPdᴵ⁴(SO₃F)₆, which decomposes at 160°C to yield Pdᴵᴵ(SO₃F)₂ and S₂O₆F₂ [7]. Xenon bis(fluorosulfate), Xe(SO₃F)₂, is also reported to reductively eliminate SO₃F radicals, which combine to form S₂O₆F₂ [8]. The two principal modes of thermal decomposition of binary fluorosulfates are:

(i) SO₃ elimination to give MFₙ or MFₙ(SO₃F)ₘ (M = Ta, Nb) [9], e.g.

\[
TaF₂(SO₃F)₃ \rightarrow TaF₃(SO₃F)₂ + SO₃
\]  

(ii) S₂O₅F₂ elimination [10], e.g.

\[
MoO(SO₃F)₄ \rightarrow MoO₂(SO₃F)₂ + S₂O₅F₂.
\]

In both of these cases the oxidation state of the metal is unchanged.

It should be noted that unusual magnetic behaviour is also observed during the synthesis of gold(III) fluoride, AuF₃. There are two methods of producing AuF₃: direct fluorination of gold metal, giving a diamagnetic product [11], and fluorination of gold
metal by BrF₃ and pyrolysis (at 180°C) of an intermediate with the composition \( \text{BrF}_2[\text{AuF}_4] \) [12], which yields a weakly paramagnetic product (\( \mu_{\text{eff}}^{295} = 0.5 \text{ BM} \)) [13].

There are very few examples of true, mononuclear Au(II) complexes [5][14]. The first was reported in 1954 by Rich and Taube, who used kinetic data to suggest that \([\text{AuCl}_4]^{2-}\) was formed in aqueous solution as a very short-lived intermediate during the reduction of \([\text{AuCl}_4]^-\) by \([\text{Fe(H}_2\text{O})_6]^{2+}\) [15]. There are reports of the possibility of Au(II) intermediates in free radical oxidations of Au(I) to Au(III), but there are no definite data to support the postulated mechanisms. It was not until 1959 that a true paramagnetic Au(II) complex, \(\text{Au(S}_2\text{CNEt}_2)_2\), was found to be stable enough for detection by ESR [16]. However, the species thought to give rise to the spectrum was not isolated. It was in 1965 that the first Au(II) complex, \((\text{Bu}_4\text{N})_2[\text{Au(S}_2\text{C}_2(\text{CN})_2)_2]\), was isolated [17].

There have been a number of mono and polynuclear compounds reported in which gold has the formal oxidation state of +2, and they can be separated into three categories:

(i) mixed valency, or "pseudo gold(II)" compounds, with linearly coordinated Au(I) (d⁸) and square planar Au(III) (d¹⁰) [5]. These compounds are diamagnetic. An example is that of AuCl₂, whose crystal structure determination showed it to be \(\text{Au}_4\text{Cl}_8\) (Figure 3-1)[18];

![Figure 3-1. Crystal Structure of \(\text{Au}_4\text{Cl}_8\)](image-url)
(ii) dimeric compounds with a gold-gold bond that renders the compound diamagnetic, e.g. \( \text{Au}_2\text{I}_2\{\mu-(\text{CH}_2)_2\text{PMe}_2\}_2 \) (Figure 3-2) \([14]\); and

![Figure 3-2. Structure of Au\(_2\)I\(_2\{\mu-(\text{CH}_2)_2\text{PMe}_2\}_2 \)](image)

(iii) monomeric \( \text{Au}(\text{II}) \) compounds with unsaturated thiolate anion ligands, e.g. \([\text{Au}(\text{mnt})_2]^{2-}\) (mnt = maleonitrile dithiolate) \([17]\). ESR data about \([\text{Au}(\text{mnt})_2]^{2-}\) have been reported, and the \( g \) values indicate that the unpaired electron is in a ligand-based orbital despite the observation of hyperfine splitting due to \(^{197}\text{Au} \left(I = \frac{3}{2}\right)\) \([19]\). There is also a carborane compound, \([\text{(C}_2\text{H}_4\text{N})_2\{\text{Au(B}_9\text{C}_2\text{H}_{11})_2\}]\), which was found to be paramagnetic, with \( \mu_{\text{eff}} = 1.79\text{BM} \), consistent with a \( d^9 \) configuration \([20]\). However, no ESR data are available to indicate whether the unpaired electron is delocalized around the gold center or the carbolide anion. A phthalocyanine complex containing \( \text{Au}(\text{II}) \) has also been reported \([21]\).

From the brief review, it appears that a true \( \text{Au}^{2+} \) center having the electron configuration \([\text{Xe}]^{4f^{14}5d^9} \), comparable to \( \text{Cu}^{2+} \) or \( \text{Ag}^{2+} \), has not been unambiguously identified. In cases where monomeric complexes of gold(II) are encountered, the ligands chosen in the past such as unsaturated dithiolates, the 1,2-dicarbolide anion, and phthalocyanine, appear to possess low lying unoccupied molecular orbitals, which allow electron delocalisation according to
anion

and hence a complex of the type

may either be viewed as a gold(II) complex or a gold(III) radical anion due to the ambiguity introduced by the vague oxidation state of the ligand.

The difficulty in obtaining Au(II) complexes can be rationalized by considering the ionization potentials of the metals in group 10: copper, silver, and gold. From the table of ionization potentials shown below (Table 3-1), it can be seen that less energy is required for gold to reach the +3 oxidation state than for copper or silver, but the most energy is required for gold to reach the +2 oxidation state.

Table 3-1. Ionization Potentials (kJ·mol\(^{-1}\)) for Group 11 Metals [22]

<table>
<thead>
<tr>
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<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>(\sum N) (_{N=1})</th>
<th>(\sum N) (_{N=1})</th>
<th>Known Positive Oxidation States*</th>
</tr>
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<tbody>
<tr>
<td>Cu</td>
<td>745</td>
<td>1958</td>
<td>3824</td>
<td>2703</td>
<td>6527</td>
<td>1, 2, 3</td>
</tr>
<tr>
<td>Ag</td>
<td>731</td>
<td>2074</td>
<td>3361</td>
<td>2805</td>
<td>6166</td>
<td>1, 2, 3</td>
</tr>
<tr>
<td>Au</td>
<td>890</td>
<td>1980</td>
<td>2943</td>
<td>2870</td>
<td>5813</td>
<td>1, (2), 3, 5</td>
</tr>
</tbody>
</table>

*most common oxidation state(s) is underscored
In square planar or distorted octahedral d⁹ complexes, the unpaired electron is in the dx²-y² orbital, which is at the highest energy level, and it should be easy to remove an electron from this orbital. Hence the +2 oxidation state for gold should be unstable, and Au(II) should disproportionate to Au(I) and Au(III).

It appears that in both instances where unusual magnetic behaviour of a supposed gold(III) compound Au(SO₃F)₃ and AuF₃ [11] was observed, their syntheses has involved a pyrolysis step. It was thought that in the preparation of Au(SO₃F)₃, a paramagnetic species was produced during this step, since the intermediate Br₃[Au(SO₃F)₄] is diamagnetic. It was decided to study the controlled pyrolysis of a diamagnetic sample of Au(SO₃F)₃ in order to obtain evidence in favour of this assumption and to detect Au²⁺ by ESR.

3.2 Syntheses

3.2.1 Pyrolysis of Au(SO₃F)₃

Au(SO₃F)₃ was prepared by the direct oxidation of the metal by S₂O₆F₂ in HSO₃F [4]. A 100 mL round bottom flask was charged with 265 mg (0.536 mmol) of Au(SO₃F)₃, evacuated, and heated at 60°C in an oil bath for one week. There was no observable change in colour from the initial bright orange, and no sublimate was visible. There was also no measurable pressure at -196°C. At room temperature, 4.9 mbar (9.8 µmol) of volatile materials were measured and removed. The temperature of the oil bath was increased to 100°C and the reactor heated for four days. An orange crystalline solid sublimed on the upper sides of the reactor. With the reactor at room temperature, 3.5 mbar (7 µmol) of volatile materials were measured and removed. The oil bath temperature was increased to 125°C and the Au(SO₃F)₃ heated for another two days. After cooling the reactor to room temperature, 2.9 mbar (5.8 µmol) of volatile materials were removed. The sublimate was scraped from the walls of the reactor and mixed with the residue, which was now slightly darker in colour. Since the pressures of the volatile
materials were low, the sublimate and residue were mixed together so that the total pressure of any volatile materials produced by further pyrolysis would be easier to measure. The mixture was heated at 125°C for another week. No more volatiles were observed at room temperature. The pyrolyzed Au(SO₃F)₃ had an overall weight loss of 17.8 mg, and microanalysis indicated that the sulfur content had decreased to 18.9% from a calculated value of 19.5%. The residue had a melting point of 138-139°C (lit. 140°C [4]). The volatile materials in the initial slow pyrolysis were at too low a pressure to be identified (at least 5 mbar pressure is needed), so two other experiments were done where the Au(SO₃F)₃ was pyrolyzed at 115°C and 145°C. The two samples were found to be ESR silent before the pyrolyses was carried out. All volatile materials (5 mbar, 0.045 mmol) were collected at room temperature; there was no measurable pressure at -196°C or -78°C. The volatile materials were identified as SO₂F₂ and SiF₄ by infrared spectroscopy [23].

3.2.2 Reduction of Au(III) to Au(II) Using Gold Metal

Approximately 3 mL HSO₃F was added to a 50 mL round bottom flask containing 255 mg Au(SO₃F)₃ (0.516 mmol) and 42 mg gold powder (0.213 mmol); the mole ratio of Au(SO₃F)₃ to gold metal was 2.42:1. The mixture was stirred at room temperature; as the Au(SO₃F)₃ dissolved, an opaque orange solution formed. Over a period of four hours the solution gradually cleared, and the colour changed to orange-red. It was then heated overnight at 65°C (ca. 10 hours). All the gold metal had dissolved, and the solution was now dark orange-brown. An orange solid precipitated after 3-4 days and was removed by vacuum filtration. The solution was pipetted into an ESR tube and spectra of the frozen liquid were taken. The solution colour was unchanged after removal of the precipitate, but the solution gradually became lighter in colour as more solid kept forming over a period of a few weeks. The filtered, dried solid was identified by microanalysis as Au(SO₃F)₂ and found to be ESR silent. It did not melt or decompose below 290°C.
<p>| | |</p>
<table>
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<tbody>
<tr>
<td>Au</td>
<td>S</td>
</tr>
<tr>
<td>Anal. calc. for O₆F₂S₂Au</td>
<td>49.85</td>
</tr>
<tr>
<td>found</td>
<td>49.50</td>
</tr>
</tbody>
</table>

3.2.3 Reaction of Cs[Au(SO₃F)₄] with Gold Metal

A 50 ml round bottom flask containing 16 mg (0.0812 mmol) gold metal was charged with 172 mg (0.237 mmol) of Cs[Au(SO₃F)₄]. The mole ratio of Cs[Au(SO₃F)₄] to gold metal was 2.9:1. Approximately 3 mL HSO₃F was added by distillation in vacuo. The Cs[Au(SO₃F)₄] dissolved to give a clear yellow solution, while the gold remained undissolved. The mixture was placed in a 60°C oil bath and heated for 5 days. No change in the mixture was observed. The temperature of the oil bath was increased to 100°C and the mixture heated for 3 days. An orange solid slowly precipitated. Unreacted gold was still visible at the bottom of the reactor, but a small amount appeared to have been consumed. The oil bath temperature was increased first to 130°C, then to 160°C, and heated for 3-4 days at each temperature. The amount of orange precipitate slowly increased. Gold metal was still present in the mixture. The reaction was repeated using a 10:1 mole ratio of Cs[Au(SO₃F)₄] to gold metal, with the same results. Neither adding more HSO₃F nor elevated temperatures could dissolve all of the metal. A suspension of the precipitate and solution was removed from the mixture using a pipette. The orange precipitate was separated from the solution by vacuum filtration, and neither solid nor solution gave rise to an ESR spectrum. The solid did not melt or decompose below 290°C. The filtered precipitate was investigated using infrared spectroscopy and the spectra were found to be consistent with Au(SO₃F)₂. Microanalysis of the precipitate gave poor results, possibly due to traces of gold metal.
3.3 Results and Discussion

Pyrolysis of a sample of diamagnetic Au(SO$_3$F)$_3$ allows us to see if any paramagnetic centers are generated, and if SO$_3$F radicals or S$_2$O$_6$F$_2$ are produced. Since Au(II) ($d^9$) has an unpaired electron, ESR spectroscopy is the best method for detecting low concentrations of this moiety. The pyrolysis was carried out slowly to avoid the possibility of disproportionation of the gold(II) center to gold(I) and gold(III). In addition, if any paramagnetic centers were generated, the slow pyrolysis would ensure that they were present in low concentrations. High concentrations of paramagnetic centers lead to line broadening in ESR spectroscopy, and any hyperfine structure that may be present would be obscured. The pyrolysis is followed by weight. Measurement and identification of any volatiles by infrared spectroscopy was undertaken.

The magnetic moment of the Au(SO$_3$F)$_3$ made via BrSO$_3$F is about 0.54 BM [3], well below the value of 1.73 BM (spin-only value) expected for a single unpaired electron. Thus, it appears that there is a very small concentration of paramagnetic species in the sample (calculated to be ca. 7%).

The amounts of volatile materials obtained during the initial pyrolysis were too small for identification by IR spectroscopy. Subsequently, two shorter pyrolysis experiments with larger amounts of Au(SO$_3$F)$_3$ were carried out. To ensure that the volatile materials produced at different temperatures were the same, one sample was heated at 115°C and another at 145°C. The melting point of Au(SO$_3$F)$_3$ is reported to be 140°C [1], so heating a sample of Au(SO$_3$F)$_3$ at 145°C allowed us to determine whether the volatile fraction produced by decomposition of Au(SO$_3$F)$_3$ was the same as the fraction produced by pyrolysis of Au(SO$_3$F)$_3$ at 115°C. The volatile byproducts in both cases were found to be SO$_2$F$_2$ and SiF$_4$ [23], with possible traces of S$_2$O$_5$F$_2$ and S$_2$O$_6$F$_2$. In spite of our efforts, we could not detect any evidence for dioxygen, O$_2$, which is a possible decomposition product.
Since evidence of SO₃F radicals was found in the ESR spectra of the pyrolyzed solid (vide infra), it seemed likely that SO₂F₂ and SiF₄ were formed by the reaction between SO₃F radicals and the glass reactor. It has been reported that SO₃F⁻ attacks glass at temperatures above 120°C [24]. To confirm that a net loss of SO₃F⁻ or its dimer S₂O₆F₂ had occurred during the pyrolysis, the solid residue from the sample that had been heated at 115°C was dissolved in HSO₃F and S₂O₆F₂ was added. After removal of the acid, excess peroxide, and all volatile materials in vacuo, the re-oxidized residue was found to have increased in weight by ca. 5.7%. Microanalysis of the residue showed it to be Au(SO₃F)₃, and it was ESR silent. The overall weight loss after the pyrolysis was 6.3%; re-oxidation of the residue resulted in a weight gain of 5.7%. The "missing" 0.6% is probably due to glass attack, since SiF₄ was found in the infrared spectrum of the volatiles during the pyrolysis.

Gold tris(fluorosulfate) is also easily reduced by gold metal in HSO₃F. When a mole ratio of 2.4:1 of Au(SO₃F)₃ to Au(s) is used, with enough HSO₃F to dissolve the Au(SO₃F)₃, the gold powder was completely consumed within 24 h, and the colour of the solution changed from clear orange to opaque dark brown. The frozen brown solution gave rise to an ESR signal. Precipitation of Au(SO₃F)₂ from a sample of the brown liquid occurred slowly, and the colour of the solution became lighter as more solid formed.

3.3.1 Vibrational Spectra

3.3.1a Pyrolyzed Au(SO₃F)₃

The pyrolysis did not lead to well-defined compounds, e.g. Au(SO₃F)₂ or AuSO₃F, unlike the silver and palladium bis(fluorosulfates) mentioned earlier. A differential thermal gravimetry experiment was done by Prof. Meyer, Hannover, Germany, to observe the thermal decomposition of Au(SO₃F)₃. It was found that heating a sample of Au(SO₃F)₃ resulted in a gradual, rather than a stepwise loss of mass and ultimately led to the crucible being coated with a thin layer of gold metal.
While there was little evidence of $S_2O_6F_2$ in the infrared spectra of the volatile materials produced by the pyrolysis, and the observation of the SO$_3$F radical in the ESR spectra was sporadic at best, the re-oxidation and ESR experiments strongly suggest that the following occurs during the pyrolysis:

$$\text{Au(SO}_3\text{F)}_3 \xrightarrow{\Delta} \text{Au(SO}_3\text{F)}_{3-x} + x \text{SO}_3\text{F} \quad (3)$$

The non-stoichiometric loss of SO$_3$F may account for our inability to detect $S_2O_6F_2$, unlike the silver and palladium analogues, which lose half a mole of $S_2O_6F_2$ each [6][7]:

$$\text{Ag(SO}_3\text{F)}_2 \rightarrow \text{Ag(SO}_3\text{F)} + \frac{1}{2} \text{S}_2\text{O}_6\text{F}_2 \quad (4)$$
$$\text{Pd(SO}_3\text{F)}_3 \rightarrow \text{"Pd(SO}_3\text{F)}_2" + \frac{1}{2} \text{S}_2\text{O}_6\text{F}_2 \quad (5)$$

The temperature at which the Au(SO$_3$F)$_3$ is pyrolyzed (115°C) is also near the temperature at which $S_2O_6F_2$ starts to react with the walls of the glass reactor [24]. The potential difficulty in detecting $S_2O_6F_2$ may also be due to its reoxidizing of sublimed Au(SO$_3$F)$_{3-x}$ in the cooler parts of the reactor. Another possible decomposition product, dioxygen, was not detected; attempts to find evidence of O$_2$ using mass spectrometry were unsuccessful. If we assume that all weight loss is due to SO$_3$F (which is not entirely correct, since the presence of SiF$_4$ indicates some glass was etched away, possibly resulting in an inflated value for the weight loss), it is possible to calculate the approximate value of $x$ in Au(SO$_3$F)$_{3-x}$ ($x = 0.33$) to give Au(SO$_3$F)$_{2.67}$. This formulation has a calculated sulfur value of 18.5%, which compares very well to the value of 18.9% obtained from microanalysis.

It is interesting to note that sublimation of Au(SO$_3$F)$_3$ in a static vacuum does not produce a paramagnetic species, but the same sublimation carried out under dynamic vacuum gives an ESR signal similar to that produced by the pyrolysis.
The molecular structure of Au(SO$_3$F)$_3$ provides a possible insight into the decomposition mechanism. Au(SO$_3$F)$_3$ is dimeric [25] in the solid state, and possibly also in solution [26]. The structure of the solid shows both bridging and terminal SO$_3$F groups (Figure 3). The environment around the Au(III) center is best described as almost square planar, with long, weak Au...O contacts to adjacent groups above and below the square plane formed by gold(III) and four oxygen atoms. The four oxygen atoms bound to the gold can be separated into two pairs that are cis to each other. One pair has an Au...O bond length of 2.02 Å, the other an Au...O bond length of 1.959 Å.

Figure 3-3. Structure of Au(SO$_3$F)$_3$
This difference in Au-O bond lengths produces local $C_{2v}$ symmetry (Figure 3-4).

![Figure 3-4. Enlarged Diagram of the Au(III) Environment](image)

It seems reasonable that with the reductive elimination of SO$_3$F$^-$ (detected by ESR spectroscopy and discussed later), one of the terminal SO$_3$F groups on an adjacent dimeric unit bridges to the reduced center (Au$^{2+}$) to form oligomers, thus restoring the square planar environment. The Au$^{2+}$ center could then be considered as a lattice defect in Au(SO$_3$F)$_3$.

The loss of a sulfur containing species, e.g. SO$_3$F$^-$, should cause changes in the vibrational spectra, particularly in the fluorosulfate stretching regions. A comparison of the infrared data of pyrolyzed, sublimed, and diamagnetic Au(SO$_3$F)$_3$ is provided in Table 3-2.
Table 3-2. Infrared Spectra of Pyrolyzed, Sublimed [4], and Diamagnetic [4] 
\( \text{Au(SO}_3\text{F)}_3 \)

<table>
<thead>
<tr>
<th>pyrolyzed ( \text{Au(SO}_3\text{F)}_3 ) (cm(^{-1})), int.</th>
<th>sublimed ( \text{Au(SO}_3\text{F)}_3 ) (cm(^{-1})), int.</th>
<th>diamagnetic ( \text{Au(SO}_3\text{F)}_3 ) (cm(^{-1})), int.</th>
<th>Tentative Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1434 w</td>
<td>1435 w, sh</td>
<td>1442 m</td>
<td>( \nu \text{SO}_3 ), t</td>
</tr>
<tr>
<td>1432 m</td>
<td>1427 m, sh</td>
<td>1425 m</td>
<td>( \nu \text{SO}_3 ), br</td>
</tr>
<tr>
<td>1407 m, sh</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1381 m, b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1220 w, sh</td>
<td>1240 vs</td>
<td>( \nu \text{SO}_3 ), t</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1220 s, sh</td>
<td></td>
</tr>
<tr>
<td>1112 m, b</td>
<td>1135 ms</td>
<td>( \nu \text{SO}_3 ), br</td>
<td></td>
</tr>
<tr>
<td>1055 w, sh</td>
<td>1055 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1037 m</td>
<td>1030 m</td>
<td>960 w, sh</td>
<td>( \nu \text{S-O...Au} )</td>
</tr>
<tr>
<td>960 w, sh</td>
<td>918 m, b</td>
<td>920 s, sh</td>
<td></td>
</tr>
<tr>
<td>924 m, b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>891 m, b</td>
<td>887 m, b</td>
<td>895 s, b</td>
<td>( \nu \text{S-F} )</td>
</tr>
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<td></td>
<td>820 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>664 w</td>
<td>682 s</td>
<td>( \nu \text{Au-O + def} )</td>
</tr>
<tr>
<td>667 w, sh</td>
<td>670 s, sh</td>
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<td></td>
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<td>461 w</td>
<td>460 m</td>
<td>( \nu \text{Au-O + def} )</td>
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</table>

The vibrational bands attributed to bridging fluorosulfate groups in pyrolyzed \( \text{Au(SO}_3\text{F)}_3 \) are split compared to the same bands arising from diamagnetic \( \text{Au(SO}_3\text{F)}_3 \). This band proliferation may be due to vibrational coupling or to factor group splittings for the fluorosulfate group. The remaining bands appear unchanged.

3.3.1b \( \text{Au(SO}_3\text{F)}_2 \)

The characterization of the orange precipitate, \( \text{Au(SO}_3\text{F)}_2 \), was initially puzzling. It was found to be diamagnetic, not paramagnetic as expected for a \( d^9 \) gold(II) center. Its vibrational spectra are considerably more complex than those of other metal(II)
bis(fluorosulfates) [27]. The vibrational spectra of Au(SO$_3$F)$_3$ appear to be more suitable for comparison to those of Au(SO$_3$F)$_2$. The vibrational data for Au(SO$_3$F)$_2$ and Au(SO$_3$F)$_3$ are listed in Table 3-3.

Table 3-3. Vibrational Spectra of Au(SO$_3$F)$_2$ and Au(SO$_3$F)$_3$

<table>
<thead>
<tr>
<th>Infrared Au(SO$_3$F)$_3$ (cm$^{-1}$),int.</th>
<th>Infrared Au(SO$_3$F)$_2$ (cm$^{-1}$),int.</th>
<th>Raman Au(SO$_3$F)$_3$ $\Delta \nu$(cm$^{-1}$),int.</th>
<th>Raman Au(SO$_3$F)$_2$ $\Delta \nu$(cm$^{-1}$),int.</th>
<th>Tentative Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1442vs</td>
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<td>1449m</td>
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<td>1400vs</td>
<td>1423m,sh</td>
<td>1423m</td>
<td>$\nu$SO$_3$, br</td>
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<td></td>
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<td>1200vs</td>
<td>1227vs</td>
<td>1199w,sh</td>
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<td></td>
</tr>
<tr>
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<td>955m, sh</td>
<td>955w</td>
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<td>610w</td>
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<td>590s</td>
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<td>546m</td>
<td>541m</td>
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</tr>
<tr>
<td>460m</td>
<td>462m</td>
<td>465m</td>
<td>456m</td>
<td>$\nu$Au$^{III}$-O$_4$</td>
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<td>450m</td>
<td>450m</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>415m</td>
<td>$\rho$SO$_3$F</td>
</tr>
</tbody>
</table>
The diamagnetism of the sample presented the possibility that Au(SO₃F)₂ could be described as a mixed valency Au(I)-Au(III) complex of the form Au⁺⁺Au⁺⁺⁺⁺(SO₃F)₄. This is analogous to the formulation of AuCl₂ as Au₄Cl₈ [5]. Au(SO₃F)₂ may even have a structure akin to Au₄Cl₈, i.e. a linearly coordinated Au(I) and a square planar Au(III) center.

Examination of the vibrational data for Au⁺⁺Au⁺⁺⁺⁺(SO₃F)₄ shows that the peak positions have shifted to slightly lower frequencies relative to Au(SO₃F)₃. There is also extensive band splitting, particularly in the bridging fluorosulfate and S-F stretching regions.

The band splitting may be caused by asymmetric fluorosulfate bridging between Au(I) and Au(III). The two metal centers are expected to exhibit different acceptor abilities towards the oxygen atoms of the fluorosulfate group. It is also possible that Au(SO₃F)₂ is polymeric, and vibrational coupling among neighboring fluorosulfate groups may cause band splittings.

Additional support for the formulation of Au(SO₃F)₂ as Au⁺⁺Au⁺⁺⁺⁺(SO₃F)₄ is the tendency for Au(II) to disproportionate to Au(I) and Au(III), and the observation that diamagnetic Au⁺⁺Au⁺⁺⁺⁺(SO₃F)₄ precipitates from an ESR active (i.e. paramagnetic) species in solution.

3.3.2 Electron Spin Resonance Spectra

3.3.2a Au(SO₃F)₂.₆₇

The slow pyrolysis produced an ESR-active species. The pyrolyzed sample, Au(SO₃F)₂.₆₇, gave an axial spectrum (Figure 3-5) with no hyperfine coupling. This is unexpected, since the nuclear spin of ¹⁹⁵Au is 3/2.
The g values used to simulate the spectrum are: $g_{xx} = 2.103$, $g_{yy} = 2.093$, $g_{zz} = 2.882$, $g_{iso} = 2.359$. The "spike" seen to the right of the major feature (A) has a g value of 2.0033 and was attributed to the SO$_3$F radical [28]. This "spike" only appears in the spectra occasionally. So far, we have been unable to determine why there is no hyperfine coupling.

3.3.2b Au(SO$_3$F)$_3$ Reduced by Gold Metal

The reduction of Au(SO$_3$F)$_3$ by gold metal resulted in a brown liquid and Au$^I$Au$^{III}$(SO$_3$F)$_4$. The frozen solution was ESR-active, giving an axial ESR spectrum with a four-line hyperfine splitting pattern (Figure 3-6). A nuclear quadrupole coupling constant was necessary in the simulation, thus precluding the possibility that the splitting was due to the presence of fluorine atoms ($I=1/2$). Including the nuclear quadrupole coupling constant in the simulations gave the correct relative line intensities (Figure 3-7).
\[ g_{zz} = 2.890 \]
\[ g_{yy} = 2.093 \]
\[ g_{xx} = 2.103 \]
\[ g_{iso} = 2.362 \]

Figure 3-6. ESR Spectrum of Frozen Au\(^{2+}\) (solv)

Figure 3-7. Au\(^{2+}\) Simulations With a Nuclear Coupling Constant (a) and Without (b).
It appears that the hyperfine coupling is consistent with an $I=3/2$ nucleus, ie. $^{197}$Au. The $g$ values used in the simulation are: $g_{xx} = 2.096$, $g_{yy} = 2.103$, $g_{zz} = 2.890$, $g_{iso} = 2.363$, $A_{xx} = 145$ Mhz, $A_{yy} = 145$ Mhz, $A_{zz} = 120$ Mhz, $A_{iso} = 136.7$ Mhz. The axial form of the $g$ values ($g_{xx} = g_{yy} \neq g_{zz}$) for Au$^{2+}$ both in solution and the solid suggests the paramagnetic Au$^{2+}$ center is in an environment very much like the Au(III), i.e. approximately square planar. Further evidence of similar environments for the two metal centers is also provided by the $g_{iso}$ values of both the solid and solution, which are identical within experimental error (2.359 vs. 2.363). A comparison of the $g$ values with other known gold(II) species in the table below shows that we have obtained the highest values so far. A large $g$ value indicates that the electron may be partly localized on an atom with a large spin-orbit coupling constant.

Table 3-4. $g$ Values of Known Gold(II) Species

<table>
<thead>
<tr>
<th>Complex</th>
<th>T(K)</th>
<th>$g_{xx}$</th>
<th>$g_{yy}$</th>
<th>$g_{zz}$</th>
<th>$g_{iso}$</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(SO$<em>3$F)$</em>{3-x}$</td>
<td>103</td>
<td>2.093</td>
<td>2.103</td>
<td>2.882</td>
<td>2.359</td>
<td>this work</td>
</tr>
<tr>
<td>Au$^{2+}$ (solv)</td>
<td>103</td>
<td>2.093</td>
<td>2.103</td>
<td>2.890</td>
<td>2.362</td>
<td>this work</td>
</tr>
<tr>
<td>Au$^I$Au$^{III}$ (SO$_3$F)$_4$(solv)</td>
<td>77</td>
<td>2.065</td>
<td>2.234</td>
<td>2.656</td>
<td>2.318</td>
<td>this work</td>
</tr>
<tr>
<td>[Au(mnt)$_2$]$^{2-a}$</td>
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<td>2.0023</td>
<td>1.9947</td>
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<td></td>
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<td>Au(phthalocyanine)</td>
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<td>[21]</td>
</tr>
<tr>
<td>Ag(SO$_3$F)$_2$</td>
<td>77</td>
<td>2.072</td>
<td>2.096</td>
<td>2.407</td>
<td>2.192</td>
<td>[6]</td>
</tr>
</tbody>
</table>

$^a$[Au(mnt)$_2$]$^{2-}$ doped into [Ni(mnt)$_2$]$^{2-}$; $^b$Temperature not given; $^c$In BrSO$_3$F the $g_{iso}$ value differs slightly from the one initially reported.

Although we have not yet arrived at a definite explanation for the absence of hyperfine coupling in the solid sample and the presence of hyperfine coupling in the solution, it is possible that the difference between the two Au$^{2+}$ ESR spectra is due to a
concentration effect. In \( \text{Au}^{2+}(\text{solv}) \), the concentration of the paramagnetic species is affected by the disproportion equilibrium to produce \( \text{Au}(\text{SO}_3\text{F})_2 \). If the concentration of \( \text{Au}^{2+}(\text{solv}) \) is much smaller than \( \text{Au}^{2+}(\text{solid}) \), then it may be possible to see hyperfine coupling in the former. It should be noted that a similar observation was made during the study of \( \text{Ag}(\text{SO}_3\text{F})_2 \) [29]. The ESR spectrum of a solid sample of \( \text{Ag}(\text{SO}_3\text{F})_2 \) showed no hyperfine structure, yet a solution of \( \text{Ag}(\text{SO}_3\text{F})_2 \) in \( \text{BrSO}_3\text{F} \) gave an ESR spectrum with some hyperfine structure (Figure 3-8).

![ESR Spectra of Ag(SO₃F)₂](image)

**Figure 3-8.** ESR Spectra of \( \text{Ag}(\text{SO}_3\text{F})_2 \) in (a) the solid state, and (b) in \( \text{BrSO}_3\text{F} \)
3.3.2c \( \text{Au}^1\text{Au}^{III}(\text{SO}_3\text{F})_4 \)

A sample of diamagnetic \( \text{Au}^1\text{Au}^{III}(\text{SO}_3\text{F})_4 \), when redissolved in HSO\(_3\)F, formed a dark red-brown solution that gave rise to an asymmetric ESR spectrum (Figure 3-9). The \( g \) values used to simulate the spectrum are \( g_{xx} = 2.656 \), \( g_{yy} = 2.234 \), and \( g_{zz} = 2.065 \) (\( g_{iso} = 2.318 \)). There is evidence of hyperfine splitting due to four fluorine atoms and formulation as \( [\text{Au}(\text{SO}_3\text{F})_4]^{2-} \) is suggested. If small amounts of \( \text{Au}(\text{SO}_3\text{F})_3 \) are added, the spectrum gradually becomes more and more symmetric, and the value of \( g_{iso} \) changes from 2.318 for the asymmetric species to 2.36 (Figure 3-10). In addition, if a sample of the dark brown liquid is sealed under vacuum in a 6 mm glass tube, over two to three weeks the solution becomes lighter in colour, and the same orange solid slowly precipitated (this was confirmed by infrared spectroscopy).

\[
\begin{align*}
g_{xx} &= 2.656 \\
g_{yy} &= 2.234 \\
g_{zz} &= 2.065 \\
g_{iso} &= 2.318
\end{align*}
\]

Figure 3-9. ESR Spectrum of \( \text{Au}^1\text{Au}^{III}(\text{SO}_3\text{F})_4 \) in HSO\(_3\)F
3.3.3 Reaction of Cs[Au(SO₃F)₄] and Gold Metal

Reacting Cs[Au(SO₃F)₄] with gold metal produces an orange precipitate as well, but some metal is always present. Neither the solution nor the solid were ESR active, indicating that no Au²⁺ appears to be formed. Analysis of the orange solid by vibrational spectroscopy, and comparison of its melting point to the solid isolated from the ESR-active solution, showed it to be Au[Au(SO₃F)₄]. Au(SO₃F)₃ is acidic in HSO₃F, while Cs[Au(SO₃F)₄] is basic (*vide supra*) [2][4]. The proposed reaction for the formation of Au[Au(SO₃F)₄] from Au²⁺(solv) may be written as follows:

\[
8 \text{HSO}_3\text{F} + 2 \text{Au}^{2+}(\text{solv}) \rightleftharpoons \text{Au}^1\text{Au}^{\text{III}}(\text{SO}_3\text{F})_{4(s)} + 4 \text{H}_2\text{SO}_3\text{F}^+ \quad (6)
\]
From the above equation, it seems that a high acidium ion concentration would stabilize \( \text{Au}^{2+} \) (solv), while a high fluorosulfate anion concentration would favour formation of \( \text{Au}^1\text{Au}^{III}(\text{SO}_3\text{F})_4 \).

Similar behaviour is observed in diamagnetic silver(II) oxide, AgO [30]. The solid is formulated as Ag\(^1\)-Ag\(^{III}\), and dissolving it in strong, aqueous mineral acids forms the bright blue Ag\(^2+\) (solv), which is detectable by ESR.

### 3.4 Conclusion

Distinct evidence for the formation of Au\(^2+\) in both the liquid and solid states has been obtained via ESR. The \( g \) values are the highest reported so far, indicating electron delocalization around the Au\(^2+\) center, and not the ligands. Pyrolysis of Au\((\text{SO}_3\text{F})_3\) resulted in reductive elimination of SO\(_3\)F radicals and formation of Au\(^2+\) as lattice defects. The ESR spectrum is axial, indicating that the paramagnetic center is in a site of high symmetry. In solution, Au\(^2+\) (solv) was produced by reduction of Au\((\text{SO}_3\text{F})_3\) by gold powder, and stabilized by the acidium ion, H\(_2\text{SO}_3\)F\(^+\). The Au\(^2+\) was unstable and disproportionated to form a mixed valency solid with the empirical formula Au\((\text{SO}_3\text{F})_2\) and formulated to be Au\(^1\)Au\(^{III}\)(SO\(_3\)F\(_4\)) by infrared and Raman spectroscopy. The attempted reduction of Cs[Au\((\text{SO}_3\text{F})_4\)] by gold powder resulted in the formation of Au\(^1\)Au\(^{III}\)(SO\(_3\)F\(_4\)). Attempts to isolate pure Au(II) have been unsuccessful to date.
References


CHAPTER 4. SYNTHESIS AND CHARACTERIZATION OF [Au(CO)2][Sb2F11]

4.1 Introduction

There are few reports of stable carbonyl complexes of the group 11 elements. No thermally stable, neutral binary carbonyl compounds of copper, silver, or gold have been isolated, although matrix isolation experiments with gold have provided evidence for Au(CO)n (n = 1, 2) [1]. Copper carbonyl cations of the type Cu(CO)n+ (n = 1-4) have been generated from either copper(I) oxide or copper(I) sulfate and CO in concentrated H2SO4 [2], and are used as carbonylation catalysts in reactions with olefins, alcohols, and hydrocarbons [3]-[5].

Souma et al. have also reported the formation of [Ag(CO)2]+, which exhibited catalytic abilities similar to the Cu(I) carbonyl cations [6], and have obtained both vibrational and 13C NMR data from the copper and silver carbonyl cations [6]. However, they were unable to isolate any of these cations. Recently, Ag(CO)[B(OTeF5)4] and [Ag(CO)2][B(OTeF5)4] have been isolated by Strauss and co-workers [7][8]. Although the silver salts were characterized by X-ray crystallography, they are thermally unstable and decompose with loss of CO.

Copper and gold are the only group 11 elements known to form thermally stable carbonyl chlorides [9]. The crystal structures of both Au(CO)Cl [10] and Cu(CO)Cl [11] are known, and differ from each other in that the gold compound consists of linear monomers, whereas the copper congener is a polymeric sheet with bridging chloride atoms. A [Cu(CO)][AsF6] species [12], and other copper carbonyl derivatives [9] have been reported in addition to some silver bis(carbonyl) complexes with the formula [Ag(CO)2][M(OTeF5)4] (M = Ti, Zn) [8].

The first gold carbonyl complex, Au(CO)Cl, was prepared in 1925 by Manchot and Gall [13], and independently reported by Kharasch and Isbell [14]. Both groups passed
carbon monoxide over gold(III) chloride at temperatures varying from 50°C to 120°C. No other gold carbonyl complexes were reported until recently. Then, three were prepared in rapid succession: Au(CO)SO₃F, made by reductive carbonylation of Au(SO₃F)₃ in HSO₃F [15], [Au(CO)₂][UF₆], prepared in HF by oxidizing gold metal with UF₆ in a CO atmosphere [16], and Au(CO)Br, made by reacting Au₂Br₂ or AuBr and CO in dibromomethane. However, Au(CO)Br could not be isolated from solution [17]. Neither the fluoride nor iodide analogues are known, and attempts to prepare Au(CO)I have been reportedly unsuccessful [17].

4.2 Synthesis of [Au(CO)₂][Sb₂F₇]

Au(CO)SO₃F (0.325 mg, 1.0 mmol) was prepared as described previously [15]. Antimony pentafluoride (10 g, 46.1 mmol) and 2 mmol CO were condensed onto the Au(CO)SO₃F. The mixture was warmed to 50°C and stirred. Two liquid phases were observed, but upon warming to 75°C for one hour, one phase formed. Cooling to room temperature caused two phases to separate out again. Excess SbF₅ and the byproduct Sb₂F₉SO₃F were removed in vacuo. Pumping the residue at 80°C to constant weight produced [Au(CO)₂][Sb₂F₇] (730 mg, 1.03 mmol). The white, crystalline solid could be heated to 130°C without obvious evolution of CO and was found to melt at 156°C.

\[
\text{Anal. calc. for C}_{20}\text{F}_{11}\text{Sb}_{2}\text{Au} \quad 27.9 \quad 3.40 \quad 34.5 \\
\text{found} \quad 29.5 \quad 3.57 \quad 33.9
\]

Satisfactory elemental analysis for Au and Sb could not be obtained because of interference between the two metals.

4.3 Results and Discussion

The solvolysis of Au(CO)SO₃F in SbF₅ under a pressure of carbon monoxide resulted in the quantitative formation of [Au(CO)₂][Sb₂F₇]. The byproduct, Sb₂F₉SO₃F, was identified by infrared spectroscopy [18]. Since the volume of both the vacuum line
and the reactor were known, the amount of carbon monoxide taken up was easily
calculated and the stoichiometry of the reaction can be written as

$$\text{Au(CO)SO}_3\text{F} + 4 \text{SbF}_5 + \text{CO} \rightarrow \text{[Au(CO)2][Sb}_2\text{F}_{11}] + \text{Sb}_2\text{F}_9\text{SO}_3\text{F}$$ (1)

Bis(carbonyl)gold(I) undecafluorodiantimonate, \([\text{Au(CO)}_2][\text{Sb}_2\text{F}_{11}]\), is the fifth
gold carbonyl species to be reported. The cation, \([\text{Au(CO)}_2]^+(\text{solv})\), was first observed \textit{in situ}
during a vibrational study of the reductive carbonylation of \(\text{Au(SO}_3\text{F)}_3\) in \(\text{HSO}_3\text{F}\)
[15], but solvent removal resulted in partial substitution of CO by \(\text{SO}_3\text{F}^-\), and
\(\text{Au(CO)SO}_3\text{F}\) was isolated. The use of a less basic anion allows us to isolate
\([\text{Au(CO)}_2][\text{Sb}_2\text{F}_{11}]\). The \([\text{Au(CO)}_2]^+\) cation is also reportedly present in \([\text{Au(CO)}_2][\text{UF}_6]\)
[16], but due to its thermal instability, incomplete vibrational and microanalysis data, an
unambiguous identification is still forthcoming.

4.3.1 Vibrational Spectra

Gold in a +1 oxidation state has been shown to exhibit linear coordination, and this
is borne out by published crystal structure data of various gold(I) complexes and theoretical
bonding calculations [19][20]. Even though no molecular structure of \([\text{Au(CO)}_2][\text{Sb}_2\text{F}_{11}]\)
is available yet, we can assume that \([\text{Au(CO)}_2]^+\) will also be linear. In that case, the
cation has \(D_{\infty h}\) symmetry, and the irreducible representation is found to be

$$\Gamma_{\text{vib}} = 2\Sigma_g^+(\text{Ra}) + 2\Sigma_u^+(\text{IR}) + \Pi_g(\text{Ra}) + 2\Pi_u(\text{IR})$$ (2)

Of the seven fundamental vibrations of \([\text{Au(CO)}_2]^+\), four are observed in the
infrared spectrum and three in the Raman spectrum. Isotopic substitution using \(^{13}\text{C}\) and
\(^{18}\text{O}\) were used to ensure assignment of the bands with minimal ambiguity. The results are
summarized in Table 4-1.
Table 4-1. Infrared and Raman Data (cm\(^{-1}\)) for [Au(CO)\(_2\)]\(^+\) and Its Isotopomers

<table>
<thead>
<tr>
<th></th>
<th>[Au(CO)(_2)](^+)</th>
<th>[Au((^{13}\text{C})\text{O})(_2)](^+)</th>
<th>[Au((^{18}\text{O})\text{C})(_2)](^+)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR</td>
<td>Raman</td>
<td>IR</td>
<td>Raman</td>
<td></td>
</tr>
<tr>
<td>2605vw</td>
<td>2547</td>
<td>2545</td>
<td>(\Sigma_u^+)</td>
<td>(\nu_2+\nu_3)</td>
</tr>
<tr>
<td>2239vw</td>
<td>2187</td>
<td>2188</td>
<td>(\Sigma_u^+)</td>
<td></td>
</tr>
<tr>
<td>2254vs</td>
<td>2199</td>
<td>2203</td>
<td>(\Sigma_g^+)</td>
<td>(\nu_1)</td>
</tr>
<tr>
<td>2217s</td>
<td>2165</td>
<td>2165</td>
<td>(\Sigma_u^+)</td>
<td>(\nu_3)</td>
</tr>
<tr>
<td>2176w</td>
<td>2125</td>
<td>2125</td>
<td>(\Sigma_u^+)</td>
<td>(\nu_3',\text{^{13}C})</td>
</tr>
<tr>
<td>406m</td>
<td>392</td>
<td>403</td>
<td>(\Pi_u)</td>
<td>(\nu_6)</td>
</tr>
<tr>
<td>400vw</td>
<td>N/O(^*)</td>
<td>N/O</td>
<td>(\Sigma_g^+)</td>
<td>(\nu_2)</td>
</tr>
<tr>
<td>354w</td>
<td>348</td>
<td>344</td>
<td>(\Sigma_u^+)</td>
<td>(\nu_4)</td>
</tr>
<tr>
<td>312sh</td>
<td>303</td>
<td>308</td>
<td>(\Pi_g)</td>
<td>(\nu_5)</td>
</tr>
<tr>
<td>105</td>
<td>105</td>
<td>100</td>
<td>(\Pi_u)</td>
<td>(\nu_7)</td>
</tr>
</tbody>
</table>


not observed

The average C-O stretching frequency of [Au(CO)\(_2\)]\(^+\) in HSO\(_3\)F was found to be 2231 cm\(^{-1}\), which was unexpectedly high [15]. Solid [Au(CO)\(_2\)][Sb\(_2\)F\(_{11}\)] has an even higher CO stretching frequency (av. 2235.5 cm\(^{-1}\)). The value of \(\nu\text{CO}\) (\(\nu_3\)) for [Au(CO)\(_2\)][UF\(_6\)] is reported at 2200 cm\(^{-1}\) [16]. The carbonyl gold(I) fluorosulfate, Au(CO)SO\(_3\)F, has C-O stretching frequencies at 2196 cm\(^{-1}\) in the infrared and 2195 cm\(^{-1}\) in the Raman [15]. Monocarbonyl gold(I) chloride, Au(CO)Cl, exhibits solvent dependent infrared active C-O stretches between 2153 cm\(^{-1}\) and 2170 cm\(^{-1}\) [21] in solution, and Raman active C-O vibrations at 2183 cm\(^{-1}\) in the solid [22]. The bromine analogue, Au(CO)Br, has infrared C-O stretching frequencies between 2151 cm\(^{-1}\) and 2159 cm\(^{-1}\) that are also dependent on the solvent used [17]. No Raman data are available for Au(CO)Br. A comparison of the stretching frequencies of the above compounds indicates that \(\nu\text{CO}\) increases with decreasing basicity of the anion, i.e. Br\(^-\) < Cl\(^-\) < SO\(_3\)F\(^-\) < UF\(_6\)\(^-\) < [Sb\(_2\)F\(_{11}\)]\(^-\).

The C-O stretching frequency of [Au(CO)\(_2\)][Sb\(_2\)F\(_{11}\)] decreases to 2199 cm\(^{-1}\) from 2254 cm\(^{-1}\) in the Raman spectrum upon substitution of \(^{13}\text{C}\) for \(^{12}\text{C}\), as expected. The
linear cation has a centre of inversion and the mutual exclusion principle holds: none of the bands observed in the infrared are coincident with those in the Raman. Comparison of the observed bands to the isoelectronic and isostructural [Au(CN)2]− [23][24] was used in the assignment of [Au(CO)2]+ bands (Table 4-2).

Table 4-2. Comparison of [Au(CO)2]+ and [Au(CN)2]− Stretching Vibrations.

<table>
<thead>
<tr>
<th>[Au(CO)2]⁺</th>
<th>[Au(CN)2]⁻</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2254</td>
<td>2162</td>
<td>ν₁</td>
</tr>
<tr>
<td>400</td>
<td>440</td>
<td>ν₂</td>
</tr>
<tr>
<td>2217</td>
<td>2142</td>
<td>ν₃</td>
</tr>
<tr>
<td>354</td>
<td>426</td>
<td>ν₄</td>
</tr>
<tr>
<td>312</td>
<td>302</td>
<td>ν₅</td>
</tr>
<tr>
<td>406</td>
<td>390</td>
<td>ν₆</td>
</tr>
<tr>
<td>105</td>
<td>120</td>
<td>ν₇</td>
</tr>
</tbody>
</table>

⁹Averaged values from references [23][24]

Since the metals and counteranions are different, useful comparison of the C-O stretching frequencies as reported is of limited utility. A comparison of C-O force constants among different metal carbonyl species may be more useful, since the magnitude of the force constants are a quantitative measure of C-O bond strengths. As can be seen from Table 4-3, the C-O force constant for [Au(CO)₂][Sb₂F₁₁] is the highest, with the exception of HCO⁺. π-Backbonding is impossible in the formyl cation, HCO⁺, so the force constant of this molecule represents an upper limit and can be used as an example of a pure σ bond. The large force constant for [Au(CO)₂][Sb₂F₁₁] implies that π-back bonding is greatly reduced.
Table 4-3. Stretching Frequencies and Force Constants of CO in Some Transition Metal Carbonyls

<table>
<thead>
<tr>
<th>Compound(^a)</th>
<th>(\nu_{\text{CO}}(\text{cm}^{-1}))^b</th>
<th>(f_r(10^2\text{Nm}^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>2143</td>
<td>18.6</td>
<td>[25]</td>
</tr>
<tr>
<td>CO(^+)</td>
<td>2184</td>
<td>19.3</td>
<td>[25]</td>
</tr>
<tr>
<td>HCO(^+)</td>
<td>2184</td>
<td>21.3</td>
<td>[26]</td>
</tr>
<tr>
<td>W(CO)(_6)</td>
<td>2126</td>
<td>17.2</td>
<td>[27]</td>
</tr>
<tr>
<td>Cr(CO)(_6)</td>
<td>2119</td>
<td>17.2</td>
<td>[27]</td>
</tr>
<tr>
<td>[Re(CO)(_6)](^+)(\text{solv})</td>
<td>2197</td>
<td>18.1</td>
<td>[27]</td>
</tr>
<tr>
<td>Cu(CO)Cl(^d)</td>
<td>2157</td>
<td>18.3</td>
<td>e</td>
</tr>
<tr>
<td>[Cu(CO)](^+)[AsF(_6)](^-)</td>
<td>2180</td>
<td>19.2</td>
<td>[27]</td>
</tr>
<tr>
<td>[Ag(CO)][B(OTeF(_5))(_4)]</td>
<td>2204</td>
<td>19.6</td>
<td>[7]</td>
</tr>
<tr>
<td>Au(CO)Br(^f)</td>
<td>2153</td>
<td>N/A(^g)</td>
<td>[17][28]</td>
</tr>
<tr>
<td>Au(CO)Cl</td>
<td>2170</td>
<td>19.0</td>
<td>[21][22][29]</td>
</tr>
<tr>
<td>Au(CO)SO(_3)F</td>
<td>2196</td>
<td>19.5</td>
<td>[15]</td>
</tr>
<tr>
<td>[Au(CO)(_2)][UF(_6)]</td>
<td>2200</td>
<td>N/A</td>
<td>[16]</td>
</tr>
<tr>
<td>[Au(CO)(_2)][Sb(_2)F(_11)]</td>
<td>2235.5</td>
<td>20.1</td>
<td>this work</td>
</tr>
</tbody>
</table>

\(^a\)Spectra taken of solids unless otherwise indicated. \(^b\)The average \(\nu_1\) frequency is given for M(CO)\(_6\) species and the average C-O stretch is given for [Au(CO)\(_2\)]\(^+\) species. \(^c\)In CH\(_3\)CN. \(^d\)In argon matrix. \(^e\)H.S. Plitt, Ph.D. thesis, U. of Munich, Germany (1991). \(^f\)In CH\(_2\)Cl\(_2\). \(^g\)not available.

The force constant for CO(g) gives the bond strength of the uncomplexed molecule, and serves as the baseline value. The order of C-O bond strength in decreasing order is HCO\(^+\), [Au(CO)\(_2\)][Sb\(_2\)F\(_11\)]\(^-\), [Ag(CO)][B(OTeF\(_5\))\(_4\)], [Au(CO)\(_2\)][UF\(_6\)], Au(CO)SO\(_3\)F, CO\(^+\), [Cu(CO)][AsF\(_6\)], and Au(CO)Cl. The large value of the force constant for the C-O bond in [Au(CO)\(_2\)][Sb\(_2\)F\(_11\)] indicates that CO behaves more like a \(\sigma\) donor than a \(\pi\) acceptor. This is consistent with the discussion in the general introduction regarding Au(I).
compounds, and their tendency for linear coordination using bonds with more $\sigma$ character than $\pi$ character.

The order of anion basicity, based on the available C-O force constants, is the same as the order established from examining the C-O stretching frequencies in the infrared, i.e. $\text{Cl}^- < \text{SO}_3\text{F}^- < [\text{Sb}_2\text{F}_{11}]^-$.  

The gold carbonyl complexes differ from the copper and silver carbonyl derivatives in that the last two lose CO readily [6]-[8], while the gold carbonyl compounds are all thermally stable and easily isolated. Table 4-4 gives the melting points of various gold carbonyl compounds.

Table 4-4. Melting Points of Gold Carbonyl Derivatives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Au(CO)}_2][\text{UF}_6]$</td>
<td>80°C</td>
<td>[16]</td>
</tr>
<tr>
<td>$\text{Au(CO)}\text{Cl}$</td>
<td>110°C-114°C</td>
<td>[13]</td>
</tr>
<tr>
<td>$\text{Au(CO)}\text{SO}_3\text{F}$</td>
<td>49-50°C$^a$</td>
<td>[15]</td>
</tr>
<tr>
<td>$[\text{Au(CO)}_2][\text{Sb}<em>2\text{F}</em>{11}]$</td>
<td>130°C</td>
<td>this work</td>
</tr>
</tbody>
</table>

$^a$decomposes at 190°C

With the exception of $\text{Au(CO)}\text{Cl}$, the melting points of the carbonyl derivatives increase as the counterions become more weakly nucleophilic.

Previously reported single crystal X-ray diffraction studies of the $[\text{Sb}_2\text{F}_{11}]^-$ ion in $[\text{H}_3\text{F}_2][\text{Sb}_2\text{F}_{11}]$ [30] and $[\text{BrF}_4][\text{Sb}_2\text{F}_{11}]$ [31] indicate that the anion has $D_{4h}$ symmetry. If we assume that the anion in $[\text{Au(CO)}_2][\text{Sb}_2\text{F}_{11}]$ also has $D_{4h}$ symmetry, the irreducible representation of the normal vibrations for $[\text{Sb}_2\text{F}_{11}]^-$ is

$$\Gamma_{\text{vib}} = 4A_{1g}(\text{Ra}) + A_{1u} + 4A_{2u}(\text{IR}) + 2B_{1g}(\text{Ra}) + B_{1u} + B_{1g}(\text{Ra}) + 2B_{2u} + 4E_g(\text{Ra}) + 5E_u(\text{IR}).$$

The data for $[\text{Sb}_2\text{F}_{11}]^-$ are listed in Table 4-5.
<table>
<thead>
<tr>
<th>[Au(CO)$_2$][Sb$<em>2$F$</em>{11}$]</th>
<th>[Au($^{13}$CO)$_2$][Sb$<em>2$F$</em>{11}$]</th>
<th>[Au(C$^{18}$O)$_2$][Sb$<em>2$F$</em>{11}$]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR. Raman</td>
<td>IR. Raman</td>
<td>IR. Raman</td>
<td></td>
</tr>
<tr>
<td>713</td>
<td>714</td>
<td>713</td>
<td>$\nu_{\text{as Sb-F}}$</td>
</tr>
<tr>
<td>697</td>
<td>697</td>
<td>697</td>
<td>$\nu_{\text{s Sb-F}}$</td>
</tr>
<tr>
<td>689</td>
<td>689</td>
<td>689</td>
<td></td>
</tr>
<tr>
<td>662</td>
<td>663</td>
<td>663</td>
<td>$\nu$ Sb-F$_{4eq}$</td>
</tr>
<tr>
<td>653</td>
<td>653</td>
<td>653</td>
<td>A$_{1g}$</td>
</tr>
<tr>
<td>598</td>
<td>599</td>
<td>598</td>
<td>E$<em>g$, B$</em>{1g}$</td>
</tr>
<tr>
<td>503</td>
<td>503</td>
<td>502</td>
<td>$\nu_{\text{as Sb-F-Sb}}$</td>
</tr>
<tr>
<td>307</td>
<td>307</td>
<td>308</td>
<td>$\delta$ Sb-F$_{ax}$</td>
</tr>
<tr>
<td>293</td>
<td>293</td>
<td>293</td>
<td>A$_{1g}$</td>
</tr>
<tr>
<td>279</td>
<td>279</td>
<td>279</td>
<td>B$_{1g}$</td>
</tr>
<tr>
<td>267</td>
<td>266</td>
<td>266</td>
<td>A$_{2u}$</td>
</tr>
<tr>
<td>230</td>
<td>229</td>
<td>229</td>
<td>B$_{2g}$, E$_u$</td>
</tr>
<tr>
<td>131</td>
<td>131</td>
<td>131</td>
<td>E$_g$</td>
</tr>
</tbody>
</table>

The vibrational band positions of [Sb$_2$F$_{11}$]$^-$ in [Au(CO)$_2$][Sb$_2$F$_{11}$] are consistent with the mutual exclusion principle in that none of the infrared and Raman bands overlap. Some difficulty was encountered in the assignment of the bands, since inconsistencies were found in the previously reported vibrational spectra of [XeF][Sb$_2$F$_{11}$] [32], Cs[Sb$_2$F$_{11}$] [33], and [C$_3$F$_3$][Sb$_2$F$_{11}$] [34], particularly regarding the assignment of $\nu$Sb-F and $\nu$Sb-F-Sb.

4.3.2 $^{13}$C NMR Spectra

The isotopic substitutions and acquisition of the $^{13}$C NMR data were carried out by Prof. H. Willner, J. Schaebs, and M. Bodenbinder at the University of Hannover, Germany. Hence, only a quick summary of the results will be given.
The existence of \([\text{Au(CO)}_2]^+\text{(solv)}\) was first postulated from vibrational data obtained during the formation of \(\text{Au(CO)SO}_3\text{F}\), and the following sequence of reactions was proposed [15]:

(i) reduction of \(\text{Au(SO}_3\text{F)}_3\)
\[
\text{Au(SO}_3\text{F)}_3 + \text{CO} \rightarrow \text{Au}^+(\text{solv}) + \text{CO}_2(\text{g}) + \text{SO}_3\text{F}^-(\text{solv}) + \text{S}_2\text{O}_5\text{F}_2(\text{l}) \tag{4}
\]

(ii) formation of \([\text{Au(CO)}_2]^+\text{(solv)}\)
\[
\text{Au}^+(\text{solv}) + 2\text{CO} \rightarrow [\text{Au(CO)}_2]^+(\text{solv}) \tag{5}
\]

(iii) dissociation with CO loss
\[
[\text{Au(CO)}_2]^+(\text{solv}) \rightarrow [\text{Au(CO)}]^+(\text{solv}) + \text{CO}(\text{g}) \tag{6}
\]

(iv) reaction with \(\text{SO}_3\text{F}^-(\text{solv})\)
\[
[\text{Au(CO)}]^+(\text{solv}) + \text{SO}_3\text{F}^-(\text{solv}) \rightarrow \text{Au(CO)SO}_3\text{F(s)} \tag{7}
\]

The reduction of \(\text{Au(SO}_3\text{F)}_3\) by CO in \(\text{HSO}_3\text{F}\) was followed by $^{13}$C NMR spectroscopy in an attempt to identify intermediate species and to observe any exchange processes that could occur. All chemical shift values quoted are relative to TMS.

The $^{13}$C NMR spectra obtained of the solutions were very simple, with singlets being the only resonances observed at all times. Initially, $^{13}$CO alone was bubbled through a sample of \(\text{HSO}_3\text{F}\) and a $^{13}$C NMR spectrum recorded. A singlet at 184 ppm was observed, and attributed to small amounts of dissolved $^{13}$CO. It should be noted that the solubility of CO in \(\text{HSO}_3\text{F}\) is very low [15]. Next, a $^{13}$C NMR spectrum of a mixture of $^{13}$CO and \(\text{S}_2\text{O}_6\text{F}_2\) to in \(\text{HSO}_3\text{F}\) gave a single resonance at 125 ppm which was attributed to $^{13}$CO$_2$. Both of the chemical shift values are consistent with previous reports of $\delta^{13}$CO and $\delta^{13}$CO$_2$ in aprotic solvents [17][28][35][36], and were unchanged even though a monoprotic solvent was used in these experiments.

In the reduction of gold(III) chloride by carbon monoxide in thionyl chloride, phosgene was reported as one of the byproducts [37]. The expected analogue in the reduction of \(\text{Au(SO}_3\text{F)}_3\) by $^{13}$CO in \(\text{HSO}_3\text{F}\), $^{13}$CO(SO$_3$F)$_2$, is not observed in the $^{13}$C NMR spectrum. It seems that this molecule is unstable, and decomposes to give $^{13}$CO$_2$. 

and S$_2$O$_5$F$_2$ [38]. The presence of both of these byproducts were confirmed by infrared spectroscopy in our study, and the amounts of these two gases was determined by PV measurements.

During the reduction of Au(SO$_3$F)$_3$ by $^{13}$CO, three singlets are initially observed: a large peak at 174 ppm, and two smaller peaks at 162 ppm and 125 ppm. At no time was any coupling of the $^{13}$C nucleus to the $^{195}$Au nucleus observed. This is also in keeping with previous reports for Au(CO)Cl [22][35]. No $^{13}$CO was detected. $^{13}$CO$_2$ is responsible for the peak at 125 ppm. Reducing the volume of solution present in the reaction vessel by pumping in vacuo removed the $^{13}$CO$_2$, which resulted in the gradual disappearance of the resonance at 125 ppm. Continued pumping resulted in the 162 ppm peak increasing in size and the 174 ppm peak decreasing. When all the solvent was removed, the white solid Au($^{13}$CO)SO$_3$F was obtained. Therefore the resonance at 174 ppm, which was initially dominant, is attributed to [Au(CO)$_2$]$^+$, while the resonance at 162 ppm, which becomes dominant at high solute concentration, can be attributed to [Au($^{13}$CO)]$^+$. This is consistent with the proposed reaction scheme for the formation of Au(CO)SO$_3$F (vide supra) [15].

The preparation of [Au(CO)$_2$][Sb$_2$F$_{11}$] involved adding SbF$_5$ to Au(CO)SO$_3$F under a pressure of CO. The $^{13}$C NMR spectrum of the solution showed a peak at 174 ppm. This was attributed to [Au($^{13}$CO)$_2$]$^+$ earlier, and appears unchanged in the sample containing SbF$_5$. Solid state magic angle spinning NMR spectroscopy of a sample of [Au($^{13}$CO)$_2$][Sb$_2$F$_{11}$](s) also exhibited a peak at 174 ppm, providing further evidence that the resonance is due to [Au($^{13}$CO)$_2$]$^+$. Evidence for exchange processes taking place between [Au($^{13}$CO)]$^+$ and [Au($^{13}$CO)$_2$]$^+$ was also found (Figure 4-1). Heating a sample of the solution containing both the 174 ppm and 162 ppm signals to 52°C from the initial temperature of 17°C caused the peaks to broaden, followed by coalescence at 37°C to a single broad peak.
Continued warming to 52°C resulted in narrowing of the signal to a sharp peak at 167 ppm.

Figure 4-1. Variable Temperature $^{13}$C NMR Spectra of a Mixture of $[\text{Au}^{(13}\text{CO})]^+$ and $[\text{Au}^{(13}\text{CO})_2]^+$ in HSO$_3$F

A kinetic study of the CO exchange between the two complexes is currently underway, which should provide some insight into the exchange mechanism.

4.4 Conclusion

$[\text{Au(CO)}_2][\text{Sb}_2\text{F}_{11}]$ has been characterized by vibrational and NMR spectroscopy. All of the fundamental vibrational frequencies of the cation were observed and assigned.
The conditions required to isolate unusual cations such as \([Au(CO)]^+\) and \([Au(CO)_2]^+\) have been determined: a very strong protonic acid (HSO₃F) is used to produce the cations and very weakly nucleophilic anions ([Sb₂F₁₁]⁻, [UF₆]⁻) are used to stabilize them. The solid \([Au(CO)_2][Sb₂F₁₁]\) is thermally stable to 130°C, and the high CO stretching frequency (ave. 2235.5 cm⁻¹) indicates very little π-back bonding. It appears that the behaviour of this new gold carbonyl compound is best described as a coordination compound where the CO molecule acts as a ligand, and not as a π-acceptor as is found in the classical transition metal carbonyls.
References


CHAPTER 5. CRYSTAL AND MOLECULAR STRUCTURE OF [Au(NCCH₃)₂][SbF₆]

Introduction

There are a number of crystal structures reported for gold(I) complexes in review articles [1][2]. All of these compounds have linear or nearly linear geometry around the gold center, as expected.

The gold-carbon bond in [Au(CO)₂][Sb₂F₁₁] was postulated to be weak due to greatly reduced π-backbonding (vide supra). This suggests that a donor molecule should be able to replace the CO ligands. The substitution reaction described here occurred accidentally during an attempt to recrystallize [Au(CO)₂][Sb₂F₁₁] from acetonitrile.

Synthesis

Upon the addition of an excess dry CH₃CN to -40-50 mg [Au(CO)₂][Sb₂F₁₁], immediate evolution of gas was observed; the gas was identified by infrared spectroscopy as carbon monoxide. White crystals suitable for single crystal X-ray diffraction were produced by slow solvent evaporation and were mounted into 0.5 mm o.d. quartz tubes and analyzed by Drs. R. Jones and J. Trotter of this Department. The composition of the white solid was confirmed by microanalysis.

\[
\begin{array}{ccc}
\text{C} & \text{H} & \text{N} \\
\text{Anal. calc. for } \text{C}_4\text{H}_6\text{N}_2\text{F}_6\text{SbAu} & 9.33 & 1.17 & 5.43 \\
\text{found} & 9.40 & 1.19 & 5.37 \\
\end{array}
\]

The crystal data are summarized in Table 5-1.
Table 5-1. Selected Crystallographic Data For [Au(NCCH₃)₂][SbF₆]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₄H₆N₂F₆AuSb</td>
</tr>
<tr>
<td>Formula wt</td>
<td>514.81</td>
</tr>
<tr>
<td>Crystal System</td>
<td>cubic</td>
</tr>
<tr>
<td>Space Group</td>
<td>Pα̅ (No. 205)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.250(2)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1076.9(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>T (K)</td>
<td>294</td>
</tr>
<tr>
<td>ρ₀ (g/cm⁻³)</td>
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</tr>
<tr>
<td>λ (Å)</td>
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</tr>
<tr>
<td>μ(Mo Kα) cm⁻¹</td>
<td>1614</td>
</tr>
<tr>
<td>Transmission Factors</td>
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</tr>
<tr>
<td>R</td>
<td>0.023</td>
</tr>
<tr>
<td>Rw</td>
<td>0.024</td>
</tr>
<tr>
<td>Number of independent measured reflections</td>
<td>527</td>
</tr>
<tr>
<td>Reflections with I ≤ 3σ(I)</td>
<td>147</td>
</tr>
<tr>
<td>No. of parameters refined</td>
<td>25</td>
</tr>
</tbody>
</table>
5.3 Results and Discussion

Single crystals of $[\text{Au(NCCH}_3)_2]\text{[SbF}_6]$ were obtained from the reaction of $[\text{Au(CO)}_2]\text{[Sb}_2\text{F}_{11}]$ with acetonitrile. Sulfur dioxide was initially used as the donor solvent, but bis(carbonyl)gold(I) undecafluorodiantimonate was too soluble. A mixture of SO$_2$ and SO$_2$FCl appeared to be a suitable mixed solvent system, but single crystals of $[\text{Au(CO)}_2]\text{[Sb}_2\text{F}_{11}]$ have not yet been obtained.

The use of a donor solvent such as acetonitrile successfully displaced the carbon monoxide groups according to

$$[\text{Au(CO)}_2]\text{[Sb}_2\text{F}_{11}] + 2 \text{CH}_3\text{CN} \rightarrow [\text{Au(NCCH}_3)_2]\text{[SbF}_6] + 2 \text{CO} + \text{SbF}_5 \quad (1)$$

Antimony pentafluoride has been reported to form SbF$_5$$^-$-NCCH$_3$ with acetonitrile, but in the presence of excess solvent the adduct is soluble [3] and was not isolated by us.

The ease with which CO is displaced by CH$_3$CN suggests further use of $[\text{Au(CO)}_2]\text{[Sb}_2\text{F}_{11}]$ in the synthesis of other cationic gold(I) complexes. The $[\text{Au(NCCH}_3)_2]^+$ cation has been reported previously [4] as the SbCl$_6$$^-$ salt and has been characterized by infrared spectroscopy of $[\text{Au(NCCH}_3)_2]\text{[SbCl}_6]$ [5]. The solvated $[\text{Au(NCCH}_3)_2]^+$ cation is also easily obtained by anodic oxidation of gold in acetonitrile [6][7], and its standard reduction potential is known [8].

$[\text{Au(NCCH}_3)_2]\text{[SbF}_6]$ forms clear and colourless cubic crystals that belong to the space group $\text{Pa}\bar{3}$ (205). An ORTEP diagram, along with the packing, are shown in Figures 5-1 and 5-2.
Figure 5-1. An ORTEP Diagram Showing the Atom Positions in [Au(NCCH$_3$)$_2$][SbF$_6$].

Figure 5-2. Stereoview and Packing in [Au(NCCH$_3$)$_2$][SbF$_6$].
In a cubic crystal, the sides of the unit cell are equal in length, and the cell axes are orthogonal. The gold and antimony atoms were found to be pseudo-body-centered with respect to each other. The cation \([Au(NCCH_3)_2]^+\) lies along the space diagonal of the cube that forms the unit cell; a three-fold symmetry axis is present along this line. The two methyl groups are in a staggered conformation, and the overall symmetry of the cation is \(D_{3d}\). The N-Au-N bond angles are exactly 180.0°. Since the carbon atom of the cyanide group is sp hybridized, the C-C≡N moiety must also be linear. The terminal carbon is sp\(^3\) hybridized and the hydrogens surrounding it form a tetrahedron. The bond angles, intramolecular distances, and interionic distances are given in Table 5-2.

Table 5-2. Bond Lengths (Å), Angles(°), and Interionic Distances (Å) with Estimated Standard Deviations for \([Au(NCCH_3)_2][SbF_6]\)

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Bond Angles</th>
<th>Interionic Distances(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au N 1.97(1)</td>
<td>N Au N' 180.0</td>
<td>Au F 3.455(5)</td>
</tr>
<tr>
<td>Sb F 1.841(5)</td>
<td>Au N C(1)180.0</td>
<td>Au H 3.51</td>
</tr>
<tr>
<td>N C(1) 1.08(1)</td>
<td>N C(1) C(2)180.0</td>
<td>F H 2.42</td>
</tr>
<tr>
<td>C(1) C(2) 1.47(2)</td>
<td>F Sb F' 180.0</td>
<td>F H 3.04</td>
</tr>
<tr>
<td>F Sb F'' 89.2(2)</td>
<td>F C(1) 3.179(7)</td>
<td></td>
</tr>
<tr>
<td>F Sb F''' 90.8(2)</td>
<td>F C(2) 3.122(7)</td>
<td></td>
</tr>
<tr>
<td>F N 3.181(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F H 3.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F C(1) 3.52(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F H 3.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N H 3.53</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Contacts out to 3.60 angstroms. Estimated standard deviations in the least significant figure are given in parentheses.*
The perfect linearity of the N≡C-C bond angle is unusual in that while it is expected theoretically, the same moiety in other transition metal complexes, e.g. cis- and trans-OsBr2(NCCH3)(CO)(PPh3)2, have N≡C-C bond angles of 178(2)° and 179(3)° respectively [9].

Of the complexes containing nitrogen atoms bound to gold atoms, the Au-N bond lengths vary from 2.018(22) to 2.097(38) Å [2][10]. These bond lengths are somewhat longer than the 1.97(1) Å found for [Au(NCCH3)2]+. An exception is the sodium bis(N-methylhydantoinato)gold(I) tetrahydrate, [(MeN.CO.N.CO.CH2)2Au]Na+·4H2O, where a bond length of 1.94 Å(ave) is found for Au-N [11]. Unfortunately, the light atom positions are usually of limited accuracy, so the Au-N bond lengths reported often have large estimated standard deviations (esd’s) [2].

Another feature that has been reported in linear Au-N containing complexes is short Au...Au contacts, i.e. an intramolecular Au-Au distance of less than ca. 3.5 Å [2]. The shortest distance between two gold atoms in [Au(NCCH3)2][SbF6] is 7.247 Å (a√2).

The C-N bond length in uncoordinated acetonitrile is 1.1571 Å [12]; this is slightly longer than the value of 1.08(1) Å found for [Au(NCCH3)2]+. There appears to be little π-back donation, since this would cause lengthening of the C-N bond distance to greater than 1.1571 Å.

The hexafluoroantimonate(V) anion, SbF6−, is a regular octahedron with bond angles of 90° within experimental error. Alkali metal hexafluoroantimonates are all reported to contain octahedral SbF6− [13][14][15], although the space group may not be cubic (e.g. LiSbF6 is rhombohedral [13]). The Sb-F bond distance in LiSbF6 is, at 1.877(6) Å, slightly longer than the 1.841(5) Å reported here. The SbF6− anion may be found in a site of lower than Oh symmetry when it is paired with transition metal complex cations in compounds such as [Ni(CH3CN)6](SbF6)2 [16] and [Ni(CD3CN)6](SbF6)2 [17]. In the latter case, the anion has C3 symmetry and Sb-F bond distances of 1.80(1) and
1.83(1) Å. In the former, the anion has bond lengths of 1.825(4) and 1.827(4) Å and $C_3$ symmetry as well. It is postulated that the distortion is due to site symmetry effects.

Conclusion

The weak gold-carbon bond, indicated in the high CO stretching frequency, and the proposed reduction in $\pi$-backbonding, allows the CO ligand to be easily replaced by acetonitrile, a stronger nucleophile. It can be seen from the molecular structure, with N-Au-N bonds that are exactly 180.0°, that the gold(I) center prefers linear coordination. The short C-N distances suggest reduced $\pi$-backbonding. In addition, the $\sigma$ donor orbital on the nitrogen atom of acetonitrile appears to be slightly antibonding, resulting in a stronger C-N bond upon coordination of the N atom to the gold center; this phenomenon is commonly observed in the vibrational spectra of acetonitrile complexes [11]. The SbF$_6^-$ anion has regular octahedral geometry.
References


CHAPTER 6. SYNTHESSES AND CHARACTERIZATIONS OF \([\text{Pt(CO)}_4]\)[\text{Pt(SO}_3\text{F)}_6]\),
\(\text{Pt(CO)}_2(\text{SO}_3\text{F})_2\), AND \([\text{Pt(CO)}_4]\)[\text{Sb}_2\text{F}_11\text{I}_2]\.

6.1 Introduction

Nickel tetracarbonyl was first prepared in 1890 from nickel metal and carbon monoxide, and is the first binary carbonyl reported [1]. Its formation and thermolysis is an important part of the Mond process, which is used to purify nickel. The thermally unstable platinum and palladium congeners were not prepared until much later, and could only be studied by co-condensation of the metal atoms with CO in an inert matrix between 4 and 10K [2][3]. A study of the neutral binary carbonyls of the group 10 elements using matrix isolation techniques was reported by Kündig et al. [4], and the physical and chemical properties of \(M(\text{CO})_n\) (\(M = \text{Pd, Ni, Pt; n = 1-4}\)) were compared. The thermal instability of \(\text{Pt(CO)}_4\), the reported tetrahedral geometry, and the observed C-O stretching frequencies (\(\nu_{\text{CO}}=2047.8\ \text{cm}^{-1}(\text{IR}); \Delta\nu_{\text{CO}}=2049\ \text{cm}^{-1}(\text{Ra,dp})\)) [4], differ substantially from the data obtained for the platinum carbonyl compounds reported in this thesis.

The continued interest in platinum and palladium carbonyl complexes is due to their potential use as carbonylation catalysts in the formation of acid chlorides and esters [6]. Platinum carbonyl complexes are many and varied [5][6]. Our interest lies with the platinum carbonyl halides. The first metal carbonyl complexes ever made were a series of platinum carbonyl chlorides, obtained by Schützenberger in 1870 [7]. He isolated three interconvertible products by sublimation: two yellow, flaky compounds analyzed as \(\text{Pt(CO)}\)\(_2\text{Cl}_2\) (mp 192°C), \(\text{Pt}_2(\text{CO})_3\)\(_4\) (mp 130°C), and white needles, found to be \(\text{Pt(CO)}_2\)\(_2\text{Cl}_2\) (mp 142°C). Schützenberger also reported the facile reactions of the platinum carbonyl chlorides with ammonia, ethylene, and phosphorus chlorides [8][9].

The bromo and iodo carbonyl halides, \(\text{Pt(CO)}\)\(_2\text{Br}_2\) and \(\text{Pt(CO)}\)\(_2\text{I}_2\), were reported by Mylius and Foerster some twenty years later [10][11]. The analogues were prepared by
dissolving Pt(CO)Cl₂ in HX (X = Br, I), followed by recrystallisation from benzene. A similar approach has been used by Calderazzo [12] to synthesize Pt(CO)₂X₂ (X = Br, I). These methods of preparing platinum carbonyl halides require forcing conditions, i.e. carbon monoxide pressures up to 210 atmospheres and temperatures exceeding 100°C [6][12]. However, under these conditions the monomeric carbonyl halides lose CO and form dinuclear complexes with halide bridges [13]. It has been reported that cis-Pt(CO)₂Cl₂ will not undergo this conversion if thionyl chloride is used as solvent. The fluoride analogues, Pt(CO)₆F₂, have yet to be discovered.

Most platinum carbonyl complexes have the metal in the +2 oxidation state [13]. These complexes are usually neutral, e.g. Pt(CO)X₂ (X = Cl, Br, I), or anionic, e.g. [Pt(CO)X₃]⁻ (X = Cl, Br, I) [5][13]. There are no reports of binary, square planar, cationic platinum carbonyls. Platinum carbonyl derivatives are also known where the metal is in the +1 (e.g. (P₅N₄)₂[Pt₂(CO)₂Cl₄]) [14] or +4 (e.g. [Pt(CO)Cl₅]⁻) oxidation state, but these are quite rare [5][13].

The majority of the C-O stretching frequencies of these platinum carbonyl halides lie above the value of free gaseous carbon monoxide (2143 cm⁻¹), with the exception of [Pt(CO)I₂]₂ (see Table 6-1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>νCO (cm⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(CO)₂Cl₂</td>
<td>2168-2180 cm⁻¹</td>
<td>[15]</td>
</tr>
<tr>
<td>Pt(CO)₂Br₂</td>
<td>2164 cm⁻¹ (benzene)</td>
<td>[16]</td>
</tr>
<tr>
<td>[Pt(CO)I₂]₂</td>
<td>2112 cm⁻¹</td>
<td>[17]</td>
</tr>
</tbody>
</table>

*a solvent dependent*
The high C-O stretching frequencies are reportedly caused by reduced π-backbonding and the slightly antibonding nature of the 5σ orbital used in σ donation to platinum [15].

Since Au(SO$_3$F)$_3$ in HSO$_3$F was so easily reduced by CO, it was decided to extend this approach to the Pt(SO$_3$F)$_4$/HSO$_3$F system to see if analogous platinum carbonyl complexes could be synthesized. If the analogy holds true, the new platinum carbonyl complexes should be easily prepared under mild conditions. The [Pt(CO)$_4$]$^{2+}$ cation, analogous to [Au(CO)$_2$]$^+$, should be obtainable and isolable, either in solution or as the fluoroantimonate(V) salt. The C-O stretching frequency of any platinum carbonyl complex obtained in this manner should be well above 2143 cm$^{-1}$.

6.2 Syntheses

6.2.1 Pt(CO)$_2$(SO$_3$F)$_3$

Platinum tetrakis(fluorosulfate), Pt(SO$_3$F)$_4$ (0.612 mg, 1.04 mmol), was made by the oxidation of platinum metal by S$_2$O$_6$F$_2$ in HSO$_3$F as described by Lee and Aubke [18]. A known amount of carbon monoxide (0.508 atm., 4.60 mmol) was introduced into the 100 mL round-bottom flask containing red-brown Pt(SO$_3$F)$_4$, and the mixture was magnetically stirred at room temperature. After 48 hours a bright yellow solid had formed, and the solution was lighter in colour (pale orange). The volatiles at -196°C, -78°C, and room temperature were measured, removed and identified by infrared spectroscopy as CO (excess), CO$_2$, and S$_2$O$_5$F$_2$, respectively. More CO was added to the mixture, and stirring of the mixture continued at room temperature. The addition was repeated until no more CO was taken up, the mixture consisted of a bright yellow solid in a clear yellow solution, and no more solid appeared to be formed. In each case all volatiles were measured and removed before any more CO was added. Total CO uptake was 2.75 mmol, and the mole ratio of Pt:CO was calculated to be 1:2.64 (or approximately 2:5). The product was isolated by vacuum filtration in approximately 80% yield, and was
identified by microanalysis as Pt(CO)$_2$(SO$_3$F)$_3$. It is slightly soluble in HSO$_3$F, and melts at 140°C with decomposition and evolution of gas.

<table>
<thead>
<tr>
<th>C</th>
<th>S</th>
<th>F</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.38</td>
<td>17.48</td>
<td>10.39</td>
<td>35.58</td>
</tr>
</tbody>
</table>

6.2.2 Pt(CO)$_2$(SO$_3$F)$_2$

Pt(CO)$_2$(SO$_3$F)$_2$ was prepared by reacting 0.516 atm CO with Pt(SO$_3$F)$_4$ (0.621 mg, 1.05 mmol) in HSO$_3$F in a 50 mL round-bottom flask. The mixture was stirred and heated at 80°C overnight. The colour of the solution was initially red-brown. A mixture consisting of a yellow solid and an orange solution was observed. With continued heating, the yellow solid gradually disappeared and the solution became clear and colourless. Excess HSO$_3$F was removed by slow pumping *in vacuo*, leaving a waxy, ivory, hygroscopic solid. Cooling to 0°C was necessary to prevent bumping. The CO uptake and all volatiles were measured and identified as before. The total CO uptake was 3.32 mmol. The Pt:CO ratio from gas volumetric measurements was 1:3.16. Microanalysis gave the empirical formula of the white solid as Pt(CO)$_2$(SO$_3$F)$_2$.

<table>
<thead>
<tr>
<th>C</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.34</td>
<td>14.27</td>
</tr>
</tbody>
</table>

Pt(CO)$_2$(SO$_3$F)$_2$ melts at 100°C to a translucent, creamy liquid.

6.2.3 [Pt(CO)$_4$][Sb$_2$F$_{11}$]$_2$

A sample of solid Pt(CO)$_2$(SO$_3$F)$_2$ (0.690 mg, 1.54 mmol) was weighed into a round bottom flask. Excess SbF$_5$ was added by vacuum distillation. Warming to 80°C was necessary to facilitate stirring the SbF$_5$. Only one liquid phase was observed at all times. Pt(CO)$_2$(SO$_3$F)$_2$ slowly dissolved in SbF$_5$. Carbon monoxide was admitted into the
reactor and a white solid formed immediately at the surface of the liquid. Rapid CO uptake was observed at room temperature; once the uptake slowed, the reactor was pressurized with a known amount of CO, then sealed and the mixture left stirring overnight at 80°C to ensure a complete reaction. The reaction was considered complete when no more CO was taken up; this was established by pressure measurements. Total CO uptake was 3.46 mmol, or 2.24 moles of CO per mole of Pt(CO)\(_2\)(SO\(_3\)F)\(_2\).

Alternatively, the SbF\(_5\) addition can be carried out while the Pt(CO)\(_2\)(SO\(_3\)F)\(_2\) is still in HSO\(_3\)F solution. In this case, excess SbF\(_5\) was added by condensation in vacuo, followed by CO. Two phases were initially visible; the viscous SbF\(_5\) at the bottom, and the HSO\(_3\)F on top. Stirring at room temperature combined the two layers. A white solid formed immediately upon contact with the gas. A known pressure of CO was left in the reactor overnight to ensure complete reaction. The reaction was assumed complete when there was no more CO uptake at room temperature. There were no measurable volatiles at any temperature (-196°C, -78°C, room temperature), apart from unreacted CO.

If the reaction was carried out solely in SbF\(_5\), the excess solvent can be removed by pumping at room temperature. If the reaction was carried out in HSO\(_3\)F/SbF\(_5\), the reactor must be cooled to -0°C before pumping, or the mixture will bump. Conversion of Pt(CO)\(_2\)(SO\(_3\)F)\(_2\) to [Pt(CO)\(_4\)][Sb\(_2\)F\(_{11}\)]\(_2\) was quantitative (calculated mw: 1227.4 g·mol\(^{-1}\) vs. expected mw: 1212.09 g·mol\(^{-1}\)). [Pt(CO)\(_4\)][Sb\(_2\)F\(_{11}\)]\(_2\) melts with decomposition to a brown liquid at 200°C.

\[
\begin{array}{c|c|c}
  & C & F \\
\hline
\text{Anal. calc. for } C\text{O}_4\text{F}_2\text{Sb}_4\text{Pt} & 3.96 & 34.48 \\
\text{found} & 4.33, 4.05 & 31.91, 35.6 \\
3.72 (Beller)
\end{array}
\]

N.B.: The carbon analyses were carried out by Mr. P. Borda of this department. Fluorine analyses (and one C analysis) were carried out by Beller Laboratories, Göttingen,
Germany. Here, as in the case of \([\text{Au(CO)}_2][\text{Sb}_2\text{F}_{11}]\), satisfactory elemental analysis for either Pt or Sb could not be obtained due to interference between the two metals.

6.3 Results and Discussion

6.3.1 \(\text{Pt(CO)}_2\text{(SO}_3\text{F)}_3\)

Reduction of \(\text{Pt(SO}_3\text{F)}_4\) in \(\text{HSO}_3\text{F}\) by \(\text{CO}\) is achieved under the same conditions as those used in the preparation of \(\text{Au(CO)SO}_3\text{F}\) [19] (room temperature, \(\text{ca.}~2\text{ atm CO, 8 h})\). However, the yellow product obtained was not analogous to \(\text{Au(CO)SO}_3\text{F}\). Monitoring the \(\text{CO}\) uptake indicated that \(\text{ca.}~\text{five moles of CO were required for two moles of Pt(SO}_3\text{F)}_4\). Following the reaction by weight was not possible due to the method of isolation (by filtration) and the slight solubility of the yellow solid in \(\text{HSO}_3\text{F}\). The empirical formula of the precipitate was found to be \(\text{Pt(CO)}_2\text{(SO}_3\text{F)}_3\) from microanalysis, and the reaction may be formulated as

\[
2 \text{Pt(SO}_3\text{F)}_4 + 5 \text{CO} \rightarrow 2 \text{Pt(CO)}_2\text{(SO}_3\text{F)}_3 + \text{CO}_2 + \text{S}_2\text{O}_5\text{F}_2
\]  

(1)

even though a product of the type \(\text{Pt(CO)}_2\text{X}_3\) (\(X = \text{anionic ligand}\)) is unprecedented [5][6][13].

The formation of phosgene, \(\text{COCl}_2\), is one of the by-products in the reduction of \(\text{Au(III)}\) or \(\text{Pt(IV)}\) halides by carbon monoxide [20], and the fluorosulfate analogue, \(\text{CO(SO}_3\text{F)}_2\), is expected to be produced. However, only \(\text{CO}_2\) and \(\text{S}_2\text{O}_5\text{F}_2\) are observed, and it has been postulated that \(\text{CO(SO}_3\text{F)}_2\) is unstable and decomposes [21] according to

\[
\text{CO(SO}_3\text{F)}_2 \rightarrow \text{CO}_2 + \text{S}_2\text{O}_5\text{F}_2
\]  

(2)

These byproducts were also found for the preparation of \(\text{Pt(CO)}_2\text{(SO}_3\text{F)}_2\) and identified by infrared spectroscopy.
It is noted that the mole ratio of Pt:CO is slightly higher than expected. This may arise from the presence of residual $S_2O_6F_2$ in the HSO$_3$F solution from the preparation of Pt(SO$_3$F)$_4$, which will oxidize CO to CO$_2$ according to

$$S_2O_6F_2 + CO \rightarrow CO_2 + S_2O_5F_2 \quad (3)$$

Another reason for the discrepancy between the expected and observed mole ratios may be slight inaccuracies in the determination of the vacuum line volume.

The yellow solid behaves differently from Au(CO)SO$_3$F. Pt(CO)$_2$(SO$_3$F)$_3$ cannot be sublimed and is moderately soluble in HSO$_3$F, while Au(CO)SO$_3$F is purified by sublimation and is completely soluble in HSO$_3$F. Unlike Pt(CO)$_2X_2$ (X=Cl, Br, I) [12], CO is not released upon heating Pt(CO)$_2$(SO$_3$F)$_3$; the solid merely decomposes. The decomposition products are identified by infrared spectroscopy as SiF$_4$ and SO$_2F_2$.

Pt(CO)$_2$(SO$_3$F)$_3$ appears to be an intermediate in the reductive carbynylation of Pt(SO$_3$F)$_4$ to Pt(CO)$_2$(SO$_3$F)$_2$, which is analogous to Au(CO)SO$_3$F. In the gold system, Au(SO$_3$F)$_3$ is completely reduced to [Au(CO)$_2$]$^+$ (which was detected in situ and later isolated), and solvent removal effected the loss of one mole of CO out of the three moles that were initially taken up [19]. The platinum system appears less easily reduced, and slightly more forcing conditions are needed for a complete reduction (vide infra). From these qualitative observations, it seems that gold is more readily oxidized by $S_2O_6F_2$ than platinum, and gold(III) is more readily reduced than platinum(IV). Table 6-2 lists the redox potentials [22] of the four metals that are implicated in the formation of non-classical metal carbonyl complexes.
Table 6-2. Redox Potentials of Selected Metals in Aqueous Acid*

<table>
<thead>
<tr>
<th>Metal</th>
<th>$E^0$ (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(II)/Ag(I)</td>
<td>1.98</td>
</tr>
<tr>
<td>Pd(IV)/Pd(II)</td>
<td>1.60</td>
</tr>
<tr>
<td>Au(III)/Au(I)</td>
<td>1.40</td>
</tr>
<tr>
<td>Pt(IV)/Pt(II)</td>
<td>1.10</td>
</tr>
</tbody>
</table>

*Standard aqueous acid, $a_{H^+} = 1.0$

It can be seen that the oxidizing ability of the metals decreases in the order Ag(II) > Pd(IV) > Au(III) > Pt(IV). This is consistent with the relative reaction rates of the reductive carbonylation of palladium [23], gold [19], and platinum in HSO$_3$F, all of which produce thermally stable products. The reaction of palladium(IV) fluorosulfate with CO is complete within one hour at room temperature [23]. The same reaction with gold(III) fluorosulfate takes ca. ten hours at room temperature [19], and the platinum(IV) fluorosulfate reaction with CO requires forcing conditions in order to effect a complete reduction of Pt(IV) to Pt(II).

Pt(CO)$_2$(SO$_3$F)$_3$ is diamagnetic and does not give rise to an ESR signal. This was unusual, since Pt(III) should be paramagnetic ($d^7$). This leads us to the possibility of a mixed valency Pt(II)-Pt(IV) complex, of the form [Pt(CO)$_4$][Pt(SO$_3$F)$_6$]. The formation of [Pt(CO)$_4$][Pt(SO$_3$F)$_6$] in the reductive carbonylation of Pt(SO$_3$F)$_4$ may be viewed in the following stepwise fashion in analogy to the reduction of Au(SO$_3$F)$_3$ by CO (vide supra) [19]:

(i) reduction of Pt(SO$_3$F)$_4$

$$\text{Pt}(\text{SO}_3\text{F})_4(\text{solv}) + \text{CO} \rightarrow \text{Pt}^{2+}(\text{solv}) + 2\ \text{SO}_3\text{F}^- + \text{CO}_2 + \text{S}_2\text{O}_5\text{F}_2$$  \hspace{1cm} (4)

(ii) stabilization of transient Pt$^{2+}$(solv) by complex formation

$$\text{Pt}^{2+}(\text{solv}) + 4\ \text{CO} \rightarrow [\text{Pt(CO)}_4]^{2+}$$  \hspace{1cm} (5)
(iii) complex anion formation with unreacted Pt(SO$_3$F)$_4$ [18]

\[
\text{Pt(SO}_3\text{F)}_4 + 2 \text{SO}_3\text{F}^- \rightarrow \text{[Pt(SO}_3\text{F)}_6]^{2-}} \quad (6)
\]

(iv) salt formation

\[
\text{[Pt(CO)}_4^{2+} + \text{[Pt(SO}_3\text{F)}_6]^{2-} \rightarrow \text{[Pt(CO)}_4]\text{[Pt(SO}_3\text{F)}_6]} \quad (7).
\]

The above equations only rationalize a possible pathway to the formation of [Pt(CO)$_4$][Pt(SO$_3$F)$_6$], and detailed $^{13}$C NMR studies are needed in order to unambiguously identify any intermediates.

The colour of [Pt(CO)$_4$][Pt(SO$_3$F)$_6$] (yellow) and its partial solubility in HSO$_3$F allows uv-visible and two conductivity measurements. The uv-visible spectrum of an extremely dilute solution shows broad peaks at $\lambda_{\text{max}} = 256$ nm and 300 nm. Electronic spectra of Pt(SO$_3$F)$_4$ and Cs$_2$[Pt(SO$_3$F)$_6$] in HSO$_3$F both have peaks at $\lambda_{\text{max}} = 245$ nm [18]. The peak at 256 nm can be attributed to the [Pt(SO$_3$F)$_6$]$^{2-}$ anion. The shift of this peak from 245 cm$^{-1}$ may be due to the presence of the [Pt(CO)$_4$]$^{2+}$ cation. The 300 nm peak may be tentatively attributed to [Pt(CO)$_4$]$^{2+}$. A uv-visible spectrum of HSO$_3$F shows a band below 200 cm$^{-1}$.

The observed change in conductivity of [Pt(CO)$_4$][Pt(SO$_3$F)$_6$] in HSO$_3$F was very small (ca. 1.6x10$^{-3}$ Ω$^{-1}$cm$^{-1}$). It is inconclusive from conductivity measurements alone whether the compound produces ions upon dissociation.

The anion, [Pt(SO$_3$F)$_6$]$^{2-}$, is an extremely weak nucleophile (the weakest after [SbF$_6$]$^-$, and [Sb$_2$F$_{11}$]$^-) based on $^{119}$Sn Mössbauer spectra of various (CH$_3$)$_2$Sn$^{2+}$ salts [24], and it is not entirely surprising, after the discussion of gold carbonyl cations, that the anion can stabilize the very electrophilic [Pt(CO)$_4$]$^{2+}$ cation. Formation of [Pt(CO)$_4$][Pt(SO$_3$F)$_6$] as a slightly soluble salt in HSO$_3$F is also favoured by the high lattice energy generated by two doubly charged ions. The cation was identified by vibrational and $^{13}$C NMR spectroscopy. The anion was also identified by vibrational spectroscopy and by $^{19}$F NMR spectroscopy.
6.3.1a Vibrational Spectra

The assignment of bands due to the cation in the vibrational spectra of $[\text{Pt( CO)}_4][\text{Pt(SO}_3\text{F)}_6]$ was based upon the assignments for $[\text{Pt(CN)}_4]^{2-}$ [25][26], and anion assignments were based on those for the $\text{Ba}^{2+}$ and $\text{ClO}_2^+$ salts of $[\text{Pt(SO}_3\text{F)}_6]^{2-}$ [18]. The vibrational data are shown in Table 6-3.

Identification of the cation was somewhat problematic. $[\text{Pt( CO)}_4]^{2+}$ is the first doubly charged carbonyl cation reported. The only known carbonyl cations to date are octahedral $[\text{M(CO)}_6]^+$ ($\text{M} = \text{Mn}, \text{Tc}, \text{Re}$) [27] and linear $[\text{M(CO)}_2]^+$ ($\text{M} = \text{Ag}$ [28], $\text{Au}$) (vide supra). Since there are no known square planar binary carbonyl cations, no data was available for comparison. However, the isoelectronic, square planar $[\text{Pt(CN)}_4]^{2-}$ anion is known and has been studied by infrared spectroscopy [29].

Infrared and Raman bands do not coincide, suggesting that the $[\text{Pt( CO)}_4]^{2+}$ cation has a center of symmetry. As expected, the C-O stretching frequencies of $[\text{Pt( CO)}_4][\text{Pt(SO}_3\text{F)}_6]$ are quite high, and are easily identified at 2235 cm$^{-1}$ and 2231 cm$^{-1}$ in the infrared, and 2281 cm$^{-1}$ and 2257 cm$^{-1}$ in the Raman. The degenerate $\text{E}_u$ mode in the infrared spectrum is slightly split into 2235 cm$^{-1}$ and 2231 cm$^{-1}$ peaks, observable only at high resolution (ca. 1 cm$^{-1}$). The average C-O stretching frequency of $[\text{Pt( CO)}_4][\text{Pt(SO}_3\text{F)}_6]$ is 2251 cm$^{-1}$, and is higher than $\nu\text{CO}$ for the gold species $[\text{Au( CO)}_2][\text{Sb}_2\text{F}_{11}]$, which has $\nu_{\text{av, CO}}$ at 2235.5 cm$^{-1}$.
Table 6-3. Vibrational Data for [Pt(CO)₄][Pt(SO₃F)₆], Ba[Pt(SO₃F)₆], and (ClO₂)₂[Pt(SO₃F)₆]

<table>
<thead>
<tr>
<th></th>
<th>[Pt(CO)₄][Pt(SO₃F)₆]</th>
<th>Ba[Pt(SO₃F)₆]</th>
<th>(ClO₂)₂[Pt(SO₃F)₆] b) Approx.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infrared $\nu$(cm⁻¹),int.</td>
<td>Raman $\Delta \nu$(cm⁻¹),int.</td>
<td>Raman $\Delta \nu$(cm⁻¹),int.</td>
<td>Infrared $\nu$(cm⁻¹),int.</td>
</tr>
<tr>
<td>2281 vs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2257 s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1395 vs 1385 s,sh</td>
<td>1402 s 1391 s,sh</td>
<td>1397 vw 1386 m</td>
<td>1415 vs 1378 s, sh</td>
</tr>
<tr>
<td>1230 m,sh</td>
<td>1252 vs 1216 s</td>
<td>1258 vs 1218 m</td>
<td>1245 m,sh 1215 vs</td>
</tr>
<tr>
<td>1190 s,sh</td>
<td>1192 s,sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>966 vs 928 s,sh</td>
<td>-1050 w 1006,1025 w</td>
<td>1012 w 925 s</td>
<td>968 vs</td>
</tr>
<tr>
<td>835 ms 815 s,sh</td>
<td>854 m 812 w</td>
<td>857 w 838 vw</td>
<td>825 vs 805 s,sh</td>
</tr>
<tr>
<td>805 vs</td>
<td>801 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>660 m 650 m,sh</td>
<td>633 vs 629 vs</td>
<td>629 vs 650 m</td>
<td>662 m</td>
</tr>
<tr>
<td>595 ms 560 m</td>
<td>580 vw 549 vw</td>
<td>583 vw 546 s</td>
<td>587 s</td>
</tr>
<tr>
<td>530 m 489 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>468 w,sh</td>
<td>460 vw,sh 446 s</td>
<td>460 m 452 m,sh</td>
<td>452 m,sh</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>420 vw 277 vs</td>
<td>422 vw 283 vs</td>
<td>411 w</td>
</tr>
<tr>
<td></td>
<td>446 s 269 vs</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>188 m 131 s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Ref. 18; b) Ref. 18; ClO₂⁺ bands at 1298, 1285, 1045 and 517 cm⁻¹ are omitted.
Other bands that may arise from the cation (e.g., Pt-C stretches) cannot be unambiguously identified, although the two bands at 530 cm\(^{-1}\) and 489 cm\(^{-1}\) have been tentatively assigned as Pt-C stretches in comparison to \([\text{Pt(CN)}_4]^{2-}\), where \(\nu_{\text{Pt-C}}\) is observed at 505 cm\(^{-1}\) and calculated to appear at 519 cm\(^{-1}\) [29].

Identification of the anion was carried out via vibrational spectroscopy. There is a three-peak pattern characteristic of the \([\text{Pt(SO}_3\text{F)}_6]^{2-}\) anion in the Raman spectrum. A moderately strong peak at ca. 630 cm\(^{-1}\), a weak peak at 450 cm\(^{-1}\) and another moderately strong peak at 280 cm\(^{-1}\) can be seen from Table 6-3. These bands correspond in part to the symmetrical Pt-O\(_6\) stretch, the asymmetrical Pt-O\(_6\) stretch, and the symmetric Pt-O\(_6\) deformation mode, respectively. These vibrations are shown in Figure 6-1.

![Figure 6-1. Selected Normal Vibrations of \([\text{Pt(SO}_3\text{F)}_6]^{2-}\)](image)

The S-F stretch for \([\text{Pt(SO}_3\text{F)}_6]^{2-}\) appears at ca. 800 cm\(^{-1}\) and is slightly split, but still in good agreement with the value found for ionic Ba[Pt(SO\(_3\)F\(_6\))] and (ClO\(_2\))\(_2\)[Pt(SO\(_3\)F\(_6\))] [18], suggesting that \([\text{Pt(CO)}_4][\text{Pt(SO}_3\text{F)}_6]\) may have some ionic character.

6.3.1b \(^{19}\)F and \(^{13}\)C NMR Spectra

The \(^{19}\)F NMR spectrum of \([\text{Pt(CO)}_4][\text{Pt(SO}_3\text{F)}_6]\) in HSO\(_3\)F exhibited a resonance at 47.4 ppm, which compares very well to the \(^{19}\)F NMR spectrum of Cs\(_2\)[Pt(SO\(_3\)F\(_6\))], which had a peak at 47.75 ppm [18]. A second, very intense peak found in the spectrum of \([\text{Pt(CO)}_4][\text{Pt(SO}_3\text{F)}_6]\) at 40.3 ppm was attributed to HSO\(_3\)F. Lee reported the HSO\(_3\)F
resonance at 40.77 ppm for a sample of Cs₂[Pt(SO₃F)₆] in HSO₃F [18]. In the ¹³C NMR spectrum, the isotopically labelled [Pt(¹³CO)₄][Pt(SO₃F)₆] gives a peak at 140.5 ppm. Two satellite bands are also observed, and are attributed to ¹³C-¹⁹⁵Pt coupling. The ¹³C-¹⁹⁵Pt coupling constant was found to be 1576±2 Hz. Table 6-4 gives the NMR parameters for [Pt(CO)₄][Pt(SO₃F)₆] and some similar compounds.

Table 6-4. NMR Parameters for Some Platinum Carbonyl Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ(¹³C)(ppm)</th>
<th>J(¹³C-¹⁹⁵Pt)(Hz)</th>
<th>Solvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pt(CO)₄][Pt(SO₃F)₆]</td>
<td>140.5</td>
<td>1576±2</td>
<td>HSO₃F</td>
<td>This work</td>
</tr>
<tr>
<td>Pt(CO)₂Cl₂</td>
<td>151.6</td>
<td>1576</td>
<td>C₆D₆</td>
<td>[16]</td>
</tr>
<tr>
<td>Pt(CO)₂Br₂</td>
<td>152.0</td>
<td>1566</td>
<td>C₆D₆</td>
<td>[16]</td>
</tr>
</tbody>
</table>

The coupling constant for [Pt(CO)₄][Pt(SO₃F)₆] compares very well to those for the chloride and bromide compounds, but the chemical shift is further upfield by 10-11 ppm. This may be due to the different solvents in which the compounds were dissolved. Shortening of the C-O bond due to reduced π-backbonding may also cause the chemical shift to move further upfield.

6.3.2 Pt(CO)₂(SO₃F)₂

The partial reduction of Pt(SO₃F)₄ in HSO₃F by CO was carried out at room temperature and -2 atmospheres of pressure. If the reaction temperature is increased to 80°C, the initial red-brown mixture first forms a yellow solid and an orange liquid. Further heating results in a clear, colourless solution. Removal of the solvent in vacuo leaves a waxy white solid. The empirical formula of this solid was determined by microanalysis to be Pt(CO)₂(SO₃F)₂. It melted at 100°C, with no evidence of CO loss (no gas evolution was observed). The CO uptake was monitored by pressure measurements, and the equation for the reaction can be written as
\[
\text{Pt(SO}_3\text{F)}_4 + 3 \text{CO} \rightarrow \text{Pt(CO)}_2(\text{SO}_3\text{F)}_2 + \text{CO}_2 + \text{S}_2\text{O}_5\text{F}_2 \quad (8)
\]

The mole ratio of Pt:CO for this reaction is calculated to be 1:3.16. Again, the mole ratio of Pt:CO is slightly higher than expected, and the presence of residual S\text{O}_6\text{F}_2 in Pt(SO\text{O}_3\text{F})_4 described earlier may account for this discrepancy (vide supra).

Pt(CO)_2(SO\text{O}_3\text{F})_2 was characterized by vibrational spectroscopy. The byproducts CO_2 and S\text{O}_5\text{F}_2 were obtained, as expected, and also identified by vibrational spectroscopy.

6.3.2a Vibrational Spectra

The infrared and Raman data for Pt(CO)_2(SO\text{O}_3\text{F})_2 and Pd(CO)_2(SO\text{O}_3\text{F})_2 [23] are listed in Table 6-5.

The CO stretches are easily identified. From their positions, the ligands appear to be terminally bound. Like [Pt(CO)_4][Pt(SO\text{O}_3\text{F})_6], the Pt-C stretches and CO deformation modes are obscured by SO\text{O}_3\text{F} vibrations. Two intense C-O vibrations in the infrared spectrum and one in the Raman spectrum of solid Pt(CO)_2(SO\text{O}_3\text{F})_2 suggest that the complex has the cis configuration. Overlapping infrared and Raman bands also indicate a non centrosymmetric molecule, which is consistent with cis-Pt(CO)_2(SO\text{O}_3\text{F})_2. Further support for our assignment of the vibrational spectra as being due to cis-Pt(CO)_2(SO\text{O}_3\text{F})_2 comes from the nearly superimposable vibrational spectra obtained for cis-Pd(CO)_2(SO\text{O}_3\text{F})_2, which was recently made in our research group. The structure of cis-Pd(CO)_2(SO\text{O}_3\text{F})_2 was subsequently confirmed by X-ray crystallography (Figure 6-2) [23].

The absence of vibrational bands in the 1100-1200 cm\(^{-1}\) region indicates that there are no bridging bidentate fluorosulfate groups. The fluorosulfate bands in the terminal region (1400-1250 cm\(^{-1}\)) are complex, possibly due to vibrational coupling. The S-F stretching bands, found around 800 cm\(^{-1}\) are consistent with ionic SO\text{O}_3\text{F}, and imply that the OSO\text{O}_2\text{F} groups in cis-Pt(CO)_2(SO\text{O}_3\text{F})_2 may be polar. A solution infrared spectrum of cis-Pt(CO)_2(SO\text{O}_3\text{F})_2 in HSO\text{O}_3\text{F} shows νCO shifting to higher frequency. The C-O
strectching frequencies are now found at 2224 and 2219 cm\(^{-1}\). This shift may be due to partial ionization of Pt(CO)\(_2\)(SO\(_3\)F)\(_2\) in HSO\(_3\)F.

Table 6-5. Vibrational Data for Pt(CO)\(_2\)(SO\(_3\)F)\(_2\) and Pd(CO)\(_2\)(SO\(_3\)F)\(_2\)

<table>
<thead>
<tr>
<th></th>
<th>Pt(CO)(_2)(SO(_3)F)(_2)</th>
<th>Pd(CO)(_2)(SO(_3)F)(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR, int.</td>
<td>Raman, int.</td>
<td>IR, int.</td>
</tr>
<tr>
<td>2219s</td>
<td>2219vs 2191w</td>
<td>2228ms 2212w,sh</td>
</tr>
<tr>
<td>2185vs</td>
<td>2181mw</td>
<td>2208s 2207ms</td>
</tr>
<tr>
<td>2145vw</td>
<td>2166w,sh</td>
<td></td>
</tr>
<tr>
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<td>1395s</td>
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<tr>
<td>1389s,sh</td>
<td>1380s 1376m 1378vs,sh</td>
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<td>799s</td>
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<tr>
<td>551s</td>
<td>554w 552mw</td>
<td></td>
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<tr>
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<tr>
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<td>514ms</td>
<td></td>
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<tr>
<td>436w</td>
<td>462ms 440ms 455mw</td>
<td></td>
</tr>
<tr>
<td>411vw</td>
<td>412w 417vw 405w</td>
<td></td>
</tr>
</tbody>
</table>

Tentative Assignment

- \(\nu_{sym}^{12}CO\)
- \(\nu_{as}^{12}CO\)
- \(\nu^{13}CO\)
- \(\nu_{sym}SO_2\)
- \(\nu S-O...Pt\)
- \(\nu SF\)
- \(\nu Pt-O, \delta SO_2\)
- \(\delta SO_3\)
- \(\delta Pt-CO (?)\)
- \(\nu Pt-O, \delta SO_3\)
- \(\rho SO_3F\)
Figure 6-2. Molecular Structure of Pd(CO)$_2$(SO$_3$F)$_2$ [23]
The average CO stretching frequency of cis-Pt(CO)2(SO3F)2 is, at 2201 cm⁻¹, somewhat lower than that of [Pt(CO)4][Pt(SO3F)6] (ν_{av} CO = 2251 cm⁻¹). The satellite bands at 2191 cm⁻¹ (Ra) and 2145 cm⁻¹ (IR) are attributed to ¹³CO naturally occurring in the sample. It was initially thought that these bands were due to traces of trans-Pt(CO)2(SO3F)2, since a report by Calderazzo showed that differences in CO stretching frequencies between the cis and trans forms of Pt(CO)2X2 (X = Cl, Br, I) were about 30 cm⁻¹, with the trans isomer absorbing at lower frequency [12]. The differences between peaks in our sample were about 27 cm⁻¹ and 40 cm⁻¹ in the Raman and infrared, respectively.

Similar splittings for the CO moieties are found for cis-Pd(CO)2(SO3F)2. Since the infrared spectrum of the palladium carbonyl complex is obtained from single crystal fragments, it is unlikely that our interpretation of trans-M(CO)2(SO3F)2 is correct. It is more likely that factor group effects and ν¹³C=O satellite bands are responsible for the small, low intensity bands.

cis-Pt(CO)2Cl2 was prepared by reductive carbonylation of PtCl4 in thionyl chloride [30]. The bromo and iodo analogues were prepared by halogen exchange of cis-Pt(CO)2Cl2 with HX (X=Br, I) [31]. Andreini et al. prepared the trans isomers by heating the cis isomers, causing CO loss to give a dinuclear species, and then forming trans-Pt(CO)2Cl2 by cleaving the halogen bridges using an excess of CO [31] according to

\[
2 \text{cis-Pt(CO)2Cl2} \rightarrow 2 \text{trans-Pt(CO)2Cl2}
\]

Formation of trans-Pt(CO)2Cl2 is consistent with the trans-directing influence of CO. However, the trans isomer is unstable, and can be easily converted to the cis form [31]. This synthetic approach does not appear to be available to us because reversible
CO dissociation-association does not seem to occur for the fluorosulfate and the corresponding dinuclear complex, Pt₂(CO)₂(SO₃F)₄, is not yet known.

In the preparation of Pt(CO)₂(SO₃F)₂, we postulate a different pathway for the formation of the complex. The reduction of Pt(SO₃F)₄(solv) initially forms [Pt(CO)₄]²⁺(solv) according to §C NMR. The cation is stabilized by the highly acidic conditions and excess CO. The excess CO is easily removed by pumping in vacuo, since CO is not very soluble in HSO₃F [19]. Like the gold system, CO may be displaced by SO₃F⁻ at the metal center. The formation of Pt(CO)₂(SO₃F)₂ can then be written as follows:

\[ [\text{Pt(CO)}_4]^{2+}(\text{solv}) + 2 \text{SO}_3\text{F}^- \rightarrow \text{cis-Pt(CO)}_2(\text{SO}_3\text{F})_2 + 2 \text{CO} \quad (10) \]

Substitution reactions on square planar Pt(II) complexes usually follows an associative pathway [32]. Since CO is an excellent trans-directing ligand, it is highly probable that cis-Pt(CO)₂(SO₃F)₂ is the sole product.

6.3.3 \[\text{Pt(CO)}_4\text{][Sb}_2\text{F}_{11}\text{]}_2\]

The first evidence of [Pt(CO)₄]²⁺ is obtained by the isolation and vibrational characterization of [Pt(CO)₄][Pt(SO₃F)₆] as an intermediate in the partial reduction of Pt(SO₃F)₄(solv) by CO. However, only the C-O stretching frequencies could be clearly identified; other vibrations appeared to overlap with SO₃F vibrations and deformation modes. With the successful preparation of [Pt(CO)₄][Sb₂F₁₁]₂, we hope to be able to confirm the identity of [Pt(CO)₄]²⁺.

[Pt(CO)₄][Sb₂F₁₁]₂ was prepared by dissolving Pt(CO)₂(SO₃F)₂ in excess SbF₅ in the presence of CO. The product is isolated by pumping in vacuo to constant weight; cooling of the reactor was necessary to prevent bumping. Conversion of Pt(CO)₂(SO₃F)₂ to [Pt(CO)₄][Sb₂F₁₁]₂ is quantitative. The byproduct, Sb₂F₉SO₃F, was identified by infrared spectroscopy. From the amount of CO taken up, the reaction can be written as:
\[
\text{Pt(CO)\textsubscript{2}(SO\textsubscript{3}F)\textsubscript{2} + 2 CO + 8 SbF\textsubscript{5} \rightarrow [Pt(CO)\textsubscript{4}][Sb\textsubscript{2}F\textsubscript{11}]\textsubscript{2} + 2 Sb\textsubscript{2}F\textsubscript{9}SO\textsubscript{3}F} \quad (11)
\]

[Pt(CO)\textsubscript{4}][Sb\textsubscript{2}F\textsubscript{11}]\textsubscript{2} melts with decomposition at 200°C to a brown liquid. Vibrational and X-ray photoelectron spectroscopy are used to characterize [Pt(CO)\textsubscript{4}][Sb\textsubscript{2}F\textsubscript{11}]\textsubscript{2}.

6.3.3a Vibrational Spectra

The vibrational data obtained from a sample of solid [Pt(CO)\textsubscript{4}][Sb\textsubscript{2}F\textsubscript{11}]\textsubscript{2} are listed in Table 6-6.

### Table 6-6. Vibrational Data for [Pt(CO)\textsubscript{4}][Sb\textsubscript{2}F\textsubscript{11}]\textsubscript{2}

<table>
<thead>
<tr>
<th>Infrared, int.</th>
<th>Raman, int.</th>
<th>Tentative Assignment</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>2289\textsubscript{vs}</td>
<td>(\nu\text{CO (A\textsubscript{1g})})</td>
</tr>
<tr>
<td></td>
<td>2267\textsubscript{s}</td>
<td>(\nu\text{CO (B\textsubscript{1g})})</td>
</tr>
<tr>
<td>2244\textsubscript{m}</td>
<td>(\nu\text{sym CO (E\textsubscript{u})})</td>
<td></td>
</tr>
<tr>
<td>2204\textsubscript{w}</td>
<td>(\nu\text{sym}^{13}\text{CO (E\textsubscript{u})})</td>
<td></td>
</tr>
<tr>
<td>707\textsubscript{vs}</td>
<td>(\nu\text{sym Sb-F\textsubscript{ax}})</td>
<td></td>
</tr>
<tr>
<td>688\textsubscript{vs}</td>
<td>686\textsubscript{w}</td>
<td>(\nu\text{sym Sb-F\textsubscript{4eq}})</td>
</tr>
<tr>
<td>675\textsubscript{s}</td>
<td>669\textsubscript{m}</td>
<td>(\nu\text{sym Sb-F\textsubscript{4eq}})</td>
</tr>
<tr>
<td>666\textsubscript{m}</td>
<td>657\textsubscript{m}</td>
<td>(\nu\text{sym Sb-F\textsubscript{4eq}})</td>
</tr>
<tr>
<td>604\textsubscript{w,sh}</td>
<td>649\textsubscript{m,sh}</td>
<td>(\nu\text{sym Sb-F\textsubscript{4eq}})</td>
</tr>
<tr>
<td>596\textsubscript{w}</td>
<td>594\textsubscript{w}</td>
<td>(\nu\text{sym Sb-F\textsubscript{4eq}})</td>
</tr>
<tr>
<td>517\textsubscript{m}</td>
<td>(\nu\text{Pt-CO})</td>
<td></td>
</tr>
<tr>
<td>503\textsubscript{w,sh}</td>
<td>(\delta\text{Pt-CO})</td>
<td></td>
</tr>
<tr>
<td>473\textsubscript{m}</td>
<td>305\textsubscript{w}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>231\textsubscript{w}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>140\textsubscript{w}</td>
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</tr>
</tbody>
</table>

The CO stretching frequency of [Pt(CO)\textsubscript{4}][Sb\textsubscript{2}F\textsubscript{11}]\textsubscript{2} is found at 2244 cm\textsuperscript{-1} in the infrared, and 2278 cm\textsuperscript{-1} (average) in the Raman. These are the highest values recorded so far for any metal carbonyl complex.
The observation of two CO stretching vibrations in the Raman and one in the infrared spectrum are consistent with a centrosymmetric [Pt(CO)₄]²⁺ cation with $D_{4h}$ symmetry. The non-coincidence of the infrared and Raman CO vibrations, as expected from the mutual exclusion rule, provide further support for $D_{4h}$ symmetry. The infrared bands at 517, 503, and 473 cm⁻¹ are tentatively attributed to $v_{\text{Pt-CO}}$ by analogy to the assignments for [Pt(CN)₄]²⁻ [26]. An attempt at a complete vibrational analysis is postponed pending the results of $^{13}$C and $^{18}$O isotopic substitution studies and force field calculations similar to those carried out for [Au(CO)₂][Sb₂F₁₁] (vide supra). A comparison of the CO stretching frequencies of [Pt(CO)₄][Pt(SO₃F)₆] and [Pt(CO)₄][Sb₂F₁₁]₂ shows that the C-O stretching frequency increases with decreasing nucleophilicity of the anion. The C-O stretching frequencies are unprecedentedly high, supporting the postulation made earlier that π-backbonding is minimal, more so in [Pt(CO)₄][Sb₂F₁₁]₂ for either of Pt(CO)₂(SO₃F)₂ or [Pt(CO)₄][Pt(SO₃F)₆].

Preliminary force constant calculations have been carried out for the [Pt(CO)₄]²⁺ cation [33] according to the method of Cotton and Kraihanzel [34], and the force constant is found to be 20.64 x 10² Nm⁻¹.

The [Sb₂F₁₁]⁻ vibrational bands appear in almost the same positions here as in [Au(CO)₂][Sb₂F₁₁], and assignments are based on $D_{4h}$ symmetry for the anion, analogous to the gold compound. Shifts in vibrational frequencies are probably due to the [Pt(CO)₄]²⁺ cation.

6.3.3b X-ray Photoelectron Spectra

[Pt(CO)₄][Sb₂F₁₁]₂ was analyzed by XPS. During the experiment, traces of the sample were left in the vacuum chamber and affected the instrument's ability to reattain ultra-high vacuum (UHV) conditions (pressure = 10⁻⁷ to 10⁻⁸ bar). Consequently, no other samples were analyzed.
All samples sent for XPS analysis contain some adventitious carbon in the form of hydrocarbons, and this is impossible to remove, no matter how carefully the sample is prepared [35]. This air-borne carbon is used as an internal reference, and the C1s peak appears at 284.6 eV [35]. C1s reference peak shifts can happen, and may be caused by the spectrometer. These shifts can be neglected because we usually measure the energy difference between two peaks. A C-O $\sigma$ bond increases the binding energy by 1.5 eV, and each additional $\pi$ bond increases the energy by approximately another 1.5 eV [36]. Thus, for a carbon atom triply bonded to oxygen the C1s peak should have a binding energy of 289.1 eV, or 4.5 eV greater than 284.6 eV. Figure 6-3 shows the X-ray photoelectron spectrum of [Pt(CO)$_4$][Sb$_2$F$_{11}$]$_2$ in the C1s region.

![Figure 6-3. C1s binding energy of [Pt(CO)$_4$][Sb$_2$F$_{11}$]$_2$.](image-url)
The C1s reference peak appears at 285 eV. The appearance of the peak at 290.5 eV is 5.5 eV greater than the energy of the reference peak and suggests that the carbon atom in [Pt(CO)₄][Sb₂F₁₁]₂ is triply bonded to the oxygen atom. The anion may be responsible for the slightly greater than expected energy shift.

6.3.4 Reaction of Cs[Pt(SO₃F)₅] and Cs₂[Pt(SO₃F)₆] with CO in HSO₃F

Neither Cs[Pt(SO₃F)₅] nor Cs₂[Pt(SO₃F)₆] in HSO₃F reacted with CO, even with extended reaction times, and elevated temperatures. An infrared spectrum of the solid produced in these reactions showed no CO stretch, and the melting points were identical to the literature values (as reported by Lee and Aubke) [18].

Redissolving Pt(SO₃F)₄ in HSO₃F and adding CO at room temperature yielded only a clear, colourless liquid, possibly Pt(CO)₂(SO₃F)₂. It was not isolable due to difficulties with removing all the acid. Warming the reactor caused a black film to form on the surface of the solution. If Pt(SO₃F)₄ was redissolved in HSO₃F and the mixture was heated immediately after adding carbon monoxide, the reaction proceeded through the yellow intermediate [Pt(CO)₄][Pt(SO₃F)₆], and Pt(CO)₂(SO₃F)₂ was eventually isolated as before.

6.4 Conclusion

Three new platinum carbonyl complexes have been prepared under mild reaction conditions. A highly acidic environment is suitable for stabilizing the hitherto unknown [Pt(CO)₄]²⁺ cation in solution, and the use of weakly nucleophilic anions such as [Pt(SO₃F)₆]²⁻ and [Sb₂F₁₁]⁻ allow isolation of these cations as the corresponding salts. It is possible to displace two carbon monoxide molecules by slow removal of HSO₃F from [Pt(CO)₄]²⁺(solv), and replace them with SO₃F molecules. Pt(CO)₂(SO₃F)₂ differs from the platinum carbonyl halides in that it does not appear to lose CO and form dinuclear complexes upon heating. All of the C-O stretching frequencies are very high, and this is attributed to CO behaving as a σ donor, with minimal π-backbonding.
References

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10. F. Mylius and F. Foerster, Ber. (1891) 24, 2424.
11. F. Foerster, Ber. (1891) 24, 3751.

23. C. Wang, unpublished results.


33. M. Bodenbinder, personal communication.


36. Dr. P. Wong, personal communication.
CHAPTER 7. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The investigation of the unusual magnetic behaviour of gold tris(fluorosulfate), Au(SO$_3$F)$_3$, using electron spin resonance spectroscopy led to the identification of a true Au$^{2+}$ center both in the solid state and in solution for the first time. Pyrolysis of solid Au(SO$_3$F)$_3$ reductively eliminated SO$_3$F radicals and generated Au$^{2+}$ centers as lattice defects. The pyrolysis of the diamagnetic intermediate, Br$_3$[Au(SO$_3$F)$_4$], in the preparation of Au(SO$_3$F)$_3$ via oxidation of gold metal by BrSO$_3$F may produce the Au$^{2+}$ defects, which would explain the observed weak paramagnetism in these samples. This is consistent with earlier observations that like Ag$^{2+}$, weakly paramagnetic samples of Au(SO$_3$F)$_3$ followed the Curie-Weiss Law. In HSO$_3$F solution, Au$^{2+}$(solv) was produced as an unstable intermediate in the reduction of solvated Au(SO$_3$F)$_3$ by gold metal. The Au$^{2+}$ species in solution disproportionated to give a mixed valency complex of the composition Au$^I$Au$^{III}$(SO$_3$F)$_4$.

A new gold carbonyl compound, [Au(CO)$_2$][Sb$_2$F$_{11}$], was prepared. Earlier solution studies of the reductive carbonylation of Au(SO$_3$F)$_3$ in HSO$_3$F had suggested the presence of [Au(CO)$_2$]$^+$(solv), but Au(CO)SO$_3$F was isolated instead. Solvolysis of Au(CO)SO$_3$F in SbF$_5$ in the presence of CO yields [Au(CO)$_2$][Sb$_2$F$_{11}$]. This is the first thermally stable complex with a binary, linear carbonyl cation, and it has been characterized by vibrational analysis and NMR studies. The average C-O stretching frequency is 2235.5 cm$^{-1}$, and indicates that carbon monoxide behaves primarily as a $\sigma$-donor ligand, with minimal $\pi$-backbonding. The Au-C bond is weak, and replacement of CO by donor ligands such as acetonitrile is facile, and gives [Au(NCCH$_3$)$_2$][SbF$_6$]. Crystals of [Au(NCCH$_3$)$_2$][SbF$_6$] are isolated by slow solvent evaporation, and the X-ray diffraction study shows the Au(I) center in a perfectly linear arrangement with the N-C-C moieties of the acetonitrile ligands. The SbF$_6^-$ anion is octahedral.
The reductive carbonylation procedure was applied to the Pt(SO$_3$F)$_4$/HSO$_3$F system, and three new platinum carbonyls are isolated: [Pt(CO)$_4$][Pt(SO$_3$F)$_6$], cis-Pt(CO)$_2$(SO$_3$F)$_2$, and [Pt(CO)$_4$][Sb$_2$F$_{11}$]$_2$. The reaction conditions are mild, in stark contrast to the preparation of Pt(CO)$_2$X$_2$ (X = Cl, Br, I), where elevated temperatures and high CO pressures are required.

[Pt(CO)$_4$][Pt(SO$_3$F)$_6$] is an intermediate isolated in the ambient temperature reductive carbonylation of Pt(SO$_3$F)$_4$ in HSO$_3$F, and provided the first evidence for the [Pt(CO)$_4$]$^{2+}$ cation. However, only C-O vibrations were successfully assigned due to overlap of most of the remaining vibrations with those of SO$_3$F. cis-Pt(CO)$_2$(SO$_3$F)$_2$ is analogous to Au(CO)SO$_3$F, and unlike the corresponding Pt(CO)$_2$X$_2$ (X = Cl, Br, I) compounds, does not appear to lose CO upon heating. The complete vibrational spectra of Pt(CO)$_2$(SO$_3$F)$_2$ have been reported and assigned by analogy to cis-Pd(CO)$_2$(SO$_3$F)$_2$, where a molecular structure has been obtained very recently in our laboratory.

[Pt(CO)$_4$][Sb$_2$F$_{11}$]$_2$ is the group 10 analogue of [Au(CO)$_2$][Sb$_2$F$_{11}$], and was prepared by solvolysis of Pt(CO)$_2$(SO$_3$F)$_2$ in SbF$_5$ in the presence of CO. All of the platinum carbonyl complexes exhibited extremely high average C-O stretching frequencies at 2251 cm$^{-1}$, 2201 cm$^{-1}$, and 2261 cm$^{-1}$ for [Pt(CO)$_4$][Pt(SO$_3$F)$_6$], cis-Pt(CO)$_2$(SO$_3$F)$_2$, and [Pt(CO)$_4$][Sb$_2$F$_{11}$]$_2$ respectively, and like the gold carbonyl, carbon monoxide acts as a $\sigma$ donating ligand with minimal $\pi$-backdonation, which is drastically different from its behaviour in classical transition metal carbonyls.

Our knowledge of thermally stable, cationic carbonyl derivatives of the noble metals has recently been extended by Mr. C. Wang in our group to palladium. While [Pd(CO)$_4$][Sb$_2$F$_{11}$]$_2$ and cis-Pd(CO)$_2$(SO$_3$F)$_2$ (the latter has been characterized by single crystal X-ray diffraction) are apparently isostructural to the corresponding Pt(II) compound described here, a third compound, cyclo-[Pd$_2$(\mu-CO)$_2$(SO$_3$F)$_2$, which has also been structurally characterized, is unique and is found to contain the square planar cation [Pd$_2$(\mu-CO)$_2$]$^{2+}$ with symmetrically bridging CO ligands.
This recent work provides a stark contrast to the thermally highly unstable silver carbonyl complexes of the type \( \text{Ag(CO)}_n\text{B(OTeF}_5\text{)}_4 \) \( (n = 1, 2) \) which decompose at room temperature. This would suggest that the search for other non-classical carbonyl derivatives should perhaps extend towards the left of group 10, with rhodium and iridium promising candidates, rather than to the right towards the post-transition metals.

In all work described here, as well as in the studies of the palladium systems, fluorosulfuric acid, with its wide liquid range (-88.98 to 162.7°C), has been found to be a very useful medium for stabilizing solvated cations like \([\text{M(CO)}_4]^{2+}\) \( (\text{M} = \text{Pt, Pd}) \) and \([\text{Au(CO)}_2]^+\). It should be possible to stabilize other carbonyl cations in \( \text{HSO}_3\text{F} \) by employing synthetic strategies described in this thesis. There is no reason why other metals, including non-transition metals or lanthanides, should not form carbonyl cations with unusual spectroscopic properties and bonding characteristics similar to the ones observed.

A number of additional suggestions for further work concern the following:

(i) A more complete characterization of the metal carbonyl cations by \( ^{13}\text{C} \) or heteronuclear NMR should be undertaken. The use of X-ray photoelectron spectroscopy started here should also be continued.

(ii) Synthetic use of the carbonyl cations should be extended. Substitution of CO by \( \text{CH}_3\text{CN} \) described here and the structural characterization of \([\text{Au(NCCH}_3)_2][\text{SbF}_6]\) is a promising start. All indications are that CO remains a very weak Lewis base and numerous potential ligands like phosphines, amines or organic sulfides appear to be promising candidates due to their better \( \sigma \) donating ability.

(iii) By analogy to the identification of \( \text{Au}^{2+} \) described in this thesis, the search for other metal cations in unusual oxidation states should be continued. Like \( \text{Au(SO}_3\text{F)}_3 \) and \( \text{AuF}_3 \), weak paramagnetism has been reported in samples of \( \text{PtF}_4 \) and \( \text{Pt(SO}_3\text{F)}_4 \), the cause of which is still unexplained.
(iv) A puzzling aspect of the metal carbonyl complexes still needs to be explained: why is the metal-carbon bond so stable in the derivatives of gold, platinum, and palladium, where all indications suggest only insignificant \( \pi \)-backbonding? The recently obtained structure of \( \text{cis-Pd(CO)}_2(\text{SO}_3\text{F})_2 \) provides evidence for significant intermolecular \( \text{O} \cdots \text{C} \) contacts involving oxygens from the fluorosulfate groups. In a \( \text{M}^{n+} \langle \text{CO} \rangle \) segment, \( \sigma \) donation is expected to generate a positive charge on carbon. To clarify this point more detailed molecular structure determinations need to be undertaken.