SYNTHESIS AND CHARACTERISATION OF
RUTHENIUM OCTAETHYLPOPHRYIN COMPLEXES

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the required standard.

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Abstract

The synthesis and characterisation of some higher valent Ru octaethylporphyrin complexes are discussed. These complexes, Ru(OEP)(X)(X') (X=X'=Br,Cl and X=SbF₆,X'=THF) are of the oxidation state IV and III, respectively, with either a triplet d⁴, S=1 intermediate spin ground state (for X=X'=Br, Cl) or a d⁵, S=1/2 low spin (for X=SbF₆,X'=THF) ground state. The alternative Ru^{III} or Ru^{II} π-cation radical formulations are ruled out. The first Ru-X bond frequencies (X=Br, 179 cm⁻¹; X=Cl, 289 cm⁻¹, KBr) in Ru-porphyrin systems are assigned. The ¹H NMR data indicate that contact contributions dominate the isotropic shifts but dipolar relaxation is responsible for the relaxation of the resonances observed. The metal-porphyrin π-bonding arises from ligand-to-metal charge transfer in all three complexes and the Ru^{III}(SbF₆) complex likely has a p-fluoro bridge with \( V_{Sb-F} = 650 \) cm⁻¹, Nujol. The simple preparative reactions have high yields (>80%) and the stability of these complexes make them excellent precursors for further chemistry in high-valent ruthenium porphyrins.
To
my Parents
and
Bhavini
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List of Abbreviations and Symbols

atm atmosphere
br broad
CHCl₃ chloroform
CH₂Cl₂ dichloromethane
CH₃CN acetonitrile
C₆H₆ benzene
cm⁻¹ wavenumber
°C degrees centigrade
CO carbon monoxide
D deuterium
d doublet
EtO ethoxide
EtOH ethanol
eV electron volt
FT Fourier transform
GHZ gigahertz
HBr hydrogen bromide
HCl hydrogen chloride
¹H proton
K degrees Kelvin
m multiplet
mCPBA meta-chloroperbenzoic acid
MeOH methanol
mg milligram
mL millilitres
mm millimeters
ms milliseconds
mW milliWatt
nm nanometer
OEP octaethylporphyrin dianion
PhIO iodosylbenzene
porp porphyrin dianion
PPh₃ triphenylphosphine
PR₃trialkylphosphine
ppm parts per million
PY pyridine
Ru ruthenium
s singlet
SbF₆ hexafluoroantimonate(V) anion
t triplet
THF tetrahydrofuran
TMP tetramesitylporphyrin dianion
TMS tetramethylsilane
T₁ spin lattice relaxation
TPP tetraphenylporphyrin dianion
μeff magnetic moment
ν infrared frequency
λmax absorption maximum
χ magnetic susceptibility
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I would like to thank Drs. B.R. James and D. Dolphin for their patience and support when each was needed and for showing me that chemistry is not everything in life! I also wish to thank Dr. F. Aubke and Dr. M. Camenzind for many interesting discussions on fluorine chemistry and general theoretical/practical chemistry, respectively; and lastly, my wife for her enduring love and support.
The insertion of ruthenium into the porphyrin core with triruthenium dodecacarbonyl \((\text{Ru}_3(\text{CO})_{12})\) results in a metal-carbonyl complex\(^1\) of the type \(\text{Ru}^{\text{II}}(\text{porphyrin})\text{CO}\) which, because of the usual synergic Ru-CO bonding\(^2\) effectively ties up one axial ligation position. Consequently, the early research\(^3\) in ruthenium porphyrin chemistry focused on the ligand trans to the CO since the trans effect\(^4\) labilises the ligand at this position. The porphyrins used were not the naturally occurring porphyrins (which may contain reactive vinyl groups, see Figure I.1) but instead were the easily synthesised, highly symmetric macrocycles octaethylporphyrin\(^5\) \((\text{H}_2\text{OEP})\), tetraphenylporphyrin\(^6\) \((\text{H}_2\text{TPP})\), and tetramesitylporphyrin\(^7\) \((\text{H}_2\text{TMP})\); these systems, because of their high symmetry (see Figure I.2), simplified characterisation by spectroscopic methods.

There are two known methods for the decarbonylation of Ru(porphyrin)CO complexes: photolysis of the CO precursor in donor solvents such as pyridine, acetonitrile or tetrahydrofuran leads to Ru(porp)(solvent)\(^8\) complexes that are primarily used as starting materials for other systems; or alternatively, the addition of tertiary phosphines \((\text{PR}_3)\) to the CO complex can form Ru(porp)(PR\(_3\))\(^2\) complexes.\(^9-11\) While some Ru(porp)(PR\(_3\))\(^2\) species exhibit the ability to decarbony-
Figure I.1: The heme unit of naturally occurring hemo-proteins (protoporphyrin IX dicarboxylic acid).
late aldehydes catalytically,\(^{12,13}\) \(\text{Ru}^{	ext{III}}(\text{OEP})(\text{PPh}_3)(\text{Br})\) (obtained by treating \(\text{Ru}(\text{OEP})(\text{PPh}_3)_2\) with \(\text{HBr/air}\)),\(^{14}\) when oxidised with excess meta-chloroperbenzoic acid (mCPBA) or iodosylbenzene (PhIO), forms a highly oxidised, monomeric complex containing a metal-oxo species formulated as the \(\pi\)-cation radical \([\text{O} = \text{Ru}^{	ext{IV}}(\text{OEP} \pi\text{-cation radical})]\text{Br}\). Both \(\text{Ru}^{	ext{III}}(\text{OEP})(\text{PPh}_3)(\text{Br})\) and \([\text{O} = \text{Ru}^{	ext{IV}}(\text{OEP} . . .)]\text{Br}\)\(^{15,16}\) in the presence of mCPBA or PhIO were found to activate the C-H bonds of organic substrates resulting in catalytic oxidation. As documented in Appendix A.I of this thesis, all attempts in this present study to isolate the \(\text{Ru}^{	ext{IV}} \pi\text{-cation radical complex led to a mixture of \(\text{Ru}^{	ext{IV}}\) \(\mu\)-oxo bridged "dimers" and triphenylphosphine oxide \((\text{O} = \text{PPh}_3)\) formed by oxidation of the liberated \(\text{PPh}_3\):}

\[
\text{excess mCPBA} \quad 2\text{Ru}^{	ext{III}}(\text{OEP})(\text{PPh}_3)\text{Br} \quad \longrightarrow \quad \text{Br} \quad \begin{array}{c} \text{Ru}^{	ext{IV}} \quad \text{O} \quad \text{Ru}^{	ext{IV}} \quad \text{Br} + 2 \text{O} = \text{PPh}_3 \\ \text{or} \quad \text{PhIO} \quad \end{array}
\]

\[
( \quad ) = \text{OEP}^{-2}
\]

Appendix A.I also documents the oxidation of the \(\text{Ru(OEP)} (\text{CH}_3\text{CN})_2\) complex using excess mCPBA. At either ambient (\(19^\circ\text{C}\)) or low (\(-60^\circ\text{C}\)) temperatures, the primary products were \(\mu\)-oxo dimers, indicating that the dimers are extremely stable "thermodynamic" sinks for \(\text{Ru(OEP)}\) chemistry.\(^{17}\)
Figure 1.2: Highly symmetric synthetic porphyrins used in research with model complexes.

R = CH₂CH₃, R' = H: octaethylporphyrin
R = H, R' = phenyl: tetraphenylporphyrin
R = H, R' = 2,4,6-trimethylbenzyl (or mesitylene): tetramesitylporphyrin
It was apparent that the formation of a high oxidation state complex would be greatly assisted by the formation of a Ru^{III} precursor which contained no oxidisable ligands that might interfere in the subsequent purification of any new high valent Ru(OEP) complexes. Although the chemistry of Ru(OEP) has expanded greatly from the initial work on the Co-complexes, relatively little research on ligand systems other than those noted above has been carried out until recently. Collman et al. have published in the past two years the preparation of Ru^{III}(OEP)(EtO)(EtOH) and several new Ru(OEP)(R)(R') compounds (where R=R'= alkyl, R=vacant with R'= carbene or carboxylate)\(^{17-19}\) via a novel K\(_2\)Ru\(^0\)(porp)) complex. Some of the transformations indicate that new and exciting organometallic chemistry is possible at ruthenium porphyrin centres. Also, Groves and Quinn have recently published the preparation of Ru\(^{VI}\)(TMP)(O)\(_2\)\(^{20}\) (a di-oxo complex) and noted its ability to oxidise olefins to epoxides.\(^{21}\) In light of these developments, it was hoped that the availability of a Ru^{III}(OEP)X complex (X=halide) would allow for further study of the activation of C-H bonds in organic substrates by ruthenium porphyrins. Collman et al.\(^{22}\) discovered an excellent Ru^{II} precursor that was obtained by the vacuum pyrolysis of Ru^{II}(OEP)(py)\(_2\). This novel compound, [Ru(OEP)]\(_2\), had no axial ligands and was found to be dimeric:

\[ \begin{array}{c}
\text{Ru}^{\text{II}} \equiv \equiv \text{Ru}^{\text{II}} \\
\text{OEP}^- \\
\end{array} \]
The work described in this thesis shows that upon oxidation of the dimer, novel Ru^{IV}(OEP)X_2 (X= Br, Cl) complexes are formed instead of the hoped for Ru^{III}(OEP)X complex. Although these Ru^{IV} complexes did not catalyse the oxidation of organic substrates, they did lead to the synthesis of many new ruthenium porphyrin complexes. The chemistry and characterisation of these new compounds and their conversion into other compounds will be discussed in this thesis.
References


Chapter II: EXPERIMENTAL.

A. Reagents and Solvents.

Tetrahydrofuran (BDH, analytical reagent grade), acetonitrile (Eastman, spectroscopic grade) and dichloromethane (Fisher, reagent grade) were refluxed under argon over calcium hydride (Fisher, purified grade) prior to freshly distilling into storage flasks. Toluene (Fisher, reagent grade) and hexanes (BDH, Omnisolv grade) were also distilled from calcium hydride prior to use. All the above solvents were stored over molecular sieves (MCB, 4A pellets) and THF was stored in the dark to prevent peroxide products from forming (all the above solvents were used without testing further for purity).

Pyridine (BDH, reagent grade) and benzene (Fisher, ACS grade) were stored over activated molecular sieves without any previous purification. Methanol (BDH, Omnisolv grade) and ethanol (Fisher, reagent grade) were used as obtained.

Deuterated solvents for NMR studies were also given special treatment: benzene-\textsubscript{d\textsubscript{6}} (SCI Isotopes, 99.5% D) and dichloromethane-\textsubscript{d\textsubscript{2}} (MSD Isotopes, 99.8% D) were vacuum distilled into anaerobic sample storage bottles in which activated molecular sieves had been previously prepared. The NMR solvents were freeze-pump-thawed thrice prior to use to remove any air or highly volatile impurities. The apparatus used for vacuum transfer of solvents and reagents is shown in
Figure II.1: Apparatus used for the transfer of solvents and reagents under anaerobic conditions.
Figure II.1. Methanol-d₄ (KOR Isotopes, 99.5% D) and chloroform-d₁ (MSD Isotopes, 99.8% D) were used as obtained.

Triphenylphosphine was supplied from MCB Chemical Co., sodium ethoxide was obtained from Aldrich Chemical Co. and both were used as supplied. Sodium dithionite was used as obtained in its purified grade from J.T. Baker Chemical Co. Ruthenium trichloride trihydrate was supplied on loan by Johnson Matthey Limited and octaethylporphyrin was kindly supplied by Dr. Tilak Wijesekera.

Argon was supplied from Linde and, when needed for rigorous conditions, purified by passing successively through an activated molecular sieve column and a Redox catalyst column (Fisher Scientific) to remove moisture and oxygen, respectively. Carbon monoxide was also supplied from Linde and used as obtained. Anhydrous HBr(g) was obtained from Matheson and technical grade HCl(g) was supplied by BDH Chemical Co. Nitrous oxide was supplied as the purified grade by Linde. The hydrogen halide and N₂O gases were used as supplied.

B. Physical Measurements.

Optical spectra were obtained using a Cary 17D spectrophotometer with 0.1, 0.5 and 10 mm pathlength quartz cells. Anaerobic spectra were recorded using an anaerobic spectro-
Figure II.2: An anaerobic optical cell.
photometer cell (see Figure II.2). All infrared spectra unless indicated otherwise were obtained using a Nicolet 5 DX-FT spectrometer utilising in all cases cesium iodide windows and Nujol. Nuclear magnetic resonance spectra were obtained on a Varian XL-300 FT spectrometer. Electron paramagnetic resonance measurements were made on a Varian E3 spectrometer utilising a liquid nitrogen Dewar for low temperature ($77^\circ$K) spectra. Anaerobic EPR and NMR spectra were obtained using anaerobic cells similar to that shown in Figure II.2. A Kratos-AEI MS902 mass spectrometer operating in the electron impact (70 eV), direct insertion mode at 200-300°C source temperatures was used for mass spectral data. Microanalyses were performed by Peter Borda of this department. Magnetic susceptibilities were measured using Evans' method, the data being recorded on an XL-300 NMR spectrometer. Equivalent conductivity measurements were made in CH$_3$CN, CH$_2$Cl$_2$, or CHCl$_3$ using a cell with a cell constant (K) of 1.0 cm$^{-1}$ and a RCM 15B1 Conductivity bridge from the Arthur H. Thomas Company. The resistance of the appropriate samples were measured and converted to conductivity using:

$$K \times 10^3 \text{ (conversion factor L} \rightarrow \text{cm}^3)$$

$$\text{Conductivity} = \frac{1 \times \text{concentration of solution} \times \text{measured resistance}}{}$$

High pressure chemistry was carried out using a Baskerville
and Lindsay High Pressure Hydrogenation autoclave.

C. Preparation of Ruthenium Complexes.

Dodecacarbonyltriruthenium(0) (1).

This starting material was prepared in earlier studies at a yield of 40% using Mantovani's method, but a new procedure based on Bruce's method was developed. RuCl$_3$.3H$_2$O (3 g) and methanol (200 mL) were placed into a high-pressure autoclave and stirred at 150°C under 70 atm of CO(g) for twenty-four hours. The reaction mixture was vented and filtered to yield crude Ru$_3$(CO)$_{12}$. The filtrate was then replaced into the autoclave with yet another 3 g of RuCl$_3$.3H$_2$O and repressurized under the conditions described previously. This process was continued until all available trichloride was exhausted. The crude Ru$_3$(CO)$_{12}$ was purified by extraction into hexanes using a Soxhlet apparatus and, upon cooling to -20 °C overnight, bright yellowish crystals were obtained which were filtered and air dried (80% yield).

$\nu$(CO) = 2058, 2020 and 1995 cm$^{-1}$. 
Carbonyl(ethanol)(octaethylporphyrinato)ruthenium(II) (2).

This precursor was made according to the method developed by Barley et al.\(^5\)

\[ \nu_{(CO)} = 1922 \text{ cm}^{-1}. \]

Bis(triphenylphosphine)(octaethylporphyrinato)ruthenium(II) (3).

This complex was also prepared by a literature method.\(^6\)

Analysis \( \text{C}_{72}\text{H}_{74}\text{N}_4\text{P}_2\text{Ru} \) (1158 g/mole), calculated: \( \text{C}=74.65, \text{H}=6.46, \text{N}=4.85\% \); found: \( \text{C}=74.73, \text{H}=6.50, \text{N}=4.85\% \).

NMR(\( \text{C}_6\text{D}_6 \), anaerobic): 1.70 (t), \( \text{CH}_3 \); 3.68 (q), \( \text{CH}_2 \); 4.20 (d), \( \text{o-H} \); 6.2-6.8 (m), \( \text{m-,p-H} \); 9.16 (s), meso-H.

(Triphenylphosphine)(octaethylporphyrinato)ruthenium(II) (4).

\[
\text{Ru}^{II}(\text{OEP})(\text{PPh}_3)_2 \xrightarrow{200^\circ\text{C}, 2 \text{ h}, 1 \times 10^{-5}\text{torr}} \begin{array}{c} \text{Ru}^{II}(\text{OEP})(\text{PPh}_3) \\ \text{+ (PPh}_3) \end{array}
\]

A far simpler method to prepare this compound than that published by James et al.\(^7\) is via pyrolysis of the bis-phosphine complex (3). \( \text{Ru}(\text{OEP})(\text{PPh}_3)_2 \) (100 mg, 0.1 mmoles) was placed into a 10 mm diameter test tube which has a vacuum line attachment (see Figure II.3). By use of an engraver, the particles which adhered to the walls were agitated to the
Figure II.3: Temperature-controlling oven apparatus for the vacuum pyrolysis of Ru(OEP) complexes.
bottom of the tube. The purple powder was then heated at 200°C at 1x10^{-5} torr vacuum for two hours using a temperature controlling tube oven (Kugelrohr oven from Büchi). The liberated triphenylphosphine appears as a white residue at the mouth of the oven and the five-coordinate phosphine complex remains at the bottom of the tube. (95% yield).

Analysis for C_{54}H_{59}N_{4}PRu(896 g/mole), calculated: C=72.40, H=6.59, N=6.26%; found: C=72.49, H=6.70, N=6.13%.

NMR(C_{6}D_{6}, anaerobic): 2.02 ppm (t), CH_{3}; 3.92 (q), CH_{2}; 4.45 (d), o-H; 6.45 (m), m-H; 6.68 (d), p-H; 9.50, meso-H.

MS (70 eV EI): 895 m/e, Ru(OEP)(PPh_{3})^{+}; 634, Ru(OEP)^{+}, 262, PPh_{3}^{+}.

Bromo(triphenylphosphine)(octaethylporphyrinato) ruthenium(III) (5).

\[
\begin{align*}
\text{CH}_2\text{Cl}_2 \\
\text{Ru}^{II}(\text{OEP})(\text{PPh}_3) + \text{HBr/O}_2 &\rightarrow \text{Ru}^{III}(\text{OEP})(\text{PPh}_3)\text{Br} + \text{HO}_2
\end{align*}
\]

An improvement over a previous method reported\textsuperscript{6} for this compound is the use of the monophosphine complex (4) instead of the bisphosphine complex (2); this avoids separation of the oxidised phosphine formed during the reaction. A 10 mL solution, made by bubbling anhydrous HBr (g) to saturation into CH\textsubscript{2}Cl\textsubscript{2}, was added to 100 mg (0.1 mmoles) of (4) under inert conditions via vacuum transfer. After exposure to air, the reaction mixture was cooled to ice-bath temperature, and
cold hexanes added to precipitate the product. The precipitate was then recrystallised twice from CH$_2$Cl$_2$-hexanes to yield a reddish powder (95% yield).

Analysis for C$_{54}$H$_{59}$N$_4$RuPBr(975g/mole), calculated: C=66.53, H=6.06, N=5.75, Br=8.11%, found: C=66.33, H=6.24, N=5.49, Br=7.85%.

Bis(pyridine)(octaethylporphyrinato)ruthenium(II) (6).

hv, 24 h, Ar

Ru$^{II}$(OEP)(CO)(EtOH) + 2 Py $\rightarrow$ Ru$^{II}$(OEP)(Py)$_2$ + CO + EtOH

This compound was prepared according to the method published by Antipas et al.$^8$ using the photolysis cell diagrammed in Figure II.4. A Hanovia 450 Watt mercury vapor lamp with a quartz water-cooler jacket was used for the photolysis (90% yield).

NMR(C$_6$D$_6$, anaerobic): 2.03 ppm(t), CH$_3$; 2.26(d), m-H; 3.97(q), CH$_2$; 4.17(m), o-H; 4.33(d), p-H; 9.74(s), meso-H.

Analysis for C$_{46}$H$_{54}$N$_6$Ru(791g/mole), calculated: C=69.79, H=6.83, N=10.62%; found: C=69.39, H=6.83, N=10.72%.

Bis(acetonitrile)(octaethylporphyrinato)ruthenium(II) (7).

hv, 24 h, Ar

Ru$^{II}$(OEP)(CO)(EtOH) + 2 CH$_3$CN $\rightarrow$ Ru$^{II}$(OEP)(CH$_3$CN)$_2$ + CO + EtOH

This complex was prepared using a photolysis procedure.
Ru(OEP)(CO)(EtOH) (130 mg, 0.2 mmoles) was placed in a test tube and CH₃CN (10 mL) added. Although the CO complex does not fully dissolve, the photolysis causes the acetonitrile to reflux and thus dissolve the starting material. After photolysis for 12 hours under argon, the solution was slowly cooled to room temperature under a purge of argon and the product precipitated as large, shiny purple crystals. These were filtered under argon, washed with acetonitrile and dried on a vacuum line at room temperature at an 80% yield. This method results in the presence of a small amount (5%) of the CO complex. Samples suitable for microanalysis and future X-ray crystal structure determination were obtained by adding dry, anaerobic CH₃CN (2 mL) to samples of the dimer [Ru(OEP)]₂ (10 mg, 0.008 mmoles) under anaerobic, vacuum conditions. The solution was then refluxed under vacuum and cooled slowly overnight to precipitate large, shiny purple crystals which were filtered, dried under vacuum at room temperature and stored under N₂(g).

\[ \nu(C≡N) = 2260 \text{ cm}^{-1}. \]

NMR(CD₂Cl₂, anaerobic): -2.70 ppm(s), CH₃CN; 1.95(t), CH₃; 3.98(q), CH₂; 9.96(s), meso-H.

Analysis for C₄₀H₅₀N₆Ru (716g/mole), calculated: C=63.69, H=6.98, N=11.73%; found: C=63.82, H=7.11, N=11.80%.
Figure II.4: Apparatus for photolysis of Ru(OEP) complexes.
Bis[(octaethylporphyrinato)ruthenium(II)] (8).

200°C, 2 h, 1x10^-5 torr

2 Ru^{II}(OEP)(Py)_2 \rightarrow [Ru^{II}](OEP)]_2 + 4 Py

This dimeric complex was prepared from complex 6 according to the method of Collman et al.10.

NMR(C_6D_6, anaerobic): 3.52 ppm(t), CH_3; 10.22(s), meso-H; 11.21 (m), CH_2; 26.13(m), CH_2.

Analysis for C_{72}H_{88}N_8Ru_2 (1268 g/mole), calculated: C=68.14, H=6.94, N=8.83%; found: C=68.49, H=7.01, N=8.91%.

Dibromo(octaethylporphyrinato)ruthenium(IV) (9).

1/2 [Ru^{II}(OEP)]_2 + HBr/Br_2* \rightarrow Ru^{IV}(OEP)(Br)_2 + HBr

* see chapter IV

To 8 (100 mg, 0.08 mmole), 10 mL of a solution, made by bubbling anhydrous HBr(g) to saturation in CH_2Cl_2, was added via vacuum transfer. The red solution was then exposed to the air, cooled to ice-bath temperature, and cold hexanes added to precipitate small reddish crystals which were filtered and recrystallised from CH_2Cl_2/ hexanes. The sample was dried at room temperature under vacuum. Large crystals suitable for an X-ray crystal structure determination were grown using vapour diffusion of n-pentane into CHCl_3 solutions of (9) under aerobic conditions (90% yield).

Analysis for C_{36}H_{44}N_4RuBr_2 (791 g/mole), calculated: C=54.55,
H=5.56,N=7.08,Br=20.08%;found:C=54.35,H=5.70,N=7.00,Br=20.09%
EPR signals were unobserved at ambient or low(77 K) temperatures in 1:1 toluene:dichloromethane.

NMR(CDCl₃,aerobic,19 °C): 60.1 ppm (broad), CH₂(16); 7.10 (br), CH₃(24); 3.90 (br), meso-H(4).

Magnetic susceptibility: \( \mu_{\text{eff}} = 2.5 \) B.M. using 2% t-butyl alcohol in CH₂Cl₂.

MS( EI, 70 eV, 280°C): 1268 m/e, [Ru(OEP)]₂⁺; 634, Ru(OEP)⁺; 80, HBr⁺.

Conductivity(at 20 °C): 0.5(CH₂Cl₂) and 12(CH₃CN) ohm⁻¹M⁻¹cm⁻¹.

UV/VIS(CH₂Cl₂,aerobic): 360 nm, sh(\( \log \epsilon = 4.75 \)), 398, Soret(4.90); 505(4.23); 535(4.16).

Dichloro(octaethylporphyrinato)ruthenium(IV) (10).

This compound was prepared using the method described for the dibromo analogue but using HCl(g) in place of HBr(g) (90% yield).

Analysis for C₃₆H₄₄N₄RuCl₂(703g/mole), calculated: C=61.23, H=6.24, N=7.94, Cl=10.07%; found: C=60.98, H=6.17, N=7.83, Cl=9.88%.

EPR signals were unobserved at ambient or low(77 K) temperatures in 1:1 toluene:dichloromethane solutions.

NMR(CDCl₃,aerobic,19 °C): 57.2 ppm, CH₂(16); 8.00, meso-H(4); 6.44, CH₃(24).

Magnetic susceptibility: \( \mu_{\text{eff}} = 2.6 \) B.M. using 5% t-butyl
alcohol in dichloromethane.

MS(EI, 70 eV, 300°C): 1268 m/e, [Ru(OEP)]$_2^+$; 634, Ru(OEP)$^+$. Conductivity (at 20°C): 0.7 ohm$^{-1}$M$^{-1}$cm(CH$_2$Cl$_2$); 14 ohm$^{-1}$M$^{-1}$cm(CH$_3$CN).

UV/VIS(CH$_2$Cl$_2$, aerobic): identical to that of the dibromide analogue.

Tetrahydrofuran(hexafluoroantimionate(V)) (octaethylporphyrinato) ruthenium(III) (11).

Ru$^{IV}$(OEP)(Cl)$_2$ + AgSbF$_6$ + THF $\rightarrow$ Ru$^{III}$(OEP)(SbF$_6$)(THF)
+ 1/2 Cl$_2$ + AgCl*

* see Chapter IV

In a Schlenk flask, 10 (100 mg, 0.13 mmoles) and silver hexafluoroantimionate(V) (86 mg, 0.25 mmoles) were dissolved in dry, degassed THF (50 mL). The resulting red suspension was stirred under dry argon for thirty minutes and then filtered through a Schlenk filter to remove the suspended reaction products (presumably AgCl). n-Pentanes (100 mL) were then cannulated into the filtrate with stirring to precipitate the product as a brown powder. This was recrystallized twice from THF/n-pentanes and dried under vacuo at 80°C for six hours (90% yield).

Analysis for C$_{40}$H$_{52}$N$_4$RuSbF$_6$O (941 g/mole), calculated: C = 51.06, H = 5.53, N = 5.95%; found: C = 51.19, H = 5.65, N = 5.87%.

NMR(CDCl$_3$, anaerobic, 19 °C): 17.5 ppm, CH$_2$(8); 6.24, meso-H(4);
EPR signals were unobserved at room temperature but at 77 K, \( g_\perp = 2.3 \) and \( g_\parallel = 2.8 \) were measured using an 1:1 THF:toluene, anaerobic solution.

Conductivity (at 20°C): 9.0 ohm\(^{-1}\)M\(^{-1}\)cm in CHCl\(_3\).

UV/VIS (CHCl\(_3\), anaerobic): 386 nm, Soret (log \( \varepsilon = 4.94 \)); 501 (4.00); 528 (4.01).
References.

Chapter III: The Characterisation of Ru^{IV}(OEP)(X)\(_2\) and Ru^{III}(OEP)(SbF\(_6\))(THF).

Section III.1: Analysis of the data for Ru(OEP)(Br)\(_2\)\(^9\) and Ru(OEP)(Cl)\(_2\)\(^10\).

A. NMR Spectroscopy.

The use of \(^1\)H NMR in diagnosing Ru(OEP) complexes is an indispensable tool, as the eight ethyl groups of OEP are sensitive probes of the symmetry about the ruthenium:

![Diagram of ethyl groups with pyrrole as mirror plane of symmetry.](image)

Figure III.1: A view of the ethyl groups with the pyrrole as the mirror plane of symmetry.

The free rotation about the C\(_1\)C\(_2\) bond results in H\(_a\) and H\(_b\) being equivalent and the rotation about the C\(_2\)C\(_3\) bond results in the methyl protons also being equivalent. Thus, for Ru(OEP) (hypothetically, without any axial ligands), one observes an A\(_2\)B\(_3\) \(^1\)H NMR pattern for the ethyl groups in their
usual chemical shift range. Since Ru(OEP) has $D_{4h}$ symmetry, the meso protons ($H_m$) would be equivalent and result in a singlet. The inclusion of axial ligands will affect the overall symmetry of the complex in two general ways: if both the axial ligands are identical, then a $D_{nh}$ symmetry will be preserved and an $A_2B_3$ spectrum would result; however, if the axial ligands are different from each other, then the $D_{nh}$ symmetry is lost and the $H_a$ and $H_b$ protons become inequivalent, resulting in two methylene peaks of equal intensity ($ABX_3$ spectrum).¹ These differences are diagrammed below:

(a) $A_2B_3$ spectrum

(b) $ABX_3$ spectrum

Figure III.2: Theoretical $^1H$ NMR spectra for OEP complexes: (a) mirror symmetry present ($x$ axis = $y$ axis), (b) no mirror symmetry present.

Complexes 9 and 10, having similar nonproton axial ligands, exhibit $^1H$ NMR spectra with only three signals ($-CH_2,-CH_3,-H_m$) because a mirror plane of symmetry is present (see Figure III.1). The chemical shifts of these three signals in $D_{nh}$ symmetry generally depend on the metal's oxida-
tion state and the axial ligands present. A Ru$^{II}$ complex with neutral axial ligands would have a d$^6$ octahedral (with tetragonal axial stretching distortion) configuration which is shown in Figure III.3:\textsuperscript{2}

$$\text{Ru}^{II},d^6 \quad \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \\
\text{(d orbitals)} \quad \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \\
\quad \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow $$

no ligand field \hspace{1cm} octahedral field \hspace{1cm} tetragonal axial stretching distortion

Figure III.3: Ligand field splitting diagram for a Ru$^{II},d^6$

A paramagnetic complex such as 9 or 10 has unpaired electrons in the metal d-orbitals, and so the chemical shifts are perturbed from their normal 0-12 ppm diamagnetic range. For paramagnetic shifts, the observed isotropic shift is based on the three sources:\textsuperscript{3}

$$(\Delta H/H)_{iso} = (\Delta H/H)_{contact} + (\Delta H/H)_{dipolar} - (\Delta H/H)_{diamagnetic}$$

The contact shift arises from the partial transfer of unpaired spin density into an orbital centered on the nucleus of interest, and is proportional to the hyperfine coupling constant $A$ (which reflects the unpaired spin density at the
nucleus); and is inversely proportional to the temperature. Dipolar shifts primarily arise from the magnetic anisotropy or inequivalence in the x,y,z axes of the metal, and are proportional to \( r^{-3} \) where \( r \) is the metal-to-proton nucleus distance. Since the dipolar shift diminishes according to a \( r^{-3} \) function, its effect is secondary to that of the contact shift in many cases where paramagnetism is present.

The \(^1\text{H} \) NMR spectra of 9 and 10 (see Figures III.5 and III.6) exhibit all the characteristics of a L→M CT system for metal-porphyrin \( \pi \)-bonding. The transfer of spin density between the metal d orbitals and the molecular orbitals of the ligand can occur via \( \sigma \) and/or \( \pi \)-bonding. For \( \pi \)-bonding, either a ligand-to-metal charge transfer (L→M CT) or a metal-to-ligand charge transfer (i.e. backbonding) (M→L CT) is possible; and which process occurs is dependent on the energy of the metal d orbitals relative to the porphyrin energy levels (see Figure III.4). If the axial ligands exert significant \( \pi \)-bonding to the metal, then the \( \text{e}_g \) orbitals of the metal become destabilised and increase in energy, bringing them closer to the energy level of the porphyrin \( \text{e}_g \pi^* \) orbital. In this case, a M→L charge transfer is likely, and the transferred charge resides largely at the porphyrin meso position, causing the \( H_{\text{meso}} \) \(^1\text{H} \) NMR signal to shift greatly up-field of TMS compared to the diamagnetic shift (the positions of the pyrrole hydrogens tend to shift slightly downfield at the same time). In the case of a weaker \( \pi \)-donor, the metal \( \text{e}_g \)
levels become less destabilised and now are nearer to the porphyrin 3eg \Pi- orbital energy level, resulting in a L\rightarrow M CT. In this case, most of the electron density is donated from the pyrrole carbons rather than the meso carbons, and thus the ethyl 1H NMR resonances shift downfield while the meso NMR resonance shifts slightly upfield. Thus, the 1H NMR spectra of 9 and 10 exhibit all the characteristics of a L\rightarrow M CT system because the methylene peak appears as a broad singlet at \sim 60 ppm, the methyl peak at \sim 7.0 ppm and the meso peak between 3-9 ppm (see Figures III.5 and III.6). The corresponding diamagnetic positions are +3.97, +2.03 and +9.74 ppm respectively for Ru^{II}(OEP)(py)\textsubscript{2}.

\[ \begin{align*}
\vdots \quad x^2-y^2 \\
\vdots \quad z^2 \\
\vdots \quad \text{PY}(\Pi^*) \\
\vdots \quad 4e_g(\Pi^*) \\
\uparrow \quad a_{2u} \\
\downarrow \quad a_{1u}(\Pi) \\
\downarrow \quad 3e_g(\Pi) \\
\vdots \quad \text{xy(n.b.)} \\
\vdots \quad \text{xz, yz}(e_g) \\
\vdots \quad \text{PY}(\Pi) \\
\end{align*} \]

porphyrin \quad metal \quad axial ligand

Figure III.4: The MO diagram for Ru(OEP)(py)\textsubscript{2} as a model for the Ru^{IV}(OEP)(X)\textsubscript{2} complexes 9 and 10.\textsuperscript{6}
Figure III.5: The $^1H$ NMR spectrum of Ru(OEP)(Br)$_2$ in CDCl$_3$, 300 MHz, 19 °C, under aerobic conditions.
Figure III.6: The $^1$H NMR spectrum of Ru(OEP)(Cl)$_2$ in CDC$_3$, 300 MHz, 19 °C, under aerobic conditions.
The assignments of the OEP peaks were deduced from the relative intensities and by the integration of the signals observed. Although chemical shifts arise mainly from contact effects for paramagnetic molecules, relaxation rates are primarily effected by dipolar relaxation terms, which diminish according to \( r^{-6} \) where \( r \) is the metal-to-proton distance. Thus, by studying the spin-lattice relaxation rates \( (T_1)^{-1} \) by the inversion-recovery NMR method (as described in the Varian XL-300 NMR operating manual)\(^9\) and intuitively correlating these values to 'r', one can assign unambiguously the NMR spectra observed (see Tables III.1 and III.2 and Figure III.7). If the relaxation rate is fast (short \( T_1 \), i.e. \( dt \) is small), then the resonant frequency width (dF) is large, and vice-versa. For this reason, the NMR spectra of 9 and 10 both have broad signals with no observed splittings or couplings.

The relative ordering of the ruthenium d-orbitals is of considerable interest because, to our knowledge, 2 and 10 are the first intermediate spin, triplet state \( S=1 \), ruthenium porphyrin complexes known. There are three possible orderings of the ruthenium's d-orbitals energy for a Ru\(^{IV} \), d\(^4\) configuration (see Figure III.8).

The \( S=2 \) configuration in Figure III.8 argues against a L\( \rightarrow \)M CT system in favour of \( \sigma \)-bonding because the \( d_{x^2-y^2} \) orbital is of \( \sigma \)-symmetry, and the orbitals needed for L\( \rightarrow \)M or M\( \rightarrow \)L CT system are of \( e_g \pi / \pi^* \) symmetry. Also, that \( S \) is
equal to one (two unpaired electrons) from magnetic measurements of 9 and 10, indicates that the S=2 high spin configuration is considered less likely than the other two (b or c in Figure III.8). These last two cases are consistent with a L→M CT picture but are not easily distinguished using common spectroscopic methods. If one chooses an axial

(a) $\mathbf{d}_{z^2}$ (b) $\mathbf{d}_{x^2-y^2}$ (c) $\mathbf{d}_{x^2-y^2}$

Figure III.8: The three possible d-orbital occupancies of Ru$^{IV}$, d$^4$ paramagnetic complexes: (a) an S=2 configuration (b) an S=1 $\mathbf{d}_{xy}^2\mathbf{d}_{xz},\mathbf{d}_{yz}$ configuration (c) an S=1 $\mathbf{d}_{xz},\mathbf{d}_{yz}^3\mathbf{d}_{xy}^1$ configuration.

stretching distortion instead of an axial compression distortion (ie. Ru-Br, 2.55 Å vs Ru-N, 2.05 Å (ave.) for Ru(OEP) (PPh$_3$)Br),$^{27b}$ then configuration c in Figure III.8 is the best representation for a Ru$^{IV}$,d$^4$ complex.

A Curie Law plot of the isotropic shift versus $T^{-1}$ should result in a straight line only if one spin state is populated over the temperature range studied. Another test for Curie behaviour is that as $T^{-1}\to 0$, the isotropic shift should approach 0 ppm (ie. the corresponding diamagnetic position) and, if both conditions are met, the compound is said to follow the Curie Law.$^{11}$ Although all the proton
Table III.1: $T_1$ Data for Ru$^{IV}$(OEP)(Br)$_2$.$^a$

<table>
<thead>
<tr>
<th>Interpulse delay (ms)$^b$</th>
<th>Intensity (CH$_2$)</th>
<th>Intensity (CH$_3$)</th>
<th>Intensity (H$_{meso}$)</th>
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</thead>
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<td>13.0</td>
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$^a$ in CDC$_3$ at 19°C (aerobic sample); intensities given as peak heights (arbitrary scale).

$^b$ Standard time delay to allow for partial relaxation of the spin magnetization vector.

$^c$ Obtained from a computer-aided curve-fitted plot of signal intensity vs. interpulse delay utilising the data above.
Table III.2: $T_1$ Data for Ru$^{IV}$-(OEP)(Cl)$_2$.\textsuperscript{a}

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<th>Intensity (CH$_3$)</th>
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<tr>
<td>500</td>
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<td>251</td>
<td>23.0</td>
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</table>

$T_1$ (ms)\textsuperscript{c}  

50.1  

89.7  

13.2

\textsuperscript{a} in CDCl$_3$ at 19°C (aerobic sample); intensities given as peak heights in an arbitrary scale.

\textsuperscript{b} standard time delay to allow for partial relaxation of the spin magnetization vector.

\textsuperscript{c} obtained from a computer-aided curve-fitted plot of signal intensity vs. interpulse delay utilising the data above.
Figure III.7: Plot of the signal intensity vs. interpulse delay to obtain the corresponding $T_1$ values for 9 and 10.
resonances of 9 and 10 gave straight lines for Curie plots, only the CH\textsubscript{3} resonances for 9 and 10 and the H\textsubscript{meso} resonance for 10 gave extrapolated intercepts near zero ppm (± 5 ppm) at T\textsuperscript{-1}→0 (see Table III.3 and Figure III.9 and III.10). The other three peaks (the CH\textsubscript{2} resonance for 9 and 10 and the H\textsubscript{meso} resonance for 9) do not follow the Curie Law. The presence of spin-orbit coupling may be the origin of the non-Curie behaviour.\textsuperscript{12}

A further point is that OEP has 22 4n+2 Huckel resonance configuration. If an electron is added or removed from the ring, the resulting radical is then stabilised by many resonance structures.\textsuperscript{13} Thus, another possible electronic configuration for 9 and 10 is that of a Π\textsuperscript{-}cation radical porphyrin complex, in which an electron has been removed (oxidation) from the ring to the metal centre in comparison to a Ru\textsuperscript{IV}(OEP) formulation. This would result in a \([\text{Ru}\textsuperscript{III}(\text{OEP}(.+))\text{X}]\text{X}^{-}\) ionic complex or an \([\text{Ru}\textsuperscript{III}(\text{OEP}(.+))\text{X}\text{2}]\) neutral complex. Morishima et al.\textsuperscript{14} have shown that such Π\textsuperscript{-}cation radical complexes, although containing an axial CO ligand, exhibit very broad \(^1\text{H}\) NMR signals in the range -60 to +60 ppm with the -CH\textsubscript{2} and -CH\textsubscript{3} \(^1\text{H}\) NMR resonances well downfield and the meso-H NMR resonance shifted well upfield of TMS. Both 9 and 10 do not exhibit this type of a \(^1\text{H}\) NMR spectrum and both are non-electrolytes.

On the strength of the \(^1\text{H}\) NMR data, the Ru(OEP)\text{X}\textsubscript{2} formulation with an intermediate spin, triplet ground state
Table III.3: Data for the Curie Plot of the Isotropic shift vs. Inverse Temperature.

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<th>shift(CH$_2$)</th>
<th>shift(H$_m$)</th>
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<td>5.79/-3.95</td>
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<td>68.0/64.0</td>
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<td>4.16/-5.58</td>
</tr>
<tr>
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<td>6.92/4.89</td>
<td>57.9/53.9</td>
<td>3.67/-6.07</td>
</tr>
<tr>
<td>50</td>
<td>3.10</td>
<td>6.13/4.10</td>
<td>52.9/48.9</td>
<td>3.23/-6.51</td>
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</tbody>
</table>

B. Data for Ru(OEP)(Cl)$_2$, 10.

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<th>$T,^\circ C$</th>
<th>$10^{-3}T^{-1}$</th>
<th>shift(CH$_3$)</th>
<th>shift(CH$_2$)</th>
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<td>82.2/78.2</td>
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</tr>
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<td>-30</td>
<td>4.12</td>
<td>8.49/6.66</td>
<td>74.7/70.7</td>
<td>9.93/0.13</td>
</tr>
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<td>7.66/5.63</td>
<td>67.7/63.7</td>
<td>9.10/-0.64</td>
</tr>
<tr>
<td>10</td>
<td>3.53</td>
<td>6.98/4.95</td>
<td>62.0/58.0</td>
<td>8.44/-1.30</td>
</tr>
<tr>
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<td>3.30</td>
<td>6.43/4.40</td>
<td>57.2/53.2</td>
<td>7.92/-1.81</td>
</tr>
<tr>
<td>50</td>
<td>3.10</td>
<td>6.06/4.04</td>
<td>53.9/49.9</td>
<td>7.61/-2.13</td>
</tr>
</tbody>
</table>

$^a$ Temperature deviation ± 0.5 °C.

$^b$ Obtained in CDCl$_3$, aerobic sample.

$^c$ Diamagnetic correction (Ru$^{II}$(OEP)(py)$_2$, C$_6$D$_6$, anaerobic):

CH$_3$=2.03, CH$_2$=3.97, H$_m$=9.74 ppm.
Figure III.9: Curie Plot for Ru(OEP)(Br)$_2$)$_2$, in the temperature range -50 to +50 °C.
Figure III.10: Curie Plot for Ru(OEP)(Cl)₂ 10, in the temperature range -50 to +50 °C.
Ru$^{IV}$,d$^4$ metal center seems almost certain. The axial bonding is due to $\sigma$ bonding with appreciable $\pi$ donor character, and the metal-porphyrin $\pi$-bonding is likely L$\rightarrow$M CT.

B. Optical Spectra.

The presence of a porphyrin $\pi$-cation radical complex is invariably indicated in the visible region of the optical spectrum: a broad peak at 620-680 nm$^{15}$ is characteristically diagnostic of a $\pi$-cation radical. The absence of such a peak in the optical spectra of 9 and 10 supports the conclusions reached by NMR, and as the optical spectra yield no further information except for identification purposes, the data are presented in Figure III.11 without discussion.

C. Infrared and Resonance Raman Spectroscopy.

The infrared spectra of 9 and 10 are both deficient of a characteristic strong peak at 1520-70 cm$^{-1}$ which is typically present in OEP $\pi$-cation radical complexes.$^{16}$ Thus, the IR spectra of these compounds again support the conclusions from the NMR data. The assignment of the Ru-X bond frequency was investigated because no such halogen frequencies within porphyrin systems have been reported to date. An assignment was attempted using FT-IR data but the presence of many bands due to water or carbon dioxide in the far-IR region (some of
Figure III.11: The optical spectrum of Ru(OEP)(X)₂ complexes in CH₂Cl₂. \( C = 2.50 \times 10^{-5} \text{ M} \), pathlength = 1.0 cm.

398 nm \( \log \varepsilon = 4.90 \)

360 nm \( \log \varepsilon = 4.75 \)

505 nm \( \log \varepsilon = 4.23 \)

535 nm \( \log \varepsilon = 4.16 \)
which may overlap with any legitimate signals present) made this task impossible. There were no intense peaks in this region, suggesting that due to the centrosymmetric nature of these compounds, some bands may be present in the resonance Raman spectra of \(9\) and \(10\). Using argon ion laser excitation at 457.9 nm, a KBr matrix (1 mg sample/100 mg KBr) was found to give the Ru-Br bond frequency at 178 cm\(^{-1}\) (no observable isotope splitting) and the Ru-Cl frequency at 289 cm\(^{-1}\) (again, no isotope splitting observed); both peaks appear as intense, but broad bands (see Figures III.12 and III.13) and the characteristic 100 cm\(^{-1}\) separation between the bromide and chloride analogues was observed. The resonance Raman spectra were measured by Dr. Laura Andersson (University of Oregon) to whom I am extremely grateful.

D. Mass Spectroscopy.

A surprising feature of the mass spectra of \(9\) and \(10\) is that their most intense peaks are due to the Ru(OEP) unit, with no parent ion being observed; the dimeric \([\text{Ru(OEP)}]_2^+\) and the monomeric \(\text{Ru(OEP)}^+\) species give rise to the most intense signals. The only other peaks resulted from the usual fragmentation pattern of the ring (see Figure III.14). By mimicking the conditions of a mass spectrometer in a laboratory experiment, it was found that \(9\) and \(10\) could be converted back to the dimer (8) in a quantitative yield (see
Figure III.12: The Raman resonance spectrum of Ru(OEP)(Br)$_2$ in a KBr matrix. (* denotes a matrix RR band).
Figure III.13: The Raman resonance spectrum of Ru(OEP)(Cl)$_2$ in a KBr matrix. (* denotes a matrix RR band).

- $672 \text{ cm}^{-1}$, porphyrin mode
- $350 \text{ cm}^{-1}$, porphyrin mode
- $289 \text{ cm}^{-1}$, $\nu_{(\text{Ru-Cl})}$
Figure III.14: The mass spectrum of Ru(OEP)(Br)$_2$. (The chloride analogue is identical except for peak at 79 m/e).
E. Magnetic Susceptibility and Electron Paramagnetic Resonance.

The solution magnetic susceptibilities of 9 and 10 were 2.5 and 2.6 B.M., respectively, and were estimated using \( \chi_m \), the molar susceptibility, which was obtained by Evans' method (B.M. = 9.27x10^{-24} \text{ J T}^{-1}): 50 \mu\text{L} of a 5% t-butyl alcohol in CH\(_2\)Cl\(_2\) solution were added to a long melting point sample tube. 9 or 10 (1-2 mg) and the 5% t-butyl alcohol solution (500 \mu\text{L}) were then added to an NMR sample tube and the melting point tube was placed co-axially inside. The \(^1\text{H} \) NMR spectrum was obtained immediately, and the separation of the two \(^1\text{H} \) NMR resonances for t-butyl alcohol (in two different environments) was measured (typically 7-9 Hz). \( \chi_g \) (gram susceptibility) was calculated. Diamagnetic corrections were made using Pascal's constants, and the resulting susceptibilities were within experimental error of the spin-only value of 2.83 B.M. for an S=1 system.

No EPR signals of 9 and 10 at either ambient or 77 K in 1:1 toluene:dichloromethane were observed. There are several possible reasons for this: the short relaxation times discussed earlier for the protons would lead to the broaden-
ing of any signal; secondly, the triplet state S=1 has zero-field splitting\textsuperscript{24} which can cause signals to be obscured; lastly, the unpaired spins can couple with each other, giving rise to spin-spin interactions which can cause a signal to be broadened.\textsuperscript{25}

The EPR spectra of these compounds would have shown the presence of a sharp signal at $g=2.00$ if a $\pi$-cation radical were present.\textsuperscript{26}

Section III.2: Analysis of the Data for Ru\textsuperscript{III}(OEP)(SbF\textsubscript{6})(THF) 11.

A. NMR Spectroscopy.

The $^1$H NMR spectrum of Ru(OEP)(SbF\textsubscript{6})(THF), 11, differs from that of 9 and 10 in two ways: 11 has two CH\textsubscript{2} peaks, each integrating to eight protons, showing that no mirror symmetry (ie. no mirror plane of symmetry) is present whereas 9 and 10 have such symmetry and exhibit only one CH\textsubscript{2} peak. Secondly, the spectrum of 11 is solvent dependent whereas spectra of the previous complexes show little solvent dependence. Spectra of 11 in CH\textsubscript{3}CN-d\textsubscript{3} or MeOH-d\textsubscript{4} appear complicated with many meso-H peaks suggesting that the SbF\textsubscript{6} unit and/or THF can be easily displaced by strongly coor-
dinating solvents. Because of solubility problems, the
measurement of the NMR spectrum of 11 is restricted to using CDC\textsubscript{3} or polar coordinating solvents; thus, the \textsuperscript{1}H NMR spectrum in CDC\textsubscript{3} is shown in Figure III.15. The CH\textsubscript{3} resonance has not shifted greatly from its diamagnetic position of 2.03 ppm whereas the meso-H and CH\textsubscript{2} peaks have shifted greatly from their diamagnetic positions. The meso-H peak has shifted from 9.74 to 6.25 ppm and the CH\textsubscript{2} peaks are at 3.80 and 17.5 ppm compared to the diamagnetic position of 3.97 ppm. The presence of two CH\textsubscript{2} peaks and their position indicates that the electronic environment on one side of the porphyrin plane is different from the other side of the porphyrin plane, with one CH\textsubscript{2} peak close to the normal diamagnetic position of 3.97 ppm. This type of \textsuperscript{1}H NMR is similar to that of the dimer [Ru(OEP)]\textsubscript{2}, (which has two CH\textsubscript{2} resonances; one at 26.1 ppm, the other at 11.2 ppm) and also to that of Ru\textsuperscript{III}(OEP)(PPh\textsubscript{3})(Br) (having two CH\textsubscript{2} resonances at 8.8 and 18.5 ppm).\textsuperscript{27} The separation between the two CH\textsubscript{2} peaks (about 10-15 ppm) in the last two cases have been ascribed to differences in metal-porphyrin charge transfer at each CH\textsubscript{2} proton site and a similar effect is postulated for 11.

The assignment of the \textsuperscript{1}H spectra of 11 was made using T\textsubscript{1} experiments as discussed in the previous NMR section (III.1.A). A similar correlation between T\textsubscript{1}'s and r (the metal-to-proton distance), as observed for 9 and 10, was found for 11 (see Table III.4 and Figure III.16), with the exception that for 11, the CH\textsubscript{2} resonance at 17.5 ppm has a
Figure III.15: The $^1$H NMR spectrum of Ru(OEP)(SbF$_6$)(THF) in CDC$_3$, 300 MHz anaerobic sample at 19 °C.
longer T₁ relaxation time than the CH₂ protons at 3.80 ppm. Since the T₁ relaxation, by definition, refers to the relaxation of a spin with the help of the surrounding lattice of solvent and other molecules present, the relaxation monitored by the CH₂ protons at 17.5 ppm must be slower than the relaxation for the other CH₂ protons at 3.80 ppm. The reason for this difference in relaxation rates is not apparent; although, presuming that the dipolar relaxation is still dominant, the r vector must be shorter for the faster relaxing protons as a consequence of the T₁'s dependence on r⁻⁶. The presence of an out-of-the-plane Ru would account for this shortening of the r₀ vector (both the [Ru(OEP)]₂ dimer and RuⅢ(OEP) (PPh₃)(Br) have an out-of-the-plane ruthenium). The use of T₁ experiments to assign a ¹H NMR spectrum does not always lead to an unambiguous solution; for example, in this case, the T₁ data cannot be used to distinguish which CH₂ resonance originates from which side of the porphyrin plane (the SbF₆ side vs the THF side). In such cases, deuterium labelling is needed for a complete assignment.

The plot of the isotropic shift vs T⁻¹ gave a straight line, indicating that only one spin state is occupied over the temperature range studied (−50 to +50 °C in CDCl₃, see Table III.5 and Figure III.17). The high temperature extrapolations to T⁻¹→0 of the isotropic shifts gave values within experimental error (± 5 ppm) of 0 ppm for all the
Table III.4: $T_1$ Data for Ru$^{III}$(OEP)(SbF$_6$)(THF).$^a$

<table>
<thead>
<tr>
<th>Interpulse $D_3$ (ms)</th>
<th>$\text{CH}_2$ (17.5 ppm) $^b$ Intensity</th>
<th>$\text{CH}_2$ (3.80 ppm) $^b$ Intensity</th>
<th>$H_m$ $^b$ Intensity</th>
<th>$\text{CH}_3$ $^b$ Intensity</th>
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<tr>
<td>5.0x10$^{-1}$</td>
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<td>-29.7</td>
<td>-209</td>
</tr>
<tr>
<td>1.0</td>
<td>-93.0</td>
<td>-20.2</td>
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<tr>
<td>4.0</td>
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</tr>
<tr>
<td>8.0</td>
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<td>-20.4</td>
<td>-128</td>
</tr>
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<td>37.0</td>
<td>10.3</td>
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</tr>
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<td>62.0</td>
<td>46.0</td>
<td>14.5</td>
<td>159</td>
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<tr>
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<td>85.4</td>
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<td>19.9</td>
<td>243</td>
</tr>
<tr>
<td>100</td>
<td>93.6</td>
<td>46.0</td>
<td>24.0</td>
<td>272</td>
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<td>61.0</td>
<td>55.4</td>
<td>337</td>
</tr>
<tr>
<td>500</td>
<td>103</td>
<td>61.1</td>
<td>55.0</td>
<td>336</td>
</tr>
<tr>
<td>$T_1$ (ms)$^c$</td>
<td>34.2</td>
<td>10.3</td>
<td>9.3</td>
<td>44.7</td>
</tr>
</tbody>
</table>

$^a$ in CDCl$_3$ at 19°C (anaerobic sample).

$^b$ peak height in an arbitrary scale.

$^c$ obtained from a computer-aided curve-fitted plot of signal intensity vs. interpulse delay utilising the data supplied above.
Figure III.16: Plot of the signal intensity vs. interpulse delay to calculate $T_1$ values.
resonances except that of the \( H_m \). The \(-CH_2\) and \(-CH_3\) data obtained from the Curie plots obeyed the Curie Law within the temperature range studied indicating that only a single ground state is populated.

The \(^{19}\mbox{F}\) NMR spectrum of \( \text{II} \) (CDCl\(_3\), anaerobic) shown in Figure III.18 has a lineshape and position vastly different from that of free KSbF\(_6\) in Freon-II. Free SbF\(_6\)\(^{-}\) appears as a broad resonance (± 10 ppm) centered at -119 ppm relative to Freon-II\(^{28}\); thus, this result indicates that the SbF\(_6\) is coordinated (\( \text{II} \) is also a non-electrolyte in CHCl\(_3\)) and not free as is suggested by the IR data discussed in section III.2.E.

B.EPR Spectroscopy.

The EPR spectrum of \( \text{II} \) is characteristic of a complex with mirror symmetry (X=Y≠Z), since one sees two signals: \( g || \) and \( g \perp \).\(^{29}\) The spectrum is shown in Figure III.19 and was obtained using X-band microwave frequency radiation (9.11 GHz) at 10 mW microwave power and a dilute 1:1 (THF:toluene) solution of \( \text{II} \) under anaerobic conditions. No signal was observed at room temperature but at -196°C (77°K), an intense signal was observed with \( g || \) at 2530 ± 20 G (\( g = 2.8 ± 0.1 \)) and \( g \perp \) at 2950 ± 20 G (\( g = 2.3 ± 0.1 \)) with no hyperfine splittings. This spectrum and its lineshape are similar to that of other Ru\(^{III}\)(OEP) complexes.\(^{27b}\) The alternative, possible formula-
Table III.5: Data for the Curie Plot of the Isotropic shift vs. Inverse Temperature for 11.

<table>
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<th>$T, \degree C$</th>
<th>$T^{-1} \times 10^3 \text{ K}^{-1}$</th>
<th>shift(CH$_3$)</th>
<th>shift(H$_m$)</th>
</tr>
</thead>
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<td></td>
<td>obs$^b$/corr$^c$</td>
<td>obs$^b$/corr$^c$</td>
</tr>
<tr>
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<td>9.31/-0.43</td>
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<tr>
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<td>4.12</td>
<td>1.35/-0.68</td>
<td>8.52/-1.22</td>
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<tr>
<td>-10</td>
<td>3.80</td>
<td>1.41/-0.62</td>
<td>7.64/-2.10</td>
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<tr>
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<td>3.53</td>
<td>1.35/-0.68</td>
<td>6.96/-2.78</td>
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<td>3.30</td>
<td>1.42/-0.61</td>
<td>6.47/-3.27</td>
</tr>
<tr>
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<td>3.10</td>
<td>1.43/-0.60</td>
<td>6.07/-3.67</td>
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<table>
<thead>
<tr>
<th></th>
<th></th>
<th>shift(CH$_2$,17ppm)</th>
<th>shift(CH$_2$,3ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>obs$^b$/corr$^c$</td>
<td>obs$^b$/corr$^c$</td>
</tr>
<tr>
<td>-50</td>
<td>4.48</td>
<td>20.6/16.6</td>
<td>3.41/-0.59</td>
</tr>
<tr>
<td>-30</td>
<td>4.12</td>
<td>19.7/15.7</td>
<td>3.53/-0.47</td>
</tr>
<tr>
<td>-10</td>
<td>3.80</td>
<td>18.7/14.7</td>
<td>3.71/-0.29</td>
</tr>
<tr>
<td>10</td>
<td>3.53</td>
<td>17.8/13.8</td>
<td>3.67/-0.33</td>
</tr>
<tr>
<td>30</td>
<td>3.30</td>
<td>17.1/13.1</td>
<td>3.74/-0.26</td>
</tr>
<tr>
<td>50</td>
<td>3.10</td>
<td>16.6/12.6</td>
<td>3.75/-0.25</td>
</tr>
</tbody>
</table>

$^a$ temperature deviation ± 0.5 °C.

$^b$ obtained in CDCl$_3$, aerobic sample.

$^c$ diamagnetic correction (Ru$^{II}$ (OEP)(py)$_2$,C$_6$D$_6$, anaerobic):

CH$_3$=2.03, CH$_2$=3.97, H$_m$=9.74 ppm.
Figure III.17: Curie Plot for Ru(OEP)(SbF₆)(THF) in the temperature range -50 to +50 °C.
Figure III.18: The $^{19}$F NMR spectrum of Ru(OEP)(SbF$_6$)(THF), 11, in CDCl$_3$ (obtained at 19 °C at 300 MHz using an anaerobic sample).
Figure III.19: The EPR spectrum of Ru(OEP)(SbF$_6$)(THF) in 1:1 THF:toluene (anaerobic) at -196 °C. (9.11 GHz X-band radiation at 10 mW microwave power).
tion of 11 as a Ru\textsuperscript{II}(OEP)(SbF\textsubscript{6})(THF) cation radical complex is ruled out. Such a radical complex would behave from an EPR point of view as an isolated organic radical which gives rise to a sharp signal at $g = 2.0$ (3200 G).

C. Optical Spectra.

As discussed in a previous section (III.1.B), the optical spectrum of a cation radical is distinctive and, since 11 does not show this characteristic absorption, a TI-cation radical formulation is ruled out. The optical spectrum of 11 is shown in Figure III.20.

D. Mass Spectroscopy.

The usual Ru(OEP) peaks were observed in the MS along with the peaks for the SbF\textsubscript{6} unit. In fact, the fragmentation pattern SbF\textsubscript{3}\textsuperscript{+}, SbF\textsubscript{2}\textsuperscript{+}, and SbF\textsuperscript{+} (178, 159, 140 m/e respectively) is readily observed (see Figure III.21) but the parent SbF\textsubscript{6}\textsuperscript{+} is not present, indicating that the SbF\textsubscript{6} unit might be thermally decomposed. No parent peak for the complex was present and the THF was the first fragment observed at m/e of 71.
Figure III.20: The optical spectrum of Ru(OEP)(SbF₆)(THF) in CHCl₃. (C = 2.29 x10⁻⁵ M, pathlength = 1.0 cm).

385 nm (log ε = 4.94)

5496 nm (4.00)

525 nm (4.01)
Figure III.21: Mass spectrum of Ru(OEP)(SbF₆)(THF).
E. Infrared Spectroscopy.

The typical \( \pi \)-cation radical peak for OEP is not present in the spectrum of 11, showing again that the cation radical formulation is inappropriate. Based on data for other \( \mu \)-fluoro metal-SbF\(_6\) compounds,\(^{30}\) the band at 650 cm\(^{-1}\) (Figure III.22) is assigned to \( \nu(Sb-F) \). This stretching frequency appears to be sharp (and not broad as would be expected for a bridging SbF\(_6\)), and is in the correct area for an ionic SbF\(_6\) complex. The IR data indicates that the SbF\(_6\) is uncoordinated,\(^{31}\) and is in conflict with the \(^{19}\)F NMR, \(^1\)H NMR, and conductivity data. These differences in data may be due to the SbF\(_6\) being weakly coordinated.\(^{30}\)
Figure III.22: The infrared spectrum of Ru(OEP)(SbF₆)(THF) in a Nujol mull.

\( \nu_{(Sb-F)} = 650 \text{ cm}^{-1} \)
References.

5. Reference 3, p. 67.


22. Ibid., p. 35.


27(a). Collman, J. P.; Barnes, C. E.; Sweeplston, P. W.; Ibers, J. A.; J.


Chapter IV: The Chemistry of the RuIV(OEP) complexes 9 and 10.

The oxidation of 9 and 10 in CH₂Cl₂ at room temperature using either mCPBA or PhIO displayed two trends: at low oxidant to porphyrin ratios (<10:1), no reaction was observed (the resonance for free oxidant could be easily observed using ¹H NMR) and this behaviour was independent of reaction time or rate of stirring. At higher ratios of oxidant to porphyrin (>15:1), these same conditions resulted in bleached solutions with concomitant loss of the porphyrin's NMR resonances and optical spectra. Clearly, the macrocycle was being destroyed by the oxidants, and the same reactivity was observed for two-phase reactions using H₂O₂ or tertiary-butylhydroperoxide in aqueous media as oxidants.

The attempted oxidation of cyclohexene in CH₂Cl₂ (0.1 M) using excess (>20x) mCPBA or PhIO in the presence of 9 or 10 (1x10⁻³ M) at 19 °C did not result in any oxidised cyclohexene products (as tested by GC), and the macrocycle was still destroyed. Regrettably, 9 and 10 do not exhibit any ability to catalyse the oxidation of this organic substrate.

Solutions of 9 and 10 in CH₂Cl₂ (1x10⁻³ M) were unaffected in the light or dark when exposed to air. They were also unchanged in the presence of trace amounts of water but the species were hydrolysed to the μ-oxo dimers [Ru(OEP)X]₂O (X=Br or OH) in excess water (x100) as studied by ¹H NMR (see
Appendix A.I). Exposure to five atmospheres of pure O$_2$ or N$_2$O for two days also resulted in unreacted solutions of 9 and 10 (again, 1x10$^{-3}$ M). Thus, these complexes are inert toward oxidants tested to date. Heating anaerobic NMR samples (CDCl$_3$, 1x10$^{-4}$ M) at 100 °C for two hours under light or dark conditions led to the thermal decomposition of the compounds.

The reaction of 9 and 10 (1x10$^{-3}$ M) with excess sodium dithionite (Na$_2$S$_2$O$_4$) in CH$_2$Cl$_2$ or with excess sodium borohydride (NaBH$_4$) in THF led to the rapid formation of Ru$^{II}$(OEP)(CO) as judged by the $^1$H NMR spectrum (see Appendix A.II.1). The source of CO for these reactions is unknown but carbonyl formation is frequently encountered during experimentation. Solutions of 9 and 10 in CH$_2$Cl$_2$ (1x10$^{-4}$ M), exposed to one atm of H$_2$ (g) for 12 hours showed no reactivity towards dihydrogen, as monitored by visible spectroscopy.

The presence of the peak for the [Ru(OEP)]$_2$ dimer in the mass spectra of 9 and 10 indicated that the complexes were being reduced in the mass spectrometer. By heating these compounds (7 mg) in an anaerobic NMR tube at 200°C and 1x10$^{-5}$ torr vacuum for one hour, the dimer was quantitatively regenerated. The $^1$H NMR of the pyrolysed product did not have any resonances due to the starting material and only one H$_m$ resonance was observed (for the dimer). Although the pressure in the vacuum line did increase during continued pumping (indicating that a volatile material was evolved), the
volatile has not yet been identified. The most likely possibility is halogen production via a radical process:

\[ \text{Ru}^{IV}(\text{OEP})(\text{X})_2 \rightarrow 1/2 \text{[Ru}^{II}(\text{OEP})]_2 + 2 \text{X}^* \text{radicals} \]

1x10^{-5} \text{ torr, 2h}

200{\degree}C

The above findings lead one to question the origin of the oxidant for the reverse Ru^{II} \rightarrow \text{Ru}^{IV} preparative reaction. Using stoichiometric amounts of Br_{2} as the oxidant did lead to the Ru^{IV} products but with side-products which made purification difficult. Chromatography under either anaerobic or aerobic conditions, using either alumina or silica gel (activity I \rightarrow IV) with a variety of solvent systems (MeOH: CH_{2}Cl_{2} or neat CH_{3}CN or neat MeOH), always resulted in decomposed products. Using excess HX(g), considered to contain trace amounts of X_{2}(g),^1 (pure, anhydrous HX(g) should be colourless but the gases obtained from suppliers have a faint yellow color) gave clean samples of 9 and 10; indeed, using excess HF(g) to oxidise the dimer did not give the analogous Ru^{IV}(OEP)(F)_{2} complex because HF(g) does not have any F_{2}(g) as a trace impurity.\(^2\) Another possible oxidant for the Ru^{II} \rightarrow \text{Ru}^{IV} oxidation was thought to be HX(g) itself.

Gaseous HX could possibly oxidise the [Ru^{II}(OEP)]_{2} dimer, consequently forming the Ru^{IV}(OEP)(X)_{2} compounds and
dihydrogen ($H_2$):

\[ 4 \text{HX}(g) + [\text{Ru}^{II}(\text{OEP})]_2 \rightarrow 2 \text{H}_2(g) + 2 \text{Ru}^{IV}(\text{OEP})(X)_2 \]

Several attempts were made to detect $H_2$ using the following procedure: in an inert atmosphere glove box, 20 mg of the $[\text{Ru}(\text{OEP})]_2$ dimer was loaded into an anaerobic flask with a side arm septum port (2 mL volume) similar to that shown in figure II.3. A saturated solution of $\text{HX}(g)$ in $\text{CH}_2\text{Cl}_2$ (1 mL) was vacuum transferred into the flask containing the dimer and the resulting solution was thawed to allow the reagents to react. Upon refreezing to 77°K to trap out the excess $\text{HX}(g)$ and solvent, a 1 mL sample of the vapor phase was withdrawn using a gastight syringe and injected directly into the GC. The formation of $H_2(g)$ could not be detected by gas chromatography (Carle GC: 6' Porapak Q column, 25°C oven temperature, 20 mL/min gas flow, 1 mL gas samples). If, accidentally, the reaction is exposed to the air before the reagents have had sufficient time to react (about 5 minutes), the corresponding $\mu$-oxo dimer $[\text{Ru}(\text{OEP})X]_2\text{O}$ is formed. The most likely source of the oxidant in the preparative reaction is trace halogen in gaseous hydrogen halide.

In an attempt to prepare $\text{Ru}^{IV}(\text{OEP})(X')_2$ ($X' = \text{SbF}_6$), two equivalents of silver hexafluoroantimonate(V) ($\text{AgSbF}_6$, 4 mg, 0.01 mmoles), and 9 or 10 (4 mg, 0.005 mmoles), were reacted in $\text{CDCl}_3$ in an NMR tube and the $^1\text{H}$ spectrum of the
reaction mixture was obtained immediately. The familiar NMR resonances for 9 and 10 were not present in the spectrum of the reaction mixture and only one porphyrin product (that is, only one $H_m$ resonance) was observed. Further spectroscopic analysis of the new product (11), along with microanalysis, indicated that it was a Ru$^{III}$ complex with only one SbF$_6$ unit per ruthenium. This result is surprising because it indicates that either Ru$^{IV}$ has oxidised Ag$^I$ to Ag$^{II}$, thereby generating a Ru$^{III}$ product (the Ag$^I$/Ag$^{II}$ reduction potential is near $-2$ V),$^3$ or that silver assists the homolytic cleavage of the Ru-X bond (giving Ru$^{III}$ and X$^*$ radicals). In light of the very high energy needed to oxidise Ag$^I$, the latter reason is most likely the cause of the reduction of ruthenium to Ru$^{III}$. The exact mechanism is unknown as yet and more work is needed in this area to verify the mechanism.
References


Chapter V: Conclusions and Suggestions for Future Studies.

The addition of \( \text{HX}(g) \) to the \([\text{Ru}^{\text{II}}(\text{OEP})]\)\(_2\) dimer results in the formation of highly oxidised, novel complexes of \( \text{Ru}^{\text{IV}} \). All the data obtained to date indicate consistently that these compounds are \( \text{Ru}^{\text{IV}}(\text{OEP})(X)\)\(_2\) (\(X=\text{Br}, \text{Cl}\)) complexes with a triplet state, intermediate spin ground state electronic configuration, and are the first such ruthenium porphyrins reported. The alternate \( \text{Ru}^{\text{III}} \) \( \pi \)-cation radical formulation is ruled out, and the first \( \text{Ru-X} \) IR/RR bond stretching frequencies (KBr pellets) have been assigned in \( \text{Ru} \) porphyrins (\(X=\text{Br}, 179 \text{ cm}^{-1}; X=\text{Cl}, 289 \text{ cm}^{-1}\)). An analysis of the relationship between metal-axial ligand/metal-porphyrin bonding, and the corresponding \(^1\text{H} \text{NMR}\) spectrum has been attempted. The halide is predicted to be a weak \( \pi \)-donor (\(p\pi\text{-d}\pi\) donation) to the metal, and consequently, the \( \text{Ru-porphyrin} \) bonding is also a ligand-to-metal charge transfer (instead of metal-to-ligand back-donation). The isotropic shift is mainly due to contact contributions but dipolar relaxation is the dominant relaxation mechanism. The oxidant responsible for the \( \text{Ru}^{\text{II}} \) to \( \text{Ru}^{\text{IV}} \) oxidation is trace \( \text{X}_2(g) \) in \( \text{HX}(g) \) and is not either the \( \text{HX} \) itself or air/O\(_2\). Both \( \text{9} \) and \( \text{10} \) appear to be easily reduced by common reducing agents but are oxidatively inert and do not have the ability to catalyse the oxidation of cyclohexene in the presence of monoxygen sources such as mCPBA or PhIO.

Similarly, \( \text{11} \) is formulated to be \( \text{Ru}^{\text{III}}(\text{OEP})(\text{SbF}_6)(\text{THF}) \).
rather than a Ru$^{II}$ π-cation radical. As with other M(porp) SbF$_6$ complexes, a μ-fluoro bridged Ru-F-SbF$_5$ type of structure is favored with $\nu_{\text{Sb-F}} = 650$ cm$^{-1}$ (Nujol). The electronic configuration is that of a Ru$^{III}$, d$^5$ low spin (S=1/2) complex.

The above compounds (9-11) are excellent precursors for further study in high oxidation state Ru porphyrin chemistry because of their ease of preparation and inherent stability. One example of this is the substitution of the alkyls in place of the halides to form the corresponding Ru(OEP)(R)$_2$ compounds (R=CH$_3$, phenyl, C$_2$H$_5$).\(^1\) Also, the substitution of an halide for the SbF$_6$ unit may form a Ru$^{III}$ (porp)(X) complex, and this complex would be an excellent precursor (as 11 may be) for studying the catalytic oxidation of organic substrates as discussed in the Introduction.

References

Appendix I: The Oxidation Chemistry of Ru\(^{III}\)(OEP)(PPh\(_3\))(Br), 5.

The original method developed by Leung\(^1\) for the synthesis of an oxo complex involved stirring 5 (100 mg, 0.1 mmoles) and mCPBA (100 mg, 0.6 mmoles) in dry, degassed CH\(_2\)Cl\(_2\) for thirty minutes under argon. A green product was then precipitated by adding cold hexanes, filtered and dried under vacuum. Based on visible and ESR spectra, Leung et al. suggested a [O=Ru\(^{IV}\)(OEP+.)]Br formulation.\(^2\) Following his procedure, a brown powder was obtained which was analysed by spectroscopic techniques. The visible spectrum of the brown product (12) was broad and diffuse (\(\lambda_{\text{max}}=384\) (log \(\varepsilon=4.80\)), 502 (3.73), and 604 (3.62) nm); the mass spectrum displayed peaks for only O=PPh\(_3\) (278 m/e), and the corresponding infrared band for \(\nu_{O=P}\) was present at 1190 cm\(^{-1}\).\(^3\) The \(^1\)H NMR spectrum of 12 had two resonances at 7.15 and 7.58 ppm for the O=PPh\(_3\) protons and three proton signals at 9.35, 4.1–4.4, 1.85 ppm (for \(-H_m\), \(-CH_2\) (two signals), and \(-CH_3\) respectively) for OEP. The %N obtained from microanalysis was very low, and was consistent with the other data which suggested contamination of 12 with O=PPh\(_3\).

Chromatography was attempted in order to separate the O=PPh\(_3\) from the porphyrin residue, using either silica gel or alumina (activity I–IV) and eluting with a CH\(_2\)Cl\(_2\)/MeOH solvent system. The NMR spectrum of the CH\(_2\)Cl\(_2\)/MeOH (1/25) eluate indicated that two species were present: O=PPh\(_3\) and a
diamagnetic porphyrin complex with the same chemical shifts as $\text{12}$. This solvent system was the only one found to elute all of the porphyrin product; unfortunately, it co-elutes the phosphine oxide. The $^1\text{H NMR}$ and visible spectra of $\text{12}$ were identical to those of the $\mu$-oxo dimer $[\text{Ru(OEP)Cl}]_2\text{O}$ reported by Collman (see Figures AI.1 and AI.2).\textsuperscript{4}

A room temperature titration of $\text{5}$ ($1\times10^{-4}$ M) in $\text{C}_6\text{D}_6$ with one-electron equivalent aliquots of mCPBA in $\text{C}_6\text{D}_6$ (the reaction being followed by NMR) showed that a small amount (<5%) of a second porphyrin compound was formed upon addition of more than ten equivalents of mCPBA. That this minor product is not present in samples which have aged or been purified by chromatography is significant. Indeed, the same titration carried out at -60 °C gave a better yield (10%) of the minor product as judged by NMR. Due to the complexity of the purification procedure, and the low yields for the minor product, a new precursor which had no oxidisable axial ligands was sought.

A NMR titration similar to that done for $\text{5}$ was attempted for $\text{Ru}^{\text{II}}(\text{OEP})(\text{CH}_3\text{CN})_2$ ($\text{Z}$) to test whether a $\text{Ru}^{\text{III}}$ precursor was really needed to study higher oxidation states of Ru. At either 19 °C or -60 °C, a titration of $\text{Z}$ ($1\times10^{-4}$ M) with mCPBA in $\text{C}_6\text{D}_6$ and $\text{CD}_2\text{Cl}_2$ (done in a septum-capped NMR tube) led to the quantitative formation of the $\mu$-oxo dimer $[\text{Ru(OEP)X}]_2\text{O}$. Because the $\text{Ru}^{\text{IV}}\mu$-oxo dimers are diamagnetic, the shifts due to the three sets of OEP protons will not vary
Figure A.I.1: The $^1$H NMR spectrum of [Ru(OEP)(X)]$_2$O in C$_6$D$_6$, 300 MHz aerobic sample at 19 °C. (Note: the $^1$H NMR spectrum of 12 is identical to that of the spectrum below with the exception that no mCPBA peaks are present.)
Figure A.I.2: The optical spectrum of [Ru(OEP)(X)]₂O in CH₂Cl₂.

384 nm (log ε = 4.80)

502 nm (3.72)

604 nm (3.62)
greatly as different anionic ligands are substituted, and the presence of the distinctive \(^1\)H NMR pattern 9.80, 4.20-3.80 (two sets), and 1.90 ppm (-H\(_m\), -CH\(_2\), and -CH\(_3\), respectively) is representative of these bridged dimers. Thus, it is apparent that a precursor which can be easily oxidised by oxygen-free reagents (to avoid \(\mu\)-oxo dimer formation) would greatly aid the synthesis of high oxidation complexes of Ru.

References.

1. Leung, T.W., personal communication.
### Appendix II: Tabulation of Spectroscopic Data for Ru Porphyrin Complexes.

Table A.II.1: Tabulation of $^1$H NMR Data.

<table>
<thead>
<tr>
<th>Ru(OEP) (L)(L')</th>
<th>$H_m$</th>
<th>$CH_2$</th>
<th>$CH_3$</th>
<th>axial ligand</th>
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<tbody>
<tr>
<td>$L=EtOH, L'=CO$</td>
<td>9.74(s)</td>
<td>4.00(q)</td>
<td>2.03(t)</td>
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<tr>
<td>$L=L'=PPh_3$</td>
<td>9.16(s)</td>
<td>4.20(q)</td>
<td>1.70(t)</td>
<td>$e$</td>
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<td>$L=\text{vacant}, L'=PPh_3$</td>
<td>9.50(s)</td>
<td>3.92(q)</td>
<td>2.02(t)</td>
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<tr>
<td>$L=Br, L'=PPh_3$</td>
<td>9.90(s)</td>
<td>8.85,18.5(m)</td>
<td>0.53(br)</td>
<td>$g$</td>
</tr>
<tr>
<td>$L=L'=py$</td>
<td>9.74(s)</td>
<td>3.97(q)</td>
<td>2.03(t)</td>
<td>$h$</td>
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<tr>
<td>$L=L'=CH_3CN$</td>
<td>9.96(s)</td>
<td>3.98(q)</td>
<td>1.95(t)</td>
<td>-2.70,CH$_3$CN</td>
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<td>Dimer</td>
<td>10.2(s)</td>
<td>11.2,26.1(m)</td>
<td>3.52(t)</td>
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</tr>
<tr>
<td>$L=L'=Br$</td>
<td>3.50(br)</td>
<td>60.1(br)</td>
<td>7.10(br)</td>
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</tr>
<tr>
<td>$L=L'=Cl$</td>
<td>8.20(br)</td>
<td>59.7(br)</td>
<td>6.34(br)</td>
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<tr>
<td>$L=\text{THF}, L'=SbF_6$</td>
<td>6.24(br)</td>
<td>17.5,3.80(br)</td>
<td>1.89(br)</td>
<td>$i$</td>
</tr>
</tbody>
</table>

---

$a$ C$_6$D$_6$(7.15 ppm), aerobic sample.

$b$ C$_6$D$_6$(7.18 ppm), anaerobic sample.

$c$ CDC$_3$(7.25 ppm), aerobic sample.

$d$ CDC$_3$(7.25 ppm), anaerobic sample.

$e$ phenyl resonances: 4.20(d), o-H; 6.2-6.8(m), m-, p-H.

$f$ phenyl resonances: 4.45(m), o-H; 6.45(m), m-H; 6.68(d), p-H.

$g$ phenyl resonances: 2.72(m), p-H; 14.6-14.8, o-, m-H.

$h$ pyridine resonances: 2.26(d), m-H; 4.17(m), o-H; 4.33(d), p-H.

$i$ THF resonances: 2.00, -1.05.
<table>
<thead>
<tr>
<th>compound</th>
<th>frequency$\text{(} \text{cm}^{-1} \text{)}$</th>
<th>assignment,$\nu$</th>
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<tr>
<td>$\text{Ru}<em>3(\text{CO})</em>{12}$, $1$</td>
<td>$2058, 2020, 1995$</td>
<td>$C=O$</td>
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<tr>
<td>$\text{Ru(OEP)(CO)(EtOH)}$, $2$</td>
<td>$1922$</td>
<td>$C=O$</td>
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<tr>
<td>$\text{Ru(OEP)(CH}_3\text{CN)}_2$, $7$</td>
<td>$2260$</td>
<td>$C≡N$</td>
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<tr>
<td>$\text{Ru(OEP)(Br)}_2$, $9$</td>
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<td>$\text{Ru-Br}$</td>
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<tr>
<td>$\text{Ru(OEP)(Cl)}_2$, $10$</td>
<td>$289$</td>
<td>$\text{Ru-Cl}$</td>
</tr>
<tr>
<td>$\text{Ru(OEP)(THF)(SbF}_6)$, $11$</td>
<td>$650$</td>
<td>$\text{Sb-F}$</td>
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