Binuclear Osmium Complexes and Related Compounds - A Synthetic and Spectroelectrochemical Study

A thesis submitted for the degree of Doctor of Philosophy at The Australian National University

by

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Declaration

Except where specific reference is made to other sources, the work presented in this thesis is the work of the author. It has not been submitted, in whole or in part, for any other degree.

David Greig Humphrey
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Abstract

This thesis is in general devoted to the synthesis and characterization of binuclear halide-bridged diosmium (and diruthenium) complexes. Particular emphasis is placed on their redox chemistry and associated spectroelectrochemistry.

An extensive range of triple-bridged, face-sharing \([\text{M}_2(\mu-\text{X})_3(\text{PR}_3)_6]\) \(X\) complexes (\(M=\text{Ru}, \text{Os}, X=\text{Cl}, \text{Br}, \text{PR}_3=\text{variation of phosphine donor ligands}\)) are prepared, along with the first example of an isostructural mixed-metal (Ru/Os) complex (Chapter 1). These complexes in general undergo two metal-based one-electron oxidations, formally spanning \(\text{M}_2^{\text{II}},\text{II}\), \(\text{M}_2^{\text{II}},\text{III}\) and \(\text{M}_2^{\text{III}},\text{III}\). A mixed-valence \([\text{Ru}_2(\mu-\text{X})_3(\text{PR}_3)_6]^2+\) complex has also been isolated for the first time, and is the subject of a more detailed magnetic study.

Where possible, the u.v./visible/near-infrared spectra of the \([\text{M}_2(\mu-\text{X})_3(\text{PR}_3)_6]^2+\) complexes are collected in three oxidation levels (Chapter 2). These spectra can in general be assigned in terms of ligand-to-metal charge-transfer, and transitions within the molecular orbital manifold described for \(D_{3h}\) systems. The mixed-valence \([\text{M}_2(\mu-\text{X})_3(\text{PR}_3)_6]^2+\) systems (both Os2 and Ru2) are thought to be valence-delocalized, while the mixed-metal (Ru/Os) complex is best described as valence-trapped. The spectroelectrochemistry of the structurally related “ruthenium blues” \([\text{Ru}_2(\mu-\text{X})_3(\text{Me}_3\text{tacn})_2]^2+\) (\(X=\text{Cl}, \text{Br}\)) is also presented for the first time.

The double-bridged, edge-sharing diosmium complexes, \([\text{Os}_2(\mu-\text{X})_2\text{X}_8]^2-\) (\(X=\text{Cl}, \text{Br}\)), are prepared by improved procedures, and shown to be important precursors to the \([\text{Os}_2(\mu-\text{X})_3\text{X}_6]^2-\) complexes (Chapter 3). The voltammetry and spectroelectrochemistry of the \([\text{Os}_2(\mu-\text{X})_2\text{X}_8]^2-\) complexes is presented for the first time, in addition to detailed variable-temperature magnetic measurements on solid samples of the \(\text{Os}_2^{\text{IV}},\text{IV}\) compounds.

The triple-bridged, face-sharing diosmium complexes, \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^1-\) and \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^3-\) are isolated for the first time as organo-soluble salts (Chapter 4). The analogous nonachloride complex is also prepared by electrolysis and characterized \textit{in situ}. The redox chemistry of the...
[Os₂(μ-X)₃X₆]²⁻ systems is presented, and can be related to that of [Ru₂(μ-X)₃X₆]²⁻, [Os₂(μ-X)₂X₈]²⁻ and [M₂(μ-X)₃(PR₃)₆]²⁺ in a systematic and periodic manner. The electronic spectra of the [Os₂(μ-X)₃X₆]²⁻ complexes are collected in three oxidation levels (z=1, 2, 3), and empirical assignments of the main spectral features are offered. Variable-temperature magnetic studies are also performed on various salts of [Os₂(μ-Br)₃Br₆]¹⁻ and [Os₂(μ-Br)₃Br₆]³⁻.

Studying the cleavage reactions of binuclear complexes [Os₂(μ-X)₃X₆]¹⁻ and [Os₂(μ-X)₂X₈]²⁻ led to the preparation and characterization of a range of monomeric complexes, of stoichiometry [OsX₅L]²⁻ and trans-[OsX₄L₂]²⁻ (Chapter 5). Their redox chemistry, u.v./visible/near-infrared and epr spectra are discussed. Plotting either E₁/₂(OsIV/III), E₁/₂(OsIII/II) or ν_max(XMCT) against stoichiometry (n in [OsX₆-nLₙ]²), yields two distinct patterns of behaviour, depending on the identity of L. For weak π-acceptors the progression is regular, while for successive incorporation of strong π-acceptors the progression is clearly non-additive. Such behaviour is not predicted by recent linear ligand additivity models.

Abbreviations

In this thesis, numerical ranges are sometimes abbreviated by the usage 12-20 000 (meaning 12 000 to 20 000) and the like; c.f. p63.
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Chapter 1

SYNTHESIS AND REDOX STUDIES OF CONFACIAL BIOCATAHERAL COMPLEXES OF RUTHENIUM AND OSMIUM, \([M_2(\mu-X)_3(PR_3)_6]^{z+}\)

1.1 INTRODUCTION

1.1.1 General

A diverse range of binuclear transition metal complexes have been synthesized over the past 30 years. Consideration of their chemical and physical properties has revealed that many of these compounds display unusual optical and magnetic phenomena, novel electron-transfer properties or enhanced reactivity. Certain examples have found use in catalysis, as models for active sites in metal containing biological systems and as building blocks for inorganic polymers. Others have displayed exotic structures.

Some well-known and interesting examples of binuclear coordination compounds are \([(NH_3)_5Ru(\mu-N_2)Ru(NH_3)_5]^{4+}\), where the two metal centres are linked by a single bridging dinitrogen group,\(^1\) or the 'classical' mixed-
valence pyrazine-bridged Creutz-Taube ion [(NH₃)₅Ru(µ-pz)Ru(NH₃)₅]⁺.²,³

Examples of dimeric compounds held together by unsupported metal-metal bonds include the octahalodimetallate complexes, of which the most famous is probably [Re₂Cl₈]²⁻.⁴ Other metal-metal bonded compounds, such as Cr₂(O₂CCH₃)₄, are "strapped together" by bidentate ligands.⁵

Organometallic binuclear systems are diverse; e.g. Fe₂(CO)₉, which has six terminal and three bridging carbonyl groups, and [Ni₂(C₅H₅)₃]⁺, where two Ni(C₅H₅)⁺ units are bridged by another C₅H₅⁻ group, giving a "triple-decker sandwich" structure.⁶,⁷

Within the large area of biologically relevant compounds, some examples are the manganese containing enzymes known as catalases, where current models consist of two manganese atoms (in a variety of oxidation states) with nitrogen donor terminal ligands, and a variety of bridging oxygen groups such as oxo, hydroxy, carboxylate etc.⁸-¹⁰ Sulfide-bridged binuclear iron complexes have also been extensively studied, as analogues of the iron-sulfur protein 2Fe-Ferredoxin.¹¹,¹²

The common link amongst these very different systems is that some particular and important aspect of their chemistry only occurs as a consequence of the bimetallic unit, and is due, at least in part, to the interaction of two metal centres.

The binuclear complexes under consideration in this thesis have confacial and conlateral biocylindrical geometries. The majority of work has been carried out on osmium and ruthenium complexes of the former; this structure consists of two octahedra sharing a common face, thus forming a triple-bridge, while the latter can be described as double-bridged, edge-sharing biocylindrical. In each case, suitable monomeric complexes can be sought which model the intrinsic electronic properties of the subunits making up the bimetallic complex.

1.1.2 Confacial Biocylindrical Complexes of Ruthenium and Osmium

There is a large and diverse range of ruthenium complexes possessing the triple-bridged, face-sharing biocylindrical structure.¹³,¹⁴ In the case of osmium, the number of examples cited in the literature are far fewer.
The bridging ligands in these compounds are small, anionic groups, such as halide (X⁻), O₂⁻, H⁻, OH⁻ or OR⁻. Terminal ligands like the hard donors X⁻, NH₃ and H₂O tend to stabilize the \{M(µ-X)₃M\}²⁺ unit in higher metal oxidation states, while soft donor ligands such as PR₃, AsR₃, CO, CS or arene stabilize \{M(µ-X)₃M\}²⁺ in low oxidation states. Almost all of the complexes synthesized in Chapter 1 are isolated in their divalent oxidation states, the exceptions being two mixed-valence compounds. A survey of the literature will therefore focus on selected M₂II,II and formally M₂II,III examples (where M=Ru, Os).

A particularly large number of Ru₂II,II compounds have been reported. The majority of these involve halide bridging groups with phosphine and arsine donor ligands at the terminal coordination sites, often in combination with other neutral (e.g. CO, CS) and anionic (e.g. halide) ligands. The first reported compounds of this class were prepared by Chatt and Hayter in 1961.¹⁵ By refluxing alcoholic solutions of RuCl₃.xH₂O and the appropriate tertiary phosphine, compounds of formula [Ru₂(µ-Cl)₃(PR₃)₆]Cl were obtained. The triple-bridged Ru₂II,II structure, [(PR₃)₃Ru(µ-Cl)₃Ru(PR₃)₃]⁺Cl⁻ (Figure 1.1), was proposed on the basis of conductivity and molecular weight measurements, assuming RuⅡ retained its six coordinate octahedral geometry. This was later confirmed, when Raspin published the structure of [Ru₂(µ-Cl)₃(PEt₂Ph)₆]¹⁺mer-[RuCl₃(PEt₂Ph)₃]¹⁻.¹⁶ The angles within the core of the binuclear unit (i.e. Ru-Clb-Ru' 87.9° (av) and Clb-Ru-Clb' 76.9° (av)), and a Ru...Ru separation of 3.443 Å, confirmed the structure did not contain a metal-metal bond.
Over the ensuing years, [Ru$_2$(µ-Cl)$_3$(PR$_3$)$_6$]Cl compounds containing a variety of phosphorus donor ligands have been synthesized. Some of the procedures are summarized in Figure 1.2.

**Figure 1.2** Preparative Routes to [Ru$_2$(µ-Cl)$_3$(PR$_3$)$_6$]Cl Complexes.

(i) Boiling aqueous ethanol, PR$_3$=PEt$_2$Ph, PEtPh$_2$, PMe$_2$Ph, PMePh$_2$,
(ii) Boiling ethanol, PR$_3$=P(OEt)$_2$Ph, P(OEt)$_3$,
(iii) Boiling alcohol (ROH, R=Me, Et), PR$_3$=P(OR)$_2$Ph, P(OR)Ph$_2$, R=Me, Et,
(iv) Refluxing toluene, PR$_3$=triphos,*
(v) Polar solvent, PR$_3$=PMe$_2$Ph (n=4), PR$_3$=PMe$_2$Ph (n=3), PR$_3$=P(OMe)$_3$ P(OMe)Ph$_2$ (n=4),
(vi) Refluxing EtOH or CH$_2$Cl$_2$, PR$_3$=PEt$_2$Ph, PEtPh$_2$, PMe$_2$Ph (n=3 or 4),
(vii) Boiling 2-methoxyethanol, PR$_3$=PEt$_2$Ph.

Since Chatt’s first preparation, many other compounds containing the {Ru(µ-Cl)$_3$Ru}$^{1+}$ core have been isolated, along with some {Ru(µ-Cl)$_3$Ru}$^{2+}$ (formally Ru$_2^{II,III}$) and {Ru(µ-Cl)$_3$Ru}$^{3+}$ complexes.

Ru$_2^{II/II}$ examples include the neutral [Ru$_2$(µ-Cl)$_3$(PR$_3$)$_5$Cl] compounds (Figure 1.3 (a)), which have a terminal chloride in addition to the three bridging chloride ligands. Their preparation can be achieved by a number of routes, depending upon the identity of the phosphine. Other related neutral complexes are [Ru$_2$(µ-Cl)$_3$(L)(PR$_3$)$_4$Cl] (L=CO, CS) (Figure 1.3 (b)), prepared by Stephenson et al., while examining the rearrangement reactions of a variety of monomeric Ru$_2^{III}$ complexes.

These compounds are just some of the many face-sharing Ru$_2^{II,II}$

* triphos=1,1,1-tris(diphenylphosphinomethyl)ethane.
complexes reported in the literature. What makes them interesting is that it was with these complexes that Heath and Stephenson first probed the redox activity of the \{(\mu-\text{Cl})_3\text{Ru}\}^{1+}\ core. In what was the first of many papers concerning the redox properties of halide-bridged diruthenium systems, these authors examined the voltammetry of the complexes described above, and suggested that as a class they undergo successive one-electron metal-based oxidations.\textsuperscript{26} Subsequent work established a wealth of redox activity associated with the \{(\text{Ru}(\mu-\text{X})_3\text{Ru})^{2+}\ core,\textsuperscript{27-30} some of which is described here.

![Figure 1.3 (a) and (b)](image)

The structures of the neutral (a) \[[\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_5\text{Cl}]\] and (b) \[[\text{Ru}_2(\mu-\text{Cl})_3(\text{CO})(\text{PR}_3)_4\text{Cl}]\] complexes.

The Effective Atomic Number (EAN) rule for summing the complement of valence electrons about a coordinated metal ion provides a convenient way of describing the redox changes in these complexes, where a \text{Ru}_{2\text{II,II}} compound is by definition a 36 electron \((2 \times 18)\) system. The stepwise removal of consecutive electrons (corresponding to metal-based oxidations) gives firstly the 35 electron species, then the 34 electron species and so on. Figure 1.4 summarizes this terminology. The entire range of 32 to 36 electron \([\text{M(\mu-\text{X})}_3\text{M}]^{2+}\) species are discussed in the course of this thesis.

![Figure 1.4](image)

Electron counting scheme for \([\text{M}_2(\mu-\text{X})_3\text{L}_6]^{2+}\ complexes, \text{M}=\text{Ru}, \text{Os.}
The \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^{1+}\) complexes first prepared by Chatt and Hayter\(^{15}\) show two reversible one-electron metal-based oxidations, spanning the 36 to 34 electron systems. Similarly, the \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_5\text{Cl}]\) complexes also display two oxidations, moved to lower potentials as a consequence of the increased halide ligation. Intuitively, the first of these oxidations, corresponding to the 35/36 electron couple, will be preferentially localized on the ruthenium centre bearing the additional (terminal) chloride ligand (see Figure 1.6 (b)). The rational shift of the metal-centred \(E^0\) to more positive potentials as \(L\) replaces halide is well documented. In particular, linear relationships between stoichiometry and metal-based electrode potentials have recently been established by Heath and Duff for the \([\text{Ru}X_{6-n}(\text{RCN})_n]^z\) series of complexes.\(^{31}\) Only one oxidation is observed in the \([\text{Ru}_2(\mu-\text{Cl})_3(L)(\text{PR}_3)_4\text{Cl}]\) (\(L=\text{CO}, \text{CS}\)) complexes, the carbonyl (or thiocarbonyl) group making the second oxidation inaccessible (see Figure 1.6 (c)).\(^{32}\)

Another particularly interesting group of triple-bridged diruthenium complexes are those of general formula \([\text{Ru}_2(\mu-\text{Cl})_3(L)_4\text{Cl}_2]\) (\(L=\text{PR}_3, \text{AsR}_3\)), isolated as neutral 35 electron mixed-valence compounds. There are three possible isomers for this stoichiometry as illustrated in Figure 1.5.

\(\text{(a)}\)

\(\text{(b)}\)

\(\text{(c)}\)

\(\text{Figure 1.5 (a), (b) and (c) The structures of the three possible isomers for complexes of stoichiometry } [\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_4\text{Cl}_2].\)
Nicholson prepared the first of these complexes, \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PBU}_3)_4\text{Cl}_2]\), in 1967.\(^{33}\) He reported that the reaction of a concentrated ethanolic solution of ruthenium trichloride and tri-n-butylphosphine yielded firstly the edge-sharing, double-bridged \([\text{Ru}_2(\mu-\text{Cl})_2(\text{PBU}_3)_4\text{Cl}_4]\) and then from filtrate the mixed-valence \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PBU}_3)_4\text{Cl}_2]\).

The proposed triple-bridged structure was later confirmed by x-ray crystallographic studies, \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PBU}_3)_4\text{Cl}_2]\) having the structure shown in part (a) of Figure 1.5.\(^{34,35}\) While this preparation appears straightforward, others have not been able to repeat Nicholson's achievement,\(^{32}\) and the great majority of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{L})_4\text{Cl}_2]\) compounds isolated until very recently have been asymmetric isomers (Figure 1.5, (c)).\(^{36}\)

The redox chemistry of the \([\text{Ru}_2(\mu-\text{Cl})_3(\text{L})_4\text{Cl}_2]\) compounds is most interesting. The voltammetry of these mixed-valence complexes, formally \(\text{Ru}^{\text{III}}/\text{II}\), in general show an oxidation and a reduction, spanning the 34 to 36 electron systems as in the \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^+\) and \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_5\text{Cl}]\) compounds.

Heath, Stephenson and co-workers were able to prepare two different isomers of stoichiometry \([\text{Ru}_2(\mu-\text{Cl})_3(\text{As}(p\text{-tol})_3)_4\text{Cl}_2]\),\(^{36}\) each with a magnetic moment corresponding to one unpaired electron.\(^{36}\) From e.s.r. studies, the isomers were shown to have structures (a) and (c) in Figure 1.5. Although the voltammetry of each of these complexes revealed an oxidation and a reduction, the separation of these couples \((\Delta E_{1/2})\) was distinctly different. \(\Delta E_{1/2}\) for asymmetric isomers is typically large, due to the different ligand environment about each metal centre. In the example described above (Figure 1.5 (c)), \(\Delta E_{1/2}=1.50\) V, as compared with 0.76 V in the symmetric isomer (Figure 1.5 (a)).

Emerging from the systematic examination of the redox properties of a number of \([\text{Ru}(\mu-\text{Cl})_3\text{Ru}]^{2+}\) complexes are certain rational structure/redox correlations. The \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^+\), \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_5\text{Cl}]\) and \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_4\text{Cl}_2]\) (asymmetric) complexes form a systematic series, in

---

* Cotton et al. have recently prepared symmetric \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_4\text{Cl}_2]\) isomers. This work will be discussed at a later point.

\(^{36}\) James et al. were also able to prepare symmetric isomers of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_4\text{Cl}_2]\), using bidentate phosphines, enforcing symmetric ligation.\(^{36}\)

\(^{36}\) \(p\)-tol=4-methylphenyl
which terminal phosphine ligands from one ruthenium atom are progressively substituted by chloride. The voltammetry of these complexes is presented schematically in Figure 1.6, along with that of [Ru$_2$(μ-Cl)$_3$(CO)(PR$_3$)$_4$Cl].

![Diagram of voltammetry](image)

**Figure 1.6 (a), (b), (c) and (d).** Schematic representation of the voltammetry of a variety of diruthenium complexes, differing only in the identity of their terminal ligands.

Adopting a localized view of the successive metal-centred couples, the effect of substitution (on Ru$_a$) is traced by the movement of the 35/36 electron couple in complexes (a), (b) and (d). The couple moves progressively to less positive potentials, by 0.74 V (on average) as each PEt$_2$Ph is replaced by Cl$^-$. Similarly the effect on the metal centre remote from the substitution (Ru$_b$) is mapped by the 34/35 electron couple, which
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moves by 0.24 V (on average) per substitution. Note also the separation of the couples ($\Delta E_{1/2}$) increases by ca. 0.5 V in such a substitution, which reflects the increasing asymmetry in the structure.

Although the full series of complexes from $[\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^+$ to $[\text{Ru}_2(\mu-\text{Cl})_3\text{Cl}_6]^{-}$ are not available, for those that are, a plot of the mean of the 34/35 and 35/36 couples versus stoichiometry gives a linear relationship (Figure 1.7). This is reminiscent of the behaviour of $[\text{RuX}_{6-n}({\text{RCN})}_n]^z$ monomers upon substitution of X by RCN, as mentioned earlier.

![Figure 1.7](image)

**Figure 1.7** Structure/redox correlations. A plot of the mean of 34/35 and 35/36 electron couples versus $n$, in $[\text{Ru}_2(\mu-\text{Cl})_3\text{Cl}_6.n(\text{PR}_3)_n]^+$ complexes.

In odd-electron binuclear systems, the question arises as to whether the electron is shared equally between the two metal centres (delocalized), or preferentially resides on one particular metal (localized or trapped). The optical spectra of such mixed-valence systems often display a band which is unique to the odd-electron configuration. Such a band, called an intervalence charge-transfer (i.v.c.t.) band, was observed in the near-infrared optical spectrum of $[\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_4\text{Cl}_2]$. Electrochemical oxidation of the $[\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_5\text{Cl}]$ and $[\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_6]^+$ complexes yielded further isoelectronic 35 electron systems, the absorption spectra of which also revealed i.v.c.t. transitions. Comparing the spectra of the three
complexes \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_6]^{2+}\), \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_5\text{Cl}]^{1+}\) and \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_4\text{Cl}_2]\), the i.v.c.t. band can be found centred at -4 400, 9 700 and 13 500 cm\(^{-1}\) respectively. Optical band shape analysis suggested the symmetric complex was best described as delocalized, while the asymmetric examples were valence trapped.\(^{38}\)

Cotton \textit{et al.}\(^{39,40}\) have recently provided some much needed structural data on \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_4\text{Cl}_2]\) complexes of the type described above. Re-examining Nicholson's reaction (with a variety of phosphines), they isolated a number of bi- and trinuclear ruthenium/chloro/phosphine complexes.\(^{39-41}\) Three different isomers of general formula \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_4\text{Cl}_2]\) were structurally characterized, as illustrated in Figure 1.5. The asymmetrically ligated isomer of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{P}Bu_3)_4\text{Cl}_2]\) (Figure 1.5 (c)) was described as being valence-trapped, thus contrasting with the symmetric isomers shown in Figure 1.5 (parts (a) and (b)), in which the odd electron is thought to be delocalized.

Other mixed-valence diruthenium compounds, about which much has been written, are the ammine-capped systems, \([\text{Ru}_2(\mu-\text{X})_3(\text{NH}_3)_6]\)\(^{2+}\). Solutions of these complexes, and the aquo analogues, \([\text{Ru}_2(\mu-\text{X})_3(\text{H}_2\text{O})_6]\)\(^{2+}\),\(^{42}\) are intensely blue in colour, on account of their i.v.c.t. bands in the visible region of the spectrum. Both the chloride and bromide complexes of \([\text{Ru}_2(\mu-\text{X})_3(\text{NH}_3)_6]\)\(^{2+}\) are known, their structures being confirmed by x-ray crystallographic studies.\(^{43,44}\) While there is general agreement in the literature that these complexes are best described as delocalized mixed-valence systems, there are conflicting views as to the assignments of the electronic spectra.\(^{45}\)

Similar compounds have been prepared by Wieghardt \textit{et al.}, with terminal macrocyclic N-donor ligands, 1,4,7-triazacyclononane and \(N, N', N''\)-trimethyl-1,4,7-triazacyclononane,\(^{46,47}\) e.g. \([\text{Ru}_2(\mu-\text{X})_3(\text{Me}_3\text{tacn})_2]\)\(^{2+}\).\(^{6}\) These mixed-valence systems are electronically delocalized, with very similar physical properties to their ammine (NH\(_3\)) analogues. For the moment, it is only necessary to stress that the related phosphine- and ammine-capped face-sharing halide-bridged complexes differ sharply in

\(^{6}\) Me\(_3\text{tacn}=N, N', N''\)-trimethyl-1,4,7-triazacyclononane.
their optical properties.

Very little thus far has been said about diosmium complexes possessing the confacial biocatalyst structure. This is simply because there are relatively few examples of such complexes, compared with the large number of ruthenium examples. For that reason, any novel diosmium complexes are of obvious interest. Aside from a number of arene-capped, alkoxy/hydroxy-bridged systems,\textsuperscript{48-51} and some triple hydrido-bridged compounds,\textsuperscript{52} the most well documented examples are the [Os\textsubscript{2}(\mu-Cl)\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]X complexes.

In their paper describing the preparation and characterization of the [Ru\textsubscript{2}(\mu-Cl)\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]X compounds,\textsuperscript{15} Chatt and Hayter also reported some diosmium complexes of the same formula. Since then, a number of routes have led to the isolation of [Os\textsubscript{2}(\mu-X)\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]X complexes. The various methods are summarized in Figure 1.8.

\begin{figure}[h]
\centering
\begin{tikzpicture}
\node (1) at (0,0) {[Os\textsubscript{2}X\textsubscript{6}]\textsuperscript{2-}};
\node (2) at (2,-1) {[Os\textsubscript{2}X\textsubscript{6}]\textsuperscript{2-}};
\node (3) at (2,-2) {[Os\textsubscript{2}(\mu-X)\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]\textsuperscript{1+}};
\node (4) at (3,-3) {mer-[OsX\textsubscript{3}(PR\textsubscript{3})\textsubscript{3}]};
\node (5) at (2,-3) {cis-[OsX\textsubscript{2}(PR\textsubscript{3})\textsubscript{4}]};
\draw (1) -- (2) node[above=0.5cm,midway]{(i)};
\draw (2) -- (3) node[left=0.5cm,midway]{(iv)};
\draw (3) -- (4) node[above=0.5cm,midway]{(ii)};
\draw (3) -- (5) node[below=0.5cm,midway]{(iii)};
\end{tikzpicture}
\caption{Preparative routes to [Os\textsubscript{2}(\mu-X)\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]X complexes.}
\end{figure}

\begin{itemize}
\item (i) Boiling aqueous ethanol, X=Cl, PR\textsubscript{3}=PMe\textsubscript{2}Ph, PMePh\textsubscript{2}, PEt\textsubscript{2}Ph, PEtPh\textsubscript{2},\textsuperscript{15}
\item (ii) Treatment with Zn/Hg under Ar at room temperature in tetrahydrofuran, X=Cl, PR\textsubscript{3}=PMe\textsubscript{2}Ph, PEt\textsubscript{2}Ph, PEtPh\textsubscript{2},\textsuperscript{53} and X=Cl, PR\textsubscript{3}=PMe\textsubscript{2}Ph, via electrochemical reduction in CH\textsubscript{2}Cl\textsubscript{2},\textsuperscript{54}
\item (iii) Refluxing iso-butanol, X=Cl, PR\textsubscript{3}=PMe\textsubscript{2}Ph,\textsuperscript{54}
\item (iv) Refluxing ethanol, X=Cl, Br, PR\textsubscript{3}=PMePh\textsubscript{2}, PEt\textsubscript{3},\textsuperscript{55}
\end{itemize}

The voltammetry of the diosmium complexes has also been recorded, and is qualitatively very similar to that of the diruthenium analogues; the complexes undergo two metal-based one-electron oxidations.\textsuperscript{32,54,55}
Three diosmium compounds have been structurally characterized, namely [Os₂(µ-Cl)₃(PEt₃)₆]PF₆, [Os₂(µ-Cl)₃(PMe₂Ph)₆]PF₆ and the mixed-valence complex [Os₂(µ-Cl)₃(PEt₃)₆](PF₆)₂. The structures of these complexes are discussed in more detail in the introduction to Chapter 2.

1.1.3 Purpose of This Work

In general, this thesis is devoted to the synthesis and spectroelectrochemical characterization of binuclear and related monomeric complexes of osmium and ruthenium. The [M₂(µ-X)₃(PR₃)₆]¹⁺ and [M₂(µ-X)₃(X)₆]³⁻ complexes (M=Ru, Os; X=Cl, Br) form important subclasses within the general class of triple-bridged, face-sharing biocatahedral systems. The effect of terminal ligation on redox stability is such that these complexes are normally isolated in different oxidation states, i.e. M²⁺,²⁺ and M²⁺,²⁺ for the terminal phosphine and halide systems respectively. In between these extremes, the ammine- and aquo-capped complexes, [Ru₂(µ-X)₃(L)₆]²⁺ (L=H₂O, NR₃), are isolated as Ru²⁺,²⁺.

Through the use of electrochemical techniques, it is possible to drive these systems to common oxidation states, M²⁺,²⁺ and M²⁺,²⁺, where comparisons of the degree of metal-metal interaction, as a function of the metal, and terminal ligation are more valid.

For the first time it has been possible to make a systematic spectroelectrochemical survey of the [M₂(µ-X)₃(PR₃)₆]²⁺ complexes, encompassing M=Ru and Os, X=Cl and Br, and a wide range of phosphine ligands. This provides the opportunity for comparison of the metal-metal interaction in isostructural/isoelectronic osmium and ruthenium complexes (over three oxidation states), and the classification of the mixed-valence 35 electron species. The syntheses and redox chemistry of the [M₂(µ-X)₃(PR₃)₆]X compounds are described in Chapter 1, and their associated spectroelectrochemistry is discussed in Chapter 2.

Spectroelectrochemical, in this sense, refers to the use of electrochemical and in situ spectroelectrochemical techniques.
1.2 SYNTHESIS OF HALO-BRIDGED DIRUTHENIUM AND DIOSMIUM COMPLEXES, \([M_2(\mu-X)_3(PR_3)_6]X\).

1.2.1 Diruthenium Complexes

The \([Ru_2(\mu-Cl)_3(PR_3)_6]Cl\) complexes, \((PR_3=PEtPh_2, PEt_2Ph, PEt_3, PMe_2Ph, P(OMe)Ph_2\) and \((PR_3)_6=(\text{triphos})_2\),\(^\dagger\) were synthesized by boiling suspensions of \([RuCl_2(PPh_3)_3]\) and the appropriate phosphine in deoxygenated absolute ethanol, or in the case of \(P(OMe)Ph_2\), methanol.

For the tridentate tripod ligand, 1,1,1-tris(diphenylphosphinomethyl)ethane (Figure 1.9), quantitative yields of the binuclear complex \([Ru_2(\mu-Cl)_3(\text{triphos})_2]Cl\) were obtained by using 2-methoxyethanol instead of absolute ethanol.\(^\ddagger\) This complex has previously been prepared in 80 % yield by heating cis-[RuCl_2(dmsol)_4] and triphos in toluene.\(^{19}\)

![Figure 1.9](image)

\(\text{Figure 1.9} \) The tridentate tripod ligand, 1,1,1-tris(diphenylphosphinomethyl)ethane.

Using 2-methoxyethanol instead of absolute ethanol in the reaction of \([RuCl_2(PPh_3)_3]\) and monomeric phosphines (\(PR_3=PEtPh_2, PEt_2Ph\)) led to the isolation of \(\text{cis-}[RuCl_2(CO)(PR_3)_3]\) complexes, and \(\text{not}\) the desired \([Ru_2(\mu-Cl)_3(PR_3)_6]Cl\) compounds. The monomeric carbonyl complexes were characterized by i.r. and n.m.r. spectroscopy.\(^{23}\) Decarbonylation of alcohols by low valent ruthenium complexes is well documented in the literature.\(^{57}\)

It was originally hoped to synthesize the analogous bromide-bridged complexes by treating \([Ru_2(\mu-OH)_3(PMe_2Ph)_6]PF_6\) with HBr. However, the

\(^\dagger\) Triphos=1,1,1-tris(diphenylphosphinomethyl)ethane.

\(^\ddagger\) Yields of \([Ru_2(\mu-Cl)_3(\text{triphos})_2]Cl\) were \(-75\%\) using absolute ethanol.
preparation of the hydroxo-bridged complex, as developed by Lindsay,\textsuperscript{32} could not be repeated here with any success. Only low yields were obtained, amongst other products which proved difficult to separate.

An alternative synthesis of \([\text{Ru}_2(\mu-\text{Br})_3(\text{PMe}_2\text{Ph})_6]\text{Br}\) was briefly mentioned by Lindsay.\textsuperscript{32} Heating mixtures of \([\text{RuBr}_2(\text{PPh}_3)_3]\) and \(\text{PMe}_2\text{Ph}\) in methanol gave the bromide-bridged complex. This method proved very successful in preparing good yields of \([\text{Ru}_2(\mu-\text{Br})_3(\text{PMe}_2\text{Ph})_6]\text{Br}\), and \([\text{Ru}_2(\mu-\text{Br})_3(\text{PET}_3)_6]\text{Br}\).

For electrochemical studies, it is advantageous to have a redox inert counter-anion. The \([\text{M}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]X\) complexes are in general isolated with halide anions, which exhibit large irreversible oxidative waves at approximately +1.2 V (versus Ag/AgCl). A convenient metathetical procedure was developed to prepare the triflate salts of the binuclear complexes. Simply dissolving the complex in dichloromethane, adding \(-25\%\) excess of a CF\(_3\)SO\(_3\)H/MeOH stock solution (\(-0.1\) mol. dm\(^{-3}\)), and gently refluxing this mixture overnight gave good yields of crystalline \([\text{M}_2(\mu-X)_3(\text{PR}_3)_6]\text{CF}_3\text{SO}_3\) compounds.

\subsection*{1.2.2 Diosmium Complexes}

The synthesis of these complexes was first attempted using the original procedure of Chatt and Hayter.\textsuperscript{15} Refluxing mixtures of \((\text{NH}_4)_2[\text{OsCl}_6]\) and the required phosphine in aqueous ethanol gave only mer-\([\text{OsCl}_3(\text{PR}_3)_3]\) compounds. Further reaction of these compounds with excess free ligand in alcoholic solvents, or reduction with Zn/Hg in dichloromethane yielded the required bimetallic complexes.\textsuperscript{53} Such procedures either consumed considerable quantities of phosphine ligands and were time consuming, or gave only low yields of \([\text{Os}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]\text{Cl}\) complexes.

The method of Heath \textit{et al.} was used to successfully prepare moderate yields of \([\text{Os}_2(\mu-\text{Cl})_3(\text{PMe}_2\text{Ph})_6]\text{Cl},\textsuperscript{54} however the versatility of this route to give other \([\text{Os}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]\text{Cl}\) complexes was not explored. Walton has also described the synthesis of a number of \([\text{Os}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]X\) compounds.\textsuperscript{55} The starting material of this reaction, the multiply bonded \([\text{Os}_2X_8]^2-\) dimer, is made from \([\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2]\), the preparation of which is not trivial.\textsuperscript{58}
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The published methods of preparing \([\text{Os}_2(\mu-X)_3(\text{PR}_3)_6]X\) complexes described above all involve the reduction of higher-valent osmium compounds. Given that dimerization only occurs to any considerable extent when the metal is in its divalent oxidation state, then reduction must precede bridge formation. The free phosphine ligand functions as an efficient reducing agent, but the presence of large excesses of free ligand must inhibit the dimerization process to some extent. With these problems in mind, an alternative procedure to triple-bridged, face-sharing binuclear complexes was sought.

The five coordinate, divalent \([\text{OsCl}_2(\text{PPh}_3)_3]\) is a well characterized Os\(^{II}\) compound.\(^{59-61}\) The reactivity of this complex is generally unexplored, which is surprising, given the lack of convenient osmium starting materials, and the diversity of complexes prepared from its ruthenium analogue.\(^{62}\)

Refluxing mixtures of \([\text{OsCl}_2(\text{PPh}_3)_3]\) and tertiary phosphines (PEt\(_3\), PEt\(_2\)Ph, PMe\(_2\)Ph) in deoxygenated absolute alcohol gave pale-yellow solutions, from which light-coloured solids were isolated. Single resonances were observed in the \(^{31}\text{P}(1\text{H})\) n.m.r. spectra of these materials, consistent with the formation of symmetric \([\text{Os}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]\)Cl complexes [equation (1.1)], as was microanalytical data. Their infra-red spectra were also indistinguishable from \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]\)Cl compounds with the same phosphine. The electrochemistry of these complexes, which will be discussed in greater detail in Section 1.3, was also consistent with the binuclear formulation.

\[
2[\text{OsCl}_2(\text{PPh}_3)_3] + 6\text{PR}_3 \xrightarrow{\text{EtOH}, \Delta} [\text{Os}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]\text{Cl} + 6\text{PPh}_3 \quad (1.1)
\]

\(\text{PR}_3 = \text{PMe}_2\text{Ph}, \text{PEt}_3, \text{PEt}_2\text{Ph}, \text{and} (\text{PR}_3)_3=\text{triphos}\)

Using 2-methoxyethanol in place of absolute ethanol in equation (1.1) gave cis-\([\text{OsCl}_2(\text{CO})(\text{PR}_3)_3]\) complexes, where \(\text{PR}_3\) is a monodentate phosphine. In contrast, in the presence of the tridentate phosphine triphos, \([\text{Os}_2(\mu-\text{Cl})_3(\text{triphos})_2]\)Cl was formed. The contrasting reactivity of \([\text{OsCl}_2(\text{PPh}_3)_3]\)/phosphine mixtures in ethanol and 2-methoxyethanol parallels that of \([\text{RuCl}_2(\text{PPh}_3)_3]\).
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The divalent \([\text{OsCl}_2(\text{PPh}_3)_3]\) has proven to be a most useful precursor to \([\text{Os}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]\text{Cl}\) compounds. The analogous bromide complex, \([\text{OsBr}_2(\text{PPh}_3)_3]\), has been previously reported, but its preparation could not be repeated. Aside from Walton's route to the bromide-bridged complexes, there are no other reports of \([\text{Os}_2(\mu-\text{Br})_3(\text{PR}_3)_6]\text{Br}\) compounds within the literature.

It was discovered that refluxing mer-\([\text{OsBr}_3(\text{PMe}_2\text{Ph})_3]\) and PMe_2Ph in deoxygenated 2-methoxyethanol gave the bromide-bridged complex \([\text{Os}_2(\mu-\text{Br})_3(\text{PMe}_2\text{Ph})_6]\text{Br}\) directly. The intention was to prepare cis-\([\text{OsBr}_2(\text{PMe}_2\text{Ph})_4]\), and then heat this species in a high-boiling alcohol to yield the bromide-bridged binuclear complex, a route analogous to that described by Heath et al. for the formation of \([\text{Os}_2(\mu-\text{Cl})_3(\text{PMe}_2\text{Ph})_6]\text{Cl}\).

Triflate salts of \([\text{Os}_2(\mu-\text{X})_3(\text{PR}_3)_6]^+\) were readily prepared by the same procedure already outlined for the \([\text{Ru}_2(\mu-\text{X})_3(\text{PR}_3)_6]\text{CF}_3\text{SO}_3\) complexes.

### 1.2.3 Mixed-Metal Binuclear Complexes

To the best of the author's knowledge, only one brief mention of a heterobinuclear triple halide-bridged Ru/Os complex appears within the literature. No voltammetric or spectroelectrochemical studies were performed on the \([(\text{PPh}_3)_2(\text{CO})\text{Ru}(\mu-\text{Cl})_3\text{OsCl}(\text{PPh}_3)_2]\) complex, due to its poor solubility in typical non-aqueous electrochemical solvents, e.g. CH_2Cl_2. Nixon et al. prepared mixed Ru/Rh triple-chloro bridged face-sharing complexes, and commented that the analogous Ru/Os compounds could not be synthesized.

A symmetrically ligated Ru/Os complex was of great interest, as the metal orbitals which make up the molecular orbital scheme for complexes of this basic structure, would no longer be degenerate. This mis-match of orbital energies may produce an asymmetric electron distribution upon oxidation (which should preferentially occur at the osmium site). Therefore the electronic spectrum of \([(\text{PR}_3)_3\text{Ru}(\mu-\text{X})_3\text{Os}(\text{PR}_3)_3]^2+\) (formally \([\text{Ru}^{II}(\mu-\text{X})_3\text{Os}^{III}]^2+\)) was of particular interest.

The tridentate triphos ligand was chosen in an effort to prepare symmetric binuclear complexes, exclusively coordinating phosphine at each
Chapter 1

of the terminal sites. Refluxing an equimolar mixture of the two precursors, [RuCl₂(PPh₃)₃] and [OsCl₂(PPh₃)₃], with an excess of triphos in 2-methoxyethanol produced yellow solutions [equation (1.2)].

\[
4 [\text{OsCl}_2(\text{PPh}_3)_3] + 4 [\text{RuCl}_2(\text{PPh}_3)_3]
\]

\[
\begin{align*}
2-\text{MeOCH}_2\text{CH}_2\text{OH} & \quad 8 \text{triphos} \\
N_2, \Delta & \quad (1.2) \\
\rightarrow & \\
[\text{Ru}_2(\mu-\text{Cl})_3(\text{triphos})_2]\text{Cl} & + [\text{Os}_2(\mu-\text{Cl})_3(\text{triphos})_2]\text{Cl} \\
+ 2 [(\text{triphos})\text{Ru}(\mu-\text{Cl})_3\text{Os(tribhos)}]\text{Cl} & + 24 \text{PPh}_3
\end{align*}
\]

The \(^{31}\text{P}(\text{H})\) n.m.r. spectrum of the yellow solid isolated from this reaction is shown in Figure 1.10. Four singlets are observed, all consistent with the formation of highly symmetric complexes in which each arm of the tripodal ligand is coordinated to a metal centre (free triphos has a resonance at -26.3 p.p.m.). The singlets at +36.5 and -17.4 p.p.m. can be assigned as [Ru₂(µ-Cl)_3(triphos)_2]Cl and [Os₂(µ-Cl)_3(triphos)_2]Cl respectively, prepared and characterized as discussed in Section 1.2.2. The remaining singlets are assigned as belonging to [(triphos)Ru(µ-Cl)_3Os(triphos)]Cl. The products of the reaction had formed in an approximately statistical ratio [equation (1.2)], i.e. 1:2:1 for Ru₂:RuOs:Os₂, as determined from integration of the n.m.r. spectrum.
Attempts at physical separation of this mixture were unsuccessful. Even the first few percent of product formed upon crystallization contained all three complexes.

Repeating the reaction with a five fold excess of \([RuCl_2(PPh_3)_3]\) limited the formation of the diosmium complex [equation (1.3)] to such an extent that essentially only two products were obtained.

\[
\begin{align*}
[OsCl_2(PPh_3)_2] + 5 [RuCl_2(PPh_3)_3] \\
2\text{-MeOCH}_2\text{CH}_2\text{OH} & \quad 6 \text{triphos} \\
N_2, \Delta \\
2 [Ru_2(\mu-\text{Cl})_3(\text{triphos})_2]Cl + [(\text{triphos})\text{Ru}(\mu-\text{Cl})_3\text{Os}(\text{triphos})]Cl \\
+ 18 \text{PPh}_3
\end{align*}
\]
The $^{31}$P($^1$H) n.m.r. spectrum of this reaction mixture (Figure 1.11) revealed only two major products, $[\text{Ru}_2(\mu-\text{Cl})_3(\text{triphos})_2]\text{Cl}$ and $[(\text{triphos})\text{Ru}(\mu-\text{Cl})_3\text{Os(triphos)}]\text{Cl}$. The small quantity of $[\text{Os}_2]^{1+}$ formed was removed upon workup of the reaction. Again the product distribution was approximately statistical.

![Figure 1.11](image)

**Figure 1.11** The $^{31}$P($^1$H) n.m.r. of product mixture from equation (1.3). Resonance (a) is from $[\text{Ru}_2(\mu-\text{Cl})_3(\text{triphos})_2]\text{Cl}$, resonance (b) $[\text{Os}_2(\mu-\text{Cl})_3(\text{triphos})_2]\text{Cl}$, and resonances (c) from $[(\text{triphos})\text{Ru}(\mu-\text{Cl})_3\text{Os(triphos)}]\text{Cl}$.

The separation of the two products was achieved by selective chemical oxidation of the heterobimetallic complex. The addition of NOPF$_6$ to a dichloromethane solution of $[\text{RuOs}]^{+}$ and $[\text{Ru}_2]^{+}$ resulted in the formation of a dark green solution over a period of several minutes. The careful addition of a small volume of diethyl ether, and cooling led to the

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## [(triphos)Ru(μ-Cl)$_3$Os(triphos)]Cl abbreviated as [RuOs]$^{2+}$, and the homobimetallic complexes as [Ru$_2$]$^{2+}$ and [Os$_2$]$^{2+}$. 

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crystallization of a dark green solid, \([(\text{triphos})\text{Ru}(\mu-\text{Cl})_3\text{Os(triphos)})](\text{PF}_6)_2\). While the solubilities of the \((\text{RuOs})^+\) and \((\text{Ru}_2)^+\) mono-cations were very similar, that of the \((\text{RuOs})^2+\) di-cation was different enough to allow its isolation (although only in low yield), free of contamination by the \((\text{Ru}_2)^+\) complex (Figure 1.12).

\[\text{Figure 1.12} \quad \text{The } 31^pJ^1H \text{ n.m.r. of } [(\text{triphos})\text{Ru}(\mu-\text{Cl})_3\text{Os(triphos)})]^+ \text{ after reduction of } [(\text{triphos})\text{Ru}(\mu-\text{Cl})_3\text{Os(triphos)})](\text{PF}_6)_2 \text{ with } n\text{Bu}_4\text{NBH}_4 \text{ in dichloromethane.}\]
1.3 VOLTAMMETRY OF BINUCLEAR COMPLEXES

1.3.1 General

The voltammetry described in this thesis was recorded in a conventional one compartment, three electrode cell. A platinum disc working electrode (0.5-1.0 mm diameter) was used, in dichloromethane or acetonitrile solutions containing \( \text{Bu}_4\text{NPF}_6 \) electrolyte, at concentrations of 0.5 and 0.1 mol. dm\(^{-3} \) respectively. The solutions were routinely deoxygenated with argon or nitrogen, and all voltammetry was performed under an argon or nitrogen cover. All potentials quoted are versus the Ag/AgCl reference electrode, against which ferrocene is oxidized at +0.55 volts (V).

Unless otherwise specified, all references made to the reversibility, irreversibility etc. of redox processes refer to voltammetric reversibility, i.e. the degree of reversibility has been determined by standard voltammetric techniques, according to a number of selected criteria.\(^6^7\) It is also appropriate at this point to make clear the distinction between voltammetric and chemical reversibility, as used in the following discussion. In the voltammetric experiment, only a small portion of the species in solution is actually oxidized or reduced, and the timescale of this process, which is typically in the order of seconds, is controlled by the scan rate. Whether or not the couple is strictly reversible depends upon the rate of heterogeneous electron transfer. This is in sharp contrast to the chemical experiment, in which the entire solution is transformed, whether by bulk electrosynthetic means, or through the use of a chemical oxidant/reductant. The timescale of this redox transformation, which may be hours, becomes the duration of the electrolysis (or the reaction time).\(^6^8\)

The voltammetric reversibility (or otherwise) of a redox process was established by standard criteria.\(^6^7\) Due to high solution resistance within the cell in non-aqueous media, a voltammetrically reversible system can produce results (to these criteria) which deviate from the theoretically predicted values.\(^6^9\) While the instrumentation used in this study does have the facility to compensate for \( iR \) drop, it is simpler (and more reliable) to study a system known to possess a voltammetrically reversible, diffusion-
controlled redox process, and see how it behaves in practice under the same conditions. The ferrocene oxidation is generally accepted to satisfy the reversibility criteria,\textsuperscript{70,71} and has been used for this purpose. Redox processes of other compounds which yield a voltammetric response identical to that of ferrocene, under the same conditions, may be regarded as being \textit{voltammetrically reversible}. The redox processes of the complexes discussed in this chapter have been analysed accordingly, and the results are summarized in the appropriate tables.

Low temperatures, typically 213K (\textdegree60°C), have been used routinely to improve reversibility by restricting rearrangement of electrode products.

\textbf{1.3.2 Voltammetry of [M}_{2}(\mu-X)_{3}(PR_{3})_{6}\text{X Complexes}}

The voltammetry of the [M\textsubscript{2}(\mu-X)\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]\textsuperscript{1+} complexes prepared in Chapter 1 are reported here, some for the first time. In dichloromethane solution at 213 K, each of these species undergoes two metal-based one-electron oxidations (Figure 1.13). Applying the EAN rule to these systems, the sequence of redox transformations therefore span the 36 to 34 electron species, as illustrated in Figure 1.4 (page 5).

The first oxidation is either reversible or quasi-reversible for all complexes, while the second oxidation is, depending upon the metal and phosphine, reversible, quasi-reversible or irreversible. The E\textsubscript{1/2} values and reversibility of these couples are summarized in Table 1.1. Examination of this data reveals some interesting similarities and differences:

(i) The osmium complexes are oxidized at potentials lower than their ruthenium analogues, by \textdegree0.2 V. The 5d valence electrons of osmium experience greater shielding from the core charge of the nucleus, and so are removed more easily (Figure 1.13).

(ii) The oxidations of all complexes move to lower potentials as the net donor-ability of the terminal phosphine increases. The order of the E\textsubscript{1/2} values qualitatively follows that predicted by phosphine basicity.\textsuperscript{11} Taking for example the [Ru\textsubscript{2}(\mu-Cl)\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]\textsuperscript{1+} complexes, the complex with the most

\textsuperscript{11} The basicity of a phosphine, i.e. pK\textsubscript{a} of R\textsubscript{3}PH\textsuperscript{+}, represents only the \textsigma-donor ability of the ligand, and does not account for \textpi-bonding.\textsuperscript{72} Electrochemical potentials are influenced by the net donor ability of the ligand, and do not partition \textsigma and \textpi effects, hence any relationships between E\textsubscript{1/2} and pK\textsubscript{a} values are purely qualitative. Steric effects can also be important in the bonding of phosphine complexes.
basic phosphine PEt₃ has oxidations at +1.09 and +1.71 V, while for the least basic ligand, P(OMe)Ph₂, the same couples occur at +1.46 and +1.97 V.

(iii) In contrast to the effect of variation of the phosphine, exchanging chloride for bromide in the bridging sites has little effect on the positions of the oxidative couples (further discussion of the effect of different halides on metal-based redox potentials can be found in Chapter 5).
The separation of successive redox couples ($\Delta E_{1/2}$) in a symmetric binuclear complex provides an indication as to the degree of electronic interaction between the two metal centres.

For a complex in which the metal atoms are non-interacting, $\Delta E_{1/2}$ is given by simple statistics, and depends only on the number of metal centres present, i.e. for a binuclear system involving two one-electron transfer steps (n=1), $\Delta E_{1/2}=(RT/nF)(\ln 4)$, or at 298 K, $\Delta E_{1/2}=36$ mV.

### Table 1.1  Electrochemical data for $[M_2(\mu-X)_3(PR_3)_6]^{1+}$, $[M_2(\mu-X)_3(triphos)_2]^{1+}$ and $[M_2(\mu-X)_3(Me_3tacn)_2]^{1+}$ Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}$ Values (V) $^a$</th>
<th>$\Delta E_{1/2}$ (V)</th>
<th>$K_c \ b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{PEtPh}_2)_6]^{1+}$</td>
<td>+1.80 (pr) +1.21 (r)</td>
<td>0.59</td>
<td>9.13 x 10$^{13}$</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{PEtPh}_2)_6]^{1+}$</td>
<td>+1.71 (r) +1.19 (r)</td>
<td>0.52</td>
<td>2.02 x 10$^{12}$</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{PEt}_3)_6]^{1+}$</td>
<td>+1.71 (r) +1.09 (r)</td>
<td>0.62</td>
<td>4.68 x 10$^{14}$</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Br}_3(\text{PEt}_3)_6]^{1+}$</td>
<td>+1.68 (r) +1.11 (r)</td>
<td>0.57</td>
<td>3.07 x 10$^{13}$</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]^{1+}$</td>
<td>+1.87 (r) +1.31 (r)</td>
<td>0.56</td>
<td>1.78 x 10$^{13}$</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Br}_3(\text{PMe}_2\text{Ph})_6]^{1+}$</td>
<td>+1.87 (r) +1.32 (r)</td>
<td>0.55</td>
<td>1.03 x 10$^{13}$</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{triphos})_2]^{1+}$</td>
<td>+1.94 (r) +1.46 (r)</td>
<td>0.48</td>
<td>2.28 x 10$^{11}$</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{P(OMe)}\text{Ph}_2)_6]^{1+}$</td>
<td>+1.97 (irr) +1.46 (qr)</td>
<td>0.51</td>
<td>1.17 x 10$^{12}$</td>
</tr>
<tr>
<td>$[\text{Os}_2\text{Cl}_3(\text{PEt}_3)_6]^{1+}$</td>
<td>+1.49 (r) +0.97 (r)</td>
<td>0.52</td>
<td>2.02 x 10$^{12}$</td>
</tr>
<tr>
<td>$[\text{Os}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]^{1+}$</td>
<td>+1.47 (r) +0.87 (r)</td>
<td>0.60</td>
<td>1.58 x 10$^{14}$</td>
</tr>
<tr>
<td>$[\text{Os}_2\text{Cl}_3(\text{Me}_3\text{tacn})_2]^{2+} \ c$</td>
<td>+1.09 (r) -0.09 (r)</td>
<td>1.19</td>
<td>1.44 x 10$^{28}$</td>
</tr>
<tr>
<td>$[\text{Os}_2\text{Br}_3(\text{Me}_3\text{tacn})_2]^{2+} \ c$</td>
<td>+1.09 (r) +0.04 (r)</td>
<td>1.05</td>
<td>7.00 x 10$^{24}$</td>
</tr>
</tbody>
</table>

$^a$ Measured in 0.5 mol. dm$^{-3}$ nBu$_4$NPF$_6$/CH$_2$Cl$_2$ at 213 K, versus Ag/AgCl, against which ferrocinium/ferrocene occurs at +0.55 V. By convention, the couples are listed as reductions. r=reversible, qr=quasi-reversible, pr=partially reversible (i.e. EC mechanism) and irr=irreversible. The numbers in parentheses refer to the EAN electron counting scheme (see Figure 1.4). $^b$ $K_c=e^{-(\Delta E_{1/2}/R.T)}$, $\Delta E=\Delta E_{1/2}$, separation of couples. $^c$ These complexes were supplied by Professor K. Wieghardt.

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* The two metal centres must be in identical ligand environments.

** The interaction can occur through direct d orbital overlap, or via a bridging group(s).
The separation of the two couples for any one complex are listed in Table 1.1, these values being essentially the same for both ruthenium and osmium (~0.55 V). Where direct comparison of $\Delta E_{1/2}$ between the two metals is possible, e.g. $X=\text{Cl}$, $\text{PR}_3=\text{PET}_3$, $\text{PET}_2\text{Ph}$, $\text{PMe}_2\text{Ph}$ and triphos, no consistent trend is observed, with the most significant difference only 60 mV (Ru>Os). Although the 5d orbitals of osmium can be considered to be more diffuse than those of ruthenium, the above results do not infer an increased Os...Os interaction. A direct structural comparison between ruthenium and osmium $[\text{M}_2(\mu-\text{Cl})_3(\text{PMe}_2\text{Ph})_6]^{1+}$ reveals a longer M-M distance for M=Os (see Chapter 2, Table 2.1). A comparison of the M-X-M' and X-M-X' angles reveals only small yet consistent differences, indicating slightly greater repulsion in the diosmium system in the 36 electron state, as compared with the known ruthenium complexes.

1.3.3 Voltammetry of $[(\text{triphos})\text{Ru}(\mu-\text{Cl})_3\text{Os(}\text{triphos})]^{2+}$

Thus far only the voltammetry of the homobimetallic complexes has been discussed. A schematic diagram of the voltammetry of the $[\text{Os}_2]^{2+}$, $[\text{Ru}_2]^{2+}$ and $[\text{RuOs}]^{2+}$ complexes is shown in Figure 1.14 (parts (a), (b) and (c)).

The first couple (35/36) in $[\text{RuOs}]^{2+}$ occurs at +1.26 V, which corresponds to the first oxidation in $[\text{Os}_2]^{2+}$, while the second couple in $[\text{RuOs}]^{2+}$ (34/35) is at +1.94 V, coinciding with the second oxidation in $[\text{Ru}_2]^{2+}$. Because the $[\text{RuOs}]^{2+}$ complex is isolated as the mixed-valence dication (z=2), the couple at +1.26 V is a reduction (Os$^{\text{III}} \rightarrow$Os$^{\text{II}}$), while that at +1.94 V is an oxidation (Ru$^{\text{II}} \rightarrow$Ru$^{\text{III}}$). Although the separation of the 34/35 and 35/36 electron couples has increased, this merely reflects the asymmetry of the complex.
The fact that the +1.26 and +1.94 V couples coincide exactly with those of their parent homobimetallic complexes implies that the Os centre in [RuOs]^{2+} cannot distinguish between Ru or Os at the other site in the heteroatom complex (the reverse of course, is also true), and therefore the metals are non-interacting. The near-infrared spectrum of the mixed-valence heterobimetallic complex will be discussed in the following chapter.
Chapter 1

1.4 SYNTHESIS AND MAGNETISM OF \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_3)_6](\text{PF}_6)_2\)

Prior to this work, mixed-valence \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^{2+}\) complexes had only ever been prepared by bulk electrolysis of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^{1+}\) species; their only form of characterization being solution measurements. \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_3)_6](\text{PF}_6)_2\) is the first mixed-valence ruthenium compound of its type to be isolated, and hence was characterized more fully.

Initial attempts at the chemical preparation of a mixed-valence \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^{2+}\) species were unsuccessful. Either the basisity of the phosphine ligands were not sufficient to permit chemical oxidation, or the oxidized products were too unstable under the reaction conditions to allow isolation. The properties of the trialkyl phosphine complex \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_3)_6]^{1+}\) however were such that preparation and isolation of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_3)_6](\text{PF}_6)_2\) was possible.

The use of NO\(^+\) as an oxidant is well documented\(^7\), and this proved successful and convenient to use, NOPF\(_6\) simply being added to a dichloromethane solution of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_3)_6]\text{CF}_3\text{SO}_3\), containing an equivalent amount of \(\text{nBu}_4\text{NPF}_6\). Gradually, with stirring at room temperature, the colour of the solution changed from yellow to bright green. The removal of \(-25\%\) of the solvent, the addition of several drops of diethyl ether and refrigeration of the solution caused the precipitation of a crystalline dark green product, the u.v./visible spectrum of which matched that of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_3)_6]^{2+}\), previously obtained through bulk electrogeneration in an OTTLE cell (see Chapter 2).

The voltammetry of the green product in dichloromethane showed two couples, at identical positions to those in \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_3)_6]\text{CF}_3\text{SO}_3\), the only difference being these couples correspond to a reduction (\(E_{1/2}=+1.09\) V), and an oxidation (\(E_{1/2}=+1.71\) V), instead of two oxidations.

The magnetic susceptibility of a powdered sample of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_3)_6](\text{PF}_6)_2\) was recorded between temperatures of 300 and 4.2 K, in a field of 10 000 gauss. The magnetic moment (\(\mu_{\text{eff}}, \text{per molecule}\)) decreases from 2.13 B.M. at 300 K to a near spin-only value of 1.74 B.M. at 4.2 K, consistent with the presence of one unpaired electron per two ruthenium centres. The size of the magnetic moment and its variation...
with temperature are in general terms typical of a low spin octahedral Ru$^{III}$ ($d^5$) monomer, since [Ru$_2$(μ-Cl)$_3$(P$\text{Et}_3$)$_6$(PF$_6$)$_2$] is formally a $S=0$, $S=1/2$ system (Ru$^{II,III}$).

Figgis and Lewis et al. have studied a number of monomeric systems$^7$ They observed moments in the order of 1.9-2.4 B.M. at room temperature, decreasing to 1.75-1.90 B.M. at ca. 80 K. Figure 1.15 shows the variation of $\mu_{\text{eff}}$ as a function of temperature and spin-orbit coupling constant ($\lambda$) for a $^2T_{2g}$ ground term where $\lambda \gg kT$.$^7$ The value of $\mu_{\text{eff}}$ at room temperature is typically greater than the spin-only moment ($\mu_{so}$), on account of orbital contribution in the T ground term. $\mu_{\text{eff}}$ also has some dependence on temperature, approaching $\mu_{so}$ as $kT/\lambda$ approaches zero.

![Figure 1.15](image)

**Figure 1.15** The variation of $\mu_{\text{eff}}$ with temperature, as a function of $kT/\lambda$ for the low spin $d^5$ Ru$^{III}$ ion ($^2T_{2g}$ ground state) with negative $\lambda$. The point marked on the curve corresponds to the free ion value of spin-orbit coupling at room temperature.

A plot of the temperature variation of $\chi_m$ and $\mu_{\text{eff}}$ (per molecule) are shown in Figure 1.16. While in broad terms the behaviour is similar to that of many other Ru$^{III}$ systems, the more precise variation of $\mu_{\text{eff}}$ with temperature is a little unusual. Between 300 and ~50 K, the moment passes through a slight but clearly noticeable depression. This is in contrast to the typical behaviour of octahedral Ru$^{III}$ complexes, such as
[Ru(NH$_3$)$_5$Cl]Cl$_2$.H$_2$O, the $\mu$$_{\text{eff}}$ versus temperature plot for which is shown inset (Figure 1.16). This subtle difference is only noted, and no explanation is offered, given the complexities associated with T terms where the effects of low symmetry ligand fields, large spin-orbit coupling constants and electron delocalization all need to be considered.

![Graph](image)

**Figure 1.16** Variation of $\mu$$_{\text{eff}}$ and $\chi$$_m$ (per molecule) with temperature for [Ru$_2$(μ-Cl)$_3$(PEt$_3$)$_6$](PF$_6$)$_2$. Inset: $\mu$$_{\text{eff}}$ versus temperature behaviour of [RuCl(NH$_3$)$_5$Cl]Cl$_2$.H$_2$O (taken from reference 76).
The X-band e.s.r. spectrum of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_3)_6](\text{PF}_6)_2\) was also recorded, in a toluene/dichloromethane glass at 37 K (Figure 1.17). The spectrum is typical of that for a \(S=\frac{1}{2}\) complex in an axial field, giving \(g\)-values of 2.32 \((g_\parallel)\) and 1.65 \((g_\perp)\).

![Figure 1.17 X-band e.s.r. spectrum of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_3)_6](\text{PF}_6)_2\) in a dichloromethane/toluene glass at 37 K.](image)

Preliminary results indicate the analogous diosmium complex can be prepared in a similar way. Further work is required on related ruthenium (and osmium) complexes to establish if the observed behaviour of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_3)_6](\text{PF}_6)_2\) is characteristic of 35 electron mixed-valence
[M₂(µ-X)₃(PR₃)₆]²⁺ systems, or intrinsic to this particular complex. In particular a detailed magnetic/e.s.r. study on a strictly *trapped* mixed-valence system would be of interest to establish if its magnetic behaviour was more typical of a monomeric complex. The magnetism of the [Ru₂(µ-X)₃(Me₃tacn)₂]²⁺ complexes has been previously recorded, the moment varying between 1.88-2.20 B.M. over the 293-98 K temperature range. Measurements to 4.2 K are required to reveal any minor variations from the normal that may be occurring in these complexes. Some similar studies to very low temperatures on monomeric Mᴵᴵ (M=Ru, Os) complexes would also be of interest, since the vast majority of literature data are only recorded to liquid nitrogen temperatures.

Electrochemical measurements were performed using a PAR model 170 electrochemical system. The cell was of a standard three electrode configuration, consisting of a polished platinum disc working electrode (0.5-1.0 mm diameter), platinum foil auxiliary electrode and a double-tipped Ag/AgCl reference electrode (Metrohm). The internal compartment of the reference electrode was filled with 0.1 M KCl. The internal compartment of the reference electrode was filled with 0.1 M KCl. The external compartment was filled with the standard electrolyte solutions, i.e. 0.5 M NaCl, 0.5 M Na₂SO₄ in CH₂Cl₂. The ferrocenium/ferrocene couple was recorded at -0.35 V in CH₂Cl₂ at room
1.5 EXPERIMENTAL

1.5.1 General Remarks

Elemental analyses were performed by the Microanalytical Services Unit at the Research School of Chemistry, A.N.U. Melting-points were determined using a Buchi 510 melting point apparatus, in evacuated, sealed melting-point tubes, and are uncorrected. Infrared spectra (4 000–500 cm\(^{-1}\)) were recorded on a Perkin Elmer 683 infrared spectrophotometer (calibrated against polystyrene film), as pressed KCl or KBr discs. Far-infrared spectra (500–150 cm\(^{-1}\)) were recorded on a Perkin Elmer 1800 fourier transform spectrophotometer, as pressed polythene discs. Absorption spectra (50 000–4 000 cm\(^{-1}\)) were recorded using a Perkin Elmer \(\lambda\) u.v./visible/near-infrared spectrophotometer. \(^{1}\)H and \(^{31}\)P\(^{1}\)H n.m.r. spectra were collected on Varian Gemini 300 and Varian XL200E instruments respectively, in 5.0 mm quartz tubes. Fast atom bombardment mass spectra were obtained on a ZAB2-SEQ mass spectrometer, in the specified matrix. A Varian Associates spectrometer (100 kHz modulation frequency) fitted with an Oxford Instruments helium flow cryostat was used to measure epr spectra. The klystron frequency was determined using a Hewlett-Packard Electronic Counter. Magnetic susceptibility data was collected by Dr. K. S. Murray and Dr. B. Mourbaraki of Monash University, using a Quantum Design MPMS SQUID (superconducting quantum-interference device) magnetometer. Calibration for field and temperature were as set by the manufacturer, and checked against a standard palladium sample (field) and [CuSO\(_4\)].5H\(_2\)O and [HgCo(CNS)\(_4\)] (temperature).

Electrochemical measurements were performed using a PAR model 170 electrochemical system. The cell was of a standard three electrode configuration, consisting of a polished platinum disc working electrode (0.5-1.0 mm diameter), platinum bar auxiliary electrode and a double-fritted Ag/AgCl reference electrode (Metrohm). The internal compartment of the reference electrode was filled with 0.45 mol. dm\(^{-3}\) \(n\)Bu\(_4\)NPF\(_6\)/0.05 mol. dm\(^{-3}\) \(n\)Bu\(_4\)NCl in CH\(_2\)Cl\(_2\). The external compartment was filled with the standard electrolyte solutions, \textit{i.e.} 0.50 mol. dm\(^{-3}\) \(n\)Bu\(_4\)NPF\(_6\) in CH\(_2\)Cl\(_2\). The ferrocinium/ferrocene couple was recorded at +0.55 V in CH\(_2\)Cl\(_2\) at room
temperature. The $n$Bu$_4$NPF$_6$ electrolyte was prepared by neutralizing 40% solutions of $n$Bu$_4$NOH (Aldrich) with HPF$_6$. The precipitate was collected by filtration, washed with large amounts of distilled water, dried and recrystallized twice from ethanol/water, before drying at 373 K under high vacuum for 24 hours. The solvent was pre-dried over KOH pellets, before distilling from CaH$_2$ just prior to use. The electrolyte solutions were deoxygenated with either N$_2$ or Ar, and the cell maintained under an inert atmosphere. Low temperature measurements were recorded in a jacketed cell, connected to a Lauda RL6 circulating cooling bath. The temperature was monitored by a Comark 2001 digital thermometer, with the probe located directly in the electrochemical solution.

1.5.2 Materials and Methods

The monodentate tertiary phosphine ligands were purchased from the Aldrich Chemical Company, and Organometallics Inc. The tridentate phosphine, 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) was supplied by Strem Chemicals Inc. Trifluoromethanesulfonic acid ("triflic acid") was vacuum distilled prior to use. All solvents were of analytical grade, and used without further purification unless stated otherwise. The following compounds were prepared according to their literature methods; [RuCl$_2$(PPh$_3$)$_3$],$^{79}$ [RuBr$_2$(PPh$_3$)$_3$],$^{80}$ [OsCl$_2$(PPh$_3$)$_3$],$^{60}$ mer-[OsCl$_3$(PMe$_2$Ph)$_3$],$^{81}$ cis-[OsCl$_2$(PMe$_2$Ph)$_4$],$^{54}$ and mer-[OsBr$_3$(PMe$_2$Ph)$_3$] as for its chloride analogue, the only difference being HBr was used instead of HCl. Standard Schlenk-line techniques were used throughout this work.$^{82}$

1.5.3 Synthesis of [Ru$_2$(µ-X)$_3$(PR$_3$)$_6$]X Complexes

The [Ru$_2$(µ-Cl)$_3$(PR$_3$)$_6$]Cl compounds were all synthesized by essentially the same procedure, starting from [RuCl$_2$(PPh$_3$)$_3$]. The bromide complexes were similarly prepared, from [RuBr$_2$(PPh$_3$)$_3$]. Below is a general procedure, accompanied by microanalytical results (Table 1.2) and more specific experimental details (Table 1.3). For electrochemical studies, a redox inert anion is preferred. A convenient, general method of converting halide salts to triflate salts was developed, and is also described below.
General Procedure for Synthesis of [Ru$_2$(µ-X)$_3$(PR$_3$)$_6$]X Complexes

The ligand (4 mmol. equivalent) was added to a stirring suspension of [RuX$_2$(PPh$_3$)$_3$] (1 mmol. equivalent) in deoxygenated absolute ethanol (~30.0 ml. per 0.25 g of [RuX$_2$(PPh$_3$)$_3$]). The mixture was then refluxed under nitrogen for the designated number of hours, producing a yellow solution. The solvent was removed in vacuo, to yield a yellow residue. The addition of a benzene/diethyl ether solution (~1/5, v/v), and swirling gave a yellow precipitate, which was collected by filtration, washed extensively with n-hexane, diethyl ether and dried in vacuo.

Metathesis of [Ru$_2$(µ-X)$_3$(PR$_3$)$_6$]X Complexes

[Ru$_2$(µ-X)$_3$(PR$_3$)$_6$]X was dissolved in a minimum volume of dichloromethane, and ~25% excess of triflic acid (CF$_3$SO$_3$H) added, in the form of a 0.10 mol. dm$^{-3}$ solution of CF$_3$SO$_3$H in methanol. This mixture was then gently refluxed under nitrogen overnight, after which the solvent was removed, and the residue recrystallized from either dichloromethane/diethyl ether or acetone/diethyl ether. On occasions it was not necessary to isolate the halide salt as described above; after removing the solvent from the reaction mixture, the CF$_3$SO$_3$H/methanol solution (100 % excess) was added directly to the residue, and the procedure continued as described here.
Table 1.2 Microanalytical data for \(\text{[Ru}_2(\mu-X)\text{X}_3\text{(PR}_3)_6\text{]}\) and \(\text{[Ru}_2(\mu-X)\text{X}_3\text{(triphos)}_2\text{]}\) compounds.\(^a,b,c\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found and Calculated Microanalytical Figures, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>(\text{[Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6\text{]}) trif</td>
<td>45.81</td>
</tr>
<tr>
<td>(\text{C}<em>4\text{H}</em>{58}\text{Cl}_3\text{F}_3\text{O}_3\text{P}_6\text{Ru}_2\text{S})</td>
<td>(45.75)</td>
</tr>
<tr>
<td>(\text{[Ru}_2\text{Br}_3(\text{PMe}_2\text{Ph})_6\text{]}) trif</td>
<td>40.86</td>
</tr>
<tr>
<td>(\text{C}<em>4\text{H}</em>{58}\text{Br}_3\text{F}_3\text{O}_3\text{P}_6\text{Ru}_2\text{S})</td>
<td>(41.45)</td>
</tr>
<tr>
<td>(\text{[Ru}_2\text{Cl}_3(\text{PETPh}_2)_6\text{]}) trif</td>
<td>57.99</td>
</tr>
<tr>
<td>(\text{C}<em>8\text{H}</em>{90}\text{Cl}_3\text{F}_3\text{O}_3\text{P}_6\text{Ru}_2\text{S})</td>
<td>(58.57)</td>
</tr>
<tr>
<td>(\text{[Ru}_2\text{Cl}_3(\text{PET}_2\text{Ph})_6\text{]}) trif</td>
<td>49.05</td>
</tr>
<tr>
<td>(\text{C}<em>6\text{H}</em>{90}\text{Cl}_3\text{F}_3\text{O}_3\text{P}_6\text{Ru}_2\text{S})</td>
<td>(50.37)</td>
</tr>
<tr>
<td>(\text{[Ru}_2\text{Cl}_3(\text{PET}_3)_6\text{]}) Cl</td>
<td>40.67</td>
</tr>
<tr>
<td>(\text{C}<em>3\text{H}</em>{78}\text{Cl}_4\text{P}_6\text{Ru}_2)</td>
<td>(41.07)</td>
</tr>
<tr>
<td>(\text{[Ru}_2\text{Br}_3(\text{PET}_3)_6\text{]}) Br</td>
<td>35.16</td>
</tr>
<tr>
<td>(\text{C}<em>3\text{H}</em>{78}\text{Br}_4\text{P}_6\text{Ru}_2)</td>
<td>(35.13)</td>
</tr>
<tr>
<td>(\text{[Ru}_2\text{Cl}_3(\text{triphos})_2\text{]}) trif</td>
<td>58.85</td>
</tr>
<tr>
<td>(\text{C}<em>8\text{H}</em>{78}\text{Cl}_3\text{F}_3\text{O}_3\text{P}_6\text{Ru}_2\text{S})</td>
<td>(58.40)</td>
</tr>
<tr>
<td>(\text{[Ru}_2\text{Cl}_3(\text{P(OMe}_2\text{Ph})_6\text{]}) trif</td>
<td>53.64</td>
</tr>
<tr>
<td>(\text{C}<em>7\text{H}</em>{78}\text{Cl}_3\text{F}_3\text{O}_9\text{P}_6\text{Ru}_2\text{S})</td>
<td>(54.07)</td>
</tr>
</tbody>
</table>

\(^a\) trif=triflate, \(\text{CF}_3\text{SO}_3^-\).

\(^b\) Calculated microanalytical figures in parentheses.

\(^c\) Throughout this thesis, analytical data are quoted to two decimal places as received from the micro-analytical laboratory. In most cases rounding to the nearest 0.05 or even to the nearest 0.1% could be a realistic simplification.
Table 1.3  Experimental details for synthesis of $[\text{Ru}_2(\mu-X)_3(\text{PR}_3)_6]X$ and $[\text{Ru}_2(\mu-X)_3(\text{triphos})_2]X$ compounds.

<table>
<thead>
<tr>
<th>Complex $^a$</th>
<th>Starting Material</th>
<th>Ligand $^b$</th>
<th>density (ρ) (g cm$^{-3}$)</th>
<th>Solvent $^c$</th>
<th>Reaction Time, (hrs.)</th>
<th>Yield (%)</th>
<th>$\delta^{31P}[^1H]$, (p.p.m.) $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{Cl}$</td>
<td>$[\text{RuCl}_2(\text{PPh}_3)_3]$</td>
<td>PMe$_2$Ph</td>
<td>0.97</td>
<td>EtOH</td>
<td>90</td>
<td>91</td>
<td>+21.0 $^e$</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Br}_3(\text{PMe}_2\text{Ph})_6]\text{Br}$</td>
<td>$[\text{RuBr}_2(\text{PPh}_3)_3]$</td>
<td>PMe$_2$Ph</td>
<td>0.97</td>
<td>EtOH</td>
<td>4</td>
<td>90</td>
<td>+18.9</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{PETh}_2\text{Ph})_6]\text{trif}$</td>
<td>$[\text{RuCl}_2(\text{PPh}_3)_3]$</td>
<td>PETh$_2$</td>
<td>1.03</td>
<td>EtOH</td>
<td>56</td>
<td>28</td>
<td>+33.3</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{PETh}_2\text{Ph})_6]\text{Cl}$</td>
<td>$[\text{RuCl}_2(\text{PPh}_3)_3]$</td>
<td>PETh$_2$</td>
<td>0.96</td>
<td>EtOH</td>
<td>85</td>
<td>82</td>
<td>+36.0</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{PETh}_3)_6]\text{Cl}$</td>
<td>$[\text{RuCl}_2(\text{PPh}_3)_3]$</td>
<td>PETh$_3$</td>
<td>0.80</td>
<td>EtOH</td>
<td>72</td>
<td>91</td>
<td>+33.7 $^e$</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Br}_3(\text{PETh}_3)_6]\text{Br}$</td>
<td>$[\text{RuBr}_2(\text{PPh}_3)_3]$</td>
<td>PETh$_3$</td>
<td>0.80</td>
<td>EtOH</td>
<td>8</td>
<td>69</td>
<td>+33.5</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{triphos})_2]\text{Cl}$</td>
<td>$[\text{RuCl}_2(\text{PPh}_3)_3]$</td>
<td>triphos</td>
<td>-</td>
<td>2-MeOEtOH</td>
<td>6</td>
<td>99</td>
<td>+36.5</td>
</tr>
<tr>
<td>$[\text{Ru}_2\text{Cl}_3(\text{P(OMe)}\text{Ph}_2)_6]\text{Cl}$</td>
<td>$[\text{RuCl}_2(\text{PPh}_3)_3]$</td>
<td>P(OMe)Ph$_2$</td>
<td>1.08</td>
<td>MeOH</td>
<td>4</td>
<td>91</td>
<td>+138.7 $^e$</td>
</tr>
</tbody>
</table>

$^a$ trif=triflate, CF$_3$SO$_3^-$.

$^b$ The metal/ligand reactant ratio was 1/4 (mol./mol.), except for $[\text{Ru}_2(\mu-\text{Cl})_3(\text{PMe}_2\text{Ph})_6]\text{Cl}$, in which it was 1/6, and $[\text{Ru}_2(\mu-\text{Cl})_3(\text{triphos})_2]\text{Cl}$, which was 1/1.

$^c$ All solvents were thoroughly deoxygenated prior to use. EtOH=ethanol, MeOH=methanol and 2-MeOEtOH=2-methoxyethanol.

$^d$ Recorded in CD$_2$Cl$_2$ unless noted otherwise. All resonances were singlets, the chemical shifts measured versus 85% H$_3$PO$_4$. Positive resonances lie to high frequency of 85% H$_3$PO$_4$, negative resonances to low frequency of 85% H$_3$PO$_4$.

$^e$ CDCl$_3$. 
1.5.4 Synthesis of [Os₂(µ-X)₃(PR₃)₆]X Complexes

The diosmium complexes were prepared by a number of routes, as discussed in Section 1.2. The literature procedures, or modifications thereof, and the more general method (from [OsCl₂(PPh₃)₃]) are all described below. The halide counter anion could be exchanged for triflate using the procedure described for the diruthenium complexes.

(i) Tri-µ-chloro-hexakis(dimethylphenylphosphine)diosmium(II/II) chloride, [Os₂(µ-Cl)₃(PMe₂Ph)₆]Cl.

The title compound was prepared by the method of Heath et al.,⁵⁴ the only difference being longer reaction times were required for reasonable yields. Cis-[OsCl₂(PMe₂Ph)₄] (0.21 g, 0.26 mmol.) was heated under N₂ in deoxygenated iso-butanol (65 ml.) for 86 hours. The solvent was removed from the reaction mixture to yield a yellow residue. Stirring this residue in benzene (10 ml.) led to the formation of a pale-yellow solid, which was collected via filtration and washed thoroughly with diethyl ether (0.13 g, 77% yield).

(ii) Tri-µ-bromo-hexakis(dimethylphenylphosphine)diosmium(II/II) bromide, [Os₂(µ-Br)₃(PMe₂Ph)₆]Br.

Mer-[OsBr₃(PMe₂Ph)₃] (0.27 g, 0.31 mmol.) was dissolved in 30 ml. of deoxygenated 2-methoxyethanol, and 0.15 ml. (1.05 mmol., p=0.97 g cm⁻³) of PMe₂Ph added to this stirring solution. The solution was then refluxed under N₂ for 40 hours., after which the solvent was removed to leave a yellow residue. The residue was shaken in a methanol/diethyl ether mixture (1/4, v/v), the precipitate collected by filtration, washed with more diethyl ether and dried in vacuo (0.19 g, 78% yield).

(iii) Tri-µ-chloro-hexakis(diethylphenylphosphine)diosmium(II/II)- chloride, [Os₂(µ-Cl)₃(PEt₂Ph)₆]Cl.

To a stirred suspension of [OsCl₂(PPh₃)₃] (0.25 g, 0.24 mmol., p=0.96 g
cm$^{-3}$) in degassed absolute ethanol (30 ml.), was added $\text{PE}_2\text{Ph}$ (0.17 ml., 0.96 mmol.), and the mixture refluxed under $\text{N}_2$ for 6 hours. The solvent was removed in vacuo, and the residue fractionally recrystallized from dichloromethane/benzene. The pale coloured precipitate was collected by filtration, washed with diethyl ether and dried under high vacuum at 313 K (0.11 g, 61%).

(iv) Tri-$\mu$-chloro-hexakis(triethylphosphine)diosmium(II/II)chloride, $[\text{Os}_2(\mu-\text{Cl})_3(\text{PEt}_3)_6]\text{Cl}$.

$\text{PEt}_3$ (0.21 ml., 1.42 mmol., $\rho=0.80$ g cm$^{-3}$) was added to a stirred suspension of $[\text{OsCl}_2(\text{PPh}_3)_3]$ (0.25 g, 0.24 mmol.) in 30 ml. deoxygenated absolute ethanol. This mixture was then refluxed under $\text{N}_2$ for 55 hours, to yield a yellow solution. The solvent was removed in vacuo, and benzene/diethyl ether added to the residue. A fine yellow precipitate was collected by filtration and washed with ether. The product was then dried under high vacuum at 313 K (0.10 g, 66%).

(v) Tri-$\mu$-chloro-bis(1,1,1-tris(diphenylphosphinomethyl)ethane) diosmium(II/II)chloride, $[\text{Os}_2(\mu-\text{Cl})_3(\text{triphos})_2]\text{Cl}$.

$[\text{OsCl}_2(\text{PPh}_3)_3]$ (0.23 g, 0.22 mmol.) and triphos (0.15 g, 0.24 mmol.) were placed in 50 ml. side-arm round bottomed flask equipped with a stirrer bead. The flask was purged with $\text{N}_2$, and 30 ml. of degassed absolute ethanol added to form a green suspension. This mixture was then refluxed under $\text{N}_2$ for 25 hours, producing a pale yellow solution. The solvent was removed, and the residue taken up in dichloromethane. The addition of a large volume of benzene precipitated a fine pale yellow solid, which was collected by filtration, washed with more benzene, diethyl ether and dried (0.17 g, 74 % yield).
Chapter 1

Table 1.4 Microanalytical and $^{31}$P[1H] n.m.r. data for $[\text{Os}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]X$ and $[\text{Os}_2(\mu-\text{Cl})_3(\text{triphos})_2]X$ compounds.

<table>
<thead>
<tr>
<th>Complex $^a$</th>
<th>Found and Calculated $^b$</th>
<th>$\delta^{31}$P[1H] $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microanalytical Figures, (%)</td>
<td>(p.p.m.)</td>
</tr>
<tr>
<td>$[\text{Os}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{trif}$</td>
<td>C 39.72 H 4.67 Cl/Br -12.25</td>
<td>-36.8 $^d$</td>
</tr>
<tr>
<td>C$<em>{49}$H$</em>{66}$Cl$_3$F$_3$O$_3$Os$_2$P$_6$</td>
<td>(40.18) (4.54)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Os}_2\text{Br}_3(\text{PMe}_2\text{Ph})_6]\text{trif}$</td>
<td>C 36.95 H 4.23 Cl/Br -11.80</td>
<td>-38.4</td>
</tr>
<tr>
<td>C$<em>{49}$H$</em>{66}$Br$_3$F$_3$O$_3$Os$_2$P$_6$</td>
<td>(36.83) (4.16) (11.63)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Os}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl}$</td>
<td>C 46.76 H 6.23 Cl/Br -11.54</td>
<td>-21.3</td>
</tr>
<tr>
<td>C$<em>{60}$H$</em>{90}$Cl$_4$Os$_2$P$_6$</td>
<td>(47.43) (5.97) (12.23)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Os}_2\text{Cl}_3(\text{PEt}_3)_6]\text{Cl}$</td>
<td>C 35.42 H 7.64 Cl/Br -14.94</td>
<td>-25.8</td>
</tr>
<tr>
<td>C$<em>{36}$H$</em>{90}$Cl$_4$P$_6$Os$_2$</td>
<td>(35.12) (7.37) (15.09)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Os}_2\text{Cl}_3(\text{triphos})_2]\text{Cl}$</td>
<td>C 55.30 H 4.38 Cl/Br 8.19</td>
<td>-17.5</td>
</tr>
<tr>
<td>C$<em>{82}$H$</em>{78}$Cl$_4$Os$_2$P$_6$</td>
<td>(55.59) (4.44) (8.00)</td>
<td></td>
</tr>
</tbody>
</table>

*a* trif=triflate, CF$_3$SO$_3^-$,  
*b* Calculated microanalytical figures in parantheses.  
*c* Recorded in CD$_2$Cl$_2$ unless stated otherwise. All resonances are singlets, the chemical shifts measured versus external 85 % H$_3$PO$_4$. Positive resonances lie to high frequency of 85 % H$_3$PO$_4$, negative resonances to low frequency of 85 % H$_3$PO$_4$.  
*d* CDCI$_3$.

1.5.5 Isolation of the Mixed-Valence $[\text{Ru}_2(\mu-\text{Cl})_3(\text{PEt}_3)_6]\text{Cl}(\text{PF}_6)_2$ Complex

Tri-µ-chloro-hexakis(triethylphosphine)diruthenium hexafluorophosphate, $[\text{Ru}_2(\mu-\text{Cl})_3(\text{PEt}_3)_6]\text{Cl}(\text{PF}_6)_2$

$[\text{Ru}_2\text{Cl}_3(\text{PEt}_3)_6]\text{Cl}$ (0.13 g, 0.124 mmol.) and nBu$_4$NPF$_6$ (0.05 g, 0.129 mmol.) were dissolved in 15.0 ml. of freshly distilled dichloromethane. To this solution was added NOPF$_6$ (0.046 g, 0.263 mmol.), and stirring was continued at room temperature under N$_2$. Gradually the colour of the solution changed from yellow to green. A small amount of the solvent was removed, diethyl ether added, and the solution stored in the cold. A green crystalline solid was collected by filtration, washed with ether and dried in air (0.08 g, 50 %).
1.5.6. Calculation of Magnetic Moments

Throughout this thesis:

\[ \mu_{\text{eff}} \text{ (in B.M.)} = 2.83 (\chi_M T)^{1/2} \]

where \( \chi_M \) is the molar susceptibility in units of \( \text{cm}^3\text{mol}^{-1} \), corrected for diamagnetic ligand and counterion contributions, and \( T \) is the absolute temperature.

1.5.7. Stirred Voltammetry

Stirred voltammetry (e.g., p96) is useful to distinguish between oxidations and reductions and thus to determine the oxidation level of a given solution. In this work, stirred voltammograms were generally obtained by stirring the solution with a magnetic follower (250 rpm) rather than by use of a rotating electrode assembly.
Chapter 1

1.6 REFERENCES


42. (a) P. E. Dumas and E. E. Mercer, Inorg. Chem., 1971, 10, 2755,
56. L. J. Yellowlees, private communication.


Chapter 2

SPECTROELECTROCHEMISTRY OF CONFACIAL BIOCTAHEDRAL COMPLEXES OF RUTHENIUM AND OSMIUM,

\[ [M_2(\mu-X)_3(PR_3)\delta]^{1+/2+/3+} \]

2.1 INTRODUCTION

Chapter 1 described the syntheses and voltammetry of a range of face-sharing halide-bridged diruthenium and diosmium complexes. In general, these complexes undergo two successive, reversible (or quasi-reversible) oxidations. Previous work established the chemical reversibility of the 35/36 electron-couple,\(^1\) such that one-electron oxidation of \([M_2(\mu-X)_3(PR_3)\delta]^{1+}\) produces the 35 electron di-cation \((d^5/d^6)\), an odd electron mixed-valence system. Immediately the question arises; is the system valence trapped, \(i.e.\) \([\text{M}^{II}(\mu-X)_3\text{M}^{III}]^{2+}\), or delocalized \([\text{M}^{II/2}(\mu-X)_3\text{M}^{II/2}]^{2+}\)?

Heath, Stephenson and co-workers considered this question for a number of 35 electron \([\text{Ru}(\mu-X)_3\text{Ru}]^{2+}\) systems, one of which was electrogenerated \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_6]^{2+}\) (Figure 2.1 (a)).\(^1\) They reported an intense intervalence charge-transfer (i.v.c.t.) band at 4 350 cm\(^{-1}\), and in accord with band shape analysis, described this mixed-valence complex as
delocalized. In contrast, the closely related \( \text{[Ru}_2(\mu-\text{Cl})_3(\text{PET}_{2}\text{Ph})_5\text{Cl}]^{1+} \) complex (Figure 2.1 (b)), with asymmetric terminal ligation, is distinctly valence localized,\(^1\) as judged by the same spectroscopic criteria. Thus we can see that while these \( \text{[Ru}_2(\mu-X)_3(\text{PR}_3)_6]^{2+} \) systems are delocalized, they are perhaps only weakly interacting, so that even a small modification causes them to become trapped. It was also reported that the spectrum of \( \text{[Ru}_2(\mu-\text{Cl})_3(\text{PET}_{2}\text{Ph})_6]^{2+} \) had an additional feature in the near-infrared region. The development of optically superior instrumentation, compared to what had previously been used, meant this complex, and related \( \text{[Ru}_2(\mu-X)_3(\text{PR}_3)_6]^{2+} \) systems, were worthy of re-examination.

Prior to the work described herein, the optical spectra of the analogous diosmium complexes had not been considered, and so it was of importance to collect the spectra of the \( \text{[Os}_2(\mu-X)_3(\text{PR}_3)_6]^{2+} \) systems, for comparison with those of the diruthenium complexes. In addition, it was of interest to see if the fully oxidized \( \text{[M}_2(\mu-X)_3(\text{PR}_3)_6]^{3+} \) complexes (\( \text{M} = \text{Ru}, \text{Os} \)) could be electrogenerated, and their spectra recorded.

This chapter describes the spectroelectrochemistry of the \( \text{[M}_2(\mu-X)_3(\text{PR}_3)_6]^{1+}/2+/3+ \) (\( \text{M} = \text{Ru}, \text{Os} \)) complexes, and also presents for the first time the anodic and cathodic spectroelectrochemistry of some isostructural ruthenium “blues”, \( \text{[Ru}_2(\mu-X)(\text{Me}_3\text{tacn})_2]^{1+}/2+/3+. \)\(^*\)

The spectra of the 35 electron systems are discussed first, due to the considerable literature on the 35 electron \( \text{[Ru}_2(\mu-X)_3(\text{NH}_3)_6]^{2+} \) ions,\(^2\) and

---

\( \text{Me}_3\text{tacn}=N, N', N''\)-trimethyl-1,4,7-triazacyclononane.

---
their aquo analogues, [Ru$_2$(µ-X)$_3$(H$_2$O)$_6$]$^{2+}$. Both of these systems have been described as delocalized mixed-valence species. The spectra of odd-electron systems are also in principle easier to interpret than those of even-electron systems. To a first approximation, electron-electron correlation terms do not need to be considered in the former, and transition energies can be assumed to be representative of orbital energy differences. Such an assumption cannot be made in an even-electron case, due to the energy associated with the unpairing of an electron.
2.2 ELECTROGENERATION OF SPECTRA

The voltammetry of the complexes synthesized in Chapter 1 revealed consecutive one-electron oxidations, yielding firstly the 35 electron, and then the 34 electron systems (Figure 2.2). Performing such oxidations in an optically transparent thin-layer electrolysis (OTTLE) cell permits in situ collection of the u.v./visible/near-infrared spectra (50 000-4 000 cm⁻¹) of the 35 and 34 electron systems (see experimental).

\[
\begin{align*}
\text{M}^{2+} & \xrightarrow{+e} [\text{MX}_3\text{M}]^{2+} \xrightarrow{+e} \text{M}^{2+} \\
34\text{e}^- & \quad \text{(d}^5, \text{d}^5) & 35\text{e}^- & \quad \text{(d}^5, \text{d}^6) & 36\text{e}^- & \quad \text{(d}^6, \text{d}^6)
\end{align*}
\]

Figure 2.2. Accessible oxidation levels of \([\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{2+}\) complexes.

In a typical experiment (Figure 2.3), a \([\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{1+}\) solution was exhaustively oxidized to yield the 35 electron species \((\text{M}^{II,III})^\#\) [(i)], after which the potential was reset and the starting spectrum regenerated [(iii)]. Having established that this was obtained intact, without the loss or gain of any features, then the complex was again oxidized to the \(\text{M}^{II,III}\) level [(iii)]. Electrogeneration of the 34 electron system was then attempted [(iv)]. Upon obtaining a final \(\text{M}^{III,III}\) spectrum, the complex was reduced to the 35 electron species once more [(v)]. The observation of isosbestic points and the regeneration of starting spectra at each step was taken as strong evidence for a chemically reversible redox process.

The reason for the conservative approach whereby \(\text{M}^{II,III}\) is taken back to \(\text{M}^{II,II}\) prior to pressing on to \(\text{M}^{III,III}\), is that if one simply progresses through the oxidation levels, \(\text{M}^{II,II} \rightarrow \text{M}^{II,III} \rightarrow \text{M}^{III,III}\), and the second oxidation is irreversible, then there is no opportunity to retrieve \(\text{M}^{II,II}\), so that the first product, \(\text{M}^{II,III}\), cannot be validated.

# The \(\text{M}^{II,III}\) description of a 35 electron system is purely an oxidation state formalism, and in this instance does not define the system as valence trapped.
All of the diosmium complexes yielded spectra of both 35 and 34 electron oxidized products, however for some of the diruthenium complexes with less basic phosphines, only spectra of the first oxidation product (35 electron) were obtained.

\[ [\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{1+} \xrightarrow{(i)} [\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{2+} \]

\[ [\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{1+} \xrightarrow{(ii)} [\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{2+} \]

\[ [\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{2+} \xrightarrow{(iii)} [\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{2+} \xrightarrow{(iv)} [\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{3+} \]

\[ [\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{2+} \xrightarrow{(v)} [\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{2+} \]

**Figure 2.3** Flow diagram showing sequence of electrogeneration of \([\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{2+}\) complexes, \(z=1, 2, 3\). See text for \((i)\rightarrow(v)\).
2.3 MIXED-VALENCE 35 ELECTRON SYSTEMS

2.3.1 Mixed-Valence $[\text{Ru}_2(\mu-X)_3(\text{Me}_3\text{tacn})_2]^{2+}$ Complexes

Although some disagreement still exists over the detailed spectral assignments of the ammine capped complexes, the main features are in general well understood. Wieghardt et al. noted the similarities between the $[\text{Ru}_2(\mu-X)_3(\text{Me}_3\text{tacn})_2]^{2+}$ spectra and those of the $[\text{Ru}_2(\mu-X)_3(\text{NH}_3)_6]^{2+}$ ions. The near-infrared/visible spectrum of $[\text{Ru}_2(\mu-\text{Cl})_3(\text{Me}_3\text{tacn})_2]^{2+}$ is presented in Figure 2.4.

![Absorbance spectrum](image)

**Figure 2.4** Electronic spectrum of $[\text{Ru}_2(\mu-\text{Cl})_3(\text{Me}_3\text{tacn})_2]^{2+}$.

The spectra are assigned on the basis of the familiar molecular orbital (m.o.) scheme for confacial biocathedral complexes in $D_{3h}$ symmetry (Figure 2.5). In the ammine-capped complexes, the interaction between the two metal centres is extensive, resulting in a large splitting of the bonding ($\sigma, \delta$) and antibonding ($\sigma^*, \delta^*$) molecular orbitals. This in turn causes considerable mixing of the $\delta$ and $\pi$ symmetry molecular orbitals, such that the normal ordering of these orbitals may be perturbed. The first band in the spectrum (Figure 2.4), at $\sim 5970 \text{ cm}^{-1}$, has been assigned as the $\delta^* \rightarrow \sigma^*$ transition. The
strong absorption at \(-14\ 700\ \text{cm}^{-1}\) arises mainly from the \(z\)-polarized \(\sigma \rightarrow \sigma^*\) excitation, although magnetic circular dichroism studies have shown this band is comprised of more than one transition.\(^7\) The two weaker bands at higher energy (22 920 and 30 600 cm\(^{-1}\)) have their origin in promotions from the \(t_{2g}\) to the \(e_g\) m.o. manifold, \(i.e.\) \(d-d\) type transitions.

![Figure 2.5 Molecular orbital scheme for confacial biocahedral complexes in \(D_{3h}\) symmetry. The allowed \(\sigma \rightarrow \sigma^*\) and \(\delta^* \rightarrow \sigma^*\) transitions for a 35 electron system are shown.](image)

The spectrum of \([\text{Ru}_2(\mu-\text{Br})_3(\text{Me}_3\text{tacn})_2]^{2+}\) is essentially the same as that of the analogous chloride, noting that all bands are moved to lower energies (Table 2.1). The metal-metal (M-M) interaction is expected to be slightly less in the bromide complex, resulting in a smaller splitting of the \(t_{2g}\) m.o. manifold. The \(\delta^* \rightarrow \sigma^*\) and \(\sigma \rightarrow \sigma^*\) transitions are therefore at lower energy. The transitions \(between\) the \(t_{2g}\) and the \(e_g\) m.o. manifold are at lower energy because of the smaller single-ion ligand field generated by bromide ligands.\(^9\)
**Table 2.1** Spectral Data for \( [\text{Ru}_2(\mu-X)_3(\text{Me}_3\text{tacn})_2]^\pm/2^+ /3^+ \) Complexes, \( X=\text{Cl}, \text{Br} \).

<table>
<thead>
<tr>
<th>Complex ( a,b )</th>
<th>Band Maxima, cm(^{-1} ) (( \epsilon, \text{M}^{-1} \text{cm}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( X=\text{Cl} )</td>
</tr>
<tr>
<td>( [\text{Ru}_2X_3(\text{Me}_3\text{tacn})_2]^1^+ )</td>
<td>20 630 (410)</td>
</tr>
<tr>
<td></td>
<td>26 250 (350)</td>
</tr>
<tr>
<td></td>
<td>36 230 (2 250)</td>
</tr>
<tr>
<td>( [\text{Ru}_2X_3(\text{Me}_3\text{tacn})_2]^2^+ )</td>
<td>5 970 (300)</td>
</tr>
<tr>
<td></td>
<td>14 700 (6 150)</td>
</tr>
<tr>
<td></td>
<td>22 920 (810)</td>
</tr>
<tr>
<td></td>
<td>30 600 (970)</td>
</tr>
<tr>
<td>( [\text{Ru}_2X_3(\text{Me}_3\text{tacn})_2]^3^+ )</td>
<td>26 710 (7 830)</td>
</tr>
<tr>
<td></td>
<td>34 770 (12 020)</td>
</tr>
</tbody>
</table>

\( a \) \( \text{Me}_3\text{tacn}=N,N',N''-\text{trimethyl}-1,4,7-\text{triazacyclononane} \).

\( b \) Extinction coefficients for \( [\text{Ru}_2(\mu-X)_3(\text{Me}_3\text{tacn})_2]^2^+ \) complexes taken from reference 8, and used to scale \( \epsilon \) for oxidized and reduced complexes.

All of these features below \(~30 \ 000 \text{ cm}^{-1} \) in the \( [\text{Ru}_2(\mu-X)_3(\text{Me}_3\text{tacn})_2]^2^+ \) complexes (\( X=\text{Cl}, \text{Br} \)) are associated with the mixed-valence spectrum, since upon reduction, these bands collapsed to leave an essentially featureless spectrum (which will be discussed in more detail in Section 2.5). Figure 2.6 shows the spectral progression upon in situ electroreduction of \( [\text{Ru}_2(\mu-\text{Cl})_3(\text{Me}_3\text{tacn})_2]^2^+ \).
Figure 2.6 Spectral progression upon reduction of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{Me}_3\text{acn})_2]^2^+\) to \([\text{Ru}_2(\mu-\text{Cl})_3(\text{Me}_3\text{acn})_2]^1^+\).

2.3.2 \([\text{M}_2(\mu-\text{X})_3(\text{PR}_3)_6]^2^+\) Complexes of Ruthenium and Osmium

Before examining the near-infrared and visible spectra of these mixed-valence complexes, it is of relevance to establish an approximate separation of the metal centres. The parent \([\text{M}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^1^+\) complexes have long metal-metal (M-M) distances; in the case of ruthenium these vary between 3.39 and 3.46 Å (Table 2.2), and 3.47 and 3.44 Å for the two structurally characterized diosmium complexes. Analogous low oxidation state ruthenium and osmium complexes typically have similar bond lengths and bonding radii. 19

When drawing conclusions about the nature of M-M interactions in confacial biocahedral complexes from structural data, it is not sufficient to consider only the M-M separation. Other factors such as the metal-bridging halide bond distance (M-X\(_b\)), and M-X\(_b\)-M'/X\(_b\)-M-X\(_b\)' bond angles also need to
be taken into account.

Cotton and Ucko described the bonding in $[\text{M}_2(\mu-X)_3X_6]^{2-}$ complexes in terms of elongation or contraction along the M-M axis.²⁰ The $[\text{M}(\mu-X)_3\text{M}]^{2+}$ core can be defined by two angles ($\alpha$, $\beta$), as well as the M-M distance ($2d'$) (Figure 2.5). In an ideal confacial bi-octahedron, $\alpha=90^\circ$ and $\beta=70.5^\circ$. This places the two metals at the centres of the planes between the terminal and bridging halides, i.e. $d'=d''$. For complexes in which M-M bonding exists; $\alpha>90^\circ$, $\beta<70.5^\circ$ and $d'/d''<1.0$, while for those in which M-M bonding does not exist; $\alpha<90^\circ$, $\beta>70.5^\circ$ and $d'/d''>1.0$. For example, $\alpha=77.2^\circ$, $\beta=87.9^\circ$ and $d'/d''=1.47$ for $[\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_6]^{1+}$, suggesting a repulsive force exists between the two ruthenium cations, in accord with the relatively long M-M separation of 3.443 Å.¹⁴

![Figure 2.7](image)

The only $[\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{2+}$ structure solved for either M=Ru or Os is $[\text{Os}_2(\mu-\text{Cl})_3(\text{PET}_3)_6](\text{PF}_6)_2$.¹¹ The M-M separation is 3.406 Å, only ~0.07 Å shorter than that in the unoxidized complex. In the absence of other information, a similar decrease in M-M separation upon oxidation may be expected in the diruthenium complexes. For the various hexakis phosphine complexes shown in Table 2, it follows that the M-M separations lies between 3.30 and 3.40 Å at the $[\text{Ru}(\mu-\text{Cl})_3\text{Ru}]^{2+}$ level. The separation in the analogous $[\text{Ru}(\mu-\text{Br})_3\text{Ru}]^{2+}$ complexes is expected to be marginally greater.
The likely M-M separation in an \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^{2+}\) complex is therefore considerably longer than in the isoelectronic \([\text{Ru}_2(\mu-\text{Cl})_3(\text{NH}_3)_6]^{2+}\) complex, where the M-M distance is 2.753 Å (Table 2.1). The geometry of the \{\text{Ru}(\mu-\text{Cl})_3\text{Ru}\}^{2+}\) core in the ammine capped complexes is consistent with the existence of a weak M-M bond, as is expected from a simple molecular orbital scheme, which predicts a formal bond order of 0.5 for the 35 electron system.

The expected longer M-M distance in the phosphine capped complexes comes as a consequence of the \(\pi\)-acid character of the terminal ligands, which reduce the polarizability of the ruthenium \(d\) orbitals, and increase the effective metal ion charges, causing greater M-M repulsion. Comparison of the voltammetry also supports this view. As discussed in Chapter 1, the separation of consecutive couples (\(\Delta E_{1/2}\)) in symmetric complexes gives an indication as to the degree of M-M interaction, the larger \(\Delta E_{1/2}\) the greater the interaction. For \([\text{Ru}_2(\mu-X)_3(\text{Me}_3\text{tacn})_2]^{2+}\), \(\Delta E_{1/2}\) (34/35-35/36 electron couples) is 1.19 and 1.05 V for \(X=\text{Cl}\) and \(\text{Br}\) respectively, but contracts to only ca. 0.6 V (or less) for \([\text{Ru}_2(\mu-X)_3(\text{PR}_3)_6]^{1+}\) complexes.

Further evidence for the likelihood of a relatively long M-M distance in the \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^{2+}\) systems comes from the structures of the symmetric mixed-valence \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_4\text{Cl}_2]\) complexes (Figure 2.8). The structural data for these complexes are also listed in Table 2.2.

The M-M separation (2.99-3.12 Å) and appropriate angles within the bridgehead indicate net repulsion between the metal atoms. Cotton suggested a weak Ru-Ru bond, however, Wieghardt et al. noted that in complexes where the M-Ru bonding is at best weak, structural data alone cannot be used to determine the existence or non-existence of a M-M bond.8
Table 2.2 Structural details for a variety of diosmium and diruthenium confacial biocahedral complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>M...M (Å)</th>
<th>M-X (Å)</th>
<th>X-M-X' (°), α</th>
<th>M-X-M' (°), β</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="PF$_6$">(PEt$_3$)$_3$Os(µ-Cl)$_3$Os(PEt$_3$)$_3$</a></td>
<td>3.473</td>
<td>2.49</td>
<td>76.9</td>
<td>88.29</td>
<td>10</td>
</tr>
<tr>
<td><a href="PF$_6$">(PMe$_2$Ph)$_3$Os(µ-Cl)$_3$Os(PMe$_2$Ph)$_3$</a></td>
<td>3.440</td>
<td>-</td>
<td>-</td>
<td>87.0</td>
<td>11</td>
</tr>
<tr>
<td><a href="PF$_6$">(PEt$_3$)$_3$Os(µ-Cl)$_3$Os(PEt$_3$)$_3$</a>$_2$</td>
<td>3.406</td>
<td>-</td>
<td>-</td>
<td>87.01</td>
<td>11</td>
</tr>
<tr>
<td>[(PMe$_2$Ph)$_3$Ru(µ-Cl)$_3$Ru(PMe$_2$Ph)$_3$]PF$_6$</td>
<td>3.39</td>
<td>2.49</td>
<td>79</td>
<td>86</td>
<td>12</td>
</tr>
<tr>
<td>[(PBu$_3$)$_3$Ru(µ-Cl)$_3$Ru(PBu$_3$)$_3$][RuCl$_4$(PBu$_3$)$_2$]</td>
<td>3.395</td>
<td>2.485</td>
<td>78.5</td>
<td>86.05</td>
<td>13</td>
</tr>
<tr>
<td>[(PEt$_2$Ph)$_3$Ru(µ-Cl)$_3$Ru(PEt$_2$Ph)$_3$][RuCl$_3$(PEt$_2$Ph)$_3$]</td>
<td>3.444</td>
<td>2.48</td>
<td>76.9</td>
<td>87.7</td>
<td>14</td>
</tr>
<tr>
<td>[(triphos)Ru(µ-Cl)$_3$Ru(triphos)]BPh$_4$</td>
<td>3.455</td>
<td>2.494</td>
<td>78.0</td>
<td>87.8</td>
<td>15</td>
</tr>
<tr>
<td>[(PMe$_2$Ph)$_2$ClRu(µ-Cl)$_3$RuCl(PMe$_2$Ph)$_2$]</td>
<td>2.9941</td>
<td>2.359</td>
<td>74.9</td>
<td>86.9</td>
<td>13</td>
</tr>
<tr>
<td>[(PMe$_3$)$_2$ClRu(µ-Cl)$_3$RuCl(PMe$_2$Ph)$_2$]</td>
<td>2.992</td>
<td>2.442</td>
<td>86.223</td>
<td>75.59</td>
<td>13</td>
</tr>
<tr>
<td>[(PBu$_3$)$_2$ClRu(µ-Cl)$_3$RuCl(PBu$_3$)$_2$]</td>
<td>3.115</td>
<td>2.436</td>
<td>83.54</td>
<td>79.44</td>
<td>16</td>
</tr>
<tr>
<td>[(NH$_3$)$_3$Ru(µ-Cl)$_3$Ru(NH$_3$)$_3$][BPh$_4$]$_2$</td>
<td>2.753</td>
<td>2.393</td>
<td>90.3</td>
<td>70.2</td>
<td>17</td>
</tr>
<tr>
<td>[(NH$_3$)$_3$Ru(µ-Br)$_3$Ru(NH$_3$)$_3$][ZnBr$_4$]$_2$</td>
<td>2.852</td>
<td>2.53</td>
<td>92.4</td>
<td>68.5</td>
<td>18</td>
</tr>
<tr>
<td><a href="PF$_6$">(Me$_3$tacn)Ru(µ-OH)$_3$Ru(Me$_3$tacn)</a>$_2$H$_2$O</td>
<td>2.401</td>
<td>1.955</td>
<td>86.7</td>
<td>75.7</td>
<td>8</td>
</tr>
<tr>
<td><a href="ClO$_4$">(Me$_3$tacn)Ru(µ-OH)$_3$Ru(Me$_3$tacn)</a>$_3$</td>
<td>2.505</td>
<td>2.06</td>
<td>88.0</td>
<td>75.0</td>
<td>8</td>
</tr>
</tbody>
</table>

*a triphos=1,1,1-tris(diphenylphosphinomethyl)ethane, b Me$_3$tacn=N, N', N''-trimethyl-1,4,7-triazacyclononane.
Chapter 2

Indeed even the semantics of what constitutes a 'bond' should be scrutinized. Whatever the exact nature of the M-M interaction in the \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_4\text{Cl}_2]\) complexes, the M-M separation in the \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^2+\) systems is not likely to be less than in these complexes. Replacing the terminal chloride with phosphine will only increase the effective positive charge on the metal centres, increasing the M-M repulsion, and weakening the M-M interaction.

The above discussion concerning likely M-M distances, and the comparatively small \(\Delta E_{1/2}\) values, establishes that the interaction in the \([\text{Ru}_2(\mu-\text{X})_3(\text{PR}_3)_6]^2+\) and \([\text{Os}_2(\mu-\text{X})_3(\text{PR}_3)_6]^2+\) complexes will be considerably less than in the ammine-capped systems.

In the unoxidized precursor complexes, \([\text{Ru}_2(\mu-\text{X})_3(\text{PR}_3)_6]^1+\), the region of the spectrum below \(-25\,000\,\text{cm}^{-1}\) is devoid of any features. Upon one-electron oxidation, intense bands grow in the region 4 000-9 000 cm\(^{-1}\). The spectral changes accompanying the one-electron oxidation of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_6]^1+\) are shown in Figure 2.9.

![Spectral progression accompanying oxidation of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_6]^1+\) to \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_6]^2+\). The step marked with an asterisk, at \(-11\,600\,\text{cm}^{-1}\), is a detector change.](image)
It should also be noted that further oxidation (to the 34 electron system) results in the collapse of the near-infrared bands, hence they are inherent to the odd electron configuration.

Comparing the spectrum of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PEt}_2\text{Ph})_6]^{2+}\) (Figure 2.9 and 2.10 (a)) with that of \([\text{Ru}_2(\mu-\text{Cl})_3(\text{Me}_3\text{tacn})_2]^{2+}\) (Figure 2.4), reveals very few similarities. This is not surprising given the expected differences in the extent of M-M interaction between the two complexes. The spectral data for the 35 electron diruthenium complexes are contained in Table 2.3. Focussing firstly on the bands in the near-infrared region of the spectrum, their positions are insensitive to the polarity of the solvent, and they are moderately intense, with \(\epsilon\) varying between 1 500 and 5 000 M\(^{-1}\) cm\(^{-1}\).

Hush has proposed a model for symmetric, weakly interacting mixed-valence complexes, in which the optical promotion of an electron between adjacent metal centres is proportional to the thermal energy barrier of electron transfer.\(^{21}\) For localized systems, class II according to the classification scheme outlined by Robin and Day,\(^{22}\) the band maxima \((\nu_{\text{max}})\) is related to the bandwidth at half maximum intensity \((\Delta\nu_{1/2})\) by the equation:

\[
\Delta\nu_{1/2} = [16(kT)\ln(2)\nu_{\text{max}}]^{1/2}, \quad \text{i.e. at } 300 \text{ K, } \Delta\nu_{1/2} = [2310\nu_{\text{max}}]^{1/2}
\]

The position, intensity and shape of the near-infrared bands listed in Table 2.3 do not adhere to the above criteria, implying a localized mixed-valence description is inappropriate.

Adopting then the m.o. bonding scheme for the \([\text{Ru}_2(\mu-X)_3(\text{PR}_3)_6]^{2+}\) complexes, the same transitions as those observed in the \([\text{Ru}_2(\mu-X)_3(\text{Me}_3\text{tacn})_2]^{2+}\) spectra are expected, albeit at different energies. The smaller splitting of the \(t_{2g}\) m.o. manifold for the \([\text{Ru}_2(\mu-X)_3(\text{PR}_3)_6]^{2+}\) complexes will result in the \(\delta^* \rightarrow \sigma^*\) and \(\sigma \rightarrow \sigma^*\) transitions being at lower energy than those in \([\text{Ru}_2(\mu-X)_3(\text{Me}_3\text{tacn})_2]^{2+}\).

The assignment of the \(\sigma \rightarrow \sigma^*\) promotions in the \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^{2+}\) spectra are not obvious, the appearance of the near-infrared region of the spectra being quite varied (Figure 2.10). In most cases two strong bands are observed, however the variation of intensities of these two bands relative to one another is quite sensitive to the identity of both halide and phosphine.
Table 2.3  Electrogenerated spectral data for \([M_2(\mu-X)\text{}_3(PR_3)_6]^{2+}\) and \([M_2(\mu-X)\text{}_3(\text{triphos})_2]^{2+}\) complexes.

<table>
<thead>
<tr>
<th>Complex(^a)</th>
<th>Band Maxima, (\text{cm}^{-1}) ((e), (M^{-1}\ \text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6])^{2+}</td>
<td>near-i.r. visible &gt;20 000 (\text{cm}^{-1})</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Br}_3(\text{PMe}_2\text{Ph})_6])^{2+}</td>
<td>17 000 (4 400)</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{PEtPh}_2)_6])^{2+}</td>
<td>4 700, 7 400 (3 440), (2 480)</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6])^{2+}</td>
<td>4 900, 6 980 (2 700), (1 610)</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{PEt}_3)_6])^{2+}</td>
<td>4 500, 6 250 (2 800), (1 500)</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Br}_3(\text{PEt}_3)_6])^{2+}</td>
<td>4 140, 6 500 (4 200), (1 600)</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{triphos})_2])^{2+,b}</td>
<td>5 300 (1 700)</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{POMePh}_2)_6])^{2+}</td>
<td>4 900, 8 420 (1 720), (1 760)</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6])^{2+}</td>
<td>5 200, 8 800 (6 600), (1 150)</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Br}_3(\text{PMe}_2\text{Ph})_6])^{2+}</td>
<td>4 950, 8 200 (4 400), (200)</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6])^{2+}</td>
<td>4 500, 7 600 (2 310), (530)</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{PEt}_3)_6])^{2+}</td>
<td>4 850, 7 770 (5 020), (720)</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{triphos})_2])^{2+,b}</td>
<td>4 910, 7 900 (5 880), (600)</td>
</tr>
<tr>
<td>([\text{RuOsCl}_3(\text{triphos})_3])^{2+}</td>
<td>7 660 (1 870)</td>
</tr>
</tbody>
</table>

\(^a\) Solutions were electrogenerated in 0.5 mol. dm\(^{-3}\) \(n\text{Bu}_4\text{NPf}_6/\text{CH}_2\text{Cl}_2\) an OTTLE cell at 213 K. \(^b\) triphos=1,1,1-tris(diphenylphosphinomethyl)ethane.
Figure 2.10 U.v./visible/near-infrared spectra of (a) [Ru$_2$(μ-Cl)$_3$(PET$_2$Ph)$_6$]+, (b) [Ru$_2$(μ-Cl)$_3$(PET$_2$Ph)$_6$]+, (c) [Ru$_2$(μ-Cl)$_3$(P(OMe)$_2$Ph)$_6$]+ and (d) [Ru$_2$(μ-Cl)$_3$(triphos)$_2$]+, electrogenerated in 0.5 mol. dm$^{-3}$ nBu$_4$NPF$_6$/CH$_2$Cl$_2$ in an OTTLE cell at 213 K. Asterisk shows detector change.
Figure 2.10 continued

U.v/visible/near-infrared spectra of (e) \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PET}_3)_6]^2^+\), (f) \([\text{Ru}_2(\mu-\text{Br})_3(\text{PET}_3)_6]^2^+\), (g) \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PM}_{2}\text{Ph})_6]^2^+\) and (h) \([\text{Ru}_2(\mu-\text{Br})_3(\text{PM}_{2}\text{Ph})_6]^2^+\) electrogenerated in 0.5 mol. dm\(^{-3}\) \(\text{nBu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2\) in an OTTLE cell at 213 K.
The lowest band is found between 4100-5100 cm\(^{-1}\), and is often the most intense. The position of the second band varies between 6250-8420 cm\(^{-1}\), and sometimes appears as a shoulder on the high energy side of the first band. There does not however appear to be any pattern to the separation of these two bands. In addition, the magnitude of the extinction coefficients appears dependent upon the basicity of the phosphine, the more basic phosphines having larger \(\varepsilon\) values (Table 2.3).

It is not apparent why there are two intense transitions. Since the intensity of both bands are the same order, it is unlikely that one of these corresponds to the \(\delta^*\rightarrow\sigma^*\) transition. In the ammine-capped systems, the intensity of the \(\sigma\rightarrow\sigma^*\) transition is \(\sim20\) times greater than \(\delta^*\rightarrow\sigma^*\). Should there be a mechanism by which the \(\sigma\rightarrow\sigma^*\) transition could be split into two components, then the spectrum can be assigned. The \(\delta^*\rightarrow\sigma^*\) transition then lies somewhere below 4000 cm\(^{-1}\).

Turning now to the near-infrared spectra of the diosmium complexes (Table 2.3), they are all very similar, with little variation upon changing the phosphine or bridging-halide. The spectral progression upon oxidation of \([\text{Os}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_6]^1+\) to \([\text{Os}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_6]^2+\) is shown below, in Figure 2.11.

\[\text{Figure 2.11. Spectral progression accompanying oxidation of } [\text{Os}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_6]^1+ \text{ to } [\text{Os}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_6]^2+.\]
The lowest energy band is consistently more intense, leading to its assignment as the $\sigma \rightarrow \sigma^*$ transition. Without knowing the reason for the splitting, i.e. the source of the higher energy component, it is difficult to postulate the cause of the difference in near-infrared spectra between osmium and ruthenium. One distinct difference between these two metal cations is the threefold increase in the size of the spin-orbit coupling constant from ruthenium to osmium, whereas differences in bond radii and electrode potentials of halogeno/phosphine complexes are not as pronounced as in for example homoleptic halide complexes. This point however is only noted, and no detailed conclusion is drawn at this stage.

In summary, those bands in the near-infrared region of the 35 electron spectrum are consistent with a delocalized mixed-valence system. A qualitative molecular orbital scheme such as that shown in Figure 2.5 is appropriate for the interacting metal centres. However, the precise ordering the levels is uncertain, on account of potentially strong mixing of the $\delta$ and $\pi$ symmetry orbitals. Any one of several perturbations such as spin-orbit coupling or the trigonal field distortion may invoke re-ordering of these levels. These perturbations are of comparable magnitude, so that it is not obvious which of these may dominate.

The intense low energy band, most prominent in Os, is assigned as the $\sigma \rightarrow \sigma^*$ transition. For the remainder of the 35 electron spectrum (both Os and Ru), there are several plausible assignments. The very broad, weak band(s) between $\sim$12-20 000 cm$^{-1}$, and the more intense higher energy feature can be accounted for in terms of the types of transitions expected in monomeric complexes, or alternatively as transitions within the $\{M(\mu-\text{Cl})_3M\}^{2+}$ core. The most likely solution is a combination of the two.

A *facial* $[MX_3(\text{PR}_3)_3]$ complex models one of the metal sites in the bimetallic complexes. Recently Levason reported the crystal structure of a *fac*-OsCl$_3$($\text{PR}_3)_3$.$^{23}$ This complex was prepared as described,$^{23}$ and its visible spectrum recorded (Figure 2.13). The band at 19 260 cm$^{-1}$ is thought to arise from P($\sigma$)$\rightarrow$Os$^{III}$(t$_{2g}$) charge-transfer, broadened through mixing in of the Cl($\pi$$\rightarrow$Os(t$_{2g}$) transition at higher energy (32 470 cm$^{-1}$).$^{24}$ The features in this spectrum are very similar to those observed between ca. 12 000 and 20 000 cm$^{-1}$ in the $[M_2(\mu-X)_3(\text{PR}_3)_6]^{2+}$ complexes (M=Ru, Os).
Figure 2.12  U.v./visible/near-infrared spectra of (a) $[\text{Os}_2(\mu-\text{Cl})_3(\text{PMe}_2\text{Ph})_6]^{2+}$, (b) $[\text{Os}_2(\mu-\text{Cl})_3(\text{PET}_2\text{Ph})_6]^{2+}$, (c) $[\text{Os}_2(\mu-\text{Cl})_3(\text{triphos})_2]^{2+}$, electrogenerated in 0.5 mol dm$^{-3}$ $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$, in an OTTLE cell at 213 K.
Although P(σ)→M(t_{2g}) charge-transfer transitions have been observed previously,\textsuperscript{23} little is known about how the energy of this transition varies with PR\textsubscript{3}. In trans-[RuX\textsubscript{4}(PR\textsubscript{3})\textsubscript{2}]\textsuperscript{1−} complexes,\textsuperscript{25} the P(σ)→M(t_{2g}) charge-transfer is a well defined single band. This is not the case in the [M\textsubscript{2}(μ-X)\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]\textsuperscript{2+} systems studied here, where the weak band(s) (ε<1 000 M\textsuperscript{-1} cm\textsuperscript{-1}) are very broad (∼4-8 000 cm\textsuperscript{-1}), and the maxima ill defined. There does however appear to be a sensible correlation between the leading edge of this band(s), and the position of the 35/36 electron couple in the bimetallic complex. The higher the couple, the lower in energy this broad absorption begins (supporting a l.m.c.t. assignment), most noticeable when comparing osmium with ruthenium. In accord with electrode potentials and as expected for a l.m.c.t. transition, the band is at lower energy in ruthenium (being easier to reduce than osmium). Alternatively, a manifold transition σ\textsuperscript{*}→π/π\textsuperscript{*} would also fit energetically and be expected to be intrinsically lower for ruthenium as compared with osmium [M\textsubscript{2}(μ-X)\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]\textsuperscript{2+} complexes.
It should also be noted that several weak bands were observed in the spectra of the [Ru2(µ-X)3(Me3tacn)2]^2+ complexes, at higher energy than the intense σ→σ* transition, and assigned provisionally as σ*→π and δ*/δ*→π/π*. It is therefore reasonable to suggest that the broad, weak features in the middle region of the [M2(µ-X)3(PR3)6]^2+ spectra arise from two different sources; firstly charge-transfer from P(σ) to metal t2g derived m.o.'s, and secondly from higher energy core transitions.

The higher energy bands (Figures 2.10, 2.11 and 2.12), centred around 26-28 000 cm⁻¹ in diruthenium, and 30-32 000 cm⁻¹ in diosmium, resemble the band at similar energy in fac-[OsCl3(PR3)3], which is largely Cl(π)→OsIII(dπ) charge-transfer. The bridging halides are not however expected to give rise to Xb(π)→M(dπ) charge-transfer transitions. Their optical "transparency" can be understood by consideration of the metal-based acceptor orbitals. From Figure 2.5, the acceptor orbital in the 35 electron systems is σ*. This orbital, which arises from the parent t2g metal orbitals, is antibonding, which by definition implies a node passes through the plane shared by the two metal centres (i.e. the shared "face"). It is on this node that the halide p orbitals lie, resulting in poor overlap of the halide donor and core acceptor orbitals. Therefore Xb(π)→M(dπ) charge-transfer is unfavourable. This discussion in general applies to triple halide bridged complexes, which have σ* or δ* acceptor orbitals (e.g. the 34 electron [Os2(µ-X)3X6]3- complexes discussed in Chapter 4). Supporting this notion was the observation that only small shifts (~1 000 cm⁻¹) were observed upon replacing chloride with bromide, rather than the predicted 6 000 cm⁻¹ shift.

The position of the higher energy feature is also essentially constant for any one metal, and varies little upon changing phosphine or the bridging-halide. Taking ruthenium as an example, the band shift between PEt3 and P(OMe)Ph2 is 200 cm⁻¹, and as noted above moves by only ~1 000 cm⁻¹ upon exchanging bromide for chloride. The main component of this band may therefore arise from a transition within the [Ru(µ-X)3Ru]²⁺ core; from those orbitals largely metal t2g in character to those e_g in character, in effect, a d-d type transition.

To conclude, the 35 electron [M2(µ-X)3(PR3)6]^2+ complexes are described as delocalized mixed-valence systems, and plausible assignments of the
spectra can be made. It should however be noted, that within this very general class of mixed-valency, there must exist varying degrees of 'delocalization', dependent presumably upon the extent of electronic interaction between the metal centres. On this basis the diruthenium complex with the strongly π-acid P(OR)Ph₂ ligands is the 'least' delocalized of the systems studied here. The near-infrared spectral differences between the diruthenium and diosmium complexes may be interpreted in terms of greater M...M interaction in the latter, even though the expected differences based on ΔE₁/₂ values are negligible.

It is interesting to speculate whether or not it is possible to achieve valence trapping (according to the strict spectroscopic criteria) in a symmetric \( \{M(µ-X)_3M\}^{2+} \) mixed-valence compound, given that even at the maximum M...M separation (with the three halide bridges still intact), the metal atoms are still relatively close (as compared with systems bridged by organic molecules such as pyrazine etc.). The kinds of mixed-valence complexes which may be expected to lie on the border of the delocalized/trapped problem are those with strongly electron withdrawing terminal ligands. Continually increasing π-acid character of the terminal ligands intuitively decreases the M-M interaction. Such a complex may be \([\text{Ru}_2(µ-\text{Cl})_3(\text{CO})_6]^{2+}\). However, other problems are envisaged with systems of this type. Even if the parent \([\text{Ru}_2(µ-\text{Cl})_3(\text{CO})_6]^{1+}\) complex could be prepared, its oxidation would be extremely difficult and may not occur prior to oxidation of the halide bridges. It may not be thermodynamically possible to generate the odd electron configuration in such an electron deficient system.

### 2.3.3 A Heterobimetallic Mixed-Valence Complex

The heterobimetallic complex,¹ \([(\text{triphos})\text{Ru}(µ-\text{Cl})_3\text{Os}(\text{triphos})]\)^2+, was isolated at the mixed-valence level, as described in chapter 1. Although this complex is not symmetrical in the strictest sense of the word, the voltammetry has shown that each metal centre cannot distinguish if its

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¹ Abbreviated as \([\text{RuOs}]^{2+}\), the homobimetallic complexes \([M_2(µ-X)_3(\text{triphos})]^{2+}\) as \([\text{Ru}]^{2+}\) and \([\text{Os}]^{2+}\) for M=Ru and Os respectively.
'partner' is osmium or ruthenium. The solvation energies of (RuOs)²⁺ can be assumed to be very similar to those of the (Ru₂)²⁺ and (Os₂)²⁺ complexes, suggesting that the relative difference in h.o.m.o. energies between osmium and ruthenium is maintained. It is therefore reasonable to suggest that the odd-electron is located on the osmium centre, i.e. a localized oxidation has occurred. Simplistically, one may have expected a ³¹P resonance from the phosphorus atoms coordinated to ruthenium centre, however a room temperature ³¹P[¹H] spectrum (+200→-200 p.p.m.) did not reveal any resonances. Paramagnetically shifted ³¹P[¹H] resonances have been reported at 1200 p.p.m. to high field of H₃PO₄, in trans-[OsX₄(PR₃)₂] complexes.²³,²⁷ The spectrum of the mixed-valence (RuOs)²⁺ species therefore needs re-collecting, over a wide spectral range with a long accumulation time. In any event, not observing a resonance does not prohibit describing the core as (Ru₃(µ-Cl)₃Os⁰)²⁺. The resonance may still be unobservable because of extensive paramagnetic broadening.

An e.s.r. spectrum of this complex was also recorded in a CH₂Cl₂/toluene glass at 40 K, however the resonance was so weak it was only just distinguishable from that of the cavity. Poor solubility of the [(triphos)Ru(µ-Cl)₃Os(triphos)](PF₆)₂ compound appears to be the limiting factor. Attempts are currently underway to prepare more soluble analogues.

Comparing the electronic spectrum of this complex (Figure 2.14) with those just discussed in Section 2.3.2 reveals some immediate differences. The single band observed in the near-infrared region is ~2 400 and 2 800 cm⁻¹ higher in energy than those in (Ru₂)²⁺ and (Os₂)²⁺ respectively, and is typically broader and less intense than those bands in the related homobimetallic complexes (see Figures 2.10 and 2.11).
Hush's model for a symmetric, weakly coupled mixed-valence system predicts a relationship between band position (\( u_{\text{max}} \)) and bandwidth at half intensity (\( \Delta u_{1/2} \)) at room temperature, \( \Delta u_{1/2} = [2310 \cdot u_{\text{max}}]^{1/2} \) (see Section 2.3.2). The predicted \( \Delta u_{1/2} \) for a band with \( u_{\text{max}} = 7660 \text{ cm}^{-1} \) is 4200 cm\(^{-1}\). The observed \( \Delta u_{1/2} \) was \(-4000 \text{ cm}^{-1}\). The exact band maximum is difficult to calculate, due to the broadness of the band. However, shifting the band maximum by even +/- 200 cm\(^{-1}\) only results in \( \Delta u_{1/2} \) values between 4150 and 4260 cm\(^{-1}\). If the Hush model is appropriate for the \( \{\text{RuOs}\}_2^{2+} \) system, then the band maximum should shift with solvent. Unfortunately the solvent dependence could not be tested. The solubility of the complex does not permit measuring the spectrum in solvents less polar than CH\(_2\)Cl\(_2\), and dissolution in potentially coordinating solvents resulted in decomposition.

It is reasonable to conclude the mixed-valence heterobimetallic system belongs in a different class to the homobimetallic complexes. The above spectral analysis suggests a weakly coupled system, as compared with the valence delocalized \( [M_2(\mu-X)_3(PR_3)_6]^{2+} \) complexes. While the \( \{\text{RuOs}\}_2^{2+} \) complex may not comply exactly with Hush's criterion for a localized mixed-
Chapter 2

valence system, in comparison to the \([M_2(\mu-X)_3(PR_3)_6]^{2+}\) system, it is essentially localized.

Now that a rational methodology has been established for preparing mixed-metal face-sharing complexes, it should be possible to prepare similar complexes with more basic and more solubilizing phosphines. A valence-trapped mixed-valence complex is likely to experience significant trigonal distortion, which can be probed by e.s.r. spectroscopy. In addition, it would be of great interest to prepare rhodium or iridium heterobimetallic complexes, i.e. \([Ru(\mu-X)_3Rh]^{3+}\), \([Ru(\mu-X)_3Ir]^{3+}\), \([Os(\mu-X)_3Rh]^{3+}\), \([Os(\mu-X)_3Ir]^{3+}\), which would 'trap' the system even further, through a greater mis-match of \(d\) orbital energies. Further study of complexes of this type may in time help in the spectral assignment of the \([M_2(\mu-X)_3(PR_3)_6]^{2+}\) complexes.
2.4 M_{2}^{III,III} [M_{2}(\mu-X)_{3}(PR_{3})_{6}]^{3+} AND [Ru_{2}(\mu-X)_{3}(Me_{3}tacn)_{2}]^{3+} COMPLEXES

2.4.1 General Remarks

The 34 electron \((d^{5}/d^{5})\) [Ru_{2}(\mu-X)_{3}(Me_{3}tacn)_{2}]^{3+} and [M_{2}(\mu-X)_{3}(PR_{3})_{6}]^{3+} complexes \((M=Ru, Os)\) have been electrogenerated from the mixed-valence 35 electron species, and their spectra are presented here for the first time. For those phosphine-capped compounds, the spectra of the fully oxidized species were collected for all the diosmium complexes, however only for the more basic phosphines \((PR_{3}=PEt_{3}, PEt_{2}Ph)\) could these spectra be electrogenerated for the diruthenium complexes.

2.4.2 [Ru_{2}(\mu-X)_{3}(Me_{3}tacn)_{2}]^{3+} Complexes

The familiar molecular orbital scheme for complexes of this type predicts a 34 electron system to be diamagnetic, and contain a M-M bond (of bond order 1.0). The Ru_{2}^{III,III} complex [Ru_{2}(\mu-OH)_{3}(Me_{3}tacn)_{2}]ClO_{4})_{3} has been isolated, its diamagnetism and structural characterization supporting the formation of a M-M bond. The halide-bridged systems similarly are expected to have considerable M-M interaction, although the M-M separation will necessarily be greater than in the hydroxide bridged complex, as a consequence of the larger bridging group.

The spectral progression accompanying the oxidation of [Ru_{2}(\mu-Br)_{3}(Me_{3}tacn)_{2}]^{2+} to the [Ru_{2}(\mu-Br)_{3}(Me_{3}tacn)_{2}]^{3+} species is presented in Figure 2.15 (a). The \(\sigma \rightarrow \sigma^{*}\) and \(\delta^{*} \rightarrow \sigma^{*}\) transitions collapse, with the growth of two intense bands at higher energy. Part (b) of Figure 2.15 shows the fully oxidized [Ru_{2}(\mu-Br)_{3}(Me_{3}tacn)_{2}]^{3+} spectrum. Similar changes occur upon oxidation of the chloride-bridged complex. The band positions and extinction coefficients for both complexes at the Ru_{2}^{III,III} level are listed in Table 2.1, along with the spectral data for the 35 and 36 electron species.

The two bands in the chloride are \(-2 000 \text{ cm}^{-1}\) higher in energy than those in the analogous bromide; however for reasons explained in Section 2.3, charge-transfer from the bridging halides into the metal-based acceptor orbitals are not expected. The two strong bands are therefore assigned as transitions within the \((Ru(\mu-X)_{3}Ru)^{3+}\) core. The bands in the chloro-
Figure 2.15  (a) Spectral progression accompanying oxidation of [Ru$_2$(µ-Br)$_3$(Me$_3$tacn)$_2$]$^{2+}$ to [Ru$_2$(µ-Br)$_3$(Me$_3$tacn)$_2$]$^{3+}$, and (b) final spectrum of [Ru$_2$(µ-Br)$_3$(Me$_3$tacn)$_2$]$^{3+}$, electrogene-rated in 0.2 mol. dm$^{-3}$ $n$Bu$_4$NPF$_6$/CH$_3$CN in an OTTLE cell at 233 K.
bridged complex are ca. 2 000 cm\(^{-1}\) higher in energy than those of the bromo-bridged species. Should these bands be due to transitions between the t\(_{2g}\) and e\(_{g}\) m.o. manifolds, then their positions will be dependent upon ligand field effects. From the spectrochemical series, the field generated by Cl is greater than that of Br, implying the transitions in the former will be found at higher energy. In addition, marginally greater M-M interaction can be expected in [Ru\(_2\)(µ-Cl)\(_3\)(Me\(_3\)tacn)\(_2\)]\(^{3+}\), on account of the smaller size of the chloro-bridging group, hence the m.o. manifold may span a wider range of energies. Depending upon which orbitals are involved in the transition, the band energy may reflect the larger splitting of the t\(_{2g}\) and e\(_{g}\) type orbitals. Given the uncertainty associated with the even-electron system on account of electron/electron correlation terms, more definitive assignments are not offered.

The hydroxy-bridged analogue, [Ru\(_2\)(µ-OH)\(_3\)(Me\(_3\)tacn)\(_2\)]\(^{3+}\), reportedly has a band at 31 850 cm\(^{-1}\), but is not known if this is the first component of a two-band spectrum, with a higher unreported component. It is reasonable to expect the core transitions in this latter complex to be higher in energy, due to the increased M-M interaction through having a smaller bridging group. A two-band spectrum was also reported for [Ru\(_2\)(µ-Cl)\(_3\)(H\(_2\)O)\(_6\)]\(^{3+}\) (27 800 and 32 200 cm\(^{-1}\)).

2.4.3 [M\(_2\)(µ-X)\(_3\)(PR\(_3\))\(_6\)]\(^{3+}\) Complexes of Osmium and Ruthenium

Oxidation of the [M\(_2\)(µ-X)\(_3\)(PR\(_3\))\(_6\)]\(^{2+}\) complexes results in collapse of those bands in the near-infrared region of the spectrum, and the growth of a prominent band ca. 11 000 cm\(^{-1}\). The spectral progressions upon oxidation of [M\(_2\)(µ-Cl)\(_3\)(PEt\(_3\))\(_6\)]\(^{2+}\) to [M\(_2\)(µ-Cl)\(_3\)(PEt\(_3\))\(_6\)]\(^{3+}\) (M=Ru, Os) are presented in Figure 2.16 (parts (a) and (b)). The spectral data for the [M\(_2\)(µ-X)\(_3\)(PR\(_3\))\(_6\)]\(^{3+}\) complexes are listed in Table 2.4.

The narrow, intense band between 10-12 000 cm\(^{-1}\), absent in the spectra of monomeric fac-[MX\(_3\)(PR\(_3\))] complexes, is tentatively assigned as a core transition, within the t\(_{2g}\) m.o. manifold. The position of this band is almost invariant upon changing M, X and PR\(_3\), as summarized below:

(i) for the same X and PR\(_3\), \(\nu_{\text{max}}\) Ru < \(\nu_{\text{max}}\) Os (\(\Delta\nu_{\text{max}}\) 800-1 200 cm\(^{-1}\)),

\(\nu_{\text{max}}\) Ru < \(\nu_{\text{max}}\) Os (\(\Delta\nu_{\text{max}}\) 800-1 200 cm\(^{-1}\)),
Figure 2.16 Spectral progression accompanying oxidation of \([\text{M}_2(\mu-\text{Cl})_3(\text{PET}_3)_6]^{12+}\) to \([\text{M}_2(\mu-\text{Cl})_3(\text{PET}_3)_6]^{3+}\) for (a) \(M=\text{Ru}\), (b) \(M=\text{Os}\), electrogenerated in 0.5 mol. dm\(^{-3}\) \(^\text{nBu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2\) in an OTTLE cell at 233 K.
(ii) for the same M and PR₃, \( \nu_{\text{max}} \) Br < \( \nu_{\text{max}} \) Cl (\( \Delta \nu_{\text{max}} \approx 1000 \text{ cm}^{-1} \)),
(iii) for M=Os and \( X=\text{Cl} \), \( \nu_{\text{max}} \) varies by only 1 110 cm\(^{-1} \) for PEt\(_3\), PEt\(_2\)Ph, PMe\(_2\)Ph and triphos.

The above observations are consistent with a \([M(\mu-X)₃M]^{3+}\) core transition (within the \( t₂g \) m.o. manifold), and similarly rules out l.m.c.t. transitions of the type \( P(\sigma)\rightarrow M^{\text{III}}(d₃) \), as considerable shifts (\( \approx 2000 \text{ cm}^{-1} \)) are expected between M=Ru and Os. Again \( X_b(\pi)\rightarrow M^{\text{III}}(d₃) \) charge-transfer need not be considered (see Section 2.3).

### Table 2.4

**Electrogeneated spectral data for \([M2(\mu-X)₃(PR₃)₆]^{3+}\) and \([M2(\mu-X)(\text{triphos})₂]^{3+}\) complexes.**

<table>
<thead>
<tr>
<th>Complex (^a)</th>
<th>Band Maxima, ( \text{cm}^{-1} ) (( \epsilon, \text{M}^{-1} \text{cm}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{PET}_2\text{Ph})_6]^{3+})</td>
<td>~4 500, 10 100, 3 850, ~12 600, ~1 800</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{PET}_3)_6]^{3+})</td>
<td>~1 110, 4 550, 4 550</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Br}_3(\text{PET}_3)_6]^{3+})</td>
<td>~4 200, 10 100, 16 800</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]^{3+})</td>
<td>5 400, 11 550, ~15 000, 32 400</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Br}_3(\text{PMe}_2\text{Ph})_6]^{3+})</td>
<td>5 300, 11 150, 9 500</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{PET}_2\text{Ph})_6]^{3+})</td>
<td>4 450, 11 260, 16 570, 31 500</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{PET}_3)_6]^{3+})</td>
<td>5 100, 11 930, 14 950, 18 460, 31 330</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{triphos})_2]^{3+})</td>
<td>5 300, 10 820, 14 340</td>
</tr>
</tbody>
</table>

\(^a\) Solutions were electrogenerated in 0.5 mol dm\(^{-3}\) \( \text{nBu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2 \) in an OTTLE cell at 213 K. \(^b\) Not observed, \(^c\) triphos=1,1,1-tris((diphenylphosphinomethyl)ethane.

Other assignments considered included a double-excitation of the neighbouring ions,\(^28\) since this intense band occurs at approximately twice the energy of a single-ion transition in Os\(^{\text{III}}\). This assignment can be
discounted by the fact that the band is in almost the same position for the diruthenium complexes. Single-ion transitions from Ru\textsuperscript{III} are not readily observed,\textsuperscript{9} since they are thought to occur around 4 000 cm\textsuperscript{-1} (and hence the double-excitation is expected \approx 8 000 cm\textsuperscript{-1}).

Interestingly, such a band has been observed in [Ir\textsubscript{2}(\mu-X)\textsubscript{3}X\textsubscript{6}]\textsuperscript{1-}, which is isoelectronic with Os\textsubscript{2}III,III\textsubscript{25}. The only inconsistency with the assignment of the intense band as a core transition is that a similar band is not observed in the isoelectronic, isostructural [M\textsubscript{2}(\mu-X)\textsubscript{3}(X)\textsubscript{6}]\textsuperscript{3-} complexes (M=Ru, Os), studied in Chapter 4. Other features in the 34 electron [M\textsubscript{2}(\mu-X)\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]\textsuperscript{3+} spectra include a very weak band between 4 000 and 5 500 cm\textsuperscript{-1}. This band is also assigned as a core transition, as it is observed for both M=Ru and Os, at similar energies.\textsuperscript{†}

The series of weak, broad bands found between 12-20 000 cm\textsuperscript{-1} in the spectra of the [M\textsubscript{2}(\mu-X)\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]\textsuperscript{2+} complexes all tend to increase in intensity upon oxidation. This observation is consistent with the conclusion drawn in Section 2.3, that some portion of this broad band(s) arises through P(\sigma)\rightarrow M\textsuperscript{III}(t\textsubscript{2g}) charge-transfer. It is uncertain what the effect oxidation will have on these transitions in this region.

The remaining feature in the spectra of the [M\textsubscript{2}(\mu-X)\textsubscript{3}(PR\textsubscript{3})\textsubscript{6}]\textsuperscript{3+} complexes are the band(s) found at \approx 30-32 000 cm\textsuperscript{-1} for M=Os, and \approx 24-28 000 cm\textsuperscript{-1} for M=Ru. The position of this band is remarkably invariant through three oxidation levels, and is effected little by the identity of the halide bridge or the terminal phosphine. This again suggests a core transition, possibly between the t\textsubscript{2g} and e\textsubscript{g} derived m.o. manifolds. The band is consistently higher in energy for M=Os, which can be explained in terms of greater single-ion 10 Dq for osmium.

Oxidation may be expected to lead to an increase in the M-M interaction, on account of shortening of the M-X\textsubscript{b} bond distances and the increase in the formal bond order (0.5 to 1.0). Opposed to this contraction within the (M(\mu-X)\textsubscript{3}M)\textsuperscript{3+} core is the increase in electrostatic repulsion between the positively charged metal cations. At the d\textsuperscript{5} level, backbonding

\textsuperscript{†} Single-ion Os\textsuperscript{III} transitions are typically found in this region, however those of Ru\textsuperscript{III} are expected at lower energy.
from the metal to the $\pi$-acid phosphine ligands will decrease, which will effectively decrease the positive charge of the metal atom. From this discussion, it is apparent a number of opposing effects may be in operation, making it unclear as to what changes are most likely to occur. The energetic invariance of the $\sim$30-32 000 cm$^{-1}$ (M=Os) and $\sim$24-28 000 cm$^{-1}$ (M=Ru) band may come as a consequence of the competing effects outlined above.

In summary, the weak band at $\sim$5 000 cm$^{-1}$ and the narrow, intense band at $\sim$11 000 cm$^{-1}$ are assigned as core transitions, most probably within the $t_{2g}$ derived m.o. manifold. The broad, weak bands in the 12-20 000 cm$^{-1}$ region of the spectrum are consistent with core transitions and $P(\sigma)\rightarrow M^{III}(t_{2g})$ charge-transfer, while the higher energy band is thought to arise from excitation between the $t_{2g}$ and $e_g$ derived m.o. manifolds.

The similarity of the diosmium and diruthenium spectra (especially below $\sim$12 000 cm$^{-1}$) suggests the degree of M-M interaction is essentially the same, unlike at the 35 electron level, where the spectra were distinctly different. In the phosphine capped systems, oxidation may have resulted in a decrease in M-M interaction, contrary to what is predicted from the simple m.o. scheme.
2.5 \( \text{M}_{2}^{\text{II,II}} [\text{M}_{2}(\mu-X)_{3}(\text{PR}_{3})_{6}]^{1+} \) AND \( [\text{Ru}_{2}(\mu-X)_{3}(\text{Me}_{3}\text{tacn})_{2}]^{1+} \) COMPLEXES

The mixed-valence \( [\text{Ru}_{2}(\mu-X)_{3}(\text{Me}_{3}\text{tacn})_{2}]^{2+} \) complexes are reversibly reduced to yield the \( [\text{Ru}_{2}(\mu-X)_{3}(\text{Me}_{3}\text{tacn})_{2}]^{1+} \) species, the spectra of which are presented here for the first time. Figure 2.17 shows the spectral progression accompanying electrosynthesis of \( [\text{Ru}_{2}(\mu-\text{Br})_{3}(\text{Me}_{3}\text{tacn})_{2}]^{1+} \).

The two low intensity bands at 19 830 and 25 180 cm\(^{-1}\) (see Table 2.1) are the spin-allowed single-ion d-d transitions, \( ^{1}A_{1g} \rightarrow ^{1}T_{1g} \) and \( ^{1}A_{1g} \rightarrow ^{1}T_{2g} \). In the \( [\text{Ru}_{2}(\mu-\text{Cl})_{3}(\text{Me}_{3}\text{tacn})_{2}]^{1+} \) complex, these same bands are at slightly higher energy, in accord with the greater ligand field associated with chloride.

![Absorbance Spectra](image)

**Figure 2.17** Spectral progression accompanying reduction of \( [\text{Ru}_{2}(\mu-\text{Br})_{3}(\text{Me}_{3}\text{tacn})_{2}]^{2+} \) to \( [\text{Ru}_{2}(\mu-\text{Br})_{3}(\text{Me}_{3}\text{tacn})_{2}]^{1+} \).

The remaining feature in these spectra are the moderately intense bands (\( \varepsilon \sim 1 \text{700-2 300 M}^{-1} \text{ cm}^{-1} \)) found above 30 000 cm\(^{-1}\) (Table 2.1). In the

---

\( ^{5} \) The reduction of the analogous chloride complex was shown in Figure 2.6, Section 2.3.
absence of other more plausible assignments, the band at 33 740 cm\(^{-1}\) for \(X=\text{Br}\) is designated as a core transition, arising from promotion between the \(t_{2g}\) and \(e_g\) m.o. manifolds, \textit{i.e.} a 10D\(_q\)-type transition. The spectrum of the analogous chloride complex, \([\text{Ru}_2(\mu-\text{Cl})_3(\text{Me}_3\text{tacl}_2)]^{1+}\), has a similarly assigned band at 36 230 cm\(^{-1}\). It is at higher energy on account of the larger effective single-ion 10D\(_q\) generated by the chloride ligands. Assignments such as m.l.c.t. can be readily dismissed, since the Me\(_3\text{tacl}\) ligand does not possess available \(\pi\)-orbitals to become involved in such processes. The fully occupied \(t_{2g}\) m.o. manifold prohibits \(N(\sigma)\rightarrow M^{II}(t_{2g})\) charge-transfer, meaning that only \(N(\sigma)\text{l.m.c.t.}\) to binuclear \(M^{II}(\pi,\pi^*)\) (c.f. Fig 2.5, p51) can occur. However this transition is likely to be found at very high energy, since the N donor orbital is expected to be greatly stabilized with respect to the metal acceptor orbital.

\textit{Table 2.5} Spectral data for \([\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{1+}\) and \([\text{M}_2(\mu-X)_3(\text{triphos})_2]^{1+}\) complexes.

<table>
<thead>
<tr>
<th>Complex (^a)</th>
<th>Principal Bands, cm(^{-1}) ((\varepsilon, M^{-1}) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]^{1+})</td>
<td>29 450 (3 730)</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Br}_3(\text{PMe}_2\text{Ph})_6]^{1+})</td>
<td>28 520 (3 740)</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{PET}Ph_2)_6]^{1+})</td>
<td>27 440 (3 180)</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{PET}Ph_2)_6]^{1+})</td>
<td>28 800 (3 130), 34 300 (6 340)</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{PET}_3)_6]^{1+})</td>
<td>27 150 (1 740), 30 270 (2 290), 36 230 (5 460)</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Br}_3(\text{PET}_3)_6]^{1+})</td>
<td>26 180 (2 100), 29 380 (2 800), 34 480 (5 440)</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{triphos})_2]^{1+, b})</td>
<td>27 230 (6 020)</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Cl}_3(\text{P(OMe)}\text{Ph}_2)_6]^{1+})</td>
<td>27 810 (4 430)</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]^{1+})</td>
<td>32 580 (7 920)</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Br}_3(\text{PMe}_2\text{Ph})_6]^{1+})</td>
<td>31 410 (6 580)</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{PET}Ph_2)_6]^{1+})</td>
<td>31 690 (5 790), 37 940 (11 020)</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{PET}_3)_6]^{2+})</td>
<td>-32 500 (sh), 34 390 (4 660), 41 050 (7 550)</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_3(\text{triphos})_2]^{2+, b})</td>
<td>31 410 (8 730)</td>
</tr>
</tbody>
</table>

\(^{a}\) Recorded in dichloromethane. \(^{b}\) triphos=1,1,1-tris(diphenylphosphinomethyl)ethane.

Turning now to the spectra of the \([\text{M}_2(\mu-X)_3(\text{PR}_3)_6]^{1+}\) complexes (\(M=\text{Ru, Os}\)), they are in general all quite similar, consisting of one or two moderately intense transitions in the region 26-30 000 cm\(^{-1}\) for \(M=\text{Ru and}\)
31-35 000 cm\(^{-1}\) for M=Os. The precise appearance of this feature(s) is dependent upon the identity of the phosphine, e.g. for \([\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]\)^{1+} complexes, two bands are clearly evident for \(\text{PR}_3=\text{PEt}_3\), a band and a shoulder for \(\text{PR}_3=\text{PEtPh}_2\) and in the case of triphos, only a single band is observed. For those complexes containing phosphines with phenyl substituents, the spectrum above \(-35 000\) cm\(^{-1}\) is dominated by ligand-based $\pi-\pi^*$ transitions. The spectra of the \([\text{M}_2(\mu-\text{Cl})_3(\text{PEt}_3)_6]\)^{1+} complexes (M=Ru, Os), shown in Figure 2.18, clearly reveal an additional band, at 36 230 cm\(^{-1}\) for M=Ru and at 41 050 cm\(^{-1}\) for M=Os. This higher energy feature is present as a shoulder in the spectra of mixed aryl/alkyl phosphine \([\text{M}_2(\mu-X)_3(\text{PR}_3)_6]\)^{1+} complexes.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{b.png}
\caption{U.v./visible spectra of \([\text{M}_2(\mu-\text{Cl})_3(\text{PEt}_3)_6]\)^{1+} complexes.  
(a) M=Os, (b) M=Ru.}
\end{figure}
These bands are not associated with internal transitions on the phosphine ligand. A series of binuclear [ZnCl$_2$(PR$_3$)$_2$] complexes were prepared specifically for the purpose of obtaining spectra of coordinated phosphine ligands. The spectra of such complexes were featureless to ca. 45 000 cm$^{-1}$. Metal-to-ligand charge-transfer (m.l.c.t.), of the type M$^{II}$(t$_{2g}$)$\rightarrow$P($\pi^*$) may have been expected, since such transitions are favoured in low spin $d^6$ complexes. This assignment can however be discounted, as the bands in the osmium spectra are consistently higher in energy than those in ruthenium. For an m.l.c.t. assignment, the reverse is required, since osmium complexes are in general easier to oxidize than those of ruthenium.

It was noted above that the N donor orbitals of Me$_3$tacn are strongly stabilized with respect to the metal acceptor orbitals ($\pi, \pi^*$), such that N(\(\sigma\))$\rightarrow$M$^{II}$(\(\pi, \pi^*\)) charge-transfer is expected at very high energy. This however is not the case with P donor ligands, where P(\(\sigma\))$\rightarrow$M charge-transfer has been observed in a number of complexes. Comparison of the spectra of [Ru$_2$(\(\mu\)-Cl)$_3$(PEt$_3$)$_6$]$_{1+}$ and [Ru$_2$(\(\mu\)-Cl)$_3$(Me$_3$tacn)$_2$]$_{1+}$ complexes (Figures 2.17 and 2.6) immediately reveals the significant contribution of the phosphine ligands. The facial arrangement of the phosphines on the metal centre creates two symmetry orbitals (A, E), hence two charge-transfer bands are expected, P(\(\sigma\))$\rightarrow$Ru$^{II}$(\(\pi, \pi^*\)).

The spectra of the [M$_2$(\(\mu\)-Cl)$_3$(PR$_3$)$_6$]$_{1+}$ complexes may therefore comprise of two types of bands, a core transition, and a m.l.c.t. band. The two different transitions can be identified by comparing the spectra of the [Ru$_2$(\(\mu\)-Cl)$_3$(PEt$_3$-nPh$_n$)$_6$]$_{1+}$ series of the complexes (n=0, 1, 2) (Figure 2.19). The shoulder on the leading edge of the first band remains approximately stationary, while the more well defined band moves progressively to higher energy, as does the more intense band. Two assignments are proposed. The low energy shoulder is assigned as the core transition, analogous to that observed in the [Ru$_2$(\(\mu\)-X)$_3$(Me$_3$tacn)$_2$]$_{1+}$ complexes. Consistent with the core assignment is the observation that the same band in [Os$_2$(\(\mu\)-Cl)$_3$(PEt$_3$)$_6$]$_{1+}$ is found at higher energy, due to the larger single-ion 10 Dq expected for osmium. Changing the bridging ligand from chloride to bromide causes the band to move to lower energy, as expected from the
s spectrochemical series (10 Dq Br<10 Dq Cl). The two higher energy bands are then assigned as \( P(\sigma) \rightarrow \text{Ru}^{ll}(\pi,\pi^*) \) charge-transfer transitions, the positions of which vary with the identity of the phosphine ligand. As required for l.m.c.t., the bands in the diosmium complexes are at higher energy.

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Figure 2.19 U.v./visible spectra of \( \{\text{Ru}_2(\mu-\text{Cl})_3(\text{PR}_3)_6\}_{1^+} \) complexes.
(a) \( \text{PR}_3=\text{PEt}_3 \), (b) \( \text{PR}_3=\text{PEt}_2\text{Ph} \), (c) \( \text{PR}_3=\text{PEtPh}_2 \).
2.6 EXPERIMENTAL

The u.v./visible/near-infrared spectra of electrogenerated species are collected in situ through the use of an OTTLE (optically transparent thin-layer electrolysis) cell, placed in the beam of a spectrophotometer.

The OTTLE cell consists of a rectangular 0.5 mm path length fused-silica (Suprasil W) cell, containing a fine platinum gauze (70% transmittance) working electrode. Positioned in the top of the cell are a miniaturized auxiliary electrode (platinum wire) and a Ag/AgCl reference electrode, separated from the bulk solution by porous glass frits. The cell is cryostatted in a gas-tight, double-glazed (Suprasil W windows) polytetrafluoroethylene cell block, enabling both the cell and its contents to be cooled (by cold nitrogen gas) to temperatures as low as 193 K. In the work described in this thesis, cooling of the electrochemical solution is essential, since the greater majority of electogenerated products are only stable at low temperatures. The entire cell/cell block is positioned in the beam of the spectrophotometer (Perkin-Elmer λ9), which permits monitoring of the spectrum while the electrolysis takes place.

Dry nitrogen gas is cooled by passing through a copper coil immersed in a Dewar of liquid nitrogen. It then travels through a heat exchanger (maintained at the desired temperature by a Bruker n.m.r. temperature controller), and is piped into the cell compartment and through the cell block. The cold gas passes through the inner windows and over the faces of the cell, cooling the cell and its contents. To prevent fogging of the outer windows, room temperature nitrogen gas is passed between the inner and outer windows. The thermocouple for the temperature controller is positioned at the point of gas outflow from the cell block. A known difference between gas outflow temperature and solution temperature within the OTTLE cell allows the required temperature to be accurately established and maintained.

A modified Thompson potentiostat is used for electrogeneration. Electrolysis is typically carried out at a potential 300 mV past the $E_{1/2}$ of the redox process in question. The electrolysis is continued until the current decays to a constant minimum, and spectral changes cease to occur. The
working criteria for reversibility are established by the observation of isosbestic points accompanying spectral changes, and the ability to regenerate starting spectra (see Section 2.2).
2.7 REFERENCES

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    247.


3.1 PRELIMINARY REMARKS

As will be explained more fully in the following chapter, the triple-bridged, face-sharing structure is quite common among metal halide complex anions. A notable exception is the case of osmium, where prior to this work, there were no conclusive reports of any such binuclear nonahalide complexes having been isolated. Two complexes that have been previously documented however, are the double-bridged edge-sharing bioctahedral species, $[\text{Os}_2(\mu-X)_2X_8]^{2-}$, for both $X=\text{Cl}$ and $\text{Br}$. The author's initial interest in these compounds stemmed from their potential use as precursors to triple-bridged binuclear complexes, $[\text{Os}_2(\mu-X)_3X_6]^{2-}$.* However, it soon became apparent that the decahalodiosmate complexes were of special interest in their own right. Although both the chloride and bromide complexes have been known for some time, aside from their structural characterization and a detailed description of vibrational spectra, suprisingly

* For further discussion see Chapter 4.
little of their chemistry has been reported. The solution chemistry of such complexes was largely unexplored. It was therefore appropriate to characterize these binuclear complexes more fully before exploring their reactivity. Our eventual success (Chapter 4) in isolating \( \text{[Os}_2(\mu-X)_3X_9]^{2-} \) adds to the value of comparative characterization of the \( \text{[Os}_2(\mu-X)_2X_8]^{2-} \) complexes.
3.2 INTRODUCTION

In 1984, two separate publications reported for the first time the syntheses and structures of \((\text{nBu}_4\text{N})_2[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]\) and \((\text{nBu}_4\text{N})_2[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]\) (Figure 3.1).\(^1,2\)

![Figure 3.1](image)

*Figure 3.1* The double-bridged, edge-sharing biocahedral structure.

Cotton and co-workers reported that the reaction of \((\text{nBu}_4\text{N})_2[\text{OsBr}_6]\) in refluxing trifluoroacetic acid (TFAA) yielded a black solid, of formula \((\text{nBu}_4\text{N})_2[\text{Os}_2\text{Br}_{10}]\) (as shown by elemental analysis).\(^1\) Repeating the same reaction in an apparatus which cycled the temperature back and forth between 310 and 315 K resulted in the isolation of a more crystalline sample. A single crystal x-ray diffraction study revealed this product was the previously unreported double-bridged edge-sharing complex, \((\text{nBu}_4\text{N})_2[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]\). The di-Os\(^{IV}\) compound was only weakly paramagnetic at room temperature, with a magnetic moment of 0.26 bohr magnetons (B.M.) per osmium.

The analogous chloride complex was isolated by a different method.\(^2\) Preetz *et al.* prepared \((\text{Et}_4\text{N})_2[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]\) by heating pentavalent \(\text{Et}_4\text{N}[\text{OsCl}_6]\) at 513 K for a short period of time. The dimerization process occurs by an internal redox reaction, involving the reduction of Os\(^V\) to Os\(^{IV}\), concomitant with the formation of an equivalent amount of gaseous chlorine. The reaction can be reversed, since treatment of salts of \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]\)\(^2\) at 393 K with Cl\(_2\) gas reforms \([\text{OsCl}_6]\)\(^1\).

The tetraethylammonium salt was converted to the tetra-n-butylammonium species, and the structure of \((\text{nBu}_4\text{N})_2[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]\) was
established by single crystal x-ray diffraction analysis. The room
temperature magnetic moment of \((\text{nBu}_4\text{N})_2[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]\) was quoted as
1.36 B.M. per osmium, significantly larger than that reported for the
analogous bromide. Preetz and Bruns later prepared the same compound by
a different route. They found that heating solid \(\text{Et}_4\text{N}[\text{OsCl}_5(\text{CO})]\) at
temperatures between 393 and 423 K displaced CO and gave quantitative
yields of \((\text{Et}_4\text{N})_2[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]\).

The structures of both the bromide and chloride complexes of
\((\text{nBu}_4\text{N})_2[\text{Os}_2(\mu-\text{X})_2\text{X}_8]\) are essentially identical, being comprised of two
octahedra which share a common edge. In each case the metal-metal
distance is quite long, 3.788(3) and 3.626(1) Å for the bromide and chloride
respectively. The metal centres deviate from ideal octahedral
environments; the \(X_b-\text{Os}-X'_b\) angle being less than 90°, and the \(\text{Os}-X_b-\text{Os'}\)
angle greater than 90° in each case (Table 3.1). For idealized octahedral
geometry, both angles should equal 90°. This distortion can be explained in
terms of lengthening of the metal-metal distance, possibly as a consequence
of metal-metal electrostatic repulsion, given that each osmium centre is in
the +4 oxidation state. This distortion, and the long Os...Os distance implies
a lack of direct metal-metal bonding.

Interestingly, this discrete binuclear edge-sharing complex models a
segment of the structure of a high temperature polymorph of \(\text{OsCl}_4\). The
latter consists of infinite linear chains of edge-sharing \([\text{Os}(\mu-\text{Cl})_4\text{Cl}_2]\)
ocahedra. Each Os atom possesses two terminal chlorides (trans to each
other), and four in-plane bridging chlorides, which share opposite edges
with adjacent Os atoms. The Os...Os distance is uniformly 3.560(1) Å along
the chain, and does not alternate between long and short metal-metal
distances, as is the case in many \([\text{M}(\mu-\text{X})_4\text{X}_2]\)_n systems having this structure.
The octahedra are distorted in a way similar to \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]\)^2, and the
magnetic moment quoted as 1.6 B.M. per \([\text{Os}(\mu-\text{Cl})_4\text{Cl}_2]\) unit.

The neutral binuclear pentavalent complex \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]\) has also
been prepared, by the reaction of \(\text{OsF}_6\) with excess \(\text{BCl}_3\) at low temperature. This complex was structurally characterized as a double-bridged edge-

\[^{**}\text{The quoted values of magnetic susceptibility and magnetic moment do not correspond. See Section 3.5 for more discussion.}\]
sharing compound, with an Os...Os distance of 3.63(7) Å. Again each osmium atom is displaced from the centre of the octahedron formed by the six chloride ligands, in a way suggestive of considerable metal-metal repulsion (Table 3.1).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Os...Os (Å)</th>
<th>Os-X-Os' (°)</th>
<th>X-Os-X' (°)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(nBu₄N)₂[Os₂Br₁₀]</td>
<td>3.788</td>
<td>96.3</td>
<td>83.7</td>
<td>1</td>
</tr>
<tr>
<td>(nBu₄N)₂[Os₂Cl₁₀]</td>
<td>3.626</td>
<td>97.54</td>
<td>82.46</td>
<td>2</td>
</tr>
<tr>
<td>OsCl₄</td>
<td>3.560</td>
<td>96.93</td>
<td>83.07</td>
<td>5</td>
</tr>
<tr>
<td>[Os₂Cl₁₀]</td>
<td>3.63</td>
<td>97</td>
<td>83</td>
<td>6</td>
</tr>
</tbody>
</table>

The decahalodiosmate dianions, [Os₂(μ-X)₂X₈]²⁻ (X=Cl, Br) are of great interest in the area of high oxidation state osmium chemistry. As mentioned in the preliminary remarks, their solution chemistry is largely unexplored. Chapter 3 describes the improved preparations of these complexes, and reports for the first time their redox chemistry spanning Os²⁺,III to Os²⁺,V, and the associated spectroelectrochemistry.
3.3 SYNTHESIS AND CHARACTERIZATION

The initial preparation of the decabromodiosmate complex, \((^{n}Bu_4N)_2[Os_2(\mu-Br)_2Br_8]\), was attempted following the method described by Cotton et al.\(^1\) This involved refluxing a mixture of \((^{n}Bu_4N)_2[OsBr_6]\) and neat TFAA, producing a black solid, reportedly the above mentioned compound. The procedure was carried out as described, and a finely divided black precipitate collected. This material repeatedly gave analyses corresponding to \(C_{16}H_{36}NOs_2Br_9\), or \(^{n}Bu_4N[Os_2Br_9]^{-}\), but given the acidic medium from which it came, \([Os_2(\mu-Br)_2Br_8]^{2-}\) could easily have crystallized as the mixed \((^{n}Bu_4N)(H))^{2+}\) salt, meaning the microanalytical figures were inconclusive.** By comparison of the far-infrared spectrum of this solid with the spectrum of the genuine material,\(^7\) it became apparent that this material was not a salt of the decabromodiosmate dianion. It was later shown that this black product, isolated from refluxing mixtures of \((^{n}Bu_4N)_2[OsBr_6]\) and TFAA, was in fact \(^{n}Bu_4N[Os_2(\mu-Br)_3Br_6]^{-}\), the hitherto unknown face-sharing, bioctahedral nonabromodiosmate complex. Details of the characterization of this complex will be discussed, along with further aspects of its chemistry in the following chapter.

However, if instead of refluxing the \((^{n}Bu_4N)_2[OsBr_6]/\text{TFAA}\) mixture, it is only warmed at 323 K (as in the case of the structurally characterized material), another dark solid was obtained, which was very similar in appearance to \(^{n}Bu_4N[Os_2(\mu-Br)_3Br_6]^{-}\). The far-infrared spectrum (Figure 3.2) of this product was identical to that shown for \((^{n}Bu_4N)_2[Os_2(\mu-Br)_2Br_8]\),\(^7\) and the analysis consistent with a compound of stoichiometry \(C_{32}H_{72}N_2Os_2Br_{10}\). The x-ray powder diffraction pattern of this compound also matched that calculated from the known structure of \((^{n}Bu_4N)_2[Os_2(\mu-Br)_2Br_8]^{-}\).

The critical factor in controlling the product of this reaction is the temperature at which the mixture is heated. Warming the TFAA solution of \((^{n}Bu_4N)_2[OsBr_6]\) yields \((^{n}Bu_4N)_2[Os_2(\mu-Br)_2Br_8]\), while contrary to Cotton's

** Calculated microanalytical figures(%):

\(^{n}Bu_4N[Os_2Br_9], C_{16}H_{36}NOs_2Br_9, C 14.32, H 2.70, N 1.04, Br 53.59

\(^{n}Bu_4N)(H)(Os_2Br_{10}), C_{16}H_{37}NOs_2Br_{10}, C 13.51, H 2.62, N 0.99, Br 56.20

\(^{n}Bu_4N)(O_4N)_2[Os_2Br_{10}], C_{32}H_{72}N_2Os_2Br_{10}, C 23.09, H 4.36, N 1.68, Br 48.01
account, refluxing produces $^\text{nBu}_4\text{N}[\text{Os}_2(\mu-\text{Br})_3\text{Br}_8]$. More discussion on the relationship of these complexes to each other will appear in the following chapter.

The tetraphenyolphosphonium salt of $[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}$ has also been prepared, and is a valuable alternative derivative. It is prepared in an
identical way to the nBu4N+ salt, except a longer reaction time is required to produce reasonable yields of (Ph4P)2[Os2(µ-Br)2Br8].

Turning now to the decachloride, [Os2(µ-Cl)2Cl8]2-, the Ph4P+ salt was first prepared using the procedure outlined by Preetz et al.,2 which starts inconveniently from pentavalent Ph4P[OsCl6]. Heating Ph4P[OsCl6] at 513 K under vacuum yielded a solid which subsequently proved to be a mixture of the desired product and (Ph4P)2[OsCl6]. It was also found that heating samples of nBu4N[OsCl5(thf)]4 under vacuum gave mixtures of the starting material, (nBu4N)2[OsCl6] and (nBu4N)2[Os2(µ-Cl)2Cl8]. All attempts to purify these mixtures by recrystallization resulted in partial decomposition of the decachlorodiosmate complex.

Given the success of the TFAA route to organo-soluble salts of [Os2(µ-Br)2Br8]2-, it was decided to explore this procedure in an attempt to prepare the analogous chloride complex. Warming a yellow solution of (nBu4N)2[OsCl6] in neat TFAA (to ~323 K) produced a green solution over a period of ~20 hours, however no product separated, even after cooling. Upon the addition of diethyl ether however, a fine green solid precipitated. While this product again proved to be a mixture of unreacted (nBu4N)2[OsCl6], and some (nBu4N)2[Os2(µ-Cl)2Cl8], it at least confirmed the latter was formed under these conditions. Repeating the reaction with a different salt of [OsCl6]2-, namely Ph4P+, led to the convenient isolation of (Ph4P)2[Os2(µ-Cl)2Cl8], free of starting material and TFAA. Using the less solubilizing counter cation results in the formation of (Ph4P)2[Os2(µ-Cl)2Cl8] as a fine green precipitate within 15 minutes of warming the (Ph4P)2[OsCl6]/TFAA mixture. A near quantitative yield (96%) of (Ph4P)2[Os2(µ-Cl)2Cl8] can now be routinely obtained from this reaction, by heating the (Ph4P)2[OsCl6]/TFAA mixture at ~323 K for 5 days.

All attempts at recrystallizing impure samples of the highly reactive decahalodiosmates resulted in their decomposition. Apparently, the

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# The composition of this mixture was determined by electrochemical studies. Given that compounds which differ only in the identity of the halide (whether it be chloride or bromide) generally have similar voltammetry, the electrochemical response of (Ph4P)2[Os2(µ-Cl)2Cl8] was expected to be similar to that of (nBu4N)2[Os2(µ-Br)2Br8].

From knowledge of the voltammetry of (nBu4N)2[Os2(µ-Br)2Br8] and (Ph4P)2[OsCl6], it was clear the mixture contained the latter complex and (nBu4N)2[Os2(µ-Cl)2Cl8].

†† The preparation of this complex (where thf =tetrahydrofuran) is described in Chapter 5.
spontaneous separation of the \((\text{A})_2\{\text{Os}_2(\mu-\text{X})_2\text{X}_8\}\) (\(\text{A}=\text{Ph}_4\text{P}, \text{nBu}_4\text{N}; \text{X}=\text{Cl}, \text{Br}\)) compounds from hot, neat TFAA is of central importance to their isolation. It also aids in their formation, in that the equilibrium shown in equation (3.1) is driven to the right by the precipitation of the decahalodiosmate from the acid. The right-hand side of equation (3.1) may be further favoured, given that in such acid concentrations the free halide may form gaseous HX.

\[
2\{\text{OsX}_4\}^{2-} \rightleftharpoons [\text{Os}_2\text{X}_{10}]^{2-} + 2\text{X}^-
\] (3.1)

In addition to the TFAA being a poor solvent for organic salts of the \([\text{Os}_2(\mu-\text{X})_2\text{X}_8]^{2-}\) (\(\text{X}=\text{Cl}, \text{Br}\)) complexes, it appears to function as a halide abstracting agent, in a way similar to trifluoromethanesulfonic ('triflic') acid in transition metal halide chemistry. The use of this very strong acid to eliminate halide (and yield labile \(\text{CF}_3\text{SO}_3^-\) complexes) from a variety of transition metal compounds has been well documented.8,9
3.4 ELECTROCHEMISTRY

As mentioned in the introduction, the electrochemistry of the double-bridged, edge-sharing decahalodiosmate complexes had not been previously reported, so is discussed here for the first time.

While the \([\text{Os}_2(\mu-\text{X})_2\text{X}_8]\)^{2-} (\text{X}=\text{Cl, Br}) compounds are quite stable in the solid state, solutions are prone to decomposition via a number of different pathways, such as reduction or attack by nucleophiles. Except under special conditions (see below), one-electron reduction of \([\text{Os}_2(\mu-\text{X})_2\text{X}_8]\)^{2-} invariably leads to the simultaneous formation of \([\text{Os}_6]\)^{2-} (through asymmetric cleavage), together with a unidentified lower oxidation state product. Coordinating solvents readily cleave the double-halide bridge, giving rise to mixtures of monomeric products. Even dry, sealed dichloromethane solutions of the bimetallic complexes show signs of decomposition over a period of several hours at room temperature (as monitored by u.v./visible spectroscopy). If however the solvent is pre-chilled to 213 K (-60 °C) before adding the complex, the stability of the complex in solution is greatly enhanced.

The voltammetry of the decahalodiosmate complexes was recorded in pre-cooled dichloromethane/electrolyte solutions. An indication of the redox processes likely to be observed in these complexes can be gained by noting that monomeric \([\text{Os}_6]\)^{2-} complexes display \text{Os}^\text{V}/\text{IV}, \text{Os}^\text{IV}/\text{III} couples and under special circumstances (see Chapter 5), an \text{Os}^\text{III}/\text{II} couple. Each \([\text{Os}_2(\mu-\text{X})_2\text{X}_8]\)^{2-} (\text{X}=\text{Cl, Br}) complex displays four metal-based one-electron transfer processes, corresponding to an oxidation and three reductions, as shown from stirred voltammagrams. For example, \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]\)^{2-} displays two \text{Os}^\text{IV}/\text{III} reductions, i.e. \text{Os}^\text{IV,IV}/\text{IV,III} and \text{Os}^\text{IV,III}/\text{III,III}, which are flanked by an \text{Os}^\text{V}/\text{IV} and an \text{Os}^\text{III}/\text{II} couple. This grouping of related couples, with wide separations in between, is characteristic of binuclear halide-bridged electrochemistry.\(^{10,11}\) The corresponding pairs to the \text{Os}^\text{V}/\text{IV} and \text{Os}^\text{III}/\text{II} couples are expected to occur outside the electrochemical window of the media used here. It is interesting to note that while \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]\) (\text{Os}^\text{V,V}) is electrochemically inaccessible under the conditions described above, it has been prepared chemically, and structurally
characterized as an edge-sharing bi-octahedral species (see Section 3.2).

Isolated as the Os$_2$IV,IV complexes, the first reduction of the decahalodiosmate di-anions to the formally Os$_2$IV,III species is quasi-reversible for both $X=\text{Cl}$ and Br, as determined by standard criteria (see Chapter 1). The second reduction, Os$_2$IV,III to Os$_2$III,III, is also quasi-reversible for both complexes. The final reduction, Os$_2$III,III to what is formally Os$_2$II,II, was found to be irreversible under all experimental conditions tried (for $X=\text{Cl}$, Br). Likewise, the oxidation from Os$_2$IV,IV to Os$_2$IV,V was also irreversible for both $X=\text{Cl}$ and Br.

An alternative way of describing these redox processes is to use the 18 electron formalism described previously in Chapter 1. If the M$_2^{II,II}$ ($d^6/d^6$) complex were to be considered as a 36 electron species, then the M$_2^{IV,IV}$ ($d^4/d^4$) complex would be regarded as a 32 electron system. Figure 3.3 summarizes the electron count through the redox changes exhibited by the [Os$_2$(µ-$X$)$_2$X$_8$]$^{2-}$ ($X=\text{Cl}$, Br) complexes.

![Figure 3.3](image-url)

**Figure 3.3** Electron counting scheme for [M$_2$(µ-$X$)$_2$X$_8$]$^{2-}$ complexes, $M=\text{Os}$

The low-temperature voltammograms of (Ph$_4$P)$_2$[Os$_2$(µ-Br)$_2$Br$_9$] are reproduced in Figure 3.4. Part (a) shows the quasi-reversible 32/33 and 33/34 electron reductions, while parts (b) and (c) encompass these same couples, plus the 34/35 electron reduction and the 31/32 electron oxidation respectively. The nature of the daughter product (marked with an asterisk), which appeared upon scanning over the irreversible 34/35 and 32/31 electron couples, will be discussed in the following chapter. At this stage it suffices to say that the positions of these waves suggest the formation of an [Os$_2$Br$_9$]$^{2-}$ species.

The voltammetry of the chloride complex is essentially the same as
Figure 3.4 Voltammetry of $[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^2-$ in 0.5 mol dm$^{-3}$ $n\text{Bu}_4\text{NPF}_6$ /CH$_2$Cl$_2$ at 213 K, scan rate =100 mV/s. Part (a) shows the 32/33 and 33/34 electron reductions only, part (b) the daughter product (*) formed after scanning over the irreversible 34/35 electron reduction, and part (c) the formation of the same daughter product (*) after scanning over the 31/32 electron oxidation.
that of the bromide, shown in Figure 3.4. The 31/32 electron oxidation in 
(Ph₄P)₂[Os₂(µ-Cl)₂Cl₈] was not always observed in dichloromethane, since it
was at times difficult to distinguish between the background and the
possible oxidation wave. Its observation was evidently dependent upon the
quality of the CH₂Cl₂ and of the electrolyte on any particular day.
Fortunately the 31/32 electron oxidation was more reliably observed in
acetonitrile. The same procedure was used with MeCN, i.e. the electrolyte
solution was chilled to 233 K (-40 °C) prior to adding the complex, and the
voltammetry again recorded.

The voltammetric data for both [Os₂(µ-X)₂X₈]²⁻ and [OsX₆]²⁻ complexes
(X=Cl, Br) are presented in Table 3.2. When comparing the voltammetry of
the monomeric and dimeric complexes, it can be more appropriate to refer
to the "centre of gravity" or "mean" of a pair of related (d⁴,4⁺→d⁵,5⁻)
couples in the binuclear complex, rather than one particular couple. The
centre of gravity of the 32/33 and 33/34 electron couples in [Os₂(µ-Br)₂Br₈]²⁻
is at +0.06 V. This represents an anodic (positive) shift of 0.43 V from the
corresponding couple in [OsBr₆]²⁻ (OsIV/III).

<table>
<thead>
<tr>
<th>Complex</th>
<th>V,IV/IV,IV (31/32)</th>
<th>IV,IV/IV,III (32/33)</th>
<th>IV,III/III,II (33/34)</th>
<th>III,III/III,II (34/35)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ph₄P)₂[Os₂Br₁₀]</td>
<td>+1.86 (irr)</td>
<td>+0.30 (qr)</td>
<td>-0.18 (qr)</td>
<td>-1.88 (irr)</td>
</tr>
<tr>
<td>(Ph₄P)₂[Os₂Cl₁₀]</td>
<td>+2.10 b (irr)</td>
<td>+0.26 (qr)</td>
<td>-0.24 (qr)</td>
<td>-1.85 (irr)</td>
</tr>
<tr>
<td>(Ph₄P)₂[OsBr₆]</td>
<td>+1.43 (r)</td>
<td>-0.37 (qr)</td>
<td>2.28 c (irr)</td>
<td></td>
</tr>
<tr>
<td>(Ph₄P)₂[OsCl₆]</td>
<td>+1.50 (r)</td>
<td>-0.49 (qr)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2  Voltammetric data for [Os₂(µ-X)₂X₈]²⁻ and [OsX₆]²⁻ complexes.

a Measured in 0.50 mol. dm⁻³ nBu₄NPF₆/CH₂Cl₂ at 213 K, versus Ag/AgCl, against which
ferrocenium/ferrocene occurs at +0.55 V. By convention the couples are listed as
reductions, the numbers in parentheses referring to the EAN electron counting scheme (see
Figure 3.3). r=reversible, qr=quasi-reversible, pr=partially reversible and
irr=irreversible.  b Measured in 0.10 mol. dm⁻³ nBu₄NPF₆/CH₃CN at 233 K, versus
Ag/AgCl.  c Only observed under "superdry " conditions. See Chapter 5 for more details.

In simple arithmetic terms, the decahalodiosmate di-anions have one
less halide per osmium than their hexahalide counterparts, and so may be
expected to be harder to oxidize. In addition, the electrostatic influence of the adjacent highly positively charged osmium centres on one another could also contribute to the increased difficulty in oxidizing the $[\text{Os}_2(\mu-X)_2X_8]^{2-}$ complexes.

The variation in metal-based redox couples with different halide ions is largely dependent upon the actual system under consideration (see Chapter 5 for further discussion). For the complexes listed in Table 3.2, there are no consistent differences in the positions of the metal-based electrode potentials between the chloride and bromide complexes. The 32/31 electron oxidation and the 34/35 electron reduction of $[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{2-}$ are respectively "harder" and "easier"† than those in the bromide complex, i.e. for the chloride, both the 31/32 and 34/35 electron couples have more positive $E_{1/2}$ values than the analogous couples in the bromide complex. The opposite is true for the 32/33 and 33/34 electron couples, where the $E_{1/2}$ values of $[\text{Os}(\mu-\text{Cl})_2\text{Cl}_8]^{2-}$ are more negative than those of $[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}$, making both of these reductions more difficult in the case of $[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{2-}$. The numerical differences in all of the above couples, except one, are small, being equal to or less than 80 mV. The one exception is the 32/31 electron oxidation, where the difference between chloride and bromide is 220 mV, however little significance can be placed on this figure since the couple is irreversible.

Similar differences in the positions of $E_{1/2}$ values between chloride and bromide are observed in the corresponding monomeric hexahalides (Table 3.2). The Os$^{V/IV}$ couple of $[\text{OsCl}_6]^{2-}$ is more positive than that of the analogous $[\text{OsBr}_6]^{2-}$, while the Os$^{IV/III}$ couple of the chloride is found negative of the bromide position. Chloride and bromide generally show greater similarity in their influence of chemical properties than any other two halide ions. In light of the wide and varied nature of results of electrochemical studies on complexes coordinating different halide ions, the small differences noted above are not unexpected.

As explained in Chapter 1, the separation of related couples in binuclear complexes is related to the degree of electronic interaction

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† Reductions become easier as $E_{\text{red}}$ becomes a larger positive number.
between the two metal centres. The separation of the 32/33 and 33/34 electron couples in the \([\text{Os}_2(\mu-X)_2X_8]^{2-}\) complexes is approximately the same, being 0.50 V for X=Cl, and 0.48 V in the case of X=Br. Calculating the comproportionation equilibrium constant \((K_c)\) of equation (3.2), yields \(K_c\) values equal to \(6.8 \times 10^{11}\) for X=Cl and \(2.3 \times 10^{11}\) for X=Br. These figures suggest the mixed-valence \([\text{Os}_2(\mu-X)_2X_8]^{3-}\) species should have considerable stability towards redox disproportionation.

\[
\begin{array}{ccc}
\text{III} & \text{III} & \text{IV} \\
\{\text{Os}(\mu-X)\text{Os}\}^{4+} + & \{\text{Os}(\mu-X)\text{Os}\}^{6+} & \overset{K_c}{\longrightarrow} 2 \{\text{Os}(\mu-X)\text{Os}\}^{5+} \\
\end{array}
\] (3.2)

There is a distinct lack of electrochemical data on structurally related systems, with which these values can be compared. The neutral \([\text{M}_2(\mu-\text{Cl})_2\text{Cl}_8]\) \((\text{M}=\text{Nb, Ta, Mo, Re})\) compounds have been studied voltammetrically, however none of these complexes retained their dimeric structure in solution.\(^{12}\) Numerous edge-sharing \([\text{M}_2(\mu-X)_2L_8]\) complexes are known, although suprisingly few have been studied electrochemically.
Chapter 3

3.5 SPECTROELECTROCHEMISTRY

3.5.1 Introduction

The moderate potentials required to access the 33 and 34 electron states of the $[\text{Os}_2(\mu-X)_2X_8]^{2-}$ complexes, along with the chemical reversibility of these couples (under special conditions), enabled the electrogeneration in solution of these previously unreported species. Carrying out such experiments in situ, in an OTTLE cell, permitted characterization of these species by means of their electronic spectra. Aside from being of interest in their own right, the spectra of the $[\text{Os}_2(\mu-X)_2X_8]^{2-}$ systems ($z=2, 3, 4$) provide an essential aspect to the general comparison of metal-metal interactions in edge-sharing and face-sharing diosmium complexes. The latter were discovered whilst attempting to prepare $[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}$ by the reported literature route.\(^1\)

Both $[\text{Os}_2(\mu-X)_2X_8]^{2-}$ complexes ($X=\text{Cl}, \text{Br}$) have been characterized by X-ray structures (see Table 3.1). The long Os...Os distance, and the distortion within the $[\text{Os}(\mu-X)_2\text{Os}]^{6+}$ core imply the $[\text{Os}_2(\mu-X)_2X_8]^{2-}$ complexes do not contain a metal-metal bond, and so can be considered as weakly interacting. Of special interest is the 33 electron species, and the question of whether the mixed-valence state is best described as localized (formally Os$_{2\ IV\,\ III}$) or delocalized. Both the $[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{3-}$ and $[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{3-}$ species have been characterized, and their properties are discussed below. In addition, detailed spectroscopic characterization of $[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{4-}$ has been carried out, and some information on $[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{4-}$ collected also.

3.5.2 Accumulation of Spectra

In dry dichloromethane at 213 K (−60 °C), it proved possible to electrogenerate solutions of $[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{3-}$ and $[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{4-}$ within the chilled OTTLE cell, and cycle back and forth between the 32, 33 and 34 electron species, without loss of any material or degradation of spectra. The spectral changes accompanying each redox step (32/33 and 33/34 electron couples) proceeded with the retention of isosbestic points.
Under identical conditions to those just described, the 32/33 electron reduction of \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{2-}\) was accompanied by a series of irreversible spectral changes. Only after considerable effort was the reduced \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{3-}\) species stabilized (through the use of \(\text{nBu}_4\text{NCl}\) as electrolyte), and its optical spectrum collected. The conversion of the \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{3-}\) to the \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{4-}\) was attempted in this same medium. Electrolysis proceeded smoothly to \(\sim 50\%\) conversion before decomposition occurred. However, from the initial stages of the electrolysis it was possible to identify conclusively at least one prominent band of the \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{4-}\) spectrum.

### 3.5.3 Visible Spectra of \([\text{Os}_2(\mu-X)_2\text{X}_8]^{z-}\) Complexes (\(z=2, 3, 4\))

The visible spectra of the 32, 33 and 34 electron species of \([\text{Os}_2(\mu-X)_2\text{X}_8]^{z-}\) (\(X=\text{Cl, Br}; z=2, 3, 4\)) are dominated by intense halide-to-metal charge-transfer bands, i.e. \(X(\pi)\rightarrow \text{Os}(d_π)\). This assignment is confirmed by several observations. Firstly, the absorption manifold in the spectrum of \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{2-}\) is found \(~6000\) cm\(^{-1}\) higher in energy than that in \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}\), as required by optical electronegativities for a halide-to-metal charge-transfer transition (Figure 3.5). A number of similar correlations can be made between the \([\text{Os}_2(\mu-X)_2\text{X}_8]^{3-}\) and \([\text{Os}_2(\mu-X)_2\text{X}_8]^{4-}\) spectra, all yielding shifts of \(~6000\) cm\(^{-1}\) between \(X=\text{Cl}\) and \(\text{Br}\) (Table 3.3).

Upon two-electron reduction of the \(\text{Os}_2^{IV,IV}\) to the \(\text{Os}_2^{III,III}\) species (\(d^4/d^4\rightarrow d^5/d^5\)), the absorption manifold moves to higher energy, by \(~8000\) cm\(^{-1}\) overall (Figure 3.6). This is again consistent with the halide-to-metal charge-transfer assignment of these bands, since the optical electronegativity of the metal centre or, in this case, of the \((\text{Os}(\mu-X)_2\text{Os})^{2+}\) core, must decrease upon reduction, from \(\text{Os}^{IV}\) to \(\text{Os}^{III}\). At any particular redox level, the band envelopes for \(X=\text{Cl}\) and \(\text{Br}\) are in general, similar. The spectra of the

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# Note that an interesting anomaly was observed between the behaviour of \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{2-}\) in the OTTLE cell and in a bulk electrosynthetic cell. In the latter, in dichloromethane at 213 K, \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{2-}\) could be reduced to the \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{4-}\) state in the bulk cell, where upon warming rearrangement occurred to yield the \([\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{3-}\) species (see Chapter 4). Under the same conditions in the OTTLE cell, a one-electron reduction of \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{2-}\) did not proceed with isosbestic points, and nor could the starting spectrum be regenerated upon reversing the potential.
bromide complexes are more structured than those of the analogous chloride, which is attributed to the larger spin-orbit coupling constant of bromide. The effect of the spin-orbit coupling constant can also be observed in the spectra of the [OsX₆]²⁻/³⁻ complexes (X=Cl, Br), where X=Br consistently gives more complicated band structure (Figures 3.7 and 3.8).

Figure 3.5 U.v./visible spectra of \([\text{Os}_2(\mu-X)_2X_8]\)²⁻ complexes. (a) X=Br, and (b) X=Cl. The sharp bands above 35 000 cm⁻¹ in spectrum (b) are due to \(\pi-\pi^*\) transitions associated with the Ph₄P⁺ cation.
Figure 3.6 U.v./visible spectra of $\text{Os}_2(\mu-\text{Br})_2\text{Br}_8^{2+}$ complexes, (a) $z=2$, (b) $z=3$, (c) $z=4$, recorded in 0.5 mol. dm$^{-3}$ $n\text{Bu}_4\text{NPF}_6$ /CH$_2$Cl$_2$ at 213 K, in an OTTLE cell.
Other comparisons between the spectra of the $[\text{Os}_2(\mu-X)X_8]^2-$ and $[\text{Os}X_6]^2-$ complexes can also be made, since the visible region of spectra of the latter are also dominated by $X(\pi)\rightarrow\text{Os}(d_\pi)$ charge-transfer. The complexities of the $[\text{Os}X_6]^2-$ spectra arise from charge-transfer from the array of halide donor orbitals. A similar such array of donor orbitals for the $[\text{Os}_2(\mu-X)X_8]^2-$ complexes would give a multitude of $X(\pi)\rightarrow\text{Os}(d_\pi)$ transitions.

The intense $X(\pi)\rightarrow\text{Os}^{1\text{V}}(d_\pi)$ charge-transfer bands are consistently lower in energy in the $[\text{Os}_2(\mu-X)X_8]^2-$ complexes. For example, in $[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^2-$, the manifold is centred at $\sim 20,000$ cm$^{-1}$ (Figure 3.5) as compared with $\sim 22,000$ cm$^{-1}$ in $[\text{OsBr}_6]^2-$ (Figure 3.7). This difference can be explained by comparing the voltammetry of the two complexes (Section 3.4). As a consequence of $[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^2-$ being more easily reduced, the halide-to-metal charge
transfer (which can be viewed as an internal reduction) is found at lower energy. Comparison of the \([\text{OsCl}_6]^{2-}\) and \([\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{2-}\) spectra, and \([\text{OsX}_6]^{3-}/[\text{Os}_2(\mu-\text{X})_2\text{X}_8]^{4-}\), reveals a similar shift in the charge-transfer manifold, for the same reason.

Figure 3.8  U.v./visible spectra of \([\text{OsX}_6]^{1-}\) complexes. (a) \(X=\text{Br}\), and (b) \(X=\text{Cl}\).

As noted above in the \([\text{Os}_2(\mu-X)_2\text{X}_8]^{2-}\) spectra, the charge-transfer manifold is blue shifted by \(-8\ 000\ \text{cm}^{-1}\) upon two electron reduction of the 32 to the 34 electron species. The shift in the \([\text{OsX}_6]^{2-}/3^{-}\) spectra were essentially the same, being \(-8\ 300\ \text{cm}^{-1}\) for \(X=\text{Cl}\), and \(8\ 200\ \text{cm}^{-1}\) for \(X=\text{Br}\) (Figure 3.6). In terms of the absorption profile (i.e. band shape), the spectra of \([\text{Os}_2(\mu-X)_2\text{X}_8]^{2-}\) and \([\text{OsX}_6]^{2-}\), shown in Figures 3.5 and 3.7, reveal few similarities. On occasions in the past the u.v./visible spectra of weakly interacting binuclear complexes have resembled those of related monomers.\(^{13}\)
Table 3.3  U.v./visible spectral data for $[\text{Os}_2(\mu-X)_2X_a]^{2-}$ complexes, 
($X=$Cl, Br, $z=2, 3, 4$).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Band Maxima, cm$^{-1}$ ($\varepsilon$, M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Os}<em>2\text{Br}</em>{10}]^{2-}$</td>
<td>10 980 (90), 13 150 (350), 19 940 (6 000), 21 600 (3 600), 23 320 (3 040), 25 130 (3 430), 26 450 (3 140), 34 150 (4 560)</td>
</tr>
<tr>
<td>$[\text{Os}<em>2\text{Br}</em>{10}]^{3-}$</td>
<td>11 980 (70), 17 720 (2 010), 19 510 (3 010), ∼20 000 sh, 21 630 (3 610), 23 700 (3 680), 25 520 (4 340)</td>
</tr>
<tr>
<td>$[\text{Os}<em>2\text{Br}</em>{10}]^{4-}$</td>
<td>14 040 (670), 16 790 (770), 26 270 (4 410), 27 220 (4 000), 31 000 (3 930)</td>
</tr>
<tr>
<td>$[\text{Os}<em>2\text{Cl}</em>{10}]^{2-}$</td>
<td>22 600 (4 390), 26 230 (16 360), 29 480 (6 680), 32 130 (8 280)</td>
</tr>
<tr>
<td>$[\text{Os}<em>2\text{Cl}</em>{10}]^{3-}$</td>
<td>26 620 (9 080), 29 690 br $c$ (7 080)</td>
</tr>
<tr>
<td>$[\text{Os}<em>2\text{Cl}</em>{10}]^{4-}$</td>
<td>∼34 500 $d$</td>
</tr>
</tbody>
</table>

$a$ Recorded in 0.50 mol. dm$^{-3} \text{nBu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ in an OTTE cell at 213 K.

$b$ Recorded in 0.10 mol. dm$^{-3} \text{nBu}_4\text{NCl}/\text{CH}_2\text{Cl}_2$ in an OTTE cell at 213 K.

$br=broad$. $d$ Electrolysis not complete.

While the general features of the charge-transfer spectra have been accounted for, the discussion thus far has not distinguished between the terminal ($X_t$) and bridging halides ($X_b$). It was noted in Chapter 2, that the bridging halides did not contribute to the spectra of the 34 and 35 electron $[M_2(\mu-X)_3(\text{PR}_3)_6]^{2+/3+}$ complexes (with $X_b(\pi)\rightarrow M(d_\pi)$ charge-transfer bands), on account of the location of the metal based acceptor orbital. The precise location of the acceptor orbital in the present systems is less certain, so that $X_b(\pi)\rightarrow \text{Os}(d_\pi)$ cannot be discounted by a similar argument.

X-ray photoelectron spectra studies suggest that the valence shell electrons on bridging halides are likely to be lower in energy than those of terminal halides$^{14}$ since $X_b$ is stabilized by two metal centres. Charge-transfer from the bridging halide ($X_b(\pi)\rightarrow M(d_\pi)$) is therefore expected at higher energy than that from the terminal halides. The orbital energy difference estimated by Walton et al., (0.5-1.2 eV) corresponds to between 4 000-9 600 cm$^{-1}$. The charge-transfer manifold in the $[\text{Os}_2(\mu-X)_2X_a]^{2-}$ ($X=$Cl, Br) complexes span ∼10 000 cm$^{-1}$, which could encompass both the $X_b(\pi)/X_t(\pi)\rightarrow M(d_\pi)$ charge-transfer. At the 34 electron level, for $X=$Br, the
span is only \( \sim 5000 \) cm\(^{-1}\).

Bruns and Preetz have previously recorded the electronic spectra of the \( (nBu_4N)_2[Os_2(\mu-X)_2X_8] \) \( (X=Cl, Br) \) complexes in polythene films at 10 K.\(^7\) They described the u.v./visible region of the spectra in terms of overlapping \( Br_b(\pi)\rightarrow Os^{IV}(d_\pi) \) and \( Br_t(\pi)\rightarrow Os^{IV}(d_\pi) \) charge-transfer transitions.

Discussion thus far has only dealt with the spectra of the 32 and 34 even electron systems, and not the mixed-valence 33 electron species. The nature of the odd electron \([Os_2(\mu-Br)_2Br_8]^{3-}\) species is of special interest. The visible spectrum of \([Os_2(\mu-Br)_2Br_8]^{3-}\) is shown in Figure 3.6, the charge-transfer manifold spanning the entire region covered by the \( Os^{IV,IV} \) and \( Os^{III,III} \) spectra.

![Figure 3.6](image.png)

**Figure 3.6** Spectral progression upon reduction of \([Os_2(\mu-Br)_2Br_8]^{2-}\) to \([Os_2(\mu-Br)_2Br_8]^{3-}\).
Given that the charge-transfer manifold was observed to move by \(~8000\, \text{cm}^{-1}\) upon reduction of the \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}\) to the \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{4-}\) species, upon-one electron reduction of \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}\) to \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{3-}\), there is very little movement of the manifold. Instead, those bands lowest in energy merely decrease in intensity. This is most readily observed in the spectral progression accompanying the reduction of \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}\) to \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{3-}\) (Figure 3.9).

The pairing of the relative electrode potentials may give an indication as to why the charge-transfer manifold does not shift upon one electron reduction. The position of an \(M^{z}/z^{-1}\) couple in general indicates the ease with which reduction occurs, which can in turn be related to the position of charge-transfer. Correlations between \(E^0\) and optical charge-transfer energies are well established.\(^{15}\) The small separation of the 32/33 and 33/34 electron couples (ca. 0.5 V), compared with the relatively large separation of the 33/34 and 34/35 electron couples (ca. 2.0 V), predicts a discontinuous shift in the charge-transfer manifold, as observed.

While the charge-transfer spectra of the mixed-valence species are very challenging, the most interesting spectral features of such systems are observed below ca. 10 000 \(\text{cm}^{-1}\). What follows is a discussion of the near-infrared region of the \([\text{Os}_2(\mu-X)_2\text{X}_8]^{3-}\), and \([\text{Os}_2(\mu-X)_2\text{X}_8]^{2-}\), \([\text{Os}_2(\mu-X)_2\text{X}_8]^{4-}\) spectra.

### 3.5.4 Near-Infrared Spectra of \([\text{Os}_2(\mu-X)_2\text{X}_8]^{z-}\) Complexes (\(z=2, 3, 4\))

The low energy spectrum of a concentrated dichloromethane solution of \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}\) is presented in Figure 3.10 (a), clearly showing a series of sharp, weak bands. Preetz and Bruns recorded similar spectra in polythene films at 10 K.\(^{7}\) The weak bands at 4 880, 9 660 and 10 980 \(\text{cm}^{-1}\) are in similar positions to single-ion transitions in \([\text{OsBr}_6]^{2-}\).\(^{16}\) In addition to those features, there are two more intense bands, at 5 300 and 13 150 \(\text{cm}^{-1}\) (the former is very sharp in comparison to the latter). These bands were thought to arise from either pair-wise transitions, or double excitations,\(^{17}\) however a conclusive assignment was not made.\(^{7}\)
Figure 3.10 Near-infrared spectra of \( \text{[Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-} \) complexes, (a) \( z=2 \), (b) \( z=3 \), (c) \( z=4 \), recorded in 0.5 mol. dm\(^{-3}\) \( n\text{Bu}_4\text{NPF}_6 /\text{CH}_2\text{Cl}_2 \) at 213 K, in an OTTLE cell. Asterisk marks detector change.
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The spectral progression obtained upon the one-electron reduction of [Os₂(µ-Br)₂Br₈]²⁻ is presented in Figure 3.11. Those bands in the parent [Os₂(µ-Br)₂Br₈]²⁻ spectrum all collapse, giving way to a series of broad, more intense bands. Note that the sharp band at 5 300 cm⁻¹ initially decreased in intensity, before being overtaken by the growing [Os₂(µ-Br)₂Br₈]³⁻ spectrum. Considerable structure is present on the band below −6 000 cm⁻¹ (Figure 3.10 (b)).

![Figure 3.11 Near-infrared spectral changes accompanying reduction of {Os₂(µ-Br)₂Br₈}²⁻ to {Os₂(µ-Br)₂Br₈}³⁻. The step at −11 600 cm⁻¹ (marked with an asterisk) is due to the detector change.](image)

Before discussing this spectrum any further, it is worthwhile to view that of [Os₂(µ-Br)₂Br₈]⁴⁻ (Os²⁺⁺⁺). Exhaustive electrolysis produces the spectrum shown in Figure 3.10 (c). The region of the spectrum below 10 000 cm⁻¹ is devoid of features except for the two bands at 5 630 and 4 780 cm⁻¹ (ε<100 M⁻¹ cm⁻¹). Tetragonally distorted monomeric Os³⁺ complexes typically display two low energy, low intensity bands, due to transitions within the spin-orbit coupled components of the ⁴T₂g ground state. The
bands in \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{4-}\) are similarly assigned as single ion intraconfigurational transitions.

Returning now to the \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{3-}\) species, the structure of the 4 000-6 000 cm\(^{-1}\) region of the spectrum appears to consist of a summation of the single ion features from \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}\) (Os\(_{\text{IV},\text{IV}}\)) and \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{4-}\) (Os\(_{\text{III},\text{III}}\)), suggesting a trapped mixed-valence system. Superimposed on the intraconfigurational type transitions are a series of intervalence charge-transfer bands. All of these bands are very weak, with \(\varepsilon \sim 320 \text{ M}^{-1} \text{ cm}^{-1}\) for the most intense band at 6 660 cm\(^{-1}\).

**Table 3.4 Near-infrared spectral data of \([\text{Os}_2(\mu-X)_{2}\text{X}_8]^{z-}\) complexes, \(X=\text{Br}, z=2, 3, 4\) and \(X=\text{Cl}, z=2, 3\).**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Band Maxima, cm(^{-1}) ((\varepsilon, \text{ M}^{-1} \text{ cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Os}<em>2\text{Br}</em>{10}]^{2-})</td>
<td>4 880 (170), 5 300 (320), 9 660 (120), 10 980 (90), 13 150 (350)</td>
</tr>
<tr>
<td>([\text{Os}<em>2\text{Br}</em>{10}]^{3-})</td>
<td>4 850 (310), 4 990 (320), 5 270 (320), 5 530 (340), 6 660 (330), 7 900 (140), 9 900 (60)</td>
</tr>
<tr>
<td>([\text{Os}<em>2\text{Br}</em>{10}]^{4-})</td>
<td>4 780 (80), 5 630 (50), 14 040 (220), 16 790 (310)</td>
</tr>
<tr>
<td>([\text{Os}<em>2\text{Cl}</em>{10}]^{2-})</td>
<td>5 000, 5 400, 9 950, 14 630 (210), 15 590 (310), 16 880 (230)</td>
</tr>
<tr>
<td>([\text{Os}<em>2\text{Cl}</em>{10}]^{3-})</td>
<td>~5 000, ~6 000, 7 100, 8 750, 10 100</td>
</tr>
</tbody>
</table>

\(a\) Recorded in 0.50 mol dm\(^{-3}\) \(n\text{Bu}_4\text{NPF}_6\)/\(\text{CH}_2\text{Cl}_2\) in an OTTLE cell at 213 K. Recorded in 0.10 mol dm\(^{-3}\) \(n\text{Bu}_4\text{NPF}_6\)/\(\text{CH}_2\text{Cl}_2\) in an OTTLE cell at 213 K. \(c\) Extinction coefficients for maxima below 11 600 cm\(^{-1}\) could not be calculated, due to instrumental problems when this data was collected.

The bandwidth of a mixed-valence transition can give an indication as to whether the system is localized or delocalized.\(^{18}\) Taking for example the band at 6 660 cm\(^{-1}\) (Figure 3.10 (b)), a bandwidth at half intensity (\(\Delta v_{1/2}\)) of 3 900 cm\(^{-1}\) is predicted. While it is difficult to accurately calculate \(\Delta v_{1/2}\) for any of the bands in Figure 3.10 (b), they are all relatively narrow (\(\Delta v_{1/2} \sim 1 500 \text{ cm}^{-1}\)). The band maxima are also insensitive to changes in the dielectric constant of the solvent; the \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{3-}\) species was electrogenerated in both dichloromethane and acetonitrile, however no detectable shifts in band
maxima were observed. Based on the criteria set out by Hush,\textsuperscript{18} this system should be classed as delocalized. While the Hush model has successfully described the mixed-valence spectra of a number of linear, single-bridged bimetallic species,\textsuperscript{19} it may be inappropriate for halide-bridged complexes such as [Os\textsubscript{2}(µ-X)\textsubscript{2}X\textsubscript{8}]\textsuperscript{2-}, where the two metal centres are physically much closer. Treating the 33 electron species as a trapped mixed-valence system assigns oxidation states of 3+ and 4+ to the metal centres in [Os\textsubscript{2}(µ-X)\textsubscript{2}X\textsubscript{8}]\textsuperscript{3-}. The observed spectra (X=Cl, Br) are not merely a superposition of the Os\textsuperscript{IV,IV} and Os\textsuperscript{III,III} spectra, nor can the spectra be similarly constructed from monomeric [OsX\textsubscript{6}]\textsuperscript{2-} and [OsX\textsubscript{6}]\textsuperscript{3-} spectra, in the crucial near-i.r. region.

In summary, the u.v./visible spectra of the [Os\textsubscript{2}(µ-Br)\textsubscript{2}Br\textsubscript{8}]\textsuperscript{2-} complexes can be explained by a series of charge-transfer transitions from the halide(\pi) orbital array to the vacancies in the metal t\textsubscript{2g} set. More specific assignments are unwarranted, until further studies have been carried out on some structurally and symmetry related monomeric and dimeric compounds. For example, the u.v./visible spectra of cis-[OsX\textsubscript{4}L\textsubscript{2}]\textsuperscript{0/1-} compounds (where L=NH\textsubscript{3} or similar) would be of interest, as this monomeric fragment models the local symmetry of one of the osmium centres in [Os\textsubscript{2}(µ-X)\textsubscript{2}X\textsubscript{8}]\textsuperscript{2-} (and the ammine ligand will contribute little to the spectrum). The weak, highly structured bands found in the near-infrared region of the [Os\textsubscript{2}(µ-Br)\textsubscript{2}Br\textsubscript{8}]\textsuperscript{3-} spectra are specific to the mixed-valence configuration. One plausible interpretation of the 4 000-6 000 cm\textsuperscript{-1} region of the spectrum involves a summation of single ion transitions from Os\textsuperscript{III} and Os\textsuperscript{IV} centres, together with intervalence features, implying a weakly interacting mixed-valence system in accord with the relatively high overall oxidation state and likely metal-metal separation (c.f. Table 3.1). In this case, further analysis is required to explain why the intervalence bands are somewhat narrower (1500 c.f. 4000 cm\textsuperscript{-1}) than predicted by the classical strictly localized model.
3.6 MAGNETISM OF [Os$_2$X$_{10}$]$^{2-}$ COMPLEXES

The magnetic susceptibility of (nBu$_4$N)$_2$[Os$_2$(µ-Cl)$_2$Cl$_8$] has been recorded previously over the 336-94 K temperature range, the magnetic moment quoted as 1.36 B.M. per osmium at 296 K. In the case of the analogous bromide complex, only a room temperature moment was reported, this being 0.26 B.M. per osmium. Given the uncertainty associated with the published values of $\chi_m$ and $\mu_{\text{eff}}$ for (nBu$_4$N)$_2$[Os$_2$(µ-Cl)$_2$Cl$_8$], and the very low moment quoted for (nBu$_4$N)$_2$[Os$_2$(µ-Br)$_2$Br$_8$], it was of interest to re-examine the magnetic properties of freshly prepared samples of these compounds.

Before discussing these results, it is appropriate to consider some of the complexities associated with the magnetism of the monomeric osmium complexes, in particular low spin $d^4$ hexahalo-osmate systems. It has been known for some time that the hexahalo-osmates show depressed moments. For the low-spin $d^4$ configuration of Os$^{IV}$ in an octahedral field, the spin only moment would be 2.83 B.M. Typical moments however are in the range of 1.5-1.7 B.M.

The large spin-orbit coupling for Os$^{IV}$ ($\lambda \approx 4000$ cm$^{-1}$) causes splittings of the $^3T_{1g}$ ground term, much larger in magnitude than the size of $kT$ (~200 cm$^{-1}$ at room temperature), and so at available temperatures only the lowest non-degenerate level ($J=0$) is populated. The susceptibility is therefore due entirely to the second order Zeeman effect, in which some contribution from a higher level ($J=1$) is mixed into the ground state. The magnetic susceptibility is then expected to be independent of temperature (T.I.P.). The magnetic moments however decrease markedly with decreasing temperature, as predicted, since the large spin-orbit coupling constant of Os$^{IV}$ means it is found on the left of the curve in Figure 3.12, where $kT/|\lambda|$ is very small. At (impossibly) high temperatures the theoretical magnetic moment ($(L(L+1)+4S(S+1))^{1/2}$) rises as high as 3.5 B.M., before settling to the high temperature limit of ~3.2 B.M.

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*It should be noted that this figure of 1.36 B.M. (per Os) does not correspond to the quoted susceptibility, of $\chi_m=2970 \times 10^{-6}$ c.g.s.u. Based on $\chi_m=2970 \times 10^{-6}$, $\mu_{\text{eff}}=1.87$ B.M. per Os. Alternatively, accepting $\mu_{\text{eff}}$/per Os)=1.36 B.M., implies $\chi_m=780 \times 10^{-6}$ c.g.s.u.*
The magnetic moments of alkali metal salts of $[\text{OsX}_6]^{2-}$ have also been observed to increase upon dilution into diamagnetic isostructural $[\text{PtX}_6]^{2-}$ lattices. This suggested an intermolecular antiferromagnetic exchange mechanism was functioning, and that the various alkali metal salts of $[\text{OsX}_6]^{2-}$ could not be assumed to be magnetically dilute, such that strong spin-orbit coupling may not be the only source of suppressed moments.

![Graph](image)

**Figure 3.12** The variation of $\mu_{\text{eff}}$ with temperature, as a function of $kT/|1/\lambda|$, for the $d^4$, $\text{Os}^{IV}$ ion ($3T_{1g}$ ground state) with negative $\lambda$. The point marked on the curve corresponds to the free-ion value of spin-orbit coupling at room temperature.

The susceptibilities of pure powdered samples of ($\text{Ph}_4\text{P})_2[\text{OsX}_6]$ compounds (X=Cl, Br) prepared in our laboratory were measured over a 300-4.2 K temperature range, in a field of 3 000 gauss. The observed magnetization values for these large molecular weight/weakly paramagnetic complexes were rather similar to those of the empty gelatin capsule sample holders. Despite this limitation, the susceptibility per osmium ($\chi_{\text{Os}}$) for both compounds (X=Cl, Br) remained essentially constant at ~1100 c.g.s. units between 300-50 K, with a slight increase at the low temperature end of this range (Figure 3.13). Below 50 K each shows a rapid
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Figure 3.13 Variation of (a) susceptibility and (b) magnetic moment with absolute temperature for \((\text{Ph}_4\text{P})_2\text{OsBr}_6\).
increase in $\chi_{Os}$, due most likely to small traces of higher spin impurities rather than any magnetic phase change of a cooperative kind. The present values are very similar to those observed previously for $R_4N^+$ and Cs$^+$ salts of $[OsX_6]^{2-}$ ($X=Cl$, Br) (see Table 3.5), and the temperature dependence of $\chi_{Os}$ in the previously studied 300-80 K range is also similar.\textsuperscript{23}

The x-ray crystal structure of $(Ph_4P)_2[OsCl_6]$ has been reported,\textsuperscript{25} and does not reveal any relatively short Os-Cl...Cl-Os contacts (the closest being 6.77 Å). This is in contrast to the Ph$_3PH^+$ salt of $[OsCl_6]^{2-}$, where Cl...Cl distances of 3.2-3.3 Å can be found.\textsuperscript{26}

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\mu_{eff}$ per molecule</th>
<th>$\mu_{eff}$ per Os</th>
<th>$10^6\chi_m$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(nBu_4N)<em>2[Os_2Cl</em>{10}]$</td>
<td>1.92</td>
<td>1.36</td>
<td>2970</td>
<td>2</td>
</tr>
<tr>
<td>$(Ph_4P)<em>2[Os_2Cl</em>{10}]$</td>
<td>2.09</td>
<td>1.48</td>
<td>1820</td>
<td>d</td>
</tr>
<tr>
<td>$(Ph_4P)_2[OsCl_6]$</td>
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<td>1.59</td>
<td>1060</td>
<td>d</td>
</tr>
<tr>
<td>$(nBu_4N)_2[OsCl_6]$</td>
<td>e</td>
<td>1.52</td>
<td>984</td>
<td>23</td>
</tr>
<tr>
<td>Cs$_2[OsCl_6]$</td>
<td>e</td>
<td>1.47</td>
<td>909</td>
<td>23</td>
</tr>
<tr>
<td>Cs$_2[OsBr_6]$</td>
<td>e</td>
<td>1.65</td>
<td>1162</td>
<td>22</td>
</tr>
<tr>
<td>(NH$_4$)$_2[OsCl_6]$</td>
<td>e</td>
<td>1.47</td>
<td>907</td>
<td>23</td>
</tr>
<tr>
<td>$(nBu_4N)<em>2[Os_2Br</em>{10}]$</td>
<td>0.37</td>
<td>0.26</td>
<td>27</td>
<td>1</td>
</tr>
<tr>
<td>$(Ph_4P)<em>2[Os_2Br</em>{10}]$</td>
<td>2.15</td>
<td>1.52</td>
<td>1940</td>
<td>d</td>
</tr>
<tr>
<td>$(Ph_4P)_2[OsBr_6]$</td>
<td>e</td>
<td>1.63</td>
<td>1120</td>
<td>d</td>
</tr>
<tr>
<td>Cs$_2[OsBr_6]$</td>
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<td>1.56</td>
<td>982</td>
<td>23</td>
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<tr>
<td>Cs$_2[OsBr_6]$</td>
<td>e</td>
<td>1.74</td>
<td>1285</td>
<td>22</td>
</tr>
<tr>
<td>(NH$_4$)$_2[OsBr_6]$</td>
<td>e</td>
<td>1.52</td>
<td>982</td>
<td>23</td>
</tr>
<tr>
<td>(Me$_4N$)$_2[OsBr_6]$</td>
<td>e</td>
<td>1.59</td>
<td>1068</td>
<td>23</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Bohr magnetons. \textsuperscript{b} Molecular susceptibility, c.g.s.u. \textsuperscript{c} These figures are not consistent, see text. \textsuperscript{d} This work. \textsuperscript{e} For monomeric complexes, $\mu_{eff}$ per molecule=$\mu_{eff}$ per Os.
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The susceptibility data, at least in the 300-50 K range, is broadly in agreement with the intermediate spin-orbit coupling model described by others.\textsuperscript{22-24} There does not appear to be any significant influence upon changing the large organic cations (\textsuperscript{n}Bu\textsubscript{4}N\textsuperscript{+}, Ph\textsubscript{4}P\textsuperscript{+}) or the halide. These observations alone, together with the large intermolecular Cl...Cl distances, imply a lack of significant spin-spin lattice interactions, despite the evidence for magnetic dilution effects mentioned above in the K\textsubscript{2}[(Os, Pt)Cl\textsubscript{6}] and (NH\textsubscript{4})\textsubscript{2}[(Os, Pt)Br\textsubscript{6}] systems. It would be interesting to compare the magnetism of (Ph\textsubscript{3}PH)\textsubscript{2}[OsCl\textsubscript{6}] with that of (Ph\textsubscript{4}P)\textsubscript{2}[OsCl\textsubscript{6}], in which the intermolecular Cl...Cl distances are distinctly different.

Turning now to the decahalodiosmate complexes, the crystal structures of (\textsuperscript{n}Bu\textsubscript{4}N)\textsubscript{2}[Os\textsubscript{2}(\mu-X)\textsubscript{2}X\textsubscript{8}] (X=Cl, Br) have both been reported.\textsuperscript{1,2} In the case of the chloride, the closest Os-Cl...Cl-Os distance is 5.94 Å, while for the bromide, there are none less than 7.0 Å. Given that the sum of the ionic radii are 3.62 and 3.92 Å for chloride and bromide respectively, it is reasonable to expect both (\textsuperscript{n}Bu\textsubscript{4}N)\textsubscript{2}[Os\textsubscript{2}(\mu-X)\textsubscript{2}X\textsubscript{8}] complexes are magnetically dilute. The magnetic data discussed here was however collected on Ph\textsubscript{4}P\textsuperscript{+} salts of [Os\textsubscript{2}(\mu-X)\textsubscript{2}X\textsubscript{8}]\textsuperscript{2-}, for which specific crystal structure data are lacking.

It is reasonable to expect the (Ph\textsubscript{4}P)\textsubscript{2}[Os\textsubscript{2}(\mu-X)\textsubscript{2}X\textsubscript{8}] compounds are magnetically dilute as well, as with the [OsX\textsubscript{8}]\textsuperscript{2-} salts, although clearly direct crystal packing information would be desirable.

Comparing the data presented here for the [Os\textsubscript{2}(\mu-X)\textsubscript{2}X\textsubscript{8}]\textsuperscript{2-} complexes with what has been previously published (Table 3.5), major differences are noted, especially in the case of the bromide. The small \(\mu_{\text{Os}}\) value of 0.26 B.M. reported for (\textsuperscript{n}Bu\textsubscript{4}N)\textsubscript{2}[Os\textsubscript{2}(\mu-Br)\textsubscript{2}Br\textsubscript{8}] is most probably in error. Despite the calculation errors by Krebs and the different temperature dependence quoted, taking \(\mu_{\text{Os}}\) as reported, it is possible the difference between the two salts of [Os\textsubscript{2}(\mu-Cl)\textsubscript{2}Cl\textsubscript{8}]\textsuperscript{2-} arises because of the different cation, since cation effects have been previously noted in \(d^3/d^3\ A_3\text{Mo}_2X_9\) systems. As the size of \(A^+\) increases, so does the internuclear (M-M) separation,\textsuperscript{27} and correspondingly a decrease in antiferromagnetic coupling occurs.\textsuperscript{28}

The variation of magnetic susceptibility with temperature of the (Ph\textsubscript{4}P)\textsubscript{2}[Os\textsubscript{2}(\mu-X)\textsubscript{2}X\textsubscript{8}] complexes (X=Cl, Br) was also explored, over the 300-4.2 K temperature range, in a field of 10 000 gauss. Part (a) of Figures 3.14
Figure 3.14 Variation of (a) susceptibility and (b) magnetic moment with absolute temperature for \((\text{Ph}_4\text{P})_2\text{Os}_2(\mu-\text{Br})_2\text{Br}_6\).
Figure 3.15 Variation of (a) susceptibility and (b) magnetic moment with absolute temperature for (Ph₄P)₂Os₂(μ-Cl)₂Cl₈.
and 3.15 plot susceptibility versus temperature for the \((\text{Ph}_4\text{P})_2[\text{Os}_2(\mu-X)X_8]\) compounds. The gradual increase in \(\chi_{\text{mol}}\) between 300 and 50 K is *not* characteristic of an exchange coupled system. Such systems, at least in first row ions, typically display broad maxima, before decreasing towards zero at low temperatures. The observed increase in susceptibility at very low temperatures (<20 K) may be caused by a small amount of monomeric impurity.

**Table 3.6** Room temperature magnetic data for tetravalent osmium complexes prepared in Chapter 3.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\mu_{\text{eff}}) per molecule (^a)</th>
<th>(\mu_{\text{eff}}) per Os (^a)</th>
<th>(10^6\chi_m) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{Ph}_4\text{P})_2[\text{Os}_2\text{Cl}_10])</td>
<td>2.09</td>
<td>1.48</td>
<td>1820</td>
</tr>
<tr>
<td>((\text{Ph}_4\text{P})_2[\text{Os}_2\text{Br}_10])</td>
<td>2.15</td>
<td>1.52</td>
<td>1940</td>
</tr>
<tr>
<td>((\text{Ph}_4\text{P})_2[\text{OsCl}_6])</td>
<td>(c)</td>
<td>1.59</td>
<td>1060</td>
</tr>
<tr>
<td>((\text{Ph}_4\text{P})_2[\text{OsBr}_6])</td>
<td>(c)</td>
<td>1.63</td>
<td>1120</td>
</tr>
</tbody>
</table>

\(^a\) Bohr magnetons. \(^b\) Molecular susceptibility, c.g.s.u. \(^c\) For monomeric complexes, \(\mu_{\text{eff}}\) per molecule=\(\mu_{\text{eff}}\) per Os.

The room temperature magnetic moments of the chloride and bromide \((\text{Ph}_4\text{P})_2[\text{Os}_2(\mu-X)X_8]\) complexes are similar (per Os) to the moments of the monomeric \((\text{Ph}_4\text{P})_2[\text{OsX}_6]\) complexes, and the wide-range temperature dependence of \(\chi_{\text{Os}}\) and \(\mu_{\text{Os}}\) also, suggesting the Os\(^{IV}\) metal centres are only weakly antiferromagnetically coupled.

The variation of the magnetic moment (per molecule) with temperature is shown in part (b) of Figures 3.14 and 3.15. The chloride and bromide complexes behave in a similar manner, the moment decreasing steadily from the room temperature values with the lowering of the temperature. At temperatures less than ~50 K, the moment approaches zero a little more rapidly, as expected since \(\mu_{\text{Os}}\) is proportional to \(T^{1/2}\), *i.e.* a parabolic relationship. The considerable temperature dependence of the magnetic moment is also characteristic of monomeric low spin Os\(^{IV}\) complexes. Indeed the most notable feature of the temperature dependence
of $\chi_{Os}$ and $\mu_{Os}$ for the $[Os_2(\mu-X)X_8]^{2-}$ complexes is how similar they are to those for the $[OsX_6]^{2-}$ species. Simplistically, this would suggest either:

(i) no spin-spin interactions occur in either class.
(ii) that the degree of coupling, be it intra or intermolecular, is similar.
(iii) the electronic coupling (whether it be weak or strong) is not expressed in the paramagnetic behaviour of these complexes due to the large spin-orbit coupling constant of Os$^{IV}$, which isolates the non-magnetic ground state from the higher $J$ levels.

The halide bridge is an efficient promoter of superexchange, such that zero exchange-coupling seems unlikely. Available structural data gives no indication that intermolecular interactions are operative. Magnetic dilution could however be confirmed by an Evans' method solution magnetic moment, or alternatively through doping $(Ph_4P)_2[Os_2(\mu-X)X_8]$ into an isostructural diamagnetic lattice. The only other anionic double-bridged decahalide complex known is $(PCl_4)_2[Ti_2(\mu-Cl)Cl_8]$. If the $Ph_4P^+$ salt of this complex could be prepared, then dilution studies may be possible.

It should also be noted that the face-sharing $Ph_4P[Os_2(\mu-Br)Br_6]$ complex, with its anticipated smaller Os...Os distance, likewise shows very similar magnetism, both in size and temperature dependence of $\chi_{Os}$ (see Chapter 4). The similarity in magnetic properties of the three structurally very different complexes, $[OsBr_6]^{2-}$, $[Os_2(\mu-Br)Br_8]^{2-}$ and $[Os_2(\mu-Br)Br_6]^{1-}$, suggests that the last point noted above may explain the relative insensitivity of the magnetic moment to varying structure and halide. Close examination of the optical spectrum could give essential information with respect to critical parameters such as the spacing of the Zeeman levels and the effective distortion from $O_h$ symmetry in the dimers. At a fundamental level, rigorous magnetic measurements are less sensitive in the context of $d^4/d^4$ systems, in contrast to $[Os_2(\mu-Br)Br_6]^{3-}$ ($d^5/d^5$), which will be discussed later.

As indicated above, much of our understanding on exchange-coupled models is based on the behaviour of 1st row $d$ block transition metal ions, in which orbital degeneracy or very large spin-orbit coupling (of the present type) can be safely ignored. Second order Zeeman effects (T.I.P.), small in 1st
row ions, are simply added on to the $\chi_{\text{dimer}}$ expression at each temperature. This may not be a viable procedure in 3rd row systems, in which $\chi_{\text{TIP}}$ is the dominant or only contribution to magnetization. Discussion is also limited by the lack of similar examples within the literature. As noted by Carlin, paramagnetic $4d$ and $5d$ transition metals are in general not well studied, especially in the case of polynuclear species. What data are available are generally only recorded down to liquid nitrogen temperatures.

Ammonium salts of the hexafluorosilicate (XeF$_6$), $\text{Ph}_4\text{P}$, and $\text{Ph}_3\text{P}$ were purchased from Strem Chemicals Incorporated, as was terphenylpyrophosphonium bromide. Tolyphenylpyrophosphonium chloride, terphenylpyrophosphonium bromide and the analogous dibromide and trifluoroacetate acid were purchased from the Aldrich Chemical Company. All of the above reagents were used as supplied except for trifluoroacetic acid, which was distilled from P$_2$O$_5$ prior to use, and stored under dry nitrogen away from the light.

The ammonium salts of the hexafluorosilicate were prepared simply by dissolving ammonium salts in the appropriate dilute hydrochloric acid and sometimes filtering is necessary to remove traces of insoluble material, and adding the organic compound. The organic salt of $\text{XeF}_6\text{Py}_2$ precipitated immediately. After filtering off, the crude material was thoroughly washed with distilled water, diethyl ether and then dried. Depending upon the organic salt, the crude product on occasions did not require recrystallization. Yields were quantitative.

### 3.7.3 Synthesis of Decahalogenosilicate Complexes

(i) Bistrifluoroacetylphenylphosphonium di-$\text{Xe}$-chloro-decafluorosilicate ($\text{XeF}_6\text{Py}_2$).

(Ph$_2$P)$_2$(XeCl$_4$) (1.87g, 0.99 mmol) was dissolved in 15.0 ml. of neat trifluoroacetic acid, and the resulting solution warmed (oil bath temperature 323 K) with stirring under $\text{N}_2$. After heating for 3 days, a considerable quantity of fine green precipitate had formed. The mixture was cooled, the precipitate filtered off, and extensively washed with a-lactone and diethyl ether. The product was then dried in vacuo at 373 K (80% yield).
3.7 EXPERIMENTAL

3.7.1 General Remarks

The spectroscopic instrumentation, electrochemical, spectroelectrochemical and magnetic apparatus has been described in Chapters 1 and 2.

3.7.2 Materials and Methods

Ammonium salts of the hexahaloosmates (X=Cl, Br) were purchased from Strem Chemicals Incorporated, as was tetraphenylphosphonium bromide. Tetraphenylphosphonium chloride, tetra-n-butylammonium bromide and the analogous chloride, and trifluoroacetic acid were purchased from the Aldrich Chemical Company. All of the above reagents were used as supplied except for trifluoroacetic acid, which was distilled from P$_2$O$_5$ prior to use, and stored under N$_2$ away from the light.

The organosoluble salts of the hexahaloosmates were prepared simply by dissolving ammonium salts in the appropriate dilute hydrohalic acid (sometimes filtering is necessary to remove traces of insoluble material), and adding the organic cation. The organic salt of [OsX$_6$]$^{2-}$ precipitated immediately. After filtering off, the crude material was thoroughly washed with distilled water, diethyl ether and then dried. Depending upon the organic cation, the crude product on occasions did not require recrystallization. Yields were quantitative.

3.7.3 Synthesis of Decahalodiosmate Complexes

(i) Bis(tetraphenylphosphonium) di-$\mu$-chloro-octachlorodiosmate(IV/IV).

(Ph$_4$P)$_2$[OsCl$_6$] (1.07g, 0.99 mmol.) was dissolved in 15.0 ml. of neat trifluoroacetic acid, and the resulting solution warmed (oil bath temperature 323 K) with stirring under N$_2$. After heating for 5 days, a considerable quantity of fine green precipitate had formed. The mixture was cooled, the precipitate filtered off, and extensively washed with n-hexane and diethyl ether. The product was then dried in vacuo at 373 K (0.67 g, 96 %).
(ii) Bis(tetraphenylphosphonium) di-µ-bromo-octabromodiosmate(IV/IV).

(Ph₄P)₂[Os₂Br₁₀] was prepared by the procedure described above. Warming 0.72 g of (Ph₄P)₂[OsBr₆] in 5.0 ml. of neat trifluoroacetic acid for 26 hours produced 0.48 g (96 %) of (Ph₄P)₂[Os₂(µ-Br)₂Br₈].

Microanalysis: Calc.(%) for C₄₈H₄₀Cl₁₀Os₂P₂; C 40.78, H 2.85, P 4.38

Found(%); C 41.03, H 2.73, P 4.29

Far Infra-red Spectrum: (polythene disc, prepared in n-hexane) 330 cm⁻¹ (s), 300 (s), 262 (s), 171 (w), 156 (w).

(iii) Bis(tetra-n-butylammonium) di-µ-bromo-octabromodiosmate(IV/IV).

The tetra-n-butylammonium salt of [Os₂(µ-Br)₂Br₈]²⁻ was prepared in essentially the same way as (Ph₄P)₂[Os₂Br₁₀]. 0.28 g of (nBu₄N)₂[OsBr₆] in 3.0 ml. of neat trifluoroacetic acid gave 0.14 g (70 %) of (nBu₄N)₂[Os₂(µ-Br)₂Br₈]. after 8 hours warming.

Microanalysis: Calc.(%) for C₃₂H₇₂Br₁₀N₂Os₂; C 23.09, H 4.36, N 1.68, Br 48.01

Found(%); C 19.76, H 4.17, N 1.46, Br 47.94

(note: the carbon figure was found to be repeatedly low.)

Far Infra-red Spectrum: (polythene disc) 235 cm⁻¹ (s), 222 (s), 198 (m).
3.8 REFERENCES


4.3. INTRODUCTION

The octahedral bicalcium structure (Figure 4.1) is commonly found among anionic complexes of the transition metals and some main group metal ions. These elements report to some triple-bridged, non-stoichiometric $\left[\text{M}_{\text{III-X}}\text{X}_3\right]^+$ complexes in the periodic table shown in Figure 4.2. The metal atoms in such complexes are found in oxidation states ranging from 2+ to 6+. Chloride and iodide complexes are most common, while several iodine and bromide have been prepared. One example of a heterobimetallic Cr/Mo complex is also known (see Figure 4.2).
Chapter 4

DISCOVERY OF NONAHALODIOSMATE COMPLEXES: SYNTHESIS, VOLTAMMETRY AND SPECTROELECTROCHEMISTRY, 
\([\text{Os}_2(\mu-X)_3X_6]^{z-}\)

4.1 INTRODUCTION

The confacial bioctahedral structure (Figure 4.1) is commonly found among anionic complexes of the transition metals and some main group metal ions. Those elements reported to form triple-bridged, face-sharing \([M_2(\mu-X)_3X_6]^{z-}\) nonahalide complexes are shaded in the periodic table shown in Figure 4.2. The metal atoms in such complexes are found in oxidation states ranging from 2+ to 4+. Chloride and bromide complexes are most common, while several iodides and fluorides have been prepared. One example of a heterobinuclear Cr/Mo complex is also known (see Figure 4.2).
Diruthenium nonahalide complexes, \([\text{Ru}_2(\mu-X)_3X_6]^{3-}\) (X=Cl, Br), are well documented. Fergusson and Greenaway found heating potassium, rubidium or cesium salts of \([\text{RuCl}_5(\text{H}_2\text{O})]^{2-}\) at 473 K under vacuum initially gave green powders, which turned brown with longer reaction times.\(^1\)

![Figure 4.1](image)

**Figure 4.1** The triple-bridged, face-sharing structure.

Figure 4.2 The shaded elements are those for which \([M_2(\mu-X)_3X_6]^{2-}\) complexes have been reported. The Lanthanide and Actinide series have been omitted, since there are no known examples of \([M_2(\mu-X)_3X_6]^{2-}\) complexes for these elements.

\[
\begin{align*}
\text{Sc}_2\text{Cl}_9 & \quad 3^-;2 \\
\text{Ti}_2\text{Cl}_9 & \quad 1^-;3 \quad [\text{Ti}_2\text{Cl}_9]^{3-};4 \\
[V_2\text{X}_9]^{3-}, & \quad X=\text{F},5 \quad \text{Cl},6 \quad \text{Br},6 \\
[\text{Cr}_2\text{X}_9]^{3-}, & \quad X=\text{F},7 \quad \text{Cl},6,8 \quad \text{Br},6,8 \\
[\text{Mn}_2\text{Cl}_9]^{5-}, & \quad 9 \\
[\text{Fe}_2\text{Cl}_9]^{3-}, & \quad 10 \\
[Nb_2\text{X}_9]^{3-}, & \quad X=\text{Cl}, \text{Br}, I,11 \\
[\text{Mo}_2\text{X}_9]^{3-}, & \quad X=\text{Cl}, \text{Br}, I,8 \quad [\text{Mo}_2\text{Cl}_9]^{2-};12 \\
[\text{Ru}_2\text{X}_9]^{3-}, & \quad X=\text{Cl},13 \quad \text{Br},14 \\
[\text{Ir}_2\text{X}_9]^{3-}, & \quad X=\text{Cl}, \text{Br}^{15} \\
[\text{Sb}_2\text{Br}_9]^{3-};16 \\
[\text{Ta}_2\text{Cl}_9]^{3-};17 \\
[W_2\text{Cl}_9]^{3-};8,18 \quad [W_2\text{X}_9]^{2-},X=\text{Cl},19 \quad \text{Br},20 \\
[\text{Re}_2\text{X}_9]^{1-},X=\text{Cl},8 \quad \text{Br},21 \\
[\text{Rh}_2\text{X}_9]^{3-},X=\text{Cl},8 \\
[\text{Rh}_2\text{Cl}_9\text{Br}_n]^{3-}, & \quad 22 \\
[\text{Tl}_2\text{Cl}_9]^{3-};8 \\
[\text{Bi}_2\text{I}_9]^{3-};8 \\
[\text{Cl}_3\text{MoCl}_3\text{CrCl}_3]^{3-};23
\end{align*}
\]
On the basis of x-ray powder photographs, magnetic and far-infrared data, they formulated the green and brown powders as salts of [Ru$_2$(μ-Cl)$_3$Cl$_6$]$^{3-}$ and [RuCl$_6$]$^{3-}$ respectively.

Then in 1981 Darriet prepared and structurally characterized crystals of Cs$_3$[Ru$_2$(μ-Cl)$_3$Cl$_6$], confirming the triple-bridged, face-sharing geometry of the complex. A solid-state method had again been used to prepare this compound, which involved heating a mixture of RuCl$_3$ and CsCl at 1123 K in an evacuated, sealed tube.

On repeating the work of Fergusson and Greenaway, Coombe found that only brown powders were obtained upon heating K$_2$[RuCl$_5$(H$_2$O)] in an evacuated, sealed Carius tube at 533 K. The far-infrared spectrum of this brown material was however consistent with the formation of K$_3$[Ru$_2$(μ-Cl)$_3$Cl$_6$]. It was later found that the reaction, as shown in equation (4.1), proceeded more efficiently if the tube was continually under evacuation while heating was in progress. Fergusson's attribution of a green colour to salts of [Ru$_2$(μ-Cl)$_3$Cl$_6$]$^{3-}$ remains a small anomaly.

$$2 \text{K}_2[\text{RuCl}_5(\text{H}_2\text{O})] \xrightarrow{\Delta} \text{K}_3[\text{Ru}_2(\mu-\text{Cl})_3\text{Cl}_6] + \text{KCl} + 2\text{H}_2\text{O} \quad (4.1)$$

Simple salts of [Ru$_2$(μ-Br)$_3$Br$_6$]$^{3-}$ can be easily synthesized from a number of starting materials, emphasizing its domination of Ru$^{III}$ bromide chemistry. Heating aqueous Br$_2$/HBr solutions of RuCl$_3$.xH$_2$O, [RuCl$_6$]$^{2-}$, [RuCl$_6$]$^{3-}$ or [RuBr$_6$]$^{2-}$ results in formation of the nonabromodiruthenate complex. The addition of KBr to these solutions yields crystalline K$_3$[Ru$_2$(μ-Br)$_3$Br$_6$]. The face-sharing biocathedral structure was confirmed by x-ray powder diffraction studies and far-infrared data. In order to carry out solution studies of [Ru$_2$(μ-X)$_3$X$_6$]$^{3-}$ complexes in non-aqueous solvents, organo-soluble tetra-n-butyl-ammonium salts of the trianion were isolated. A simple metathesis was performed by dissolving K$_3$[Ru$_2$(μ-Br)$_3$Br$_6$] or the K$_3$[Ru$_2$(μ-Cl)$_3$Cl$_6$]/KCl mixture in dilute aqueous acid, and adding the appropriate form of $^n$Bu$_4$NX. The ($^n$Bu$_4$N)$_3$[Ru$_2$(μ-X)$_3$X$_6$] compounds (X=Cl, Br) precipitated immediately from solution, allowing easy isolation. To date, only one organic salt of
[\text{Ru}_2(\mu-\text{X})_3\text{X}_6]^{3-} \text{ has had its structure determined, that being (MeEtim)}_3[\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6]^+_.^{14}

The prolific number of redox levels accessible electrochemically in the \((\text{nBu}_4\text{N})_3[\text{Ru}_2(\mu-\text{X})_3\text{X}_6] \text{ (X=Cl, Br)} \) compounds was first demonstrated by Heath, Stephenson and coworkers.\textsuperscript{26} In dichloromethane at 233 K, these complexes display a quasi-reversible reduction and two reversible oxidations. The electrogenerated products were too unstable to allow isolation, however utilization of a number of \textit{in situ} spectroelectrochemical techniques permitted further characterization of these species.

Magnetic studies on various salts of [\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6]^{3-} \text{ complexes have shown their room temperature magnetic moments are sensitive to the identity of the cation, varying from 0.75 B.M. per Ru for the potassium salt, to 1.01 B.M. per Ru for the cesium salt.}^1 More recently it was noted that magnetic measurements on powder samples of (\text{nBu}_4\text{N})_3[\text{Ru}_2(\mu-\text{X})_3\text{X}_6] \text{ (X=Cl, Br)} \text{ were very similar to those obtained by Evans solution methods.}^2\textsuperscript{27}

Some solution magnetic susceptibility measurements have been performed on electrogenerated solutions of [\text{Ru}_2(\mu-\text{X})_3\text{X}_6]^{2-}.\textsuperscript{26} At 273 K, magnetic moments of 3.76 and 4.40 B.M. per molecule were recorded for the [\text{Ru}_2(\mu-\text{Cl})_3\text{Cl}_6]^{2-} \text{ and } [\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6]^{2-} \text{ species respectively. Such high moments (three unpaired electrons) were suggestive of weakly coupled Ru\textsuperscript{II}I(d^5) \text{ and } \text{Ru}\textsuperscript{IV}(d^4) \text{ centres. The [Ru}_2(\mu-\text{X})_3\text{X}_6]^{1-} \text{ complexes were more difficult to electroganerate in bulk, and decomposed at temperatures above ca. 230 K.}

The changes in the optical spectra accompanying these redox progressions have also been studied.\textsuperscript{24,28} The electronic spectra of the [\text{Ru}_2(\mu-\text{X})_3\text{X}_6]^{1-}/2^{-}/3^{-}/4^{-} (\text{X=Cl, Br}) \text{ species have all been recorded. With the exception of the starting complex, } [\text{Ru}_2(\mu-\text{X})_3\text{X}_6]^{3-}, \text{ these species were all electrosynthesized \textit{in situ} at low temperature in an OTTLE cell. The spectra of mixed-valence } [\text{Ru}_2(\mu-\text{X})_3\text{X}_6]^{2-} \text{ and } [\text{Ru}_2(\mu-\text{X})_3\text{X}_6]^{4+} \text{ complexes (X=Cl, Br) are particularly interesting, showing transitions in the near-infrared region of the spectrum.}^{#}

\textsuperscript{*} \text{MeEtim}=1\text{-methyl-3-ethylimidazolium cation.}

\textsuperscript{#} \text{The spectra of the } [\text{Ru}_2(\mu-\text{X})_3\text{X}_6]^{2-} \text{ complexes (X=Cl, Br) will be discussed more fully where appropriate, in company with to those of the analogous osmium complexes.}
Osmium is an obvious absence from this family of \([M_2(\mu-X)_3X_6]^{2-}\) complexes, instead forming \([\text{Os}_2(\mu-X)_2X_8]^{2-}\) and \([\text{Os}_2X_8]^{2-}\), both unknown for ruthenium. Given the amount of data on the nonahalodiruthenate complexes, it was of great importance to investigate the analogous osmium systems, and provide another comparison of 4d versus 5d binuclear complexes. The obvious question arose of how does the metal-metal interaction vary between Ru and Os, as a function of oxidation state? This also related to the electronic classification of mixed-valence species. Such complexes with π-donor halides at the terminal positions also contrast those isostructural \([\text{Os}_2(\mu-X)_3(\text{PR}_3)_6]^2+\) compounds discussed in Chapter 2.

Compounds of stoichiometry \([\text{Os}_2(\mu-X)_3X_6]^{2-}\) (X=Br, z=0 and 3) have appeared within the literature, albeit only briefly. In 1942 Hieber and Stallmann\(^{33}\) prepared a black/brown material, claimed to be \([\text{Os}_2\text{Br}_9].6\text{H}_2\text{O}\), by the method of Moraht and Wischin.\(^{34}\) The procedure involved boiling “osmic acid” (\(\text{H}_2\text{OsO}_4\)) with excess of HBr, in the presence of alcohol for 2 days, after which the mixture was evaporated to give black/brown crystals, of formula \([\text{Os}_2\text{Br}_9].6\text{H}_2\text{O}\). No structure was proposed. To the author’s knowledge, the only other report of a complex of stoichiometry \([\text{Os}_2X_9]^{2-}\) was that of Emerson and Fergusson.\(^{35}\) They proposed the temporary formation of \(\text{Cs}_3[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\) as an intermediate in the aerial decomposition of \(\text{Cs}_3[\text{OsBr}_4].\text{H}_2\text{O}\) to \(\text{Cs}_2[\text{OsBr}_6],\) as evidenced by x-ray powder diffraction data of the mixtures.

The mechanism by which formation of the face-sharing, triple-bridged structure occurs, is believed to proceed via a double-bridged intermediate. Phosphorus n.m.r. studies have suggested such a species on route to \([M_2(\mu-\text{Cl})_3(\text{PR}_3)_6]^+\) (M=Ru, Os) complexes.\(^{36,37}\) Equilibria are also known to exist between edge and face-sharing Mo and W compounds.\(^{38,39}\) With the above in mind, the double-bridged, edge-sharing \([\text{Os}_2(\mu-X)_2X_8]^{2-}\) complexes provided a logical precursor with which to attempt the syntheses of the triple-bridged, face-sharing \([\text{Os}_2(\mu-X)_3X_6]^{3-}\) species. The tendency of transition metal halide complexes to expel halide upon reduction is well documented.\(^{37,40}\) One plausible route to the triple-bridged structure involved the expulsion of a single halide ion upon (the two electron) reduction of \([\text{Os}_2(\mu-X)_2X_8]^{2-}\), culminating in the sharing of a third halide to
satisfy the octahedral coordination requirements of each osmium centre (Figure 4.3).

Thus the work described in this chapter focuses on the synthesis of organo-soluble forms of the missing nonahalodiosmate complexes, and the investigation of their redox activity and associated spectroelectrochemistry.

Figure 4.3 Proposed mechanism for the formation of the triple-bridged nonahalodiosmate complex.
4.2 SYNTHESIS AND CHARACTERIZATION OF NONABROMODIOSMATE COMPLEXES, \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{1-}\) and \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{3-}\)

4.2.1 Chemical Preparation

Attempts to prepare \((\text{nBu}_4\text{N})_2[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]\), by the method described by Cotton et al., led to the isolation of a black solid, the far-infrared spectrum of which did not match that of the desired complex, recorded independently by Bruns and Preetz. Gradual accumulation of evidence, as outlined below, led to the conclusion that in fact this dark material was itself the previously unknown nonabromodiosmate complex.

Vigorous heating a mixture of \((\text{nBu}_4\text{N})_2[\text{OsBr}_6]\) and neat trifluoroacetic acid (TFAA) yielded a black solid, which was isolated by filtration and dried in vacuo. Initial attempts at obtaining any solution characterization of this material failed as a result of its extreme reactivity. Solutions of the solid in dichloromethane had a transient dark blue/black colour, which changed rapidly to dark orange. The u.v./visible spectra of these orange solutions only revealed features attributable to the starting material of the reaction, \([\text{OsBr}_6]^{2-}\). The material behaved similarly in a wide variety of solvents, and so characterization was initially limited to the use of techniques which required only solid samples of the black material.

Infrared spectroscopy and elemental analysis established that the dark solid contained only C, H and N (from \(\text{nBu}_4\text{N}^+\) cations), along with Os and Br. The ligation of the trifluoroacetate anion was considered, as it potentially can function as a monodentate and/or bidentate ligand. Both coordination modes of the \(\text{CF}_3\text{CO}_2^-\) anion can however be readily distinguished by the characteristic \(\nu_{\text{sym}}(\text{CO}_2)\) and \(\nu_{\text{asym}}(\text{CO}_2)\) stretching bands. All the bands in the infrared spectrum could be attributed to the \(\text{nBu}_4\text{N}^+\) cation. In addition, this material repeatedly gave C, H, N and Br analyses corresponding to \(\text{C}_{16}\text{H}_{36}\text{NO}_{\text{S}2}\text{Br}_9\).

The observation that the unknown material could be dissolved in dry, prechilled 213 K (-60 °C) dichloromethane, giving blue/black solutions which did not undergo any rapid colour changes, led to the solution characterization of this compound. Its enhanced stability in such an
environment gave access to a variety of other experimental techniques which resulted in its identification.

The voltammetry of the compound in pre-cooled dichloromethane revealed three reductions, at +1.07, +0.35 and -1.27 V (versus Ag/AgCl). The first two reductions were reversible, the third only partially reversible. A stirred d.c. voltammogram indicated each reduction involved the same number of electrons. From the relatively small separation of the couples, two possibilities were apparent. The solid was either a one to one mixture of two monomeric species, or a binuclear complex. The electrochemistry of the starting material, (nBu₄N)₂[OsBr₆], is well established so its presence could be discounted. The pattern of redox-couples closely resembled those in the [Ru₂(µ-X)₃X₆]⁴⁻/³⁻/²⁻/¹⁻ systems, while the positions explained the reactivity of the solid, as a very strong oxidant.

The doubly reduced species, assumed to be an Os₂³⁺,³⁺ complex, was successfully prepared by step-wise bulk electrolytic addition of two electrons, the one-electron nature of each step being confirmed by coulometry. The bulk reduced product (now a brown/yellow solution), had couples in an identical place to those in the original material, hence no structural change had occurred upon reduction. This reduced solution was warmed to room temperature, and while the reversibility of the couples suffered, no apparent decomposition of the bulk Os₂³⁺,³⁺ solution occurred.

Some of the reduced solution was syringed into the OTTLE cell, and the u.v./visible spectrum of the Os₂³⁺,³⁺ species recorded. The spectra of the oxidized Os₂³⁺,⁴⁺ and Os₂⁴⁺,⁴⁺ products were then recorded in turn, by reversible electrogeneration at 213 K. The spectrum of the most highly oxidized form closely resembles that of [Ru₂(µ-Br)₃Br₆]¹⁻, which had previously been electrogenerated (see Figure 4.4).

One of the most persuasive pieces of evidence for the constitution of the unknown compound came from its behaviour in prechilled acetonitrile, as monitored by a.c. and cyclic voltammetry. The voltammetry in acetonitrile at 233 K was identical to that observed in cold dichloromethane.

---

∞ Routine voltammetry of (nBu₄N)₂[OsBr₆] reveals an oxidation at +1.43 V and a reduction at -0.37 V, see Chapter 5 for more details.

§ This would have been impractical for the black, highly reactive Os₂⁴⁺,⁴⁺ solution.
Upon warming, it was apparent that a chemical transformation was taking place, with the appearance of new couples (in a one to one ratio), at the expense of those associated with the unknown material. From the knowledge of expected shifts in electrode potentials accompanying substitution of halide by nitrile, and the voltammetry of [OsBr₆]²⁻, these products were tentatively identified as [OsBr₅(MeCN)]¹⁻ and trans or cis-[OsBr₄(MeCN)₂]. Accordingly, these monomeric complexes were then prepared independently, and their voltammetry recorded, confirming these assignments. The postulate, as to the identity of the species formed upon warming acetonitrile solutions of the unknown material, was correct [equation (4.2)], and striking evidence for the asymmetric cleavage of a nine halide precursor. Nonahalodiiridate complexes have also been observed to cleave asymmetrically. It is also of note that carrying out the same experiment with (ⁿBu₄N)₂[Os₂(µ-Br)₂Br₆] yields only ᵐBu₄N[OsBr₅(MeCN)].

\[
\text{unknown material} \xrightarrow{\text{MeCN}} ᵐBu₄N[OsBr₅(MeCN)] + trans-[OsBr₄(MeCN)₂]
\] (4.2)

The preparation and characterization of ᵐBu₄N[OsBr₅(MeCN)] and trans-ⁿBu₄N[OsBr₄(MeCN)₂] is described in Chapter 5.
The above observations were all consistent with the black solid, isolated from the vigorous refluxing of \( (\text{nBu}_4\text{N})_2[\text{OsBr}_6] \) in TFAA, having the formula \( \text{nBu}_4\text{N}[\text{Os}_2\text{Br}_9] \). While this unknown material was being characterized, an authentic sample of \( (\text{nBu}_4\text{N})_2[\text{Os}_2(\mu-\text{Br})_2\text{Br}_8] \) was prepared (under mild conditions),\(^\dagger\) with very different physical properties to those described here for the nonabromide.

The two-electron reduction product of \( [\text{Os}_2\text{Br}_9]^{1-} \) (i.e. \( [\text{Os}_2\text{Br}_9]^{3-} \)), could also be prepared chemically, and isolated as an organo-soluble \( \text{nBu}_4\text{N}^+ \) salt. The addition of two consecutive equivalents of \( \text{nBu}_4\text{NBH}_4 \) to a prechilled dichloromethane solution of \( \text{nBu}_4\text{N}[\text{Os}_2\text{Br}_9] \) yielded a brown/yellow solution. The u.v./visible spectrum of this solution was identical to that of the electrochemically reduced species, confirming the product of chemical and electrochemical reduction were the same. Dark coloured needles of composition \( (\text{nBu}_4\text{N})_3[\text{Os}_2\text{Br}_9] \) (as shown by elemental analysis) were isolated from this solution.

The u.v./visible spectra and voltammetry of the \( [\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6]^{2-} \) and diosmium complexes (formulated as \( [\text{Os}_2\text{Br}_9]^{2-} \)) for \( z=1, 2, 3 \), could be related in a rational and systematic way, suggesting these complexes were structurally related. The far-infrared spectrum of the reduced diosmium compound gave conclusive evidence to its structure.

A comparison of the far-infrared spectra of \( (\text{nBu}_4\text{N})_3[\text{Os}_2\text{Br}_9] \) and \( (\text{nBu}_4\text{N})_3[\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6] \) revealed some striking similarities (Figure 4.5), only expected in isostructural compounds. The far-infrared spectra of confacial biocahedral \( [\text{M}_2(\mu-\text{X})_3\text{X}_6]^{2-} \) complexes have been thoroughly studied.\(^{44,45}\) From the infrared active vibrations predicted by \( \text{D}_{3h} \) molecular symmetry, two metal-terminal halide (M-X\(_t\)) stretches (\( A_2'' , E' \)) and two metal-bridging halide (M-X\(_b\)) stretches (\( A_2'' , E' \)) are expected, the latter being lowest in energy. At even lower energy, weaker metal-halide deformation modes are predicted.

The far-infrared spectrum of \( (\text{nBu}_4\text{N})_3[\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6] \) was recorded in a polythene disc at room temperature, and is shown in Figure 4.5. The strong bands at 258 and 231 cm\(^{-1} \) are assigned as the Ru-Br\(_t\) stretching bands.\(^1\)

\(^\dagger\) See Chapter 3.
Figure 4.5  Far-infrared spectra of (a) $^{n}$Bu$_4$N[Os$_2$(μ-Br)$_3$Br$_6$], (b)Ph$_4$P[Os$_2$(μ-Br)$_3$Br$_6$] (c) ($^{n}$Bu$_4$N)$_3$[Os$_2$(μ-Br)$_3$Br$_6$] and (d) ($^{n}$Bu$_4$N)$_3$[Ru$_2$(μ-Br)$_3$Br$_6$], recorded in polythene discs at room temperature. The dashed lines on spectrum (c) indicate the positions (and approximate intensities) of the bands in the spectrum of ($^{n}$Bu$_4$N)$_3$[Ir$_2$(μ-Br)$_3$Br$_6$], measured under the same conditions.
Scaling these bands to account for the mass difference between Ru and Os predicts Os-Br\textsubscript{t} bands at 230 and 205 cm\textsuperscript{-1}. The two strong bands observed in (nBu\textsubscript{4}N)\textsubscript{3}[Os\textsubscript{2}(\mu-Br)\textsubscript{3}Br\textsubscript{6}] (polythene disc, room temperature) occur at 223 and 203 cm\textsuperscript{-1}, and are assigned as the Os-Br\textsubscript{t} stretching bands. The band at lower energy (181 cm\textsuperscript{-1}) is an Os-Br\textsubscript{b} stretching vibration (Figure 4.5). The same simple scaling cannot be performed for the M-X\textsubscript{b} stretches, which are far less sensitive to mass changes. A similar spectrum was also observed for (nBu\textsubscript{4}N)\textsubscript{3}[Ir\textsubscript{2}(\mu-Br)\textsubscript{3}Br\textsubscript{6}]\textsuperscript{15}, further supporting the triple-bridged, face-sharing structure of (nBu\textsubscript{4}N)\textsubscript{3}[Os\textsubscript{2}(\mu-Br)\textsubscript{3}Br\textsubscript{6}] (and nBu\textsubscript{4}N[Os\textsubscript{2}(\mu-Br)\textsubscript{3}Br\textsubscript{6}]).

In the solid state, the effect of counter cations on the far-infrared spectra, and on the dimensions of the binuclear structure in general, have been previously noted.\textsuperscript{45} The resolution of the two Os-Br\textsubscript{t} stretching bands of [Os\textsubscript{2}(\mu-Br)\textsubscript{3}Br\textsubscript{6}]\textsuperscript{1-} is dependent upon the identity of the cation (Figure 4.5). Only a single broad band is observed in nBu\textsubscript{4}N[Os\textsubscript{2}(\mu-Br)\textsubscript{3}Br\textsubscript{6}], while for Ph\textsubscript{4}P[Os\textsubscript{2}(\mu-Br)\textsubscript{3}Br\textsubscript{6}] two bands are clearly visible.

In summary, it has been established that warming (nBu\textsubscript{4}N)\textsubscript{2}[Osb\textsubscript{6}] in TFAA gives the double-bridged, edge-sharing compound (nBu\textsubscript{4}N)\textsubscript{2}[Os\textsubscript{2}(\mu-Br)\textsubscript{2}Br\textsubscript{8}] in high yield, as described in Chapter 3. Alternatively, vigorous refluxing of this same mixture exclusively yields the highly reactive triple-bridged, face-sharing complex (nBu\textsubscript{4}N)[Os\textsubscript{2}(\mu-Br)\textsubscript{3}Br\textsubscript{6}]. Chemical reduction of this latter compound produces more tractable (nBu\textsubscript{4}N)\textsubscript{3}[Os\textsubscript{2}(\mu-Br)\textsubscript{3}Br\textsubscript{6}]. The precise role of TFAA is not known, but the acid presumably functions as a halide abstrating agent, in addition to being a very poor solvent for the product, (nBu\textsubscript{4}N)[Os\textsubscript{2}(\mu-Br)\textsubscript{3}Br\textsubscript{6}]. The same chemistry works equally well beginning with (Ph\textsubscript{4}P)\textsubscript{2}[OsBr\textsubscript{6}], although longer reaction times in TFAA are required to produce clean samples of Ph\textsubscript{4}P[Os\textsubscript{2}(\mu-Br)\textsubscript{3}Br\textsubscript{6}], and not mixtures of the latter and (Ph\textsubscript{4}P)\textsubscript{2}[Os\textsubscript{2}(\mu-Br)\textsubscript{2}Br\textsubscript{8}].

The monosubstituted compound, nBu\textsubscript{4}N[OsBr\textsubscript{5}(MeCN)], was also heated vigorously in TFAA, to establish if substituted binuclear complexes could be synthesized. Again, a finely divided black solid was filtered off, which was subsequently also proven to be (nBu\textsubscript{4}N)[Os\textsubscript{2}(\mu-Br)\textsubscript{3}Br\textsubscript{6}]. The stability of the Os\textsubscript{IV} oxidation state in the TFAA environment is such that each metal centre retains as many bromide ligands as possible. On
reflection, reduction to Os\textsuperscript{III} would most probably have to occur to retain coordination of the neutral nitrile ligand (in preference to halide) upon dimerization.

4.2.2 Electrochemical Synthesis.

Prior to the unexpected discovery of \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{1-}\), the original strategy to prepare \([\text{Os}_2(\mu-\text{X})_3\text{X}_6]^{3-}\) complexes envisaged reduction of the double-bridged \([\text{Os}_2(\mu-\text{X})_2\text{X}_8]^{2-}\) species, followed by expulsion of halide concomitant with the formation of the tervalent triple-bridged structure.

A direct indication that the route outlined above may yield the desired complex in a highly controlled process arose while investigating the redox chemistry of \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}\) in dichloromethane (see Chapter 3). The same daughter product was formed at the electrode upon generation of the 35 or 31 electron species (both the 34/35 and 31/32 electron couples are irreversible). The cyclic voltammograms showing the formation of the daughter product were shown in Figure 3.4, in Chapter 3. The alternating current voltammogram for the 34/35 electron reduction is presented here in Figure 4.6. After scanning over the irreversible 34/35 electron couple, the return scan reveals the formation of a species with couples at -1.27, +0.35 and +1.07 V, \textit{i.e.} \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{2-}\). This process can be described as an ECE mechanism. Unexpectedly, the oxidation of \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}\) to what is nominally \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{1-}\) resulted in the formation of a daughter product with the same redox processes. A possible mechanism yielding \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{2-}\) may involve Os-Br bond cleavage through oxidation of a coordinated bromide, and reduction of the Os\textsuperscript{V} centre.

The next step was to transfer the observations from the voltammetric experiment to the bulk electrosynthetic cell. Taking \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}\) in dichloromethane at 213 K, and performing a two electron reduction gave the hitherto unknown tervalent species, \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{4-}\). Warming this solution to \(\sim 243\) K resulted in the disappearance of those waves corresponding to the decabromodiosmate complex, and the growth of a new species. With time and further warming (to 273 K), the rearrangement to \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{3-}\) was complete. The product from the electrochemical reduction and subsequent rearrangement of \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}\), was
Figure 4.6 Volammetric evidence for the formation of $\text{[Os}_2(\mu-\text{Br})_3\text{Br}_6]^{2-}$ from $\text{[Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}$. Part (a) shows the a.c. voltammogram of $\text{[Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}$. After scanning over the irreversible 34/35 electron reduction, the return sweep reveals the formation of a daughter product. Part (b) shows the return scan, starting from -2.0 V. The hatched peaks correspond to $\text{[Os}_2(\mu-\text{Br})_3\text{Br}_6]^{2-}$. Voltammetry recorded in 0.5 mol. dm$^{-3}$ $^n\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ at 213 K. $v=20$ mVs$^{-1}$ and $\omega=205$ Hz. See Figure 3.4 for the accompanying cyclic voltammogram.
[Os₂(µ-Br)₃Br₆]³⁻, as judged by u.v./visible spectra and electrochemistry.

### 4.2.3 Structural Studies

Despite considerable endeavour, a crystal structure of (nBu₄N)[Os₂(µ-Br)₃Br₆] or (Ph₄P)₃[Os₂(µ-Br)₃Br₆] has as yet not been obtained. An x-ray powder diffraction pattern of (nBu₄N)₃[Os₂(µ-Br)₃Br₆] reveals this material is essentially amorphous, with very little long range order within the crystal lattice. The tetra-n-butylammonium cation has a reputation for causing disorder in structures, although within this study three nBu₄N⁺ salts of monomeric complexes have had their structures solved (see Chapter 5). The tetraphenylphosphonium salt gives a more encouraging powder pattern, with several sharp lines being observed at low angles. Crystals of this latter salt were not however of sufficient quality for single crystal diffraction studies.
4.3 SYNTHESIS OF NONACHLORODIOSMATE COMPLEXES, [Os$_2$Cl$_4$]$^3^-$

4.3.1 Chemical Preparation.

Given the success of the TFAA route to the synthesis of nBu$_4$N[Os$_2$(µ-Br)$_3$Br$_6$], it was hoped the analogous chloride complex could be prepared in an identical manner. This however was not to be, as refluxing (nBu$_4$N)$_2$[OsCl$_6$] in neat TFAA yielded only dark yellow/brown solutions. Removal of the acid from these solutions gave intractable oils.

As discussed in the previous chapter, only the tetraphenylphosphonium salt of [Os$_2$(µ-Cl)$_2$Cl$_8$]$^{2^-}$ could be isolated in a pure form, the tetra-n-butylammonium salt being too soluble in neat TFAA to precipitate directly from the reaction mixture. It was reasonable to suggest that products of the [OsCl$_6$]$^{2^-}$/refluxing TFAA reaction would again be more readily isolated using the Ph$_4$P$^+$ salt of the hexachloroosmate.

However, the reaction of (Ph$_4$P)$_2$[OsCl$_6$] with refluxing TFAA proceeded in a similar way to that beginning with (nBu$_4$N)$_2$[OsCl$_6$], giving dark yellow/brown solutions which did not yield any solid material, even upon cooling. Products were again difficult to isolate from this reaction mixture, and at present remain unidentified. Infrared spectroscopy of some residues suggests incorporation of the trifluoroacetate anion has occurred.

Accordingly, it is important to consider the reasons for the success of TFAA in preparing salts of [Os$_2$(µ-Br)$_3$Br$_6$]$^{1^-}$. The mono-anion is very reactive in solution, only being stable under special conditions (i.e. dry, chilled non-coordinating solvents). Its isolation may only be possible through its insolubility in TFAA, the transformation from the double to the triple-bridged structure occurring heterogeneously. Therefore, if A[Os$_2$(µ-Cl)$_3$Cl$_6$] (where A=mono-cation) does not precipitate immediately upon its formation, further reaction may well occur. The apparent difference in reactivity of the chloride and bromide may lie simply in their different solubilities.

4.3.2 Electrochemical Preparation.

The success of the electrochemical reductive halide elimination route
to $[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{3-}$, and our ability prepare $(\text{Ph}_4\text{P})_2[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]$ in near quantitative yields, suggested this was still a feasible route to the $[\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{3-}$ species. The reaction was carried out in a way exactly analogous to that of the bromide, with critical attention to applied potential and temperature over the various phases of the reaction. Bulk reduction of the $[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{2-}$ to the $[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{4-}$ species, followed by warming gave a product whose voltammetry and optical spectra (in three different oxidation levels) are consistent with the formation of $[\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{3-}$.

Aside from the above characterization, a solution far-infrared spectrum of the electrogenerated material was recorded. The solvent, dichloromethane, has a band at 286 cm$^{-1}$ in the expected $\nu$(Os-Cl) region. The solvent was removed in vacuo, and the electrolyte/$[\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{3-}$ mixture taken up in dibromomethane. The spectrum is presented in Figure 4.7. The dominant feature is a strong band at 308 cm$^{-1}$, and a less intense feature at 254 cm$^{-1}$.

![Figure 4.7](image)

**Figure 4.7** Solution far-infrared spectrum of $[\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{3-}$ (in dibromomethane). The dashed lines indicate the positions (and approximate intensities) of the bands in the spectrum of $[\text{Ir}_2(\mu-\text{Cl})_3\text{Cl}_6]^{3-}$, measured under the same conditions. * designates solvent bands.

The addition of a solution of $[\text{Rh(bipy)}_3](\text{CF}_3\text{SO}_3)_3$ to the dichloromethane mixture of $[\text{Os}_2\text{Cl}_9]^{3-}$ and electrolyte resulted in the
immediate precipitation of $[\text{Rh(bipy)}_3][\text{Os}_2\text{Cl}_9]$ as a fine brown powder. Unfortunately the $[\text{Rh(bipy)}_3]^{3+}$ salt of $[\text{Os}_2\text{Cl}_9]^{3-}$ was too insoluble for our purposes.

Following the success of the electrochemical route to $[\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{3-}$, chemical reduction of $[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{2-}$ was attempted. A number of reductants were tried, however none were successful in producing solutions of $[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{4-}$ at 213 K. Some of the reductants did not function at that temperature. The only material isolated from each attempt was $(\text{Ph}_4\text{P})_2[\text{OsCl}_6]$, underlining the inherent instability of $[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^{3-}$ towards cleavage reactions.

### 4.3.3 Final Comment

Having discovered a logical route to the nonahalodiosmate complexes, and another less obvious method of preparing $[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{1-}$, the question remains as to why these complexes have not previously been synthesized.

There are several contributing explanations. Firstly, the number of convenient osmium starting materials, in any oxidation state, is extremely limited. In Chapter 1, $[\text{OsCl}_5(\text{PPh}_3)_3]$ was used with great success to prepare $[\text{Os}_2(\mu-\text{Cl})_3(\text{PR}_3)_6]\text{Cl}$ compounds, however its promise as a useful osmium reagent lies in the area of low oxidation state chemistry. The majority of high oxidation state osmium chemistry begins with either OsO$_4$, or $[\text{OsX}_5]^{2-}$ complexes. The former requires reduction, which can be difficult to control, the latter is often substitution inert except under vigorous conditions.

The synthesis of the diruthenium $[\text{Ru}_2(\mu-\text{X})_3\text{X}_6]^{3-}$ complexes offers no guidance for the osmium chemist. Considering the chloride first, an osmium analogue of the ruthenium starting material, $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$, does not exist. As will be shown in Chapter 5, $[\text{Os}^{\text{III}}\text{Cl}_5\text{L}]^{2-}$ species are only stable when L is a strong $\pi$-acceptor, such as CO. The stable oxidation state for $[\text{OsX}_5\text{L}]^{2-}$ complexes where L is a labile leaving group, is Os$^{\text{IV}}$ (see Chapter 5). In the case of the bromide, $[\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6]^{3-}$ is prepared by repeated treatment of $\text{RuCl}_3.x\text{H}_2\text{O}$ with $\text{HBr}/\text{Br}_2$ solutions. Given the uncertainty associated with the actual constituents of hydrated ruthenium trichloride,
often simply called "commercial ruthenium(III) trichloride", it is not feasible to design a similar osmium synthesis, and in any event [Os₂(µ-Br)₃Br₆]³⁻ simply does not have the same stability and dominance of Os³⁺/Br chemistry. Osmium trichloride, OsCl₃, is a known material, although it does not appear to be readily available commercially. It should also be added that aqueous osmium chemistry (in the absence of a hydrohalic acid) can become complicated through the formation of oxide and hydroxide species. In the presence of an acid HX, yet without other ligands which may inhibit the synthesis of bimetallic units, the stability of [OsX₆]²⁻ is such that it is often formed.

The heart of the problem lies in the control of oxidation states. As was mentioned briefly in chapter 3, heating [Os⁴⁺Cl₅(thf)]¹⁻ under vacuum yields the double-bridged complex, [Os₂(µ-Cl)₂Cl₈]²⁻. The dimerization of monomeric Os⁴⁺ complexes preferentially gives [Os₂(µ-X)₂X₈]²⁻ complexes. Although [OsX₅L]¹⁻ species such as [Os⁴⁺Cl₅(thf)]¹⁻ are easily reduced, upon doing so they often lose halide, becoming most susceptible to attack by traces of water and other lewis bases. As will be shown in Chapter 5, trans-[OsX₄L₂]¹⁻ complexes are in most cases very stable species.
4.4 VOLTAMMETRY OF NONAHALODIOSMATE COMPLEXES.

4.4.1 General

The voltammetry of the \([\text{Os}_2(\mu-X)_3X_6]^{2-}\) \((X=\text{Cl}, z=1, X=\text{Br}, z=1, 3)\) complexes, especially that of \(\text{nBu}_4\text{N}[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\), has already been referred to in describing their discovery and characterization. Each of these compounds display three metal-based redox processes; in the case of \([\text{Os}_2(\mu-X)_3X_6]^{3-}\) \((X=\text{Cl}, \text{Br})\), two oxidations and a reduction, while for \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\)^1, three reductions are recorded, all in identical positions to the couples in the reduced form of the complex, \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\)^3-. These couples span the 32 to 35 electron systems, as shown in Figure 4.8. The one-electron nature of all these steps was established by analysis of the c.v. and a.c.v. responses, and confirmed by coulometric measurements. Table 4.1 lists the voltammetric data for the \([\text{Os}_2(\mu-X)_3X_6]^{2-}\) complexes.

\[
\begin{align*}
\text{IV} & : M-X-M + e^- \rightarrow (\text{MX}_3\text{M})^{4+} \\
\text{III} & : M-X-M + e^- \rightarrow (\text{MX}_3\text{M})^{2+} \\
\text{II} & : M-X-M + e^- \rightarrow (\text{MX}_3\text{M})^{1+} \\
\text{I} & : M-X-M + e^- \rightarrow (\text{MX}_3\text{M})^{0+}
\end{align*}
\]

Figure 4.8 Electrochemically accessible oxidation levels of \([\text{Os}_2(\mu-X)_3X_6]^{2-}\) complexes.

The cyclic and alternating current voltammograms of \(\text{nBu}_4\text{N}[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\), recorded in dichloromethane at 213 K, are shown in Figure 4.9. Each wave is labelled according to the formal oxidation state changes of the osmium centres accompanying electron transfer. The first two reductions in this complex (and similarly the two oxidations in the \([\text{Os}_2(\mu-X)_3X_6]^{3-}\) species), are reversible on a both a voltammetric and bulk electrosynthetic timescale. The 34/35 electron reduction in all three diosmium complexes listed in Table 4.1 is only partially reversible \(i.e.\) an EC mechanism.

The variation of metal-based electrode potentials with halides is
Table 4.1 Voltammetric Data for [Os₂(µ-X)₃X₆]²⁻ and [Ru₂(µ-X)₃X₆]²⁻ complexes, X=Cl, Br.

<table>
<thead>
<tr>
<th>Complex</th>
<th>E₁/₂ Values (V)</th>
<th>ΔE₁/₂ (V)</th>
<th>Kc b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IV,IV/III III,III (32/33 e⁻)</td>
<td>III,III,II (34/35 e⁻)</td>
<td></td>
</tr>
<tr>
<td>(nBu₄N)₃[Os₂Br₉]</td>
<td>+1.07 (r)</td>
<td>+0.95 (r)</td>
<td>-0.59 (qr)</td>
</tr>
<tr>
<td>(nBu₄N)[Os₂Br₉]</td>
<td>+1.07 (r)</td>
<td>+0.95 (r)</td>
<td>-0.59 (qr)</td>
</tr>
<tr>
<td>(nBu₄N)₃[Os₂Cl₉]</td>
<td>+1.26 (r)</td>
<td>+0.95 (r)</td>
<td>-0.59 (qr)</td>
</tr>
<tr>
<td>(nBu₄N)₃[Ru₂Br₉]</td>
<td>+1.46 (r)</td>
<td>+0.95 (r)</td>
<td>-0.59 (qr)</td>
</tr>
<tr>
<td>(nBu₄N)₃[Ru₂Cl₉]</td>
<td>+1.70 (r)</td>
<td>+0.95 (r)</td>
<td>-0.59 (qr)</td>
</tr>
</tbody>
</table>

a Measured in 0.5 mol·dm⁻³ nBu₄NPF₆/CH₂Cl₂ at 213 K, versus Ag/AgCl, against which ferrocinium/ferrocene occurs at +0.55 V. By convention, the couples are listed as reductions, the number in parentheses referring to the to the EAN electron counting scheme. r=reversible, qr=quasi-reversible, pr=partially reversible (i.e. EC mechanism) and irr=irreversible.

b Kc = e(ΔE/F/RT), ΔE = ΔE₁/₂, separation of 34/35 and 35/36 electron couples.
Figure 4.9 Cyclic and alternating current voltammograms of \((\text{Bu}_4\text{N})\text{Os}_2(\mu-\text{Br})_3\text{Br}_6\) in 0.5 mol. dm\(^{-3}\) \(\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2\) at 213 K, versus Ag/AgCl. Scan rate=100 mV/s for c.v. and 20 mV/s for a.c.v., with \(\omega=205\) Hz. The dashed vertical lines indicate the positions of the analogous couples in \([\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6]^{2-}\).
discussed at length in Chapter 5. Generally, only small differences are observed in $E_{1/2}$ values upon replacing Cl by Br, with no pattern as to the likely ordering of the two, i.e. Cl>Br or Cl<Br. The maximum difference in any one particular couple of the $[\text{Os}_2(\mu-X)X_6]^3-$ complexes, between the chloride and bromide, is 280 mV. This occurs between the 34/35 electron couples, the chloride being more negative than the bromide.** The 32/33 electron couples differ by 190 mV, however on this occasion the chloride is more positive than the bromide. The remaining 33/34 electron couples are only separated by 20 mV. There is no consistent directional shift in $E_{1/2}$ values between chloride and bromide, an effect also noted in the $[\text{Ru}_2(\mu-X)_2X_6]^3-$ systems (see Section 4.4.2).

Figure 4.10 presents the cyclic and alternating current voltammograms of $[\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^3-$, the product formed in situ upon rearrangement of $[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]^4-$: The final oxidation, the 33/32 electron couple, is partly concealed by the oxidation of free chloride, formed in the rearrangement process (see Section 4.3).

![Figure 4.10](image)

**Figure 4.10** Cyclic and alternating current voltammograms of $[\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^3-$, recorded in 0.5 mol. dm$^{-3}$ nBu$_4$NPF$_6$/CH$_2$Cl$_2$ solutions, at 213 K versus Ag/AgCl.

The replacement of six terminal halides by six phosphines has considerable effect on the available oxidation states, consistent with the $\pi$-
bonding nature of the ligands. The only redox process observed in both complexes is the 34/35 electron couple, which moves from -1.55 V in \([\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{3-}\) to +1.47 V in \([\text{Os}_2(\mu-\text{Cl})_3(\text{PEt}_3)_6]^{1+}\), a shift of ca. 3.0 V.

### 4.4.2 Comparison of Osmium and Ruthenium Nonahalodimetallate Complexes

The redox processes displayed by the \([\text{M}_2(\mu-X)_3X_6]^{2-}\) complexes (M=Ru, Os, X=Cl, Br) are summarized in Table 4.1. The dioxinum complexes are more easily oxidized, and more difficult to reduce than their ruthenium analogues. Relativistic effects increase shielding of the osmium 5d valence electrons from the core charge of the nucleus, and hence they are more easily removed. It is for this reason that higher oxidation state osmium complexes are in general more stable than their ruthenium counterparts. The isolation of \(\text{A}[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\) (A=\(n\text{Bu}_4\text{N}^+, \text{Ph}_4\text{P}^+\)) is testimony to this effect. The pattern of shifts in \(E_{1/2}\) values upon exchanging chloride for bromide was identical for the \([\text{Os}_2(\mu-X)_3X_6]^{2-}\) and \([\text{Ru}_2(\mu-X)_3X_6]^{2-}\) complexes.

The separations of the 32/33 and 33/34 electron couples are consistently greater in the \([\text{Os}_2(\mu-X)_3X_6]^{2-}\) complexes, indicative of an increase in the metal-metal (M-M) interaction. This is supported by magnetic measurements (Section 4.6), which reveal \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{3-}\) is essentially diamagnetic, unlike \([\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6]^{3-}\), which has a room temperature moment of 1.67 B.M. per molecule.

This difference described above is in contrast to what is observed in the \([\text{M}_2(\mu-X)_3(\text{PR}_3)_6]X\) compounds, where the separation of the 34/35 and 35/36 couples is both smaller and approximately equal (~0.5 V) for ruthenium and osmium.## The difference lies in the identity of the terminal ligands. With \(\pi\)-donating terminal halides, the ability of a 5d element to engage in M-M \((d\pi-d\pi)\) bonding is promoted, the larger \(\Delta E_{1/2}\) being indicative of a more pronounced Os-Os interaction. Conversely, the effect of the \(\pi\)-acceptor phosphines is to attenuate this difference between osmium and ruthenium, resulting in smaller and more similar metal-metal interactions.

## The estimated 34/35 versus 35/36 electron gap for \([\text{Ru}_2(\mu-\text{Cl})_3\text{Cl}_6]^{3-}\) is ~0.9 V.
The comproportionation constants (K_c) for equation (4.3) are also listed in Table 4.1, these being calculated from the separation of the 32/33 and 33/34 electron couples. The value of K_c gives an indication as to the stability of the mixed-valence complex. Electrogenerated solutions of [Ru_2(µ-X)3X_6]^2- were only stable at temperatures below 273 K. The K_c values for the osmium complexes are orders of magnitude greater than those of ruthenium, and in each case chloride are larger than bromide. Given the modest potential required to oxidize [Os_2(µ-X)3X_6]^3+ to [Os_2(µ-X)3X_6]^2-, it may be possible to chemically perform this oxidation, and isolate the mixed-valence species for further magnetic studies.

\[ \begin{align*}
\text{III} & \quad \text{III} \\
\{\text{Os}(µ-X)3\text{Os}\}^{3+} & + \{\text{Os}(µ-X)3\text{Os}\}^{5+} \quad K_c \quad 2\{\text{Os}(µ-X)3\text{Os}\}^{4+} \\
\text{IV} & \quad \text{IV} \\
\end{align*} \] (4.3)

4.4.3 Comparison of Osmium and Other 3rd Row Nonahalodimetallate Complexes

The face-sharing [M_2(µ-X)3X_6]^2- complexes are well known for M=W, Re and Ir (see introduction). The preparation of the diosmium complexes completes the series of 3rd row transition metal [M_2(µ-X)3X_6]^2- complexes from W to Ir (Table 4.2). Heath et al. have made a comprehensive study of the redox chemistry of the 4d and 5d hexahalometallates. The E_{1/2} values were found to vary in an orderly manner across the periodic table, which was explained in terms of central ion core-charge and interelectronic correlations. The deviation at the d^3 I d^4 couple in [MCI_6]^2-/3- complexes is due to the onset of spin-pairing, as a result of putting the fourth electron into the t^2g shell. This is not the pattern of E_{1/2} values which would be predicted on the basis of the classical binuclear
molecular orbital scheme (refer to Figure 4.12), where the redox active orbital is $\delta, \delta^*, \delta^*$ and $\sigma^*$ for $M_{2}^{IV,IV}=W_2, Re_2, Os_2$ and $Ir_2$ bimetallic complexes respectively. Accordingly, these data suggest that in the higher oxidation states the localized ion effects are the dominant perturbation on the electronic structure and metal-metal interaction is not sufficient to alter that periodic trend of monomeric complexes.

Table 4.2  $E_{1/2}$ values for third row transition metal (nBu$_4$N)$_3[M_2(\mu-Cl)_3Cl_6]$ complexes (M=W, Re, Os, Ir).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}$ Values (V)$^a$</th>
<th>mean of 32/33-33/34 couples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IV,IV/IV,III (32/33)</td>
<td>IV,III/III,III (33/34)</td>
</tr>
<tr>
<td>(nBu$_4$N)$_3[W_2Cl_9]^b$</td>
<td>+0.68</td>
<td>-0.06</td>
</tr>
<tr>
<td>(nBu$_4$N)$_3[Re_2Cl_9]^b$</td>
<td>+0.75</td>
<td>-0.17</td>
</tr>
<tr>
<td>(nBu$_4$N)$_3[Os_2Cl_9]$</td>
<td>+1.26</td>
<td>+0.33</td>
</tr>
<tr>
<td>(nBu$_4$N)$_3[Ir_2Cl_9]$</td>
<td>+1.77</td>
<td>+1.03</td>
</tr>
</tbody>
</table>

$^a$ Measured in 0.5 mol. dm$^{-3}$ nBu$_4$NPf$_6$/CH$_2$Cl$_2$ at 213 K, versus Ag/AgCl, against which ferrocinium/ferrocene occurs at +0.55. By convention the couples are listed as reductions, the numbers in parentheses referring to the EAN electron counting scheme. $^b$ Reference 49.

Figure 4.11  Trend in the mean of the 32/33-33/34 electron couple for $[M_2(\mu-Cl)_3Cl_6]^{3-}$ complexes (M=W, Re, Os, Ir).
Plotting either of what are formally \( M_{2}^{IV,IV/IV,III} \) or \( M_{2}^{IV,III/II,II,II} \) couples versus \( M \) yields essentially the same relationship. It is however more appropriate to plot the centre of gravity, if we wish to follow the underlying trend from \( W \) to \( Ir \), without perturbation due to variation in \( \Delta E_{1/2} \) across the series.

\[
\begin{align*}
\sigma^* & \quad - \quad - \quad - \quad - \\
\delta^* & \quad - \quad - \quad \# \quad \# \\
\delta & \quad - \quad - \quad \# \quad \# \quad \# \\
\sigma & \quad - \quad - \quad - \quad - \quad - \\
W_{2}^{IV,IV} & \quad \text{(d}^2/d^2) \\
Re_{2}^{IV,IV} & \quad \text{(d}^3/d^3) \\
Os_{2}^{IV,IV} & \quad \text{(d}^4/d^4) \\
Ir_{2}^{IV,IV} & \quad \text{(d}^5/d^5) \\
\end{align*}
\]

**Figure 4.12** Molecular orbital schemes for the \([M_{2}(\mu-Cl)_{3}Cl_{6}]^{1-} \) complexes (\( M=W, \text{Re, Ir, Os} \)). The vacant \( \pi/\pi^* \) orbitals derived from the \( e_8 \) \( d \) orbitals have been omitted purposely.
4.5 SPECTROELECTROCHEMISTRY OF NONAHALODIOSMATE COMPLEXES

4.5.1 Introductory Remarks

Considerable insight into the electronic structure of the \([M_2(\mu-X)_3X_6]^{2-}\) complexes can be obtained from the empirical assignment of their electronic spectra. Spectroscopic comparisons of diruthenium and diosmium, addressed initially in \([M_2(\mu-X)_3(PR_3)_6]^{2+}\) systems, are again of concern in the \([M_2(\mu-X)X_6]^{2-}\) complexes. In addition, the identification of intervalence charge-transfer bands in the spectra of mixed-valence complexes can provide information as to the classification of system, \textit{i.e.} localized or delocalized.

The discussion which follows seeks to assign the general features of the electronic spectra of the nonahalide \([M_2(\mu-X)_3X_6]^{2-}\) complexes (\(M=\text{Os, Ru, X=Cl, Br; } z=1, 2, 3\)). The spectrum of any one of these complexes alone would be difficult to assign. However, within the above family of systematically related complexes, it is possible to vary \textit{every} element of the structure, \textit{i.e.} the identity of the metal, the halide, and the prevailing oxidation level. From a knowledge of the expected spectral changes accompanying variation of these factors, persuasive assignments can be made. These preferred assignments are tabulated in Tables 4.3, 4.4, 4.5, and the considerations leading to these assignments are detailed below.

4.5.2 General Considerations

A number of possible transitions associated with atoms or groups of atoms (termed \textit{chromophores}) can be identified within the triple-bridged face-sharing \([M_2(\mu-X)_3L_6]^{2-}\) structure.

\textbf{Single-ion Transitions.}

Consider firstly single-ion transitions associated with a single metal centre. In \(\text{Ru}^{	ext{III}}\) and \(\text{Ru}^{	ext{IV}}\), ligand-field bands are often obscured by charge-transfer absorptions, while intraconfigurational transitions are generally at energies \(<4\ 000\ \text{cm}^{-1}\),\textsuperscript{50} and therefore are essentially outside our spectroscopic window (typically 45 000-4 000 cm\(^{-1}\)). Osmium \(d-d\) bands suffer
the same fate as those of ruthenium, however, for Os^{III} and Os^{IV}, intraconfigurational bands can typically be observed in the 10 000-5 000 cm\(^{-1}\) region. The remaining single-atom chromophores are the terminal (X\(_t\)) and bridging halides (X\(_b\)), which alone do not make any contribution to the spectrum in the region of most interest, i.e. below ~35 000 cm\(^{-1}\).

**Charge-Transfer from Bridging Halides.**

Chromophores involving groups of atoms include transitions arising from the metal/bridging halide and metal/terminal halide fragments, M(X\(_b\))\(_3\) and M(X\(_t\))\(_3\). As was noted in Chapter 2, the bridging halide ligands do not in general make a contribution to the electronic spectra of [M\(_2\)(µ-X)\(_3\)L\(_6\)]\(^2+\) complexes through X\(_b\)(π)→M(d\(_{π}\)) charge-transfer transitions. This was evidenced by the fact that only marginal changes in the spectra of the [Ru\(_2\)(µ-X)\(_3\)(PR\(_3\))\(_6\)]\(^1+/2+/3+\), [Ru\(_2\)(µ-X)\(_3\)(Me\(_3\)tacn)\(_2\)]\(^1+/2+/3+\) and [Os\(_2\)(µ-X)\(_3\)(PR\(_3\))\(_6\)]\(^1+/2+/3+\) complexes were observed upon changing chloride for bromide, and not the expected 6 000 cm\(^{-1}\) shift repeatedly observed in monomeric complexes for X(π)→M(d\(_{π}\)) charge-transfer transitions. Transitions from the bridging halides need not be considered any longer.

**Charge-Transfer from Terminal Halides.**

Another spectroscopic chromophore to consider is charge-transfer involving the facially arranged terminal halides. The local geometry about any one of the metal centres is approximately octahedral, with a facial arrangement of ligands X (in this case X\(_t\)), and L (here L=X\(_b\)), i.e. the single-ion chromophore approaches a fac-[MX\(_3\)L\(_3\)] system. The charge-transfer spectra of such monomeric complexes are well understood.\(^5\) Two X(π)→M(d\(_{π}\)) charge-transfer transitions are predicted, arising through promotion from the A and E symmetry orbitals of the three-halide array.

The fac-[RuX\(_3\)(Me\(_3\)tacn)] (X=Cl, Br) complexes are ideal for the purpose of defining the chromophore containing three facially arranged halides. The spectra of both the chloride and bromide RuX\(_3\)(Me\(_3\)tacn) complexes are shown in Figure 4.13, their systematic relationship to one another clearly evident. As required by optical electronegativities for a X(π)→M(d\(_{π}\)) charge-transfer transition, the bands in the spectrum of the chloride complex are at higher energy than those in the bromide, the size of the shifts precisely as observed in other monomeric systems, i.e. ~ 6 000 cm\(^{-1}\).\(^4\) The terminal
halides in an \([M_2(\mu-X)_3(X)_6]^{2-}\) complex are therefore expected to give rise to two \(X(\pi)\rightarrow M(d_\pi)\) charge-transfer bands (A and E as above), the positions of which should move in an orderly fashion as the oxidation level of the bimetallic complex varies.

![Absorbance (Arbitrary Units)](image)

**Figure 4.13** The u.v./visible spectra of fac-[RuX3(Me3lacn)] complexes, (a) \(X=Cl\), (b) \(X=Br\).

**Principles of Halide-to-Metal Charge-Transfer.**

Upon reduction of monomeric \([MX_6]^{2-}\) complexes with a \(d^n\) configuration where \(n\leq 5\), the \(X(\pi)\rightarrow M(d_\pi)\) charge-transfer manifold is shifted to higher energies. The size of the shift, estimated from optical electronegativities or measured directly, is typically ca. 8 000 cm\(^{-1}\). For example, the charge-transfer manifold moves by \(-8 300\) cm\(^{-1}\) from \([OsCl_6]^{2-}\) to \([OsCl_6]^{3-}\) (Figure 4.14).

A ligand-to-metal charge-transfer (l.m.c.t.) transition can in general be viewed as an 'internal reduction', and therefore its position is dependent upon the identity of the metal, or more correctly the reducibility of the metal centre. Electrode potentials can be used to establish the ease with which a complex is reduced. Comparing ruthenium and osmium, the latter is more difficult to reduce, therefore l.m.c.t. transitions (more specifically \(X(\pi)\rightarrow M(d_\pi)\) charge-transfer) are found at higher energy in osmium.
complexes.

The following points summarize the expected relationships for $X_{\pi}(\pi) \rightarrow M(d_{\pi})$ charge-transfer transition energies in the spectra of the $[M_2(\mu-X)_{3}(X)_6]^{2-}$ complexes;

- $X_{\pi}(\pi) \rightarrow M^{III}(d_{\pi}) > X_{\pi}(\pi) \rightarrow M^{IV}(d_{\pi})$,
- $\text{Cl}_{2}(\pi) \rightarrow M(d_{\pi}) > \text{Br}_{2}(\pi) \rightarrow M(d_{\pi})$,
- $X_{\pi}(\pi) \rightarrow \text{Os}(d_{\pi}) > X_{\pi}(\pi) \rightarrow \text{Ru}(d_{\pi})$.

![Absorbance vs Wavenumber](image)

Figure 4.14 The blue shift of the $X(\pi) \rightarrow M(d_{\pi})$ charge-transfer manifold upon reduction of $[\text{OsCl}_6]^{2-}$ to $[\text{OsCl}_6]^{3-}$.

Core Transitions.

The remaining chromophore to discuss is that involving the two metal centres, bridged by the three halide atoms, *i.e.* $[M(\mu-X)_{3}M]^{2+}$. These five atoms define the "core" of the biocathedron. In Chapter 2, the spectra of the electrogenerated $[\text{Ru}_2(\mu-X)_{3}(\text{Me}_3\text{tacn})_2]^{3+}$ species were discussed. These are dominated by two intense transitions, the positions of these bands moving only marginally between $X=\text{Cl}$ and $\text{Br}$. It was concluded that these bands arose from transitions between orbitals derived from the $[M(\mu-X)_{3}M]^{2+}$ core, *i.e.* "core transitions". While not being especially
sensitive to the identity of the halide bridge (X=Cl, Br), such transitions are likely to be affected by other factors, such as the effective single-ion ligand field, 10 Dq, and in particular the degree of metal-metal interaction, this in turn being influenced by the metal oxidation states and terminal ligands. The uncertainty surrounding the analysis of such transitions lies in assessing which of these factors will have the dominating effect. There is also the challenge of predicting the likely changes in core transition energies upon altering the identity of the metal, the terminal ligands and the oxidation level of the \( \{M(\mu-X)_3M\}^{2+} \) core.

A further problem not widely appreciated is that the connection between orbital energies and transition energies is much more tenuous in closed shell (even electron) systems, because unquantified electron/electron correlation terms are prominent. Such terms are to a large extent self-cancelling in odd electron systems, where transition energies can be taken as a more direct measure orbital spacing.

The greater the metal-metal interaction, the more pronounced the core transitions are likely to become. Given the uncertainty associated with the assignment of such transitions, the first group of complexes to be discussed are the \( [M_2(\mu-X)_3X_6]^{1-} \) species, where intuitively the metal-metal interactions within the \( [M_2(\mu-X)_3X_6]^{1-} \), \( [M_2(\mu-X)_3X_6]^{2-} \) and \( [M_2(\mu-X)_3X_6]^{3-} \) series are at a minimum.

### 4.5.3 Electronic Spectra of \( [M_2(\mu-X)_3X_6]^{1-} \) Complexes

In the u.v./visible spectra of all the \( M_2^{IV,IV} [M_2(\mu-X)_3X_6]^{1-} \) complexes (M=Os, Ru, Ir; X=Cl, Br), the dominant feature is the leading band (\( \alpha \) in Figure 4.15), assigned as the A-symmetry \( X_1(\pi) \rightarrow M^{IV}(d_\pi) \) charge-transfer band. For each metal, the band is at higher energy in the case of the chloride, as required for a \( X(\pi) \rightarrow M(d_\pi) \) charge-transfer transition. The shift between X=Cl and Br is \( \sim 5000 \text{ cm}^{-1} \) in the case of Ru and Ir, and \( \sim 6000 \text{ cm}^{-1} \) for Os (Table 4.3). Shifts of similar size are observed on monomeric complexes.

For any one halide, the order of the band maxima, from lowest to highest is Ir<<Ru<<Os. Since l.m.c.t. transitions in general can be viewed as
'internal reductions', the positions of the 32/33 electron reduction should also reflect this trend. From Table 4.3, it can be seen 32/33 electron reduction is easiest for Ir, and hardest for Os, further supporting the assignment of this main band as the A symmetry $X_t(\pi) \rightarrow M^{IV}(d_{\pi})$ charge-transfer transition.

![Spectra of complexes](image)

**Figure 4.15** The u.v./visible spectra of $[M_2(\mu-Cl)_3Cl_6]^{1-}$ complexes, (a) $M=$Os, (b) $R$Ru, electrogenerated in an OTTLE cell in 0.5 mol. dm$^{-3}$ $n$Bu$_4$NPFe$_6$/CH$_2$Cl$_2$ at 213 K. Note that spectrum (b) was only recorded to 5 000 cm$^{-1}$.
Table 4.3 U.v./visible data and $E_{1/2}$ values for $[M_2(\mu-X)_3X_6]^\text{1-}$ complexes, $M=$Ru, Os, Ir, $X=$Cl, Br.

<table>
<thead>
<tr>
<th>[M$_2$X$_9$]$^\text{1-}$</th>
<th>$E_{1/2}$ (V)$^b$ (32/33 e-)</th>
<th>Band Assignments (cm$^{-1}$)</th>
<th>$E_{1/2}$ (V)$^b$ (32/33 e-)</th>
<th>Band Assignments (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex$^a$</td>
<td></td>
<td>α</td>
<td>β</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>15 600</td>
<td>21 000</td>
<td>10 700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23 150$^d$</td>
<td>26 750</td>
<td>17 150$^e$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17 100$^f$</td>
<td>21 700</td>
<td>12 000$^g$</td>
</tr>
<tr>
<td>Ir</td>
<td>1.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os$^c$</td>
<td>1.26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>1.70</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Electrognerated in 0.5 mol. dm$^{-3}$ CH$_2$Cl$_2$/$^\text{m}$Bu$_4$NPF$_6$ in an OTTLE cell at 213 K. $^b$ Recorded in 0.5 mol. dm$^{-3}$ $^\text{n}$Bu$_4$NPF$_6$/CH$_2$Cl$_2$ at 213 K, versus Ag/AgCl. The numbers in parentheses refer to the EAN electron counting scheme (see Figure 4.8). $^c$ Near-infrared bands at 4 450 cm$^{-1}$ ($\varepsilon$=450 M$^{-1}$ cm$^{-1}$) for X=Cl, and at $-4$ 500 cm$^{-1}$ ($\varepsilon$=1 000 M$^{-1}$ cm$^{-1}$) for X=Br. $^d$ $\varepsilon$=8 200 M$^{-1}$ cm$^{-1}$. $^e$ $\varepsilon$=8 440 M$^{-1}$ cm$^{-1}$. $^f$ $\varepsilon$=7 860 M$^{-1}$ cm$^{-1}$. $^g$ $\varepsilon$=6 050 M$^{-1}$ cm$^{-1}$. $\varepsilon$ values for other bands can be calculated directly from the appropriate spectrum (see figures).
The expected E-symmetry $\chi_t(\pi) \rightarrow M^{IV}(d_{\pi})$ charge-transfer band ($\beta$ in Figure 4.15) can be readily assigned to the less intense, higher energy band in the spectra of the $[M_2(\mu-\text{Cl})_3\text{Cl}_6]^{1-}$ complexes. In the case of the nonabromodimetallates however, this second band is not as obvious. The spectra of the $[M_2(\mu-\text{Br})_3\text{Br}_6]^{1-}$ complexes (M=Ru, Os, Ir) all bear striking mutual resemblance in this region, despite the different electron count (Ru, Os versus Ir). There are consistently more features in the $[M_2(\mu-\text{Br})_3\text{Br}_6]^{1-}$ spectra, which may arise from the greater spin-orbit coupling constant of bromide ligands, where the relevant donor states are orbitally degenerate. Careful examination of the nonachloride spectra also reveals some evidence for the splitting of the second band. Taking $[\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{1-}$ as an example, a shoulder can be seen on the blue side of band $\beta$ in Figure 4.15. In the spectra of monomeric chromophores (Figure 4.13), $[\text{RuX}_3(\text{Me}_3\text{tacn})]$, the higher energy E band is again typically broader than the A band.

The spectral data for the $[M_2(\mu-X)_3X_6]^{1-}$ complexes are summarized in Table 4.3. The main features of the spectra are assigned in terms of $\chi_t(\pi) \rightarrow M(d_{\pi})$ charge-transfer. The leading band in the spectrum, band $\alpha$, always remains intact, however the second of the predicted $\chi_t(\pi) \rightarrow M(d_{\pi})$ charge-transfer bands tends to split into two or more features ($\beta, \gamma$). This is most noticeable for $X=\text{Br}$. A transition associated with the $[M(\mu-X)_3M]^{2+}$ core is not obvious in the principle u.v./visible manifold§§ of the $[M_2(\mu-X)_3X_6]^{1-}$ complexes. As shown in Chapter 2, core transitions tend to be relatively insensitive to the identity of the bridging halide. The $\chi_t(\pi) \rightarrow M(d_{\pi})$ charge-transfer manifold shifts by ~6 000 cm$^{-1}$ from $[\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{1-}$ to $[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{1-}$, without any additional bands being observed which could be assigned to a core transition. The similarities between the Os$^{IV,IV}$ and Ru$^{IV,IV}$ spectra for a given halide are striking. Should a core transition be part of this manifold, then significant differences between osmium and ruthenium, let alone iridium, with its different electron count, may be expected, on account of their contrasting 10 Dq values, spin-orbit coupling constants and capacity for metal-metal bonding.

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§§ Between 20-30 000 cm$^{-1}$ for $X=\text{Cl}$, and 15-25 000 cm$^{-1}$ for $X=\text{Br}$.  

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See Section 4.2 for the spectra of the $[M_2(\mu-\text{Br})_3\text{Br}_6]^{1-}$ complexes (M=Ru, Os).
4.5.4 Electronic Spectra of \([M_2(\mu-X)_3X_6]^{2-}\) Complexes

**Visible Region.**

The spectra of the formally \(M_2^{IV,III}\) mixed-valence \([M_2(\mu-X)_3X_6]^{2-}\) complexes are more complicated in appearance than those of their \([M_2(\mu-X)_3X_6]^{1-}\) congeners. They can still however be cross matched and accounted for on the basis of \(X_1(\pi)\rightarrow M(d_{\pi})\) charge-transfer from the terminal halides, together with an intervalence charge-transfer (i.v.c.t.) band associated with the odd electron configuration (within the \(M(\mu-X)_3M\)^{4+} core).

![Figure 4.16](image.png)

*Figure 4.16* The u.v./visible spectra of the \([Ru_2(\mu-X)_3X_6]^{2-}\) complexes, (a) \(X=Cl\), (b) \(X=Br\), electrogenerated in an OTTLE cell in 0.5 mol. dm\(^{-3}\) \(n\text{Bu}_4\text{NPF}_6/CH_2Cl_2\) at 213 K.
Compare firstly the \([\text{Ru}_2(\mu-\text{X})_3\text{X}_6]^{2-}\) spectra (X=Cl, Br) (Figure 4.16). The broad bands at 10 300 and 9 500 cm\(^{-1}\) have been assigned as the i.v.c.t. transition (\(\phi\)) in the chloride and bromide respectively (more discussion later).\(^{24}\) The remainder of the spectrum between \(\sim 15-20\) 000 cm\(^{-1}\) is accounted for by Cl\((\pi)\rightarrow \text{Ru}(d_\pi)\) charge-transfer from the terminal halides. A similarly spaced group of bands are found at lower energy in the bromide spectrum, as expected for Br\((\pi)\rightarrow \text{Ru}(d_\pi)\) charge-transfer. Focussing on the central band in each manifold (Figure 4.16 (a) and (b)) labelled \(\alpha\), the shift of this band between the two spectra is 5 700 cm\(^{-1}\). It is possible to connect the other bands in the spectra in the same way. For reasons not fully explored, the bromide spectra are again more structured. These results are summarized in Table 4.4.

The position of the i.v.c.t. band is insensitive to the identity of the halide, shifting by only 800 cm\(^{-1}\) between the \([\text{Ru}(\mu-\text{Cl})_3\text{Ru}]^{4+}\) and \([\text{Ru}(\mu-\text{Br})_3\text{Ru}]^{4+}\) species. The two bands are also of comparable width and intensity in the two systems. Because the X\((\pi)\rightarrow \text{Ru}(d_\pi)\) charge-transfer manifold is at lower energy for X=Br, the i.v.c.t. band in \([\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6]^{2-}\) is partly obscured.

<table>
<thead>
<tr>
<th>([\text{M}_2\text{X}_9]^{2-}) Complex (^a)</th>
<th>Band Assignments (cm(^{-1}))</th>
<th>i.v.c.t. band</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ru}_2\text{Cl}_9]^{2-})</td>
<td>(\text{X}<em>1(\pi)\rightarrow \text{Os}(d</em>\pi)) Charge-Transfer</td>
<td>(\alpha)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>16 500</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>11 000</td>
</tr>
<tr>
<td>([\text{Ru}_2\text{Br}_9]^{2-})</td>
<td></td>
<td>22 400</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Cl}_9]^{2-})</td>
<td></td>
<td>16 000</td>
</tr>
<tr>
<td>([\text{Os}_2\text{Br}_9]^{2-})</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Electrogenerated in 0.5 mol. dm\(^{-3}\) \(\text{nBu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2\) in an OTTLE cell at 213 K. \(^b\) \(\varepsilon=5\) 500 M\(^{-1}\) cm\(^{-1}\). \(^c\) \(\varepsilon=4\) 100 M\(^{-1}\) cm\(^{-1}\). \(^d\) Near-infrared bands at 8 270 (\(\varepsilon=110\) M\(^{-1}\) cm\(^{-1}\)) and 5 240 cm\(^{-1}\) (\(\varepsilon=840\) M\(^{-1}\) cm\(^{-1}\)) for X=Cl, and 4 700 cm\(^{-1}\) (\(\varepsilon=780\) M\(^{-1}\) cm\(^{-1}\)) for X=Br. \(^e\) \(\varepsilon=7\) 200 M\(^{-1}\) cm\(^{-1}\). \(^f\) \(\varepsilon=7\) 260 M\(^{-1}\) cm\(^{-1}\). \(\varepsilon\) values for other bands can be calculated from the appropriate spectrum.
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Turning now to the visible spectra of the diosmium complexes (Figure 4.17), the various bands in \([\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{2-}\) and \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{2-}\) manifolds can be labelled in a similar way (Table 4.4). Systematic shifts of between 5 300 and 6 800 cm\(^{-1}\) are observed, in accord with the assignment of these bands as terminal halide-to-metal charge-transfer. Comparing the spectra of \([\text{Os}_2(\mu-\text{X})_3\text{X}_6]^{2-}\) and \([\text{Ru}_2(\mu-\text{X})_3\text{X}_6]^{2-}\) complexes, band \(\alpha\), is typically 7-8 000 cm\(^{-1}\) higher in osmium for a given halide, again in accord with \(X_t(\pi)\rightarrow M(d_{\pi})\) charge-transfer transitions.

![Figure 4.17](image)

**Figure 4.17** The u.v./visible spectra of the \([\text{Os}_2(\mu-\text{X})_3\text{X}_6]^{2-}\) complexes, (a) \(X=\text{Cl}\), (b) \(X=\text{Br}\), electrogenerated in an OTTLE cell in 0.5 mol. dm\(^{-3}\) \(\text{nBu}_4\text{NPF}_6 /\text{CH}_2\text{Cl}_2\) at 213 K.
The i.v.c.t. transition in the diosmium complexes cannot be identified from the \([\text{Os}_2(\mu-X)_3X_6]^{2-}\) spectra alone. Examination of the spectral progression accompanying reduction of \([\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^1-\) to \([\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^2-\) (Figure 4.18) provides strong evidence that the i.v.c.t. band in \([\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^2-\) is in fact concealed by the charge-transfer manifold.

![Absorbance (Arbitrary Units)](image)

**Figure 4.18** The spectral changes accompanying reduction of \([\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^1-\) to \([\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^2-\).

At the foot of the charge-transfer manifold, a broad unresolved band grows. This feature cannot be associated with \(X_t(\pi)\rightarrow M(d_{\pi})\) charge-transfer, since it is expected to move to higher energy upon reduction. This is then assigned as a portion of the i.v.c.t. band, unresolved with the remainder of the band being concealed under the charge-transfer manifold. It is difficult to define the energy of the i.v.c.t. transition, however, given that the onset of the band occurs ca. 16 000 cm\(^{-1}\), and that the bandwidth at half intensity is unlikely to be greater than 5 000 cm\(^{-1}\), then the band maximum may lie between 18-19 000 cm\(^{-1}\).

If, by analogy with what is observed in ruthenium, the i.v.c.t. transition
is at marginally lower energy in the bromide, then this again would place this corresponding band near 18 000 cm$^{-1}$ in $[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{2-}$, now fully under the charge-transfer manifold. In accord with this reasoning, there is no anomalous growth of absorption on the red side of the $X_1(\pi)\rightarrow M(d_{\pi})$ charge-transfer band upon reduction of $[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{1-}$.

The $[\text{Ru}_2(\mu-X)_3X_6]^{2-}$ species have been previously described as localized mixed-valence systems, involving weakly interacting Ru$^{\text{III}}$ and Ru$^{\text{IV}}$ centres,\textit{i.e.} a class II species using the nomenclature developed by Robin and Day.\textsuperscript{53} This was concluded on the outcome of band shape analysis according to the model proposed by Hush,\textsuperscript{54} and was further supported by solution magnetic susceptibility studies.\textsuperscript{26} The magnetic susceptibility of electrogenerated solutions of $[\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6]^{2-}$ were indicative of weakly coupled $d^5/d^4$ centres (three unpaired electrons in total), as opposed to the one unpaired electron in the delocalized molecular orbital (m.o.) model. However, in a situation where a truly localized trapped-valence state prevails, the predictions of the molecular orbital bonding scheme have no force, since the conventional m.o. approach implicitly assumes a symmetric structure and a symmetric distribution of electrons between the two metal centres.

In the absence of any magnetic data on the $[\text{Os}_2(\mu-X)_3X_6]^{2-}$ complexes, and lacking the possibility of i.v.c.t. band shape analysis, it is unclear how to describe the 33 electron mixed-valence system, \textit{i.e.} localized or delocalized.

**Near-Infrared Region.**

Two weak bands ($\varepsilon<800$ M$^{-1}$ cm$^{-1}$) are observed in the near-infrared spectral region of the $[\text{Os}_2(\mu-X)_3X_6]^{2-}$ complexes. Upon reduction to the $[\text{Os}_2(\mu-X)_3X_6]^{3-}$, a highly structured band grows, at a position typical of single-ion intraconfigurational transitions in monomeric Os$^{\text{III}}$ complexes. Equally, oxidation to the $[\text{Os}_2(\mu-X)_3X_6]^{1-}$ species results in collapse of the bands, and the growth of a comparable single-ion feature attributable to an intraconfigurational transition on Os$^{\text{IV}}$. The spectra of the $[\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{2-}$ (z=2, 3) species are shown in Figure 4.19. The near-infrared spectra of $[\text{Os}_2(\mu-X)_3X_6]^{2-}$ thus contrast those of isovalent $[\text{Os}_2(\mu-X)_2X_8]^{3-}$ (Chapter 3, Section 3.4), where a complicated series of bands was observed, and attributed to broad intervalence charge-transfer and sharp single-ion
Figure 4.19 Near-infra-red spectra of (a) [Os₂(μ-Cl)₃Cl₆]²⁻, (b) spectral progression upon reduction of [Os₂(μ-Cl)₃Cl₆]²⁻ to [Os₂(μ-Cl)₃Cl₆]³⁻, and (c) [Os₂(μ-Cl)₃Cl₆]³⁻, as discussed on p168. The step at ~7 680 cm⁻¹ is due to a filter change.
transitions.
It has been previously noted that there are no similar bands in the near-infrared region of the analogous \([\text{Ru}_2(\mu-X)_3X_6]^{2-}\) spectra.

### 4.5.5 Electronic Spectra of \([\text{M}_2(\mu-X)_3X_6]^{3-}\) Complexes

The spectra of the \([\text{M}_2(\mu-X)_3X_6]^{3-}\) complexes (\(\text{M}=\text{Ru}, X=\text{Cl, Br}\)) have been briefly discussed by several authors. Cotton \textit{et al.} have completed a theoretical study on the \([\text{Ru}_2(\mu-\text{Cl})_3\text{Cl}_6]^{3-}\) anion, using the SCF-X\(\alpha\)-SW method to calculate a \((a_1')^2(e_1')^4(e_1'')^4(a_2'')^0\) ground state. They then attempted to assign the electronic spectrum in terms of transitions within the metal-metal core, on the basis of this model. They found that the observed spectrum was not at all consistent with that predicted, and attributed this to the poor resolution of the photoacoustic spectrum of \(\text{Cs}_3[\text{Ru}_2(\mu-\text{Cl})_3\text{Cl}_6]\).

More recently Seddon \textit{et al.} used this same molecular orbital (m.o.) scheme to propose a tentative assignment of the spectrum of \([\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6]^{3-}\). In contrast to Cotton’s assignments, Seddon \textit{et al.} concluded that the observed bands originated from orbitals which were largely bromide in character, \textit{i.e.} l.m.c.t. from the bridging and terminal halides into vacant metal acceptor orbitals.

Both groups have considered only one complex, \([\text{Ru}_2(\mu-\text{Cl})_3\text{Cl}_6]^{3-}\) or \([\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6]^{3-}\), whereas in the present work the spectra of the four related complexes have been compared; \([\text{Ru}_2(\mu-X)_3X_6]^{3-}\) and the previously unavailable \([\text{Os}_2(\mu-X)_3X_6]^{3-}\) (\(X=\text{Cl, Br}\)). It is argued below that neither of the above assignments is satisfactory, and a better explanation of the \([\text{M}_2(\mu-X)_3X_6]^{3-}\) spectra can only be achieved by assigning the spectrum as a combination of \(X_1(\pi)\rightarrow M^{\text{III}(d_{\pi})}\) charge-transfer and core transitions between orbitals which are essentially metal based in character.

**Visible Region.**

Upon examining the spectra of \([\text{Ru}_2(\mu-X)_3X_6]^{3-}\) (\(X=\text{Cl, Br}\)) presented in Figure 4.20, it becomes apparent that the most prominent feature in each spectrum (band \(\alpha\)) cannot be assigned as \(X_1(\pi)\rightarrow\text{Ru}(d_{\pi})\) charge-transfer in both cases, since the maxima differ by only 2 900 cm\(^{-1}\). Instead a more
appealing solution lies in the assignment of bands $\beta$ and $\gamma$ as $X_1(\pi) \rightarrow \text{Ru}(d_{\pi})$ charge-transfer; the shifts between Cl and Br being 6 200 and 5 700 cm$^{-1}$ for $\beta$ and $\gamma$ respectively (Table 4.5).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{spectrum.png}
\caption{The electronic spectra of $[\text{Ru}_2(\mu-X)_3X_6]^3^-$ complexes, (a) $X=\text{Cl}$, (b) $X=\text{Br}$.}
\end{figure}
The β and γ bands occur at sensible energies for \(X(\pi) \rightarrow Ru(d_{\pi})\) charge-transfer. In monomeric facial \([RuX_3(Me_3tacln)]\) complexes, the \(X(\pi) \rightarrow Ru(d_{\pi})\) charge-transfer span the regions as follows; for \(X=Cl\), 25-29 000 cm\(^{-1}\), for \(X=Br\), 19-26 000 cm\(^{-1}\). The \(X(\pi) \rightarrow Ru(d_{\pi})\) charge-transfer bands just assigned for the \([Ru_2(\mu-X)X_6]^{3-}\) complexes \((X=Cl, Br)\) fall in this region, in fact the lowest energy band in both the monomeric and bimetallic complexes is coincident for any one halide.

<table>
<thead>
<tr>
<th>Complex ([M_2X_9]^{3-})</th>
<th>Near-i.r. Band</th>
<th>Core Band</th>
<th>(X(\pi) \rightarrow Os(d_{\pi})) Charge-Transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>([Ru_2Cl_9]^{3-})</td>
<td>5 600</td>
<td>22 600 (^b)</td>
<td>25 150</td>
</tr>
<tr>
<td>([Ru_2Br_9]^{3-})</td>
<td>5 250</td>
<td>19 700 (^c)</td>
<td>(\sim 19 000)</td>
</tr>
<tr>
<td>([Os_2Cl_9]^{3-})</td>
<td>5 600</td>
<td>26 600 (^d)</td>
<td>28 800</td>
</tr>
<tr>
<td>([Os_2Br_9]^{3-})</td>
<td>5 400</td>
<td>24 400 (^e)</td>
<td>(\sim 22 500)</td>
</tr>
<tr>
<td>(\sim 5 600)</td>
<td>23 250</td>
<td>(\sim 23 600)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Recorded in 0.5 mol dm\(^{-3}\) \(nBu_4NPF_6/CH_2Cl_2\) in an OTTLE cell at 213 K. \(^b\) \(\varepsilon=9 400 M^{-1} cm^{-1}\). \(^c\) \(\varepsilon=6 050 M^{-1} cm^{-1}\). \(^d\) \(\varepsilon=9 000 M^{-1} cm^{-1}\), estimated value, since this complex was only prepared in situ, and not isolated. \(^e\) \(\varepsilon=6 170 M^{-1} cm^{-1}\).

In addition, upon two-electron oxidation from \([Ru_2(\mu-X)X_6]^{3-}\) to \([Ru_2(\mu-X)X_6]^{1-}\), the charge-transfer manifold has moved to by \(\sim 8 100\) cm\(^{-1}\) and 7 600 cm\(^{-1}\) to lower energy for \(X=Cl\) and \(Br\) respectively. Such shifts are typical of what is observed for monomeric Ru/X systems upon oxidation from Ru\(^{III}\) to Ru\(^{IV}\),\(^{40}\) providing further evidence that the \(X(\pi) \rightarrow Ru(d_{\pi})\) charge-transfer assignments are correct for the \([Ru_2(\mu-X)X_6]^{3-}\) complexes.

Having located the \(X(\pi) \rightarrow Ru(d_{\pi})\) charge-transfer bands, the remaining feature of the spectra (band \(\alpha\)) is assigned as a core transition. Similarly assigned bands were not obvious in the spectra of the \([Ru_2(\mu-X)X_6]^{1-}\) and \([Ru_2(\mu-X)X_6]^{2-}\) complexes. Although the m.o. scheme formally predicts
metal-metal bonding to decrease upon ascending from the 32 to the 34 electron system, intuitively the opposite is expected. Metal-metal repulsion is greatly diminished in the $M_2^{III,III}$ systems, and $d$ orbital contraction will be less pronounced, so considerable $d$ orbital overlap can be envisaged, resulting in the formation of more significant metal-metal interactions. Such a notion is supported by magnetic measurements, discussed at length in Section 4.6. Accordingly, a more pronounced core transition in the spectra of the $[Ru_2(\mu-X)_3X_6]^{3-}$ complexes is not unexpected.

As described in Chapter 2, the spectra of the $[Ru_2(\mu-X)_3(Me_3tacn)_2]^{3+}$ complexes were assigned in terms of two prominent core transitions, these spectra not being complicated by $X_I(1t)\rightarrow Ru(d_{1t})$ charge-transfer bands. The core bands were relatively insensitive to the identity of the halide bridge, shifting by only $\sim 2000$ cm$^{-1}$ to lower energy upon replacing Cl by Br. From Table 4.5, this same shift in band $\alpha$ is $2900$ cm$^{-1}$ for the $[Ru_2(\mu-X)_3X_6]^{3-}$ complexes.

Consideration of the spectra of the diosmium nonahalides in a similar way yields a fully consistent analogous assignment. The band assignments are summarized in Table 4.5, and the spectra shown in Figures 4.21 and 4.22. The $X_I(\pi)\rightarrow M^{III}(d_{1t})$ charge-transfer bands ($\beta, \gamma$) are at higher energy for osmium (compared with ruthenium), as predicted from electrode potentials. The core transition likewise is found at higher energy, which could come as a consequence of the greater single-ion 10 $Dq$ value for osmium, or as is equally likely, through increased metal-metal interaction within the $\{Os(\mu-X)_3Os\}^{3+}$ core, culminating in an increased spread of the m.o. manifold.

**Near-Infrared Region.**

The highly structured band found between 5-6 000 cm$^{-1}$ in the spectra of the $[Os_2(\mu-X)_3X_6]^{3-}$ complexes is reminiscent of a single-ion transition. The spectra of concentrated solutions of the isoelectronic $[Ru_2(\mu-X)_3X_6]^{3-}$ complexes show a feature in a similar position. However these bands are distinctly lacking in fine structure, and are significantly less intense ($\epsilon<100$ M$^{-1}$ cm$^{-1}$) than the structured bands observed in the spectra of the diosmium complexes ($\epsilon\sim 800-1200$ M$^{-1}$ cm$^{-1}$). Although at similar energy, the bands in the diosmium spectra may have a different assignment to those
in diruthenium. The bands in the spectra of the latter were tentatively assigned by Kennedy as core $\delta^* \rightarrow \sigma^*$ transitions.\textsuperscript{28}

*Figure 4.21* The electronic spectra of $\text{[Os}_2(\mu-X)_3X_3]^3^{-}$ complexes, (a) $X=\text{Cl}$, (b) $X=\text{Br}$. 

The assignments in the $\text{[M}_3\mu-X_3X_3]^3^{-}$ spectra are probably not fully clarified.
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Figure 4.22 The spectral changes accompanying reduction of \( [\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{2-} \) to \( [\text{Os}_2(\mu-\text{Cl})_3\text{Cl}_6]^{3-} \).

4.5.6 Summary

The visible and near-infrared spectra of the \([\text{M}_2(\mu-X)_3\text{X}_6]^{1/-2/-3-}\) complexes have been empirically assigned, i.e. assigned according to transition type. In addition, all of these species have intense, high energy bands in the u.v. region of the spectrum, some of which are presumably \( X_t(\pi)\rightarrow M(e_g) \) transitions, however, no attempt has been made to correlate this data.

The visible spectra of the \([\text{M}_2(\mu-X)_3\text{X}_6]^{1/-2/-3-}\) complexes (\( \text{M}=\text{Ru, Os and X=Cl, Br} \)) are all systematically related, the spectra being accounted for in terms of terminal halide-to-metal charge-transfer, core transitions, and in the \([\text{M}_2(\mu-X)_3\text{X}_6]^{2-}\) complexes, an intervalence charge-transfer band (only readily observed for \( \text{M}=\text{Ru} \)). Whether the mixed-valence \([\text{Os}_2(\mu-X)_3\text{X}_6]^{2-}\) species is best described as localized or delocalized is unclear, and further magnetic studies are warranted.

The assignments in the \([\text{M}_2(\mu-X)_3\text{X}_6]^{3-}\) spectra are perhaps not as
conclusive as for \([M_2(\mu-X)X_6]^{2-}\) and \([M_2(\mu-X)X_6]^{1-}\) however \(X_1(\pi)\to M(d_{\pi})\) charge-transfer transitions alone cannot account for all the prominent features. For this reason a core transition is also assigned. The spectral similarities between the osmium and ruthenium derivatives, so evident in the \([M_2(\mu-X)X_6]^{1-}\) and \([M_2(\mu-X)X_6]^{2-}\) complexes, are no longer as obvious for the \([M_2(\mu-X)X_6]^{3-}\) species, though we can trace a one-to-one correlation between the \([Ru_2(\mu-X)X_6]^{3-}\) and \([Os_2(\mu-X)X_6]^{3-}\) band systems.

The near-infrared spectra of the \([Os_2(\mu-X)X_6]^{1-}\) and \([Os_2(\mu-X)X_6]^{3-}\) complexes (\(X=Cl, Br\)) reveal weak, vibronically structured bands, reminiscent of intraconfigurational transitions in monomeric OsIV and OsIII complexes. The mixed-valence \([Os_2(\mu-X)X_6]^{2-}\) species have two broader bands in this region of the spectrum, neither of which shows any signs of resolved vibronic structure.

The above conclusions are taken up again in Section 4.7, which examines the nature of the bonding in the \([Os_2(\mu-X)X_6]^{1-/2-/3-}\) systems.
4.6 VARIABLE TEMPERATURE MAGNETIC STUDIES

The magnetic susceptibilities of powdered samples of $\mathrm{nBu}_4\mathrm{N}[\mathrm{Os}_2(\mu-\mathrm{Br})_3\mathrm{Br}_6]$ and $\mathrm{Ph}_4\mathrm{P}[\mathrm{Os}_2(\mu-\mathrm{Br})_3\mathrm{Br}_6]$ have been recorded between temperatures of 300 and 4.2 K, in a field of 10 000 gauss. Part (a) of Figure 4.23 shows the susceptibility per osmium ($\chi_{\mathrm{Os}}$) of $\mathrm{Ph}_4\mathrm{P}[\mathrm{Os}_2(\mu-\mathrm{Br})_3\mathrm{Br}_6]$ is almost constant between 300-50 K, before rising sharply below ~30 K. The sudden increase in $\chi_{\mathrm{Os}}$ at low temperature is most probably due to the presence of an impurity with Curie-like paramagnetic behaviour. The magnetic moment of $\mathrm{Ph}_4\mathrm{P}[\mathrm{Os}_2(\mu-\mathrm{Br})_3\mathrm{Br}_6]$ (part (b) of Figure 4.23) is observed to decrease steadily with temperature.

The variable temperature magnetic behaviour of $[\mathrm{Os}_2(\mu-\mathrm{Br})_3\mathrm{Br}_6]^{1-}$ described above is very similar with that of $[\mathrm{OsBr}_6]^{2-}$ and $[\mathrm{Os}_2(\mu-\mathrm{Br})_2\mathrm{Br}_6]^{2-}$, previously discussed in Chapter 3. In each of these complexes (all $d^4/d^4$) the magnetic susceptibility is essentially invariant with temperature, as expected since the paramagnetism arises entirely from the second order Zeeman effect (T.I.P.). A sudden increase in $\chi_{\mathrm{Os}}$ at very low temperatures is observed in all three complexes, which is attributable to traces of higher spin impurities. Since $\chi_{\mathrm{Os}}$ is constant with respect to temperature, the effective magnetic moment per osmium ($\mu_{\mathrm{Os}}$) is proportional to $T^{1/2}$, and so $\mu_{\mathrm{Os}}$ decreases in a parabolic manner upon lowering the temperature. The magnetic moments do not approach zero at the low temperature limit on account of the paramagnetic impurity. The room temperature magnetic moments of the $[\mathrm{Os}_2(\mu-\mathrm{Br})_2\mathrm{Br}_6]^{2-}$ and $[\mathrm{Os}_2(\mu-\mathrm{Br})_3\mathrm{Br}_6]^{1-}$ complexes are only slightly smaller than that of $[\mathrm{OsBr}_6]^{2-}$ (Table 4.6).

It is still uncertain whether the similarities noted above are due to very weak, almost zero antiferromagnetic coupling between the Os$^{IV}$ ions in $[\mathrm{Os}_2(\mu-\mathrm{Br})_2\mathrm{Br}_6]^{2-}$ and $[\mathrm{Os}_2(\mu-\mathrm{Br})_3\mathrm{Br}_6]^{1-}$; alternatively the magnetic measurements may simply be insensitive to the degree of Os$^{IV}$...Os$^{IV}$ interaction, as discussed in Section 3.5 of Chapter 3. Whatever the answer, should the $[\mathrm{Os}_2(\mu-\mathrm{Br})_3\mathrm{Br}_6]^{1-}$ complexes contain a strong metal-metal bond, then the magnetic moment is expected to be lowered considerably.

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$^\dagger\dagger$ The introductory discussion in Section 3.5 of Chapter 3, concerning the magnetism of Os$^{IV}$ complexes, is again of relevance here.
The magnetism of the \((\text{Ph}_4\text{P})_3[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\) \((d^5/d^5)\) was also recorded under identical conditions to those described above for the \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\) complexes. The magnetic properties of \((\text{Ph}_4\text{P})_3[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\) are distinctly different from those of \((\text{Ph}_4\text{P})[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\) (Table 4.6). The former complex is essentially diamagnetic at room temperature, with a magnetic moment of 0.28 B.M. per Os\(^{III}\). Such a low moment is in accord with the formation of a metal-metal bond. The magnetic moment decreases as the temperature is lowered, although there is considerable scatter in these points, on account of the very weak paramagnetism (Figure 4.24). The magnetic susceptibility is essentially constant between 300-100 K, before increasing rapidly at very low temperatures. The low temperature behaviour is attributable to a trace of monomeric impurity in the sample.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\mu_{\text{eff}}) per molecule (^a)</th>
<th>(\mu_{\text{eff}}) per Os (^a)</th>
<th>(10^6 \chi_m) (^b)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{Ph}_4\text{P})_2[\text{OsBr}_6])</td>
<td>c</td>
<td>1.63</td>
<td>1120</td>
<td>d</td>
</tr>
<tr>
<td>\text{Ph}_4\text{P}[\text{Os}_2\text{Br}_9]</td>
<td>2.01</td>
<td>1.42</td>
<td>1690</td>
<td>d</td>
</tr>
<tr>
<td>\text{nBu}_4\text{N}[\text{Os}_2\text{Br}_9]</td>
<td>2.16</td>
<td>1.52</td>
<td>1900</td>
<td>d</td>
</tr>
<tr>
<td>((\text{Ph}_4\text{P})_2[\text{Os}<em>2\text{Br}</em>{10}])</td>
<td>2.15</td>
<td>1.52</td>
<td>1940</td>
<td>d</td>
</tr>
<tr>
<td>((\text{Ph}_4\text{P})_3[\text{OsBr}_9])</td>
<td>0.40</td>
<td>0.28</td>
<td>35</td>
<td>d</td>
</tr>
<tr>
<td>((\text{nBu}_4\text{N})_3[\text{Ru}_2\text{Br}_9])</td>
<td>1.67</td>
<td>1.18</td>
<td>580</td>
<td>34</td>
</tr>
</tbody>
</table>

\(^a\) Bohr magnetons. \(^b\) c.g.s.u. \(^c\) For monomeric complexes, \(\mu_{\text{eff}}\) per molecule=\(\mu_{\text{eff}}\) per Os. \(^d\) This work.

A previous magnetic study on a powdered sample of \((\text{nBu}_4\text{N})_3[\text{Ru}_2(\mu-\text{Br})_3\text{Br}_6]\) revealed the magnetic susceptibility decreased from its room temperature value of 580 c.g.s.u., to \(-370\) c.g.s.u. at 115 K (Table 4.6).\(^{27}\) At lower temperatures \(\chi_{\text{Ru}}\) increased sharply, due to some

\(^{27}\) A dichloromethane/toluene glass of \((\text{Ph}_4\text{P})_3[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\) was also e.s.r. silent at 40 K.
Figure 4.23 Variation of (a) susceptibility (per Os) and (b) magnetic moment (per Os) with absolute temperature for Ph₄P[Os₂(μ-Br)₃Br₆].
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Figure 4.24 Variation of (a) susceptibility (per Os) and (b) magnetic moment (per Os) with absolute temperature for \((\text{Ph}_4\text{P})_3\text{Os}_2(\mu\text{-Br})_3\text{Br}_6\).
paramagnetic impurity. The weak paramagnetism was explained in terms of a low lying triplet state 
\((\text{a}_1')^2(\text{e}_1')^4(\text{e}_1'')^3(\text{a}_2'')^1)\), thermally populated at room 
temperature. The observed decrease in \(\chi_{\text{Ru}}\) upon cooling was in accord with 
this explanation. As noted above, there is very little variation of \(\chi_{\text{Os}}\) with 
temperature in the \((\text{Ph}_4\text{P})_3[\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\) complex (Figure 4.24, part (a)). 
This may be due to greater splitting of the \(\delta^*/\sigma^*\) orbitals, a consequence of 
the increased \(d\) orbital overlap in the diosmium system. The triplet state is 
therefore not populated to any large extent at room temperature.

The difference between the diruthenium and diosmium systems is 
suggestive of a stronger metal-metal bond in the latter mentioned complex. 
This point is discussed further in Section 4.7, where the bonding in these 
systems is discussed in conjunction with voltammetric and spectroscopic 
measurements presented in Sections 4.4 and 4.5.
4.7 SUMMARY

The triple-bridged, face-sharing diosmium complexes, \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{1-}\) and \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{3-}\), have been isolated for the first time as organo-soluble salts. The analogous chloride complex has been prepared and characterized in situ.

The results described in Sections 4.2 and 4.3 have established that the double-bridged \([\text{Os}_2(\mu-X)_2X_8]^{2-}\) complex is an intermediate in the formation of the triple-bridged \([\text{Os}_2(\mu-X)_3X_6]^{1-}\) species from \([\text{OsX}_6]^{2-}\). Figure 4.25 summarizes the relationships between the \([\text{OsX}_6]^{2-}\), \([\text{Os}_2(\mu-X)_2X_8]^{2-}\) and \([\text{Os}_2(\mu-X)_3X_6]^{2-}\) complexes. The TFAA transformation of \([\text{Os}_2(\mu-X)_2X_8]^{2-}\) to \([\text{Os}_2(\mu-X)_3X_6]^{1-}\), step 2, was not established for \(X=\text{Cl}\). The remainder of the scheme is appropriate for both \(X=\text{Cl}\) and \(\text{Br}\). The precise role by which TFAA functions in steps 1 and 2 is not clearly understood, except to say it presumably acts as a halide abstracting agent, and is a very poor solvent for the reaction products. The formation of the triple-bridged complex by redox induced elimination of halide from \([\text{Os}_2(\mu-X)_2X_8]^{4-}\) is perhaps the more rational route, and it applies to both \(X=\text{Cl}\) and \(\text{Br}\).

The redox chemistry of the \([\text{Os}_2(\mu-X)_3X_6]^{2-}\) complexes has been presented, and can be related to that of the \([\text{Os}_2(\mu-X)_2X_8]^{2-}\), \([\text{Ru}_2(\mu-X)_3X_6]^{2-}\), \([\text{M}_2(\mu-\text{Cl})_3\text{Cl}_6]^{2-}\) (\(\text{M}=\text{W}, \text{Re}, \text{Ir}\)) and \([\text{Os}_2(\mu-X)_3(\text{PR}_3)_6]^{2+}\) complexes in a systematic and periodic manner. The electronic spectra of the \([\text{Os}_2(\mu-X)_3X_6]^{2-}\) complexes (\(X=\text{Cl}, \text{Br}\)) were collected in three different oxidation levels (\(z=1, 2, 3\)), and compared with those of the \([\text{M}_2(\mu-X)_3X_6]^{2-}\) systems (\(\text{M}=\text{Ru}, \text{Ir}, X=\text{Cl}, \text{Br}\) and \(z=1, 2, 3\)). Empirical assignments of the main spectral features have been offered, and variable temperature magnetic studies were also carried out on various salts of \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{1-}\) and \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{3-}\).

At the outset of this work we were interested in the variation of metal-metal bonding as a function of oxidation level, and identity of the metal ion, i.e. osmium versus ruthenium. Comparing the data collected here on the diosmium complexes, with that previously obtained by Coombe, Heath and Kennedy on the diruthenium and iridium systems, enables some purely descriptive (qualitative) bonding comparisons to be made.

The u.v./visible spectra of the \([\text{M}_2(\mu-X)_3X_6]^{1-}\) complexes (\(\text{M}=\text{Ru}, \text{Os}, \text{Ir}\),
Figure 4.25 Reaction scheme depicting chemical and electrochemical transformations of [OsBr₆]²⁻, [Os₂(μ-Br)₂Br₈]³⁻ and [Os₂(μ-Br)₃Br₆]²⁻. All processes are in CH₂Cl₂ except 1 and 2, which are in TFAA (silicon oil bath temperatures are quoted for 1 and 2). Hatched complexes are short lived in electrochemical solutions.
X=Cl, Br) are all very similar. The principal bands can be assigned as 
$X_t(\pi) \rightarrow M_{1V}(d_{\pi})$ charge-transfer transitions, with no indication of any prominent core transitions. The periodic variation of $E_{1/2}(32/33)$ through the $[M_2(\mu-Cl)_3Cl_6]^2-$ series (M=W, Re, Os, Ir) and the paramagnetism of $[Os_2(\mu-Br)_3Br_6]^{1-}$ suggests the $[Os_2(\mu-X)_3X_6]^{1-}$ complexes do not contain a strong metal-metal bond. Application of the molecular orbital scheme to these systems assumes direct metal-metal interactions are the dominant bonding influence. However, such an assumption ignores the tendency of high oxidation states to diminish metal-metal interactions, through $d$ orbital contraction and electrostatic repulsion.

The main features in the visible spectra of the $[M_2(\mu-X)_3X_6]^{2-}$ complexes can be assigned in terms of $X_t(\pi) \rightarrow M(d_{\pi})$ charge-transfer, and in the case of M=Ru, an i.v.c.t. transition. Analysis of this i.v.c.t. band by Kennedy and Heath suggests a valence-trapped situation prevails in the $[Ru_2(\mu-X)_3X_6]^{2-}$ complexes.

Previous magnetic studies on electrogenerated solutions of $[Ru_2(\mu-X)_3X_6]^{2-}$ found three unpaired electrons, indicative of weakly coupled $d^5/d^4$ centres. As in the $[M_2(\mu-X)_3X_6]^{1-}$ systems, the molecular orbital bonding description is inappropriate for $[M_2(\mu-X)_3X_6]^{2-}$, since it proposes just one unpaired electron in the strongly metal-metal bonded system (Figure 4.26).

It remains unclear how to classify the mixed-valence $[Os_2(\mu-X)_3X_6]^{2-}$ complexes. The i.v.c.t. band in these complexes, clearly visible in the trapped $[Ru_2(\mu-X)_3X_6]^{2-}$ species, is thought to be concealed underneath the $X_t(\pi) \rightarrow M(d_{\pi})$ charge-transfer manifold. Given that the separation of the 32/33 and 33/34 electron couples is considerably greater in the diosmium complexes, and the intrinsic tendency of 5$d$ transition metals to be more involved in metal-metal bonding (through the greater radial extension of their $d$ orbitals), it is reasonable to expect greater metal-metal interaction in the diosmium systems (as compared with that in diruthenium). Further studies of the 33 electron system are required in order to gain a better understanding of the bonding interactions within the $[M(\mu-X)M]^4+$ core.

Optical and magnetic data suggests the non metal-metal bonded description of the 32 and 33 electron systems is no longer appropriate at the 34 electron level. The diamagnetism of $(Ph_4P)\text{[Os}_2\text{(μ-Br)}_3\text{Br}_6]$ suggests the
formation of a metal-metal bond. In accord with this increased metal-metal interaction, the electronic spectra of the \([M_2(\mu-X)_3X_6]^{3-}\) complexes reveal a core transition, as well as the expected \(X_t(\pi)\rightarrow\text{M}^{\text{III}}(d^5)\) charge-transfer bands. The abrupt change in the degree of metal-metal bonding upon reaching the 34 electron level can be rationalized in terms of expansion of the \(d\) orbitals, and a decrease in the electrostatic repulsion between the metal centres. The molecular orbital bonding scheme becomes appropriate for such systems (Figure 4.26).

\[
\begin{align*}
\sigma^* & \quad \text{---} & \text{---} & \text{---} \\
\delta^* & \quad \text{#} & \text{---} & \text{#} \\
\delta & \quad \text{---} & \text{#} & \text{#} \\
\sigma & \quad \text{#} & \text{#} & \text{#} \\
M_2^{\text{IV,IV}} & \quad (d^4/d^4) & \text{---} & \text{---} \\
M_2^{\text{IV,III}} & \quad (d^4/d^5) & \text{---} & \text{---} \\
M_2^{\text{III,III}} & \quad (d^5/d^5) & \text{---} & \text{---}
\end{align*}
\]

**Figure 4.26** Molecular orbital schemes for \([M_2(\mu-X)_3X_6]^{3-}\) complexes, \(M=\text{Ru, Os}\). The vacant \(\pi/\pi^*\) orbitals derived from the \(eg\) \(d\) orbitals have been omitted purposely.

The difference between 4\(d\) and 5\(d\) transition metal elements also becomes apparent for the first time at the 34 \(M_2^{\text{III,III}}\) electron level. On the basis of magnetic measurements it is suggested that the metal-metal bond in the diosmium \([\text{Os}_2(\mu-X)_3X_6]^{3-}\) complexes is appreciably stronger than in their diruthenium analogues. This is comparable with what is observed in the \([M_2(\mu-X)_3X_6]^{3-}\) complexes (\(M=\text{Mo, W}\)), where the metal-metal bond strength increases considerably from \([\text{Mo}_2(\mu-X)_3X_6]^{3-}\) to \([\text{W}_2(\mu-X)_3X_6]^{3-}\)\(^{56}\).

The difference in metal-metal bonding between osmium and ruthenium in the \([M_2(\mu-X)_3X_6]^{3-}\) complexes stands in contrast to the
[M₂(µ-X)₃(PR₃)₆]³⁺ systems, where the metal-metal interactions are thought to be very similar (and weak). The bonding differences between the isoelectronic {Os(µ-X)₃Os}³⁺ cores can be rationalized in terms of the π-bonding properties of the terminal phosphine and halide ligands.

4.3.3 Synthesis of Homoleptic Térnary Complexes

(1) Tetra-n-butylammonium tri-µ-bromo-bis(-aza-tetradentate (IV, IV)

(Ph₃P)₄PBr₂ was weighed into a 150 ml round bottomed flask, and 30 ml of neat trifluoroacetic acid added with stirring. The resulting dark mixture was cooled vigorously under N₂ for 8 hours. The fine, dark precipitate which had formed was collected by filtration, washed with fresh trifluoroacetic acid, and dried under nitrogen. The essentially dry material was then pumped under high vacuum at 273 K for 8 hours (0.54 g, 91%).

Microanalysis: Cδ (%) for C₁₄H₂₆Br₂N₂O₄: C 42.2, H 2.0, N 5.6, Br 32.90

Found (％): C 42.76, H 2.74, N 5.07, Br 31.97

4.3.5 Materials and Methods
4.8 EXPERIMENTAL

4.8.1 General Remarks

The voltammetric, spectroelectrochemical and magnetic apparatus have been previously discussed in Chapters 1 and 2, as was the spectroscopic instrumentation. Constant potential bulk electrosynthesis was performed in a jacketed, three compartment H-cell. The working electrode consisted of a platinum mesh basket, the auxiliary electrode of a platinum wire coil, and the reference electrode was as described for voltammetric measurements. The contents of the cell were cooled using a Lauda RL6 circulating bath, previously described in Chapter 1.

4.8.2 Materials and Methods

The reagents used were those listed in chapter 3, with the addition of nBu₄NBH₄, which was supplied by the Aldrich Chemical Company. Ph₄PBH₄ was synthesized by a variation of a literature procedure, from NaBH₄ (B.D.H.) and Ph₄PCl (Aldrich). The starting materials were all prepared as described in Chapter 3, and the (nBu₄N)₃[Ru₂(µ-X)₃X₆] (X=Cl, Br) compounds by improved literature routes.

4.8.3 Synthesis of Nonahalodiosmate Complexes

(i) Tetra-n-butylammonium tri-µ-bromo-hexabromodiosmate(IV,IV)

(nBu₄N)₂[OsBr₆] (0.64 g, 0.23 mmol.) was weighed into a 10.0 ml. round bottomed flask, and 5.0 ml. of neat trifluoroacetic acid added with stirring. The resulting dark mixture was boiled vigorously under N₂ for 8 hours. The fine, dark precipitate which had formed was collected by filtration, washed with fresh trifluoroacetic acid, and dried under nitrogen. The essentially dry material was then pumped under high vacuum at 373 K for 8 hours (0.34 g, 91%).

Microanalysis: Calc.(%) for C₁₆H₃₆Br₉NOs₂; C 14.32, H 2.70, N 1.04, Br 53.59
Found (%); C 14.75, H 2.74, N 1.07, Br 53.57
Far Infra-red Spectrum: (polythene disc, prepared in n-hexane) 234 cm$^{-1}$ (s), 197 (m).

This compound was also prepared by two other procedures, each involving different starting materials. Vigorous boiling of (nBu$_4$N)$_2$[Os$_2$(µ-Br)$_2$Br$_8$] or nBu$_4$N[OsBr$_5$(MeCN)] in neat trifluoroacetic acid also yielded nBu$_4$N[Os$_2$(µ-Br)$_3$Br$_6$].

(ii) Tetraphenylphosphonium tri-µ-bromo-hexabromodiosmate(IV,IV)

The tetraphenylphosphonium salt of [Os$_2$(µ-Br)$_3$Br$_6$]$^{1-}$ was prepared in essentially the same way as nBu$_4$N[Os$_2$(µ-Br)$_3$Br$_6$]. 0.31 g of (Ph$_4$P)$_2$[OsBr$_6$] in 2.50 ml. of neat trifluoroacetic acid gave 0.15 g (91 %) of Ph$_4$P[Os$_2$(µ-Br)$_3$Br$_6$] after 120 hours of vigorous boiling.

Microanalysis: Calc. (%) for C$_{24}$H$_{20}$Br$_9$Os$_2$P: C 20.03, H 1.40, P 2.15

Found (%): C 20.40, H 1.37, P 2.46

Far Infra-red Spectrum: (polythene disc, prepared in n-hexane) 235 cm$^{-1}$ (s), 222 (s), 184 (m).

(iii) Tris(Tetra-n-butylammonium) tri-µ-bromo-hexabromodiosmate (III,III)

nBu$_4$N[Os$_2$(µ-Br)$_3$Br$_6$] (46.3 mg, 3.45 x 10$^{-5}$ mol.) was dissolved under nitrogen in 10.0 ml. of freshly distilled, deoxygenated dichloromethane, prechilled using an acetone/dry ice bath to 203 K. Two mole equivalents of an nBu$_4$NBH$_4$/CH$_2$Cl$_2$ solution (i.e. 1.06 ml. of an 0.069 M solution) was then added dropwise to this stirring solution, the temperature maintained at 203 K. The reduction was monitored by u.v./visible spectroscopy, and on occasions it was necessary to add 10-20 % excess of the borohydride solution to achieve complete reduction to the [Os$_2$(µ-Br)$_3$Br$_6$]$^{3-}$ species. The mixture was then stirred for 2-3 hours, the temperature rising slowly. The brown/yellow solution was then transferred to a Schlenk flask, and degassed diethyl ether added to the point of crystallization. Refrigeration then
yielded fine, dark coloured needles of \((nBu_4N)_3[Os_2(\mu-Br)_3Br_6]\), which could be filtered off, washed with ether and dried (32 mg, 52 %).

**Microanalysis:** Calc.(%) for \(C_{48}H_{108}Br_9N_3Os_2\); C 31.56, H 5.96, N 2.30, Br 39.36

Found (%); C 31.25, H 6.26, N 2.23, Br 39.21

**Far Infra-red Spectrum:** (polythene disc, prepared in n-hexane) 223 cm\(^{-1}\) (s), 203 (s), 181 (m).

(iv) **Tris(tetraphenylphosphonium) tri-\(\mu\)-bromo-hexabromo-diosmate\(\text{III,III}\)**

Using \(Ph_4P[Os_2(\mu-Br)_3Br_6]\) and \(Ph_4PBH_4\) by the procedure described above, yielded \((Ph_4P)_3[Os_2(\mu-Br)_3Br_6]\) as thin green/yellow plates, in 68 % yield.

**Microanalysis:** Calc.(%) for \(C_{72}H_{60}Br_9Os_2P_3\); C 40.83, H 2.86, P 4.39

Found (%); C 40.17, H 2.71, P 4.28

(v) **Tris(tetra-n-butylammonium) tri-\(\mu\)-chloro-hexachloro-diosmate\(\text{III,III}\)**

Solutions of the above complex were electrogenerated in a bulk electrosynthetic cell, described in Section 4.8.1. \((Ph_4P)_2[Os_2(\mu-Cl)_2Cl_8]\) (typically 50 mg) was dissolved in the deoxygenated precooled electrolyte solution (0.5 mol. dm\(^{-3}\) \(nBu_4NPd_6/CH_2Cl_2\)), under an argon cover. Electrolysis at -0.8 V, 203 K was continued until the current decayed to essentially zero, the linear stirred voltammogram showing \([Os_2(\mu-Cl)_2Cl_8]\)\(^4-\) had been formed. The solution was then slowly warmed, rearrangement beginning at -233 to 243 K. When the rearrangement was complete (at -273 K), as shown by c.v. and a.c.v., the solution was transferred under argon to a Schlenk flask, for further use.
4.9 REFERENCES

Chapter 4

52. L. Dubicki, private communication.

The final chapter of this thesis is principally concerned with monomeric complexes. Synthetic strategies have been developed to yield a wide variety of osmium complexes. Their redox chemistry and charge-transfer spectra are presented, and some fundamental consequences of these physical measurements are discussed. The interest in such monomeric complexes stems from the possibility of isolating structurally distinct Os(V) complexes as air-stable precursors for further studies. Upon warming, air-stable, asymmetrical derivatives of [Os(NCO)(CO)2][O2] and [Os(NCO)(CO)2][O2] are formed, important these broader...
SYNTHESIS, CHARACTERIZATION AND SPECTROELECTROCHEMISTRY OF SUBSTITUTED MONOMERIC OSMIUM HALIDE COMPLEXES.

5.1 INTRODUCTION

5.1.1 Preliminary Remarks

The final chapter of this thesis is principally concerned with monomeric complexes. Synthetic strategies have been developed to yield a wide variety of osmium complexes. Their redox chemistry and charge-transfer spectra are presented, and some fundamental consequences of these physical measurements are discussed.

The interest in such monomeric complexes came as a consequence of recording the voltammetry of halide-bridged binuclear complexes in acetonitrile. Upon warming chilled acetonitrile solutions of \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]\)\(^{1-}\) and \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]\)\(^{2-}\), it became apparent these binuclear
species were undergoing cleavage reactions to yield monomeric products. By comparison with the voltammetry of \([\text{OsBr}_6]^{2-}\), predictions could be made as to the identity of these cleavage products. We postulated the simultaneous formation of \([\text{OsBr}_5(\text{MeCN})]^{-}\) and \([\text{OsBr}_4(\text{MeCN})_2]\) (trans or cis) from \([\text{Os}_2(\mu-\text{Br})_3\text{Br}_6]^{-}\), while in the case of \([\text{Os}_2(\mu-\text{Br})_2\text{Br}_8]^{2-}\), \([\text{OsBr}_5(\text{MeCN})]^{-}\) was the only predicted product.

It was this work that initiated our interest in the predictability of metal-based redox potentials in osmium chemistry. Consideration of this problem raises several questions; firstly by how much does the metal-based electrode couple shift upon substitution of A by B (e.g. \([\text{MA}_6] \rightarrow [\text{MA}_5\text{B}]\)), and is this shift additive for further substitutions? (i.e. \([\text{MA}_5\text{B}] \rightarrow \text{cis/trans}-[\text{MA}_4\text{B}_2] \rightarrow \text{mer/fac}-[\text{MA}_3\text{B}_3]\) etc). Also, what is the effect of different isomers on a particular redox couple? With these questions in mind, our study on substituted monomeric halide complexes began. Our predictions to the identity of the cleavage products were later proven to be correct, through chemically preparing these compounds, and recording their electrochemistry separately.

A systematic voltammetric and spectroscopic study was recently carried out on a series of ruthenium complexes, \([\text{RuX}_{6-n}(\text{RCN})_n]^{2-}\) (X=Cl, Br; R=Me, Ph; n=0-6). The voltammetry of these compounds revealed that strict linear relationships exist between the metal-based redox couples and the stoichiometry of the complex. Similarly, the progression of optical charge-transfer energies through the series (both halide-to-metal and metal-to-nitrile) reflect this variation of electrode potentials with stoichiometry. From such data a map of the relative frontier orbital energies of the system can be pieced together. A natural extension of this work is to compare and contrast these results with those from the analogous osmium series. The synthesis of a number of osmium halo/nitrile complexes (some for the first time) provides such an opportunity.

The compounds we wished to study may be described as ‘binary’ complexes, which involve only two kinds of ligands in the coordination sphere of the central metal ion. One of these ligands being a halide ion (X), and the other a \(\pi\)-acceptor ligand (L). Such compounds, of general formula \([\text{OsX}_{6-n}\text{L}_n]^{2-}\), can be considered as substitution products (for n=0\(\rightarrow\)5) of the
hexahaloosmates, \([\text{OsX}_6]^{2-}\) (i.e. \(n=0\)).

Redox induced substitution reactions have been used with considerable success in the past to generate substituted forms of transition metal complexes\(^2\)\(^-\)\(^4\). The preparative emphasis in the present study has been placed on developing reliable chemical routes to such complexes.

The majority of the complexes prepared here fall into two main categories, according to their stoichiometry. For a range of ligands \(L\), pentahalo-monosubstituted compounds of general formula \([\text{OsX}_5L]^{2-}\) have been synthesized. Previous reports on compounds of this type appear in Section 5.1.2 of this introduction. Section 5.1.3 then describes the literature of the tetrahalo-bisubstituted complexes, \(\text{trans-}[\text{OsX}_4L_2]^{2-}\) and \(\text{trans-}[\text{OsX}_4LL']^{2-}\). Finally section 5.1.4 briefly lists some previously prepared binary complexes of other stoichiometries (\(n=3\) or less). In this work, only a small number of complexes have been prepared which fall into this category, as compared with a large number of reported literature examples. Only representative examples of complexes of these formulae have been described here, and the reader referred to several reviews for a more comprehensive account of the literature.

Chapter 5 describes the syntheses and characterization of the monomeric complexes, along with their electrochemistry and charge-transfer spectra. Some consequences of the voltammetric and spectroscopic results are then discussed, in reference to ligand parameterization and ligand additivity.

\(5.1.2\) A Review of Pentahalo-monosubstituted Osmate Complexes

A considerable number of complexes of general formula \([\text{OsX}_5L]^{2-}\) have been previously isolated, for a diverse range of ligands \(L\). The only known halo/nitrile complexes of osmium are those of stoichiometry \([\text{OsX}_5L]^{1-}\) (\(X=\text{Cl, Br}; L=\text{MeCN}\)).\(^5\) These complexes were prepared by photolysis of neat acetonitrile solutions of \([\text{OsX}_6]^{2-}\) at selected wavelengths. Magnuson has also reported the formation of \([\text{OsBr}_5(\text{MeCN})]^{1-}\).\(^6\) He found the very unstable pentavalent species \([\text{OsBr}_6]^{1-}\) decomposed in acetonitrile to afford
[OsBr₅(MeCN)]⁻. He also recorded the electronic spectrum and voltammetry of this complex, which will be discussed in more detail at a later stage.

The photochemical method mentioned above was also used to prepare the mono-pyridine complex [OsCl₅(py)]⁻, and later the analogous bromide complex, [OsBr₅(py)]⁻. The corresponding iodo complex could not be isolated by this route; irradiation of [OsI₆]⁻ in pyridine preferentially yields mer-[OsI₃(py)₃] instead. The [OsI₅(py)]⁻ anion has however been successfully synthesized by a chemical route. Whereas the reaction of hexahaloosmates with pyridine in polar solvents gives complexes of the type mer-[OsX₃(py)₃] and [OsX₂(py)₄] (cis and trans) (X=Cl, Br, I), the same reagents in non-polar solvents yield mono-substituted products, [OsX₅(py)]⁻ for X=Cl, Br and I. ⁸

Several papers have mentioned the formation of [OsCl₅(NH₃)]²⁻, via the reduction of [OsCl₅N]²⁻. Taube et al. detailed this synthesis in a report on the characterization and reactivity of Os⁴⁺ ammines, where they isolated an air sensitive Cs⁺ salt of [OsCl₅(NH₃)]²⁻. The preparation of this compound involved reducing an acidified aqueous solution of the nitrido complex K₂[OsCl₅N]. The complex K₂[OsCl₅N], is strictly another example of a pentahalo-monosubstituted complex, however we are mainly concerned with those in which the Os-L bond is considered to be of single bond order. In the case of [OsCl₅N]²⁻, the nitrido group is regarded as a triply bonded ligand.¹¹

Nitrosyl complexes of the type [OsX₅(NO)]²⁻ (X=Cl, Br, I) appeared within the literature as early as 1903,¹² when such compounds were prepared by the action of the appropriate hydrohalic acid on salts of [Os(NO)(OH)(NO₂)₄]²⁻. More recently a number of other routes to such complexes have been discovered,¹² even for the case where X=F. One of the more general routes to [OsX₅(NO)]²⁻ (X=Cl, Br, I) complexes involves treating [OsX₅]²⁻ with the nitrite ion (NO₂⁻) and the appropriate acid, HX.¹³ Recently Bhattacharyya et al. reported another route the pentahalo-nitrosylosmate complexes.¹⁴ The procedure involved treating [Os(NO)(C₅O₄)₂]¹⁻ with hot concentrated HX (X=Cl, Br, I), yielding amongst other products, the [OsX₅(NO)]²⁻ species.
Pentahalo-monocarbonyl complexes have also received considerable attention within the literature. In 1967, Cleare and Griffith claimed to isolate Cs$_3$[OsCl$_5$(CO)], by heating Na$_2$OsCl$_6$ in formic acid, followed by the addition of CsCl.$^{15}$ A later paper dealing with the vibrational spectra of carbonyl and nitrosyl platinum metal complexes also reported the synthesis of the corresponding bromide complex in the same manner.$^{16}$ Both of these reports however incorrectly claimed these complexes contained osmium in its divalent oxidation state. The same authors subsequently noted this mistake, and correctly formulated these complexes as tervalent Cs$_2$[OsCl$_5$(CO)] i.e. Os$^{III}$.\textsuperscript{17}

Another route to such complexes appeared in 1975, when Preetz and Johannsen briefly commented that treatment of an acetone solution of trans-[OsBr$_4$(CO)$_2$]$^{1-}$ with HBr yielded [OsBr$_5$(CO)]$^{2-}$.\textsuperscript{18} Then in 1977 Preetz published a more detailed account of the preparation of [OsX$_5$(CO)]$^{2-}$ complexes (X=Cl, Br, I).\textsuperscript{19} The procedure involved firstly preparing an acetone solution of trans-[OsBr$_4$(CO)$_2$]$^{1-}$ from Na$_2$OsBr$_6$ and CO, and then treating this solution with concentrated HBr to yield the desired complex. The analogous chloro and iodo complexes can then be generated from [OsBr$_5$(CO)]$^{2-}$, by reaction with the appropriate hydrohalic acid. However Bottomly \textit{et al.} later reported that such reactions in their hands yielded only mixtures of [OsX$_5$(CO)]$^{2-}$ and trans-[OsX$_4$(CO)(S)]$^{1-}$ complexes (S=MeOH, H$_2$O, Me$_2$CO).\textsuperscript{20}

Preetz and Bruns have also isolated the Os$^{IV}$ pentachloromonocarbonyl complex, through the action of chlorine on a CH$_2$Cl$_2$ solution of the trans-[OsX$_4$(CO)$_2$]$^{1-}$ anion (X=Br, I).\textsuperscript{21} Treating a solution of [OsCl$_5$(CO)]$^{1-}$ with free bromide or iodide results in immediate reduction of this complex to yield the [OsCl$_5$(CO)]$^{2-}$ di-anion. The [OsCl$_5$(CO)]$^{1-}$ anion proved to be a useful precursor to a variety of other osmium complexes, including the pentavalent [OsCl$_6$]$^{1-}$ and the double-bridged [Os$_2$(µ-Cl)$_2$Cl$_8$]$^{2-}$.$^{21}$

The electronic spectra of the aquo-pentahaloosmate anions [OsX$_5$(H$_2$O)]$^{1-}$ have appeared on numerous occasions within the literature.$^{22}$ Solutions of [OsX$_5$(H$_2$O)]$^{1-}$ have been prepared through the photolysis or hydrolysis of hexachloroosmates in aqueous media.$^{5,23}$ The mono-aquo
species can in turn undergo deprotonation (in solutions of high pH) to yield the hydroxo complex \([\text{OsX}_5(\text{OH})]^{2-}\).\(^{24}\)

While halo/phosphine complexes of osmium are common, only one example of an \([\text{OsX}_5(\text{PR}_3)]^{2-}\) compound appears to have been isolated.\(^{25}\) The preparation involved treating a boiling acetone solution of \([\text{Os(NHPPh}_3]\text{Cl}_4(\text{PPPh}_3)].(\text{CH}_3)_2\text{CO}\) with one equivalent of \([\text{Ph}_4\text{As}][\text{H}_5\text{O}_2]\text{Cl}_2\). The products, \([\text{Ph}_4\text{As}][\text{OsCl}_5(\text{PPPh}_3)]\) and \([\text{Ph}_3\text{PNH}_2]\text{Cl}\), were obtained in stoichiometric quantities.

It is worth noting that of all the complexes mentioned above, only two have been structurally characterized, those being the nitrosyl complexes \([\text{OsF}_5(\text{NO})]^{2-}\) and \([\text{OsBr}_5(\text{NO})]^{2-}\). For the fluoride complex, structures for both the (Cs\(^+\))\(^2\) and mixed (Na\(^+\))(K\(^+\)) salts are reported, each containing a water of crystallization per complex.\(^{26}\) The bromide complex also formed with water molecules of crystallization (two in this case), and the cation was 1,10-phenanthrolinium.\(^{14}\)

Very few of the \([\text{OsX}_5\text{L}]^{1-}\) complexes discussed above have had their voltammetry recorded. In his study of pentavalent hexahaloosmate complexes,\(^6\) Magnuson recorded the voltammetry of \([\text{OsBr}_5(\text{MeCN})]^{1-}\), observing a reduction at +0.02 V (versus the saturated calomel reference electrode). Magnuson also described the electrochemical preparation of \([\text{OsBr}_5(\text{MeCN})]^{1-}\). In MeCN at room temperature, the Os\(^{IV}/III\) couple of \([\text{OsBr}_6]^{2-}/^{3-}\) is irreversible at normal scan rates, and the generation of a daughter product can be seen by the appearance of small wave at ~0.0 V, \emph{i.e} 0.6 V more anodic than the hexahalide reduction (at -0.55 V). This was of course the Os\(^{IV}/III\) couple of \([\text{OsBr}_5(\text{MeCN})]^{2-}\), this species being formed at the electrode through loss of bromide from electrogenerated \([\text{OsBr}_6]^{3-}\). In Preetz’s most recent description of \([\text{OsCl}_5(\text{CO})]^{1-}\),\(^{21}\) he reported the voltammetry of this monosubstituted product. The Os\(^{IV}/III\) reduction was found at +0.623 V, versus the saturated mercury/mercurous sulphate reference electrode. The voltammetry of the \((\text{Ph}_4\text{P})_2[\text{OsX}_5(\text{NO})] (X=\text{Cl}, \text{Br})\) compounds in acetonitrile, and in dimethylformamide in the case of X=I, revealed oxidations of varying reversibility at +0.94, +0.96 and +1.08 V respectively, versus the saturated calomel electrode.\(^{14}\)

In summary, a number of complexes of formula \([\text{OsX}_5\text{L}]^{2-}\) have been
previously documented. What becomes apparent upon consideration of their syntheses is the diversity of procedures used in their preparation. An effective and systematic route to complexes of this general formula has been sought in the present work.

Before any sensible comparisons can be made of the metal-based redox couples, the voltammetry of the \([\text{OsX}_5\text{L}]^{2-}\) complexes needs to be recorded in a systematic manner, preferably in a common solvent versus the same reference electrode. Moreover there are great benefits from low temperature measurements, where redox-linked dissociation can be inhibited and reversibility is enhanced.

### 5.1.3 A Review of Tetrahalo-bisubstituted Osmate Complexes

Turning now to complexes of stoichiometry \([\text{OsX}_4\text{L}_2]^{2-}\) we find the great majority of these examples are \textit{trans} isomers. The most well documented examples are \textit{trans} OsIV complexes, with phosphines or arsines as the neutral ligands. Leigh \textit{et al.} were able to isolate selected compounds of this formula \((X=\text{Br}, L=\text{P}^n\text{Pr}_3; X=\text{Cl}, L=\text{P}^n\text{Bu}_2\text{Ph}, \text{P}^n\text{Pr}_3, \text{As}^n\text{Pr}_3)\) from ethanol/hydrohalic acid solutions of osmium tetroxide and the respective ligand.\(^{27}\) This product could not be isolated for some of the more soluble phosphines and arsines. Short reaction times were also critical, otherwise reduction to OsIII and further substitution occurred to yield \textit{mer}-\(\text{OsCl}_3\text{L}_3\) \((L=\text{AsR}_3, \text{PR}_3)\) complexes. Another route to the \textit{trans}-\([\text{OsX}_4\text{L}_2]\) compounds was given in the same paper; this involved the slow oxidation of \textit{mer}-\(\text{OsCl}_3\text{L}_3\) \((L=\text{P}^n\text{Bu}_2\text{Ph}, \text{P}^n\text{Pr}_3, \text{P}^n\text{Pr}_2\text{Ph}, \text{PMe}_2\text{Ph}, \text{As}^n\text{Pr}_3, \text{AsMe}_2\text{Ph})\) with dry carbon tetrachloride. \textit{Trans}-\([\text{OsCl}_4(\text{SbPh}_3)_2]\) has also been prepared by this route.\(^{28}\) Douglas and Shaw found this second method gave only low yields of the desired phosphine and arsine complexes.\(^{29}\) They reported \textit{trans}-\([\text{OsCl}_4\text{L}_2]\) compounds were more readily synthesized by treating a dichloromethane/carbon tetrachloride solution of \textit{mer}-\(\text{OsCl}_3\text{L}_3\) \((L=\text{PEt}_2\text{Ph}, \text{AsEt}_2\text{Ph})\) with chlorine, whilst the mixture was under irradiation.

Some years later, Armstrong and Walton isolated \textit{trans}-\([\text{OsX}_4(\text{PR}_3)_2]\) complexes with trialkyl phosphines \((\text{PR}_3=\text{PEt}_3, \text{P}^n\text{Pr}_3, \text{P}^n\text{Bu}_3)\) in low yield, whilst attempting to prepare \(\text{OsO}_2\text{Cl}_2(\text{PR}_3)_2\) species. The procedure was
essentially the same as that used by Leigh et al. except the mixture was cooled rather than heated upon combination of the reactants.

A neutral tetrachloro trans complex involving two Ph₂AsCH₂AsPh₂ ligands has also been reported, from refluxing a water/alcohol mixture of (NH₄)₂[OsCl₆] in the presence of the free ligand. Each di-arsine ligand coordinates in a monodentate fashion.²⁸

Recently Levason et al. described the formation, spectroscopy and electrochemistry of a number of trans-[OsX₄L₂]⁰⁻ complexes.³¹ They prepared the neutral phosphine and arsine derivatives (L=PPh₃, PEt₃, PEt₂Ph, PEtPh₂, AsEt₃, AsPh₃) by Leigh's first method (see above), with some minor variations in the case of PPh₃ and AsPh₃. Complexes with antimony, selenium and nitrogen donor atom ligands were also synthesized, some for the first time. Trans-[OsX₄(SbPh₃)₂] was obtained from the oxidation of mer-OsX₃(SbPh₃)₃ with X₂ in dichloromethane, and trans-[OsX₄(SeMe₂)₂] from the reaction of [OsX₆]²⁻ with the free ligand in n-butanol. The neutral bis-pyridine complexes, trans-[OsX₄(py)₂] were also prepared in this work, by lengthy heating of Na₂[OsX₆] in an ethanol/pyridine mixture. Alternatively, tervalent trans-[OsCl₄(py)₂]¹⁻ was obtained directly by pyrolysis of (pyH)₂[OsCl₆] under nitrogen, and may be oxidized with chlorine to trans-[OsCl₄(py)₂].

Other tervalent mono-anions of the same general stoichiometry, trans-[OsX₄L₂]¹⁻, have also been synthesized. The reaction of tertiary phosphines with alcoholic solutions of the triple bonded diosmium dimer, [Os₂X₈]²⁻, gives trans-[OsX₄(PR₃)₂]¹⁻ complexes.³²,³³ Good yields are obtained for both X=Cl, Br, and a range of trialkyl and mixed alkyl/aryl phosphines. A new general route to the anionic Os³⁺ complexes was also given by Levason et al.³¹ This involved refluxing ethanol solutions of the neutral Os¹⁵ compounds with ascorbic acid. Such a procedure had previously been successful in synthesizing the analogous iridium complexes.³⁴

The trans geometry of the tetravalent [OsX₄L₂] compounds (L=PR₃, AsR₃) was determined spectroscopically,³⁵ and confirmed through crystallographic studies.³⁶,³⁷ Tervalent trans-Ph₄P[OsCl₄(PEt₃)₂] and trans-nBu₄N[OsCl₄(py)₂] complex has also been structurally characterized, although the details for the latter have yet to be published.³³
Other $[\text{OsX}_4 L_2]^{2-}$ and $[\text{OsX}_4 L_4]^{2-}$ complexes to have been prepared and characterized include trans-$[\text{OsX}_4 (\text{CO})_2]^{2-}$ (X=Br, I, ref 19) and trans-$[\text{OsX}_4 (\text{CO})(\text{L})]^{-1}$ (X=Cl, Br, I) where L=H$_2$O and py. While the latter two complexes do not strictly fall into the category of binary complexes defined earlier, they are equally interesting and hence included here. The passage of CO through an acetone solution of Na$_2[\text{OsBr}_6]$ for 24 hours, followed by the addition of a $nR_4N^+$ salt and cooling resulted in the isolation of trans-$nR_4N[\text{OsBr}_4(\text{CO})_2]$. Reduction of this complex to the Os$^{II}$ di-anion was achieved with potassium hydroxide in ethanol. Trans-$[\text{OsX}_4 (\text{CO})(\text{H}_2\text{O})]^{1-}$ was formed during the hydrolysis of $[\text{OsX}_5 (\text{CO})]^{2-}$ (X=Cl, Br, I) at room temperature. Further substituted complexes are also formed, however the products can be separated by ionophoresis. The treatment of $[\text{OsX}_5 (\text{CO})]^{2-}$ or trans-$[\text{OsX}_4 (\text{CO})_2]^{1-}$ with anhydrous pyridine in the presence of bentonite yielded trans-$[\text{OsX}_4 (\text{CO})(\text{py})]^{1-}$ complexes. Bottomley et al. also isolated trans-$[\text{OsX}_4 (\text{CO})(\text{S})]^{1-}$ complexes, where S=H$_2$O, Me$_2$CO and MeOH, whilst trying to prepare the pentahalo-carbonyl species $[\text{OsX}_5 (\text{CO})]^{2-}$ according to literature procedures. The solvent molecule in trans-$[\text{OsX}_4 (\text{CO})(\text{S})]^{1-}$ was readily displaced by $o-C_6H_4(\text{AsMe}_2)_2$, to give trans-$[\text{OsX}_4 (\text{CO})(\text{diars})]^{1-}$, where the diarsine functions only as a monodentate ligand. Similarly, trans-$[\text{OsX}_4 (\text{CO})(\text{PPh}_3)]^{1-}$ was isolated from an acetone solution of trans-$[\text{OsX}_4 (\text{CO})(\text{H}_2\text{O})]^{1-}$ and the free phosphine. These transformations illustrate the considerable lability of the ligand trans to carbonyl in tervalent trans-$[\text{OsX}_4 (\text{CO})(\text{L})]^{1-}$ complexes.

Most recently Walton et al. synthesized a number of trans-$[\text{OsX}_4 (\text{CNR})_2]^{1-}$ and trans-$[\text{OsX}_4 (\text{CO})(\text{L})]^{1-}$ complexes, from the triply bonded $[\text{Os}_2\text{X}_8]^{2-}$ dimer. The di-isonitrile complexes were prepared by stirring ethanol suspensions of $[\text{Os}_2\text{X}_8]^{2-}$ with the desired ligand, while heating mixtures of $[\text{Os}_2\text{X}_8]^{2-}$/EtOH under CO gave trans-$[\text{OsX}_4 (\text{CO})(\text{EtOH})]^{1-}$. Further reaction of this latter complex with a variety of ligands L gave trans-$[\text{OsX}_4 (\text{CO})(\text{L})]^{1-}$ complexes (L=thf, PR$_3$, py, dmso etc.). These complexes were extensively characterized by a variety of techniques, including epr spectroscopy and cyclic voltammetry.

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* diars=$o-C_6H_4(\text{AsMe}_2)_2$. 
Studies on the electrochemistry of trans-$\text{[OsCl}_4(\text{O}_2)]$ in hydrochloric acid media report trans-$\text{[OsCl}_4(\text{H}_2\text{O}_2)]^{0/1}$ species,\textsuperscript{22} but such complexes have yet to be isolated.

Cis isomers of stoichiometry $[\text{OsX}_4\text{L}_2]^{2-}$ are far less common than their trans analogues. Cis-$[\text{OsX}_4(\text{CO})_2]^{2-}$ is one such example. Refluxing $[\text{OsX}_6]^{2-}$ in formic acid 16 or allyl alcohol yields the cis complex, as the cesium or tetraalkylammonium salts.\textsuperscript{41} Thermolysis apparently isomerizes the trans complex to the cis form.\textsuperscript{18} The cis arrangement of carbonyls in these compounds has been assigned by infrared spectroscopy. The cis isomer of $[\text{OsCl}_4(\text{py})_2]$ has also been briefly reported, in a study on the redox induced step-wise substitution of $[\text{OsCl}_4]^{2-}$.\textsuperscript{42}

Examples of cis isomers involving bidentate ligands, namely bipyridine, phenanthroline and ethylenediamine.\textsuperscript{43-45} Such ligands enforce a cis geometry in order to satisfy their bidentate coordination requirements. Similarly, the potentially tridentate phosphine ligand PhP(\text{CH}_2\text{CH}_2\text{PPh}_2)_2 occupies cis coordination sites in $[\text{OsCl}_4(\text{PhP(\text{CH}_2\text{CH}_2\text{PPh}_2)_2})]$, and hence functions only as a bidentate ligand.\textsuperscript{46}

5.1.4 Further Substituted Osmium Halo Complexes, $[\text{OsX}_{6-n}\text{L}_n]^{(n=3, 4)}$

As mentioned earlier, only limited examples of further substituted compounds have been prepared. For the stoichiometry $[\text{OsX}_3\text{L}_3]$, routes to mer-$[\text{OsX}_3\text{L}_3]$ (X=halide, L=PR$_3$, AsR$_3$) are numerous and well established, and the reader is referred to a selection of papers which adequately describe this work.\textsuperscript{12,47} Similarly, the preparation of ammine,\textsuperscript{10} carbonyl,\textsuperscript{48} and pyridine\textsuperscript{12,47,49} compounds of this type are also well established. The overwhelming majority of complexes of this formula are meridional isomers, although facial compounds $[\text{OsX}_3\text{L}_3]$ are known, for L=PR$_3$, AsR$_3$, SbR$_3$, py,\textsuperscript{47} CO.\textsuperscript{48} The structure of fac-$[\text{OsCl}_3(\text{PET}_2\text{Ph})_3]$ was recently solved by Levason et al.\textsuperscript{47} Prior to this, the facial geometry of the halophosphine complexes was based on spectroscopic evidence.\textsuperscript{35}

For the next stoichiometry in the series, cis/trans-$[\text{OsX}_2\text{L}_4]$, a large number of compounds are known, for a wide range of ligands L. However, no new complexes of this stoichiometry have been prepared here, so their
chemistry will not be detailed. The reader is instead referred to a number of articles which summarize much of this work.\textsuperscript{10, 12, 33, 50, 51}
5.2 SYNTHESIS AND CHARACTERIZATION OF MONOMERIC OSMIUM COMPLEXES

5.2.1 Monosubstituted Complexes of Stoichiometry \([\text{OsX}_5L]\)^2-

(i) \(L=\text{acetonitrile, pyridine.}\)

As outlined in the introduction, Preetz and Hasunpusch prepared \([\text{OsX}_5(\text{MeCN})]\)^1- (X=Cl, Br) and \([\text{OsCl}_5(\text{py})]\)^1- through the photochemical irradiation of acetonitrile or pyridine solutions of the hexahaloosmates, \([\text{OsX}_6]^2-\). This appeared an attractive route to compounds of general formula \([\text{OsX}_5L]\)^1- (where X=Cl, Br and L=\(\pi\)-acceptor ligand). However, attempts to repeat their results failed. Photolysis was carried out at a wavelength of 350 nm initially, and then 251 nm. After a reaction time of 10 hours (at both wavelengths), no change in the u.v./visible spectra of these solutions was observed.

It appears the photochemical activation of the hexahaloosmate complexes is highly dependent upon the wavelength of irradiation. Preetz and Hasunpusch obtained quantum yields between 10^-2 and 10^-3 after irradiation at wavelengths of 313, 334, 366, 405 and 436 nm. The photochemistry of the hexahaloosmates remains largely unexplored, and further work is required to establish under what conditions reactivity might reliably be achieved. This could prove to be a very fruitful area of synthetic osmium chemistry.

Our failure to synthesize these compounds photochemically prompted the development of other general routes, the aim being to be able to introduce a variety of ligands L to the osmium site. The first route explored was the use of stoichiometric amounts of Ag+ salts to remove halide (as AgX) from \([\text{OsX}_6]^2-\), in the presence of a ligand L, in order to prepare the mono-substituted pentahaloosmate species.

This method has proven successful in preparing \([\text{OsX}_5(\text{MeCN})]\)^1- and \([\text{OsX}_5(\text{py})]\)^1- in good yield (X=Cl, Br and the cation \(\text{nBu}_4\text{N}^+\) or \(\text{Ph}_4\text{P}^+\)). Stirring warm acetonitrile or pyridine solutions of \((\text{nBu}_4\text{N})_2[\text{OsX}_6]\) (X=Cl, Br) in the presence of one mole equivalent of AgCF_3SO_3 yields the desired complexes. The temperature is critical. For the reactions mentioned above,
heating to reflux leads to mixtures of mono and further substituted products, while at room temperature no reaction occurs for at least 24 hours. At a selected intermediate temperature, the reaction proceeds smoothly, its progress conveniently monitored by visible spectroscopy. As a precautionary measure, the reactions were routinely protected from the light.

The identity of these complexes was initially established by their infrared and visible spectra matching those reported in the literature for these compounds. The compound \( n\text{Bu}_4\text{N}[\text{OsBr}_5(\text{MeCN})] \) has since had its structure determined by a single crystal x-ray diffraction study (see Appendix 1).

In the past Ag\(^+\) salts have successfully been used to abstract halide from organometallic osmium compounds. It should be noted that Ag\(^+\) can also function as an efficient oxidant, should the compound have a readily accessible oxidation (\( E^{\text{ox}} \sim +0.40\ \text{V}, \) versus Ag/AgCl). Incorporation of Ag\(^+\) into the product is further possible complication. Hinckley et al. prepared an osmium/silver complex while looking at possible methods of chloride substitution in salts of \([\text{OsCl}_6]^{2-}\). Upon reacting an excess of AgNO\(_3\) with an acetonitrile solution of PPh\(_3\) and \((n\text{Bu}_4\text{N})_2[\text{OsCl}_6]\), a red solution was formed which deposited crystals of OsCl\(_6\)Ag\(_2\)(PPh\(_3\))\(_4\). The structure consists of a central octahedral \([\text{OsCl}_6]^{2-}\) unit, to which is bonded two \([\text{Ag}(\text{PPh}_3)_2]^{1+}\) fragments, one on either side of the central octahedron. Each Ag\(^+\) cation has approximately tetrahedral geometry, and bridges two equatorial chlorides, producing the symmetric Ag.Os.Ag adduct. The formation of such a complex is not unexpected, given the readiness with which Ag\(^+\) coordinates phosphine ligands.

Another convenient route to the \([\text{OsCl}_5(\text{MeCN})]^{1-}\) complex was also established. Stirring \((\text{Ph}_4\text{P})_2[\text{Os}_2(\mu-\text{Cl})_2\text{Cl}_8]\) in acetonitrile for an extended period of time gave respectable yields of \(\text{Ph}_4\text{P}[\text{OsCl}_5(\text{MeCN})]\).

\((ii)\ L=\text{carbonyl}.

Given the success of the Ag\(^+\) route in the preparation of MeCN and py complexes, the same method was tried in an attempt to synthesize \([\text{OsX}_5(\text{CO})]^{2-}\). Passage of CO through a warm 1,2-dichloroethane solution of
(nBu4N)2[OsX6] (X=Cl, Br) containing one mole equivalent of AgCF3SO3 resulted in the isolation of the trans-disubstituted species, [OsX4(CO)2]−, and not the monosubstituted product. The disubstituted compounds were identified spectroscopically. It is perhaps not surprising that this reaction yielded trans-[OsX4(CO)2]−, given the strong trans effect of CO, and the large excess of CO present during the reaction.

The procedure of Johannsen and Preetz was also tried in an attempt to isolate salts of the [OsX5(CO)]2− complexes (X=Cl, Br, I). They postulated the formation of the [OsBr5(CO)]2− species was facilitated through substitution of one of the carbonyl groups by an acetone ligand, which might in turn be replaced by a bromide ion. We find that the reaction does in fact proceed through a trans-[OsBr4(CO)(Me2CO)]− intermediate. Acetone solutions of trans-[OsBr4(CO)2]− at room temperature change colour from intense purple to orange/brown over a period of 30 minutes. The visible spectra of such solutions match that of trans-[OsBr4(CO)(Me2CO)]−, this compound having been previously isolated by another route (Section 5.2.2). The addition of aqueous HBr to such solutions brought about further changes in the visible spectra, however these were not consistent with the formation of [OsBr5(CO)]2−. Intractable oils were obtained upon working up these reactions.

Having noted the lability of a carbonyl ligand in trans-[OsBr4(CO)2]−, a 10% excess of nBu4NBr was added to a dry dichloromethane solution of the dicarbonyl. The solution slowly changed colour, and after 6 hours stirring at room temperature the visible spectrum matched that reported for [OsBr5(CO)]2−. The infrared spectrum of the isolated red/brown product has a strong νCO band at 1953 cm−1, compared with literature values of 1959 and 1956 cm−1 for the tetramethylammonium and tetraethylammonium salts of [OsBr5(CO)]2− respectively. Subsequent analytical and spectroscopic data confirmed the identity of the product as (nBu4N)2[OsBr5(CO)]2−. The analogous chloride complex was synthesized in an identical manner, by starting with trans-nBu4N[OsCl4(CO)2]. A similar

§ It is interesting to note that as the size of the tetraalkylammonium cation increases, the carbonyl stretching frequency decreases. Likewise, as the inorganic cations get larger, in the order K+, Rb+, and Cs+, again the carbonyl stretching frequency decreases, from 2015 to 2006 and 1967 cm−1 respectively.
transformation has been previously performed with [RhI₄(CO)₂]⁻, where the addition of excess iodide yielded [RhI₅(CO)]²⁻.56

(iii) \( L=\text{tert-butyl isonitrile} \).§

Until recently, very few isonitrile complexes of osmium had been reported, and the majority of those that are known contain osmium in a low oxidation state, most commonly Os²⁺.

The first attempt to prepare such complexes resulted in the formation of the \( \text{trans} \) disubstituted species, [OsX₄(CNBuᵗ)₂]⁻. The procedure involved warming 1,2-dichloroethane solutions of \((nBu₄N)_2[OsX₆](X=Cl, Br)\), containing an equivalent of AgCF₃SO₃, and a slight excess of the ligand CNBuᵗ. Small yields of the \( \text{trans} \)-nBu₄N[OsX₄(CNBuᵗ)₂] compounds (X=Cl, Br) were isolated. This complex was also unknown until a recent paper (which appeared after our study was complete) reported its preparation.40 Its synthesis is discussed in more detail in Section 5.2.2.

Another attempt at synthesizing the mono-substituted species was made using the decachlorodiosmate compound, \((Ph₄P)_2[Os₂(µ-Cl)₂Cl₈]\). A 1,2-dichloroethane/CNBuᵗ solution of the dimer was stirred at room temperature. The visible spectrum of the mixture changed quickly, however the most distinguishable new features were those of [OsCl₆]²⁻. Working up the reaction gave a quantity of \((Ph₄P)_2[OsCl₆]\), a very small amount of the desired product, \((Ph₄P)[OsCl₅(CNBuᵗ)]\), and other uncharacterized species. The complex \((Ph₄P)[OsCl₅(CNBuᵗ)]\) was charaterized by its infrared and u.v./visible spectroscopy, elemental analyses and fast atom bombardment (FAB) mass spectroscopy. The negative-ion FAB mass spectra in general did not give molecular ions ([M]⁻) for the [OsX₅L]⁻ complexes, only fragments corresponding to [OsX₅]⁻, [OsX₄]⁻ and [OsX₃]⁻. The spectrum of \( Ph₄P[OsCl₅(CNBuᵗ)] \) was recorded in a 3-nitrobenzyl alcohol (NBA) matrix \((m/z=153)\). The molecular ion for the [OsCl₅(CNBuᵗ)]⁻ anion was not observed, however the base peak at \( m/z=414.8 \) corresponds to the loss of one chloride from [M]⁻, i.e. the [OsCl₄(CNBuᵗ)]⁻ fragment. The less intense peaks at \( m/z=366.7 \) and 331.6 are assigned as [OsCl₅]⁻ and [OsCl₄]⁻ ions. The peak at \( m/z=567.8 \) involves the

§ tert-butyl isonitrile=CNBuᵗ.
The incorporation of the matrix, \([\text{OsCl}_4(\text{CNBu}^t)+\text{NBA}]^-\). The results of the negative-ion FAB mass spectra of all the \([\text{OsX}_5\text{L}]^-\) complexes are summarized in Table 5.1.

**Table 5.1** Mass spectral data for \([\text{OsX}_5\text{L}]^-\) complexes.

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<th>Complex</th>
<th>m/z</th>
<th>% of base peak</th>
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</tr>
<tr>
<td>([\text{OsCl}_5(\text{thf})]^-)</td>
<td>366.7</td>
<td>66</td>
<td>([\text{OsCl}_5]^-)</td>
</tr>
<tr>
<td></td>
<td>331.6</td>
<td>62</td>
<td>([\text{OsCl}_4]^-)</td>
</tr>
<tr>
<td>([\text{OsCl}_5(\text{Me}_2\text{CO})]^-)</td>
<td>366.7</td>
<td>45</td>
<td>([\text{OsCl}_5]^-)</td>
</tr>
<tr>
<td></td>
<td>331.6</td>
<td>100</td>
<td>([\text{OsCl}_4]^-)</td>
</tr>
<tr>
<td></td>
<td>296.8</td>
<td>16</td>
<td>([\text{OsCl}_3]^-)</td>
</tr>
</tbody>
</table>

$^a$ Recorded in 3-Nitrobenzyl alcohol (NBA) matrix.

By far the most successful route to the \([\text{OsX}_5(\text{CNBu}^t)]^-\) complex
involves firstly the preparation of a solvated $[\text{OsX}_5(S)]^{1-}$ complex. A mixture of $[\text{OsX}_6]^2-$ ($X=\text{Cl}, \text{Br}$) and one mole equivalent of AgCF$_3$SO$_3$ was warmed in a 50/50 (v/v) solution of tetrahydrofuran/1,2-dichloroethane. The resulting solutions were believed to consist largely of $[\text{OsX}_5(\text{thf})]^{1-}$. This was later confirmed by isolating the chloride complex from solution (see discussion below). The solutions were filtered through a bed of celite (to remove AgX), and the solvent evaporated in vacuo. The residue was then taken up in freshly distilled dichloromethane, and CNBu$^+$ added. In the case of the bromide, the solution changes from deep red to purple within minutes. The colour change for the chloride is less spectacular, but the reaction equally efficient. Good yields of various organic salts of $[\text{OsX}_5(\text{CNBu})]^1-$ ($X=\text{Cl}, \text{Br}$) can be isolated by this route.

The dichloromethane solutions of presumed $[\text{OsX}_5(\text{thf})]^{1-}$ are quite unstable, being very sensitive to moisture, and reverting largely back to $[\text{OsX}_6]^2-$ if left overnight. An attempt was made to isolate a product from one of these solutions, in an effort to characterize this species more fully. The solvated species prepared from $\left(\text{nBu}_4\text{N}\right)_2[\text{OsCl}_6]$ was chosen, as it appeared to be the more stable than the analogous bromide. The product proved difficult to crystallize, but eventually an orange/yellow solid was collected. This too was quite unstable, degenerating to an oil over a period of two days when stored at room temperature under nitrogen. The procedure was therefore repeated, beginning instead with $\left(\text{Ph}_4\text{P}\right)_2[\text{OsCl}_6]$. A microcrystalline yellow precipitate was readily isolated, which to date appears indefinitely stable when stored under the same conditions as the analogous short-lived $\text{nBu}_4\text{N}^+$ salt.

The solid gave elemental analysis corresponding to $\text{Ph}_4\text{P}[\text{OsCl}_5(\text{thf})].\text{Ph}_4\text{PCF}_3\text{SO}_3$. Non-coordinated anionic triflate was identified in the infrared spectrum. The nature of this complex was confirmed by recording its voltammetry in dichloromethane. The cyclic voltammogram revealed an oxidation and two reductions, typical of those observed for other $[\text{OsCl}_5(L)]^{1-}$ complexes where $L$ is a weak $\pi$-acceptor (see Section 5.3). Voltammetric techniques can be very useful in the

---

† thf=tetrahydrofuran.
‡ Similar double-salts form between Ph$_4$PCF$_3$SO$_3$ and other Ph$_4$P[OsX$_5$L] compounds.
characterization of compounds, especially when a body of data is already available for similar complexes. The u.v./visible spectra of both the chloride and bromide complexes were also consistent with this formulation. The positions of the maxima were appropriate for halide(\pi)-to-metal(Os\textsuperscript{IV}) charge-transfer transitions.**

A molecular ion corresponding to [OsCl\textsubscript{5}(thf)]\textsuperscript{1-} was not observed in the negative-ion FAB mass spectrum of this compound, only [OsCl\textsubscript{5}]\textsuperscript{1-} (m/z=366.7) and [OsCl\textsubscript{4}]\textsuperscript{1-} (m/z=331.6) fragments were identified. Given the lability of the thf ligand, it is not surprising the molecular ion was not observed. Even where L is a more tightly bound ligand, the negative-ion FAB mass spectra of [OsX\textsubscript{5}L]\textsuperscript{1-} complexes do not always give molecular ions (see Table 5.1).

(iv) \textit{L}=acetone.

Prior to discovering the increased stability of Ph\textsubscript{4}P[OsCl\textsubscript{5}(thf)], other such complexes with potentially labile leaving groups were considered. Such a complex is the acetone species. Prepared initially by the action of AgCF\textsubscript{3}SO\textsubscript{3} on acetone solutions of [OsCl\textsubscript{6}]\textsuperscript{2-}, the nBu\textsubscript{4}N[OsCl\textsubscript{5}(Me\textsubscript{2}CO)] complex does have far greater stability than its tetrahydrofuran analogue, especially in the solid state.

The most convenient method of preparing the Ph\textsubscript{4}P\textsuperscript{+} salt of this complex was to simply stir (Ph\textsubscript{4}P)\textsubscript{2}[Os\textsubscript{2}(\mu-Cl)\textsubscript{2}Cl\textsubscript{8}] in ‘dry’ acetone\textsuperscript{#}, taking care to exclude water from the reaction mixture. From such reactions, crystalline golden brown materials were isolated, which analysed as Ph\textsubscript{4}P[OsCl\textsubscript{5}(Me\textsubscript{2}CO)]. Yields were typically about 75%.

The voltammetry of this complex was characteristic of that of a [OsX\textsubscript{5}L]\textsuperscript{1-} complex in which L is a weak \pi-acceptor (Section 5.3). In dichloromethane, an oxidation and two reductions were observed, the first of which was reversible at 213 K.

The negative-ion FAB mass spectrum of Ph\textsubscript{4}P[OsCl\textsubscript{5}(Me\textsubscript{2}CO)] was also similar to that of other [OsX\textsubscript{5}L]\textsuperscript{1-} compounds. Fragments corresponding to [OsCl\textsubscript{5}]\textsuperscript{1-}, [OsCl\textsubscript{4}]\textsuperscript{1-} and [OsCl\textsubscript{3}]\textsuperscript{1-} were observed (see Table 5.1), although the molecular ion was not found.

** Detailed discussion of the solution u.v./visible spectra will follow in Section 5.4

\textsuperscript{#} i.e. acetone equilibrated with dried molecular sieves.
Acetone can function as either a $\eta^1$ $\sigma$-bound ligand (coordinating through O), or as a $\eta^2$ $\pi$-bound ligand (coordinating through both C and O). In diamagnetic complexes, the binding mode of acetone is readily determined by $^{13}$C n.m.r. spectroscopy; the CO $^{13}$C resonance for the $\eta^1$ ligand being within ~20 p.p.m. of free acetone signal (which occurs at ~200 p.p.m.), while for the $\eta^2$ case, the same resonance is usually observed around 80 p.p.m. The C=O stretching frequency ($\nu_{CO}$) is also sensitive to coordination. In the case of $\eta^1$ acetone ligands, these absorptions are commonly found in the 1500-1700 cm$^{-1}$ region. Previous studies on $\eta^2$ bound ketones and aldehydes have assigned the C=O stretch in the range 1000-1200 cm$^{-1}$.58,59

The $^1$H and $^{13}$C N.M.R. spectra of Ph$_4$P[OsCl$_5$(Me$_2$CO)] did not reveal any resonances which could be confidently assigned to the coordinated acetone ligand. The tetravalent [OsX$_5$L]$^{1-}$ complexes are in general weakly paramagnetic, and so the signals may be very broad and hence not observed.

The infrared spectrum of Ph$_4$P[OsCl$_5$(Me$_2$CO)] reveals a moderately intense band at 1 684 cm$^{-1}$, which was assigned as $\nu_{CO}$, indicating the acetone ligand binds through a lone pair of the CO oxygen, as a $\eta^1$ acetone ligand. The analogous bromide complex was also synthesized, by an analogous method. The $\nu_{CO}$ stretch of acetone in Ph$_4$P[OsBr$_5$(Me$_2$CO)] was found at 1609 cm$^{-1}$. The $\nu_1$ ($\nu_{AB}$) stretching frequency of diatomic ligands trans to halide usually decreases down the series Cl$, Br$, I$, as the M-X bond strength decreases.61 Considering the O-bound acetone ligand in similar terms, the $\nu_{CO}$ in the bromide compound would be expected to lie at lower energy than that in the analogous chloride species. This is in fact what is observed. In the [OsX$_5$(MeCN)]$^{1-}$ (X=Cl, Br) complexes, $\nu_{CN}$ of acetonitrile is also lowest in energy in the case of the bromide.

Taube et al. characterized [Os(NH$_3$)$_5$(Me$_2$CO)]$^{2+}$, in which the acetone ligand is bound through both the carbon and oxygen ($\eta^2$) to the metal centre.59 Upon oxidation of this compound (Os$^{II}$/III), the coordination mode of the acetone ligand changes to $\eta^1$. Such changes in the binding modes of ligands (called linkage isomerization) accompanying redox change are well documented.62 Given that the acetone ligand coordinates to Os$^{III}$ through an oxygen $\sigma$ bond, similar coordination to Os$^{IV}$ is not suprising.
While the electron richness of the \([\text{OsCl}_5]^{1-}\) site may be expected to be greater than that of \([\text{Os(NH}_3)_5]^{3+}\) (as evidenced by \(E_{1/2}\) of acetone complexes) the \(\sigma\) binding mode of acetone is still expected to be favoured at Os\(^{IV}\).

Although the coordinated ligand was not identified from n.m.r. experiments, what was observed in the proton n.m.r., aside from the \(\text{Ph}_4\text{P}^+\) cation resonances, was a free acetone signal at 2.15 p.p.m. Given that this compound was synthesized in acetone, such a resonance may have been due to the presence of residual solvent. However, repeated recrystallization of this material from dichloromethane/diethyl ether gave no different results, indicating a dissociative equilibria maybe occurring. Based on the integration of the cation resonances, the amount of free acetone represents \(-12\%\) of that initially in solution, in the form of coordinated acetone. The replacement of the labile acetone ligand with a ligand \(L\) can be conveniently monitored by \(^1\text{H}\) n.m.r. spectroscopy. An n.m.r solution of \(\text{Ph}_4\text{P}[\text{OsCl}_5(\text{Me}_2\text{CO})]\) spiked with an equivalent of acetonitrile, initially shows the presence of both uncoordinated acetone (2.15 p.p.m.) and acetonitrile (1.99 p.p.m.). With time, the intensity of the free acetone singlet increases, while that of the acetonitrile decreases. Associated with the exchange is a definite change in colour of the solution, from the light orange of the acetone complex to yellow of the acetonitrile species. The u.v./visible spectrum of the latter matches that previously recorded for \([\text{OsCl}_5(\text{MeCN})]^{1-}\).

The synthetic versatility of this labile acetone complex remains largely unexplored. The addition of acetonitrile, pyridine or tert-butyl isonitrile to dichloromethane solutions of \(\text{Ph}_4\text{P}[\text{OsX}_5(\text{Me}_2\text{CO})]\) results in the formation of the respective \([\text{OsX}_5L]^{1-}\) complexes.

\((v)\) \(L=\text{nitrosyl}\)

The preparation of tervalent \([\text{OsCl}_5(\text{NO})]^{1-}\) was also attempted using \(\text{Ag}^+\) to abstract \(\text{Cl}^-\) from 1,2-dichloroethane solutions of \([\text{OsCl}_6]^{2-}\), in the presence of \(\text{NO}^+\). The reaction mixture became an intense purple colour after warming the vessel for \(-5\) hours. The u.v./visible spectrum of this solution shows an intense band at \(-19\,620\,\text{cm}^{-1}\). The features of this absorption spectrum were identical to those of \([\text{RuCl}_5(\text{NO})]^{1-}\), except that the osmium spectrum was blue shifted (as expected for halide-to-metal
charge-transfer transitions) by ~4 300 cm\(^{-1}\). The [RuCl\(_5\)(NO)]\(^{1-}\) anion was electrogenerated from [RuCl\(_5\)(NO)]\(^{2-}\) at very positive potentials (ca. +1.6 V versus Ag/AgCl).

The \(n\)Bu\(_4\)N\(^+\) salt proved very difficult to crystallize, so the preparation was repeated beginning with the Ph\(_4\)P\(^+\) salt of [OsCl\(_6\)]\(^{2-}\). The purple solid isolated from this reaction was very highly oxidizing, and decomposed over a period of weeks. The u.v./visible spectrum of the decomposition product(s) revealed bands assignable to [OsCl\(_6\)]\(^{2-}\).**

If instead the complex is isolated in its divalent oxidation state, then the material has considerably greater stability. The synthesis of this complex involves firstly preparing a purple solution of [OsCl\(_5\)(NO)]\(^{1-}\) (as above), and then reducing Os\(^{III}\) to Os\(^{II}\) by adding one equivalent of Ph\(_4\)PBH\(_4\); the colour of the solution fades immediately to pale yellow, after which diethyl ether is added to precipitate (Ph\(_4\)P\(_2\))([OsCl\(_5\)(NO)]). Purple solutions of the tervalent species, [OsCl\(_5\)(NO)]\(^{1-}\), are readily prepared by oxidation of dichloromethane solutions of [OsCl\(_5\)(NO)]\(^{2-}\) with NOPF\(_6\).

5.2.2 Disubstituted Complexes of Stoichiometry \([\text{Os}X_4L_2]^{2-}\)

(i) \(L=\text{acetonitrile}\).

The previously unreported bis-acetonitrile complexes were synthesized by the chemical reduction of acetonitrile solutions of the monosubstituted complexes, \([\text{Os}X_5(\text{MeCN})]^{1-}\) (X=Cl, Br). In the case of X=Cl, the n-tetrabutylammonium salt was difficult to crystallize, and repeatedly gave poor elemental analyses. The tetraphenylphosphonium salt on the other hand was more easily isolated, and provided satisfactory analysis. However, it has appreciably poorer solubility than the \(n\)Bu\(_4\)N\(^+\) salt.

These compounds were characterized initially by their u.v./visible

** One possible mechanism of decomposition may involve disproportionation, according to the equation below. The visible spectrum of the Os\(^{II}\) species will be essentially featureless, and its II/III oxidation may be at an extreme potential, given that the analogous couple occurs at +1.2 V in [OsCl\(_5\)(NO)]\(^{1-}\).

\[
2 \text{[Os}^{III}\text{Cl}_5\text{(NO)}]^{1-} \rightarrow \text{[Os}^{II}\text{Cl}_4\text{(NO)}_2]^{2-} + \text{[Os}^{IV}\text{Cl}_6]^{2-}
\]
spectra, which matched in profile those of the analogous ruthenium compounds. As with the \([\text{OsX}_5\text{L}]^{1-}\) complexes, negative-ion FAB mass spectra also proved very useful in the identification of reaction products. In each case molecular ions \(([M]^{1-})\) were observed for the \([\text{OsX}_4(\text{MeCN})_2]^{1-}\) anions, at \(m/z = 413.9\) for \(X = \text{Cl}\) and at \(m/z = 591.7\) for \(X = \text{Br}\). The base peak for both complexes belonged to the \([M-2\text{MeCN}]^{1-}\) fragment, with the isotope splitting pattern matching that calculated for \([\text{OsX}_4]^{1-}\). The \([\text{M-MeCN}]^{1-}\) fragment was also present in the spectra of both compounds. While no evidence of the organic cation was found, the alcohol matrix (NBA) readily combined with the molecular ion to produce \([M+NBA]^{1-}\) and \([M+2\text{NBA}]^{1-}\) ions.

**Table 5.2** Mass spectral data for some trans-\([\text{OsX}_4\text{L}_2]^{1-}\) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(m/z)</th>
<th>% of base peak</th>
<th>Fragment (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{OsCl}_4(\text{MeCN})_2]^{1-})</td>
<td>719.9</td>
<td>8</td>
<td>([M + 2 \text{NBA}]^{1-})</td>
</tr>
<tr>
<td></td>
<td>566.9</td>
<td>28</td>
<td>([M + \text{NBA}]^{1-})</td>
</tr>
<tr>
<td></td>
<td>413.9</td>
<td>52</td>
<td>([\text{OsCl}_4(\text{MeCN})]^{1-})</td>
</tr>
<tr>
<td></td>
<td>372.8</td>
<td>15</td>
<td>([\text{OsCl}_4]^{1-})</td>
</tr>
<tr>
<td></td>
<td>331.8</td>
<td>100</td>
<td>([\text{OsBr}_4(\text{MeCN})_2]^{1-})</td>
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<tr>
<td></td>
<td>897.7</td>
<td>8</td>
<td>([\text{OsBr}_4(\text{MeCN})]^{1-})</td>
</tr>
<tr>
<td></td>
<td>744.7</td>
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<td>([\text{OsBr}_4]^{1-})</td>
</tr>
<tr>
<td></td>
<td>591.7</td>
<td>76</td>
<td>([\text{OsBr}_4(\text{MeCN})_2]^{1-})</td>
</tr>
<tr>
<td></td>
<td>552.6</td>
<td>21</td>
<td>([\text{OsBr}_4(\text{MeCN})]^{1-})</td>
</tr>
<tr>
<td></td>
<td>509.6</td>
<td>100</td>
<td>([\text{OsBr}_4]^{1-})</td>
</tr>
<tr>
<td>([\text{OsCl}_4(\text{CO})_2]^{1-})</td>
<td>512.8</td>
<td>13</td>
<td>([\text{OsCl}_4(\text{CO}) + \text{NBA}]^{1-})</td>
</tr>
<tr>
<td></td>
<td>359.8</td>
<td>100</td>
<td>([\text{OsCl}_4(\text{CO})]^{1-})</td>
</tr>
<tr>
<td>([\text{OsBr}_4(\text{CO})_2]^{1-})</td>
<td>565.6</td>
<td>23</td>
<td>([\text{OsBr}_4(\text{CO})_2]^{1-})</td>
</tr>
<tr>
<td></td>
<td>537.6</td>
<td>39</td>
<td>([\text{OsBr}_4(\text{CO})]^{1-})</td>
</tr>
</tbody>
</table>

\(^a\) Recorded in 3-Nitrobenzyl alcohol (NBA) matrix.

Chemical reduction of \([\text{OsBr}_5(\text{MeCN})]^{1-}\) with organo-soluble salts of \(\text{BH}_4^-\) was monitored voltammetrically. Two products are formed initially upon addition of the reducing agent to an acetonitrile solution of the
complex. With time, one product gives way to the other. This process was speeded up by heating the reaction vessel. Given that the couples of the trans isomer were identified upon isolation of the complex, the positions of the other couples (~230 mV anodic of the trans) correspond to the transient product being the cis isomer. In these circumstances, voltammetric monitoring of the reaction is most convenient and informative.

(ii) \( L = \text{carbonyl} \).

As previously mentioned (Section 5.2.1), the tervalent di-carbonyl complexes were first prepared while attempting to isolate the monocarbonyls, \( [\text{OsX}_5(\text{CO})]^{2-} \). The procedure involved passing CO gas through a warm 1,2-dichloroethane solution of \((\text{tBu}_4\text{N})_2[\text{OsX}_6] \) (X=Cl, Br), containing one mole equivalent of AgCF\(_3\)SO\(_3\). This reaction yielded the \( \text{trans} \)-\( \text{tBu}_4\text{N}[\text{OsX}_4(\text{CO})_2] \) compounds. A similar procedure using two mole equivalents of AgCF\(_3\)SO\(_3\) gives an identical product. These products were first characterized spectroscopically, the infrared and u.v./visible spectra matching those in the literature for \( \text{trans} \)-[OsBr\(_4\)(CO)\(_2\)]\(^{1-}\).\(^{19}\) The negative-ion FAB mass spectra were again informative, although more complicated than those of the bisacetonitrile complexes. In the case of X=Cl, the [M]\(^{1-}\) molecular-ion for \( \text{trans} \)-[OsCl\(_4\)(CO)\(_2\)]\(^{1-}\) was not observed. The most abundant peak corresponded to [OsCl\(_4\)(CO)]\(^{1-}\) (m/z=359.8). A number of other peaks were also observed at higher m/z values, which could be identified as Os/Cl/CO/NOBA aggregates, formed through the re-combination of fragments inside the spectrometer. Where X=Br, the molecular-ion for \( \text{trans} \)-[OsBr\(_4\)(CO)\(_2\)]\(^{1-}\) was observed, in addition to the [OsBr\(_4\)(CO)]\(^{1-}\) fragment. Re-combination of fragments apparently occurs giving aggregates at high m/z values, as with the chloride complex.

The structure of \( \text{trans} \)-\( \text{tBu}_4\text{N}[\text{OsBr}_4(\text{CO})_2] \) has been confirmed by a single crystal x-ray diffraction study (see Appendix 2).

The route applied above is similar in principle to that used by Preetz et al.,\(^{19}\) but lacks the complication of a coordinating solvent. He described the formation of \( \text{trans} \)-[OsX\(_4\)(CO)\(_2\)]\(^{1-}\) (X=Br, I) complexes by the action of CO on acetone solutions of Na\(_2[\text{OsX}_6]\) (X=Br, I). In this reaction the two moles of Na\(^+\) ion could function as the halide abstracting reagent. Given the capacity
Chapter 5

trans-[OsX₄(CO)₂]⁻ to form trans-[OsX₄(CO)(S)]⁻ complexes in a variety of solvents (including acetone, see (iv)), it is somewhat suprising the di-carbonyl was isolated from the conditions described. Preetz et al. only reported the isolation of the bromide and iodide trans-[OsX₄(CO)₂]⁻ complexes, and not the chloride analogue, although they hint at its presumed existence.⁶⁴ The latter complex has been prepared and isolated here for the first time.

(iii) \(L=\text{tert-butyl isonitrile.}\)

The tert-butyl isocyanide complexes, trans-[OsX₄(CNBut)₂]⁻ (X=Cl, Br) were first prepared in low yields while attempting to isolate salts of [OsX₅(CNBut)]⁻ (Section 5.2.1). As with the other complexes of this formula, the di-isonitrile compounds were characterized by infrared and u.v./visible spectroscopy, and negative-ion FAB mass spectrometry.

A more successful route was however devised. Heating a 1,2-dichloroethane solution of \((\text{Ph}_4\text{P})_2[\text{Os}_2(\mu-X)X]_8\) to reflux in the presence of a small excess of CNBut gives high yields of trans-\(\text{Ph}_4\text{P}[\text{OsX}_4(\text{CNBut})_2]\) compounds (X=Cl, Br).

(iv) Mixed Complexes, \(L=\text{Carbonyl, } L'=\text{other } \pi\text{-acceptor ligands.}\)

The trans-[OsX₄(CO)₂]⁻ complexes are excellent precursors for a range of trans-[OsX₄(CO)(L)]⁻ complexes. Simply stirring dry dichloromethane solutions of trans-[OsX₄(CO)₂]⁻ in the presence of the incoming ligand L results in substitution of CO by L. Complexes of this type have been prepared for L=MeCN and CNBut, for both X=Cl Br, and were characterized by infrared and u.v./visible spectroscopy, and negative-ion FAB mass spectrometry. The mass spectral data for the trans-[OsX₄L₂]⁻ complexes are contained in Table 5.2. The structure of trans-\(n\text{Bu}_4\text{N}[\text{OsBr}_4(\text{CO})(\text{MeCN})]\) has also been determined (see Appendix 3). The nitrile ligand in this latter complex can however be removed. Boiling trans-[OsX₄(CO)(MeCN)]⁻ in acetone for several minutes yields trans-[OsX₄(CO)(Me₂CO)]⁻.

It is suprising that Preetz et al were able to isolate salts of trans-[OsBr₄(CO)₂]⁻, given that their preparation was carried out in acetone. Dissolving trans-[OsX₄(CO)₂]⁻ (X=Cl, Br) in acetone yields trans-
[OsX₄(CO)(Me₂CO)]⁻ (X=Cl, Br) over a period of an hour at room temperature. The substitution of carbonyl by acetone may possibly be suppressed with the large excess of CO present.

Chapter 5

It is appropriate to summarize the results described for these novel complexes before describing the volatility of the substituted ethylene complexes. Several authors have previously quoted electrode potentials for some or all of the [OsX₄(CO)(X=Cl, Br) compounds. In nearly all cases for the dichloromethanes, the [OsX₄Cl]⁻ (X=Cl, Br) complexes display a reversible oxidation to Os(V=VIII), and a quasi-reversible reduction (Os(V=VII)) at 223 K. Figure 31 shows the cyclic voltammetry of [OsBr₄Cl]⁻ recorded in dichloromethane at 223 K under routine conditions.

Figure 31 Cyclic voltammetry of [OsBr₄Cl]⁻ in 8.5 mM Me₂SO at 223 K, scan rate = 50 mV/s.

Under special conditions, a third redox process can be observed. This experiment requires extremely dry conditions, as a special cell was used for this purpose. A number of designs of vacuum-tight electrochemical cells have been published within the literature. The cell used here is of independent design, but remains essentially the same features. The variable-tight cell consists of a central compartment both required electrodes, attached to which is a number of sidearms, all of which can be independently isolated. The procedure for the use of the cell involves firstly...
5.3.1 Voltammetry of Hexahaloosmate Complexes, [OsX₆]²⁻

It is appropriate to summarize the redox behaviour of the hexahalide complexes before describing the voltammetry of the substituted haloosmate compounds. Several authors have previously quoted electrode potentials for some or all of the [OsX₆]²⁻ (X=F, Cl, Br) compounds. In freshly distilled dichloromethane, the [OsX₆]²⁻ (X= Cl, Br) complexes display a reversible oxidation (OsIV/III), and a quasi-reversible reduction (OsIV/III) at 223 K. Figure 5.1 shows the cyclic voltammetry of [OsBr₆]²⁻ recorded in dichloromethane at 223 K under routine conditions.

![Cyclic voltammogram of (nBu₄N)₂[OsBr₆] in 0.5 mol dm⁻³ nBu₄NPF₆/CH₂Cl₂ at 223 K, scan rate =100 mV/s.](image)

Figure 5.1 Cyclic voltammogram of (nBu₄N)₂[OsBr₆] in 0.5 mol dm⁻³ nBu₄NPF₆/CH₂Cl₂ at 223 K, scan rate =100 mV/s.

Under special conditions, a third redox process can be observed. This experiment requires extremely dry conditions, so a special cell was used for this purpose. A number of designs of vacuum-tight electrochemical cells have been published within the literature. The cell used here is of independent design, but retains essentially the same features. The vacuum-tight cell consists of a central compartment (with required electrodes), attached to which is a number of sidearms, all of which can be independently isolated. The procedure for the use of the cell involves firstly
loading different sidearms with the necessary components, i.e. electrolyte, compound and internal reference material. The cell and its contents are then thoroughly dried, and the solvent distilled directly onto the electrolyte. Once sealed under argon or nitrogen, the cell is ready for use. The solvent/electrolyte mixture is transferred to the central compartment of the cell by opening the appropriate tap and rotating the entire apparatus. After establishing the background potential limits, the compound under investigation is similarly transferred to the central compartment. Finally, when the voltammetry has been satisfactorily recorded, the reference material is moved to the main cell compartment for calibration of the observed couples.

Figure 5.2 presents the cathodic region of both the cyclic and a.c. voltammograms of $[\text{OsBr}_6]^{2-}$ in dichloromethane at 223 K, measured in the cell described above. Only under these extremely dry conditions can the irreversible Os$^{III/II}$ couple be observed. The analogous couple in $[\text{OsCl}_6]^{2-}$ was not observed, even under such stringent conditions.

![Figure 5.2 Voltammetry of ($^n\text{Bu}_4\text{N})_2[\text{OsBr}_6]$ in specially designed vacuum tight cell, under identical conditions to those listed in Figure 5.1.](image-url)
The voltammetric data recorded for the hexahaloosmate complexes are presented in Table 5.3. The variation in metal-based redox couples with different halide ions is largely dependent upon the actual system under consideration. Aside from the identity of the halide, the metal, the redox process in question and the other ancillary ligands are also of importance. Perusal of the literature reveals the spread of $E_{1/2}$ with halide is extremely varied, depending upon the nature of the complex being studied. For example, in a low oxidation state complex with only a single halide and other soft, $\pi$-acceptor ligands, the shifts in $E_{1/2}$ upon changing the halide may be very small.71 Alternatively, in higher oxidation state complexes with hard $\sigma/\pi$-donor ligands, such as the hexahalides, the spread in $E_{1/2}$ may be large.67

<p>| Table 5.3 $E_{1/2}$ data for $[\text{OsX}_6]^{2-}$ and $[\text{OsX}_5L]^-$ complexes. |</p>
<table>
<thead>
<tr>
<th>Complex</th>
<th>V/IV</th>
<th>IV/III</th>
<th>III/II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{OsCl}_6]^{2-}$</td>
<td>+1.50 (r)</td>
<td>-0.49 (qr)</td>
<td>$b$</td>
</tr>
<tr>
<td>$[\text{OsBr}_6]^{2-}$</td>
<td>+1.43 (r)</td>
<td>-0.37 (qr)</td>
<td>-2.28 (irr)</td>
</tr>
<tr>
<td>$[\text{OsCl}_5(\text{MeCN})]^-$</td>
<td>+2.02 (pr)</td>
<td>+0.21 (r)</td>
<td>-1.47 (pr)</td>
</tr>
<tr>
<td>$[\text{OsBr}_5(\text{MeCN})]^-$</td>
<td>+1.85 (pr)</td>
<td>+0.25 (r)</td>
<td>-1.45 (pr)</td>
</tr>
<tr>
<td>$[\text{OsCl}_5(\text{py})]^-$</td>
<td>+1.89 (pr)</td>
<td>+0.07 (r)</td>
<td>--1.5 (irr)</td>
</tr>
<tr>
<td>$[\text{OsBr}_5(\text{py})]^-$</td>
<td>+1.78 (pr)</td>
<td>+0.17 (r)</td>
<td>-1.31 (qr)</td>
</tr>
<tr>
<td>$[\text{OsCl}_5(\text{CNBu})]^-$</td>
<td>+0.37 (r)</td>
<td>+0.37 (r)</td>
<td>-1.00 (irr)</td>
</tr>
<tr>
<td>$[\text{OsBr}_5(\text{CNBu})]^-$</td>
<td>+1.80 (irr)</td>
<td>+0.50 (r)</td>
<td>-0.95 (irr)</td>
</tr>
<tr>
<td>$[\text{OsCl}_5(\text{Me}_2\text{CO})]^-$</td>
<td>+1.6 (irr)</td>
<td>-0.02 (r)</td>
<td>-1.84 (pr)</td>
</tr>
<tr>
<td>$[\text{OsCl}_5(\text{thf})]^-$</td>
<td>+1.88 (irr)</td>
<td>-0.05 (r)</td>
<td>-1.85 (irr)</td>
</tr>
<tr>
<td>$[\text{OsCl}_5(\text{CO})]^2-$</td>
<td>$b$</td>
<td>+1.20 (pr)</td>
<td>-0.60 (irr)</td>
</tr>
<tr>
<td>$[\text{OsBr}_5(\text{CO})]^2-$</td>
<td>$b$</td>
<td>+1.16 (r)</td>
<td>-0.36 (irr)</td>
</tr>
</tbody>
</table>

$^a$ Recorded in 0.5 mol. dm$^{-3}$ $n\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ at 213 K, versus $\text{Ag}/\text{AgCl}$. $r$=reversible, qr=quasi-reversible, pr=partially reversible, irr=irreversible $b$ Not observed.

The ability of the halide to stabilize high oxidation states decreases from fluoride through to iodide, as the charge/ionic radii ratio decreases, along with the $\pi$-donor ability of the halide.72 The ease with which
complexes are oxidized (or the difficulty with which they are reduced) often follows this same progression, with the oxidation potentials (of complexes) increasing along the series F-, Cl-, Br-, I-. However, it should be noted that this is not always the case, and the reverse order has also been observed. On occasions the difference in redox potentials between fluoride and the other heavier halides is significant, followed by only small shifts amongst chloride, bromide and iodide, and not necessarily in the periodic order. This non-uniform change has been observed in other physicochemical measurements on a number of systems. The availability of empty d-orbitals for back-donation from the metal on chloride, bromide and iodide, but not fluoride, can often account for the discontinuity in observed results.

The OsV/IV couple of [OsCl₆]²⁻ is more positive than that of the analogous [OsBr₆]²⁻, while the OsIV/III couple of the chloride is found negative of the bromide position. Chloride and bromide are generally speaking more alike in their influence of chemical properties than any other two halide ions. In light of the wide and varied nature of results of electrochemical studies on complexes coordinating different halide ions, the small differences noted above are not unexpected. Similar variations have also been observed in the substituted complexes about to be described, however the dependence of \( E_{1/2} \) on halide will not be discussed further, except in special circumstances.

### 5.3.2 Voltammetry of [OsX₅L]²⁻ Complexes

(i) L=acetonitrile, pyridine, acetone, tetrahydrofuran and tert-butyl isonitrile.

In the standard +2.0→-2.0 volt electrochemical window routinely provided by solvents such as dichloromethane and acetonitrile (versus Ag/AgCl), three metal-based redox steps are observed for the [OsX₅L]²⁻ compounds (L=MeCN, py, Me₂CO, thf, CNBu). All the commonly available osmium oxidation states (II→V) can be generated at the working electrode, although some of these species are very unstable. Associated with each of the above tetravalent complexes are two reductions (Os⁴⁺/³⁻ & Os³⁻/²⁻) and an oxidation (Os⁴⁺/⁵⁺). The cyclic voltammogram of \( n\text{Bu}_4\text{N}[\text{OsCl}_5(\text{MeCN})] \) recorded in dichloromethane at 213 K is presented in
Figure 5.3, showing the reversible Os$^{IV}$/III reduction, and the partially reversible Os$^{III}$/II and Os$^{IV}$/V couples. The voltammetric results for all the [OsX$_5$L]$^{2-}$ complexes are summarized in Table 5.3.

\[ \text{Os}^{IV/III} \quad \text{Os}^{III/II} \]

Volts
(vs Ag/AgCl)

\[ +2.0 \quad +1.0 \quad 0.0 \quad -1.0 \quad -2.0 \]

The availability of various oxidation states associated with the [OsX$_5$L]$^{2-}$ compounds are very much dependent upon the nature of the ligand L. Replacing a halide ion with any $\pi$-basic ligand results in an anodic shift of the metal-based redox couples, the magnitude of the shift being dependent upon the strength of the $\pi$-acceptor ligand. The stronger the $\pi$-acceptor ligand, the more accessible the lower oxidation states become.

At low temperature in dichloromethane, the first reduction is uniformly reversible or quasi-reversible for all complexes under discussion here in this section. The second reduction in general is not as reversible as the first, although this does vary somewhat from complex to complex. The return wave of a cyclic voltammogram is usually smaller than the forward wave, and the peak separation in the order of 300 mV. The Os$^{IV}$/V oxidation generally has poor reversibility, depending upon the identity of L.
(ii) \( L = \text{Carbonyl} \).

The pentahalomonocarbonyl complexes differ from those compounds just described in that only two redox couples are observed in the typical voltammetric window. The strong \( \pi \)-acceptor capabilities of the carbonyl ligand mean the Os\( V/IV \) couple becomes inaccessible. Both the chloride and bromide complexes are isolated as tervalent dianions, \( i.e. \) [Os\( \text{III}X_5(\text{CO}) \)]\(^{2-}\). In dichloromethane, under Ar, these complexes display an oxidation (Os\( \text{III}/IV \)) and a reduction (Os\( \text{III}/\text{II} \)). The oxidation is reversible when \( X = \text{Br} \), but only partially-reversible for \( X = \text{Cl} \). While the voltammetry of the chloride complex suggests the Os\( IV \) complex could not be prepared synthetically, Preetz \textit{et al.} isolated salts of the tetravalent [Os\( \text{Cl}_5(\text{CO}) \)]\(^{1-}\) complex, through the action of Cl\(_2\) on \( \text{trans-}[\text{OsX}_4(\text{CO})_2]^{1-} \) (\( X = \text{Br}, \text{I} \)).\(^{21}\) Presumably the oxidation of the metal centre occurs prior to halide substitution.

The reductions of the [Os\( X_5(\text{CO}) \)]\(^{2-}\) complexes are irreversible, even at 213 K. From Figure 5.4, one can see the reduction is completely irreversible, as no return wave is observed.

![Cyclic voltammogram of (Ph\(_4\)P)\(_2\)[OsCl\(_5\)(CO)] in 0.5 mol. dm\(^{-3}\) \( n\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2\) at 213 K.]

Continuing the scan reveals another electroactive species, not present
in the initial scan of this region. This is an example of a ECE mechanism, whereby following electron-transfer, a chemical transformation takes place, yielding another electroactive species.\textsuperscript{68} The identity of the daughter product of this reduction is at present still unknown. There are no obvious additional ligands present, since the reduction is performed in CH\textsubscript{2}Cl\textsubscript{2} under argon. The daughter product occurs 0.31 V anodic of the [OsCl\textsubscript{5}(CO)]\textsuperscript{2-} reduction (\textit{i.e.} at -0.29 V). It is possible traces of water are being coordinated, or alternatively a five coordinate species may be being formed. If the voltammetry is performed under N\textsubscript{2}, the cyclic voltammogram has an essentially identical appearance, except the daughter product is now found 0.46 V anodic of the [OsCl\textsubscript{5}(CO)]\textsuperscript{2-} reduction (\textit{i.e.} at -0.14 V). This species is tentatively identified as the Os\textsuperscript{III/II} couple of \textit{trans-}[OsCl\textsubscript{4}(CO)(N\textsubscript{2})]\textsuperscript{1-}. The bromide complex, [OsBr\textsubscript{5}(CO)]\textsuperscript{2-} behaves in a similar manner, yielding putative [OsBr\textsubscript{4}(CO)]\textsuperscript{2-} and [OsBr\textsubscript{4}(CO)(N\textsubscript{2})]\textsuperscript{1-}. With time, the voltammograms of the chloride complex become less well defined. The forward wave of the oxidation in particular, becomes undefined, through the encroachment of a large irreversible wave. The position of this irreversible wave corresponds to that of free chloride. This suggests chloride is slowly dissociating from the complex. In contrast, the voltammetry of [OsBr\textsubscript{5}(CO)]\textsuperscript{2-} in CH\textsubscript{2}Cl\textsubscript{2} does not degrade with time, and there is no evidence of bromide release.

\textit{(iii) L=Nitrosyl.}

The voltammetry of the pentachloronitrosyl complex is very straightforward. In CH\textsubscript{2}Cl\textsubscript{2} at 213 K, this complex undergoes a reversible Os\textsuperscript{II/III} oxidation at +1.21 V. This is similar to what Heath \textit{et al.} recorded for the voltammetry of the analogous ruthenium complex, the only difference being the latter complex was, as expected, more difficult to oxidize.\textsuperscript{63} The position of the Os\textsuperscript{III/II} couple represents a considerable shift in E\textsubscript{1/2}(Os\textsuperscript{III/II}) from other [OsX\textsubscript{5}L]\textsuperscript{2-} complexes; for example E\textsubscript{1/2}(Os\textsuperscript{III/II}) of [OsCl\textsubscript{5}(MeCN)]\textsuperscript{1-} occurs at -1.47 V, a shift of 2.68 V. Bhattacharyya \textit{et al.} recorded the room temperature voltammetry of the [OsX\textsubscript{5}(NO)]\textsuperscript{2-} (X=Cl, Br, I) complexes in acetonitrile, and described the reversibility of the Os\textsuperscript{II/III} oxidation in the chloride compound as being 'nearly reversible'.\textsuperscript{14}
5.3.3 Voltammetry of trans-[OsX₄L₂]²⁻ Complexes

The voltammetry of the bis-substituted complexes are all very similar, with each complex showing an oxidation (Os³⁺/IV) and a reduction (Os³⁻/II). As in the [OsX₅L]²⁻ compounds, the positions of these couples varies according to the π-acceptor strength of the neutral ligands, the stronger the π-acceptor, the more difficult the oxidation and the easier the reduction become. The electrode potentials associated with these complexes are summarized in Table 5.4.

Table 5.4  $E_{1/2}$ data for trans-[OsX₄L₂]¹⁻ and trans-[OsX₄LL']¹⁻ complexes, and mer-[OsCl₃(MeCN)₃].

<table>
<thead>
<tr>
<th>Complex a</th>
<th>$E_{1/2}$ (V) b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V/IV</td>
</tr>
<tr>
<td>[OsCl₄(MeCN)₂]¹⁻</td>
<td>c</td>
</tr>
<tr>
<td>[OsBr₄(MeCN)₂]¹⁻</td>
<td>c</td>
</tr>
<tr>
<td>[OsCl₄(CO)₂]¹⁻</td>
<td>c</td>
</tr>
<tr>
<td>[OsBr₄(CO)₂]¹⁻</td>
<td>c</td>
</tr>
<tr>
<td>[OsCl₄(CO)(MeCN)]¹⁻</td>
<td>c</td>
</tr>
<tr>
<td>[OsBr₄(CO)(MeCN)]¹⁻</td>
<td>c</td>
</tr>
<tr>
<td>[OsCl₄(CNBut)₂]¹⁻</td>
<td>c</td>
</tr>
<tr>
<td>[OsBr₄(CNBut)₂]¹⁻</td>
<td>c</td>
</tr>
<tr>
<td>[OsCl₄(CO)(CNBut)²]¹⁻</td>
<td>c</td>
</tr>
<tr>
<td>[OsBr₄(CO)(CNBut)²]¹⁻</td>
<td>c</td>
</tr>
<tr>
<td>[OsBr₄(CO)(Me₂CO)]¹⁻</td>
<td>c</td>
</tr>
<tr>
<td>mer-[OsCl₃(MeCN)₃]</td>
<td>c</td>
</tr>
</tbody>
</table>

a  All [OsX₄L₂]¹⁻ complexes are trans isomers. b  Recorded in 0.5 mol. dm⁻³ $n$Bu₄NPF₆/CH₂Cl₂ at 213 K, versus Ag/AgCl. r=reversible, qr=quasi-reversible, pr=partially reversible, irr=irreversible. c  Not observed.

With the exception of trans-[OsBr₄(CO)₂]¹⁻, the Os⁴⁺/IV oxidation was uniformly reversible or quasi-reversible at low temperature for all compounds on a voltammetric timescale. The Os³⁺/IV oxidation of trans-[OsBr₄(CO)₂]¹⁻ is only partially reversible under the same conditions. The reversibility of the Os³⁻/II reduction was more varied. For the trans-[OsX₄(MeCN)₂]¹⁻, trans-[OsX₄(CNBut)₂]¹⁻, trans-[OsX₄(CO)(CNBut)₂]¹⁻ (X=Cl,
Br) complexes, the reduction was quasi-reversible in each case.

The voltammetry of the above complexes is essentially the same when recorded in acetonitrile at low temperature, although care must be taken with the dicarbonyl complexes, to ensure substitution does not take place. The substitution of carbonyl by acetonitrile can in fact be conveniently monitored by voltammetric techniques. The dichloromethane/acetonitrile solvent mixture is prechilled to 233 K prior to adding the complex. Upon warming, the waves corresponding to trans-[OsX₄(CO)₂]⁻ decrease in height, with the growth of new waves from trans-[OsX₄(CO)(MeCN)]⁻.

![Cyclic voltammogram of trans-Ph₄P[OsCl₄(MeCN)₂] in 0.1 mol dm⁻³ nBu₄NPF₆/MeCN, at (a) room temperature and (b) 233 K.](image)

**Figure 5.5** Cyclic voltammogram of trans-Ph₄P[OsCl₄(MeCN)₂] in 0.1 mol dm⁻³ nBu₄NPF₆/MeCN, at (a) room temperature and (b) 233 K.

At room temperature in acetonitrile, the OsIII/II reduction of trans-[OsX₄L₂]⁻ complexes tends to become irreversible. Figure 5.5, parts (a) and (b) show the cyclic voltammogram of trans-[OsCl₄(MeCN)₂]⁻ at both 293 and 233 K. A classical ECE mechanism operates at room temperature. Figure 5.5 does not show the next cyclic scan over the newly produced species, but this wave is in fact reversible. The daughter product has its OsIII/II couple 0.73 V.
more anodic than the Os$^{III/II}$ couple of trans-[OsCl$_4$(MeCN)$_2$]$^{1-}$. Such a shift corresponds to the expulsion of chloride from the reduced Os$^{II}$ centre, followed by the coordination of acetonitrile, giving mer-[OsCl$_3$(MeCN)$_3$], as identified by its u.v./visible spectrum. Similar shifts were observed in the analogous ruthenium system. Part (b) of Figure 5.5 shows the effect of cooling upon the Os$^{III/II}$ reduction. The couple becomes quasi-reversible, with no evidence for the formation of any daughter products.

5.3.4 Voltammetry of Further Substituted Complexes

The electrochemistry of the mer-OsX$_3$(MeCN)$_3$ compounds (X=Cl, Br) in dichloromethane reveals an oxidation (Os$^{III/IV}$) and a reduction (Os$^{III/II}$), both of which are quasi-reversible at room temperature. The positions of these couples are listed in Table 5.5, with those of the trans-[OsX$_4$L$_2$]$^{1-}$ complexes.

The well known mer-OsX$_3$(PR$_3$)$_3$ compounds display very similar electrochemistry, which has been previously documented. The mer-OsCl$_3$(PMe$_2$Ph)$_3$ complex in particular has been comprehensively studied by Heath et al. They found that reduction of the neutral species in non-coordinating media resulted in the formation of the triple chloro-bridged binuclear complex, [Os$_2$(µ-Cl)$_3$(PMe$_2$Ph)$_6$]Cl. Carrying out this same experiment with mer-[OsX$_3$(MeCN)$_3$] did not yield a binuclear complex. Air free solutions of the mono-anion, [mer-OsX$_3$(MeCN)$_3$]$^{1-}$, were in fact stable at room temperature. At this same temperature, a strong difference was observed in the behaviour of the phosphine and nitrile complexes, when recorded in coordinating solvents (S). Reduction of mer-[OsCl$_3$(PMe$_2$Ph)$_3$] yielded [OsCl$_2$(PMe$_2$Ph)$_3$(S)] almost immediately, however the bulk reduction of mer-[OsX$_3$(MeCN)$_3$] in acetonitrile again gives only the mer-[OsX$_3$(MeCN)$_3$]$^{1-}$ species. This anion is quite stable, and only shows signs of decomposition after several hours at room temperature. The decomposition product is almost certainly an isomer of [OsX$_2$(MeCN)$_4$]. The new species has two oxidations, 0.70 and 0.65 volts more anodic than the respective couples in the monomeric starting complex. These shifts are consistent with the loss of halide (also detected in the cyclic voltammogram)
and the coordination of a further nitrile ligand. The electrolysis was performed under argon, as nitrogen coordinates quite readily to OsII. The identity of the isomer remains unknown, although if this chemistry parallels that of the phosphines, the cis isomer will be formed.
5.4 CHARGE-TRANSFER SPECTRA OF MONOMERIC COMPLEXES

5.4.1 General

Many of the compounds whose preparation has been described in an earlier part of this chapter are intensely coloured complexes, through absorption in the visible region of the spectrum. Colour in transition metal compounds often arises because of transitions within unfilled $d$ shells. In many cases however, the colour comes, at least in part, as a consequence of electron transfer from the metal to the ligand, or the converse, from the ligand to the metal. When such processes, termed charge-transfer transitions, occur in the visible region of the spectrum, the complex is coloured. There are two principal types of charge-transfer transitions, namely ligand-to-metal (l.m.c.t.) or metal-to-ligand charge-transfer (m.l.c.t.).

The latter type of charge-transfer processes occur more commonly in transition metal complexes where the metal has a full complement of $d_{\pi}$ electrons, i.e. a $t_{2g}^6$ configuration. Metal-to-ligand charge-transfer spectra will not be discussed at length in this chapter, since only one complex, $[\text{OsCl}_5(\text{NO})]^2-$, was isolated with osmium in its divalent oxidation state. Some Os$^{II}$ species were however characterized in situ by spectroelectrogeneration, so mention of their spectra will be made at the appropriate place.

The u.v./visible spectra of $d^n$ heavy metal hexahalide complexes (where $d \leq 6$) are dominated by l.m.c.t. bands. The study of l.m.c.t. spectra really began in 1959, when Jørgenson published his pioneering work "Electron Transfer Spectra of Hexahalide Complexes". In this paper he presented an explanation of the u.v./visible spectra of the known $d^n$ heavy metal hexahalide complexes. These spectra are characterized by intense halide-to-metal charge-transfer excitations, which can be viewed as an "internal" redox step, or one-electron promotion [equation (5.1)].

$$[\text{M}^n(X_6^{6-})] \xrightarrow{\text{hv}} [\text{M}^{n-1}(X_6^{5-})]$$

(5.1)
In simple terms, the energy of this l.m.c.t. transition is dependent upon two factors; firstly, the oxidizing power of the metal (i.e. how easily the metal is reduced), and secondly the reducing power of the ligand (i.e. how easily the ligand is oxidized). For hexahalide complexes \([M(d^n)X_6]^{2-}\), of fixed \(X\) and \(n\), the halide-to-metal charge-transfer energy decreases upon moving across the 2nd and 3rd row d-block elements, and increases in going from 4d to 5d metals. Similarly, for a fixed \(M\) and \(n\), the halide-to-metal charge-transfer manifold is found at progressively lower energy upon descending down the halide group F, Cl, Br and I, as the ligand becomes easier to oxidize.

From a large body of data, Jørgenson noted these systematic shifts in charge-transfer energies with the orderly variation of ligands and metals within complexes of the same symmetry and coordination number. Assuming the energy of a charge-transfer transition was proportional to the electronegativity difference between the donor and acceptor orbitals, optical electronegativities were calculated for individual ligands and metals, based on the position of the first Laporte allowed band in the charge-transfer spectra. A value of 3.9 was chosen for fluoride (to match the Pauling electronegativity value), and so the ligand-to-metal charge-transfer energy was given by the expression in equation (5.2), where \(\chi_{\text{opt}}(X)\) and \(\chi_{\text{opt}}(M)\) are the optical electronegativities of the ligand donor and metal acceptor orbitals respectively. The 30 000 cm\(^{-1}\) constant relates the \(\chi_{\text{opt}}\) scale to the Pauling electronegativity scale.

\[
\nu_{\text{LMCT}} (\text{in cm}^{-1}) = 30 000[\chi_{\text{opt}}(X) - \chi_{\text{opt}}(M)] \quad (5.2)
\]

What the equation fails to take into account however is the interelectronic repulsion correction, which unfortunately is not trivial. The value of optical electronegativities lies in their ability to predict approximate shifts in \(\nu_{\text{LMCT}}\) energies accompanying ligand, metal or oxidation state changes in complexes of the same symmetry. Care must however be exercised in their use, especially in complexes with two or more kinds of ligands.

While the range of complexes available to spectroscopists has grown enormously since Jørgensons early work, the 4d and 5d hexahalometalates
still remain the most studied series of compounds. Before considering the charge-transfer spectra of the these complexes in any detail, it is worthwhile to consider what types of l.m.c.t. transitions may occur in such systems. A simplified molecular orbital scheme for metal-halide interactions is shown in Figure 5.1. Examination of this diagram reveals four types of l.m.c.t. transitions are possible, listed below in order of increasing energy.

(i) ligand(\(\pi\))-to-metal(\(t_{2g}\))
(ii) ligand(\(\pi\))-to-metal(\(e_g\))
(iii) ligand(\(\sigma\))-to-metal(\(t_{2g}\))
(iv) ligand(\(\sigma\))-to-metal(\(e_g\))

Building up the molecular orbital diagram for the [MX\(_6\)]\(^{2-}\) complex reveals a more complicated situation. The six halides around the central metal ion set up twelve occupied \(\pi\)-orbitals and six occupied \(\sigma\)-orbitals. The \(\pi\)-orbitals are split (primarily because of halide-halide interactions) into four groups of symmetry \(t_{1g}, t_{1u}, t_{2u}, t_{2g}\), while the \(\sigma\)-orbitals transform to \(a_{1g}, e_g,\) and a \(t_{1u}\) group. There has been some disagreement within the literature as to the ordering of the \(\pi\)-orbitals, but it is generally accepted that the order is as quoted above, with the \(t_{1g}\) being highest in energy, and the \(t_{2g}\) lowest. The \(\sigma\)-orbital ordering, from highest to lowest, is believed to be \(e_g, t_{1u}, a_{1g}\).
Chapter 5

The l.m.c.t. transitions can still be viewed as belonging to one of the four types listed above. Instead of there being one transition of type (i), four are now expected, from each of the \( \pi \) symmetry orbitals, into the metal acceptor orbital.

The ground state of the metal ion is also of importance. In a \( d^5 \) ion, the single vacancy in the \( t_{2g} \) set of \( d \) orbitals means the excited state has only one possible metal-based configuration, that being \( d^6 \). Interelectronic repulsion need not be considered any further. For \( d^4 \) ions, the situation is more complicated, as more than one state is possible for the \( d^5 \) ion generated by excitation, e.g. \([\text{RuCl}_6]^2-\).

One may then expect, for a \( d^5 \) ion with only one hole in the \( t_{2g} \) set, the four lowest energy charge-transfer bands to be assigned as ligand(\( \pi \))-to-metal(\( t_{2g} \)) transitions (one from each of the four triplet levels). This is in fact how the spectrum of \([\text{IrCl}_6]^2-\) is interpreted (Figure 5.7). Selection rules account for the intensity differences.

![Figure 5.7](image-url)  

*Figure 5.7*  U.v./visible spectrum of \([\text{IrCl}_6]^2-\).

The \( t_{1u}(\text{Cl} \pi) \rightarrow t_{2g}(d_{\pi}) \) and \( t_{2g}(\text{Cl} \pi) \rightarrow t_{2g}(d_{\pi}) \) promotions are very weak, since these transitions are Laporte (\( g \leftrightarrow g \)) forbidden. The spectra of the chloride complexes are most readily assigned, as the spin-orbit coupling constant of chloride is not large enough to produce observable splittings of the triply degenerate halide donor levels. The larger spin-orbit coupling constants of bromide and iodide make the spectra of the \([\text{MBr}_6]^2-\) and \([\text{MI}_6]^2-\)
complexes more complicated. Further transitions at higher energy are also observed in the example shown Figure 5.7. Donation from the highest σ-orbital into the metal t$_{2g}$ orbitals occurs at ~32 250 cm$^{-1}$, this being a type (iii) transition. Another complex in the class of low spin d$^5$ ions is [OsCl$_6$]$^{3-}$ (Figure 5.8). Its spectrum is very similar in profile (but blue shifted) to that of the isoelectronic [IrCl$_6$]$^{2-}$, and is assigned analogously.

The halide-to-metal charge-transfer spectra of the [OsX$_6$]$^{2-}$ (X=F, Cl, Br, I) species have also been recorded and assigned. While the d$^4$ configuration of Os$^{IV}$ may have been expected to give complicated spectra, through having more than one possible excited state, this is not the case and the spectra in general have similar features to the d$^5$ systems (Figure 5.9). This occurs through a further restriction (j-j selection rule) that only acquires importance under extreme spin-orbit coupling, as in 5d elements.

![Figure 5.8](image_url)  
**Figure 5.8** U.v./visible spectrum of [OsCl$_6$]$^{3-}$.

The one-electron promotion model, successful in describing the spectra of d$^4$ and d$^5$ hexahalometalates, can also be applied to substituted complexes. As stated above, the two main bands in the spectra of d$^5$ [MX$_6$]$^{2-}$ complexes arise from transitions between a triply degenerate halide donor orbitals (t$_{1u}$, t$_{2u}$) and the t$_{2g}$ metal acceptor orbital. Any one component of these symmetry donor orbitals only encompasses $p$ orbitals from four of the six halides, such that even in the hexahalide complexes, the important charge-transfer chromophore is the planar array of four halides. Fortunately the
replacement of one or two axial halides with other ligands acts to simplify rather than disrupt this basis, through removing excess three-fold degeneracy associated with six halides around the metal centre. The dominant [MX₄] chromophore is retained upon substitution to the [MX₅L] and trans-[MX₄L₂] complexes.

![Absorbance vs Wavenumber](image)

**Figure 5.9** U.v./visible spectrum of [OsCl₆]²⁻.

The solution spectra of the [OsX₅L]²⁻ and trans-[OsX₄LL']²⁻ (L=L' and L≠L') complexes are now discussed. The charge-transfer spectra of the latter are in general more readily interpreted than those of the [OsX₅L]²⁻ species, and so are described first.

### 5.4.2 Spectra of the trans-[OsX₄L₂]¹⁻ and trans-[OsX₄LL']¹⁻ complexes.

Several features of the low spin d⁵ trans-[MX₄L₂]¹⁻ system make complexes of this type an ideal place to start when discussing the charge-transfer spectra of substituted heavy metal halide complexes. Consider firstly the structure, which ideally belongs to the D₄h symmetry point group. The axial trans ligands do not interact to any large extent with the equatorial halides, so to a first approximation any mixing of the X and L orbitals can be neglected. It is therefore reasonable to expect distinct l.m.c.t transitions,
from the halides $X(\sigma$ and $\pi$), and the ligands $L(\sigma)$, to the metal acceptor orbitals. This situation is informative, in that the charge-transfer energies can be assigned directly to energy gaps between the bonding and non-bonding (or anti-bonding) molecular orbitals. Those transitions in which the ligand donor orbitals are coplanar with the metal acceptor orbitals, are likely to have the greatest intensity. This principle was established by Jørgenson, and comes through the need for efficient orbital overlap between the donor and acceptor orbitals involved in the transition.

Also of significance is the orientation of the metal acceptor orbital in the $d^5$ trans-$[MX_4L_2]^{1-}$ complexes. The unique vacancy in the ground state of the metal ion will occur in the $t_{2g}$ orbital highest in energy. $\pi$-donating halide ligands have a destabilizing influence on the metal $t_{2g}$ orbitals, such that the orbital of highest energy will be that which experiences the greatest degree destabilization, i.e. that orbital which interacts with the greatest number of halides. The singly occupied orbital therefore lies in the plane of the four halide ions. Taking the $z$-axis as running parallel to the L-Os-L' bond axis, then it is the $d_{xy}$ orbital which contains the electronic hole.

If the unique hole lies in the $d_{xy}$ orbital, any promotions from the $\sigma$-orbital of the neutral ligand to a metal $t_{2g}$ orbital are likely to be weak in intensity, since the donor and acceptor orbitals are orthogonal. In addition, if the occupied donor orbitals of ligands $L$ are relatively low in energy (as compared with those orbitals of the halides), then such transitions will in general occur at high energies, thereby not complicating the visible region of the spectrum. The likelihood of $L(\sigma)\rightarrow M(d_{\pi})$ transitions being either very weak in intensity or occurring at high energies, means the ligand $L$ can be regarded as essentially being 'optically transparent' (over the visible region of the spectrum). This then places considerable significance on the plane of four halide ions as being the important chromophore responsible for the charge-transfer spectra of these complexes. In summary, the nature of the $d^5$ trans-$[MX_4L_2]^{1-}$ system means the charge-transfer spectra can be assigned with confidence in terms of the $[MX_4]^{1-}$ halide donor orbital array, which itself is readily recognized as a subset of the $[MX_6]^{2-}$ chromophore.

* described by a negative $e_{\pi}$ parameter in the angular overlap model.
Heath and Duff recently mapped the halide symmetry orbitals for the complete series of compounds varying in stoichiometry from \([MX_6]^{2-}\) to \([MXL_5]^{2-}\) (where X=halide, L=nitrile).\(^1\) For trans isomers of stoichiometry \([MX_4L_2]^{1-}\), the important ligand donor orbitals are those set up by the \(\pi\)-orbitals of the planar tetrahalide array, these being \(a_{2g}\), \(e_u\) and \(b_{2g}\).\(^2\) The ground state of the \(d^5\) configuration is \(^2B_{2g}\), such that a series of transitions from the ligand donor orbitals to the metal acceptor orbital are expected (Figure 5.10).\(^2\) The spectra for ruthenium and osmium complexes are in general very similar in profile, and differ only in the energies of the transitions.

\[\text{Figure 5.10} \quad \text{U.v./visible spectrum of trans-[RuCl}_4\text{(MeCN)}_2\text{]}^{1-}.\]

The visible region of the solution spectra are dominated by a series of intense absorptions, assigned as ligand-to-metal charge-transfer bands, or more specifically \(X(\pi)\rightarrow\text{Os}^{\text{III}}(d_{\pi})\) transitions (where X=halide). This general assignment was confirmed with the changes observed in the spectra upon replacing chloride with bromide (Figure 5.11). Accompanying this exchange of halides was a bathochromic movement in the absorption manifold, of on average \(-6\ 300\ \text{cm}^{-1}\). The shift matches that predicted for halide-to-metal
charge-transfer transitions based on the different optical electronegativity values for chloride and bromide.

![Absorbance (Arbitrary Units)](image)

**Figure 5.11** U.v./visible spectra of [OsX₄(MeCN)₂]⁺, (a) X=Br, (b) X=Cl.

Looking firstly at the spectra of the chloride complexes, they all appear very similar. The spectra are dominated by a strong central band, flanked by weaker, less intense features. This intense band is assigned as the favoured in-plane (allowed) eᵤ→b₂g transition (Figure 5.10), which involves co-planar donation from the halide symmetry orbital to the metal acceptor orbital.
The weak leading band in all of these spectra has been assigned as the $a_{2g} \rightarrow b_{2g}$ transition. While this is also an in-plane transition, selection rules show that it is Laporte-forbidden. The other weak band on the high energy side of the principal $e_u \rightarrow b_{2g}$ transition is more readily observed in some complexes than others. This transition has been assigned as the $b_{2g} \rightarrow b_{2g}$ promotion, which is again Laporte forbidden. The principal band in these spectra appears as a doublet, most obvious in [OsCl$_4$(MeCN)$_2$]$^-$: The doublet arises through the splitting of the degenerate $E_u$ state by halide-based spin-orbit coupling ($\xi$). This effect is most readily seen in comparing a series of complexes which differ only in the identity of the halide ion. Preetz et al. have prepared such complexes, namely the [OsX$_4$(CO)(L)]$^-$ (X=Cl, Br, I; L=H$_2$O, py) series.$^{38,39}$ As the spin-orbit coupling constant of the halide ion becomes larger (down the Cl$^-$, Br$^-$, I$^-$ series), so does the splitting of the principle band.

It is also necessary to remember the trans neutral ligands (L) may have $\sigma$ or $\pi$ orbitals of appropriate energy to give rise to L$\rightarrow$Os$^{III}$(d$_\pi$) transitions. Such bands are likely to be relatively weak in intensity, given that the donor and acceptor orbitals in such transitions are not co-planar. Levason and co-workers noted such weak transitions in trans-[OsX$_4$L$_2$]$^-$ complexes (L=PR$_3$, AsR$_3$, SbR$_3$, X=Cl, Br) $^{31}$ in the 11 000-15 000 cm$^{-1}$ region. The exact position of these bands was dependent upon the actual phosphine, arsine or stibine ligand. The spectra of the trans-[OsX$_4$LL$'$]$^-$ and trans-[OsX$_4$L$_2$]$^-$ compounds studied here did not reveal any bands in the visible region which could be assigned as ligand(L)-to-metal($t_{2g}$) charge-transfer transitions. It is likely the neutral ligands present in these complexes do not have the relatively high energy occupied orbitals required for L$\rightarrow$Os$^{III}$(d$_\pi$) transitions to intrude.

The identity of the ligands L and L$'$ does however contribute to the position of the halide-to-metal absorption manifold. The stronger the $\pi$-acceptor ligands, the lower the position of the halide-to-metal charge-transfer manifold. For example, in the trans-[OsCl$_4$(CO)$_2$]$^-$ complex, the $e_u \rightarrow b_{2g}$ doublet is centred around 30 060 cm$^{-1}$, while in the trans-[OsCl$_4$(CO)$_2$]$^-$ species the same transition occurs at 26 660 cm$^{-1}$. The more strongly $\pi$-accepting ligands function to decrease the electron density on the metal centre, meaning the l.m.c.t. transitions, which can be viewed as an
internal reduction, occur at lower energy. This shift in the halide-to-metal charge-transfer manifold is paralleled in the movement of the metal-based electrode reduction potentials. The $E_{1/2}(\text{Os}^{III}/\text{II})$ values move anodically (to more positive potentials) with increasing $\pi$-acceptor strength of the ligands L and L'.

Examination of the spectra of the analogous bromide complexes prompts two immediate observations. Firstly, the charge-transfer manifold is red shifted from that of the analogous chloride by ca. 6 000 cm$^{-1}$. This magnitude and direction of shift are in accord with the different optical electronegativities of the two halides, as explained previously in the description of the hexahalide spectra. In addition, the principal $e_u \rightarrow b_{2g}$ transition is now distinctly comprised of two components. The greater splitting of this $e_u \rightarrow b_{2g}$ transition arises from the larger spin-orbit coupling constant of bromide. The two components of this band are separated by between 1200-2200 cm$^{-1}$, the free ion $\xi$ value for bromide being $\sim$2 200 cm$^{-1}$ (and $\sim$650 cm$^{-1}$ for Cl).²

Each of the tervalent trans-$[\text{OsX}_4\text{L}_2]^{1-}$ and trans-$[\text{OsX}_4\text{LL'}]^{1-}$ compounds studied displays two metal-based redox processes, (these being an oxidation and a reduction) as discussed in Section 5.3. Accompanying the changes in oxidation state of the metal centre are changes associated with the charge-transfer spectra. Performing the electrolysis in situ, in an OTTLE cell, allows the spectral changes to be monitored while the oxidation or reduction takes place.

Accompanying the oxidation of the trans-$[\text{OsX}_4\text{L}_2]^{1-}$ complexes to the neutral species, was a red shift in the halide-to-metal charge-transfer manifold. The magnitude of the shift, ca. 5 700 and 4 900 cm$^{-1}$ for X=Cl and Br respectively, is approximated by the difference in optical electronegativities of the Os$^{III}$ and Os$^{IV}$ metal ions, as calculated by Jørgenson for the hexahalides.²² Precise assignments of the Os$^{IV}$ spectra are complicated by the fact that there are now two vacancies in the metal acceptor orbitals, yielding a number of different states associated with the $d^5$ configuration of the excited state. For any given halide, the spectra are however very similar.

Where reduction to the $[\text{OsX}_4\text{LL'}]^{2-}$ or $[\text{OsX}_4\text{L}_2]^{2-}$ species (Os$^{II}$) was
possible, the halide-to-metal($t_{2g}$) charge-transfer manifold collapsed, to yield essentially featureless visible spectra, as expected with the fully occupied $t_{2g}$
Figure 5.12 All spectra recorded in an OTTLE cell in 0.5 mol. dm$^{-3}$ Bu$_4$NPF$_6$/CH$_2$Cl$_2$ at 213 K. (a) Spectral progression upon reduction of trans-[OsBr$_4$(CNBu$_4$)$_2$]$^{2-}$, (b) u.v./visible spectrum of trans-[OsBr$_4$(CNBu$_4$)$_2$]$^{2-}$ and (c) spectral progression upon oxidation of trans-[OsBr$_4$(CNBu$_4$)$_2$]$^{2-}$.
set. Promotion from the halide donor orbitals to the single hole in the $t_{2g}$ set of $d$-orbitals is no longer possible. Ligand-to-metal charge-transfer into the metal $e_g$ orbitals can still occur, but most probably in the u.v. region of the spectrum. The other form of charge-transfer, metal-to-ligand, becomes predominant with the $d^6$ metal configuration. The Os$^{	ext{II}}$ spectra were generated for the $[\text{OsBr}_4(\text{CO})_4]^-$, $[\text{OsCl}_4(\text{CO})(\text{MeCN})]^-$, $[\text{OsX}_4(\text{CO})(t-\text{BuNC})]^-$ ($X=\text{Cl, Br}$) and $[\text{OsX}_4(t-\text{BuNC})_2]^-$ ($X=\text{Cl, Br}$) complexes. This data is summarized in Table 5.5.

The visible region of the above mentioned spectra are essentially featureless, with no evidence for any low energy m.l.c.t. bands. The higher energy region of the spectrum typically consists of a series of poorly defined bands. The spectra of the chloride and bromide complexes of $[\text{OsX}_4(\text{CNBu}_4)^2-$, isolated as $\text{Ph}_4\text{P}^+$ salts, are complicated by $\pi-\pi^*$ transitions associated with the aromatic portion of the cation (at $\sim 36$ 400, 37 500 and 38 400 cm$^{-1}$). The $\pi-\pi^*$ transitions appear to be superimposed on broad bands at $\sim 32$ 000 and 37 000 cm$^{-1}$. A well resolved band was observed in the spectrum of $[\text{OsBr}_4(\text{CO})_2]^2-$, at 34 440 cm$^{-1}$. In addition, two very weak transitions ($\epsilon \sim 350$ M$^{-1}$ cm$^{-1}$) were found at 22 300 and 29 500 cm$^{-1}$. These can be assigned as the spin-allowed $d-d$ transitions, $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$. 
Table 5.5 U.v./visible spectral data for trans-\([\text{Os}X_4L_2]^{2-}\) complexes, \(z=0, 1, 2\).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Band Maxima (\text{cm}^{-1}), ((\text{M}^{-1}\text{ cm}^{-1})) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{Os}^4, z=0)</td>
</tr>
<tr>
<td>([\text{OsCl}_4(\text{MeCN})_2]^{2-})</td>
<td>19 490 (310), 24 490 (12 540), 27 060 (4 710), 32 770 (3 910)</td>
</tr>
<tr>
<td>([\text{OsBr}_4(\text{MeCN})_2]^{2-})</td>
<td>13 880 (270), 16 240 (2 770), 19 710 (13 560), 22 730 (1 420), 25 650 (850), 27 690 (1 640)</td>
</tr>
<tr>
<td>([\text{OsCl}_4(\text{CO})_2]^{2-})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{OsBr}_4(\text{CO})_2]^{2-})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{OsCl}_4(\text{CO})(\text{MeCN})]^{2-})</td>
<td>16 200 (380), 20 580 (8 630), 25 000 (4 660)</td>
</tr>
<tr>
<td>([\text{OsBr}_4(\text{CO})(\text{MeCN})]^{2-})</td>
<td>13 050 (1 470), 15 680 (9 350), 19 420 (2 410), 23 900 (1 320), 26 330 (1 150)</td>
</tr>
<tr>
<td>([\text{OsCl}_4(\text{CNBu})_2]^{2-})</td>
<td>18 490 (160), 23 080 (6 850), 26 370 (1 390), 31 140 (1 080)</td>
</tr>
</tbody>
</table>

\(^a\) Numbers in parentheses indicate relative intensities.

\(\text{CNBu}^+\) is \(\text{CNBu}^{3+}\), the t-butylimido ligand.
<table>
<thead>
<tr>
<th>Complex</th>
<th>χ max (g/cm²)</th>
<th>χ min (g/cm²)</th>
<th>χ max (g/cm²)</th>
<th>χ min (g/cm²)</th>
<th>χ max (g/cm²)</th>
<th>χ min (g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[OsBr₄(CNBut)₂]²⁻</td>
<td>12 370 (230), 13 230 (410), 15 300 (1 650), 16 780 (8 420), 17 780 (9 100), 19 340 (2 740), 24 760 (970), 27 320 (1 620)</td>
<td>19 370 (470), 21 820 (6 220), 23 020 (4 790), 24 880 (1 490), 26 430 (1 130), 31 830 (1 210)</td>
<td>16 480 (360), 20 940 (11 600), 25 250 (3 230)</td>
<td>22 940 (420), 26 480 (8 840), 36 180 (3 380)</td>
<td>39 500 (7 510)</td>
<td>-37 000 br</td>
</tr>
<tr>
<td>[OsCl₄(CO)(CNBut)]²⁻</td>
<td>16 480 (360), 20 940 (11 600), 25 250 (3 230)</td>
<td>22 940 (420), 26 480 (8 840), 36 180 (3 380)</td>
<td>39 500 (7 510)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[OsBr₄(CO)(CNBut)]²⁻</td>
<td>10 020 (360), 15 630 (10 870), 19 100 (2 320), 24 320 (1 960), 35 160 (4 660)</td>
<td>17 100 (580), 19 700 (8 810), 21 170 (6 040), 22 870 (1 410), 24 660 (1 250), 30 230 (1 480), 37 540 (8 020)</td>
<td>28 300 (640)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[OsBr₄(CO)(Me₂CO)]²⁻</td>
<td>-</td>
<td>16 500 (260), 19 400 (4 810), 21 640 (4 130), 30 070 (1 030), 38 430 (3 920)</td>
<td>-</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>mer-[OsCl₃(MeCN)]₃</td>
<td>-</td>
<td>25 130 (1 270), 28 840 (7 480)</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Recorded in 0.5 mol dm⁻³ nBu₄PF₆/CH₂Cl₂, in an OTTLE cell at 213 K. Featureless spectrum.*
5.4.3 Spectra of [OsX₅L]²⁻ Complexes

Having considered the charge-transfer spectra which result essentially from the [OsX₄]¹⁻ chromophore, it is now appropriate to consider that from [OsX₅]²⁻. The [OsX₅]²⁻ chromophore can be thought of as a summation of the planar [OsX₄]¹⁻ and apical (X)¹⁻ components. Given that the donor orbital on this apical halide is not coplanar with the vacant metal acceptor orbital, the transition from this particular halide may be unfavoured and relatively weak. The series of orbitals from the halide array associated with the [MX₅L] (C₄ᵥ symmetry) closely resemble those set up by the trans-[MX₄L₂] case, with the noted difference that the inversion centre is no longer present. As was the case with the compounds of stoichiometry trans-[OsX₄L₂]²⁻, the Os¹II d⁵ configuration is the simplest place to start, where the single vacancy lies in the plane of the dₓᵧ orbital (taking the z-axis as running parallel to X-Os-L).

The Os¹II solution spectra of the [OsCl₅L]²⁻ complexes are presented in Figures 5.13 and 5.14, and the data tabulated in Table 5.6. The u.v./visible region of the spectra can be generally assigned as chloride-to-metal charge-transfer transitions. This was established by noting the bathochromic spectral shifts upon exchanging chloride for bromide. The absorption profiles are very similar, the most outstanding feature in each spectrum being a single, somewhat asymmetric band. The position of this maximum reflects the π-acceptor strength of the ligand L; the stronger the π-acceptor, the less negative the value of E₁/₂(Os¹II/II), and the lower the energy of this principle l.m.c.t. band.

The [OsCl₅L]²⁻ complexes (L = MeCN, py, CNBu⁴, z=1) were isolated with osmium in its tetravalent oxidation state. In dichloromethane at 213 K, the Os⁴/III reductions were reversible on an electrosynthetic timescale, enabling in situ electrogeneration of the Os²⁺ spectra in an OTTLLE cell. The electrogenerated spectrum of the [OsCl₅(MeCN)]²⁻ species is relatively simple, consisting of a broad, asymmetric band at ~32 700 cm⁻¹, assigned as the e→b₂ promotion. The weak Laporte forbidden transition (a₂→b₂) lies at the foot of the principal e→b₂ absorption band, while those more intense features at 38 000-40 000 cm⁻¹ arise from transitions from chloride orbitals of lower energy.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Band Maxima cm$^{-1}$, (M$^{-1}$ cm$^{-1}$) $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Os$^{IV}$, $z=1$</td>
</tr>
<tr>
<td>[OsCl$_5$(MeCN)]$_2$</td>
<td>26 860 (11 840), 34 020 (12 460)</td>
</tr>
<tr>
<td>[OsBr$_5$(MeCN)]$_2$</td>
<td>18 690 (4 380), 21 300 (8 250), 29 980 (1 840)</td>
</tr>
<tr>
<td>[OsCl$_5$(py)]$_2$</td>
<td>23 560 (1 230), 26 940 (5 910), 31 060 (2 630), 33 970 (3 250)</td>
</tr>
<tr>
<td>[OsBr$_5$(py)]$_2$</td>
<td>17 000 (2 100), 19 430 (4 880), 21 550 (10 410), 24 250 (1 180)</td>
</tr>
<tr>
<td>[OsCl$_5$(CNBu$_1$)]$_2$</td>
<td>25 (1 140), 28 970 (410)</td>
</tr>
<tr>
<td>[OsBr$_5$(CNBu$_1$)]$_2$</td>
<td>18 690 (8 220), 20 230 (8 080), 28 640 (2 780), 34 900 (5 970)</td>
</tr>
<tr>
<td>[OsCl$_5$(CO)]$_2$</td>
<td>-</td>
</tr>
<tr>
<td>[OsBr$_5$(CO)]$_2$</td>
<td>-</td>
</tr>
<tr>
<td>[OsCl$_5$(thf)]$_2$</td>
<td>28 090 (21 650)</td>
</tr>
<tr>
<td>[OsBr$_5$(thf)]$_2$</td>
<td>20 050, 22 500, 25 480, 28 800 $^b$</td>
</tr>
<tr>
<td>[OsCl$_5$(Me$_2$CO)]$_2$</td>
<td>28 540 (8 400)</td>
</tr>
<tr>
<td>[OsBr$_5$(Me$_2$CO)]$_2$</td>
<td>19 980, 22 700, 25 850 $^b$</td>
</tr>
<tr>
<td>[OsCl$_5$(NO)]$_2$</td>
<td>-</td>
</tr>
</tbody>
</table>

$a$ Recorded in 0.5 mol dm$^{-3}$ nBu$_4$NPF$_6$/CH$_2$Cl$_2$, in an OTTLE cell at 213 K. $^b$ These complexes were prepared in situ, and not isolated.
The spectrum of $[\text{OsCl}_5\text{(py)}]^2-$, shown in Figure 5.13, contains some features not attributable to chloride-to-metal charge-transfer. The principal band in $[\text{OsCl}_5\text{(py)}]^-$ (Os$^{IV}$) at $\sim 27,000 \text{ cm}^{-1}$ collapses upon reduction, confirming its assignment as a chloride-to-metal charge-transfer transition. Accompanying the collapse of the band at $\sim 27,000 \text{ cm}^{-1}$ was the growth of another feature at $33,560 \text{ cm}^{-1}$. This is the expected position for a Cl($\pi$)$\rightarrow$Os$^{III}$ charge-transfer transition, being $\sim 6,000 \text{ cm}^{-1}$ from that in Os$^{IV}$ manifold. The broad band at $25,180 \text{ cm}^{-1}$ in $[\text{OsCl}_5\text{(py)}]^2-$, which grew upon reduction cannot be assigned as chloride-to-metal charge-transfer.

*Figure 5.13* U.v./visible spectra of (a) $[\text{OsCl}_5\text{(MeCN)}]^2-$ and (b) $[\text{OsCl}_5\text{(py)}]^2-$.
The spectral changes which occurred upon reduction of \([\text{OsC}_5\text{(py)}]\)\(^1\) were fully reversible, and proceeded with isosbestic points. The complete starting spectrum was also regenerated at the application of the appropriate potential, such that the band at 25 180 cm\(^{-1}\) is not due to a decomposition product. If the electrogenerated product was in equilibrium with another species, then isosbestic points can still be observed. If such a process was occurring, then the position of equilibrium (and hence spectrum) should be effected by temperature, concentration and excess ligand(s). A possible reaction accompanying reduction of the metal centre involves the loss of halide. If such a mechanism is occurring, then the presence of free halide in the reaction should suppress the dissociation, and shift the position of equilibrium. The reduction was therefore performed in a large excess of tetraethylammonium chloride. The electrolysis progressed in an identical manner to what had occurred previously. The resultant reduced spectrum was the same as that shown in Figure 5.13, thus ruling out the possibility of a dissociative process.

Pyridine is known to possess relatively low \(\pi\) orbitals, capable of participating in a \(\text{py}(\pi)\rightarrow\text{Os}^{\text{III}}\) charge-transfer promotion. An extra band also appears to present in the \(\text{Os}^{\text{IV}}\) spectrum. Ligand-to-metal charge-transfer bands are expected to move to higher energy upon reduction of \(\text{Os}^{\text{IV}}\) to \(\text{Os}^{\text{III}}\). It is difficult to tell if a similar band is present in the analogous bromide complex, as the \(\text{Br}(\pi)\rightarrow\text{Os}^{\text{III}}\) charge-transfer occurs in this region. Further work is required to establish the origin of this band.

The other compounds of the \([\text{OsC}_5\text{L}]^{2^-}\) stoichiometry studied were [\(\text{OsC}_5\text{(CNBu}^\text{t})]\)\(^2^-\), [\(\text{OsC}_5\text{(CO)}]\)\(^2^-\) and [\(\text{OsC}_5\text{(NO)}]\)\(^2^-\) (Figure 5.14). Adopting the \(\text{NO}^+\) formalism, the nitrosyl complex was isolated with osmium in its di-valent oxidation state, meaning the \(\text{Os}^{\text{III}}\) state had to be electrogenerated in the standard way. The u.v./visible spectra of these complexes clearly resemble each other. In each case the Laporte forbidden band is clearly visible, on the low energy side of the dominant \(e\rightarrow\text{b}_2\) transition. At higher energy the \(\text{b}_2\rightarrow\text{b}_2\) transition can be found for the carbonyl and nitrosyl species.
Figure 5.14 U.v./visible spectra of (a) \( [\text{OsCl}_5(\text{CNBu}^+)]^{2-} \), (b) \( [\text{OsCl}_5(\text{CO})]^{2-} \) and (c) \( [\text{OsCl}_5(\text{NO})]^{1-} \).
Weaker transitions are found on both the high and low energy sides of this main band, these being most visible in the isonitrile, carbonyl and nitrosyl spectra (Figure 5.14). This pattern of an intense band flanked by weaker features has already been observed in the charge-transfer spectra of the trans-[OsX4L2]1- series. The similarities between the [OsX5L]2- and [OsX4L2]2- spectra are most obvious when L is a strong π-acceptor, as is the case in the isonitrile and carbonyl complexes. Such similarities in the $d^5$ absorption spectra arises from the dominant [OsCl4]$^{1-}$ component in each chromophore. The contribution from the apical halide in the [OsX5L]2- complexes is not expected to significant, since its donor orbital is not coplanar with the metal acceptor orbital. Possibilities for the $X_{apical}(\pi)\rightarrow M(d_\pi)$ charge-transfer include;

(i) the transition being very weak, since the halide donor orbital is not coplanar with the metal acceptor orbital.

(ii) the transition is significant but superimposed on that from [OsX4]$^{1-}$;

(iii) the transition is significant but shifted from that of [OsX4]$^{1-}$.

Evidence to date suggests that two of the above points may apply in different situations. Preetz prepared a series of [OsCl4X(py)]1- complexes (X=Br, I), and recorded their visible spectra.7 Bands appropriate to $X(\pi)\rightarrow Os^{IV}(d_\pi)$ charge-transfer were observed, in addition to Cl(\pi)→OsIV(d_\pi) charge-transfer bands, providing evidence for (ii).

The previous section described how the preparation of the [OsX5(CO)]2- complexes was achieved through exploiting the lability of one of the carbonyl ligands in trans-[OsX4(CO)]21-. Hoping to prepare [OsCl4X(CO)]2- complexes (X=Br, I), trans-[OsCl4(CO)]21- was dissolved in CH2Cl2 and a stoichiometric amount of I- added. No significant changes were observed in the u.v./visible spectrum of the complex, even after stirring for 24 hours at room temperature with a 100 fold excess of I-. Similar reactions were attempted with trans-[OsBr4(CO)]21- and different halide anions. On no occasion was there evidence for $X_{apical}(\pi)\rightarrow Os^{III}(d_\pi)$ charge-transfer. Assuming that substitution has taken place, and that scrambling has not occurred, the apical halide appears "silent". This then contrasts what was
observed in the spectra of the [OsCl₄X(py)]¹⁻ complexes. The strong π-acceptor carbonyl group may reduce effective orbital overlap between the metal centre and the apical halide to such an extent that the charge-transfer is not observed. These preliminary observations are worthy of further study.

Considering the [OsCl₅L]²⁻ complexes as a whole, there appears to be a division in spectral types. The spectra of the L=MeCN and py are and (at the OsIII level), the L=MeCN, py spectra appear marginally different to the L=t-BuNC, CO, NO⁺ cases. The latter are more similar to trans-[OsCl₄L₂]¹⁻ complexes, which suggests the apical halide is essentially optically transparent when L is a strong π-acceptor. For the weaker π-acceptors, this same halide becomes more prominent, its contribution being superimposed upon that from the four halide array.

Most of the [OsBr₅L]²⁻ compounds analogous to those chlorides discussed above were also prepared, and their charge-transfer spectra interpreted in a similar way. The spectra of the d⁵ [OsBr₅L]²⁻ species are presented in Figure 5.15. (L=py, MeCN, CNBu¹, CO). For the pyridine, acetonitrile and isonitrile complexes, the OsIII spectra were electrogenerated in the OTTLE cell, from the respective OsIV compounds. Salts of the carbonyl, [OsBr₅(CO)]²⁻ were isolated with osmium in its trivalent oxidation state. The spectra of these complexes are perhaps not as similar in profile as those of the chlorides, and generally appear to be more complex. The dominant feature in each of these spectra is again assigned as the e→b₂ promotion, which essentially describes the electron-donation from the equatorial bromides to the single vacancy in the metal t₂g orbital. The greater complexity of the bromide spectra comes as a consequence of a more pronounced perturbation of the orbitally degenerate halide donor state, E. This perturbation is caused by the spin-orbit coupling constant of the halide. Whereas the spectra of the chloride complexes appeared as broadened, asymmetric bands, those of the bromides actually show some splitting of the main transition. This is due to the larger spin-orbit coupling constant of bromide.

As with the trans-[OsX₄L₂]¹⁻ complexes, the bromide-to-metal charge-transfer manifold occurs at lower energy than in analogous chloride
complexes. For a given ligand L, the principal band is red shifted by between 6 400-6 600 cm⁻¹ upon replacing chloride by bromide.

The data for the available Os⁴⁺ spectra is listed in Figure 5.6, and the data summarized in Table 5.6. The spectra are in general more complicated than those of their Os³⁺ analogues, however systematic correlations are still observed.

![Figure 5.15](image.png)

**Figure 5.15** U.v./visible spectra of [OsBr₅L]²⁻ complexes, (a) L=py, (b) L=MeCN, (c) L=CNBu⁴, (d) L=CO.
5.5 NEAR-INFRARED AND EPR SPECTRA OF TERVALENT OSMIUM COMPLEXES

The $\text{trans-[OsX}_4\text{L}_2]^-$, $\text{trans-[OsX}_4\text{LL'}]^-$ and $[\text{OsX}_5\text{L}]^{2-}$ complexes are expected to have large tetragonal ligand-field distortion (along the 4-fold symmetry axis) on account of the axial coordination of ligands of varying π-acceptor strength. Low symmetry ligand fields of this type and the large spin-orbit constant associated with Os$^{III}$ lift the sixfold degeneracy of the $2T_2$ ground term, giving rise to three Kramers doublets, as shown in Figure 5.16. For these complexes there is no doubt as to the ordering of the terms. The $d_{xz}$ and $d_{yz}$ orbitals are clearly stabilized to a greater extent than $d_{xy}$ by the axial π-acceptor ligands. The $2B_2$ orbital-singlet ($e_g^4 b_{2g}^1$) is therefore found lowest in energy.

![Figure 5.16](image)

**Figure 5.16** Successive splitting of the $2T_2$ ground term by an axial field and spin-orbit coupling. Total degeneracies are given in parentheses. The $\Gamma_7 \rightarrow \Gamma_6$ and $\Gamma_7 \rightarrow \Gamma_7$ intraconfigurational transitions are shown.

Epr spectroscopy can provide valuable information about $d$ orbital splitting and metal-ligand covalency in paramagnetic transition metal complexes. These complexes belong to $C_{4v}$ or $D_{4h}$ symmetry groups. For such systems two g values are predicted, corresponding to g tensor
components parallel ($g_z=g_{||}$) and perpendicular ($g_x=g_y=g_{\perp}$) to the fourfold axis. The degree of splitting of the $^2B_2$ and $^2E$ states is reflected in the values of $g_{||}$ and $g_{\perp}$, which vary as a function of $\Delta/\lambda$ and $k$ (Figure 5.17), according to the simple theoretical model proposed by Stevens $^{80}$ and Bleaney & O'Brien $^{81}$ (where $\Delta$ is the effective tetragonal field, $\lambda$, which has a positive sign, is the effective spin-orbit coupling constant for the $^2T_2(t_2^5)$ multiplet, and $k$ the classical orbital reduction factor). Thus epr data can be used to define axial distortion. Unfortunately this model gives two numerical solutions for the case where $\Delta/\lambda$ has a positive sign, such that the analysis of an individual complex can be ambiguous.

\[ \Delta/\lambda \] (\(\lambda\) positive)

Figure 5.17 Variation of $g$ as a function of $\Delta/\lambda$.

The X-band epr spectra of the present family of thirteen complexes were measured in dichloromethane/toluene glasses at 40 K. The results are tabulated in Table 5.7. The data for the chloride complexes shows that $g_{||}$ and $g_{\perp}$ are all very similar for those complexes containing at least one carbonyl group. For these complexes, the simple model gives two solutions for $k$ and $\Delta/\lambda$;

(a) $k=1.2$ and $\Delta/\lambda=0.3$,

and (b) $k=0.8$ and $\Delta/\lambda=3$.

The effective parameter $k$ contains two dominant contributions; (i) the first order orbital reduction factor (for the $^2T_2(t_2^5)$ multiplet), whose value is reduced from unity by covalency, and (ii) the second order contribution...
arising from coulombic mixing of the $^2T_2(t^2_2)$ and $^2T_2(t^2_2e)$ states. The latter increases the value of $k$ by 0.1-0.15 for Os$^{III}$. Solution (a) is rejected because $k$ is too large and $\Delta/\lambda$ reasonably small.

Table 5.7  Epr data for tervalent osmium complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$X=Cl$</th>
<th>$X=Br$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g_{</td>
<td></td>
</tr>
<tr>
<td>[OsX$_5$(NO)]$^1$-</td>
<td>2.00</td>
<td>2.17</td>
</tr>
<tr>
<td>[OsX$_4$(CO)$_2$]$^1$-</td>
<td>1.61</td>
<td>2.45</td>
</tr>
<tr>
<td>[OsX$_5$(CO)]$^2$-</td>
<td>1.57</td>
<td>2.46</td>
</tr>
<tr>
<td>[OsX$_4$(MeCN)(CO)]$^1$-</td>
<td>1.64</td>
<td>2.44</td>
</tr>
<tr>
<td>[OsX$_4$(CNBut)(CO)]$^1$-</td>
<td>1.59</td>
<td>2.46</td>
</tr>
<tr>
<td>[OsX$_4$(CNBut)$_2$]$^1$-</td>
<td>1.20</td>
<td>2.55</td>
</tr>
<tr>
<td>[OsX$_4$(MeCN)$_2$]$^1$-</td>
<td>c</td>
<td>c</td>
</tr>
</tbody>
</table>

$a$ This complex was not prepared.  $b$ Not observed.  $c$ This complex was too insoluble to record its epr spectrum.

Taking $k$ as $\sim0.8$, gives a value of $\Delta/\lambda\sim3$. Inspection of Figure 5.17 shows that these complexes fall in the region to the right hand side of the minima in $g_{||}$, indicating considerable tetragonal distortion is present in such systems. For the analogous bromide complexes, $g_{\perp}$ is again essentially constant, although the $g_{||}$ values are more varied. Analysis of the data in the same way as that for the chlorides gives $k\sim0.9-1.0$, and $\Delta/\lambda\sim3$.

There is a greater separation of the $g_{||}$ and $g_{\perp}$ values in the bisisonitrile complexes, trans-[OsX$_4$(CNBut)$_2$]$^1$-. These values give $k\sim0.85$ and 0.92 for $X=Cl$ and $Br$ respectively, similar to those obtained for the [OsX$_4$L(CO)]$^1$- complexes. The corresponding values of $\Delta/\lambda$ are $\sim2.0$ for $X=Cl$ and $Br$. This value of $\Delta/\lambda$ is significantly smaller than that for complexes containing one carbonyl group. Unfortunately solubility problems prevented collecting data for the bis-acetonitrile complexes. From the $g_{\perp}$ value that was obtained for trans-[OsBr$_4$(MeCN)$_2$]$^1$-, and assuming $k\sim0.90$, then the model gives two solutions, $\Delta/\lambda\sim1$ and $\Delta/\lambda\sim2.7$. 

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The first solution is consistent with the established trend in increasing \( \pi \)-acceptor ability;

\[
\text{CO} > \text{RNC} > \text{RCN}
\]

Single-ion transitions within the \( ^2T_2 \) ground state of low-spin \( d^5 \) Os\(^{III} \) complexes (termed intraconfigurational transitions) provide another means of assessing the degree of tetragonal distortion. Concentrated solutions of \( \text{trans-[OsX}_4\text{L}_2]^1- \), \( \text{trans-[OsX}_4\text{LL}^1]^1- \), \( \text{[OsX}_5\text{(CO)}]^{2-} \) and \( \text{[OsCl}_5\text{(NO)}]^1- \) complexes revealed two weak, low energy bands, assigned as the Laporte-forbidden \( \Gamma_7 \rightarrow \Gamma_6 \) and \( \Gamma_7 \rightarrow \Gamma_7 \) intraconfigurational transitions (Figure 5.18).

Table 5.8 summarizes the near-infrared spectral data for the Os\(^{III} \) complexes. For large \( \Delta/\lambda \) with a positive sign, the average of the two transition energies is proportional to the value of \( \Delta/\lambda \), and the splitting approaches the asymptotic limit of \( \lambda \). For those complexes containing one carbonyl ligand, the average energy of the two band spectrum varies between 8 190 and 8 840 cm\(^{-1} \) (\( X=\text{Cl} \)), while for \( \text{trans-[OsCl}_4\text{(CNBut)}_2]^1- \) it is distinctly lower in energy, at 7 170 cm\(^{-1} \). In the bis-acetonitrile complex, \( \text{trans-[OsCl}_4\text{(MeCN)}_2]^1- \), the centre of gravity can be found at 6 000 cm\(^{-1} \).

**Table 5.8** Near-infrared spectral data for tervalent osmium complexes.

<table>
<thead>
<tr>
<th>Complex ( b,c )</th>
<th>Band Maxima cm(^{-1} ), (M(^{-1} ) cm(^{-1} )) ( a )</th>
<th>( X=\text{Cl} )</th>
<th>( X=\text{Br} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{[OsCl}_5\text{(NO)}]^1- )</td>
<td>10 800 (15), 11 500 (20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{[OsX}_4\text{(CO)}_2]^1- )</td>
<td>7 780 (30), 9 890 (20)</td>
<td>7 530 (40), 9 110 (70)</td>
<td></td>
</tr>
<tr>
<td>( \text{[OsX}_5\text{(CO)}]^2- )</td>
<td>7 200 (35), 9 180 (30)</td>
<td>6 620 (20), 8 390 (60)</td>
<td></td>
</tr>
<tr>
<td>( \text{[OsX}_4\text{(CO)}(\text{MeCN})]^1- )</td>
<td>7 780 (30), 9 860 (30)</td>
<td>7 200 (50), 8 840 (65)</td>
<td></td>
</tr>
<tr>
<td>( \text{[OsX}_4\text{(CO)}(\text{CNBut})]^1- )</td>
<td>7 600 (15), 9 550 (20)</td>
<td>6 990 (25), 8 650 (50)</td>
<td></td>
</tr>
<tr>
<td>( \text{[OsX}_4\text{(CNBut)}_2]^1- )</td>
<td>6 140 (20), 8 200 (25)</td>
<td>5 750 (30), 7 460 (30)</td>
<td></td>
</tr>
<tr>
<td>( \text{[OsX}_4\text{(MeCN)}_2]^1- )</td>
<td>5 170 (25), 6 830 (20)</td>
<td>4 900 (30), 6 300 (25)</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) Recorded in dichloromethane at room temperature. \( b \) All \( \text{[OsX}_4\text{L}_2]^1- \) and \( \text{[OsX}_4\text{LL}^1]^1- \) complexes are trans isomers. \( c \) Each complex is isolated in its tervalent oxidation state, except \( \text{[OsCl}_5\text{(NO)}]^1- \), which was prepared by NOPF\(_6\) oxidation of \( \text{[OsCl}_5\text{(NO)}]^2- \). \( d \) This complex was not prepared.
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Figure 5.18 Near-infrared spectra of trans-[OsBr₄L'L]- complexes, (a) L=L'=CO, (b) L=CO, L'=MeCN, (c) L=L'=MeCN
The near-infrared optical data confirm what was suggested from the epr measurements, that the degree of tetragonal distortion increases along the series \( \text{trans-}[\text{OsX}_4(\text{MeCN})_2]^{1-} \), \( \text{trans-}[\text{OsX}_4(\text{CNBu})_2]^{1-} \), \( [\text{OsX}_4(\text{CO})L]^{2-} \) (\( L=\text{MeCN} \), \( \text{CNBu} \), \( \text{CO}, z=1 \) and \( L=\text{X}, z=2 \)). This order essentially maps the increase in the combined \( \pi \)-acceptor strength of the two axial ligands. The complex which experiences the greatest tetragonal distortion however is \( [\text{OsCl}_5(\text{NO})]^{1-} \). The epr spectrum reveals \( g_{\parallel} \) and \( g_{\perp} \) are very close together, indicating the most probable solution places \( [\text{OsCl}_5(\text{NO})]^{1-} \) to the far right of Figure 5.17. The near-infrared spectrum supports this conclusion, the average energy of the two band spectrum being at 10 930 cm\(^{-1}\). The exceptional \( \pi \)-acid character of the nitrosyl ligand causes the greatest degree of tetragonal distortion. It is also of interest to note that for the \( \text{trans-}[\text{OsX}_4(\text{MeCN})_2]^{1-} \), \( \text{trans-}[\text{OsX}_4(\text{MeCN})(\text{CO})]^{1-} \) and \( \text{trans-}[\text{OsX}_4(\text{CO})_2]^{1-} \) series of complexes, the average energy of the two transitions does not vary in consistent manner with progressive substitution of the \( \text{trans} \) ligands. This non-additive influence of the \( \text{trans} \) ligands is taken up in the following section.

The near-infrared and epr spectra provide complementary information with which to consider the nature of the tetragonal distortion in low spin \( d^5 \text{Os}^{III} \) systems. Work is continuing to prepare a bis-nitrile complex which has sufficient solubility to enable its epr spectrum to be recorded.
5.6 LIGAND ADDITIVITY AND NON-ADDITIVITY

5.6.1 Introduction

In recent times there has been an increased interest in the additive effect ligands have on electrochemical potentials. Linear correlations have been found to exist between redox potentials and stoichiometry, in a diverse range of organometallic and coordination compounds. Fenske had earlier suggested that the oxidation potentials in the \([\text{Mn(CO)}_{6-n}\text{(CNMe)}_n]^{1+}\) series of complexes could be linearly correlated with the energy of the HOMO, as calculated by Fenske-Hall methods. Bursten built upon these ideas, in a model for trends in the \(E^0\) for binary complexes \([\text{ML}_{6-n}\text{L'}_n]\) which focussed on the change in \(d_n\) orbital energy of the redox-active orbital through interaction with ligands \(L\) and \(L'\). Pickett et al. established the concept of ligand parameters, in order to quantify the overall donor capabilities of a range of ligands. Lever recently used similar principles to define parameters for a large number of ligands, and using these parameters predicted the redox potentials for a wide and varied range of organometallic and coordination compounds. Unique to the second of these models is the assumption that the effects of the ligands are arithmetically additive, so that successive substitutions lead to equal shifts in electrode potentials.

With these models in mind, the attention of the reader is drawn to a seemingly simple system recently studied in this laboratory. The relationship between \(E^0\) and composition has been observed to vary in either a linear or non-linear fashion, depending upon the nature of the ligands occupying the axial sites of an octahedron.

The complexes in question are of trans-\([\text{OsX}_4\text{LL'}]^{2-}\) stoichiometry, their preparation, characterization, voltammetry and optical spectra having been presented in Chapter 5. For convenience, the voltammetric and \(X(\pi)\rightarrow\text{Os}^{III}(d\rho)\) charge-transfer data for complexes (1) to (18) is summarized in Table 5.9.
Table 5.9 Summary of electrode potentials and charge-transfer maxima for monomeric osmium complexes.

<table>
<thead>
<tr>
<th>Complex (a)</th>
<th>(E_{1/2} (V)) (b, c)</th>
<th>(\nu_{max} (cm^{-1})) (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V/IV</td>
<td>IV/III</td>
</tr>
<tr>
<td>1 ([\text{OsBr}_6]^{3-})</td>
<td>+1.43</td>
<td>-0.37</td>
</tr>
<tr>
<td>2 ([\text{OsBr}_5(\text{MeCN})]^{2-})</td>
<td>+1.85</td>
<td>+0.25</td>
</tr>
<tr>
<td>3 ([\text{OsBr}_4(\text{MeCN})]^{2+})</td>
<td>+0.82</td>
<td>-0.77</td>
</tr>
<tr>
<td>4 ([\text{OsBr}_5(\text{CO})]^2-)</td>
<td>+1.16</td>
<td>-0.36</td>
</tr>
<tr>
<td>5 ([\text{OsBr}_4(\text{CO})]^2-)</td>
<td>+1.84</td>
<td>+0.27</td>
</tr>
<tr>
<td>6 ([\text{OsBr}_4(\text{CO})(\text{MeCN})]^{1-})</td>
<td>+1.53</td>
<td>-0.08</td>
</tr>
<tr>
<td>7 ([\text{OsBr}_5(\text{CNBu})]^{2-})</td>
<td>+1.80</td>
<td>+0.50</td>
</tr>
<tr>
<td>8 ([\text{OsBr}_4(\text{CNBu})]^{2+})</td>
<td>+0.94</td>
<td>-0.66</td>
</tr>
<tr>
<td>9 ([\text{OsBr}_4(\text{CO})(\text{CNBu})]^{1-})</td>
<td>+1.47</td>
<td>-0.07</td>
</tr>
<tr>
<td>10 ([\text{OsCl}_6]^{3-})</td>
<td>+1.50</td>
<td>-0.49</td>
</tr>
<tr>
<td>11 ([\text{OsCl}_5(\text{MeCN})]^{2-})</td>
<td>+2.02</td>
<td>+0.21</td>
</tr>
<tr>
<td>12 ([\text{OsCl}_4(\text{MeCN})]^{2+})</td>
<td>+0.79</td>
<td>-1.00</td>
</tr>
<tr>
<td>13 ([\text{OsCl}_5(\text{CO})]^2-)</td>
<td>+1.20</td>
<td>-0.60</td>
</tr>
<tr>
<td>14 ([\text{OsCl}_4(\text{CO})]^2-)</td>
<td>+1.64</td>
<td>-0.10</td>
</tr>
<tr>
<td>15 ([\text{OsCl}_4(\text{CO})(\text{MeCN})]^{1-})</td>
<td>+1.59</td>
<td>-0.15</td>
</tr>
<tr>
<td>16 ([\text{OsCl}_5(\text{CNBu})]^{2-})</td>
<td>+0.37</td>
<td>-1.00</td>
</tr>
<tr>
<td>17 ([\text{OsCl}_4(\text{CNBu})]^{2+})</td>
<td>+1.01</td>
<td>-0.69</td>
</tr>
<tr>
<td>18 ([\text{OsCl}_4(\text{CO})(\text{CNBu})]^{1-})</td>
<td>+1.55</td>
<td>-0.19</td>
</tr>
</tbody>
</table>

\(a\) All complexes are listed as Os\(\text{III}\) species. \(b\) Not observed. \(c\) In 0.5 mol. dm\(^{-3}\) \(n\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2\) at 213 K, versus Ag/AgCl, against which \([\text{Fe(C}_5\text{H}_5)_2]^+/\text{O}\) occurs at +0.55 V. \(d\) For those complexes not isolated as Os\(\text{III}\), this species was electrogenerated in 0.5 mol. dm\(^{-3}\) \(n\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2\) at 213 K, in an OTTLE cell.

5.6.2 \([\text{OsX}_6-n(\text{MeCN})_n]^{2-}\) Series: \(n=0, 1, 2\).

The variation of \(E_{1/2}\) (both Os\(\text{III}/\text{II}\) and Os\(\text{IV}/\text{III}\)) with composition for the \([\text{OsX}_6-n(\text{MeCN})_n]^{2-}\) (\(n=0, 1, 2\)) complexes (1), (2), (3) and (10), (11), (12) is plotted in Figure 5.19 (a) and (b). This series of nitrile complexes shows essentially linear variation of \(E_{1/2}\) with \(n\). For \(X=\text{Br}\), the Os\(\text{III}/\text{II}\) couple shifts by \(-0.8\) V at the first substitution of Br by MeCN, and then by \(-0.7\) V at the second substitution. The corresponding shifts in the Os\(\text{IV}/\text{III}\) couple are 0.62 and 0.57 V. In the case of \(X=\text{Cl}\), the Os\(\text{III}/\text{II}\) couple was not observed in \([\text{OsCl}_6]^{2-}\).
The average shifts in $E_{1/2}$ per substitution are obtained from the gradient of the line of best fit, and are summarized below:

For $X=Br$, IV/III 0.59 V/Br  
$X=Br$, III/II 0.75 V/Br  
$X=Cl$, IV/III 0.52 V/Cl  
$X=Cl$, III/II 0.57 V/Cl

Recently Heath and Duff studied the trends in $E_{1/2}$ and $u_{\text{max}}$ for the $[\text{RuX}_{6-n}(\text{RCN})_n]^2^-$ $(n=0\rightarrow6)$ complexes, and found a linear relationship between $E_{1/2}$ and $n$ spanning the entire series. It remains to be seen if the linearity is conserved in the osmium system for all of $n=0\rightarrow6$. Yellowlees and Taylor established similar linear relationships in the $[\text{OsCl}_{6-n}^n(\text{py})_n]^2^-$ series $(n=0\rightarrow4)$.

Correlations between electrochemical potentials and charge-transfer spectroscopic data have been established by a number of authors. Figure 5.20 presents the u.v./visible spectra for the Os$^{\text{III}}$ complexes $[\text{OsCl}_6]^3^-$, $[\text{OsCl}_5(\text{MeCN})]^2^-$ and trans-$[\text{OsCl}_4(\text{MeCN})_2]^1^-$, these being dominated by Cl($\pi$)$\rightarrow$Os$^{\text{III}}$(d$\pi$) charge-transfer. The manifold clearly moves linearly with composition.

**Figure 5.19** $E_{1/2}$ versus composition for $[\text{OsX}_{6-n}(\text{MeCN})_n]$ complexes, $n=0, 1, 2$, (a) $X=Br$, (b) $X=Cl$. 
Figure 5.20  U.v./visible spectra of (a) [OsCl₆]³⁻, (b) [OsCl₅(MeCN)]²⁻ and (c) trans-[OsCl₄(MeCN)]²⁻.
5.6.3 \textit{[OsX}_{6-n}(L)_n}^z Series: L=CO, CNBu, n=0, 1, 2.

Treating the electrochemical and spectroscopic data for the halide/carbonyl and halide/isonitrile complexes in the same way as that of the halide/nitrile complexes, reveals distinctly different behaviour of $E_{1/2}$ and $\nu_{\text{max}}$ with composition.

A plot of $E_{1/2}$ (Os^{III/II} and Os^{IV/III}) versus stoichiometry for the halide/carbonyl compounds (1), (4) and (5) is shown in Figure 5.21. The Os^{III/II} couple shifts by $\sim$1.9 V upon the first substitution of bromide by carbonyl, and then by only $\sim$0.6 V at the second substitution. This distinctly non-additive effect is also observed in the Os^{IV/III} couple. Similar shifts in $E_{1/2}$ occur in the analogous chloride complexes (10), (13) and (14). Such behaviour is in direct contrast to what was observed in the halide/nitrile complexes discussed in Section 5.6.2, and is not predicted by current ligand additivity models.

The shifts in $\nu_{\text{max}}$ of the charge-transfer manifold with composition parallel the patterns established by voltammetry. Figure 5.22 shows the u.v./visible spectra of the [OsCl$_6$]$^{3-}$, [OsCl$_5$(CO)]$^{2-}$ and [OsCl$_4$(CO)]$^{1-}$ complexes. The non-linear progression of the charge-transfer bands (Cl($\pi$)$\rightarrow$Os^{III}$d_{\pi}$) is clearly evident, the manifold being red shifted by $\sim$8
000 cm\(^{-1}\) at the first substitution (CO replacing Cl), and then by only \(\sim 300\) cm\(^{-1}\) at the second. In the bromide complexes, (1), (4) and (5), the shifts are essentially the same, being \(\sim 8\) 300 and \(\sim 1 \ 000\) cm\(^{-1}\) at the first and second substitutions respectively.
Figure 5.22 U.v./visible spectra of (a) \([\text{OsCl}_6]^{3-}\), (b) \([\text{OsCl}_5(\text{CO})]^{2-}\) and (c) trans-\([\text{OsCl}_4(\text{CO})_2]^{1-}\).
Turning now to the isonitrile complexes, the variation of $E_{1/2}$ and $\nu_{\text{max}}$ with composition is again non-additive, although the differences are not as pronounced as in the halide/carbonyl complexes. The results of the voltammetric and spectroscopic measurements are summarized in graphical form in Figure 5.23.

$$E_{1/2} \ (V)$$

<table>
<thead>
<tr>
<th>$n$</th>
<th>0</th>
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<tr>
<td>IV/III</td>
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<td>III/II</td>
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Figure 5.23 $E_{1/2}$ and $\nu_{\text{max}}$ versus stoichiometry for $[\text{OsBr}_{6-n}(\text{CNBu})_n]^{2-}$ complexes, $n=0, 1, 2$.

**5.6.4 Trans-[OsX$_4$L_L']$_2^-$ Series, L, L'=MeCN, CO, CNBu.**

Aside from the $[\text{OsX}_6]^{2-}$, $[\text{OsX}_5L]^{2-}$, $[\text{OsX}_4L_2]^{2-}$ series discussed in Sections 5.6.2 and 5.6.3, the trans-[OsX$_4$L_L']$_2^-$ complexes with two different neutral ligands allow formation of further series, namely trans-[OsX$_4$L$_2$]$_2^-$, trans-[OsX$_4$L_L']$_2^-$, trans-[OsX$_4$L'L$_2$]$_2^-$, with which to consider ligand additivity relationships. Two such series can be considered here, for both chloride and bromide, and combinations of CO/MeCN and CO/CNBut.

Both of these series yield non-linear variation of of $E_{1/2}$ and $\nu_{\text{max}}$ with composition. Figure 5.24 shows the u.v./visible spectra of the first series, for both $X=$Cl and Br. Note that in the case of the bromide spectra, (b), (d) and (f), the horizontal axis is offset by 5 000 cm$^{-1}$. 
Figure 2.24 U.v./visible spectra of trans-[OsX₄LL']¹⁻ complexes, (a) X=Cl, L=L'=MeCN, (b) X=Br, L=L'=MeCN, (c) X=Cl, L=CO, L'=MeCN, (d) X=Br, L=CO, L'=MeCN, (e) X=Cl, L=L'=CO, (f) X=Br, L=L'=CO.
5.6.5 CONCLUSION

Electrochemical (E_{1/2}) and charge-transfer spectral data (\( \nu_{\text{max}} \)) has been used to establish two distinctly different types of behaviour associated with the \( \{\text{OsX}_4\}^{2-} \) site, depending on the identity of the ligands \( L \) and \( L' \). For the \([\text{OsX}_{6-n}(\text{MeCN})_n]^2 \) (\( X=\text{Cl, Br; } n=0, 1, 2 \)) series of complexes, \( E_{1/2} \) and \( \nu_{\text{max}} \) vary in a linear manner with composition. However, for those complexes involving the replacement of halide by strong \( \pi \)-acid ligands, \([\text{OsX}_{6-n}(L)_n]^2 \) (\( X=\text{Cl, Br; } n=0, 1, 2; L=\text{CO, CNBu}^l \)) \( E_{1/2} \) and \( \nu_{\text{max}} \) move in a distinctly non-linear fashion with composition.

This contrasting behaviour can be accounted for in terms of the differing \( \pi \)-donor/acceptor strengths of the ligands \( L \) and \( L' \), and the polarizability of the \( \{\text{OsX}_4\}^{2-} \) site. Much of the previous work concerned with ligand additivity has involved complexes with strong \( \pi \)-acid ligands, often in conjunction with first row transition metals. The presence of strong \( \pi \)-acid ligands on the metal site attenuates the effects of other incoming ligands, through decreasing the site polarizability. In the case under discussion here, the \( \pi \)-donor halides contribute to the electron density on the metal centre. This, coupled with having a third row transition metal, produces a relatively electron rich site.

It is apparent that certain combinations of ligands and metals do not comply with recent models of ligand additivity. The purpose of this discussion has been to highlight some of the limitations of these models, which in turn can only lead to the improvement of our understanding of a concept as fundamental to inorganic chemists, as ligand additivity.
5.7 EXPERIMENTAL

5.7.1 General Remarks

The instrumentation and apparatus used in the chapter has been described previously in Chapters 1 to 4.

5.7.2 Materials and Methods

Organo-soluble salts of \([\text{OsX}_6]^{2-}\) (X=Cl, Br) were prepared as described in Chapter 3. In addition to the reagents used in Chapters 3 and 4, AgCF$_3$SO$_3$ and tert-butyl isonitrile were purchased from the Aldrich Chemical Company. All solvents were distilled according to standard procedures$^90$ and stored under nitrogen in the dark when not in use.

5.7.3 Synthesis of \([\text{OsX}_5L]^{2-}\) Complexes

(i) Tetra-n-butylammonium pentachloro(pyridine)osmate(IV)

AgCF$_3$SO$_3$ (0.18 g, 0.72 mmol) was added to a stirring yellow solution of \((\text{nBu}_4\text{N})_2\text{OsCl}_6\) (0.64 g, 0.72 mmol) in 25 ml. of pyridine. The resulting orange solution was then heated under N$_2$ (oil bath temperature ~363 K) with the exclusion of light for 30 hours. Removal of the solvent yielded a yellow residue which was recrystallized from a minimum volume of boiling acetone. Fine yellow needles formed upon the addition of diethyl ether and cooling. The product was collected by filtration, washed with diethyl ether and dried \textit{in vacuo} (0.37 g, 75%).

Microanalysis: Calc. (%) for C$_{21}$H$_{41}$Cl$_5$N$_2$Os; C 36.60, H 6.00, N 4.07

Found (%); C 36.42, H 6.15, N 4.05

Infra-red Spectrum: (KCl disc) 2 965 cm$^{-1}$ (m), 2 875 (m), 1 610 (m), 1 482 (s), 1 453 (s), 1 381 (w), 1 223 (w), 1 165 (w), 1 073 (m), 1 049 (w), 1 018 (w), 766 (m), 690 (s), 650 (w).


(ii) Tetra-n-butylammonium pentabromo(pyridine)osmate(IV)

This compound was obtained in 60 % yield using a similar procedure to that described for the preparation of its chloride analogue, noting that the reaction time was reduced to 18 hours in an oil bath at ~333 K.

Microanalysis: Calc. (%) for C$_{21}$H$_{41}$Br$_5$N$_2$O$_s$; C 27.68, H 4.53, N 3.07

Found (%); C 27.74, H 4.53, N 3.04

Infra-red Spectrum: (KBr disc) 2 962 cm$^{-1}$, 2 872 (s), 1 604 (s), 1 487 (m), 1 472 (s), 1 448 (s), 1 380 (w), 1 362 (w), 1 222 (m), 1 075 (s), 1 045 (m), 1 013 (s), 880 (w), 767 (s), 737 (w), 692 (s), 643 (w).

(iii) Tetra-n-butylammonium pentachloro(acetonitrile)osmate(IV)

A mixture of (nBu$_4$N)$_2$OsCl$_6$ (0.77 g, 0.87 mmol) and AgCF$_3$SO$_3$ (0.23 g, 0.88 mmol) in 25 ml of acetonitrile was heated under N$_2$ (oil bath temperature ~333 K) with the exclusion of light for 5 hours. The solvent was removed under vacuum and the residue recrystallized from boiling acetonitrile. The addition of diethyl ether and cooling yielded a yellow microcrystalline precipitate which was collected by filtration, washed with diethyl ether and dried in vacuo (0.40 g, 71 %).

Microanalysis: Calc. (%) for C$_{18}$H$_{39}$Cl$_5$N$_2$O$_s$; C 33.20, H 6.04, N 4.30

Found (%); C 33.14, H 6.30, N 4.21

Infra-red Spectrum: (KCl disc) 2 960 cm$^{-1}$ (s), 2 915 (s), 2 870 (s), 2 325 (m), 2 300 (s), 1 481 (s), 1 475 (s), 1 421 (w), 1 380 (s), 1 350 (w), 1 275 (w), 1 170 (w), 1 150 (m), 1 106 (w), 1 058 (w), 1 026 (m), 1 018 (w), 955 (w), 878 (s), 838 (w), 794 (m), 741 (s).

(iv) Tetra-n-butylammonium pentabromo(acetonitrile)osmate(IV)

This complex was prepared in 60 % yield using a procedure identical to that described for its chloride analogue.

Microanalysis: Calc. (%) for C$_{18}$H$_{39}$Br$_5$N$_2$O$_s$; C 24.76, H 4.50, N 3.21

Found (%); C 24.88, H 4.61, N 3.22

Infra-red Spectrum: (KBr disc) 2 960 cm$^{-1}$ (s), 2 925 (s), 2 870 (s), 2 310 (m),
(v) Tetra-n-butylammonium pentabromo(tert-butyl isonitrile)osmate(IV)

\[(\text{Bu}_4\text{N})_2\text{OsBr}_6\ (0.62\ g, 0.54\ mmol)\] was dissolved in a solution consisting of 10.0 ml. of 1,2-dichloroethane and 15.0 ml. of tetrahydrofuran. To this was added AgCF$_3$SO$_3$ (0.14 g, 0.54 mmol.), and the resulting mixture warmed (oil bath temperature -323 K) under N$_2$ in the absence of light. After 4 hours warming, the mixture was cooled, and filtered under N$_2$ through a bed of celite. The solvent was removed in vacuo to give a red/brown residue, which was subsequently taken up in 25 ml. of freshly distilled dichloromethane. To this solution was syringed a small excess of tert-butyl isonitrile (73 µL., 0.64 mmol., ρ=0.74 g cm$^{-3}$). Within minutes the colour of the solution had changed from red/brown to deep purple. The solution was stirred at room temperature under N$_2$ for an hour, after which the solvent and unreacted ligand were removed in vacuo. The residue was again dissolved in a minimum volume of dichloromethane, and diethyl ether added to induce crystallization of the product. Cooling produced a microcrystalline purple product which was collected by filtration, washed with diethyl ether, and dried in vacuo at 313 K (0.33 g, 68 %).

Microanalysis: Calc.(%) for C$_{21}$H$_{45}$Br$_5$N$_2$Os; C 27.56, H 4.96, N 3.06

Found(%); C 27.63, H 5.26, N 2.99

Infra-red Spectrum: (KBr disc) 2963 cm$^{-1}$ (s), 2938 (s), 2875 (s), 2116 (s), 1471 (s), 1374 (m), 1236 (w), 1 v196 (m), 1109 (w), 1062 (w), 1032 (w), 925 (w), 884 (w), 734 (w), 523 (w).

(vi) Tetraphenylphosphonium pentachloro(tert-butyl isonitrile)osmate(IV)

This complex was prepared in 53 % yield from (Ph$_4$P)$_2$[OsCl$_6$], using a procedure identical to that described for its bromide analogue.
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Microanalysis: Calc.(%) for C_{29}H_{29}Cl_{5}NO_{5}P; C 44.09, H 3.70, N 1.77

Found(%); C 41.77, H 3.70, N 1.31

Infra-red Spectrum: (KCl disc) 3 055 cm\(^{-1}\) (w), 2 212 (s), 1 483 (m), 1 434 (s), 1 273 (w), 1 183 (w), 1 105 (s), 995 (w), 762 (w), 753 (w), 747 (w), 720 (s), 688 (s), 523 (s).

(vii) Bis(tetraphenylphosphonium) pentachloro(carbonyl)osmate(III)

A small excess of Ph\(_4\)PCl (26.3 mg, 7.02x10\(^{-5}\) mol.) was added under N\(_2\) to a dichloromethane solution of trans-Ph\(_4\)P[OsCl\(_4\)(CO)\(_2\)] (50.3 mg, 6.92x10\(^{-5}\) mol.). The resulting mixture was stirred under N\(_2\) at room temperature for 20 hours, after which diethyl ether was added to precipitate a fine, light-yellow coloured solid. The precipitate was collected by filtration, washed with diethyl ether and dried in air (0.06, 81%).

Microanalysis: Calc.(%) for C\(_{49}\)H\(_{40}\)Cl\(_{5}\)O\(_{5}\)P\(_{2}\); C 54.78, H 3.75, P 5.77

Found(%); C 51.77, H 3.70, P 5.31

Infra-red Spectrum: (KCl disc) 3 420 cm\(^{-1}\) (m), 3 060 (w), 1 954 (s), 1 585 (m), 1 484 (m), 1 442 (s), 1 438 (s), 1 340 (w), 1 315 (w), 1 279 (s), 1 266 (s), 1 226 (m), 1 188 (w), 1 165 (w), 1 146 (s), 1 106 (s), 1 031 (s), 984 (m), 751 (m), 721 (s), 689 (s), 634 (s), 570 (w), 525 (s).

(viii) Bis(tetra-n-butylammonium) pentabromo(carbonyl)osmate(III)

This compound was prepared in 43 % yield from (nBu\(_4\)N)\(_2\)[OsBr\(_6\)] and nBu\(_4\)NBr by a procedure analogous to that described for (Ph\(_4\)P)\(_2\)[OsCl\(_5\)(CO)].

Microanalysis: Calc.(%) for C\(_{33}\)H\(_{72}\)Br\(_5\)O\(_{5}\)O; C 35.94, H 6.58, N 2.54

Found(%); C 31.77, H 5.70, N 3.06

Infra-red Spectrum: (KCl disc) 3 680 cm\(^{-1}\) (m), ~3 300 (m), 2 960 (s), 2 865 (s), 1 944 (s), 1 902 (w), 1 616 (w), 1 488 (s), 1 465 (s), 1 380 (s), 1 279 (w), 1 253 (w), 1 172 (w), 1 150 (m), 1 107 (w), 1 055 (w), 1 026 (m), 876 (s), 800 (m), 740 (s), 573 (m).
(ix) Tetraphenylphosphonium pentachloro(tetrahydrofuran)osmate(IV)

\[(\text{Ph}_4\text{P})_2[\text{OsCl}_6] (0.28 \text{ g, 0.26 mmol.}) \text{ and } \text{AgCF}_3\text{SO}_3 (0.07 \text{ g, 0.26 mmol.})\]
were added under \(N_2\) to a solution of 1,2-dichloroethane/tetrahydrofuran (50 ml., 1/1, v/v). The fine dark precipitate which formed initially, changed to dark red upon warming (with the exclusion of light). The mixture was then gently refluxed for \(~20\) hours, yielding a yellow solution and a fine white precipitate. After cooling, the precipitate was filtered off, and the solvent removed from the filtrate. Fractional recrystallization from dichloromethane/diethyl ether gave a micocrystalline yellow product, which was collected by filtration, washed with diethyl ether and dried (0.28 g, 85 %). This complex was isolated as a 1:1 mixture with \(\text{Ph}_4\text{PCF}_3\text{SO}_3\), as shown by the microanalysis and infra-red spectrum.

**Microanalysis:** Calc.(%) for \(\text{C}_{53}\text{H}_{48}\text{Cl}_5\text{O}_4\text{OsP}_2\text{S}\); C 50.23, H 3.82, P 4.89
Found (%); C 49.72, H 4.00, P 4.55

**Infra-red Spectrum:** (KCl disc) 3 055 cm\(^{-1}\) (w), 1 585 (m), 1 484 (m), 1 442 (s), 1 435 (s), 1 342 (w), 1 315 (w), 1 280 (s), 1 267 (s), 1 228 (m), 1 188 (w), 1 165 (w), 1 146 (s), 1 109 (s), 1 034 (s), 996 (m), 850 (m), 754 (m), 722 (s), 690 (s), 615 (w), 569 (w), 525 (s).

(x) Tetraphenylphosphonium pentachloro(acetone)osmate(IV)

\[(\text{Ph}_4\text{P})_2[\text{O}_2(\mu-\text{Cl})_2\text{Cl}_8] (0.12 \text{ g, 8.49x10}^{-5} \text{ mol.})\]
was dissolved in 25 ml. of acetone and stirred in a sealed flask at room temperature. After stirring for three days, the solvent was removed under vacuum, and the residue fractionally recrystallized from dichloromethane/diethyl ether. A golden brown/yellow material was collected by filtration, washed with diethyl ether and dried *in vacuo* (0.08 g, 62 %).

**Microanalysis:** Calc.(%) for \(\text{C}_{27}\text{H}_{26}\text{Cl}_5\text{O}_4\text{OsP}\); C 42.40, H 3.43, P 4.05
Found (%); C 41.83, H 3.83, P 3.96

**Infra-red Spectrum:** (KCl disc) 3 379 cm\(^{-1}\) (w), 3 59 (w), 2 924 (w), 1 684 (m), 1 584 (m), 1 496 (s), 1 482 (m), 1 435 (m), 1 340 (w), 1 311 (w), 1 292 (m), 1 186 (m), 1 164 (m), 1 170 (s), 1 066 (m), 1 025 (m), 996 (m), 835 (m), 812 (m), 784
(m), 764 (m), 752 (m), 723 (s), 690 (s), 527 (s).

\[(\text{xi}) \text{Bis(tetraphenylphosphonium) pentachloronitrosylosmate(II)}\]

\[(\text{Ph}_4\text{P})_2[\text{OsCl}_6] (0.33 \text{ g}, 0.31 \text{ mmol.}) \text{ was dissolved with warming in 30 ml. of 1,2-dichloroethane. \text{AgCF}_3\text{SO}_3 (0.08 \text{ g}, 0.31 \text{ mmol.}) and NOPF}_6 (0.06 \text{ g}, 0.37 \text{ mmol.}) \text{ were then added to this solution under N}_2. \text{ Warming this mixture (with the exclusion of light) in an oil bath at 333 K for 5 hours gave an intensely purple coloured solution, to which was added Ph}_4\text{PBH}_4 (0.10 \text{ g}, 0.37 \text{ mmol.}). \text{ A fine precipitate began to form upon removal of the solvent from the pale yellow coloured solution. A small volume of diethyl ether was added and the mixture cooled. The microcrystalline off-white precipitate was collected by filtration, washed with diethyl ether and dried under high vacuum at 313 K. This complex was isolated as a 1:1 mixture with Ph}_4\text{PCF}_3\text{SO}_3, \text{ as shown by the microanalysis and infra-red spectrum (0.28 g, 59 \%).}\]

**Microanalysis:** Calc. (%) for C\text{73H}_{60}\text{Cl}_{15}\text{F}_{3}\text{NO}_4\text{OsP}_3\text{S}; C 56.04, H 3.86, N 0.90

Found (%); C 55.52, H 3.72, N 0.61

**Infra-red Spectrum:** (KCl disc) 3 060 cm\(^{-1}\) (w), 1 795 (s), 1 586 (w), 1 485 (m), 1 452 (s), 1 438 (s), 1 325 (w), 1 282 (s), 1 268 (s), 1 229 (m), 1 190 (w), 1 166 (w), 1 149 (m), 1 109 (s), 1 035 (s), 987 (m), 860 (w), 840 (w), 803 (w), 754 (m), 724 (s), 692 (s), 687 (m), 618 (w), 570 (w), 556 (w), 526 (s).

### 5.7.4 Synthesis of trans-[OsX\(_4\)L\(_2\)]\(^2+\) Complexes

\[(i) \text{Trans tetraphenylphosphonium tetrachlorobis(acetonitrile)-osmate(III)}\]

\[(\text{Ph}_4\text{P})_2\text{OsCl}_6 (0.70 \text{ g}, 0.65 \text{ mmol.}) \text{ was dissolved with warming under N}_2 \text{ in 40 ml. of freshly distilled acetonitrile. Added to this solution was AgCF}_3\text{SO}_3 (0.33 \text{ g}, 1.29 \text{ mmol}, and the mixture warmed at \sim 333 K (oil bath temperature) for 1 hour. After the addition of Ph}_4\text{PBH}_4 (0.25 \text{ g}, 0.71 \text{ mmol}, warming was continued for a further 16 hours. The mixture was then filtered through fluted filter paper, which was subsequently rinsed with dichloromethane. The volume of the solvent was then reduced in vacuo.}\]
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Cooling yielded an orange precipitate, which was filtered off, washed with diethyl ether and dried \textit{in vacuo} at 313 K for 10 hours. (0.34 g, 70%).

**Microanalysis:** Calc. (%) for C$_{28}$H$_{26}$Cl$_4$N$_2$PO$_s$; C 44.63, H 3.48, N 3.72

Found (%); C 44.88, H 3.41, N 3.73

**Infra-red Spectrum:** (KCl disc) 3 062 cm$^{-1}$ (m), 2 068 (m), 2 007 (m), 1 586 (m), 1 549 (w), 1 484 (s), 1 438 (s), 1 380 (w), 1 337 (w), 1 314 (w), 1 277 (w), 1 182 (w), 1 165 (w), 1 111 (s), 1 027 (w), 995 (s), 944 (w), 758 (m), 749 (w), 722 (s), 687 (s), 614 (w), 526 (s).

\textbf{(ii) Trans tetra-n-butylammonium tetrabromobis(acetonitrile) osmate(III)}

$^n$Bu$_4$NBH$_4$ (0.08 g, 0.31 mmol) was added to a stirring solution of $^n$Bu$_4$N[OsBr$_5$(MeCN)] (0.25 g, 0.29 mmol) in 20 ml. of freshly distilled acetonitrile. The resulting red/orange solution was left stirring under N$_2$ overnight. A condenser was then fitted to the reaction vessel and the solution warmed at 313 K for a further 24 hours. The addition of diethyl ether and cooling yielded a fine yellow microcrystalline precipitate. The product was filtered off, washed with diethyl ether and dried \textit{in vacuo} (0.13 g, 54%).

**Microanalysis:** Calc. (%) for C$_{20}$H$_{42}$Br$_4$N$_2$Os; C 28.79, H 5.07, N 5.04

Found (%); C 28.40, H 5.16, N 4.90

**Infra-red Spectrum:** (KCl disc) 2 950 cm$^{-1}$ (s), 2 910 (s), 2 865 (m), 1 466 (s), 1 108 (w), 1 060 (w), 1 032 (w), 947 (w), 922 (w), 893 (w), 878 (w), 735 (w).

\textbf{(iii) Trans tetra-n-butylammonium tetrachlorobis(carbonyl) osmate(III)}

($^n$Bu$_4$N)$_2$[OsCl$_6$] (0.27 g, 0.30 mmol.) was dissolved in 30 ml. of 1,2-dichloroethane. To this yellow solution was added AgCF$_3$SO$_3$ (0.08 g, 0.31 mmol), and carbon-monoxide bubbled through the resulting mixture, for \textasciitilde 20 hours. The reaction mixture was then filtered through fluted filter paper (twice), and the volume of filtrate solvent reduced \textit{in vacuo}. The addition of diethyl ether resulted in the formation of a fine, yellow precipitate, which was filtered off and dried in air (0.16 g, 84%).
Microanalysis: Calc. (%) for C_{18}H_{36}Cl_{4}NO_{2}Os; C 34.29, H 5.75, N 2.22

Found (%); C 35.38, H 7.13, N 2.41

Infra-red Spectrum: (KCl disc) 2 962 cm\(^{-1}\) (s), 2 874 (m), 1 990 (s), 1 946 (w), 1 625 (w), 1 482 (s), 1 380 (m), 1 350 (w), 1 270 (m), 1 224 (w), 1 153 (m), 1 108 (w), 1 067 (w), 1 030 (m), 878 (m) 795 (w), 738 (m), 636 (m), 566 (m).

Solution (CH\(_2\)Cl\(_2\)) 1 991 cm\(^{-1}\) (s)

(iv) Trans tetra-n-butylammonium tetrabromobis(carbonyl) osmate(III)

To a solution of (nBu\(_4\)N)\(_2\)OsBr\(_6\) (0.64 g, 0.55 mmol) in 30 ml. of 1,2-dichloroethane, was added AgCF\(_3\)SO\(_3\) (0.29 g, 1.10 mmol) with stirring, with the exclusion of light. The reaction mixture was then warmed (oil bath temperature ~318 K) and carbon monoxide bubbled through the solution for 18 hours. After cooling a fine dark precipitate was removed by filtration, and the volume of solvent reduced in vacuo. Diethyl ether was added until the product began to crystallize. Cooling at ~263 K produced long dark purple coloured needles. The crystals were filtered off, washed with diethyl ether and dried on the frit (0.36 g, 82% yield).

Microanalysis: Calc. (%) for C_{18}H_{36}Br_{4}NO_{2}Os; C 26.75, H 4.49, N 1.73

Found (%); C 26.89, H 4.54, N 1.87

Infra-red Spectrum: (KBr disc) 2 962 cm\(^{-1}\) (s), 2 933 (m), 2 874 (m), 2 043 (s), 2 016 (sh), 1 481 (m), 1 460 (m), 1 381 (m), 1 261 (w), 1 176 (w), 1 151 (w), 1 106 (w), 1 028 (m), 884 (m), 800 (w), 738 (m), 592 (s).

Solution (CH\(_2\)Cl\(_2\)) 2 040 cm\(^{-1}\) (s)

(v) Trans tetra-n-butylammonium tetrachloro(carbonyl)(acetonitrile) osmate(III)

Trans - nBu\(_4\)N[OsCl\(_4\)(CO)\(_2\)] (0.13 g, 0.21 mmol.) was dissolved in 5.0 ml. of freshly distilled acetonitrile and stirred at room temperature under N\(_2\) overnight. The solvent was then stripped from reaction mixture, and the resulting residue fractionally recrystallized from boiling acetonitrile/diethyl ether. Cooling initially yielded an oil, however upon standing at ~263 K for several days a yellow microcrystalline solid formed. The product was
collected by filtration, washed with diethyl ether and dried on the frit (0.08 g, 60% yield).

**Microanalysis:** Calc. (%) for C\textsubscript{19}H\textsubscript{39}Cl\textsubscript{4}N\textsubscript{2}O\textsubscript{8}; C 35.46, H 6.11, N 4.35  
Found (%); C 35.70, H 6.24, N 4.10  
**Infra-red Spectrum:** (KCl disc) 2 965 cm\textsuperscript{-1} (s), 2 927 (m), 2 871 (m), 2 328 (w), 2 303 (w), 2 007 (s), 1 482 (m), 1 458 (w), 1 380 (w), 1 176 (w), 1 151 (w), 1 107 (w), 1024 (m), 882 (m), 796 (w), 740 (m), 587 (s), 526 (w).

**(vi) Trans tetra-n-butylammonium tetrabromo(carbonyl)(acetonitrile) osmate(III)**

This complex was prepared in 62% yield in an identical manner to that of the analogous chloride complex.

**Microanalysis:** Calc. (%) for C\textsubscript{19}H\textsubscript{39}Br\textsubscript{4}N\textsubscript{2}O\textsubscript{8}; C 27.78, H 4.79, N 3.41  
Found (%); C 28.35, H 4.59, N 3.49  
**Infra-red Spectrum:** (KBr disc) 2 964 cm\textsuperscript{-1} (s), 2 925 (w), 2 871 (m), 2 327 (w), 2 302 (w), 2 006 (s), 1 972 (sh), 1 610 (w), 1 480 (m), 1 380 (m), 1 178 (w), 1 152 (w), 1 120 (w), 1 107 (w), 1 025 (w), 884 (m), 800 (w), 738 (m), 582 (m), 526 (w).

**(vii) Trans tetra-n-butylammonium tetrabromo(carbonyl)(acetone) osmate(III)**

Recrystallization of trans-\textsuperscript{n}Bu\textsubscript{4}N[OsBr\textsubscript{4}(CO)(MeCN)] from boiling acetone yielded a brown microcrystalline precipitate. Spectroscopic characterization established the acetonitrile had been replaced by acetone.

**Microanalysis:** Calc. (%) for C\textsubscript{20}H\textsubscript{42}Br\textsubscript{4}NO\textsubscript{2}O\textsubscript{8}; C 28.65, H 5.05, N 1.67  
Found (%); C 26.38, H 4.85, N 1.55  
**Infra-red Spectrum:** (KBr disc) 3 359 cm\textsuperscript{-1} (s), 2 963 (s), 2 935 (m), 2 875 (m), 1 972 (s), 1 827 (w), 1 610 (m), 1 470 (m), 1 381 (m), 1 163 (w), 1 067 (w), 1 035 (w), 883 (w), 738 (w), 575 (w), 559 (w).
(viii) Trans tetraphenylphosphonium tetrachlorobis(tert-butyl isonitrile)osmate,

(Ph₄P)₂[Os₂(μ-Cl)₂Cl₈] (0.28 g, 0.20 mmol.) was dissolved in 20 ml. of 1,2-dichloroethane, and tert-butyl isocyanide (0.36 ml., 3.17 mmol.) added. The green mixture was then refluxed with stirring under N₂ for 18 hours, giving a yellow solution. The solvent was removed in vacuo, and the residue recrystallized from dichloromethane/diethyl ether. The pale yellow microcrystalline precipitate was collected by filtration, washed with diethyl ether and dried in vacuo at 313 K (0.25 g, 76%).

Microanalysis: Calc.(%) for C₃₄H₃₈Cl₄N₂OsP; C 48.75, H 4.57, N 3.34

Found(%); C 53.67, H 4.96, N 3.06

Infra-red Spectrum: (KBr disc) 3 055 cm⁻¹ (m), 2 982 (m), 2 145 (s), 1 583 (m), 1 483 (m), 1 453 (w), 1 437 (s), 1 397 (w), 1 356 (m), 1 338 (w), 1 314 (w), 1 231 (w), 1 199 (m), 1 106 (s), 1 037 (w), 995 (s), 760 (m), 723 (s), 690 (s), 615 (w), 548 (m), 523 (s).

(ix) Trans tetraphenylphosphonium tetrabromobis(tert-butyl isonitrile)osmate(III)

This complex was prepared in 61% yield from (Ph₄P)₂[Os₂(μ-Br)₂Br₈] by a procedure similar to that described for its chloride analogue

Microanalysis: Calc.(%) for C₃₄H₃₈Cl₄N₂OsP; C 40.21, H 3.77, N 2.76

Found(%); C 44.55, H 3.91, N 2.44

Infra-red Spectrum: (KBr disc) 2 980 cm⁻¹ (w), 2 130 (s), 1 582 (w), 1 483 (w), 1 441 (m), 1435 (m), 1 366 (w), 1 203 (w), 1 108 (m), 996 (w), 763 (w), 722 (m), 689 (m), 523 (s).

(x) Trans tetra-n-butylammonium tetrabromo(carbonyl)(tert-butyl isonitrile)osmate(III)

To a solution of trans-nBu₄N[OsBr₄(CO)₂] (0.20 g, 0.25 mmol.) dissolved in 15.0 ml. of freshly distilled dichloromethane, was added tert-butyl isonitrile (0.28 ml., 2.48 mmol.). This mixture was then stirred overnight at room temperature under N₂, after which the solvent and excess isonitrile
ligand were removed by heating *in vacuo*. The resulting residue was fractionally recrystallized from dichloromethane/diethyl ether, and the dark green microcrystalline product collected by filtration, washed with diethyl ether and dried in air (0.14 g, 67%).

**Microanalysis:** Calc. (%) for C$_{22}$H$_{45}$Br$_4$N$_2$O$_8$; C 30.60, H 5.25, N 3.24

Found (%); C 30.70, H 5.37, N 3.29

**Infra-red Spectrum:** (KBr disc) 2 962 cm$^{-1}$ (m), 2 875 (m), 2 214 (s), 2 003 (s), 1 472 (m), 1 373 (w), 1 205 (w), 880 (w), 734 (w), 588 (m).

(xi) **Trans** tetra-n-butylammonium tetrachloro(carbonyl)(tert-butyl isonitrile)osmate(III)

This complex was prepared by a similar procedure to that of the analogous bromide complex. Upon completion of the reaction, and removal of the solvent, the product residue was recrystallized from tetrahydrofuran/n-hexane and diethyl ether.

**Microanalysis:** Calc. (%) for C$_{22}$H$_{45}$Cl$_4$N$_2$O$_8$; C 38.54, H 6.62, N 4.09

Found (%); C 38.71, H 6.87, N 4.00

**Infra-red Spectrum:** (KCl disc) 2 960 cm$^{-1}$ (s), 2 935 (m), 2 875 (m), 2 220 (s), 2 012 (s), 1 471 (m), 1 372 (w), 1 235 (w), 1 200 (m), 885 (w), 738 (w), 589 (m).

### 5.7.5 Synthesis of Mer-Trichlorotris(acetonitrile)osmium(III)

**Trans**-(Ph$_4$P)[OsCl$_4$(CH$_3$CN)$_2$] (0.13 g, 0.17 mmol.) was dissolved with warming in 30 ml. of distilled acetonitrile. To this yellow solution was added one mole equivalent of AgCF$_3$SO$_3$, (0.046 g, 0.18 mmol.) resulting in the immediate precipitation of a fine red solid. The mixture was then refluxed with stirring under N$_2$ for 3 days, to give a yellow solution containing a fine light coloured solid. The solid was filtered off, and the yellow solution passed down a silica-gel column (eluted with acetonitrile). A yellow fraction was collected, and the solvent was removed *in vacuo*. The residue was then recrystallized from dichloromethane/diethyl ether, yielding a fine pale orange precipitate (0.10 g, 66%). This complex was isolated as a 1:1 mixture with Ph$_4$PCF$_3$SO$_3$, as shown by the microanalysis.
and the infra-red spectrum.

**Microanalysis:** Calc. (%) for $\text{C}_{31}\text{H}_{29}\text{Cl}_3\text{F}_3\text{N}_3\text{O}_3\text{OsPS}$; C 40.00, H 3.22, N 4.63

Found (%); C 38.30, H 2.99, N 4.70

**Infra-red Spectrum:** (KCl disc) 3 064 cm$^{-1}$ (w), 2 972 (m), 2 915 (m), 1 587 (w), 1 487 (m), 1 443 (s), 1 437 (s), 1 280 (s), 1 265 (s), 1 227 (m), 1 188 (w), 1 147 (s), 1 109 (s), 1 033 (s), 996 (m), 952 (w), 758 (m), 752 (m), 722 (s), 689 (s), 634 (s), 614 (w), 570 (w), 525 (s), 447 (w).
5.8 REFERENCES

83. L. Dubicki, private communication.

Crystal Structure of $\text{nBu}_4\text{N}[\text{OsBr}_5(\text{MeCN})]$  

$n\text{Bu}_4\text{N}[\text{OsBr}_5(\text{MeCN})]$, $\text{C}_{18}\text{H}_{39}\text{Br}_5\text{N}_2\text{Os}$, $M_r = 873.24$, triclinic, $P\overline{1}$, $a = 10.038$ (1), $b = 11.837$ (1), $c = 12.541$ (1) Å, $\alpha = 70.99$ (1), $\beta = 85.49$ (1), $\gamma = 87.55$ (1) °, $V = 1404.3$ Å$^3$, $Z = 2$, $D_x = 2.065$ Mg m$^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 18.05$ mm$^{-1}$, $F(000) = 824$, $T = 293$ K, $R = 0.031$ for 3801 observed reflections.

[Diagram showing the crystal structure with atom labeling]

*Figure A.1* Thermal ellipsoid diagram of $[\text{OsBr}_5(\text{MeCN})]^{1-}$ anion showing atom labelling. Ellipsoids show 50% probability levels except H atoms which were drawn as small circles of arbitrary radius.
**Table A.1**  Interatomic distances (Å) and angles (°) for non-hydrogen atoms of \( ^{n}Bu_4N[OsBr_5(MeCN)] \)

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Crystal Structure of \textit{trans}-nBu\textsubscript{4}N[OsBr\textsubscript{4}(CO)\textsubscript{2}]

\((n\text{Bu}_4\text{N})[\text{OsBr}_4(\text{CO})_2], C_{18}H_{36}Br_4N_0_2O_5, M_r = 808.3, \text{monoclinic, } P2_1/c, a = 12.957 (1), b = 12.306 (1), c = 18.132 (1) \text{ Å}, \beta = 106.97 (1) ^\circ, V = 2765.4 \text{ Å}^3, Z = 4, D_x = 1.941 \text{ Mg m}^{-3}, \lambda(\text{Cu } K\alpha) = 1.5418 \text{ Å}, \mu = 16.5 \text{ mm}^{-1}, F(000) = 1532, T = 298 \text{ K}, R = 0.031 \text{ for } 3496 \text{ observed reflections.}

\textit{Figure A.2} Thermal ellipsoid diagram of \textit{trans-}\{\text{OsBr}_4(\text{CO})_2\}\textsuperscript{1-} anion showing atom labelling. Ellipsoids show 50\% probability levels.
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Crystal Structure of $\text{nBu}_4\text{N}[\text{OsBr}_4(\text{CO})(\text{MeCN})]$}

$n\text{Bu}_4\text{N}[\text{OsBr}_4(\text{CO})(\text{MeCN})]$, $C_{19}H_{39}Br_4NO_2$, $M_r = 821.3$, monoclinic, $P2_1/n$, $a = 12.805 (1)$, $b = 12.281 (2)$, $c = 18.711 (2)$ Å, $\beta = 99.26 (1)$ °, $V = 2904.1$ Å$^3$, $Z = 4$, $D_x = 1.878$ Mg m$^{-3}$, $\lambda(\text{Cu K\alpha}) = 1.5418$ Å, $\mu = 14.9$ mm$^{-1}$, $F(000) = 1564$, $T = 293$ K, $R = 0.068$ for 4011 observed reflections.

*Figure A.3.* Thermal ellipsoid diagram of $[\text{OsBr}_4(\text{CO})(\text{MeCN})]^{1-}$ anion showing atom labelling. Ellipsoids show 50% probability levels. H atoms not located.
**Table A.3** Interatomic distances (Å) and angles (°) for non-hydrogen atoms of trans-(nBu₄N)[OsBr₄(CO)(MeCN)].

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C(32)-C(33)-C(34)  115(2)  N(1)-C(41)-C(42)  116(1)
C(41)-C(42)-C(43)  113(1)  C(42)-C(43)-C(44)  118(2)
Crystal structure of cis-[OsCl₂(PMe₂Ph)₄]

[OsCl₂(PMe₂Ph)₄], C₃₂H₄₄Cl₂O₈P₄, Mr = 817.7, monoclinic, C2/c, a = 22.451 (2), b = 8.516 (1), c = 18.485 (2) Å, β = 106.16 (1)°, V = 3394.6 Å³, Z = 4, Dₓ = 1.592 Mg m⁻³, λ(Mo Kα) = 0.71069 Å, μ = 4.12 mm⁻¹, F(000) = 1624, T = 298 K, R = 0.017 for 3662 observed reflections.

**Figure A.4.** Thermal ellipsoid diagram of cis-[OsCl₂(PMe₂Ph)₄], showing atom labelling. Ellipsoids show 50% probability levels. H atoms not located.
Table A.4  Interatomic distances (Å) and angles (°) for non-hydrogen atoms of cis-[OsCl₂(PMe₂Ph)₄].

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