

Electrochemical and Spectroelectrochemical Studies

on Mixed Halo/Pyridine Osmium complexes

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Declaration

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

K.J.Taylor

For all my Family
especially Duncan Jack Adam
and to Katherine.

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Abstract

The complexes $[\text{OsCl}_{6-n}\text{py}_n]^{(n-y)+}$, where $n = 0, 1, 2(\text{trans}), 2(\text{cis}), 3(\text{mer}), 4(\text{trans}), 5$ and 6 , and y varies between 2 and 4 , have been synthesised via redox induced substitution reactions of $[\text{OsCl}_6]^{2-}$. The series has been fully characterised using electrochemical and spectroelectrochemical techniques. Several key members namely $\text{trans}-[\text{TPA}][\text{OsCl}_4\text{py}_2]$, $\text{cis}-[\text{OsCl}_4\text{py}_2]$, $\text{trans}-[\text{OsCl}_2\text{py}_4]$ and $[\text{OsPY}_6][\text{BF}_4]_2$, have also been examined by X-ray crystallography. Voltammetric data derived from these complexes has been compared to $E_{1/2}$ values predicted by two recent models. $E_{1/2}$ values for the series $[\text{OsCl}_{6-n}\text{py}_n]^{(n-y)}$, where $y = 3$ and 2 , are dependent on n but independent of the isomeric form adopted. However, we propose that $E_{1/2}$ values for the series $[\text{OsCl}_{6-n}\text{py}_n]^{(n-4)+}$ are dependent not only on n and the isomeric form, but also on the precise coordination mode of the pyridine ligands.

As a comparison some members of the series $[\text{OsBr}_{6-n}\text{PY}_n]^{(n-y)+}$ and $[\text{OsI}_{6-n}\text{PY}_n]^{(n-y)+}$, and complexes $[\text{TBA}][\text{OsCl}_5\text{L}]$, where $\text{L} = \text{PhCN}$, 2 , 3 and 4 -cyanopyridine and $3,4$ -dicyanopyridine, have also been synthesised and characterised using the methods described above. Kinetic studies on the reduction of $[\text{OsCl}_6]^{2-}$ in the presence of pyridine, dmf and CO suggest Cl^- loss is the rate determining step for this process.

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Chapter 1: Introductory remarks; some examples of redox induced reactions; an outline of the principles of ligand additivity theory; an introduction to the interpretation of u.v./vis. electronic absorption spectra; an outline of the material contained in the ensuing chapters.

'Care, gentle reader, should be taken to examine one's motives before attempting the arduous task to which a detailed examination of this thesis would amount. For, unless one possesses a keen interest in the redox activated substitution reactions of osmium complexes and the spectroscopic and electrochemical data derived therefrom, such perusal of this volume may indeed prove excessively taxing.'

A.R.Brown (1990)

1.1 Introductory remarks.

The work contained in this thesis concerns the electrochemical and spectroelectrochemical examination of compounds of the general formula $[\text{OsX}_{6-n}\text{L}_n]\text{Y}^{-n}$, where X is chloride, bromide or iodide, L is a π -accepting ligand such as pyridine, n takes values between nought and six, and y varies between five and two. The compounds are all produced from redox-induced substitution reactions of hexahaloosmate(IV) starting materials.

The family of complexes have been extensively studied with particular regard to their electronic properties using the techniques of electrochemistry and U.V./Vis./near I.R. absorption spectroscopy. The electrochemical data are discussed in relation to ligand additivity arguments. The notoriously difficult task of assigning bands in the u.v./vis. absorption spectra to specific electronic transitions is facilitated by the comparison of the many closely related spectra. The dependence of the electronic properties on n and y is also discussed.

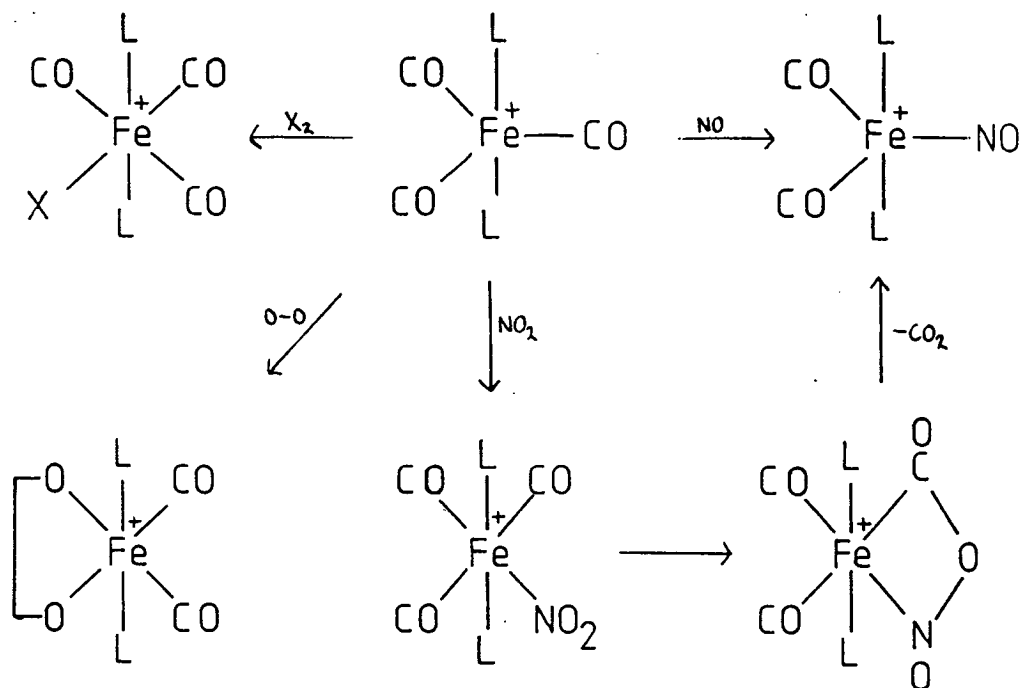
By way of introduction some examples of redox-induced processes, namely: i) oxidative substitution, ii) reductive substitution, iii) oxidative ligand-based dimerisation, iv) oxidation by a 'non-innocent' oxidant, v) oxidative metal-based dimerisation and vi) redox-induced isomerisation, are drawn from the chemical

literature. These examples are followed by an outline of ligand additivity theory. Next a guide to the interpretation of U.V./Vis Absorption Spectra is given. Emphasis is placed on the types of spectral phenomena encountered for complexes of the general formula $[\text{OsX}_{6-n}\text{PY}_n]^{\text{Y}+}$ (X= halogen). Finally, an outline of the material contained in the following chapters is given.

1.2. Some Examples of Redox-Induced Processes.

i) Connelly et al.^{1,2,3} have shown that oxidation of *trans*- $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$ to the green crystalline one-electron oxidation product $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2][\text{PF}_6]$ by $\text{Ag}[\text{PF}_6]$ results in the facile reaction of the oxidised complex with moities such as NO_2 , NO , Cl_2 , Br_2 , I_2 and 1,2 diketone to which the original complex is inert (Scheme 1.1). The reactions show examples of both oxidative addition, eg: in the addition of NO_2 , and oxidative substitution, eg: in the replacement of CO by NO. The reaction with NO_2 is particularly interesting in that the product, after thermolysis, is $[\text{Fe}(\text{CO})_2(\text{NO})(\text{PPh}_3)_2]^+$ which is formed via the intermolecular linking of CO and NO_2 followed by the elimination of CO_2 , as monitored by infra-red spectroscopy.

ii) When $[\text{OsCl}_3(\text{PMe}_2\text{Ph})_3]$ is reduced electrochemically⁴ at -0.5V vs. Ag/AgCl in a solution of

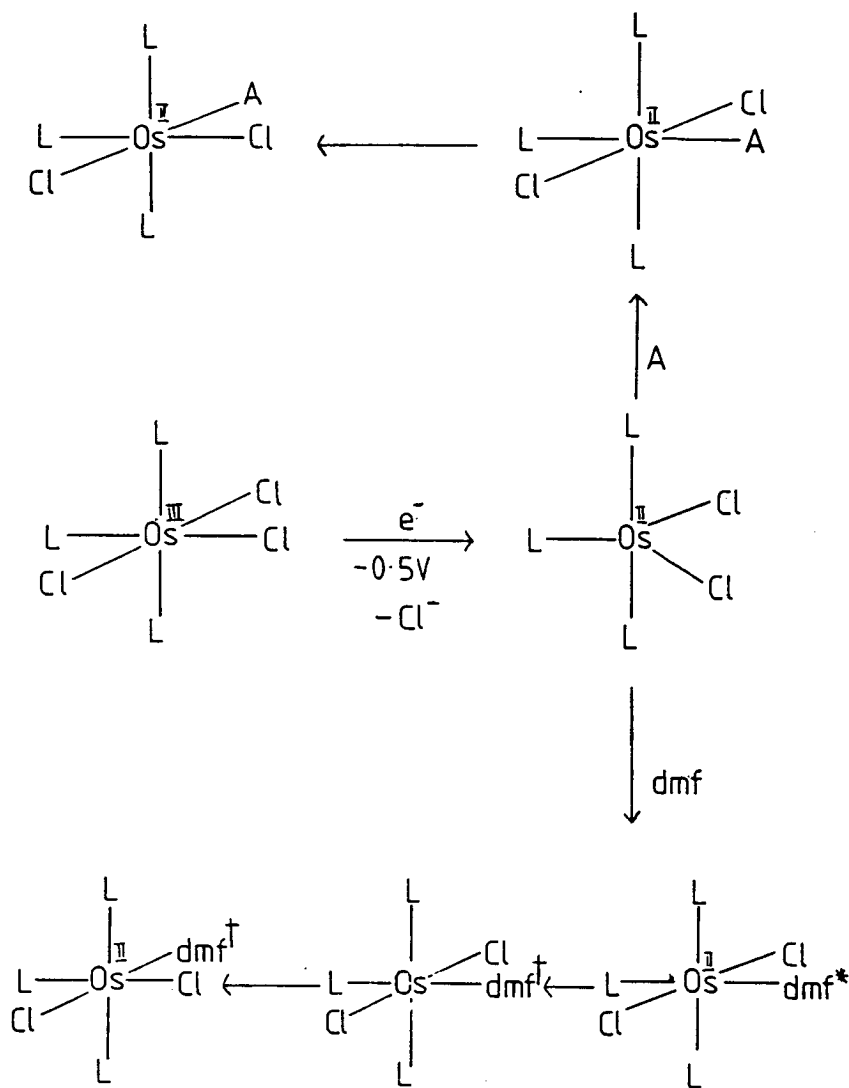


$L = PPh_3$ $X_2 = \text{halogen}$ $O-O = 1,2 \text{ diketone}$

Scheme 1.1. Reactions of the $[Fe(CO)_3(PPh_3)_2]^+$ Cation.

$[0.5M [TBA][BF_4]/ CH_2Cl_2]$, the resulting greenish-yellow solution contains free Cl^- ions, as identified by cyclic voltammetry which can be removed by addition of a stoichiometric amount of $Na[BF_4]$. The neutral five coordinate $[OsCl_2(PMe_2Ph)_3]$ species was characterised by nuclear magnetic resonance spectroscopy. This is an example of redox-induced reductive elimination.

However, a bulk reductive electrolysis of $[OsCl_3(PMe_2Ph)_3]$, in either coordinating solvents, such as acetonitrile or dimethylformamide, or in methylene chloride saturated by a stream of a gaseous coordinating ligand, such as carbon monoxide or dinitrogen, results in the reductive substitution reactions shown in scheme 1.2.

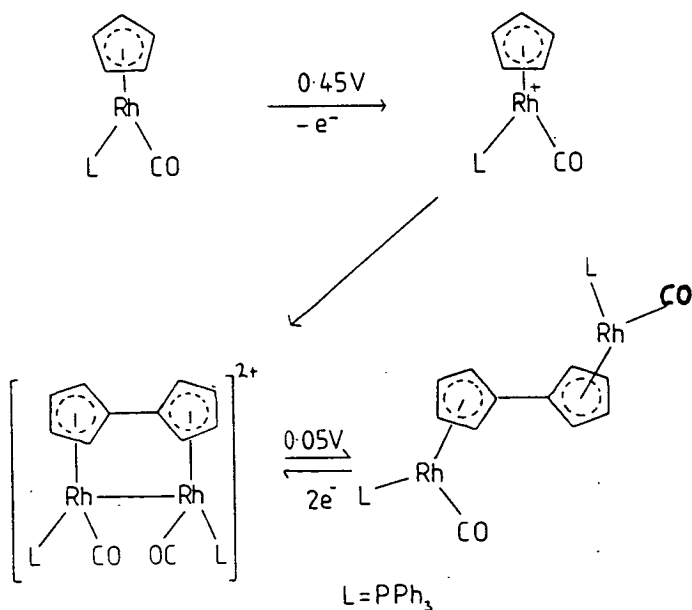


$L = \text{PMePh}$, $A = \text{MeCN}, \text{CO}, \text{C}_4\text{H}_6, \text{N}_2$. † = N bound, * = O bound.

Scheme 1.2 Addition Reactions of the Five Coordinate Intermediate $[\text{Os(II)Cl}_2(\text{PMe}_2\text{Ph})_3]$.

Studies using nuclear magnetic resonance generally show that the species with the substituent *trans*- to a phosphine ligand is formed initially, followed by a subsequent reorganisation to the thermodynamically favoured *cis*- isomer.

iii) The cyclic voltammogram^{3,5} of $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Cp}]$ shows an irreversible oxidation wave at 0.45V vs. s.c.e. coupled with a reversible daughter product wave centered at 0.05V. The chemical oxidation of $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Cp}]$ by $[\text{FeCp}_2]^+$ or $[\text{N}_2\text{C}_6\text{H}_4\text{F-p}]^+$ leads to the production of the daughter product, the fulvalene complex: $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\eta^5:\eta'^5\text{-C}_{10}\text{H}_8)]^{2+}$ (Scheme 1.3). The $\text{Rh}(\text{CO})(\text{PPh}_3)$ groups in this species are *cis*- to one another with respect to the fulvalene ligand. This compound has a long metal-metal bond (2.93Å) and the structure is strained with the C_{10}H_8 bridge bent and twisted.^{3,6}



Scheme 1.3

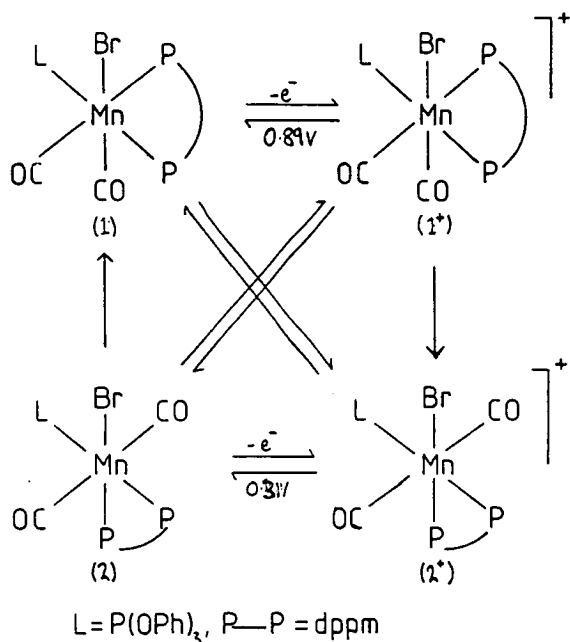
Scheme 1.3 Reaction Scheme for the Oxidation of $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Cp}]$.

Interestingly, $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\eta^5:\eta'^5\text{C}_{10}\text{H}_8)]$, which was chemically reduced by sodium amalgam from $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\eta^5:\eta'^5\text{-C}_{10}\text{H}_8)]^{2+}$ has the two $\text{Rh}(\text{CO})(\text{PPh}_3)$ groups *trans*- to each other with respect to the fulvalene ligand.^{3,6}

iv) When $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Cp}]$ is reacted with $\text{Ag}[\text{PF}_6]$,^{3,5} the silver (I) ion does not oxidise the parent species to the fulvalene complex discussed above. Instead the Ag^+ acts as a 'non-innocent' oxidant giving the adduct $[\text{Ag}\{\text{Rh}(\text{CO})(\text{PPh}_3)\text{Cp}\}_2][\text{PF}_6]$ which is an air stable, crystalline solid.

v) In contrast to $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Cp}]$, when $[\text{Rh}(\text{CO})\{\text{P}(\text{OPh})_3\}\text{Cp}]$ is oxidised, either by $[\text{FeCp}_2]^+$ or electrolytically, the dimer $[\text{Rh}_2(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2\text{Cp}_2]^{2+}$ is produced.⁷ This compound exhibits a Rh-Rh bond (2.81Å) and no linking of the cyclopentadiene ligands.

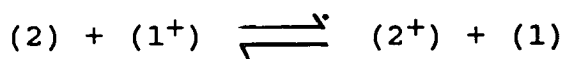
vi) The electrochemical oxidation of *cis*- $[\text{MnBr}(\text{CO})_2\{\text{P}(\text{OPh})_3\}(\text{dppm})]$ (1), where $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$, results in rapid oxidative isomerisation to *trans*- $[\text{MnBr}(\text{CO})_2\{\text{P}(\text{OPh})_3\}(\text{dppm})]^+$ (2^+) as shown in the square scheme (scheme 1.4).^{3,8} The reduction of (2^+) results in slow reductive isomerisation to the neutral *cis* starting material (1). (The oxidation potentials of the two isomers (1) and (2) are in considerable variance, the



Scheme 1.4

Scheme 1.4 Electrochemical Oxidative Isomerisation of *cis*-[MnBr(CO)₂{P(OPh)₃}(dppm)].

reason for this discrepancy is discussed in section 1.3.). However, the simple scheme described above is complicated by the fact that addition of small amounts of *trans*-[MnBr(CO)₂{P(OPh)₃}(dppm)]⁺ (2⁺) to the neutral *trans*- isomer (2) results in the quantitative formation of neutral *cis*-[MnBr(CO)₂{P(OPh)₃}(dppm)] (1).^{3,9} Although the equilibrium constant for the two oxidised species lies well in favour of the *trans*- isomer (2⁺), the cross reaction (see below) is favoured by 0.58V.



It is this cross reaction that provides the driving force for a catalytic cycle. This has synthetic implications in that a slow electrochemical reduction of (2^+) will result in (2) being in contact with (2^+) , resulting in the formation of (1). However, if the reduction is performed quickly ie. chemically, the formation of (1) by this means would be hindered.

1.3 Ligand additivity.

Ligand additivity theory is an attempt to quantify the electronic effects that a set of ligands have on a metal centre. Ligand additivity has recently been the subject of an excellent review.¹⁰ Several experimental techniques have been employed in order to classify ligands according to their donor-acceptor properties, these include electronic spectroscopy, I.R. spectroscopy, N.M.R. spectroscopy, core and valence photoelectron spectroscopy, Mossbauer spectroscopy and electrochemistry. Here the theories as applied to electrochemical data are given. The present discussion concentrates on metal-based, as opposed to ligand-based, electron transfer reactions.

Considering a chemical species in solution, with reference to the discussion of electrochemical techniques given in appendix 1, the point at which either an oxidative or reductive current flows can be related to the standard potential E^0 for the chemical species in

solution. Several studies have shown that these standard potentials can be related to the energy change involved in removing or adding an electron to a chemical species, which in turn can be related to the energies of the lowest unoccupied molecular orbital (L.U.M.O.) and the highest unoccupied molecular orbital (H.O.M.O.) respectively. Electrochemical studies on aromatic hydrocarbons have shown linear relationships between both reduction potentials and the calculated L.U.M.O.'s,¹¹ and oxidation potentials and the calculated H.O.M.O.'s.¹²

Similar correlations have been made for inorganic systems. The most notable of these is the examination of the series of manganese complexes $[\text{Mn}(\text{CO})_{6-n}(\text{CNMe})_n]^+$. A linear correlation between the number of isocyanide ligands present in the complexes $[\text{Mn}(\text{CO})_{6-n}(\text{CNMe})_n]^+$, and their respective oxidative potentials has been observed.¹³ It was proposed that the additive change in the oxidation potentials was due to the additive electronic effect on the H.O.M.O. which resulted from replacing successive carbonyl ligands with isocyanide ligands. This view was supported when the energies of the H.O.M.O.'s were calculated using the nonempirical Fenske-Hall M.O. method.¹³ A plot of the calculated H.O.M.O. energies against the experimentally determined oxidation potentials yielded a linear correlation, with the compounds with H.O.M.O.'s at lower energy showing greater oxidative potentials. The authors concluded that although the

oxidation potential was a measure of the energy difference between the reduced and oxidised species, which would inherently include other variables such as solvent effects, it was nevertheless reasonable that for a series of closely related compounds the linear correlation between oxidation potential and H.O.M.O. energy should be observed, since the electron involved in the oxidation should always be derived from the H.O.M.O.

These initial studies provided the basis upon which various models could be proposed in an attempt to correlate the large amount of electrochemical data pertaining to transition metal complexes, in terms of the electronic effects the ligands have on the metal centre.

The pioneering model was that of Pickett and Pletcher.¹⁵ They considered the series of compounds discussed above, as well as some other metal carbonyl complexes, and proposed that for the series of electrochemical couples $[M(CO)_{6-n}L_n]Y^+/(Y+1)^+$ where $n = 0, 1, trans-2, mer-3, cis-4$ and 5, the following tenets could be expected:

1. For a series of related complexes, if the oxidation potentials are measured in the same inert solvent with the same reference electrode, then they should be a measure of the relative H.O.M.O. energies for the series, provided that the M.O.'s are not drastically perturbed by the oxidation and that the change in free energy of solvation is approximately constant throughout

the series.

2. The change in the oxidation potential induced by the replacement of CO by L is independent of n and is a function of the ligand L only.

3. The effect of changing the charge of a series, for a given L, is to add a constant, proportional to the charge, to the oxidation potential.

Hence the following relationship (1) was proposed:

$$E^0 = A + n(\delta E^0 / \delta n)_L + QY \quad 1$$

where A is a constant characteristic of the reference potential and solvent system, $(\delta E^0 / \delta n)_L$ is a parameter dependent on the nature of L, which defines the change in E^0 when one CO is replaced by L, and Q_Y is a charge parameter. This latter quantity was defined by comparing E^0 values for some isoelectronic complexes that only differed in overall charge, such as $[V(CO)_6]^{-/0}$ and $[Cr(CO)_6]^{0/+}$, and, $[Cr(CO)_5Br]^{-/0}$ and $[Mn(CO)_5Br]^{0/-}$. The six examples which were used for the determination of this charge parameter yielded an average value 1.48 for Q. Using equation (1), some 'ligand inductive parameters', $(\delta E^0 / \delta n)_L$, for several ligands found in metal carbonyl complexes, were calculated.

The main disadvantage of the model proposed by Pickett and Pletcher was that only the number and type of ligand around the metal centre were considered, the

stereochemical positions of the ligands were ignored and hence the model predicts the same oxidation potential for a pair of isomers. It should be remembered that when the Pickett and Pletcher model was proposed, there were few examples of electrochemical data on pairs of isomers. There are now many examples of isomeric pairs of compounds exhibiting quite different oxidation potentials. For instance, in the extended series of complexes $[\text{Mn}(\text{CO})_{6-n}(\text{CNMe})_n]^+$, *cis* and *trans*- $[\text{Mn}(\text{CO})_2(\text{CNMe})_4]^+$ show oxidation potentials at 1.28 and 1.44V vs. s.c.e. respectively and *mer* and *fac*- $[\text{Mn}(\text{CO})_3(\text{CNMe})_3]^+$ exhibit oxidative $E_{1/2}$ values at 1.73 and 1.90V vs. s.c.e.¹⁶ Another example of this difference is illustrated in the complexes *cis*- and *trans*- $[\text{MnBr}(\text{CO})\{\text{P}(\text{OPh})_3(\text{dppe})\}]$ (1.2 vi). These differences in E_0 were first discussed in 1974 by Wimmer, Snow and Bond, using a qualitative bonding scheme.¹⁷ They suggested that the H.O.M.O. in the *cis* isomer of $[\text{Mn}(\text{CO})_2(\text{CNMe})_4]^+$ is involved in one π -back bonding interaction with the CO whereas *trans*- $[\text{Mn}(\text{CO})_2(\text{CNMe})_4]^+$ will have no such interaction (fig. 1.1). Similarly the H.O.M.O. in *fac*- $[\text{Mn}(\text{CO})_3(\text{CNMe})_3]^+$ will be involved in 2 π -back bonding interactions whereas *mer*- $[\text{Mn}(\text{CO})_3(\text{CNMe})_3]^+$ will only be involved in one (fig. 1.1). Since CO is a better π -acceptor than CNMe, the more backbonding interactions the H.O.M.O. in these complexes has with CO ligands, the more it will be stabilised, thus

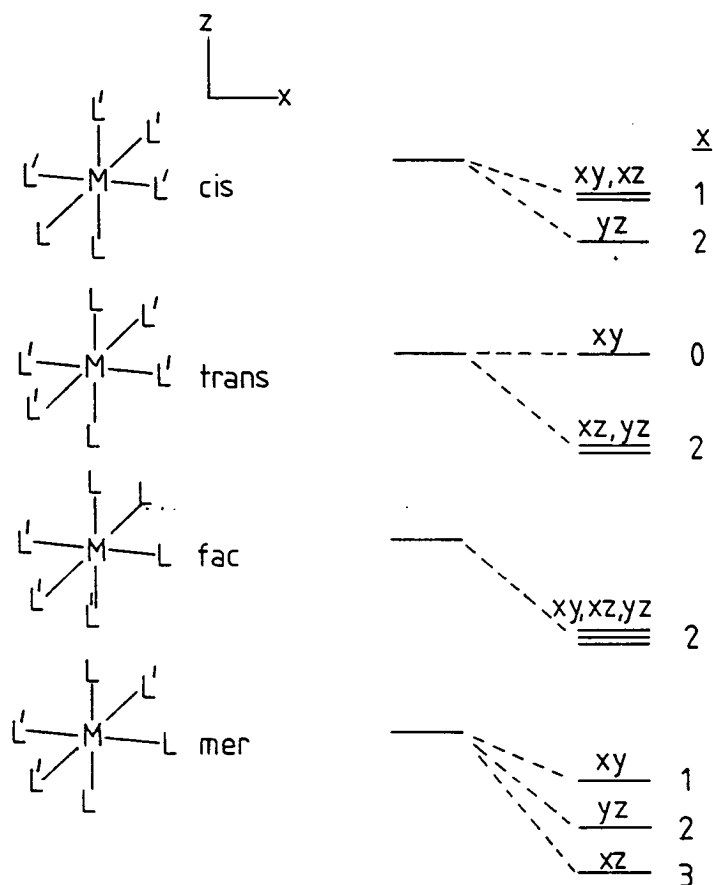


Figure 1.1 Qualitative Diagram showing the Energetic Splitting of the Metal Based d Orbitals for ML_nL_{6-n} where $n = 2, 3$.

making it more difficult to oxidise. This is borne out experimentally.

The ligand additivity model of Bursten gives a quantitative basis to this qualitative model.¹⁸ Bursten noted that all seven members of the series $[Mn(CO)_{6-n}(CNMe)_n]^+$ $n = 0, 1, cis-2, trans-2, fac-3, mer-3, cis-4$ and 5, show a linear correlation between oxidation potential and calculated H.O.M.O. energy. It was subsequently shown that the calculated energetics of the

metal-based M.O.'s obeyed the simple additive equation:

$$\epsilon_i = a + bn + cx_i \quad \underline{2}$$

where ϵ_i is the orbital energy of the i^{th} M.O., x_i is the number of CO ligands with which the metal d orbital can interact and a, b , and c are empirically derived parameters.

These observations led Bursten to propose his ligand additivity model, which then encompassed binary ligand substitution series of the type $ML_nL'_{n-6}$, where L and L' were ligands such as CO and CNMe, and M was a low spin d^6 metal centre such as Cr(0), Mn(I) or Re(I). The model was also used to include octahedral d^1 complexes.¹⁹

The basis of the model for d^6 metal centres is to consider the electronic effect the ligands have on the three metal based $d\pi$ (d_{xy} , d_{xz} and d_{yz}) orbitals which are the three main contributors to the three H.O.M.O.'s. It was assumed that these metal-based $d\pi$ orbitals interact with the ligands principally through a set of empty orthogonal π^* orbitals based on the ligands. It was then postulated that for such binary ligand systems that the energetic effect of the ligands upon the metal based $d\pi$ orbitals was only dependent on: a) the number of each type of ligand and b) the number of each type with which the $d\pi$ orbital can interact. Furthermore, both these dependences are linear. Hence

$$\epsilon_i = \overset{\text{M}}{a^0} + \overset{\text{M}}{nb^L} + \overset{\text{M}}{(6-n)b^{L'}} + \overset{\text{M}}{x_i c^L} + \overset{\text{M}}{(4-x_i)c^{L'}} \quad \underline{3}$$

where a^0 is a characteristic of the specific metal and oxidation state being considered, b^L and $b^{L'}$ are constants dependent on the gross energetic effect of the metal binding to L and L' respectively, c^L and $c^{L'}$ are constants describing the energetic effect of the interaction between the i^{th} metal $d\pi$ orbital and L and L' respectively, and x_i is the number of ligands of the type L the i^{th} metal orbital can interact with.

Equations 2 and 3 form the basis of the ligand additivity model. Their form implies the following:

1. The gross ligand effects upon the metal centre atom must be isomer independent, that is, the average orbital energy of the three metal based $d\pi$ M.O.'s must depend only on n .
2. The gross effect of ligand replacement upon the metal atom is independent of n .
3. The three metal-based $d\pi$ orbitals do not rehybridize upon ligand replacement, even though they may be allowed to do so by symmetry.
4. The effect of one of the $d\pi$ orbitals interacting with L and not L' is independent of n .
5. The orbital energy of any of the metal-based $d\pi$ orbitals depends only on the number and type of each ligand available for bonding and is independent of the

stereochemistry of the ligands about the metal.

To apply this model to electrochemical data, a linear correspondence between the energy of the H.O.M.O. and the oxidation potential must be assumed.

$$E_{1/2} = k_1(-\epsilon_{\text{HOMO}}) + k_2 \quad \underline{4}$$

where k_1 and k_2 are empirically derived parameters. From this relation and equations 2 and 3 we can see that:

$$E_{1/2} = A + Bn + Cx_{\text{HOMO}} \quad \underline{5}$$

$$A = A_M^0 + 6B_M^L + 4C_M^L ; \quad B = B_M^L - B_M^{L'} ; \quad C = C_M^L - C_M^{L'} \quad \underline{6}$$

where x_{HOMO} is the number of ligands L with which the highest occupied $d\pi$ orbital can interact and A, B and C are empirically derived parameters which can be related to a, b and c using equation 4.

The $E_{1/2}$ values predicted by this model are dependent on the precise electronic configuration at the metal centre. Table 1.1 (overleaf) details these precise predictions. It should be noted that these predictions assume that the spin pairing energy is greater than any splitting within the metal $d\pi$ orbitals.

Bursten's predictions fit well with a substantial range of compounds. The electrochemical data he successfully applied his model to are derived from the

Predicted $E_{1/2}$ values for d^n configurations, $n = 1-6$, of $ML_nL'^{6-n}$, where L is a more stabilising ligand than L'

		Low spin state of M					
		d^6, d^5, d^4, d^3		d^1		d^2	
Compound	n	x_{HOMO}	$E_{1/2}$	x_{HOMO}	$E_{1/2}$	x_{HOMO}	$E_{1/2}$
ML'_6	0	0	A	0	A	0	A
MLL'_5	1	0	A+B	1	A+B+C	1	A+B+C
$t-ML_2L'^4$	2	0	A+2B	2	A+2B+2C	2	A+2B+2C
$c-ML_2L'^4$	2	1	A+2B+C	2	A+2B+2C	1	A+2B+C
$m-ML_3L'^3$	3	1	A+3B+C	3	A+3B+3C	2	A+3B+2C
$f-ML_3L'^3$	3	2	A+3B+2C	2	A+3B+2C	2	A+3B+2C
$t-ML_4L'^2$	4	2	A+4B+2C	4	A+4B+4C	2	A+4B+2C
$c-ML_4L'^2$	4	2	A+4B+2C	3	A+4B+3C	3	A+4B+3C
ML_5L'	5	3	A+5B+3C	4	A+5B+4C	3	A+5B+3C
ML_6	6	4	A+6B+4C	4	A+6B+6C	4	A+6B+4C

The electrochemical couples that have been tested are as follows:

$[\text{Mn}(\text{CO})_n(\text{CNMe})_{6-n}]^{1+/2+}$ in CH_2Cl_2 where $n = 0, 1, t-2, c-2, m-3, f-3$.

$[\text{Mn}(\text{CO})_n(\text{CNMe})_{6-n}]^{1+/2+}$ in MeCN where $n = 0, 1, t-2, m-3, c-4, 5$.

$[\text{Mn}(\text{CO})_n(\text{CNPh})_{6-n}]^{1+/2+}$ in CH_2Cl_2 where $n = 0, 1, t-2, c-2, m-3, f-3, c-4$.

$[\text{Cr}(\text{CO})_n(\text{CNMe})_{6-n}]^{0/1+}$ in CH_2Cl_2 where $n = f-3, c-4, 5$.

$[\text{Cr}(\text{CO})_n(\text{CNPh})_{6-n}]^{0/1+}$ in CH_2Cl_2 where $n = 0, 1, c-2, f-3, c-4, 5, 6$.

$[\text{Nb}(\text{NCMe})_n\text{Cl}_{6-n}]^{-2+n/-1+n}$ in MeCN where $n = 0, 1, c-2$.

$[\text{Ta}(\text{CNMe})_n\text{Cl}_{6-n}]^{-2+n/-1+n}$ in MeCN where $n = 0, 1, c-2$.

compounds listed below table 1.1

The biggest disadvantage of the method is that in order to calculate an $E_{1/2}$ potential, the values for A, B, and C must be known. $E_{1/2}$ values for three members of a substitution series must be known in order to obtain A, B and C. Another interesting point is that the model has only been applied to d^1/d^0 and low spin d^6/d^5 couples. Neither of these couples is likely to involve rehybridization of the orbitals on oxidation. d^5/d^4 and d^4/d^3 oxidation couples would be likely to involve such a reorganisation. This would be likely to result in a departure from the linear correlation between oxidation potential and the energy of the H.O.M.O. Finally the values of constants A, B and C do reflect some limited physical meaning namely: parameter A reflects the metal in a particular oxidation state, ligand parameter B is related to π -acceptance, π -donation and σ -donation, ligand parameter C is only related to π -donation and π -acceptance.

Other workers have attempted to produce models which, with knowledge of some parameters pertaining to a metal centre and the surrounding ligands, will directly predict $E_{1/2}$ values. Initially Chatt, Leigh and Pickett developed their ligand parameters,²⁰ more recently Lever has proposed 'Ligand Parametrization.'²¹

Chatt et al. defined their ligand parameter as follows:

$$P_L = E_{1/2}^{\text{OX}}[\text{Cr}(\text{CO})_5\text{L}] - E_{1/2}^{\text{OX}}[\text{Cr}(\text{CO})_6] \quad 7$$

in other words P_L is the ligand induced change in the oxidative $E_{1/2}$ potential as compared to $\text{Cr}(\text{CO})_6$. The following ligand constants P_L were experimentally derived:

Ligand	P_L	Ligand	P_L	Ligand	P_L
N^+	1.46	CNMe	-0.43	I^-	-1.15
NO^+	1.40	NCMe	-0.58	NCO^-	-1.16
CO	0.00	py	-0.59	Br^-	-1.17
N_2	-0.07	NH_3	-0.77	Cl^-	-1.19
$\text{P}(\text{OPh})_3$	-0.18	CF_3CO_2^-	-0.78	H^-	-1.22
PPh_3	-0.35	NCS^-	-0.88	N_3^-	-1.26
CNPh	-0.38	CN^-	-1.00	OH^-	-1.55
NCPH	-0.40				

These ligand parameters were plotted against the oxidative $E_{1/2}$ values found for several related series of compounds $\text{trans-}[\text{MYL}(\text{dppe})_2]^+$, where $\text{MY} = \text{Mo}(\text{NO}^+)$, $\text{Mo}(\text{CO})$, $\text{Mo}(\text{N}_2)$, $\text{Mo}(\text{NCPH})$, $\text{Mo}(\text{N}_3^-)$, $\text{Fe}(\text{H})$, $\text{Re}(\text{N}_2)$; $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ with L being the variable ligand. The plots were all linear but had different slopes. The authors proposed the following relation:

$$E_{1/2} = E_S + \beta(P_L). \quad 8$$

where E_S , the intrinsic electron richness of $[MY(dppe)_2]$, is the standard $E_{1/2}$ potential for $[MYL(dppe)_2]$ for $L = CO$, P_L is 0 where $L = CO$; and β , the site polarisability, is the dimensionless slope of a $E_{1/2}$ vs P_L plot.

Lever has recently extended this sort of model to embrace electrochemical data not only pertaining to organometallic chemistry, but also to coordination chemistry as a whole.²¹ His model is based on ligand parameters E_L calculated from electrochemical data derived from a vast range of complexes with the general formula $[Ru(bipy)_nL_{6-2n}]Y^+$.

In order to obtain these ligand parameters Lever first considered the oxidative couple: $Ru(bipy)_3^{2+/3+}$. This occurs at 1.53V vs N.H.E. in acetonitrile. Since this complex contained six Ru-N bonds the E_L for $1/2(bipy)$ was defined as $1.53/6 = 0.255V$. He went on to examine the $E_{1/2}$ values for the $Ru(II)/Ru(III)$ couples for a series of compounds $[Ru(bipy)_nL_{6-2n}]^{2+}$. The E_L value for each ligand $E_L(L)$ was derived from the following relation:

$$E_{obs}(Ru(III)/Ru(II)) = 2n \times 0.255 + (6 - 2n)E_L(L) \quad 9$$

Thus the $E_L(L)$ parameter could be derived from three types of compound, namely: $[Ru(bipy)_2L_2]^{2+}$, $[Ru(bipy)L_4]^{2+}$ and $[RuL_6]^{2+}$. In this way $E_L(L)$ values for over 100 ligands were defined. These values were subsequently used to define the best average value for $E_L(bipy)$ which turned

out to be 0.59V. The $E_L(L)$ values were all recalculated using this new value for $E_L(\text{bipy})$. Using these recalculated $E_L(L)$ values, $E_L(L)$ values for all the Ru(II) complexes not containing bipy were then calculated.

Using this collection of $E_L(L)$ values we can now predict $E_{1/2}$ values for compounds of the type $\text{RuX}_x\text{Y}_y\text{Z}_z$ utilising the following equation:

$$E_{\text{calc}} = xE_L(X) + yE_L(Y) + zE_L(Z) \quad \underline{10}$$

$$\text{or } E_{\text{calc}} = [\Sigma E_L] \quad \underline{11}$$

When the calculated $E_{1/2}$ values, E_{calc} , are plotted against the observed potentials, E_{obs} , the equation of the best fit line through the points is:

$$E_{\text{obs}} = 0.97[\Sigma E_L] + 0.04 \quad \underline{12}$$

A line passing through the origin with a gradient of 1, would have been the result had the calculated data matched up exactly to the experimental values.

To allow these $E_L(L)$ parameters to be of use in the prediction of $E_{1/2}$ values for metals other than ruthenium, Lever suggests similar least squares analysis plots of $[\Sigma E_L]$ versus E_{obs} should be plotted yielding the relation:

$$E_{\text{obs}} = S_M[\Sigma E_L] + I_M \quad 13$$

where S_M and I_M are constants for all complexes containing a particular metal with similar oxidation state, spin state and coordination sphere.

1.4 An Introduction to the Interpretation of U.V/Vis. Electronic Absorption Spectra, with specific reference to the spectra of the complexes $[\text{OsX}_{6-n}\text{PY}_n]^{(n-Y)+}$ ($X = \text{halogen}$).

The assignment of absorption bands to specific electronic transitions is notoriously difficult. However the comparative study of spectra of several closely related species is often helpful in this regard.

In the series of complexes $[\text{OsCl}_{6-n}\text{PY}_n]^{(n-Y)+}$ the osmium metal centre is always in an octahedral coordination site and hence the d orbitals will be split into two subsets, the t_{2g} or $d\pi$ orbitals and the e_g or $d\sigma$ orbitals in O_h symmetry. However, most of the complexes we are considering have considerably lower symmetry than O_h and thus the degeneracy of the t_{2g} and e_g orbitals will be removed, but the ' t_{2g} ' set may still be regarded as $d\pi$ orbitals and the e_g set as $d\sigma$ orbitals.

The possible low energy transitions in $[\text{OsCl}_{6-n}\text{PY}_n]^{X-}$ complexes are shown schematically in figure 1.2. There are three main types of transition which we must consider, namely:

- 1) metal-based
- 2) ligand-based
- 3) charge transfer

We appreciate that within the concept of delocalised molecular orbitals of coordination compounds these distinctions are in most instances an approximation. However they do provide a starting point from which the discussion of the assignments of the electronic transitions can proceed.

1) Metal-based transitions are considered to occur between molecular orbitals predominantly localised on the metal centre; usually these concern excitations from the $d\pi$ to the $d\sigma$ orbitals, d-d transitions. We are unable to observe these bands in our osmium complexes because the $d\pi$ - $d\sigma$ gap is large and hence transitions between these orbitals will be masked by the very much more intense charge transfer bands. However, in electron deficient complexes, eg Os(III) species, the possibility arises of electronic transitions within the metal-based nondegenerate $d\pi$ orbitals. These transitions known as $d\pi \rightarrow d\pi$ transitions occur at low energy and are weak. An example of such a transition is illustrated in the near infra-red spectrum of $[\text{Os}(\text{bipy})_3]^{3+}$.²²

2) Ligand-based transitions are primarily between molecular orbitals predominantly localised on the ligands and are frequently referred to as ligand-centred or

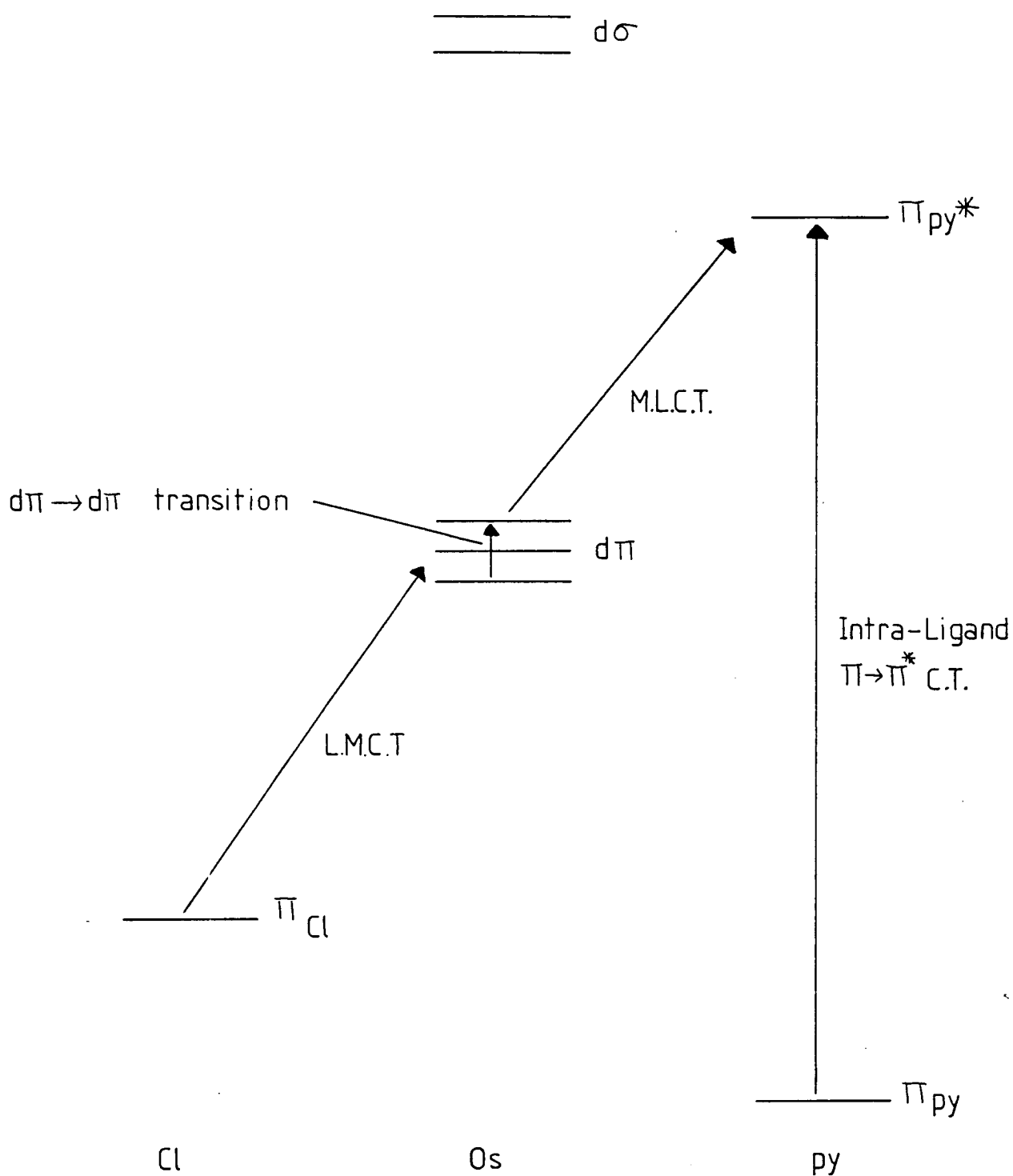


Figure 1.2 Qualitative Molecular Orbital Diagram Showing the Possible Electronic Transitions for Complexes of the type $[\text{OsCl}_{6-n}\text{py}_n]^{(n-y)+}$.

intraligand transitions. They almost invariably involve $\pi \rightarrow \pi^*$ excitations. Thus, in the present complexes pyridine based $\pi \rightarrow \pi^*$ transitions, at moderately high energies, will be important.

3) Charge transfer transitions between orbitals of different localisation cause displacement of electronic charge from the ligands to the metal (L.M.C.T.) or from the metal to the ligand (M.L.C.T.). Such transitions are often intense and usually occur above $10,000\text{cm}^{-1}$.

L.M.C.T. bands occur in the visible region of the spectrum if the ligands have lone pairs of relatively high energy (π -donors) and the metal has low-lying empty or partially empty orbitals.

M.L.C.T. transitions are most commonly observed in complexes containing an aromatic ligand. If the empty π^* orbitals of the ligand lie at sufficiently low energy and the metal centre is relatively electron rich then the M.L.C.T. transition will occur at low energy.

1.5 An outline of the material contained in the ensuing chapters.

Chapter 2 contains electrochemical and spectral data pertaining to the series of complexes $[\text{OsCl}_{6-n}\text{PY}_n]^{(n-Y)+}$. The electrochemical data is treated using the ligand additivity arguments discussed above. Where possible the

bands in the u.v./vis. electronic absorption spectra are assigned to specific electronic transitions.

Chapter 3 deals with electrochemical and spectral data derived from the series $[\text{OsBr}_{6-n}\text{PY}_n]^{(n-Y)+}$ and $[\text{OsI}_{6-n}\text{PY}_n]^{(n-Y)+}$ in a similar fashion.

Chapter 4 is devoted to a discussion of the kinetics of the reductive substitutions of $[\text{OsCl}_6]^{2-}$.

Chapter 5 compares spectral and electrochemical data collected for complexes of the general formula $[\text{OsCl}_5\text{L}]Y^-$, where L is a range of substituted pyridines and CO.

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Chapter 2. Introduction; synthesis, electrochemistry and spectroelectrochemistry of the series $[\text{OsCl}_{6-n}\text{py}_n]^{(n-y)+}$; discussion of this electrochemical and spectral data; experimental details.

'...and the man whose turn it was to play....was the First Grave Digger.

A word about this human wen. He was - if there can be said to be grades in such sub-species - the star performer of the Wrecking Crew. The lunches of fifty-seven years had caused his chest to slip down to the mezzanine floor, but he was still a powerful man, and had in his youth been a hammer thrower of some repute. He differed from his colleagues - the Man With the Hoe, Old Father Time, and Consul, the Almost Human - in that, while they were content to peck cautiously at the ball, he never spared himself in his efforts to do it a violent injury. Frequently he had cut a blue dot almost in half with his niblick. He was completely muscle-bound, so that he seldom achieved anything beyond a series of chasms in the turf, but he was always trying, and it was his secret belief that, given two or three miracles happening simultaneously, he would one of these days bring off a snifter.'

2.1 Introduction

Complexes of the form $[\text{OsCl}_{6-n}\text{PY}_n]^{(n-y)+}$, where $n = 0, 1, 2$ (*cis* and *trans* isomers), 3 (*mer*), 4 (*trans*), 5, 6 and y varies from 2 to 4, have been prepared and examined electrochemically and spectroelectrochemically. In this chapter the redox behaviour of all the complexes is compared and discussed using ligand additivity arguments. The u.v/vis. absorption spectra of the complexes obtained from spectroelectrochemical studies are compared and the bands therein assigned to possible electronic transitions.

2.2.1 Electrochemistry and Spectroelectrochemistry of $[\text{OsCl}_6]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 230K.

The electrochemical behaviour of tetrabutylammonium hexachloroosmate(IV) ($[\text{TBA}]_2[\text{OsCl}_6]$)¹, I^{2-} , in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 230K was studied using the techniques outlined in Appendix 1. A cyclic voltammogram (fig. 2.1) of I^{2-} shows a reduction step at -0.56V (process A) and an oxidation process at +1.38V (process B). Both redox steps are reversible and a coulometric study revealed that each process involved one electron. The redox-active centre for both processes is considered to be the Os(IV) metal ion which has a d^4 low-spin electronic configuration (t_{2g}^4). Thus the oxidation step will produce $[\text{OsCl}_6]^-$ which may be formulated as $[\text{Os(V)Cl}_6]^-$ (t_{2g}^3), I^- , and

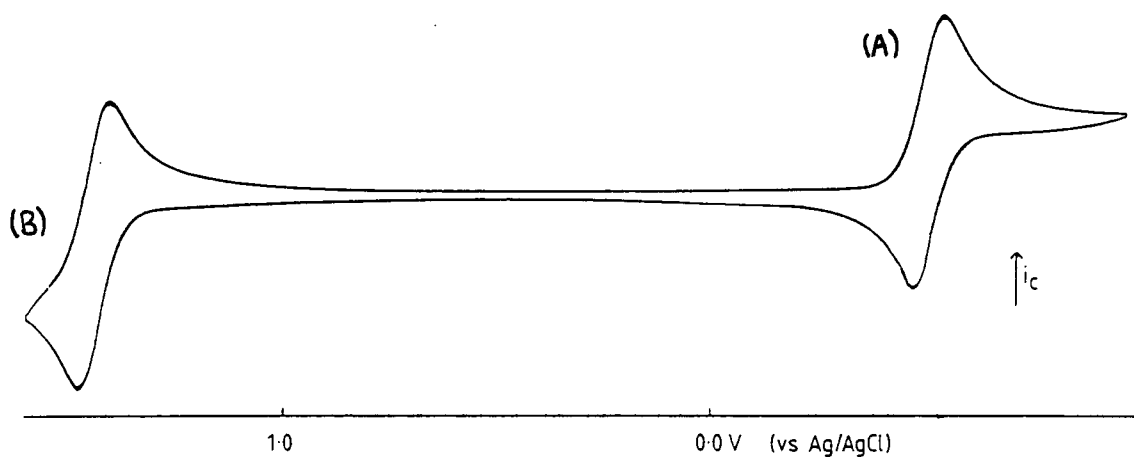


Figure 2.1 Cyclic Voltammetry of $[\text{OsCl}_6]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M}$ $[\text{TBA}][\text{BF}_4]$ at 230K.

the reduction step results in $[\text{OsCl}_6]^{3-}$ or $[\text{Os(III)Cl}_6]^{3-}$ (t_{2g}^5), I^- .

The electronic u.v./vis. spectra of I^{2-} , I^{3-} and I^- were examined under similar conditions at an optically transparent thin layer electrode (O.T.T.L.E.) (see appendix 1). The spectrum of yellow $[\text{OsCl}_6]^{2-}$ (fig. 2.2) is dominated by two strong bands (I and II). These bands have been assigned as $\text{Cl}^- \pi \rightarrow \text{Os(IV)} d\pi(2t_{2g})$ transitions involving different chloride based orbitals.^{2,3} The spectra of claret $[\text{Os(V)Cl}_6]^-$ (fig. 2.3) and pale yellow

$[\text{Os(III)Cl}_6]^{3-}$ (fig. 2.4) exhibit absorption bands of similar molar absorbance at lower and higher energy respectively. These shifts are as would be expected for L.M.C.T.'s (ie. L.M.C.T. bands move to lower energy on removal of an electron from the metal centre) and are therefore assigned as $\text{Cl}^- \pi \rightarrow \text{Os(V)d}\pi$ or $\text{Os(III)d}\pi$ transitions. $[\text{OsCl}_6]^{2-}$ and $[\text{OsCl}_6]^{3-}$ have $^3\text{T}_{2g}$ and $^2\text{T}_{2g}$ ground states respectively whereas $[\text{OsCl}_6]^-$ has a $^4\text{A}_{2g}$ ground state. This may explain why the band shapes in the spectra of the two former complexes are similar whereas the latter is quite different from these two.

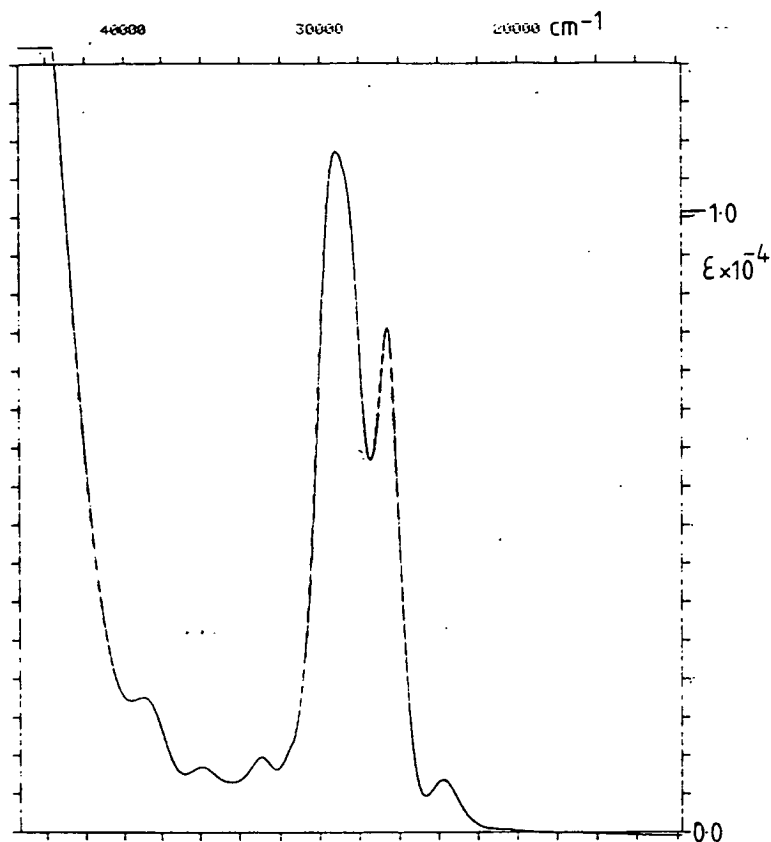


Figure 2.2 U.V./Vis. Absorption Spectrum of $[\text{OsCl}_6]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 230K.

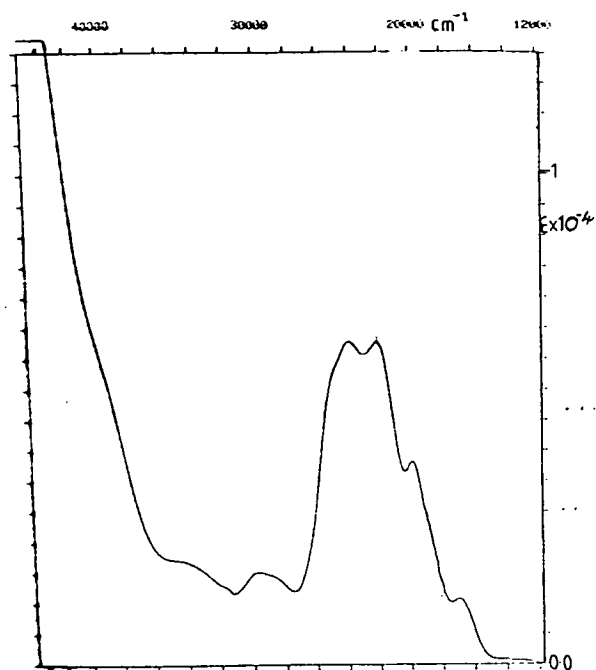


Figure 2.3 U.V./Vis. Absorption Spectrum of $[\text{OsCl}_6]^-$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 230K.

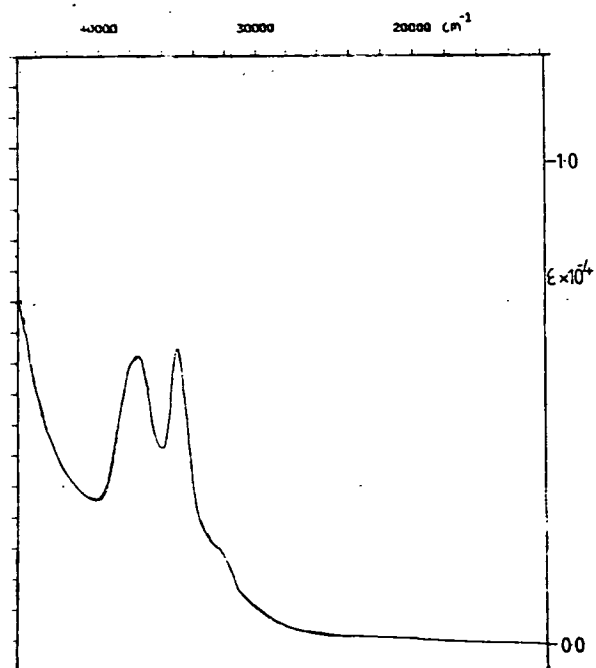


Figure 2.4 U.V./Vis. Absorption Spectrum of $[\text{OsCl}_6]^{3-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 230K.

2.2.2 The Reductive Electrochemistry and Spectroelectrochemistry of $[\text{OsCl}_6]^{2-}$ in pyridine/0.1M $[\text{TBA}][\text{BF}_4]$ at 290K.

A cathodic cyclic voltammogram of $[\text{TBA}]_2[\text{OsCl}_6]$ in pyridine/0.1M $[\text{TBA}][\text{BF}_4]$ at 290K (fig. 2.5) shows an irreversible reduction at -0.56V (process 1) followed by oxidation of a daughter product at -0.02V (process 2). A second scan includes reduction of the daughter product (process 3). A coulometric study shows both the irreversible reduction and the oxidation of the daughter product to involve $1e^-$.

A further coulometric experiment at -0.75V was executed with $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ doped with a tenfold excess of pyridine to $[\text{OsCl}_6]^{2-}$ which confirmed the $1e^-$ steps cited above. A stirred voltammogram of the final solution showed a 1:1 ratio of free chloride (oxidation wave at 1.2V) to daughter product. The daughter product is therefore suggested to be $[\text{OsCl}_5\text{py}]^{2-}$. Detailed mechanistic studies of the redox induced substitution of chloride by py is given in Chapter 4.

A spectroelectrochemical reduction of $[\text{TBA}]_2[\text{OsCl}_6]$ in pyridine/0.1M $[\text{TBA}][\text{BF}_4]$ was performed at the O.T.T.L.E. (fig. 2.6). The blood orange product displayed an intense band at $25\,000\text{ cm}^{-1}$ which is at lower energy than the L.M.C.T. bands of $[\text{OsCl}_6]^{2-}$ and $[\text{OsCl}_6]^{3-}$ and is thus interpreted as a M.L.C.T. transition ($\text{Os(III)}d\pi \rightarrow \text{py}\pi^*$).

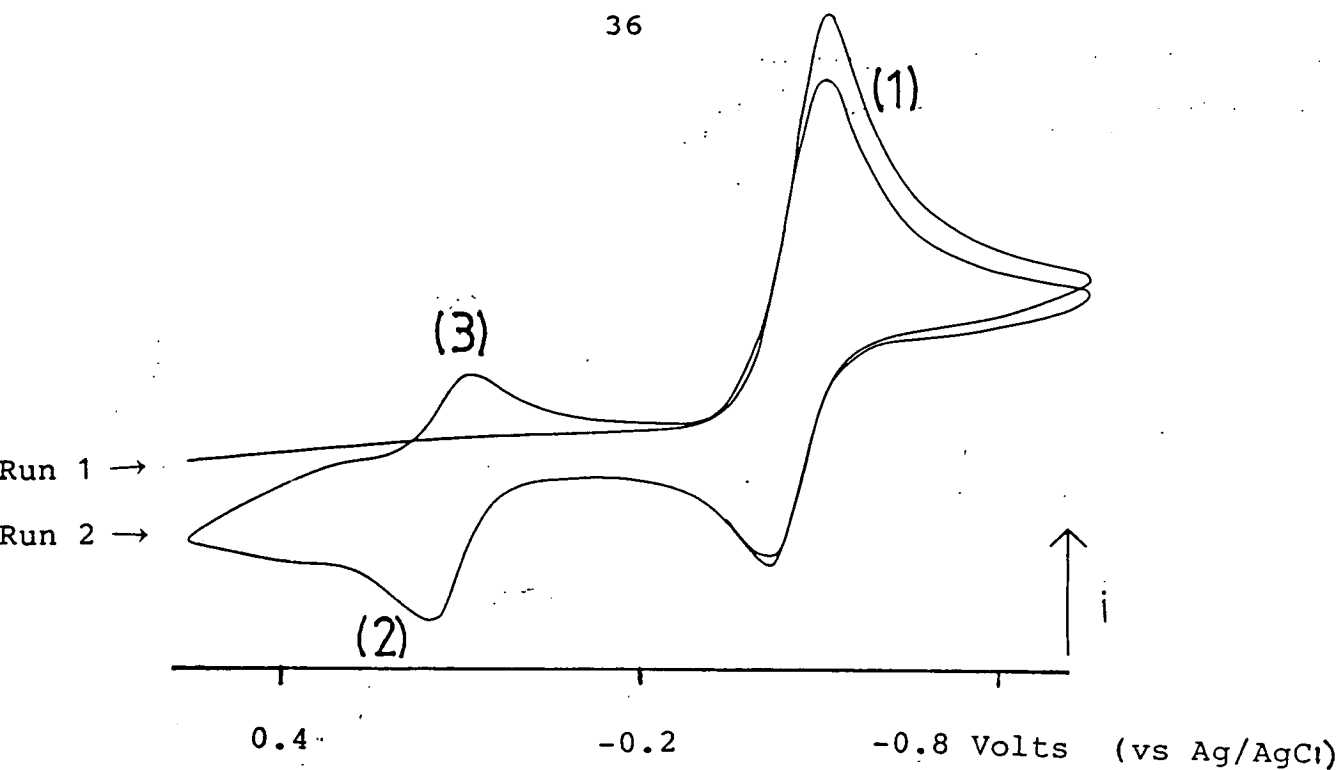


Figure 2.5 Cyclic Voltammogram of $[\text{OsCl}_6]^{2-}$ in pyridine/0.1M $[\text{TBA}][\text{BF}_4]$ at 290K.

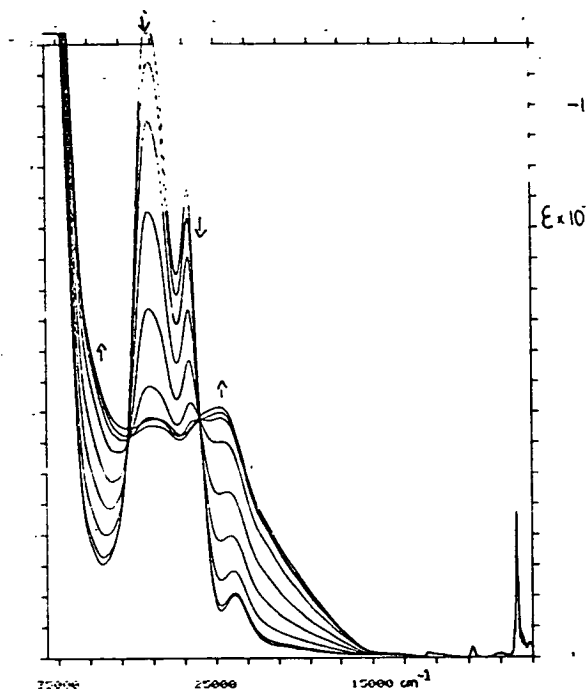


Figure 2.6 U.V./Vis. Absorption Spectra showing the spectroelectrochemical conversion of $[\text{OsCl}_6]^{2-}$ to $[\text{OsCl}_5\text{py}]^{2-}$ at -0.8V in pyridine/0.1M $[\text{TBA}][\text{BF}_4]$ at 290K.

2.2.3 Preparation, Electrochemistry and Spectroelectrochemistry of $[\text{TBA}][\text{OsCl}_5\text{py}]$.

The reductive substitution of $[\text{TBA}]_2[\text{OsCl}_6]$ by pyridine was effected in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ doped with 10 molar equivalents of pyridine, either by bulk electrolysis performed at -0.75V or by the addition of cobaltacene as chemical reducing agent. The resulting $[\text{OsCl}_5\text{py}]^{2-}$, which is not air stable, was oxidised either by bulk electrolysis at 0.2V or chemically using the oxidising agent $[\text{NO}][\text{BF}_4]$. The lemon yellow, air stable, product $[\text{TBA}][\text{OsCl}_5\text{py}]$ was isolated by thin layer chromatography.

Cyclic voltammetry and a.c.voltammetry of $[\text{TBA}][\text{OsCl}_5\text{py}]$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 290K (fig. 2.7) shows an electrochemically reversible reduction at -0.02V and a reversible oxidation at 1.83V . A stirred voltammogram shows waves of similar height for the reduction and oxidation, hence, since we know the reduction involves one electron, the oxidation must be a one electron step. Pyridine is a π - accepting ligand but is itself not easily reduced, hence both redox processes of $[\text{Os}(\text{IV})\text{Cl}_5\text{py}]^-$ are again considered to be metal-based.

The spectroelectrochemistry of $[\text{TBA}][\text{OsCl}_5\text{py}]$ was examined in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K at the O.T.T.L.E. The spectrum of $[\text{Os}(\text{IV})\text{Cl}_5\text{py}]^-$ shows good correspondence with a spectrum in the literature⁴,

obtained from a sample prepared by photolysis of $[\text{OsCl}_6]^{2-}$ in pyridine. The bands at lowest energy in the spectrum of $[\text{Os(IV)Cl}_5\text{py}]^-$, by comparison with $[\text{OsCl}_6]^{2-}$, must correspond to L.M.C.T. transitions ($\text{Cl}^- \pi \rightarrow \text{Os(IV)d}\pi$) (fig. 2.8). Upon reduction to $[\text{Os(III)Cl}_5\text{py}]^{2-}$ we would predict that the $\text{Cl}^- \rightarrow \text{Os}$ C.T. transitions should move to higher energy as in isoelectronic $[\text{OsCl}_6]^{3-}$. This is not what is observed experimentally (fig. 2.9) and hence the band at lowest energy at $25\,000\text{ cm}^{-1}$ is considered to be due to a M.L.C.T. ($\text{Os(III)d}\pi \rightarrow \text{py}\pi^*$) transition. Oxidation to $[\text{OsCl}_5\text{py}]$ results in a spectrum (fig. 2.10) that is similar in band position to that of $[\text{OsCl}_6]^-$ (fig. 2.3) and thus we assign the bands at low energy ($22\,900\text{ cm}^{-1}$) to L.M.C.T. transitions ($\text{Cl}^- \pi \rightarrow \text{Os(V)d}\pi$). The band shapes are dissimilar since the symmetry around the two osmium(V) centres, and hence the ground states, are different.

2.2.4 Initial Preparation and Electrochemistry of *cis*- and *trans*- $[\text{OsCl}_4\text{py}_2]^-$.

An a.c.voltammogram of $[\text{OsCl}_5\text{py}]^{2-}$ left in a solution of $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ doped with pyridine at 310K for 96 hours gave the electrochemical response shown in figure 2.11. Waves II and IV corresponded respectively to the $[\text{OsCl}_5\text{py}]^{2-}/[\text{OsCl}_5\text{py}]^-$ and $[\text{OsCl}_5\text{py}]^-/[\text{OsCl}_5\text{py}]$ couples discussed in section 2.2.3. Processes III and V are shifted about 0.5V positive relative to waves II and IV

Electrochemical response of $[\text{OsCl}_5\text{py}]^{1-}$
in $\text{CH}_2\text{Cl}_2 / 0.5\text{M} [\text{Bu}_4\text{N}]^+[\text{BF}_4]^-$ at 290K

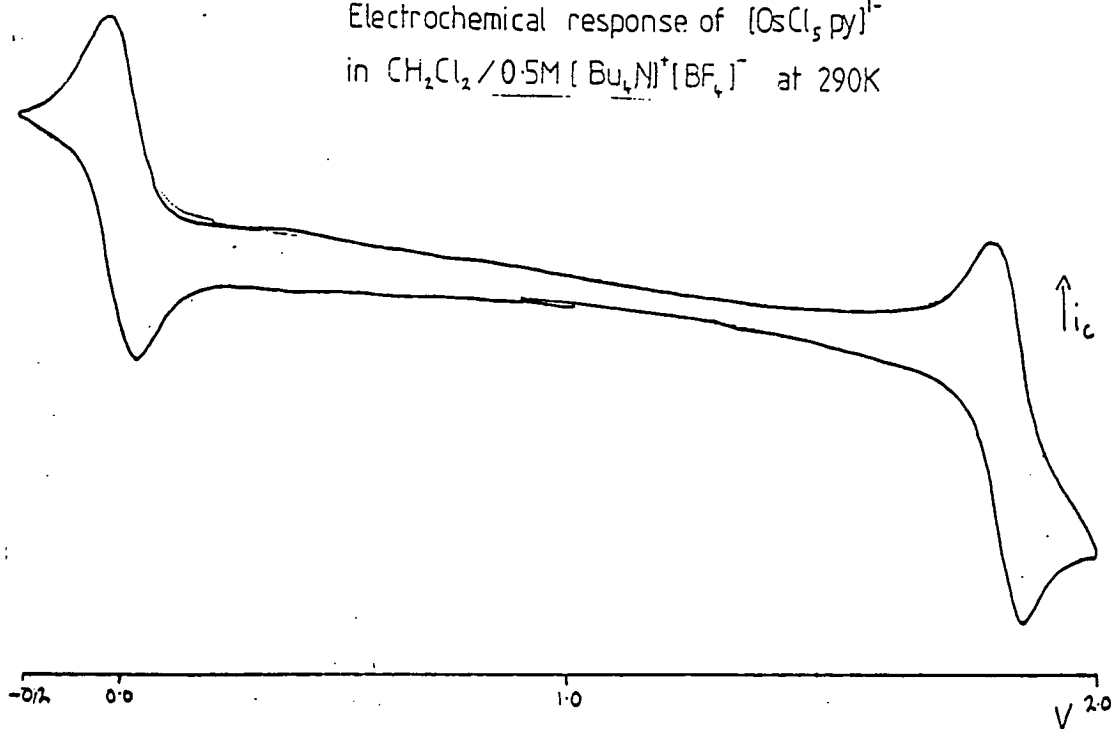


Figure 2.7 Cyclic Voltammogram of $[\text{OsCl}_5\text{py}]^{1-}$ in $\text{CH}_2\text{Cl}_2 / 0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 290K.

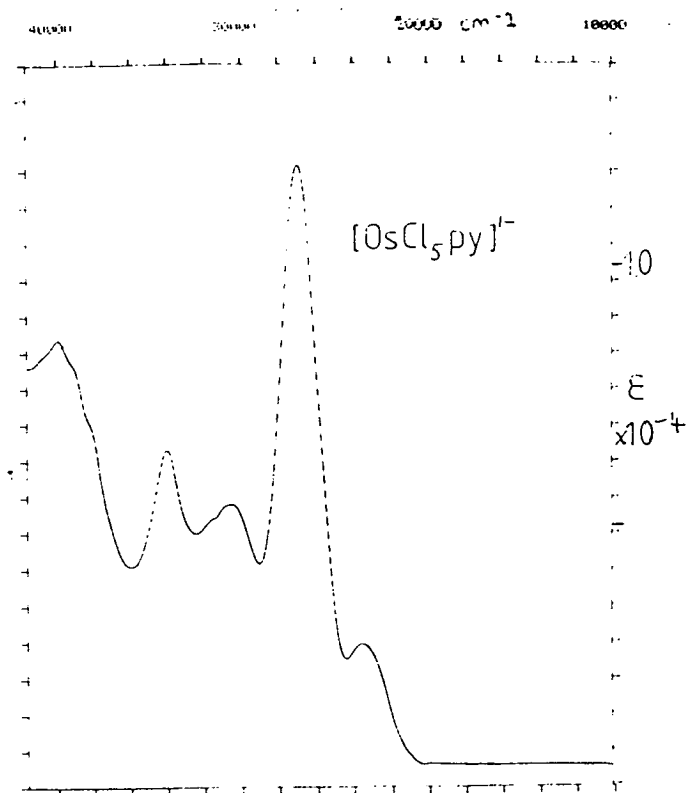


Figure 2.8 U.V./Vis. Absorption Spectrum of $[\text{OsCl}_5\text{py}]^{1-}$ in $\text{CH}_2\text{Cl}_2 / 0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 240K.

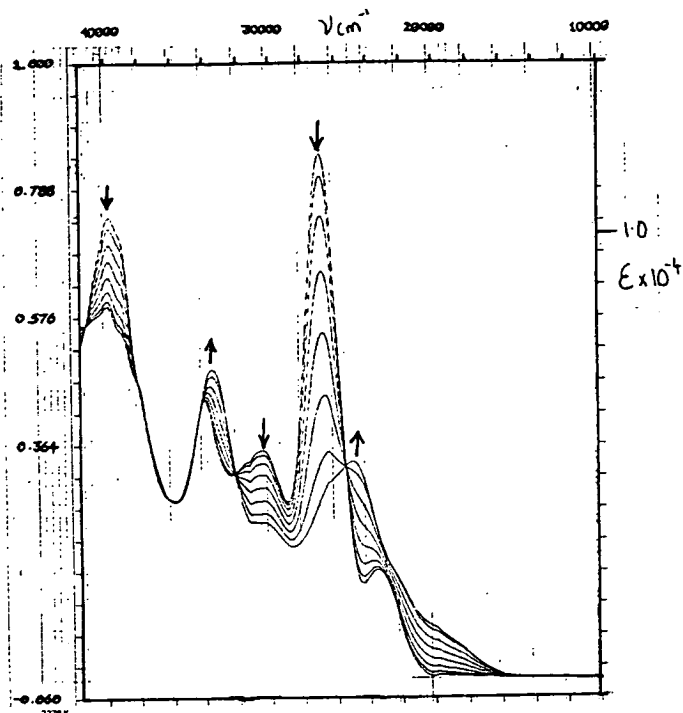


Figure 2.9 U.V./Vis. Absorption Spectra Showing the Spectroelectrochemical Conversion of $[\text{OsCl}_5\text{py}]^-$ to $[\text{OsCl}_5\text{py}]^{2-}$ at -0.2V in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 240K .

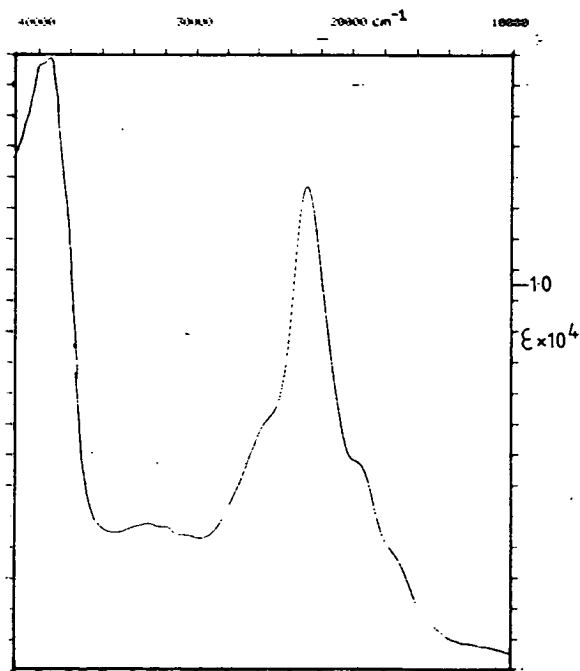


Figure 2.10 U.V./Vis. Absorption Spectrum of $[\text{OsCl}_5\text{py}]$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 240K .

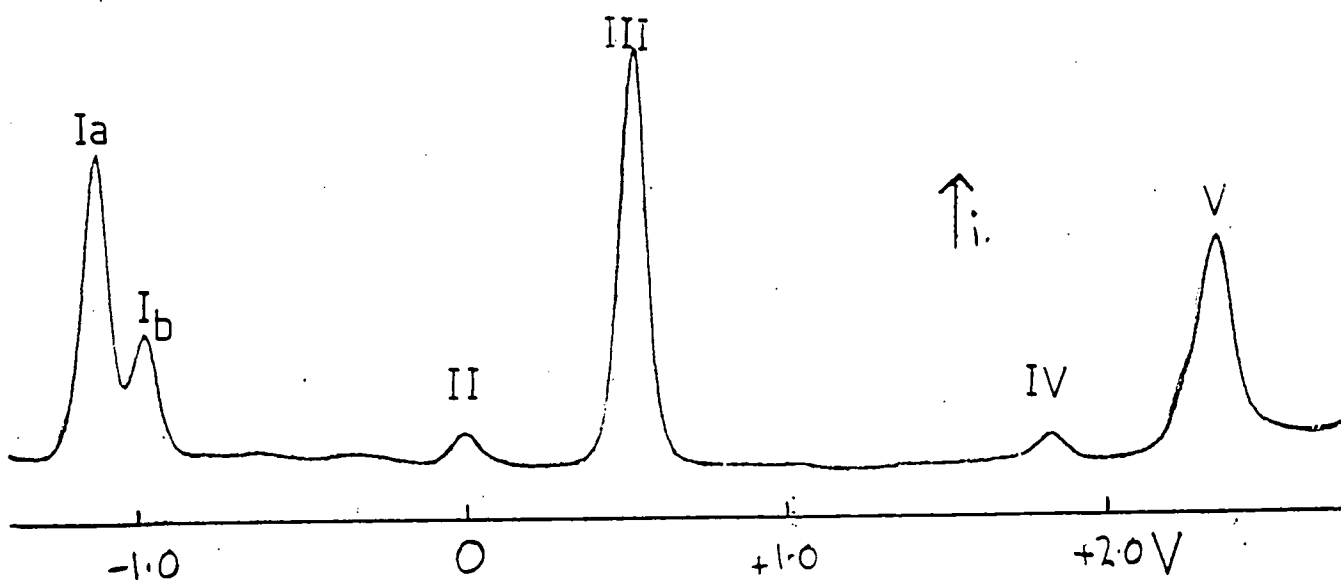


Figure 2.11 A.C. Voltammogram Showing a Solution of $[\text{OsCl}_5\text{py}]^{2-}$ in CH_2Cl_2 /doped with pyridine/0.5M $[\text{TBA}][\text{BF}_4]$ at 290K, after 96 hours at 310K.

which suggest substitution of a further chloride ligand by a pyridine. Hence these processes seem to relate to $[\text{OsCl}_4\text{py}_2]^- / [\text{OsCl}_4\text{py}_2]$ and $[\text{OsCl}_4\text{py}_2] / [\text{OsCl}_4\text{py}_2]^+$ couples respectively. A further process at -1.0V (wave I) is also observed but this wave unlike III and V is distinctly split into Ia and Ib.

Bulk electrolysis of the solution at 0.8V (oxidation of process III) in order to produce $[\text{OsCl}_4\text{py}_2]$, resulted in the precipitation of a fine orange solid. An a.c.voltammogram of the resulting solution showed that wave Ia had completely disappeared, III and V had decreased in height and were now of similar area to wave Ib which was almost unaltered. Since *trans*- $[\text{OsCl}_4\text{py}_2]$ is neutral and would be expected to exhibit no dipole moment process Ia was assigned as the *trans*- $[\text{OsCl}_4\text{py}_2]^{2-} / [\text{OsCl}_4\text{py}_2]^-$ couple whilst process Ib was attributed to the *cis*- $[\text{OsCl}_4\text{py}_2]^{2-} / [\text{OsCl}_4\text{py}_2]^-$ couple. As in the previously discussed sections all the redox processes are considered to be metal centred.

The infrared spectra of *trans*- $[\text{OsCl}_4\text{py}_2]$ and *cis*- $[\text{OsCl}_4\text{py}_2]$ (see 2.2.6) are shown in figure 2.12. The two regions of interest are the Os-Cl stretching region 300-400 cm^{-1} and the pyridine deformation range 1600-600 cm^{-1} (table 2.1). The former region shows two bands for *trans*- $[\text{OsCl}_4\text{py}_2]$ (point group D_{2h}) and four bands for the *cis*- $[\text{OsCl}_4\text{py}_2]$ (C_{2v}). These observations are in agreement with the number predicted by considering possible I.R.

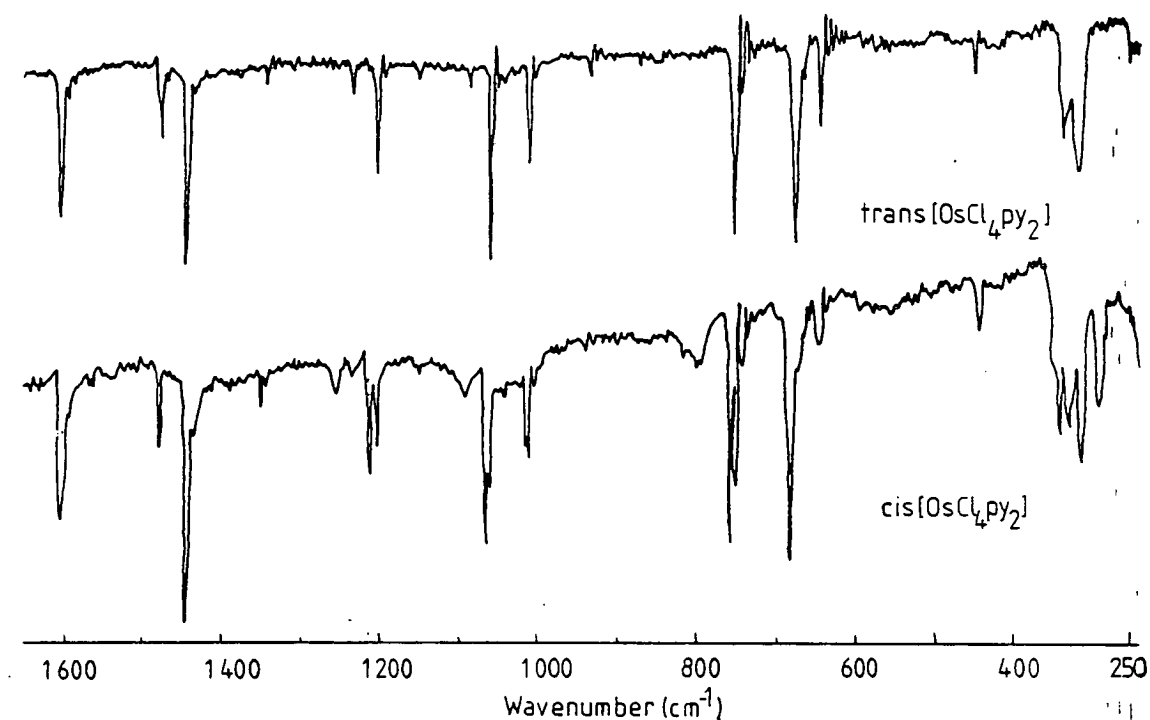


Figure 2.12 The Infra-Red Spectra of *trans*-[OsCl₄py₂] and *cis*-[OsCl₄py₂] measured in KBr discs.

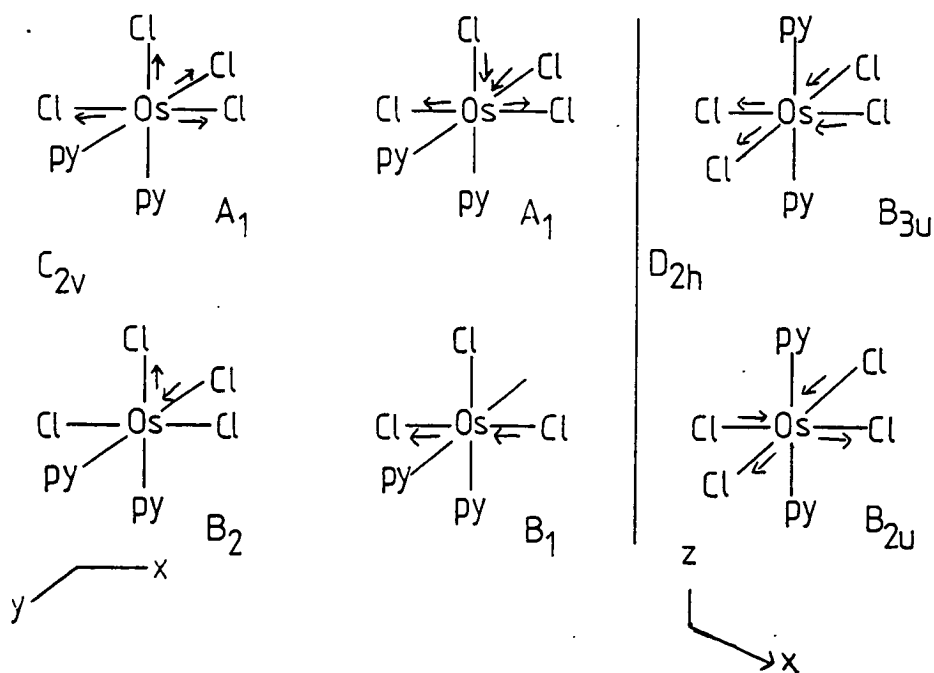


Figure 2.13 Os-Cl Stretching Modes for *trans*- and *cis*-[OsCl₄py₂]

active stretching modes for the two point groups above (fig. 2.13). The pyridine deformations are in similar positions for the two complexes but for the *cis*-[OsCl₄py₂] isomer each of the bands are split. This is a reflection of the lower symmetry in this molecule.

Table 2.1. Position of the bands in the I.R. spectra* of *cis*- and *trans*- [Os(IV)Cl₄py₂].

	<i>trans</i> -[Os(IV)Cl ₄ py ₂]	<i>cis</i> -[Os(IV)Cl ₄ py ₂]
	1 608	1 605 1 594(sh)
	1 480	1 480
	1 450	1 470 1 440(sh)
	1 208	1 213 1 207
Pyridine stretches + deformations	1 062	1 065 1 060
	1 012	1 015 1 010
	758	759 751
	680	682 674
Os-Cl stretches	342	342
	320	330
		318
		293

* Spectra obtained from KBr disks.

2.2.5 Preparation, X-Ray Single Crystal Structure, Electrochemistry and Spectroelectrochemistry of *trans*-[TPA][OsCl₄py₂].

An orange suspension of *trans*-[OsCl₄py₂] in a 1:1 CH₂Cl₂/methanol mixture was chemically reduced using a methanol/hydrazine mixture. Upon addition of [TPA][OH] solution red crystals of [TPA][OsCl₄py₂] accrued.

An X-ray single crystal structure determination confirmed the pyridine ligands were in the *trans* configuration. The structure shows an Os-N bond distance of 2.08Å and an Os-Cl bond length of 2.37Å. A list of bond lengths, bond angles and torsion angles is given in table 2.2. The pyridine rings are coplanar as illustrated in figure 2.14.

An a.c. voltammogram of a solution of these crystals in CH₂Cl₂/0.5M [TBA][BF₄] at 290K shows a reduction wave at -1.16V and two oxidation processes at 0.54V and 2.35V. Stirred voltammetry coupled to a coulometric analysis of the oxidation at 0.54V showed the processes to be one electron steps. Thus the reductive wave is formulated as an Os(III)/Os(II) process and the two oxidative steps as Os(III)/Os(IV) and Os(IV)/Os(V) processes.

A reductive electrogeneration of *trans*-[Os(III)Cl₄py₂]⁻ in CH₂Cl₂/0.5M[TBA][BF₄] at 230K was executed at the O.T.T.L.E. (fig.2.15). The electronic configuration of the Os centre in *trans*-[Os(II)Cl₄py₂]²⁻

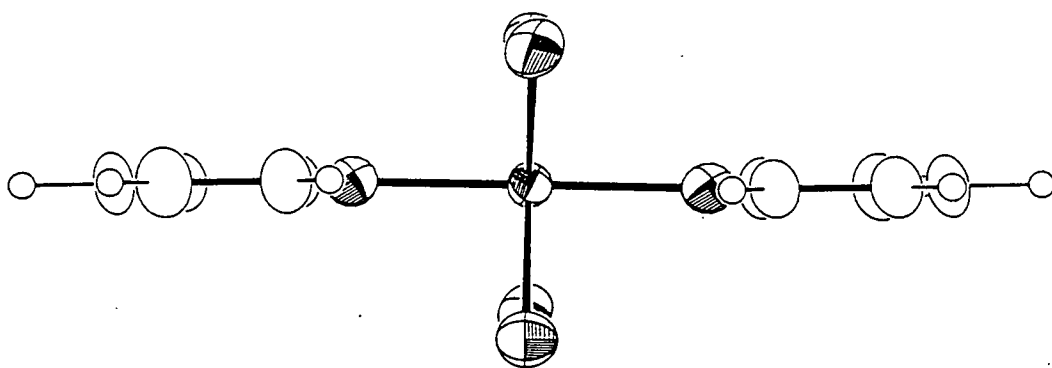
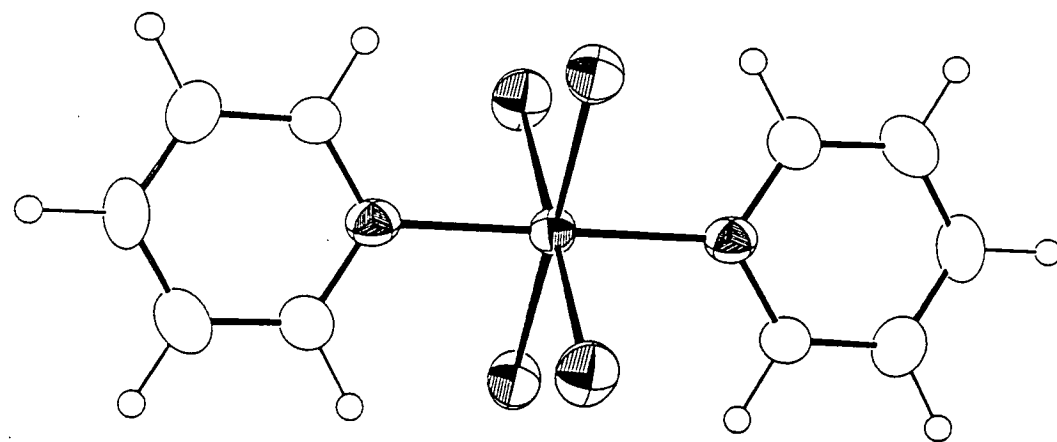


Figure 2.14 Views of the $\text{trans-[OsCl}_4\text{py}_2\text{]}^-$ Anion.

Table 2.2 Bond Lengths (Å), Angles and Torsion Angles (degrees) with Standard Deviations for the Anion *trans*-[OsCl₄py₂]⁻.

Os -Cl(1)	2.3691(21)	C(5) - C(6)	1.395(13)
Os -Cl(2)	2.3664(21)	N -C(11)	1.521(13)
Os - N(1)	2.077(6)	N -C(21)	1.521(11)
N(1) - C(2)	1.343(10)	C(11) -C(12)	1.512(16)
N(1) - C(6)	1.366(10)	C(12) -C(13)	1.515(17)
C(2) - C(3)	1.382(11)	C(21) -C(22)	1.517(13)
C(3) - C(4)	1.375(12)	C(22) -C(23)	1.522(15)
C(4) - C(5)	1.370(14)		

Cl(1) - Os -Cl(2)	89.86(7)	C(3) - C(4) - C(5)	119.2(9)
Cl(1) - Os - N(1)	90.75(17)	C(4) - C(5) - C(6)	119.0(9)
Cl(2) - Os - N(1)	90.33(18)	N(1) - C(6) - C(5)	122.3(8)
Os - N(1) - C(2)	122.3(5)	C(11) - N -C(21)	111.5(7)
Os - N(1) - C(6)	120.7(5)	N -C(11) -C(12)	115.7(9)
C(2) - N(1) - C(6)	117.1(6)	C(11) -C(12) -C(13)	110.4(9)
N(1) - C(2) - C(3)	123.0(7)	N -C(21) -C(22)	115.9(7)
C(2) - C(3) - C(4)	119.4(8)	C(21) -C(22) -C(23)	109.6(8)

Cl(1) - Os - N(1) - C(2)	139.2(6)	N(1) - C(2) - C(3) - C(4)	0.5(12)
Cl(1) - Os - N(1) - C(6)	-41.7(6)	C(2) - C(3) - C(4) - C(5)	0.4(13)
Cl(2) - Os - N(1) - C(2)	-130.9(6)	C(3) - C(4) - C(5) - C(6)	-0.5(14)
Cl(2) - Os - N(1) - C(6)	48.1(6)	C(4) - C(5) - C(6) - N(1)	-0.4(14)
Os - N(1) - C(2) - C(3)	177.8(6)	C(21) - N -C(11) -C(12)	-55.8(11)
C(6) - N(1) - C(2) - C(3)	-1.3(11)	C(11) - N -C(21) -C(22)	-53.6(10)
Os - N(1) - C(6) - C(5)	-177.9(7)	N -C(11) -C(12) -C(13)	175.1(9)
C(2) - N(1) - C(6) - C(5)	1.2(12)	N -C(21) -C(22) -C(23)	177.9(7)

is d^6 (t_{2g}^6) and hence we would expect its low energy spectrum to be dominated by M.L.C.T. transitions ($Osd\pi \rightarrow py\pi^*$). The full metal sub-shell precludes the observation of any low energy L.M.C.T. transitions ($Cl^- \pi \rightarrow Osd\pi$). We therefore assign the low energy transitions in the spectrum of purple $trans-[OsCl_4py_2]^{2-}$ to M.L.C.T. transitions which move to higher energy upon reoxidation to yellow $[OsCl_4py_2]^-$. The u.v./vis spectrum of $[OsCl_4py_2]^-$ reported by Walton et al.⁵, prepared by the reflux of $[TBA]_2[Os_2Cl_8]$ with pyridine in d.m.f., gave similar band positions to the spectrum reported above,

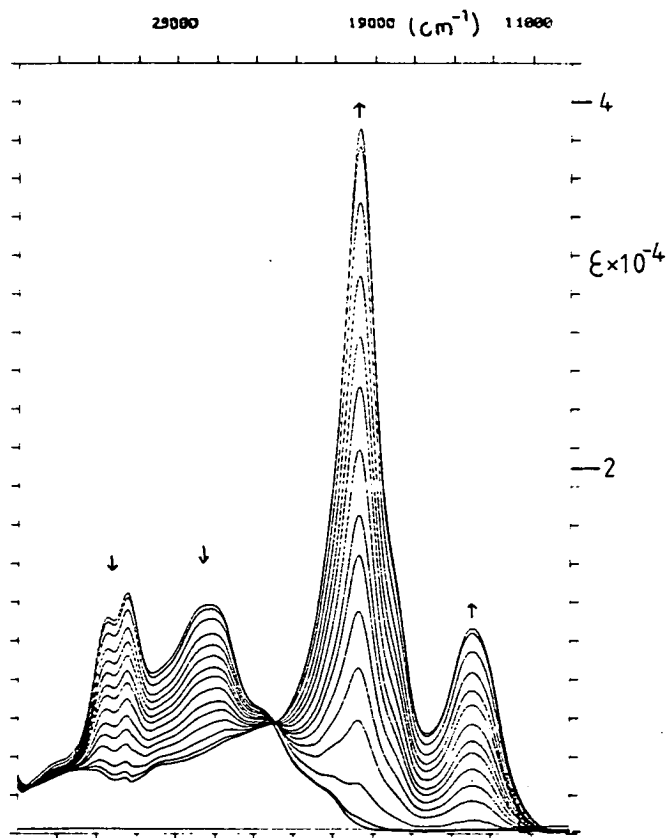


Figure 2.15 U.V./Vis. Absorption Spectra Showing the Spectroelectrochemical Conversion of $trans-[OsCl_4py_2]^-$ to $[OsCl_4py_2]^{2-}$ at $-1.4V$ in $CH_2Cl_2/0.5M [TBA][BF_4]$ at $230K$.

however voltammetric data on this sample does not agree with our data.

Our observations are at considerable variance with the preparation and characterisation of $[\text{Os(IV)Cl}_4\text{py}_2]$ recently reported in the literature.⁶ The solid reported is blue-purple, not orange as we observe, and is soluble in methylene chloride. Furthermore the assignment of the u.v./vis. spectrum of this blue-purple material invokes a $\text{py}\sigma \rightarrow \text{Os(IV)}d\pi$ transition to explain a band observed at $18\,830\text{cm}^{-1}$. With regards to the present work this appears most unlikely (see 2.3.2). The infra-red spectrum and electrochemical behaviour of the blue-purple material are also different to that which we have observed. The reported preparation involves a prolonged reflux of $\text{Na}_2[\text{OsCl}_6]$ in pyridine containing ethanol. We tentatively suggest that the blue-purple material contains osmium in a lower oxidation state, and is, perhaps, dimeric.

2.2.6 Preparation, X-Ray Single Crystal Structure Electrochemistry and Spectroelectrochemistry of *cis*- $[\text{OsCl}_4\text{py}_2]$.

$[\text{TBA}]_2[\text{OsCl}_6]$ was chemically reduced using cobaltacene in a solution of CH_2Cl_2 doped with pyridine. After four days at 310K the resulting solution was oxidised using $[\text{NO}][\text{BF}_4]$. All solid material, primarily *trans*- $[\text{OsCl}_4\text{py}_2]$, was removed and the resulting yellow solution purified by thin layer chromatography.

Recrystallisation from a CH_2Cl_2 /diethylether mixture yielded orange crystals of *cis*- $[\text{OsCl}_4\text{py}_2]$.

A single crystal structure determination confirmed the *cis* arrangement of the pyridine ligands and showed Os-N bond distances of 2.113(8) and 2.118(9)Å. Where chlorides were *trans* to pyridine, the Os-Cl bond lengths were 2.229(3)Å and 2.340(3)Å. The two mutually *trans*- Os-Cl bonds showed bond lengths of 2.309(3)Å as illustrated in figure 2.16. A list of bond lengths and angles is given in table 2.3. The planes of the two pyridine rings mutually describe an angle of 59.62 degrees. The differences in bond lengths between the *cis* and *trans* isomers may well be a reflection of the different oxidation states of the complexes.

A.c. voltammetry of *cis*- $[\text{OsCl}_4\text{py}_2]$ combined with stirred voltammetry in CH_2Cl_2 at 290K shows 2 reductions at -0.98V, 0.54V and an oxidation at 2.35V. A coulometric study on the wave at 0.54V confirmed the two former processes as $1e^-$ steps.

Spectroelectrochemical reductions of *cis*- $[\text{OsCl}_4\text{py}_2]$ were performed at the O.T.T.L.E. in a solution of $\text{CH}_2\text{Cl}_2/0.5\text{M}[\text{TBA}][\text{BF}_4]$ at 230K. L.M.C.T. bands ($\text{Cl}^- \pi \rightarrow \text{Os(IV)}d\pi$) observed in the spectrum of yellow $[\text{Os(IV)Cl}_4\text{py}_2]$ move to higher energy upon reduction to yellow $[\text{Os(III)Cl}_4\text{py}_2]^-$ (fig. 2.17). M.L.C.T. bands ($\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$) appear at low energy upon reduction to purple $[\text{OsCl}_4\text{py}_2]^{2-}$ (fig. 2.18).

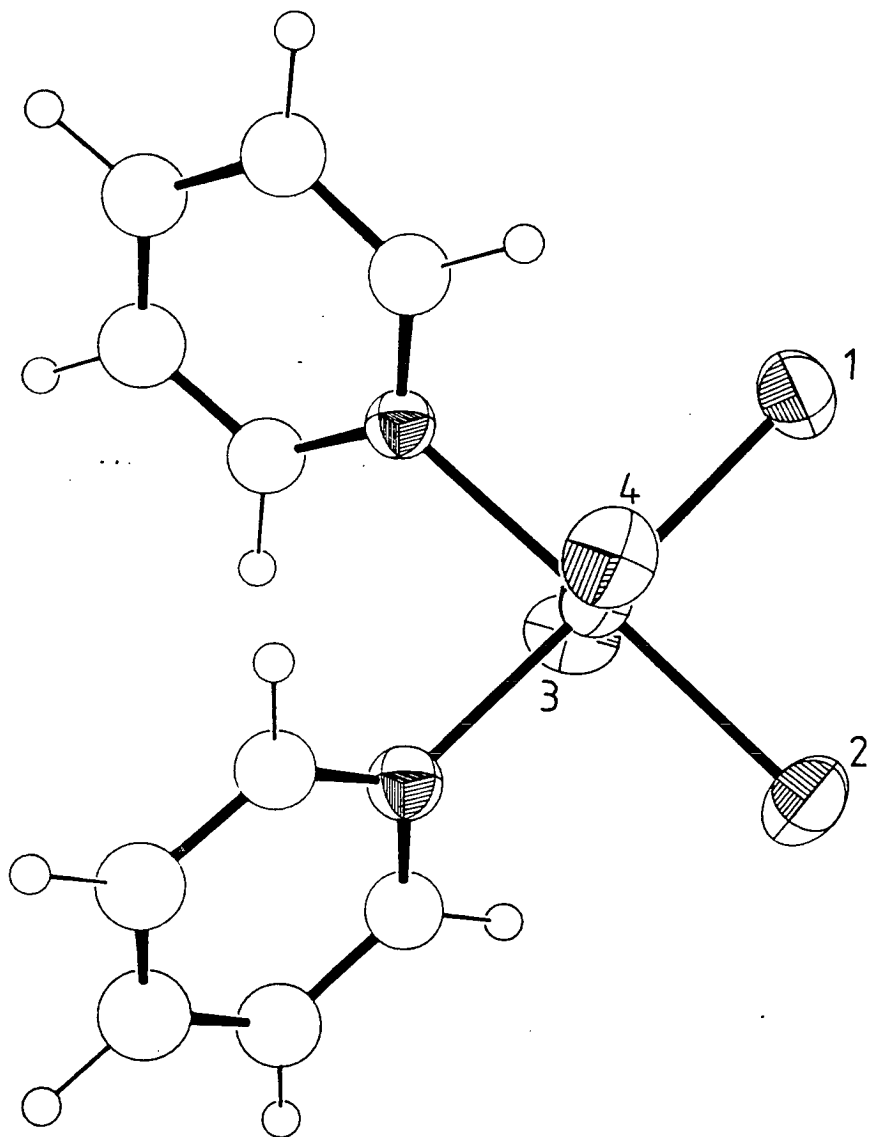


Figure 2.16 View of *cis*-[OsCl₄py₂].



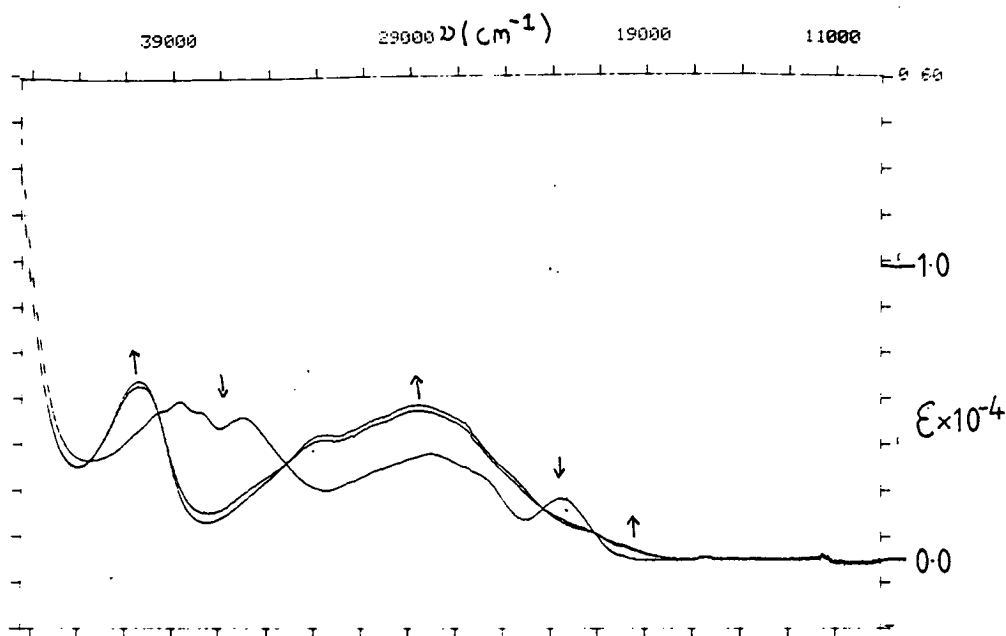


Figure 2.17 U.V./Vis. Absorption Spectra Showing the Spectroelectrochemical Conversion of *cis*-[OsCl₄py₂] to [OsCl₄py₂]⁻ at 0.4V in CH₂Cl₂/0.5M [TBA][BF₄] at 230K.

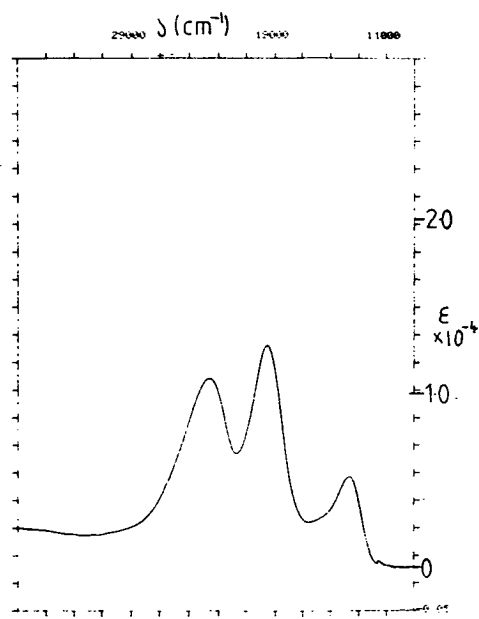


Figure 2.18 U.V./Vis. Absorption Spectrum of *cis*-[OsCl₄py₂]²⁻ in CH₂Cl₂/0.5M [TBA][BF₄] at 230K.

Table 2.3. Bond Lengths (Å) and Angles (degrees) with Standard Deviations for *cis*-[OsCl₄py₂].

Os	-Cl(1)	2.309(3)	C(53) -C(54)	1.344(18)
Os	-Cl(2)	2.309(3)	C(54) -C(55)	1.376(16)
Os	-Cl(3)	2.299(3)	C(55) -C(56)	1.373(16)
Os	-Cl(4)	2.340(3)	N(61) -C(62)	1.359(14)
Os	-N(51)	2.113(8)	N(61) -C(66)	1.338(14)
Os	-N(61)	2.118(9)	C(62) -C(63)	1.367(16)
N(51)	-C(52)	1.339(14)	C(63) -C(64)	1.369(18)
N(51)	-C(56)	1.349(14)	C(64) -C(65)	1.390(18)
C(52)	-C(53)	1.374(17)	C(65) -C(56)	1.375(16)

Cl(1)-Os-Cl(2)	177.45(11)	Os-N(51)-C(56)	121.9(7)
Cl(1)-Os-Cl(3)	91.34(11)	C(52)-N(51)-C(56)	117.4(9)
Cl(1)-Os-Cl(4)	90.59(10)	N(51)-C(52)-C(53)	120.8(10)
Cl(1)-Os-N(51)	88.94(23)	C(52)-C(53)-C(54)	122.0(12)
Cl(1)-Os-N(61)	89.38(25)	C(53)-C(54)-C(55)	118.0(11)
Cl(2)-Os-Cl(3)	91.10(11)	C(54)-C(55)-C(56)	118.6(11)
Cl(2)-Os-Cl(4)	90.06(10)	N(51)-C(56)-C(55)	123.2(10)
Cl(2)-Os-N(51)	88.60(23)	Os-N(61)-C(62)	121.2(7)
Cl(2)-Os-N(61)	89.87(25)	Os-N(61)-C(66)	120.1(7)
Cl(3)-Os-Cl(4)	92.13(11)	C(62)-N(61)-C(66)	118.5(9)
Cl(3)-Os-N(51)	178.35(24)	N(61)-C(62)-C(63)	121.7(10)
Cl(3)-Os-N(61)	90.02(25)	C(62)-C(63)-C(64)	119.9(11)
Cl(4)-Os-N(51)	89.49(23)	C(63)-C(64)-C(65)	118.6(12)
Cl(4)-Os-N(61)	177.85(25)	C(64)-C(65)-C(66)	119.1(11)
N(51)-Os-N(61)	88.4(3)	N(61)-C(66)-C(65)	122.1(10)
Os-N(51)-C(52)	120.7(7)		

2.2.7 Preparation, Electrochemistry and Spectroelectrochemistry of *mer*-[OsCl₃py₃].

[OsCl₃py₃] can be prepared either electrochemically, from a bulk electrolysis of [TBA]₂[OsCl₆] in pyridine at 290K at an applied potential of -1.8V with subsequent oxidation of the resulting [OsCl₃py₃]⁻ at -0.2V, or chemically, by heating K₂[OsCl₆] in a glycerol/pyridine mixture at 360K for 3 hours. A crystallographic study⁷ has shown that *mer*-[OsCl₃py₃] is the isomeric species present.

An a.c.voltammogram of *mer*-[OsCl₃py₃] in CH₂Cl₂/0.5M [TBA][BF₄] at 290K (fig. 2.19) shows three waves I, II and III. A coulometric study shows that steps I and II involve one electron reduction and oxidation processes respectively.

A spectroelectrochemical study in CH₂Cl₂/0.5M [TBA][BF₄] at 240K at the O.T.T.L.E. was undertaken. The low energy bands in the spectrum of deep green [Os(II)Cl₃py₃]⁻ must be due to M.L.C.T. (Os(II)d π $\rightarrow$ py π^*) since the metal has a low spin d⁶ electronic configuration (fig. 2.20). The spectrum of pale yellow [Os(IV)Cl₃py₃]⁺ (fig. 2.21) shows L.M.C.T. (Cl⁻ π $\rightarrow$ Os(IV)d π) which are assigned by comparison with previously assigned Os(IV) species (sections 2.2-2.6). The electronic absorption spectrum of yellow *mer*-[Os(III)Cl₃py₃] (fig.2.22) shows one asymmetric band at 31 600cm⁻¹. A previous note of

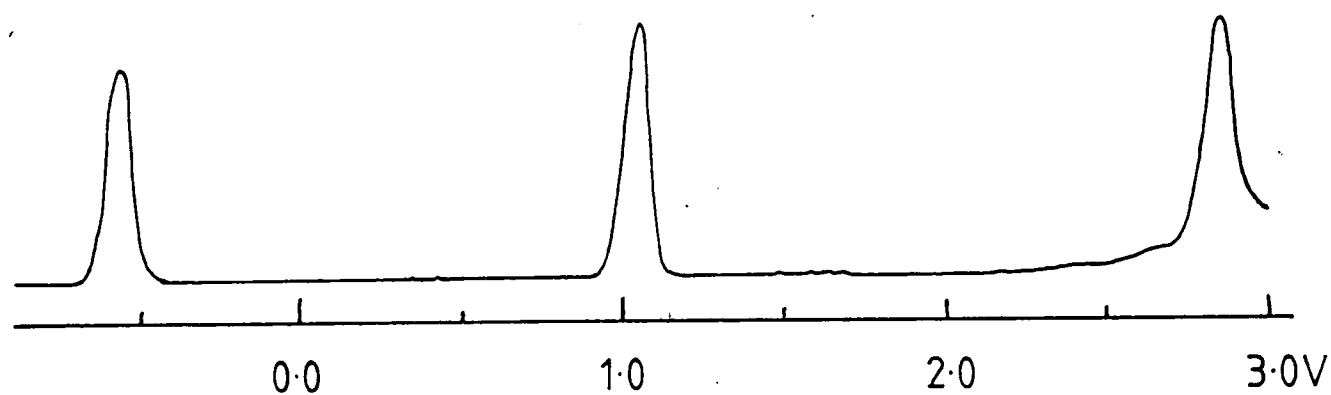


Figure 2.19 A.C.Voltammogram of *mer*-[OsCl₃py₃] in CH₂Cl₂/0.5M [TBA][BF₄] at 290K.

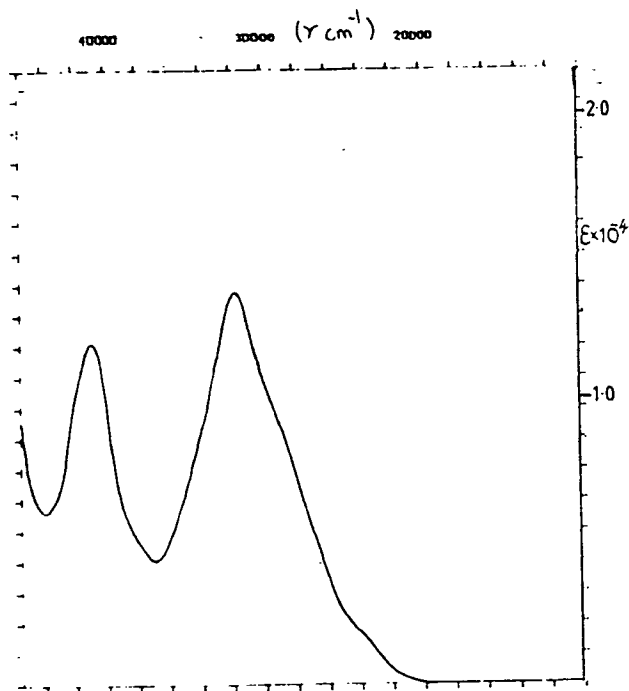


Figure 2.20 U.V./Vis. Absorption Spectrum of *mer*-[OsCl₃py₃]⁻ in CH₂Cl₂/0.5M [TBA][BF₄] at 240K.

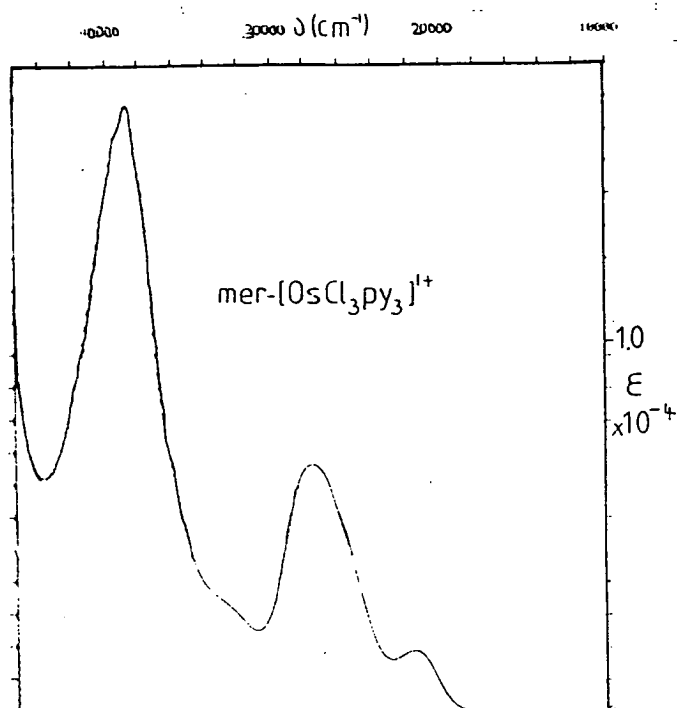


Figure 2.21 U.V./Vis. Absorption Spectrum of $\text{mer-}[\text{OsCl}_3\text{py}_3]^+$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K.

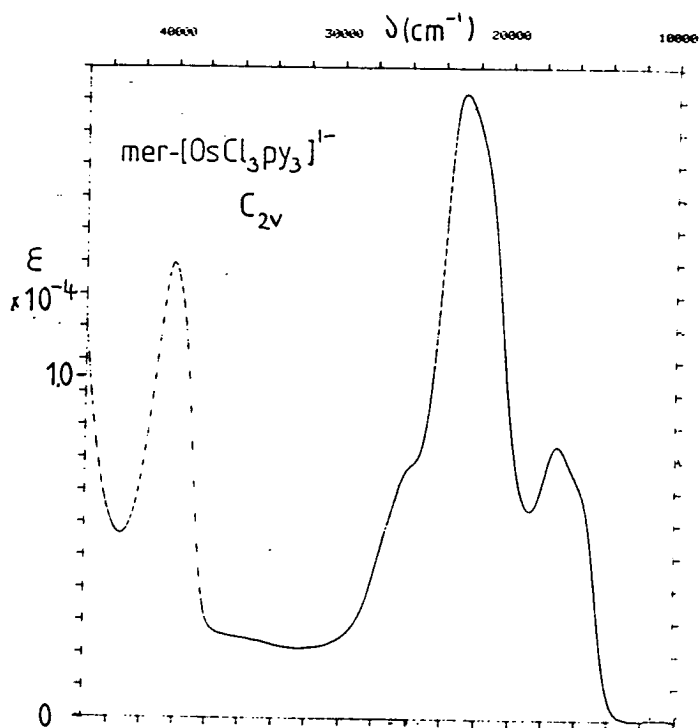


Figure 2.22 U.V./Vis. Absorption Spectrum of $\text{mer-}[\text{OsCl}_3\text{py}_3]$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K.

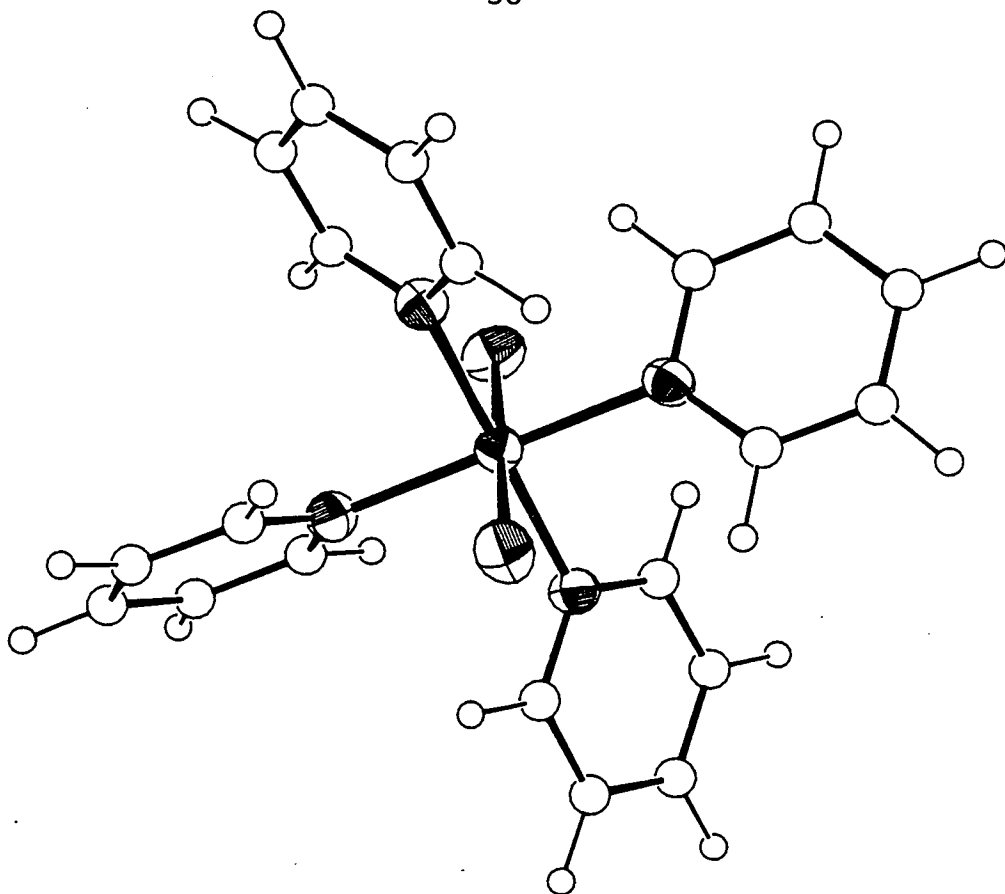
this species has been reported.⁸ By comparison with the spectra of $[\text{OsBr}_3\text{py}_3]$ and $[\text{OsI}_3\text{py}_3]$ *vide infra* this band can be assigned as a superposition of both L.M.C.T. ($\text{Cl}^- \pi \rightarrow \text{Os(III)}d\pi$) and M.L.C.T. ($\text{Os(III)}d\pi \rightarrow \text{py}\pi^*$).

The spectrum of *mer*- $[\text{OsCl}_3\text{py}_3]\text{Cl}$, prepared from the oxidation of *mer*- $[\text{OsI}_3\text{py}_3]$ in CH_2Cl_2 by chlorine, is reported in the literature.⁹ The absorption bands are at lower energy and have much lower extinction coefficient than the bands we have observed. When we generated this species spectroelectrochemically as described above, it was noted that this species was subject to rapid decomposition at temperatures above 270K.

2.2.8. Preparation, X-Ray Single Crystal Structure, Electrochemistry and Spectroelectrochemistry of *trans*- $[\text{OsCl}_2\text{py}_4]$.

Trans- $[\text{OsCl}_2\text{py}_4]$ was prepared by heating a solution of $[\text{OsCl}_3\text{py}_3]^-$ in py at 370K for 3 hours. $[\text{OsCl}_3\text{py}_3]^-$ was prepared from the reduction of *mer*- $[\text{OsCl}_3\text{py}_3]$ either by a bulk electrolysis or chemically using $\text{Na}[\text{BH}_4]$ as reductant. The chemical preparation is modified from a preparation devised by Buckingham et al.¹⁰ Purple crystals accrued from a methylene chloride/ methanol/ hydrazine hydrate solution of *trans*- $[\text{OsCl}_2\text{py}_4]$.

A single crystal structure determination of *trans*- $[\text{OsCl}_2\text{py}_4]$ shows Os-N bond distances of 2.07Å and

Figure 2.23 View of *trans*-[OsCl₂py₄].Table 2.4 Bond Lengths (Å), Angles and Torsion Angles (degrees) with Standard Deviations for *trans*-[OsCl₂py₄]

Os - Cl	2.3992(17)	C(2) - C(3)	1.402(13)
Os - N(1)	2.071(6)	C(3) - C(4)	1.382(14)
N(1) - C(2)	1.362(11)	C(4) - C(5)	1.368(14)
N(1) - C(6)	1.357(10)	C(5) - C(6)	1.368(12)

Cl - Os - N(1)	90.07(19)	C(2) - N(1) - C(6)	117.7(7)
Cl - Os - Cl(')	179.91(6)	N(1) - C(2) - C(3)	121.0(8)
Cl - Os - N(1'')	89.99(19)	C(2) - C(3) - C(4)	120.2(9)
N(1) - Os - N(1'')	179.9(3)	C(3) - C(4) - C(5)	117.5(9)
N(1) - Os - N(1')	90.2(3)	C(4) - C(5) - C(6)	121.1(9)
Os - N(1) - C(2)	120.5(5)	N(1) - C(6) - C(5)	122.3(8)
Os - N(1) - C(6)	121.9(5)		

C(6) - N(1) - C(2) - C(3)	0.1(12)	C(2) - C(3) - C(4) - C(5)	1.2(14)
C(2) - N(1) - C(6) - C(5)	-1.3(12)	C(3) - C(4) - C(5) - C(6)	-2.4(14)
N(1) - C(2) - C(3) - C(4)	-0.1(14)	C(4) - C(5) - C(6) - N(1)	2.5(14)

Os-Cl bond lengths of 2.40Å. The pyridine rings are all tilted out of the N₄ plane by some 48.02 degrees as illustrated in fig. 2.23. The angles mutually described by the pyridine planes are 64.32, 83.96 and 62.51 degrees. A list of bond lengths, angles and torsion angles can be found in table 2.4.

The average Fe-N and Fe-Cl bond distances in the analogous *trans*-[FeCl₂py₄] complex¹¹, are 2.23 and 2.43Å respectively. These bond lengths are longer than those found in the osmium analogue. We attribute this difference to the different spin configurations adopted by the complexes. Since [FeCl₂py₄] has a high-spin d⁶ configuration it has less electron density available for back donation into the pyridine π -accepting orbitals than the low spin osmium species, hence the Fe-N bond length is greater. This results in less steric interaction between pyridine ligands, *trans* pyridine ligands are coplanar, since the pyridine rings are able to assume electronically preferred positions.

A cyclic voltammogram of *trans*-[OsCl₂py₄] in CH₂Cl₂/0.5M [TBA][BF₄] at 290K shows two reversible one electron oxidations at -0.07V and 1.53V (as confirmed by stirred voltammetry and coulometry).

A sample of *trans*-[Os(II)Cl₂py₄] in CH₂Cl₂/0.5M [TBA][BF₄] at 240K was examined at the O.T.T.L.E. The bands at low energy in the spectrum of deep red *trans*-[OsCl₂py₄] (fig. 2.24) are assigned as M.L.C.T.

transitions ($\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$). Upon oxidation to yellow $[\text{Os(III)}\text{Cl}_2\text{py}_4]^+$ these bands move to higher energy (fig. 2.25). Further oxidation to yellow $[\text{Os(IV)}\text{Cl}_2\text{py}_4]^{2+}$ is accompanied by the appearance of bands at lower energy (fig. 2.26) which can be assigned as L.M.C.T. transitions ($\text{Cl}^-\pi \rightarrow \text{Os(IV)}d\pi$).

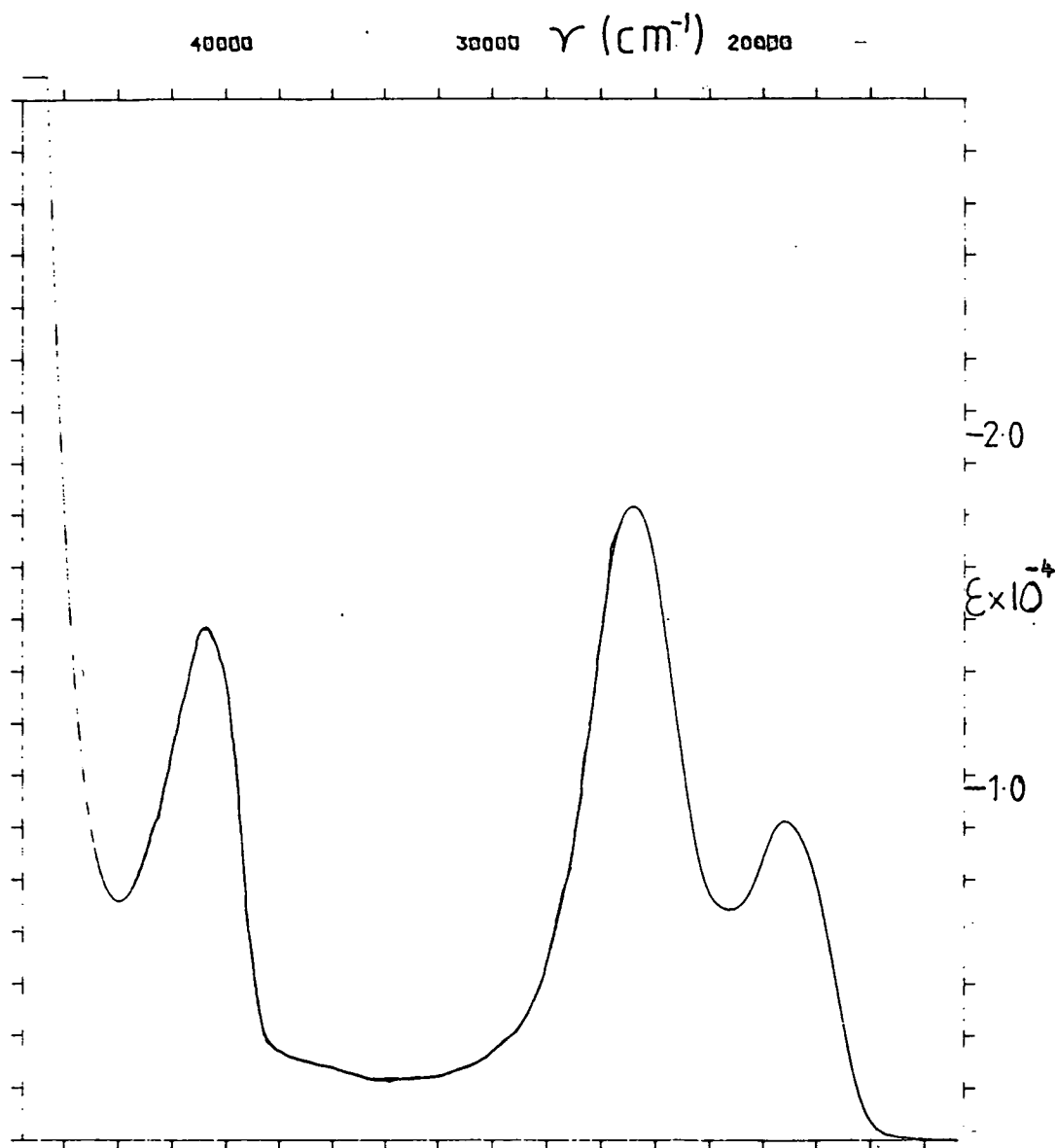


Figure 2.24 U.V./Vis. Absorption Spectrum of $\text{trans-[OsCl}_2\text{py}_4]$ in $\text{CH}_2\text{Cl}_2/0.5\text{M [TBA][BF}_4\text{]}$ at 240K.

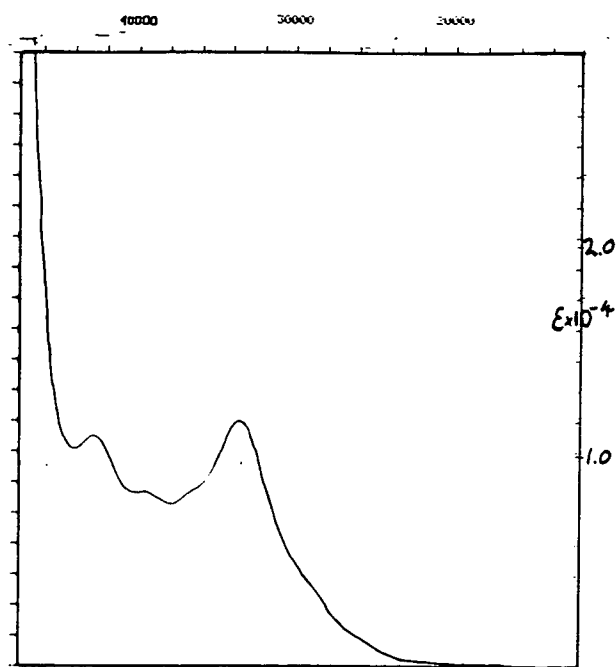


Figure 2.25 U.V./Vis. Absorption Spectrum of $\text{trans-}[\text{OsCl}_2\text{py}_4]^+$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K.

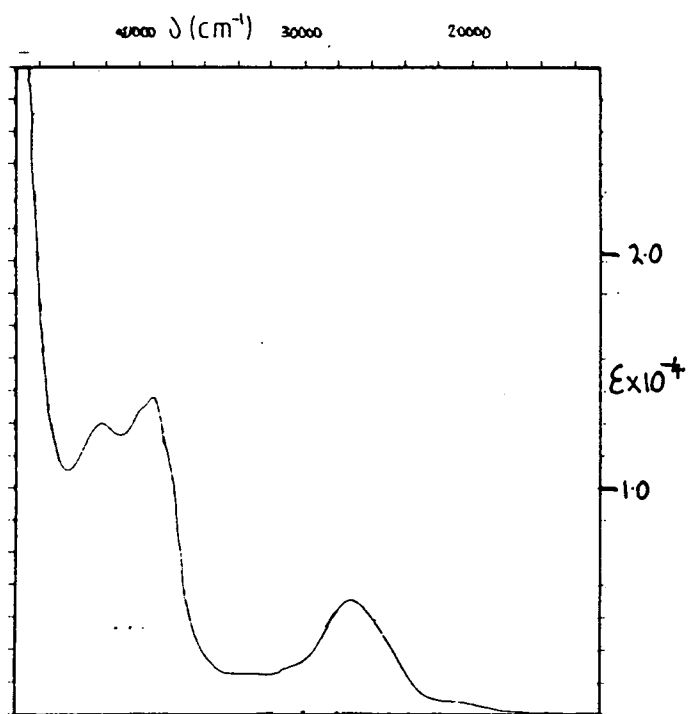


Figure 2.26 U.V./Vis. Absorption Spectrum of $\text{trans-}[\text{OsCl}_2\text{py}_4]^{2+}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K.

2.2.9 Preparation, Electrochemistry and Spectroelectrochemistry of $[\text{OsClpy}_5][\text{PFTPb}]$.

$[\text{OsClpy}_5][\text{PFTPb}]$ was prepared as follows. A solution of $\text{K}_2[\text{OsCl}_6]$ in a 5:1 ethanediol/pyridine mixture was heated at 450K for 3 hours. The solution was poured onto a solution of hydrazine hydrate and filtered. The filtrate was treated with an aqueous solution of lithium pentafluorotetraphenylborate, $\text{Li}[\text{PFTPb}]$. The resulting bright red/orange precipitate was purified using thin layer chromatography and recrystallised from a methylene chloride/methanol/hydrazine hydrate mixture.

Cyclic voltammetry and a.c. voltammetry of a solution of $[\text{OsClpy}_5][\text{PFTPb}]$ in 0.5M $[\text{TBA}][\text{BF}_4]$ CH_2Cl_2 revealed two redox steps at +0.49 and +2.02V. Both processes were shown to be oxidations by stirred voltammetry. The former oxidative process was confirmed as a one electron step by a coulometric study.

Spectroelectrochemical oxidations of $[\text{OsClpy}_5]^+$ in CH_2Cl_2 0.5M $[\text{TBA}][\text{BF}_4]$ at 200K were performed at the O.T.T.L.E. The bands at low energy in the spectrum of orange $[\text{OsClpy}_5]^+$ (fig. 2.27) were assigned as $\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$ C.T. transitions on the basis that the metal has a low spin d^6 configuration. Upon oxidation to $[\text{Os(III)Clpy}_5]^{2+}$ these M.L.C.T transition bands move to higher energy and are seen in the spectrum (fig. 2.28) superposed with $\text{Cl}^-\pi \rightarrow \text{Os(III)}d\pi$ C.T. transitions (these

assignments are made by a comparison with the Os(III) species already studied in this chapter). The spectrum of $[\text{Os(IV)Clpy}_5]^{3+}$ exhibits low energy $\text{Cl}^- \pi \rightarrow \text{Os(IV)d}\pi$ C.T. transitions (fig. 2.29) assigned thus on the basis of a comparison with the Os(IV) species previously discussed.

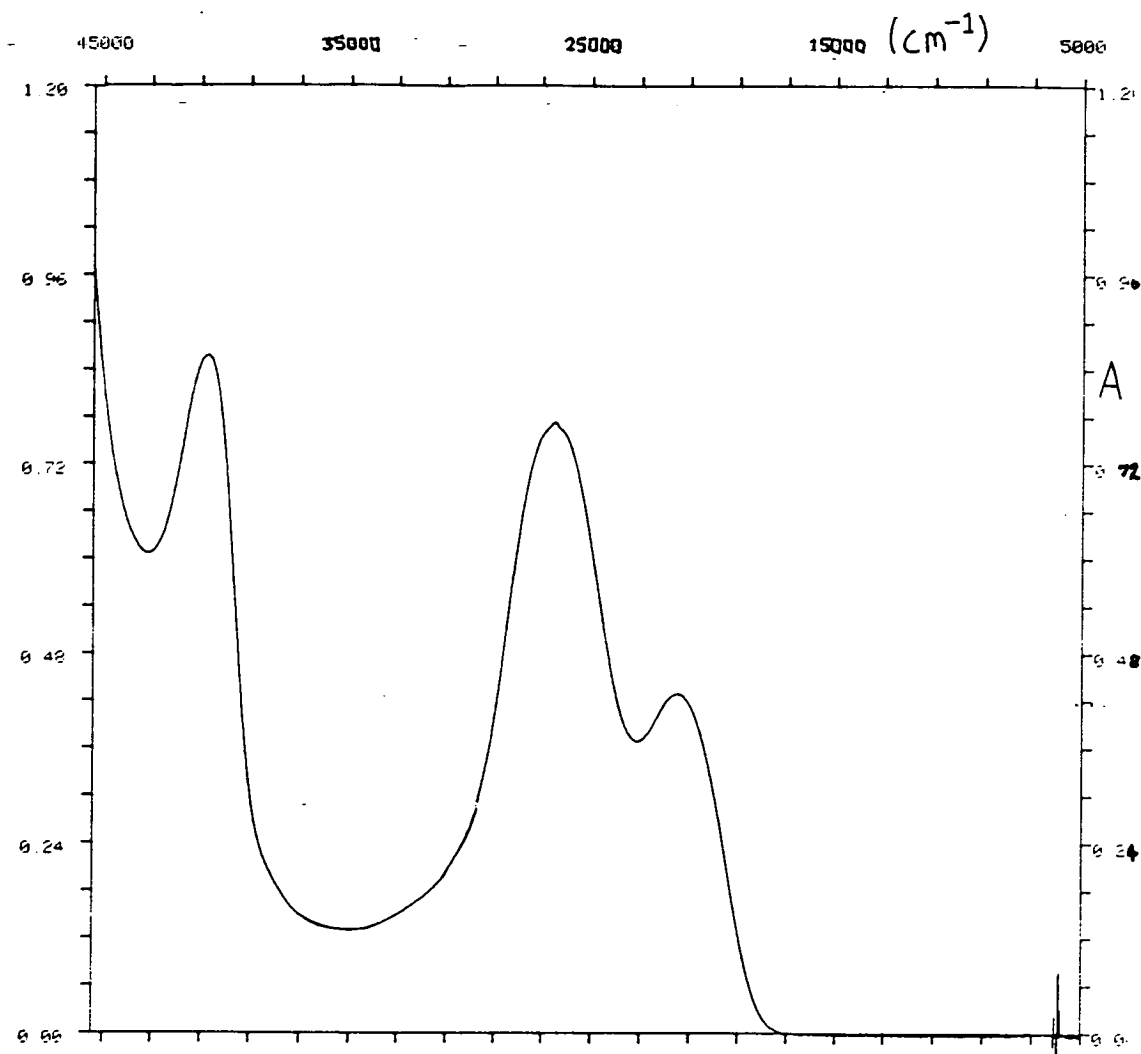


Figure 2.27 U.V./Vis. Absorption Spectrum of $[\text{OsClpy}_5]^{3+}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 200K.

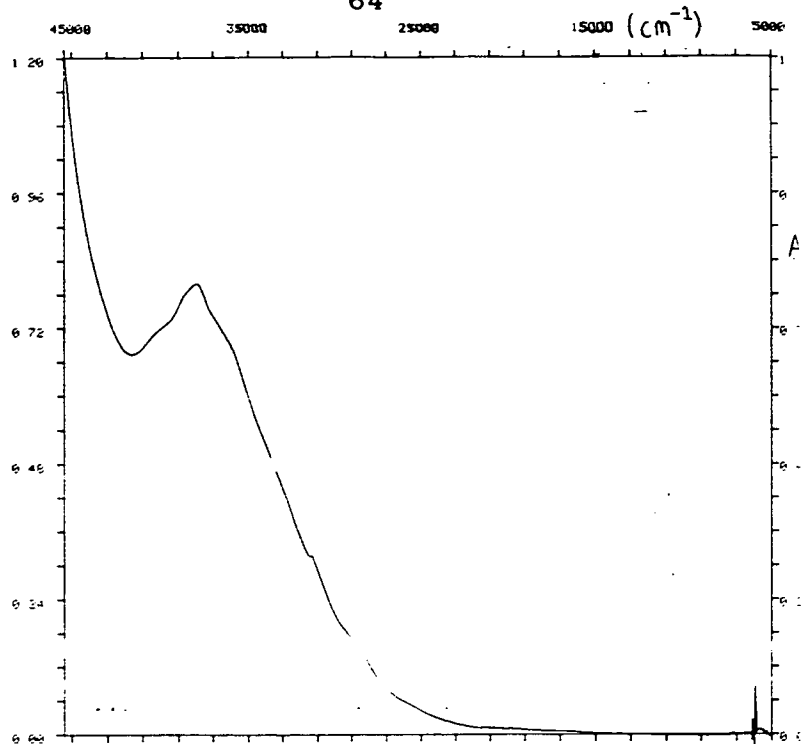


Figure 2.28 U.V./Vis. Absorption Spectrum of $[\text{OsCl}_2\text{py}_4]^{2+}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 200K.

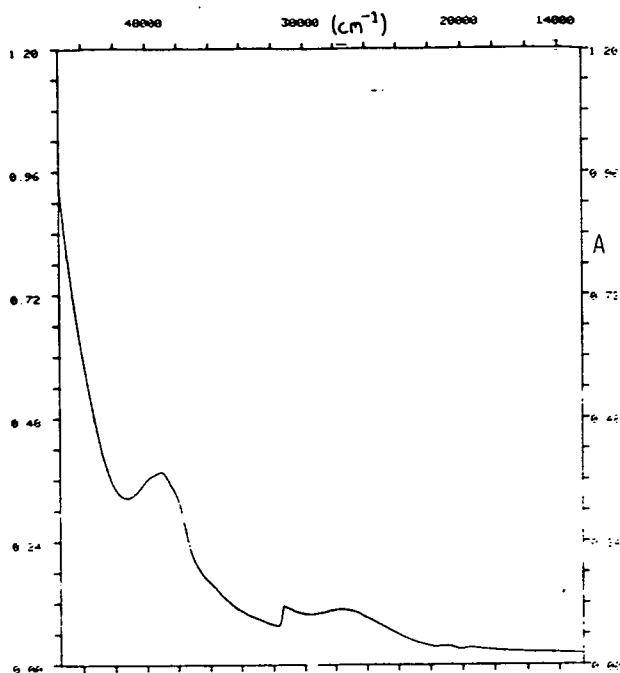


Figure 2.29 U.V./Vis. Absorption Spectrum of $[\text{OsClpy}_5]^{3+}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 200K.

2.2.10 Preparation, X-Ray Single Crystal Structure, Electrochemistry and Spectroelectrochemistry of $[\text{OsPy}_6][\text{BF}_4]_2$.

$[\text{NH}_4]_2[\text{OsCl}_6]$ was refluxed in pyridine in the presence of zinc dust and sodium tetrafluoroborate for 150 hours and then filtered. Sodium chloride and zinc chloride were separated from the solid material produced by washing with small volumes of water. Slow evaporation of a nitromethane solution of the material yielded small yellow crystals.

A crystal structure determination of $[\text{OsPy}_6][\text{BF}_4]_2$ shows an average Os-N bond distance of 2.11Å. A list of bond lengths and angles is shown in table 2.5. With respect to the table the pyridine rings are all tilted out of the plane described by N_B , N_C , N_D and N_E by 87.27, 46.69, 35.16, 31.32, 32.08 and 89.06 degrees. Table 2.6 shows the angles the pyridine rings mutually describe. The structure is illustrated in fig. 2.30.

The structure of $[\text{OsPy}_6]^{2+}$ can be compared to the structures of $[\text{Rupy}_6]^{2+}$ and $[\text{Fepy}_6]^{2+}$ 12,13. $[\text{OsPy}_6]^{2+}$ is isostructural with $[\text{Rupy}_6]^{2+}$. The average Ru-N bond length is 2.12Å compared to 2.11Å for the Os-N bonds. The average Fe-N bond length, 2.26Å, is much longer. This difference is due to the iron species adopting a high spin electronic configuration as discussed in section 2.2.8 Pyridines trans to one another in the $[\text{Fepy}_6]^{2+}$ structure

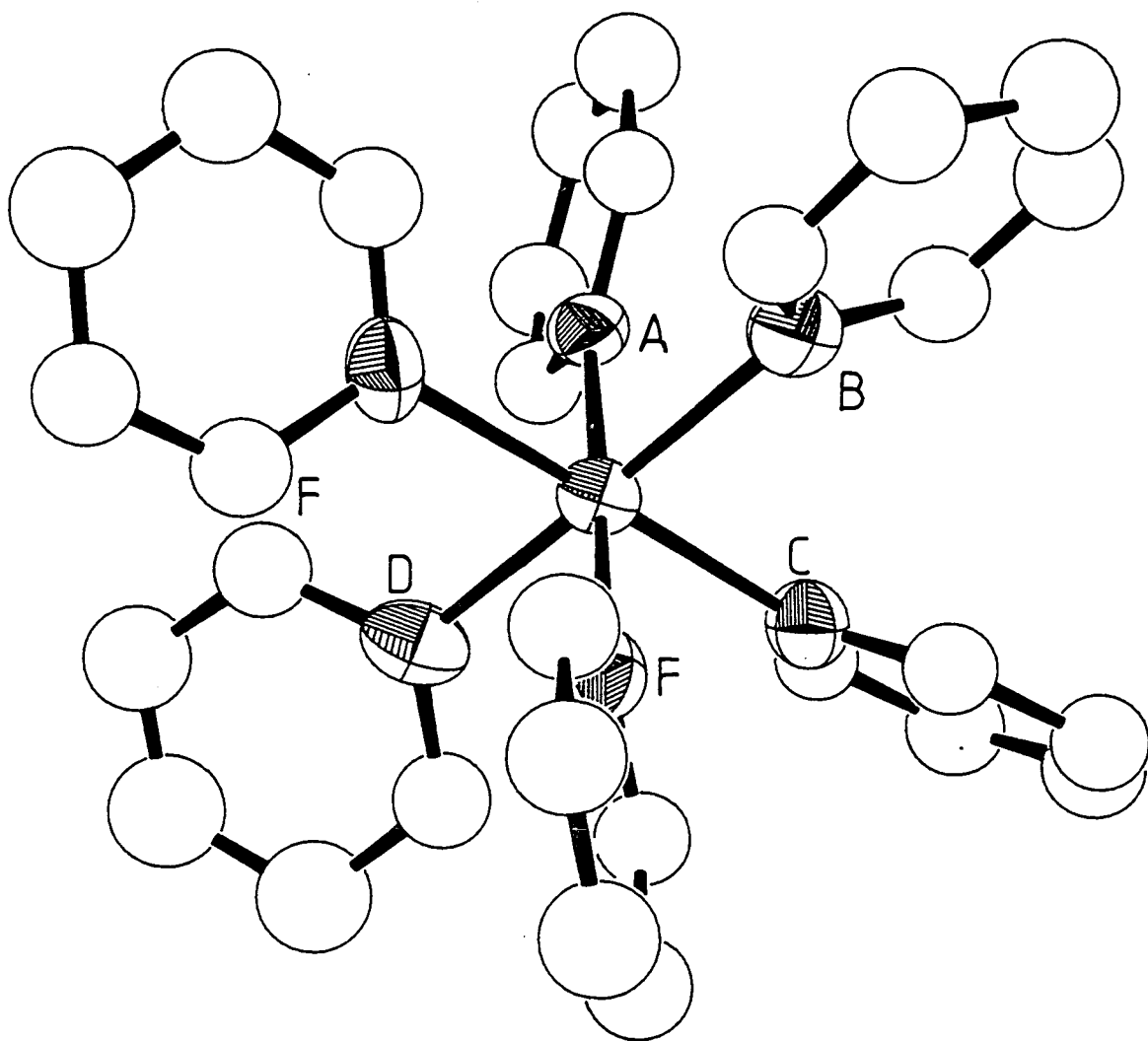


Figure 2.30 View of the [OsPy₆]²⁺ Dication.

Table 2.5 Bond Lengths(Å) and Angles (degrees) with Standard Deviations for the Dication [Os₂py₆]²⁺.

Os -N(1A)	2.122(6)	C(3C) -C(4C)	1.353(14)
Os -N(1B)	2.097(6)	C(4C) -C(5C)	1.386(14)
Os -N(1C)	2.115(6)	C(5C) -C(6C)	1.349(13)
Os -N(1D)	2.104(6)	N(1D) -C(2D)	1.341(10)
Os -N(1E)	2.093(6)	N(1D) -C(6D)	1.335(10)
Os -N(1F)	2.137(6)	C(2D) -C(3D)	1.390(13)
N(1A) -C(2A)	1.368(11)	C(3D) -C(4D)	1.385(14)
N(1A) -C(6A)	1.364(10)	C(4D) -C(5D)	1.404(13)
C(2A) -C(3A)	1.411(12)	C(5D) -C(6D)	1.357(12)
C(3A) -C(4A)	1.323(13)	N(1E) -C(2E)	1.370(12)
C(4A) -C(5A)	1.391(14)	N(1E) -C(6E)	1.351(10)
C(5A) -C(6A)	1.395(13)	C(2E) -C(3E)	1.426(15)
N(1B) -C(2B)	1.361(12)	C(3E) -C(4E)	1.371(16)
N(1B) -C(6B)	1.344(9)	C(4E) -C(5E)	1.364(16)
C(2B) -C(3B)	1.430(13)	C(5E) -C(6E)	1.405(13)
C(3B) -C(4B)	1.321(12)	N(1F) -C(2F)	1.336(10)
C(4B) -C(5B)	1.393(13)	N(1F) -C(6F)	1.380(11)
C(5B) -C(6B)	1.374(11)	C(2F) -C(3F)	1.382(12)
N(1C) -C(2C)	1.370(10)	C(3F) -C(4F)	1.368(14)
N(1C) -C(6C)	1.320(10)	C(4F) -C(5F)	1.391(13)
C(2C) -C(3C)	1.403(12)	C(5F) -C(6F)	1.391(13)
N(1A) - Os -N(1B)	88.34(23)	Os -N(1C) -C(6C)	126.2(5)
N(1A) - Os -N(1C)	92.19(23)	C(2C) -N(1C) -C(6C)	115.6(6)
N(1A) - Os -N(1D)	87.48(23)	N(1C) -C(2C) -C(3C)	122.2(7)
N(1A) - Os -N(1E)	91.55(23)	C(2C) -C(3C) -C(4C)	118.6(9)
N(1A) - Os -N(1F)	179.00(22)	C(3C) -C(4C) -C(5C)	119.6(9)
N(1B) - Os -N(1C)	87.37(23)	C(4C) -C(5C) -C(6C)	117.9(9)
N(1B) - Os -N(1D)	175.82(23)	N(1C) -C(6C) -C(5C)	126.0(8)
N(1B) - Os -N(1E)	92.93(23)	Os -N(1D) -C(2D)	124.0(5)
N(1B) - Os -N(1F)	92.47(23)	Os -N(1D) -C(6D)	121.6(5)
N(1C) - Os -N(1D)	92.60(23)	C(2D) -N(1D) -C(6D)	114.4(7)
N(1C) - Os -N(1E)	176.25(23)	N(1D) -C(2D) -C(3D)	125.0(8)
N(1C) - Os -N(1F)	88.43(22)	C(2D) -C(3D) -C(4D)	117.8(9)
N(1D) - Os -N(1E)	87.37(24)	C(3D) -C(4D) -C(5D)	118.5(9)
N(1D) - Os -N(1F)	91.71(23)	C(4D) -C(5D) -C(6D)	117.5(8)
N(1E) - Os -N(1F)	87.82(23)	N(1D) -C(6D) -C(5D)	126.7(8)
Os -N(1A) -C(2A)	120.6(5)	Os -N(1E) -C(2E)	118.8(6)
Os -N(1A) -C(6A)	122.3(5)	Os -N(1E) -C(6E)	125.0(5)
C(2A) -N(1A) -C(6A)	117.0(7)	C(2E) -N(1E) -C(6E)	116.2(7)
N(1A) -C(2A) -C(3A)	121.2(8)	N(1E) -C(2E) -C(3E)	122.5(9)
C(2A) -C(3A) -C(4A)	121.0(8)	C(2E) -C(3E) -C(4E)	119.3(10)
C(3A) -C(4A) -C(5A)	118.9(9)	C(3E) -C(4E) -C(5E)	118.3(11)
C(4A) -C(5A) -C(6A)	119.6(9)	C(4E) -C(5E) -C(6E)	120.9(10)
N(1A) -C(6A) -C(5A)	121.9(8)	N(1E) -C(6E) -C(5E)	122.7(8)
Os -N(1B) -C(2B)	119.4(6)	Os -N(1F) -C(2F)	122.2(5)
Os -N(1B) -C(6B)	125.2(5)	Os -N(1F) -C(6F)	121.1(5)
C(2B) -N(1B) -C(6B)	115.1(7)	C(2F) -N(1F) -C(6F)	116.6(7)
N(1B) -C(2B) -C(3B)	122.2(8)	N(1F) -C(2F) -C(3F)	122.9(7)
C(2B) -C(3B) -C(4B)	119.5(8)	C(2F) -C(3F) -C(4F)	120.6(9)
C(3B) -C(4B) -C(5B)	119.9(8)	C(3F) -C(4F) -C(5F)	118.3(9)
C(4B) -C(5B) -C(6B)	117.8(8)	C(4F) -C(5F) -C(6F)	118.6(9)
N(1B) -C(6B) -C(5B)	125.5(7)	N(1F) -C(6F) -C(5F)	122.8(8)
Os -N(1C) -C(2C)	118.1(5)		

Table 2.6 Angles Mutually Described by the Pyridine Planes in the Dication $[\text{OsPy}_6]^{2+}$.

Plane	B	C	D	E	F
A	59.58	66.37	70.77	76.84	30.33
B		54.29	77.34	59.85	77.96
C			52.44	67.03	56.50
D				32.40	87.39
E					63.32

are co-planar, which is the electronically preferred orientation. In the ruthenium and osmium analogues these pyridines are staggered. We suggest this is due to a steric interaction between adjacent pyridine ligands resulting from the shorter metal-pyridine bond present for these two complexes.

A cyclic voltammogram of $[\text{OsPy}_6][\text{BF}_4]_2$ in a $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ CH_2Cl_2 solution reveals a reversible, one electron oxidation at +0.96V (as confirmed by coulometry). No reductive processes are observable.

A spectroelectrochemical study was performed at the O.T.T.L.E. in which $[\text{OsPy}_6]^{2+}$ was oxidised at 240K in

$\text{CH}_2\text{Cl}_2/0.5\text{M}$ [TBA][BF_4]. The spectrum of yellow $[\text{Os}(\text{II})\text{py}_6]^{2+}$ (fig. 2.31) is dominated by $\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$ C.T. transitions. Upon oxidation to $[\text{Os}(\text{III})\text{py}_6]^{3+}$ (fig. 2.32) these L.M.C.T transitions move to higher energy and are superposed with $\text{py}\pi \rightarrow \text{py}\pi^*$ intraligand C.T.'s (which are mentioned in section 2.3.2).

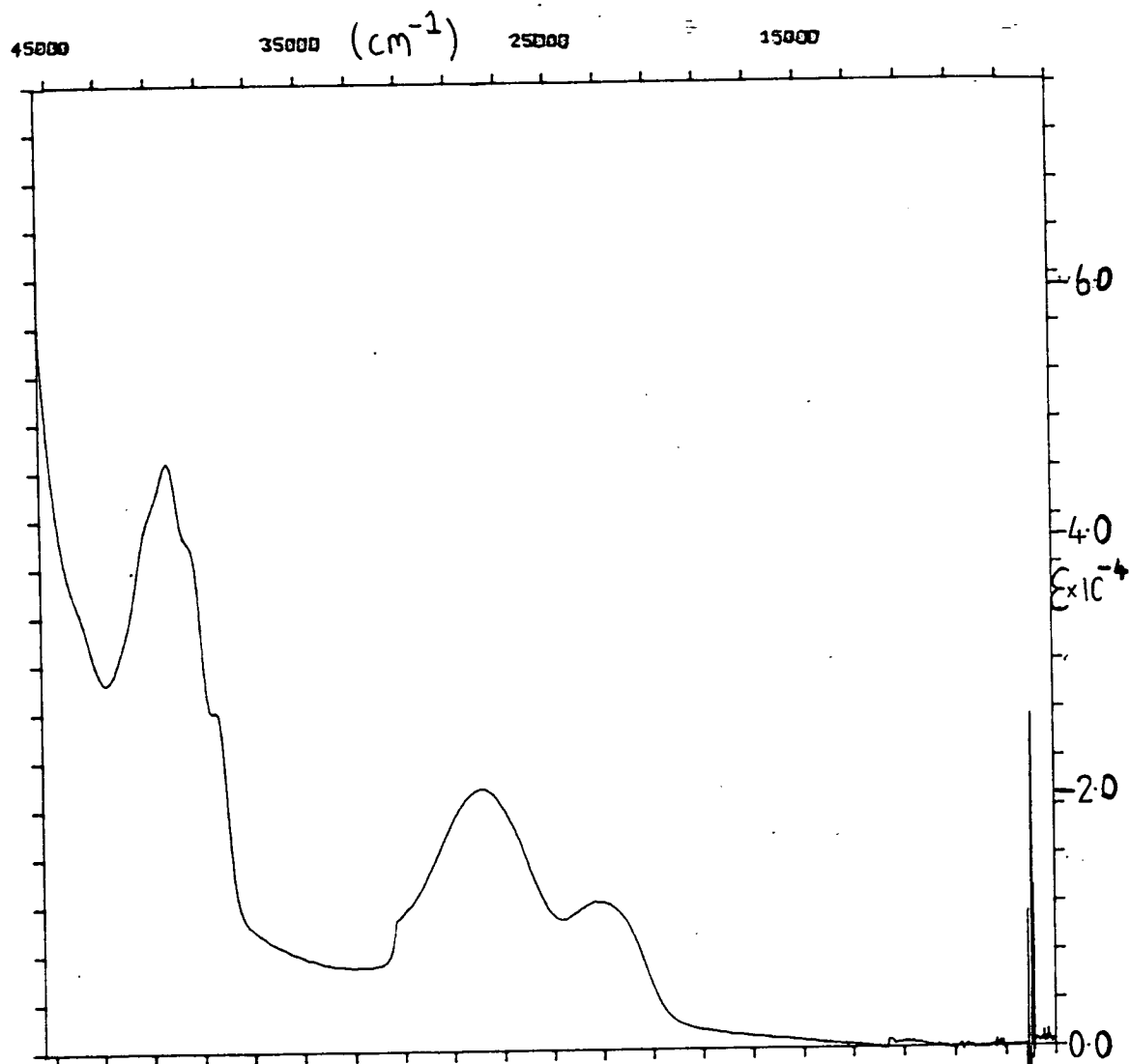


Figure 2.31 U.V./Vis. Absorption Spectrum of $[\text{Os}(\text{py})_6]^{2+}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M}$ [TBA][BF_4] at 240K.

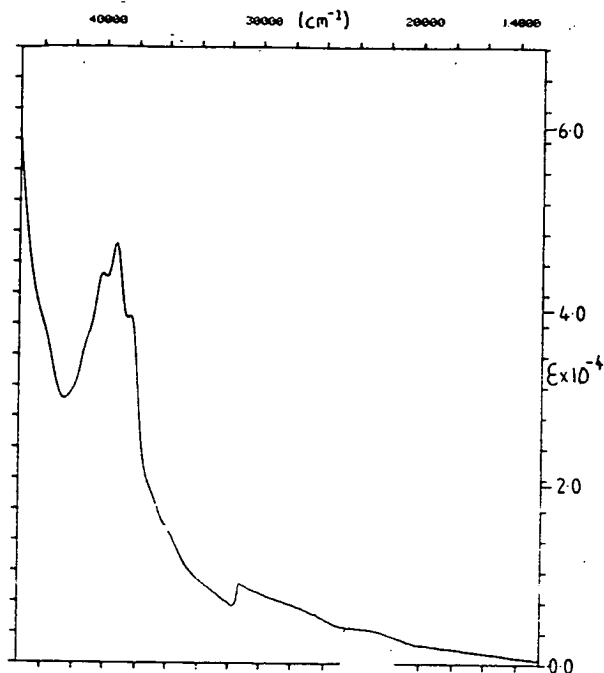
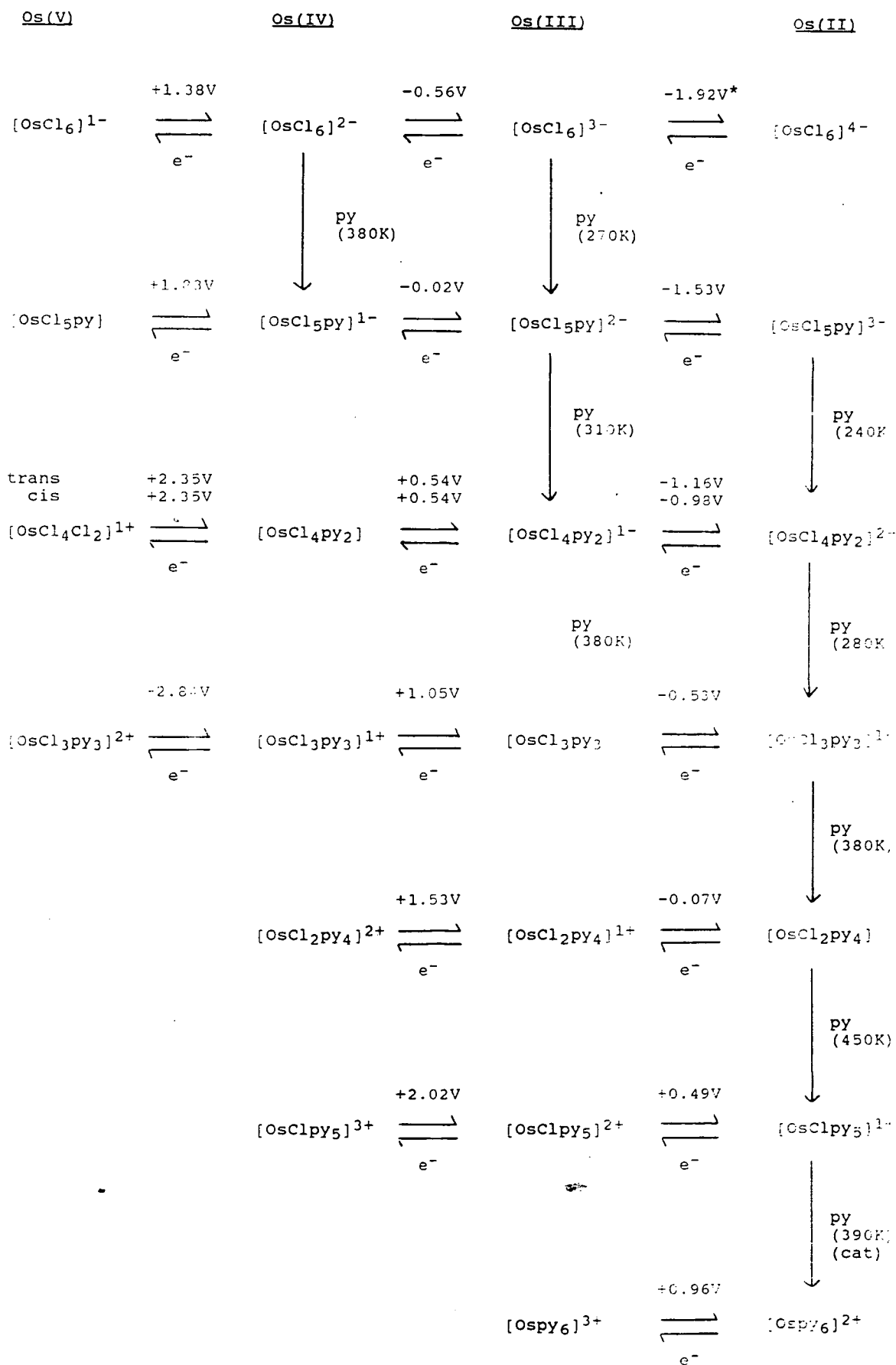


Figure 2.32 U.V./Vis. Absorption Spectrum of $[\text{OsPy}_6]^{3+}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 240K.

2.3.1 Discussion of the $E_{1/2}$ values obtained for the series $[\text{OsCl}_{6-n}\text{Py}_n]^{(n-y)+}$.

The voltammetric data collected in the previous sections are presented in scheme 2.1. The assembled results are one of the most extended body of data for a related family of complexes collected to date. Note that as Cl^- ligands are sequentially replaced by py ligands so the $E_{1/2}$ values for corresponding couples move to more positive potentials. This is a reflection of replacement of a π -donating ligand by a π -accepting ligand, stabilising lower oxidation states. In figure 2.33 $E_{1/2}$

Scheme 2.1 Voltammetric Data and Reaction Scheme for the series $[\text{OsCl}_{6-n}\text{py}_n]^{(n-y)+}$.



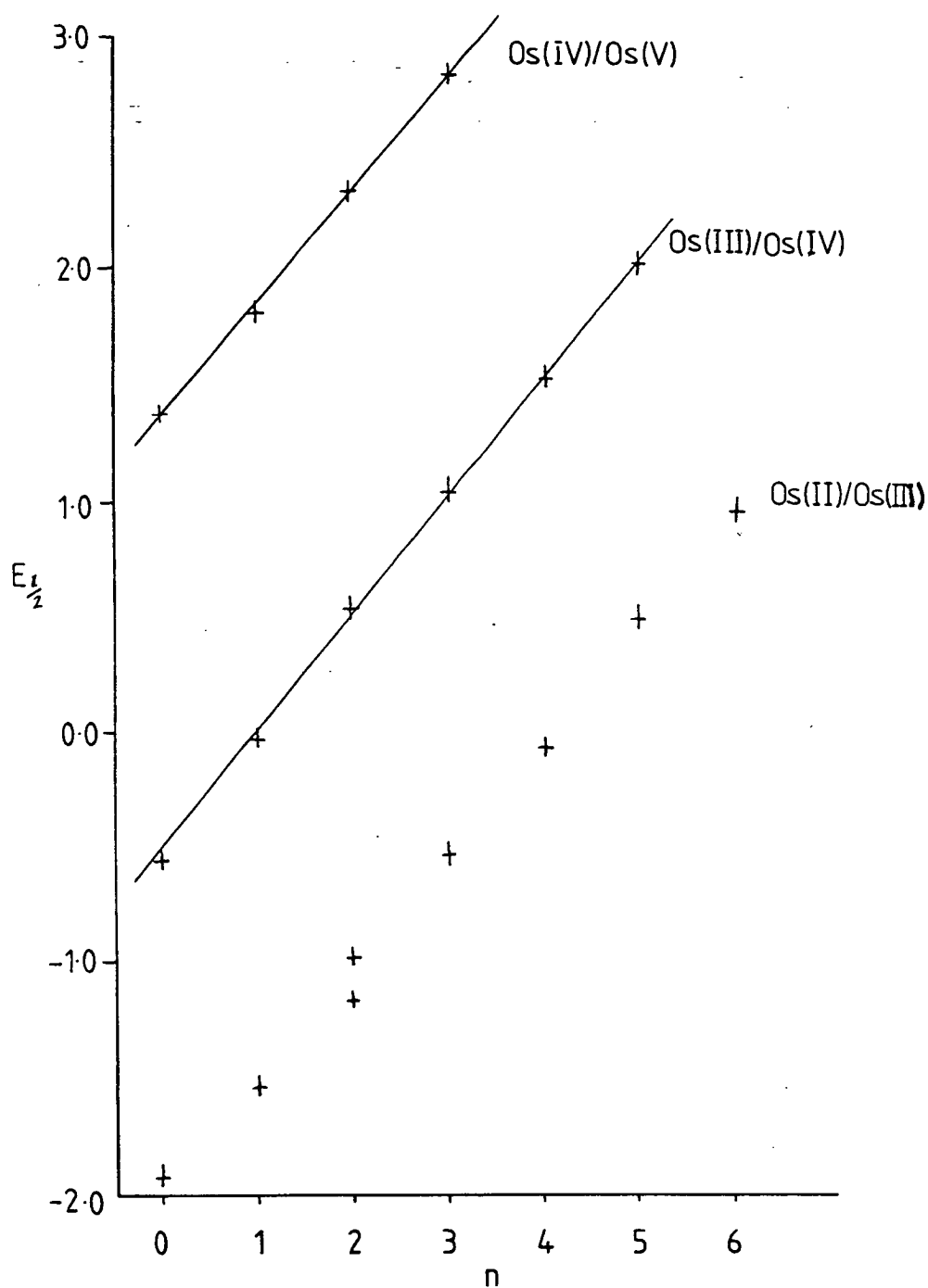


Figure 2.33 Graph Showing n against $E_{1/2}$ for the Series $[\text{OsCl}_{6-n}\text{py}_n](n-y)^+$.

values are plotted against n , where n corresponds to the number of pyridine ligands in the complexes $[\text{OsCl}_{6-n}\text{py}_n]^{(n-2)+}$. Below, the electrochemical results are compared to values calculated using 'Ligand Parametrization'¹⁴ and then fitted to Bursten's 'Ligand Additivity'¹⁵ model.

The $E_{1/2}$ values for the Os(III)/Os(II) couples can be compared to the values predicted by the 'Electrochemical Parametrization of Metal Redox Couples' proposed by Lever¹⁴.

The general equation (see chapter 1) for the prediction of an $E_{1/2}$ values is:

$$E_{\text{calc}} = S_M[\sum E_L] + I_M + C_{\text{ref}} \quad \underline{1}$$

where: E_{calc} is the calculated $E_{1/2}$ value, S_M and I_M are constants for a specific redox couple of all the complexes of a given metal with the same stereochemistry and spin state, (in this case Os(III)/Os(II) couples of octahedral, low spin complexes), $\sum E_L$ is the sum of the electronic contributions of each ligand around the metal, C_{ref} corrects potentials collected using a S.H.E. to values relative to a Ag/AgCl reference electrode. Inserting the values for S_M , I_M calculated by Lever for Os(III)/Os(II) couples we have:

$$E_{\text{calc}} = 1.01[\sum E_L] - 0.40 - 0.105 \quad \underline{2}$$

Using values of $E_L(\text{Cl}^-) = -0.24\text{V}$ and $E_L(\text{py}) = 0.25\text{V}$, E_{calc} can be obtained for the series under study (table 2.7). These are compared graphically with the experimental values in fig. 2.34. The predicted values show good correlation with the experimental values, E_{calc} always falling within 200mV of E_{obs} . However, the method does not take into account any isomer effects and in a more precise model (see later) these clearly must be taken into account.

There are no values currently available for S_M and I_M for Os(IV)/Os(III) and Os(V)/Os(IV) couples. Plots of the experimental $E_{1/2}$ values versus $[\Sigma E_L]$ give good straight line plots (fig. 2.35). Least square analyses of these plots show that:

for Os(IV)/Os(III) couples, $S_m = 1.05 \pm 0.02$

$I_m = 1.095 \pm 0.02$

and for Os(V)/Os(IV) couples, $S_m = 1.00 \pm 0.02$

$I_M = 2.905 \pm 0.02$

Comparing the three plots in fig. 2.35, a much better correspondence between ΣE_L and E_{obs} is observed for the Os(IV)/Os(III) and Os(V)/(IV) couples than for the Os(III)/Os(II) couples. This difference can be explained by considering the relative energies of the electrons involved in the various redox steps. The H.O.M.O. in the Os(II) species, which lies in the metal-based $d\pi$ orbitals (see figure 2.38), lies at higher energy than those in the Os(III) and Os(IV) complexes, hence it is more susceptible

Table 2.7 $[\Sigma E_L]$, E_{calc} and Experimental $E_{1/2}$ Values for the series $[OsCl_{6-n}py_n]^{(n-4)+}$.

Redox Process	$\Sigma E_L(V)$	$E_{calc}^a(V)^b$	$E_{obs}(V)^b$
$[OsCl_6]^{4-}/3-$	-1.44	-1.945	-1.92
$[OsCl_5py]^{3-}/2-$	-0.95	-1.455	-1.53
$[OsCl_4py_2]^{2-}/1-$	-0.46	-0.965	-1.16 (-0.95) ^c
$[OsCl_3py_3]^{1-}/0$	+0.03	-0.475	-0.53
$[OsCl_2py_4]^{0}/1+$	+0.52	+0.015	-0.07
$[OsClpy_5]^{1+}/2+$	+1.01	+0.515	+0.49
$[Os py_6]^{2+}/3+$	+1.50	+1.010	+0.96

^a $E_{calc} = 1.01(\Sigma E_L) - 0.40 - 0.105$

^b Volts versus Ag/AgCl that gave a $FeCp_2/FeCp_2^+$ at 0.56V.

^c *cis* value in parentheses.

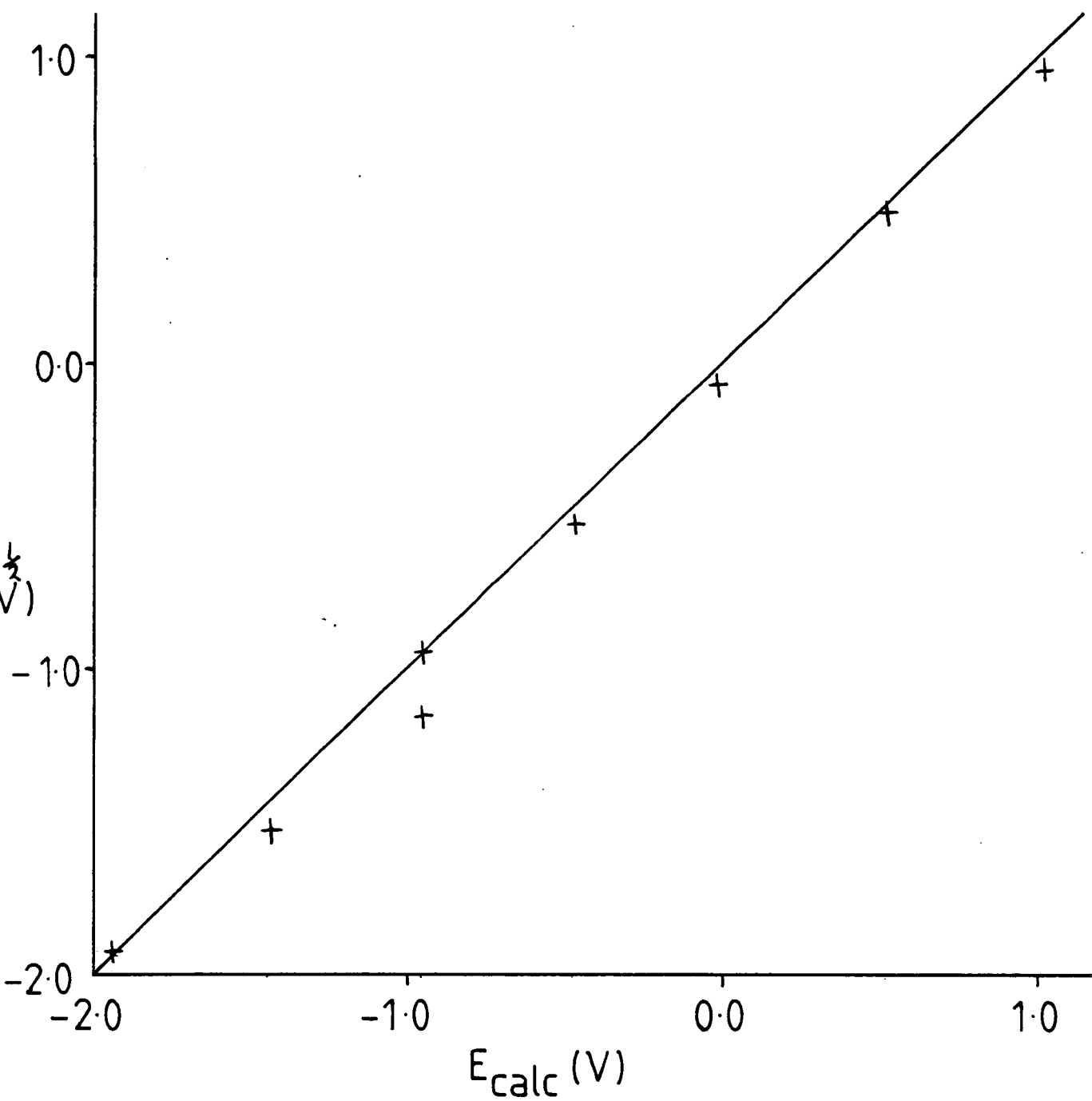


Figure 2.34 Graph showing E_{calc} against experimental $E_{1/2}$ values for the series $[\text{OsCl}_{6-n}\text{py}_n]^{(n-4)+/(n-3)+}$.

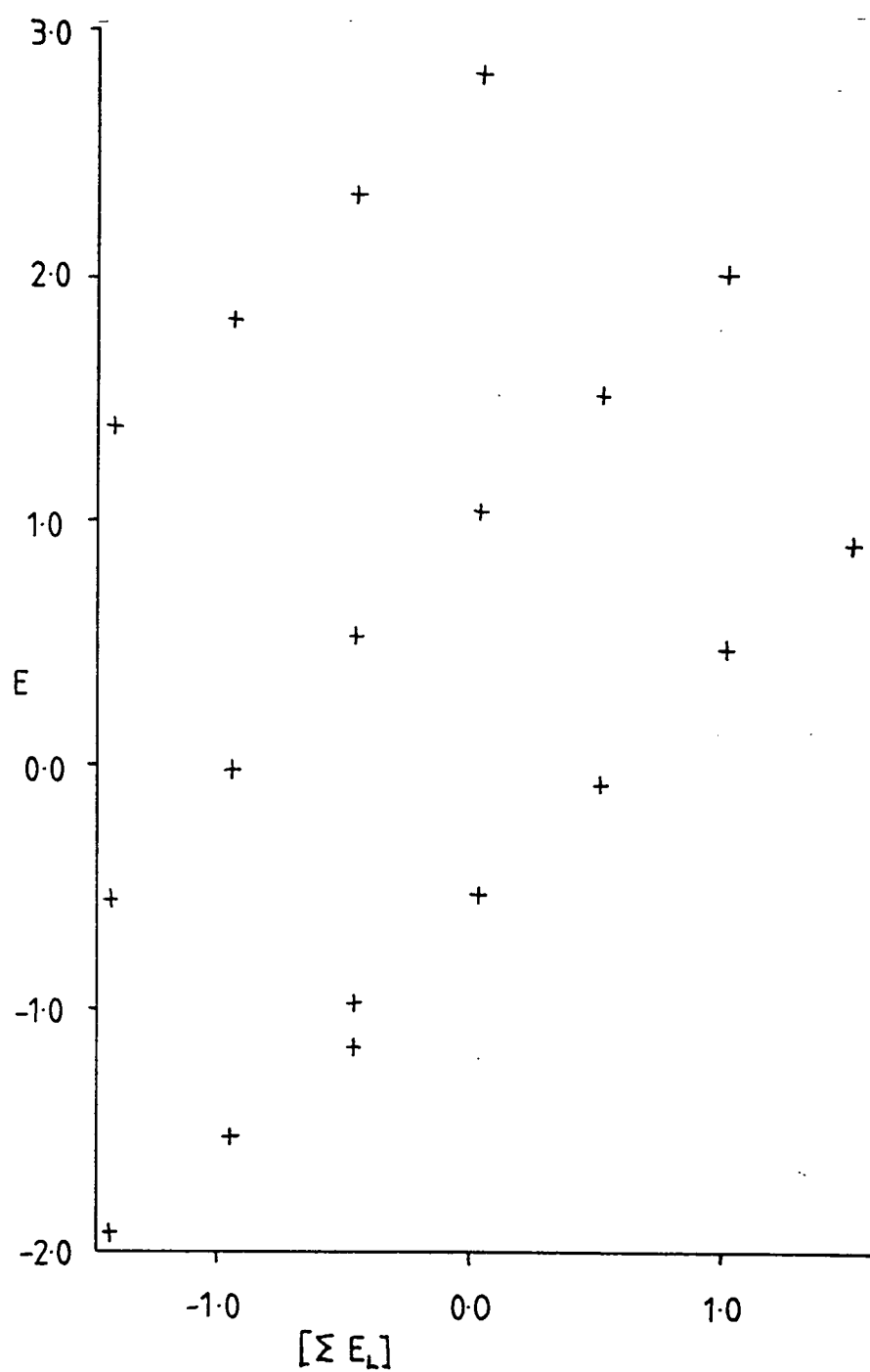


Figure 2.35 Graph showing $[\Sigma E_L]$ against $E_{1/2}$ for the series $[\text{OsCl}_{6-n}\text{py}_n]^{(n-Y)+}$.

to π - interactions with surrounding ligands that have π - accepting character (equally we would expect the H.O.M.O. in Os(IV) complexes to be more susceptible to interactions with ligands with π - donating properties, since the H.O.M.O. is at lower energy in this oxidation state than in Os(II) complexes). In the Os(II) species interactions of the H.O.M.O. with π - accepting ligands, as we shall consider, are isomer dependent.

We can conclude that 'Electrochemical Parametrization' has given reliable but rough predictions of $E_{1/2}$ values for the Os(III)/Os(II) couples. Values for S_m and I_M have been obtained for the Os(IV)/Os(III) and Os(V)/Os(IV) couples which will assist in any future calculations of this type. However, the method ignores the subtle possibility that the energy of the H.O.M.O. might be altered by isomer dependent π - interactions with the surrounding ligands. In order to gain an appreciation of these effects we must fit the redox data collected to Bursten's 'Ligand Additivity' model.¹⁵

Summarising the theory presented in section 1.3, the equation governing the value of a particular redox potential is:

$$E_{1/2} = A + Bn + Cx_{HOMO} \quad \underline{3}$$

where, in this instance,

$$A = A_{Os(II/III)}^0 + 6B_{Os(II/III)}^{Cl} + 4C_{Os(II/III)}^{Cl} \quad 4$$

$$B = B_{Os(II/III)}^{py} - B_{Os(II/III)}^{Cl} \quad 5$$

$$C = C_{Os(II/III)}^{py} - C_{Os(II/III)}^{Cl} \quad 6$$

Briefly, parameter A is constant for a given redox couple. Parameter B (like Lever's $[\sum E_L]$) is isomer independent and reflects the overall change in stabilisation of the metal centre that arises from the replacement of a Cl^- by a py ligand. Parameter C reflects the effect upon a given $d\pi$ orbital (the H.O.M.O.) of replacing a Cl^- by a py. It is this parameter that is isomer dependent. Values of n and x_{HOMO} and the predicted oxidative $E_{1/2}$ (E_{BLA}) for each complex are tabulated below.

	n	x_{HOMO}	Predicted E_{BLA}
$[OsCl_6]^{(n-y)+}$	0	0	A
$[OsCl_5py]^{(n-y)+}$	1	0	A + B
<i>trans</i> - $[OsCl_4py_2]^{(n-y)+}$	2	0	A + 2B
<i>cis</i> - $[OsCl_4py_2]^{(n-y)+}$	2	1	A + 2B + C
<i>mer</i> - $[OsCl_3py_3]^{(n-y)+}$	3	1	A + 3B + C
<i>trans</i> - $[OsCl_2py_4]^{(n-y)+}$	4	2	A + 4B + 2C
$[OsClpy_5]^{(n-y)+}$	5	3	A + 5B + 3C
$[Ospy_6]^{(n-y)+}$	6	4	A + 6B + 4C

According to the ligand additivity model, the values of these coefficients should be similar for oxidations of Os(II), Os(III) and Os(IV) species (that is for metal centres with spin configurations: low spin d^6 , d^5 and d^4 , $y = 4, 3, 2$, respectively). Inspection of the $E_{1/2}$ versus n graph (fig. 2.33) shows linear, isomer independent plots for the Os(IV)/Os(III) and Os(V)/Os(IV) redox couples. This either implies C is negligible for the electrons involved in these redox processes, or that the model is not appropriate for these particular redox couples. Values of A and B obtained by least squares analysis of these plots are given below.

	A	B
Os(IV)/Os(III)	-0.54 ± 0.01	0.53 ± 0.01
Os(V)/(Os(IV)	1.37 ± 0.02	0.49 ± 0.01

One of the premises contained in Bursten's ligand additivity model is that the metal-based $d\pi$ orbitals do not rehybridize upon oxidation. If this premise is violated, the underlying principle of the model, that is that oxidation potential is proportional to the H.O.M.O. energy, would break down, since the energy of the oxidised state would then be dependent on the energy of all three $d\pi$ orbitals. The energy involved in spin pairing is

around 0.5eV (4000cm^{-1}). The energy gaps between the $d\pi$ orbitals are smaller than this, as observed spectroscopically in $d\pi \rightarrow d\pi$ bands at ca. $5\ 000\text{cm}^{-1}$ (see fig. 2.28), which derive their energy from both d-d splitting and spin pairing components. Hence it seems likely that for oxidations of low spin d^5 and d^4 complexes, that is when an electron is removed from the H.O.M.O., such a rehybridization would take place. Hence the ligand additivity model would not be appropriate for these complexes.

The Os(III)/Os(II) plot is not linear, moreover, as predicted by the 'Ligand Additivity' model, nearly linear portions are observed for $n = 0, 1, 2(\text{trans})$, and $n = 2(\text{trans}), 3, 4, 5, 6$. Values of A and B are obtained from the first portion ($n = 0, 1, 2(\text{trans})$) of the graph. Using these values for A and B, C can be calculated for each couple. The average value for C is given below.

	A	B	C
Os(III)/Os(II)	-1.92 ± 0.01	0.38 ± 0.01	0.18

The redox couples predicted by these values of A, B and C (E_{BLA}) against the experimental $E_{1/2}$ values are shown in Table 2.8 and are plotted in figure 2.36.

Values for the constants from which A, B and C are derived (see equations 4, 5 and 6) cannot be derived from

Table 2.8 Comparison of $E_{1/2}$ Values (E_{BLA}) Calculated by the Ligand Additivity Model^a and Experimental $E_{1/2}$ Values for the Series $[OsCl_{6-n}py_n]^{(n-4)-}$.

Redox Process	E_{BLA}	$E_{obs}(V)^b$	C^c
$[OsCl_6]^{4-}/3-$	-1.92	-1.92	-
$[OsCl_5py]^{3-}/2-$	-1.535	-1.53	-
$t-[OsCl_4py_2]^{2-}/1-$	-1.15	-1.16	-
$c-[OsCl_4py_2]^{2-}/1-$	-0.97	-0.95	0.20
$m-[OsCl_3py_3]^{1-}/0$	-0.585	-0.53	0.235
$t-[OsCl_2py_4]^{0}/1+$	-0.02	-0.07	0.155
$[OsClpy_5]^{1+}/2+$	+0.545	+0.49	0.16
$[OsPy_6]^{2+}/3+$	+1.11	+0.96	0.14

^a Values calculated using values of $A = -1.92$, $B = 0.385$ and the average value of $C = 0.18$.

^b Volts versus $Ag/AgCl$.

^c C is calculated for each couple using the experimental $E_{1/2}$ values and $A = -1.92$, $B = 0.385$.

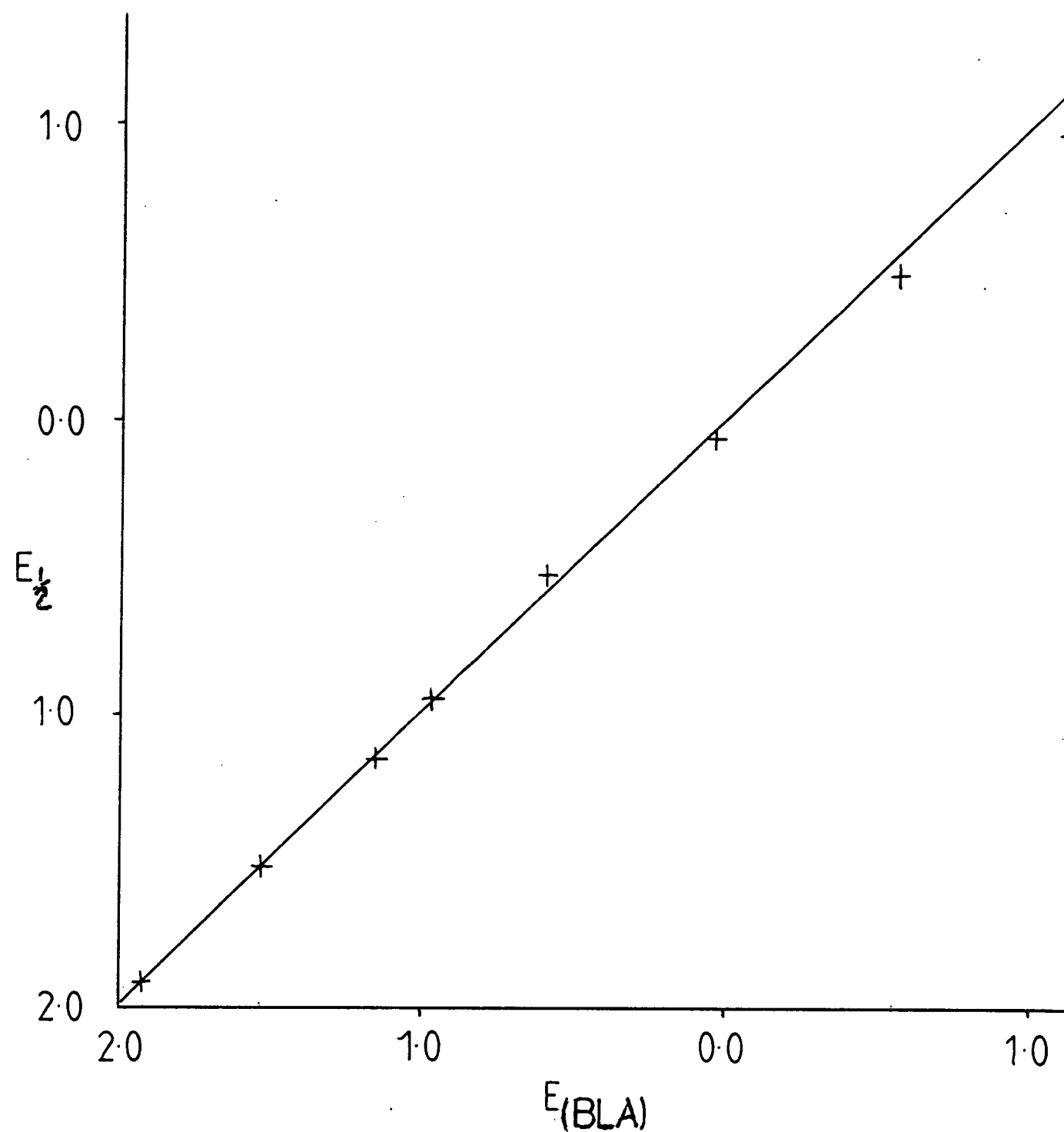


Figure 2.36 Graph Showing $E_{1/2}$ Values Calculated Using the 'Ligand Additivity' Model (E_{BLA}) against the Experimental $E_{1/2}$ values for the series $[OsCl_{6-n}PY_n]^{(n-4)+}$

this data alone. In order to obtain these constants a similar series must be developed with both the py and the chloride replaced by a similar ligand, the constants could then be solved simultaneously. The following chapter describes two series in which Cl^- is replaced by Br^- and I^- .

The value of C varies with the number of pyridines, n , around the metal, as shown in table 2.8 and graphically in figure 2.37. We can observe a general decrease in the value as more pyridines become ligated. This can be explained by considering the precise mode of coordination of the pyridine ligands. Compared to the small, linear molecules (CO and CNMe) that Bursten has based his model on, pyridine is a large planar molecule. The electronically preferred orientation of the pyridine ligands would give maximum overlap between the pyridine π^* acceptor orbitals, which lie perpendicular to the ring, and the metal $d\pi$ orbitals. In order to achieve this maximum overlap, all the pyridine ligands in the compounds *trans*- and *cis*- $[\text{OsCl}_4\text{py}_2]^{2-}$, *mer*- $[\text{OsCl}_3\text{py}_3]^{1-}$, and *trans*- $[\text{OsCl}_2\text{py}_4]$ would lie either in the same plane or perpendicular to one another. X-ray crystal structure determinations have shown that when pyridines are *cis* to one another they do not coordinate in this fashion, presumably due to a steric interaction between the α hydrogens on adjacent ligands. Rather, they coordinate in a fashion that best satisfies the electronic and steric

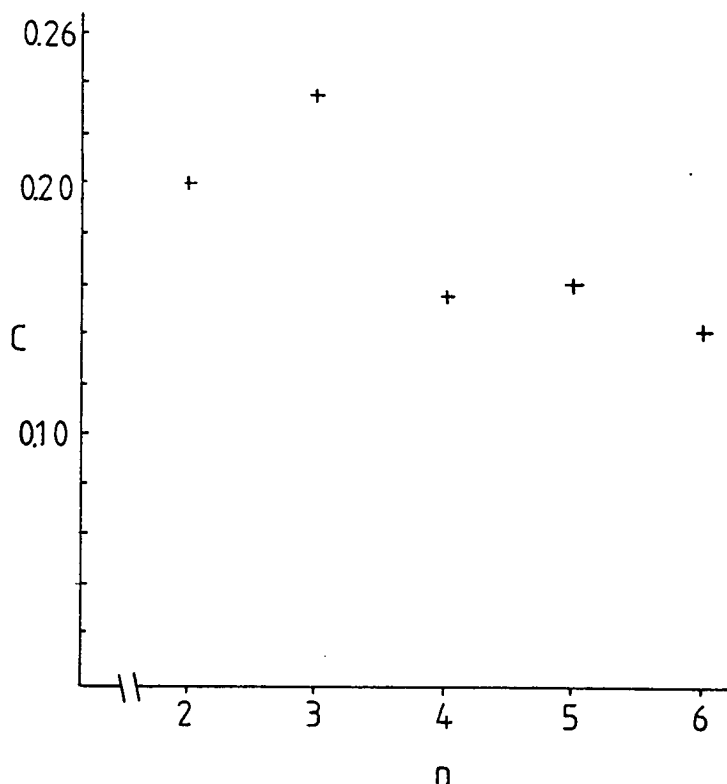


Figure 2.37 Graph Showing Parameter C against n for the Series $[\text{OsCl}_{6-n}\text{py}_n](n-4)^+$.

constraints put upon them. Bursten's ligand additivity model assumes each ligand has two orthogonal π^* orbitals which will always be aligned in the most electronically favourable fashion. We propose that because the pyridine π^* orbitals found in complexes of the type $[\text{OsCl}_{6-n}\text{py}_n](n-4)^+$ are not always able to lie in the most electronically favourable position, the ligand additivity model is not entirely appropriate for these complexes. Moreover, as the number of pyridines around the metal centre increases, the pyridines' coordination will be

increasingly dictated by steric, rather than electronic factors. This will result in the metal $d\pi$ orbitals becoming less efficiently stabilised by the pyridine π^* orbitals, which accounts for the observed general decrease in C as more pyridines become coordinated.

In conclusion, we would argue that the electrochemical data we have obtained for the Os(II)/Os(III) reinforces the 'ligand additivity' model proposed by Bursten for oxidations of d^6 complexes. In addition we propose that the precise orientation of the ligands, with respect to the metal based $d\pi$ orbitals, influences the oxidation potentials.

As a result of these conclusions we would predict that the oxidation potential of *fac*-[Os(II)Cl₃py₃]⁻ will be lower than for the corresponding *mer*- isomer, but the difference will not be as large as Bursten's model predicts, due to parameter C being reduced due to sterically crowded pyridine ligands. Bursten's model predicts that there would be no difference in the oxidation potentials for *cis* and *trans*-[Os(II)Cl₂py₄]. We would argue that the *cis* isomer would be more difficult to oxidise than the *trans* isomer due to parameter C being smaller for the *cis* isomer. This would be due to steric factors preventing the pyridine ligands being orientated in the electronically favoured positions. As yet neither isomer has been synthesised successfully in this laboratory to test these predictions.

2.3.2 Discussion of the u.v.visible electronic absorption spectra of the series $[\text{OsCl}_{6-n}\text{py}_n]^{(n-y)+}$.

The position and extinction coefficients of the absorption bands from all the u.v./vis spectra obtained in the spectroelectrochemical experiments detailed in sections 2.2.1-2.2.9 are listed in along with probable assignments in Table 2.8 at the end of this section. The types of electronic transitions we would expect for complexes of this type has been expounded upon in section 1.4. and are shown in figure 1.2.

If the complex being examined contains pyridine, any band at high energy ($> 40\,000\text{cm}^{-1}$) must be assigned, at least in part, to $\text{py}\pi \rightarrow \text{py}\pi^*$ C.T. transitions. These transitions occur at $40\,000\text{cm}^{-1}$ in free pyridine (fig. 2.38), and their position does not alter significantly on complexation, as can be observed in the spectra of $[\text{OsCl}_5\text{py}]Y^-$, where $y = 2,1,0$, (figs. 2.8, 2.9, 2.10.)

Assignment of bands to charge transfer transitions in the complexes containing Os(II) is usually unambiguous since the $d\pi$ orbitals on the Os centre are full and thus the low energy transitions will be M.L.C.T, $\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$.

The low energy spectrum of $[\text{Os}(\text{py})_6]^{2+}$ as shown in figure 2.31 has two intense absorptions at $23\,300$ and $27\,900\text{cm}^{-1}$ which may be assigned as triplet and singlet $\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$ transitions since the complex contains only pyridine ligands. The spectrum of $[\text{Os}(\text{bipy})_3]^{2+}$ also

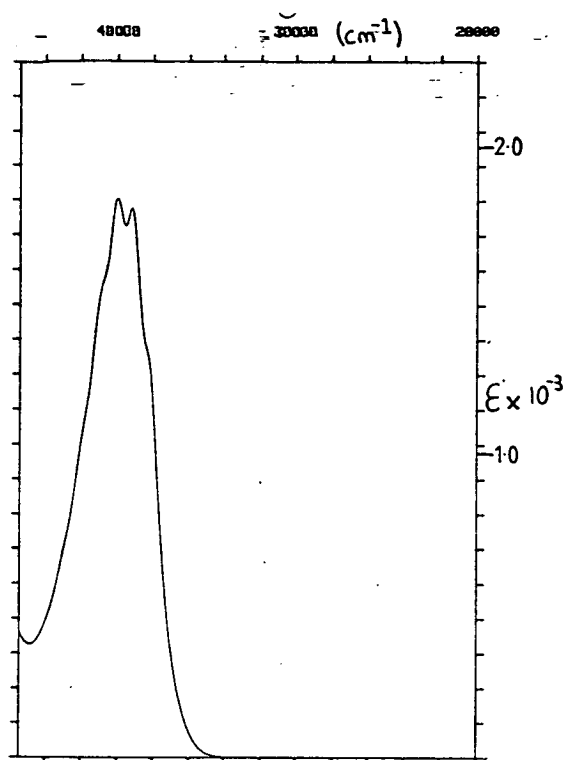


Figure 2.38 U.V./Vis. Absorption Spectrum of Pyridine in CH₂Cl₂ at 290K.

shows two low energy absorption bands which have been assigned to singlet and triplet M.L.C.T. transitions.¹⁶ The spin orbit coupling term for Os(II) is large (ca. 3 000cm⁻¹)¹⁷ hence the singlet/triplet nomenclature tends to become meaningless in such heavy metal complexes. We can therefore assign the two absorption bands observed in the spectrum of [OsPy₆]²⁺ to 'singlet' and 'triplet' M.L.C.T. transitions. Low energy bands occur in the spectra of *trans*-[Os(II)Cl₄Py₂]²⁻, *cis*-[Os(II)Cl₄Py₂]²⁻, *mer*-[Os(II)Cl₃Py₃]¹⁻, *trans*-[Os(II)Cl₂Py₄] and [Os(II)ClPy₅]¹⁺ (see figures 2.15, 2.18, 2.20, 2.24, 2.27 and 2.31 respectively) and are similarly assigned to

M.L.C.T. transitions. The energies of these bands are plotted against n , the number of coordinated pyridines, in figure 2.40. The energy of the M.L.C.T. band increases by approximately 2000cm^{-1} with each additional coordinated pyridine.

This can be rationalised by considering the effect of the complete ligand set on the metal-based $d\pi$ orbitals. If we assume that all the Os(II) complexes examined have the $\text{py}\pi^*$ -based L.U.M.O. at a similar energy and roughly equal Os-N bond distances, then replacement of a chloride by a pyridine will result in stabilisation of the $d\pi$ orbitals. Thus as π -donors are replaced by π -accepting ligands so the oxidation potential for the Os(II)/Os(III) couple should become more positive and the M.L.C.T. band should occur at higher energy. Both of these predictions are observed experimentally.

Another interesting feature of figure 2.40 is the difference in energy between the triplet and singlet M.L.C.T. transitions. As the number of pyridine ligands on the complexes increase so the energy separation between the triplet and singlet M.L.C.T. transitions decreases. This can be explained by a consideration of the factors determining the energies of the singlet and triplet transitions. These factors are the coulomb energy, which is an electrostatic term and the exchange energy, which is a quantum mechanical term. Considering a more simple example first¹⁸, the only difference between a ^3S and ^1S

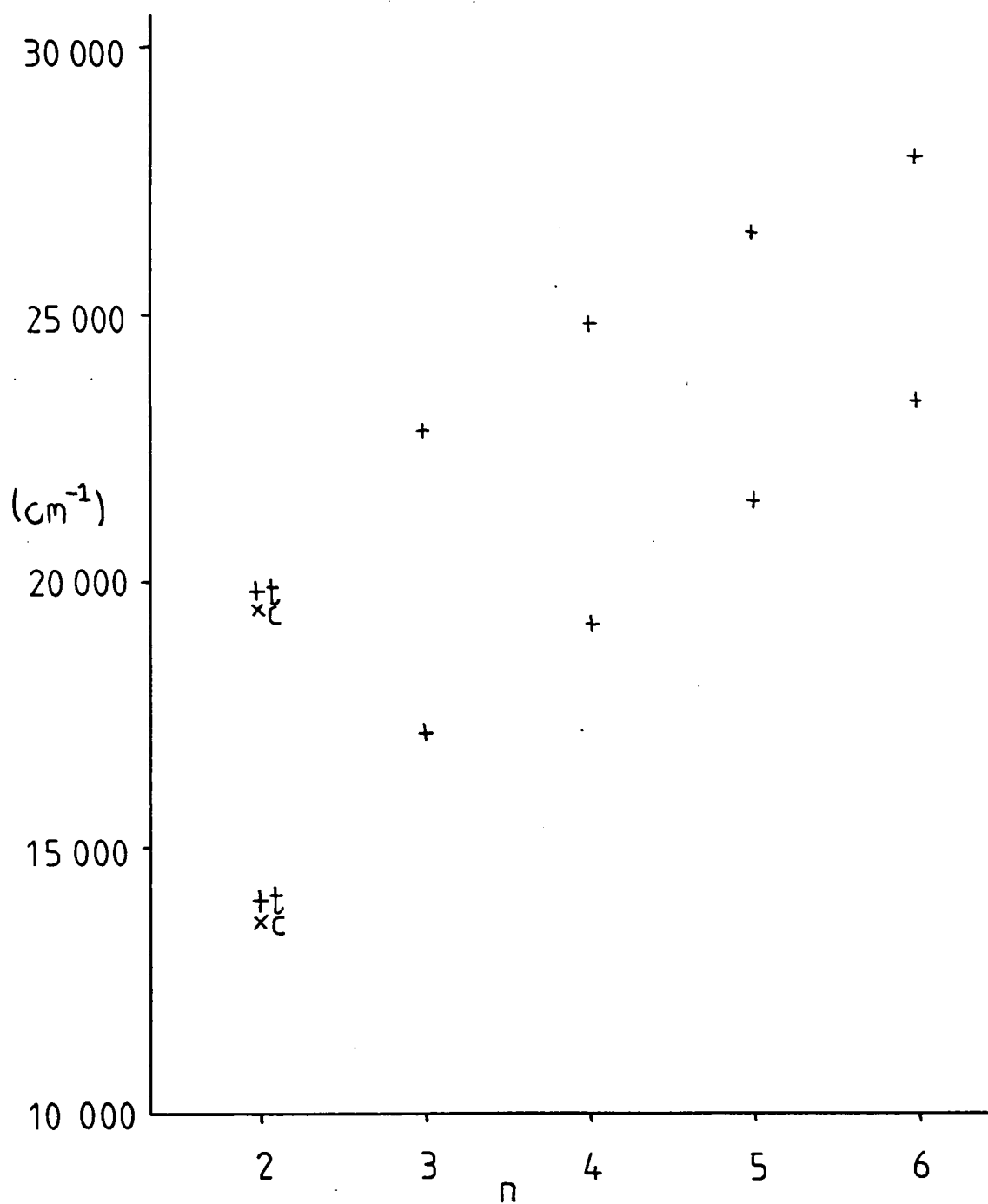


Figure 2.39 Graph Showing Energies of 'Singlet' and 'Triplet' Bands against n for the Series $[\text{OsCl}_{6-n}\text{py}_n]^{(n-4)+}$.

states of He is in the sign of the exchange energy. They are both subject to the same electrostatic/coulombic contributions, and both have an exchange energy, but it is a stabilising (negative) term for the triplet state and a destabilising (positive) term for the singlet. The exchange energy is a correlation energy - for the triplet state the electrons tend to be well separated, but for the singlet they are more likely to be closer and therefore of higher energy (due to electrostatic repulsion). A classical argument to explain this would be that the parallel spins of the triplet state help to keep the electrons apart and therefore lower the energy, and vice versa for the antiparallel singlet spins. Hence, returning to the spectra of $[\text{OsCl}_{6-n}\text{py}_n]^{(n-4)+}$, increasing the number of coordinated pyridine ligands results in the environment for the excited electron becoming more delocalised. Therefore both the positive and negative exchange energy contributions will be reduced.

It is noted that the singlet, triplet nomenclature used here is not entirely appropriate due to the large degree of spin orbit coupling for an osmium (II) centre which renders the spin quantum number almost meaningless. Thus the "triplet" to "singlet" intensity ratio becomes much larger than would be expected for lighter metal centres.

The extinction coefficients of the main $\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$ C.T. transitions increase with increasing number of

coordinated pyridines, providing the complexes have pyridines coordinated in a similar fashion. There is a general increase in the extinction coefficients throughout the series: $c\text{-[Os(II)Cl}_4\text{py}_2\text{]}^{2-}$, $m\text{-[Os(II)Cl}_3\text{py}_3\text{]}^{1-}$, $t\text{-[Os(II)Cl}_2\text{py}_4\text{]}$ and $[\text{Os py}_6]^{2+}$. This is as expected since the possibility of a transition occurring is proportional to the oscillator strength of a band and the probability of the transition increases with increasing number of pyridine ligands. $t\text{-[Os(II)Cl}_4\text{py}_2\text{]}^{2-}$ shows a more intense absorption which may be due to the different mode of coordination of the pyridines in this complex compared to the other Os(II) species considered (the pyridines are co-planar in this case).

A study of which $\text{Os(II)} \rightarrow \text{py}\pi^*$ C.T. transitions are electronically allowed and hence will carry appreciable intensity can be found in Appendix 2. The conclusion of these studies is that the complexes with the lowest symmetry, namely $c\text{-[OsCl}_4\text{py}_2\text{]}^{2-}$ and $m\text{-[OsCl}_3\text{py}_3\text{]}^{1-}$ which have local C_{2v} symmetry at the Os(II) centre, would be expected to have two singlet transitions from nondegenerate Os(II) $d\pi$ orbitals to the lowest energy combination of $\text{py}\pi^*$ orbitals. In contrast to this the other Os(II) species, which all have higher local symmetry at the metal centre (but not the same symmetry in every case), would only be expected to show one intense band. The absorption spectra of $c\text{-[OsCl}_4\text{py}_2\text{]}^{2-}$ and $m\text{-[OsCl}_3\text{py}_3\text{]}^{1-}$, shown in figures 2.18 and 2.20

respectively, show two intense bands with a low energy triplet related to them whereas the other Os(II) species only exhibit one singlet low energy M.L.C.T. band (see figures 2.15, 2.24, 2.27 and 2.31).

The low energy absorption bands in the spectra of all the Os(IV) and Os(V) species examined are dominated by $\text{Cl}^- \pi \rightarrow \text{Os(IV)} d\pi$ or $\text{Os(V)} d\pi$ L.M.C.T. transitions. M.L.C.T. bands involving π^* orbitals of py will occur at higher energies and cannot be distinguished from other C.T. transitions in this region. Calculations on which combinations of $\text{Cl}^- \pi$ orbitals give rise to electronically allowed transitions to the metal $d\pi$ orbitals are complicated and lie beyond the scope of this work. The main C.T. band in each Os(IV) spectrum tends to lie around $27\,000\text{cm}^{-1}$ with its corresponding triplet band at $23\,000\text{cm}^{-1}$.

The individual spectra of Os(III) complexes are more difficult to interpret than the related Os(II), Os(IV) and Os(V) species since these exhibit both M.L.C.T. and L.M.C.T. bands which are often superimposed on one another. However, when the spectra of all eight Os(III) complexes are considered together, a greater understanding of the composition of each individual spectrum can be attained.

Os(III) $d\pi \rightarrow \text{py}\pi^*$ charge transfer transitions.

Bearing in mind the steady increase in energy that was observed for the M.L.C.T. transitions in the spectra of

$[\text{Os(II)Cl}_{6-n}\text{py}_n]^{(4-n)-}$ as n increases, one might suggest that a similar increase in the energy of the M.L.C.T. transitions as chlorides are replaced by pyridines will occur in the spectra of the Os(III) complexes. The band at $25\,000\text{cm}^{-1}$ in the spectrum of $[\text{Os(III)Cl}_5\text{py}]^{2-}$ (fig. 2.9) has been assigned as a $\text{Os(III)} \rightarrow \text{py}\pi^*$ C.T. transition (see section 2.2.2 and 2.2.3). In the spectrum of $[\text{Os py}_6]^{3+}$ (fig. 2.32) there is no charge transfer band at lower energy than the shoulder at $36\,000\text{cm}^{-1}$ on the $\text{py}\pi \rightarrow \text{py}\pi^*$ intraligand C.T. transitions. These two observations lead to the conclusion that as n increases the $\text{Os(III)}d\pi \rightarrow \text{py}\pi^*$ C.T. charge transfer bands are indeed shifted to higher energy. Assuming this shift is fairly regular, (about $2\,500\text{cm}^{-1}$ for each extra pyridine), we can make the following additional assignments:

Compound	$\nu_{\text{max}}(\text{cm}^{-1})$	Assignment
$t\text{-}[\text{Os(III)Cl}_4\text{py}_2]^-$	27 400	$\text{Os(III)}d\pi \rightarrow \text{py}\pi^*$
$c\text{-}[\text{Os(III)Cl}_4\text{py}_2]^-$	28 600	$\text{Os(III)}d\pi \rightarrow \text{py}\pi^*$

Using these arguments the following approximations can also be made regarding the likely position of the $\text{Os(III)}d\pi \rightarrow \text{py}\pi^*$ C.T. transitions in the complexes where these bands are masked by either $\text{Cl}^-\pi \rightarrow \text{Os(III)}d\pi$ or $\text{py}\pi \rightarrow \text{py}\pi^*$ C.T. transitions:

Compound	$\nu_{\max}(\text{cm}^{-1})$
$m\text{-[Os(III)Cl}_3\text{py}_3]$	30 500
$t\text{-[Os(III)Cl}_2\text{py}_4]^+$	33 000
$[\text{Os(III)Clpy}_5]^{2+}$	35 500
$[\text{Os(III)py}_6]^{3+}$	38 000

$\text{Cl}^-\pi \rightarrow \text{Os(III)}d\pi$ charge transfer transitions

Elucidating the position of these bands is more difficult than for the M.L.C.T. transitions discussed above since they occur at higher energy. The composition of these bands is also more complex since there are several allowed accessible $\text{Cl}^-\pi \rightarrow \text{Os(III)}d\pi$ transitions. However we can observe that the energy of these bands (as for the L.M.C.T. transitions in the Os(IV) complexes) is fairly independent of the number of pyridines around the complex. The bands tend to occur around $33\,000\text{cm}^{-1}$.

In some of the Os(III) spectra, weak bands at low energy were observed. These bands are assigned as metal based $d\pi \rightarrow d\pi$ transitions. An example of this can be seen in the spectrum of $[\text{Os(III)Clpy}_5]^{2+}$ (figure 2.28) where the band maximum is at $5\,700\text{cm}^{-1}$ ($\epsilon = \text{ca. } 300\text{ mol}^{-1}\text{cm}^{-1}\text{dm}^3$).

Thus the complete assignment for the bands in the observed spectra of all the species discussed is given in Table 2.8.

Table 2.9 Positions ($\nu_{\max}$) and Extinction Coefficients (ϵ) of Bands in the Electronic Absorption Spectra for the series $[\text{OsCl}_{(6-n)}\text{PY}_n]^{(n-Y)+}$ in CH_2Cl_2 / 0.5M $[\text{TBA}][\text{BF}_4]$.

Compound	$\nu_{\max}(\text{cm}^{-1})$	$\epsilon(\text{mol}^{-1}\text{cm}^{-1}\text{dm}^3)$	Assignment
$[\text{Os(V)Cl}_6]^-$	17 000	1 370	$\text{Cl}^- \pi \rightarrow \text{Os(V)} d\pi$
	19 870	4 220	$\text{Cl}^- \pi \rightarrow \text{Os(V)} d\pi$
	22 000	6 780	$\text{Cl}^- \pi \rightarrow \text{Os(V)} d\pi$
	24 000	6 780	$\text{Cl}^- \pi \rightarrow \text{Os(V)} d\pi$
	29 600	1 920	$\text{Cl}^- \pi \rightarrow \text{Os(V)} d\pi$
$[\text{Os(IV)Cl}_6]^{2-}$	23 800	900	$\text{Cl}^- \pi \rightarrow \text{Os(IV)} d\pi$
	26 700	8 410	$\text{Cl}^- \pi \rightarrow \text{Os(IV)} d\pi$
	29 200	11 370	$\text{Cl}^- \pi \rightarrow \text{Os(IV)} d\pi$
	33 600	1 250	$\text{Cl}^- \pi \rightarrow \text{Os(IV)} d\pi$
	35 800	1 090	$\text{Cl}^- \pi \rightarrow \text{Os(IV)} d\pi$
	39 000	2 240	$\text{Cl}^- \pi \rightarrow \text{Os(IV)} d\pi$
$[\text{Os(III)Cl}_6]^{3-}$	35 200	10 460	$\text{Cl}^- \pi \rightarrow \text{Os(III)} d\pi$
	37 600	10 210	$\text{Cl}^- \pi \rightarrow \text{Os(III)} d\pi$
$[\text{Os(V)Cl}_5\text{py}]$	22 900	12 580	$\text{Cl}^- \pi \rightarrow \text{Os(V)} d\pi$
	39 200	13 820	$\text{Cl}^- \pi \rightarrow \text{Os(V)} d\pi$

/ continued

Compound	$\nu_{\max}(\text{cm}^{-1})$	$\epsilon (\text{mol}^{-1}\text{cm}^{-1}\text{dm}^3)$	Assignment
[Os(IV)Cl ₅ py] ⁻	23 500	2 430	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	27 000	11 790	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	30 600	5 140	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	34 100	6 290	
	40 000	8 360	py $\pi \rightarrow$ py π^*
[Os(III)Cl ₅ py] ²⁻	25 000	4 930	Os(III) $\rightarrow$ py π^*
	33 600	6 960	Cl ⁻ $\pi \rightarrow$ Os(III)d π
	39 900	10 390	py $\pi \rightarrow$ py π^*
<i>t</i> -[Os(III)Cl ₄ py ₂] ⁻	27 400	12 500	Os(III) $\rightarrow$ py π^*
	31 400	13 150	Cl ⁻ $\pi \rightarrow$ Os(III)d π
	32 500	11 810	Cl ⁻ $\pi \rightarrow$ Os(III)d π
<i>t</i> -[Os(II)Cl ₄ py ₂] ²⁻	13 970	11 210	Os(II) $\rightarrow$ py π^*
	19 790	39 230	Os(II) $\rightarrow$ py π^*
<i>c</i> -[Os(IV)Cl ₄ py ₂]	22 400	2 110	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	26 300	3 240	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	35 400	5 480	
	38 300	6 030	py $\pi \rightarrow$ py π^*
<i>c</i> -[Os(III)Cl ₄ py ₂] ⁻	28 600	5 360	Os(III)d $\pi \rightarrow$ py π^*
	32 700	4 220	Cl ⁻ $\pi \rightarrow$ Os(III)d π
/ continued	40 400	6 090	py $\pi \rightarrow$ py π^*

Compound	$\nu_{\max}(\text{cm}^{-1})$	$\epsilon (\text{mol}^{-1}\text{cm}^{-1}\text{dm}^3)$	Assignment
$c\text{-}[\text{Os}(\text{II})\text{Cl}_4\text{py}_2]^{2-}$	13 550	5 190	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	19 460	12 660	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	23 500	10 710	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
$m\text{-}[\text{Os}(\text{IV})\text{Cl}_3\text{py}_3]^+$	27 500	10 810	$\text{Cl}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	38 700	12 200	$\text{py}\pi \rightarrow \text{py}\pi^*$
$m\text{-}[\text{Os}(\text{III})\text{Cl}_3\text{py}_3]$	31 700	9 690	$\text{Cl}^-\pi \rightarrow \text{Os}(\text{III})d\pi$
			$\text{Os}(\text{III})d\pi \rightarrow \text{py}\pi^*$
	40 900	8 440	$\text{py}\pi \rightarrow \text{py}\pi^*$
$m\text{-}[\text{Os}(\text{II})\text{Cl}_3\text{py}_3]^-$	17 120	6 350	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	22 830	14 530	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	40 200	10 580	$\text{py}\pi \rightarrow \text{py}\pi^*$
$t\text{-}[\text{Os}(\text{IV})\text{Cl}_2\text{py}_4]^{2+}$	27 200	5 070	$\text{Cl}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	39 100	14 220	$\text{py}\pi \rightarrow \text{py}\pi^*$
	42 600	13 040	$\text{py}\pi \rightarrow \text{py}\pi^*$
$t\text{-}[\text{Os}(\text{III})\text{Cl}_2\text{py}_4]^+$	33 500	11 650	$\text{Os}(\text{III})d\pi \rightarrow \text{py}\pi^*$
	42 800	10 920	$\text{py}\pi \rightarrow \text{py}\pi^*$
$t\text{-}[\text{Os}(\text{II})\text{Cl}_2\text{py}_4]$	19 160	8 890	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	24 800	17 640	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	40 800	14 400	$\text{py}\pi \rightarrow \text{py}\pi^*$

Compound	$\nu_{\max}(\text{cm}^{-1})$	$\epsilon(\text{mol}^{-1}\text{cm}^{-1}\text{dm}^3)$	Assignment
[Os(IV)Clpy ₅] ³⁺	27 600		Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	38 900		py $\pi \rightarrow$ py π^*
[Os(III)Clpy ₅] ²⁺	37 800		py $\pi \rightarrow$ py π^*
[Os(II)Clpy ₅] ⁺	21 500		Os(II)d $\pi \rightarrow$ py π^*
	26 500		Os(II)d $\pi \rightarrow$ py π^*
	40 800		py $\pi \rightarrow$ py π^*
[Os(III)py ₆] ³⁺	39 300	46 950	py $\pi \rightarrow$ py π^*
[Os(II)py ₆] ²⁺	23 100	11 450	Os(II)d $\pi \rightarrow$ py π^*
	27 900	20 620	Os(II)d $\pi \rightarrow$ py π^*
	40 300	46 400	py $\pi \rightarrow$ py π^*
Pyridine	39 200	1 790	py $\pi \rightarrow$ py π^*
	40 000	1 820	py $\pi \rightarrow$ py π^*

2.4 Experimental.

Throughout the course of this work C,H,N analysis was not used since the technique, in our experience, has proved unreliable for complexes containing osmium. Generally, to check the purity of a compound, its electrochemical response was examined. The electrochemical response of an electroactive species is a very sensitive indicator of purity, although it is recognised that this technique will not detect non-electroactive material.

$K_2[OsCl_6]$ and $[NH_4]_2[OsCl_6]$ were used as supplied by Johnson Matthey. The tetrabutylammonium salt, $[TBA]_2[OsCl_6]$, was obtained by metathesis. $K_2[OsCl_6]$ (1g) was dissolved in 1 molar hydrochloric acid (100ml). Tetrabutylammoniumhydroxide solution (40% by weight) was added dropwise until no further precipitation occurred. The fine yellow precipitate produced was dried under vacuum for 48 hours.

$[TBA][OsCl_5py]$ was prepared as follows. $[TBA]_2[OsCl_6]$ (0.05g) was dissolved in 10ml $CH_2Cl_2/0.1ml$ pyridine. When the solution had been degassed and was under nitrogen, an excess (0.02g) of cobaltacene was added and the solution stirred for 3 minutes. Excess cobaltacene was filtered off and the solution oxidised using $[NO][BF_4]$. Excess $[NO][BF_4]$ was filtered off and $[TBA][OsCl_5py]$ separated from $[CoCp_2][BF_4]$ using thin

layer chromatography. A silica gel plate, layer thickness 0.25mm, was eluted using CH_2Cl_2 . The more mobile yellow $[\text{TBA}][\text{OsCl}_5\text{py}]$ was dried under vacuum for 24 hours.

The preparation of *trans*- $[\text{TPA}][\text{OsCl}_4\text{py}_2]$ is shown below. $[\text{TBA}]_2[\text{OsCl}_6]$ (0.05g) in a $\text{CH}_2\text{Cl}_2/0.5\text{M}[\text{TBA}][\text{BF}_4]$ (7 ml)/ py (0.05ml) solution underwent a bulk electrolysis at -0.75V to yield $[\text{OsCl}_5\text{py}]^{2-}$. This solution was warmed under nitrogen for 96 hours at 310K yielding a mixture of *cis*- and *trans*- $[\text{OsCl}_4\text{py}_2]^-$. The solution then underwent a bulk electrooxidation at 0.8V to yield *cis*- $[\text{OsCl}_4\text{py}_2]$ (yellow solution) and *trans*- $[\text{OsCl}_4\text{py}_2]$ (orange solid). The orange solid was filtered off, suspended in 1:1 CH_2Cl_2 /methanol solution (2ml) and reduced chemically by addition of a 1:20 hydrazine hydrate/methanol mixture until the reduction was complete. Addition of 0.1ml $[\text{TPA}][\text{OH}]$ solution (20% by weight) to the yellow solution yielded small red crystals of *trans*- $[\text{TPA}][\text{OsCl}_4\text{py}_2]$.

In order to prepare *cis*- $[\text{OsCl}_4\text{py}_2]$, a solution of $[\text{Os(III)Cl}_5\text{py}]^{2-}$ in $\text{CH}_2\text{CH}_2/\text{py}$ was prepared as in the synthesis of $[\text{TBA}][\text{Os(IV)Cl}_5\text{py}]^-$ above. This blood orange solution was warmed at 310K under nitrogen for 96 hours. The resulting pale orange solution of *cis*- and *trans*- $[\text{OsCl}_4\text{py}_2]^-$ was oxidised using $[\text{NO}][\text{BF}_4]$. The solid material, *trans*- $[\text{OsCl}_4\text{py}_2]$ and excess $[\text{NO}][\text{BF}_4]$, was removed and the resulting yellow solution was purified by thin layer chromatography (as above). Orange crystals of *cis*- $[\text{OsCl}_4\text{py}_2]$ were obtained upon recrystallisation,

specifically solvent diffusion from a CH_2Cl_2 /diethylether mixture.

mer- $[\text{OsCl}_3\text{py}_3]$ was prepared by heating $\text{K}_2[\text{OsCl}_6]$ (0.25g) in a glycerol (2.5 ml)/ pyridine (0.5ml) mixture, under nitrogen at 360K for three hours. The mixture was poured onto cold water (15ml). The resulting solid material was filtered off and purified using thin layer chromatography (as above). Dark orange crystals can be obtained upon crystallisation from either CH_2Cl_2 /hexane or CH_2Cl_2 /diethylether mixtures.

trans- $[\text{OsCl}_2\text{py}_4]$ was made by heating $[\text{OsCl}_3\text{py}_3]$ (0.2g) to 380K in a 5:1 glycerol/pyridine mixture (2ml) and adding $\text{Na}[\text{BH}_4]$ (0.02g). After 30 minutes the mixture was poured onto cold water and the resulting solid material purified by thin layer chromatography (as above). Dark purple crystals of *trans*- $[\text{OsCl}_2\text{py}_4]$ were produced from a 20:20:1 CH_2Cl_2 /methanol/hydrazine hydrate (to avoid oxidation) solution. A F.A.B. mass spectrum of these crystals showed a peak at $m/z = 578$. This corresponds to the parent ion $[\text{OsCl}_2\text{py}_4]^+$. The spectrum exhibited the complex isotopic distribution expected for a complex containing both osmium and chloride. Details are given in table 2.10.

$[\text{OsClpy}_5][\text{PFTPb}]$ was prepared by heating $\text{K}_2[\text{OsCl}_6]$ (0.5g) in a pyridine (1ml) / ethanediol (5ml) mixture at 450K for 3 hours under N_2 . The resulting mixture was poured onto a solution of hydrazine hydrate in water. All

solid material precipitated (mainly $[\text{OsCl}_2\text{py}_4]$) was filtered off and the filtrate treated with a saturated solution of lithium tetrakis-(pentafluorophenyl) borate. The resulting psychedelic orange solid was filtered and purified using thin layer chromatography (as above). Small red/orange crystals were produced from a 10:20:1 CH_2Cl_2 /methanol/hydrazine hydrate solution. A F.A.B. mass spectrum of these crystals showed a peak corresponding to the parent ion, $[\text{OsClpy}_5]^+$, at $m/z = 622$. Further details are given in table 2.10.

$[\text{OsPy}_6][\text{BF}_4]_2$ was prepared by heating $[\text{NH}_4]_2[\text{OsCl}_6]$ (0.5g), zinc dust (0.5g) and sodium tetrafluoroborate (0.5g) in pyridine (10ml) at 390K for 150 hours. When the mixture was filtered, stirred with 2ml water (to remove any sodium chloride or zinc chloride), filtered again and washed with water (2 x 1ml) and diethylether (2 x 5ml), a yellow orange powder of $[\text{OsPy}_6][\text{BF}_4]_2$ was obtained. Small yellow crystals were produced by allowing a solution of the orange powder in nitromethane to evaporate.

Tetrabutylammonium-tetrafluoroborate $[\text{TBA}][\text{BF}_4]$ was prepared by slowly adding tetrafluoroboric acid (30 ml, 30% solution) to tetrabutylammonium hydroxide (100 ml, 40% by weight), stirring and diluting as required. The pH of the solution was monitored using pH paper. When the pH of the solution was between 7-5, the white solid material produced was filtered and washed with distilled water (4 x 30ml). The product was recrystallised by dissolving

Table 2.10 Mass-spectral¹ data for the complexes [OsCl₂py₄] and [PFTFB][OsClpy₅].²

Complex	Mass number of peak(m/z)	Probable ion
[OsCl ₂ py ₄]	578	[OsCl ₂ py ₄] ⁺
	499	[OsCl ₂ py ₃] ⁺
	420	[OsCl ₂ py ₂] ⁺
[OsClpy ₅] ⁺	622	[OsClpy ₅] ⁺
	543	[OsClpy ₄] ⁺
	464	[OsClpy ₃] ⁺

¹ Both spectra were recorded using 3-nitro-benzyl alcohol as the matrix.

² The spectra both showed complex isotopic distribution.

in a hot water/methanol mixture, performing a hot filtration and leaving to cool. The resulting white needle crystals were then filtered and dried *in vacuo* at 80°C for 48 hours.

Methylene chloride CH₂Cl₂ was purified by storing over KOH for two weeks followed by reflux and distillation over P₂O₅. All other solvents and materials were used as supplied.

Electrochemical and spectroelectrochemical

measurements were performed using the methods and equipment described in appendix 1.

2.5 References

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Chapter 3. Introduction; synthesis, electrochemistry and spectroelectrochemistry of some members of the series: $[\text{OsBr}_{6-n}\text{PY}_n]^{(n-Y)+}$ and $[\text{OsI}_{6-n}\text{PY}_n]^{(n-Y)+}$; discussion of the electrochemical and spectroelectrochemical data; experimental.

'I am never merry when I hear sweet music'.
'The reason is, your spirits are attentive:
The man that hath no music in himself,
Nor is not moved with concord of sweet sounds,
Is fit for treasons, stratagems and spoils;
The motions of his spirit are dull as night,
And his affections dark as Erebus:
Let no such man be trusted'.

William Shakespeare

(The Merchant of Venice, Act V Scene I)

3.1 Introduction.

In the previous chapter electrochemical and spectral data for complexes of the type $[\text{OsCl}_{6-n}\text{py}_n]^{(n-Y)+}$ were examined. A useful method of extending the ligand additivity model discussed, as well as to clarify some band assignments in the electronic spectra (notably for the Os(III) complexes), was to change either the halide or the pyridine ligands by another ligand. This chapter relates the replacement of chloride by bromide and iodide.

Complexes of the form $[\text{OsBr}_{6-n}\text{py}_n]^{(n-Y)+}$, where $n = 0, 1, 2$ (*cis* and *trans* isomers), 3 (*mer*), 4 (*trans*), and $[\text{OsI}_{6-n}\text{py}_n]^{(n-Y)+}$, where $n = 0, 1, 3$ (*mer*), 4 (*trans*) and $y = 2$ to 4, have been prepared. These sets of compounds follow roughly the same reaction scheme as the $[\text{OsCl}_{6-n}\text{py}_n]^{(Y-n)-}$ series, however since bromide and iodide are more labile ligands than chloride, milder reaction conditions were generally required to effect the reactions. The redox behaviour of all the complexes is analysed using ligand additivity arguments. Bands in the electronic u.v/vis. spectra of the complexes, obtained from the spectroelectrochemical studies, are assigned and the spectra of related complexes are compared.

3.2.1 Electrochemistry and spectroelectrochemistry of $[\text{OsBr}_6]^{2-}$ $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 230K.

The electrochemical properties of tetrabutylammonium hexabromoosmate(IV) ($[\text{TBA}]_2[\text{OsBr}_6]$), II^{2-} , in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 230K were studied using the methods described in Appendix 1. A cyclic voltammogram (fig. 3.1) of II^{2-} shows a reductive step at -0.36V (process A) and an oxidative process at 1.38V (Process B). Both redox steps are reversible at this temperature, and a coulometric examination showed that both steps involved one electron. The Os(IV) metal centre is considered to be the redox-active site for both processes. Hence the reduction step produces $[\text{Os(III)Br}_6]^{3-}$, (II^{3-}), and the oxidation $[\text{Os(V)Br}_6]^-$, (II^-).

The electronic u.v./vis. spectra of II^{2-} , II^{3-} and II^- were obtained under similar conditions using the O.T.T.L.E. The spectrum of blood red $[\text{OsBr}_6]^{2-}$ contains two groups of bands (C) and (D) (fig. 3.2). Group (C) have been assigned as $\text{Br}^-(\pi) \rightarrow \text{Os(IV)}d\pi \ 2t_{2g}$ transitions, while Group (D) involves $\text{Br}^-(\pi) \rightarrow \text{Os(IV)}d\sigma \ 2e_g$ transitions.¹ We would not agree with the latter assignment. The difference in energy between the two sets of bands provides a measure of Δ (the difference in energy between the t_{2g} and e_g metal based d orbitals). The difference in energy between group C and D is only ca. $20\ 000\text{cm}^{-1}$, whereas we know the Δ value for Os(IV)

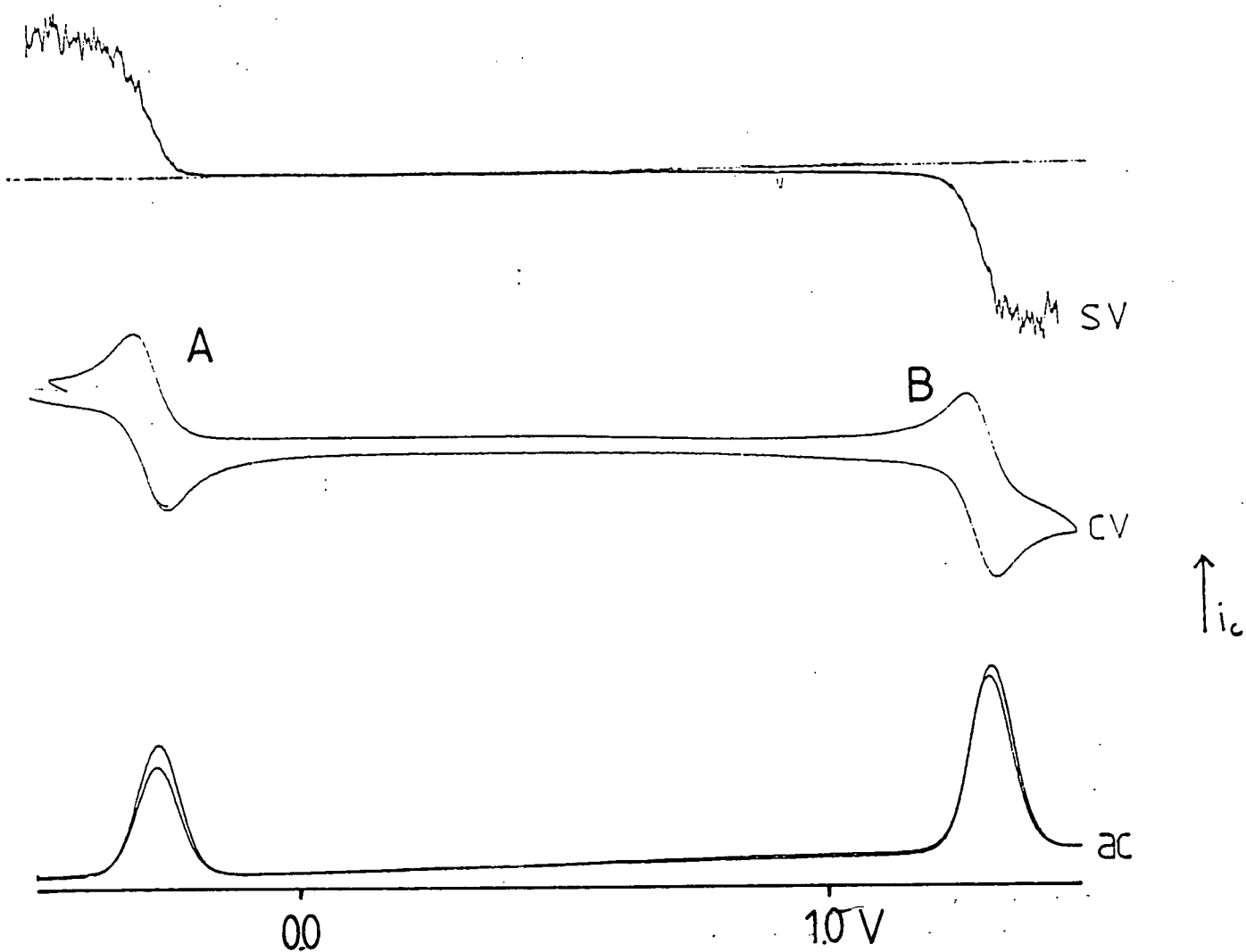


Figure 3.1 Cyclic, A.C. and Stirred Voltammograms of $[\text{OsBr}_6]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 230K.

complexes to be around $30\,000\text{cm}^{-1}$. Hence we would also assign group D as $\text{Br}^-\pi \rightarrow \text{Os(IV)}d\pi$ C.T. transitions. The spectra of yellow $[\text{Os(III)Br}_6]^{3-}$ (fig. 3.3) and $[\text{Os(V)Br}_6]^-$ (fig. 3.4) contain bands of similar extinction coefficient at higher and lower energy respectively. These observations are consistent with the energetic changes we would expect for L.M.C.T. transitions upon oxidation or reduction of the metal. The spectra are compared with their chloride and iodide analogues in section 3.3.2.

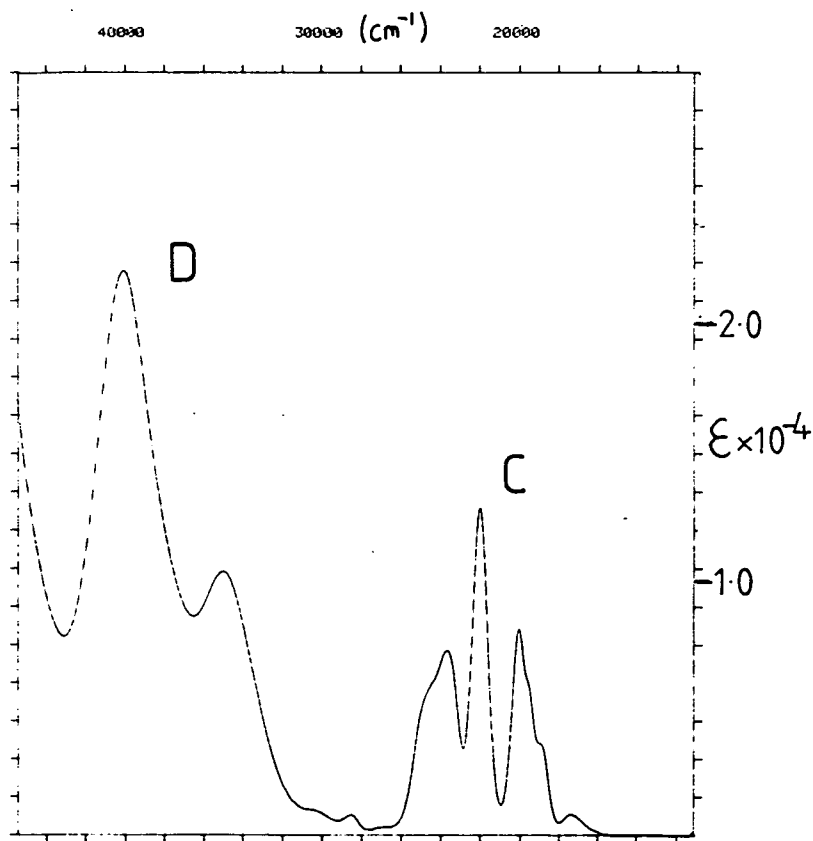


Figure 3.2 U.V./Vis. Absorption Spectrum of $[\text{OsBr}_6]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 230K.

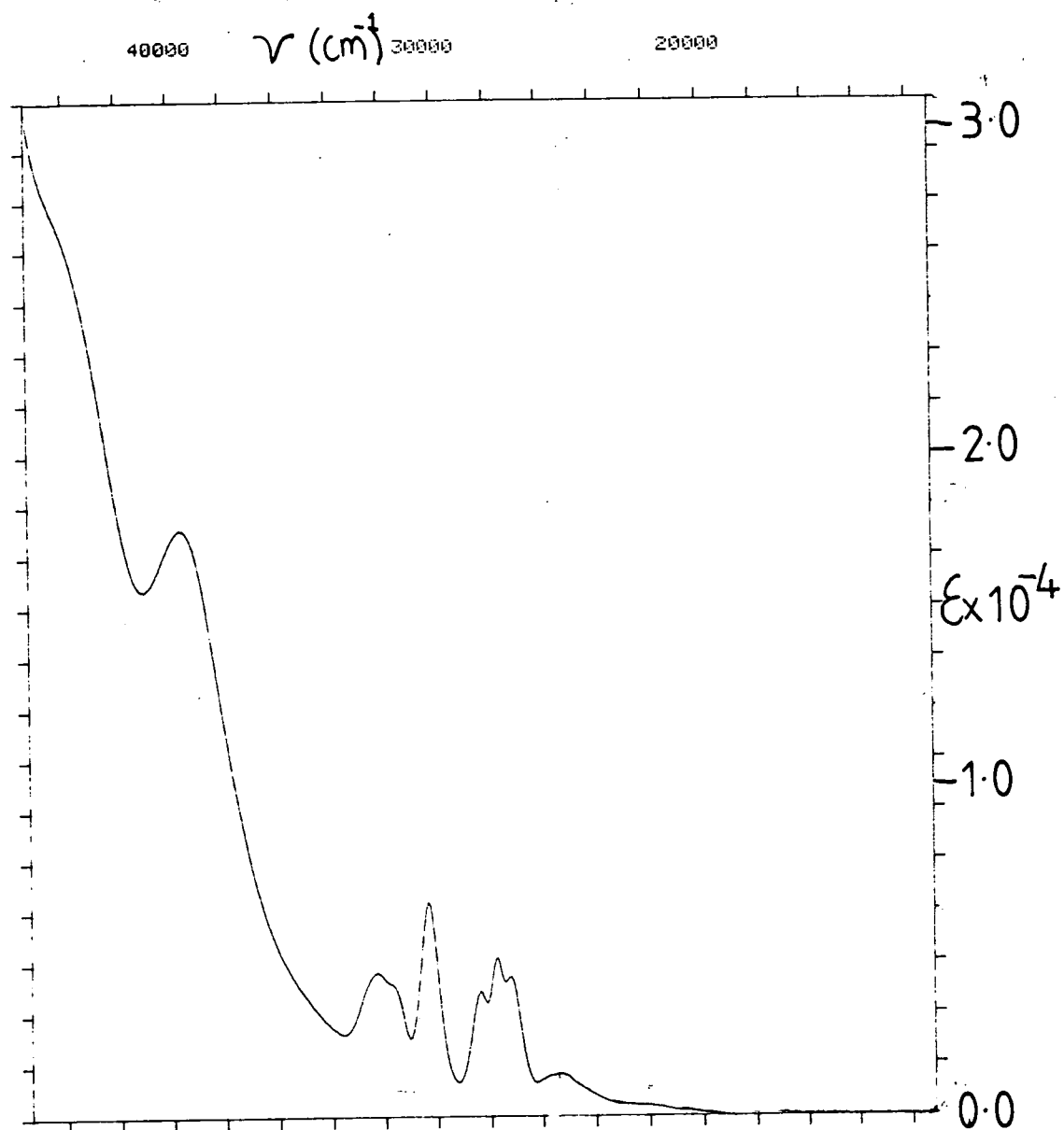


Figure 3.3 U.V./Vis. Absorption Spectrum of $[\text{OsBr}_6]^{3-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 230K.

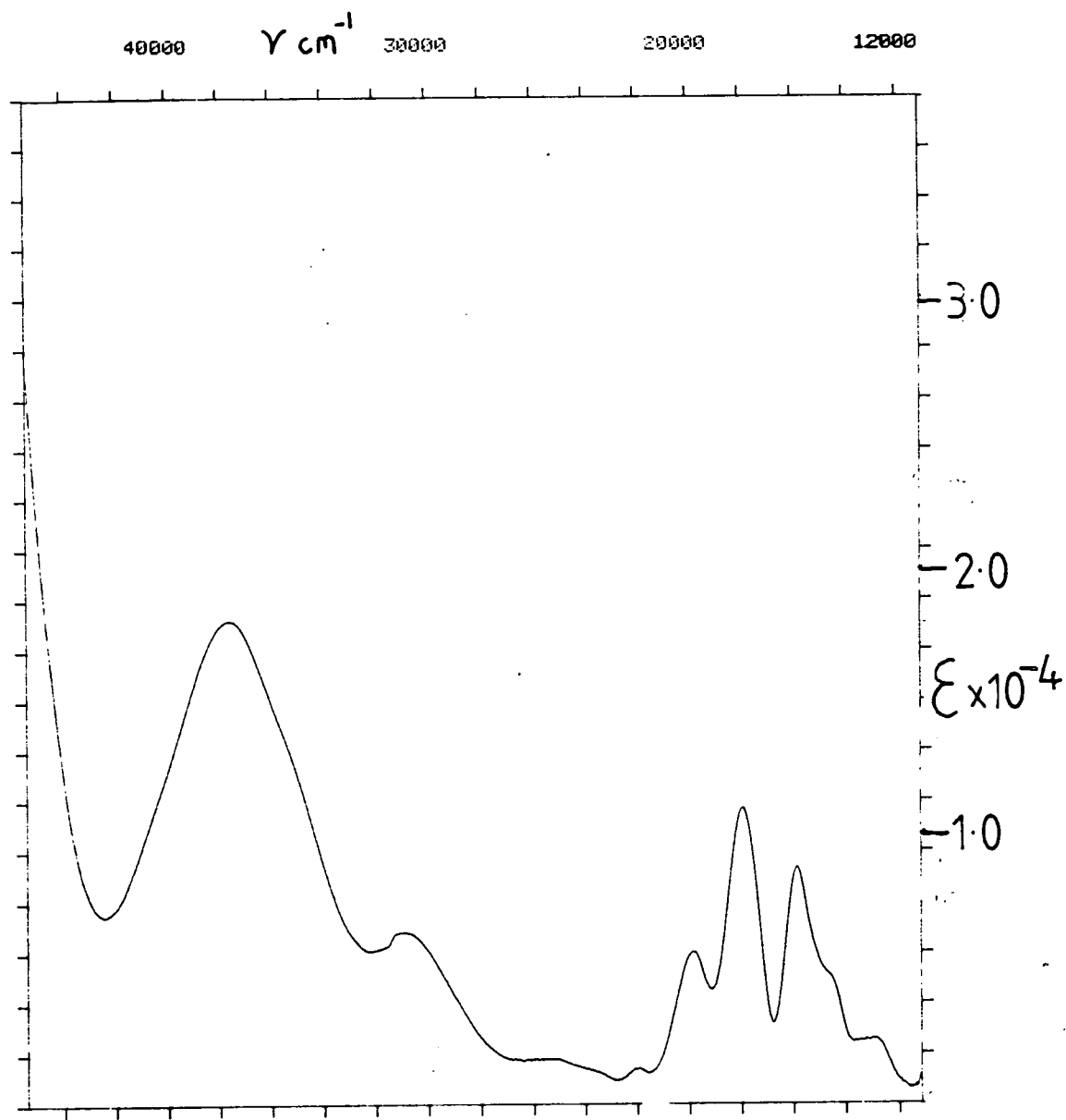


Figure 3.4 U.V./Vis. Absorption Spectrum of $[\text{OsBr}_6]^-$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 230K.

3.2.2 Preparation, Electrochemistry and Spectroelectrochemistry of [TBA][OsBr₅py]

The reductive substitution of [TBA]₂[OsBr₆] was performed by a bulk electrolysis at -0.6V in CH₂Cl₂/0.5M[TBA][BF₄] doped with 10 molar equivalents of pyridine at 290K. The resulting [Os(III)Br₅py]²⁻ was oxidised at 0.3V to the air stable [Os(IV)Br₅py]⁻, which was subsequently purified by thin layer chromatography.

Cyclic voltammetry and a.c.voltammetry of [TBA][OsBr₅py] in CH₂Cl₂/0.5M[TBA][BF₄] at 290K shows a reversible reduction at +0.10V and a reversible oxidation at 1.72V. Stirred voltammetry reveals that both steps involved similar number of electrons. An irreversible reduction was also observed at -1.42V. All processes are assumed to be metal based and to involve one electron.

The spectroelectrochemical reduction of [OsBr₅py]⁻ was undertaken in CH₂Cl₂/0.5M[TBA][BF₄] at 270K at the O.T.T.L.E. The bands at lowest energy (E) in the spectrum of purple [OsBr₅py]⁻, by comparison with [OsCl₅py]⁻ and [OsBr₆]²⁻, must correspond to Br⁻(π) $\rightarrow$ Osd π L.M.C.T. transitions (fig. 3.5). This spectrum shows good agreement with a sample prepared in the literature by the photolysis of [OsBr₆]²⁻ in pyridine³. Upon reduction to red [OsBr₅py]²⁻ we would predict that these L.M.C.T. transitions would move to higher energy, also, by analogy with [OsCl₅py]²⁻, we would also expect an Os(III)d $\pi \rightarrow$ py π^*

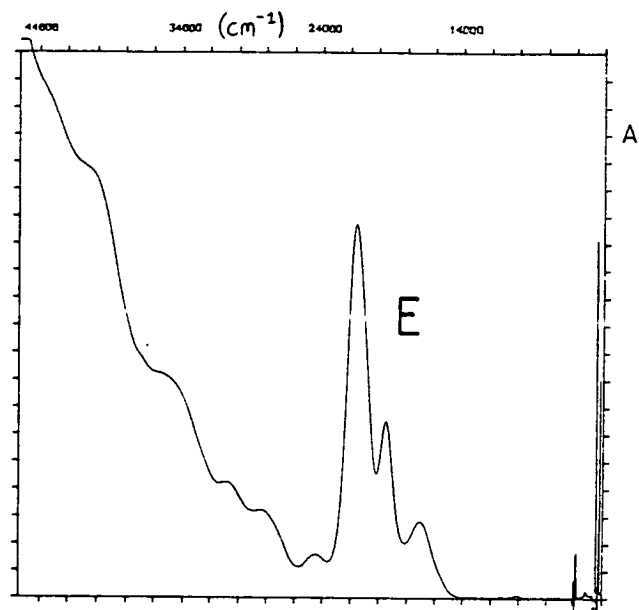


Figure 3.5 U.V./Vis. Absorption Spectrum of $[\text{OsBr}_5\text{py}]^-$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 270K.

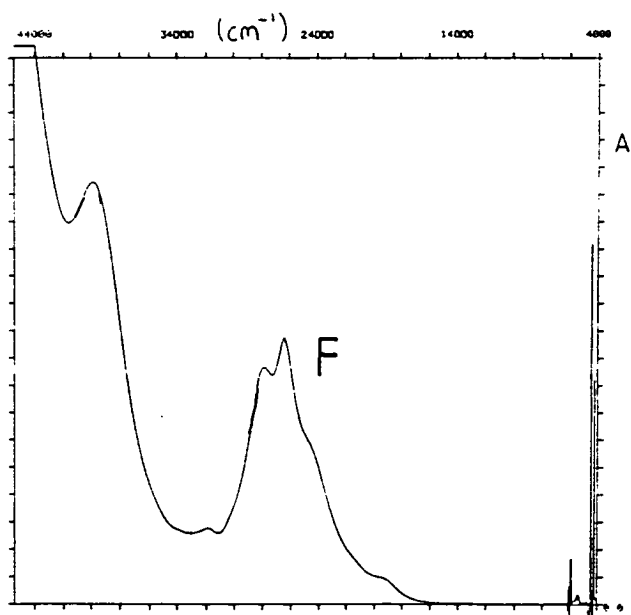


Figure 3.6 U.V./Vis. Absorption Spectrum of $[\text{OsBr}_5\text{py}]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 270K.

M.L.C.T. Reasoning thus, the bands (F) in the spectrum of $[\text{OsBr}_5\text{py}]^{2-}$ (fig. 3.6) are assigned as a superposition of $\text{Br}^-(\pi) \rightarrow \text{Os(III)}\pi$ and $\text{Os(III)}\pi \rightarrow \text{py}\pi^*$ transitions.

3.2.3 Preparation and Electrochemistry of *trans*- $[\text{OsBr}_4\text{py}_2]$

A bulk electrolysis of $[\text{TBA}]_2[\text{OsBr}_6]$ was performed at -0.6V at 290K in $\text{CH}_2\text{Cl}_2/0.5\text{M}[\text{TBA}][\text{BF}_4]$ doped with a 10 molar equivalent of pyridine. The solution of $[\text{OsBr}_5\text{py}]^{2-}$ was stored for 24 hours under N_2 at 300K. The resulting solution was oxidised at 0.8V yielding a dark turquoise solid, assigned as *trans*- $[\text{Os(IV)Br}_4\text{py}_2]$ by comparison with the insoluble *trans*- $[\text{Os(IV)Cl}_4\text{py}_2]$, and a violet-blue solution which contained mainly *cis*- $[\text{Os(IV)Br}_4\text{py}_2]$.

Cyclic and a.c. voltammetric studies on *trans*- $[\text{OsBr}_4\text{py}_2]^-$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 290K showed two reversible one-electron oxidations at 0.60V and 2.20V and a reversible reduction at -0.96V.

3.2.4 Preparation, Electrochemistry and Spectroelectrochemistry of *cis*- $[\text{OsBr}_4\text{py}_2]$

A blue/violet solution of *cis*- $[\text{OsBr}_4\text{py}_2]$ was prepared in the fashion described above and purified using thin layer chromatography.

Cyclic voltammetry and a.c.voltammetry of

cis-[OsBr₄py₂] in CH₂Cl₂/0.5M [TBA][BF₄] at 290K revealed a reversible oxidation at +2.15V and two one-electron reductions at +0.60V and -0.83V.

Spectroelectrochemical reductions of *cis*-[OsBr₄py₂] in CH₂Cl₂/0.5M [TBA][BF₄] were performed at the O.T.T.L.E. The low energy bands (G) in the spectrum of *cis*-[Os(IV)Br₄py₂] (fig. 3.7), by analogy with [OsBr₅py]⁻, are assigned as Br⁻(π) $\rightarrow$ Os(IV)d π transitions. The spectrum of *cis*-[Os(III)Br₄py₂]⁻ (fig. 3.8) shows bands (H) which, by comparison with [OsBr₅py]²⁻, can be seen to be a superposition of Br⁻(π) $\rightarrow$ Os(III)d π and Os(III) $\rightarrow$ py π^* charge transfer transitions. The low energy bands (I) in the electronic absorption spectrum of *cis*-[Os(II)Br₄py₂]²⁻ (fig. 3.9) are assigned as Os(II)d π $\rightarrow$ py π^* M.L.C.T transitions, since the metal contains a full t_{2g}⁶ subshell, and closely resemble the analogous bands in the spectrum of *cis*-[OsCl₄py₂]²⁻.

3.2.5. Preparation, X-ray Crystal Structure, Electrochemistry and Spectroelectrochemistry of *mer*-[OsBr₃py₃]

[NH₄]₂[OsBr₆] was heated in a 5:1 glycerol/pyridine mixture at 380K for two hours. The resulting *mer*-[OsBr₃py₃] was purified by thin layer chromatography and recrystallised from a CH₂Cl₂/diethylether mixture.

The X-ray crystal structure confirmed the pyridine

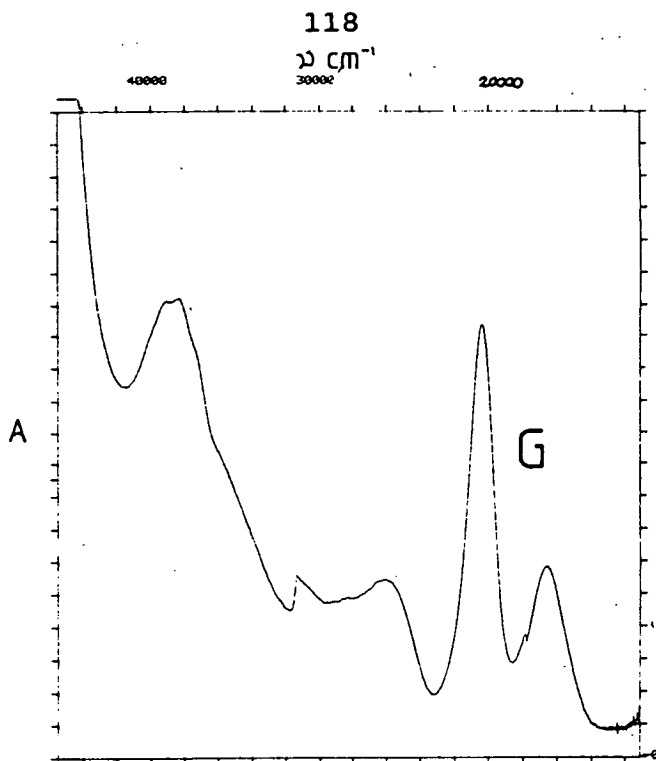


Figure 3.7 U.V./Vis. Absorption Spectrum of *cis*-[OsBr₄py₂] in CH₂Cl₂/0.5M [TBA][BF₄] at 230K.

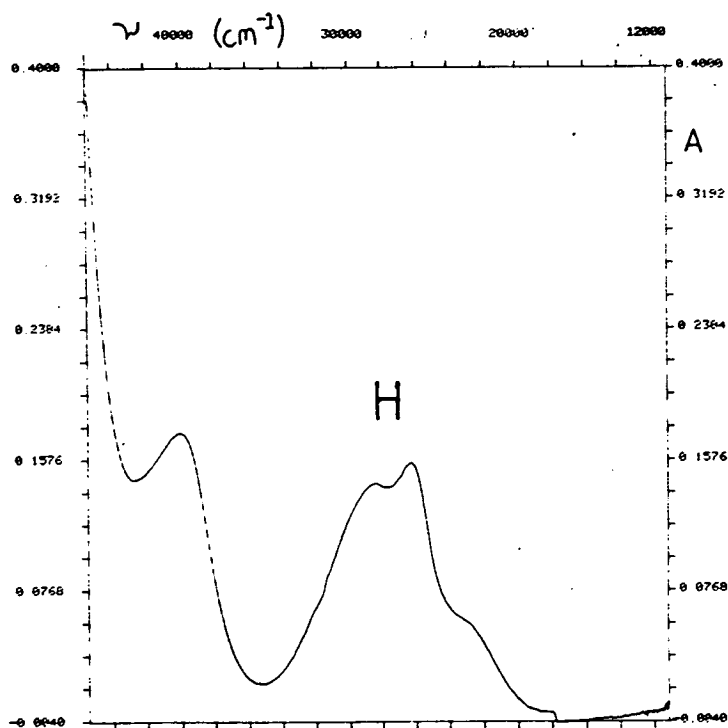


Figure 3.8 U.V./Vis. Absorption Spectrum of *cis*-[OsBr₄py₂]⁻ in CH₂Cl₂/0.5M [TBA][BF₄] at 230K.

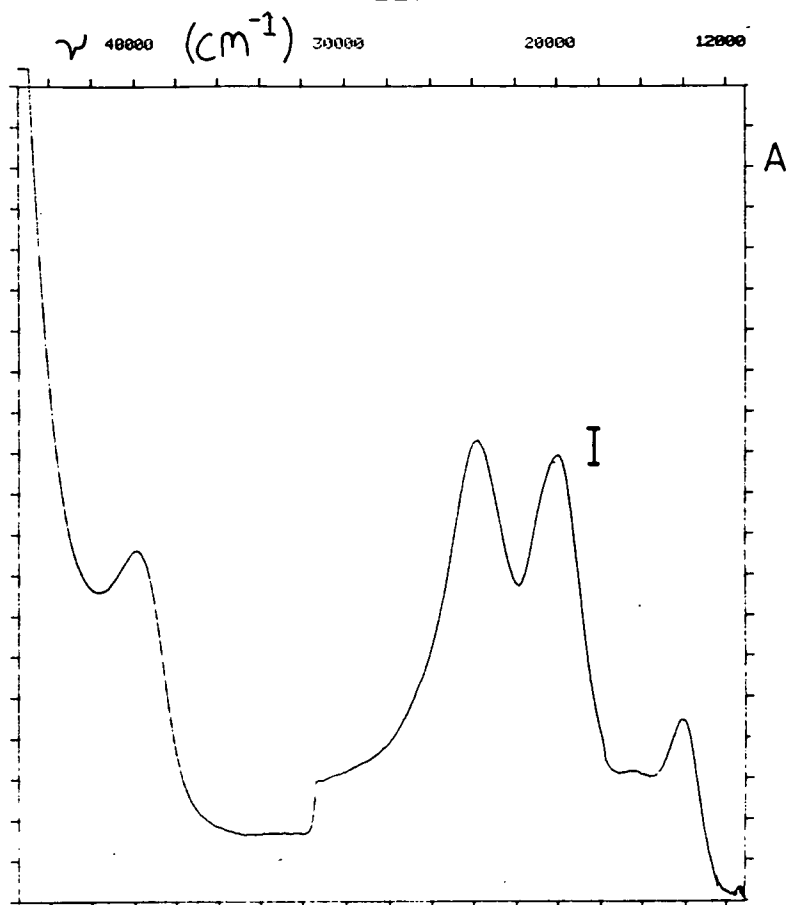


Figure 3.9 U.V./Vis. Absorption Spectrum of $\text{cis-}[\text{OsBr}_4\text{py}_2]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 230K.

ligands were in the *mer*-configuration. The pyridine rings were tilted out of the plane as illustrated in figure 3.10. The molecule exhibits an average Os-Br and Os-N bond lengths of 2.51Å and 2.12Å respectively. A full list of bond lengths, angles and selected torsion angles is given in table 3.1. These bond lengths compare with average Os-Cl and Os-N bond lengths of 2.36Å and 2.09Å exhibited in *mer*- $[\text{OsCl}_3\text{py}_3]$.⁴ The Os-N distance is shorter in *mer*- $[\text{OsBr}_3\text{py}_3]$ since Br^- is a poorer π -donor than Cl^- and hence less electron density is available for

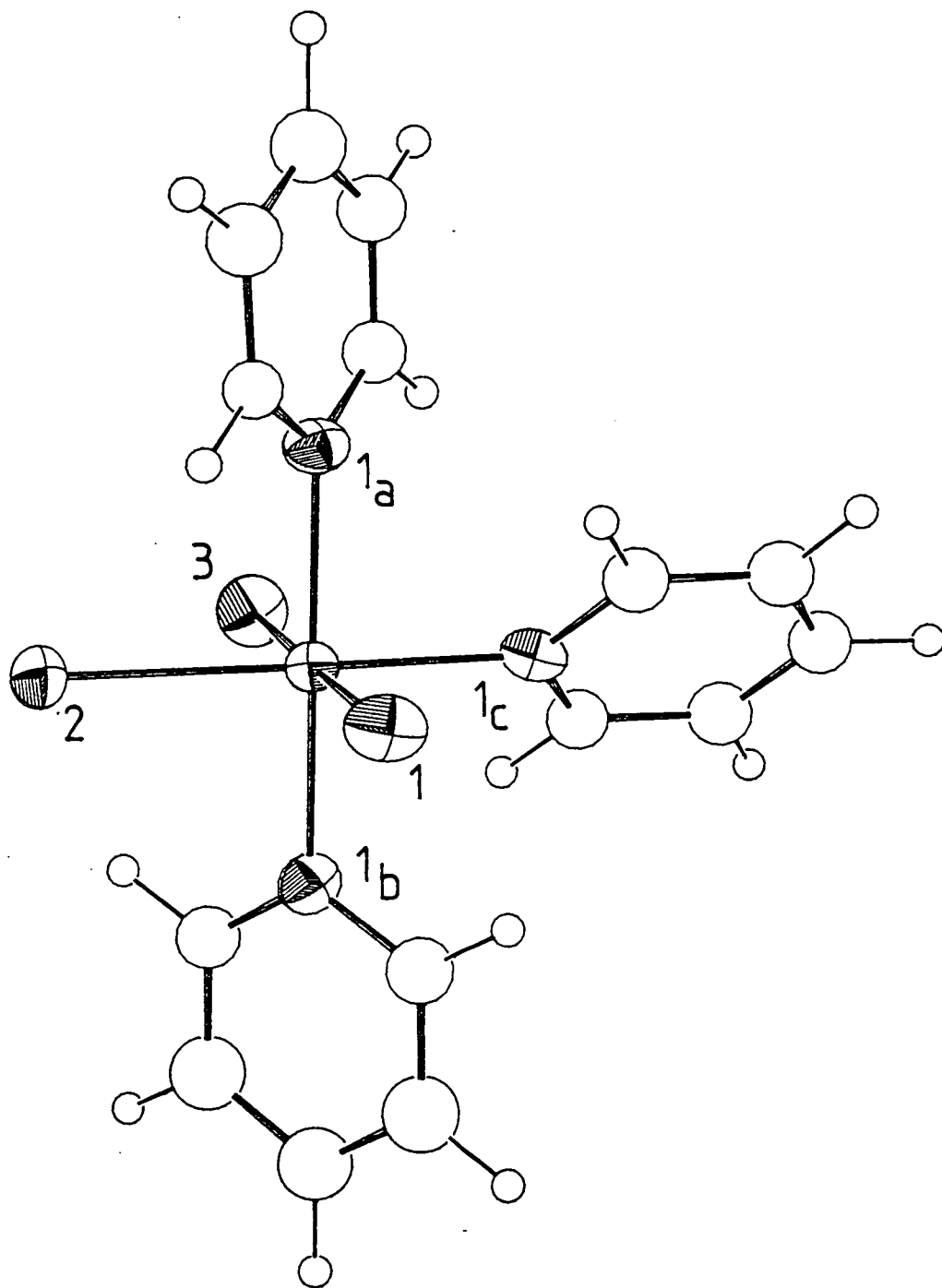


Figure 3.10 View of *mer*-[OsBr₃py₃].

Table 3.1 Bond Lengths (Å), Angles and Selected Torsion Angles (degrees) with Standard Deviations for [OsBr₃py₃].

Os -Br(1)	2.5054(11)	N(1B) -C(2B)	1.329(13)
Os -Br(2)	2.5164(11)	N(1B) -C(6B)	1.363(13)
Os -Br(3)	2.4991(12)	C(2B) -C(3B)	1.372(16)
Os -N(1A)	2.102(8)	C(3B) -C(4B)	1.391(16)
Os -N(1B)	2.111(8)	C(4B) -C(5B)	1.333(17)
Os -N(1C)	2.108(8)	C(5B) -C(6B)	1.396(16)
N(1A) -C(2A)	1.373(12)	N(1C) -C(2C)	1.360(13)
N(1A) -C(6A)	1.363(12)	N(1C) -C(6C)	1.353(14)
C(2A) -C(3A)	1.351(14)	C(2C) -C(3C)	1.391(15)
C(3A) -C(4A)	1.381(15)	C(3C) -C(4C)	1.368(16)
C(4A) -C(5A)	1.389(16)	C(4C) -C(5C)	1.354(15)
C(5A) -C(6A)	1.366(14)	C(5C) -C(6C)	1.367(15)
Br(1) - Os -Br(2)	91.77(4)	C(3A) -C(4A) -C(5A)	118.0(10)
Br(1) - Os -Br(3)	178.55(4)	C(4A) -C(5A) -C(6A)	119.9(10)
Br(1) - Os -N(1A)	90.00(21)	N(1A) -C(6A) -C(5A)	121.8(9)
Br(1) - Os -N(1B)	90.09(23)	Os -N(1B) -C(2B)	122.7(7)
Br(1) - Os -N(1C)	89.50(23)	Os -N(1B) -C(6B)	119.1(7)
Br(2) - Os -Br(3)	89.68(4)	C(2B) -N(1B) -C(6B)	118.1(9)
Br(2) - Os -N(1A)	90.13(21)	N(1B) -C(2B) -C(3B)	123.8(10)
Br(2) - Os -N(1B)	90.02(23)	C(2B) -C(3B) -C(4B)	117.8(10)
Br(2) - Os -N(1C)	178.51(23)	C(3B) -C(4B) -C(5B)	119.2(11)
Br(3) - Os -N(1A)	90.07(21)	C(4B) -C(5B) -C(6B)	121.2(11)
Br(3) - Os -N(1B)	89.84(23)	N(1B) -C(6B) -C(5B)	119.8(10)
Br(3) - Os -N(1C)	89.05(23)	Os -N(1C) -C(2C)	119.3(6)
N(1A) - Os -N(1B)	179.8(3)	Os -N(1C) -C(6C)	122.1(7)
N(1A) - Os -N(1C)	89.1(3)	C(2C) -N(1C) -C(6C)	118.5(9)
N(1B) - Os -N(1C)	90.7(3)	N(1C) -C(2C) -C(3C)	119.8(9)
Os -N(1A) -C(2A)	121.5(6)	C(2C) -C(3C) -C(4C)	120.6(10)
Os -N(1A) -C(6A)	120.7(6)	C(3C) -C(4C) -C(5C)	118.9(10)
C(2A) -N(1A) -C(6A)	117.7(8)	C(4C) -C(5C) -C(6C)	120.0(10)
N(1A) -C(2A) -C(3A)	121.8(9)	N(1C) -C(6C) -C(5C)	122.2(10)
C(2A) -C(3A) -C(4A)	120.6(10)		
C(6A) -N(1A) -C(2A) -C(3A)	0.1(14)	C(2B) -C(3B) -C(4B) -C(5B)	-2.5(17)
C(2A) -N(1A) -C(6A) -C(5A)	1.2(14)	C(3B) -C(4B) -C(5B) -C(6B)	1.5(19)
N(1A) -C(2A) -C(3A) -C(4A)	-0.5(16)	C(4B) -C(5B) -C(6B) -N(1B)	0.4(18)
C(2A) -C(3A) -C(4A) -C(5A)	-0.4(16)	C(6C) -N(1C) -C(2C) -C(3C)	1.2(14)
C(3A) -C(4A) -C(5A) -C(6A)	1.6(16)	C(2C) -N(1C) -C(6C) -C(5C)	-0.9(15)
C(4A) -C(5A) -C(6A) -N(1A)	-2.0(15)	N(1C) -C(2C) -C(3C) -C(4C)	-0.8(16)
C(6B) -N(1B) -C(2B) -C(3B)	-0.1(16)	C(2C) -C(3C) -C(4C) -C(5C)	0.1(17)
C(2B) -N(1B) -C(6B) -C(5B)	-1.1(15)	C(3C) -C(4C) -C(5C) -C(6C)	0.3(17)
N(1B) -C(2B) -C(3B) -C(4B)	1.9(17)	C(4C) -C(5C) -C(6C) -N(1C)	0.2(17)

donation into the low lying $\text{py}\pi^*$ orbitals. The rings are tilted in a similar fashion in each structure, the rings being tilted out of the N_3 plane by 48.3, 47.6 and 42.7 degrees in $\text{mer-}[\text{OsBr}_3\text{py}_3]$.

Cyclic voltammetry and a.c.voltammetry of $\text{mer-}[\text{OsBr}_3\text{py}_3]$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 290K showed two reversible redox steps, an oxidative process at +1.17V and a reductive step at -0.42V. A coulometric study revealed that both processes involved one electron.

A spectroelectrochemical examination of orange $\text{mer-}[\text{OsBr}_3\text{py}_3]$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K was undertaken. The spectrum of green $\text{mer-}[\text{Os(II)Br}_3\text{py}_3]^-$ (fig. 3.11) is dominated by bands that must be attributed to $\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$ transitions (H) since the t_{2g}^6 metal subshell is fully occupied. These M.L.C.T transitions move to higher energy on oxidation to $\text{mer-}[\text{Os(III)Br}_3\text{py}_3]$ and are superimposed by $\text{Br}^-(\pi) \rightarrow \text{Os(III)}d\pi$ transitions in band (I) in the electronic absorption spectrum (fig. 3.12). The absorption spectrum of $\text{mer-}[\text{Os(IV)Br}_3\text{py}_3]^+$ (fig. 3.13) contains bands at lower energy (J) than any observed in the $\text{mer-}[\text{Os(III)Br}_3\text{py}_3]$ spectrum and must therefore be assigned as $\text{Br}^-(\pi) \rightarrow \text{Os(IV)}d\pi$ L.M.C.T. transitions.

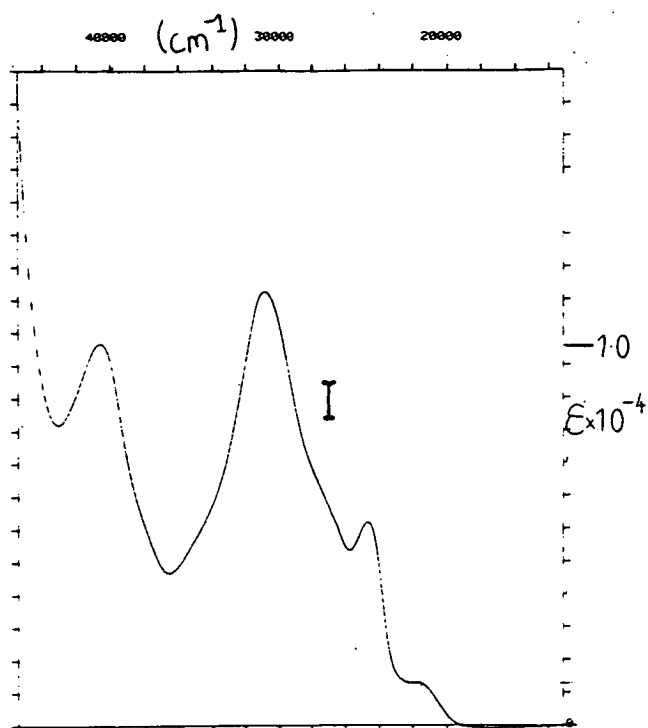


Figure 3.11 U.V./Vis. Absorption Spectrum of $\text{mer-}[\text{OsBr}_3\text{py}_3]$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K.

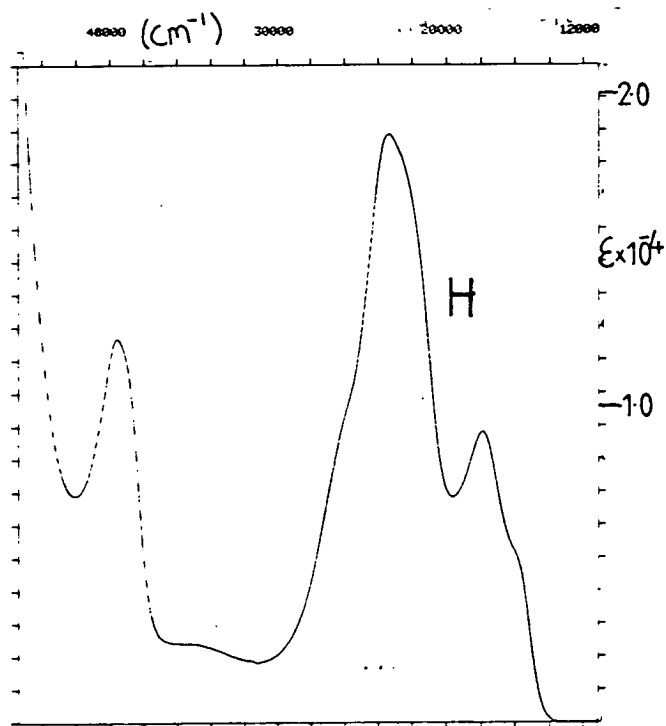


Figure 3.12 U.V./Vis. Absorption Spectrum of $\text{mer-}[\text{OsBr}_3\text{py}_3]^-$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K.

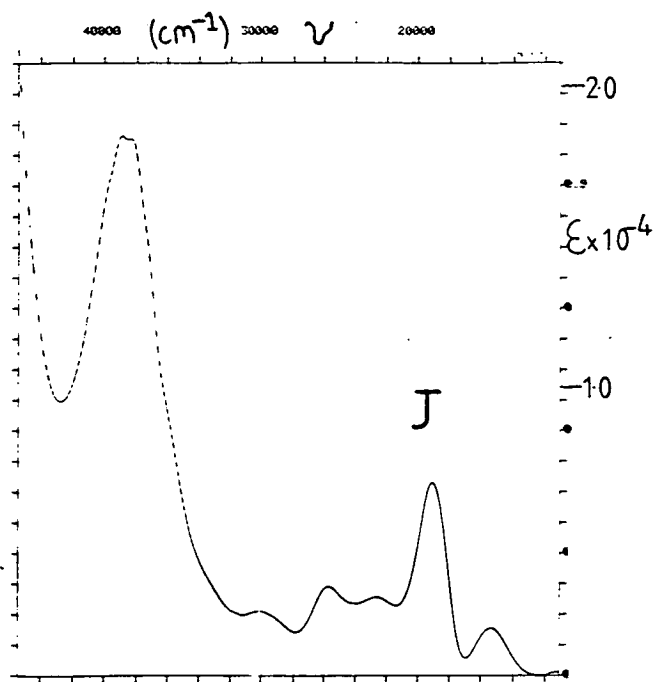


Figure 3.13 U.V./Vis. Absorption Spectrum of $\text{mer-}[\text{OsBr}_3\text{py}_3]^+$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K.

3.2.6 Preparation, Electrochemistry and Spectroelectrochemistry of $\text{trans-}[\text{OsBr}_2\text{py}_4]$

A suspension of $[\text{NH}_4]_2[\text{OsBr}_6]$ in a 5:1 glycerol/pyridine mixture was heated at 380K for three hours whereupon an equimolar amount of $\text{Na}[\text{BH}_4]$ was added. Thin layer chromatography was used to purify the resulting $\text{trans-}[\text{OsBr}_2\text{py}_4]$ which could be recrystallised from a $\text{CH}_2\text{Cl}_2/\text{diethylether}$ mixture.

Cyclic and a.c.voltammetric studies on $\text{trans-}[\text{OsBr}_2\text{py}_4]$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ revealed two reversible oxidative steps at 0.03V and 1.56V. Coulometric studies showed that both processes involved one electron.

The electronic absorbance spectrum of crimson $\text{trans-[OsBr}_2\text{py}_4\text{]}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M [TBA][BF}_4\text{]}$ (fig. 3.14) is dominated by bands (K) which, since the electronic configuration at the metal is t_{2g}^6 , must be assigned as $\text{Os(II)d}\pi \rightarrow \text{py}\pi^*$ M.L.C.T transitions. The spectrum of orange $\text{trans-[Os(III)Br}_2\text{py}_4\text{]}^+$ was obtained by a spectroelectrochemical oxidation at the O.T.T.L.E. (fig. 3.15). The spectrum contains bands (L) which are attributed, by analogy with the other Os(III) species in this series, to a combination of $\text{Os(III)d}\pi \rightarrow \text{py}\pi^*$ and $\text{Br}^-(\pi) \rightarrow \text{Os(III)}$ charge transfer transitions. Finally, the charge transfers (M) observed in the spectrum of $\text{trans-[Os(IV)Br}_2\text{py}_4\text{]}^{2+}$ are attributed to $\text{Br}^-(\pi) \rightarrow \text{Os(IV)d}\pi$ transitions (fig. 3.16).

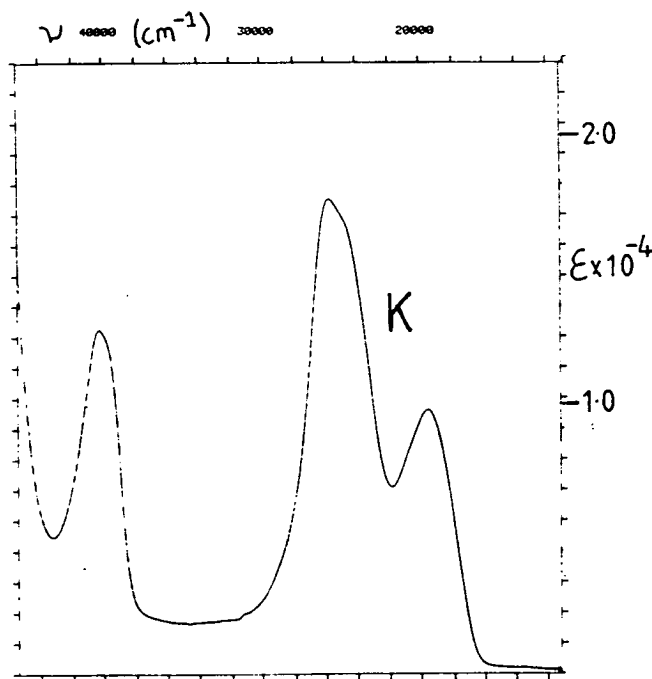


Figure 3.14 U.V./Vis. Absorption Spectrum of $\text{trans-[OsBr}_2\text{py}_4\text{]}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M [TBA][BF}_4\text{]}$ at 240K.

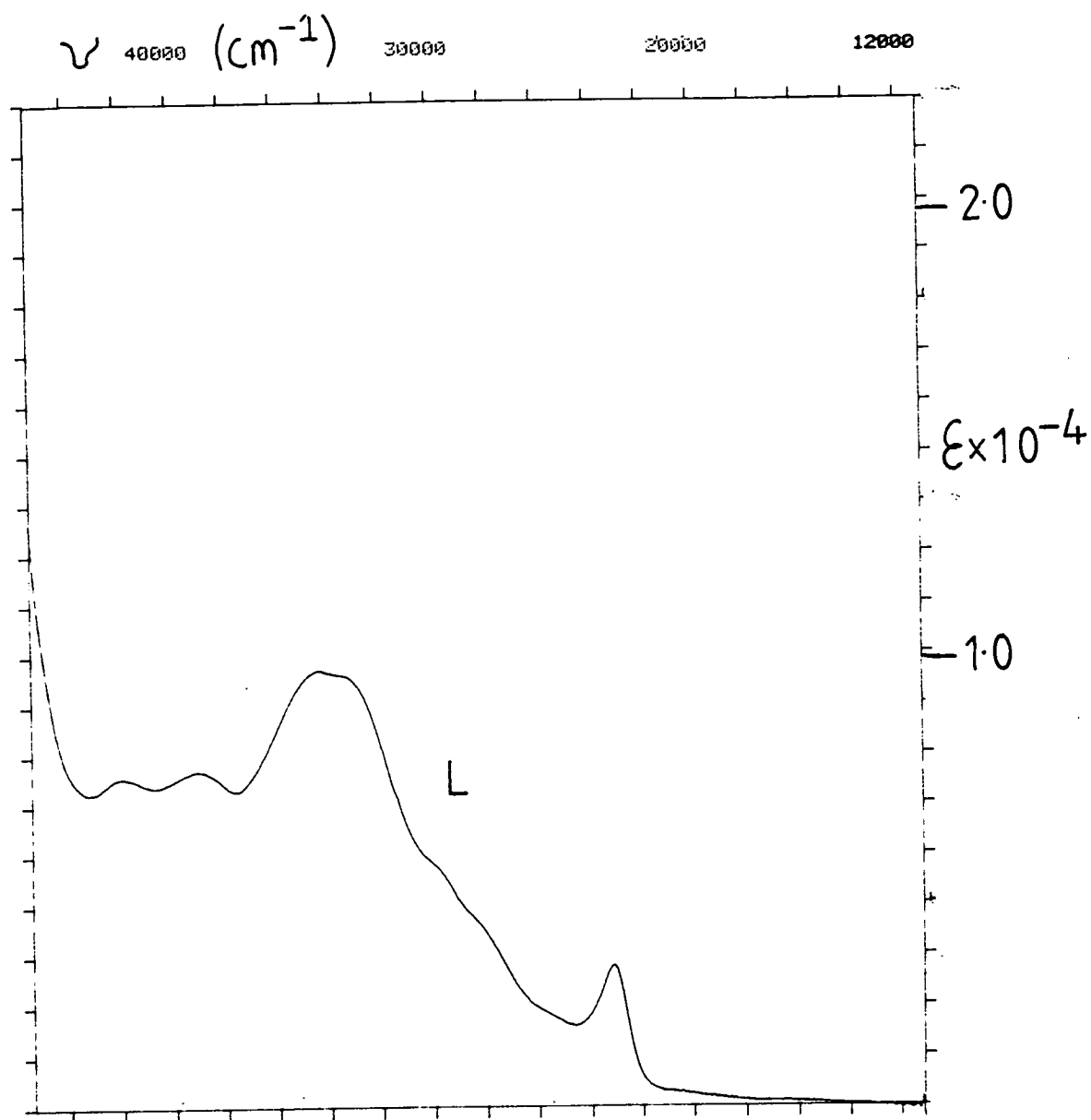


Figure 3.15 U.V./Vis. Absorption Spectrum of $\text{trans-}[\text{OsBr}_2\text{py}_4]^+$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K.

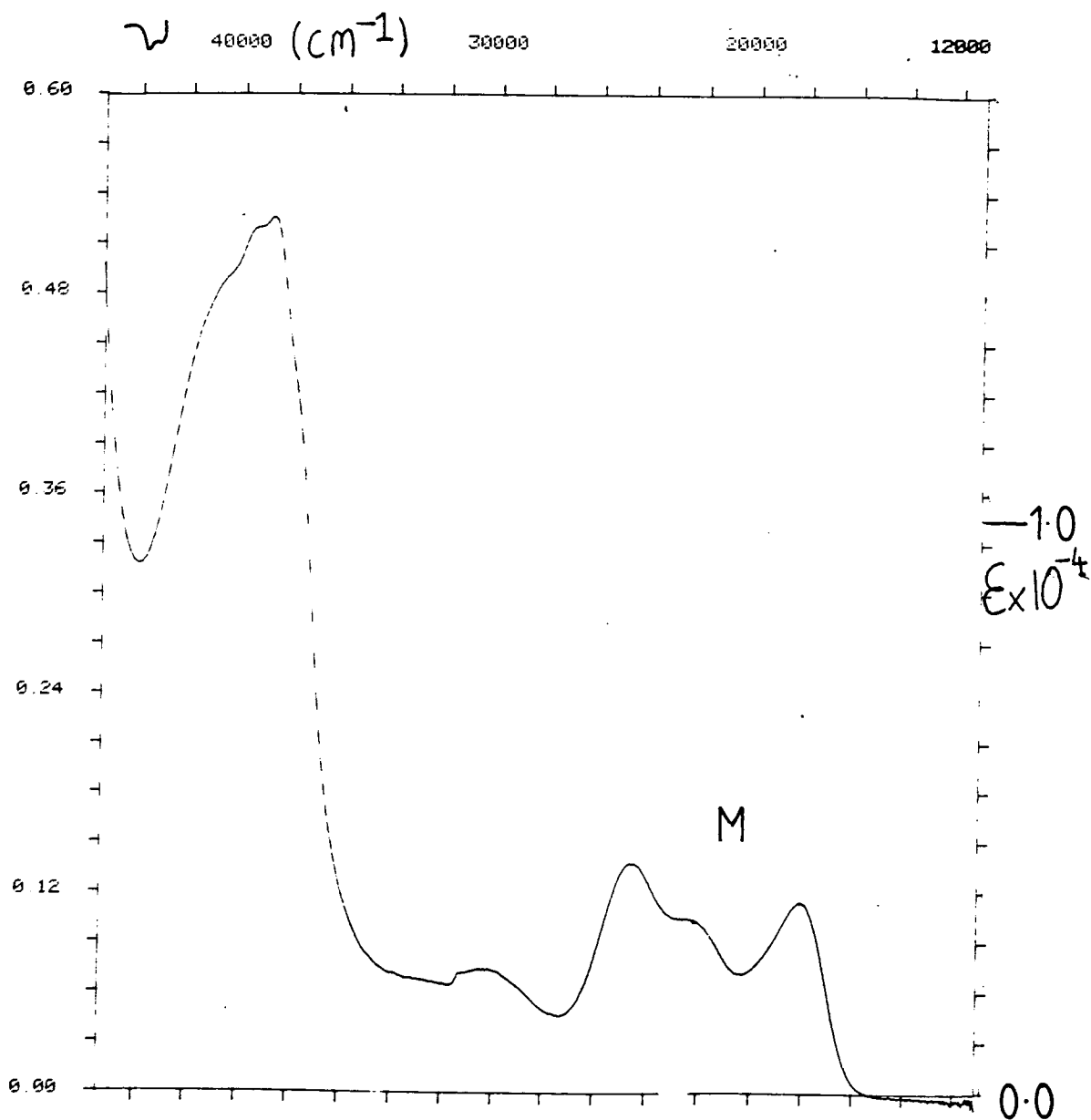


Figure 3.16 U.V./Vis. Absorption Spectrum of $\text{trans-}[\text{OsBr}_2\text{py}_4]^{2+}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 240K.

3.2.7 Preparation, Electrochemistry and Spectroelectrochemistry of $[\text{NH}_4]_2[\text{OsI}_6]$

$[\text{NH}_4]_2[\text{OsCl}_6]$ was heated in a 1.0M solution of $[\text{NH}_4][\text{I}]$ in 55% HI at 360K for 2 hours. The resulting $[\text{NH}_4]_2[\text{OsI}_6]$ was filtered off from the solution.

A cyclic voltammogram in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 290K revealed an irreversible reduction (fig. 3.17) and a complex oxidative step (fig. 3.18). Upon cooling to 230K the reductive step (I) at -0.31V became more reversible, however the oxidation (II) retained it's complexity (fig. 3.19). When the potential was stepped out to +1.1V in order to partially oxidise $[\text{OsI}_6]^{2-}$, for various periods of time, and then scanned negative, back to 0V at 100mVs^{-1} , the height of the return wave (III) was found to increase the longer the oxidative potential was applied. These observations imply oxidative decomposition coupled with a plating or absorbance of an unspecified compound on the electrode.

The reduction was examined spectroelectrochemically in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{I}]$ at 200K at the O.T.T.L.E. The two sets of absorption bands A and B in the spectrum of $[\text{OsI}_6]^{2-}$ (fig. 3.20) have been assigned as $\text{I}^-(\pi) \rightarrow \text{Os(IV)}d\pi(2t_{2g})$ and $\text{I}^-(\pi) \rightarrow \text{Os(IV)}d\sigma(2e_g)$ charge transfer transitions respectively.¹ As for $[\text{OsBr}_6]^{2-}$ we disagree with the latter assignment, favouring further $\text{I}^-\pi \rightarrow \text{Os(IV)}d\pi$ transitions to be responsible for set B. Upon

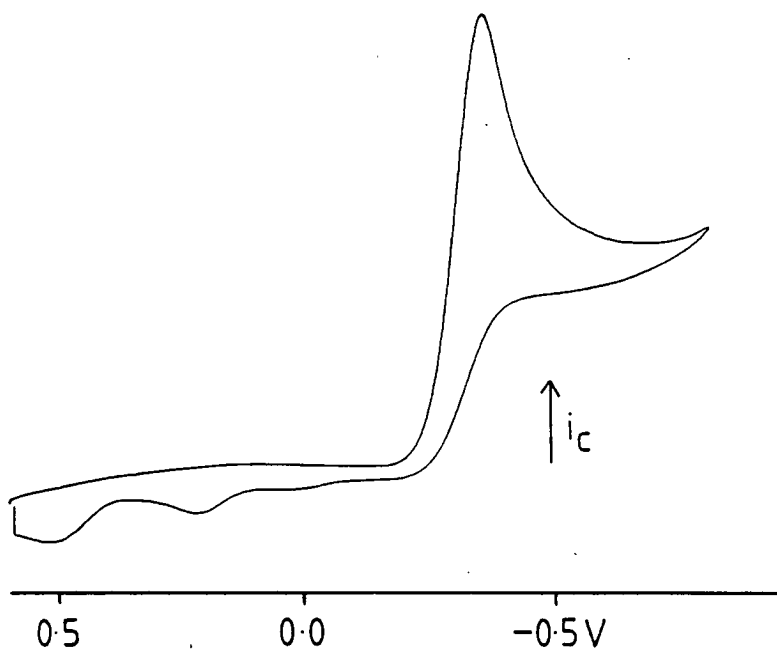


Figure 3.17 Cathodic Cyclic Voltammogram of $[\text{OsI}_6]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 290K.

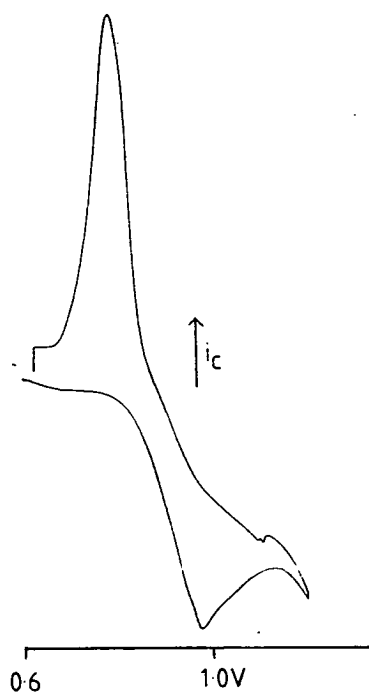


Figure 3.18 Anodic Cyclic Voltammogram of $[\text{OsI}_6]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 290K.

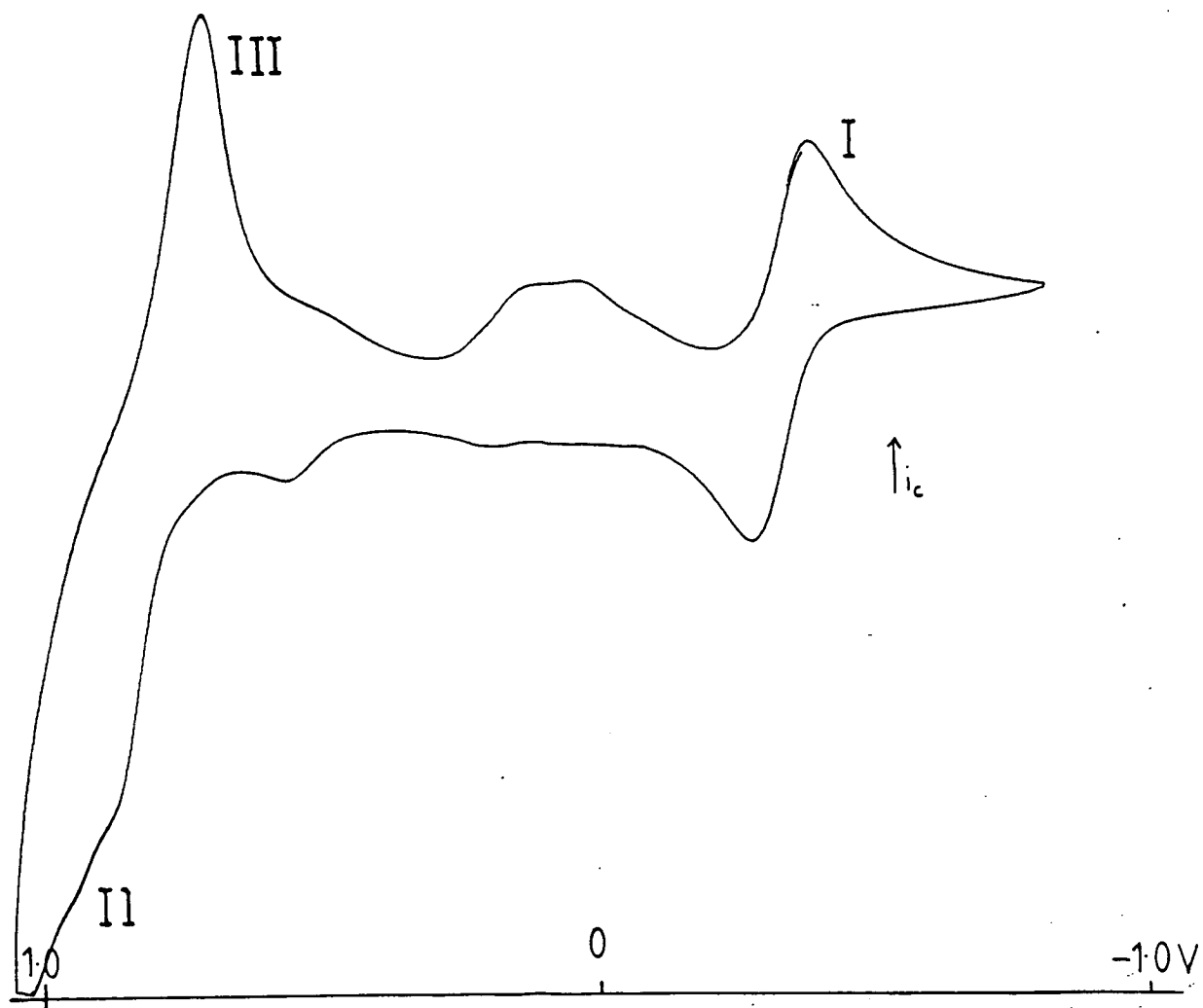


Figure 3.19 Cyclic Voltammogram of $[\text{OsI}_6]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 230K.

reduction at -0.6V the low energy absorption bands (A) decay and are replaced by bands at higher energy (C) (fig. 3.21). Upon reoxidation at 0.0V the original spectrum of $[\text{OsI}_6]^{2-}$ is replicated. These changes are similar to those observed in the one electron metal-based reductions of $[\text{OsCl}_6]^{2-}$ and $[\text{OsBr}_6]^{2-}$. Due to the instability of the reduced species, no coulometric data is available for this reduction. The similarity to the $[\text{OsCl}_6]^{2-}$ and $[\text{OsBr}_6]^{2-}$ is the main basis upon which this reduction is attributed to a one electron metal based process. Hence the reduction product is formulated as $[\text{Os(III)I}_6]^{3-}$ and bands C are assigned as $\text{I}^-(\pi) \rightarrow \text{Os(III)d}\pi$ L.M.C.T. transitions.

3.2.8 Preparation, Electrochemistry and Spectroelectrochemistry of $[\text{TBA}][\text{OsI}_5\text{py}]$

$[\text{NH}_4]_2[\text{OsI}_6]$ was dissolved in a $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ solution containing a 100 fold molar excess of pyridine. The dark blue/violet solution was stirred at 290K for 2 hours. A cyclic voltammogram of the resulting grasshopper green solution showed the emergence of a reductive process at +0.04V. which is 0.35V more positive than the parent couple. This corresponds to a shift that would be expected for replacement of one iodide by a pyridine. On this basis the product is confidently predicted to be $[\text{OsI}_5\text{py}]^-$. $[\text{TBA}][\text{OsI}_5\text{py}]$ was purified using thin layer chromatography.

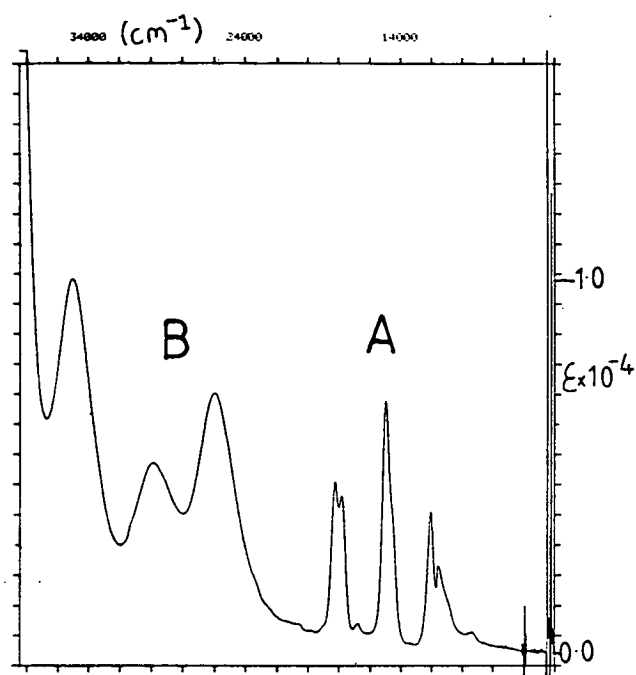


Figure 3.20 U.V./Vis. Absorption Spectrum of $[\text{OsI}_6]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{I}]$ at 200K.

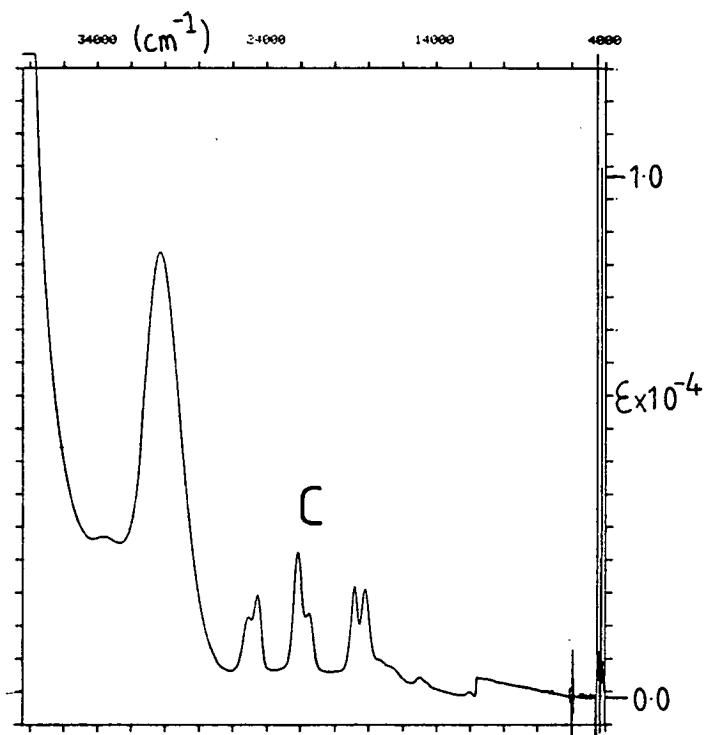


Figure 3.21 U.V./Vis. Absorption Spectrum of $[\text{OsI}_6]^{3-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{I}]$ at 200K.

A spectroelectrochemical reduction of $[\text{OsI}_5\text{py}]^-$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 260K was performed at the O.T.T.L.E. (fig. 3.22). The electronic absorbance spectrum of $[\text{Os(IV)I}_5\text{py}]^-$ (fig. 3.23) shows two sets of bands (C) and (D). Absorption bands (C) and (D) by analogy with the bands observed in the spectrum of $[\text{Os(IV)I}_6]^{2-}$ are assigned as $\text{I}^-(\pi) \rightarrow \text{Os(IV)d}\pi(2\text{t}_{2\text{g}})$ and $\text{I}^-(\pi) \rightarrow \text{Os(IV)d}\pi(2\text{t}_{2\text{g}})$ respectively. This spectrum shows good correspondence with a sample of $[\text{TBA}][\text{OsI}_5\text{py}]$ prepared by Preetz et al.⁵ The low energy bands (E) in the absorbance spectrum of $[\text{Os(III)I}_5\text{py}]^{2-}$ (fig. 3.24), are assigned as $\text{I}^-(\sigma+\pi) \rightarrow \text{Os(III)d}\pi$ charge transfer transitions since they appear at similar energy to bands (C) observed in the spectrum of $[\text{Os(III)I}_6]^{3-}$. Band (F) at 27 100 is assigned as an $\text{Os(III)d}\pi \rightarrow \text{py}\pi^*$ M.L.C.T. transition by comparison with bands of similar energy observed in the spectra for $[\text{OsCl}_5\text{py}]^{2-}$ and $[\text{OsBr}_5\text{py}]^{2-}$ examined hitherto.

3.2.9 Preparation, Electrochemistry and Spectroelectrochemistry of *mer*- $[\text{OsI}_3\text{py}_3]$

$[\text{NH}_4]_2[\text{OsI}_6]^{2-}$ was heated in a 5:1 glycerol/pyridine mixture for 30 minutes at 360K. The resulting purple *mer*- $[\text{OsI}_3\text{py}_3]$ was purified using thin layer chromatography and could be recrystallised from a CH_2Cl_2 /methanol mixture.

The redox behaviour of *mer*- $[\text{OsI}_3\text{py}_3]$ was studied using

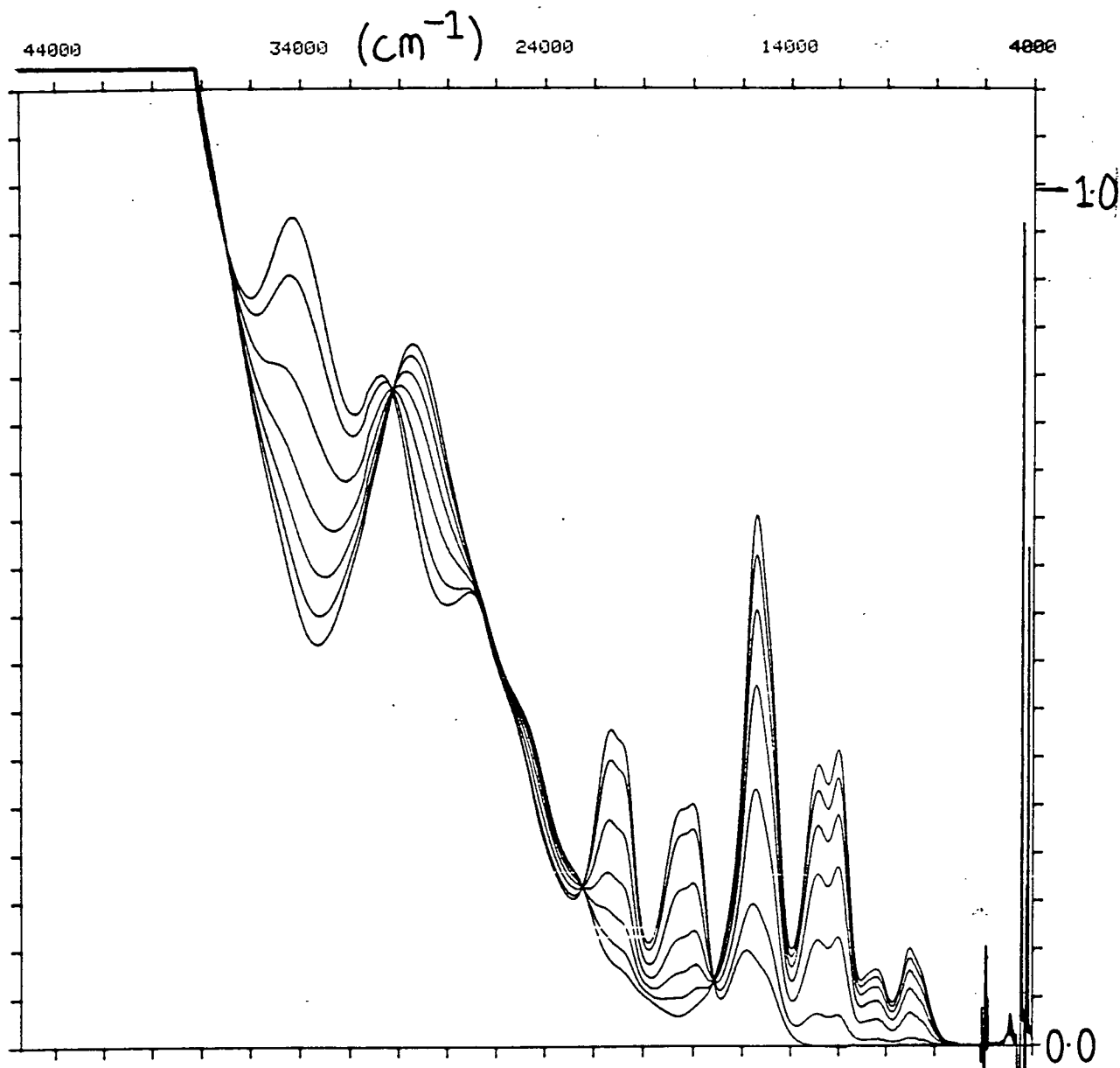


Figure 3.22 U.V./Vis. Absorption Spectra Showing the Spectroelectrochemical conversion of $[\text{OsI}_5\text{py}]^-$ to $[\text{OsI}_5\text{py}]^{2-}$ at -0.2V in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 260K .

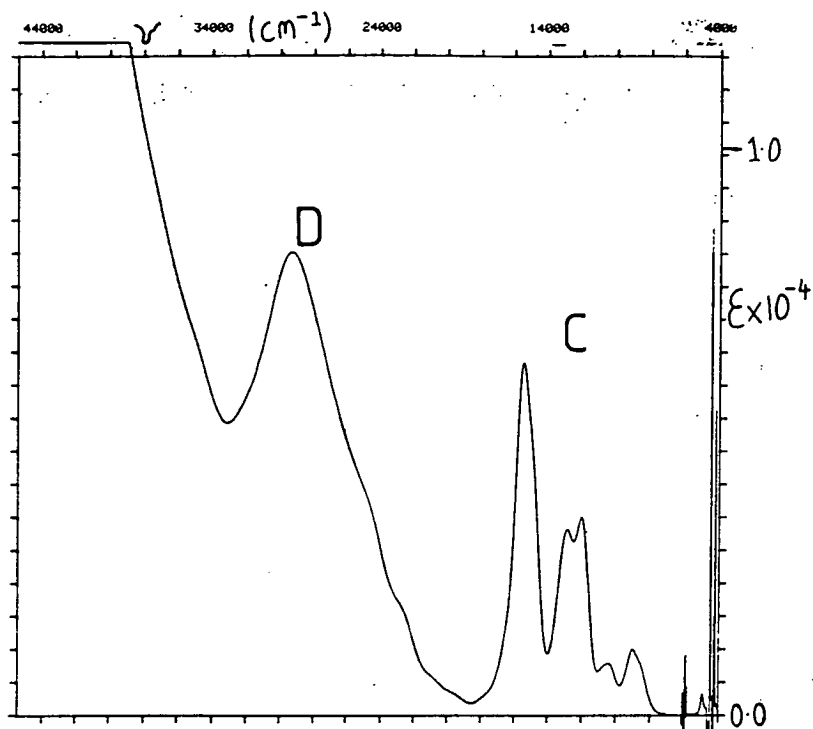


Figure 3.23 U.V./Vis. Absorption Spectrum of $[\text{OsI}_5\text{py}]^-$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 260K.

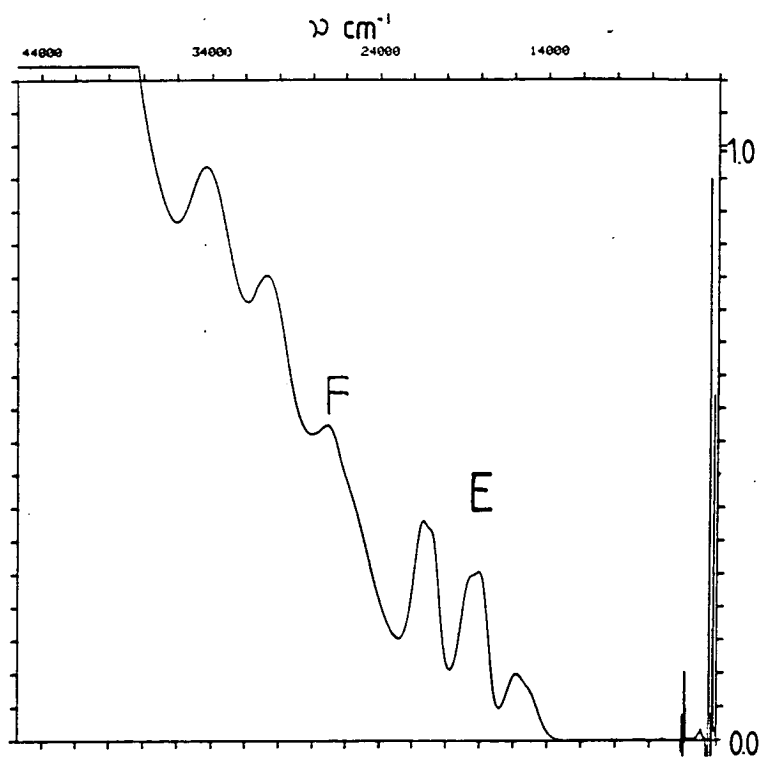


Figure 3.24 U.V./Vis. Absorption Spectrum of $[\text{OsI}_5\text{py}]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 260K.

cyclic voltammetry and a.c.voltammetry. These studies showed an oxidative process at 1.01V and a reduction step at -0.36V. Stirred voltammetry showed both the processes involved one electron.

The spectroelectrochemistry of *mer*-[OsI₃py₃] was examined in CH₂Cl₂/ 0.5M [TBA][BF₄] at 240K using an O.T.T.L.E. The spectrum of *mer*-[OsI₃py₃] (fig. 3.25) shows two main sets of absorption bands (G) and (H). The low energy bands are assigned, since they occur at similar energy to those observed for [Os(III)I₆]³⁻ and [Os(III)I₅py]²⁻, as I⁻(π) $\rightarrow$ Os(III)d π charge transfer transitions. The band at 29 900 is attributed to a Os(III)d π $\rightarrow$ py π^* M.L.C.T. transition, by comparison with the spectra of *mer*-[Os(III)Cl₃py₃] and *mer*-[Os(III)Br₃py₃]. The low energy bands (I) in the electronic spectrum of *mer*-[Os(II)I₃py₃]⁻ (fig. 3.26) must be assigned as Os(II)d π $\rightarrow$ py π^* transitions since the electronic configuration is t_{2g}⁶ at the metal. The high energy band (J) is at lower energy than those observed in the spectra of *mer*-[OsCl₃py₃]⁻ and *mer*-[OsBr₃py₃]⁻ and must therefore be due to either an iodide intraligand transition or a I⁻(π) $\rightarrow$ Os(II)d σ transition. The spectrum of [Os(IV)I₃py₃]⁺ (fig. 3.27) is dominated by I⁻(π) $\rightarrow$ Os(IV)d π transitions (K), assigned thus by comparison with the absorption bands observed in the spectra of [OsI₆]²⁻ and [OsI₅py]⁻.

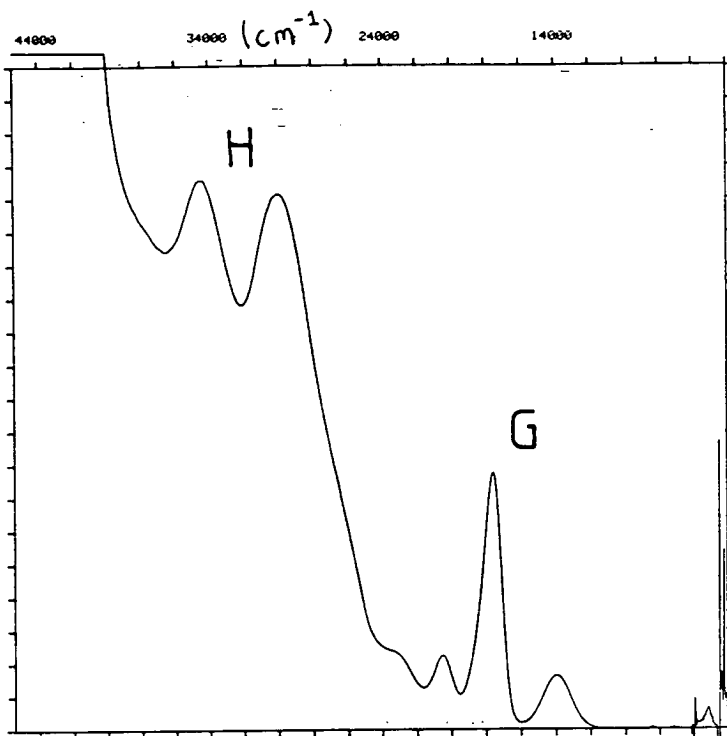


Figure 3.25 U.V./Vis. Absorption Spectrum of $\text{mer-}[\text{OsI}_3\text{py}_3]$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K.

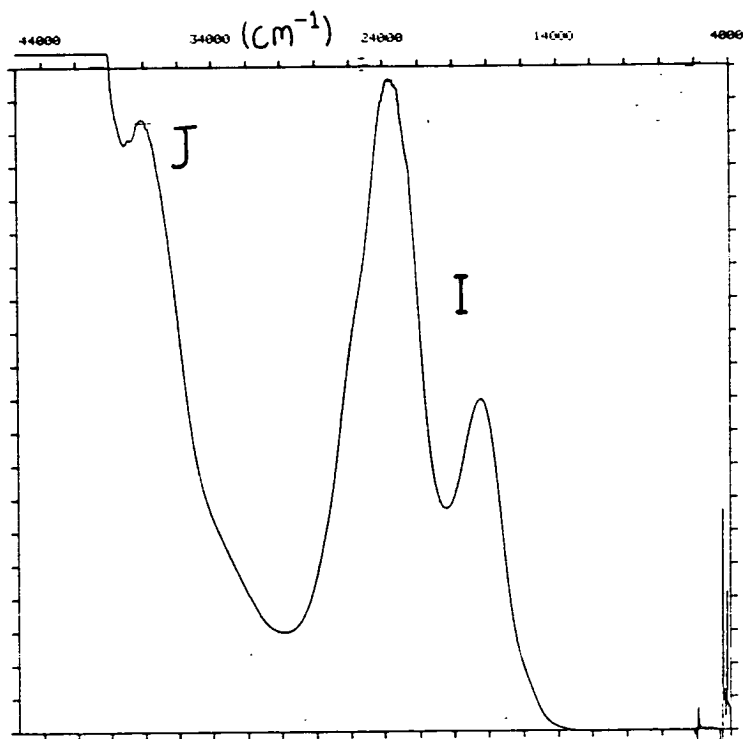


Figure 3.26 U.V./Vis. Absorption Spectrum of $\text{mer-}[\text{OsI}_3\text{py}_3]^-$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K.

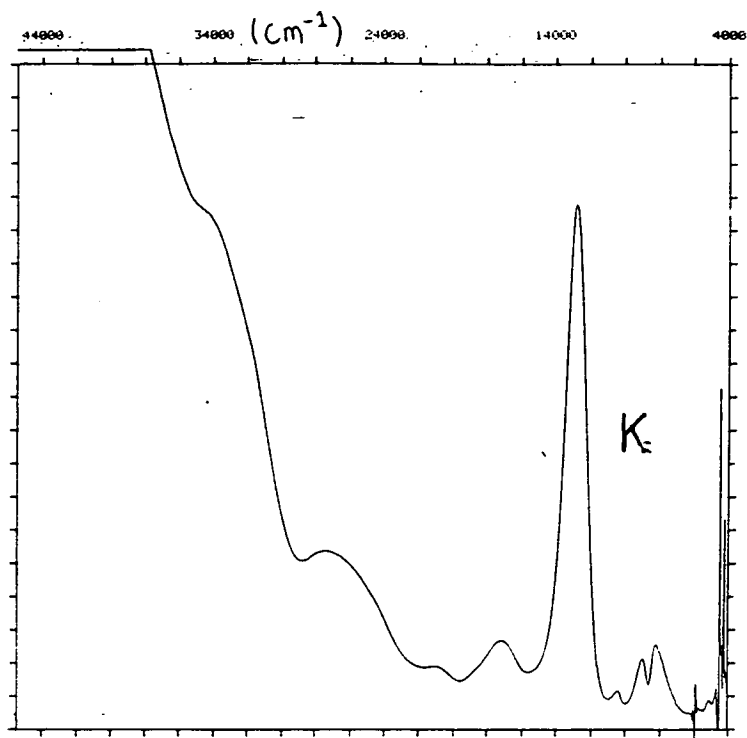


Figure 3.27 U.V./Vis. Absorption Spectrum of $\text{mer-}[\text{OsI}_3\text{py}_3]^+$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 240K.

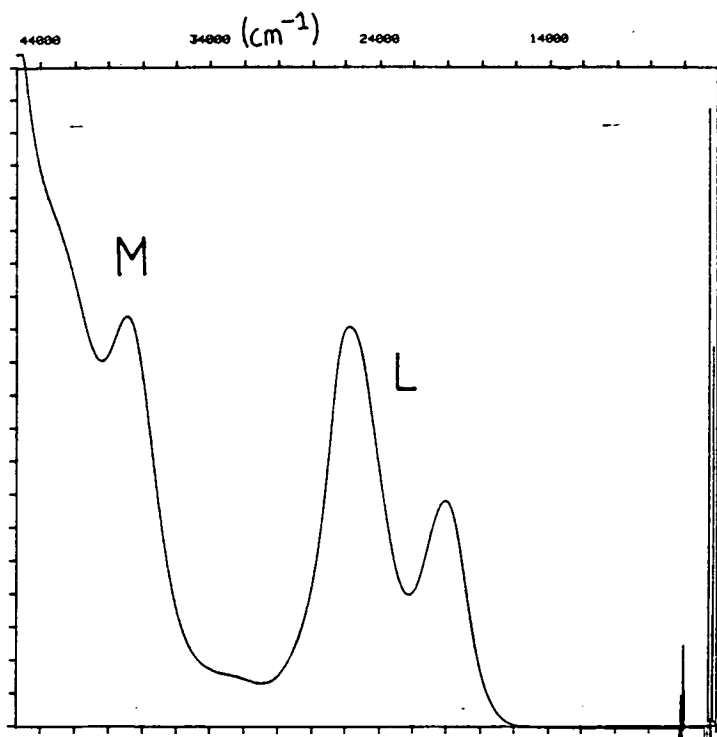


Figure 3.28 U.V./Vis. Absorption Spectrum of $\text{trans-}[\text{OsI}_2\text{py}_4]$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 240K.

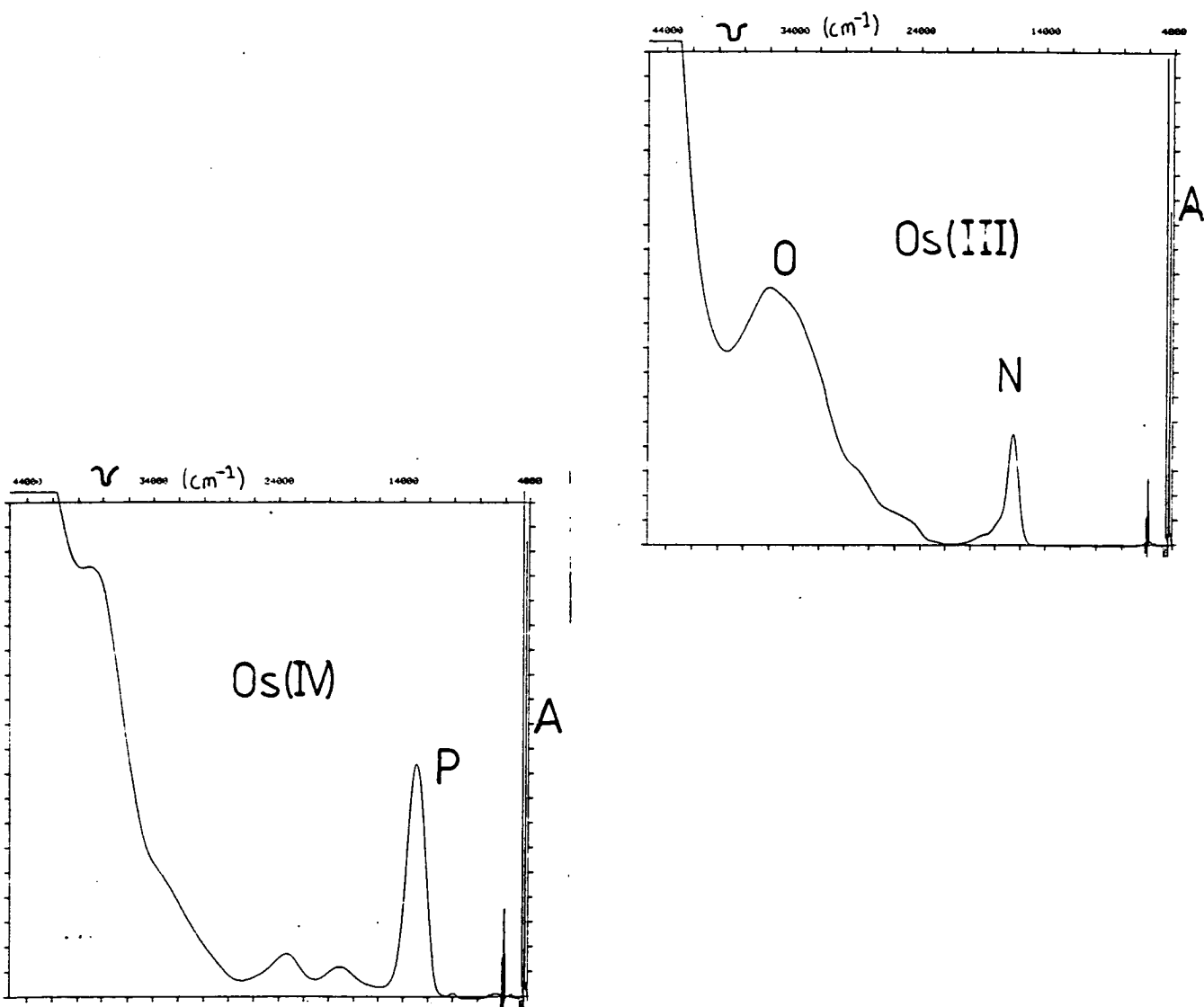
3.2.10 Preparation, Electrochemistry and Spectroelectrochemistry of *trans*-[OsI₂py₄]

[NH₄]₂[OsI₆] was heated in a 5:1 glycerol/pyridine mixture at 360K for 3 hours. The resulting deep red *trans*-[OsI₂py₄] was purified using thin layer chromatography.

Cyclic voltammetry and a.c.voltammetry were employed to examine the redox behaviour of the compound. In CH₂Cl₂/0.5M [TBA][BF₄] at 290K two reversible one electron oxidations were observed at 0.14V and 1.42V.

A spectroelectrochemical examination of *trans*-[OsI₂py₄] in CH₂Cl₂/0.5M [TBA][BF₄] at 240K was undertaken. The spectrum of *trans*-[Os(II)I₂py₄] is shown in figure 3.28. The two sets of bands (L) and (M) are assigned, in a similar manner to those in the spectrum of *mer*-[Os(II)I₂py₄]⁻ (above), as Os(II)d π $\rightarrow$ py π^* transitions and either iodide intraligand or I⁻(π) $\rightarrow$ Os(II)d σ charge transfer transitions respectively. Since the absorption band (N) in the spectrum of *trans*-[OsI₂(III)py₄]⁺ (fig. 3.29) lies at lower energy than bands (L) in the spectrum of [Os(II)I₂py₄] it must be attributed to an I⁻(π) $\rightarrow$ Os(III)d π charge transfer transition. Absorption bands (O), by comparison with the spectra of *trans*-[OsCl₂py₄]⁺ and *trans*-[OsBr₂py₄]⁺, can be assigned, at least in part, to an Os(III)d π $\rightarrow$ py π^* charge transfer transition. The spectrum of *trans*-[OsI₂py₄]²⁺ (fig. 3.30) is dominated by

absorption bands (P), which are of similar energy to the L.M.C.T transitions previously observed for iodide containing Os(IV) species. Hence the bands are attributed to $I^-(\pi) \rightarrow Os(IV)d\pi$ charge transfer transitions.



Figures 3.29 and 3.30 U.V./Vis. Absorption Spectra of $trans-[OsI_2py_4]^+$ and $trans-[OsI_2py_4]^{2+}$ respectively in $CH_2Cl_2/0.5M [TBA][BF_4]$ at 240K.

3.31 Discussion of the $E_{1/2}$ values obtained for the series $[\text{OsBr}_{6-n}\text{py}_n]^{(n-Y)}$ and $[\text{OsI}_{6-n}\text{py}_n]^{(n-Y)}$ and a comparison with $E_{1/2}$ values for the series $[\text{OsCl}_{6-n}\text{py}_n]^{(n-Y)}$.

The voltammetric data collected in the preceding sections is presented in schemes 3.1 and 3.2. As for the $[\text{OsCl}_{6-n}\text{py}_n]^{(n-Y)+}$ series discussed in chapter 2, there is a net positive shift in $E_{1/2}$ values as π -donating bromide and iodide ligands are replaced by π -accepting pyridine ligands. Figures 3.31 and 3.32 show $E_{1/2}$ values plotted against the number of pyridine ligands present (n).

$E_{1/2}$ values for the series $[\text{OsBr}_{6-n}\text{py}_n]^{(n-Y)+}$ can be predicted using Ligand Parametrization.⁶ Tables 3.2, 3.3 and figure 3.33 show the predicted values, E_{calc} , against the actual values, E_{obs} . For the Os(III)/Os(II) redox couples Lever's values of S_M and I_M are employed. The values for S_M and I_M calculated for Os(IV)/Os(III) and Os(V)/Os(IV) couples in section 2.31 are used to predict $E_{1/2}$ values for the Os(IV)/Os(III) and Os(V)/Os(IV) couples considered here.

The model predicts reasonable values for all the redox processes, although predicted values for the Os(IV)/Os(V) couples are too high and the values calculated for the Os(III)/Os(II) couples are isomer independent.

Values for parameters A, B and C in Bursten's Ligand Additivity Model⁷ (see 1.3 and 2.31) have been calculated for the series $[\text{OsBr}_{6-n}\text{py}_n]^{(n-Y)+}$, and are tabulated

below. The average value of C is given for the Os(II)/Os(III) couples and assumed to be negligible for the other couples.

Couple	A	B	C
Os(III)/Os(II)	-1.88	0.46	0.06
Os(IV)/Os(III)	-0.37±0.03	0.49±0.03	—
Os(V)/Os(IV)	1.36±0.05	0.41±0.04	—

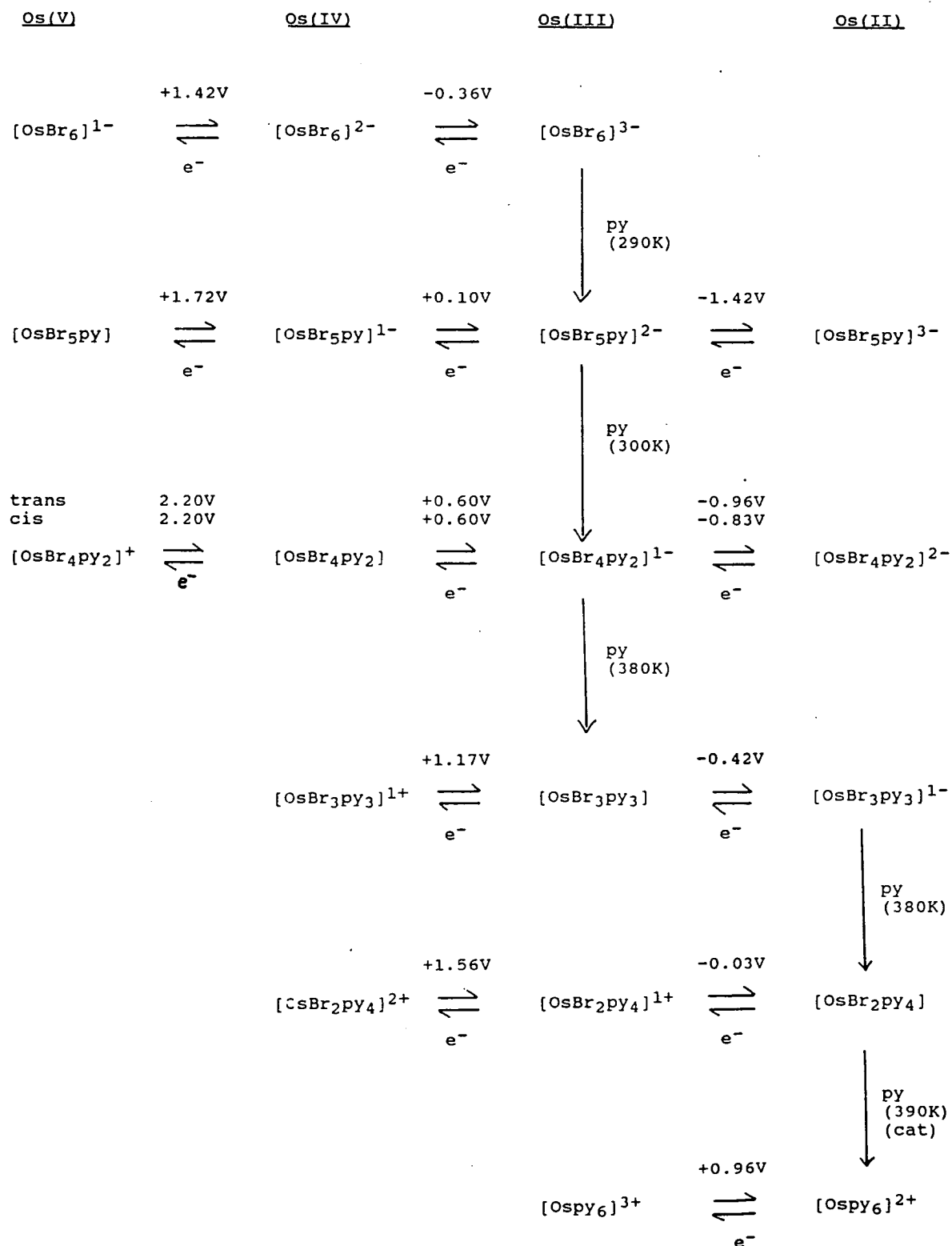
Ligand parametrization can also be used to predict $E_{1/2}$ values for the series $[\text{OsI}_{6-n}\text{PY}_n]^{(n-Y)+}$. These values are calculated as for the $[\text{OsBr}_{6-n}\text{PY}_n]^{(n-Y)+}$ series above and are shown in Table 3.4 and Fig 2.34. The predictions are, once again, reasonable.

Values for parameters A and B in Burstens ligand additivity model are given for the $[\text{OsI}_{6-n}\text{PY}_n]^{n-2/n-3}$ couples (C is assumed to be negligible). Although three values are available for $[\text{OsI}_{6-n}\text{PY}_n]^{n-3/n-4}$ couples, unfortunately only a value of B+C can be obtained. The low value of B+C however implies that C is smaller than for the $[\text{OsCl}_{6-n}\text{PY}_n]^{n-3/n-4}$ and $[\text{OsBr}_{6-n}\text{PY}_n]^{n-2/n-3}$ systems. This would be expected since the halides become weaker π -donors down the series Cl^- , Br^- , I^- .

Couple

Os(IV)/Os(III)	A = -0.35	B = 0.44
Os(III)Os(II)	—	B+C = 0.44

Scheme 3.1 Voltammetric Data and Reaction Scheme for the Series $[\text{OsBr}_{6-n}\text{py}_n]^{(n-y)}$.



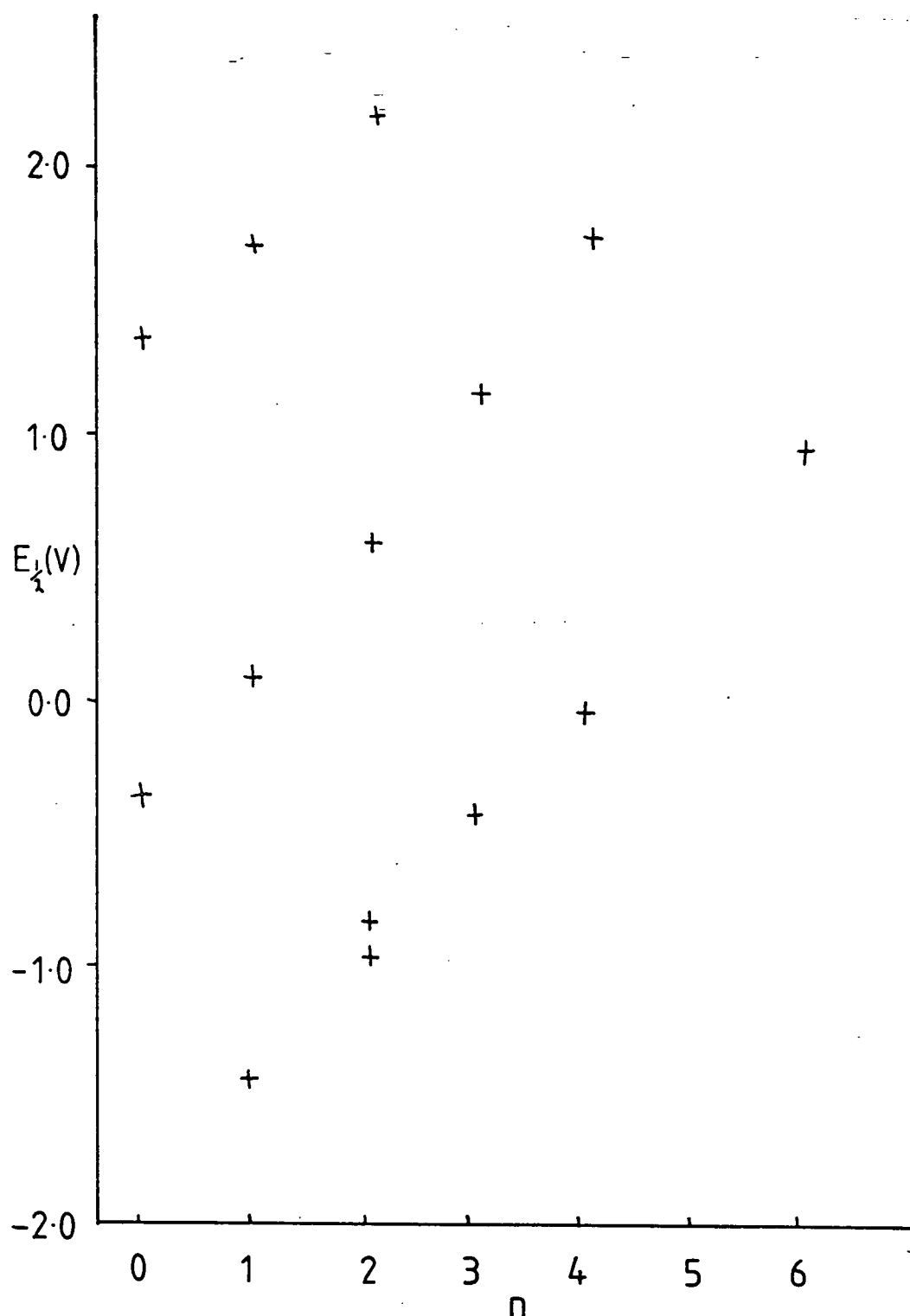
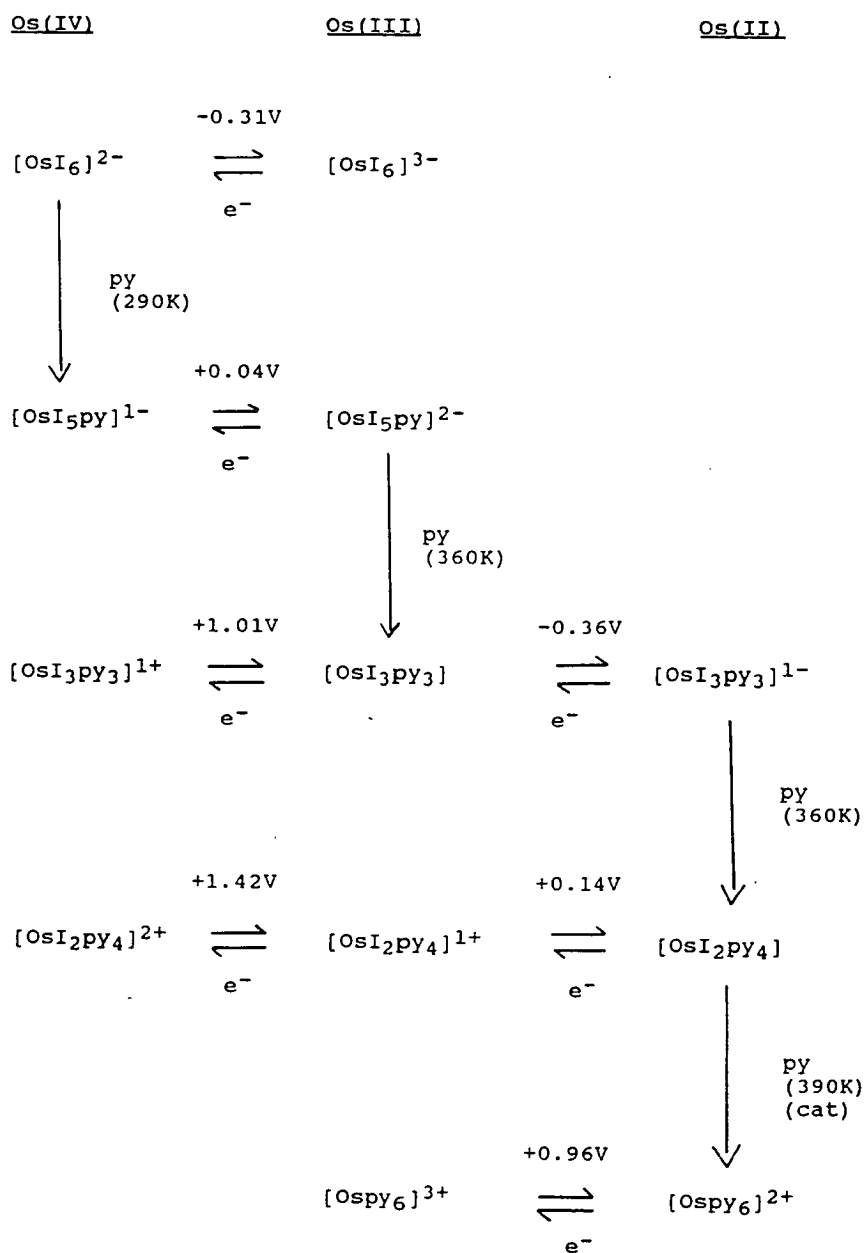


Figure 3.31 Graph Showing n against $E_{1/2}$ for the Series $[\text{OsBr}_{6-n}\text{PY}_n]^{(n-y)+}$.

Scheme 3.2 Voltammetric Data and Reaction Scheme for the Series $[\text{OsI}_{6-n}\text{py}_n]^{(n-y)+}$.



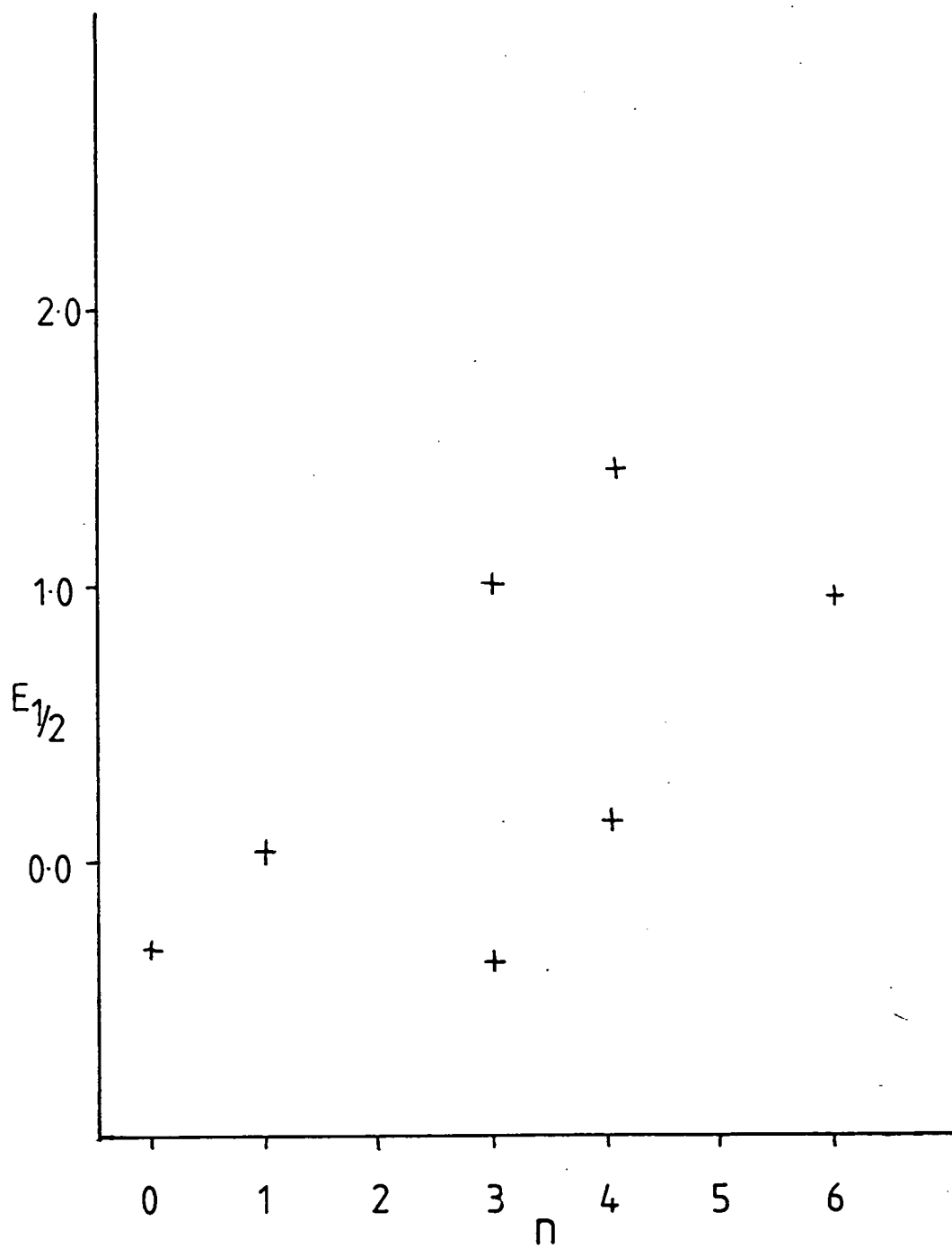


Figure 3.32 Graph Showing n against $E_{1/2}$ for the Series $[\text{OsI}_{6-n}\text{py}_n]^{(n-y)+}$.

Table 3.2 $[\Sigma E_L]$, E_{calc} and Experimental $E_{1/2}$ Values for the Series $[\text{OsBr}_{6-n}\text{py}_n]^{(n-4)+}$.

Redox Process	$\Sigma E_L(\text{V})$	$E_{\text{calc}}^{\text{a}}(\text{V})^{\text{b}}$	$E_{\text{obs}}(\text{V})^{\text{b}}$
$[\text{OsBr}_5\text{py}]^{3-/2-}$	-0.85	-1.36	-1.42
$[\text{OsBr}_4\text{py}_2]^{2-/1-}$	-0.38	-0.89	-0.96 (-0.83) ^c
$[\text{OsBr}_3\text{py}_3]^{1-/0}$	+0.09	-0.41	-0.42
$[\text{OsBr}_2\text{py}_4]^{0/1+}$	+0.56	-0.06	-0.03

^a $E_{\text{calc}} = (1.01)\Sigma E_L - 0.40 - 0.105$

^b Volts versus Ag/AgCl.

^c $E_{1/2}$ value for *cis* isomer in brackets.

Table 3.3 Comparison of Observed $E_{1/2}$ Values and Redox Data Calculated Using Ligand Parameterisation for the Series $[\text{OsBr}_{6-n}\text{py}_n]^{(n-3)/(n-2)}$ and $[\text{OsBr}_{6-n}\text{py}_n]^{(n-2)/(n-1)}$.

Redox Process	$\Sigma E_L(\text{V})$	$E_{\text{calc}}^{\text{a}}(\text{V})^{\text{b}}$	$E_{\text{obs}}(\text{V})^{\text{b}}$
$[\text{OsBr}_6]^{3-/2-}$	-1.32	-0.40	-0.36
$[\text{OsBr}_5\text{py}]^{2-/1-}$	-0.85	+0.10	+0.10
$[\text{OsBr}_4\text{py}_2]^{1-/0}$	-0.38	+0.59	+0.60 ^c
$[\text{OsBr}_3\text{py}_3]^{0/1+}$	+0.09	+1.08	+1.17
$[\text{OsBr}_2\text{py}_4]^{1+/2+}$	+0.56	+1.58	+1.56
$[\text{OsBr}_6]^{2-/1-}$	-1.32	+1.48	+1.38
$[\text{OsBr}_5\text{py}]^{1-/0}$	-0.85	+1.95	+1.72
$[\text{OsBr}_4\text{py}_2]^{0/1+}$	-0.38	+2.42	+2.20

^a Os(IV)/Os(III) steps $E_{\text{calc}} = (1.05)\Sigma E_L + 1.095 - 0.105$

Os(V)/Os(IV) couples $E_{\text{calc}} = (1.00)\Sigma E_L + 2.905 - 0.105$

^b Volts versus Ag/AgCl

^c $E_{1/2}$ values for *cis* and *trans* isomers are similar.

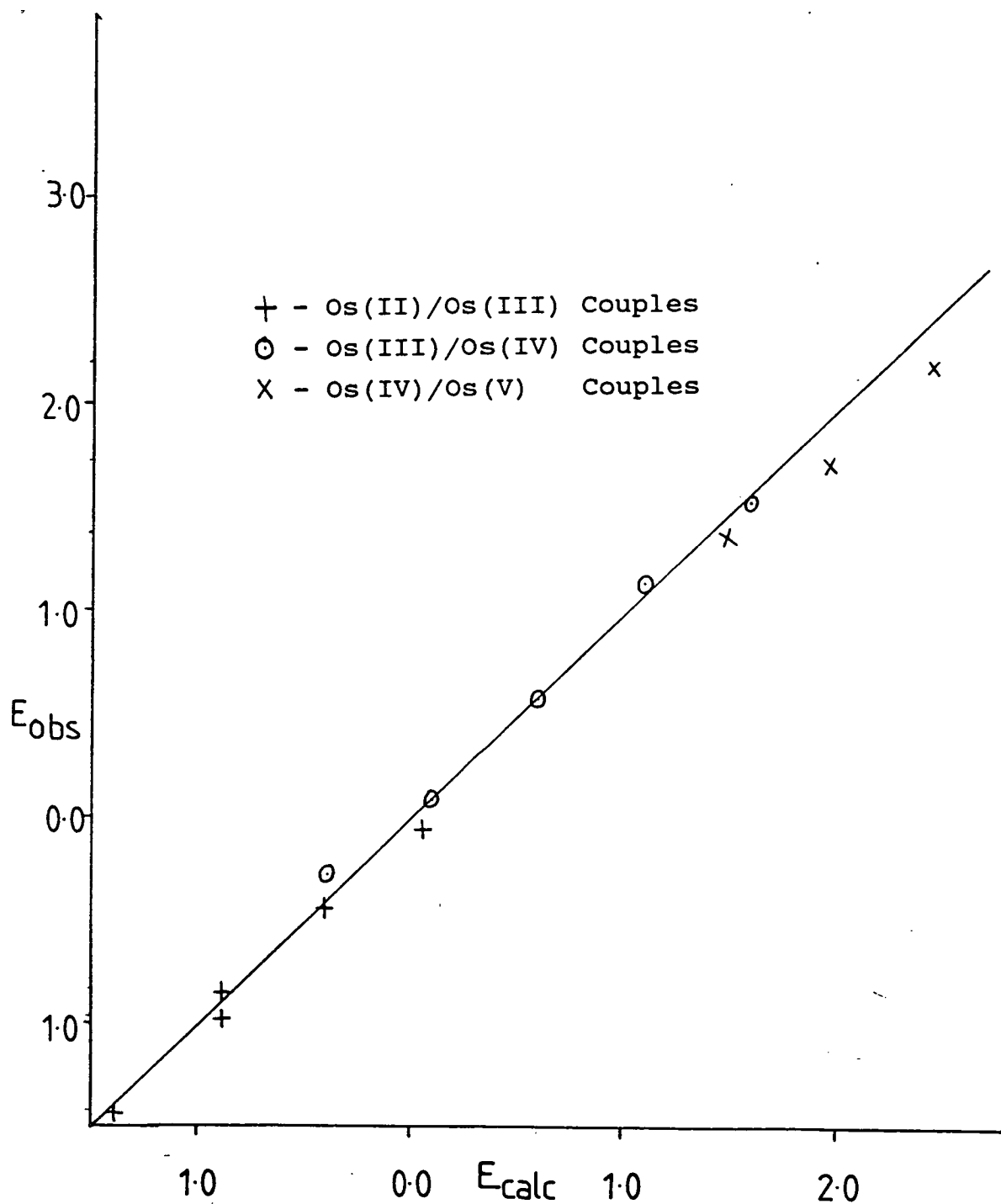


Figure 3.33 Graph Showing E_{calc} against Experimental $E_{1/2}$ Values for the series $[OsBr_{6-n}Py_n](n-y)^+$.

Table 3.4 Comparison of Observed $E_{1/2}$ Values and Redox Data Calculated Using Ligand Parameterization for the series $[\text{OsI}_{6-n}\text{py}_n]^{(n-y)}$.

Redox Process	$\Sigma E_L(\text{V})$	$E_{\text{calc}}^{\text{a}}(\text{V})^{\text{b}}$	$E_{\text{obs}}(\text{V})^{\text{b}}$
$[\text{OsI}_6]^{2-/3-}$	-1.44	-0.52	-0.31
$[\text{OsI}_5\text{py}]^{1-/2-}$	-0.95	+0.01	+0.04
$[\text{OsI}_3\text{py}_3]^{1+/0}$	+0.03	+1.09	+1.01
$[\text{OsI}_2\text{py}_4]^{2+/1+}$	+0.52	+1.54	+1.42
$[\text{OsI}_3\text{py}_3]^{0/1-}$	+0.03	-0.47	-0.36
$[\text{OsI}_2\text{py}_4]^{1+/0}$	+0.52	+0.02	+0.14

^a Os(III)/Os(II) steps $E_{\text{calc}} = (1.01)\Sigma E_L - 0.40 - 0.105$

Os(IV)/Os(III) couples $E_{\text{calc}} = (1.05)\Sigma E_L + 1.095 - 0.105$

^b Volts versus Ag/AgCl

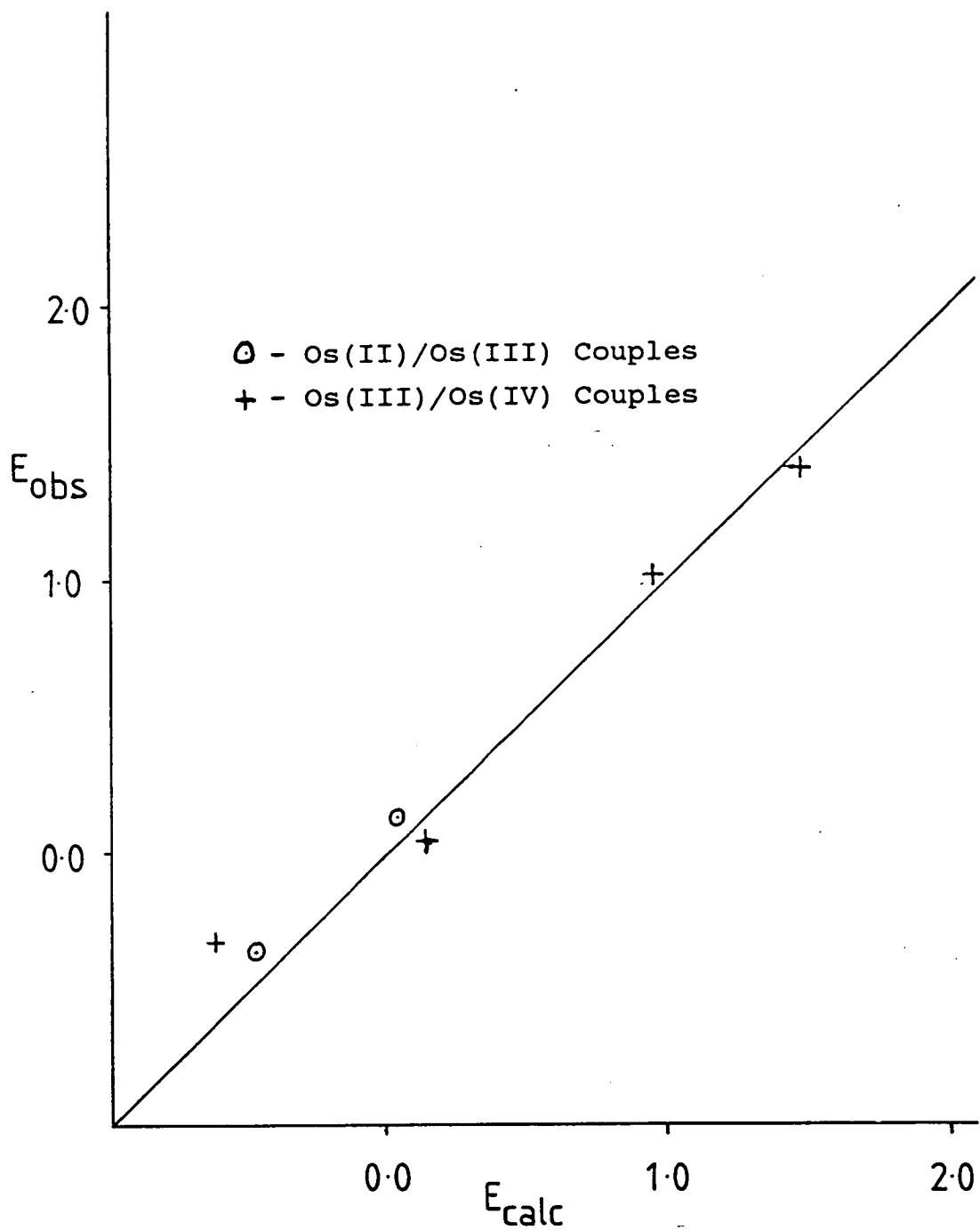


Figure 3.34 Graph Showing E_{calc} against Experimental $E_{1/2}$ Values for the series $[\text{OsI}_{6-n}\text{py}_n]^{(n-y)+}$.

3.3.2 Discussion of the U.V./Visible Absorption Spectra Obtained for the Series $[\text{OsBr}_{6-n}\text{PY}_n]^{(n-Y)+}$ and $[\text{OsI}_{6-n}\text{PY}_n]^{(n-Y)+}$

The positions of the bands in the u.v./visible electronic absorption spectra of the series $[\text{OsBr}_{6-n}\text{PY}_n]^{(n-Y)+}$ and $[\text{OsI}_{6-n}\text{PY}_n]^{(n-Y)+}$ are listed together with assignments to probable electronic transitions in tables 3.5 and 3.6 (see later).

The halide to metal C.T. transitions in the u.v./visible absorption spectra of hexahaloosmate(IV) complexes (figs. 2.2, 3.2 and 3.20) move to lower energy along the series: $[\text{OsCl}_6]^{2-}$, $[\text{OsBr}_6]^{2-}$, $[\text{OsI}_6]^{2-}$, this is because the energy of the ligand based π^- electrons increases: $3d < 4d < 5d$, thereby reducing the energy gap between the metal based $d\pi$ orbitals and the ligand orbitals. The form of the spectra also becomes more complicated as the halide becomes heavier, this is because the spin-orbit coupling coefficient for the halides increases : $\text{Cl}^- < \text{Br}^- < \text{I}^-$, which results in a greater number of more electronic transitions being observed in the spectrum of $[\text{OsI}_6]^{2-}$ than in the spectrum of $[\text{OsCl}_6]^{2-}$.

The electronic absorption spectra of the complexes $[\text{Os(IV)X}_{6-n}\text{PY}_n]^{n-2}$, where $\text{X} = \text{Br}^-$ or I^- , characteristically exhibit L.M.C.T. transitions. Assignment of each band to a specific transition, from one

of the various combinations of halide π orbitals to the metal based $d\pi$ orbitals, would be very complicated, especially since spin orbit coupling is so prevalent, and lies outwith the bounds of this work.

Complexes of the form $[\text{Os(II)}\text{X}_{6-n}\text{py}_n]^{(n-4)}$, where $\text{X} = \text{Br}^-$ or I^- , show u.v./vis. absorption spectra that are very similar to their $[\text{Os(II)}\text{Cl}_{6-n}\text{py}_n]^{n-4}$ analogues. This observation is consistent with the band assignments made in section 2.3.2, namely that the low energy bands are due to $\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$ C.T. transitions. The energy of these M.L.C.T. transitions increases slightly (by ca. 500cm^{-1}) as the halide is changed from Cl^- to Br^- to I^- in corresponding complexes ($[\text{Os(II)}\text{X}_{6-n}\text{py}_n]^{(n-4)}$ $n = 3, 4$). For instance, when we consider complexes of the form $\text{mer-}[\text{Os(II)}\text{X}_3\text{py}_3]^-$ the energies of the main $\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$ charge transfer band and the corresponding triplet transition vary with X as follows:

X^-	=	Cl^-	Br^-	I^-
'Triplet transition':		17 120	17 910	18 420
'Singlet transition':		22 830	23 390	23 700

The halide π orbitals become more diffuse as we move down the series Cl^- , Br^- , I^- , and hence become weaker π -donors, therefore destabilising the metal $d\pi$ orbitals less efficiently. This will result in an increase in the

energy gap between the metal $d\pi$ orbitals and the $py\pi^*$ orbitals, which agrees with the results above.

The spectra that provide the most useful comparison with the series examined in section 2.3.2. are those corresponding to complexes of the form $[Os(III)X_{6-n}PY_n]^{n-3}$, where $X = Br^-$ or I^- and $n = 0$ to 6. The comparison is useful since in the spectra of the series $[Os(III)Cl_{6-n}PY_n]^{n-3}$ M.L.C.T. transitions were superimposed on L.M.C.T. transitions. We expect the $X^- \pi \rightarrow Os(III)d\pi$ C.T. transitions to move to lower energy as we move down the series Cl^- , Br^- , I^- . Hence, assuming the the M.L.C.T. transfer remains at roughly the same energy with change of halide (the $[Os(II)X_{6-n}PY_n]^{(n-4)+}$ above suggest a change of no more than $1\ 500\text{cm}^{-1}$), both L.M.C.T. and M.L.C.T. transitions should be observed in the same spectrum and bands assigned with a reasonable degree of accuracy.

For example, consider the spectra of the series $[Os(III)X_3py_3]$, where $X = Cl^-$, Br^- , I^- . The spectrum of $[OsCl_3py_3]$ exhibits two bands at $31\ 700$ and $40\ 900\ \text{cm}^{-1}$. The band at $40\ 900$ has been assigned as a $py \rightarrow py\pi^*$ intraligand C.T. transition. The form of the band at $31\ 700\text{cm}^{-1}$ is not symmetrical and cannot be confidently assigned as either a M.L.C.T. or a L.M.C.T. transition. The spectrum of $[OsBr_3py_3]$ exhibits bands at $21\ 400$, $24\ 700$ and $30\ 900\text{cm}^{-1}$. Clearly the two bands at lower energy are due to $Br^- \pi \rightarrow Os(III)d\pi$ C.T. transitions since we

would expect the bands to occur at lower energy and be more numerous than those observed for $\text{Cl}^{-\pi} \rightarrow \text{Os(III)}d\pi$ C.T. transitions (see above). The band at $30\,900\text{cm}^{-1}$ can be assigned as an $\text{Os(III)} \rightarrow \text{py}\pi^*$ C.T. transition. The spectrum of $[\text{OsI}_3\text{py}_3]$ exhibits bands at $13\,940$, $17\,580$, $20\,500$, $29\,900$, $34\,400\text{cm}^{-1}$. The first three can be confidently assigned as $\text{I}^{-\pi} \rightarrow \text{Os(III)}d\pi$ C.T. transitions (since we expect these bands to occur at lower energy and be more numerous than those occurring for $\text{Cl}^{-\pi} \rightarrow \text{Os(III)}d\pi$ and $\text{Br}^{-\pi} \rightarrow \text{Os(III)}d\pi$). The next band is probably due to an $\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$ C.T. transition, while the band at $34\,400\text{cm}^{-1}$ is probably due to a $\text{I}^{-\pi} \rightarrow \text{Os(III)}d\pi$ C.T. transition. The observations we have made on the spectra $[\text{OsBr}_3\text{py}_3]$ and $[\text{OsI}_3\text{py}_3]$ allow us to confidently assign the band at $31\,700$ in the spectrum of $[\text{Os(III)Cl}_3\text{py}_3]$ to a superposition of a $\text{Os(III)}d\pi \rightarrow \text{py}\pi^*$ and $\text{Cl}^{-\pi} \rightarrow \text{Os(III)}d\pi$ C.T. transitions.

Using similar reasoning for the other sets of $[\text{Os(III)X}_{6-n}\text{py}_n]^{n-3}$ data, we arrive at the assignments listed in tables 3.5 and 3.6.

Table 3.5 Positions ($\nu_{\max}$) and Extinction Coefficients (ϵ) of Bands in the Electronic Absorption Spectra for the series $[\text{OsBr}_{(6-n)}\text{py}_n]^{(n-Y)}$ in CH_2Cl_2 /0.5M $[\text{TBA}][\text{BF}_4]$.

Compound	$\nu_{\max}(\text{cm}^{-1})$	$\epsilon (\text{mol}^{-1}\text{cm}^{-1}\text{dm}^3)$	Assignment
$[\text{Os(V)Br}_6]^-$	12 800	2 430	$\text{Br}^-\pi \rightarrow \text{Os(V)}d\pi$
	15 860	8 610	$\text{Br}^-\pi \rightarrow \text{Os(V)}d\pi$
	17 930	10 860	$\text{Br}^-\pi \rightarrow \text{Os(V)}d\pi$
	19 900	5 620	$\text{Br}^-\pi \rightarrow \text{Os(V)}d\pi$
	30 900	6 370	$\text{Br}^-\pi \rightarrow \text{Os(V)}d\pi$
	37 600	17 980	$\text{Br}^-\pi \rightarrow \text{Os(V)}d\pi$
$[\text{Os(IV)Br}_6]^{2-}$	17 300	1 030	$\text{Br}^-\pi \rightarrow \text{Os(IV)}d\pi$
	20 100	7 560	$\text{Br}^-\pi \rightarrow \text{Os(IV)}d\pi$
	22 030	12 360	$\text{Br}^-\pi \rightarrow \text{Os(IV)}d\pi$
	23 700	6 990	$\text{Br}^-\pi \rightarrow \text{Os(IV)}d\pi$
	35 100	10 000	$\text{Br}^-\pi \rightarrow \text{Os(IV)}d\pi$
	40 100	21 100	$\text{Br}^-\pi \rightarrow \text{Os(IV)}d\pi$
$[\text{Os(III)Br}_6]^{3-}$	27 100	4 200	$\text{Br}^-\pi \rightarrow \text{Os(III)}d\pi$
	27 700	4 830	$\text{Br}^-\pi \rightarrow \text{Os(III)}d\pi$
	28 300	3 740	$\text{Br}^-\pi \rightarrow \text{Os(III)}d\pi$
	30 300	6 520	$\text{Br}^-\pi \rightarrow \text{Os(III)}d\pi$
	32 300	4 380	$\text{Br}^-\pi \rightarrow \text{Os(III)}d\pi$
	39 600	17 870	$\text{Br}^-\pi \rightarrow \text{Os(III)}d\pi$

continued/

Compound	$\nu_{\max}(\text{cm}^{-1})$	$\epsilon (\text{mol}^{-1}\text{cm}^{-1}\text{dm}^3)$	Assignment
[Os(IV)Br ₅ py] ⁻	17 090		Br ⁻ $\pi \rightarrow$ Os(IV)d π
	19 520		Br ⁻ $\pi \rightarrow$ Os(IV)d π
	21 600		Br ⁻ $\pi \rightarrow$ Os(IV)d π
	24 500		Br ⁻ $\pi \rightarrow$ Os(IV)d π
[Os(III)Br ₅ py] ²⁻	26 500		Br ⁻ $\pi \rightarrow$ Os(III)d π
	27 800		Os(III)d $\pi \rightarrow$ py π^*
	39 700		py $\pi \rightarrow$ py π^*
c-[Os(IV)Br ₄ py ₂]	16 500		Br ⁻ $\pi \rightarrow$ Os(IV)d π
	20 380		Br ⁻ $\pi \rightarrow$ Os(IV)d π
	26 200		Br ⁻ $\pi \rightarrow$ Os(IV)d π
	39 200		py $\pi \rightarrow$ py π^*
c-[Os(III)Br ₄ py ₂] ⁻	26 300		Br ⁻ $\pi \rightarrow$ Os(III)d π
	28 400		Os(III) $\rightarrow$ py π^*
	40 100		py $\pi \rightarrow$ py π^*
c-[Os(II)Br ₄ py ₂] ²⁻	14 120		Os(II)d $\pi \rightarrow$ py π^*
	20 000		Os(II)d $\pi \rightarrow$ py π^*
	23 800		Os(II)d $\pi \rightarrow$ py π^*
	39 900		py $\pi \rightarrow$ py π^*

continued/

Compound	$\nu_{\max}(\text{cm}^{-1})$	$\epsilon(\text{mol}^{-1}\text{cm}^{-1}\text{dm}^3)$	Assignment
$m\text{-}[\text{Os}(\text{IV})\text{Br}_3\text{py}_3]^+$	15 350	1 650	$\text{Br}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	19 130	6 610	$\text{Br}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	22 500	2 710	$\text{Br}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	25 700	3 060	$\text{Br}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	30 200	2 190	$\text{Br}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	38 900	18 430	$\text{py}\pi \rightarrow \text{py}\pi^*$
$m\text{-}[\text{Os}(\text{III})\text{Br}_3\text{py}_3]$	21 400	1 130	$\text{Br}^-\pi \rightarrow \text{Os}(\text{III})d\pi$
	24 700	5 410	$\text{Br}^-\pi \rightarrow \text{Os}(\text{III})d\pi$
	30 900	11 510	$\text{Os}(\text{III})d\pi \rightarrow \text{py}\pi^*$
	40 600	10 160	$\text{py}\pi \rightarrow \text{py}\pi^*$
$m\text{-}[\text{Os}(\text{II})\text{Br}_3\text{py}_3]^-$	17 910	9 220	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	23 390	18 680	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	39 600	12 190	$\text{py}\pi \rightarrow \text{py}\pi^*$
$t\text{-}[\text{Os}(\text{IV})\text{Br}_2\text{py}_4]^{2+}$	18 170	4 710	$\text{Br}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	22 200	2 980	$\text{Br}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	24 600	3 940	$\text{Br}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	30 400	2 130	$\text{Br}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	38 800	14 950	$\text{py}\pi \rightarrow \text{py}\pi^*$
$t\text{-}[\text{Os}(\text{III})\text{Br}_2\text{py}_4]^+$	23 100	3 770	$\text{Br}^-\pi \rightarrow \text{Os}(\text{III})d\pi$
	34 300	9 870	$\text{Os}(\text{III})d\pi \rightarrow \text{py}\pi^*$
	38 800	7 600	$\text{py}\pi \rightarrow \text{py}\pi^*$
	42 000	7 490	$\text{py}\pi \rightarrow \text{py}\pi^*$
$t\text{-}[\text{Os}(\text{II})\text{Br}_2\text{py}_4]$	19 550	9 780	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	25 700	17 640	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	40 300	12 790	$\text{py}\pi \rightarrow \text{py}\pi^*$

Table 3.6 Positions ($\nu_{\max}$), Extinction Coefficients (ϵ) and assignments of Bands in the Electronic Absorption spectra for the series $[\text{OsI}_{(6-n)}\text{PY}_n]^{(n-Y)+}$ in CH_2Cl_2 /0.5M $[\text{TBA}][\text{BF}_4]$.

Compound	$\nu_{\max}(\text{cm}^{-1})$	$\epsilon(\text{mol}^{-1}\text{cm}^{-1}\text{dm}^3)$	Assignment
$[\text{Os}(\text{IV})\text{I}_6]^{2-}$	9 400	390	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{IV})\text{d}\pi$
	11 550	2 290	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{IV})\text{d}\pi$
	12 140	3 910	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{IV})\text{d}\pi$
	14 940	6 200	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{IV})\text{d}\pi$
	17 800	4 080	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{IV})\text{d}\pi$
	18 210	4 360	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{IV})\text{d}\pi$
	26 100	7 370	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{IV})\text{d}\pi$
	29 100	5 530	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{IV})\text{d}\pi$
	34 900	10 060	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{IV})\text{d}\pi$
$[\text{Os}(\text{III})\text{I}_6]^{3-}$	18 200	1 960	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{III})\text{d}\pi$
	18 810	2 030	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{III})\text{d}\pi$
	21 600	1 470	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{III})\text{d}\pi$
	22 100	2 700	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{III})\text{d}\pi$
	24 600	1 840	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{III})\text{d}\pi$
	25 100	1 470	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{III})\text{d}\pi$
	30 300	8 230	$\text{I}^{-}\pi \rightarrow \text{Os}(\text{IV})\text{d}\pi$

continued/

Compound	$\nu_{\max}(\text{cm}^{-1})$	$\epsilon (\text{mol}^{-1}\text{cm}^{-1}\text{dm}^3)$	Assignment
[Os(IV)I ₅ py] ⁻	9 038	1 200	I ⁻ $\pi \rightarrow$ Os(IV) d π
	10 440	930	I ⁻ $\pi \rightarrow$ Os(IV) d π
	12 020	3 500	I ⁻ $\pi \rightarrow$ Os(IV) d π
	12 860	3 280	I ⁻ $\pi \rightarrow$ Os(IV) d π
	15 460	6 200	I ⁻ $\pi \rightarrow$ Os(IV) d π
	29 300	8 160	I ⁻ $\pi \rightarrow$ Os(IV) d π
[Os(III)I ₅ py] ²⁻	15 810	1 050	I ⁻ $\pi \rightarrow$ Os(III) d π
	18 040	2 630	I ⁻ $\pi \rightarrow$ Os(III) d π
	21 300	3 420	I ⁻ $\pi \rightarrow$ Os(III) d π
	27 100	4 910	Os(III) d $\pi \rightarrow$ py π^*
	30 700	7 260	I ⁻ $\pi \rightarrow$ Os(III) d π
	34 300	8 960	I ⁻ $\pi \rightarrow$ Os(III) d π
<i>m</i> -[Os(IV)I ₃ py ₃] ⁺	8 235		I ⁻ $\pi \rightarrow$ Os(IV) d π
	8 945		I ⁻ $\pi \rightarrow$ Os(IV) d π
	10 370		I ⁻ $\pi \rightarrow$ Os(IV) d π
	12 840		I ⁻ $\pi \rightarrow$ Os(IV) d π
	17 160		I ⁻ $\pi \rightarrow$ Os(IV) d π
	27 400		I ⁻ $\pi \rightarrow$ Os(IV) d π

continued/

Compound	$\nu_{\max}(\text{cm}^{-1})$	Assignment
$m\text{-}[\text{Os}(\text{III})\text{I}_3\text{py}_3]$	5 138	$\text{Os}(\text{III})d\pi \rightarrow d\pi$
	13 940	$\text{I}^-\pi \rightarrow \text{Os}(\text{III})d\pi$
	17 580	$\text{I}^-\pi \rightarrow \text{Os}(\text{III})d\pi$
	20 500	$\text{I}^-\pi \rightarrow \text{Os}(\text{III})d\pi$
	29 900	$\text{Os}(\text{III})d\pi \rightarrow \text{py}\pi^*$
	34 400	$\text{I}^-\pi \rightarrow \text{Os}(\text{III})d\pi$
$m\text{-}[\text{Os}(\text{II})\text{I}_3\text{py}_3]^-$	18 420	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	23 700	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	38 200	$\text{py}\pi \rightarrow \text{py}\pi^*$
$t\text{-}[\text{Os}(\text{IV})\text{I}_2\text{py}_4]^{2+}$	12 940	$\text{I}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	19 130	$\text{I}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	23 320	$\text{I}^-\pi \rightarrow \text{Os}(\text{IV})d\pi$
	39 000	$\text{py}\pi \rightarrow \text{py}\pi^*$
$t\text{-}[\text{Os}(\text{III})\text{I}_2\text{py}_4]^+$	16 450	$\text{I}^-\pi \rightarrow \text{Os}(\text{III})d\pi$
	35 700	$\text{Os}(\text{III})d\pi \rightarrow \text{py}\pi^*$
		$\text{py}\pi \rightarrow \text{py}\pi^*$
$t\text{-}[\text{Os}(\text{II})\text{I}_2\text{py}_4]$	20 050	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	25 700	$\text{Os}(\text{II})d\pi \rightarrow \text{py}\pi^*$
	38 900	$\text{py}\pi \rightarrow \text{py}\pi^*$

3.4 Experimental

$[\text{NH}_4]_2[\text{OsCl}_6]$ and $[\text{NH}_4][\text{OsBr}_6]$ were used as supplied by Johnson Matthey.

$[\text{TBA}]_2[\text{OsBr}_6]$ was metathesised from $[\text{NH}_4]_2[\text{OsBr}_6]$ as follows. $[\text{NH}_4]_2[\text{OsBr}_6]$ (1.0g) was dissolved in a 1.0M hydrobromic acid (50ml). A solution of $[\text{TBA}][\text{OH}]$ (40% by weight), was added dropwise until no further precipitation occurred. The blood red solid was filtered off and dried under vacuum for 48 hours.

$[\text{TBA}][\text{OsBr}_5\text{py}]$ was prepared by the reductive electrosynthesis of $[\text{TBA}]_2[\text{OsBr}_6]$ (25 mg) in a solution of $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ (7ml)/py (0.03ml) at -0.6V (290K). The resulting solution $[\text{OsBr}_5\text{py}]^{2-}$ was reoxidised at 0.3V yielding air stable $[\text{OsBr}_5\text{py}]^-$, which was purified by thin layer chromatography on a silica plate, using CH_2Cl_2 as the eluent.

trans- $[\text{OsBr}_4\text{py}_2]$ was prepared in the following fashion. A sample of $[\text{TBA}]_2[\text{OsBr}_6]$ was reduced electrochemically to $[\text{OsBr}_5\text{py}]^{2-}$ as above. The solution was left in this oxidation state for twelve hours at 300K. The solution, which contained mainly *trans*- and *cis*- $[\text{OsBr}_4\text{py}_2]^-$, was then oxidised at 0.8V and the turquoise blue solid *trans*- $[\text{OsBr}_4\text{py}_2]$ was filtered off. *cis*- $[\text{OsBr}_4\text{py}_2]$ was obtained by passing the filtrate up a silica gel thin layer chromatography plate, the required product being found in the most mobile band.

mer-[OsBr₃py₃] was obtained by heating [NH₄]₂[OsBr₆] (0.2g) in glycerol(3ml)/pyridine(0.6ml) at 380K under nitrogen for two hours. The mixture was poured onto cold water (10ml) and the solid material filtered off. The solid was purified using thin layer chromatography (silica gel plate, CH₂Cl₂ eluent). The red solid was recrystallised from a CH₂Cl₂ diethylether mixture.

trans-[OsBr₂py₄] was synthesised as follows.

[NH₄]₂[OsBr₆] (0.2g) was heated in a glycerol(3ml)/py(0.6ml) mixture at 380K for three hours under nitrogen. A sample of Na[BH₄] (20mg) was added and, after ten minutes, the mixture was poured onto cold water. The solid material was filtered off and purified using thin layer chromatography (as above). The compound was recrystallised from a CH₂Cl₂/diethyl ether mixture.

[NH₄]₂[OsI₆] was prepared by refluxing [NH₄]₂[OsCl₆] (1.5g) in a 1.0M solution of [NH₄][I] in hydriodic acid (55%, 5ml) at 360K for two hours. The solid [NH₄]₂[OsI₆] produced was filtered and carefully washed with three 0.5ml portions of water and diethyl ether. The product was dried under vacuum for 24 hours.

[TBA][OsI₅py] was produced by reacting [NH₄]₂[OsI₆] (0.02g) with a CH₂Cl₂(10ml)/ pyridine(0.05ml) mixture under nitrogen at 290K for three hours. The resulting solution was purified using t.l.c (silica gel plate, CH₂Cl₂ eluent).

mer-[OsI₃py₃] was produced by heating [NH₄]₂[OsI₆] (0.1g) in a glycerol(2ml)/pyridine(0.4ml) mixture at 380K for

half an hour. The resulting solution was poured into cold water (5ml) and the solid material filtered off. The resulting purple solid was filtered off and purified by CH_2Cl_2 elution up a silica gel thin layer chromatography plate. The material could be recrystallised from a CH_2Cl_2 /methanol/hydrazine hydrate 20:20:1 mixture.

trans- $[\text{OsI}_2\text{py}_4]$ was obtained by heating $[\text{NH}_4]_2[\text{OsI}_6]$ (0.2g) in a glycerol (3ml) pyridine (0.6ml) mixture at 380K for three hours. The resulting solution was poured onto cold water (10ml) and the solid material filtered off. This was purified using thin layer chromatography (as above).

$[\text{TBA}][\text{BF}_4]$ and CH_2Cl_2 were used as described in chapter 2.

3.5 References.

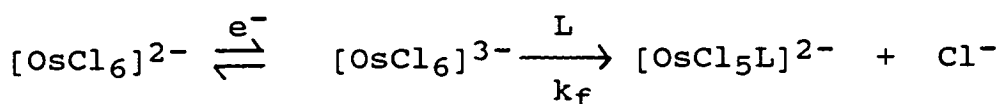
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Chapter 4 Analysis of cyclic voltammograms of the $[\text{OsCl}_6]^{2-}/^{3-}$ couple yields rate constants for the reaction of $[\text{OsCl}_6]^{3-}$ with py, dmf and CO; the rate of reaction of $[\text{OsCl}_6]^{3-}$ with py in CH_2Cl_2 is also determined using convolution techniques; the rates of reaction of $[\text{OsCl}_6]^{3-}$, $[\text{OsBr}_6]^{3-}$ and $[\text{OsI}_6]^{3-}$ with py in CH_2Cl_2 are compared using the former method.



4.1 Introduction

The pseudo-first order rate constant of a chemical reaction coupled to a charge transfer process can be obtained through analysis by cyclic voltammetry.¹ The reduction of $[\text{OsCl}_6]^{2-}$ in the presence of a suitable substituent is an example of such a process and can be described as a reversible charge transfer followed by an irreversible chemical reaction, an EC mechanism²:



A typical reductive cyclic voltammogram of $[\text{OsCl}_6]^{2-}$ is shown in figure 4.1. The ratio of the heights of the cathodic and anodic peak currents gives information on the amount of $[\text{OsCl}_6]^{3-}$ that has reacted. With the notation of figure 4.1, the principal variables determining the experimental timescale of the experiment are the half wave potential ($E_{1/2}$), the potential between $E_{1/2}$ and the switching potential E_λ , and the scan rate (∂). Nicholson and Shain calculated a large number of theoretical cyclic voltammetric curves varying both k_f and ∂ and the switching potential. For a constant value of the parameter $k_f\tau$ (where τ is the time in seconds from $E_{1/2}$ to E_λ), the ratio of anodic to cathodic peak currents was found to be constant. Thus a working curve was constructed relating the ratio of the peak currents i_a/i_c to $k_f\tau$, which allows k_f to be calculated for any single cyclic voltammogram.

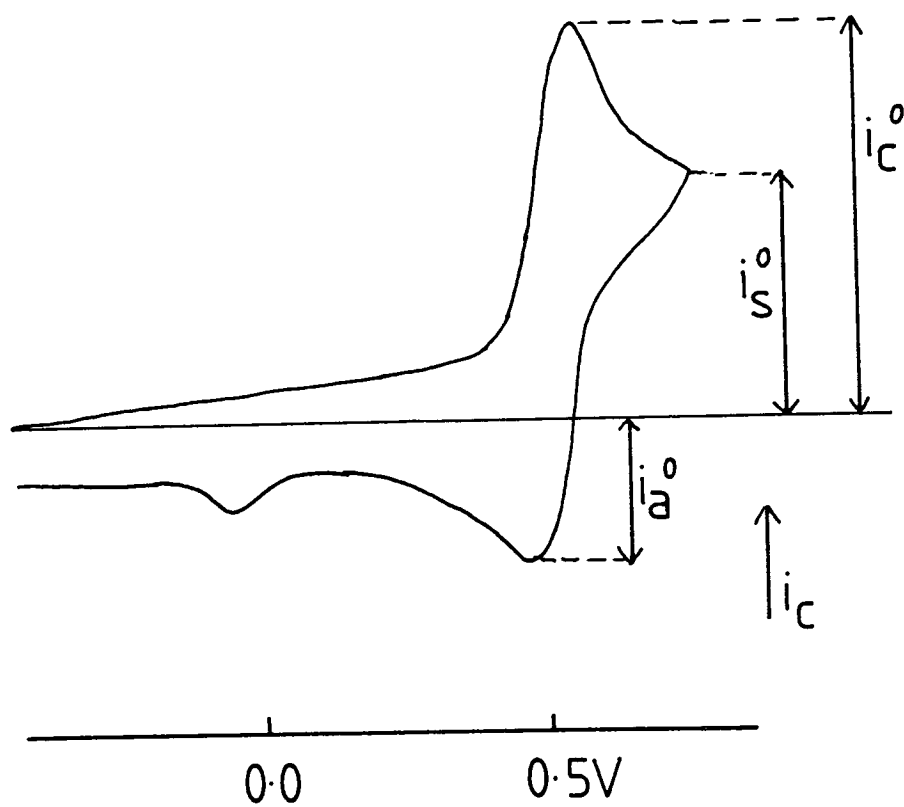


Figure 4.1 Cathodic Cyclic Voltammogram of $[\text{OsCl}_6]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ in the Presence of Pyridine.

The values required to plot this curve are given below:

i_a/i_c	$k_{fr}(s^{-1})$	$\log k_{fr}$
1.00	0.004	-2.398
0.986	0.023	-1.638
0.967	0.035	-1.456
0.937	0.066	-1.180
0.900	0.105	-0.979
0.828	0.195	-0.710
0.727	0.350	-0.456
0.641	0.525	-0.280
0.628	0.550	-0.260
0.551	0.778	-0.109
0.486	1.050	+0.021
0.466	1.168	+0.067
0.415	1.557	+0.192

To calculate i_a/i_c the following equation was used:²

$$i_a/i_c = i_a^0/i_c^0 + 0.485(i_s^0)/i_c^0 + 0.086 \quad \underline{1}$$

A significant disadvantage of this method of calculating K_f is that it uses only three points on the entire cyclic voltammetric curve.

The use of 'Kinetic Convolutions' is another method of calculating pseudo-first order rate constants. Normally a convolution is defined by the integral:

$$I_1 = I_1(t) = \int_0^t i(u) / \sqrt{\pi(t-u)} du \quad \underline{2}$$

where $i(u)$ is the current measurement made at time u .

Each convolution is estimated via a Gamma function algorithm.² A kinetic convolution is similar in form to an I_1 convolution as shown above, except that each segment is further scaled by the exponential factor containing a 'test' value of the apparent first order rate constant k_f :

$$I_2 = I_2(t) = \int_0^t i(u) \exp(-k_f(t-u)) / \sqrt{\tau(t-u)} du \quad \underline{3}$$

This method uses all of the cyclic voltammogram to calculate k_f which should give rise to a better estimate of K_f than the former method.

4.2 Kinetic data for the substitution of $[\text{OsCl}_6]^{3-}$ with pyridine, dmf and CO.

The pseudo-first order rate constants (s^{-1}) obtained for the reductive substitution of $[\text{OsCl}_6]^{2-}$ obtained using the method of Nicolson and Shain are given below:

Temp(K)	py ^a	dmf ^a	$\text{CH}_2\text{Cl}_2/\text{py}^b$	$\text{CH}_2\text{Cl}_2/\text{dmf}^b$	$\text{CH}_2\text{Cl}_2/\text{CO}^c$
273	0.03	0.21	0.09	0.09	0.09
283	0.12	0.50	0.17	0.18	0.12
293	0.40	1.10	0.31	0.34	0.19
303	1.46	2.29	0.54	0.64	0.38

a 0.1M [TBA][BF₄].

b 0.5M [TBA][BF₄], the CH₂Cl₂ solution contained a ten molar excess of substituent.

c 0.5M [TBA][BF₄], the CH₂Cl₂ solution contained an unknown amount of carbon monoxide.

(It should be noted that the value obtained for a particular rate constant was dependent on the scan rate used, not as predicted by the Nicolson and Shains' model. The k_f produced tended to increase by ca. 40% on increasing the scan rate from 100 to 400mVs⁻¹. Hence, when comparing rate constants, only results obtained from cyclic voltammograms with scan rates of 100mVs⁻¹ are quoted here).

The results show that the rate of reaction is dependent on the solvent system. All the results in methylene chloride are very similar, the rate constant for the CH₂Cl₂/CO system being low due to a low concentration of dissolved carbon monoxide in CH₂Cl₂. Dmf is known to readily solvate chloride ions and, since the rate of reaction is quicker in dmf, it seems reasonable to suggest that the rate of reaction depends on how well chloride is solvated after dissociation. The rate determining step for the substitution reaction appears to be chloride loss.

The rate constants produced for these substitutions of [OsCl₆]³⁻ are very large when compared with similar substitutions of [OsCl₆]²⁻. These latter reactions were

performed by heating the $[\text{TBA}]_2[\text{OsCl}_6]$ in the appropriate solvent and monitoring product formation by u.v./vis. absorption spectroscopy. The results obtained are listed below

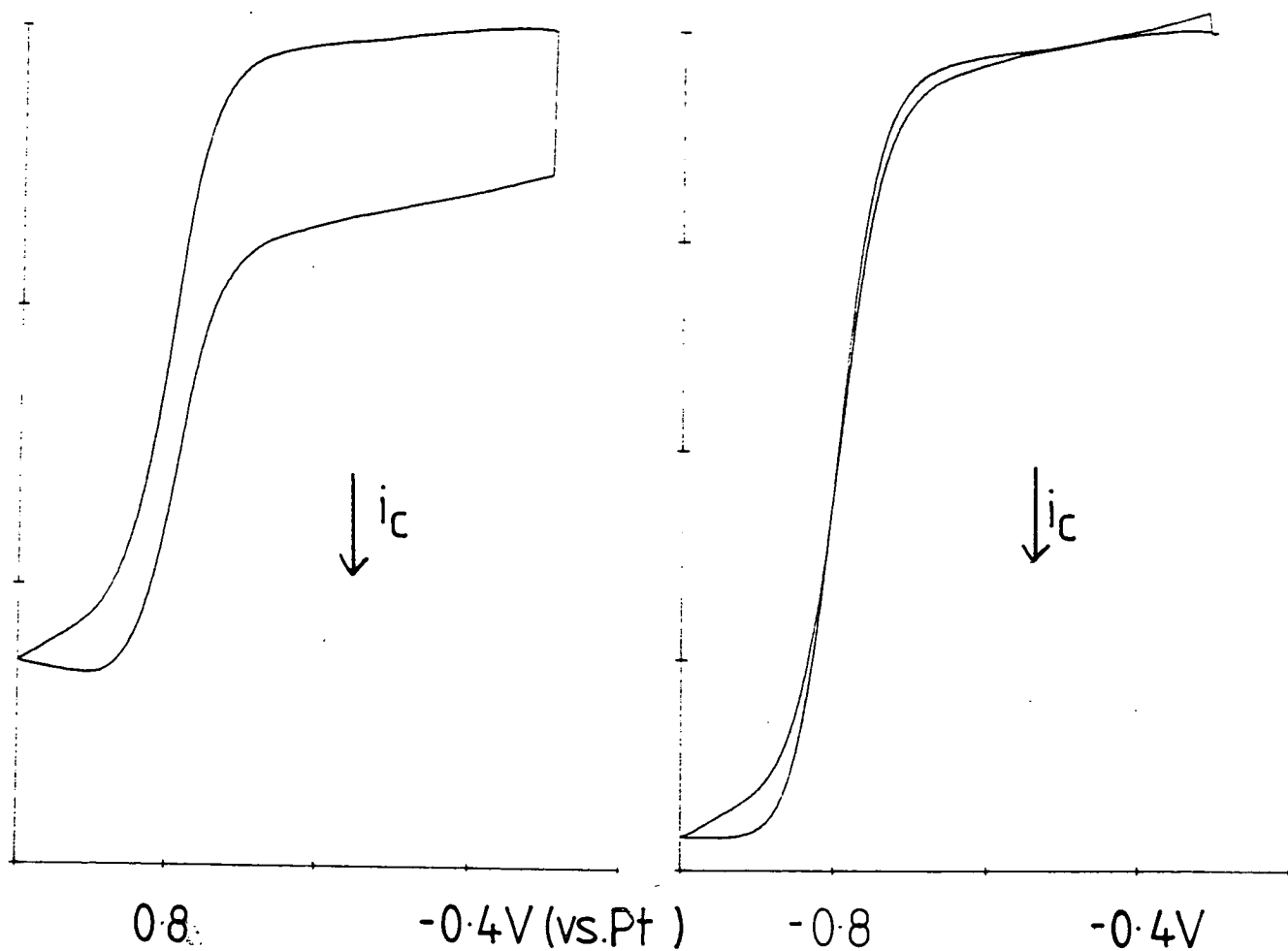
Solvent	Temperature (K)	$k_4 (\text{s}^{-1})$
pyridine	385	1.23×10^{-4}
Dmf	393	2.06×10^{-4}
	403	5.39×10^{-4}
	414	1.45×10^{-3}
	425	3.99×10^{-3}

If these rates are extrapolated to the working temperature of the $[\text{OsCl}_6]^{3-}$ substitutions, using an Arrhenius type plot ($\ln k$ vs $1/T$), we can see that the rate of reaction for the $[\text{OsCl}_6]^{3-}$ substitutions is some ten orders of magnitude greater than for $[\text{OsCl}_6]^{2-}$.

4.3 Kinetic data determined by 'kinetic convolutions' for the substitution of $[\text{OsCl}_6]^{3-}$ by pyridine in $\text{CH}_2\text{Cl}_2/0.5\text{M}$ $[\text{TBA}][\text{BF}_4]$

A pseudo first order rate constant of 0.16s^{-1} ^{was obtained} _^ for the substitution of $[\text{OsCl}_6]^{3-}$ by py in the solvent system described above at 283K. This result is comparable to the

result obtained by the previous method (0.17s^{-1}). Again, however, the calculated rate constants were found to increase with increased scan rate. The result quoted above was obtained using a scan rate of 100mVs^{-1} . Figure 4.2 and 4.3 show the convolution curve uncorrected and corrected respectively for chemical reaction of $[\text{OsCl}_6]^{3-}$ with py.



Figures 4.2 and 4.3 Convolutions of Cyclic Voltammetric Data of a Reduction of $[\text{OsCl}_6]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M}$ $[\text{TBA}][\text{BF}_4]$ /Doped with Pyridine, Corrected and Uncorrected Respectively for Reaction of $[\text{OsCl}_6]^{3-}$ with Pyridine.

4.4 A comparison of the relative rates of reaction of $[\text{OsCl}_6]^{3-}$, $[\text{OsBr}_6]^{3-}$, and $[\text{OsI}_6]^{3-}$ with py in $\text{CH}_2\text{Cl}_2/0.5\text{M}$ $[\text{TBA}][\text{BF}_4]$ at 293K, calculated using the methods of Nicholson and Shain.

Complex	$k_f(\text{s}^{-1})$
$[\text{OsCl}_6]^{3-}$	0.19
$[\text{OsBr}_6]^{3-}$	0.40
$[\text{OsI}_6]^{3-}$	18.1

The values quoted were taken from $\text{CH}_2\text{Cl}_2/0.5\text{M}$ $[\text{TBA}][\text{BF}_4]$ solutions containing ten molar equivalents of pyridine. The rate for $[\text{OsI}_6]^{3-}$ was extrapolated from a rate constants obtained from voltammograms performed between 240 and 260K, using the Arrhenius relation $\ln k \propto 1/T$.

The pseudo first order rate constants can be seen to increase as follows $[\text{OsCl}_6]^{3-} < [\text{OsBr}_6]^{3-} < [\text{OsI}_6]^{3-}$. This is as we would predict since iodide is a better leaving group than chloride. Another factor contributing to the observed increase may be that iodide is being solvated more easily than bromide or chloride in CH_2Cl_2 .

4.5 Experimental.

Cyclic voltammograms were recorded using the experimental procedures and equipment described in appendix 1. Note that particular care was taken to perform each rate constant experiment under strictly temperature controlled conditions.

The Convolution and 'kinetic convolution' experiments were performed using an EG+G P.A.R. Potentiostat/Galvanostat Model 273 coupled to the Condecon software package on a IBM Personal System/2 Model 30 Computer.

4.6 References.

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Chapter 5. Introduction; electrochemistry and spectroelectrochemistry of the species $[\text{TBA}][\text{OsCl}_5\text{L}]$ where $\text{L} = \text{PhCN}, 2\text{-cypy}, 3\text{-cypy}, 4\text{-cypy}, 3,4\text{-dcypy}$; an examination of the products of the reduction of $[\text{OsCl}_6]^{2-}$ in the presence of CO .

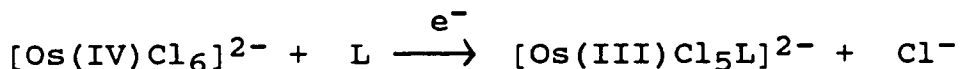
Why is it that the hate of a man - even of a man like Franco - dies with his death, and yet the love, the love which he had begun to feel for Father Quixote, seemed now to live and grow in spite of the final separation and the final silence - for how long, he wondered with a kind of fear, was it possible for that love of his to continue? And to what end?

Monsignor Quixote

Graham Greene

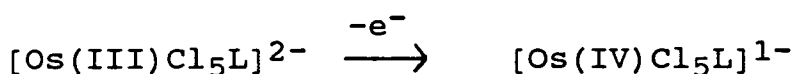
5.1 Introduction.

This chapter relates reductive substitution reactions of $[\text{OsCl}_6]^{2-}$ of the form:



where L = Benzonitrile (PhCN), 2-cyanopyridine (2-cypy), 3-cyanopyridine (3-cypy), 4-cyanopyridine (4-cypy), 3,4-dicyanopyridine (3,4-dcypy) and carbon monoxide (CO).

These reductions were performed by bulk reductive electrolysis of $[\text{OsCl}_6]^{2-}$ in a solution of $\text{CH}_2\text{Cl}_2/0.5\text{M}$ $[\text{TBA}][\text{BF}_4]$ that contained ten molar equivalents of the desired substituent L (for L = CO the reduction was performed in a CO saturated $\text{CH}_2\text{Cl}_2/0.5\text{M}$ $[\text{TBA}][\text{BF}_4]$ solution.) Except when CO was the substituent, air sensitive Os(III) compounds were produced. These were rendered air stable via oxidation to the Os(IV) species:



The products of all the reactions were all characterised electrochemically and, where possible, spectroelectrochemically. The results obtained provide a valuable insight into the electronic properties of the ligands, as well as helping in the confirmation of some of the assignments made in the interpretation of the u.v./vis. absorption spectra contained in chapter 2.

5.2.1 Electrochemistry and spectroelectrochemistry of [TBA][Os(IV)Cl₅PhCN].

Cyclic and a.c.voltammetric studies on a solution of [TBA][OsCl₅PhCN] in a CH₂Cl₂/0.5M [TBA][BF₄] at 290K revealed two reductive steps at 0.16V and -1.24V and an oxidation at 1.92V. The reduction at 0.16V was shown to be a one electron step by a coulometric experiment. The oxidative and first reductive step were reversible under the conditions described at the platinum microelectrode, whereas the second reduction was irreversible. Since PhCN is a π - acceptor, but is not itself easily reduced, the redox steps are all postulated as one electron metal based processes.

A spectroelectrochemical study of [TBA][OsCl₅PhCN] in CH₂Cl₂/0.5M [TBA][BF₄] at 240K was performed at the O.T.T.L.E. The intense bands at low energy in the spectrum of [OsCl₅PhCN]⁻ (fig. 5.1) can, by analogy with the spectrum of [Os(IV)Cl₅py]⁻ be assigned as Cl⁻ $\pi \rightarrow$ Os(IV)d π C.T. transitions. The low energy band in the spectrum of [Os(III)Cl₅PhCN]²⁻ (fig. 5.2) occurs at lower energy than any of the bands observed in the spectrum of [Os(IV)Cl₅PhCN]⁻, and hence is assigned as a Os(III)d $\pi \rightarrow$ PhCN π^* transition. The spectrum of [Os(V)Cl₅PhCN] (fig. 5.3) is dominated by Cl⁻ $\pi \rightarrow$ Os(V) transitions. The low energy end of the spectrum closely resembles that of [Os(V)Cl₅py].

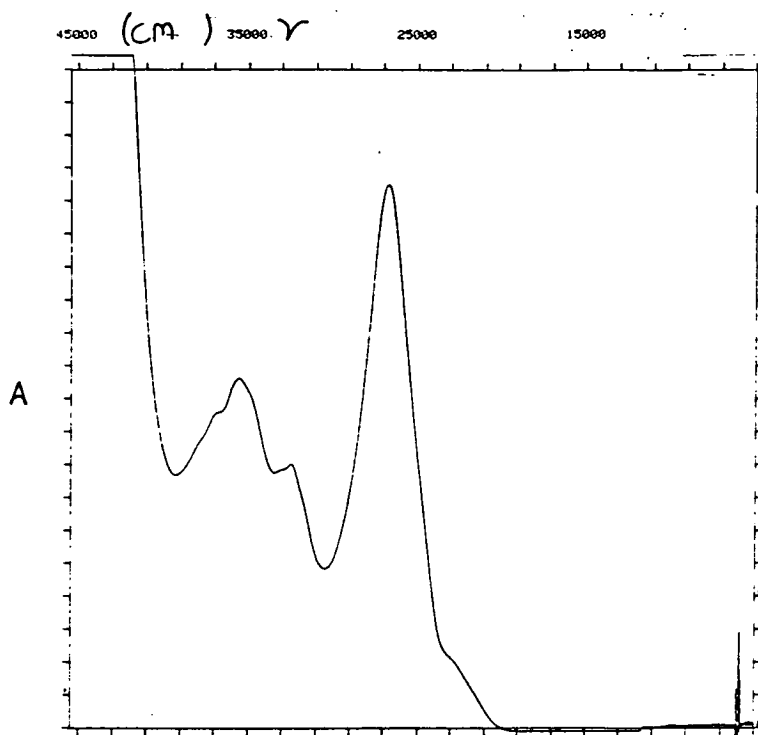


Figure 5.1 U.V./Vis. Absorption Spectrum of $[\text{OsCl}_5\text{PhCN}]^-$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 240K.

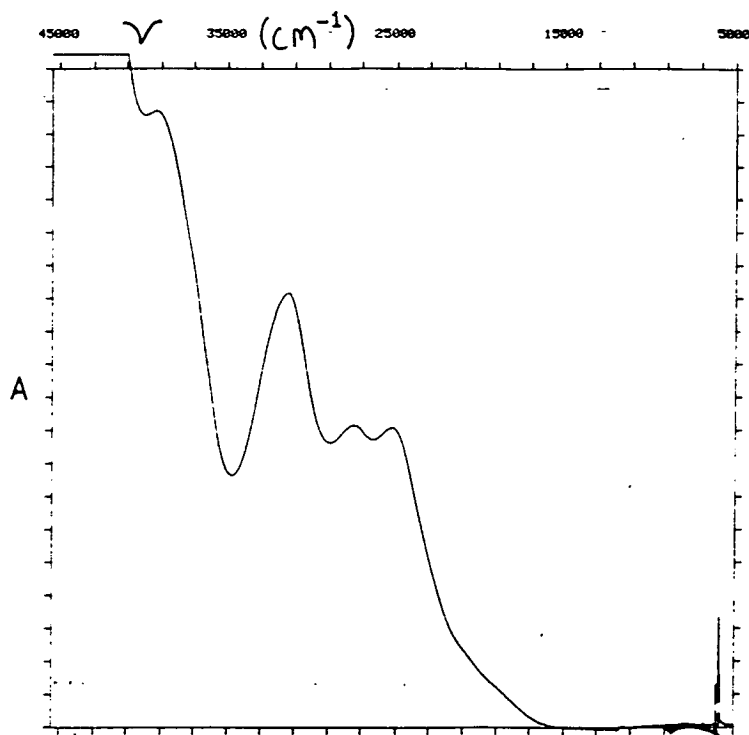


Figure 5.2 U.V./Vis. Absorption Spectrum of $[\text{OsCl}_5\text{PhCN}]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 240K.

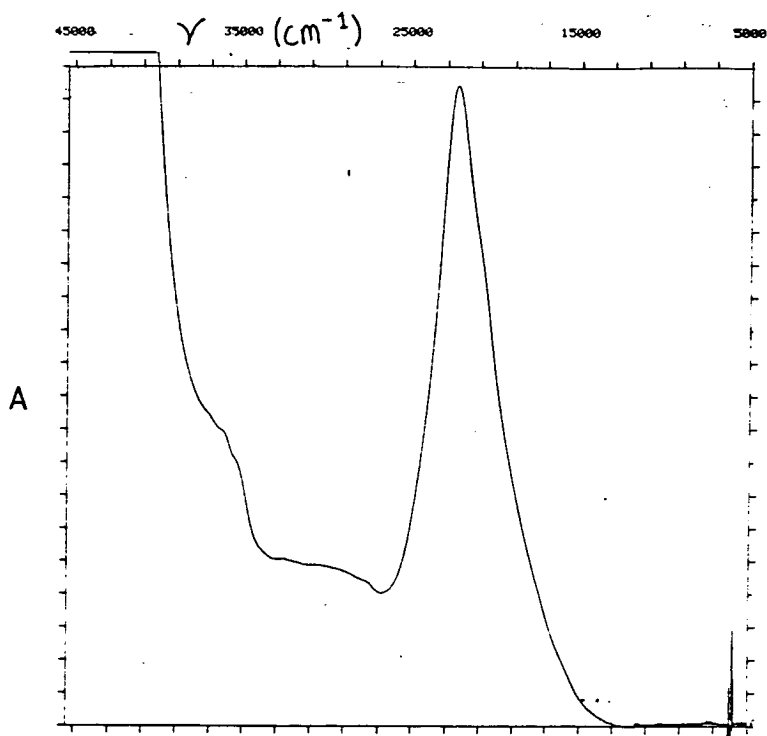


Figure 5.3 U.V./Vis. Absorption Spectrum of $[\text{OsCl}_5\text{PhCN}]$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K.

5.2.2 Electrochemical synthesis and electrochemical analysis of $[\text{TBA}][\text{OsCl}_5(2\text{-cypy})]$, $[\text{TBA}][\text{OsCl}_5(3\text{-cypy})]$ and $[\text{TBA}][\text{OsCl}_5(4\text{-cypy})]$.

When $[\text{TBA}]_2[\text{OsCl}_6]$ undergoes a bulk reductive electrolysis at -0.75V and 285K in a $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ solution containing a ten molar excess of 2,3, or 4-cypy, the products exhibit an electrochemistry more complex than had been observed in previous reductive substitutions of $[\text{OsCl}_6]^{2-}$ (e.g. with pyridine 2.2.3 and benzonitrile 5.2.1). For example, when 2-cypy is added, an a.c voltammogram of the product of the electrolysis (solution A, see fig. 5.4) reveals two sets of oxidative

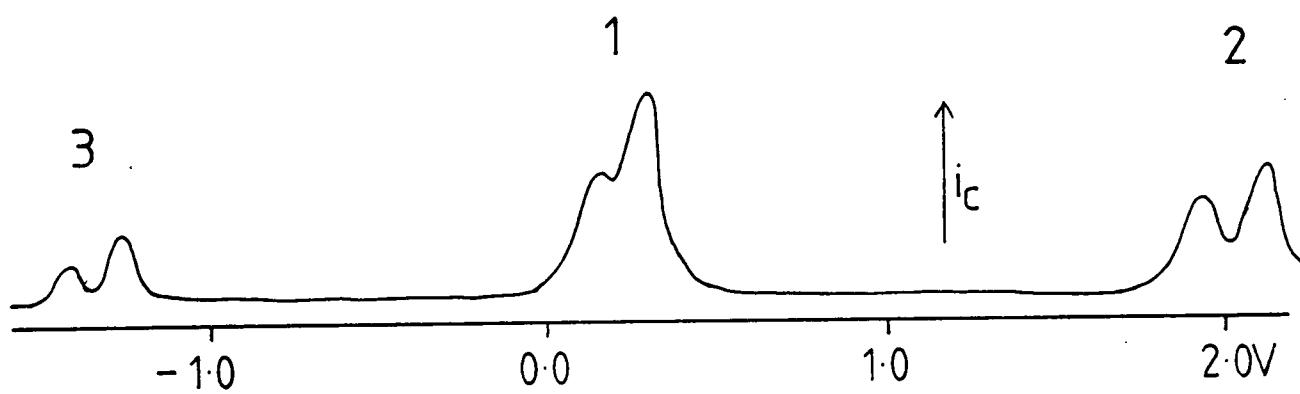


Figure 5.4 A.C. Voltammogram of solution A.

steps at 0.12 and 0.22V (set 1) and 1.92 and 2.11V (set 2). A set of reductive processes are also seen at -1.27 and -1.13V (set 3). Cyclic voltammetry shows that all the redox steps are reversible under the conditions at the platinum microelectrode within the timescale of the experiment.

When a bulk oxidative electrolysis of the products was performed at +0.30V, a coulometric plot showed that the total charge required to induce both the oxidative steps at 0.12 and 0.22V was equal to the charge involved in the initial one electron reduction of $[\text{OsCl}_6]^{2-}$. These observations can be explained by considering that 2-cypy can bind to the metal centre either through the ring nitrogen or through the terminal nitrogen in the cyano group (fig. 5.5). Hence we propose that the sets of closely spaced redox couples (1,2 and 3) correspond to similar redox processes for the two closely related molecules of $[\text{OsCl}_5(2\text{-cypy})]^-$ that arise from the two separate binding modes of 2-cyanopyridine.

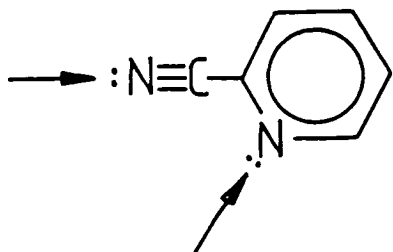


Figure 5.5 Possible Binding Sites for 2-Cyanopyridine.

Table 5.1 includes the values of redox couples for complexes of the form $[TBA][OsCl_5L]$, where $L = py, PhCN, 2-cypy$. From these data we observe that the $Os(III)/Os(IV)$ couple $[OsCl_5PhCN]^{2-/-}$ occurs at a more positive potential than that for $[OsCl_5py]^-$. Benzonitrile is a better π - acceptor than pyridine, which results in a greater stabilisation of the $Os(III)$ oxidation state for the former substituted complex than the latter. Hence we propose that, for each pair of couples, the process lying at the more positive potential corresponds to the complex containing cyanopyridine bound through the terminal nitrogen in the cyano group.

Stirred voltammetry on the products (solution A) shows that the redox steps all involve the same number of electrons. By comparison with our previous work (chapter 2), we can assign sets 1 and 2 to metal based $Os(III)/Os(IV)$ and $Os(IV)/Os(V)$ couples respectively. However set 3 cannot be confidently assigned as metal based since cyanopyridines have a reductive electrochemistry¹, which suggests that this extreme cathodic process might be ligand based. Information on the electronic nature of the reduced species $[OsCl_5(2-cypy)]^{3-}$ (such as a u.v.vis absorption spectrum), would be required before the site of the reductive process can be assigned.

Similar results are obtained when 3-cypy and 4-cypy are used as the substituents in the reductive substitution

Table 5.1 Voltammetric Data¹ for Complexes $[\text{OsCl}_5\text{L}]^-$ where L = py, PhCN, 2-cypy, 3-cypy, 4-cypy and 3,4-dcypy.

L	$[\text{OsCl}_5\text{L}]^{0/-}$	$[\text{OsCl}_5\text{L}]^{-/2-}$	$[\text{OsCl}_5\text{L}]^{2-/3-}$
Py	1.83V	-0.02V	-1.53V
PhCN	1.92V	0.16V	-1.24V
2-Cypy a)	1.92V	0.12V	-1.27V
b)	2.11V	0.22V	-1.13V
3-Cypy a)	1.92V	0.13V	-1.33V
b)	—	0.21V	-1.12V
4-Cypy a)	1.90V	0.17V	-1.16V*
b)	—	0.28V	-1.06V
3,4-Dcypy ²	1.98V	0.28V	-0.83V*

¹ Volts versus Ag/AgCl ($\text{FeCp}_2/\text{FeCp}_2^+ = 0.56\text{V}$)

² Bound through the ring N

a) is bound through the ring N, b) is CN bound.

of $[\text{OsCl}_6]^{2-}$. The electrochemical data obtained is listed in table 5.1. Note that the exact position of the cyano group on the pyridine ring makes very little difference either to redox properties of the $[\text{OsCl}_5\text{L}]^n$ species or to the relative proportions of the two isomers produced.

In order to separate the two products formed in these experiments it is necessary to electrolyse the Os(III) species initially produced, to the corresponding Os(IV) species, since the compounds are less susceptible to aerial decomposition in this higher oxidation state. The two products from each of the three reactions can be separated via thin layer chromatography at a silica gel plate using CH_2Cl_2 as the eluent. Unfortunately only the more mobile of the two compounds can be successfully recovered from the plate, thus enabling a full electrochemical and spectroelectrochemical study of this isomer only.

An electrolyte free sample of the $[\text{Os}(\text{IV})\text{Cl}_5(4\text{-cypy})]^{1-}$ complex was obtained using cobaltacene in CH_2Cl_2 to chemically reduce $[\text{TBA}]_2[\text{OsCl}_6]$ in the presence of 4-cypy. The $[\text{Os}(\text{III})\text{Cl}_5(4\text{-cypy})]^{2-}$ produced was then chemically oxidised with $[\text{NO}][\text{BF}_4]$. The products were separated using thin layer chromatography. An a.c.voltammogram of the more mobile complex in a $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ solution revealed only two reductions at 0.17V and -1.16V and an oxidation at 1.90V. This response corresponds to the species we tentatively

attributed to $[\text{OsCl}_5(4\text{-cypy})]^-$, where the 4-cypy is bound through the ring nitrogen.

This compound was successfully recrystallised by allowing diethyl ether to slowly diffuse into a solution of the compound in CH_2Cl_2 . Small yellow crystals suitable for a Röntgen-ray analysis were produced.

The single crystal structure determination of $[\text{TBA}][\text{OsCl}_5(4\text{-cypy})]$ shows the ligand bound through the ring nitrogen (fig. 5.6) with a Os-N bond length of $2.12\text{\AA}$. The average Os-Cl bond length is $2.33\text{\AA}$, the chloride *trans*- to the 4-cypy exhibiting a slightly shorter bond to osmium ($2.3095(24)\text{\AA}$) than the other chloride ligands. A list of bond lengths and angles are given in table 5.2.

5.2.3. Electrochemical synthesis and electrochemical analysis of $[\text{TBA}][\text{OsCl}_5(3,4\text{-dcypy})]$.

A solution of $[\text{TBA}]_2[\text{OsCl}_6]$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ reductively electrolysed at -0.75V in the presence of a ten molar excess of 3,4-dicyanopyridine reveals an electrochemistry even more complex than that of a solution when 2, 3 and 4-cypy were the substituents. The complexity arises since 3,4-dicyanopyridine has three possible binding sites, either through the ring nitrogen or via either of the terminal cyano groups.

The products, once electrolysed to the stable Os(IV) oxidation state, can be separated using thin layer

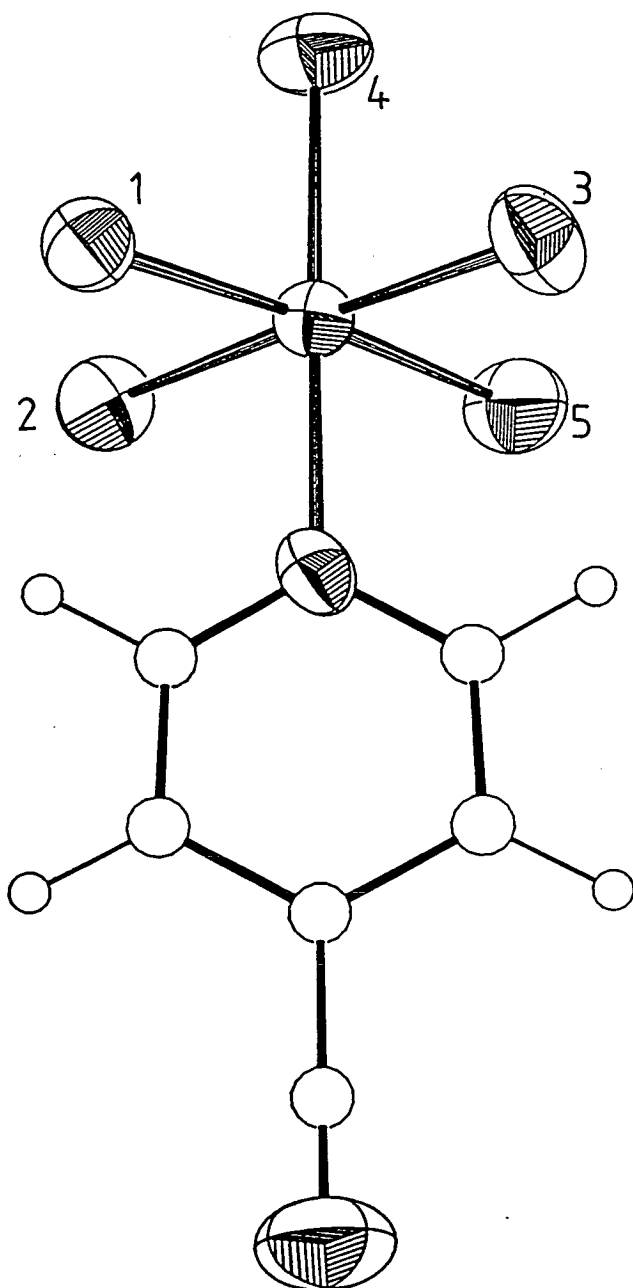


Figure 5.6 View of the $[\text{OsCl}_5(4\text{-cypy})]^-$ Anion.

Table 5.2 Bond Lengths (Å) and Angles (degrees) with Standard Deviations for the $[\text{OsCl}_5(4\text{-cypy})]^-$ Anion.

Os - Cl(1)	2.3390(23)	N - C(21)	1.509(10)
Os - Cl(2)	2.3354(21)	N - C(31)	1.541(10)
Os - Cl(3)	2.3293(25)	N - C(41)	1.516(10)
Os - Cl(4)	2.3095(24)	C(11) - C(12)	1.509(12)
Os - Cl(5)	2.3194(24)	C(12) - C(13)	1.532(13)
Os - N(1)	2.123(6)	C(13) - C(14)	1.517(14)
N(1) - C(2)	1.345(10)	C(21) - C(22)	1.534(13)
N(1) - C(6)	1.330(10)	C(22) - C(23)	1.506(14)
C(2) - C(3)	1.384(12)	C(23) - C(24)	1.468(16)
C(3) - C(4)	1.388(12)	C(31) - C(32)	1.536(12)
C(4) - C(5)	1.378(12)	C(32) - C(33)	1.513(13)
C(5) - C(6)	1.375(12)	C(33) - C(34)	1.514(14)
C(4) - C(4')	1.451(12)	C(41) - C(42)	1.520(12)
C(4') - N(4')	1.123(13)	C(42) - C(43)	1.513(14)
N - C(11)	1.510(10)	C(43) - C(44)	1.511(15)

Cl(1) - Os - Cl(2)	89.53(8)	C(5) - C(4) - C(4')	120.6(8)
Cl(1) - Os - Cl(3)	88.30(8)	C(4) - C(5) - C(6)	118.1(8)
Cl(1) - Os - Cl(4)	91.55(8)	N(1) - C(6) - C(5)	124.2(8)
Cl(1) - Os - Cl(5)	177.48(8)	C(4) - C(4') - N(4')	178.7(10)
Cl(1) - Os - N(1)	88.84(18)	C(11) - N - C(21)	111.6(6)
Cl(2) - Os - Cl(3)	176.04(8)	C(11) - N - C(31)	106.1(6)
Cl(2) - Os - Cl(4)	92.12(8)	C(11) - N - C(41)	111.9(6)
Cl(2) - Os - Cl(5)	89.89(8)	C(21) - N - C(31)	111.4(6)
Cl(2) - Os - N(1)	88.62(17)	C(21) - N - C(41)	105.6(6)
Cl(3) - Os - Cl(4)	91.24(8)	C(31) - N - C(41)	110.3(6)
Cl(3) - Os - Cl(5)	92.13(8)	N - C(11) - C(12)	116.4(6)
Cl(3) - Os - N(1)	88.03(18)	C(11) - C(12) - C(13)	108.9(7)
Cl(4) - Os - Cl(5)	90.91(8)	C(12) - C(13) - C(14)	112.1(8)
Cl(4) - Os - N(1)	179.16(18)	N - C(21) - C(22)	115.6(7)
Cl(5) - Os - N(1)	88.70(18)	C(21) - C(22) - C(23)	109.5(8)
Os - N(1) - C(2)	121.1(5)	C(22) - C(23) - C(24)	115.1(9)
Os - N(1) - C(6)	121.9(5)	N - C(31) - C(32)	116.9(7)
C(2) - N(1) - C(6)	117.0(7)	C(31) - C(32) - C(33)	108.1(7)
N(1) - C(2) - C(3)	123.3(8)	C(32) - C(33) - C(34)	113.2(8)
C(2) - C(3) - C(4)	117.9(8)	N - C(41) - C(42)	116.5(7)
C(3) - C(4) - C(5)	119.4(8)	C(41) - C(42) - C(43)	110.1(7)
C(3) - C(4) - C(4')	120.0(8)	C(42) - C(43) - C(44)	112.2(8)

chromatography (as above). Again, unfortunately, only the most mobile product can be successfully removed from the plate. When a.c. voltammetry is performed on the most mobile band 0.5M CH_2Cl_2 two reductions can be observed at 0.28V and -0.83 V, an oxidation at 1.98V is also observed. 3,4-Dicyanopyridine is a better π - acceptor than any of the cyanopyridines discussed in 5.2.2., and itself exhibits a reduction at -1.11V (see fig. 5.7). The oxidation at 1.98V and the reduction at 0.28V are attributed to Os(IV)/Os(V) and Os(IV)/Os(III) couples respectively. A spectroelectrochemical examination would determine whether the second reduction was metal or ligand based (see 5.2.4.). We suggest that in the isolated

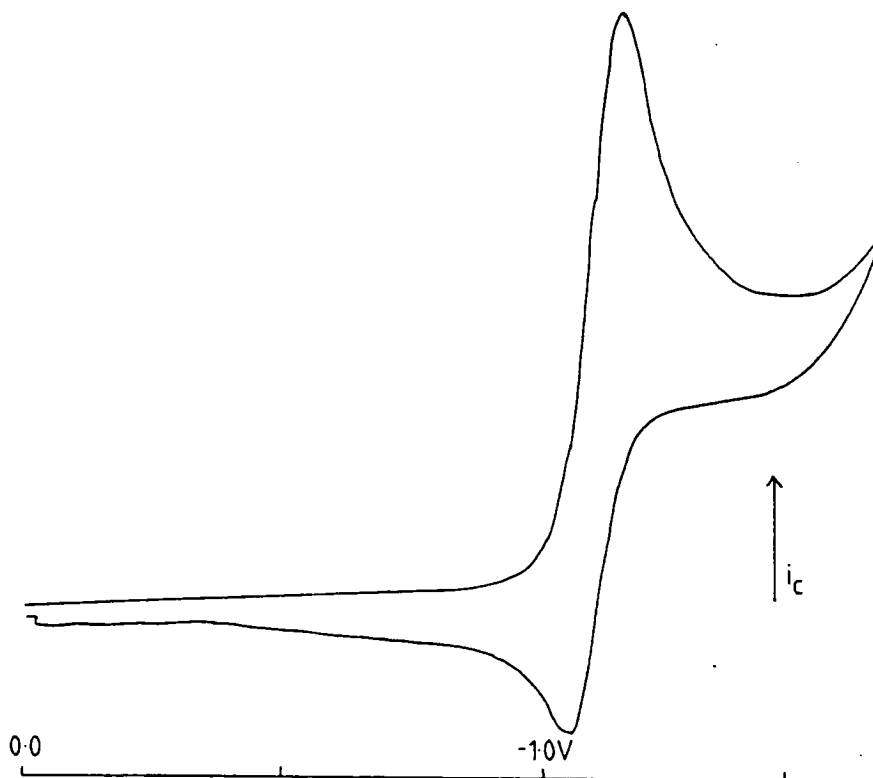


Figure 5.7 Cyclic Voltammogram of 3,4, dicyanopyridine in CH_2Cl_2 /0.5M [TBA][BF_4] at 290K.

product the 3,4-dicyanopyridine is bound through the ring nitrogen, since the Os(III)/Os(IV) redox couple occurs at a more negative potential than that found for cyano-bound $[\text{Os(IV)Cl}_5(4\text{-cypy})]^-$. We suggest that the other couples observed in the original solution can be assigned to the cyano-bound complexes.

5.2.4. Spectroelectrochemical studies on $[\text{TBA}][\text{OsCl}_5\text{L}]$ where L = 2-cypy, 3-cypy, 4-cypy and 3,4-dcypy (L bound to the metal via the ring nitrogen).

The species listed below were successfully generated and examined spectroelectrochemically at the O.T.T.L.E. :

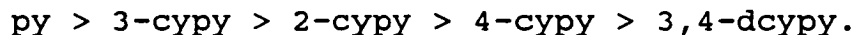
<u>Ligand</u>	<u>Os(V)</u>	<u>Os(IV)</u>	<u>Os(III)</u>	<u>'Os(III)'⁻</u>
2-cypy			$[\text{OsCl}_5\text{L}] \xrightleftharpoons{e^-} [\text{OsCl}_5\text{L}]^{2-}$	
3-cypy		$[\text{OsCl}_5\text{L}] \xrightleftharpoons{e^-} [\text{OsCl}_5\text{L}] \xrightleftharpoons{e^-} [\text{OsCl}_5\text{L}]^{2-}$		
4-cypy		$[\text{OsCl}_5\text{L}] \xrightleftharpoons{e^-} [\text{OsCl}_5\text{L}] \xrightleftharpoons{e^-} [\text{OsCl}_5\text{L}]^{3-}$		
3,4-dcypy		$[\text{OsCl}_5\text{L}] \xrightleftharpoons{e^-} [\text{OsCl}_5\text{L}] \xrightleftharpoons{e^-} [\text{OsCl}_5\text{L}]^{3-}$		

The complete spectral data set obtained is listed along with probable assignments of the absorption bands in table 5.3. The types of electronic transitions that one

would expect to observe using u.v./vis. absorption spectroscopy in complexes of this type have been outlined in section (1.4).

The u.v./vis. absorption spectra of all the Os(IV) species, bound through the ring nitrogen, are similar showing intense $\text{Cl}^- \rightarrow \text{Os(IV)}d\pi$ C.T. transition at about $27\,000\text{cm}^{-1}$ with a corresponding 'triplet' transition at $23\,000\text{cm}^{-1}$. Such a pattern is exhibited in the spectrum of $[\text{Os(IV)Cl}_5(4\text{-cypy})]^-$ (fig. 5.8)

The spectra of all the Os(III) species show a low energy $\text{Os(III)}d\pi \rightarrow \text{L}\pi^*$ C.T. transition. Such a transition is shown in the spectrum of $[\text{OsCl}_5(4\text{-cypy})]^{2-}$ (fig. 5.9). The energy of the main M.L.C.T. transition in the Os(III) complexes $[\text{OsCl}_5\text{L}]^{2-}$ varies in the following fashion:



This trend can be explained by considering the relative π -accepting abilities of the ligands. A pyridine ring containing a CN^- group will have a greater π -accepting capability due to the cyano group's electron withdrawing ability. The π -accepting qualities of 2-cypy and 4-cypy will be further enhanced compared to 3-cypy by conjugative effects. The slightly higher energy of the $\text{Os(III)} \rightarrow 2\text{-cypy} \pi^*$ transition may reflect a steric interaction between the cyano group and the chloride ligands, which results in the ring being tilted out of its preferred electronic orientation.

The spectra of the reduction products of

$[\text{Os}(\text{III})\text{Cl}_5(4\text{-cypy})]^{2-}$ and $[\text{Os}(\text{III})\text{Cl}_5(3,4\text{-dcypy})]^{2-}$, are most interesting since their form indicates whether the reduction is metal or ligand based. If these reductions were metal based, by analogy with the $[\text{OsCl}_{6-n}\text{PY}_n]^{(n-3)/(n-4)}$ spectra previously examined, we would expect the M.L.C.T. transitions to move to lower energy by some $8000\text{-}9000\text{cm}^{-1}$. The spectra of the reduction products do not exhibit such a trend (see figs. 5.10 and 5.11), hence the reduction must be assigned as ligand based. Thus the bands at $19\,260$ and $19\,800\text{cm}^{-1}$ must be assigned as $\text{Os}(\text{III})d\pi \rightarrow L^- \pi^* \text{C.T.}$ transitions.

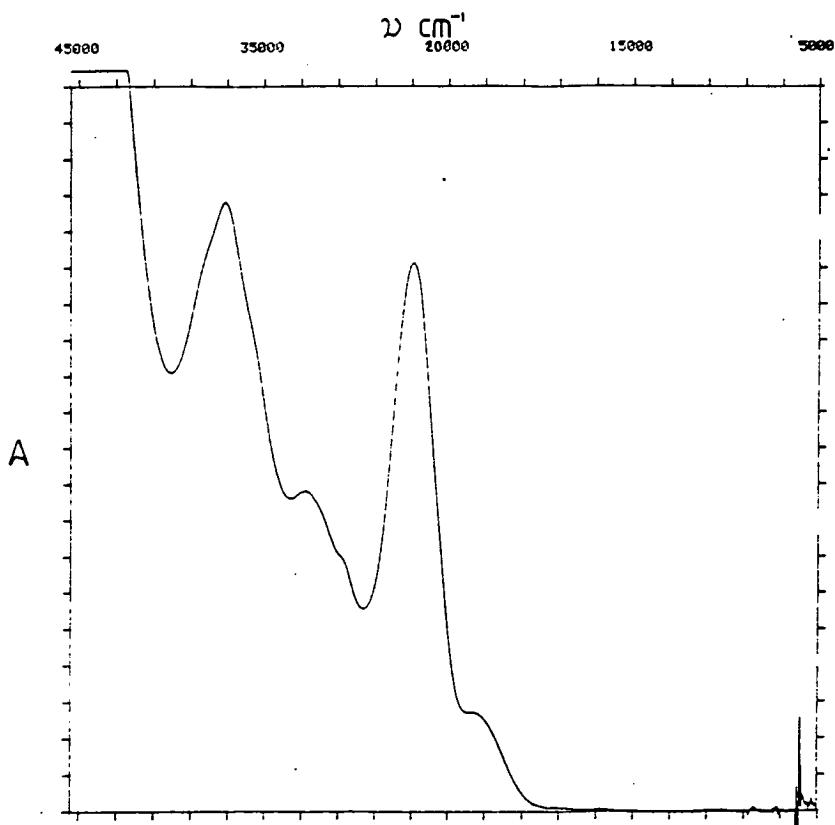


Figure 5.8 U.V./Vis. Absorption Spectrum of $[\text{OsCl}_5(4\text{-cypy})]^-$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 240K .

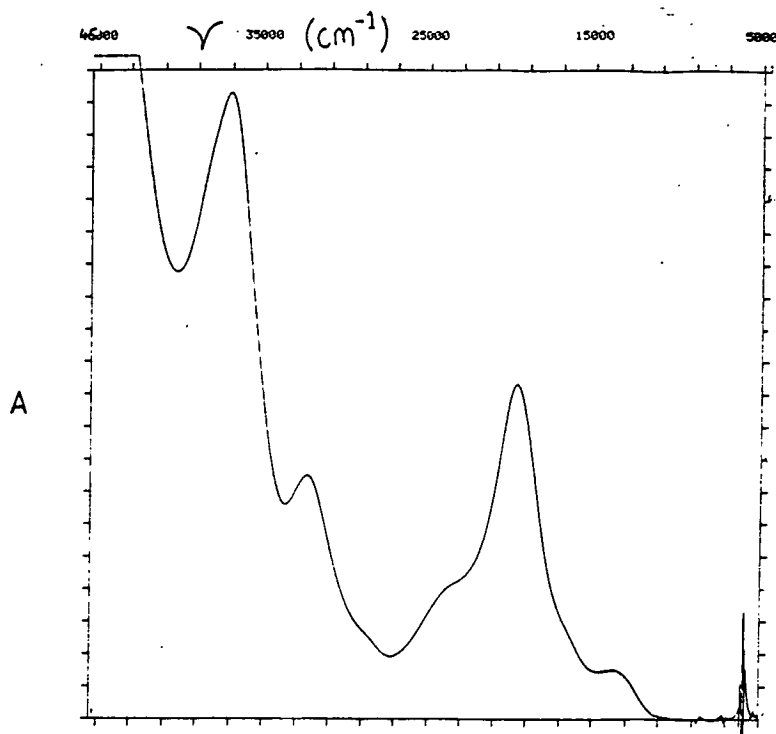


Figure 5.9 U.V./Vis. Absorption Spectrum of $[\text{OsCl}_5(4\text{-cypy})]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 240K.

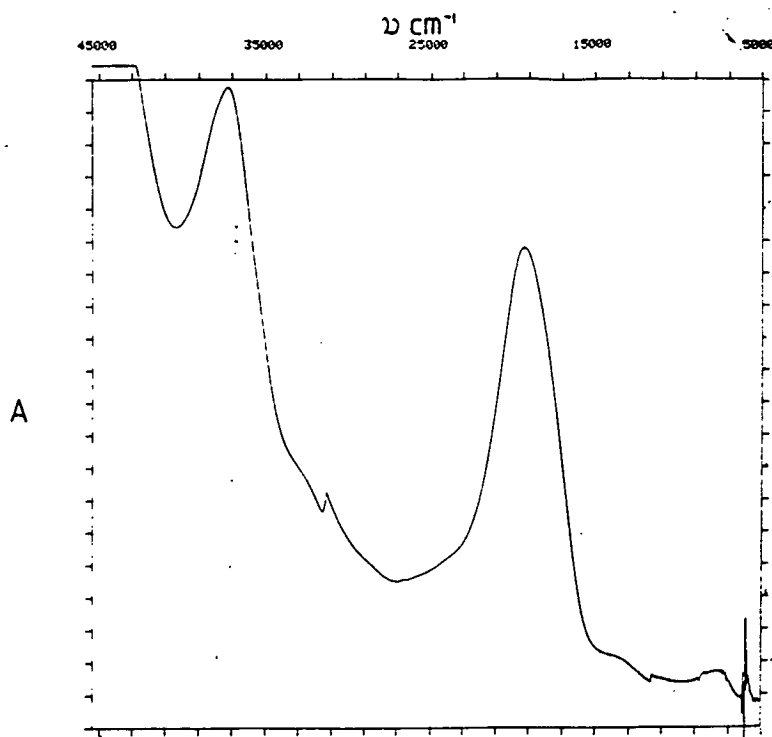


Figure 5.10 U.V./Vis. Absorption Spectrum of $[\text{OsCl}_5(4\text{-cypy})]^{3-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 240K.

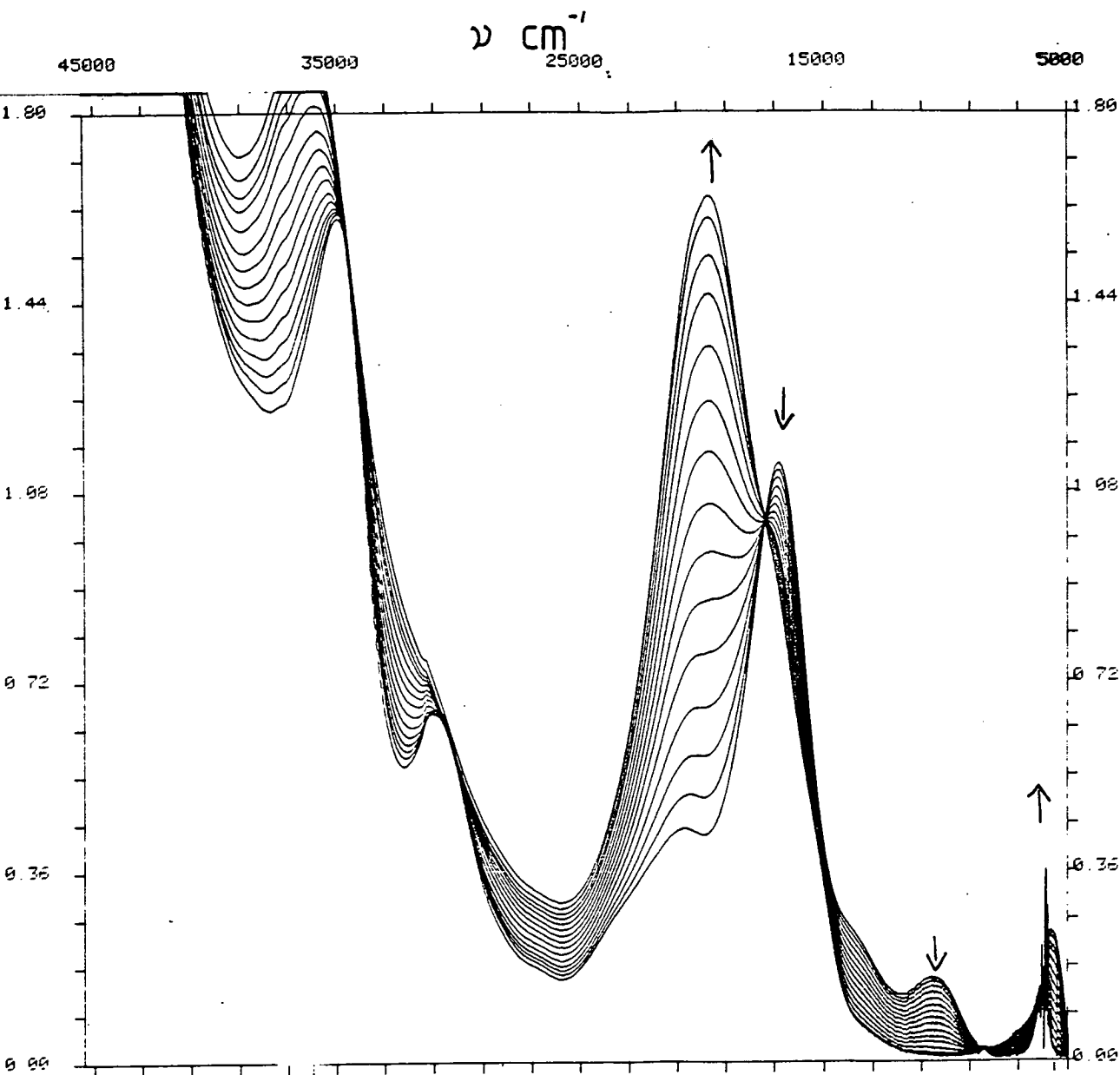


Figure 5.11 Spectra Showing the Spectroelectrochemical Reduction of $[\text{OsCl}_5(3,4\text{-dcypy})]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M}$ $[\text{TBA}][\text{BF}_4]$ at -1.6V and 240K .

Table 5.3 Positions ($\nu_{\max}$) of Bands in the Electronic Absorption Spectra in 0.5M [TBA][BF₄] CH₂Cl₂ for the Compounds [TBA][OsCl₅L] where L = PhCN, 2-cypy, 3-cypy, 4-cypy, 3,4-cypy.

Compound	$\nu_{\max}(\text{cm}^{-1})$	Assignment.
[Os(V)Cl ₅ PhCN]	22 380	Cl ⁻ $\pi \rightarrow$ Os(V)d π
[Os(IV)Cl ₅ PhCN] ⁻	26 700	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	32 500	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	35 600	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
[Os(III)Cl ₅ PhCN] ²⁻	25 300	Os(III)d $\pi \rightarrow$ PhCN π^*
	27 500	Os(III)d $\pi \rightarrow$ PhCN π^*
	31 400	Cl ⁻ $\pi \rightarrow$ Os(III)
[Os(IV)Cl ₅ (2-cypy)] ⁻	27 000	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	32 900	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	37 900	L $\pi \rightarrow$ L π^*
[Os(III)Cl ₅ (2-cypy)] ²⁻	20 100	Os(III)d $\pi \rightarrow$ L π^*
	32 000	Cl ⁻ $\pi \rightarrow$ Os(III)d π
	37 900	L $\pi \rightarrow$ L π^*

continued/

Compound	$\nu_{\max}(\text{cm}^{-1})$	Assignment.
[Os(V)Cl ₅ (3-cypy)]	22 900	Cl ⁻ $\pi \rightarrow$ Os(V)d π
	26 900	Cl ⁻ $\pi \rightarrow$ Os(V)d π
	38 100	L $\pi \rightarrow$ L π^*
[Os(IV)Cl ₅ (3-cypy)] ⁻	23 500	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	27 200	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	33 600	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	38 300	L $\pi \rightarrow$ L π^*
[Os(III)Cl ₅ (3-cypy)] ²⁻	22 200	Os(III)d $\pi \rightarrow$ L π^*
	33 000	Cl ⁻ $\pi \rightarrow$ Os(III)d π
	38 200	L $\pi \rightarrow$ L π^*
[Os(IV)Cl ₅ (4-cypy)] ⁻	27 000	Cl ⁻ $\pi \rightarrow$ Os(IV)d π
	37 100	L $\pi \rightarrow$ L π^*
[Os(III)Cl ₅ (4-cypy)] ²⁻	5 900	Os(III)d $\pi \rightarrow$ d π
	19 650	Os(III)d $\pi \rightarrow$ L π^*
	32 300	Cl ⁻ $\pi \rightarrow$ Os(III)d π
	37 000	L $\pi \rightarrow$ L π^*
[Os(III)Cl ₅ (4-cypy)] ³⁻	19 260	Os(III)d $\pi \rightarrow$ L ⁻ π^*
	31 300	Cl ⁻ $\pi \rightarrow$ Os(III)d π
	37 300	L $\pi \rightarrow$ L π^*

continued/

Compound	$\nu_{\max}(\text{cm}^{-1})$	Assignment.
$[\text{Os(IV)Cl}_5(3,4\text{-dcypy})]^-$	26 600	$\text{Cl}^-\pi \rightarrow \text{Os(IV)}$
	35 300	$\text{L } \pi \rightarrow \text{L } \pi^*$
$[\text{Os(III)Cl}_5(3,4\text{-dcypy})]^{2-}$	6 200	$\text{Os(III)d}\pi \rightarrow \text{d}\pi$
	10 570	$\text{Os(III)d}\pi \rightarrow \text{L } \pi^*$
	16 780	$\text{Os(III)d}\pi \rightarrow \text{L } \pi^*$
	30 900	$\text{Cl}^-\pi \rightarrow \text{Os(IV)d}\pi$
	34 900	$\text{L } \pi \rightarrow \text{L } \pi^*$
$[\text{Os(III)Cl}_5(3,4\text{-dcypy})]^{3-}$	5 550	$\text{Os(III)d}\pi \rightarrow \text{d}\pi$
	19 800	$\text{Os(III)d}\pi \rightarrow \text{L}^-\pi^*$
	ca.36 500	$\text{L}^-\pi \rightarrow \text{L}^-\pi^*$

5.3.1 Reductive substitutions of $[\text{OsCl}_6]^{2-}$ in the presence of CO.

A bulk reductive electrolysis at -0.8V of $[\text{TBA}]_2[\text{OsCl}_6]$, in a solution of $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ saturated with CO gas, at 230K was performed. A coulometric study showed the reductive step involved two electrons. The cyclic voltammogram of the resulting solution (containing substance X and free chloride ions), shown in figure 5.12, exhibits three redox processes. With the notation of the figure, process C corresponds to the oxidation of free chloride. Stirred voltammetry shows that steps A and B are oxidations, and that the heights of waves A to C are in the ratio 1:2. In addition the height of wave A is similar to that of the starting material before the reduction took place. We can conclude that the bulk electrolysis corresponds to a two electron reduction from Os(IV) to Os(II) with concurrent loss of two chloride ligands.

The chemical reversibility of process A was demonstrated by a bulk oxidative electrogeneration of substance X under CO at $+0.3\text{V}$ which also confirmed the redox process involved one electron. Cyclic voltammetry and stirred voltammetry of the resulting solution showed a similar electrochemical response, except that process A had become a reductive step.

A solution infra-red spectrum of these products

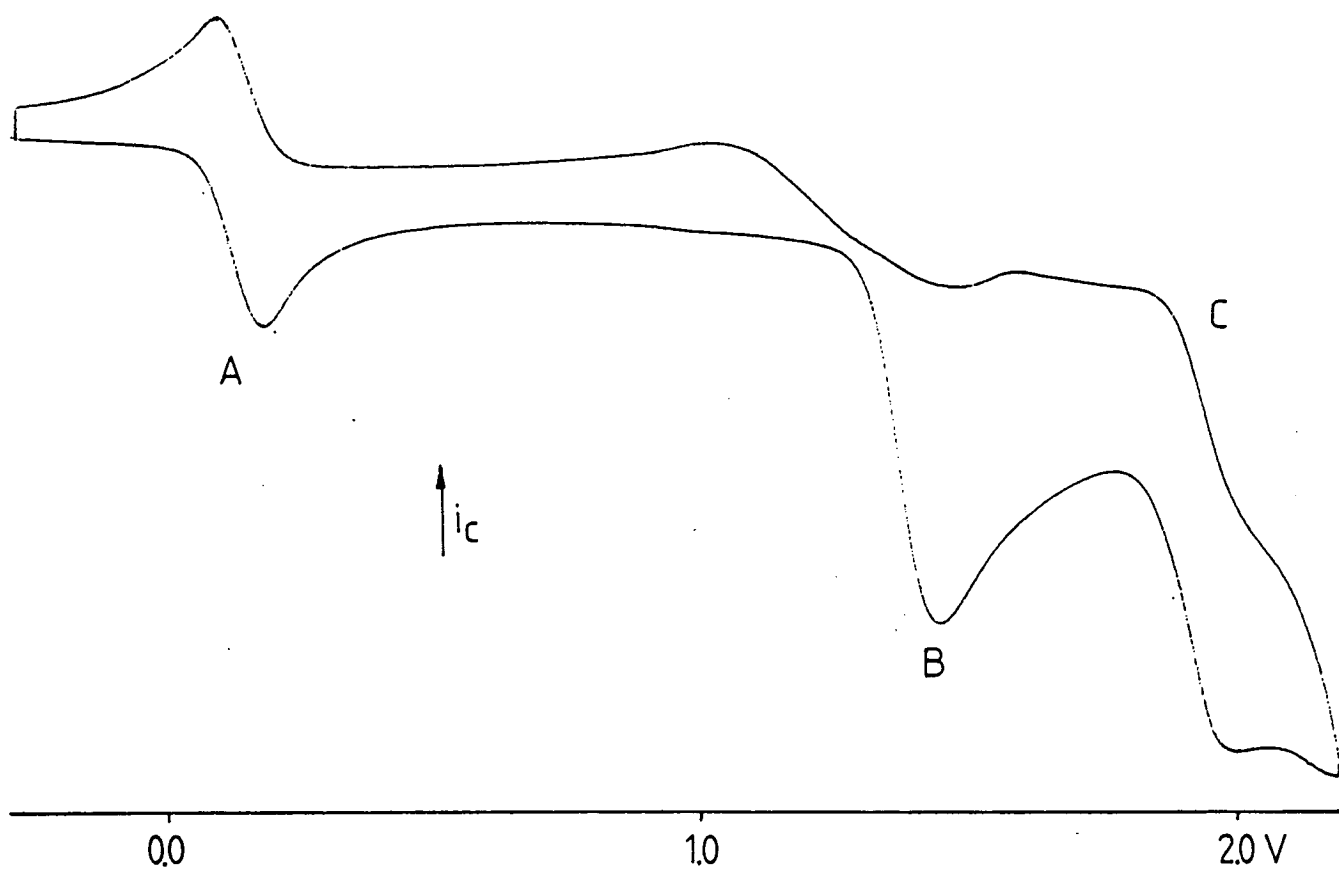


Figure 5.12 Cyclic Voltammogram of the Products of the Reduction of $[\text{OsCl}_6]^{2-}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M } [\text{TBA}][\text{BF}_4]$ at 240K under CO.

reveals a CO stretching frequency at 1915cm^{-1} for substance (X) and 2040cm^{-1} for $[\text{X}]^+$. We would expect the frequency of the CO stretch to increase as the metal oxidation state is increased since there are less electrons available for back donation into the $\text{CO } \pi^*$ orbitals.

On the nature of substance X we can conclude that it contains Os(II), four chloride ligands and at least one carbonyl moiety.

A spectroelectrochemical oxidation of compound X at 230K, was performed at the O.T.T.L.E. Figure 5.13 shows the u.v./vis. absorption spectrum of compound X. When compound X is oxidised bands appear at lower energy. (fig. 5.14). We suggest that the main band in the spectrum of compound X is due to an $\text{Os(II)}d\pi \rightarrow \text{CO}\pi^*$ C.T. transition. We would attribute the band in the spectrum of compound $[\text{X}]^+$ to $\text{Cl}^-\pi \rightarrow \text{Os(III)}d\pi$ C.T. transition, in keeping with assignments made in chapter 2.

When the solution of compound X is warmed from 230K to 290K the electrochemical response of the solution is altered. An a.c.voltammogram (fig.5.15) shows processes A and B being replaced by processes D and E. The free chloride ion response (observable only using d.c. methods) remains unaltered.

An infra red spectrum of this solution (which contained substance Y and free Cl^- ions) shows a band at 1870cm^{-1} which we assign to a carbonyl stretch.

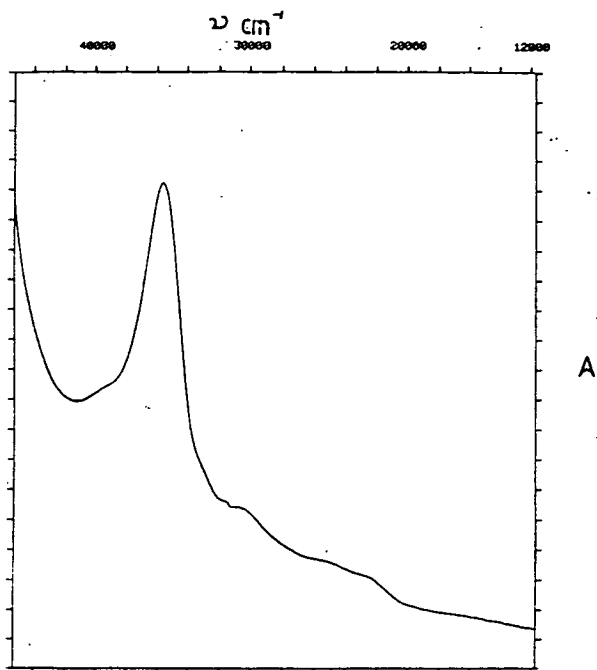


Figure 5.13 U.V./Vis. Absorption Spectrum of Substance X in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 230K.

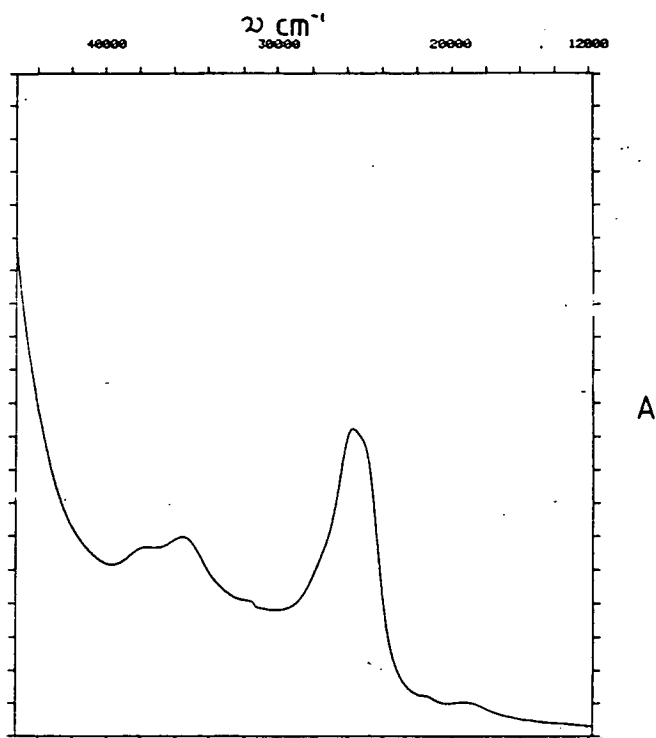


Figure 5.14 U.V./Vis. Absorption Spectrum of Substance $[\text{X}]^+$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 230K.

Spectroelectrochemical oxidations of compound Y were performed at the O.T.T.L.E. at 240K. The spectrum of compound Y (fig. 5.16) exhibits bands between 30 000 and 40 000 cm^{-1} , since the compound contains Os(II) coordinated to carbonyl and chloride ligands, we can attribute these bands to $\text{Os(II)}d\pi \rightarrow \text{CO}\pi^*$ C.T. transitions. This spectrum shows good correspondence with a solution of $\text{cis-}[\text{Os}(\text{CO})_2\text{Cl}_4]^{2-}$, prepared by Preetz et al.² (see experimental). Upon oxidation to $[\text{Y}]^+$ bands (fig. 5.17) at lower energy were produced. These can be assigned as $\text{Cl}^-\pi \rightarrow \text{Os(III)}d\pi$ transitions. Further oxidation to $[\text{Y}]^{2+}$ results in bands at even lower energy (fig. 5.18), which we can attribute to $\text{Cl}^-\pi \rightarrow \text{Os(IV)}$ C.T. transitions.

Infra red spectra of solutions of substance Y and $[\text{Y}]^+$ show bands at 1870 cm^{-1} and 1995 cm^{-1} respectively which correspond to carbonyl stretches.

Attempts to isolate substances X and Y from the electrolytic solution were unsuccessful. However when the solution of substance X (which still contained free chloride ions) were evaporated under vacuum or under a stream of CO gas, a compound (compound Z) with a new electrochemistry was produced.

A cyclic voltammogram of compound Z is shown in figure 5.19. Two electrochemical processes are observable, an irreversible reduction (process F) and a reversible oxidation (process G). Stirred voltammetry showed that both steps involved a similar number of electrons. A bulk

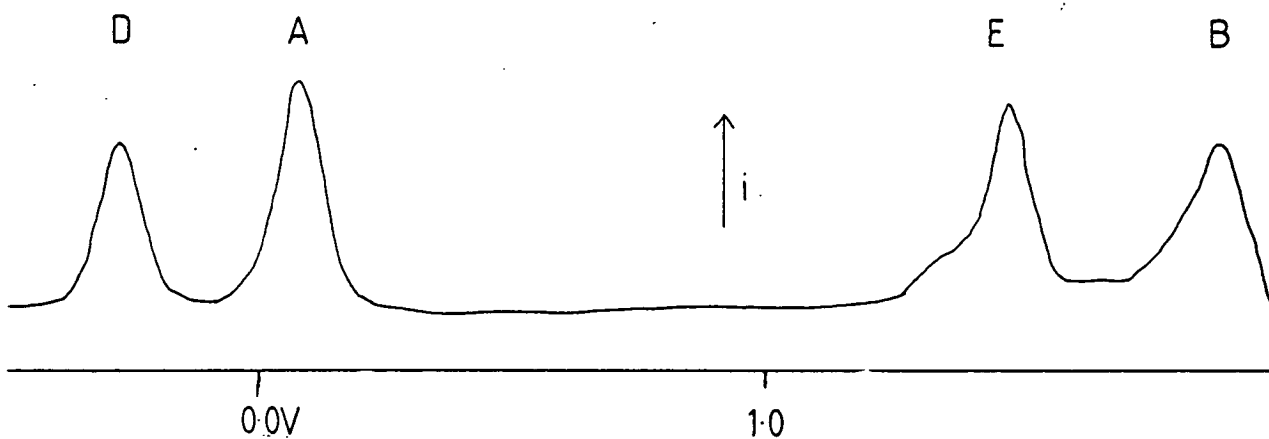


Figure 5.15 A.C. Voltammogram on a Solution of Substance X in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ on Warming to 290K under CO .

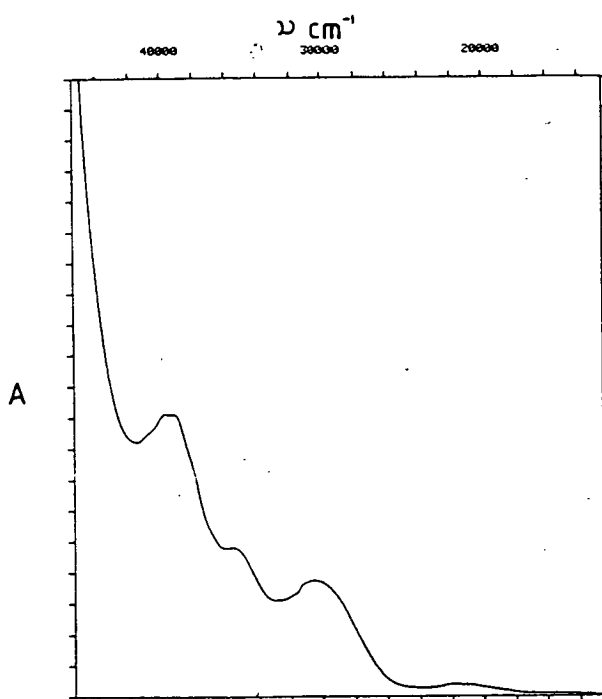


Figure 5.16 U.V./Vis. Absorption Spectrum of Substance [Y] in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 270K.

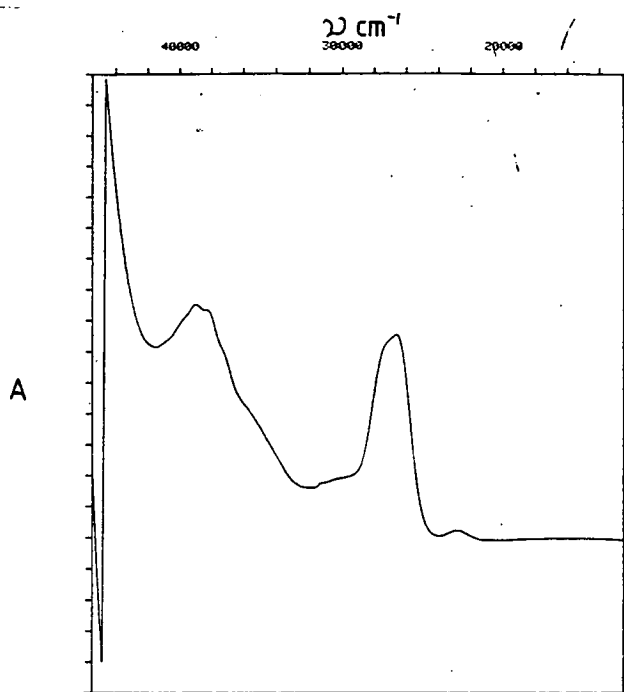


Figure 5.17 U.V./Vis. Absorption Spectrum of Substance $[Y]^+$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 270K.

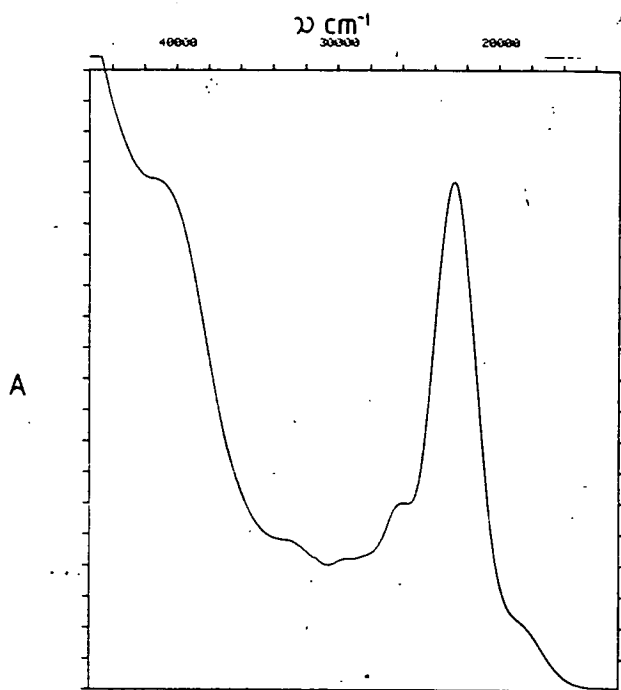


Figure 5.18 U.V./Vis. Absorption Spectrum of Substance $[Y]^{2+}$ in $\text{CH}_2\text{Cl}_2/0.5\text{M} [\text{TBA}][\text{BF}_4]$ at 270K.

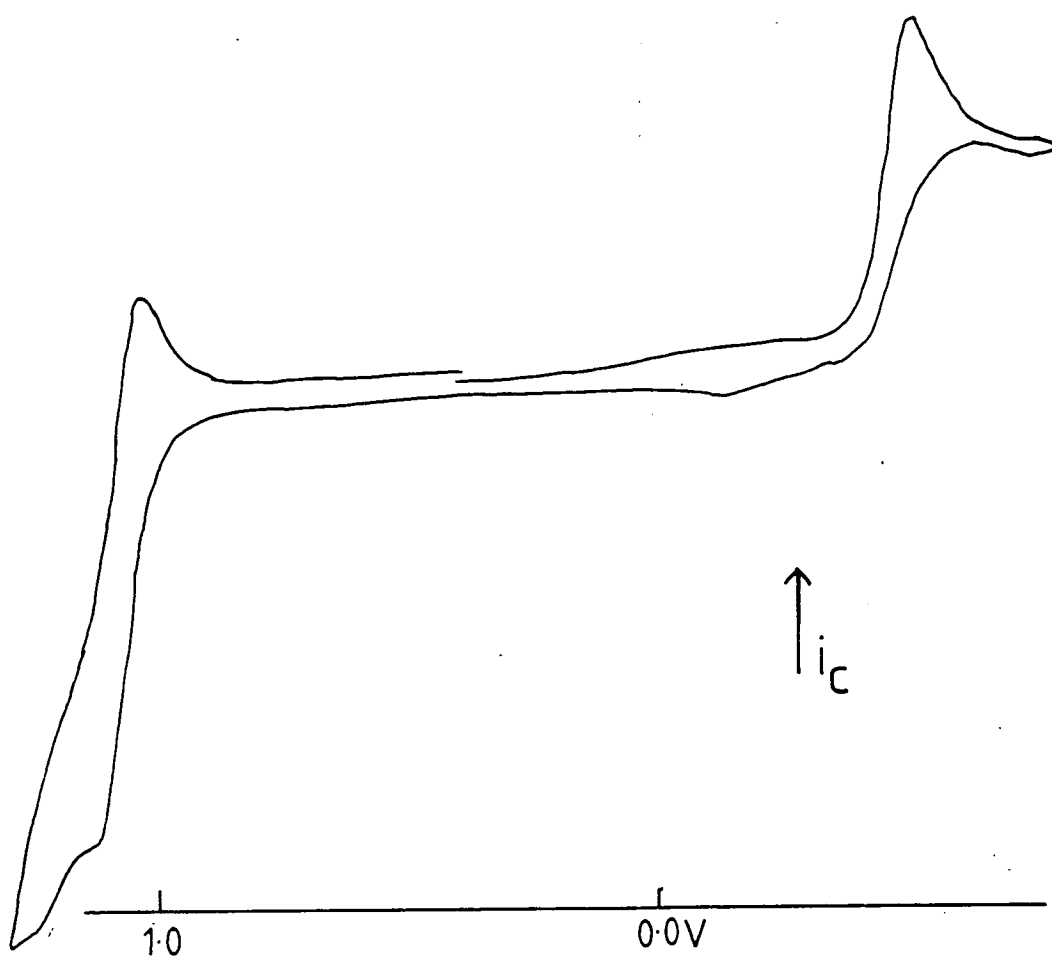


Figure 5.19 Cyclic Voltammogram of Substance Z in CH_2Cl_2 /0.5M [TBA][BF_4] at 290K.

reductive electrolysis of a $\text{CH}_2\text{Cl}_2/0.5\text{M}[\text{TBA}][\text{BF}_4]$ solution of substance Z at 230K under CO resulted in the production of substance X.

The u.v.vis. absorption spectrum of compound Z is shown in figure 5.20. This is in close correspondence with a spectrum of $[\text{Os}(\text{III})(\text{CO})\text{Cl}_5]^{2-}$ from the literature.³ A spectroelectrochemical oxidation of a solution of substance Z in $\text{CH}_2\text{Cl}_2/0.5\text{M}[\text{TBA}][\text{BF}_4]$ at +1.4V at 260K at the O.T.T.L.E. gave rise to the spectra in figure 5.21. The spectrum of substance $[\text{Z}]^+$ exhibits bands at lower energy than were observed in the spectrum of Z. This is the shift we would expect for $\text{Cl}^- \pi \rightarrow \text{Os}(\text{III})d\pi$ and $\text{Os}(\text{IV})d\pi$ C.T. transitions.

Infra-red spectra of these solutions of Z and $[\text{Z}]^+$ show bands corresponding to carbonyl stretches at 1960cm^{-1} and 2010cm^{-1} respectively. The stretching frequency of the former complex shows good correspondence with literature values for $[\text{Os}(\text{CO})\text{Cl}_5]^{2-}$ of 1957cm^{-1} ³ and 1968cm^{-1} ^{4,5,6} the latter species has not been previously observed.

On the basis of the observations above we can confidently state that substances Z and $[\text{Z}]^+$ are the complexes $[\text{Os}(\text{III})(\text{CO})\text{Cl}_5]^{2-}$ and $[\text{Os}(\text{IV})(\text{CO})\text{Cl}_5]^-$. Substances Y, $[\text{Y}]^+$ and $[\text{Y}]^{2+}$ are the complexes $\text{cis}-[\text{Os}(\text{II})(\text{CO})_2\text{Cl}_4]^{2-}$, $\text{cis}-[\text{Os}(\text{III})(\text{CO})_2\text{Cl}_4]^-$ and $\text{cis}-[\text{Os}(\text{IV})(\text{CO})_2\text{Cl}_4]^0$. Substance X is clearly a precursor to $\text{cis}-[\text{Os}(\text{II})(\text{CO})_2\text{Cl}_4]^{2-}$. $\text{Trans}-[\text{Os}(\text{II})(\text{CO})_2\text{Cl}_4]^{2-}$

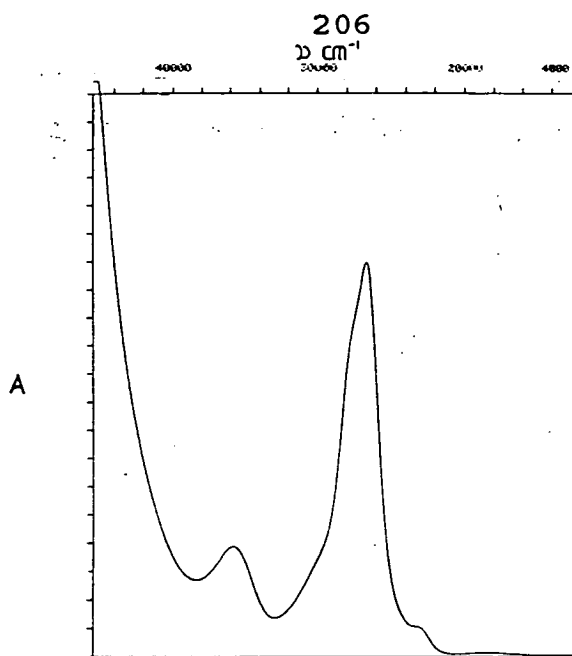


Figure 5.20 U.V./Vis. Absorption Spectrum of Substance [Z] in $\text{CH}_2\text{Cl}_2/0.5\text{M}$ [TBA][BF_4] at 270K.

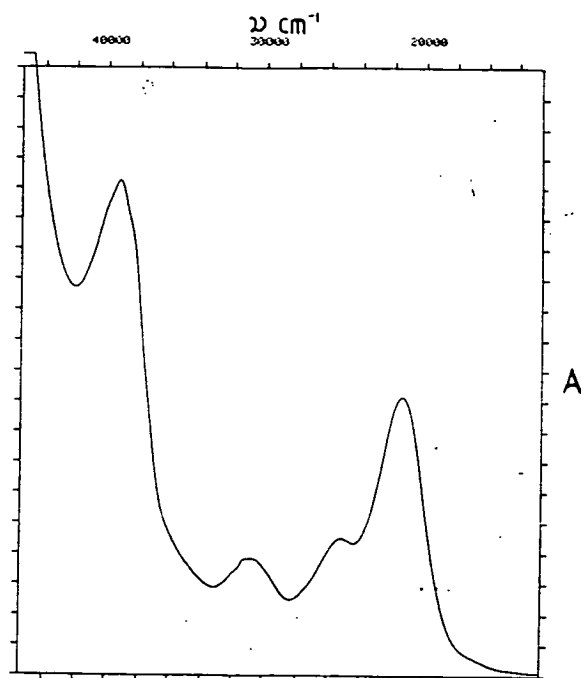
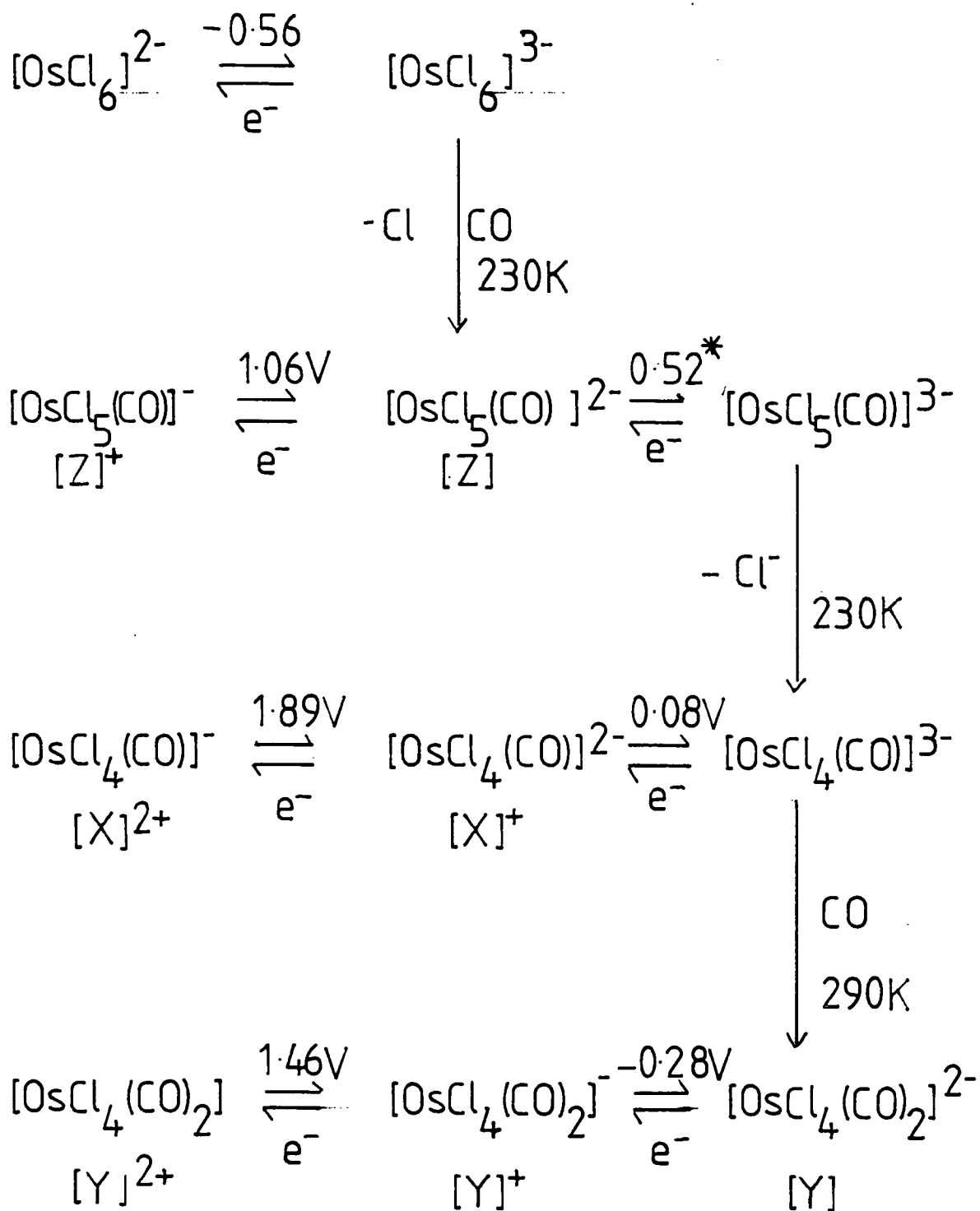


Figure 5.21 U.V./Vis. Absorption Spectrum of Substance $[\text{Z}]^+$ in $\text{CH}_2\text{Cl}_2/0.5\text{M}$ [TBA][BF_4] at 270K.

seems a likely formulation for substance X given the observations above. However the oxidations of X are found at more positive potentials than those observed for $\text{cis-}[\text{Os(II)(CO)}_2\text{Cl}_4]^{2-}$. This is not in agreement with ligand additivity arguments (see 2.31 and 1.3), which predict the *cis* isomer will be more difficult to oxidise than the corresponding *trans* isomer. Also *trans*-CO ligands are not favoured electronically although $\text{trans-}[\text{Os(CO)}_2\text{X}_4]^{2-}$ has been observed for $\text{X} = \text{Br}^-$ and I^- but not for $\text{X} = \text{Cl}^-$.⁷ Hence we suggest that substance X is the five coordinate species $[\text{Os(II)(CO)Cl}_4]^{2-}$. The extremely chemically irreversible nature of the reduction of $[\text{Os(III)(CO)Cl}_5]^{2-}$, which suggests rapid chloride loss, and decomposition to $[\text{Os(III)Cl}_5(\text{CO})]^{2-}$ upon evaporation in chloride containing, CO saturated CH_2Cl_2 solution, both suggest this species as a likely formulation. Further characterisation of substance X is required before a more confident formulation can be made.

Scheme 5.1 shows the reaction scheme described above, together with the electrochemical data obtained. Table 5.4 lists the bands in the electronic u.v./vis. absorption spectra of the substances described above together with probable assignments. Table 5.5 gives the carbonyl stretches observed in the solution infra-red spectra described above.

Scheme 5.1 Voltammetric Data and Reaction Scheme for the Reductive Substitution of $[\text{OsCl}_6]^{2-}$ in the presence of CO.



* Chemically Irreversible - E_p^F value.

Table 5.4 Positions of Bands ($\nu_{\max}$) in the U.V./Vis. Absorption Spectra of Complexes X, $[X]^+$, Y, $[Y]^+$, $[Y]^{2+}$, Z, $[Z]^+$.

Substance	Probable Complex	$\nu_{\max}(\text{cm}^{-1})$
X	$[\text{Os}(\text{II})\text{Cl}_4\text{CO}]^{2-}$	35 600
$[X]^+$	$[\text{Os}(\text{III})\text{Cl}_4\text{CO}]^-$	25 800
Y	<i>cis</i> - $[\text{Os}(\text{II})\text{Cl}_4(\text{CO})_2]^{2-}$	30 500 39 800
$[Y]^+$	<i>cis</i> - $[\text{Os}(\text{III})\text{Cl}_4(\text{CO})_2]^-$	26 800 37 200
$[Y]^{2+}$	<i>cis</i> - $[\text{Os}(\text{IV})\text{Cl}_4(\text{CO})_2]$	21 300 25 600 39 400
Z	$[\text{Os}(\text{III})\text{Cl}_5\text{CO}]^{2-}$	26 800 35 800
$[Z]^+$	$[\text{Os}(\text{IV})\text{Cl}_5\text{CO}]^-$	22 800

Table 5.5 Bands Observed in the Solution Infra-Red Spectra of Compounds X, $[X]^+$, Y, $[Y]^+$, Z and $[Z]^+$.

Substance	Probable Complex	Position of Carbonyl Stretching Frequencies (cm^{-1}).
X	$[\text{Os(II)Cl}_4\text{CO}]^{2-}$	1915
$[X]^+$	$[\text{Os(III)Cl}_4\text{CO}]^-$	2040
Y	<i>cis</i> - $[\text{Os(II)Cl}_4(\text{CO})_2]^{2-}$	1870
$[Y]^+$	<i>cis</i> - $[\text{Os(III)Cl}_4(\text{CO})_2]^-$	1995
Z	$[\text{Os(III)Cl}_5\text{CO}]^{2-}$	1960
$[Z]^+$	$[\text{Os(IV)Cl}_5\text{CO}]^-$	2010

5.4 Experimental.

All electrochemical and spectroelectrochemical measurements were performed using the techniques described in appendix 1.

The chemical preparation of *cis*- $[\text{Os}(\text{CO})_2\text{Cl}_4]^{2-}$ as per Preetz et al.² was attempted as follows:

Na_2OsCl_6 (300mg) and allyl alcohol (75 ml) were refluxed for 7 days. A u.v/vis. spectrum of the resulting orange solution corresponded very closely to a spectrum of substance Y. Unfortunately attempts to isolate a solid material by freeze drying and addition of ethanol (10ml) and tetrabutylammonium chloride (500mg) were unsuccessful.

5.5 References

1. J.Volke and V.Scala, J.Electroanal.Chem., 1972, 36, 383.
2. F.H.Johannsen, W.Preetz, A.Scheffler, J.Organomet.Chem., 1975, 102, 527.
3. F.H.Johannsen and W.Preetz, J.Organomet.Chem., 1977, 135, 221.
4. M.J.Cleare and W.P.Griffith, J.Chem.Soc.(A), 1969, 372.
5. M.J.Cleare and W.P.Griffith, J.Chem.Soc.(A), 1970, 2788.
6. M.J.Cleare, H.P.Fritz, W.P.Griffith, Spectrochim. Acta, 1972, 28A, 2019.
7. W.Preetz and F.H.Johannsen, J.Organomet.Chem., 1975, 86, 397.

Appendix 1 Electrochemical Techniques.

'Not many people are interested in what somebody else is thinking, or what they have to say. The best you can hope for is they'll listen to you so you'll have to listen to them. Everybody's loading shit on everybody else. Sometimes, somebody'll act like they're listening, but they're only waiting back in their minds for you to say something, something they can jump on or kick off on themselves. For me, conversation's usually a bore.'

Birdy

William Wharton

A.1.1. Introduction.

Electrochemical experiments have been performed throughout the course of this work. This appendix gives an outline of the various techniques employed. The text will discuss the choice of: electrodes, solvent system and cell design. Following this cyclic voltammetry, stirred voltammetry, a.c. voltammetry, bulk electrolysis and spectroelectrochemistry will be considered.¹

A.1.2. Electrodes.

All the electrochemical experiments considered here require a three electrode configuration, namely a working electrode, a reference electrode and a counter (auxilliary) electrode. Potential difference is applied between the working electrode and the reference electrode and current monitored between the working electrode and the counter electrode.

The form of a working electrode is dictated by the type of experiment one wishes to perform. In organic media platinum electrodes are generally employed, since they are stable over a wide potential range.

The reference electrode, as it's name implies, maintains a constant reference potential throughout the course of the experiment. A reference electrode must satisfy the following requirements:

- i) It must have a reversible couple which obeys the Nernst equation.
- ii) This couple must occur at a potential that is invariant with respect to temperature and time.
- iii) The internal resistance of this component should be high compared to the other electrodes. This helps prevent current flow to the reference electrode, which leaves it unpolarised and hence stable.
- iv) It must not cause contamination of the test solution or be itself contaminated. In order to prevent this a salt bridge is generally employed.

The reference electrodes generally employed in organic solvents are: Ag/Ag^+ in polar organic solvents (e.g. acetonitrile) and Ag/AgCl in non polar solvents (e.g. methylene chloride).

The counter electrode used for electrochemical experiments in organic media is constructed of an inert material such as platinum and should have a much larger surface area than the working electrode.

A.1.3. Solvent system.

A solvent system contains a solvent and supporting electrolyte. The choice of solvent² is dictated by sample stability and solubility. There are other requirements for an electrochemical solvent, namely a usable potential range, a suitably high dielectric constant, an accessible temperature range, a low vapour pressure, a low enough

viscosity, an acceptable toxicity and an ease of purification. If the solvent has donor or coordinating properties these should also be borne in mind. In spectroelectrochemical experiments absorption in the U.V. may not be desirable.

Supporting electrolyte is present in a solvent system in order to increase the conductivity of the solution. In the experiments discussed here the electrolyte concentration varies between 0.1 and 0.5M depending on the solvent. This increased conductivity results in a decrease in resistance between the working and counter electrodes and reduces the uncompensated solution resistance between the working and reference electrodes. The vast excess of electrolyte ions compared to sample ions results in:

- i) The structure of the double layer adjacent to the working electrode being largely determined by the electrolyte ions.
- ii) Migration of the test species between the working and counter electrodes being eliminated as a means of mass transport.

The same considerations discussed above with regard to the choice of solvent should be borne in mind when choosing an electrolyte for a solvent system.

A.1.4. Cell design.

All electrochemical experiments described here were

performed in electrochemical cells which incorporated the following design features:

- i) Optimised electrode geometry in order to achieve a symmetric electrical field at the working electrode.
- ii) Low internal resistance is important when using organic solvents with low conductivity and when passing high currents. This is achieved by placing the electrodes closely together which results in the area of the working electrode being kept necessarily small ($\text{ca. } 7.9 \times 10^{-7} \text{ m}^2$), so that all points on the surface will be effectively equidistant from the larger counter electrode.
- iii) A variable temperature capability.
- iv) Easy assembly and disassembly.
- v) Isolation from the surrounding environment.
- vi) A facility for the purging of dissolved dioxygen from the electrochemical solvent.
- vi) The facility to separate working and counter electrodes must be present for any bulk electrolysis.
- vii) For a spectroelectrochemical experiment all the above conditions must be satisfied along with the additional requirement of an optically transparent electrode.

Figure A.1.1. shows a typical cell for cyclic voltammetry, stirred voltammetry and a.c. voltammetry. Figures A.1.2. and A.1.3. show cells for a bulk electrolysis and a spectroelectrochemical bulk electrolysis respectively.

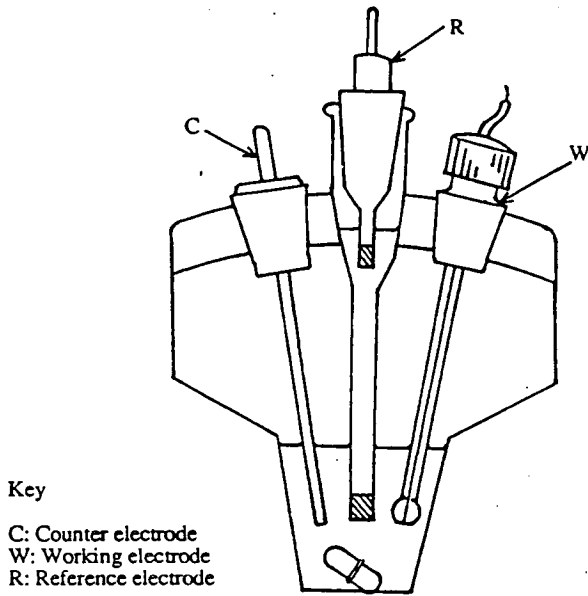


Figure A.1.1 Typical Cell for Conventional Electrochemistry.

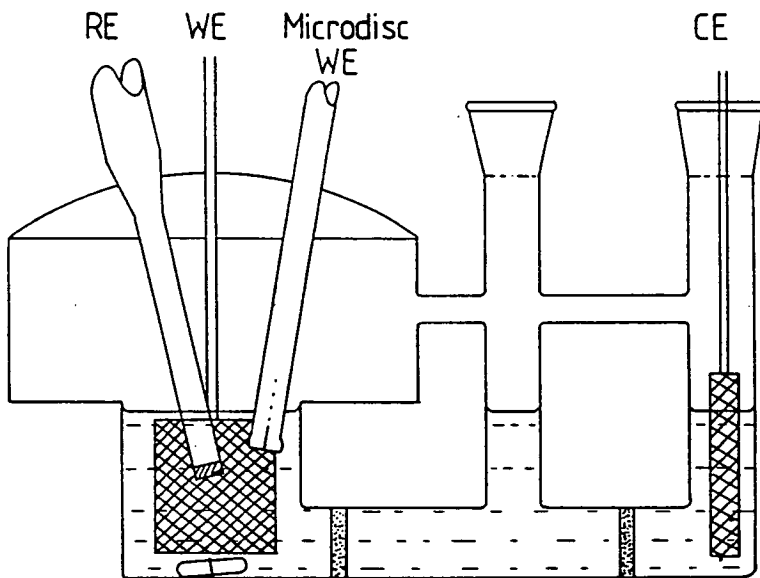
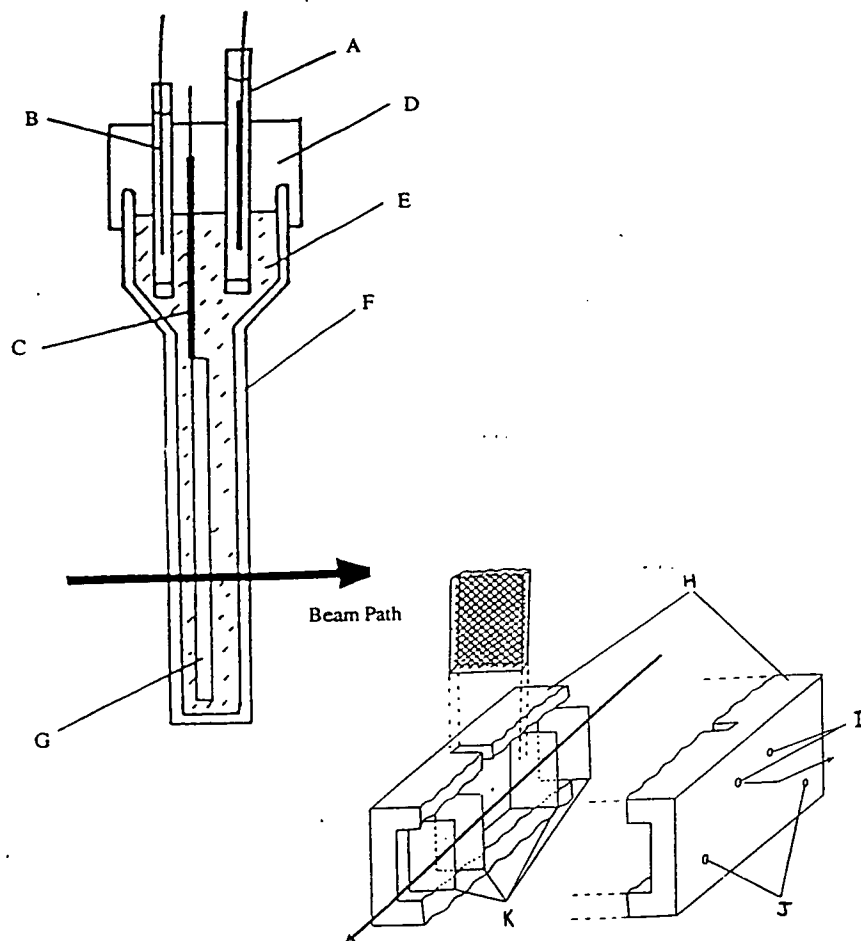


Figure A.1.2 Three Compartment Cell for Controlled Potential Bulk Electrolysis.



Key

- A: Counter electrode
- B: Reference electrode
- C: Working electrode connection protected from bulk solution by PTFE sleeve
- D: PTFE cell cap
- E: Test solution
- F: 0.1cm Infrasil quartz cell containing Pt grid working electrode
- G: Pt grid working electrode
- H: PTFE block
- I: Variable temperature nitrogen inlet ports
- J: Dry nitrogen inlet ports (to prevent fogging of inner quartz windows)
- K: Infrasil Quartz cell block windows

Figure A.1.3. Design of the Optically Transparent Thin Layer Electrode (O.T.T.L.E.) and Gas Tight PTFE Block.

A.1.5. Cyclic voltammetry.

Cyclic voltammetry uses stationary electrodes in a quiescent (unstirred) solution. In this work a platinum microdisc and platinum bar were employed as the working and counter electrodes respectively. The large amount of supporting electrolyte present in the test solution results in negligible mass transport of the test species by either migration or convection. This leaves diffusion as the only means of mass transport of the test species to the solution/working electrode interface.

The potential of the working electrode is ramped linearly with time from, to, and back to chosen potentials (fig. A.1.4.). The scan rate, v , for this is typically between 20 and 500mVs^{-1} (100mVs^{-1} for all cyclic voltammograms in this text). The current, i , which flows at the working electrode is measured as a function of applied potential, E .

An electroactive test species which exhibits electron transfer at an electrode falls into one of four classes:

- i) Reversible: where electron transfer is more rapid than diffusion of the test species to the electrode.
- ii) Quasi-Reversible: where the rate of electron transfer and diffusion is similar.
- iii) Irreversible: where the rate of electron transfer is slower than diffusion to the electrode surface.
- iv) Partially-Reversible: where an irreversible chemical reaction follows a reversible or quasi-reversible electron

transfer.

A typical cyclic voltammogram for a reversible species is shown in figure A.1.4. The current response takes the form of asymmetric peaks. An increase (or decrease) in cathodic current occurs when the test species begins to be reduced (or oxidised) at the electrode. This electron transfer increases rapidly with increasing E , depleting the concentration of unreacted test species at the electrode. When this depletion is large enough, the current reaches a peak and the electron transfer becomes diffusion controlled. Beyond this peak the potential ramp is reversed at the "switching potential". When the reduced (oxidised) test material at the electrode is re-oxidised (re-reduced) a return peak is observed at a more positive (negative) potential than for the forward peak. The shape of this peak is governed by similar electron transfer and diffusion rate factors.

The parameters obtained from a cyclic voltammetric experiment can be used to determine the nature of a particular charge transfer reaction. The parameters that are most important in this respect are the forward and reverse peak currents and potentials respectively: i_p^F , i_p^R , E_p^F , E_p^R . The particular criteria for each particular type of electron transfer are listed in table A.1.1. The average potential between E_p^F and E_p^R is the $E_{1/2}$ for the particular redox process being examined.

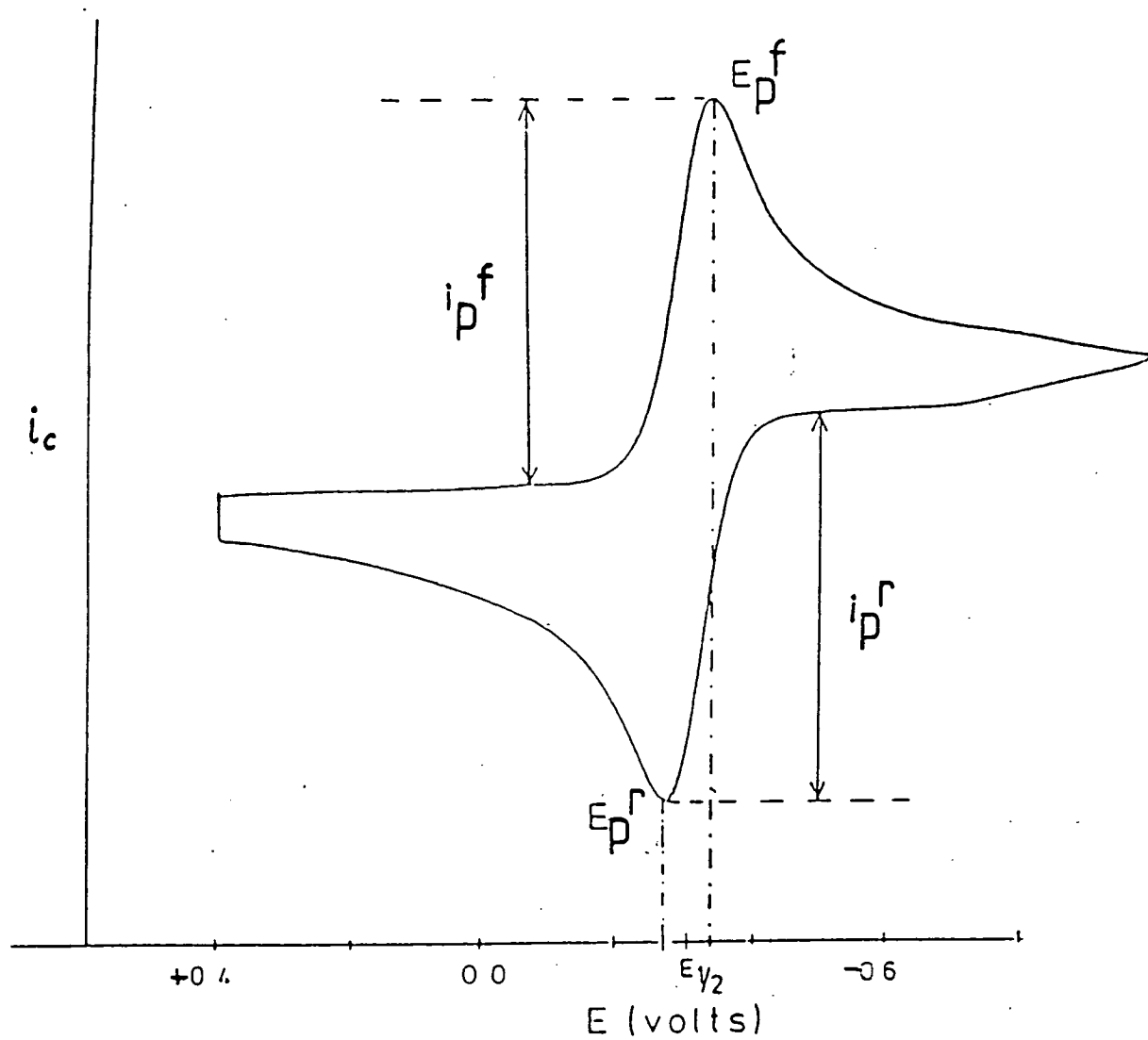


Figure A.1.4. A Typical Voltammetric Response for a Reversible Process.

Table A.1.1. Reversibility Criteria for Electron Transfer Examined Using Cyclic Voltammetry and A.C.Voltammetry.

With respect to the parameters described in the text:

Cyclic Voltammetry

Reversible	E_p is independent of v . $E_p^F - E_p^R = 59/n$ mV at 25°C. $1/2[E_p^F + E_p^R] = E_{1/2}$, independent of concentration. $i_p/v^{1/2}$ (current function) is independent of v . $i_p^R/i_p^F = 1$ and is independent of v .
Quasi-reversible	E_p shifts with v . $E_p^F - E_p^R$ increases as v increases. $i/v^{1/2}$ is independent of v . i_p^R/i_p^F generally = 1.
Partially-reversible	E_p increases by $30/n$ mV for a ten fold increase of v , at low v . $i_p/v^{1/2}$ is independent of v . i_p^R/i_p^F tends to 1 as v increases.
Irreversible	E_p shifts with v . $i_p/v^{1/2}$ is independent of v There is no peak i_p^R .

A.C.Voltammetry

For a reversible process:

- i) E_p is independent of ω
- ii) $\omega^{1/2} = 90/n$ mV at 25°C and is independent of ω .
- iii) A plot of i_p versus $\omega^{1/2}$ gives a straight line that passes through the origin.

A.1.6. Stirred Voltammetry.

In order to determine whether a redox process is an oxidation or a reduction, stirred voltammetry must be used. This experiment involves the application of a single, slow (20mVs^{-1}), linear potential ramp at the working electrode (platinum microdisc) in a uniformly stirred solution. Electron transfer at the electrode is governed by convection and diffusion. A cathodic current flow, indicates a reduction, while an anodic current flow indicates an oxidation. By convention cathodic currents are displayed up the page. A stirred voltammogram obtained for a test species which exhibited both a reversible reduction and a reversible oxidation is shown in figure A.1.5. along with the corresponding cyclic and a.c. voltammograms.

A.1.7. A.C. Voltammetry.

Alternating current (a.c.) voltammetry involves the superposition of a small alternating potential on a linear potential ramp, a scan rate of 20mVs^{-1} was used throughout

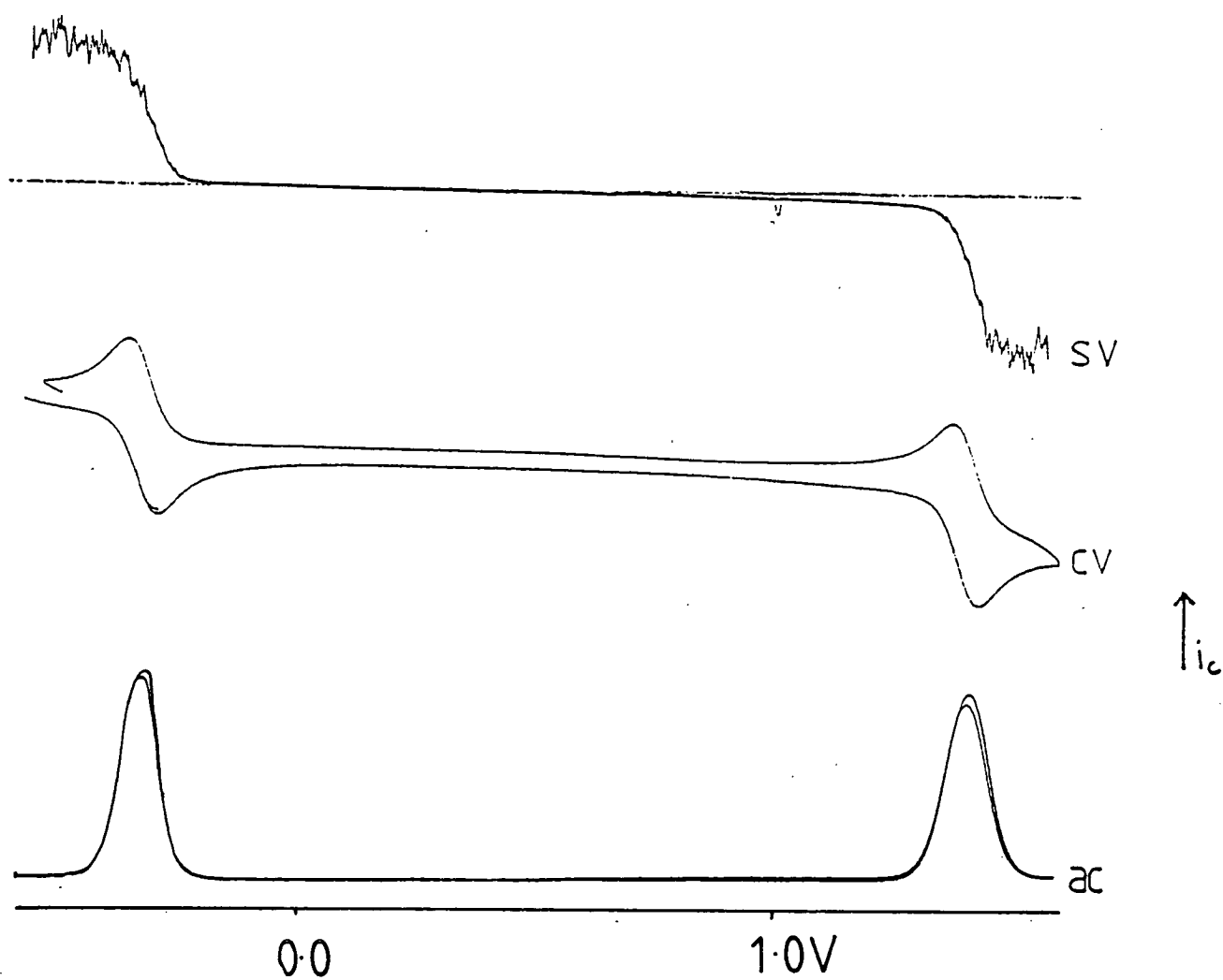


Figure A.1.5. Typical Cyclic, Stirred and A.C. Voltammetric Responses for a Complex Exhibiting Reversible Oxidation and Reduction Processes.

this work. The superimposed alternating potential is usually periodic with time and often takes the form of a sinusoidal wave (fig. A.1.6.). The amplitude of this wave is relatively small. The net a.c. current which flows is recorded as a function of the linear d.c. potential. For a test species exhibiting a reversible electron transfer, the signal recorded (fig. A.1.6.) is a symmetric peak centered on the $E_{1/2}$ observed in the corresponding cyclic voltammogram. The peaked form of the wave can be explained by a consideration of the resulting alternating current. In order for an alternating current to flow we need both oxidisable and reducible material in solution. This condition is satisfied only at potentials when a mixture of reduced (or oxidised) and unaltered test material is present at the electrode. The alternating current reaches a maximum when an equimolar amount of material of reduced (or oxidised) and unreacted test material is present.

In an a.c. voltammetric experiment the frequency of the alternating potential component, ω , can be altered. This effectively controls the timescale of the experiment and provides a more stringent check for departure from reversibility than conventional cyclic voltammetry allows. Table A.1.1. lists the criteria for reversibility in a.c. voltammetry.

The two main advantages of a.c. voltammetry over conventional cyclic voltammetry are:

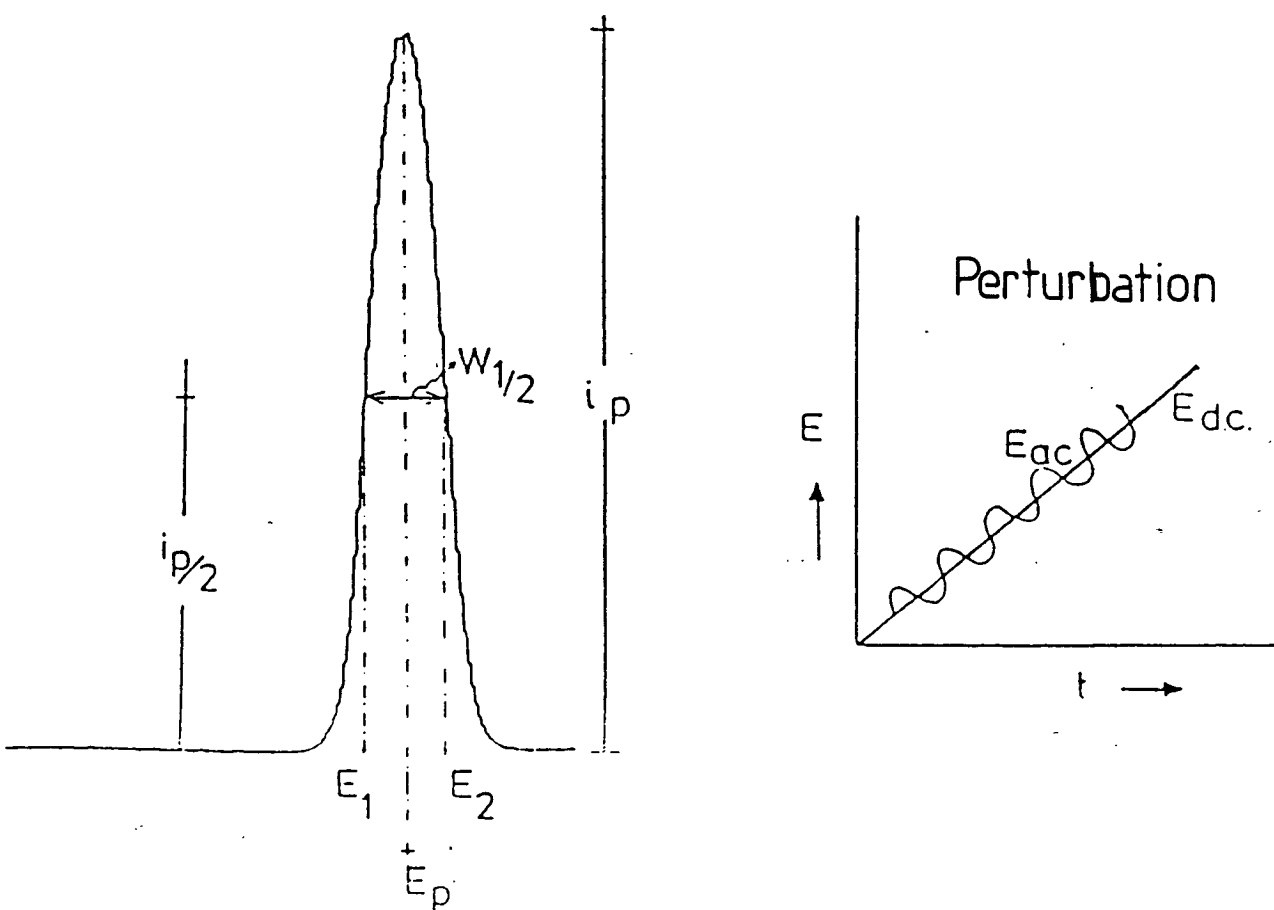


Figure A.1.6. Typical A.C. Voltammogram for a Reversible Process.

- i) An increase in sensitivity to analyte concentrations of 10^{-6} - 10^{-7} mol dm $^{-3}$ as opposed to 10^{-4} - 10^{-5} mol dm $^{-3}$ for conventional cyclic voltammetry. This results since the a.c. method discriminates between two types of current which have differing phase relationships: background "capacitive" current and "faradaic" current which results from reduction and oxidation of the test species. This distinction is made possible by phase sensitive detection of the faradaic current.
- ii) Improved resolution to separation of waves as close together as 40mV (conventional cyclic voltammetry requires 150mV separation for resolution).

A.1.8. Bulk Electrolysis - Electrosynthesis - Coulometry.

There are two types of electrolysis: potentiostatic, where the potential is fixed and the current is monitored with time, and galvanostatic where a chosen current is forced to flow through the cell. Potentiostatic electrolysis was used throughout this work.

In a bulk electrolysis a chosen potential is applied at a large working electrode, in this work a platinum basket electrode, and an electron transfer is performed on all the test species in the stirred solution. A reference electrode is placed in the centre of the basket electrode. A platinum microdisc working electrode is also present in this compartment to facilitate examination of the redox

properties of the test species and the electrolysis products. In order to avoid the counter electrode reversing the electron transfer step, it is placed in a compartment separated from the working electrode by a glass frit, which allows electrons to pass through it but which is impermeable to test species (fig. A.1.2.).

In order for an electron transfer to be fully achieved at the working electrode a potential of at least 60mV negative (positive) of the $E_{1/2}$ value for the reduction (oxidation) should be chosen. The current flowing at the working electrode can be measured and a plot against time yields a coulometric plot (fig. A.1.7.). The area under the curve yields the charge which has passed during the course of the experiment, Q . Assuming a 100% efficiency we can relate this charge to the amount of material and the number of electrons involved in the electron transfer using the relation:

$$Q = nFM \quad 1$$

where n is the number of electron involved in the electron transfer, M = number of moles of test species present and F is Faradays constant ($96\,485\text{ Cmol}^{-1}$).

Once a bulk electrolysis has been performed the electrochemistry of the resulting species should always be examined using the platinum disc microelectrode. If the redox step is chemically reversible then the initial test species should in practice be regenerated in total.

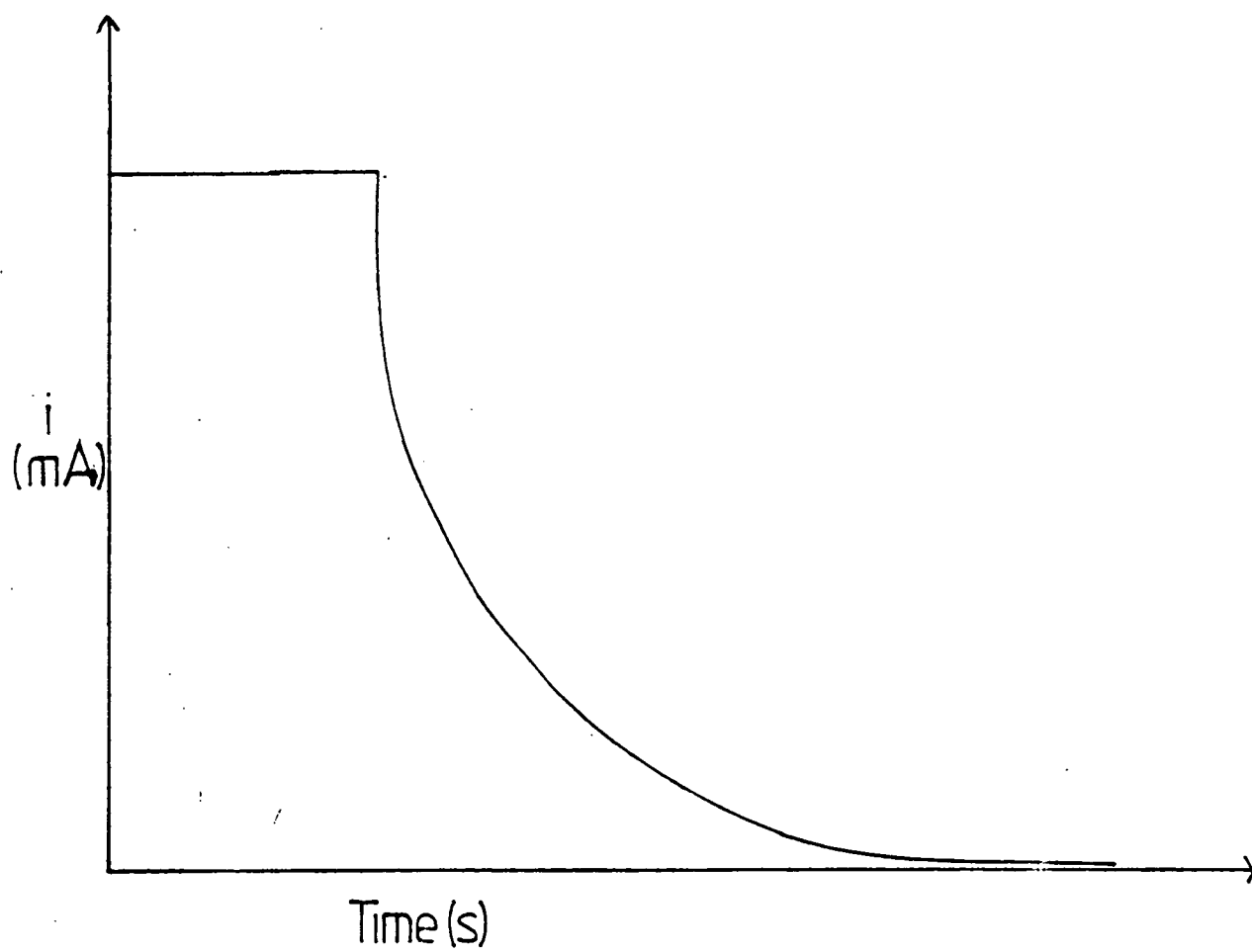


Figure A.1.7. A Characteristic Current-Time Response (Coulometric Plot) for Controlled Potential Electrolysis.

A.1.9. Bulk Spectroelectrolysis - Spectroelectrosynthesis.

Using the cell shown in figure A.1.3., reactions taking place while an electron transfer is being executed at the working electrode can be monitored *in situ* by electronic u.v./vis. absorption spectroscopy.³ The optically transparent thin layer electrode (O.T.T.L.E.) consists of a platinum/rhodium gauze working electrode (transparency ca.-40%) fitted into a quartz cell with a path length of 0.5mm. A quartz extension is fitted to the cell which acts as a reservoir for the test solution. To complete the conventional three electrode configuration a platinum wire counter electrode and a Ag/AgCl reference electrode are placed into this reservoir, both electrodes being separated from the test solution by porous frits which allow current to flow through them but are impermeable with respect to the test species. The quartz extension has a tight fitting P.T.F.E. top, which prevents solutions purged of dioxygen being exposed to the gaseous environment.

The assembly described above is placed into a gas tight P.T.F.E. block (fig. A.1.3.) which in turn is placed in the spectrometer. Temperature control is achieved by passing dry, pre-cooled nitrogen between the inner pair of quartz windows and the cell. The temperature is monitored using a thermocouple connected to a digital thermometer. To prevent the inner pair of quartz windows from fogging,

dry nitrogen is passed between the inner and outer quartz windows and the sample compartment of the spectrometer is flushed with dry nitrogen.

As for a conventional bulk electrolysis (as described in section A.1.7.), if the electron transfer process being examined is thought to be a reversible process, then this should be confirmed by a full regeneration of the starting material.

A.1.10. Experimental.

All electrochemical measurements were performed in the solvent systems and experimental conditions described in the text. In addition all solutions were argon purged. Unless otherwise stated the scan rates used were 100mVs^{-1} for cyclic voltammetry and 20mVs^{-1} for stirred voltammetry and a.c.voltammetry.

All potentials are quoted against a Ag/AgCl reference electrode against which the ferrocene/ferrocinium couple is measured at +0.56 Volts.

Cyclic voltammetric and a.c. voltammetric measurements and bulk electrolysis were performed using a PAR Model 170 Electrochemistry System connected to a Hewlett Packard 7045A X-Y Recorder.

Spectroelectrochemical experiments were performed using a Perkin-Elmer Lambda 9 Spectrophotometer in conjunction with a Metrohm-Herisau Polarecord E 506

Potentiostat.

Solutions were thermostated using a Haake Model Q
Thermostated Bath Circulator.

Temperature was monitored using Comark 5000 Digital
Thermometer connected to a Thermocouple.

A.1.11 References.

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2. C.K.Mann, Electroanal.Chem. 1969, 3, 57-134.
3. G.A.Heath, L.J.Yellowlees, and P.S.Braterman, J.Chem.Soc., Chem.Commun., 1981, 287.

Appendix 2 Determination of the allowed M.L.C.T.
transitions for the complexes $[\text{Os(II)Cl}_{6-n}\text{PY}_n]^{(n-4)+}$.

Now the day has wearied me.
And my ardent longing shall
the stormy night in friendship
enfold like a tired child.

Hands, leave all work;
brow, forget all thought.
Now all my senses
long to sink themselves in slumber.

And the spirit unguarded
longs to soar on free wings,
so that, in the magic circle of night,
it may live deeply, and a thousandfold.

Going to sleep Hermann Hesse
(translation - William Mann)

A.2.1 Introduction.

The number of $\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$ transitions expected for the complexes $\text{trans-}[\text{OsCl}_4\text{py}_2]^{2-}$, $\text{cis-}[\text{OsCl}_4\text{py}_2]^{2-}$, $\text{mer-}[\text{OsCl}_3\text{py}_3]^-$, $\text{trans-}[\text{OsCl}_2\text{py}_4]$, $[\text{OsClpy}_5]^+$, $[\text{OsPy}_6]^{2+}$ are calculated. The calculations are performed using the following local symmetries about the osmium centre:

O_h - $[\text{OsPy}_6]^{2+}$

D_{4h} - $\text{trans-}[\text{OsCl}_4\text{py}_2]^{2-}$ and $\text{trans-}[\text{OsCl}_2\text{py}_4]$

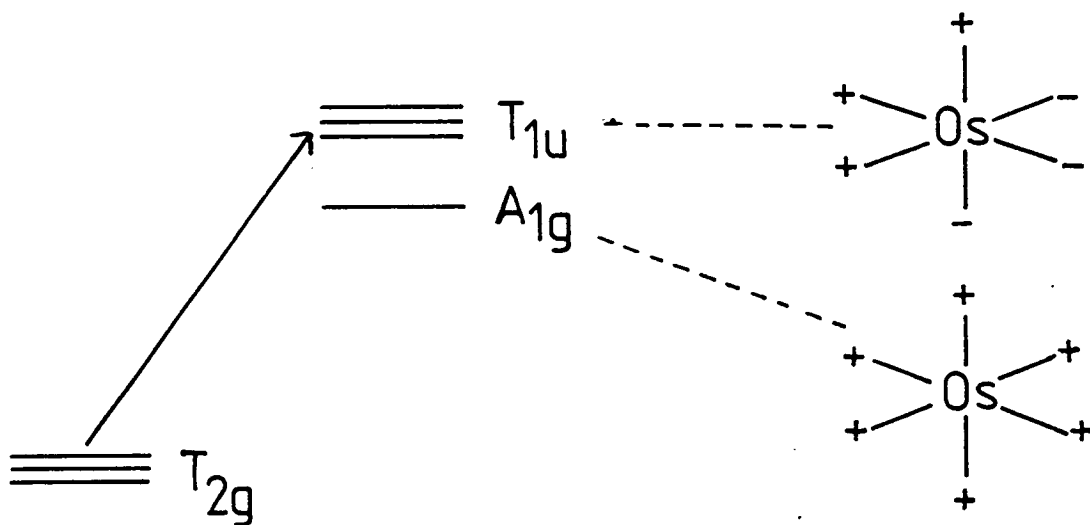
C_{4v} - $[\text{OsClpy}_5]^+$

C_{2v} - $\text{cis-}[\text{OsCl}_4\text{py}_2]^{2-}$ and $\text{mer-}[\text{OsCl}_3\text{py}_3]^-$.

The L.U.M.O. of pyridine is calculated using the M.O. scheme for pyridine shown in figure A.2.1. When calculating the symmetry of the excited state only the orbitals on nitrogen and osmium atoms are considered. Whether a specific transition is allowed is determined by multiplying the ground state term (G.S.) by the operators (OP.) for an electronic transition by the excited state term (E.S.). For a particular transition to be allowed it must be fully symmetric. To satisfy this condition the product $\text{G.S.} \times \text{OP.} \times \text{E.S.}$ must contain the fully symmetric A term.

A.2.2 Determination of the allowed $\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$ charge transfer transitions for the complexes $[\text{OsPy}_6]^{2+}$, $t\text{-}[\text{OsCl}_4\text{py}_2]^{2-}$, $t\text{-}[\text{OsCl}_2\text{py}_4]$, $[\text{OsClpy}_5]^+$, $c\text{-}[\text{OsCl}_4\text{py}_2]^{2-}$ and $m\text{-}[\text{OsCl}_3\text{py}_3]^-$.

$[\text{OsPy}_6]^{2+}$ local symmetry - O_h



Combination of pyridine orbitals: A_{1g} , T_{1u}

G.S. = A_{1g}

O.P. = T_{1u}

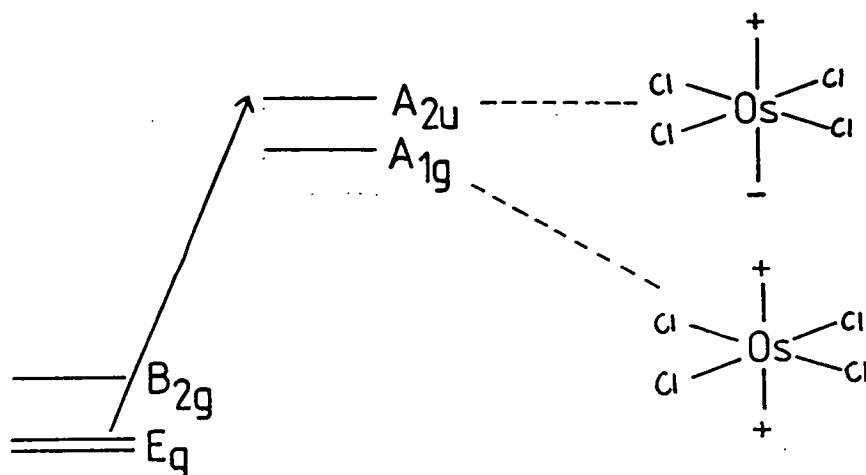
E.S. = $T_{2g} \times A_{1g} = T_{2g}$

$T_{2g} \times T_{1u} = A_{2u} + E_u + T_{1u} + T_{2u}$

$A_{1g} \times T_{1u} \times T_{2g} = A_{2u} + E_u + T_{1u} + T_{2u}$

$A_{1g} \times T_{1u} \times (A_{2u} + E_u + T_{1u} + T_{2u}) = T_{2g} + T_{1u} + T_{2u} + A_{1g} + E_g + T_{1g} + T_{2g}$
 $+ A_{2g} + E_g + T_{1g} + T_{2g}$

$[OsCl_4py_2]^{2-}$ local symmetry - D_{4h}



Combinations of pyridine orbitals: A_{1g} , A_{2u}

$$G.S. = A_{1g}$$

$$O.P. = A_{2u}, E_u$$

$$E.S. = A_{1g} \times B_{2g}, A_{1g} \times E_g = B_{2g}, E_g$$

$$= A_{2u} \times B_{2g}, A_{2u} \times E_g = B_{1u}, E_u$$

$$A_{1g} \times A_{2u} \times B_{2g} = B_{1u}$$

$$A_{1g} \times A_{2u} \times E_g = E_u$$

$$A_{1g} \times E_u \times B_{2g} = E_u$$

$$A_{1g} \times E_u \times E_g = A_{1u} + A_{2u} + B_{1u} + B_{2u}$$

$$A_{1g} \times A_{2u} \times B_{1u} = B_{2g}$$

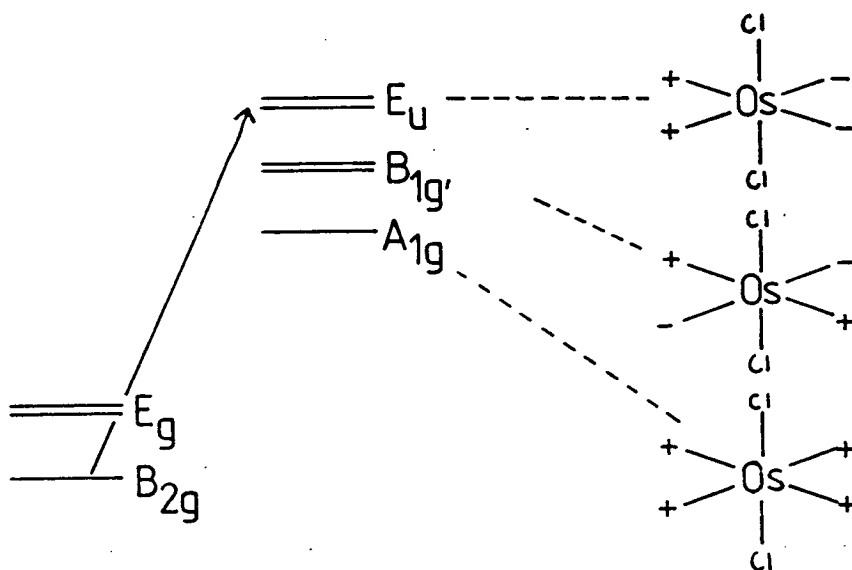
$$A_{1g} \times A_{2u} \times E_u = E_g$$

$$A_{1g} \times E_u \times B_{1u} = E_g$$

$$A_{1g} \times E_u \times E_u = A_{1g} + A_{2g} + B_{1g} + B_{2g}$$

$[OsCl_2py_4]$

local symmetry - D_{4h}



Combinations of pyridine orbitals: A_{1g}, B_{1g}, E_u .

G.S. = A_{1g}

OP. = A_{2u}, E_u

E.S. = $A_{1g} \times B_{2g}, A_{1g} \times E_g = B_{2g}, E_g$

$B_{1g} \times B_{2g}, B_{1g} \times E_g = A_{2g}, E_g$.

$E_u \times B_{2g}, E_u \times E_g = E_u, (A_{1g} + A_{2g} + B_{1g} + B_{2g})$

$A_{1g} \times A_{2u} \times B_{2g} = B_{1u}$

$A_{1g} \times A_{2u} \times E_g = E_u$

$A_{1g} \times E_u \times B_{2g} = E_u$

$A_{1g} \times E_u \times E_g = A_{1u} + A_{2u} + B_{1u} + B_{2u}$

$$A_{1g} \times A_{2u} \times A_{2g} = A_{1u}$$

$$A_{1g} \times A_{2u} \times E_g = E_u$$

$$A_{1g} \times E_u \times A_{2g} = E_u$$

$$A_{1g} \times E_u \times E_g = A_{1u} + A_{2u} + B_{1u} + B_{2u}$$

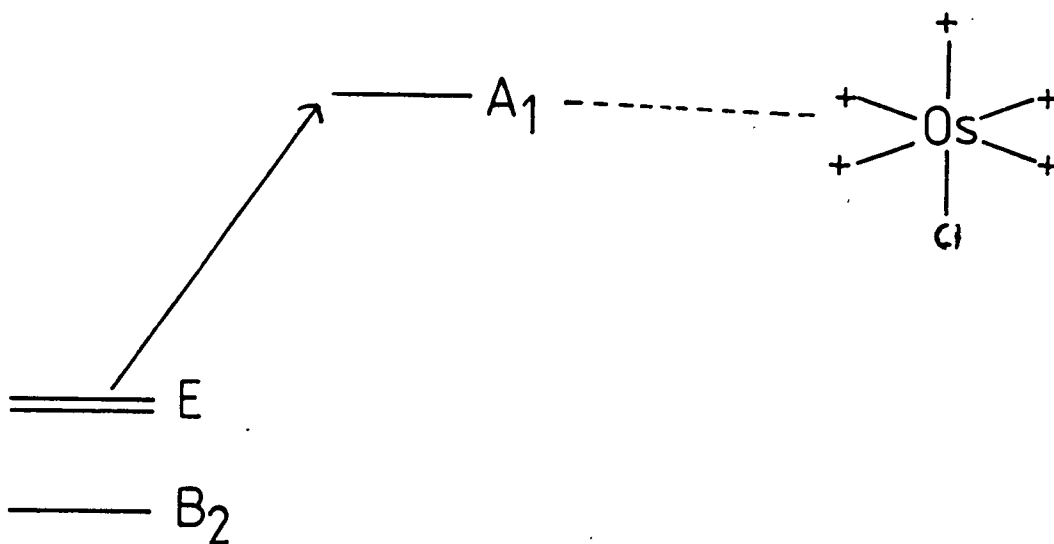
$$A_{1g} \times A_{2u} \times E_u = E_g$$

$$A_{1g} \times A_{2u} \times (A_{1g} + A_{2g} + B_{1g} + B_{2g}) = A_{2u} + A_{1u} + B_{2u} + B_{1u}$$

$$A_{1g} \times E_u \times E_u = A_{1g} + A_{2g} + B_{1g} + B_{2g}$$

$$A_{1g} \times E_u \times (A_{1g} + A_{2g} + B_{1g} + B_{2g}) = 4E_u$$

$[\text{OsCl}(\text{py}_5)]^+$ local symmetry - C_{4v}



Pyridine orbitals A_1

G.S. = A_1

OP. = A_1, E

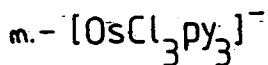
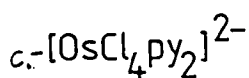
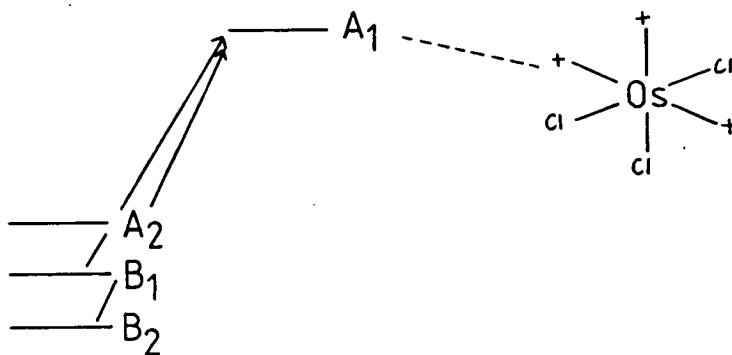
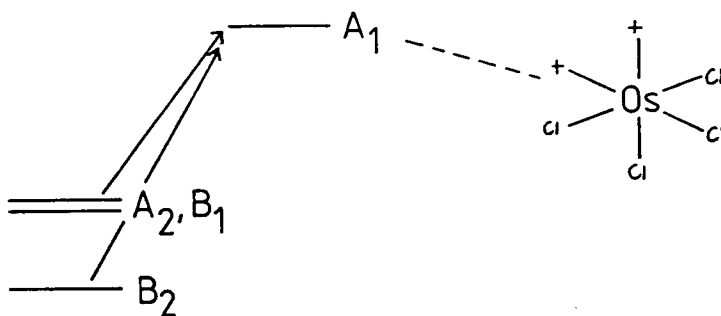
E.S. = $B_2 \times A_1, E \times A_1 = B_2, E$

$A_1 \times A_1 \times B_2 = B_2$

$A_1 \times A_1 \times E = E$

$A_1 \times E \times B_2 = E$

$A_1 \times E \times E = A_1 + A_2 + B_1 + B_2$

local symmetry - C_{2v} local symmetry - C_{2v} Combination of the pyridine orbitals: A_1 Os(II)G.S. = A_1 OP. = A_1, B_1, B_2 E.S. = $(A_2, B_1, B_2) \times A_1 = A_2, B_1, B_2$

$$A_1 \times A_1 \times A_2 = A_2 \quad A_1 \times B_1 \times A_2 = B_2 \quad A_1 \times B_2 \times A_2 = B_1$$

$$A_1 \times A_1 \times B_1 = B_1 \quad A_1 \times B_1 \times B_1 = A_1 \quad A_1 \times B_2 \times B_1 = A_2$$

$$A_1 \times A_1 \times B_2 = B_2 \quad A_1 \times B_1 \times B_2 = A_2 \quad A_1 \times B_2 \times B_2 = A_1$$

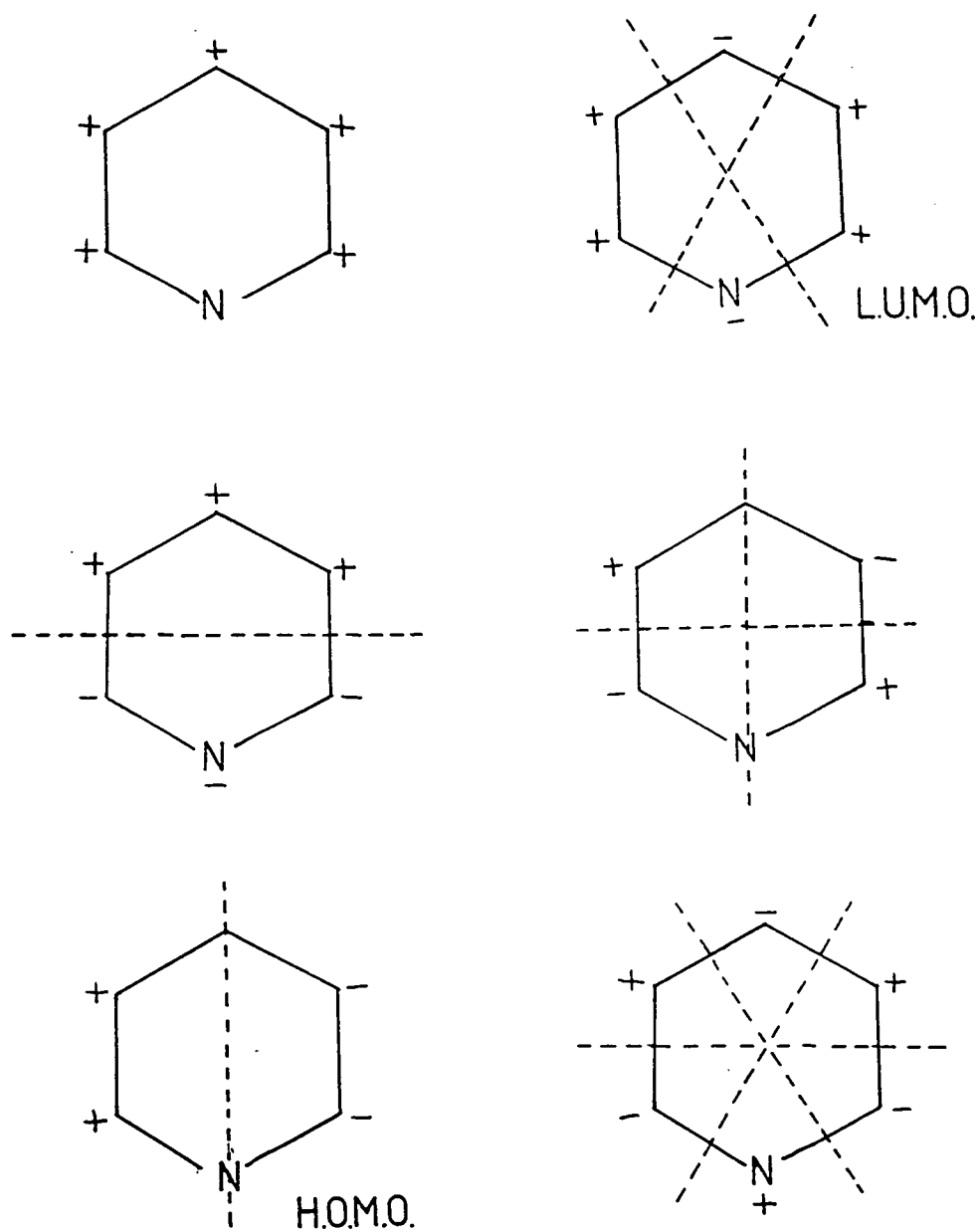


Figure A.2.1 M.O. Scheme for Pyridine.

A.2.3. Discussion on the relationship between these determinations and the observed spectra.

The determinations above show that for the compounds $[\text{OsPy}_6]^{2+}$, $[\text{OsClpy}_5]^+$, *trans*- $[\text{OsCl}_2\text{py}_4]$ and *trans*- $[\text{OsCl}_4\text{py}_2]^{2-}$ only one transition is allowed whereas for *cis*- $[\text{OsCl}_4\text{py}_2]^{2-}$ and *mer*- $[\text{OsCl}_3\text{py}_3]^-$ two transitions are expected. These observations agree with the band patterns observed in the actual spectra. These determinations also explain some other trends in the observed spectra and, when combined with information obtained from the band energies of the spectra, allow us to probe the splitting of the $d\pi$ orbitals.

The 'singlet' $\text{Os(II)}d\pi \rightarrow \text{py}\pi^*$ ($E_g \rightarrow A_{2u}$) transition for *trans*- $[\text{OsCl}_4\text{py}_2]^{2-}$ is observed at lower energy than the corresponding transfer for *cis*- $[\text{OsCl}_4\text{py}_2]^{2-}$ ($B_1 \rightarrow A_1$). Using the empirical 'ligand additivity' model of Bursten we would expect the appropriate metal based orbitals to both be stabilised by $a+2b+2c$. Hence we must conclude that the energy of the pyridine acceptor orbitals is lower for the *trans*- $[\text{OsCl}_4\text{py}_2]^{2-}$ than for *cis*- $[\text{OsCl}_4\text{py}_2]$. This might be expected since the pyridine π -orbitals in the *cis*-isomer are able to accept electron density from the π -donating chloride ligands that lie *trans* to them.

The two allowed transitions in the spectrum of *cis*- $[\text{OsCl}_4\text{py}_2]^{2-}$ lie some 4 040 cm^{-1} apart. Since both transitions are to the same acceptor level, this difference

in energy seems to provide a measure of the splitting in the non-degenerate metal based $d\pi$ orbitals. The splitting between the two corresponding transitions ($B_1 \rightarrow A_1$ and $B_1 \rightarrow A_1$) in the *mer*-[OsCl₃py₃]⁻ is smaller, ca. 3 000cm⁻¹. This splitting is slightly smaller than the energy observed for the metal based $d\pi \rightarrow d\pi$ transitions for Os(III) complexes, which occur at ca. 5 500cm⁻¹, since the $d\pi \rightarrow d\pi$ transitions also contain a spin pairing term.

Throughout these calculations it was assumed that the splitting in the metal-based $d\pi$ orbitals was larger than the difference in energy between the combinations of $py\pi^*$ orbitals. A consequence of this assumption is that we must consider the pyridine rings as essentially non-interacting. We would suggest this assumption would become more valid as more pyridines became coordinated. Since the positions of the pyridine orbitals become governed by steric rather than electronic factors, it becomes impossible for the orbitals to stabilise one another efficiently. A series of molecular orbital calculations on this series of complexes would reveal whether this assumption was reasonable.

List of Abbreviations and Notes

Å	Angstrom (10^{-10}m)
A.C.	alternating current
Bipy	2,2'-bipyridine
Cp	cyclopentadiene
C.T.	charge transfer
Cypy	cyanopyridine
Dcypy	dicyanopyridine
D.C.	direct current
Dmf	N,N- dimethylformamide
dppe	(1,2-diphenylphosphino)ethane
dppm	(1,2-diphenylphosphino)methane
E	potential
E.S.	excited state
F.A.B.	fast atom bombardment
G.S.	ground state
H.O.M.O.	highest occupied molecular orbital
I.R.	infra-red
K	degrees Kelvin
L.U.M.O.	lowest unoccupied molecular orbital
Me	methyl
M.O.	molecular orbital
N.M.R.	nuclear magnetic resonance
3-NOBA	3-nitrobenzylalcohol
OP	operator

O.T.T.L.E.	optically transparent thin layer electrode
Ph	phenyl
P.T.F.E	polytetrafluoroethylene
py	pyridine
S.C.E.	standard calomel electrode
TBA	tetrabutylammonium
TPA	tetrapropylammonium
T.L.C.	thin layer chromatography
U.V.	ultra violet
V	volts
Vis.	visible
X	halogen
ϵ	extinction coefficient ($\text{cm}^{-1} \text{mol}^{-1} \text{dm}^{-3}$)
ν_{max}	frequency of highest absorption
∂ or ν	scan rate
ω	frequency of the alternating component of the applied potential in a.c. voltammetry

Unless otherwise stated, all E values are quoted versus a Ag/AgCl reference which showed a ferrocine/ferricinium couple at +0.56V.

List of Lecture Courses and Meetings Attended.

Electronic Structures of Inorganic Complexes

by Dr. L.J. Yellowlees.

Recent Advances in Inorganic Chemistry

by Drs. A.J. Welch, L.J. Yellowlees

S.K. Chapman and M. Schroder.

Electroanalytical Methods

by Dr. H.H.J. Girault.

The Lanthanides and Actinides

by Dr. S. Cradock

Departmental Research Seminars and Colloquia.

University of Strathclyde Inorganic Club Conferences,
1988, 1989, 1990.

Butler Postgraduate Electrochemistry Meetings, University
of Edinburgh, 1988, 1989, 1990.

Fifth Ames Symposium, University of Edinburgh, 1988.

I.S.E. Conference University of Strathclyde, 1988.

R.S.C. Dalton Division Autumn Meeting, Birmingham, 1988.

R.S.C. Scottish Dalton Group Meetings, 1988, 1989, 1990.

R.S.C. Platinum Metals Conference, Cambridge, 1990.