PREPARATIONS AND OXIDATION-REDUCTION POTENTIALS OF SOME OSMIUM COMPLEXES

THESIS
SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE
AUSTRALIAN NATIONAL UNIVERSITY

D. A. BUCKINGHAM

The work described in this thesis was carried out in the Biological Inorganic Chemistry Section of the John Curtin School of Medical Research under the supervision of Professor F. P. Dwyer. The work described is the candidate's own.

Signed

D. A. Buckingham.

December 1961

PREFACE

During the last five years a systematic study has been made in these laboratories of the chemistry of the Group(VIII) elements, iron, ruthenium, and osmium. This study has been concerned with the preparations of mono-, bis-, and tris- 1,10 phenanthroline and 2,2' dipyridyl complexes, and an investigation into their thermodynamic and kinetic stabilities. Much of the work on iron and ruthenium has now been completed, and this thesis presents the results of a preparative and thermodynamic study on the last member of the group, osmium.

The preparations of mono- and bis- 1,10 phenanthroline, 2,2' dipyridyl, and 2,2',2" terpyridyl complexes of osmium(II), (III) and (IV) are described in PART ONE. The bis(dipyridyl)-phenanthrolineosmium(II) and bis(phenanthroline)dipyridyl-osmium(II) ions have been resolved into their optical isomers, and an improved method is presented for the preparation of the tris(phenanthroline)- and tris(dipyridyl)- osmium(II) complexes. An extensive series of substituted complexes of osmium(II) and osmium(III) has been isolated. These compounds are largely based on the parent mono- or bis- dipyridyl osmium complexes and involve in addition the co-ordination of phenanthroline, ethylenediamine, glycine, acetylacetone, oxalate, pyridine, ammonia, chlorine, bromine, iodine, thiocyanate, hydroxide, and additional organic ligands.

It has been realised for some time that simple model metal complex systems offer much promise in elucidating problems in metal-enzyme and metal-porphyrin chemistry. This is especially so when considering redox potentials. Although much useful information has been obtained from the iron tris-phenanthroline and dipyridyl couples, little precise information is available on the effect of the overall charge on the oxidation potential, or the effects that might be anticipated from various ligands when substituted into a standard complex structure. It is found that the osmium complexes described in PART ONE provide an ideal system whereby a quantitative investigation of the oxidation-reduction relationships between a complex in two different oxidation states can be studied.

The measurement and interpretation of such potentials for a variety of osmium(II)/osmium(III) couples is discussed in PART TWO.

This work has been carried out under the supervision of Professor F. P. Dwyer. To him I extend my sincerest thanks for help willingly given both in experimental work, and in

the interpretation of the redox potentials. It has been a pleasure to work under such guidance. Thanks must also be recorded to Dr. A. Sargeson, who at all times has been only too willing to discuss critically all phases of the work. Mention must also be made of useful discussions with Professor A. N. Hambly (Aust. Nat. Univ.), Dr. N. S. Hush (Univ. of Bristol), and with my scholar associates Messrs. T. E. MacDermott, B. Bosnich, and C. J. Hawkins. This appreciation would be incomplete without thanking Mrs. M. A. Cuthbertson for typing the thesis draft, and Mr. G. H. Searle for critically reviewing the draft and for proof reading the final thesis. For the microanalyses for nitrogen recorded in this work the candidate is indebted to Dr. J. Fildes of the microanalytical section of the Department of Medical Chemistry.

Finally I must thank the Australian National University for the award of a scholarship during the tenure of which this work was carried out.

NOMENCLATURE

All chemical compounds are formulated and named as instructed by a recent publication by the International Union of Pure and Applied Chemistry (J.A.C.S. 82, 5517, 1960).

Some common abbreviations used are:-

phen	1,10' phenanthroline
bipy	2,2' bipyridine (as the organic base)
dipy	2,2' dipyridyl (as the ligand)
tpy	2,2',2" terpyridine
py	pyridine
aca H	acetylacetone
gly H	glycine
ox	oxalate
en	ethylenediamine

CONTENTS

Page

PREFACE

PART I

CHAPTER II Preparations and Reactions of Mono-Dipyridyl and Phenanthroline Complexes of Osmium(II), (III) and (IV)

PART II

CHAPTER V Introduction to Oxidation-Reduction Potentials

CHAPTER VI

CHAPTER VII

PART I

CHAPTER ONE

INTRODUCTION TO PREPARATIVE WORK

Since the advent in 1891 of Werner's theory of co-ordination an impressive amount of research has been carried out on metals of the transition series. A review of the chemical literature shows, however, that the vast majority of this work has been concentrated on elements of the first transition series and a similar, detailed study has not been made on the chemistry of the heavier, third transition elements such as osmium.

There are several reasons for this apparent lack of interest. Firstly, osmium is not a common element (1) and has been until recently commercially available only as the metal, osmium tetroxide, and osmium trichloride. These meterials are expensive, especially when a large scale programme of preparative work is proposed. From a preparative viewpoint, a major difficulty has been the lack of an octahedral complex of definite composition, which can be prepared in high yield from the above available material, and which lends itself to a wide variety of further preparations. Many attempts have been made to use osmium tetroxide directly for preparing octahedral osmium complexes.

However, the first products of reduction are invariably osmyl, or oxyosmyl complexes which are very resistant to further reaction (2). Similarly, the use of $OsCl_3$ and $OsCl_4$ is limited, as reaction in aqueous solution invariably leads to the formation of the black insoluble dioxide, OsO_2 (3). It was realised that compounds of the type R_2OsX_6, (X=Cl,Br) would be more useful but the early methods of preparing these compounds were difficult and poor yields were obtained. Even these compounds decompose to osmium dioxide in basic solution.

Finally, the inherent difficulty in preparing osmium complexes is the metal's strong preference to co-ordinate irreversibly to oxygen. For this reason the great majority of complexes contain osmium in the anion (e.g. osmates, osmyls, oxy-osmyls, osmiamates). In this respect osmium resembles molybdenum and tungsten. This preference for oxygen prevents the use of aqueous solvents for preparing many of its complexes, and necessitates the use of organic solvents, pyrolysis techniques, or reacting directly with the co-ordinating ligand such as used in preparing the ethylenediamine complexes.

For the above reasons, preparative osmium chemistry was largely neglected until 1951. In that year, however, methods were published for preparing the hexachloro-complexes of osmium, in high yields from osmium tetroxide. Since then several workers have used these compounds to prepare a variety of osmium (II), (III) and (IV) complexes. The methods and experimental conditions used in preparing these complexes are relevant to PART I of this thesis, and a brief review of the more recent investigations is outlined below.

HEXAHALOOSMATES

Ammonium hexachloroosmate (IV) appears to have been first prepared (4,5) by heating a mixture of osmium and potassium chloride with chlorine, leaching the residue, and adding ammonium chloride. Wintrebert in 1903 found a better method of preparation (6). This involved reacting osmium tetroxide with potassium nitrite to form the osmiamate, $K[OsO_3N]$, from which potassium hexachloroosmate was thrown out on repeated evaporations with boiling concentrated hydrochloric acid. Despite the claims of Wintrebert the yield obtained using this method is never more than 40 - 50% (7,8). Similarly, potassium hexabromoosmate had been prepared by reacting sodium tetrasulfitodioxoosmate (VI) (9), or ammonium tetranitrodioxo-osmate (VI) (6) with concentrated hydrobromic acid. More recently Dwyer and Hogarth have prepared both the bromo- and chloro- compounds in almost quantitative yields from osmium tetroxide (7, 10, 11). The $OsCl_6^{2-}$ ion was prepared by reacting a 12 M hydrochloric acid solution of OsO_4 with ferrous chloride, and the ammonium or potassium salt could be crystallised out by adding ammonium or potassium chloride.

$$OsO_4 + 4FeCl_2 + 10HCl \longrightarrow H_2OsCl_6 + 4FeCl_3 + 4H_2O$$

K_2OsBr_6 could be prepared in a similar fashion, although in this case a reducing agent was not necessary - an observation noted previously by Gilchrist (12).

Both K_2OsCl_6 and K_2OsBr_6 are easily hydrolysed in dilute acid or aqueous solution and the products formed are extremely resistant to reconversion to the hexahaloosmate (IV) ion (13,14). The stability of these oxygen containing complexes is evident from the observation that $(NH_4)_2[Os\ Cl_5\ OH]$ can be boiled with concentrated hydrochloric acid in the presence of ammonium chloride without the formation of any ammonium hexachloroosmate (IV) (7).

Ammonium hexaiodoosmate (IV) appears to have been first prepared by reacting potassium osmiamate with hydroiodic acid (15). Very recently Nyholm has shown that it can be isolated as the acetone soluble fraction on reacting osmium tetroxide with iodide ions in 2N hydrochloric acid (16). Aqueous solutions of H_2OsF_6 have recently been prepared by ion exchange methods and small quantities of the salts M_2OsF_6 ($M=NH_4$, NMe_4, Na) have been isolated (17).

ARSINE COMPLEXES

Dwyer, Nyholm and Tyson found that when a tertiary arsine such as AsR_3 (R = Me,Ph) is refluxed with a solution of a hexahaloosmate in the corresponding halogen acid, reduction takes place and complexes of the type $[OsX_3(AsR_3)_3]$, X = Cl,Br separate as red needles (18). The bromo compound exists in two forms, the higher melting form being converted into the lower melting form by dissolution in benzene, while the reverse change could be effected by solution in alcohol containing hydrobromic acid. The authors suggest the equilibrium,

$$2[OsBr_3(AsR_3)_3] \rightleftharpoons [OsBr_3(AsR_3)_3]_2$$

in which the dimer could have either of the possible formulations $[OsBr_x(AsR_3)_{6-x}][OsBr_{6-x}(AsR_3)_x]$; x = 0,1,2. The corresponding iodo compound was not isolated due to further reduction to the bivalent state with the formation of the dark purple compound, $[Os\,I_2(Ph_2MeAs)_3]_2$. Continued reflux in the presence of hypophosphorous acid resulted in the formation of the pale, bivalent complexes, $[Os\,X_2(AsR_3)_4]$. Both the bivalent and tervalent complexes were found to have strong reducing properties. In a continuation of their systematic investigation of the co-ordinating ability of o-phenylenebis(dimethyl) arsine, Nyholm and co-workers have prepared a series of osmium(II), (III), and (IV) complexes containing two molecules of this ligand (19). The diamagnetic osmium(II) compounds were prepared by refluxing ammonium hexahaloosmate (IV) with an excess of the diarsine in alcoholic solution. They were found to be monomeric in nitrobenzene as are the Fe and Ru complexes (20,21). Nyholm postulates that the two bound halogen atoms occupy trans positions. However if double bonding contributes significantly to the metal-diarsine bond the cis configuration would appear more reasonable due to the possibility of forming three strong π bonds in this configuration, (c.f.p....). 67 Oxidation was effected with the appropriate halogen and the paramagnetic ($\mu = 1.85-1.93$) osmium (III) complexes, $[Os\ X_2\ D_2]X$, isolated. Reaction with 15 N nitric acid resulted in further oxidation, and the blue-black osmium (IV) complex ions, $[Os\ X_2\ D_2]^{2+}$ were isolated as the soluble perchlorates.

ETHYLENEDIAMINE COMPLEXES

Dwyer and Hogarth found that when ammonium hexabromoosmate (IV) is added to anhydrous ethylenediamine at 10°, an exothermic reaction occurs with the formation of a pink osmium (IV) complex containing three molecules of ethylenediamine, two of which have lost a proton from one of the bound nitrogen atoms (22,23).

$$(NH_4)_2\ OsBr_6 + en \xrightarrow{10^\circ} [Os\ en\ (en\text{-}H)_2]\ Br_2$$

This compound acts as a weak mono acid base (pK = 8.2) accepting one proton in slightly acidic solution to form a compound containing three ionizable Br atoms, and only one ethylenediamine molecule with a H atom deficiency.

$$[\text{Os en (en-H)}_2]^{2+} \underset{\text{OH}^-}{\overset{\text{H}^+}{\rightleftarrows}} [\text{Os en}_2\ \text{(en-H)}]^{3+}$$

Both of these complexes can be reduced with sodium dithionite to form the paramagnetic (μ = 1.6-1.7 B.M.) tris(ethylenediamine) osmium (III) ion which has been isolated as the yellow iodide. All attempts to resolve this compound failed. $[\text{Os en (en-H)}_2]\text{I}_2$ was found to react with further ethylenediamine at 100° in an oxygen free atmosphere to form an unstable green compound containing four molecules of ethylenediamine. To account for its stability the authors proposed that the fourth ethylenediamine also acts as a bidentate ligand and that the substance is an 8- covalent complex of osmium (IV).

$$[\text{Os en (en-H)}_2]\text{I}_2 \xrightarrow[100^\circ]{\text{en}} [\text{Os en}_2\ \text{(en-H)}_2]\text{I}_2$$

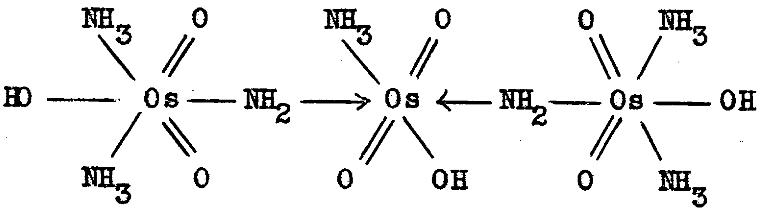
This compound is oxidized spontaneously on exposure to the air with the formation of a further two 8-covalent complexes. The less soluble of these was paramagnetic (μ = 1.6-1.8 B.M.) and brown in aqueous solution. The analyses were consistent with the formulation $[\text{Os en (en-H)}_3]\text{I}_2$ indicating a complex of osmium (V). The more soluble green compound was diamagnetic as is required for a 8-covalent complex of osmium (VI). Both compounds were found to be interconvertible.

$$\begin{tikzcd}
{[\text{Os en}_2\ \text{(en-H)}_2]^{2+}} \arrow[r, "\text{O}_2"] & {[\text{Os en (en-H)}_3]^{2+}} \arrow[d, shift left, "\text{Ce(IV)}"] \\
 & {[\text{Os (en-H)}_4]^{2+}} \arrow[u, shift left, "\text{Na}_2\text{S}_2\text{O}_3"]
\end{tikzcd}$$

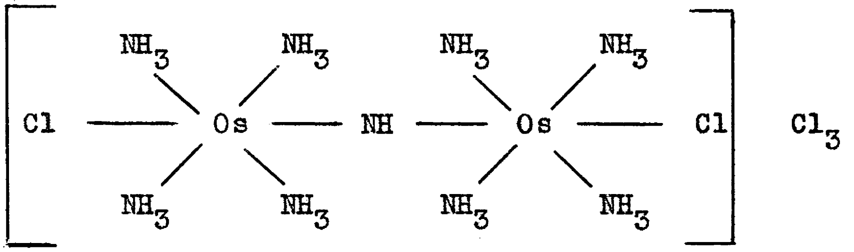
In a separate study Healy investigated the reaction between K_2OsCl_6 and N,N' disalicylylidine ethylenediamine but due to his choice of solvent (aqueous methanol), a variety of colored products of indefinite composition were obtained (24).

AMMINES

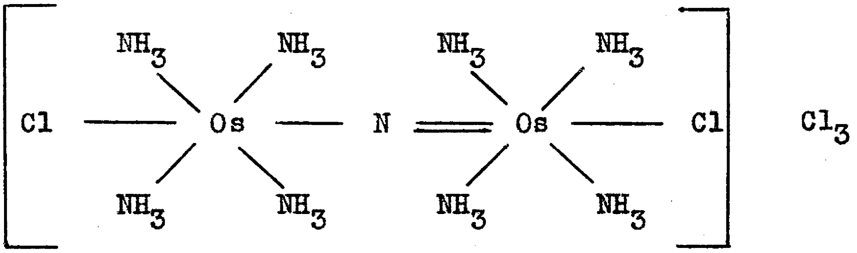
Prior to 1951, $[Os\ O_2\ (NH_3)_4]X_2$ was the only known ammine complex of osmium (25). The curious substance potassium osmiamate $K[OsO_3N]$, a compound of octavalent osmium, has been prepared by treatment of osmium tetroxide with ammonia and aqueous potassium hydroxide (26,27). It reacts with hydrochloric acid with the liberation of chlorine and degradation to the sexa-valent $[Os\ Cl_5\ N]^{2-}$ ion, which is reducible with stannous chloride to $K_2[Os\ Cl_5\ (NH_2)]$ (28). Hair and Robinson have recently shown that reacting osmium tetroxide with liquid ammonia at -25° results in the formation of an unstable orange solid of the composition $OsO_4 \cdot NH_3$, which on warming forms osmiamic acid, $HOsO_3N$ (29). Continued treatment with liquid ammonia results in the formation of an unstable compound of the probable structure, (30)



Attempts to prepare osmium ammines by direct reaction of potassium hexachloro- or hexabromo-osmate with aqueous ammonia lead to hydrolysis and the ultimate separation of osmium dioxide (31). Similarly, solutions of osmium(III) hexahalo-complexes darken in color and ultimately yield a black precipitate when treated with an aqueous ammoniacal solution (32,33). Preliminary experiments by Dwyer and Hogarth showed that direct ammonolysis with liquid ammonia could not be achieved in the tetravalent state (31), and that the osmium must first be reduced to the strongly reducing trivalent state and then treated with dry NH_3 in the absence of oxygen or water. This reaction was carried out in a steel autoclave at 285° and a pressure of 2 atmospheres, and low yields (10 - 20%) of the light fawn halopentammineosmium(III) halide resulted. The bromo-compound was isolated as the bromide, iodide, nitrate and perchlorate, but the co-ordinated chlorine atom in $[Os\,Cl\,(NH_3)_5]Cl_2$ is more labile and prevented the preparation of salts such as $[Os\,Cl\,(NH_3)_5]I_2$. If larger quantities of starting material were used, a water soluble yellow compound was formed. This analysed as $[Os_2\,(NH_3)_8NH\,Cl_2]Cl_3$ and structures I and II were proposed, of which II was preferred by analogy with the nitrido complexes $M_2[Os\,Cl_5\,N]$ (28). Structure I contains both osmium(III) and osmium(IV) valence states.



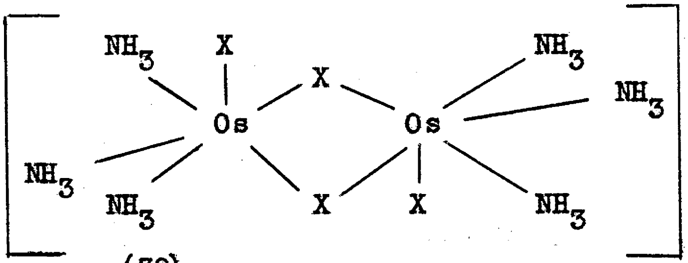
I



II

The light yellow color of the compound mitigates against such a structure. This compound was also prepared by Watt and Vaska by reacting K_2OsBr_6 with liquid ammonia at 25° (34). The observed diamagnetism also supports structure (II) above.

Dwyer and Hogarth have prepared the hexammine osmium(III) ion, $[Os\ (NH_3)_6]^{3+}$ by reacting $(NH_4)_2OsBr_6$ with ammonia gas in an autoclave at 285-290° and a pressure of two and a half atmospheres (35). Up to 50% yields of the iodo sulphate were obtained and the paramagnetism ($\mu = 2.1$ B.M.) (36) found for this compound is similar to that found for the analogous Ru ammines. The higher than "spin only" value is usual for complexes of the second and third transition series (37,38). If the hexammineosmium(III) iodo-sulphate or bromide is heated to 230° it loses one molecule of ammonia and the light brown halopentammineosmium(III) complex ion is formed (39). When heated to a higher temperature the pentammine decomposes to a black substance of empirical formula $OsX_3(NH_3)_3$, X = Br, I. From magnetic evidence and conductometric studies the halogen bridged structure



has been proposed (39). Further heating of this compound results in oxidation, and the products include OsO_4 and halogen. Watt and Vaska have shown that if K_2OsBr_6 is reacted with liquid ammonia for 12 hours at 30°, approximately half the osmium is converted into an amber ammonia insoluble product which was identified as hexammineosmium(III) hexabromoosmate(III) (40). This substance is insoluble in all common organic solvents but slowly dissolves in 48% hydrobromic acid. From the resulting solution white, crystalline, hexammineosmium(III) bromide was isolated on adding alcohol.

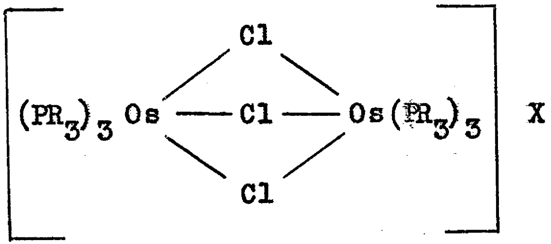
$$[Os(NH_3)_6][OsBr_6] + 3HBr \xrightarrow[\text{days}]{\text{several}} [Os(NH_3)_6]Br_3 + H_3OsBr_6$$

If potassium or ammonium hexabromoosmate is reacted with liquid ammonia at -34° in the presence of ammonium bromide the insoluble product $[Os(NH_3)_6][OsBr_6]$ is again formed but not in as high a yield as/the same reaction at 25° (41). At 90° the products are similar to those obtained over longer periods at 25° (41).

PHOSPHINE COMPLEXES

If ammonium hexachloroosmate is refluxed with diethylphenylphosphine the bright red osmium(II) nonelectrolyte $[Os\ Cl_3\ (PEt_2Ph)_3]$, is formed $^{(42)}$. On treating this compound with ethanol and potassium hydroxide, or 2-methoxyethanol, an unusual reaction occurs in which a hydride ion and carbon monoxide are transferred from the alcohol or alkoxide ion to the metal atom, with the formation of the hydridocarbonyl complex $[Os\ H\ Cl\ (CO)(PEt_2Ph)_3]$. This compound shows new bands in the infra red spectrum which are attributed to OsH and CO stretching frequencies. By using triphenylphosphine as ligand these authors have shown that the compounds previously prepared by Vaska $^{(43)}$ and formulated as $[Os\ X\ (Ph_3P)_3]$, X = Cl, Br, have the composition $[Os\ H\ X\ (CO)(PPh_3)_3]$. The measured diamagnetism is fully in accord with their being complexes of osmium(II) rather than of osmium(I) as originally proposed $^{(43)}$. More recent studies using ^{14}C labelled ethylene glycol as solvent have shown that one carbon atom of the solvent is incorporated in the complex molecule $^{(44)}$. An important clue as to the course of this reaction is provided by the isolation of the ruthenium complex $[Ru\ Cl_3\ (Ph_3P)_2\ (CH_3OH)]$ from reaction in methanolic solution $^{(45)}$. This suggests that co-ordination of the solvent occurs as an early step, with subsequent decomposition to carbon monoxide.

If $(NH_4)_2OsCl_6$ is reacted with a monotertiary phosphine PR_3, (R = Ph Et_2, Et Ph_2, Me Ph_2), in aqueous ethanolic solution a different reaction occurs (46). The reaction products may be recrystallised from ethanol as yellow plates and have been assigned the dimeric chloro-bridged structure



$X = Cl, ClO_4, BPh_4$

on the basis of molecular weight and conductivity measurements. By reacting this compound with a ditertiary phosphine $\left(C_2H_4(PR_2)_2;\ CH_2(PPh_2)_2;\ o\text{-}C_6H_4(PEt_2)_2\right)$ in the absence of a solvent the monotertiary phosphine is displaced and complexes of the type cis [Os Cl_2 (diphosphine)$_2$] are formed (46,47). The cis configuration was confirmed from dipole moment measurements. The analogous trans complex was prepared by directly refluxing the ditertiary phosphine with $(NH_4)_2OsCl_6$ in aqueous ethanol for several hours. The two chlorine atoms of either the cis or trans isomers can be replaced without stereochemical change by refluxing with lithium iodide in acetone.

cis (or trans) $[Os\ Cl_2\left(C_2H_4(PEt_2)_2\right)_2] + LiI$

cis (or trans) $[Os\ I_2\left(C_2H_4(PEt_2)_2\right)_2]$

However if the cis isomer is treated with lithium aluminium hydride in ether or tetrahydrofuran, and alcohol is added, complexes of the type <u>trans</u> [Os H X (diphosphine)$_2$] are formed (48). Continued reaction results in both halogen atoms being removed and [Os H_2 (diphosphine)$_2$] results. The remaining chlorine atom in <u>trans</u> [Os H X (diphosphine)$_2$] can be readily replaced by I^-, SCN^-, CN^- or NO_2^- by treating with the corresponding alkali metal salt in acetone under a nitrogen atmosphere (48).

OXYGEN CHELATING COMPLEXES

No oxalato, glycinato, or carbonato complexes of osmium have been described.

Only one acetylacetone compound has been prepared. Dwyer and Sargeson found that if the hexachloroosmate(III) anion is refluxed with acetylacetone in the presence of potassium bicarbonate (pH 6-7), a red solution is formed from which tris(acetylacetonato)osmium(III) can be extracted with chloroform (49).

$$OsCl_6^{2-} \xrightarrow[N_2]{Ag} OsCl_6^{3-} \xrightarrow[KHCO_3]{aca} [Os\ aca_3]$$

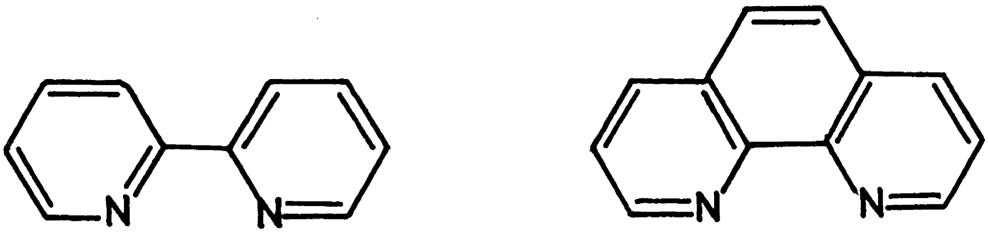
The compound forms as dark red plates which have a magnetic moment (μ = 1.81 B.M.) consistent with the presence of an osmium(III) atom.

CHAPTER TWO

PREPARATION AND REACTIONS OF MONO-DIPYRIDYL AND PHENANTHROLINE COMPLEXES OF OSMIUM(II), (III) AND (IV)

2.1 INTRODUCTION

The intense red color which results from the addition of 2,2'-bipyridine to iron(II) salts was first observed in 1898 by Blau (50). Since then the co-ordination compounds derived from I, as well as from the similarly constituted 1,10-phenanthroline, II, with many different metal ions have been extensively studied and recently reviewed (51).



I

II

Fig. 2·11

The elements of the iron triad iron, ruthenium, and osmium, in the bi- and ter- valent states form complexes of great stability with phenanthroline and bipyridine. As both these chelating ligands are relatively weak bases it is evident that much more is involved than the simple functional grouping

-C=N-C-C-N=C-. A comparison with ethylenediamine, a much stronger base with the same atomic grouping, is instructive. Trisethylenediamineiron(II) chloride is a weakly colored substance easily hydrolyzed by water. It is paramagnetic with ionic or 4s $4p^3$ $4d^2$ bonds (52). The deeply colored bipyridine and phenanthroline compounds, on the other hand, are decomposed only slowly by acids and their diamagnetism (64) indicates strong covalent $3d^2$ 4s $4p^3$ bonds. The similar complexes of ruthenium and osmium resist boiling concentrated acids and alkalis.

The source of stability in these complexes with phenanthroline and bipyridine arises from synergic bonding in which electrons are transferred from σ orbitals on the N atoms to the empty $d(e_g)$, s, and p orbitals of the metal (σ bonding); and from the $d(t_{2g})$ orbitals of the metal to the empty π molecular orbitals of the conjugated amine (π bonding). This double bond interaction involving σ and π orbitals of both metal atom and ligand results in a large ligand field stabilization energy, favouring the formation of the complex (Fig. 2.12).

Comparison of the infrared spectra of these complexes with those of the free ligands (53) reveals shifts in the absorption bands which are in agreement with the above interpretation. It is perhaps even more significant that the o-phenanthroline molecule is rendered active towards coupling with diazonium salts on complexing (54). The shifts observed in the visible spectra

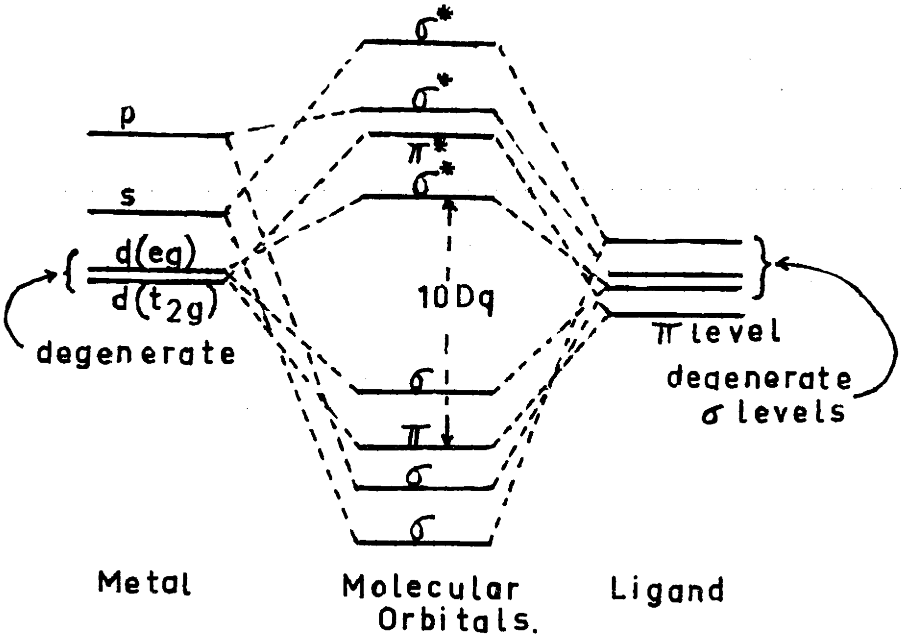
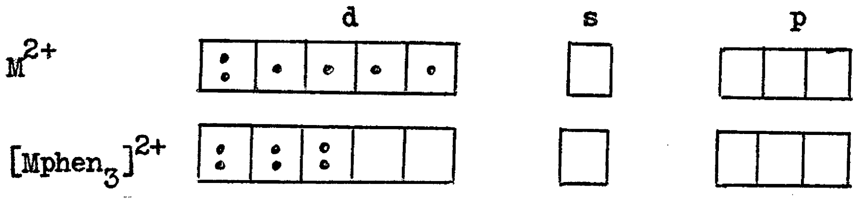


Fig 2·12

are also in accord with this view (55,53). The fact that 3,3'- disubstituted dipyridyls, which cannot form chelate rings coplanar with the aromatic rings of the ligand, show an impaired ability to form the characteristic iron(II) and copper(I) complexes lends further support (56,57). As a direct consequence of this strong bonding, the tris complexes of Fe, Ru and Os are of the low spin type in which the six outer d electrons of the free metal ion are paired in the d(t$_{2g}$) orbitals leaving the two d(e$_g$) orbitals for use in octahedral bonding.



It is very probable that the π component of the metal ligand bond is largely responsible for spin pairing since it can increase the ligand field splitting both directly (cf. Fig. 2.12), and indirectly, by delocalizing the bonding electrons over the molecule as a whole, and hence reducing the exchange energy favouring the high spin state (58). The stability constants of several 3- and 4- substituted pyridine complexes of silver(I) are consistent with this view (59).

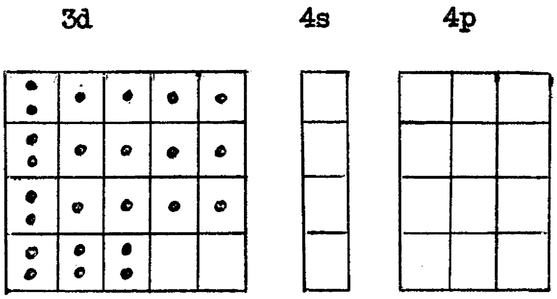
Irving and Williams (60) suggested that orbital stabilization may occur with the chelation of the first, second or third ligand molecule. Basolo and Dwyer (61) have shown that both the bis(phenanthroline) and bis(dipyridyl) iron(II) complexes are paramagnetic with four unpaired electrons, and Dwyer and Broomhead (62) have found similar magnetic moments for the mono-phenanthroline and di-pyridyl derivatives. This indicates that orbital stabilization resulting from the rearrangement of the six outer electrons in the ferrous ion must occur on chelation of the <u>third</u> ligand molecule.

$Fe(H_2O)_6^{2+}$

$[FeBCl_2]$ $\mu = 5.7-5.8$ (7)

$[FeB_2Cl_2]$ $\mu = 5.1-5.2$ (6)

$[FeB_3]^{2+}$ $\mu = 0$ (9)



A similar situation is found in the bis(dipyridyl)- and bis(phenanthroline)-iron(III) complexes which have magnetic moments corresponding to five unpaired electrons (63). The magnetic moments of the corresponding tris complexes, however, depend on the attached anion; $[Fedipy_3]Cl_3$ and $[Fephen_3]Cl_3$ are paramagnetic with moments of 5.91 Bohr magnetons, while $[Fedipy_3]_2[PtCl_6]_3$ and $[Fephen_3]_2[PtCl_6]_3$ have moments corresponding to one unpaired electron (64).

The above situation results in the mono- and bis- iron(II) complexes being unstable in aqueous solution and they rapidly disproportionate to give the more stable tris complexes (62). The analogous iron(III) complexes are stable in non-aqueous solvents but in aqueous solution are susceptible to reduction followed by disproportionation (63).

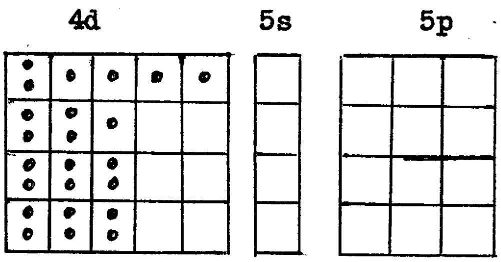
In the ruthenium complexes, however, magnetic measurements (see below) show that spin pairing occurs on co-ordination of the <u>first</u> chelate ligand.

Ru^{2+}

$(BipyH)[RuCl_4\ dipy]$ $\mu = 2.1$ (65)

$[RuCl_2\ dipy_2]$ $\mu = 1.1$ (65)

$[Ru\ dipy_3]^{2+}$



Therefore no additional electronic rearrangement is necessary to form the tris complex from the mono- or bis-complex ions and this results in both these latter two ions being stable in aqueous solution. For this reason Dwyer and Goodwin were able to prepare an extensive series of substituted derivatives of mono- and bis-phenanthroline and dipyridyl complexes (65).

As we pass from iron to osmium the d orbitals of the metal atom extend further into space and become more diffuse (67). It would therefore be expected that osmium would form stronger π bonds with ligands such as phenanthroline and dipyridyl than does iron or ruthenium. Since the stability of the metal complexes with these ligands depends to a large extent on the strength of the π bond (c.f.p.16) the mono- and bis- osmium complexes would therefore be expected to be of greater stability than the similarly constituted iron and ruthenium compounds. There is therefore justification for assuming that, as in the ruthenium complexes, electron rearrangement takes place on co-ordination of the first ligand molecule, and that the mono- and bis- phenanthroline and dipyridyl complexes would be stable towards disproportionation in aqueous solution. Because of this, and the further possibility that these osmium complexes would be stable in more than one oxidation state, they seemed to offer ideal material for a variety of chemical studies: mechanisms of substitution reactions, and the effect of the ligand on oxidation potentials. To make these studies a practical proposition it is essential that economical methods of preparation be found. These methods are described in this and the following two chapters.

Whereas the tris complexes of iron ruthenium and osmium have been known for many years, it is only recently that a study of the mono- complexes has been made. Spectroscopic evidence has been advanced (68,69) for the existence of the ion $Fe(dipy)^{2+}$ as an intermediate in the equilibrium, $Fe^{2+} + 3dipy \rightleftharpoons [Fe(dipy)_3]^{2+}$, and this pale yellow ion has been identified in sulphuric acid solutions of the base in the presence of a large excess of the iron(II) salt. No similar reaction occurs with ferric ions in aqueous media but rather the diol $[Fe\ OH\ dipy_2]_2X_4$ is formed (71). Jaeger (70) claimed to have obtained $FeSO_4.dipy$ as a crystalline solid, but when mixed with barium chloride only the tris compound $[Fe\ dipy_3]Cl_2$ resulted. The existence of the pale yellow $Fe(phen)^{2+}$ ion was first demonstrated in sulphuric acid solutions of the base in the presence of a large excess of the ferrous salt (72), and recently Harris and Lockyer (63) have isolated salts of the $[Fe\ Cl_4\ phen]^-$ ion from acetone-dioxane solution. From conductometric and spectrophotometric studies in nitrobenzene these authors showed that establishment of the equilibrium,

$$[Fe\ Cl_2\ phen_2]^+ + 2\ Cl^- \rightleftharpoons [Fe\ Cl_4\ phen]^- \rightleftharpoons Fe\ Cl_4^-$$

is very rapid, and that in aqueous solution the mono phenanthroline-iron(III) complexes are very susceptible to reduction followed by disproportionation to the tris species. Recently in this laboratory Broomhead and Dwyer (62) have prepared a number of complexes of the type $[M\ Cl_2\ phen]$ and $[M\ Cl_2\ dipy]$, where M = Fe(II), Fe(III), Ni(II), Mn(II) or Cr(III). The iron(II) complexes were prepared by the addition of the base to a tenfold excess of ferrous chloride in molar hydrochloric acid, while the iron(III) complexes were best prepared in dimethylformamide solution. The iron(II) compounds were found to be paramagnetic with magnetic moments (μ = 5.7-5.8 B.M.) indicating that they are of the high spin type.

From spectrophotometric studies of the stepwise formation of the tris(dipyridyl)ruthenium(II) ion it has been concluded that mono and bis derivatives occur as intermediates (73). Green $[Ru\ (H_2O)_2\ dipy_2]\ (ClO_4)_3$ was isolated and it was proposed that the reaction in sulphuric acid using commercial ruthenium trichloride (a mixture of Ru(III) and Ru(IV) halides) follows the sequence,

$$\begin{array}{lllll} Ru(III) & \rightleftharpoons & Ru\ dipy^{3+} & \rightleftharpoons & [Ru(H_2O)_2\ dipy_2]^{3+} \\ Ru(IV) & \rightleftharpoons & Ru\ dipy_2^{2+} & \rightleftharpoons & [Ru\ dipy_3]^{2+}\ . \end{array}$$

Recently, Dwyer and Goodwin (65) in an extensive investigation of the phenanthroline and dipyridyl complexes of ruthenium, have isolated mono -(dipyridyl) and -(phenanthroline) ruthenium(III) complexes by addition of the base to an acidic solution of potassium pentachloroaquoruthenate(III). The complex ions were isolated as the bipyridinium and phenanthrolinium salts of the $[Ru\ Cl_4\ B]^-$ ion which on oxidation with cerium(IV) gave the dark violet ruthenium(IV) complexes, $[Ru\ Cl_4\ B]$. The four co-ordinated chlorine atoms were replaced by a variety of other ligands including other halogens, water, ammonia, pyridine, ethylenediamine, oxalate, and acetylacetone, and the resulting complex ions obtained in several oxidation states.

There is only one reported instance of the formation of a mono- dipyridyl or phenanthroline complex of osmium. Swinehart (74) in a spectrophotometric study of the reaction between osmium trichloride and bipyridine at 100° in sulphuric acid, reports the initial formation of a purple complex ion at low concentrations of bipyridine. Continuous variation and mole ratio studies identified the purple as $Os\ dipy^{3+}$ with aquo or hydroxyl groups occupying the other co-ordination positions. A similar reaction occurred in hydrochloric acid. Solutions containing a moderate excess of bipyridine formed equilibrium mixtures of mono and bis complexes. The tris complex ion $[Os\ dipy_3]^{2+}$ was obtained only after several weeks of refluxing in the presence of excess bipyridine. There has been no reported isolation of mono-phenanthroline or dipyridyl osmium complexes in the solid state. In the following account the preparation and reactions of some of these compounds is described.

2.2 POTASSIUM AND AMMONIUM HEXACHLORO- AND HEXABROMO- OSMATE(IV)

The osmium(IV) complex salts $(NH_4)_2OsCl_6$, K_2OsCl_6, and K_2OsBr_6 were prepared as described by Dwyer and Hogarth (10,11). This method consists of reducing osmium(VIII) oxide with ferrous chloride in 12M hydrochloric acid (10), or with 47% hydrobromic acid (11), when reduction to the osmium(IV) valence state occurs. The complex anion OsX_6^{2-} (X = Cl,Br) may be isolated by adding the appropriate ammonium or potassium halide. Two minor alterations in experimental procedure were suggested (75) to the author and resulted in an almost quantitative yield of the osmium(IV) salts. These involved cooling the glass ampoule containing the OsO_4 in an ice-bath before breaking, and secondly adding the OsO_4 to the hydrochloric acid and not vice versa as is instructed in the above references. These alterations prevented the loss of OsO_4 vapour before reaction and so improved the final yield.

All subsequent osmium preparations outlined in this and subsequent chapters, used either the ammonium or potassium salts of the above hexahalo- complexes as starting material.

2.3 PREPARATION OF TETRACHLOROPHENANTHROLINE OSMIUM(IV) AND TETRACHLORODIPYRIDYL OSMIUM(IV)

(a) Direct Preparation

The preparation of (BH)[Os Cl_4 B] was attempted in a similar manner to Dwyer and Gibson's preparation of the analogous ruthenium derivatives (65). In a typical experiment ammonium hexachloro-osmate(IV) was reduced with half a molecule of hydrazine hydrochloride in the presence of two molecules of hydrochloric acid. The mixture was refluxed under an inert atmosphere of carbon dioxide for one hour, by which time it had changed to a dark brown-yellow solution typical of osmium(III) (33).

$$OsCl_6^{2-} \xrightarrow[CO_2]{N_2H_4.HCl} OsCl_6^{3-}$$

After adding phenanthroline (2 moles) to the cold solution it was kept at 25°-30° for four days by which time a grey crystalline precipitate had formed. Chlorine and nitrogen analyses of this compound indicated that it was not (PhenH)[Os Cl_4 phen] as expected. A similar experiment using silver wool instead of hydrazine hydrochloride as reducing agent resulted in a similar product which did not analyse correctly for chlorine or nitrogen. The preparation of (Bipy H)[Os Cl_4 dipy] was attempted in a similar manner, but again analyses figures indicated incomplete reaction. These results indicate that the co-ordination of one molecule of phenanthroline is not as simple as had been anticipated and a variety of experimental conditions would have to be tried. Preparative experiments based on the above procedure were not continued.

(b) Indirect Preparation

If one molecule of phenanthroline is added to a hot solution of potassium hexachloroosmate(IV) in 3N hydrochloric acid a yellow-orange insoluble precipitate of the salt, (K, Phen H)Os Cl_6 is formed in almost quantitative yield.

$$K_2OsCl_6 + \text{phen} \xrightarrow[90^\circ]{3N,\ HCl} (K,\ \text{phenH})OsCl_6$$

This compound is insoluble in water, acetone, and dilute hydrochloric acid. A similar reaction at 90° using one molecule of bipyridine results in the organic base being diprotonated and the formation of an orange precipitate of the bipyridinium salt, $(BipyH_2)OsCl_6$.

$$K_2OsCl_6 + \text{bipy} \xrightarrow[90^\circ]{3N,\ HCl} (BipyH_2)OsCl_6$$

Such a reaction is possible with bipyridine in strongly acidic conditions since the two aromatic rings can rotate about the single bond joining them to form a structure (a), (Fig. 2.31) in which it is possible to protonate both nitrogen atoms. In the case of phenanthroline, (b), no rotation is possible in the rigid planar molecule, and models show that it is impossible sterically to attach a proton to each of the basic nitrogen atoms.

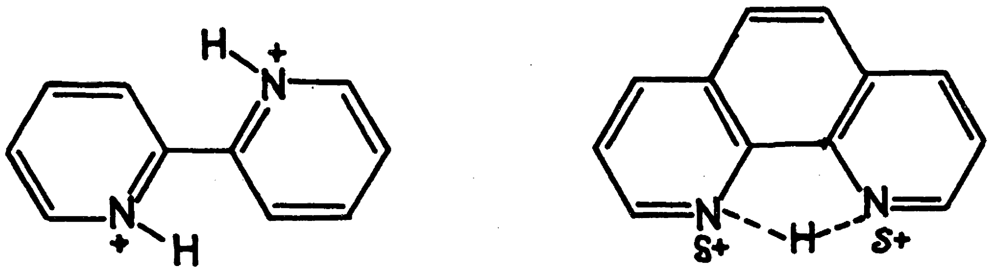


Fig. 2·31

Studies carried out recently in strongly acidic solutions have indicated the existence of the $BipyH_2^{2+}$ ion (76), but this is the first reported isolation of it in a stable compound. A similar reaction occurs with potassium hexabromoosmate(IV), and $(BipyH_2)OsBr_6$ has been separated as an almost black microcrystalline precipitate.

Pyrolysis of $(K,PhenH)OsCl_6$ at 290° in a Woods metal bath results in the phenanthroline molecule becoming chelated to the osmium with the liberation of hydrogen chloride, and the formation of the nonelectrolyte tetrachlorophenanthrolineosmium(IV).

$$(K,PhenH)OsCl_6 \xrightarrow[65\ mins]{290^{\circ}} [Os\ Cl_4\ phen] + HCl + KCl$$

The pyrolysed material is purified by reduction with hypophosphorous acid in 3N hydrochloric acid when the brown-orange osmium(III) anion, $[Os\ Cl_4\ phen]^-$ is formed. This may be reoxidized to the brick-red osmium(IV) nonelectrolyte with chlorine gas.

$$[Os\ Cl_4\ phen] \xrightarrow[H_3PO_2]{HCl} [Os\ Cl_4\ phen]^- \xrightarrow{Cl_2} [Os\ Cl_4\ phen]$$

In a similar manner pyrolysis of $(BipyH_2)OsCl_6$ at 290° results in the formation of the orange-brown nonelectrolyte, tetrachlorodipyridylosmium(IV).

$$(BipyH_2)OsCl_6 \xrightarrow[60\ mins]{290^\circ} [Os\ Cl_4\ dipy] + 2HCl$$

This may be purified in a similar manner to the mono phenanthroline complex by reduction to the osmium(III) state with hypophosphorous acid and oxidation with chlorine gas.

Both $[Os\ Cl_4\ phen]$ and $[Os\ Cl_4\ dipy]$ are obtained as light colored powders which are insoluble in water, ethanol, methanol and chloroform, but are slightly soluble in dimethylformamide to give brown solutions. By the above preparative method 80-85% yields of the osmium(IV) complexes are obtained.

2.4 SALTS OF THE TETRACHLOROPHENANTHROLINE- AND TETRACHLORODIPYRIDYL-OSMIUM(III) ANION

If $[Os\ Cl_4\ B]$, (B = phen, dipy) is suspended in 1.5 M hydrochloric acid and refluxed with hypophosphorous acid for 12 - 48 hours, the nonelectrolyte slowly dissolves to form a brown-orange solution from which the complex osmium(III) anion, $[Os\ Cl_4\ B]^-$, may be isolated as the potassium salt by addition of potassium chloride.

$$[Os\ Cl_4\ B] \xrightarrow[1.5\ M\ HCl]{H_3PO_2} [Os\ Cl_4\ B]^- \xrightarrow{KCl} K[Os\ Cl_4\ B]$$

Both the phenanthroline- and dipyridyl- osmium(III) complexes form as brown microcrystals which are very soluble in water, ethanol and methanol to give orange-brown solutions.

Addition of solid phenanthroline or bipyridine to the complex anion $[Os\ Cl_4\ B]^-$ in 1 M hydrochloric acid results in the immediate precipitation of the phenanthrolinium or bipyridinium salts. These compounds separate as sparingly soluble dark brown microcrystals containing one molecule of water of crystallisation. The following complexes have been characterised:-

$(PhenH)[Os\ Cl_4\ phen].H_2O$ $(PhenH)[Os\ Cl_4\ dipy].H_2O$

$(BipyH)[Os\ Cl_4\ phen].H_2O$ $(BipyH)[Os\ Cl_4\ dipy].H_2O$

Both the potassium and organic base cations are readily removed by oxidation with cerium(IV) or chlorine, to form the respective osmium(IV) complexes.

$$(BH)[Os\ Cl_4\ B] \xrightarrow{Cl_2} [Os\ Cl_4\ B] + B + H^+$$

A factor of great importance in determining the method of preparing complex ions is the rate at which substitution reactions involving these ions takes place. The difference in rates of substitution in inorganic reactions are extreme (77). Complexes which undergo substitution reactions at a fast rate are termed "labile", while "inert" complexes are those which undergo reactions either at a slow rate or not at all. Taube (78) has arbitrarily defined a labile system as one for which substitution reactions are complete within one minute at room temperature. Although the complex ion $[Os\ Cl_4\ B]^-$ would be termed inert in accordance with Taube's definition, the four chlorine atoms may be replaced at varying rates by other organic and inorganic ligands. Thus, although over a week is required to displace the first chlorine atom in $K[Os\ Cl_4\ dipy]$ by a water molecule at room temperature, substitution occurs much more rapidly at higher temperatures. In this respect ethylene glycol proved very useful for carrying out several substitution reactions because of its high boiling point (198°).

Although all four chlorine atoms may be replaced by other uni- or bi- dentate ligands, the organic base molecule is very firmly bound and cannot be replaced. Thus the complex ion shows no tendency to disproportionate to give the tris complex.

In the preparation of the following substituted derivatives of osmium(II) and (III), $K[Os\ Cl_4\ B]$ is in most cases used as starting material because of its easy solution in aqueous media. In some instances, however, the osmium(IV) non-electrolyte $[Os\ Cl_4\ B]$, has been used, particularly when ethylene glycol is the reacting medium.

2.5 HYDROLYSIS DERIVATIVES

If an aqueous solution of potassium tetrachlorodipyridylosmate(III) is allowed to stand at 30° the chlorine atoms slowly dissociate and are replaced by aquo or hydroxy groups*. The

---

* No attempt was made to isolate complex salts from this solution.

process is accompanied by a slow color change from orange-brown to a brownish-green and by a marked increase in conductivity of the solution. In table 2.51 values of the conductivity of a M/1000 aqueous solution of K[Os Cl_4 dipy], measured over a period of 17 days are listed.

TABLE 2.51

Time (hrs.)	Molecular Conductivity
0	91.1 $ohms^{-1}$
3	96.5 "
24	105.8 "
48	109.4 "
192	139.4 "
408	194.5 "

If a solution of K[Os Cl_4 dipy] in 0.5 N sulphuric acid is allowed to stand at 30° its color does not appreciably change but dark brown crystals of trichloroaquodipyridylosmium(III) slowly separate.

$$[\mathrm{Os\ Cl_4\ dipy}]^- \xrightarrow[\text{20 days}]{0.5\ \mathrm{N\ H_2SO_4}} [\mathrm{Os\ Cl_3\ (H_2O)\ dipy}]$$

The acid has not prevented aquation but has arrested base hydrolysis. The molecular conductivity of an aqueous solution was found to be 20.6 $ohms^{-1}$, indicating a non-electrolyte.

In order to determine the final product of hydrolysis of the ion [Os Cl_4 dipy]$^-$, an aqueous solution of potassium tetrachlorodipyridylosmate(III) was evaporated to dryness on a steam-bath many times. The solution slowly turned green-brown and then a reddish-brown color from which an insoluble brown powder was isolated after 30 evaporations. This material was almost insoluble in warm water, but was moderately soluble in dimethylformamide from which it could be recrystallised by addition of ether. The compound is a non-electrolyte in dimethylformamide, and chlorine and nitrogen analyses are in agreement with a structure such as

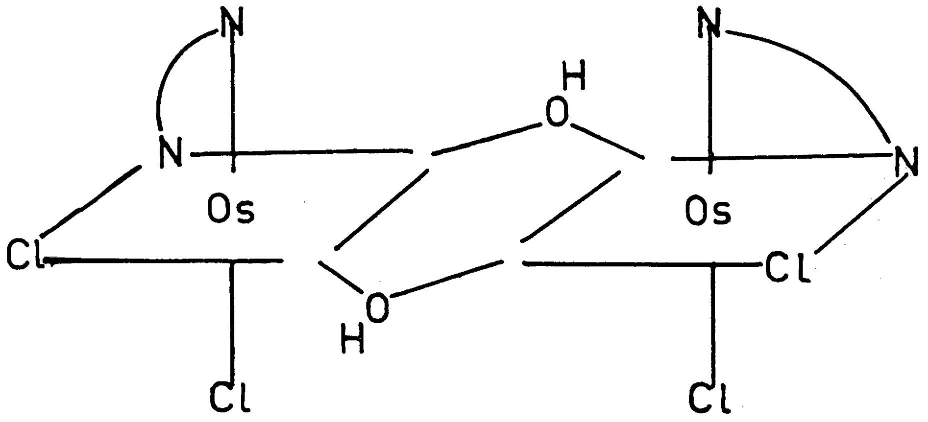


Fig. 2·51

in which two hyroxy groups join together two osmium(III) atoms.

2.6 PYRIDINE DERIVATIVES

If K[Os Cl_4 dipy] is refluxed with pyridine in aqueous solution for 5 minutes dark brown crystals of trichloropyridinedipyridylosmium(III) separate on cooling.

$$K[Os\ Cl_4\ B] + py \xrightarrow[5\ mins]{H_2O} [Os\ Cl_3\ py\ B]$$

This compound could also be prepared by refluxing the non-electrolyte $[Os\ Cl_4\ dipy]$ with pyridine in glycerol for 4 minutes. Immediate reduction to the osmium(III) valence state occurred and $[Os\ Cl_3\ py\ dipy]$ separated as fine brown insoluble needles.

$$[Os\ Cl_4\ dipy] + py \xrightarrow[4\ mins]{glycerol} [Os\ Cl_3\ py\ dipy]$$

This compound is insoluble in water and chloroform and only very slightly soluble in ethanol to give a brown solution. On continued refluxing the aqueous ethanolic solution turns brown, characteristic of the $[Os\ Cl_2\ py_2\ dipy]^+$ ion (which has not been isolated in the solid state) and then slowly to an orange-brown color as the third chlorine atom is replaced by pyridine. Reduction to the osmium(II) valence state occurs at this stage and the orange-brown $[Os\ Cl\ py_3\ dipy]^+$ ion has been isolated as the perchlorate, iodide, and chloride.

$$[Os\ Cl_3\ py\ dipy] \xrightarrow{py} [Os\ Cl_2\ py_2\ dipy]^+ \xrightarrow[8\ hrs]{py} [Os\ Cl\ py_3\ dipy]^+$$

The $[Os\ Cl\ py_3\ dipy]^+$ ion may also be prepared by refluxing tetrachlorodipyridylosmium(IV) or potassium tetrachlorodipyridylosmate(III) with pyridine in ethylene glycol for 40 minutes. The solvent acts as the reducing agent and an almost quantitative yield of the osmium(II) complex ion is obtained on removing the ethylene glycol and adding sodium iodide to an aqueous solution.

$$[\mathrm{Os\ Cl_4\ dipy}] + \mathrm{py} \xrightarrow[\text{40 mins.}]{\text{ethylene glycol}} [\mathrm{Os\ Cl\ py_3\ dipy}]^+$$

Displacement of the remaining co-ordinated halogen atom may be effected by a similar reaction. If chlorotripyridinedipyridylosmium(II) chloride is refluxed with sodium bromide or sodium iodide in ethylene glycol in the presence of excess pyridine for 60 minutes, the co-ordinated chlorine atom is replaced by bromine or iodine respectively, and the complex ions $[\mathrm{Os\ X\ py_3\ dipy}]^+$ (X = Br, I) may be crystallised by adding sodium iodide to an aqueous solution.

$$[\mathrm{Os\ Cl\ py_3\ dipy}]^+ + \mathrm{NaX} \xrightarrow[\text{60 mins}]{\text{ethylene glycol}} [\mathrm{Os\ X\ py_3\ dipy}]^+ + \mathrm{NaCl}$$

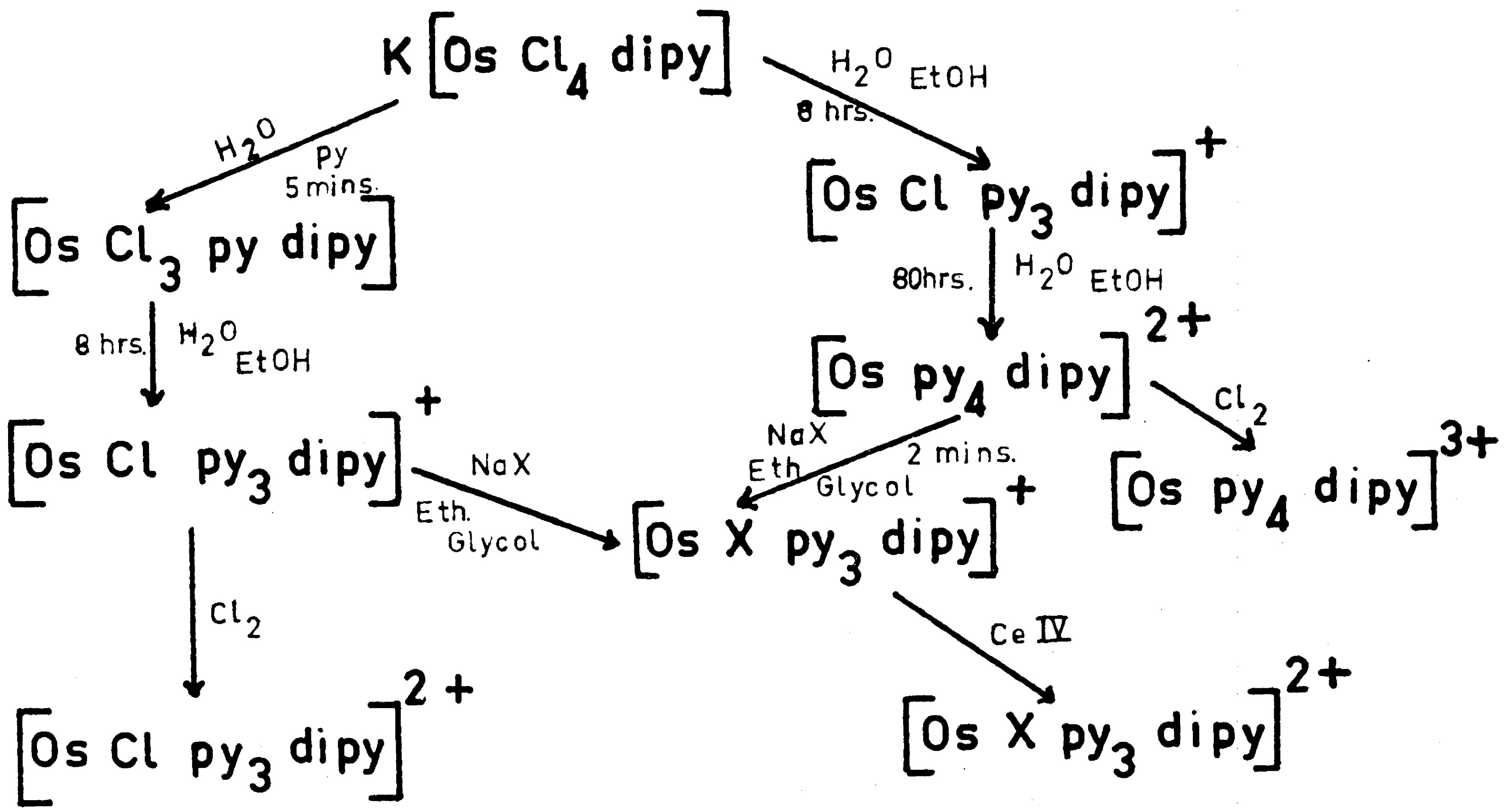
The complex iodides $[\mathrm{Os\ X\ py_3\ dipy}]\mathrm{I.H_2O}$ (X = Cl, Br, I) are all orange-brown in color and can be recrystallised from methanol by addition of ether. They may be converted to their respective chlorides with silver chloride without displacement of the co-ordinated halogen X. The chlorides may be recrystallised from aqueous solution by addition of sodium chloride.

The halotrispyridinedipyridylosmium(II) chlorides can be oxidized to the osmium(III) state with cerium(IV) ions and crystallised as the perchlorates by addition of perchloric acid.

$$[\mathrm{Os\ X\ py_3\ dipy}]^+ \xrightarrow{\mathrm{Ce(IV)}} [\mathrm{Os\ X\ py_3\ dipy}]^{2+} \quad (\mathrm{X = Cl,\ Br,\ I})$$

The chloro complex forms as orange-yellow crystals, the bromo compound is yellow-orange, and the iodo complex a light green in color. Absorption spectra of the osmium(II) and osmium(III)

Fig. 2·61 PYRIDINE DERIVATIVES.



complexes are given on page 38a.

When trichloropyridinedipyridylosmium(III) is refluxed with pyridine in aqueous ethanolic solution for 80 hours, slow displacement of the three chlorine atoms by pyridine occurs and the green tetrakis(pyridine)dipyridylosmium(II) ion may be crystallised by addition of sodium iodide or sodium perchlorate

$$[\mathrm{Os\ Cl_3\ py\ dipy}] + \mathrm{py} \xrightarrow[\substack{\text{80 hours} \\ \mathrm{NaH_2PO_2}}]{\text{ethanol/water}} [\mathrm{Os\ py_4\ dipy}]^{2+}$$

Unlike the analogous ruthenium complex ion $[\mathrm{Ru\ py_4\ dipy}]^{2+}$ the co-ordinated pyridines in $[\mathrm{Os\ py_4\ dipy}]^{2+}$ cannot be displaced by inorganic anions in aqueous solution. On refluxing with sodium halide in ethylene glycol, however, the corresponding halotris(pyridine)dipyridylosmium(II) halide is formed almost immediately. This proved an alternative method of preparing these complexes.

$$[\mathrm{Os\ py_4\ dipy}]^{2+} + \mathrm{NaX} \xrightarrow[\text{2 mins}]{\text{ethylene glycol}} [\mathrm{Os\ X\ py_3\ dipy}]\mathrm{X}$$

Oxidation of $[\mathrm{Os\ py_4\ dipy}](\mathrm{ClO_4})_2$ with cerium(IV) ions, results in the formation of the red osmium(III) complex ion $[\mathrm{Os\ py_4\ dipy}]^{3+}$ which has been separated as the salmon pink perchlorate.

$$[\mathrm{Os\ py_4\ dipy}]^{2+} \xrightarrow{\mathrm{Ce(IV)}} [\mathrm{Os\ py_4\ dipy}]^{3+}$$

2.7 ACETYLACETONE, ETHYLENEDIAMINE, AND GLYCINE DERIVATIVES

If $\mathrm{K[Os\ Cl_4\ dipy]}$ is refluxed with acetylacetone for 40 minutes, the solution slowly darkens and dark brown crystals of dichloroacetylacetonedipyridylosmium(III) crystallize out on cooling.

$$K[Os\ Cl_4\ dipy] + Haca \xrightarrow[40\ mins]{Reflux} [Os\ Cl_2\ aca\ dipy] + H^+$$

This nonelectrolyte is insoluble in water but soluble in chloroform to give a crimson-red solution from which it may be recrystallised by addition of ether.

If the aqueous ethanolic solution is refluxed for a further 8 hours in the presence of excess acetylacetone and calcium carbonate, the solution turns a brown-yellow color from which the complex ion $[Os\ aca_2\ dipy]^+$ has been isolated by addition of sodium iodide. Calcium carbonate is added to take up protons.

$$K[Os\ Cl_4\ dipy] + 2Haca \xrightarrow[8\ hrs]{Reflux} [Os\ aca_2\ dipy]^+ + 2H^+$$

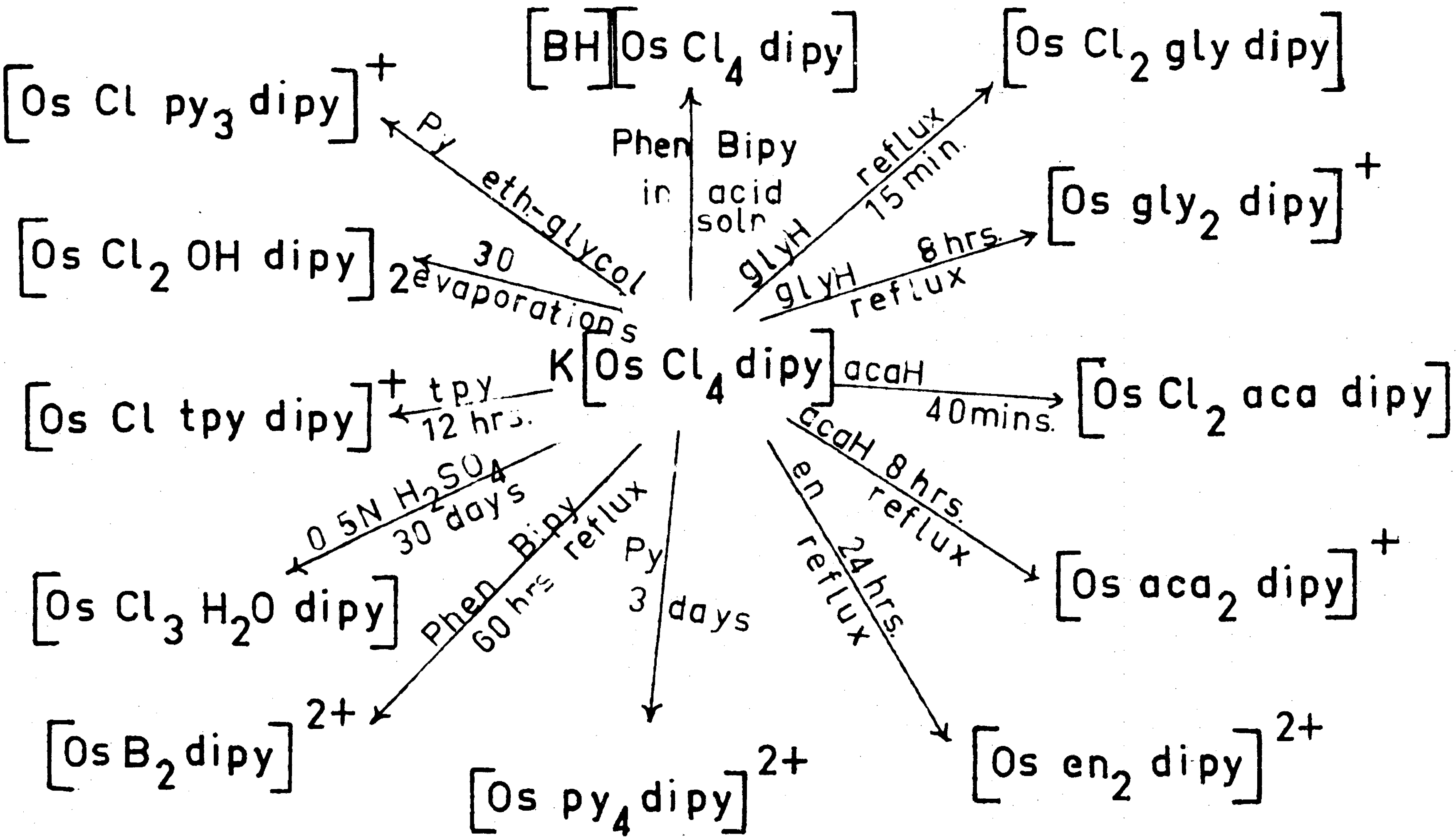
The osmium(III) complex iodide is sparingly soluble in water to give a yellow-brown solution, and may be reduced to the red-brown osmium(II) complex, $[Os\ aca_2\ dipy]$, with sodium dithionite. This compound has not been isolated in the solid state.

In a similar manner if an aqueous solution of $K[Os\ Cl_4\ dipy]$ is reacted with glycine, the nonelectrolyte dichloroglycinatodipyridylosmium(III) initially forms, but on continued refluxing in aqueous ethanol a second molecule of glycine co-ordinates and the resulting complex ion, $[Os\ gly_2\ dipy]^+$, can be isolated as the soluble iodide.

$$K[Os\ Cl_4\ dipy] + Hgly \xrightarrow[15\ mins]{Reflux} [Os\ Cl_2\ gly\ dipy] + H^+ \xrightarrow[8\ hrs]{Reflux} [Os\ gly_2\ dipy]^+$$

Oxidation of the osmium(III) ions, $[Os\ aca_2\ dipy]^+$ and $[Os\ gly_2\ dipy]^+$ results in the decomposition of the complexes. When a cerium(IV) solution is added to a cold aqueous solution of bis(acetylacetonato)dipyridylosmium(III) chloride, the brown solution darkens slightly and after a short time free acetylacetone can be detected. A similar reaction occurs with bis(glycinato) dipyridylosmium(III) chloride, the color changing to a brownish-green from which the osmium(IV) complex ion $[Os\ gly_2\ dipy]^{2+}$ could not be isolated. The osmium(III) complexes could not be regenerated by reducing the oxidized solutions. It is very probable in these large complex ions, that instead of removing an electron from the central metal atom, oxidation involves the removal of an electron from the attached ligand (79). This would result in a marked decrease in basicity of the donor atoms of the ligand and a resultant decrease in stability of the complex ion. Such a mechanism has, in fact, been recently observed by Gibson and Ingram (80) who showed by an electron spin resonance study that oxidation of methaemoglobin removed an electron from the peripheral carbon atoms and not from the metal which was taken as formally remaining in the +3 state. A similar mechanism for the above osmium complexes would account for the detection of free ligand in the oxidized solutions and also for the inability to regenerate the osmium(III) complex ions.

Fig. 2·71 DERIVATIVES OF K[Os Cl$_4$ dipy]



If K[Os Cl_4 dipy] is refluxed in aqueous ethanolic solution with ethylenediamine for 12 hours the solution slowly turns orange-brown from which the complex ion, $[Os\ en_2\ dipy]^{2+}$ may be isolated by adding sodium perchlorate.

$$K[Os\ Cl_4\ dipy] + 2\ en \xrightarrow{Reflux} [Os\ en_2\ dipy]^{2+}$$

This compound is very soluble in water, methanol and acetone, to give yellow-brown solutions. Oxidation with cerium(IV) ions gave a red-brown solution but this was not investigated in detail.

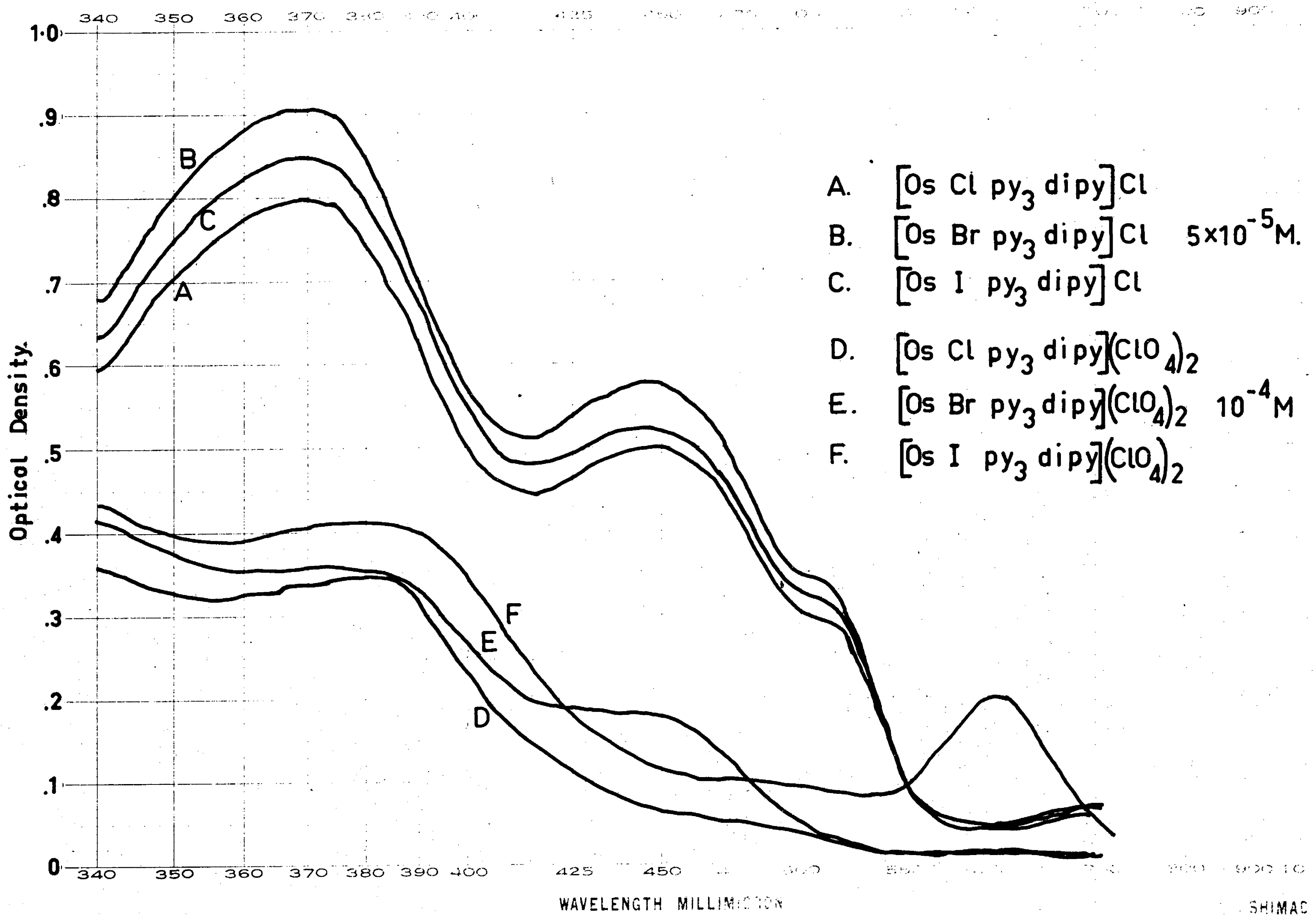
2.8 PYRIDINE DERIVATIVES OF POTASSIUM HEXACHLORO- AND HEXABROMO- OSMATE(IV)

If potassium hexachloroosmate(IV) is refluxed with pyridine in anhydrous dimethylformamide, the solution gradually turns yellow as the starting material dissolves, and then yellow-brown, from which the non-electrolyte trichlorotri(pyridine)osmium(III) may be precipitated with ether following removal of liberated potassium chloride.

$$K_2OsCl_6 + 3\ py \xrightarrow[90\ minutes]{DMF} [Os\ Cl_3\ py_3] + 2KCl + \frac{1}{2}\ Cl_2$$

$[Os\ Cl_3\ py_3]$ forms as an orange-brown powder which is insoluble in water but soluble in chloroform to give a yellow solution. It is oxidized by cerium(IV) ions to give a yellow-orange solution of presumably the $[Os\ Cl_3\ py_3]^+$ ion but this has not been isolated.

If pyridine is added to a suspension of K_2OsCl_6 in


A. [Os Cl py$_3$ dipy]Cl
B. [Os Br py$_3$ dipy]Cl 5×10^{-5}M.
C. [Os I py$_3$ dipy]Cl
D. [Os Cl py$_3$ dipy](ClO$_4$)$_2$
E. [Os Br py$_3$ dipy](ClO$_4$)$_2$ 10^{-4}M
F. [Os I py$_3$ dipy](ClO$_4$)$_2$
A
B
C
D
E
F
Optical Density.
1·0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
340
350
360
370
380
390
400
425
450
WAVELENGTH MILLIMICRON
SHIMAC

glycerol and the solution refluxed for one hour, fine dark red needles of dichlorotetrakis(pyridine)osmium(II) separate.

$$K_2OsCl_6 + 4\ py \xrightarrow[1\ hr]{glycerol} [Os\ Cl_2\ py_4]$$

These are insoluble in water and methanol, but soluble in chloroform to give a bright red solution. In a similar manner $[Os\ Br_2\ py_4]$ may be prepared as red-violet crystals by refluxing ammonium hexabromoosmate(IV) with pyridine in glycerol.

2.9 EXPERIMENTAL

Potassium Phenanthrolinium Hexachloroosmate(IV)

K_2OsCl_6 (1 g.) was suspended in hydrochloric acid (15 ml. 3 N) at 80°, and phenanthroline monohydrate (0.38 g.) dissolved in hydrochloric acid (5 ml. 1 N) was slowly added with stirring. The orange-yellow precipitate of potassium phenanthrolinium hexachloroosmate(IV) immediately formed. The solution was stirred for a further ten minutes in an ice-bath and the product was separated on a glass filter, washed with a small quantity of dilute hydrochloric acid and acetone, and air-dried at 50° (yield = 1.2 g.).

Analysis:

Calculated for $(K,phenH)OsCl_6$	Os,34.2;	N, 4.5;	Cl, 34.2
Found	Os,34.6;	N, 4.7;	Cl, 34.6

N,N' Dihydrobipyridinium Hexachloroosmate(IV)

K_2OsCl_6 (1 g.) was suspended in hydrochloric acid (15 ml. 3N) at 80° and bipyridine (0.35 g.) dissolved in hydrochloric acid (3 ml. 3N) was slowly added with continuous stirring. The orange precipitate of N,N' dihydrobipyridinium hexachloroosmate(IV) immediately separated. The solution was kept well mixed for a further 10 minutes before cooling in an ice-bath. The product was separated on a glass filter, washed with dilute hydrochloric acid and acetone, and dried at 50°. (Yield = 1.13 g.)

Analysis:

Calculated for $(BipyH_2)OsCl_6$	Os, 33.9;	N, 5.0;	Cl, 38.0
Found	Os, 34.0;	N, 5.0;	Cl, 38.1

Ammonium Phenanthrolinium Hexachloroosmate(IV)

$(NH_4)_2OsCl_6$ (0.5 g.) was suspended in hydrochloric acid (8 ml. 3N) at 80° and phenanthroline monohydrate (0.23 g.) dissolved in hydrochloric acid (5 ml. 1N) was slowly added with continuous stirring. The yellow-orange precipitate of ammonium phenanthrolinium hexachloroosmate(IV) immediately formed. The solution was cooled in an ice-bath and the product separated on a glass filter and washed with a small quantity of dilute hydrochloric acid and acetone, and air dried at 50°. (Yield = 0.65 g., 95%)

Analysis:

Calculated for $(NH_4PhenH)OsCl_6$	Os, 31.6;	N, 7.0;	Cl, 35.4
Found	Os, 31.3;	N, 7.1;	Cl, 35.6

N,N' Dihydrobipyridinium Hexabrommosmate(IV)

$(NH_4)_2OsBr_6$ (0.5 g.) was suspended in hydrobromic acid (8 ml. 3N) at 80°, and bipyridine (0.12 g.) dissolved in hydrobromic acid (1 ml. 2N) was added to the hot solution. Immediately a black microcrystalline precipitate of N,N' dihydrobipyridinium hexabromoosmate(IV) separated. The solution was cooled in an ice-bath and the product was separated on a glass filter and washed with dilute hydrobromic acid and acetone, and dried at 50°.

Analysis:

Calculated for	$(BipyH_2)OsBr_6$	Br, 57.9
Found		Br, 57.7

Tetrachlorophenanthrolineosmium(IV)

Potassium phenanthrolinium hexachloroosmate(IV) (1 g.) was pyrolysed in a Woods metal bath at 290° for 60 minutes. As the temperature was raised the color slowly changed from orange-yellow to orange-brown and finally to dark brown. Evolution of hydrogen chloride was first observed at 250° and the gas was emitted rapidly at 280°. The pyrolysed material was extracted by reduction to the osmium(III) valence state by refluxing with hypophosphorous acid (5 drops) in hydrochloric acid (30 ml. 2 N) until it had all dissolved (12 - 24 hrs.). The warm orange-brown solution was filtered and the osmium(III) anion, $[Os\ Cl_4\ phen]^-$, oxidized to tetrachlorophenanthroline-osmium(IV) by bubbling chlorine gas through the solution for 5 minutes. The brick red microcrystalline precipitate was filtered, washed with distilled water and ether, and dried at 60°. (Yield = 0.72 g., 85%)

Analysis:

Calculated for $[Os\,Cl_4\,phen]$	Os, 37.1;	N, 5.5;	Cl, 27.7
Found	Os, 36.8;	N, 5.5;	Cl, 27.6

Tetrachlorodipyridylosmium(IV)

N,N' dihydrobipyridinium hexachlorosmate(IV) (1 g.) was pyrolysed in a Woods metal bath at 295° for 60 minutes. Strict control of this temperature is important and intermittent mixing essential. As the temperature was raised the color changed from orange to brown and finally to dark brown. Evolution of hydrogen chloride gas was first observed at 240°, but at no stage was it emitted as quickly as in the preparation of the analogous phenanthroline complex. The pyrolysed material was extracted by reduction to the osmium(III) valency state by refluxing with hypophosphorous acid (3 drops) in hydrochloric acid (30 ml. 2N) until it had all dissolved. The orange-brown solution was cooled to room temperature, filtered and tetrachlorodipyridylosmium(IV) precipitated by oxidizing with chlorine gas (5 mins). The orange-brown microcrystalline precipitate was filtered, washed with dilute hydrochloric acid, distilled water, and finally with ether, and dried at 60°. (Yield = 0.74 g., 85%)

Analysis:

Calculated for $[Os\,Cl_4\,dipy]$	Os 38.9;	N, 5.75;	Cl, 29.0
Found	Os 38.4;	N, 5.9 ;	Cl, 28.6

Potassium Tetrachlorophenanthrolineosmate(III)

Tetrachlorophenanthrolineosmium(IV) (1 g.) was reduced with hypophosphorous acid (5 drops) in hydrochloric acid (30 ml. 1.5N) by refluxing for 12 hours. To the filtered solution was carefully added potassium chloride, when brown crystals of potassium tetrachlorophenanthrolineosmium(III) separated on cooling and scratching in an ice-bath. These were filtered, washed with iced water and ether, and dried at 50°. (Yield = 0.92 g.) A small amount of tetrachlorophenanthrolineosmium(IV) could be recovered from the filtrate by oxidation with chlorine gas.

Analysis:

Calculated for $K[Os\ Cl_4\ phen]$	Os, 34.6;	N, 5.1;	Cl, 25.8;
Found	Os, 34.1;	N, 5.2;	Cl, 25.8;

Ammonium Tetrachlorophenanthrolineosmate(III)

Reduction of tetrachlorophenanthrolineosmium(IV) and treatment with ammonium chloride, as for the preparation of the potassium salt, yielded the corresponding ammonium salt. This was washed with iced water and ether, and air-dried at 50°.

Analysis:

Calculated for $NH_4[Os\ Cl_4\ phen]$	N, 7.9;	Cl, 26.8;
Found	N, 7.7;	Cl, 26.7;

Potassium Tetrachlorodipyridylosmate(III)

Tetrachlorodipyridylosmium(IV) (1 g.) was reduced by refluxing with hypophosphorous acid (2 drops) in hydrochloric acid (30 ml. 2N) for 12 hours. The orange-brown solution was cooled to room temperature, filtered, and potassium chloride carefully added to the filtrate when dark brown crystals of potassium tetrachlorodipyridylosmate(III) separated on scratching in an ice-bath. These were filtered, washed with iced water and ether, and dried at 50°. (Yield = 0.96 g.). A small amount of tetrachlorodipyridylosmium(IV) could be recovered from the filtrate by oxidation with chlorine gas.

Analysis:

Calculated for K[Os Cl_4 dipy]   Os, 36.1;   N, 5.3;   Cl, 26.9

Found   Os, 35.8;   N, 5.6;   Cl, 26.2

Phenanthrolinium Tetrachlorophenanthrolineosmate(III)

Tetrachlorophenanthrolineosmium(IV) (1 g.) was reduced by refluxing with hypophosphorous acid (6 drops) in hydrochloric acid (30 ml. 1.5 N) for 12 hours. To the filtered dark orange-brown solution was added water (20 ml.) and then phenanthroline mono hydrate (0.42 g.) dissolved in hydrochloric acid (5 ml. 1 N). Black micro-crystalline plates of phenanthrolinium tetrachlorophenanthrolineosmate(III) immediately separated. The product was allowed to crystallise by standing the solution in an ice-bath for 2 hours. The solution was filtered through a glass filter and the product washed with iced water and ether and air dried at 50°. (Yield = 1.22 g. = 88%)

The osmium(III) complex remaining in solution could be recovered from the filtrate, by converting to the insoluble tetrachlorophenanthrolineosmium(IV) with chlorine gas.

Analysis:

Calculated for [PhenH][Os Cl_4 phen].H_2O Cl, 19.9;   N, 7.9

Found   Cl, 19.9;   N, 7.5

Phenanthrolinium Tetrachlorodipyridylosmate(III)

Tetrachlorodipyridylosmium(IV) (1 g.) was reduced by refluxing with hypophosphorous acid (5 drops) in hydrochloric acid (30 ml. 1.5N) for 12 hours. The orange-brown solution was cooled to room temperature, filtered, and phenanthroline monohydrate (0.44 g.) dissolved in dilute hydrochloric acid (5 ml.) was added slowly to the solution with scratching. Phenanthrolinium tetrachlorodipyridylosmate(III) immediately formed as fine dark brown needles. The solution was cooled in an ice-bath for 2 hours, filtered, and the product washed with a small quantity of iced water and ether, and dried at 50°. (Yield = 1.03 g.) The osmium(III) complex remaining in solution could be recovered by converting it to tetrachlorodipyridylosmium(IV) with chlorine gas. (0.17 g.)

Analysis:

Calculated for [PhenH][Os Cl_4 dipy].H_2O	Cl, 20.7;	N, 8.2;
Found	Cl, 21.0;	N, 8.2;

Bipyridinium Tetrachlorophenanthrolineosmate(III)

Tetrachlorophenanthrolineosmium(IV) (0.5 g.) was reduced by refluxing with hypophosphorous acid (3 drops) in hydrochloric acid (10 ml. 1.5N) for 12 hours. To the filtered orange-brown solution was added distilled water (20 ml.) and then solid bipyridine (0.17 g.) On cooling in an ice-bath and scratching, dark brown microcrystalline plates of bipyridinium tetrachlorophenanthrolineosmate(III) separated. The product was filtered, washed with iced water and ether, and dried at 50°. (Yield = 0.5 g.) As above, tetrachlorophenanthrolineosmium(IV) could be recovered from the filtrate by oxidation with chlorine gas.

Analysis:

Calculated for $[BipyH][Os\ Cl_4\ phen].H_2O$ Cl, 20.7; N, 8.2;

Found Cl, 21.1; N, 8.0;

Bipyridinium Tetrachlorodipyridylosmate(III)

Tetrachlorodipyridylosmium(IV) (0.5 g.) was reduced by refluxing with hypophosphorous acid (3 drops) in hydrochloric acid (10 ml. 1.5N) for 12 hours. To the filtered orange-brown solution was added distilled water (20 ml.) and then solid bipyridine (0.2 g.). On scratching dark brown crystals of bipyridinium tetrachlorodipyridylosmate(III) began to separate. The solution was cooled in an ice-bath for one hour, and the product removed on a sintered filter and washed with a small quantity of iced water and ether, and dried at 50°. (Yield = 0.54 g.)

Analysis:

Calculated for $[BipyH][Os\ Cl_4\ dipy].H_2O$ Cl, 21.4; N, 8.5;

Found Cl, 21.4; N, 8.2;

Trichloroaquodipyridylosmium(III) dihydrate

$K[Os\ Cl_4\ dipy]$ (0.15 g.) was dissolved in dilute sulphuric acid (10 ml. 0.5N) and allowed to stand at 30°. After 5 days brown crystals began to deposit and after 20 days these were removed, washed with dilute sulphuric acid and iced water, and dried at 35°. The product was only sparingly soluble in water to give a brown-yellow solution. A M/1000 aqueous solution had a conductivity of 20.6 ohms^{-1} indicating a non-electrolyte.

Analysis:

Calculated for $[Os\ Cl_3\ H_2O\ dipy].2H_2O$	N, 5.5; Cl, 21.0
Found	N, 5.4; Cl, 20.8

Tetrachlorobis(dipyridyl)-μ diol-diosmium(III)

K$[Os\ Cl_4\ dipy]$ (0.15 g.) was dissolved in water and evaporated to dryness on a steam bath 30 times. The original brown solution slowly turned green-brown, and then a yellow-brown as an insoluble residue began to form. After 30 evaporations this insoluble material was removed, washed with water, and recrystallised from dimethylformamide/ethanol by addition of ether. It formed as a dark brown powder which was slightly soluble in warm water to give a reddish-brown solution.

Analysis:

Calculated for $[Os_2\ Cl_4\ (OH)_2\ dipy_2]$	Cl, 16.3
Found	Cl, 16.6

Trichloropyridinedipyridylosmium(III)

Potassium tetrachlorodipyridylosmate(IV) (0.5 g.) was dissolved in warm water (10 ml.) and refluxed with pyridine (1 ml.) for 7 minutes. Dark brown crystals of trichloropyridinedipyridyl osmium(III) soon separated. These were washed with cold water, ethanol and ether, and dried at 35°.

Analysis:

Calculated for [Os Cl_3 py dipy]	N, 7.9; Cl, 20.0
Found	N, 8.1; Cl, 19.9

Trichloropyridinephenanthrolineosmium(III)

This was prepared in the same manner as above from potassium tetrachlorophenanthrolineosmate(IV) (0.3 g.). The dark brown crystals of [Os Cl_3 py phen] were insoluble in water but slightly soluble in chloroform to give an orange-yellow solution.

Analysis:

Calculated for [Os Cl_3 py phen]	Cl, 19.1
Found	Cl, 19.3

Chlorotri(pyridine)dipyridylosmium(II) iodide

(A) Reaction in aqueous solution K[Os Cl_4 dipy] (0.5 g.) was dissolved in water (15 ml.) and ethanol (10 ml.), and refluxed with pyridine (3 ml.) for 12 hours. The solution slowly changed from a deep brown color to the orange-brown of the [Os Cl py_3 dipy]$^+$ ion, which was isolated by evaporating the solution to dryness on a steam-bath and adding sodium iodide to an aqueous solution of the residue. The brown crystals of chlorotri(pyridine)dipyridylosmium(II) iodide were recrystallised from hot water by adding sodium iodide, washed with iced water, and dried at 35°.

(B) Reaction in Ethylene glycol Tetrachlorodipyridylosmium(IV) (0.5 g.) was suspended in ethyleneglycol (7 ml.) and refluxed with pyridine (2 ml.) for 40 minutes. The solution quickly turned orange-brown from which the $[Os\ Cl\ py_3\ dipy]^+$ ion was separated by evaporating the viscous solution to dryness on a steam-bath and adding sodium iodide to an ice-cold aqueous solution of the residue. The fine dark brown crystals of chlorotri(pyridine)dipyridylosmium(II) iodide which separated were washed with iced water and dried at 35°.

Analysis:

Calculated for $[Os\ Cl\ py_3\ dipy]I.3H_2O$	N, 8.75;	Halogen 20.3
Found	N, 8.6;	Halogen 20.3

Chlorotri(pyridine)dipyridylosmium(II) chloride

$[Os\ Cl\ py_3\ dipy]I$ (0.5 g.) was suspended in warm water (80 ml.) and shaken with excess silver chloride for 15 minutes until it had completely dissolved. Silver halides were removed and the orange-brown filtrate evaporated to 20 ml. and cooled in an ice-bath. On adding sodium chloride and scratching, dark brown crystals of the complex chloride deposited. These were washed with a small quantity of iced water and dried at 30°.

Analysis:

Calculated for $[Os\ Cl\ py_3\ dipy]Cl.3H_2O$	N, 9.9
Found	N, 9.8

Bromotri(pyridine)dipyridylosmium(II) bromide

$[Os\ Cl\ py_3\ dipy]Cl$ (0.5 g.) was dissolved in ethylene glycol (7 ml.) and refluxed with sodium bromide (2 g.) and pyridine (1 ml.) for 1 hour. The viscous solution was poured into water (50 ml.) and cooled in an ice-bath when bromotri(pyridine)dipyridylosmium(II) bromide separated on adding excess sodium bromide. This was separated on a glass filter and washed with iced water, and dried at 35°. It could be recrystallised from methanol/ether as dark brown-orange prisms.

Analysis:

Calculated for [Os Br py_3 dipy]Br.$2H_2O$	N, 9.0;	Br, 20.5;
Found	N, 8.6;	Br, 20.4;

Bromotri(pyridine)dipyridylosmium(II)chloride

This was prepared from [Os Br py_3 dipy]Br (0.4 g.) with silver chloride as described above for the chloro-chloride compound. The dark brown crystals are very soluble in water to give an orange-brown solution.

Analysis:

Calculated for [Os Br py_3 dipy]Cl.$2H_2O$	N, 9.5
Found	N, 9.6

Iodotri(pyridine)dipyridylosmium(II) iodide

[Os Cl py_3 dipy]Cl (0.5 g.) was suspended in ethylene glycol (7 ml.) and refluxed with sodium iodide (2 g.) and pyridine (1 ml.) for 1 hour. The viscous solution was poured into water (70 ml.), excess sodium iodide added, and the solution cooled in an ice-bath for 30 minutes. The dark precipitate of iodotri(pyridine)dipyridylosmium(II) iodide was collected on a glass filter, washed with iced water and dried at 35°. It could be recrystallised from methanol/ether as a dark brown microcrystalline powder which is sparingly soluble in water.

Analysis:

Calculated for [Os I py_3 dipy]I	N, 8.0; I, 29.1
Found	N, 7.9; I, 29.1

Iodotri(pyridine)dipyridylosmium(II) chloride

This was prepared from [Os I py_3 dipy]I using silver chloride as described above for the chloro-chloride compound. The dark brown crystals are more soluble than the chloro-chloride to give an orange-brown solution.

Analysis:

Calculated for [Os I py_3 dipy]Cl.$3H_2O$	N, 8.7
Found	N, 8.6

Chlorotri(pyridine)dipyridylosmium(III) perchlorate

[Os Cl py_3 dipy]I (0.2 g.) was converted to the chloride with silver chloride and the volume adjusted to 10 ml. Chlorine was bubbled through the cold solution which quickly turned the yellow color of the osmium(III) complex. The solution was filtered and sodium perchlorate added to the filtrate in an ice-bath when lemon-yellow crystals of chlorotri(pyridine)dipyridylosmium(III) perchlorate formed on scratching. These were washed with dilute ice-cold perchloric acid and ether, and dried at 30°.

Analysis:

Calculated for $[Os\ Cl\ py_3\ dipy](ClO_4)_2 \cdot H_2O$	N, 8.4
Found	N, 8.5

Bromotri(pyridine)dipyridylosmium(III) perchlorate

$[Os\ Br\ py_3\ dipy]Cl$ (0.2 g.) was dissolved in water (30 ml.) and dilute nitric acid (2 drops, 3N) added. Excess cerium(IV) ammonium nitrate was added, and on stirring the solution turned a bright yellow-orange. On adding concentrated perchloric acid dropwise to the filtered solution in an ice-bath and scratching, yellow-orange crystals of bromotri(pyridine)-dipyridylosmium(III) perchlorate formed. These were wahed with dilute perchloric acid and ether, and dried at 30°.

Analysis:

Calculated for $[Os\ Br\ py_3\ dipy](ClO_4)_2 \cdot H_2O$	N, 7.95
Found	N, 8.1

Iodotri(pyridine)dipyridylosmium(III)perchlorate

This was prepared as above by oxidizing a cold solution of $[Os\ I\ py_3\ dipy]Cl$ with cerium(IV) ammonium nitrate. The product formed as light green microcrystals which were soluble in water to give an olive-green solution.

Analysis:

Calculated for $[Os\ I\ py_3\ dipy](ClO_4)_2$	N, 7.9
Found	N, 8.1

Tetrakis(pyridine)dipyridylosmium(II) iodide

$[Os\ Cl_3\ py\ dipy]$ (0.4 g.) was suspended in water (14 ml.)

and ethanol (4 ml.) and refluxed with pyridine (1 ml.) and sodium hypophosphite (3 drops, 8%) for 80 hours. After 3 hours a further 20 ml. of water were added. The solution slowly changed from brown to green-brown and finally to a green-yellow color. After evaporation to dryness, the residue was dissolved in water (20 ml.) and the solution filtered. Addition of sodium iodide to the ice-cold solution resulted in the formation of dark green crystals of tetrakis-(pyridine)dipyridylosmium(II) iodide. These were recrystallised from hot water and sodium iodide, the required compound separating as the most soluble fraction. The product was washed with iced water, and dried at 40°.

Analysis:

Calculated for $[\mathrm{Os\ py_4\ dipy}]\mathrm{I_2{\cdot}2H_2O}$	N, 8.8; I, 26.6
Found	N, 8.6; I, 26.4

Tetrakis(pyridine)dipyridylosmium(II) perchlorate

To a warm aqueous solution of the above iodide, sodium perchlorate was added, and the dark green crystals of the perchlorate filtered and dried at 40°. These are sparingly soluble in cold water to give a green solution.

Analysis:

Calculated for $[\mathrm{Os\ py_4\ dipy}](\mathrm{ClO_4})_2{\cdot}\mathrm{2H_2O}$	N, 9.35
Found	N, 9.55

Tetrakis(pyridine)dipyridylosmium(III) perchlorate

$[\mathrm{Os\ py_4\ dipy}](\mathrm{ClO_4})_2$ (0.12 g.) was suspended in warm water (10 ml.) and oxidized with chlorine until it had dissolved to give a red solution. This was filtered, cooled in an ice-bath, and sodium perchlorate added, when salmon-pink microcrystals of the osmium(III) complex deposited. These were separated on a glass filter, washed with dilute ice-cold perchloric acid and ether, and dried at 40°.

Analysis:

Calculated for $[\mathrm{Os\ py_4\ dipy}](\mathrm{ClO_4})_3 \cdot 2\mathrm{H_2O}$	N, 8.4
Found	N, 8.4

Dichloroacetylacetonatodipyridylosmium(III)

K[Os $\mathrm{Cl_4}$ dipy] (0.2 g.) was dissolved in warm water (10 ml.) and refluxed with acetylacetone (0.5 ml.) for 40 minutes. On cooling in an ice-bath dark brown crystals of dichloroacetylacetonatodipyridylosmium(III) separated. These were collected on a glass filter, washed with water and a small amount of ethanol, and dried at 30°. The product is insoluble in water but soluble in chloroform from which it may be recrystallised by addition of ether.

Analysis:

Calculated for $[\mathrm{Os\ Cl_2\ aca\ dipy}]$	N, 5.4
Found	N, 5.6

Bis(acetylacetonato)dipyridylosmium(III) iodide

K[Os $\mathrm{Cl_4}$ dipy] (0.2 g.) was dissolved in warm water (10 ml.) and refluxed with acetylacetone (0.5 ml.) in the presence of excess calcium carbonate (0.5 g.). The solution slowly turned yellow-brown as the initial deposit of [Os Cl_2 aca dipy] dissolved. After 8 hours the yellow-brown solution was filtered and sodium iodide added to the filtrate in an ice-bath. Dark brown crystals of bis(acetylacetonato)dipyridylosmium(III) iodide deposited and these were washed with iced water and dried at 30°.

Analysis:

Calculated for [Os aca_2 dipy]I.H_2O N, 4.1; I, 18.4

Found N, 4.4; I, 18.7

Dichloroglycinatodipyridylosmium(III)

K[Os Cl_4 dipy] (0.2 g.) was dissolved in warm water (10 ml.) and glycine (0.2 g.) added. The solution was refluxed for 15 minutes, and the solution cooled in an ice-bath when dark brown crystals of dichloroglycinatodipyridylosmium(III) deposited. These were removed on a glass filter, washed with cold water, ethanol and ether, and dried at 35°.

Analysis:

Calculated for [Os Cl_2 gly dipy].H_2O N, 8.25

Found N, 8.0

Bis(glycinato)dipyridylosmium(III) iodide

K[Os Cl_4 dipy] (0.2 g.) was dissolved in water (10 ml.) and refluxed with glycine (0.2 g.) in the presence of excess calcium carbonate (0.3 g.) for 8 hours. The yellow-brown solution was filtered and sodium iodide added to the ice-cold filtrate when dark brown crystals of bis(glycinato)dipyridylosmium(III) iodide deposited. These were washed with iced water and dried at 30°.

Analysis:

Calculated for $[Os\ gly_2\ dipy]I.2H_2O$	N, 8.5
Found	N, 8.4

Bis(ethylenediamine)dipyridylosmium(II)iodide

K$[Os\ Cl_4\ dipy]$ (0.3 g.) was dissolved in water (15 ml.) and ethanol (5 ml.) and refluxed with ethylenediamine (0.5 ml.). After 12 hours the orange-brown solution was evaporated to dryness, dissolved in water (10 ml.) and sodium iodide added to the ice-cold solution. Dark brown crystals of bis(ethylenediamine)dipyridylosmium(II)iodide separated. These were recrystallised from hot water by adding sodium iodide, and dried at 40°.

Analysis:

Calculated for $[Os\ en_2\ dipy]I_2.H_2O$	N, 11.4;	I, 34.4
Found	N, 11.0;	I, 34.4

Bis(ethylenediamine)dipyridylosmium(II)perchlorate

This was prepared from a warm solution of the above iodide by adding sodium perchlorate and cooling in an ice-bath. The dark brown crystals of the complex perchlorate which separated were washed with iced water on a glass filter and dried at 40°.

Analysis:

Calculated for $[Os\ en_2\ dipy](ClO_4)_2 \cdot H_2O$	Cl, 10.4
Found	Cl, 10.9

Trichlorotri(pyridine)osmium(III)

K_2OsCl_6 (0.5 g.) was suspended in dimethylformamide (10 ml.) and refluxed with pyridine (2 ml.) for 2 hours. The solution slowly turned yellow-brown and the potassium chloride which deposited was filtered off from the cold solution, and ethanol (8 ml.) added to the filtrate. On adding ether a brown powder of trichlorotri(pyridine)osmium(III) deposited which was washed with excess water and alcohol, and dried at 30°.

Analysis:

Calculated for $[Os\ Cl_3\ py_3]$	N, 7.9
Found	N, 7.7

Dichlorotetrakis(pyridine)osmium(II)

K_2OsCl_6 (0.4 g.) was suspended in glycerol (3 ml.) at 80° and refluxed with pyridine (0.5 ml.) for 1 hour. The solution soon darkened and fine needles of dichlorotetrakis-(pyridine)osmium(II) separated. The viscous mixture was poured into cold water, filtered, and the product washed several times with cold water, and dried at 40°.

Analysis:

Calculated for $[Os\ Cl_2\ py_4]$	Cl, 12.3;	N, 9.7
Found	Cl, 12.5;	N, 9.6

Dibromotetrakis(pyridine)osmium(II)

$(NH_4)_2OsBr_6$ (1.5 g.) was suspended in warm glycerol (8 ml. 80°) and refluxed with pyridine (2 ml.) for 1 hour. The dark green-brown compound which initially separated, $[Os\ Br_3\ py_3]$, soon redissolved to give a red-black solution from which dark red crystals of dibromotetrakis(pyridine)-osmium(II) separated. The viscous mixture was poured into water (200 ml.), filtered, and the product washed with cold water and alcohol, and dried at 40°.

Analysis:

Calculated for $[Os\ Br_2\ py_4]$	Br, 24.0; N, 8.4
Found	Br, 24.0; N, 8.2

CHAPTER THREE

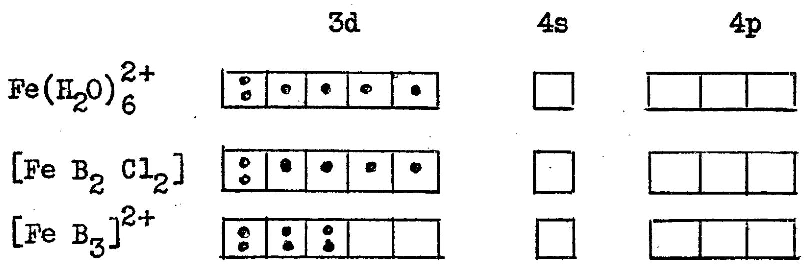
THE PREPARATIONS AND REACTIONS OF BIS- DIPYRIDYL AND PHENANTHROLINE COMPLEXES OF OSMIUM(II), (III) AND (IV)

3.1 INTRODUCTION

A variety of bis(1,10-phenanthroline) and bis(2,2'-dipyridyl) complexes of iron and ruthenium have recently been isolated (81,82) and in this chapter the preparation and properties of the analogous osmium(II), (III) and (IV) complexes are described.

The blue bis(phenanthroline)- and violet bis(dipyridyl)-iron(II) complexes, $[Fe\ Cl_2\ phen_2]$, $[Fe\ Cl_2\ dipy_2]$ were originally prepared (61) by heating $[Fe\ phen_3]Cl_3$ or $[Fe\ dipy_3]Cl_3$ *in vacuo* at 110° over concentrated sulphuric acid. A similar reaction at 255° with $[Fe\ phen_3]Br_2$ resulted in the formation of the blue dibromo complex $[Fe\ Br_2\ phen_2]$, but loss of phenanthroline from $[Fe\ phen_3]I_2$ did not occur even at this temperature. More recently in this laboratory (81) both the bis(phenanthroline)- and bis(dipyridyl)- complexes have been prepared by addition of the base to a two-fold excess of anhydrous ferrous chloride suspended in dimethylformamide.

Both the bis(dipyridyl)- and bis(phenanthroline)- iron(II) complexes have been found to be paramagnetic with four unpaired electrons (61). This contrasts with the well known diamagnetism found in the tris(phenanthroline)- and tris(dipyridyl)-iron(II) complexes (64), and indicates that orbital stabilization resulting from rearrangement of the six outer electrons in the ferrous ion to give three shared electron pairs, must occur on chelation of the third ligand molecule.



The bis iron(II) complexes are unstable in aqueous solution and rapidly disproportionate giving the corresponding tris complexes and the aquated ferrous ion.(1).

$$[\mathrm{Fe\ Cl_2\ phen_2}] \rightleftharpoons [\mathrm{Fe\ phen_3}]^{2+} + \mathrm{Fe(H_2O)_6^{2+}}$$

The analogous iron(III) complex salts are stable in non-aqueous solvents but in aqueous solution are susceptible to reduction followed by disproportionation (63).

$$[\mathrm{Fe\ Cl_2\ phen_2}]^{+} + \longrightarrow [\mathrm{Fe\ Cl_2\ phen_2}] \rightleftharpoons [\mathrm{Fe\ phen_3}]^{2+} + \mathrm{Fe(H_2O)_6^{2+}}$$

Taube (78) has suggested that disproportionation into the extreme forms can be expected for any system in which electron rearrangement takes place at some stage in the series of successive substitutions.

The first evidence for the existence of bis(phenanthroline)-

and bis(dipyridyl)- complex ions of ruthenium, was obtained from spectrophotometric studies of the step-wise formation of the tris(dipyridyl)ruthenium(II) ion (73). One substance, the green $[Ru\ (H_2O)_2\ dipy_2](ClO_4)_3$ was isolated and it was proposed that the reaction in sulphuric acid using commercial ruthenium trichloride (a mixture of Ru(III) and Ru(IV) chlorides) yielded first a monoaquodipyridyl-ruthenium(III) complex, then a bis-complex which easily underwent reduction, and finally the tris-ruthenium(II) complex resulted. Evidence was also obtained for chloro and chloroaquo species in hydrochloric acid. Dwyer and Gyarfas (83) found that if $[Ru\ dipy_3]Cl_2$ is heated in vacuo over a long period it slowly loses one molecule of dipyridyl. They isolated the dark violet dichlorobis(dipyridyl)ruthenium(II) complex $[Ru\ Cl_2\ dipy_2]$, but could not isolate the analogous phenanthroline complex by this method. More recently Dwyer and Goodwin (82) have carried out a full investigation of bis(phenanthroline)- and bis(dipyridyl)- complexes of ruthenium(II), (III) and (IV). Good yields of $[Ru\ Cl_2\ phen_2]$ and $[Ru\ Cl_2\ dipy_2]$ were obtained by pyrolysing at 300° the phenanthrolinium or bipyridinium salts of tetrachlorophenanthrolineruthenate(IV) and tetrachlorodipyridylruthenate(IV). In contrast to the analogous iron(II) complexes, these bis-ruthenium(II) compounds were found to be very stable towards disproportionation in aqueous solution (c.f. 2.1 page 20) and an extensive series of substituted derivatives was obtained by replacing the co-ordinated chlorine atom by water, ammonia, pyridine, ethylenediamine, oxalate, acetylacetone, phenanthroline and bipyridine.

The first reported preparation of bis(phenanthroline)- or bis(dipyridyl)- complexes of osmium in any valence state was in 1950 when Burstall, Dwyer and Gyarfas found that on pyrolysing potassium hexachloroosmate(IV) with bipyridine at 260-80° a mixture of dichlorobis(dipyridyl)osmium(III) chloride, and tris(dipyridyl)osmium(II) chloride was formed (84).

$$K_2OsCl_6 + \text{dipy} \xrightarrow{260\text{-}280^\circ} [Os\ Cl_2\ \text{dipy}_2]Cl + [Os\ \text{dipy}_3]Cl_2$$

The yield of the bis(dipyridyl) compound was however low. More recently Swinehart (74) has followed spectrophotometrically the reaction between osmium trichloride and bipyridine in hydrochloric acid and sulphuric acid solutions. Due to the slow rate of reaction these investigations were carried out at 100°. The author identified the bis(dipyridyl) ion $[Os\ Cl_2\ \text{dipy}_2]^+$ by comparing its absorption spectrum with that of the complex isolated by Burstall, Dwyer and Gyarfas (84) but did not isolate it in the solid state. However the complex $[Os\ (OH)_2\ \text{dipy}_2](ClO_4)$ was isolated from sulphuric acid solution, and an aqueous solution of this ion on oxidation with cerium(IV) ions turned yellow due presumably to the formation of the osmium(IV) ion, $[Os\ (OH)_2\ \text{dipy}_2]^{2+}$.

In the following account the preparation and properties of a variety of bis(phenanthroline)- and bis(dipyridyl)-complexes of osmium(II), (III) and (IV) are described. Due to the accessibility of the three oxidation states, and the probability that disproportionation into the tris species would not occur these compounds seemed to offer ideal material for a variety of chemical studies:- mechanisms of substitution reactions and effect of the ligand on oxidation potentials.

3.2 PREPARATION OF DICHLOROBIS(PHENANTHROLINE)OSMIUM(III)CHLORIDE, DICHLOROBIS(DIPYRIDYL)OSMIUM(III)CHLORIDE, AND DICHLOROPHENANTHROLINEDIPYRIDYLOSMIUM(III)CHLORIDE

(A) From Phenanthrolinium and Bipyridinium Hexachloroosmate(IV)

If phenanthroline monohydrate is added to a solution of ammonium hexachloroosmate(IV) in 3N hydrochloric acid a fine yellow microcrystalline precipitate of phenanthrolinium hexachloroosmate(IV)

$$(\mathrm{PhenH})_2\mathrm{OsCl}_6$$

results. A similar reaction at room temperature using bipyridine results in the formation of a mixture of $(\mathrm{BipyH})_2\mathrm{OsCl}_6$ and the diprotonated species $(\mathrm{BipyH}_2)\mathrm{OsCl}_6$ (c.f. page 26) but on reducing the acid concentration and by fractional precipitation at 5° the yellow

$$(\mathrm{BipyH})_2\mathrm{OsCl}_6$$

can be obtained.

Both these compounds are sparingly soluble in water, methanol and ethanol.

If the phenanthrolinium hexachloroosmate(IV) is pyrolysed at 300° in a Woods metal bath the two phenanthroline molecules outside the complex ion become chelated to the metal, and hydrogen chloride and chlorine are given off. The residue left after pyrolysis, principally $[\mathrm{Os\ Cl_2\ phen_2}]\mathrm{Cl}$, may be extracted with aqueous methanol and the ion $[\mathrm{Os\ Cl_2\ phen_2}]^+$ can be isolated as the brown sparingly soluble perchlorate.

It was found however, that the pyrolysed material contained a small amount of the osmium(II) non-electrolyte $[\mathrm{Os\ Cl_2\ phen_2}]$, and a better method of extraction consists of refluxing the pyrolysed material in absolute methanol, oxidizing the osmium(II) complex with chlorine gas, and separating $[\mathrm{Os\ Cl_2\ phen_2}]\mathrm{Cl}$ by addition of ether.

$$\begin{array}{l} [\mathrm{Os\ Cl_2\ phen_2}] \\ [\mathrm{Os\ Cl_2\ phen_2}]\mathrm{Cl} \end{array} \xrightarrow[\mathrm{Cl_2}]{\mathrm{MeOH}} [\mathrm{Os\ Cl_2\ phen_2}]\mathrm{Cl}$$

Yields however tend to be low (60 - 70%), and an analytically pure sample of the chloride is obtained only after repeated recrystallizations from methanol/ether.

The bis(dipyridyl) complex $[\mathrm{Os\ Cl_2\ dipy_2}]\mathrm{Cl}$ can be prepared in a similar manner by pyrolysis of bipyridinium hexachloroosmate(IV) but yields of only 50 - 60% are obtained due to the loss by sublimation of free bipyridine in the pyrolysis.

The yields of both the bis(phenanthroline)- and bis(dipyridyl)-

complexes may be improved by pyrolysing a paste of the organic salt in ethylene glycol but in no case are they greater than 75%.

(B) Pyrolysis of (PhenH)[Os Cl_4 phen] and (BipyH)[Os Cl_4 dipy]

If phenanthrolinium tetrachlorophenanthrolineosmate(III) (c.f. Section 2.4) is pyrolysed at 290° it loses hydrogen chloride and chlorine, the metal being reduced to the bivalent state in the process. The residue which consists mainly of dichlorobis(phenanthroline)osmium(II) is extracted with anhydrous methanol, and after concentration is oxidized with chlorine gas to the osmium(III) complex chloride which is precipitated with ether.

$$(\text{PhenH})[\text{Os Cl}_4\ \text{phen}] \xrightarrow[30\ \text{mins}]{290^{\circ}} [\text{Os Cl}_2\ \text{phen}_2] \xrightarrow[\text{Cl}_2]{\text{MeOH}} [\text{Os Cl}_2\ \text{phen}_2]\text{Cl}$$

Extraction with aqueous methanol results in the formation of insoluble hydroxy or hydroxy-bridged products which resist re-conversion to the $[\text{Os Cl}_2\ \text{phen}_2]^+$ ion.

The bis(dipyridyl) complex $[\text{Os Cl}_2\ \text{dipy}_2]\text{Cl}$, can be prepared in a similar fashion by pyrolysis of bipyridinium tetrachlorodipyridylosmate(III) although the yield is not as high due to the loss by sublimation of free bipyridine.

A simpler and more economical method of preparing the above compounds consists of refluxing the appropriate phenanthrolinium or bipyridinium salt in dimethylformamide solution for 20 minutes by which time the organic base has chelated to the metal with the formation of the respective osmium(III) chlorides $[\mathrm{Os\,Cl_2\,phen_2}]\mathrm{Cl}$ and $[\mathrm{Os\,Cl_2\,dipy_2}]\mathrm{Cl}$. These can be separated by precipitation with ether and recrystallization from methanol/ether.

By this method the mixed chelate complex dichlorophenanthrolinedipyridylosmium(III) chloride may also be prepared.

$$(\mathrm{PhenH})[\mathrm{Os\,Cl_4\,dipy}] \xrightarrow[\text{Reflux 40 mins}]{\text{D.M.F.}} [\mathrm{Os\,Cl_2\,phen\,dipy}]\mathrm{Cl}$$

(C) Direct preparation from Potassium Hexachloroosmate(IV)

The preparation of dichloro- bis(phenanthroline)- and bis(dipyridyl)- osmium(III) chlorides can be accomplished directly in 95% yield by addition of the required amount of base to potassium hexachloroosmate(IV) in anhydrous dimethylformamide solution. On refluxing, the brown color of the bis complex soon develops and potassium chloride is precipitated.

$$\mathrm{K_2OsCl_6} + 2\mathrm{B} \xrightarrow[\text{40 mins reflux}]{\text{D.M.F.}} 2\mathrm{KCl} + [\mathrm{Os\,Cl_2\,B_2}]\mathrm{Cl} + {}^1/_2\mathrm{Cl_2}$$

After removal of the potassium chloride and addition of ethanol, the osmium(III) chloride is precipitated by addition of ether.

In a similar manner, the addition of phenanthroline or bipyridine to potassium hexabromoosmate(IV) results in the formation of the analogous dibromo compounds, $[\mathrm{Os\,Br_2\,phen_2}]\mathrm{Br}$ and $[\mathrm{Os\,Br_2\,dipy_2}]\mathrm{Br}$.

Both the dibromo and dichloro osmium(III) complexes can be recrystallised by dissolving in hot methanol and precipitating with ether. They form as brown microcrystals which are soluble in warm water, methanol and ethanol to give brown-yellow solutions. Absorption spectra are given on page 82b and are similar to the curve obtained by Swinehart (74) for the $[Os\ Cl_2\ dipy_2]^+$ ion in hydrochloric acid solution.

Due to the simplicity of method and high yields obtained, the above reaction was used to prepare the bis(phenanthroline)- and bis(dipyridyl)- derivatives outlined below.

3.3 OSMIUM(II) AND OSMIUM(IV) COMPLEX IONS

The above dichloro and dibromo osmium(III) complexes may be reduced to the osmium(II) state with sodium dithionite when the non-electrolytes

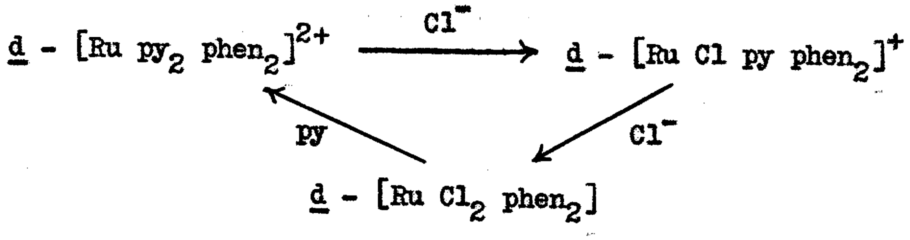
$[Os\ X_2\ phen_2].H_2O$

$[Os\ Cl_2\ phen\ dipy].H_2O$ (X = Cl, Br)

$[Os\ X_2\ dipy_2].H_2O$

separate as dark almost black crystals. These compounds are insoluble in cold water but are soluble in chloroform to give purple, purple-red, and ruby-red colors respectively.

Although the complex ions $[Os\ Cl_2\ B_2]^+$ have not been resolved into their optical isomers, there is good reason for believing that the two chlorine atoms occupy <u>cis</u> positions. In this configuration two strong π bonds form at right angles to the chelate ligands, while the *trans* isomer would involve the possible use of only one π orbital of the central metal atom (51). Further, reaction of $[\mathrm{Os\ Cl_2\ dipy_2}]$ with excess phenanthroline results in the formation of only the $[\mathrm{Os\ phen\ dipy_2}]^{2+}$ ion (90), which is most easily accounted for by a simple reaction involving replacement of two *cis* chlorine atoms. More conclusive evidence has recently been obtained in this laboratory with the analogous ruthenium system (88). $[\mathrm{Ru\ py_2\ phen_2}]\mathrm{Cl_2}$ has been resolved into its optical isomers which gives proof of the *cis* configuration of the two pyridines. Reaction of *d* - $[\mathrm{Ru\ py_2\ phen_2}]\mathrm{Cl_2}$ with chloride ions, results in the successive replacement of the pyridine molecules and the formation of the *optically active* non-electrolyte, *d* - $[\mathrm{Ru\ Cl_2\ phen_2}]$. Further, full retention of activity was observed when this compound was converted back to the *d* - $[\mathrm{Ru\ py_2\ phen_2}]^{2+}$ ion.



This proves the *cis* configuration in dichlorobis(phenanthroline) ruthenium(II). It is very probable that a similar situation occurs in $[\mathrm{Os\ py_2\ B_2}]\mathrm{Cl_2}$ and $[\mathrm{Os\ Cl_2\ B_2}]$.

The dichloro- bis(dipyridyl)- and bis(phenanthroline)-osmium(III) complex ions are unaffected by cerium(IV) ions in aqueous solution, but in 15N nitric acid immediate oxidation to the dark green osmium(IV) complex ions,

$$[Os\ Cl_2\ dipy_2]^{2+} \quad \text{and} \quad [Os\ Cl_2\ phen_2]^{2+}$$

occurs*. Addition of perchloric acid to an ice-cold solution of the above ions failed to isolate the complex perchlorates, and addition of water caused immediate reduction to the osmium(III) state.

The two chlorine atoms of $[Os\ Cl_2\ phen_2]$ and the similar dipyridyl compound $[Os\ Cl_2\ dipy_2]$ are readily replacable. However the two organic molecules are firmly chelated and cannot be replaced. Unlike the corresponding iron(II) complexes described by Basolo and Dwyer (61), $[Os\ Cl_2\ B_2]$ shows no tendency to disproportionate to give tris complex salts. The two chlorine atoms are however more difficult to displace than the similarly constituted ruthenium complexes (82), and in general more drastic conditions and longer times for reaction are required.

3.4 PYRIDINE DERIVATIVES

If dichlorobis(dipyridyl)- or dichlorobis(phenanthroline)-osmium(III) chloride is refluxed with pyridine in aqueous ethanolic solution for 12 hours the orange-brown $[Os\ Cl\ py\ B_2]^+$ (B = dipy, phen) ion results.

---

* Nyholm (21) found a similar situation in the dihalobis(diarsine)-osmium(III) complexes.

$$[Os\ Cl_2\ B_2]Cl + py \xrightarrow[\text{12 hours}]{\text{reflux}} [Os\ Cl\ py\ B_2]Cl.$$

This has been separated as the perchlorate, iodide and chloride. The bromo complex ion, $[Os\ Br\ py\ dipy_2]^+$ may be prepared in a similar manner.

These compounds may be more conveniently prepared by refluxing the dihalo- bis(dipyridyl)- or bis(phenanthroline)-osmium(II) complexes with pyridine in ethylene glycol for 20 minutes. Almost quantitative separations of the complex ions are obtained by evaporating off the ethylene glycol and adding sodium iodide to the aqueous solution in each case.

$$[Os\ X_2\ B_2] + py \xrightarrow[\text{20 mins}]{\text{ethylene glycol}} [Os\ X\ py\ B_2]^+ + X^-$$

X = Cl, Br

B = dipy, phen

Displacement of the co-ordinated halogen atom may be effected by a similar reaction. If chloropyridinebis(dipyridyl) osmium(II) iodide is pyrolysed with sodium iodide in ethylene glycol for 20 minutes, and a small amount of pyridine added and the mixture refluxed for a further 5 minutes, the iodine atom displaces the co-ordinated chlorine to form the $[Os\ I\ py\ dipy_2]^+$ complex ion.

$$[Os\ Cl\ py\ dipy_2]I + NaI + py \xrightarrow[\text{glycol}]{\text{ethylene}} [Os\ I\ py\ dipy_2]^+ + Cl^-$$

This may be separated as the iodide and converted to the chloride with silver chloride.

The complex iodides $[Os\ X\ py\ dipy_2]I.H_2O$ $(X = Cl, Br, I)$ are all orange-brown in color and can be recrystallised from methanol by addition of ether. They may be converted to the respective chlorides with silver chloride without displacement of the co-ordinated halogen, X. The chlorides may be recrystallised from aqueous solution by addition of sodium chloride.

The halopyridinebis(dipyridyl)osmium(II) chlorides can be oxidized to the osmium(III) state with cerium(IV) ions and separated as the perchlorates by addition of perchloric acid.

$$[Os\ X\ py\ dipy_2]Cl \xrightarrow{Ce(IV)} [Os\ X\ py\ dipy_2]^{2+}$$

$$(X = Cl, Br, I)$$

The chloro complex separates as orange-yellow crystals, the bromo compound is yellow, and the iodo a light green in color. Absorption spectra of the osmium(II) and osmium(III) complexes are given on page 82a.

When chloropyridinebis(dipyridyl)- or bis(phenanthroline)-osmium(II) chloride is refluxed with pyridine in aqueous ethanolic solution for 100 hours slow displacement of the remaining chloro group by pyridine occurs and the green bis(pyridine)- complexes may be separated by addition of sodium perchlorate or sodium iodide.

$$[\mathrm{Os\ Cl\ py\ B_2}]\mathrm{Cl} + \mathrm{py} \xrightarrow[\text{100 hours}]{\text{Ethanol/water}} [\mathrm{Os\ py_2\ B_2}]^{2+}$$

(B = dipy, phen) (green)

Oxidation with chlorine or cerium(IV) ions results in the red osmium(III) complex ions

$$[\mathrm{Os\ py_2\ B_2}]^{3+}$$

which have also been separated as their perchlorates.

Unlike the analogous ruthenium ion $[\mathrm{Ru\ py_2\ dipy_2}]^{2+}$ (82) the co-ordinated pyridines in $[\mathrm{Os\ py_2\ dipy_2}]^{2+}$ cannot be displaced by inorganic anions in aqueous solution but on refluxing with sodium halide in ethylene glycol the corresponding halopyridinebis(dipyridyl) osmium(II) halide is formed.

$$[\mathrm{Os\ py_2\ dipy_2}]\mathrm{X_2} \xrightarrow[\text{Ethylene glycol}]{\text{NaX}} [\mathrm{Os\ X\ py\ dipy_2}]\mathrm{X}$$

This proved an alternative method of preparing these compounds.

3.5 AMMINE DERIVATIVES

Reaction of $[\mathrm{Os\ Cl_2\ B_2}]$ (B = phen, dipy) with ammonia in aqueous solution under a variety of conditions failed to result in any ammine complexes being formed. Only hydroxy or hydroxy-bridged compounds were isolated. However if ammonia gas is bubbled through a refluxing solution of $[\mathrm{Os\ Cl_2\ dipy_2}]$ in ethylene glycol the red-brown complex ion $[\mathrm{Os\ Cl\ NH_3\ dipy_2}]^+$ forms in about 20 minutes. This has been separated as both the iodide and chloride. Continued passage of ammonia results in the formation of a dark brown solution (15 hours) from which an insoluble brown compound is obtained on removal of ethylene glycol. This compound is almost insoluble in water, methanol, and ethanol, and is a non-electrolyte in dimethylformamide solution. Analysis is consistent with an imido-bridged structure such as

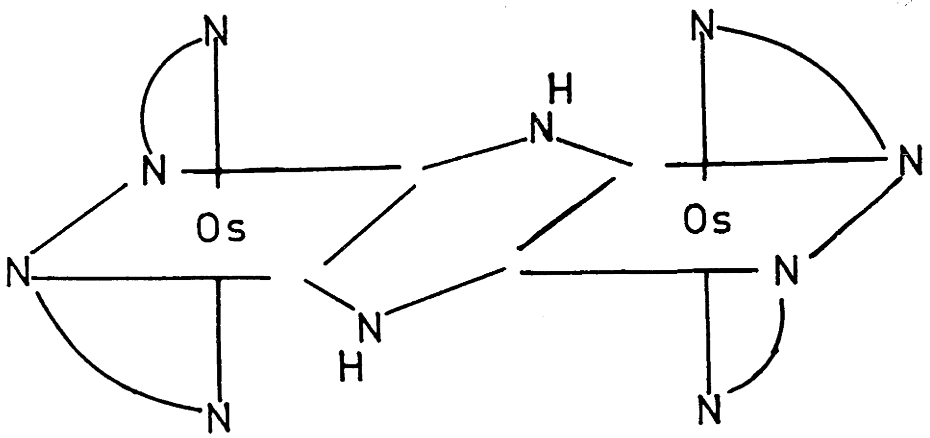


Fig. 3·51

in which each osmium atom is in the bivalent state.

Chloroamminobis(dipyridyl)osmium(II) chloride can be oxidized with cerium(IV) ions to give a brown solution from which a sparingly soluble perchlorate may be isolated. Chlorine analysis indicated the compound $[Os\ Cl\ NH_2\ dipy_2]ClO_4$ but conductivity studies and nitrogen analysis best fit a structure such as

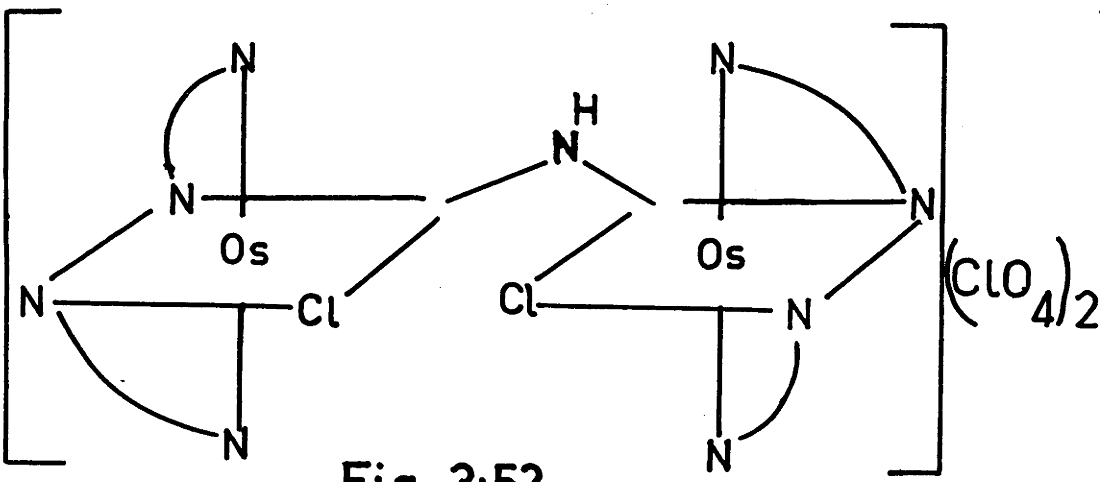


Fig. 3·52

When $[Os\ Cl_2\ dipy_2]$ is treated with liquid ammonia in an autoclave at 250-80° the two chlorine atoms are slowly removed and the orange-brown complex ion $[Os\ (NH_3)_2\ dipy_2]^{2+}$ is formed. This has been isolated as the iodide.

$$[Os\ Cl_2\ dipy_2] + NH_{3\,liq.} \xrightarrow[\text{Pressure}\quad 200\ \text{atmos.}]{250\ -\ 280^{\circ}} [Os\ (NH_3)_2\ dipy_2]^{2+}$$

Oxidation of the chloride with silver nitrate results in a green-brown solution which on warming turns green-yellow, while oxidation with cerium(IV) ions forms an orange-yellow solution. No solid compounds have been isolated.

3.6 ACETYLACETONE, ETHYLENEDIAMINE, GLYCINE, OXALATE DERIVATIVES

The two chlorine atoms in $[Os\ Cl_2\ B_2]$ (B = dipy, phen) can be replaced by acetylacetone on refluxing in aqueous ethanolic solution for 6 hours.

$$[\mathrm{Os\ Cl_2\ B_2}] + \mathrm{acaH} \xrightarrow{\text{Reflux}} [\mathrm{Os\ aca\ B_2}]^+ + \mathrm{H}^+ + 2\mathrm{Cl}^-$$

The complex ions $[\mathrm{Os\ aca\ B_2}]^+$ have been isolated as the iodides, perchlorates, and chlorides. The complex chlorides are very soluble in water and chloroform to give red-violet solutions. By this method the complex ion $[\mathrm{Os\ aca\ phen\ dipy}]^+$ has been prepared and appears to be the first reported metal complex ion containing three _different_ chelate groups.

Oxidation with mild oxidizing agents such as ferric chloride yield the orange-brown osmium(III) complex ions $[\mathrm{Os\ aca\ B_2}]^{2+}$ which have been separated as their soluble perchlorates. No evidence was obtained for an osmium(IV) complex ion.

$$[\mathrm{Os\ aca\ B_2}]^+ \xrightarrow{\mathrm{FeCl_3}} [\mathrm{Os\ aca\ B_2}]^{2+}$$

In a similar manner reaction of $[\mathrm{Os\ Cl_2\ dipy_2}]$ with glycine in aqueous ethanolic solution results in the formation of the $[\mathrm{Os\ gly\ dipy_2}]^+$ complex ion which has been separated as the iodide. It is soluble in water and organic solvents to give brown solutions.

The two chlorine atoms in $[\mathrm{Os\ Cl_2\ dipy_2}]$ can be readily replaced by the oxalato group and the red-brown sparingly soluble non-electrolyte oxalatobis(dipyridyl)osmium(II), $[Os\ ox\ dipy_2]$ is formed. This substance is sparingly soluble in water, and only slightly soluble in methanol ethanol and chloroform to give red-violet solutions.

$$[Os\ Cl_2\ dipy_2] + Na_2ox \xrightarrow{\text{Reflux}} [Os\ ox\ dipy_2] + 2Cl^-$$

It may be oxidized with cerium(IV) ions or chlorine to give a brown solution of probably the osmium(III) complex ion $[Os\ ox\ dipy_2]^+$ but this has not been isolated.

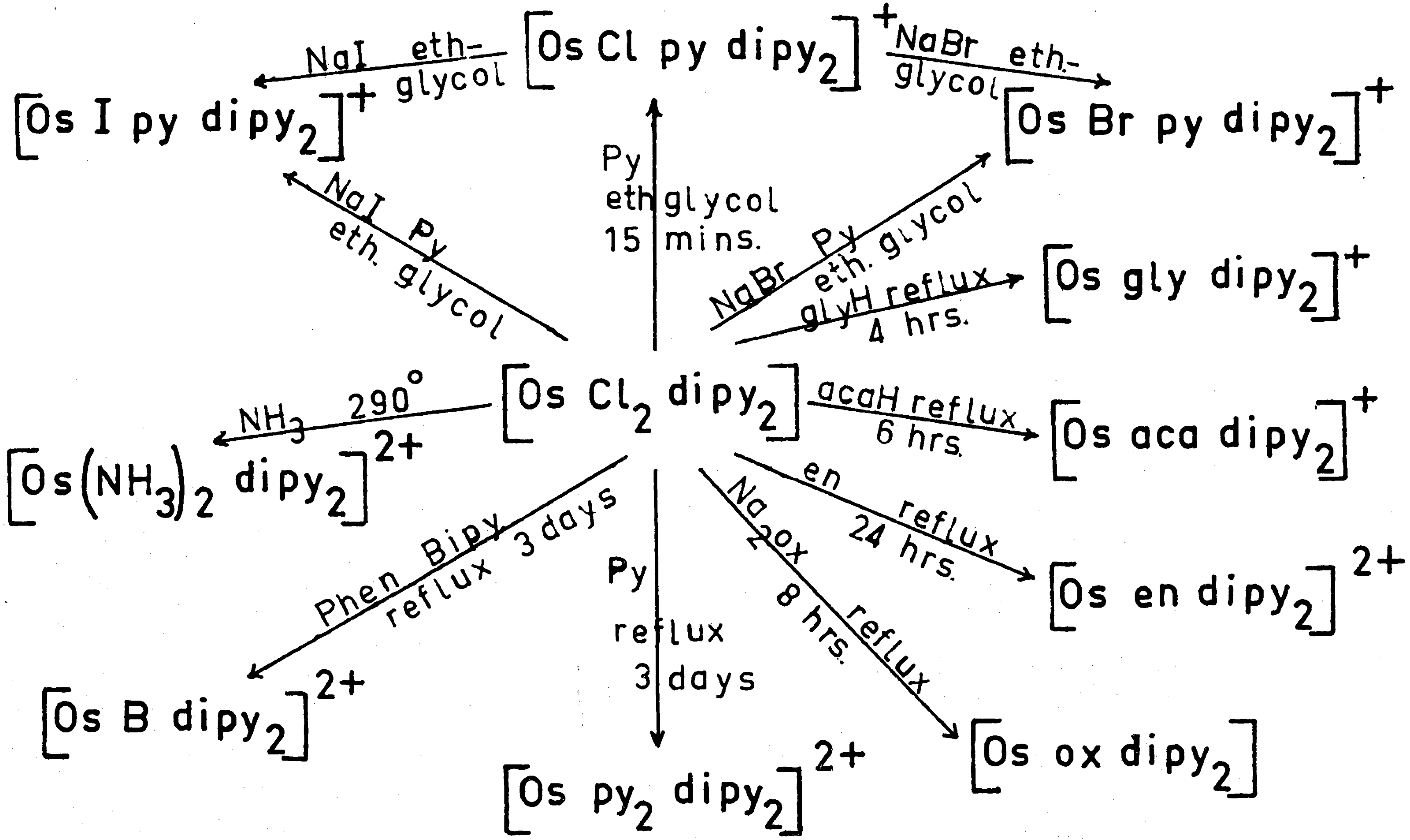
The phenanthroline complex, $[Os\ ox\ phen_2]$ is obtained by an identical reaction.

If the osmium(III) complex $[Os\ Cl_2\ B_2]Cl$ is refluxed with ethylenediamine in aqueous ethanolic solution for 4 hours an orange-brown color develops from which the complex ions $[Os\ en\ B_2]^{2+}$ (B = dipy, phen) ion can be isolated by addition of sodium iodide.

$$[Os\ Cl_2\ B_2] + en \xrightarrow{\text{reflux}} [Os\ en\ B_2]^{2+} + 2Cl^-$$

As with the $[Os\ (NH_3)_2\ dipy_2]^{2+}$ ion, oxidation of $[Os\ en\ dipy_2]^{2+}$ is not simple. On passing chlorine gas through the solution the color gradually changes to a red-violet and then to a brownish-green. These two compounds were not investigated in detail but analysis of their perchlorates indicated that they were not the simple osmium(III)

DERIVATIVES OF $[Os\,Cl_2\,dipy_2]$



complex [Os en $dipy_2$]$(ClO_4)_3$. It is probable that they involve removal of a hydrogen ion from the co-ordinated ethylenediamine as was found in the similarly constituted tris(ethylenediamine)- complexes of osmium (23).

3.7 PREPARATION AND RESOLUTION OF BIS(PHENANTHROLINE) DIPYRIDYL OSMIUM(II) AND BIS(DIPYRIDYL)PHENANTHROLINE OSMIUM(II) SALTS

Bis(phenanthroline)dipyridylosmium(II) chloride may be obtained by refluxing [Os Cl_2 $phen_2$] with one molecule of bipyridine in aqueous ethanolic solution for 48 hours, and the green-brown complex ion has been isolated as the iodide or perchlorate.

A similar reaction using [Os Cl_2 $dipy_2$] and one molecule of phenanthroline results in the formation of the green bis(dipyridyl)phenanthrolineosmium(II) chloride which has also been isolated as the iodide and perchlorate.

$$[\mathrm{Os\ Cl_2\ B_2}] + \mathrm{B'} \xrightarrow[\text{48 hours}]{\text{Reflux}} [\mathrm{Os\ B'B_2}]^{2+}$$

(B = phen, B' = dipy)
(B = dipy, B' = phen)

These two osmium(II) complex ions may be oxidized to the osmium(III) valence state with cerium(IV) ions and the reddish-blue complex ions, [Os phen $dipy_2$]$^{3+}$ and [Os dipy $phen_2$]$^{3+}$ have been isolated as their soluble perchlorates.

$$[\mathrm{Os\ B'\ B_2}]^{2+} \xrightarrow{\mathrm{Ce(IV)}} [\mathrm{Os\ B'\ B_2}]^{3+}$$

The great stability of the tris(dipyridyl) and tris(phenanthroline) complexes of osmium(II) is reflected in the ease with which they may be separated into their stable optical isomers. The resolution of tris(dipyridyl) osmium(II) chloride was achieved by Burstall, Dwyer and Gyarfas in 1950 through the d-antimonyl tartrates (84). Tris(phenanthroline)osmium(II) chloride has also been separated into stable dextro and laevo isomers, again through the d-antimonyl tartrates (86). The optically active forms of both tris(dipyridyl) and tris(phenanthroline) osmium(II) perchlorates have been oxidized without disturbance of the asymmetry of the complex ions, and the crystalline perchlorates of the d- and l- forms of the ions, $[\mathrm{Os\ phen_3}]^{3+}$ and $[\mathrm{Os\ dipy_3}]^{3+}$ have been isolated (87). The osmium(II) salts may be regenerated from the active osmium(III) forms with complete retention of configuration.

When a solution of sodium d-antimonyl tartrate was added to a concentrated aqueous solution of dl-$[\mathrm{Os\ phen_2\ dipy}]\mathrm{Cl_2}$ immediate precipitation of the crystalline diastereoisomer d-$[\mathrm{Os\ phen_2\ dipy}]$ d-$(\mathrm{SbO\text{-}tart})_2$ occurred. The diastereoisomer was converted to the active complex perchlorate by solution in dilute sodium hydroxide followed by precipitation with sodium perchlorate. The d-$[\mathrm{Os\ phen_2\ dipy}](\mathrm{ClO_4})_2$ so obtained was crystallised to constant rotation, the optically active form separating as the most soluble fraction. The perchlorate of the laevo complex ion was obtained from the original laevo filtrate and several recrystallisations from water were necessary before the optically active laevo-rotatory complex salt was obtained optically pure.

The optical isomers were stable in aqueous solution and could be kept indefinitely without loss of rotation. The specific rotations of the active perchlorates are given in Table 3.71. No rotation was observed in the Na_D line, the wave-length of which is close to an absorption maximum for each of these solutions.

When a solution of d-antimonyl tartrate was added to a concentrated solution of dl-$[Os\ dipy_2\ phen]Cl_2$ the least soluble diastereoisomer, d-$[Os\ dipy_2\ phen]$ d-$(SbOtart)_2$ could be separated on evaporating and cooling. Both diastereoisomers are fairly soluble. The optically active antimonyl tartrate was converted to the active perchlorate by solution in water followed by precipitation with sodium perchlorate.

The laevo perchlorate was obtained from the filtrate left after removal of the dd-diastereoisomer by fractional precipitation with sodium perchlorate. In order to obtain this salt optically pure several recrystallisations from hot water were necessary. The optically active forms of $[Os\ dipy_2\ phen](ClO_4)_2$ were stable in solution and did not racemise even in boiling water. The specific rotations are given in Table 3.71.

TABLE 3.71

$[\alpha]_{5461}^{20}$ Values for Osmium Complexes

	d-Isomer	l-Isomer
$[\mathrm{Os\ phen_3}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ (86)	+ 3670°	- 3570°
$[\mathrm{Os\ phen_3}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$ (87)	+ 380°	- 360°
$[\mathrm{Os\ phen_2\ dipy}](\mathrm{ClO_4})_2\cdot2\mathrm{H_2O}$	+ 2850°	- 2800°
$[\mathrm{Os\ phen_2\ dipy}]^{3+}$ (in soln.)	+ 300°	
$[\mathrm{Os\ dipy_2\ phen}](\mathrm{ClO_4})_2\cdot2\mathrm{H_2O}$	+ 2250°	- 2100°
$[\mathrm{Os\ dipy_2\ phen}]^{3+}$ (in soln.)	+ 270°	
$[\mathrm{Os\ dipy_3}]\mathrm{I_2}\cdot3\mathrm{H_2O}$ (84)	+ 2100°	- 2200°
$[\mathrm{Os\ dipy_3}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$ (89)	+ 265°	- 280°

The enantiomorphous forms of the $[\mathrm{Os\ phen_2\ dipy}]^{2+}$ and $[\mathrm{Os\ dipy_2\ phen}]^{2+}$ ions could be oxidized with chlorine to the corresponding red osmium(III) complex ions. The resulting solutions were found to be still optically active, although the magnitude of the rotation in the Hg_{5461} line had decreased almost tenfold. The original rotations of the osmium(II) complex salts were restored unchanged on reduction of the osmium(III) complex salts with sodium dithionite. The specific rotations of the $[\mathrm{Os\ phen_2\ dipy}]^{3+}$ and $[\mathrm{Os\ dipy_2\ phen}]^{3+}$ are given in Table 3.71 together with the specific rotations obtained previously by Dwyer and co-workers for the tris(dipyridyl) and tris(phenanthroline) osmium(II) and osmium(III) ions.

3.8 IMPROVED METHOD FOR THE PREPARATION OF THE TRIS(PHENANTHROLINE)OSMIUM(II) AND TRIS(DIPYRIDYL)OSMIUM(II) IONS

Tris(dipyridyl)osmium(II) bromide was first prepared by Burstall, Dwyer and Gyarfas (84) by heating a mixture of ammonium hexabromoosmate(IV) with excess bipyridine at 280°. The dark green complex ion $[\mathrm{Os\ dipy_3}]^{2+}$ was separated in 80% yield by fractional precipitation with aqueous potassium iodide. A similar reaction using potassium hexachloroosmate(IV) resulted in the formation of a mixture of dichlorobis(dipyridyl)osmium (III) chloride and tris(dipyridyl)osmium(II) chloride. Difficulties were encountered in the formation of the corresponding tris(phenanthroline)osmium(II) complex ion. Unlike bipyridine, o-phenanthroline has no reducing properties at 280° and an added reducing agent was necessary. Dwyer, Gibson and Gyarfas tried a variety of reducing agents and ultimately prepared the complex by heating phenanthroline with ammonium hexabromoosmate(IV) in glycerol at 280 - 300°, the solvent acting as the reducing agent (86).

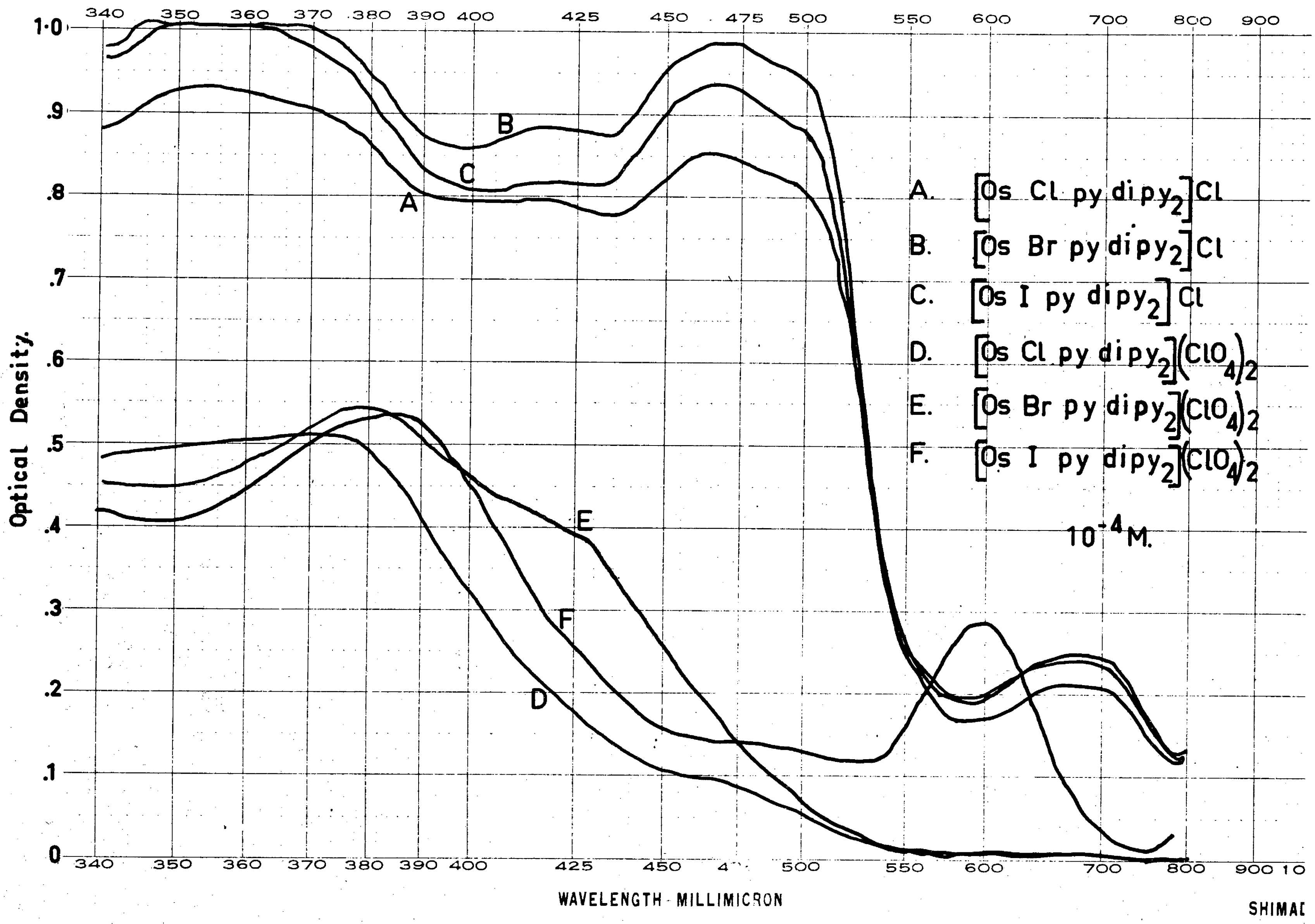
Both the complex ions $[\mathrm{Os\ dipy_3}]^{2+}$ and $[\mathrm{Os\ phen_3}]^{2+}$ have now been prepared in almost quantitative yields by refluxing the corresponding base with amonium hexabromoosmate(IV) or potassium hexachloroosmate(IV) in dimethylformamide solution. The bis complex ions $[Os\ X_2\ dipy_2]^+$ and $[Os\ X_2\ phen_2]^+$ (X = Cl, Br) are formed initially with liberation of potassium chloride or amonium bromide. On addition of water and ethanol further reduction slowly occurs with the ultimate formation of the green and brown-green tris complex ions $[Os\ dipy_3]^{2+}$ and $[Os\ phen_3]^{2+}$. These complex ions were isolated from the reaction mixture after evaporation to dryness and treatment with hydrochloric acid.

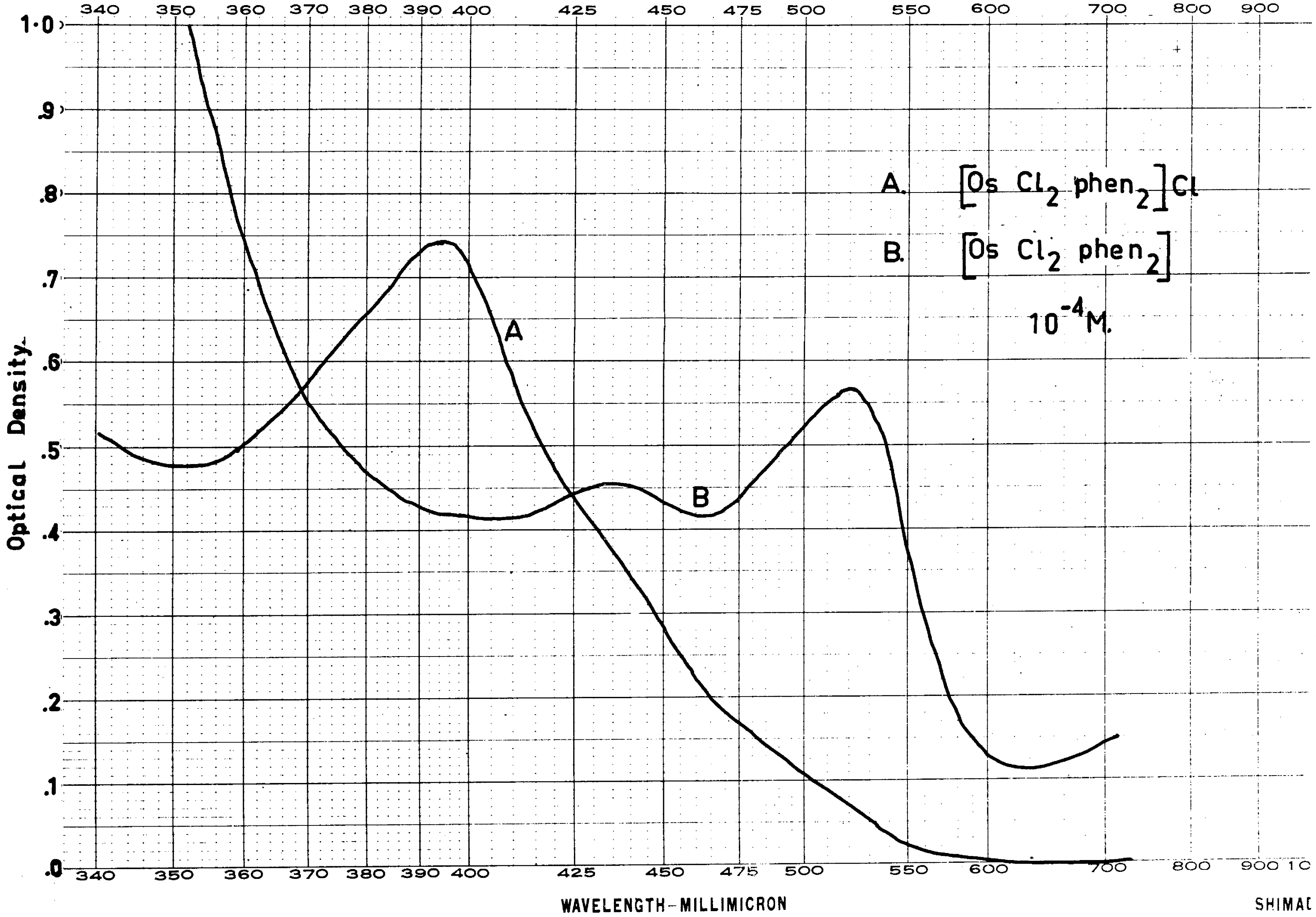
$$K_2OsX_6 + 2B \xrightarrow[\text{D.M.F.}]{\text{Reflux}} [Os\ X_2\ B_2]\ X \xrightarrow[\text{Reflux 24 hours}]{\text{Aqueous-ethanol}} [Os\ B_3]\ X_2$$

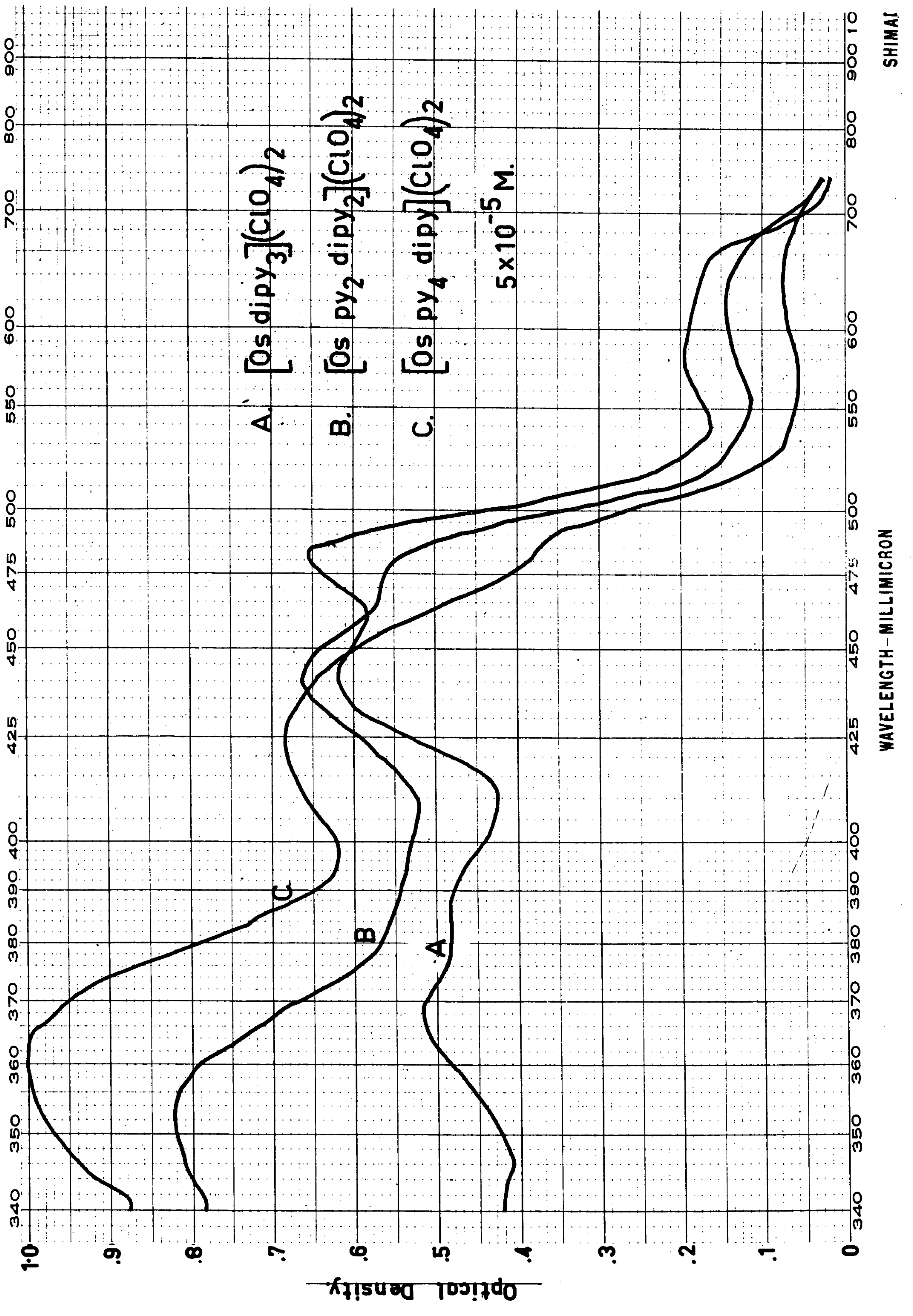
Tris(dipyridyl)osmium(II) iodide formed as dark green almost black crystals, while the tris phenanthroline derivative crystallised as dark brown-black flakes with a green reflex.

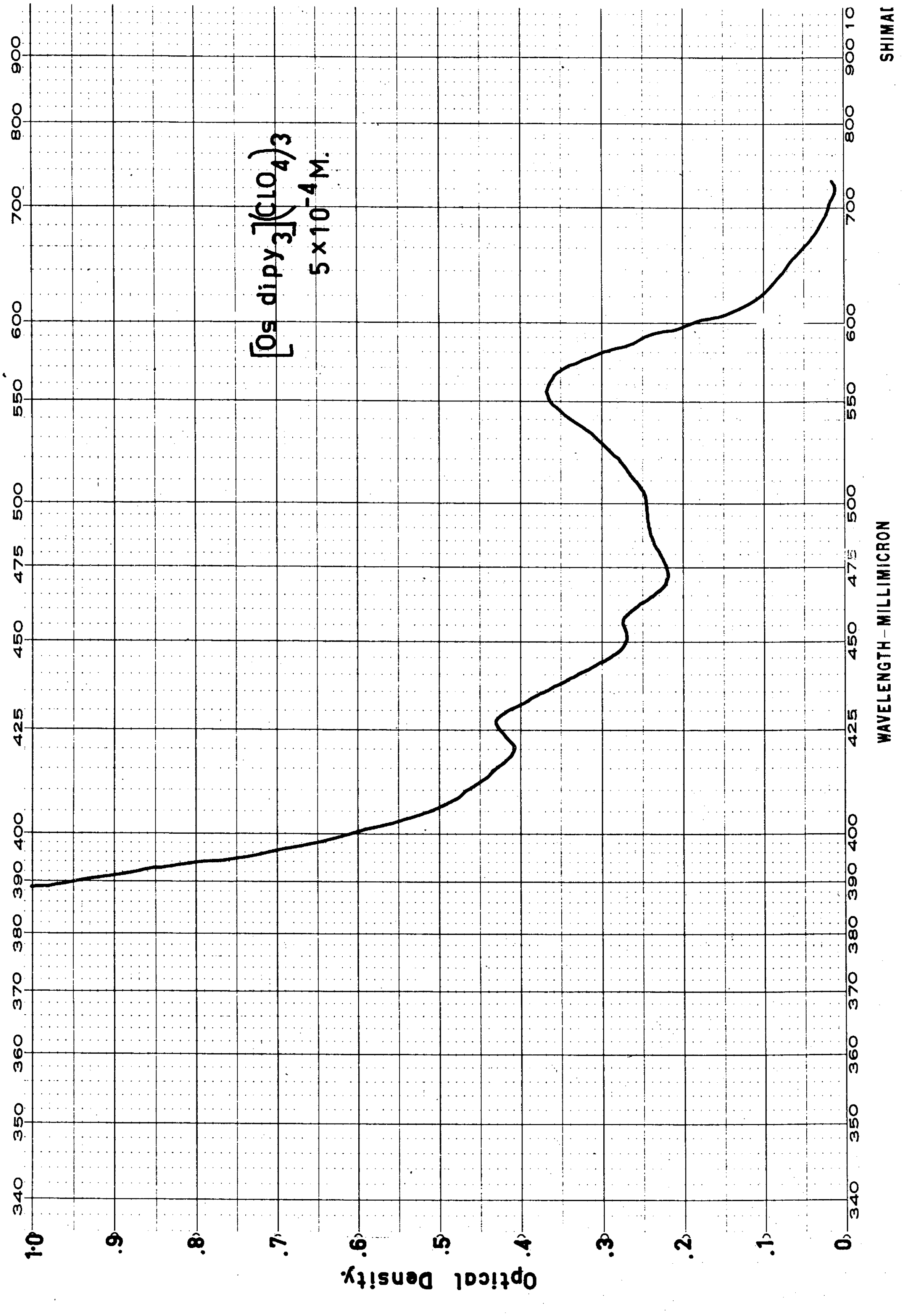
Both the tris(dipyridyl)- and tris(phenanthroline)-osmium(II) perchlorates were oxidized to the dark red and blue-red osmium(III) ions respectively with chlorine and separated as their soluble perchlorates.

$$\underset{\text{(green)}}{[Os\ B_3]^{2+}} \xrightarrow{Cl_2} \underset{\text{(red)}}{[Os\ B_3]^{3+}}$$


A. $[\mathrm{Os\ Cl\ py\ dipy_2}]\mathrm{Cl}$
B. $[\mathrm{Os\ Br\ py\ dipy_2}]\mathrm{Cl}$
C. $[\mathrm{Os\ I\ py\ dipy_2}]\mathrm{Cl}$
D. $[\mathrm{Os\ Cl\ py\ dipy_2}](\mathrm{ClO_4})_2$
E. $[\mathrm{Os\ Br\ py\ dipy_2}](\mathrm{ClO_4})_2$
F. $[\mathrm{Os\ I\ py\ dipy_2}](\mathrm{ClO_4})_2$
10^{-4}M.
A
B
C
D
E
F
Optical Density.
1·0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
340
350
360
370
380
390
400
425
450
475
500
550
600
700
800
900
10
WAVELENGTH MILLIMICRON
SHIMAI


A. $[OsCl_2\,phen_2]Cl$
B. $[OsCl_2\,phen_2]$
10^{-4}M.
A
B
Optical Density.
1·0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
340
350
360
370
380
390
400
425
450
475
500
550
600
700
800
900
WAVELENGTH-MILLIMICRON


A. $[Os\,dipy_3](ClO_4)_2$
B. $[Os\,py_2\,dipy_2](ClO_4)_2$
C. $[Os\,py_4\,dipy](ClO_4)_2$
5×10^{-5} M.
A
B
C
340
350
360
370
380
390
400
425
450
475
500
550
600
700
800
900
10
WAVELENGTH-MILLIMICRON
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1·0
Optical Density
SHIMA


[Os dipy$_3$](ClO$_4$)$_3$
5×10^{-4}M.
Optical Density.
1·0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
WAVELENGTH-MILLIMICRON
340
350
360
370
380
390
400
425
450
475
500
550
600
700
800
900
1000
SHIMA

3.9 EXPERIMENTAL

Phenanthrolinium Hexachloroosmate(IV)

Ammonium hexachloroosmate(IV) (1 g.) was dissolved in hydrochloric acid (30 ml., 2N) by warming, and a solution of phenanthroline monohydrate (0.4 g.) in hydrochloric acid (5 ml., 1N) added slowly with scratching to the cold solution. Crystallization of the product as a yellow microcrystalline powder was instantaneous. It was washed with dilute hydrochloric acid, alcohol and ether and dried at 60°.

Analysis:

Calculated for $(phenH)_2OsCl_6$	Os, 24.8;	Cl, 27.8;	N, 7.3
Found	Os, 24.7;	Cl, 28.1;	N, 7.1

Bipyridinium Hexachloroosmate(IV)

Ammonium hexachloroosmate (0.3 g.) was dissolved in hydrochloric acid (12 ml., 2N) by warming and carefully cooled in ice to make a supersaturated solution. This was slowly added with scratching to a solution of bipyridine (0.8 g.) dissolved in hydrochloric acid (5 ml., 1N). The microcrystalline yellow precipitate which immediately formed was filtered and washed with a small quantity of iced water, alcohol, and ether.

The filtrate was almost neutralised (pH 4) with ammonia and recooled, and the process repeated with a similar quantity of ammonium hexachloroosmate (0.3 g.) and the yellow precipitate washed as above, and dried at 70°. Total yield = 0.75 g.

This yield of bipyridinium hexachloroosmate(IV) could not be improved by repeating the above procedure without precipitation of some ammonium hexachloroosmate(IV).

Analysis:

Calculated for $(BipyH)_2OsCl_6$ Os, 26.5; Cl, 29.7; N, 7.8

Found Os, 26.4; Cl, 29.8; N, 8.0

Phenanthrolinium Hexabromoosmate(IV)

Ammonium hexabromoosmate (1 g.) was dissolved in hydrobromic acid (40 ml., 2N) by warming and a solution of phenanthroline monohydrate (0.54 g.) in hydrobromic acid (5 ml., 1N) added to the solution at room temperature. On scratching and cooling in an ice-bath a fine brown microcrystalline powder separated. This product was washed with dilute hydrobromic acid, a small quantity of alcohol and finally ether and dried at 60°.

Analysis:

Calculated for $(PhenH)_2OsBr_6$ Br, 46.5; N, 5.4

Found Br, 46.1; N, 5.4

Dichlorobis(phenanthroline)osmium(III) chloride

(A) From Phenanthrolinium Hexachloroosmate(IV)

$(phenH)_2OsCl_6$ (1 g.) was heated to 300° in a Woods metal bath. As the temperature rose hydrogen chloride and chlorine were evolved and at 240° the substance melted to give a dark brown syrupy liquid. As the temperature rose the liquid became more viscous and finally at 300° solidified to a brittle mass. It was kept at 300° for 20 minutes. On cooling the dark brown residue was ground to a fine powder and refluxed in methanol (100 ml.) for 2 hours with periodic bubbling of chlorine through the solution. Much of the residue dissolved to give a brown solution. This was filtered, evaporated to a small volume, and ether added when dichlorobis(phenanthroline)- osmium(III) chloride separated as a gum. This was recrystallised from methanol/ ether to give a brown microcrystalline product which was dried at 40°.

Analysis:

Calculated for $[Os\,Cl_2\,phen_2]Cl.H_2O$	N, 8.9; Cl, 17.0
Found	N, 8.8; Cl, 16.9

(B) From Phenanthrolinium Tetrachlorophenanthrolineosmate(III)

(phenH)$[Os\,Cl_4\,phen]$ (1 g.) was pyrolysed at 295° in a Woods metal bath. Hydrogen chloride and chlorine were evolved at 160° and the substance melted at 240° to give a dark liquid. As the temperature rose the liquid became more viscous and at 295° solidified. This temperature was held for 20 minutes. The pyrolysed material was ground to a fine powder, refluxed in methanol (100ml.) for two hours and chlorine bubbled through the hot solution periodically. The solution was filtered, reduced in volume, and ether added when a brown precipitate of the product separated. This was recrystallised from methanol/ether and dried at 40°.

Analysis:

Calculated for $[Os\ Cl_2\ phen_2]Cl.H_2O$	N, 8.9; Cl, 17.0
Found	N, 8.7; Cl, 16.8

(C) Direct Method in Dimethylformamide

Potassium hexachloroosmate(IV) (1 g.) was suspended in anhydrous dimethylformamide (20 ml.) and refluxed with phenanthroline monohydrate (0.89 g.) for 1 hour. As the potassium hexachloroosmate(IV) dissolved the solution slowly changed from orange-brown to brown and crystals of potassium chloride separated. The solution was cooled after 1 hour, the potassium chloride filtered off, absolute ethanol (20 ml.) added, and dichlorobis(phenanthroline)osmium(III) chloride precipitated by addition of ether. The product was washed by decantation with ether, filtered, and dried at 40°. It could be recrystallised from methanol/ether and formed as dark brown microcrystals which were dried at 100° in an air-oven. (Yield 1.85 g.)

Analysis:

Calculated for $[Os\ Cl_2\ phen_2]Cl$	N, 9.2; Cl, 17.5
Found	N, 9.0; Cl, 17.2

Dichlorobis(dipyridyl)osmium(III)chloride

(a) $[Os\ Cl_2\ dipy_2]Cl$ was made from $(bipyH)_2OsCl_6$ or $(bipyH)[Os\ Cl_4\ dipy]$ by a similar procedure to that outlined above for the preparation of the analogous phenanthroline complex.

(b) Potassium hexachloroosmate(IV) (1.9 g.) was suspended in dimethylformamide (40 ml.) and refluxed for 1 hour with bipyridine (1.3 g.). After 15 minutes crystals of potassium chloride began to separate and the solution darkened in color. After 1 hour the solution was cooled, the potassium chloride removed, and methanol (30 ml.) added. On addition of ether brown microcrystals of the product separated which were washed by decantation with ether and dried in an air-oven at 100°. Yield 2.3 g., 95%.

Dichlorobis(dipyridyl)osmium(III) chloride could be recrystallised from methanol/ether and formed as light brown flakes soluble in organic solvents to give brown solutions.

Analysis:

Calculated for $[\mathrm{Os\ Cl_2\ dipy_2}]\mathrm{Cl}$	N, 9.2;	Cl, 17.5
Found	N, 9.0;	Cl, 17.2

Dichlorophenanthrolinedipyridylosmium(III) chloride

Phenanthrolinium tetrachlorodipyridylosmate(III) (1 g.) was suspended in dimethylformamide (20 ml.) and heated under reflux for 30 minutes. The starting material quickly dissolves to give a blue-violet solution which slowly turns an orange-brown color as the phenanthroline chelates to the metal. After 30 minutes the cold solution was filtered, ethanol (40 ml.) added, and dichlorophenanthrolinedepyridylosmium(III) chloride precipitated as brown microcrystals on addition of ether. The product was washed with ether and dried in an air-oven at 100°.

It could be recrystallised from methanol/ether to give dark brown flakes which are soluble in organic solvents to give brown solutions.

Analysis:

Calculated for [Os Cl_2 phen dipy]Cl	N, 8.85;	Cl, 16.8
Found	N, 8.6;	Cl, 16.95

Dichlorobis(phenanthroline)osmium(III)chloride and dichlorobis(dipyridyl)osmium(III)chloride were prepared from (PhenH)[$OsCl_4$phen] and (BipyH)[$OsCl_4$dipy] respectively, by an identical procedure.

Dibromobis(dipyridyl)osmium(III) bromide

Ammonium hexabromoosmate(IV) (1.2 g.) was suspended in dimethylformamide (25 ml.) and heated under reflux with bipyridine (0.6 g.) for 1 hour. The solution slowly turned a dark brown and ammonium chloride was liberated. After 1 hour the solution was cooled, the ammonium chloride filtered off, and ethanol (20 ml.) added to the filtrate. On addition of ether, dibromobis(dipyridyl)osmium(III) bromide precipitated as brown flakes. The product was washed by decantation with ether and dried at 100° in an air-oven.

Dibromobis(dipyridyl)osmium(III)bromide can be recrystallised from methanol/ether to give brown flakes which are moderately soluble in warm water to give a yellow-brown solution.

Analysis:

Calculated for $[Os\,Br_2\,dipy_2]Br$	N, 7.55;	Br, 32.2
Found	N, 7.3;	Br, 33.0

Dibromobis(phenanthroline)osmium(III)bromide

Ammonium hexabromoosmate(IV) (0.5 g.) was reacted with phenanthroline monohydrate (0.31 g.) in dimethylformamide (10 ml.) in an identical manner to that described above for the preparation of the similar dipyridyl compound. The product was recrystallised from methanol/ether and dried at 100°. It formed as brown flakes soluble in organic solvents to give brown solutions.

Analysis:

Calculated for $[Os\,Br_2\,phen_2]Br$	Br, 30.3
Found	Br, 30.8

Dichlorobis(phenanthroline)osmium(II)

Dichlorobis(phenanthroline)osmium(III) chloride (1 g.) was dissolved in dimethylformamide (20 ml.) and methanol (10 ml.) and a dilute solution of sodium dithionite in water (200 ml.) slowly added to the cold solution. On cooling in an ice-bath and scratching dark purple crystals of dichlorobis(phenanthroline) osmium(II) formed. These were separated in a glass filter, washed with plenty of water, methanol, and ether, and dried at 40°.

Dichlorobis(phenanthroline)osmium(II) is insoluble in water but soluble in chloroform (from which it may be recrystallised) to give a deep purple solution.

Analysis:

Calculated for $[\mathrm{Os\ Cl_2\ phen_2}].\mathrm{H_2O}$ N, 8.8; Cl, 11.1

Found N, 8.8; Cl, 11.4

Dichlorobis(dipyridyl)osmium(II)

This compound was prepared as above by reducing a solution of dichlorobis(dipyridyl)osmium(III) chloride (1 g.) in dimethylformamide/methanol with sodium dithionite solution. Dichlorobis(dipyridyl)osmium(II) separated on cooling as dark red-purple crystals which are insoluble in water and only slightly soluble in chloroform to give a mulberry-red solution. Drying was at 40°.

Analysis:

Calculated for $[\mathrm{Os\ Cl_2\ dipy_2}].\mathrm{H_2O}$ N, 9.5; Cl, 12.0

Found N, 9.5; Cl, 12.2

Dichlorophenanthrolinedipyridylosmium(II)

This was prepared as above by reducing dichlorophenanthrolinedipyridylosmium(III) chloride with sodium dithionite solution. The osmium(II) complex separated as dark violet crystals which are slightly soluble in chloroform to give a red-purple solution.

Analysis:

Calculated for $[\mathrm{Os\ Cl_2\ phen\ dipy}].\mathrm{H_2O}$ N, 9.1;

Found N, 9.15

Dibromobis(dipyridyl)osmium(II)

Dibromobis(dipyridyl)osmium(III) bromide (1 g.) was dissolved in dimethylformamide (20 ml.) and methanol (10 ml.), and a dilute solution of sodium dithionite in water (100 ml.) was added. On cooling in an ice-bath and scratching dark, almost black crystals of dibromobis(dipyridyl)osmium(II) separated. The product was washed with excess water, methanol, and ether and dried at 40°.

Dibromobis(dipyridyl)osmium(II) is insoluble in water but moderately soluble in chloroform to give a red-brown solution.

Analysis:

Calculated for $[Os\ Br_2\ dipy_2].H_2O$	Br, 23.5;	N, 8.2
Found	Br, 22.9;	N, 8.1

Chloropyridinebis(dipyridyl)osmium(II) iodide

(A) Reaction in Aqueous Ethanolic Solution

Dichlorobis(dipyridyl)osmium(III) chloride (0.5 g.) was dissolved in water (10 ml.) and methanol (10 ml.) and refluxed for 12 hours with pyridine (2 ml.). The color of the solution slowly changed from brown to the deep brown-orange of the $[Os\ Cl\ py\ dipy_2]^+$ ion, which was isolated by evaporating the solution to dryness on a steam bath and adding sodium iodide to an aqueous solution of the residue. The dark crystals of chloropyridinebis(dipyridyl)osmium(II) iodide were recrystallised from hot water by adding sodium iodide, washed with iced water, and dried at 35°.

(B) Reaction in Ethylene Glycol

Dichlorobis(dipyridyl)osmium(II) (1.8 g.) was refluxed with pyridine (4 ml.) in ethyleneglycol (15 ml.) for 10 minutes. The viscous reaction mixture quickly turns a brown-orange and reaction is essentially complete in 5 minutes. The reaction mixture was poured into water (100 ml.) and solid sodium iodide added. On cooling in an ice-bath, dark orange crystals of chloropyridinebis(dipyridyl)osmium(II) iodide separated. These were washed with dilute sodium iodide solution, and iced water and dried at 40°. Recrystallisation was most conveniently carried out in methanol by adding ether and the product separated as dark brown crystals with an orange reflex.

Analysis:

Calculated for $[\mathrm{Os\ Cl\ py\ dipy_2}]\mathrm{I.H_2O}$ N, 9.2; Halogen = 21.3

Found N, 9.1; Halogen = 21.8

Chloropyridinebis(phenanthroline)osmium(II) iodide

This was prepared in a similar manner to the above by refluxing dichlorobis(phenanthroline)osmium(II) (1 g.) with pyridine (2 ml.) in ethylene glycol (8 ml.). Chloropyridinebis(phenanthroline)osmium(II) iodide separated as dark orange plates which were recrystallised from methanol/ether, and dried at 40°.

Analysis:

Calculated for $[\mathrm{Os\ Cl\ py\ phen_2}]\mathrm{I.H_2O}$ N, 8.6; Halogen = 20.1

Found N, 8.7; Halogen = 20.2

Bromopyridinebis(dipyridyl)osmium(II) iodide

This was prepared as above by refluxing dibromobis(dipyridyl) osmium(II) (0.5 g.) with pyridine (1 ml.) in ethylene glycol (4 ml.) for 10 minutes. Bromopyridinebis(dipyridyl)osmium(II) iodide separated as dark plates which were recrystallised from methanol/ether and dried at 40°. The product is sparingly soluble in water to give a brown solution and more soluble in organic solvents to give orange-red colours.

Analysis:

Calculated for $[\mathrm{Os\ Br\ py\ dipy_2}]\mathrm{I.H_2O}$	N, 8.7;	Halogen, 25.6
Found	N, 8.7;	Halogen, 25.8

Bromopyridinebis(phenanthroline)osmium(II) iodide

The method was as above. Bromopyridinebis(phenanthroline) osmium(II) iodide separated as dark brown plates which were recrystallised from methanol/ether and dried at 40°.

Analysis:

Calculated for $[\mathrm{Os\ Br\ py\ phen_2}]\mathrm{I.H_2O}$	Halogen, 24.3
Found	Halogen, 24.4

Iodopyridinebis(dipyridyl)osmium(II) iodide

Chloropyridinebis(dipyridyl)osmium(II) iodide (0.5 g.) was refluxed with sodium iodide (0.5 g.) in ethylene glycol (5 ml.) for 20 minutes. Pyridine (1 ml.) was added and the solution refluxed for a further 5 minutes, cooled, and poured into water (50 ml.) On adding sodium iodide and cooling in an ice-bath almost black crystals of iodopyridinebis(dipyridyl)-

osmium(II) iodide separated. These were washed with iced water and dried at 30°. They could be recrystallised from methanol/ether in which they gave a brown-orange solution.

Analysis:

Calculated for $[Os\ I\ py\ dipy_2]I.H_2O$	I, 29.7;	N, 8.3
Found	I, 29.6;	N, 8.1

Halopyridinebis(dipyridyl)osmium(II) chlorides

The chloro-, bromo-, and iodo- pyridinebis(dipyridyl)-osmium(II) iodides (0.5 g.) were converted to their respective chlorides by shaking their warm aqueous solutions with silver chloride for 10 minutes. The solution was evaporated to a small volume, filtered, and sodium chloride added to an ice-cold solution. On scratching brown crystals of the complex chloride formed which were removed after 1 hour and washed several times with dilute ice-cold hydrochloric acid, and dried at 40°.

The complex chlorides are all very soluble in water, methanol and ethanol to give brown solutions.

Analysis:

	Calculated N	Found N
$[Os\ Cl\ py\ dipy_2]Cl.3H_2O$	9.9	9.8
$[Os\ Br\ py\ dipy_2]Cl.3H_2O$	9.3	9.3
$[Os\ I\ py\ dipy_2]Cl.2H_2O$	9.0	9.1

Halopyridinebis(dipyridyl)osmium(III) perchlorates

Halopyridinebis(dipyridyl)osmium(II) chloride (0.2 g.) was dissolved in water (20 ml.) and cooled in an ice-bath.

Dilute nitric acid (2 drops, 3N) was added followed immediately by excess cerium(IV) ammonium nitrate, and the solution vigorously stirred. The oxidised solution of the chloro complex was yellow-orange, the bromo orange, and the iodo a deep green color. To the filtered solution was added sodium perchlorate and on scratching in an ice-bath the osmium(III) perchlorates formed. The products were separated on a glass filter, washed with dilute ice-cold perchloric acid and ether, and dried at 35°.

Analysis:

	Calculated N	Found N
$[Os\ Cl\ py\ dipy_2](ClO_4)_2 \cdot H_2O$	8.4	8.15
$[Os\ Br\ py\ dipy_2](ClO_4)_2 \cdot H_2O$	8.0	8.0
$[Os\ I\ py\ dipy_2](ClO_4)_2$	7.7	7.75

Bispyridinebis(dipyridyl)osmium(II) iodide

Dichlorobis(dipyridyl)osmium(II) (0.5 g.) was converted to chloropyridinebis(dipyridyl)osmium(II) chloride by refluxing with pyridine (1 ml.) in ethylene glycol (5 ml.) for 10 minutes. The solution was diluted to 200 ml. with water and refluxed with pyridine (6 drops) for 70 hours. The solution slowly changed from brown to the dark green of bispyridinebis(dipyridyl)osmium (II) chloride. The solution was evaporated to dryness, the residue dissolved in water (20 ml.), filtered, and cooled in an ice-bath. On adding sodium iodide and scratching, dark green crystals of the complex iodide separated. These were removed on a glass filter, washed with dilute sodium iodide solution and a small quantity of iced water. The dark green plates were recrystallised from hot water with sodium iodide, and dried at 35°.

Analysis:

Calculated for $[\mathrm{Os\ py_2\ dipy_2}]\mathrm{I_2.2H_2O}$	N, 8.8;	I, 26.7
Found	N, 8.5;	I. 26.7

Bispyridinebis(dipyridyl)osmium(II) perchlorate

The complex iodide (0.3 g.) was dissolved in hot water (30 ml.) and sodium perchlorate added. On cooling in an ice-bath dark green crystals of the complex perchlorate separated. These were washed with iced water and dried at 35°.

Analysis:

Calculated for $[\mathrm{Os\ py_2\ dipy_2}](\mathrm{ClO_4})_2.3\mathrm{H_2O}$	N, 9.2
Found	N, 9.1

Bispyridinebis(phenanthroline)osmium(II) iodide

Dichlorobis(phenanthroline)osmium(II) (0.5 g.) was converted to chloropyridinebis(phenanthroline)osmium(II) chloride by refluxing with pyridine (1 ml.) in ethylene glycol (5 ml.) for 10 minutes. The solution was diluted to 200 ml. with water and refluxed with pyridine (6 drops) for 100 hours. The solution slowly changed from brown to the green-brown of bispyridinebis(dipyridyl)osmium(II) chloride. The solution was evaporated to dryness on a steam-bath, and the residue dissolved in water (20 ml.), filtered, and cooled in an ice-bath. On adding sodium iodide and scratching dark brown crystals of the complex iodide separated. These were washed on a glass filter with sodium iodide solution and a small quantity of iced water. The brown-green plates were recrystallised from hot water with sodium iodide and dried at 35°.

Analysis:

Calculated for $[\mathrm{Os\ py_2\ phen_2}]\mathrm{I_2.2H_2O}$	N, 8.4;	I, 25.4
Found	N, 8.4;	I, 25.3

Bispyridinebis(phenanthroline)osmium(II) perchlorate

The complex iodide was dissolved in hot water and on adding sodium perchlorate and cooling in an ice-bath, dark brown crystals of the complex perchlorate separated. These were washed with iced water and dried at 35°.

Analysis:

Calculated for $[\mathrm{Os\ py_2\ phen_2}](\mathrm{ClO_4})_2.3\mathrm{H_2O}$	N, 8.6
Found	N, 8.5

Bispyridinephenanthrolinedipyridylosmium(II) iodide

This compound was prepared in a similar manner to the above bis(dipyridyl)- and bis(phenanthroline)- complexes, by firstly converting dichlorophenanthrolinedipyridylosmium(II) to chloropyridinephenanthrolinedipyridylosmium(II) chloride in ethylene glycol, then refluxing with pyridine in aqueous ethanol for 100 hours. The complex iodide was recrystallised from hot water with sodium iodide and dried at 35°. It was soluble in water to give a brown-green solution.

Analysis:

Calculated for [Os py_2 phen dipy]I_2	I, 26.1
Found	I, 26.0

Bispyridinebis(dipyridyl)osmium(III) perchlorate

[Os py_2 $dipy_2$]$(ClO_4)_2$ (0.2 g.) in hot water (15 ml.) was oxidized with chlorine to give a mulberry-red solution. Sodium perchlorate was added to the filtered ice-cold solution, when dark red microcrystals of bispyridinebis(dipyridyl)osmium(III) perchlorate separated. These were washed with dilute perchloric acid and ether, and dried at 30°.

Analysis:

Calculated for [Os py_2 $dipy_2$]$(ClO_4)_3 \cdot 2H_2O$	N, 8.4
Found	N, 8.4

Bispyridinebis(phenanthroline)osmium(III) perchlorate

This was prepared from [Os py_2 $phen_2$]$(ClO_4)_2$ (0.2 g.) by oxidation with chlorine in the same manner as described above for the dipyridyl complex. Bispyridinebis(phenanthroline) osmium(III) perchlorate is soluble in water to give a red-blue dichroic solution.

Analysis:

Calculated for [Os py_2 $phen_2$]$(ClO_4)_3 \cdot H_2O$	N, 8.2
Found	N, 8.2

Chloroamminobis(dipyridyl)osmium(II) iodide

[Os Cl_2 $dipy_2$] (0.4 g.) was suspended in anhydrous ethylene glycol (5 ml.) and ammonia gas bubbled through the refluxing solution. The color quickly changed to a deep brick-red. After 15 minutes the reaction mixture was evaporated to dryness, and to the filtered aqueous solution of the residue sodium iodide was added. On cooling in an ice-bath, dark brown-red crystals of the complex iodide separated which could be recrystallised from hot water. Drying was at 35°.

Chloroamminobis(dipyridyl)osmium(II) iodide is soluble in hot water, methanol, and acetone to give brick-red solutions. A $^{M}/1000$ solution in water had a conductivity of 83.8 ohms^{-1} indicating a 1:1 electrolyte.

Analysis:

Calculated for $[Os\ Cl\ NH_3\ dipy_2]I$	N, 10.3
Found	N, 10.5

Chloroamminobis(dipyridyl)osmium(II) chloride

The complex iodide from above was converted to the chloride with silver chloride and the aqueous solution evaporated to dryness. The residue was dissolved in methanol and crystallised by adding ether, and the product dried at 35°.

$[Os\ Cl\ NH_3\ dipy_2]Cl$ is very soluble in water and organic solvents to give brick-red solutions.

Analysis:

Calculated for $[Os\ Cl\ NH_3\ dipy_2]Cl$	N, 12.0
Found	N, 11.9

Tetra(dipyridyl)-μ imido-diosmium(II)

Ammonia gas was bubbled through a refluxing solution of $[Os\ Cl_2\ dipy_2]$ (0.2 g.) in ethylene glycol for 15 hours, when the solution slowly changed from brick-red to dark brown. The solution was evaporated to dryness, the residue dissolved in dimethylformamide, and precipitated with ether as a fine brown powder. The product which was almost insoluble in water and ethanol, was dried at 40°.

Analysis:

Calculated for $[Os_2(NH)_2dipy_4]$	N, 13.5
Found	N, 13.2

Dichlorotetra(dipyridyl)-μ imido-diosmium(II) perchlorate

$[Os\ Cl\ NH_3\ dipy_2]Cl$ (0.2 g.) was dissolved in water (15 ml.) and cooled in an ice-bath. Nitric acid (3 drops, 3N) was added followed immediately by excess Ce(IV) ammonium nitrate when the solution turned greenish-brown. On adding sodium perchlorate the complex perchlorate formed as brown microcrystals which were recrystallised from hot water containing a small amount of cerium(IV) ions. The product was washed with dilute perchloric acid and ether, and dried at 35°.

Analysis:

Calculated for $[Os_2\ Cl_2\ NH\ dipy_4](ClO_4)_2$	N, 9.9
Found	N, 9.8

Diamminobis(dipyridyl)osmium(II) iodide

$[Os\ Cl_2\ dipy_2]$ (0.3 g.) was heated in a steel autoclave (100 ml. capacity) with liquid ammonia (about 8 ml.). The autoclave was prepared as described by Hogarth (8), and enclosed air allowed to escape before heating. The temperature was held at 120° for 4 hours, then slowly raised to 260° and held constant for a further 4 hours before allowing to cool slowly overnight. The remaining liquid ammonia was allowed to boil off and the red-brown residue extracted with water (10 ml.) in which it gave an orange-brown solution. Sodium iodide was added to the filtered solution, and on cooling in an ice-bath dark brown crystals of diamminobis-(dipyridyl)osmium(II) iodide formed. These were recrystallised from warm water and sodium iodide, washed with a small quantity of iced water and dried at 30°.

A $^{M}/1000$ aqueous solution had a conductivity of 197 $ohms^{-1}$ indicating a 1:2 electrolyte.

Analysis:

Calculated for $[Os(NH_3)_2dipy_2]I_2.2H_2O$	N, 10.2;	I, 30.7
Found	N, 10.3;	I, 30.6

Acetylacetonatobis(dipyridyl)osmium(II) chloride

Acetylacetone (2 ml.) was added to $[Os\ Cl_2\ dipy_2]$ (1 g.) suspended in water (40 ml.) and alcohol (10 ml.), and the mixture refluxed for 6 hours in the presence of excess calcium carbonate. The excess alcohol was evaporated off, the solution filtered, and the filtrate extracted with chloroform (30 ml.) The intensely red-brown chloroform extract was dried with anhydrous sodium sulphate, evaporated to a small volume and on the addition of ether, acetylacetonatobis(dipyridyl)osmium (II) chloride crystallised as dark orange-brown plates. These were dried at 35°.

Analysis:

Calculated for [Os aca $dipy_2$]Cl	N, 8.8; Cl, 5.8
Found	N, 8.6; Cl, 6.25

Acetylacetonatobis(dipyridyl)osmium(II) perchlorate

Sodium perchlorate was added to an aqueous solution of the above chloride when brown microcrystals of the complex perchlorate immediately separated. These were washed with iced water and dried at 35°. The complex perchlorate is sparingly soluble in water to give a crimson solution.

Analysis:

Calculated for [Os aca $dipy_2$]$ClO_4 \cdot 2H_2O$	N, 7.6
Found	N, 7.7

Acetylacetonatobis(phenanthroline)osmium(II) chloride

This was prepared from [Os Cl_2 $phen_2$] (0.8 g.) in the same manner as described above for the dipyridyl compound. [Os aca $phen_2$]Cl formed as dark purple plates, very soluble in water to give a violet-purple solution.

Analysis:

Calculated for [Os aca $phen_2$]Cl	N, 8.2
Found	N, 8.0

Acetylacetonatophenanthrolinedipyridylosmium(II) chloride

This was prepared from [Os Cl_2 phen dipy] (0.5 g,) as described above. [Os aca phen dipy]Cl formed as dark plates soluble in water to give a crimson-purple solution.

Analysis:

Calculated for [Os aca phen dipy]Cl	N, 8.45
Found	N, 8.4

Acetylacetonatobis(dipyridyl)osmium(III) perchlorate

[Os aca $dipy_2$]Cl (0.2 g.) was dissolved in methanol (5 ml.) and warm water (2 ml.), and ferric chloride was added. Immediate oxidation to the orange-brown osmium(III) complex occurred, which was separated as a brown powder by addition of perchloric acid to the ice-cold solution. The complex was recrystallised from hot water and perchloric acid, washed with ether, and dried at 30°.

Analysis:

Calculated for [Os aca $dipy_2$]$(ClO_4)_2 \cdot H_2O$	N, 6.8
Found	N, 6.8

Acetylacetonatobis(phenanthroline)osmium(III) perchlorate

This was prepared from [Os aca $phen_2$]Cl (0.2 g.) as described above, and formed as orange-brown crystals.

Analysis:

Calculated for [Os aca $phen_2$]$(ClO_4)_2 \cdot H_2O$	N, 6.65
Found	N, 6.6

Glycinatobis(dipyridyl)osmium(II) iodide

Glycine (0.7 g.) was added to [Os Cl_2 $dipy_2$] (0.5 g.) suspended in water (25 ml.) and alcohol (2 ml.), and the mixture refluxed with calcium carbonate for 4 hours. The solution was evaporated to dryness and sodium iodide added to an ice-cold aqueous solution of the residue, when dark brown crystals of glycinatobis(dipyridyl)osmium(II) iodide deposited. The product was recrystallised from hot water and sodium iodide, washed with a small quantity of iced water and dried at 40°. A $^{M}/1000$ aqueous solution had a conductivity of 90 ohms^{-1} indicating a 1:1 electrolyte.

Analysis:

Calculated for $[\text{Os gly dipy}_2]\text{I}.2\text{H}_2\text{O}$	N, 9.5
Found	N, 9.6

Oxalatobis(dipyridyl)osmium(II)

$[\text{Os Cl}_2\ \text{dipy}_2]$ (0.2g.) was suspended in water (30 ml.) and alcohol (15 ml.) and refluxed with sodium oxalate (0.5 g.) for 8 hours. The starting material slowly dissolved to give a brick-red solution from which the non-electrolyte oxalatobis-(dipyridyl)osmium(II) deposited as dark crimson crystals on evaporating off the alcohol and cooling in an ice-bath. The product was collected on a glass filter, washed with iced water, a small quantity of alcohol, and finally ether, and dried at 35°.

Analysis:

Calculated for $[\text{Os ox dipy}_2].\text{H}_2\text{O}$	N, 9.2
Found	N, 9.3

Oxalatobis(phenanthroline)osmium(II)

This was prepared from $[\text{Os Cl}_2\ \text{phen}_2]$ (0.2 g.) in the same manner as described above. Oxalatobis(phenanthroline)osmium(II) crystallised as dark violet crystals almost insoluble in water and sparingly soluble in methanol and ethanol to give crimson-purple solutions.

Analysis:

Calculated for $[\text{Os ox phen}_2]$	N, 8.8
Found	N, 8.7

Ethylenediaminebis(dipyridyl)osmium(II) iodide

$[\text{Os Cl}_2\ \text{dipy}_2]\text{Cl}$ (0.6 g.) was suspended in water (20 ml.) and ethanol (15 ml.) and refluxed for 4 hours with ethylenediamine (5 ml.). The color slowly changed from brown to orange-brown, and the complex iodide was separated by evaporating off the alcohol, filtering and adding sodium iodide to the ice-cold solution. The dark brown crystals were recrystallised from hot water and sodium iodide, washed with iced water, and dried at 40°. A $^{M}/1000$ aqueous solution had a conductivity of 203 ohms^{-1} indicating a 1:2 electrolyte.

Analysis:

Calculated for $[\text{Os en dipy}_2]\text{I}_2.2\text{H}_2\text{O}$	N, 9.9
Found	N, 9.8

Ethylenediaminebis(phenanthroline)osmium(II) iodide

This was prepared from $[\text{Os Cl}_2\ \text{phen}_2]\text{Cl}$ (0.3 g.) in the same manner as described above for the dipyridyl complex. $[\text{Os en phen}_2]\text{I}$ formed as dark brown crystals which are moderately soluble in water to give a brown-orange solution.

Analysis:

Calculated for $[\text{Os en phen}_2]\text{I}_2.2\text{H}_2\text{O}$	N, 9.3
Found	N, 9.4

Bis(phenanthroline)dipyridylosmium(II) iodide

[Os Cl_2 $phen_2$] (1.4 g.) was suspended in water (100 ml.) and ethanol (20 ml.) and refluxed for 48 hours with bipyridine (0.36 g.). The solution slowly turned the green-brown color of the [Os dipy $phen_2]^{2+}$ ion. The solution was evaporated to 70 ml. on a steam bath, filtered, and sodium iodide added to the ice-cold solution. On standing almost black crystals of bis(phenanthroline)dipyridylosmium(II) iodide separated. These were recrystallised from hot water and sodium iodide, washed with a small quantity of iced water, and dried at 35°.

Analysis:

Calculated for [Os dipy $phen_2]I_2 \cdot 2H_2O$	N, 8.4;	I, 25.4
Found	N, 8.2;	I, 25.4

Bis(phenanthroline)dipyridylosmium(II) perchlorate

The complex iodide above was dissolved in hot water, filtered, and crystallised as the complex perchlorate by adding sodium perchlorate and cooling in an ice-bath. The product was dried at 35°.

Analysis:

Calculated for [Os dipy $phen_2](ClO_4)_2 \cdot 2H_2O$	N, 8.8
Found	N, 8.85

Bis(dipyridyl)phenanthrolineosmium(II) iodide

[Os Cl_2 $dipy_2$] (1 g.) was suspended in water (70 ml.) and ethanol (14 ml.), and refluxed for 48 hours with phenanthroline monohydrate (0.35 g.). The solution slowly turned dark green-brown as the phenanthroline co-ordinated to form the $[\text{Os phen dipy}_2]^{2+}$ ion. The volume was reduced to 30 ml., filtered, and sodium iodide added to the ice-cold filtrate. On standing dark green-brown bis(dipyridyl)phenanthroline-osmium(II) iodide crystallised. This was recrystallised from hot water and sodium iodide, washed with iced water, and dried at 35°.

Analysis:

Calculated for $[\text{Os phen dipy}_2]I_2 \cdot 3H_2O$	N, 8.5;	I, 25.6
Found	N, 8.5;	I, 25.9

Bis(dipyridyl)phenanthrolineosmium(II) perchlorate

The complex iodide above was dissolved in hot water, the solution filtered, and sodium perchlorate added, when the complex perchlorate crystallised on cooling in an ice-bath. It formed as dark green-brown crystals, which were dried at 35°. The product was soluble in water and organic solvents to give dark green solutions.

Analysis:

Calculated for $[\text{Os phen dipy}_2](ClO_4)_2 \cdot 2H_2O$	N, 9.15
Found	N, 9.1

Bis(phenanthroline)dipyridylosmium(III) perchlorate

$[\text{Os dipy phen}_2](ClO_4)_2$ (0.2 g.) was dissolved in the minimum quantity of hot water and the solution cooled in an ice-bath. Nitric acid (3 drops, 3N) was added, followed immediately by cerium(IV) ammonium nitrate, when the red-blue dichroic osmium(II) complex formed on stirring. On addition of sodium perchlorate and scratching, dark red crystals of the perchlorate separated. These were washed on a glass filter with dilute ice-cold perchloric acid and ether, and dried at 35°.

Analysis:

Calculated for $[\mathrm{Os\ dipy\ phen_2}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$	N, 8.2
Found	N, 8.3

Bis(dipyridyl)phenanthrolineosmium(III) perchlorate

This was prepared from $[\mathrm{Os\ phen\ dipy_2}](\mathrm{ClO_4})_2$ (0.2 g.) in a similar manner to the above $[\mathrm{Os\ dipy\ phen_2}]^{3+}$ ion. The product separated as dark red crystals which were dried at 35°. They are soluble in cold water to give a reddish-blue solution.

Analysis:

Calculated for $[\mathrm{Os\ phen\ dipy_2}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$	N, 8.4
Found	N, 8.35

Dextro-bis(phenanthroline)dipyridylosmium(II) perchlorate

$[\mathrm{Os\ dipy\ phen_2}]\mathrm{I_2}$ (1 g.) in water was converted to the chloride with silver chloride and the volume adjusted to 20 ml. To the warm solution (40°) sodium antimonyl tartrate (0.41 g.) was added slowly with scratching when on cooling in an ice-bath (15 mins.) dark brown crystals of the diastereoisomer d-$[\mathrm{Os\ dipy\ phen_2}]$ d-$(\mathrm{SbO\text{-}tart})_2\cdot x\mathrm{H_2O}$ separated. This was collected on a sintered filter and washed with iced water.

The diastereoisomer was dissolved in dilute sodium hydroxide (20 ml. $^N/20$) solution and shaken with fine paper pulp for 10 minutes, filtered, and sodium perchlorate added to the filtrate. On cooling in an ice-bath almost black crystals of the dextro perchlorate separated. This was recrystallised from hot water and sodium perchlorate, the optically active form separating as the most soluble fraction. It was dried at 35°.

A 0.002% solution in water gave $\alpha_{5461} = +0.057^\circ$ (mean value)

$$\text{whence } [\alpha]_{5461}^{20} = +2{,}850^\circ$$

$$\text{and } [M]_{5461}^{20} = +26{,}850^\circ$$

Analysis:

Calculated for d-$[\mathrm{Os\ dipy\ phen_2}](\mathrm{ClO_4})_2.2\mathrm{H_2O}$ N, 8.8

Found N, 8.8

Laevo-bis(phenanthroline)dipyridylosmium(II) perchlorate

To the filtrate left after the removal of the dd-diastereoisomer above, sodium perchlorate was added and the impure laevo perchlorate crystallised. This was obtained optically pure after several recrystallisations from hot water. The active form was more soluble than the racemic complex.

A 0.002% solution in water gave $\alpha_{5461} = -0.056^\circ$ (mean value)

$$\text{whence } [\alpha]_{5461}^{20} = -2{,}800^\circ$$

$$\text{and } [M]_{5461}^{20} = -26{,}400^\circ$$

Analysis:

Calculated for l-[Os dipy $phen_2](ClO_4)_2.2H_2O$	N, 8.8
Found	N, 8.9

Dextro-bis(dipyridyl)phenanthrolineosmium(II) perchlorate

[Os phen $dipy_2]I_2$ (1 g.) in hot water (40 ml.) was shaken with silver antimonyl tartrate (0.8 g. 2 molecules) for 10 minutes and filtered from silver iodide. The solution was concentrated on a steam-bath until on cooling in an ice-bath approximately half the substance had crystallised as the diastereoisomer d-[Os phen $dipy_2$] d-$(SbO\text{-}tart)_2.xH_2O$. This was separated on a sintered glass filter and washed with a small quantity of iced water. The diastereoisomer was dissolved in dilute sodium hydroxide solution (15 ml. $^N/20$) and the active perchlorate separated by adding sodium perchlorate to an ice-cold solution. It was recrystallised several times from hot water and sodium perchlorate, the active form separting as the most soluble fraction.

A 0.002% solution in water gave $\alpha_{5461} = +0.045^\circ$ (mean value)

$$\text{whence } [\alpha]^{20}_{5461} = +2,250$$

$$\text{and } [M]^{20}_{5461} = +20,650^\circ$$

Analysis:

Calculated for [Os phen $dipy_2](ClO_4)_2.2H_2O$	N, 9.15
Found	N, 9.0

Laevo-bis(dipyridyl)phenanthrolineosmium(II) perchlorate

The filtrate left after removal of the dd-diastereoisomer above was diluted to 100 ml. with warm water and fractionally precipitated with sodium perchlorate. The most soluble fractions which were strongly laevo-rotatory were recrystallised several times from hot water and sodium perchlorate, and dried at 35°.

A 0.002% solution gave $\alpha_{5461} = -0.042^\circ$ (mean value)

$$\text{whence } [\alpha]^{20}_{5461} = -2{,}100^\circ$$

$$\text{and } [M]^{20}_{5461} = -19{,}270^\circ$$

Analysis:

Calculated for $[\text{Os phen dipy}_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	N, 9.15
Found	N, 9.2

The Persistence of Optical Activity on Oxidation

Solutions of the above two dextro perchlorates were each treated with chlorine gas until the color changed from green-brown to reddish-blue. The oxidized solutions were filtered and examined for optical activity. The osmium(III) complex ions had no detectible rotations in the Na_D line but had small rotations in the Hg green line. The original rotations of the osmium(II) complex ions were restored unchanged on reduction with sodium dithionite and dilution with water.

A 0.02% solution of d-$[\text{Os phen}_2 \text{ dipy}]^{2+}$ gave on oxidation

$$\alpha_{5461} = +0.06^\circ \text{ (mean value)}$$

$$\text{whence } [\alpha]^{20}_{5461} = +300^\circ$$

A 0.02% solution of d-[Os dipy$_2$ phen]$^{2+}$ gave on oxidation

$$\alpha_{5461} = +0.054^{\circ} \quad \text{(mean value)}$$

$$\text{whence } [\alpha]^{20}_{5461} = +270^{\circ}$$

Tris(phenanthroline)osmium(II) iodide

Ammonium hexabromoosmate(IV) (0.5 g.) was suspended in dimethylformamide (10 ml.) and refluxed with phenanthroline monohydrate (0.4 g.) for 1 hour. The solution initially turned almost black then slowly changed to a dark green-brown color. After 1 hour, water (10 ml.), and excess phenanthroline (0.1 g.) were added and the solution refluxed for a further 10 hours by which time complete convertion to the green-brown tris complex had occurred. The solution was evaporated to dryness then the residue evaporated twice from dilute hydrochloric acid (10 ml., 3N) to ensure complete removal of dimethylformamide. The residue was dissolved in water (25 ml.) and tris(phenanthroline)osmium(II) iodide crystallised on adding sodium iodide to the solution in an ice-bath. The product was recrystallised from hot water and sodium iodide, and formed as dark brown-green plates which were dried at 35°. (Yield, 0.7 g.)

Analysis:

Calculated for [Os phen$_3$]I$_2$.H$_2$O	N, 8.4
Found	N, 8.5

Tris(dipyridyl)osmium(II) iodide

Ammonium hexabromoosmate(IV) (1.5 g.) was suspended in dimethylformamide (30 ml.) and refluxed with bipyridine (1.1 g.) for 40 minutes. Water (30 ml.) was then added and the solution refluxed for a further 12 hours by which time complete convertion to the green tris complex had occurred. The solution was evaporated to dryness and the evaporation repeated twice with hydrochloric acid (20 ml. 3N). The residue was dissolved in hot water (50 ml.) and crystallised as the iodide by adding sodium iodide to the filtered solution. The product was recrystallised from hot water and sodium iodide, and dried at 35°. (Yield, 1.8 g.).

Analysis:

Calculated for $[\mathrm{Os\ dipy_3}]\mathrm{I_2.H_2O}$	N, 9.1
Found	N, 9.0

CHAPTER FOUR

THE PREPARATIONS AND REACTIONS OF MONO- 2,2',2",TERPYRIDINE COMPLEXES OF OSMIUM (II), (III) AND (IV)

4.1 INTRODUCTION

The terdentate ligand 2,2'2",terpyridine (tpy) co-ordinates to many metal ions of the transition series (91). The chelate complexes derived from Cu(II), Ag(I), Ag(II), Zn(II), Cd(II), Hg(II), Pd(II), Pt(II), Ir(III), Ru(II) and Fe(II), contain one molecule of the base, while those from Fe(II), Co(II), Co(III), Ni(II), Ru(II), Os(II), Cr(III) and In(III) contain two (92).

Terpyridine (Fig. 4.11) co-ordinates through all three nitrogen atoms. Since the bond from each nitrogen atom to the metal must lie in the plane of the pyridine ring and resonance requires co-planarity of the three rings, it follows that all bonds from the chelate must be planar. With octahedral co-ordination Morgan and Burstall(93) considered three arrangements of the two chelate molecules in the $[M\ tpy_2]^{2+}$ ions, but the conditions of co-planarity require that the molecules of the base are arranged in two equatorial planes at right angles (Fig. 4.12). This has recently been demonstrated by X-ray analysis of terpyridyldichlorozinc(II) (94).

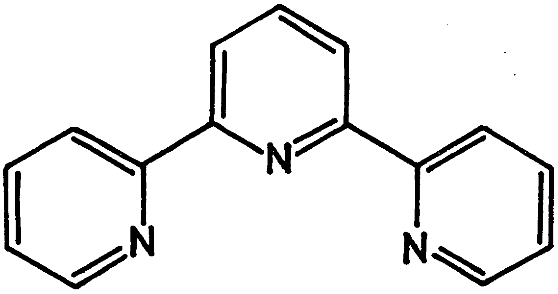


Fig. 4·11

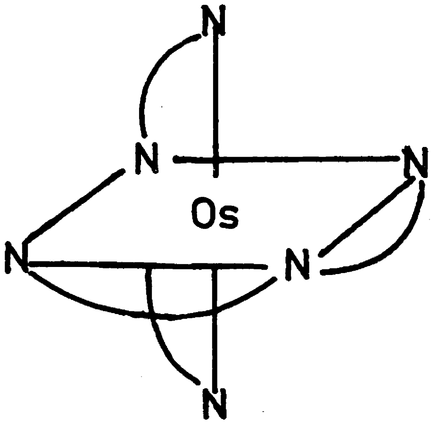


Fig. 4·12

Bis(terpyridyl)iron(II) salts are prepared by addition of the base to aqueous solutions of ferrous salts and the complex ion is characterised by its intense purple color. Oxidizing agents such as cerium(IV) salts and chlorine change the color to green, but although the ion $[\mathrm{Fe\ tpy_2}]^{3+}$ undoubtedly exists in these oxidized solutions no crystalline compound has been isolated. This has been attributed (95) to both its tendency to undergo reduction (E = - 1.076 volts) and its ability to lose one of the terdentate molecules.

The red ruthenium(II) and dark brown osmium(II) bis complex molecules have been prepared (91) by the pyrolysis of mixtures of the base with ruthenium(III) chloride and ruthenium metal, and with potassium hexachloroosmate(IV) and osmium metal respectively. However, both the compounds have been prepared (96) by a much simpler and more economical procedure involving heating potassium pentachlorohydroxyruthenate(IV) or ammonium hexabromoosmate(IV) respectively with the base in glycerol at 200°. These substances show a stability towards acids and alkalis comparable to that of the analogous phenanthroline and dipyridyl derivatives.

The green ruthenium(III) and osmium(III) bis(terpyridyl)-complexes are readily obtained by oxidation of the bivalent cations (91). Bis(terpyridyl)osmium(III) ion has been isolated as the crystalline perchlorate (95), but the analogous ruthenium ion can be obtained only in solution. The redox potentials for the $[M\ tpy_2]^{2+/3+}$ systems are given in Table 4.11 and in all cases show a marked preference for the bivalent state (97).

TABLE 4.11

Redox Potentials for $M\ tpy_2^{2+}/M\ tpy_2^{3+}$ Systems

Acid concn.	Fe	Ru	Os
0.1 f	- 1.076	- 1.281	- 0.9512
1.0 f	- 0.927	- 1.202	- 0.9070

Until recently no mono-terpyridyl complexes of Fe or Ru had been isolated. However recently Broomhead and Dwyer (62) have isolated the non-electrolyte dichloroterpyridyl iron(II) from a solution of ferrous chloride and the base in 1N hydrochloric acid in an inert atmosphere. This spin free (μ = 4.60 B.M.) complex is purple-red in solution and is assumed to have a distorted trigonal bipyramidal structure analogous to that of the Cd(II) Zn(II) and Cu(II) complexes (94).

Ruthenium(II) complexes containing one molecule of each of the bases bipyridine and terpyridine have also been prepared in this laboratory (82). The parent compound chlorodipyridylterpyridylruthenium(II) chloride was prepared by refluxing tetrachlorodipyridylruthenium(IV) with the base in aqueous alcoholic solution. The co-ordinated chlorine atom could be replaced by either pyridine or aquo groups, and the complex ions $[\mathrm{Ru\ py\ dipy\ tpy}]^{2+}$ and $[\mathrm{Ru\ H_2O\ dipy\ tpy}]^{2+}$ have been isolated as their perchlorates. A kinetic study on the rate of substitution of the chloro group in the $[\mathrm{Ru\ Cl\ dipy\ tpy}]^{+}$ ion is being carried out as a fundamental approach to the use of these substances as inhibitors of sulphydryl enzymes.

No evidence has been found from the literature for the preparation of any osmium complex containing one molecule of terpyridine. The methods used by Dwyer and Goodwin (82) in their study of the ruthenium complexes are in many cases adapted in the following investigations, but in several cases new methods of preparation have been developed. A wide variety of complexes of osmium(II), (III) and (IV) has been prepared for the first time.

4.2 PREPARATION OF TRICHLOROTERPYRIDYLOSMIUM(III) AND ITS PYRIDINE DERIVATIVES

Preliminary experiments using potassium hexachloroosmate(IV) and one molecule of the base in aqueous solution yielded a variety of colored products of indefinite compositions. These included dark colored hydrolysis products of the $[OsCl_6]^{2-}$ ion which for the most part were insoluble. Experiments carried out in glycerol and ethylene glycol using one molecule of the base yielded only the bis(terpyridyl) osmium(II) ion isolated many years ago by Morgan and Burstall (91). In view of this information three alternative methods of attack suggested themselves. (1) The possibility of preparing $(tpyH_2)OsCl_6$ and its subsequent pyrolysis in a similar manner to the preparation of tetrachlorodipyridylosmium(IV) (c.f. section 2.3 page 28). (2) The reduction of the $OsCl_6^{2-}$ ion to $OsCl_6^{3-}$ with hydrazine or silver wool (33), and the reaction of this ion with terpyridine in an inert atmosphere. (3) The possibility of direct synthesis in a non-aqueous solvent. Of these three possible methods only the last was investigated in detail.

When potassium hexachloroosmate(IV) is suspended in dimethylformamide (D.M.F.) and refluxed in the presence of one molecule of terpyridine, the non-electrolyte trichloroterpyridylosmium(III) could be isolated after three hours as a dark brown insoluble powder.

$$K_2OsCl_6 + tpy \xrightarrow{D.M.F.} [Os\ Cl_3\ tpy] + 2KCl + {}^1/{}_2Cl_2$$

This compound dissolves readily in concentrated nitric acid to give probably the yellow-brown osmium(IV) complex ion $[Os\ Cl_3\ tpy]^+$ but this was not isolated.

$$[Os\ Cl_3\ tpy] \xrightarrow{HNO_3} [Os\ Cl_3\ tpy]^+$$

Two of the three co-ordinated chlorine atoms may be readily replaced by refluxing the osmium(III) complex with pyridine in ethylene glycol. The complex ion $[Os\ Cl\ py_2\ tpy]^+$ thus obtained was isolated as both the iodide and chloride, and oxidation with chlorine gas resulted in the formation of the brown-yellow osmium(III) complex ion.

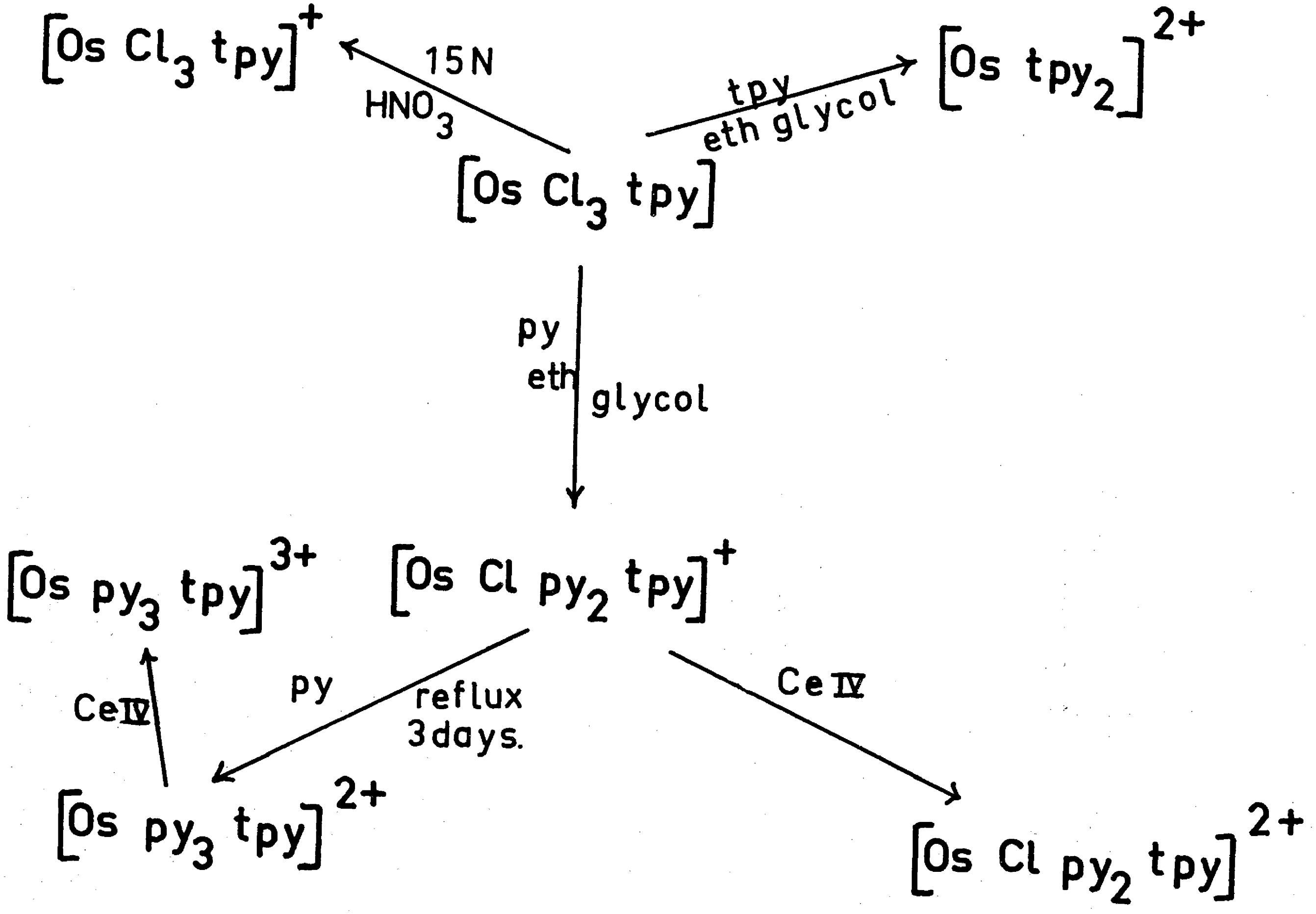
$$\underset{\text{(brown-orange)}}{[Os\ Cl\ py_2\ tpy]^+} \xrightarrow{Cl_2} \underset{\text{(brown-yellow)}}{[Os\ Cl\ py_2\ tpy]^{2+}}$$

This was isolated as the water soluble perchlorate.

Continued refluxing of chlorobis(pyridine)terpyridylosmium(II)chloride with pyridine in aqueous ethanolic solution results in the formation of the brown $[Os\ py_3\ tpy]^{2+}$ complex ion which has been isolated as the perchlorate. Oxidation with cerium(IV) ions or chlorine yields the green osmium(III) complex ion $[Os\ py_3\ tpy]^{3+}$ which has also been crystallised as the water soluble perchlorate.

$$\underset{\text{(brown)}}{[Os\ py_3\ tpy]^{2+}} \xrightarrow[Cl_2]{Ce(IV)} \underset{\text{(green)}}{[Os\ py_3\ tpy]^{3+}}$$

Fig. 4·21 Derivatives of $[OsCl_3tpy]$.



Unlike the similar ruthenium complexes (82) the co-ordinated pyridine in the above complex ions is very firmly bound and cannot be displaced even on continued refluxing in hydrochloric acid solution.

4.3 PREPARATION OF CHLORODIPYRIDYLTERPYRIDYLOSMIUM(II) CHLORIDE

When tetrachlorodipyridylosmium(IV) is suspended in aqueous alcohol and refluxed with terpyridine for 48 hours in the presence of sodium hypophosphite as a reducing agent, the starting material slowly dissolves to form the red-brown $[\mathrm{Os\ Cl\ dipy\ tpy}]^+$ ion. The complex chloride may be precipitated by the addition of concentrated hydrochloric acid and forms as almost black micro-crystals.

$$[\mathrm{Os\ Cl_4\ dipy}] + \mathrm{tpy} \xrightarrow[\mathrm{EtOH/H_2O}]{\mathrm{NaH_2\ PO_2}} [\mathrm{Os\ Cl\ dipy\ tpy}]\,\mathrm{Cl}$$

It may be recrystallised from hot water by the addition of hydrochloric acid and is soluble in methanol, ethanol and acetone to give dark red solutions. If, in the above preparation, potassium tetrachlorodipyridylosmate(III) is used as starting material, only 12 hours refluxing is necessary.

A more economical method of preparation involves refluxing one molecule of tetrachlorodipyridylosmium(IV) with terpyridine in ethylene glycol for 20 minutes. The higher temperature and reducing conditions of the solvent allow an almost quantitative yield of the complex chloride.

The [Os Cl dipy tpy]$^+$ ion has been isolated as the chloride, bromide, and iodide.

Oxidation with cerium(IV) ammonium nitrate or chlorine results in the formation of the orange-yellow osmium(III) ion which has been isolated as both the chloride and perchlorate.

$$\underset{\text{(red-brown)}}{[\mathrm{Os\ Cl\ dipy\ tpy}]^{+}} \xrightarrow{\mathrm{Cl_2}} \underset{\text{(orange-yellow)}}{[\mathrm{Os\ Cl\ dipy\ tpy}]^{2+}}$$

This ion may be reversibly reduced to the osmium(II) complex with sodium dithionite.

4.4 REPLACEMENT OF THE CO-ORDINATED CHLORINE ATOM OF [Os Cl dipy tpy]Cl BY INORGANIC ANIONS

Unlike the chlorodipyridylterpyridylruthenium(II) ion (99) the co-ordinated chlorine atom in the chlorodipyridylterpyridylosmium(II) ion is difficult to replace by other unidentate inorganic anions. Treatment of an aqueous solution of [Os Cl dipy tpy]Cl with either sodium bromide or sodium iodide merely results in the eventual isolation of the chloro bromide [Os Cl dipy tpy]Br or chloro iodide [Os Cl dipy tpy]I respectively. Repeated evaporation to dryness from concentrated hydrobromic acid results only in the oxidation of the chloro chloride complex to the osmium(III) valence state by free bromine. Analysis indicated that no replacement of the co-ordinated chlorine atom had occurred, and the original osmium(II) complex could be recovered on reduction.

If however the chloro chloride complex is refluxed in aqueous alcoholic solution with silver acetate, the dark green osmium(III) complex ion

$$[\mathrm{Os_2\ O\ dipy_2\ tpy_2}]^{4+}$$

is slowly formed (c.f. section 4.7, page 132). When the filtered solution is refluxed with hydrobromic acid in the presence of sodium hypophosphite as reducing agent the solution slowly darkens to the red-brown color of the $[\mathrm{Os\ Br\ dipy\ tpy}]^{+}$ ion from which dark red-brown crystals of the bromo bromide are formed on evaporation and cooling.

$$[\mathrm{Os_2\ O\ dipy_2\ tpy_2}]^{4+} + 2\mathrm{HBr} \xrightarrow{\mathrm{NaH_2PO_2}} 2[\mathrm{Os\ Br\ dipy\ tpy}]^{+} + \mathrm{H_2O}$$

If a similar reaction is carried out using sodium iodide instead of hydrobromic acid, a black insoluble precipitate forms which does not redissolve on continued reflux. This material appeared to be the silver iodide complex

$$[\mathrm{Os_2\ O\ dipy_2\ tpy_2}](\mathrm{AgI_2})_4$$

as it slowly dissolves in warm nitric acid to give the crimson-red osmium(IV)-osmium(III) oxo complex ion (c.f. section 4.7, page 131) and silver iodide. Repeated variations in experimental conditions and procedure failed to produce any evidence for the iodo complex ion.

Replacement of the co-ordinated chlorine atom could be effected more conveniently at a higher temperature by using ethylene glycol as solvent. The non-aqueous nature of the solvent prevented the formation of any stable hydroxy-aquo compounds, and the high boiling point (195°) considerably reduced the time for reaction. The chlorine atom is replaced by bromine, iodine, thiocyanate, or nitrite by refluxing the chloro chloride complex with the respective sodium or potassium salt in ethylene glycol. The complexes have been isolated as their bromides, iodides etc. respectively, and these may be converted into their more soluble chlorides.

$$\begin{tikzcd}
{[\mathrm{Os\ Cl\ dipy\ tpy}]\mathrm{Cl} + 2\mathrm{NaX}} \arrow[r, "\text{Ethylene glycol}"] & {[\mathrm{Os\ X\ dipy\ tpy}]\ \mathrm{X} + 2\mathrm{NaCl}} \arrow[d, "\mathrm{AgCl}"] \\
{(\mathrm{X} = \mathrm{Cl},\ \mathrm{Br},\ \mathrm{I},\ \mathrm{SCN})} & {[\mathrm{Os\ X\ dipy\ tpy}]\mathrm{Cl}}
\end{tikzcd}$$

In the case of the co-ordination of the NO_2^- group, the solution was refluxed for a shorter time (3 minutes) otherwise considerable decomposition occurred. The nitritodipyridylterpyridylosmium(II) ion has only been isolated as the iodide. (It is unknown how the nitro group is co-ordinated.)

All these compounds are soluble in water, methanol and ethanol, to an extent depending on the inorganic anion and in all cases are red-brown in solution similar to the chloro chloride complex.

It was found that the co-ordinated pyridine molecule in the $[\mathrm{Os\ py\ dipy\ tpy}]^{2+}$ ion, and acetonitrile in the $[\mathrm{Os\ CH_3CN\ dipy\ tpy}]^{2+}$ ion (see following sections) could be displaced by a halogen atom by refluxing with sodium halide in ethylene glycol.

$$\begin{matrix}[\mathrm{Os\ py\ dipy\ tpy}]^{2+} \\ [\mathrm{Os\ CH_3CN\ dipy\ tpy}]^{2+}\end{matrix} \xrightarrow[\text{Ethylene glycol}]{\text{Na X}} [\mathrm{Os\ X\ dipy\ tpy}]^{+}$$

A similar reaction does not occur in aqueous solution.

The bromo-, iodo-, and thiocyanato- osmium(II) complexes have been oxidized with cerium(IV) ions to their respective osmium(III) complexes, which have been isolated as their soluble perchlorates. The bromo derivative has also been obtained by oxidation with bromine in hydrobromic acid, and has been isolated as the orange bromo bromide.

$$[\mathrm{Os\ Br\ dipy\ tpy}]^{+} \xrightarrow[\mathrm{Br_2}]{\mathrm{Ce(IV)}} \underset{\text{(orange)}}{[\mathrm{Os\ Br\ dipy\ tpy}]^{2+}}$$

$$[\mathrm{Os\ I\ dipy\ tpy}]^{+} \xrightarrow{\mathrm{Ce(IV)}} \underset{\text{(green)}}{[\mathrm{Os\ I\ dipy\ tpy}]^{2+}}$$

$$[\mathrm{Os\ NCS\ dipy\ tpy}]^{+} \xrightarrow{\mathrm{Ce(IV)}} \underset{\text{(purple-red)}}{[\mathrm{Os\ NCS\ dipy\ tpy}]^{2+}}$$

Similar oxidation of the nitritoosmium(II) complex ion results in a yellow brown solution containing, presumably, the osmium(III) ion $[\mathrm{Os\ NO_2\ dipy\ tpy}]^{2+}$, but the color quickly fades and this complex ion has not been isolated.

4.5 NITRILE AND AMMINE DERIVATIVES OF [Os Cl dipy tpy]Cl

(a) Nitriles

When chlorodipyridylterpyridylosmium(II) chloride is refluxed for 48 hours with either acetonitrile or propionitrile in aqueous alcoholic solution, the co-ordinated chlorine atom is removed and the color changes from red-brown to brown of the complex ions,

$$[\mathrm{Os\ CH_3CN\ dipy\ tpy}]^{2+} \quad \text{and} \quad [\mathrm{Os\ C_2H_5CN\ dipy\ tpy}]^{2+}$$

These complex ions have been isolated as the iodides and perchlorates and are readily soluble in water, methanol, and ethanol, to give dark brown solutions. The co-ordinated nitrile group is firmly attached and the complex ion cannot be converted back to the chloro chloride by refluxing in hydrochloric acid, as is found with similar platinium(II) nitriles (107).

Oxidation with cerium(IV) ions generates the dichroic green-red osmium(III) ions,

$$[\mathrm{Os\ RCN\ dipy\ tpy}]^{2+} \xrightarrow{\mathrm{Ce(IV)}} [\mathrm{Os\ RCN\ dipy\ tpy}]^{3+}$$

$$(\mathrm{R} = \mathrm{CH_3},\ \mathrm{C_2H_5})$$

of which the acetonitrile compound has been isolated as the green perchlorate. Aqueous solutions of these osmium(III) complexes are not stable and quickly change from green-red to a brown-yellow color and the original osmium(II) complex ions cannot be regenerated. Results of a conductivity study of this reaction are shown in Table 4.51.

TABLE 4.51

Conductivity of a $^{M}/1000$ aqueous solution of [Os CH_3CN dipy tpy]$(ClO_4)_3$

TIME (mins)	CONDUCTIVITY (in $ohms^{-1}$)	COLOR
0	278	green
5	322	green-brown
10	360	brown
25	394	"
55	408	brown-yellow
120	410	"

The pH of the brown-yellow solution (pH = 4.0 - 4.5) suggests that the nitrile group has been slowly replaced by a hydroxyl group, with the accompanying reduction in charge of the complex ion, and elimination of a proton.

$$\underset{\text{(green-red)}}{[\text{Os } CH_3CN \text{ dipy tpy}]^{3+}} + H_2O \longrightarrow \underset{\text{(brown-yellow)}}{[\text{Os OH dipy tpy}]^{2+}} + H^+$$

Reduction of the brown-yellow solution with sodium dithionite results in a red-brown solution while reaction with dilute nitric acid results in a crimson-red color similar to that of the osmium(III)-osmium(IV) complex ion $[Os_2\ O\ dipy_2\ tpy_2]^{5+}$. (c.f. section 4.7, page 131)

(b) Ammines

Several unsuccessful attempts were made to replace the chlorine atom in the [Os Cl dipy tpy]$^+$ ion with ammonia.

(1) In aqueous ammoniacal solution no reaction occurred, the complex chloride being recovered after 48 hours refluxing.

(2) Reaction with dry ammonia gas in ethylene glycol at 195° or in glycerol at 290° again results in no reaction.

(3) When the chloro chloride is reacted with ammonia gas in the absence of oxygen in an autoclave at 300° and at high pressure (5 ml. liquid NH_3 in 100 ml. cylinder) for 8 hours, again no reaction appeared to take place.

It therefore appears that the complex chloride is extremely stable and strongly resists the replacement of the last anionic ligand with the uncharged ammonia molecule. It is expected that the [Os NH_3 dipy tpy]$^{2+}$ ion would have a brown color in solution similar to the analogous pyridine and nitrile derivatives.

4.6 PYRIDINE AND SUBSTITUTED PYRIDINE DERIVATIVES OF [Os Cl dipy tpy]Cl

The co-ordinated chlorine atom may be replaced by pyridine by refluxing an aqueous solution of the chloro chloride with pyridine for 36 hours. The complex ion, [Os py dipy tpy]$^{2+}$ has been isolated as both the iodide and perchlorate both of which are soluble in water, methanol, and ethanol, to give brown solutions.

Oxidation with chlorine gas or cerium(IV) ions results in a green-red dichroic solution similar in color to the osmium(III) nitrile derivatives (c.f. section 4.5(a), page 125) and the osmium(III) complex ion, $[\mathrm{Os\ py\ dipy\ tpy}]^{3+}$ has been isolated as the soluble perchlorate. Unlike the osmium(III) nitrile derivatives, however, the pyridine complex ion is stable towards decomposition in aqueous solution.

β-picoline, γ-picoline, 4-ethyl pyridine, and 4-isopropyl pyridine all co-ordinate similarly, and their osmium(II) complexes have been isolated as the soluble perchlorates. Oxidation with cerium(IV) ions yields, in all cases, the green-red osmium(III) complex ions which have also been isolated as their soluble perchlorates.

$$\underset{\text{(brown)}}{[\mathrm{Os\ Rpy\ dipy\ tpy}]^{2+}} \xrightarrow{\mathrm{Ce(IV)}} \underset{\text{(green-red)}}{[\mathrm{Os\ Rpy\ dipy\ tpy}]^{3+}}$$

(R = 3-Me, 4-Me, 4-Et, 4-i.pr)

α-picoline failed to co-ordinate and Coutauld molecular models showed that this is due to the steric hindrance of the 2-methyl group.

The osmium(II)-pyridine compounds are stable in aqueous solution, and the pyridine molecules are not removed on refluxing for 2 hours with hydrochloric acid. However by refluxing with sodium halides in ethylene glycol solution, the co-ordinated pyridine is replaced by the halide ion. The complex ions

$$[\mathrm{Os\ X\ dipy\ tpy}]\mathrm{Cl} \qquad (\mathrm{X = Cl, Br, I})$$

prepared by this method are identical with those prepared by the more direct method (c.f. section 4.4, page 123).

4.7 HYDROLYSIS AND OXO DERIVATIVES OF [Os Cl dipy tpy]Cl

The base and neutral hydrolysis of the chlorodipyridylterpyridylosmium(II) ion was studied by following the change in conductivity with time of a $^{M}/1000$ solution of the complex in $^{M}/1000$ sodium hydroxide solution and water respectively. The results are given in Tables 4.71 and 4.72.

TABLE 4.71 Base Hydrolysis

Temperature	Time (hrs.)	$^{M}/1000$ NaOH (ohms^{-1})	$^{M}/1000$ [Os Cl dipy tpy]Cl + $^{M}/1000$ NaOH (ohms^{-1})	Difference
20° (approx.)	0	207.6	270.6	63.0
"	1.5	217.8	282.4	64.6
"	4.5	215.8	283.4	67.6
"	12.5	206.4	274.7	68.3
95°	1.5	145.2	227.5	82.3

Fig. 4·71 Derivatives of $[\mathrm{Os\,Cl\,dipy\,tpy}]\mathrm{Cl}$

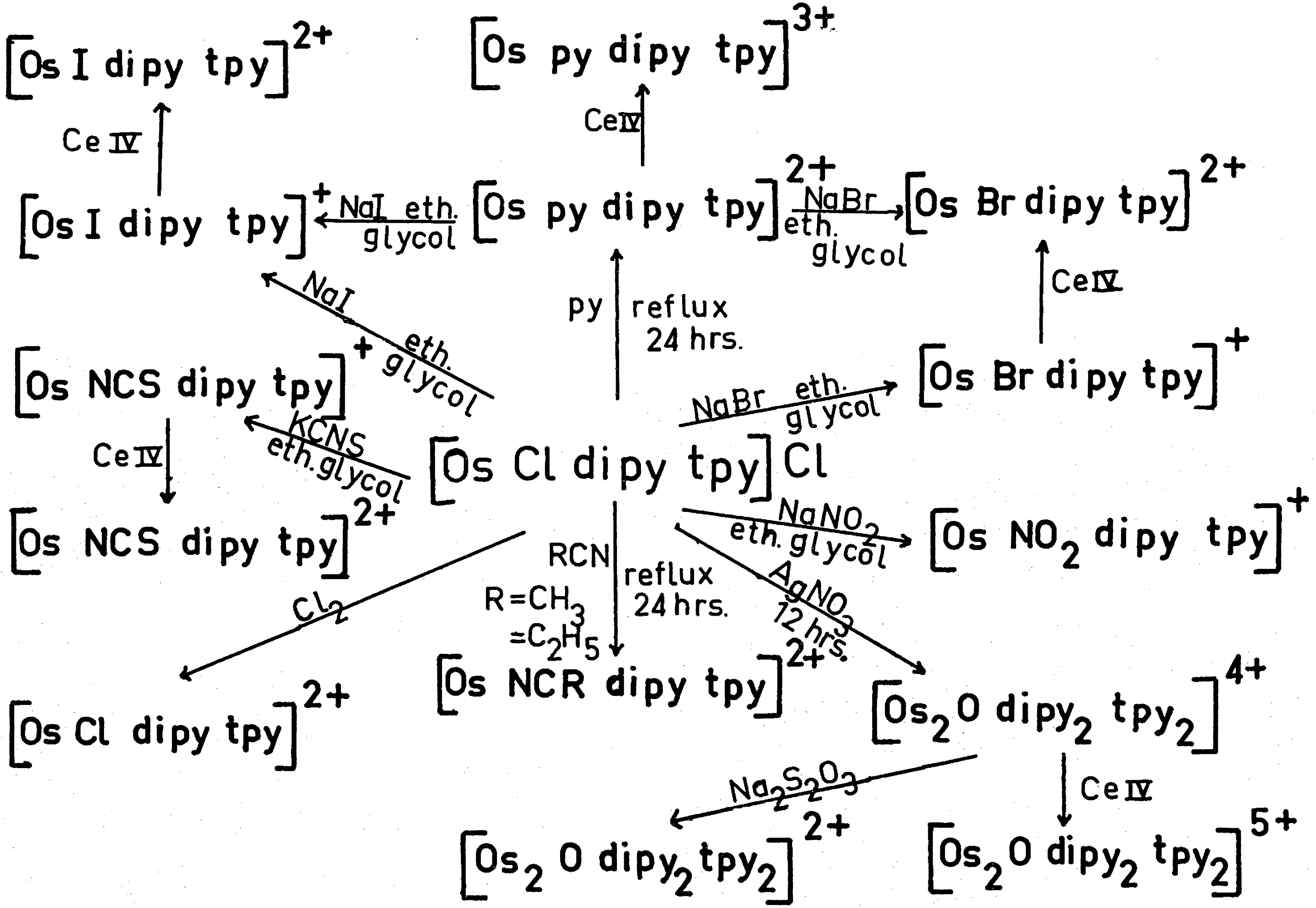
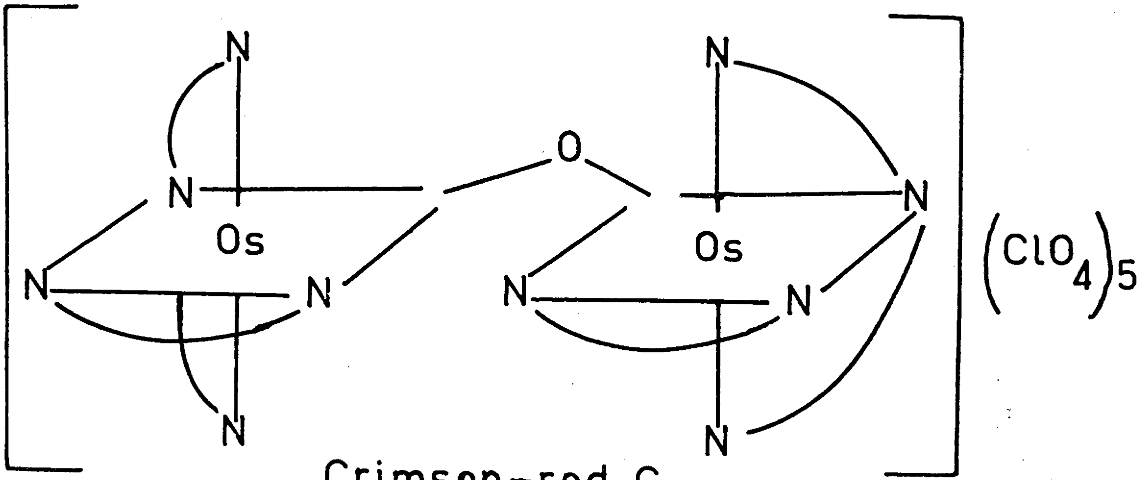


TABLE 4.72 Neutral Hydrolysis

Temperature	Time (hrs.)	Water (ohms^{-1})	$^{M}/1000$ [Os Cl dipy tpy]Cl (ohms^{-1})	Difference
20° (approx.)	0	2.4	101.5	99.1
"	1.5	2.8	105.1	102.3
"	4.5	2.7	104.0	101.3
"	12.5	3.4	102.5	99.1
95°	1.5	82.4	174.2	91.8

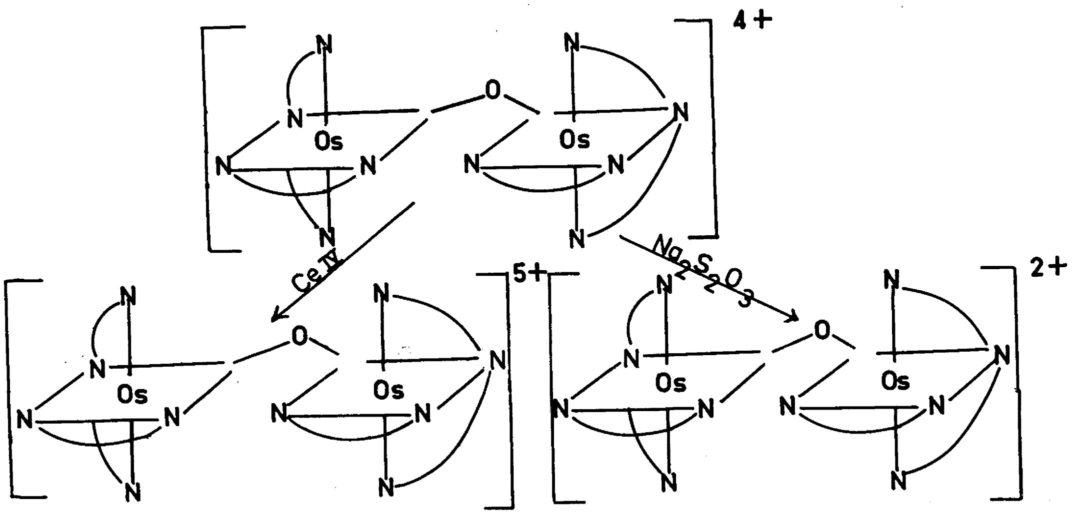
The above results indicate that aquation or base hydrolysis does not occur even when the temperature is raised to 95°. It would be expected that if hydrolysis did occur, the conductivity of the solution would decrease in the case of hydroxyl attack, and increase in the case of displacement of the chlorine atom by water. Thus the co-ordinated chlorine atom appears to be very firmly bound, and this is in keeping with the difficulty found in replacing it with other inorganic anions in aqueous solution. It therefore appears that the $[\text{Os Cl dipy tpy}]^+$ ion will be of little value for kinetic studies of substitution reactions in aqueous solution.

If an aqueous solution of chlorodipyridylterpyridylosmium(II) chloride is refluxed with silver nitrate, the solution quickly turns brown-orange due to oxidation to the osmium(III) complex ion, $[\text{Os Cl dipy tpy}]^{2+}$, which on continued refluxing gradually changes to a green-blue color. From the solution a dark blue soluble perchlorate (A) can be isolated which is stable in both acidic and alkaline conditions, and has a conductivity (210 $ohms^{-1}$) characteristic of a 1:2 electrolyte. Analyses indicate the presence of five nitrogen atoms and two perchlorate groups per molecule. Reduction of (A) with sodium dithionite gives a brown-red solution from which a soluble perchlorate (B) can be isolated by addition of sodium perchlorate. Oxidation of (A) or (B) with cerium(IV) ions gives rise to an intense crimson-red solution from which a dark red perchlorate (C) may be obtained. An aqueous solution of (C) slowly reduces to (A) on standing overnight and is immediately reduced on making the solution alkaline. It is stable indefinitely in acidic solution. A $^{M}/1000$ aqueous solution of (C) has a conductivity intermediate between that expected for a 1:2 and 1:3 electrolyte (265 $ohms^{-1}$). Analyses of (C) do not correspond to a hydroxy complex of osmium(IV) such as $[Os\ OH\ dipy\ tpy](ClO_4)_3$ or to an oxo derivative such as $[Os\ O\ dipy\ tpy](ClO_4)_2$. The analysis figures fit almost exactly those expected for a structure such as



Crimson-red C

in which a formally quadrivalent osmium atom is joined to a trivalent osmium atom through a bridging oxygen atom. Such a structure is in accord with the compound's high color, both atoms assuming an intermediate valency by resonance interaction. It is also in accord with the observed intermediate conductivity. The stable blue-green osmium(III) species (A) may then be formulated as an oxo bridged structure incorporating two trivalent osmium atoms, reduction with dithionite giving rise to the red-brown complex $[Os_2\,O\,dipy_2\,tpy_2](ClO_4)_2$, (B). The absorption spectra of (A), (B) and (C) are shown on pages 139c and 139d and it can readily be seen that (A) and (B) have spectra similar to analogous osmium(III) and osmium(II) complexes, while thatfor (C) differs markedly from that obtained for any other osmium compound.



4.8 INFRA RED STUDY ON THE CO-ORDINATION OF THIOCYANATE IN [Os NCS dipy tpy]Cl.H_2O

The thiocyanate anion, CNS^-, can co-ordinate to a metal atom through either the S or N atoms (100). The method of co-ordination has recently been investigated by several authors (101,102,103), by differentiating between the frequencies assigned to the fundamental modes of the triatomic group approximating to CN and CS stretching. Michell and Williams (101) studied the CN stretching frequency for a variety of inorganic complexes and drew a rough correlation between the band frequencies and the binding of the ligand. However these authors were unable to draw an exact, general, correlation as to bond type and attributed this to a variety of structural factors.

From a very recent investigation of the CS stretching frequency a more exact diagnosis appears to be possible (104). From a comparison of the observed CS frequencies in complexes of known structure Turco and Pecile were able to show that the symmetrical ν_1 band occurs between 690 cm^{-1} and 720 cm^{-1} for M-SCN compounds and in the range 780 - 860 cm^{-1} for M-NCS compounds. They have substantiated their argument with an imposing list of experimental data.

In the light of this information, the infra red spectrum of $[Os\ NCS\ dipy\ tpy]Cl.H_2O$ was investigated to obtain information as to the nature of the bonding of the thiocyanate group. It was expected that M-SCN bonding would be preferred, for the following reasons:-

(1) Previous infra red studies on the thiocyanate complexes of the heavier metals (e.g. Pt, Pd, Re) have shown that donation of electrons from the central metal atom to the empty d_π orbitals on the S atom is an important factor in stabilizing the MS bond;

(2) The redox potential of the $[Os\ NCS\ dipy\ tpy]^{+/2+}$ couple (c.f. section 6.4, page 186) is most easily interpreted as resulting from significant $d_\pi - d_\pi$ bonding from the central Os atom to the thiocyanate group.

The infra red spectra of [Os NCS dipy tpy]Cl.H_2O and [Os Cl dipy tpy]Cl.H_2O are compared in Figs. 4.81 and 4.82.

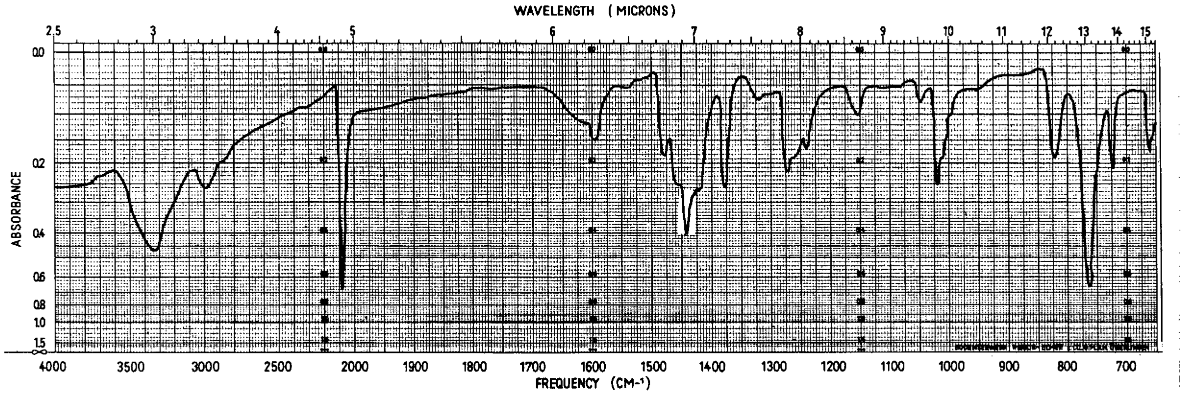


Fig. 4.81

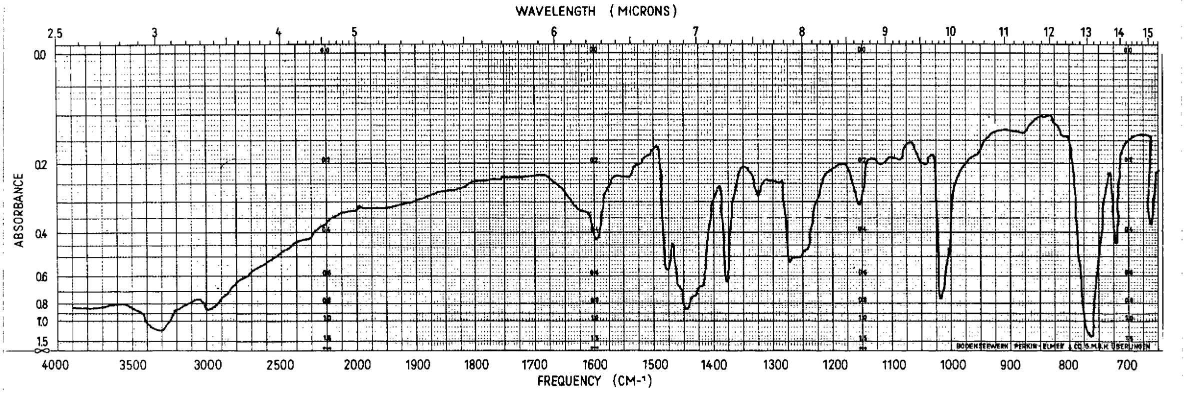


Fig. 4.82

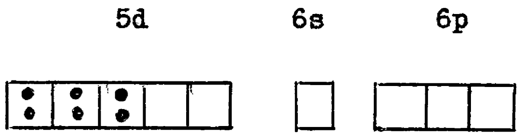
From the above spectra it can readily be seen that the thiocyanato chloride complex differs from the chloro chloride compound by bands at 2085 cm^{-1} (ν_2) and 820 cm^{-1} (ν_1). On the basis of the above discussion ν_2 can be attributed to the symmetrical CN stretching, and ν_1 to the CS stretching. The CS band occurs in the middle of the region (780 - 860 cm^{-1}) expected (104) for a M-N bond.

The CN bond is also in the region (2060 - 2105 cm^{-1}) found for nitrogen bonding in organic isothiocyanates, R-NCS $^{(105)}$.

The infra red evidence therefore suggests that in the above complex the osmium atom is bonded to nitrogen rather than sulphur. This result may be explained by a similar argument to that used by Turco and Pecile $^{(104)}$ for the substituted platinium and palladium complexes. These authors found that whereas $K_2Pt(SCN)_4$ and $K_2Pd(SCN)_4$ showed a CS stretching frequency in agreement with MS bonding ($\hat{\nu}_1$ = 697 cm^{-1}, 703 cm^{-1} respectively), the complexes formed when two thiocyanato groups were replaced by trialkyl phosphine molecules (i.e. $Pt(PR_3)_2(NCS)_2$; $Pd(PR_3)_2(NCS)_2$) have CS stretching frequencies indicative of MN bonds. This change from MS to MN bonding was explained by considering that strong π-electron acceptors such as PR_3 form strong π bonds with electrons from the metal $d(t_{2g})$ orbitals. This decreases the availability of these electrons for forming π bonds to the sulphur atom of the thiocyanato group. This mechanism would reduce the stability of the MS bond resulting from such $d_\pi - d_\pi$ interactions and the authors consider that a stage is reached in such heavy metal complexes where a change over from MS to MN bonding can occur.

A similar interpretation can be applied to the [Os NCS dipy tpy]Cl molecule. The osmium(II) atom contains six 5d electrons, which, due to the strong ligand field, are paired in the three d(t_{2g}) orbitals to give a diamagnetic molecule.

$[\mathrm{Os\ NCS\ dipy\ tpy}]^+$



It is just these d(t_{2g}) orbitals which have the correct symmetry and directional characteristics to form π bonds to surrounding ligands (106). Since the stability of the dipyridyl and terpyridyl complexes of osmium(II) has been attributed to the formation of strong π bonds (c.f. section 2.1, page 16) it would be expected that the six metal d(t_{2g}) electrons would be primarily involved in the formation of such bonds to the terpyridyl and dipyridyl ligands in [Os NCS dipy tpy]Cl. They would therefore be less available for bonding with the vacant π orbitals on the sulphur atom of the thiocyanate group. It is therefore reasonable to expect that in this complex molecule an Os-NCS bond is preferred as co-ordination through the nitrogen atom does not depend to such a large extent on the formation of a strong π component.

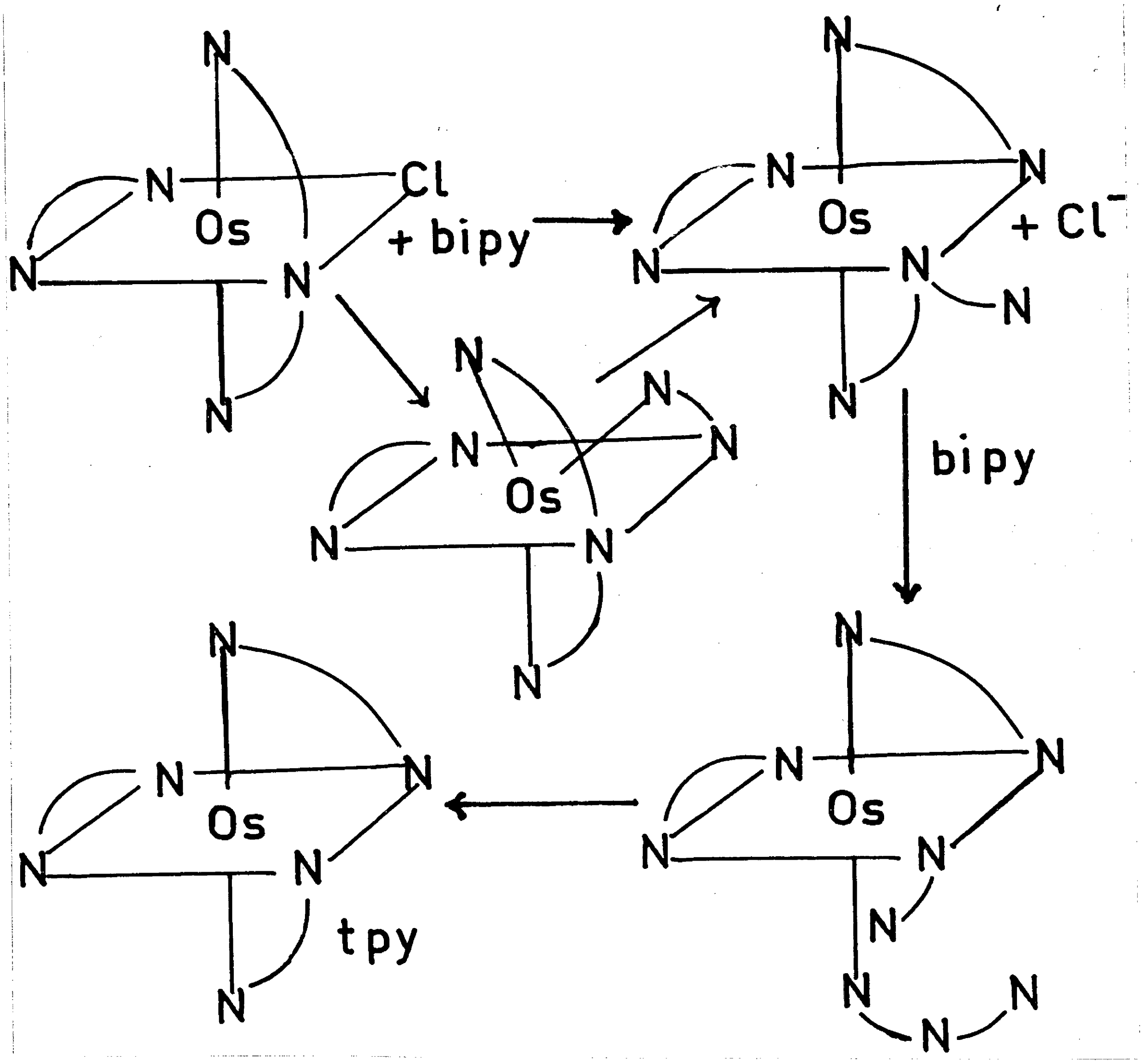
4.9 ATTEMPTED PREPARATION OF A 7-COVALENT OSMIUM COMPLEX

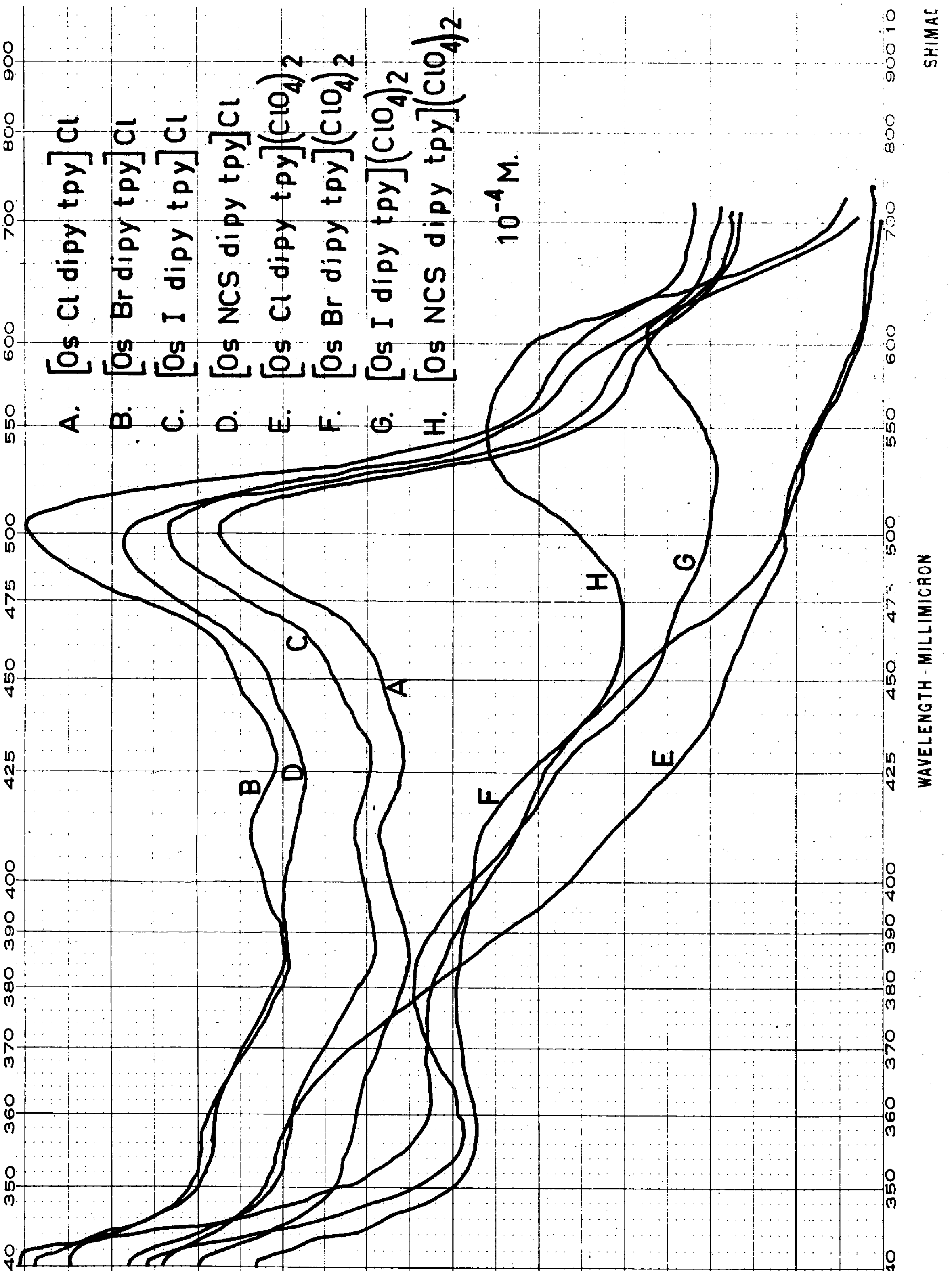
In 1955 Dwyer and Hogarth found that treatment of bis-(β-aminoethylamido)ethylenediamineosmium(IV) iodide, $[\mathrm{Os\ en\ (en{-}H)_2}]\mathrm{I}$, with anhydrous ethylenediamine at 100° in the absence of oxygen gave rise to a deep green solution from which was isolated a compound containing four ethylenediamine molecules (23). These authors present evidence which indicates that all four ethylenediamines act as bidentate ligands and that the isolated compound was an 8-covalent complex of osmium(IV). It was suggested to the present author by Professor Dwyer that a similar reaction might occur if chlorodipyridylterpyridylosmium(II) chloride is reacted with phenanthroline or bipyridine, resulting in the replacement of the chlorine atom by the chelate group with the formation of a 7-covalent osmium complex.

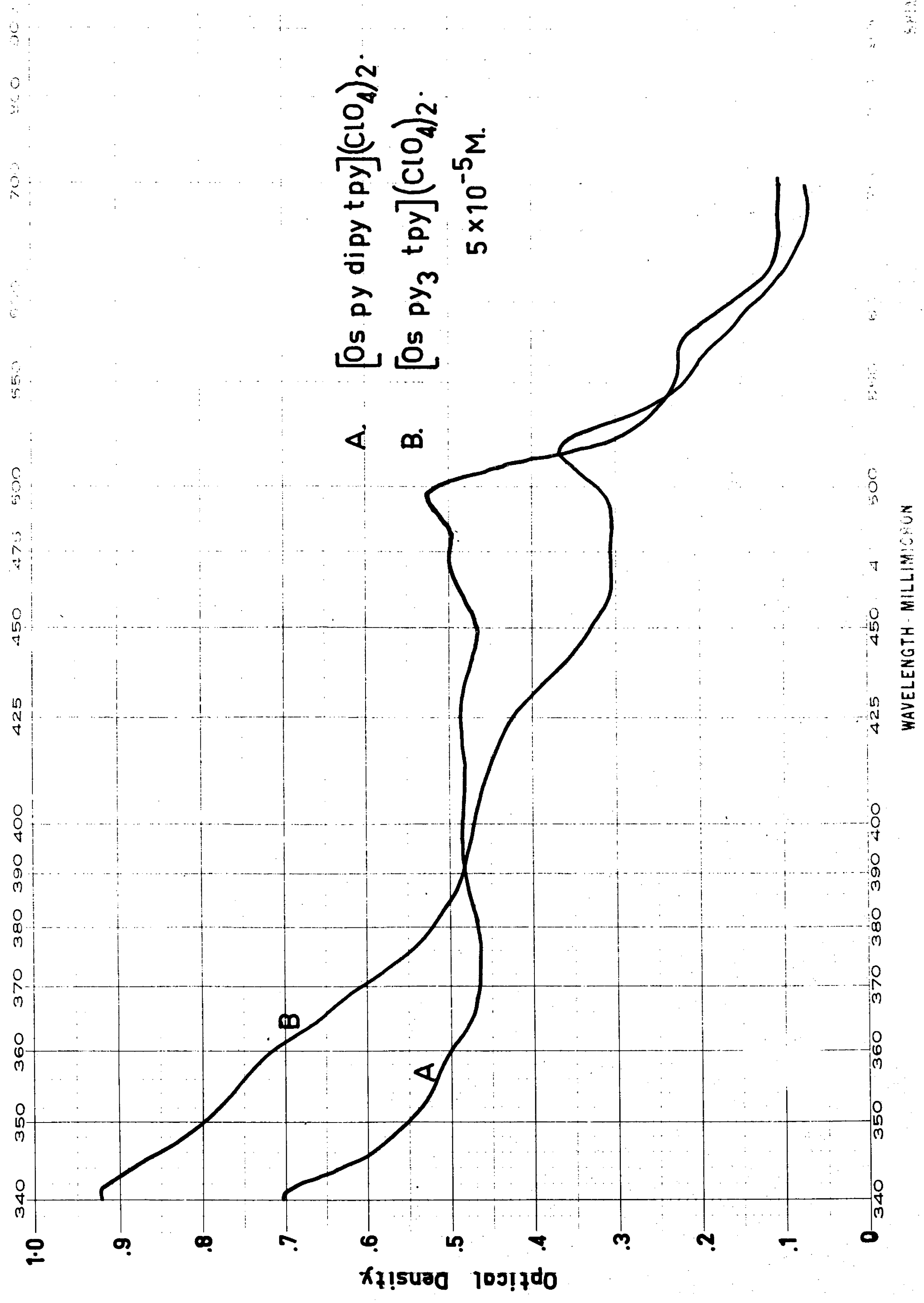
When chlorodipyridylterpyridylosmium(II) chloride was reacted with bipyridine in aqueous alcoholic solution no color change had occurred after 48 hours refluxing. When a similar reaction was carried out in an ethylene glycol/glycerol mixture a brownish-green product formed from which the green tris(dipyridyl) osmium(II) ion, and unreacted starting material, were isolated.

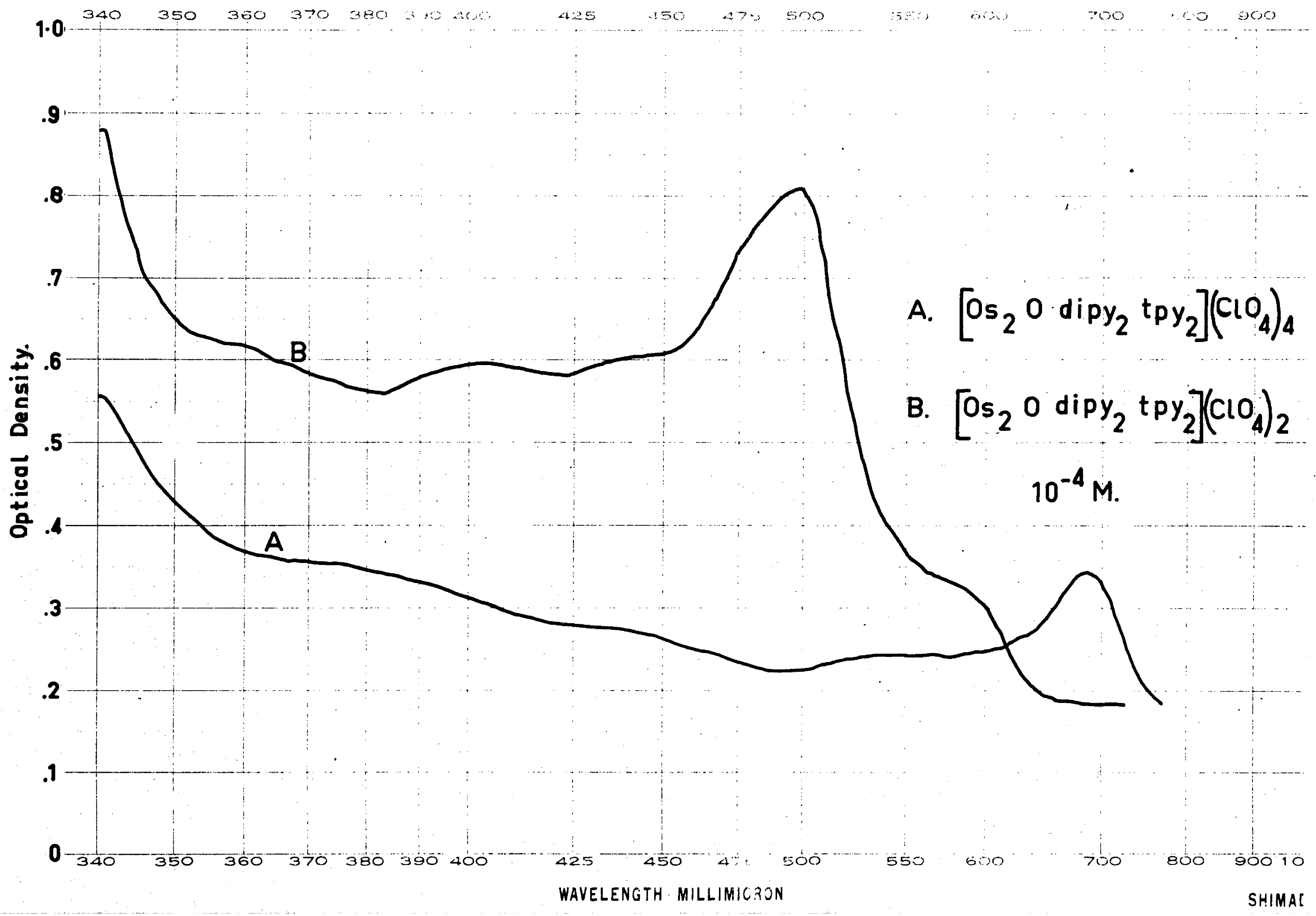
$$[\mathrm{Os\ Cl\ dipy\ tpy}]\mathrm{Cl} + 2\ \mathrm{dipy} \longrightarrow [\mathrm{Os\ dipy_3}]\mathrm{Cl_2} + \mathrm{tpy}$$

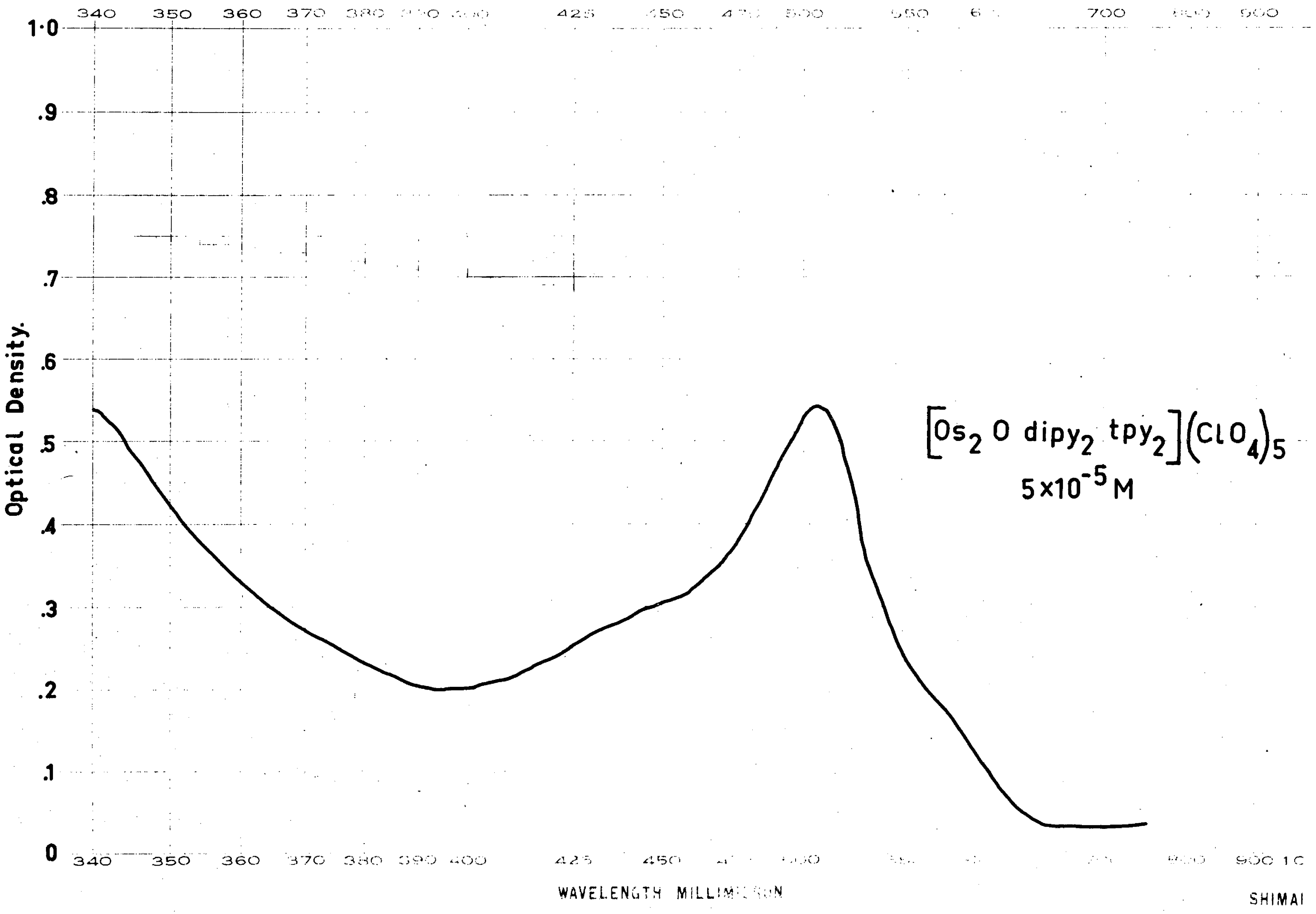
It is evident that chelation of bipyridine produces either an unstable 7-covalent intermediate which breaks down with exclusion of terpyridine, or that a bimolecular attack takes place in which chelation of bipyridine is accompanied by displacement of terpyridine to give products. A possible mechanism for replacement of the terpyridyl ligand is shown below.




A. [Os Cl dipy tpy] Cl
B. [Os Br dipy tpy] Cl
C. [Os I dipy tpy] Cl
D. [Os NCS dipy tpy] Cl
E. [Os Cl dipy tpy] (ClO4)2
F. [Os Br dipy tpy] (ClO4)2
G. [Os I dipy tpy] (ClO4)2
H. [Os NCS dipy tpy] (ClO4)2
10-4 M.
A
B
C
D
E
F
G
H
Optical Density.
1·0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
WAVELENGTH - MILLIMICRON
340
350
360
370
380
390
400
425
450
475
500
550
600
700
800
900
1000
SHIMA


A. [Os py dipy tpy](ClO$_4$)$_2$.
B. [Os py$_3$ tpy](ClO$_4$)$_2$.
5×10^{-5}M.
A
B
Optical Density
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1·0
WAVELENGTH- MILLIMICRON
340
350
360
370
380
390
400
425
450
475
500
550
700


A. $[Os_2O\,dipy_2\,tpy_2](ClO_4)_4$
B. $[Os_2O\,dipy_2\,tpy_2](ClO_4)_2$
10^{-4} M.
A
B
Optical Density.
1·0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
340
350
360
370
380
390
400
425
450
475
500
550
600
700
800
900
WAVELENGTH MILLIMICRON
SHIMAI



$[Os_2O\,dipy_2\,tpy_2](ClO_4)_5$
5×10^{-5} M

4.10 EXPERIMENTAL

Trichloroterpyridylosmium(III)

Potassium hexachloroosmate(IV) (1 g.) was suspended in dimethylformamide (20 ml.) and refluxed with terpyridine (0.53 g.) for two hours. The K_2OsCl_6 rapidly dissolves to give a reddish solution, which slowly turns red-brown and crystals of potassium chloride are precipitated. When cold, the potassium chloride was filtered off and ethanol (20 ml.) added to the filtrate. On adding ether, and scratching, a fine brown powder of trichloroterpyridylosmium(III) deposited. This was separated on a glass filter, washed with distilled water, ethanol, and ether, and dried at 40°. (Yield 0.83 g. 75%)

Trichloroterpyridylosmium(III) is insoluble in water and chloroform, slightly soluble in methanol, and more soluble in dimethylformamide to give a brown solution.

Analysis:

Calculated for $[Os\,Cl_3\,tpy]$	N, 7.93;	Cl, 20.1
Found	N, 7.95;	Cl, 20.5

Chlorobis(pyridine)terpyridylosmium(II) iodide

Trichloroterpyridylosmium(III) (0.4 g.) was suspended in ethylene glycol (10 ml.) and refluxed with pyridine (1 ml.) for 30 minutes. The non-electrolyte slowly dissolved to give a brown solution. The reaction mixture was evaporated to dryness on a steam-bath, the residue dissolved in distilled water (20 ml.), filtered, and sodium iodide added to the ice-cold solution. Chlorobis(pyridine)terpyridylosmium(II) iodide immediately precipitated as brown micro-crystals, which were washed with iced water and a small amount of ice cold ethanol. The product was recrystallised from hot water and sodium iodide, and dried at 40°. [Os Cl py_2 tpy]I is soluble in warm water, methanol and ethanol to give orange-brown solutions.

Analysis:

Calculated for [Os Cl py_2 tpy]I.H_2O	N, 9.2;	Halogen 21.3
Found	N, 9.0;	Halogen 21.5

Chlorobis(pyridine)terpyridylosmium(II) chloride

Chlorobis(pyridine)terpyridylosmium(II) iodide (0.2 g.) was suspended in hot water (20 ml.) and shaken with excess silver chloride for 10 minutes. The silver halides were filtered off and the filtrate evaporated to dryness on the steam-bath. The product was dissolved in distilled water (5 ml.), filtered, and chlorobis(pyridine)terpyridylosmium(II) chloride crystallised by addition of sodium chloride to the ice cold filtrate. The dark brown micro-crystals were washed with ice-cold dilute hydrochloric acid, ether, and dried at 40°.

The product is very soluble in water, methanol and ethanol to give red-brown solutions. A $^{M}/1000$ aqueous solution had a conductivity of 99.6 $ohms^{-1}$, indicative of a 1:1 electrolyte.

Analysis:

Calculated for $[Os\ Cl\ py_2\ tpy]Cl.H_2O$ N, 10.5; Cl, 10.6

Found N, 10.2; Cl, 10.8

Chlorobis(pyridine)terpyridylosmium(III) perchlorate

Chlorobis(pyridine)terpyridylosmium(II) chloride (0.15 g.) was dissolved in water (10 ml.) and oxidised with chlorine gas when the solution turned a light yellow-orange of the osmium(III) complex ion. Perchloric acid (70%) was added dropwise to the ice-cold filtered solution when light yellow-orange crystals of chlorobis(pyridine)terpyridylosmium(III) perchlorate separated on scratching. These were washed with ice-cold dilute perchloric acid and ether, and dried at 40°. A $^{M}/1000$ aqueous solution had a conductivity of 190.2 $ohms^{-1}$ indicative of a 2:1 electrolyte.

Analysis:

Calculated for $[Os\ Cl\ py_2\ dipy](ClO_4)_2.H_2O$ N, 8.4

Found N, 8.4

Tris(pyridine)terpyridylosmium(II) perchlorate

Trichloroterpyridylosmium(III) (0.25 g.) was refluxed with pyridine (2 ml.) in ethylene glycol for 1 hour. The red-brown solution was poured into water (200 ml.) and refluxed with ethanol (20 ml.) and pyridine (2 ml.) for 80 hours, by which time the solution had turned dark brown. This was evaporated to dryness on a steam-bath and the residue dissolved in water (20 ml.) and filtered. On adding sodium perchlorate to the ice-cold solution, tris(pyridine)terpyridylosmium(II) perchlorate crystallised as dark brown prisms. These were recrystallised from hot water and sodium perchlorate, collected on a glass filter and washed with a small quantity of ice-cold water and dried at 40°.

Tris(pyridine)terpyridylosmium(II) perchlorate is soluble in water, methanol, and ethanol to give dark brown solutions. A $^{M}/1000$ aqueous solution had a conductivity of 197.2 $ohms^{-1}$ indicating a 1:2 electrolyte.

Analysis:

Calculated for $[Os\ py_3\ tpy](ClO_4)_2.2H_2O$	N, 9.4;	Cl, 7.9
Found	N, 9.3;	Cl, 8.2

Tris(pyridine)terpyridylosmium(III) perchlorate

Tris(pyridine)terpyridylosmium(II) perchlorate (0.15 g.) was suspended in warm water (10 ml.) and oxidised with chlorine until it had dissolved to give a green solution. Perchloric acid (70%) was added dropwise to the ice-cold filtered solution, when light green crystals of tris(pyridine)terpyridylosmium(III) perchlorate formed on scratching. These were removed on a glass filter, and washed with ice-cold dilute perchloric acid and ether, and dried at 40°.

Analysis:

Calculated for $[Os\ py_3\ tpy](ClO_4)_3.H_2O$	N, 8.6
Found	N, 8.7

Chlorodipyridylterpyridylosmium(II) chloride

(a) From Tetrachlorodipyridylosmium(IV) in Aqueous Ethanolic Solution [Os Cl_4 dipy] (1.77 g.) was suspended in water (100 ml.) and ethanol (40 ml.), and terpyridine (1 g.) was added. The mixture was refluxed with sodium hypophosphite (2 ml.) for 48 hours by which time it had turned red-brown. The ethanol was evaporated off on a steam-bath and the solution filtered. Concentrated hydrochloric acid was added to the ice-cold solution (100 ml.) when fine dark almost black crystals of chlorodipyridylterpyridylosmium(II) chloride immediately deposited on scratching. The product was washed with dilute hydrochloric acid, and recrystallised from hot water and hydrochloric acid. The dark plates were washed with iced water and dried at 40°. (Yield 1.5 g.)

(b) From Potassium Tetrachlorodipyridylosmate(III) in Aqueous Ethanolic Solution K[Os Cl_4 dipy] (0.5 g.) was dissolved in water (40 ml.) and ethanol (10 ml.) and refluxed with terpyridine (0.25 g.) for 12 hours, by which time reduction to the brick-red $[Os\ Cl\ dipy\ tpy]^+$ ion had occurred. Excess ethanol was removed on a steam-bath, and the complex chloride separated as in (a) above. (Yield 0.5 g.)

(c) From Tetrachlorodipyridylosmium(IV) in Ethylene Glycol

[Os Cl_4 dipy] (1 g.) and terpyridine (0.5 g.) were refluxed in ethylene glycol (10 ml.) for 30 minutes. On reaching the boiling point the solution quickly turned deep red which did not alter on further refluxing. Ethanol (20 ml.) was added to the cold solution, and chlorodipyridylterpyridylosmium(II) chloride precipitated on addition of ether. The product was recrystallised from hot water and hydrochloric acid, as in (a) above. (Yield 1.2 g., 86%)

Chlorodipyridylterpyridylosmium(II) chloride is soluble in water, methanol, and ethanol to give brick red solutions. A $^{M}/1000$ aqueous solution had a conductivity of 97 ohms^{-1} characteristic of a 1:1 electrolyte.

Analysis:

Calculated for [Os Cl dipy tpy] Cl.H_2O	N, 10.5; Cl, 10.6
Found	N, 10.5; Cl, 10.4

Chlorodipyridylterpyridylosmium(II) bromide

[Os Cl dipy tpy]Cl was dissolved in hot water (90°) and excess sodium bromide added to the hot solution. On cooling in an ice-bath, dark, almost black micro-crystals of the chlorobromide complex formed. These were washed with dilute sodium bromide solution and iced water, and dried at 40°.

Analysis:

Calculated for [Os Cl dipy tpy] Br.H_2O	Halogen 16.1
Found	Halogen 16.1

Chlorodipyridylterpyridylosmium(II) iodide

This was prepared in a similar manner to the above bromide, by adding sodium iodide to a hot solution of [Os Cl dipy tpy]Cl. The iodide crystallised as dark prisms which were only slightly soluble in water to give a brick-red solution.

Analysis:

Calculated for [Os Cl dipy tpy] I.H_2O	Halogen 21.4
Found	Halogen 21.5

Bromodipyridylterpyridylosmium(II) bromide

Chlorodipyridylterpyridylosmium(II) bromide (0.7 g.) was suspended in ethylene glycol (5 ml.), and sodium bromide (0.5 g.) added. The solution was refluxed for 40 minutes, then evaporated to dryness on the steam-bath. The residue was dissolved in the minimum volume of hot water, filtered, and sodium bromide added to the hot filtrate. Bromodipyridylterpyridylosmium(II) bromide crystallised as dark plates on cooling in an ice-bath. The product was recrystallised from methanol/ether and dried at 40°.

Analysis:

Calculated for [Os Br dipy tpy] Br.H_2O	N, 9.2;	Br 21.0
Found	N, 9.5;	Br 21.0

Bromodipyridylterpyridylosmium(II) chloride

Bromodipyridylterpyridylosmium(II) bromide (0.5 g.) was suspended in warm water (50 ml., 40°) and shaken with excess silver chloride for 15 minutes. The silver halides were filtered off and the volume of the filtrate reduced to 15 ml. on the steam-bath. Addition of concentrated hydrochloric acid to the ice-cold solution resulted in dark plates of bromodipyridylterpyridylosmium(II) chloride.

These were washed with ice-cold dilute hydrochloric acid, a small quantity of iced water and finally ether, and dried at 40°.

Analysis:

Calculated for [Os Br dipy tpy]Cl.$2H_2O$	N, 9.6;	Halogen 15.7
Found	N, 9.7;	Halogen 15.4

Iododipyridylterpyridylosmium(II) iodide

Chlorodipyridylterpyridylosmium(II) iodide (0.5 g.) was suspended in ethylene glycol (5 ml.) and solid sodium iodide (0.5 g.) added. The solution was refluxed for 35 minutes then poured into water (20 ml.). Addition of excess sodium iodide resulted in the complete precipitation of the complex iodo iodide, which was separated and washed with iced water and ether. It was recrystallised from methanol/ether to give fine, almost black, micro-crystals which were dried at 40°. (Yield 0.5 g.)

The product is slightly soluble in cold water to give a brick-red solution.

Analysis:

Calculated for [Os I dipy tpy]I	N, 8.4;	I, 30.4
Found	N, 8.5;	I, 30.0

Iododipyridylterpyridylosmium(II) chloride

Iododipyridylterpyridylosmium(II) iodide (0.4 g.) was suspended in warm water (50 ml., 40°) and methanol (4 ml.) and shaken with excess silver chloride for 15 minutes. The silver halides were removed and the volume of the filtrate reduced to 15 ml. on the steam-bath. After filtration, addition of concentrated hydrochloric acid to the ice-cold solution resulted in black micro-crystals of iododipyridylterpyridylosmium(II) chloride. These were washed with ice-cold dilute hydrochloric acid, a small quantity of iced water and finally ether. The product was recrystallised from methanol/ether and dried at 40°.

Analysis:

Calculated for [Os I dipy tpy]Cl	N, 9.4; Halogen 21.9
Found	N, 9.4; Halogen 22.1

Isothiocyanatodipyridylterpyridylosmium(II) thiocyanate

Chlorodipyridylterpyridylosmium(II) chloride (0.5 g.) was suspended in ethylene glycol (3 ml.) and potassium thiocyanate (0.5 g.) added. The mixture was refluxed for 35 minutes then poured into an aqueous potassium thiocyanate solution. On cooling in an ice-bath, the product crystallised and was removed on a glass filter, washed with dilute potassium thiocyanate solution and iced water, and dried. The product was recrystallised by dissolving in the minimum volume of warm methanol, filtering,reducing the volume to 30 ml. and slowly adding ether. On scratching, isothiocyanatodipyridylterpyridylosmium(II) thiocyanate formed as black micro-crystals which are moderately soluble in warm water to give a red-brown solution, similar in color to the other halo osmium(II) complexes.

Analysis:

Calculated for [Os NCS dipy tpy]CNS.H_2O N, 13.7

Found N, 13.4

Isothiocyanatodipyridylterpyridylosmium(II) chloride

Isothiocyanatodipyridylterpyridylosmium(II) thiocyanate (0.5 g.) was suspended in water (50 ml., 40°) and methanol (4 ml.) and shaken with excess silver chloride for 15 minutes. The silver halides were removed and the filtrate evaporated to dryness with a stream of air. The residue was dissolved in the minimum volume of warm water (10 ml.), filtered, and the complex isothiocyanato chloride crystallised by adding sodium chloride to the ice-cold solution. The product was removed on a glass filter, washed with a small quantity of ice-cold dilute hydrochloric acid, iced water, and ether, and dried at 40°.

A $^{M}/1000$ aqueous solution had a conductivity of 103 ohms^{-1} indicating a 1:1 electrolyte.

Analysis:

Calculated for [Os NCS dipy tpy] Cl.$2H_2O$ N, 11.9

Found N, 11.7

Nitritodipyridylterpyridylosmium(II) iodide

Chlorodipyridylterpyridylosmium(II) chloride (0.2 g.) was refluxed in ethylene glycol (3 ml.) with excess sodium nitrite (0.2 g.) for 3 minutes, by which time the color had changed from red-brown to orange-brown. Further heating displaces dipyridyl and reduces the yield. The warm mixture was poured into an aqueous solution of sodium iodide, when nitritodipyridylterpyridylosmium(II) iodide crystallised on cooling in an ice-bath and scratching. The impure product was washed with sodium iodide solution, a small quantity of iced water, and finally ether. It was recrystallised from hot water by the addition of sodium iodide and dried at 35°.

Analysis:

Calculated for [Os NO_2 dipy tpy] I.$2H_2O$	I, 16.1;	N, 10.7
Found	I, 16.2;	N, 10.5

Chlorodipyridylterpyridylosmium(III) chloride

Chlorodipyridylterpyridylosmium(II) chloride (0.2 g.) was suspended in warm water (5 ml.) and chlorine gas bubbled through the solution until the color had changed from red-brown to orange-brown. The solution was evaporated to dryness on a steam-bath and the residue dissolved in the minimum volume of ethanol and filtered. On addition of ether to the ice-cold solution and scratching, light brown micro-crystals of chlorodipyridylterpyridylosmium(III) chloride formed. The product was collected on a glass filter, washed with ether, and dried at 40°.

Chlorodipyridylterpyridylosmium(III) chloride is very soluble in water to give an orange-brown solution. A $^{M}/1000$ aqueous solution had a conductivity of 195.3 $ohms^{-1}$ indicating a 1:2 electrolyte.

Analysis:

Calculated for [Os Cl dipy tpy] $Cl_2 \cdot H_2O$ N, 9.9; Cl, 15.1

Found N, 9.8; Cl, 15.0

Chlorodipyridylterpyridylosmium(III) perchlorate

[Os Cl dipy tpy] Cl (0.3 g.) was oxidized with chlorine as described above, and to the ice-cold filtered solution several drops of perchloric acid added. On scratching brown micro-crystals of the osmium(III) perchlorate formed. These were washed on a glass filter with ice-cold dilute perchloric acid and ether, and dried at 40°. The complex perchlorate is soluble in water, methanol, and ethanol to give orange-brown solutions.

Analysis:

Calculated for [Os Cl dipy tpy]$(ClO_4)_2 \cdot H_2O$ N, 8.4

Found N, 8.4

Bromodipyridylterpyridylosmium(III) bromide

To a solution of [Os Br dipy tpy] Br (0.5 g.) in water (20 ml.) was added hydrobromic acid (5 ml., 47%) which contained free bromine and the solution evaporated to dryness on a steam bath. The bromine oxidized the complex to the osmium(III) state. This was repeated with a further quantity of hydrobromic acid to ensure complete oxidation and the light brown residue recrystallised from ethanol/ether as described above for the analogous osmium(III) chloro complex. Bromodipyridylterpyridylosmium(III) bromide is soluble in water, methanol, and ethanol, to give orange-red solutions.

A $^{M}/1000$ aqueous solution had a conductivity of 200.1 ohms^{-1} indicating a 1:2 electrolyte.

Analysis:

Calculated for [Os Br dipy tpy] $Br_2.H_2O$	N, 8.4; Br, 28.4
Found	N, 8.5; Br, 28.1

Bromodipyridylterpyridylosmium(III) perchlorate

[Os Br dipy tpy]Cl (0.2 g.) was dissolved in warm water (15 ml.) and cooled in an ice-bath. Dilute nitric acid (3 drops, 3N) and a small quantity of cerium(IV) ammonium nitrate were added and the solution stirred vigorously. The orange-brown osmium(III) complex ion was separated by adding sodium perchlorate and scratching, when light brown micro-crystals formed. These were separated on a glass filter, washed with dilute perchloric acid and ether, and dried at 40°.

Analysis:

Calculated for [Os Br dipy tpy]$(ClO_4)_2$	N, 8.15
Found	N, 8.1

Iododipyridylterpyridylosmium(III) perchlorate

A solution of iododipyridylterpyridylosmium(II) chloride (0.15 g.) in water (30 ml.) was cooled in an ice-bath and dilute nitric acid (4 drops, 3N) and excess cerium(IV) ammonium nitrate added. The solution was stirred vigorously until the color had changed to a deep green, filtered, and sodium perchlorate added to the filtrate. On scratching light green crystals of iododipyridylterpyridylosmium(III) perchlorate formed which were separated on a glass filter, washed with ice-cold dilute perchloric acid and ether, and dried at 40°.

The complex could be recrystallised from hot water and sodium perchlorate. A $^{M}/1000$ solution in water had a conductivity of 212.5 $ohms^{-1}$ indicating a 1:2 electrolyte.

Analysis:

Calculated for $[Os\ I\ dipy\ tpy](ClO_4)_2$ N, 7.7

Found N, 7.8

Isothiocyanatodipyridylterpyridylosmium(III) perchlorate

To a solution of $[Os\ NCS\ dipy\ tpy]Cl$ (0.15 g.) in water (35 ml.) was added nitric acid (2 drops, 3N) and immediately excess cerium(IV) ammonium nitrate, and the solution stirred vigorously. The dichroic, purple-red solution which formed was cooled in an ice-bath and sodium perchlorate added, when on scratching dark green crystals of the complex perchlorate formed. These were separated on a glass filter, washed with dilute perchloric acid and ether, and dried at 40°. The product was recrystallised from hot water by addition of sodium perchlorate and separated as above. A $^{M}/1000$ aqueous solution had a conductivity of 215.3 $ohms^{-1}$.

Analysis:

Calculated for $[Os\ NCS\ dipy\ tpy](ClO_4)_2.H_2O$ N, 9.8

Found N, 9.9

Pyridinedipyridylterpyridylosmium(II) iodide

[Os Cl dipy tpy]Cl (0.5 g.) was suspended in water (20 ml.) and redistilled pyridine (4 ml.) added. On refluxing, the solution gradually changed from red-brown to a deep brown color, the reaction being complete in 48 hours. The solution was evaporated to dryness on a steam-bath, the residue dissolved in water (15 ml.) and sodium iodide added to the filtered ice-cold filtrate. On scratching, dark brown crystals of pyridinedipyridylterpyridylosmium(II) iodide formed which were separated on a glass filter, washed with a small quantity of ice-cold sodium iodide solution, iced water, and dried at 40°. The product was recrystallised from hot water by addition of sodium iodide. Pyridinedipyridylterpyridylosmium(II) iodide is soluble in water, methanol, ethanol, and dimethylformamide to give brown solutions. A $^{M}/1000$ aqueous solution had a conductivity of 192 ohms^{-1} indicating a 1:2 electrolyte.

Analysis:

Calculated for [Os py dipy tpy] $I_2 \cdot H_2O$	N, 9.0;	I, 27.2
Found	N, 9.1;	I, 27.1

Pyridinedipyridylterpyridylosmium(II) perchlorate

Addition of sodium perchlorate to a warm aqueous solution of the above iodide resulted in the formation of dark brown crystals of the complex perchlorate. Crystallisation was encouraged by cooling in an ice-bath, and the filtered product washed with a small quantity of iced water, and dried at 40°.

Analysis:

Calculated for $[\mathrm{Os\ py\ dipy\ tpy}](\mathrm{ClO_4})_2 \cdot \mathrm{H_2O}$	N, 9.6
Found	N, 9.6

3-methylpyridinedipyridylterpyridylosmium(II) perchlorate

[Os Cl dipy tpy] Cl (0.4 g.) was suspended in water (15 ml.) and ethanol (2 ml.) and freshly distilled (140.3°/716.2 mm B.D.H.) β-picoline (2 ml.) added. The solution was refluxed for 48 hours and evaporated to dryness on a steam-bath. The residue was dissolved in distilled water (15 ml.), filtered, and sodium perchlorate added to the ice-cold filtrate. On scratching dark brown crystals of the complex perchlorate immediately separated. These were collected on a glass filter, washed with ice-cold dilute sodium perchlorate solution, iced water and finally ether. The complex was recrystallised by dissolving in the minimum volume of dimethylformamide, filtering, adding an equal volume of ethanol and crystallising out with ether. Drying was at 40°. (Yield 0.37 g.)

Analysis:

Calculated $[\mathrm{Os\ CH_3py\ dipy\ tpy}](\mathrm{ClO_4})_2$	N, 9.6
Found	N, 9.7

4-methylpyridineterpyridylosmium(II) perchlorate

This was prepared as above using freshly distilled

(140°/710 mm "Lights") γ-picoline, and the product recrystallised from ethanol/ether.

Analysis:

Calculated [Os CH_3py dipy tpy]$(ClO_4)_2$ N, 9.6

Found N, 9.8

4-ethylpyridinedipyridylterpyridylosmium(II) perchlorate

This was prepared in a similar manner using freshly distilled 4-ethylpyridine (162.4°/714 mm "Monsanto chemicals") and the product recrystallised from dimethylformamide/ethanol by adding ether.

Analysis:

Calculated for [Os C_2H_5py dipy tpy]$(ClO_4)_2$ N, 9.5

Found N, 9.8

4-isopropylpyridinedipyridylterpyridylosmium(II) perchlorate

This was prepared using redistilled 4-isopropylpyridine (176.5-177.5°/118 mm "Monsanto chemicals") and the product recrystallised from dimethylformamide/ethanol/ether.

Analysis:

Calculated for [Os C_3H_7 dipy tpy]$(ClO_4)_2$ N, 9.3

Found N, 9.4

Pyridinedipyridylterpyridylosmium(III) perchlorate

[Os py dipy tpy]$(ClO_4)_2$ (0.2 g.) was suspended in distilled water (15 ml.) and warmed to 70°. Chlorine was bubbled through the solution which quickly turned a dichroic green-red color of the osmium(III) complex cation. Perchloric acid was added to the filtered solution, and on scratching and cooling in an ice-bath, dark green crystals of pyridinedipyridylterpyridylosmium(III) perchlorate separated. These were removed on a glass filter, washed with a small quantity of ice-cold dilute perchloric acid and ether, and dried at 40°.

[Os py dipy tpy]$(ClO_4)_3$ is soluble in water to give a light green-red solution. A $^M/1000$ solution had a conductivity of 298.1 ohms^{-1} indicating a 1:3 electrolyte.

Analysis:

Calculated for [Os py dipy tpy]$(ClO_4)_3 2H_2O$ N, 8.5

Found N, 8.4

3-methylpyridinedipyridylterpyridylosmium(III) perchlorate
4-methylpyridinedipyridylterpyridylosmium(III) perchlorate
4-ethylpyridinedipyridylterpyridylosmium(III) perchlorate
4-isopropylpyridinedipyridylterpyridylosmium(III) perchlorate

These osmium(III) complex perchlorates were prepared by oxidation of the respective osmium(II) complex perchlorates as described above for the unsubstituted pyridine compound.

Nitrogen Analyses:	Calculated	Found
[Os 3-CH_3py dipy tpy]$(ClO_4)_3.2H_2O$	8.3	8.3
[Os 4-CH_3py dipy tpy]$(ClO_4)_3.2H_2O$	8.3	8.6
[Os 4-C_2H_5py dipy tpy]$(ClO_4)_3.2H_2O$	8.2	8.2
[Os 4-C_3H_7py dipy tpy]$(ClO_4)_3.2H_2O$	8.1	8.3

Acetonitriledipyridylterpyridylosmium(II) perchlorate

[Os Cl dipy tpy]Cl (0.5 g.) was dissolved in water (20 ml.) and ethanol (4 ml.) and refluxed with acetonitrile (2 ml.) for 48 hours. The brown solution was evaporated to dryness, the residue dissolved in distilled water (10 ml.), filtered, and sodium perchlorate added to the filtrate. On cooling in an ice-bath dark brown crystals of acetonitrile-dipyridylterpyridylosmium(II) perchlorate formed. These were removed on a glass filter, washed with dilute ice-cold sodium perchlorate solution, and iced water. The product was recrystallised from hot water by addition of sodium perchlorate and dried at 35°. (Yield 0.37 g.)

$[Os\ CH_3CN\ dipy\ tpy](ClO_4)_2$ is soluble in warm water to give a dark brown solution. A $^{M}/1000$ aqueous solution had a conductivity of 196.6 $ohms^{-1}$ indicative of a 1:2 electrolyte.

Analysis:

Calculated for $[Os\ CH_3CN\ dipy\ tpy](ClO_4)_2 \cdot H_2O$	N, 10.0
Found	N, 10.2

Propionitriledipyridylterpyridylosmium(II) perchlorate

This was prepared from [Os Cl dipy tpy]Cl (0.5 g.) in a similar manner to that described above. (Yield 0.36 g.)

Analysis:

Calculated for $[Os\ C_2H_5CN\ dipy\ tpy](ClO_4)_2 \cdot H_2O$	N, 9.85
Found	N, 9.8

Acetonitriledipyridylterpyridylosmium(III) perchlorate

$[Os\ CH_3CN\ dipy\ tpy](ClO_4)_2$ (0.15 g.) was dissolved in warm water (10 ml.) and the solution cooled to room temperature. Dilute nitric acid (3 drops, 3N) and excess cerium(IV) ammonium nitrate were quickly added and the solution stirred vigorously in an ice-bath. Sodium perchlorate was added to the deep green solution and on scratching dark green crystals of acetonitriledipyridylterpyridylosmium(III) perchlorate separated. These were removed on a glass filter, washed with ice-cold dilute perchloric acid and ether, and dried at 40°.

$[\mathrm{Os\ CH_3CN\ dipy\ tpy}](\mathrm{ClO_4})_3$ is very soluble in water to give a green solution which quickly turns brown, and on standing overnight, to brown-yellow. The green color of the osmium(III) complex ion could not be regenerated on addition of an oxidizing agent such as cerium(IV) ammonium nitrate.

Analysis:

Calculated for $[\mathrm{Os\ CH_3CN\ dipy\ tpy}](\mathrm{ClO_4})_3\cdot 2\mathrm{H_2O}$ N, 8.8

Found N, 8.7

Reaction between Bipyridine and Chlorodipyridylterpyridylosmium(II) chloride in ethylene glycol/glycerol Solution

[Os Cl dipy tpy]Cl (0.2 g.) and bipyridine (0.07 g.) were refluxed in an ethylene glycol/glycerol mixture for 15 minutes. The brown-green solution was evaporated to dryness on a steam-bath and the residue dissolved in water (15 ml.) and filtered. Sodium iodide was added to the ice-cold filtrate and the dark brown precipitate which immediately formed was filtered and washed with ice-cold water. It was recrystallised from hot water and sodium iodide, and an $^{M}/1000$ aqueous solution had a conductivity of 104.5 ohms^{-1} indicating a 1:1 electrolyte. The green filtrate remaining after the separation of the above compound was evaporated to 10 ml. and excess sodium perchlorate added to the ice-cold solution. Fine dark green micro-crystals separated on standing in the refrigerator overnight. These were separated, and recrystallised from hot water and sodium perchlorate. A $^{M}/1000$ aqueous solution had a conductivity of 205 ohms^{-1}. Oxidation with cerium(IV) ammonium nitrate resulted in a red solution characteristic of the tris (dipyridyl)osmium(III) cation.

Both the brick-red complex initially isolated and the dark green perchlorate were analysed. The results indicate that the former is unreacted starting material,while the latter is tris(dipyridyl)osmium(II) perchlorate.

Analysis:

Calculated for $[Os\ Cl\ dipy\ tpy]Cl.H_2O$	Cl, 10.6
Found	Cl, 10.4
Calculated for $[Os\ dipy_3](ClO_4)_2.2H_2O$	N, 9.4
Found	N, 9.4

PART II

CHAPTER FIVE

INTRODUCTION TO OXIDATION-REDUCTION POTENTIALS

5.1 DEFINITION

For two complex ions ML_x^{n+} and $ML_x^{(n+1)+}$, which have the same chemical composition, and which differ only in their charge, the potential E for the cell system,

$$\mathrm{Pt} \;\Big|\; ML_x^{n+},\ ML_x^{(n+1)+} \;\Big\|\; H^+_{a(H^+)\,=\,1} \;\Big|\; H_2(1\ \mathrm{atm.})$$

is related to the standard thermodynamic potential E_o by the expression

$$E = E_o - \frac{RT}{F} \ln \frac{a(ML_x^{(n+1)+})\ a(H_2)^{1/2}}{a(ML_x^{n+})\ a(H^+)} \qquad 5.11$$

where R = gas constant

T = absolute temperature

F = Faraday

a = activity of the ion

E_o is the potential of the system when all the ions involved in the cell reaction are at unit activity.

It is convenient to regard the measured potential E, as resulting from the two separate cell reactions which together make up the total cell reaction. E_o may then be regarded as being equal to the difference in two potentials E_o^1 and E_o^2, characteristic of the redox half-cell, and the hydrogen electrode, respectively. Equation 5.11 then becomes

$$E = \left[E_o^1 - \frac{RT}{F} \ln \frac{a(ML_x^{(n+1)+})}{a(ML_x^{n+})} \right] - \left[E_o^2 - \frac{RT}{F} \ln \frac{a(H^+)}{a(H_2)^{1/2}} \right] \qquad 5.12$$

and expresses the E.M.F. of the cell system in terms of the potentials of the separate half-cells involved. However, it is experimentally extremely difficult to measure such single electrode potentials because of the necessity of having two separate half-cells to complete the electrical circuit. Theoretically, also, single electrode potentials have no strict thermodynamic significance since their calculation involves a knowledge of the activity of individual ionic species. Because of the extensive use of such single electrode potentials it has therefore been necessary to define an arbitrary zero of potential such that at a pressure of one atmosphere and in a solution of hydrogen ions of unit activity, the potential of the reversible hydrogen electrode is zero at all temperatures. When these conditions apply, equation 5.12 reduces to

$$E = E_o^1 - \frac{RT}{F} \ln \frac{a(ML_x^{(n+1)+})}{a(ML_x^{n+})} \qquad 5.13$$

in which the potential for the cell reaction

$$ML_x^{n+} + H^+ \rightleftharpoons ML_x^{(n+1)^+} + \tfrac{1}{2} H_2$$

is related to the standard thermodynamic potential, E_o^1 characteristic only of the redox half-cell.

All potential values recorded in this thesis refer to the above cell reaction. Such potentials are termed relative single electrode potentials.

When the activities of the two complex ions, ML_x^{n+} and $ML_x^{(n+1)^+}$, are unity, the measured potential is the standard value E_o for the cell. This may be related to the overall standard free energy change, ΔG^o, by the expression, for a one electron change

$$\Delta G^o = - FE_o \qquad 5.14$$

In this way, E_o may be related to the standard enthalpy and entropy changes,

$$\Delta G^o = - FE_o = \Delta H^o - T \Delta S^o \qquad 5.15$$

5.2 REVERSIBILITY

Equation 5.14 is valid for reversible changes only, a condition rigorously fulfilled if (108)

(1) no changes take place in the cell without the passage of the current;

(2) every change which takes place during the passage of the current may be reversed by reversing the direction of the current;

(3) the net result of all the chemical changes which take place within the cell system is known.

Condition (1) implies that the potential of the cell system should be constant with respect to time. If this condition were rigorously enforced very few potential measurements could be accepted. No sharp distinction can be drawn between potentials which change rapidly with time, and slower drifts. In redox systems changes of the latter sort can usually be traced to: (a) instability of the oxidant or reductant ion towards dissociation, hydrolysis, or oxidation and reduction; (b) changes in the state of aggregation of a constituent, including precipitation; (c) action of residual oxygen, or (d) the slow accommodation of the electrode. When the system is poorly poised, as it is near 100% reduction or oxidation, or at 50% reduction when the concentrations of the cell constituents are low, the rapidity of the drift due to any one of the above causes will be accentuated.

The second condition for reversibility implies that the same potential should be found irrespective of whether the given state is reached by reducing the oxidant $ML_x^{(n+1)^+}$, oxidizing the reductant ML_x^{n+}, or by preparing the appropriate mixture of oxidant and reductant ions. It also requires that the electrodes respond quickly and definitely to the setting of the potentiometer. With an inactive, or poorly poised system, a steady potential reading is difficult to obtain. As well as depending on the reversibility of the oxidation-reduction reaction, the above conditions imply that the oxidant and reductant ions rapidly come to equilibrium with the surface of the inert electrode. The rate of attainment of this equilibrium between the redox solution and the electrode varies according to the system being studied and the electrode employed.

The last condition for reversibility results from the necessity of knowing the activities of all the ions involved in the overall cell reaction before E_o can be calculated. Provided this reaction is reversible, E_o may then be related to thermodynamic quantities by equation 5.15. Stoichiometric relations are particularly difficult to define for complex ions which undergo slow dissociation or hydrolysis in aqueous solution.

For the osmium complexes studied in this work, electron transfer between the oxidant and reductant ions is extremely fast, $(K > 10^5 M^{-1} sec^{-1})$ (109). This establishes the reversibility of the redox system

$$OsL_6^{n+} \rightleftharpoons OsL_6^{(n+1)^+} + e.$$

Osmium complexes are also coordinately saturated and are extremely stable towards dissociation or hydrolysis in aqueous solution. The reasons for this stability have been discussed in PART 1. The cell reaction is therefore extremely simple, being uncomplicated by dissociative or hydrolytic side reactions. In addition, steady potentials are rapidly established (5 mins.) using gold electrodes. This establishes the reversibility of the cell system. Platinum electrodes were found to be less reliable in this respect due to difficulty in keeping the electrode surfaces clean.

5.3 LIQUID JUNCTIONS

In the setting up of a cell system for measuring oxidation-reduction potentials of inorganic complex ions, it is necessary to employ a liquid junction between the reference and redox half-cells. Such a junction involves at potential balance, the diffusion of components from one half-cell towards the other and this gives rise to a small potential at the junction. This process is irreversible and cannot be dealt with by the theories of thermodynamic equilibria (110).

In the measurement of potentials in inorganic systems two alternatives are available to allow for the liquid junction. The junction may be set up in a reproducible manner and its potential calculated by approximate methods (111), or an attempt can be made to eliminate, or at least minimize, the junction potential. Since reproducible "continuous mixture" junctions are difficult to set up and maintain, and the junction potential involved is even more difficult to calculate, it is usual to minimize the potential by using a potassium chloride or ammonium chloride salt bridge. In such cases, the junction potential results almost entirely from the diffusion of these ions across the solution interface. Since the anion and cation of these bridge electrolytes have almost identical transference numbers in aqueous solution, the junction potential is largely eliminated. Investigations by several workers have shown that for a saturated potassium chloride bridge the liquid junction potential is probably less than 1 m.v. (112,113). Provided the concentrations of the ions in the redox half-cell are small, such a junction is reproducible (114).

5.4 MEASUREMENT OF REDOX POTENTIALS

There are very few inorganic systems for which accurate standard potentials can be obtained. This is primarily due to such systems usually having potentials outside the range in which both oxidized and reduced ions are stable in solution. The stability of a complex ion towards oxidation or reduction in aqueous solution, is determined largely by the redox potential of the couple relative to the potential of the oxygen-water couple. This latter couple is strongly pH dependent.

$$2H_2O \longrightarrow O_2 + 4H^+ (10^{-7}M) + 4e \quad E_o = - 0.815 \text{ v.}$$

If the potential of the complex couple is less negative than - 0.815 v. the reductant would be expected to oxidize in moist air or in solution. If more negative, the oxidant should reduce, and water be oxidized to oxygen. Fortunately the H_2O/O_2 couple is highly reversible, as otherwise the number of "stable" oxidation states would be very limited. Generally for systems where the potential is less negative than - 0.815 v. (e.g. $Fe(aq)^{2+}/ Fe(aq)^{3+}$; $E_o = - 0.772$v.) the reducing agent will gradually oxidize in air. However significant oxidation of water, with the liberation of oxygen, does not usually occur until the potential is more negative than about - 1.5 v. (eg. $Co(aq)^{2+}/ Co(aq)^{3+}$; $E_o = - 1.83$ v.) Within the potential range - 0.8 v. to - 1.5 v. both oxidation states of a couple are reasonably stable. With some couples outside this range both components are unstable.

The method of measuring oxidation-reduction potentials is governed largely by the potential of the system and the stability of the complex ions towards dissociation and hydrolysis. The most accurate method involves measuring the potential of a system containing equimolar amounts of the oxidized and reduced species. This is applicable only when both forms can be isolated pure in the solid state, or at least in solution. Such ideal conditions are relatively rare. If one of the forms is unstable the redox potential may be determined by adding to a solution of the stable form exactly half the equivalent amount of oxidizing or reducing agent, depending on whether the reduced or oxidized form, respectively, is the more stable. The potential is then measured at short intervals after addition of the oxidizing or reducing agent. When the potential values obtained are plotted against time, a maximum or minimum value is obtained, and this is taken as the redox potential. The third, and perhaps the most widely applied method, is the determination of the half-equivalence point in a potentiometric titration. The accuracy of this method is limited since, during the titration, the potential is continually changing and the electrode has insufficient time to reach equilibrium. In addition, if one of the forms is unstable, the stable form will be regenerated to some extent during the titration. To minimize this error the titration must be carried out relatively quickly.

The potentials of the osmium couples given in the following chapter have all been obtained by mixing equal quantities of the oxidant and reductant complex ions. The potentials all lie within the range - 0.2 to - 0.9 volts, a region in which both the oxidized and reduced ions are relatively stable in aqueous solution, under an atmosphere of nitrogen. In the presence of oxygen slow oxidation of the reductant ions would be expected to occur for couples with potentials more positive than approximately - 0.8 volts (c.f. section 5.4, page 168). Further, as discussed in PART 1, the osmium complexes are co-ordinately saturated and extremely stable towards dissociation in aqueous solution. It has therefore been possible to obtain accurate standard potential data (± 0.2 m.v.).

5.5 FACTORS GOVERNING OXIDATION-REDUCTION POTENTIALS

It is usual to consider that the introduction of a ligand L, which co-ordinates to both oxidant and reductant ions according to the reactions

$$M_{aq}^{n^+} + xL \rightleftharpoons ML_x^{n^+}$$

$$M_{aq}^{(n+1)^+} + xL \rightleftharpoons ML_x^{(n+1)^+}$$

effects a reduction in the activities of both aquated ions. It is then possible to compare the standard potential E_o for the couple $ML_x^{n+} / ML_x^{(n+1)+}$, with $E_{o(aq)}$ of the corresponding aquo couple $M_{aq}^{n+} / M_{aq}^{(n+1)+}$ using the expression (115)

$$E_{o(c)} = E_{o(aq)} - \frac{RT}{F}\left[\ln K_{n+} - \ln K_{(n+1)+}\right] \qquad 5.51$$

where K_{n+} and $K_{(n+1)+}$ are the stability constants characteristic of the reduced and oxidized complex ions.

For the systems studied in this work the complex ions do not dissociate in solution and the ligand co-ordinates irreversibly to the metal ion. $E_{o(aq)}$ for the $Os_{aq}^{2+}/Os_{aq}^{3+}$ couple is not known with any certainty ($E_o \simeq +0.4$ volts) as the simple aquated ions are incapable of existence in solution. Equation 5.51 is of no use in such systems. It is therefore desirable that a more general treatment be available to discuss the factors governing redox potentials. In the following account a general expression is developed, which expresses oxidation-reduction potentials in terms of the bond interaction energies, solvation energies, ligand field stabilization energies, and entropy changes involved. This expression willbe used in Chapter 7 in discussing the potentials obtained for various osmium couples, and an attempt made to indicate the relative significance of each factor. It is, however, of general applicability.

In section 5.1 it was shown that the oxidation-reduction potential for a complex ion couple in aqueous solution is a measure of the free energy change ΔG^o associated with the reaction,

$$ML_x^{n+}(aq) + H^+_{aq} \longrightarrow ML_{x(aq)}^{(n+1)+} + \tfrac{1}{2}H_{2(g)}$$

the two being related by the expression

$$\Delta G^o = -FE_o \qquad 5.52$$

ΔG^o may be expressed in terms of the free energy of the reactant and product ions,

$$\Delta G^o = \Delta G^o(ML_x^{(n+1)+})_{aq} - \Delta G^o(ML_x^{n+})_{aq} + \Delta G^o(\tfrac{1}{2}H_2)_g - \Delta G^o(H^+)_{aq} \qquad 5.53$$

However, since the potential of the redox system is referred to the standard hydrogen electrode, the last two terms in equation 5.53 are constant for all potential measurements. The free energy change for the redox half-cell may therefore be expressed,

$$\Delta G^o_{redox} = \Delta G^o(ML_x^{(n+1)+})_{aq} - \Delta G^o(ML_x^{n+})_{aq} \qquad 5.54$$

The observed potential thus depends on the difference in free energy between the two complex ions of the redox couple. An insight into the factors which contribute to the free energy of a complex ion may be obtained by considering the cycle shown in figure 5.51. It is important to note that the following treatment can be applied to all redox systems, irrespective of whether such changes can occur in practice. The important requirement is that a reversible equilibrium is set up between the two ions in solution. These ions may either be the simple aquated species ($L = H_2O$) or the complex ions.

$$\begin{tikzcd}
M^{m+}_{g,v} \arrow[r, shift left, "I_m"] \arrow[d, shift right, "\Delta G_c^{n+}"'] & M^{(m+1)+}_{g,v} + e_g \arrow[l, shift left] \arrow[d, shift right] \\
ML^{n+}_{x_g} \arrow[u, shift right] \arrow[d, shift right, "\Delta G^{n+}_{soln}"'] & ML^{(n+1)+}_{x_g} \arrow[u, shift right, "\Delta G_c^{(n+1)+}"'] \arrow[d, shift right] \\
ML^{n+}_{x_{aq}} \arrow[u, shift right] \arrow[r, shift left] & ML^{(n+1)+}_{x_{aq}} + e_g \arrow[l, shift left] \arrow[u, shift right, "\Delta G^{(n+1)+}_{soln}"']
\end{tikzcd}$$

Fig. 5·51

In figure 5.51, $M_{g,v}^{m+}$ and $M_{g,v}^{(m+1)+}$ represent the reduced and oxidized gaseous metal ions in their valence states; i.e. with the same number of d electrons that they have in the final complex ion. I_m is the ionization potential for removing the (m+1)th electron from $M_{g,v}^{m+}$. As I_m is an enthalpy term, a small entropy term $\overline{S}^{o}_{e_g}$ must also be considered in the ionization process. $\overline{S}^{o}_{e_g}$ is the Sackur standard entropy of the gaseous electron and is equal to 3.62 cal. deg.$^{-1}$ mole^{-1} (116). ΔG_c^{n+} and $\Delta G_c^{(n+1)+}$ represent the free energy changes associated with the co-ordination of the ligand L_g, in the gas phase. ΔG_{soln}^{n+} and $\Delta G_{soln}^{(n+1)+}$ give the free energies associated with dissolving the gaseous complex ions in water. By considering figure 5.51 equation 5.54 may now be expanded,

$$\Delta G^{o}_{redox} = I_m + \overline{S}^{o}_{e_g} + \Delta G_c^{(n+1)+} - \Delta G_c^{n+} + \Delta G_{soln}^{(n+1)+} - \Delta G_{soln}^{n+} \qquad 5.55$$

The total free energy change for the redox half-cell is seen to depend on the ionization potential of the reduced gaseous ion, modified by the free energies of co-ordination and solution of each ion. It is these last two terms which determine the observed variation in redox potential for different co-ordination complexes of the same metal.

A similar cycle to 5.51 can be considered for the standard hydrogen half-cell, and the sum of the free energy changes, $\sum \Delta G^o_{H_2/H^+}$, may be related to the absolute potential of the hydrogen electrode.

The potential of the redox half-cell <u>relative</u> to the standard hydrogen electrode can then be expressed,

$$-FE_o = \sum \Delta G^o_{redox} - \sum \Delta G^o_{H_2/H^+} \qquad 5.56$$

$$= I_m + \Delta(\Delta G^o_c) + \Delta(\Delta G^o_{soln}) + \bar{S}^o_{e_g} - \sum \Delta G_{H_2/H^+}$$

$$= I_m + \Delta(\Delta G^o_c) + \Delta(\Delta G^o_{soln}) - C \qquad 5.57$$

where $C = \sum G^o_{H_2/H^+} - \bar{S}^o_{e_g}$ = constant.

From equation 5.57, it can be seen that the variation in E_o for different co-ordination complexes of the same metal is dependent only on differences in the free energies of co-ordination and solution of the oxidant and reductant ions.

ΔG_c and ΔG_{soln} may be separated into their respective enthalpy and entropy terms,

$$\Delta G_c = \Delta H_c - T \Delta S_c \qquad 5.58$$

$$\Delta G_{soln} = \Delta H_{soln} - T \Delta S_{soln} \qquad 5.59$$

ΔH_c measures the total bond energy resulting from the co-ordination of the ligand, L. This bond energy is composed of two terms. These are the M - L interaction energy resulting from the formation of a metal-ligand bond, and the ligand field stabilization energy resulting from the splitting of the degenerate d orbitals of the free gaseous ion. The former energy factor results from electrostatic and covalent interactions, polarization effects, and steric interactions. The ligand field factor has received adequate treatment elsewhere (117,118) and will not be discussed here. We therefore have,

$$\Delta H_c = \Delta H_{IE} + \Delta H_{LF} \qquad 5.510$$

The two entropy terms ΔS_c and ΔS_{soln} will be combined,

$$\Delta S = \Delta S_c + \Delta S_{soln} \qquad 5.511$$

ΔS^{n+} is a measure of the entropy change for the reaction,

$$M_g^{m+} + xL_g \longrightarrow ML_{x,aq}^{n+}$$

and can be expressed,

$$\Delta S^{n+} = \overline{S}^{o}(ML_x^{n+})_{aq} - x\,\overline{S}^{o}(L)_g - \overline{S}^{o}(M^{m+})_g \qquad 5.512$$

Similarly,

$$\Delta S^{(n+1)+} = \overline{S}^{o}(ML_x^{(n+1)+})_{aq} - x\overline{S}^{o}(L)_g - \overline{S}^{o}(M^{(m+1)+})_g$$

$$5.513$$

where $\overline{S}^{o}$ represents the partial molal entropy.

Combining 5.512 and 5.513,

$$\Delta(\Delta S) = \Delta S^{(n+1)+} - \Delta S^{n+} = [\bar{S}^o(ML_x^{(n+1)+})_{aq} - \bar{S}^o(ML_x^{n+})_{aq}] + [\bar{S}^o(M^{m+})_g - \bar{S}^o(M^{(m+1)+})_g] \qquad 5.514$$

The terms in $\bar{S}^o(M^{m+})_g$ resulting from contributions of the degeneracy of the ground levels on splitting will be small ($<$ 2 e.u. (119)). For differently charged ions this value will vary only slightly as a result of contributions from the d shell to the vibrational entropy (120). The last term in equation 5.514 will therefore be very small, and for complex couples containing the same central metal ion, will be constant. Therefore, to a very good approximation,

$$\Delta(\bar{S}^o) = \bar{S}^o(ML_x^{(n+1)+})_{aq} - \bar{S}^o(ML_x^{n+})_{aq} \qquad 5.515$$

Combining equations 5.55, 5.57, 5.58, 5.59, 5.510, 5.511 and 5.515, we have

$$\Delta G_o = I_m + [\Delta H^{(n+1)+}_{I.E.} - \Delta H^{n+}_{I.E.}] + [\Delta H^{(n+1)+}_{soln} - \Delta H^{n+}_{soln}] + [\Delta H^{(n+1)+}_{L.F.} - \Delta H^{n+}_{L.F.}] - T\,\Delta(\bar{S}^o) - C \qquad 5.516$$

Equation 5.514 relates the free energy difference between the oxidant and reductant ions in terms of heat and entropy changes. An attempt is made in Chapter 7 to assess the relative importance of each of the terms in brackets for the osmium couples recorded in this thesis.

CHAPTER SIX

6.1 DETERMINATION OF E_o (Debye-Huckel Theory)

For the reaction

$$ML_x^{n+} \rightleftharpoons ML_x^{(n+1)+} + e$$

the potential E of the system is related to the standard potential E_o by the expression,

$$E = E_o - \frac{RT}{F} \ln \frac{a_{ox}}{a_{red.}} \quad . \qquad 6.11$$

The activity of both the oxidant and reductant complex ions may be split into concentration (C) and activity (f) terms, i.e.

$$E = E_o - \frac{RT}{F} \ln \frac{C_{ox}}{C_{red.}} - \frac{RT}{F} \ln \frac{f_{ox}}{f_{red}} \qquad 6.12$$

where C = concentration in moles./litre

f = mean ionic activity coefficient.

When $C_{ox} = C_{red}$,

$$E = E_o - \frac{RT}{F} \ln \frac{f_{ox}}{f_{red}} \qquad 6.13$$

At low ionic strengths (< 0.1) the activity coefficient f may be expressed by the limiting form of the Debye-Huckel law (121),

$$\log f = - A z^2 \sqrt{I} \qquad 6.14$$

(where A is a constant, and z is the charge on the complex ion). Using 6.14, equation 6.13 may then be written

$$E = E_o + \frac{2.303\ RTA}{F} (2n + 1) \sqrt{I} \qquad 6.15$$

At 25° in water, A = 0.511 (122). Insertion of the values for R, T, and F, gives

$$E = E_o + 0.0301\ (2n + 1) \sqrt{I} \qquad 6.16$$

This equation gives the potential of the system as a function of the charge n on the reductant ion and the ionic strength of the solution. Under ideal conditions at 25° a plot of the measured potential E against $\sqrt{I}$ should then give a straight line of slope 0.0301 (2n + 1). Extrapolation to zero ionic strength gives the standard potential, E_o, of the redox system.

Since the limiting form of the Debye-Huckel law holds only below an ionic strength of approximately 0.1 (123), the ionic strength in the present study was never greater than 0.03. The concentrations of the redox solutions were between 6.25×10^{-5} and 2.5×10^{-4} M with respect to each ion, and the ionic strength was varied between 0.002 and 0.03 by adding measured amounts of a 0.05 M potassium chloride solution.

6.2 DETERMINATION OF $\overline{S}^o\ (OsL_x^{(n+1)+})_{aq} - \overline{S}^o\ (OsL_x^{n+})_{aq}$

Assuming ΔH^o remains constant over the temperature range

$10^\circ - 30^\circ$, it follows from equation 5.14 and 5.15 that

$$\Delta S^\circ = F \frac{\partial E_o}{\partial T} \qquad 6.21$$

$$= \frac{96,500}{4.2} \frac{\partial E_o}{\partial T} \quad \text{e.u.} \qquad 6.22$$

For the redox reaction,

$$OsL^{n+}_{x,aq} + H^{+}_{aq} \rightleftharpoons OsL^{(n+1)+}_{x,aq} + 1/2\ H_{2},g$$

$$\Delta S^\circ = \bar{S}^\circ(OsL_x^{(n+1)+})_{aq} - \bar{S}^\circ(OsL_x^{n+})_{aq} + 1/2\bar{S}^\circ(H_2)_g - \bar{S}^\circ\ (H^+)_{aq} \qquad 6.23$$

At unit activity $\bar{S}^\circ\ (H^+) = 0$ by definition, and at a pressure of one atmosphere $\bar{S}^\circ(H_2)_g = 31.2$ e.u. (124)

Equation 6.23 rearranges

$$\Delta(\bar{S}^\circ) = \bar{S}^\circ\ (OsL_x^{(n+1)+})_{aq} - \bar{S}^\circ\ (OsL_x^{n+})_{aq} = \Delta S^\circ - 15.6 \qquad 6.24$$

where ΔS° is defined by equation 6.22.

Equation 6.24 has been used to calculate the difference between the partial molal entropies of the oxidized and reduced complex ions.

6.3 EXPERIMENTAL METHOD

Equal molar quantities of the osmium(II) and osmium(III) complexes were accurately weighed out to make the final solution between $^{M}/4000$ and $^{M}/8000$ with respect to each ion. The concentration of the redox solution depended on the couple being studied and was governed by the solubility of the osmium(II) complex.

The osmium(II) complex was dissolved in the minimum volume of conductivity water and transferred to a clean 100 ml. standard flask. The osmium(III) complex was similarly dissolved in conductivity water and added to the osmium(II) solution. The volume was then adjusted to 100 ml. In cases where the potential of the couple was more negative then - 0.6 volts, one drop of 0.1M nitric acid was added to stabilize the higher oxidation state (125). This, in effect, lowers the potential of the water/oxygen couple (c.f. 5.4 , page 168). The redox solution was allowed to stand with occasional mixing for at least one hour before use. In this time the saturated calomel cell was accurately standardized (to ± 0.05 m.v.) against a quinhydrone electrode as described below (c.f. 6.51, page 191).

After one hour, exactly 10 ml. of the redox solution and 10 ml. of conductivity water were pipetted into a previously cleaned redox cell (section 6.52), and the gold electrodes placed in position. The redox cell was transferred to the constant temperature bath, the electrodes connected to the potentiometer, and a slow stream of nitrogen (at 25°) bubbled through the solution. After 20 minutes the nitrogen supply was stopped, the saturated potassium chloride salt bridge carefully wiped, inserted into the cell system, and the potentiometer quickly adjusted until no deflection was observed on the galvanometer at full sensitivity adjustment. The potentiometer was then connected to the second gold electrode and a similar reading taken. The maximum deviation in these readings was 0.2 m.v. and the average value was taken as the potential of the cell system.

Succeeding measurements were made on solutions containing 10 ml. of the redox solution and conductivity water, adjusted so that the total volume remained at 20 ml. The solutions were allowed 15 minutes to equilibrate with the electrodes, and the potential measured as before.

By this method potential values over the ionic strength range I = 0.002 to 0.03 have been obtained. The measured potentials were plotted against $\sqrt{I}$ and extrapolated to zero ionic strength to give the potential $E_{o,cell}$ for the cell,

$$\mathrm{Au} \; \left| \; \underset{(a=1)}{ML_x^{n+}} \quad \underset{(a=1)}{ML_x^{(n+1)+}} \; \right\| \; KCl_{sat} \; Hg_2Cl_2 \; \Big| \; Hg \; / \; Pt$$

The standard oxidation-reduction potential E_o is obtained from the expression

$$E_o = E_{o,cell} - E_{calomel} \qquad 6.31$$

Potential measurements have been repeated on freshly prepared redox solutions. The maximum deviation between separate runs is 0.5 m.v., and usually agreement to 0.2 m.v.

has been obtained.

In some instances different preparations have been used to prepare the redox solutions, and in a few cases the complexes have been prepared from different starting compounds (c.f. PART I).

6.4 EXPERIMENTAL RESULTS

In the following tables are recorded the standard redox potentials at infinite dilution for several series of osmium couples. Experimental points are shown on the appended Debye-Huckel plots.

TABLE 6.41

(n = 2, T = 25°C; Theoretical Debye-Huckel Slope = 15.0 m.v./ 0.1 $\sqrt{I}$)

Couple	Conc. of Redox Solution	Ionic Strength Range	E	$E_{calomel}$	E_o	Slope $\sqrt{I}$ Plot (m.v./0.1 $\sqrt{I}$)
$[\mathrm{Os\ dipy_3}](\mathrm{ClO_4})_2 \cdot \mathrm{H_2O}$	$^{M}/4000$	0.00225	-0.6385	0.2451	-0.8836	12.6
$[\mathrm{Os\ dipy_3}](\mathrm{ClO_4})_3 \cdot \mathrm{H_2O}$		0.02725				
$[\mathrm{Os\ py\ dipy\ tpy}](\mathrm{ClO_4})_2 \cdot \mathrm{H_2O}$	$^{M}/4000$	0.00225	-0.6249	0.2451	-0.8700	13.4
$[\mathrm{Os\ py\ dipy\ tpy}](\mathrm{ClO_4})_3 \cdot 2\mathrm{H_2O}$		0.02725				
$[\mathrm{Os\ py_2\ dipy_2}](\mathrm{ClO_4})_2 \cdot 2\mathrm{H_2O}$	$^{M}/4000$	0.00225	-0.5888	0.2451	-0.8339	12.6
$[\mathrm{Os\ py_2\ dipy_2}](\mathrm{ClO_4})_3 \cdot 2\mathrm{H_2O}$		0.02725				
$[\mathrm{Os\ py_3\ tpy}](\mathrm{ClO_4})_2$	$^{M}/4000$	0.00225	-0.5537	0.2451	-0.7986	15.2
$[\mathrm{Os\ py_3\ tpy}](\mathrm{ClO_4})_3$		0.02725				
$[\mathrm{Os\ py_4\ dipy}](\mathrm{ClO_4})_2 \cdot 2\mathrm{H_2O}$	$^{M}/4000$	0.00225	-0.5582	0.2451	-0.8033	12.4
$[\mathrm{Os\ py_4\ dipy}](\mathrm{ClO_4})_3 \cdot 2\mathrm{H_2O}$		0.02725				

TABLE 6.42

(n = 2, T = 25°C; Theoretical Debye-Huckel Slope = 15.0 m.v./ 0.1 $\sqrt{I}$)

Couple	Conc. of Redox Solution	Ionic Strength Range	E	$E_{calomel}$	E_o	Slope $\sqrt{I}$ Plot (m.v./0.1 $\sqrt{I}$)
[Os py dipy tpy]$(ClO_4)_2 \cdot H_2O$ [Os py dipy tpy]$(ClO_4)_3 \cdot 2H_2O$	M/4000	0.00225 0.02725	-0.6249	0.2451	-0.8700	13.4
[Os Rpy dipy tpy]$(ClO_4)_2$ [Os Rpy dipy tpy]$(ClO_4)_3 \cdot 2H_2O$ R = 4 - CH_3	M/4000	0.00225 0.02725	-.6054	0.2449	-0.8503	13.4
[Os Rpy dipy tpy]$(ClO_4)_2$ [Os Rpy dipy tpy]$(ClO_4)_3 \cdot 2H_2O$ R = 3 - CH_3	M/4000	0.00225 0.02725	-0.6208	0.2449	-0.8657	13.4
[Os Rpy dipy tpy]$(ClO_4)_2$ [Os Rpy dipy tpy]$(ClO_4)_3 \cdot 2H_2O$ R = 4 - C_2H_5	M/4000	0.00225 0.02725	-0.6123	0.2449	-0.8572	12.7
[Os Rpy dipy tpy]$(ClO_4)_2$ [Os Rpy dipy tpy]$(ClO_4)_3 \cdot 2H_2O$ R = 4 - C_3H_7	M/4000	0.00225 0.02725	-0.6146	0.2449	-0.8595	13.3

TABLE 6.43

($n = 1$, $T = 25^{\circ}$; Theoretical Debye-Huckel Slope = 9.0 m.v./0.1 $\sqrt{I}$)

Couple	Conc. of Redox Solution	Ionic Strength Range	E	$E_{calomel}$	E_o	Slope $\sqrt{I}$ Plot (m.v./0.1 $\sqrt{I}$)
[Os Cl dipy tpy]$Cl.H_2O$ [Os Cl dipy tpy]$Cl_2.H_2O$	M/4000	0.00225 0.02725	-0.3171	0.2451	-0.5622	6.7
[Os Br dipy tpy]$Cl.2H_2O$ [Os Br dipy tpy]$Br_2.H_2O$	M/8000	0.0005 0.0255	-0.3219	0.2451	-0.5670	6.7
[Os I dipy tpy]Cl [Os I dipy tpy]$(ClO_4)_2$	M/8000	0.0005 0.0255	-0.3209	0.2451	-0.5660	6.7
[Os NCS dipy tpy]$Cl.2H_2O$ [Os NCS dipy tpy]$(ClO_4)_2.H_2O$	M/16,000	0.00025 0.02025	-0.3722	0.2451	-0.6173	6.9

T A B L E 6.44

(n = 1, T = 25°; Theoretical Debye-Huckel Slope = 9.0 m.v./0.1 $\sqrt{I}$)

Couple	Conc. of Redox Solution	Ionic Strength Range	E	$E_{calomel}$	E_o	Slope $\sqrt{I}$ Plot (m.v./0.1 $\sqrt{I}$)
$[Os\ Cl\ py\ dipy_2]Cl.3H_2O$	M/8000	0.0005	-0.2372	0.2451	-0.4823	7.0
$[Os\ Cl\ py\ dipy_2](ClO_4)_2.H_2O$		0.0205				
$[Os\ Br\ py\ dipy_2]Cl.3H_2O$	M/8000	0.0005	-0.2410	0.2451	-0.4861	6.9
$[Os\ Br\ py\ dipy_2](ClO_4)_2.H_2O$		0.0205				
$[Os\ I\ py\ dipy_2]Cl.2H_2O$	M/8000	0.0005	-0.2424	0.2451	-0.4875	7.1
$[Os\ I\ py\ dipy_2](ClO_4)_2$		0.0205				
$[Os\ aca\ dipy_2](ClO_4).2H_2O$	M/8000	0.0005	0.0912	0.2451	-0.1539	6.1
$[Os\ aca\ dipy_2](ClO_4)_2.H_2O$		0.0205				

(Note For the $[Os\ aca\ dipy_2]^{+/2+}$ couple the redox solution was prepared in freshly boiled-out conductivity water. A similar 0.05 M potassium chloride solution was prepared.)

TABLE 6.45

(n = 1, T = 25°C. Theoretical Debye-Huckel Slope = 9.0 m.v./0.1 $\sqrt{I}$)

Couple	Conc. of Redox Solution	Ionic Strength Range	E	$E_{calomel}$	E_o	Slope $\sqrt{I}$ Plot (m.v./0.1 $\sqrt{I}$)
[Os Cl py_3 dipy]Cl.$3H_2O$ [Os Cl py_3 dipy]$(ClO_4)_2$.H_2O	M/8000	0.0005 0.0205	-0.1796	0.2451	-0.4247	6.9
[Os Br py_3 dipy]Cl.$2H_2O$ [Os Br py_3 dipy]$(ClO_4)_2$.H_2O	M/8000	0.0005 0.0205	-0.1983	0.2451	-0.4434	6.3
[Os I py_3 dipy]Cl.$3H_2O$ [Os I py_3 dipy]$(ClO_4)_2$	M/8000	0.0005 0.0205	-0.2055	0.2451	-0.4506	6.3

TABLE 6.46

$[Os\ dipy_3](ClO_4)_3 \cdot H_2O$ / $[Os\ dipy_3](ClO_4)_3 \cdot H_2O$ Couple

Temperature (°C)	Conc. of Redox Solution	Ionic Strength Range	E	$E_{calomel}$	E_o	Slope $\sqrt{I}$ Plot (m.v./0.1 $\sqrt{I}$)
10	$^M/_{4000}$	0.00225 0.02725	-0.6382	0.2553	-0.8935	12.6
25	$^M/_{4000}$	0.00225 0.02725	-0.6385	0.2451	-0.8836	12.7
30	$^M/_{4000}$	0.00225 0.02725	-0.6381	0.2424	-0.8805	12.8

$$\frac{\partial E_o}{\partial T} = 6.6 \times 10^{-4} \text{ volts}/^\circ C.$$

$$\Delta S^\circ = 15.2 \text{ e.u. (equation 6.22)}$$

$$\Delta(\overline{S}^\circ) = 15.2 - 15.6 = -0.4 \text{ e.u.}$$

TABLE 6.47

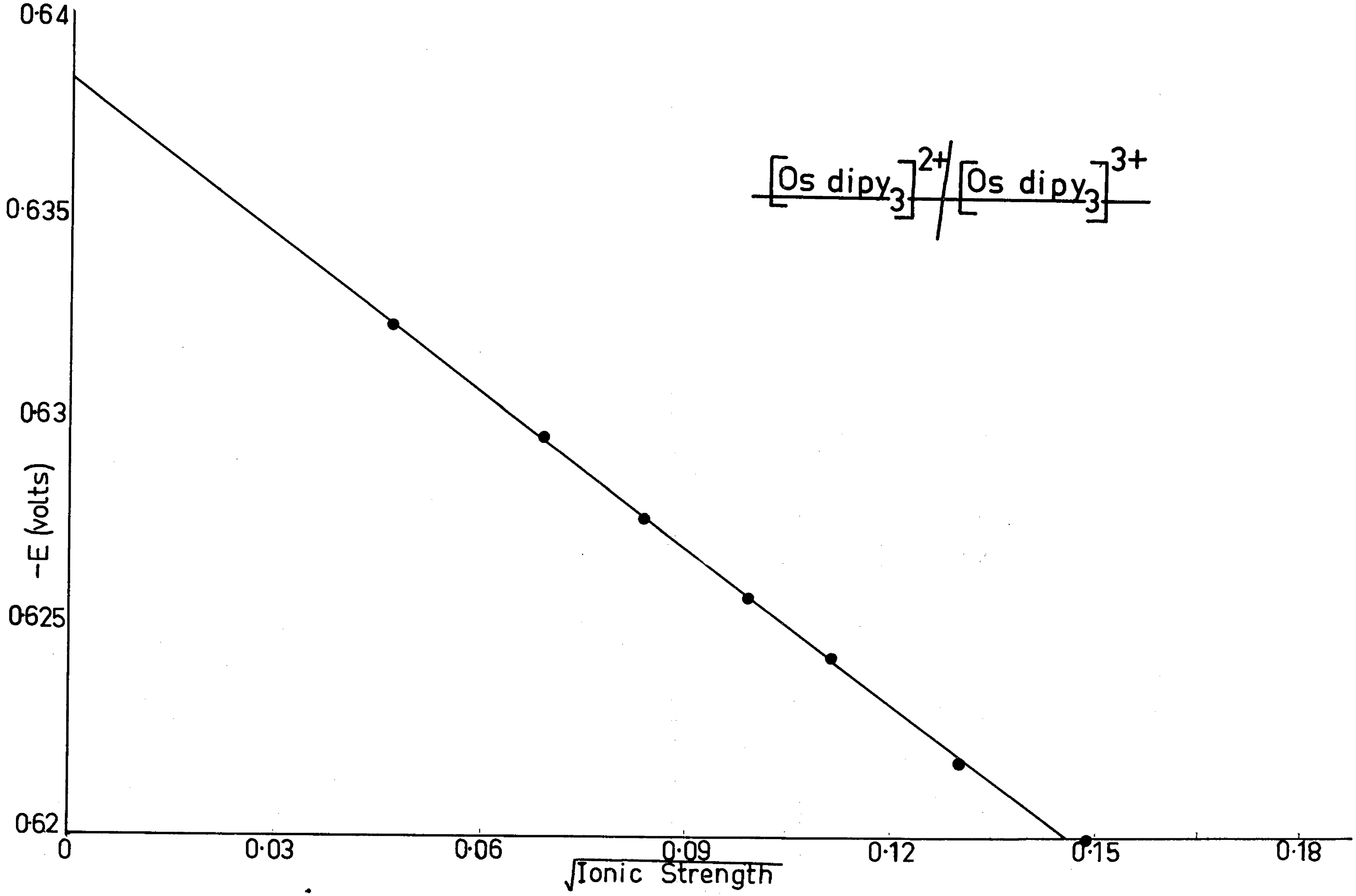
$[Os\ Cl\ py\ dipy_2]Cl.3H_2O$ / $[Os\ Cl\ py\ dipy_2](ClO_4)_2.H_2O$ Couple

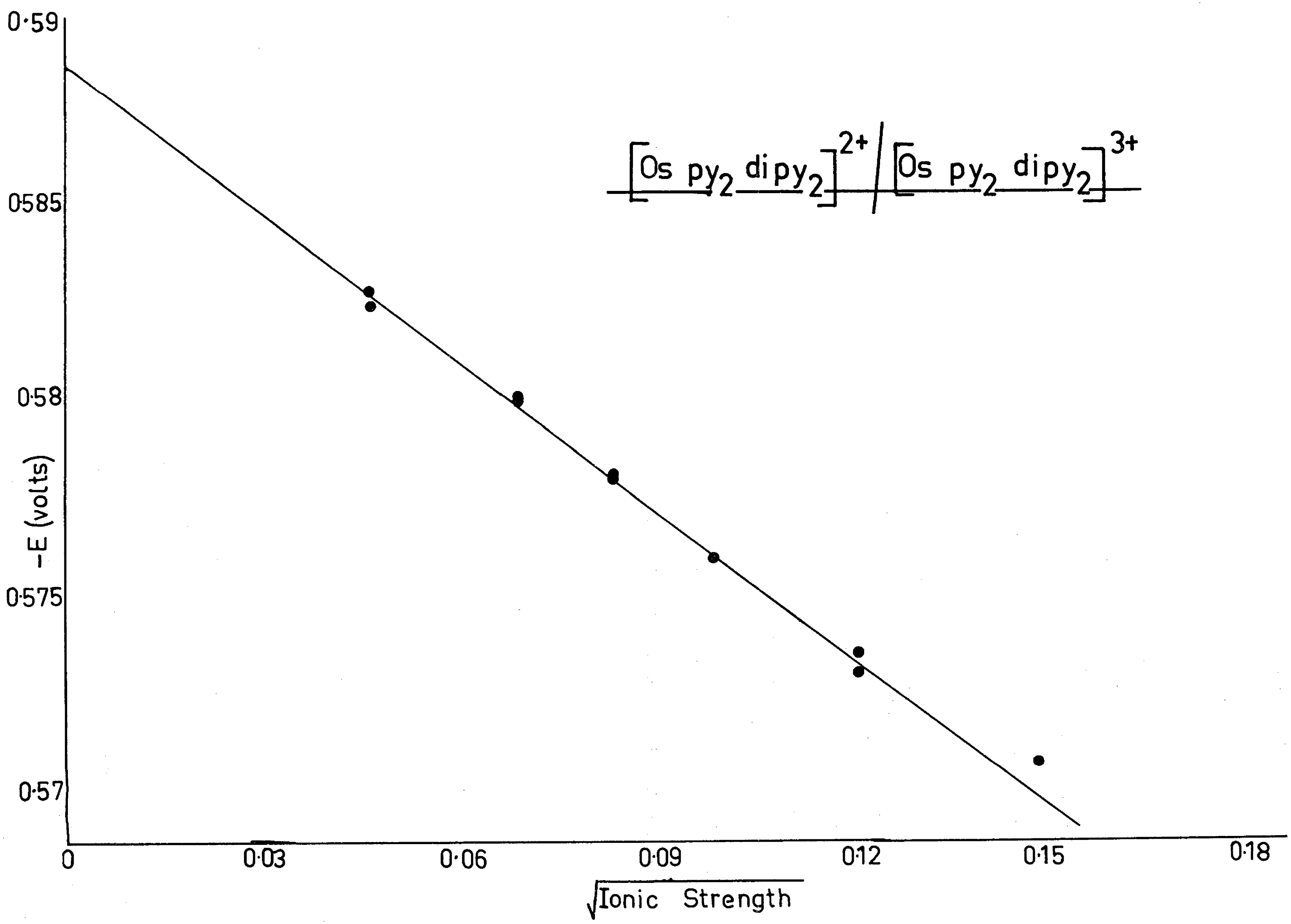
Temperature (^oC)	Conc. of Redox Solution	Ionic Strength Range	E	$E_{calomel}$	E_o	Slope $\sqrt{I}$ Plot (m.v./0.1 $\sqrt{I}$)
10	M/8000	0.0005 0.0205	-0.2393	0.2553	-0.4946	6.8
25	M/8000	0.0005 0.0205	-0.2372	0.2451	-0.4823	7.0
30	M/8000	0.0005 0.0205	-0.2348	0.2424	-0.4772	7.1

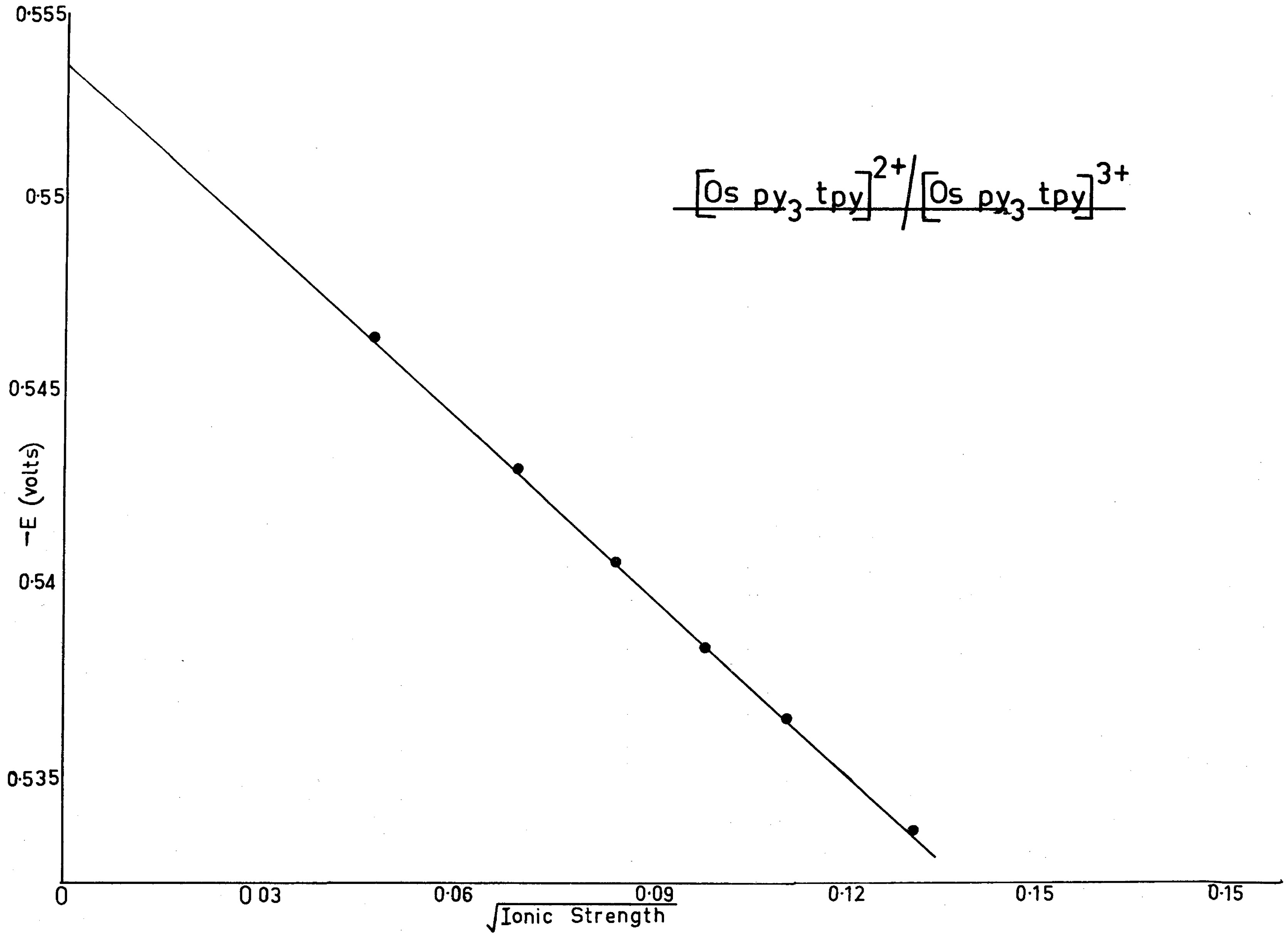
$$\frac{\partial E_o}{\partial T} = 9 \times 10^{-4} \text{ volts}/^oC$$

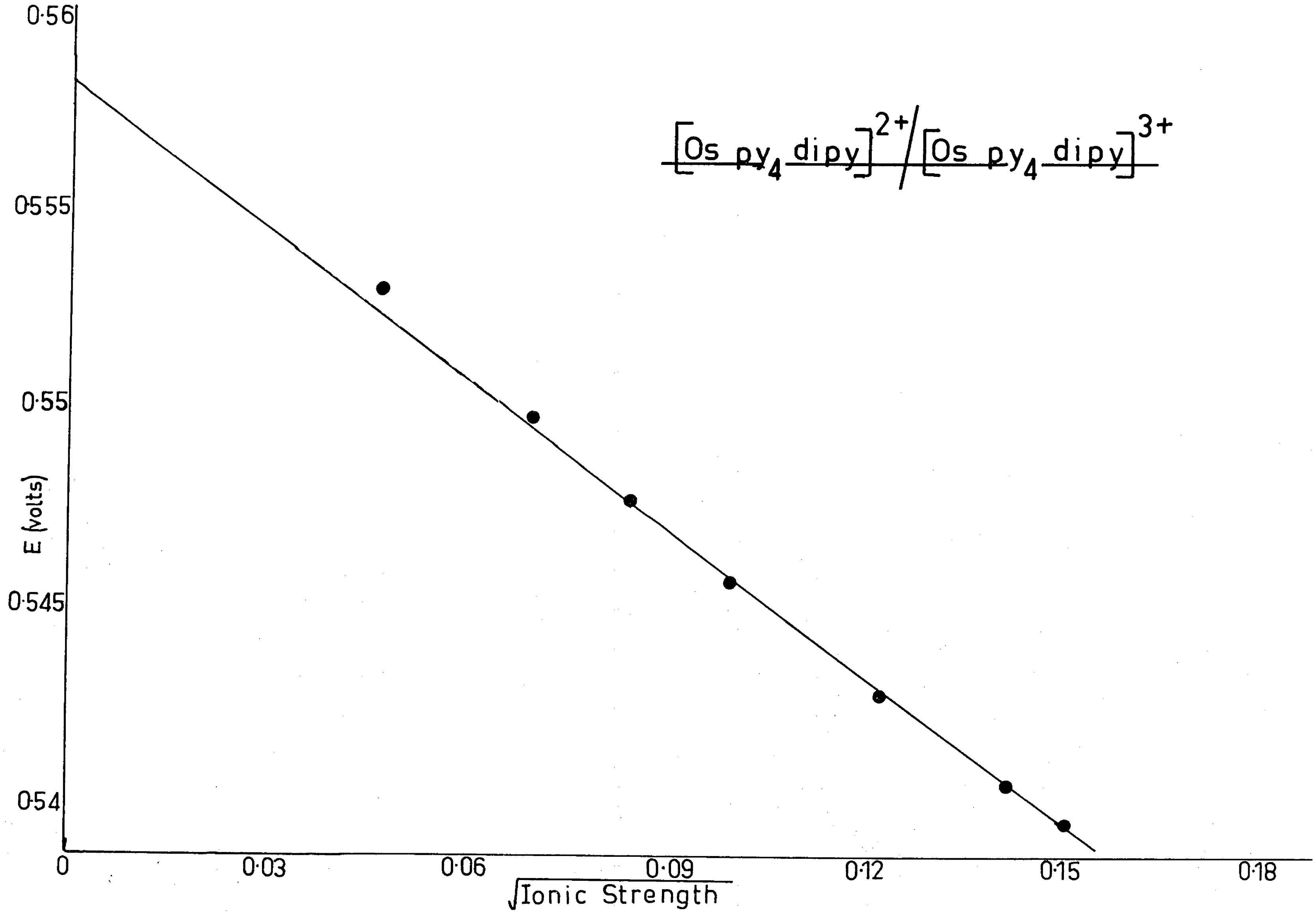
$$\Delta S^o = 20.7 \text{ e.u.} \quad \text{(equation 6.22)}$$

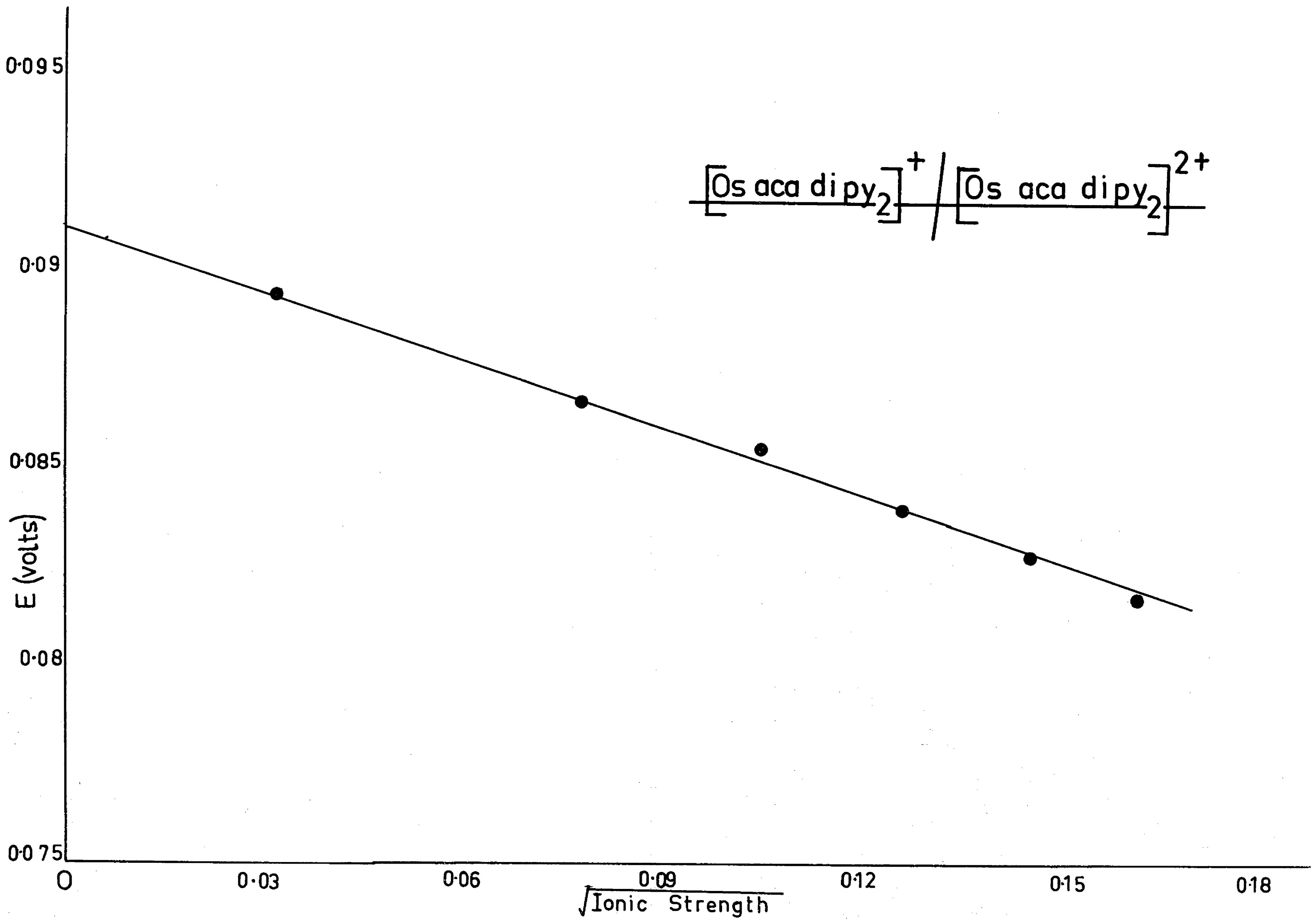
$$\Delta(\bar{S}^o) = 20.7 - 15.6 = 5.1 \text{ e.u.}$$

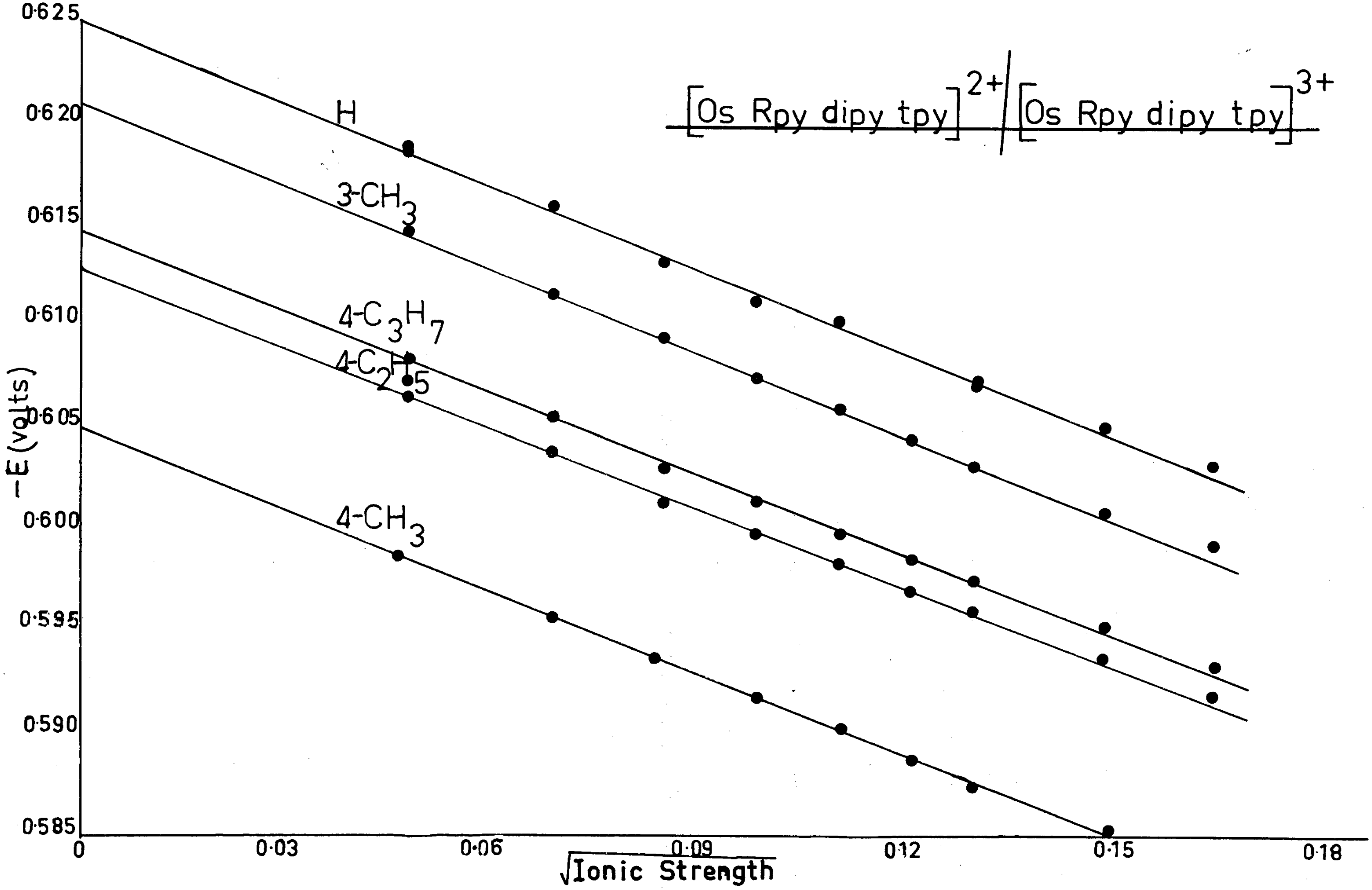

[Os dipy3]2+/[Os dipy3]3+
0·64
0·635
0·63
0·625
0·62
−E (volts)
0
0·03
0·06
0·09
0·12
0·15
0·18
√Ionic Strength


[Os py2 dipy2]2+ / [Os py2 dipy2]3+
-E (volts)
0·59
0·585
0·58
0·575
0·57
0
0·03
0·06
0·09
0·12
0·15
0·18
√Ionic Strength

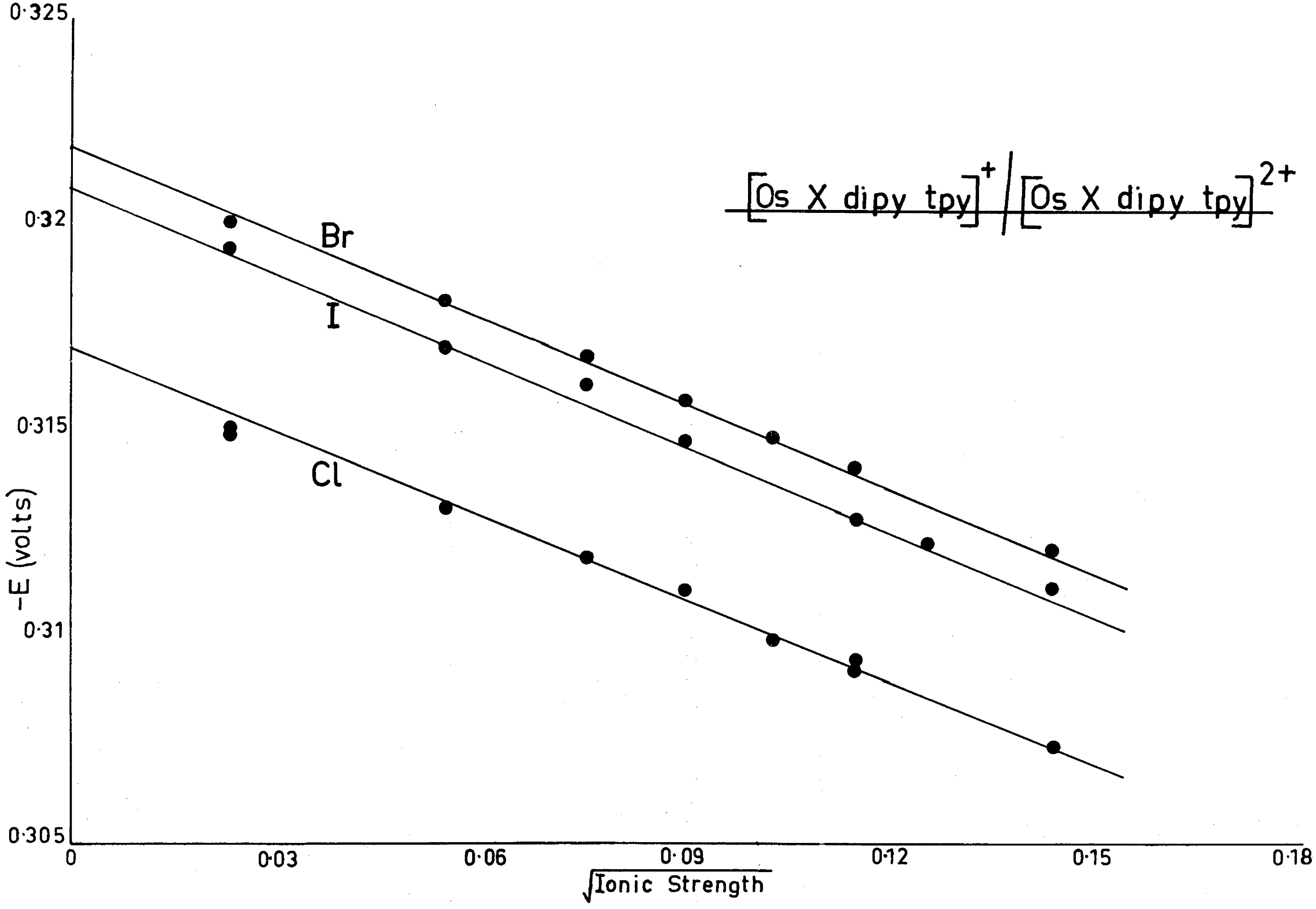

[Os py3 tpy]2+/[Os py3 tpy]3+
−E (volts)
0·555
0·55
0·545
0·54
0·535
0
0 03
0·06
0·09
0·12
0·15
0·15
√Ionic Strength

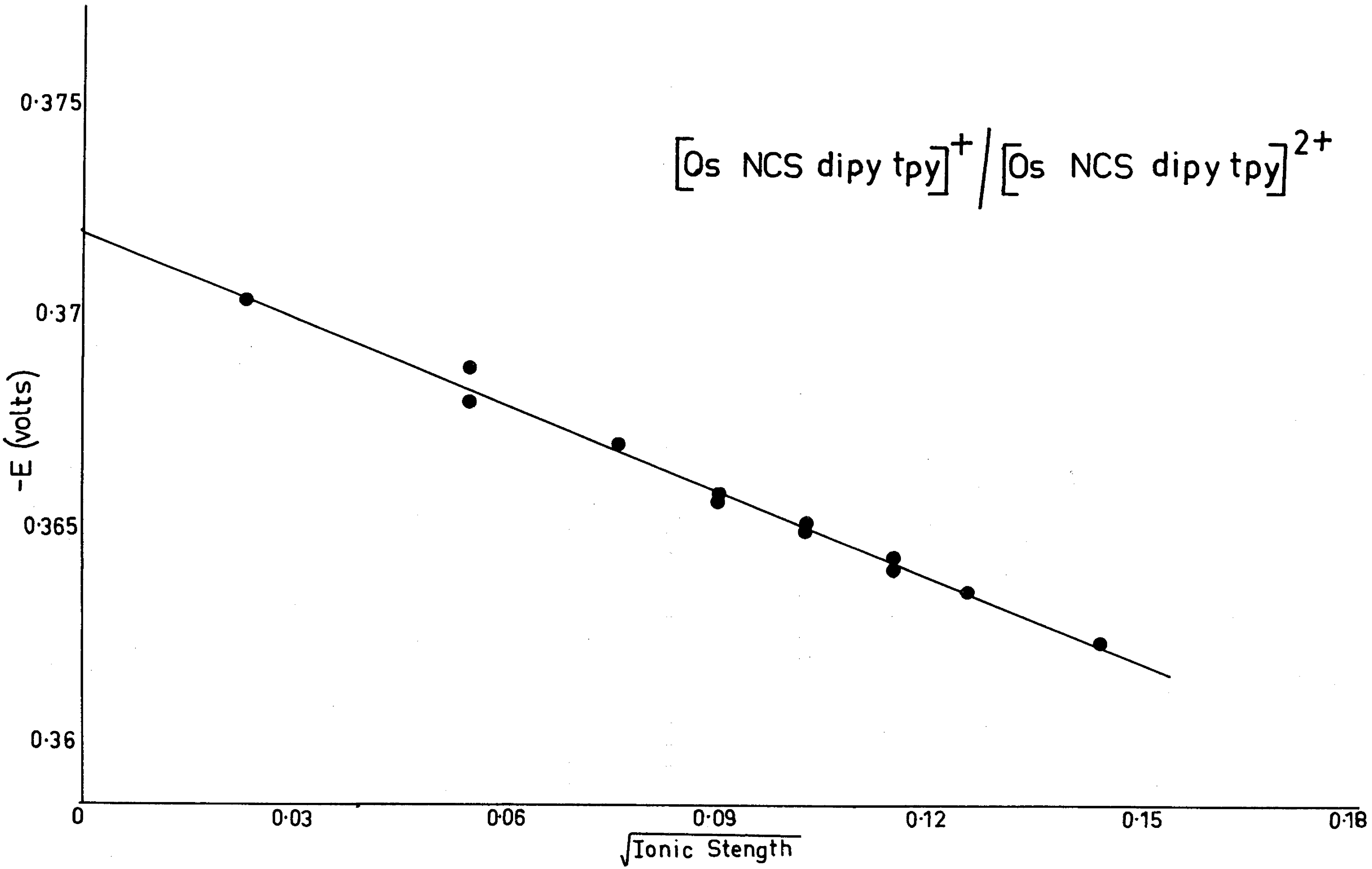

$[Os\ py_4\ dipy]^{2+}/[Os\ py_4\ dipy]^{3+}$
E (volts)
0·56
0·555
0·55
0·545
0·54
0
0·03
0·06
0·09
0·12
0·15
0·18
$\sqrt{\text{Ionic Strength}}$


$[\mathrm{Os\ aca\ dipy_2}]^{+} / [\mathrm{Os\ aca\ dipy_2}]^{2+}$
E (volts)
0·095
0·09
0·085
0·08
0·075
0
0·03
0·06
0·09
0·12
0·15
0·18
$\sqrt{\text{Ionic Strength}}$

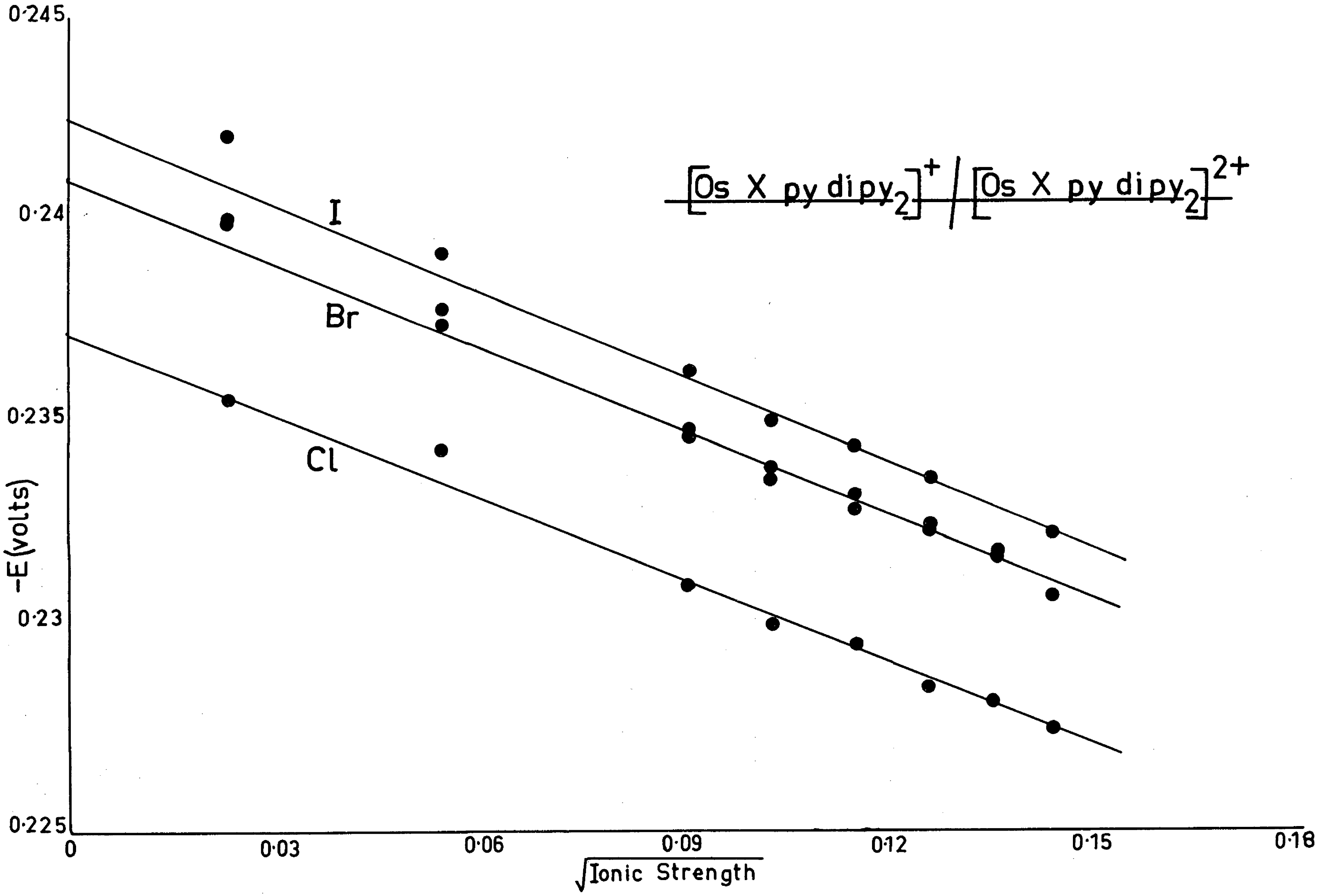


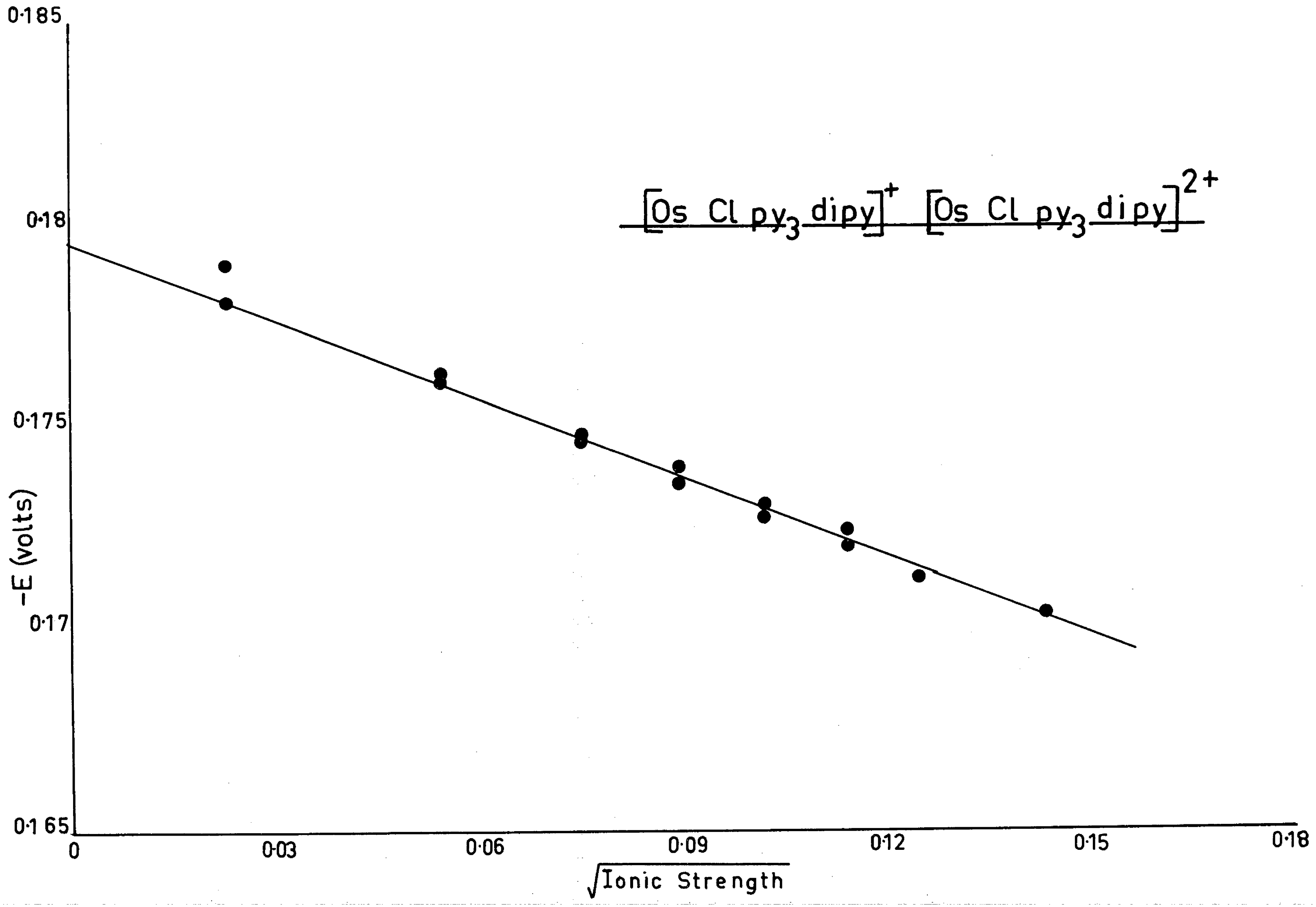
$[\mathrm{Os\ Rpy\ dipy\ tpy}]^{2+} / [\mathrm{Os\ Rpy\ dipy\ tpy}]^{3+}$
H
3-CH$_3$
4-C$_3$H$_7$
4-C$_2$H$_5$
4-CH$_3$
−E (volts)
0·625
0·620
0·615
0·610
0·605
0·600
0·595
0·590
0·585
0
0·03
0·06
0·09
0·12
0·15
0·18
√Ionic Strength

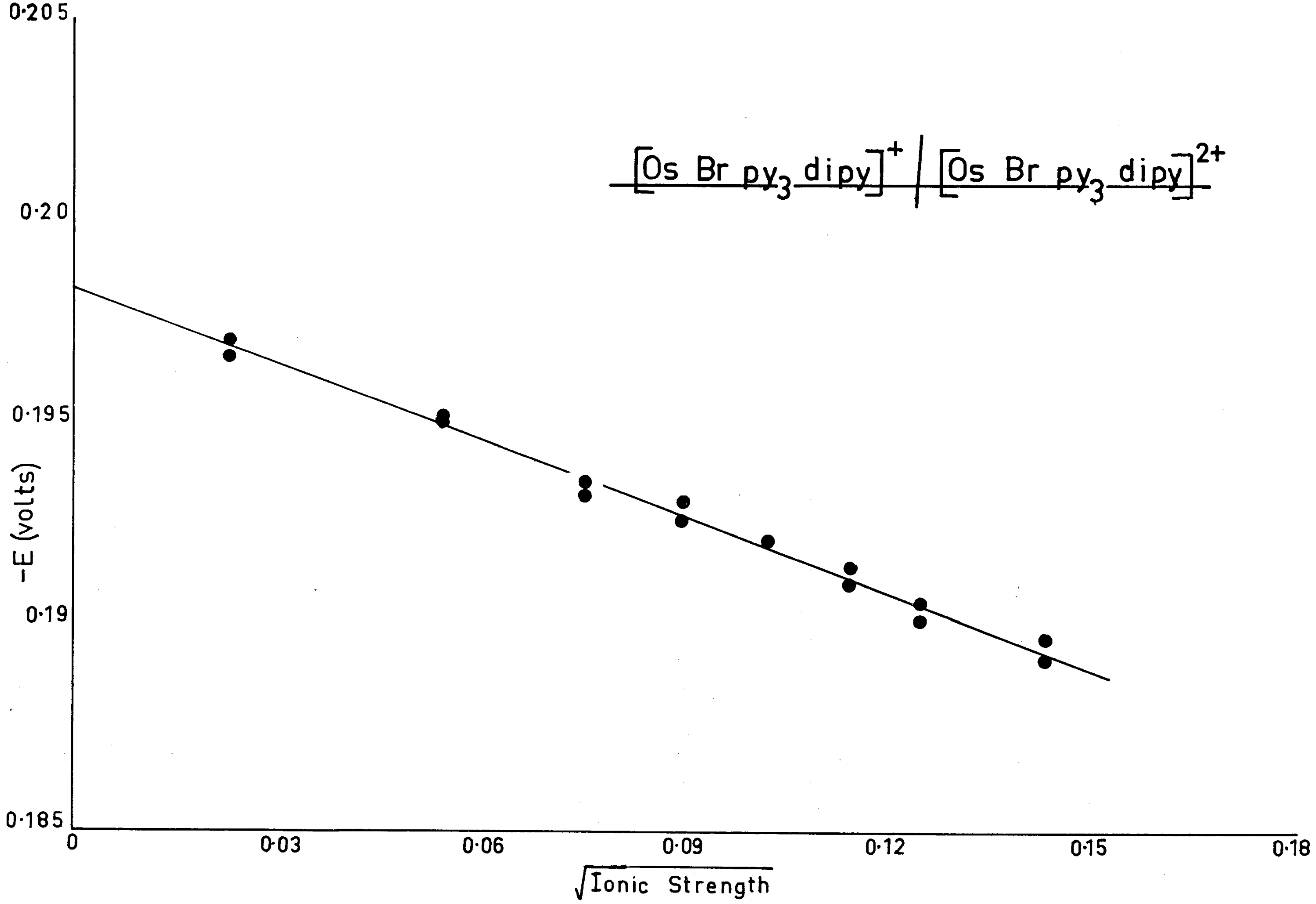

[Os X dipy tpy]$^{+}$ / [Os X dipy tpy]$^{2+}$
Br
I
Cl
0·325
0·32
0·315
0·31
0·305
-E (volts)
0
0·03
0·06
0·09
0·12
0·15
0·18
√Ionic Strength

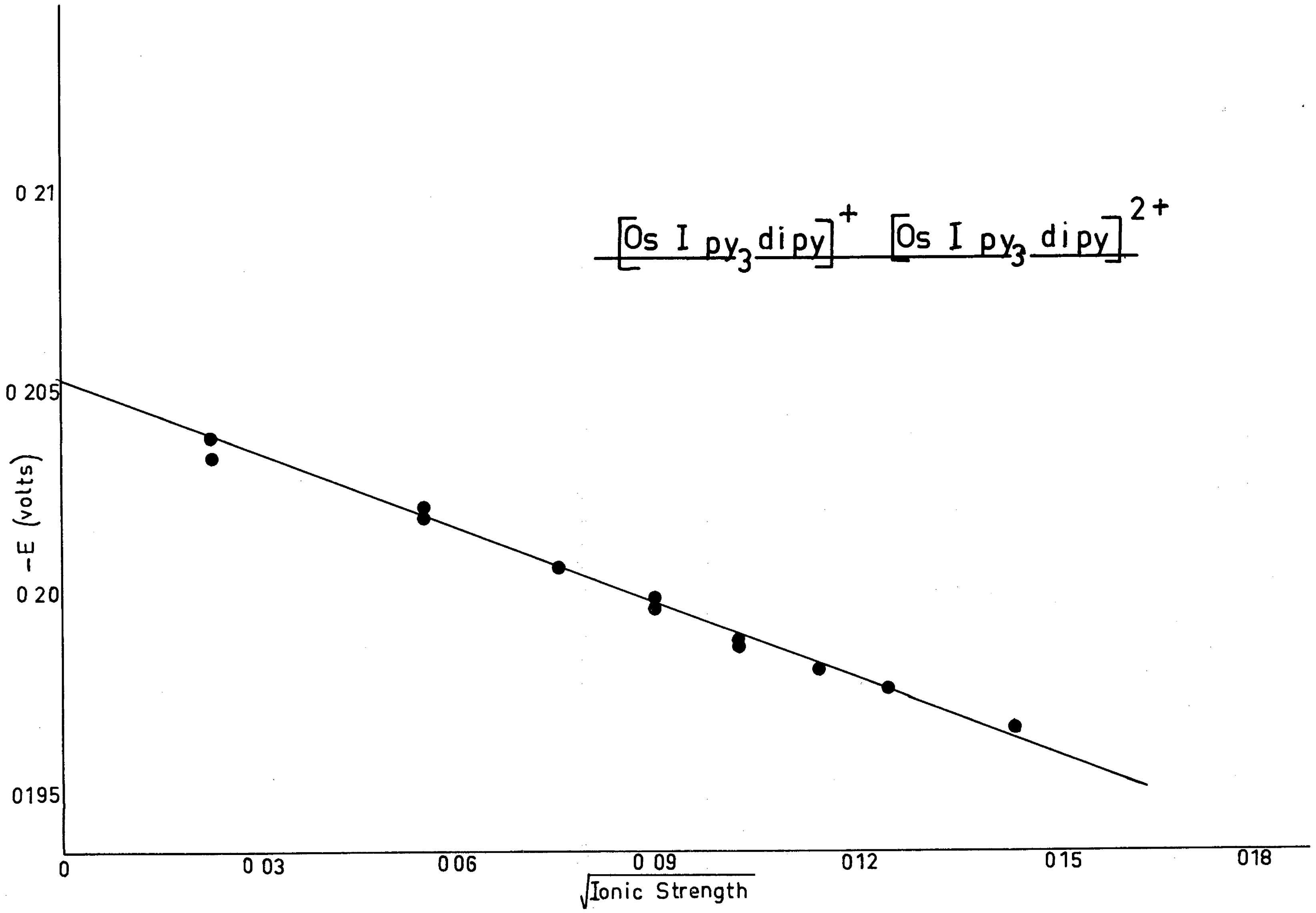


$[\text{Os NCS dipy tpy}]^{+} / [\text{Os NCS dipy tpy}]^{2+}$


[Os X py dipy$_2$]$^+$ / [Os X py dipy$_2$]$^{2+}$
I
Br
Cl
-E(volts)
0·245
0·24
0·235
0·23
0·225
0
0·03
0·06
0·09
0·12
0·15
0·18
√Ionic Strength


[Os Cl py3 dipy]+ [Os Cl py3 dipy]2+
-E (volts)
0·185
0·18
0·175
0·17
0·1 65
0
0·03
0·06
0·09
0·12
0·15
0·18
√Ionic Strength


$[\mathrm{Os\ Br\ py_3\ dipy}]^{+} / [\mathrm{Os\ Br\ py_3\ dipy}]^{2+}$
0·205
0·20
0·195
0·19
0·185
-E (volts)
0
0·03
0·06
0·09
0·12
0·15
0·18
$\sqrt{\text{Ionic Strength}}$


$[\mathrm{Os\,I\,py_3\,dipy}]^{+}$ $[\mathrm{Os\,I\,py_3\,dipy}]^{2+}$
0 21
0 205
-E (volts)
0 20
0195
0
0 03
0 06
0 09
012
015
018
√Ionic Strength

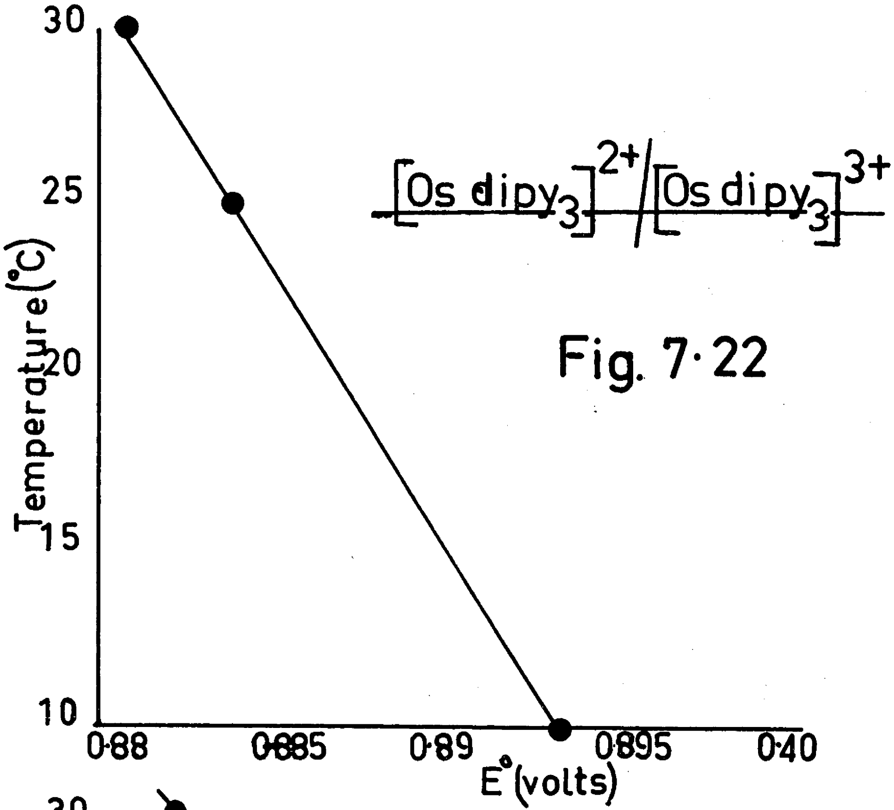


Fig. 7·22

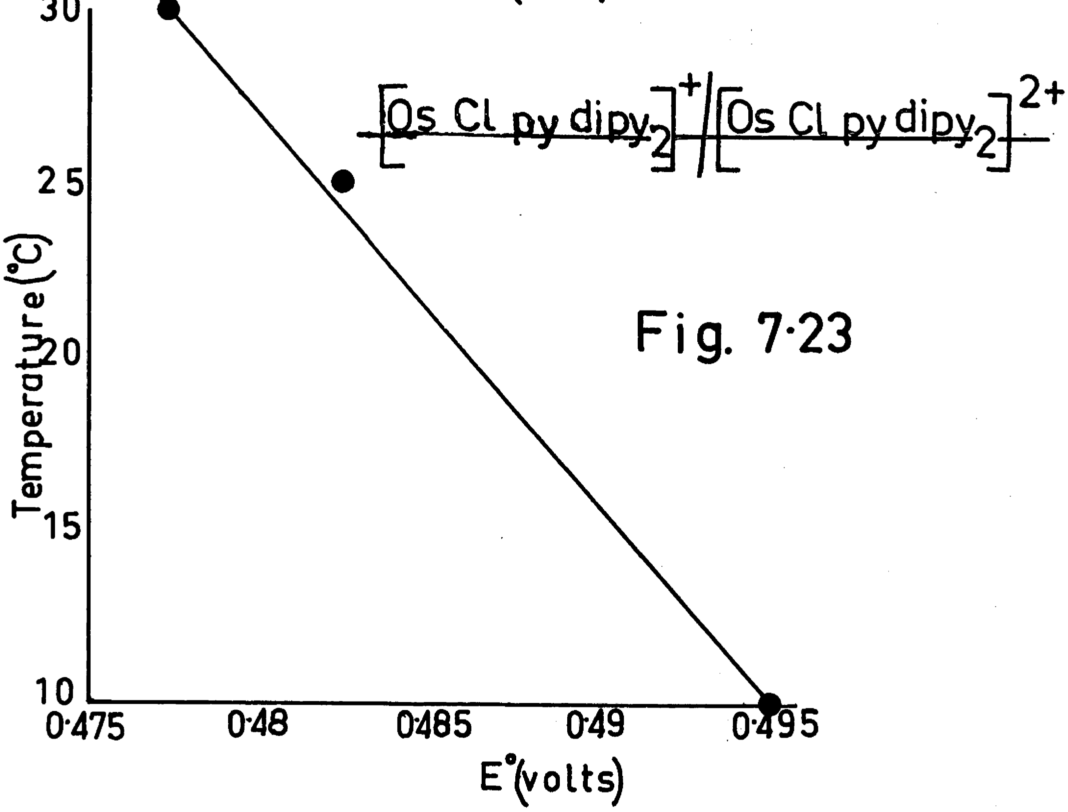


Fig. 7·23

6.51 CALIBRATION OF CALOMEL HALF-CELL

Two saturated calomel half-cells were prepared as described by Daniels, Mathews, and Williams (126). They were left in a constant temperature bath at 25 ± 0.01° for six weeks before use.

Before each series of experiments the potential of the calomel was determined against the quinhydrone electrode (127). The latter was prepared by dissolving a small quantity of twice recrystallised quinhydrone in potassium hydrogen phthalate buffer solution (0.05 M) and allowing to equilibrate with a gold electrode at 25° under a slow stream of nitrogen. After 20 minutes the nitrogen supply was stopped, the salt bridge inserted, and the potential measured. This was repeated with fresh quinhydrone solutions until the potential was reproduced to within 0.05 m.v. Provided the above procedure was followed, the potential of the calomel was found to be very constant (± 0.1 m.v.) over a period of 18 months. The calomel cells were not disturbed in the constant temperature bath during this time.

After the potential measurements at 25° had been completed, series of measurements at 30 ± 0.01° and 10 ± 0.05° were carried out. The calomel half-cells were allowed two weeks to equilibrate at each temperature, and restandardised against the quinhydrone electrode. The potentials of the saturated calomel cells at 25°, 30° and 10° are given in Table 6.51.

TABLE 6.51

Temperature	Measured Potential	Quinhydrone Potential (128)	Calomel Potential
25°	0.21720	0.4623	0.2451
	0.21703		0.2453
30°	0.21222	0.4546	0.2424
	0.21218		0.2424
10°	0.23011	0.4854	0.2553
	0.23015		0.2552

6.52 Redox Cells

The redox cells were constructed from 50 ml. tall-sided beakers fitted with rubber stoppers. Each stopper was drilled with four holes, two for the gold electrodes, one for the nitrogen inlet and one for the salt bridge. The cells were cleaned in chromic acid, thoroughly washed with distilled water, and rinsed with conductivity water before use. Several such cells were used in each experiment, so that separate solutions could be prepared and equilibrated to constant temperature while the potential of another solution was being measured.

6.53 Electrodes

It was found that reproducible potentials (to ± 0.2 m.v.) could be obtained using gold electrodes. The redox solution and electrodes were found to equilibrate within 5 minutes.

The electrodes ($^1/2''$ x $^1/2''$) were prepared from gold sheet connected to a platinum wire sealed through glass. They were etched by washing with hot aqua regia and rinsed many times with distilled water. When not in use the electrodes were kept in distilled water, or in a solution of the redox mixture during a series of measurements.

6.54 Other Equipment

The potential of the cell system was measured using a "Pye" vernier potentiometer (Cat. No. 7568) capable of reading to 0.01 m.v. A "Scalamp" high resistance galvanometer (Model 7904/S) was used as a null-point instrument to obtain potential balance.

CHAPTER SEVEN

In Chapter Five the expression,

$$\Delta G^{o} = I_{m} + \Delta(\Delta H_{I.E.}) + \Delta(\Delta H_{soln}) + \Delta(\Delta H_{L.F.}) - T\,\Delta(\overline{S}^{o}) - C$$

was developed (Equation 5.516, page 177) in which the standard free energy change ΔG^{o} for the reaction

$$OsL_{x}^{n+} \longrightarrow OsL_{x}^{(n+1)+} + e$$

is related to the ionization potential of the free gaseous ion Os^{2+}; and to differences in interaction energy ($\Delta H_{I.E.}$), ligand field stabilization energy ($\Delta H_{L.F.}$), solvation energy (ΔH_{soln}), and partial molal entropy ($\overline{S}^{o}$), between the oxidant and reductant ions. The terms I_{m} and C cancel when comparing couples with the same central metal atom.

The preferment of one particular oxidation state over another cannot usually be attributed to the operation of any one of the above factors; all factors must be considered. In this chapter the potentials of the osmium(II)/osmium(III) couples listed in Chapter Six are discussed in relation to the above expression. These couples have been divided into four groups to demonstrate the effect of

(i) charge
(ii) chelation
(iii) substitution in the ligand, and
(iv) co-ordinated halogens

on the relative stabilities of the two oxidation states.

To put each effect into its correct perspective the factors governing the potentials of some related metal complex systems are compared with those of the osmium couples.

7.1 Effect of Charge

Very little precise information is available on the effect of the overall charge on the oxidation-reduction potential. An increase in the charge on a complex ion involves an unfavourable entropy increase resulting from the more ordered arrangement of solvent molecules in the vicinity of the higher charged ion. Thus the entropy contribution $\bar{S}^o(Fe^{3+})_{aq} - \bar{S}^o(Fe^{2+})_{aq}$, to the stabilization of the ferrous ion in the $Fe^{2+}_{aq} / Fe^{3+}_{aq}$ couple is 43 e.u. (129) which is equivalent to 0.557 volts at 298°K ($E_o = -0.771$ v.). Where oxidation involves a decrease in charge on the complex ion, as in anionic complexes, the entropy of hydration should stabilize the oxidized form. For example the entropy contribution $\overline{S}^o$ $(Fe(CN)_6^{3-})_{aq}$ - $\overline{S}^o$ $(Fe(CN_6^{4-})_{aq}$ to the stabilization of the ferric state is 48 e.u.(130), or 0.62 volts at 298°K (E_o = - 0.36 v). By comparing the above aquo and cyanide couples it can be seen that E_o is increased by approximately 1.18 volts from entropy considerations alone. Thus entropy effects are important in determining the potentials of such systems.

However entropy effects are not governed entirely by charge, the size of the complex ion also being important. As the latter increases, the entropy contribution to the potential is quickly reduced. This effect is shown in Table 7.11.

In the first two iron complexes entropy considerations play an important role in **determining** the potential, and this may be related directly to the orientation of water molecules about the complex ions. However, on increasing the ionic size the entropy contribution to the potential decreases. That this is not a charge effect can be seen by considering the phenanthroline and dipyridyl complexes of Fe, Ru, and Os. Even though the charge on these ions is the same as in the $Fe(H_2O)_6^{2+}/Fe(H_2O)_6^{3+}$ couple, the $\Delta(\overline{S}^o)$ contribution to the potential has fallen significantly on co-ordination of the large organic ligand. For the Fe and Ru couples, the entropy contribution has actually changed

TABLE 7.11

Couple	$\Delta(\bar{S}^{\circ})$	Reference
$[Fe(H_2O)_6]^{2+}$ - $[Fe(H_2O)_6]^{3+}$	- 43	129
$[Fe(CN)_6]^{4-}$ - $[Fe(CN)_6]^{3-}$	48	130
$[Fe(CN)_4dipy]^{2-}$ - $[Fe(CN)_4dipy]^{-}$	34.6	131
$[IrCl_6]^{3-}$ - $[IrCl_6]^{2-}$	19.6	132
$[Fe(CN)_2dipy_2]^{0}$ - $[Fe(CN)_2dipy_2]^{+}$	17.8	131
$[Fe\ dipy_3]^{2+}$ - $[Fe\ dipy_3]^{3+}$	8.2 ± 2	131
$[Fe\ phen_3]^{2+}$ - $[Fe\ phen_3]^{3+}$	5.2 ± 2	131
$[Os\ Cl\ py\ dipy_2]^{+}$ - $[Os\ Cl\ py\ dipy_2]^{2+}$	5.1 ± 1	133
$[Ru\ dipy_3]^{2+}$ - $[Ru\ dipy_3]^{3+}$	0.2 ± 2	131
$[Os\ dipy_3]^{2+}$ - $[Os\ dipy_3]^{3+}$	$- 0.4 \pm 1$	133
	- 0.8	134

sign; i.e. the more highly charged ion is stabilized. In the tris(dipyridyl) osmium couple the entropy contribution is almost zero. Obviously here the charge plays a very minor role. This may possibly be related to shielding of the central metal ion by the large organic molecules, so that its charge has little effect on the surrounding water molecules in the second co-ordination sphere. It is important to realize, however, that the entropy term as defined (c.f. page 177) contains not only a hydrational component, but also a term resulting from the co-ordination of the ligand in the gas phase. This latter term may well become important when considering complexes containing multidentate chelate rings.

Table 7.12 details the effect on the entropy contribution of reducing the overall charge for some iron (131) and osmium couples (133).

TABLE 7.12

Couple	E_o (volts)	ΔH^o (K cals)	$T\Delta(\bar{S}^o)$ $(T=298^o)$ (K cals)
$[Os\ dipy_3]^{2+}/^{3+}$	-0.8836	20.49	0.1
$[Os\ Cl\ py\ dipy_2]^{+}/^{2+}$	-0.4823	9.58	1.5
$[Fe\ dipy_3]^{2+}/^{3+}$	-1.12	32.7	2.4
$[Fe(CN)_2\ dipy_2]^{o}/^{+}$	-0.8	29	5
$[Fe(CN)_4\ dipy]^{2-}/^{-}$	-0.541	27.4	10.3
$[Fe(CN)_6]^{4-}/^{3-}$	-0.36	27	14.3

For the iron couples, it can readily be seen that as the size of the complex ion diminishes the observed change in E_o between successive couples is increasingly determined by $\Delta(\bar{S}^o)$. It is expected that the $\Delta(\Delta H_{soln})$ term will also increase with increase in charge, and will stabilize the oxidized complex ion in the tris(dipyridyl)- couple and the reduced ion in the hexacyano-couple. However the heat of solution term is less significant in complex ions than in simple aquated ions because of the larger size of the former. It therefore appears that any decrease in $\Delta(\Delta H_{soln})$ is almost exactly counterbalanced by an increase in $\Delta(\Delta H_{I.E.})$ resulting from the replacement of a neutral dipyridyl molecule by the charged cyanide ion. The ligand field contribution $\Delta(\Delta H_{L.F.})$ is expected to remain essentially constant throughout the series due to the similarity in ligand field stabilization energies of cyanide and dipyridyl (135).

By substituting a chloride ion for a pyridine molecule in several osmium couples it has been possible to obtain a series of related couples in which the charges differ by one unit. The E_o values obtained for the various couples are listed in Table 7.13.

TABLE 7.13

Couple	E_o (volts)	ΔE_o (volts)
$[\mathrm{Os\ py\ dipy\ tpy}]^{2+\quad 3+}$	-0.8700	0.3078
$[\mathrm{Os\ Cl\ dipy\ tpy}]^{+\quad 2+}$	-0.5622	
$[\mathrm{Os\ py_2\ dipy_2}]^{2+\quad 3+}$	-0.8339	0.3516
$[\mathrm{Os\ Cl\ py\ dipy_2}]^{+\quad 2+}$	-0.4823	
$[\mathrm{Os\ py_4\ dipy}]^{2+\quad 3+}$	-0.8033	0.3786
$[\mathrm{Os\ Cl\ py_3\ dipy}]^{+\quad 2+}$	-0.4247	

On reducing the charge the osmium(III) complex is stabilized by 0.30 - 0.38 volts (approximately 7 - 9 k cals). $\Delta(\bar{S}^{o})$ for such couples (Table 7.11) is of the order of 0 - 5 e.u. (i.e. 0 - 0.07 volts at 25°). The change in potential,

ΔE_o, can therefore be largely attributed to enthalpy effects. This probably results from a significant increase in the interaction energy term $\Delta(\Delta H_{I.E.})$ on replacing pyridine by the charged chloride ion. The electrostatic energy of binding will increase significantly for both oxidized and reduced ions, but due to the higher charge and smaller radius of the osmium(III) ion will result in a net stabilization of this complex.

The $\Delta(\Delta H_{L.F.})$ term will also increase on reduction of the charge, since the extra stabilization of the reduced complex resulting from π bonding to pyridine, will be substantially reduced on co-ordination of a chloride ion. The osmium(III) complex will be the less affected by this reduction in π bonding (c.f. page 209). However, this term will be small in comparison to the large change in $\Delta(\Delta H_{I.E.})$.

The solvation energy, ΔH_{soln}, depends on both the charge and size of the complex ion. It may be estimated using the familiar Born equation (136) (giving the ΔG_{soln} term) and the variation of the dielectric constant of water with temperature. On substituting values for constants, we get

$$\Delta H_{soln} = -\frac{167}{R} n^2 \text{ k cals} \qquad 7.11$$

where R = radius of the complex ion

n = charge on the ion.

This expression is valid only for large, spherically symmetric ions $^{(137)}$. For all the couples listed in Table 7.13 the oxidant ion will be stabilized due to the large negative value of $\Delta(\Delta H_{soln})$. However, since ΔH_{soln} depends on the square of the charge $\Delta(\Delta H_{soln})$ will stabilize the oxidized species to a greater extent for the higher charged couple. This effect will be large and act in opposition to the interaction energy term $\Delta(\Delta H_{I.E.})$. The effect of the radius of the complex ion on ΔH_{soln} resulting from replacement of pyridine by a chloride ion is expected to be small and very similar for both the oxidized and reduced ions.

The "charge effect" may therefore be largely attributed to changes in the interaction energy term, $\Delta(\Delta H_{I.E.})$, and the heat of solution term, $\Delta(\Delta H_{soln})$ of equation 5.516. These two terms act in opposition and result in a small net stabilization of the osmium(III) complex ion on reducing the overall charge. $\Delta(\Delta H_{L.F.})$ supplements $\Delta(\Delta H_{I.E.})$ but its effect on ΔE_o is small in comparison. The entropy contribution $T\,\Delta(\bar{S}^o)$ is negligible.

A similar but more marked stabilization of the osmium(III) complex ion results when dipyridyl is replaced by acetylacetone (Table 7.14).

TABLE 7.14

Couple	E_o (volts)	ΔE_o (volts)
$[\mathrm{Os\ dipy_3}]^{2+}$ - $[\mathrm{Os\ dipy_3}]^{3+}$	-0.8836	0.7297
$[\mathrm{Os\ aca\ dipy_2}]^{+}$ - $[\mathrm{Os\ aca\ dipy_2}]^{2+}$	-0.1539	

ΔE_o may be attributed to similar causes to those described above. A further decrease in $\Delta H^{n+}_{L.F.}$ and $\Delta H^{n+}_{I.E.}$ results from the loss of approximately one third of the stability of the reduced complex ion resulting from π bonding. It is also likely that the more electronegative oxygen atoms of the acetylacetonato group can take up the extra charge of the oxidized ion to a greater extent than does dipyridyl with a resultant stabilization of the osmium(III) complex.

7.2 Chelate Effect

Thermodynamic data have confirmed the preparative chemists' impression, that multidentate complexes are usually more stable towards dissociation than their unidentate analogues, even though the base strengths of the ligands in the former may be the same or less than those in the latter. As an example one may compare the relatively stable chelate complex ion $[\mathrm{Ni\ en_3}]^{2+}$ with the analogous, but less stable, non-chelate complex ion $[\mathrm{Ni(CH_3NH_2)_6}]^{2+}$.

The former is stable in solution at high dilution, but $[Ni(CH_3NH_2)_6]^{2+}$ hydrolyses under the same conditions (138).

The magnitude of this "chelate effect" depends on the metal ion involved (139). If it were essentially an entropy effect as Schwarzenbach claimed (140) it would be expected to be almost independent of the metal ion (141). A recent evaluation of the heat and entropy effects involved on chelation has shown that enthalpy changes are negligible for metals where there is no ligand field stabilization, but are significant for other metals (142,143,144). This would suggest that for unidentate and bidentate ligands of similar basic strength the chelate effect may be attributed to $\Delta H_{L.F.}$ and ΔS factors.

In considering complexes which can exist in more than one oxidation state, the effect of linking ligands together should be to increase the stability of the complex in all oxidation states, though not necessarily equally. Very little data is available to assess this effect on the <u>relative</u> stabilities of oxidation states. Consideration of the potentials of the cobalt couples (145)

$$Co(NH_3)_6^{2+} - Co(NH_3)_6^{3+} \qquad E_o = -\,0.05\ v.$$

$$Co(en_3)^{2+} - Co(en_3)^{3+} \qquad E_o = 0.259\ v.$$

shows that ethylenediamine favours the cobalt(III) state to a greater extent than ammonia. Ethylenediamine is the stronger base, (pK_a(en) = 10.2; pK_a(NH_3) = 9.2) (146). The greater availability of the electron pair in ethylenediamine should result in the easier removal of an electron from the cobalt(II) atom, with a resulting stabilization of the higher oxidation state. However, both the above cobalt(II) complexes are spin free with $4s4p^34d^2$ bonding, while the cobalt(III) complexes use inner $3d^24s4p^3$ bonds. A slow activity step is involved in the electron transfer reaction, and the redox couples may well be irreversible. In such systems, where electron rearrangement occurs on oxidation, the potentials are determined largely by the activation energy involved in the electron transfer process. This invariably results in a pseudo high stability of the spin paired complex ion. In Table 7.21 and Table 7.22 are listed the standard potentials of a series of Os(II)/Os(III) couples, in which dipyridyl is successively replaced by pyridine (Table 7.21), and terpyridyl by dipyridyl and pyridine (Table 7.22).

TABLE 7.21

Couple	E_0(volts)	ΔE_0(volts)
Os $dipy_3^{2+}$ - Os $dipy_3^{3+}$	-0.8836	0.0497
Os py_2 $dipy_2^{2+}$ - Os py_2 $dipy_2^{3+}$	-0.8339	0.0306
Os py_4 $dipy^{2+}$ - Os py_4 $dipy^{3+}$	-0.8033	

TABLE 7.22

Couple	E_o (volts)	ΔE_o (volts)
$Os\ tpy_2^{2+} - Os\ tpy_2^{3+}$	-0.9866 (95)	0.1166
$Os\ py\ dipy\ tpy^{2+} - Os\ py\ dipy\ tpy^{3+}$	-0.8700	0.0714
$Os\ py_3\ tpy^{2+} - Os\ py_3\ tpy^{3+}$	-0.7986	

As discussed in Section 7.1, it is expected that entropy effects play only a minor role in determining the potential changes between the above couples. It was shown that reduction of the charge on the couple resulted in only a small change (0 - 0.07 volts) in $T\ \Delta(\bar{S}^{o})$. Therefore, for couples with the same charge the hydrational entropy contribution to ΔE_o should be even smaller.

Similarly, for the couples listed above, changes in $\Delta(\Delta H_{soln})$ are expected to be small due to the constant charges and similar sizes of the large oxidized and reduced ions (147). The octahedral covalent radii of osmium(II) and osmium(III) are nearly identical (148). Further justification for assuming $\Delta(\Delta H_{soln})$ remains essentially constant is provided by a comparison of the potentials of the Os(II)/Os(III) couples with the analogous Ru(II)/Ru(III) potentials obtained by Dwyer and Goodwin (Table 7.23) (149).

TABLE 7.23

Couple	Osmium (I=0)		Ruthenium (IN., H_2SO_4) (149)	
	E_o	ΔE_o	E_o	ΔE_o
$M\ dipy_3^{2+} - M\ dipy_3^{3+}$	-0.8836		-1.257	
		0.0497		0.01
$M\ py_2\ dipy_2^{2+} - M\ py_2\ dipy_2^{3+}$	-0.8339		-1.25	
		0.0306		0.00
$M\ py_4\ dipy^{2+} - M\ py_4\ dipy^{3+}$	-0.8033		-1.246	
$M\ tpy_2^{2+} - M\ tpy_2^{3+}$	(95) -0.9866		(95) -0.927	
		0.1166		-0.26
$M\ py\ dipy\ tpy^{2+} - M\ py\ dipy\ tpy^{3+}$	-0.8700		-1.19	
		0.0714		
$M\ py_3\ tpy^{2+} - M\ py_3\ tpy^{3+}$	-0.7986			

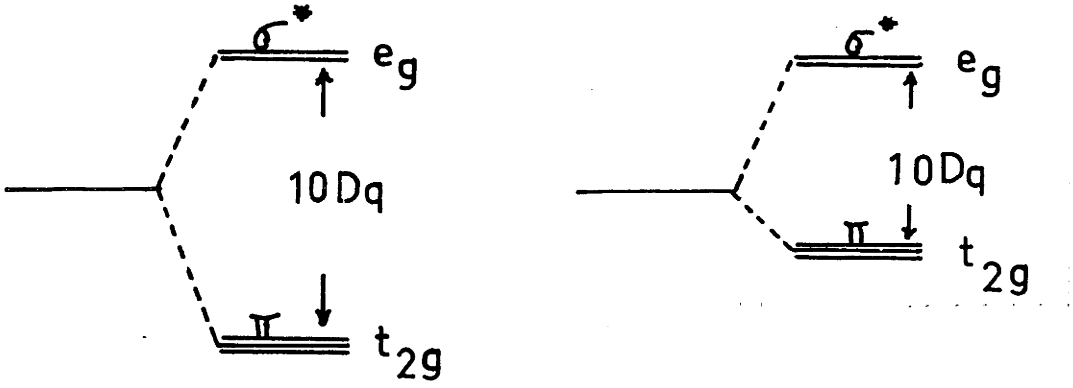
It would be expected that the $\Delta(\Delta H_{soln})$ term would be very similar in the two cases, and if significant would result in a similar trend in potential. The large magnification of the "chelate effect" observed in the osmium couples therefore probably arises largely from $\Delta H_{I.E.}$ and $\Delta H_{L.F.}$ effects.

Pyridine ($pK_a = 5.2$) is a slightly stronger base than bipyridine ($pK_a = 4.3$), and the increase in potential on successively replacing dipyridyl by two pyridine molecules (Table 7.21) can be interpreted on this basis. However, both bipyridine and pyridine are weaker bases than terpyridine (pK_a(av.) = 7.1) and the significant increase in potential observed (Table 7.22) when terpyridyl is replaced by dipyridyl and pyridine cannot be correlated with the availability of electrons on the donor nitrogen atoms.

The enthalpy changes which accompany the formation of the conjugate acid of a ligand reflect differences in electron density at the ring nitrogen atoms, whereas those accompanying the formation of metal complexes will be affected by both σ and π bonding between the metal atom and the ligand. A linear correlation between the stability of a metal complex and the pK_a of the conjugate acid of the ligand is only possible when π effects are very small or essentially constant throughout the series being studied (150,151). As discussed in Section 2.1 (page 16), the stability towards dissociation of dipyridyland terpyridyl osmium complexes can be largely attributed to π bonding. Further, the redox electron involved in oxidation probably comes from the $d(t_{2g})$ orbitals of the metal. It is just these orbitals which are used to form π bonds with the ligand (c.f. Figure 2.2, page 17). Therefore the potentials of osmium complexes should depend <u>directly</u> on the energies of the π molecular orbitals in both the oxidized and reduced ions, i.e. on the relative amounts of π bonding involved. On replacing terpyridyl or dipyridyl by pyridine, the conjugated chelate ring system is broken and the $d(t_{2g})$ electrons are raised in energy (Fig. 7.21) *.

---

* Fig. 7.21 (b) is not strictly accurate as some splitting of the t_{2g} and e_g molecular orbitals will result from tetragonal distortion of the molecule.



$[\mathrm{Os\ dipy_3}]^{2+}$ $[\mathrm{Os\ py_4\ dipy}]^{2+}$

Fig. 7·21

Evidence suggests that pyridine also forms π bonds with metal atoms $^{(59)}$, but they are probably not as strong as those formed by dipyridyl or terpyridyl.

In $[\mathrm{Os\ tpy_2}]^{2+}$ and $[\mathrm{Os\ dipy_3}]^{2+}$ the maximum number of strong π bonds will be present. In the oxidized ions only weaker bonds can form as the $d(t_{2g})$ level now has a deficiency of electrons. This will result in a marked reduction in $\Delta(\Delta H_{I.E.})$ and $\Delta(\Delta H_{L.F.})$ and a consequent stabilization of the osmium(II) state.

In $[\mathrm{Os\ py_2\ dipy_2}]^{2+}$ only two strong π bonds at right angles, and a third weaker π bond to pyridine can form. In $[\mathrm{Os\ py_2\ dipy_2}]^{3+}$ two weak π bonds are still possible. $\Delta(\Delta H_{I.E.})$ and $\Delta(\Delta H_{L.F.})$ therefore increase with a consequent stabilization of the osmium(III) valence state.

On further substitution of pyridine, $\Delta H^{2+}_{I.E.}$ and $\Delta H^{2+}_{L.F.}$ are further decreased by a reduction in π bonding, and this further stabilizes the osmium(III) state.

The potentials given in Table 7.22 can be explained similarly. Figures 7.22 and 7.23 show graphically the increase in E_o on reducing the number of chelate ligands.

Further support for the above interpretation of the "chelate effect" is provided by comparing the potentials of the couples listed in Table 7.24. Here the overall charges on the ions have been reduced by one unit from those in Table 7.21 by having one co-ordinated chlorine atom.

TABLE 7.24

Couple	E_o (volts)	ΔE_o (volts)
$[Os\ Cl\ dipy\ tpy]^+$ - $[Os\ Cl\ dipy\ tpy]^{2+}$	-0.5622	0.0799
$[Os\ Cl\ py\ dipy_2]^+$ - $[Os\ Cl\ py\ dipy_2]^{2+}$	-0.4823	0.0576
$[Os\ Cl\ py_3\ dipy]^+$ - $[Os\ Cl\ py_3\ dipy]^{2+}$	-0.4247	

ΔE_o is significantly larger than the corresponding value for the higher charged couple. If $\Delta(\Delta H_{soln})$ was the main factor determining ΔE_o it would be expected that on lowering the charge, ΔE_o would decrease since ΔH_{soln}

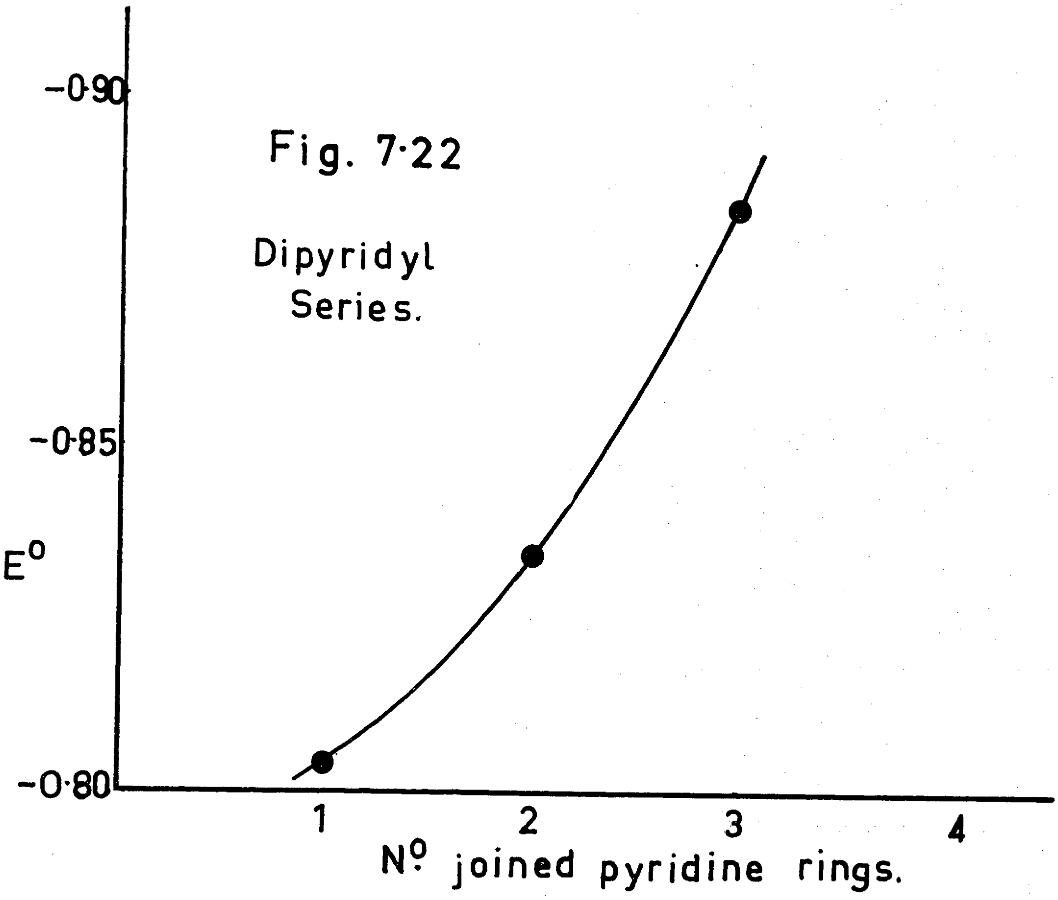
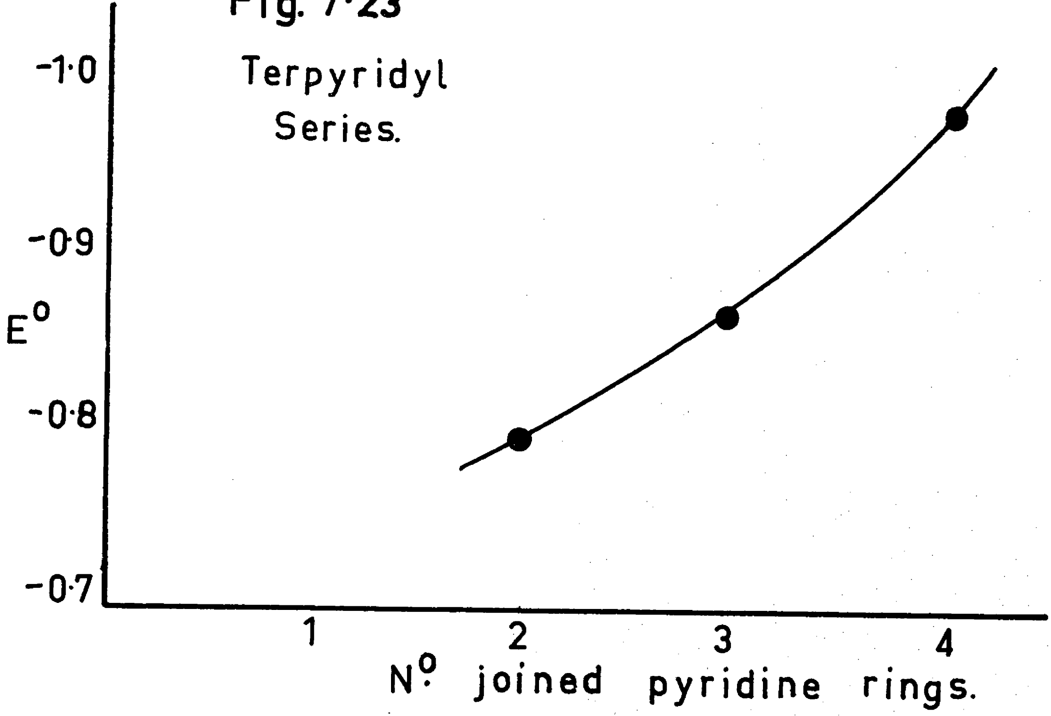


Fig. 7·22

Dipyridyl Series.

Fig. 7·23



Terpyridyl Series.

depends on the square of the charge on the complex ion. Thus $\Delta(\Delta H_{soln})$ should be smaller for the ML_x^+/ML_x^{2+} couple than for the similar ML_x^{2+}/ML_x^{3+} couple, and should result in a decrease in ΔE_o in the former series. The observed increase in ΔE_o is most easily understood as arising from the increased stabilization of the osmium(II) complex by π bonding, being successively eliminated on replacing the chelate ligands by pyridine, i.e. by $\Delta(\Delta H_{I.E.})$ and $\Delta(\Delta H_{L.F.})$ effects.

It is interesting to compare the above trends in potential with those observed for the analogous ruthenium couples (149) (Table 7.23). The "chelate effect" is increased almost tenfold in the dipyridyl series, while the potential trend in the terpyridyl series is reversed. The latter result may possibly arise from both an increase in π bonding and a reduction in the effect of basic strength and steric strain on the $\Delta(\Delta H_{I.E.})$ term.

The "chelate effect" in the above osmium complexes may therefore be largely attributed to changes in the interaction energy term $\Delta(\Delta H_{I.E.})$ and ligand field term $\Delta(\Delta H_{L.F.})$ of equation 5.516. The contributions of $\Delta(\Delta H_{soln})$ and $\Delta(\overline{S}^o)$ are expected to be small due to the constancy of the charge and size of the complex ions involved.

7.3 Effect of Substituents in the Ligand

Substitution in the ligand may affect the oxidation-reduction potential in four ways. It may:-

(i) influence the basicity of the donor atoms

(ii) affect the π bonding ability of the ligand

(iii) affect the entropy and enthalpy of solution of the complex ion, or

(iv) by purely steric effects prevent the ligand from acquiring the orientation about the central metal ion most favourable to co-ordination.

This last effect has been extensively studied for substituted phenanthrolines and dipyridyls, and it has been found, for instance, that substitution in both the 6 and 6' positions of dipyridyl completely prevents co-ordination of the two nitrogen atoms to iron (152).

The effect of substitution in the ligand on the basicity of the donor atoms, and the stability of the derived co-ordination compounds, has also been extensively studied by observing changes in the oxidation-reduction potentials of the couples,

$$[\mathrm{M\ phen_3}]^{2+} - [\mathrm{M\ phen_3}]^{3+} \qquad \text{and}$$

$$[\mathrm{M\ dipy_3}]^{2+} - [\mathrm{M\ dipy_3}]^{3+}$$

where M = Fe (153,154,155) and Ru (156). The values of the potentials of the various couples have been listed by Brandt, Dwyer, and Gyarfas (51). A similar study has recently been made by James and Williams on some Cu(I)/Cu(II) phenanthroline and dipyridyl systems (157). Electron attracting substituents (NO_2, Br, Cl) render oxidation of the complex more difficult (potentials more negative than those of the unsubstituted complexes), while electron donating groups have the opposite effect. Ewens obtained a linear relationship between the redox potentials of several 5-substituted phenanthroline complexes and the logarithms of the dissociation constants of the corresponding para-substituted benzoic acids (158). More recently Brandt and Gullstrom determined the dissociation constants of the substituted phenanthrolines themselves, and observed a direct correlation with the oxidation potential (159). Thus the variation in potential can be directly related to the basicity of the nitrogens in the substituted phenanthrolines. A similar correlation between potential and basic strength occurs for the ruthenium couples (156). These relationships can be accounted for if the pK_a is taken as a measure of the availability of the electron cloud around the ring nitrogens and its resultant effect upon the electrons around the central metal ion.

However, recent studies have shown that these linear correlations are only obtained for a series of ligands which are structurally very closely related, form π bonds to similar extents, and form the same number and size of chelate rings (151,160,161). Thus minor deviations in the straight line plot of E_o against pK_a for a series of 8-hydroxyquinoline iron couples have been explained in terms of π donor or acceptor properties of the substituents on the ligand (150). Similarly, the stabilities of some bis(pyridine) silver(I) complexes have been attributed to dative d_π bonding to the metal ion (59). The stabilities of 3-cyanopyridine silver(I) and of 5-cyano-8-hydroxyquinoline iron(II) are enhanced in comparison with their corresponding proton complexes, as the cyano substituent is a good π acceptor. For the same reason the stability of the iron(III) complex containing the latter ligand is depressed, as π bonding is considered to occur in the opposite direction (162).

In Table 7.31 are listed the potentials obtained for a series of osmium couples in which alkyl substituents are placed in the 3- and 4- positions of the co-ordinated pyridine molecule. Figure 7.31 shows a plot of the observed standard potentials against the pK_a's of the substituted pyridines. There is no linear relationship.

TABLE 7.31

E_o Values for [Os Rpy dipy tpy]$^{2+}$ [Os Rpy dipy tpy]$^{3+}$ Couple

Substituent R	pK_a (163)	E_o
H	5.17	-0.8700
$4,CH_3$	6.02	-0.8503
$3,CH_3$	5.68	-0.8657
$4,C_2H_5$	6.02	-0.8572
$4,C_3H_7$	6.02	-0.8595

This non-linearity may be ascribed to enthalpy and/or entropy considerations. The ΔH changes which accompany the formation of the conjugate acid of the ligand mainly reflect differences in σ electron density on the donor atoms, whereas those accompanying the formation of metal complexes will be affected by π bonding between the metal ions and ligand, and will also be more sensitive to steric hindrance.

The entropy changes accompanying the association of a proton with various anions are roughly constant according to the Pitzer rule (164), but those accompanying the association with amines such as terpyridine, bipyridine, and pyridine are more variable. Bulky substituents in the ligand will be expected to increase the structure breaking effect of the metal complex on the solvent, and this will result in an increase in the solvation entropy. This may well be different for the two oxidation states of the metal and result in a small change in $\Delta(\overline{S}^o)$.

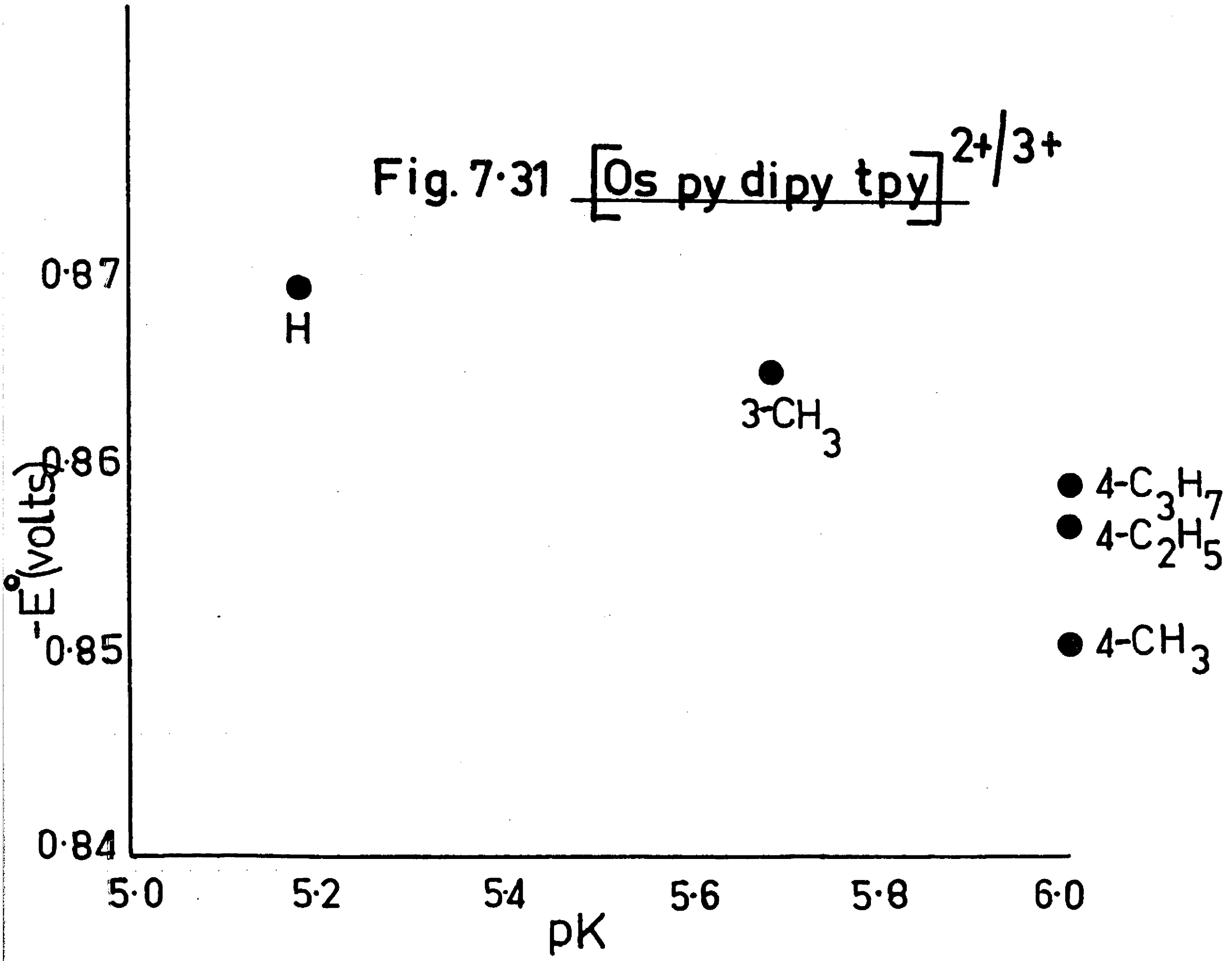


Fig. 7·31 $[\mathrm{Os\ py\ dipy\ tpy}]^{2+/3+}$

Similarly the substituting of alkyl groups on the periphery of the complex ion will also alter the solvation energy term ΔH_{soln}, and result in a variation in $\Delta(\Delta H_{soln})$ through the series studied.

However, if the terms in $\bar{S}^{o}$ and ΔH_{soln} were of primary importance in determining the deviations from linearity, it would be expected that there would be a regular trend in E_o as the size of the substituent increased along the series

$H < CH_3 < C_2H_5 < C_3H_7$. From Figure 7.31 it can be seen that this is not the case.

A more satisfactory explanation can be found in the $\Delta H_{I.E.}$ and $\Delta H_{L.F.}$ terms, by considering π donor properties of the substituents. Such π bonding does not affect the pK_a of the ligand. Thus while the 3,CH_3 substituent is unable to affect the π electron density on the N atom, the 4,CH_3 group will be able to distribute the positive charge of the central metal over its hydrogen atoms by entering into resonance with the central metal atom (Figure 7.32). Since this involves donation of negative charge to the metal atom, it will be more effective in the osmium(III) complex ion, where there is a deficiency of electrons in the π molecular orbital.

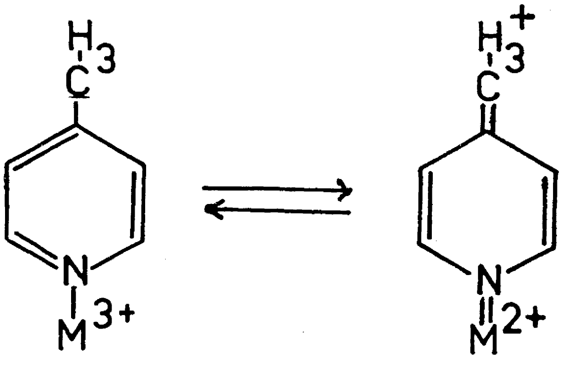


Fig. 7·32

This type of interaction stabilizes the osmium(III) complex ion. It is probable that in the osmium(II) complex π bonding will occur in the opposite direction (165). Due to the increased π electron density in the pyridine ring, the back donation of charge from the metal d(t_{2g}) orbitals will not be as effective when R = 4,CH_3, as in the unsubstituted derivative and will destabilize the osmium(II) complex ion. The combined effect on the potential will therefore result from an increase in both $\Delta(\Delta H_{I.E.})$ and $\Delta(\Delta H_{L.F.})$.

When the 4,CH_3 group is replaced by 4,C_2H_5, the stabilization of the osmium(III) complex decreases due to a reduction in the resonance interaction (Figure 7.33).

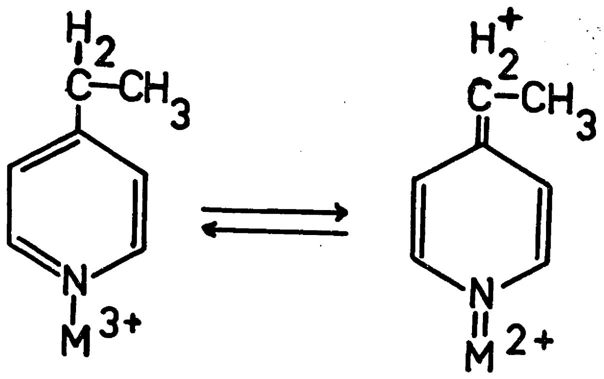


Fig. 7·33

This results from a reduction in the number of hydrogen atoms in the para position over which the positive charge of the central metal ion can be spread (Baker-Nathen effect $^{(166)}$). $\Delta(\Delta H_{I.E.})$ and $\Delta(\Delta H_{L.F.})$ will therefore be decreased, and this would account for the observed stabilization of the osmium(II) ion. A similar explanation can be given for the further observed decrease in E_o for the 4,C_3H_7 complex couple.

It is possible, therefore, to explain the observed trend in E_o for the substituted pyridine complex couples. However because the E_o differences are small, it is difficult to attribute them to any one cause, and both heat and entropy terms in equation 5.516 probably contribute.

7.4 Effect of Co-ordinated Halogens

The data available to show the effect of substituting one ligand by another of similar nature on the relative stabilities of the oxidation states is very limited. Two systems relevant to the present study are those of Ir and Ru. For the complex couples

$Ir\,Cl_6^{3-} - Ir\,Cl_6^{2-}$ $E_o = -1.017$ volts (167)

$Ir\,Br_6^{3-} - Ir\,Br_6^{2-}$ $E_o = -0.99$ volts (168)

the more positive value for the bromo system was anticipated in view of the greater stability towards reduction of the bromoiridate(IV) ion.

The values may be interpreted on the basis of the respective electronegativities of the co-ordinated halogens. Since bromine is less electronegative than chlorine, it would be expected that an electron could be removed more easily from the bromo complex. However, the large $\Delta(\overline{S}^o)$ term involved (c.f. Table 7.11), together with the uncertainty in the $IrCl_6^{3-} / IrCl_6^{2-}$ potential (132) may mean that the above is only part of the explanation.

Dwyer and Goodwin measured the potentials of the system $[\mathrm{Ru\ X\ py_3\ dipy}]^{+} / [\mathrm{Ru\ X\ py_3\ dipy}]^{2+}$ (X = Cl, Br) by the half-equivalence method in IN acid (149). They found a <u>decrease</u> in potential on substituting bromine for chlorine. This cannot be accounted for on the basis of the electronegativities, and the authors postulated the formation of π bonds between the metal and the halogen.

A similar trend in potential is observed in the present study. Table 7.41 lists the standard potentials for a series of halo- osmium couples.

TABLE 7.41

E_o Values for $[\mathrm{Os\ X\ py_3\ dipy}]^{+}$ - $[\mathrm{Os\ X\ py_3\ dipy}]^{2+}$ Couple

X	E_o	ΔE_o
Cl	-0.4247	0.0187
Br	-0.4434	0.0072
I	-0.4506	

The increase in potential on substituting bromine for chlorine cannot be explained on the basis of the electronegativities. An opposing factor, which must be considered if the potential is to be ascribed to $\Delta H_{I.E.}$ or $\Delta H_{L.F.}$ effects, is the possibility of the formation of π bonds to the halogens.

The relative stabilities of the halogen complexes have been much discussed. The sequence of stability constants is F $>$ Cl $>$ Br $>$ I for most metal halo complexes, but the reverse order is found with platinum(II), copper(I), silver(I), mercury(II) and thallium(III) complexes (169). This has been attributed to the increasing covalent character of the MX bond resulting from π bonding between filled d_π orbitals of the metal and vacant d_π orbitals in the halogen (170). An alternative explanation in terms of increased polarizing power of the central metal ion, has also been proposed (171). Poe and Vaidya (172) have criticized the possibility of d_π bonding to halogens in these "heavy" metal complexes by showing that although the stability order is Cl $<$ Br $<$ I, the actual bond strengths are in the order Cl $>$ Br $>$ I. They suggest that the observed "B class" character arises from the larger entropies and heats of solution of the bromo and iodo complexes. However, recently Westland and Westland (173) have obtained direct N.M.R. evidence for double bonding to co-ordinated halogens from a study of the trans effect in complexes of the type $[Pt\ py_2\ X_2]$ (X = Cl, Br, I, NO_2).

In the osmium(II) complex ions, three strong π bonds can theoretically be formed using the six $d(t_{2g})$ electrons of the metal (c.f. page 16). In the osmium(III) complexes, however, back donation of charge to the halogens will be significantly restricted due to the higher positive charge on the central metal atom, and the t_{2g} orbitals not being completely filled.

As it is generally accepted that the formation of π bonds contributes to the stability of a complex (67), the oxidation state in which the strongest π bonds can form will be expected to be stabilized the most. The stability order for the osmium(II) complexes would therefore be expected to increase, $Cl < Br < I$, and the potential of the Os(II) / Os(III) couples to increase, $I < Br < Cl$. The two factors, electronegativity and the π bonding ability of the ligand, are acting in opposition, and from $\Delta H_{I.E.}$ and $\Delta H_{L.F.}$ considerations it appears that the π bonding is the over-riding factor.

However, these changes in potential can equally well be ascribed to entropy and ΔH_{soln} changes. For hypothetical simple ions of the same charge and size as the above osmium complexes, the entropy differences caused by differing degrees of hydration can be estimated from the Born equation (174), or from empirical relations such as those suggested by Powell and Latimer (175). $\overline{S}^{o}(ML_x)_{aq}$ decreases as the size of the complex ion increases and as its charge decreases. $\Delta(\overline{S}^{o})$ will therefore be negative and probably decrease as chlorine is successively replaced by bromine and iodine. Opposed to this entropy effect will be the ΔH_{soln} differences between the various couples. $(-\Delta H)_{soln}$ will increase as the size decreases. Thus $\Delta(\Delta H_{soln})$ will probably decrease as chlorine is replaced by bromine and iodine, i.e. the osmium(III) state will be progressively stabilized. It has beenshown previously (page 197-9) that ΔS and ΔH_{soln} effects are at a minimum when considering large complex ions, but when small potential changes are involved these effects should not be ignored.

In an attempt to distinguish between $\Delta H_{I.E.}$, $\Delta H_{L.F.}$, and solvation effects, the potentials of a further series of osmium couples were measured. These are tabulated in the following two tables.

TABLE 7.42

E_o Values for $[Os\ X\ py\ dipy_2]^+$ - $[Os\ X\ py\ dipy_2]^{2+}$ Couples

X	E_o	ΔE_o
Cl	-0.4823	0.0038
Br	-0.4861	0.0014
I	-0.4875	

TABLE 7.43

E_o Values for $[Os\ X\ dipy\ tpy]^+$ - $[Os\ X\ dipy\ tpy]^{2+}$ Couples

X	E_o	ΔE_o
Cl	-0.5622	0.0048
Br	-0.5670	-0.0010
I	-0.5660	

On comparing Tables 7.41, 7.42 and 7.43, it can be seen that the ΔE_o values decrease as the co-ordinated pyridines are successively replaced by dipyridyl and terpyridyl. This is most simply explained as arising from a reduction in π bonding to the halogens, consequent on an increase in π bonding to the aromatic ring system, i.e. by $\Delta H_{I.E.}$ and $\Delta H_{L.F.}$ effects. Such an increase in π bonding arises from the increased delocalization of metal $d(t_{2g})$ electrons over the increasingly conjugated aromatic ligand-metal system, and a consequent withdrawal of metal $d(t_{2g})$ electrons from the osmium-halogen bond. If heats and entropies of solution were the major factors determining ΔE_o, it would be expected that similar values would be obtained, as the osmium(II) and osmium(III) complex ions will have very similar sizes in each series.

The effect of co-ordinated halogens on the potentials of the osmium couples is therefore most easily accounted for by changes in the $\Delta(\Delta H_{I.E.})$ and $\Delta(\Delta H_{L.F.})$ terms of equation 5.516. However, because of the small observed change in E_o between the various couples, contributions to ΔG^o from $\Delta(\Delta H_{soln})$ and $\Delta(\overline{S}^o)$ terms cannot be ignored.

REFERENCES

1. Cochrane J. J. Chem. Ed. 31, 407, (1954)
2. Sidgwick N. V. "The Chemical Elements and their Compounds" Oxford Univ. Press, 1950, p. 1499
3. idem p. 1492, 1494
4. Berzelius J. J. Ann. chim. et phys. 40, 257, (1829)
5. Gutbier A. and Maisch K. Ber. 42, 4239, (1909)
6. Wintrebert L. Ann. chim. et phys. [7] 28, 15, (1903)
7. Dwyer F. P. and Hogarth J. W. J. Proc. Roy. Soc. N.S.W. 84, 194, (1951)
8. Hogarth J. W. B.Sc. Thesis, University of Sydney, 1951
9. Rosenheum A. and Sassevath Z. anorg. Chem. 21, 122, (1899)
10. Dwyer F. P. and Hogarth J. W. Inorganic Synthesis Vol. V, 206, (1957)
11. idem ibid Vol. V, 204, (1957)
12. Gilchrist R. Bur. Standards J. Research 9, 279, (1932)
13. Dwyer F. P.,and Gibson N. A. Nature 165, 1012, (1950)
14. Mellor D. P. J. Proc. Roy. Soc. N.S.W. 77, 145, (1944)
15. Wintrebert L. Ann. Chim. Phys. [7] 28, 133, (1903)
16. Nyholm R. S., Fenn E., Owston P. G. and Turco A. J. Inorg. and Nuc. Chem. 17, 387, (1961)
17. Hepworth M. A., Robinson P. L. and Westland G. J. J.C.S., 1958, 611
18. Dwyer F. P., Nyholm R. S. and Tyson B. T. J.Proc. Roy. Soc. N.S.W. 81, 272, (1947)
19. Nyholm R. S. and Sutton G. J. J.C.S., 1958, 572
20. Nyholm R. S. J.C.S., 1950, 851
21. Nyholm R. S. and Sutton G. J. J.C.S., 1958, 567
22. Dwyer F. P. and Hogarth J. W. J.A.C.S., 75, 1008, (1953)
23. idem ibid 77, 6152, (1955)
24. Healy E. A. Diss. Abstracts 19, 951, (1958)

25. Gibbs W. J.A.C.S. 3, 238, (1881)

26. Fritsche J. and Struve H. J. prakt. Chem. 41, 97, (1847)

27. Brizard L. Ann. chim. Phys. 21, 373, (1900)

28. Werner A. and Dinklage K. Ber. 34, 3702, (1901)

29. Hair M. L. and Robinson P. L. J.C.S., 1960, 2775

30. Watt G. W. and Potrafke E. M. J. Inorg. and Nucl. Chem. 17, 248, (1961)

31. Dwyer F. P. and Hogarth J. W. J. Proc. Roy. Soc. N.S.W. 84, 117, (1951)

32. Dwyer F. P., McKenzie H. A. and Nyholm R.S. ibid 79, 183, (1945)

33. Dwyer F. P., Humpoletz J. E. and Nyholm R. S. ibid 80, 242, (1947)

34. Watt G. W. and Vaska L. J. Inorg. and Nuc. Chem. 6, 246, (1958)

35. Dwyer F. P. and Hogarth J. W. J. Proc. Roy. Soc. N.S.W. 85, 113, (1952)

36. Mellor D. P. A.N.Z.A.A.S. Brisbane May 1951

37. Figgis B., Lewis J., Nyholm R. S. and Peacock R. D. Trans. Far. Soc. 26, 103, (1958)

38. Earnshaw A, Figgis B. N., Lewis J. and Peacock R. D. J.C.S. 1961, 3132

39. Sutton G. J. Aust. J. Chem. 14, 33, (1961)

40. Watt G. W. and Vaska L. J. Inorg. and Nuc. Chem. 5, 308, (1958)

41. idem ibid 7, 66, (1958)

42. Chatt J. and Shaw B. L. Chem. and Industry 290, (1961)

43. Vaska L. Z. Naturforschg. 156, 56, (1960)

44. Vaska L. and DiLuzio J. W. J.A.C.S. 83, 1262, (1961)

45. Vaska L. Chem. and Ind. 1402, (1961)

46. Chatt J. and Hayter R. G. J.C.S. 1961, 896

47. idem Proc. Chem. Soc. 153, (1959)

48. idem J.C.S. 1961, 2605

49. Dwyer F. P. and Sargeson A. J.A.C.S. 77, 1285, (1955)

50. Blau F. Monatsh. Chem. 19, 647, (1898)

51. Brandt W. W., Dwyer F. P. and Gyarfas E. C. Chem. Rev. 54, 959, (1954)

52. Hein F. Chemische Koordinationslehre. S. Hirzel. Zurich (1950)

53. Busch D. H. and Bailar J. C. J.A.C.S. 78, 1137, (1956)

54. Kuznetsov V. I. Zhur. Obshchei Khim. 20, 807, (1950) c.f. C.A. 45, 1452f (1951)

55. Jorgensen C. K. Acta Chem. Scand. 11, 176 (1957)

56. Smith G. F. and Cagle F. W. J.A.C.S. 69, 1860, (1947)

57. Smith G. F. and Wilkins D. H. Anal. Chim. Acta. 9, 538, (1953)

58. Orgel L. E. 10th Solvay Conference Report Brussels 1956, p. 289

59. Basolo F. and Murmann R. K. J.A.C.S. 77, 3484, (1955)

60. Irving H. and Williams R. J. P. J.C.S. 1953, 3192

61. Basolo F. and Dwyer F. P. J.A.C.S. 76, 1454, (1954)

62. Dwyer F. P. and Broomhead J. A. Aust. J. Chem. 14, 250, (1961)

63. Harris C. M. and Lockyer T. N. Chem. and Ind. 1231, (1958)

64. Selwood P. W. "Magnetochemistry" Second Edition Interscience Pub. (1956) p. 215

65. Dwyer F. P. and Goodwin H. A. Unpublished work

66. Figgis B. J.Inorg. and Nuc. Chem. 8, 476, (1958)

67. Craig D. P., Maccoll A., Nyholm R. S., Orgel L. E. and Sutton L. E. J.C.S. 1954, 332

68. Krumholz P. J.A.C.S. 71, 3654, (1949)

69. Baxendale J. H. and George P. Trans. Far. Soc. 46, 55, (1950)

70. Jaeger F. M. and van Dijk J. A. Z. Anorg. Chem. 227, 273, (1950)

71. Gaines A., Hammett L. P. and Walden G. H. J.A.C.S. 58, 1668, (1936)

72. Kolthoff I. M., Leussing D. L. and Lee T. S. J.A.C.S. 72, 3178, (1950)

73. Miller R. R., Brandt W. W. and Sr. Marine Puke J.A.C.S. 77, 3178, (1955)

74. Swinehart Ph.D. Thesis, Purdee University, 1956
75. Hogarth J. W. Private Communication
76. Krumholz P. J. Phys. Chem. 60, 87, (1956)
77. Basolo F. Chem. Revs. 52, 459, (1953)
78. Taube H. ibid 50, 69, (1952)
79. Dwyer F. P. Report on Haematin Enzyme Symposium Canberra Aug.-Sept. 1959
80. Gibson J. F. and Ingram D. J. Nature 178, 871, (1956)
81. Broomhead J. A. and Dwyer F. P. Unpublished work
82. Dwyer F. P. and Goodwin H. A. ibid
83. Dwyer F. P. and Gyarfas E.C. Personal Communication
84. Burstall F. H., Dwyer F. P. and Gyarfas E.C. J.C.S. 1950, 953
85. Dwyer F. P. and Gyarfas E. C. J. Proc. Roy. Soc. N.S.W. 85, 135, (1951)
86. Dwyer F. P., Gyarfas E.C. and Gibson N. ibid 84, 68, (1950)
87. Dwyer F. P. and Gyarfas E. C. J.A.C.S. 73, 2322, (1951)
88. Bosnich B. Private Communication
89. Dwyer F. P. and Gyarfas E. C. J.A.C.S. 74, 4699, (1952)
90. This work Section 3.7 page 77
91. Morgan G. and Burstall F. H. J.C.S. 1932, 20
92. Brandt W. W., Dwyer F. P. and Gyarfas E. C. Chem. Revs. 54, 972 (1954)
93. Morgan G. and Burstall F. H. J.C.S. 1937, 1649
94. Corbridge D.E. C. and Cox E. C. J.C.S. 1956, 594
95. Dwyer F. P. and Gyarfas E. C. J.A.C.S. 76, 6320, (1954)
96. Dwyer F. P. Unpublished work
97. Dwyer F. P. Aust. Revs. Pure and App. Chem. 1, 77, (1951)
98. Bosnich B. and Dwyer F. P. Private Communication
99. Bosnich B. Private Communication
100. Bailar J. C. and Busch D. H. "The Chemistry of the Co-ordination Compounds" Ed. Bailar; Reinhold 1956, p. 57
101. Mitchell P. C. H. and Williams R. J.P. J.C.S. 1960, 1912

102. Kinell P. and Strandberg B. Acta. Chem. Scand. 13, 1607, (1959)

103. Chamberlain M. N. and Bailar J. C. J.A.C.S. 81, 6412, (1959)

104. Turco A. and Pecile C. Nature 191, 67, (1961)

105. Lieber E., Rao C. N. R. and Ramachandran J. Spectrochim. Acta. 13, 296, (1959)

106. Orgel L. E. Solvay Conference Report Brussels 1956, p. 289

107. Lebedinskii and Galovnya Ann secteur platine, Inst. Chim. gen (U.S.S.R.) 16, 57, (1939)

108. Harned H. S. and Owen B. B. "The Physical Chemistry of Electrolyte Solutions" Reinhold 1950, p. 297

109. Eichler E. and Wahl A. C. J.A.C.S. 80, 4145, (1958)

110. Clark W. M. "Oxidation-Reduction Potentials of Organic Systems" Williams and Wilkins 1960, p. 244

111. Glasstone S. "An Introduction to Electrochemistry" van Nostrand 1942, p. 212

112. McInnes D. A. and Yeh Y. L. J.A.C.S. 43, 2563, (1921)

113. Guggenheim E. A. J.A.C.S. 52, 1315, (1930)

114. Reference 111, p. 218

115. Perrin D. D. J.C.S., 1959, 290

116. de Bethune A. J. J. Chem. Phys. 29, 616, (1958)

117. Basolo F. and Pearson R.G. "Mechanisms of Inorganic Reactions" Wiley and Sons 1958, p. 52

118. Orgel L. E. "An Introduction to Transition Metal Chemistry" Methuen 1960, Chapter 3.

119. Benjamin L. and Gold V. Trans. Far. Soc. 50, 797 (1954)

120. George P. and McClure D. S. Progress in Inorganic Chemistry Vol. I, p. 381

121. Robinson R.A. and Stokes R. H. "Electrolyte Solutions" Second Edition Butterworths (1959), p. 230

122. idem p. 468

123. Dwyer F. P., McKenzie H. A. and Nyholm R. S. J.Proc. Roy. Soc. N.S.W. 78, 260, (1946)

124. Latimer W. M. Oxidation Potentials Second Edition Prentice-Hall p. 30

125. Dwyer F. P. and Gyarfas E. C. J.A.C.S. 74, 4699 (1952)

126. Daniels F., Mathews J. H. and Williams J. W. "Experimental Physical Chemistry" Third Edition McGraw-Hill (1941), p. 373

127. idem. p. 197

128. Dwyer F. P. Personal Communication

129. Latimer W. M. "Oxidation Potentials" Prentice-Hall (1952), p. 221

130. George P., Hanania G. I. H. and Irvine D. H. J.C.S. 1959, 2548

131. George P., Hanania G. I. H. and Irvine D. H. J.C.S. 1959, 2548

132. idem ibid 1957, 3048

133. This work, Chapter 6

134. Calculations based on data of Barnes G.T., Dwyer F. P. and Gyarfas E. C. Trans. Far. Soc. 48, 269, (1952)

135. Basolo F. and Pearson R. G. "Mechanisms of Inorganic Reactions" Wiley and Sons (1958) p. 44

136. Born M. Z. Physik 1, 45, (1920)

137. Reference 135, p. 64

138. Diehl H. Chem. Revs. 21, 84, (1937)

139. Bjerrum J. and Nielsen E. J. Acta. chem. Scand. 2, 307, (1948)

140. Schwarzenbach G. Helv. chim. Acta. 35, 2344, (1952)

141. Rossotti F. J.C. "Modern Co-ordination Chemistry" Interscience Pub. (1960), p. 58

142. Spike C. G. and Parry R. W. J.A.C.S. 75 2726, 3770, (1953)

143. Bertsch C. R., Fenelius W.C. and Block B. P. J. Phys. Chem. 62, 444, (1958)

144. Poulsen I. and Bjerrum J. Acta chem. Scand. 9, 1407, (1955)

145. Bjerrum J. "Metal Ammine Formation in Aqueous Solution" P. Haase, Copenhagen (1941) p.223, 235

146. Schwarzenbach G., Bjerrum J., Sillen L. G. Stability Constants. I.U.P.A.C., Chem. Soc. London, 1957-8

147. Barnes G. T., Backhouse J. R., Dwyer F. P. and Gyarfas E. C. J.Proc. Roy. Soc. N.S.W. 89, 151, (1956)

148. Pauling, L. "Nature of the Chemical Bond" Cornell University Press (1948) Second Edition, p. 182

149. Goodwin H. A. Ph.D. Thesis University of Sydney 1959

150. Tomkinson J. C. and Williams R. J. P. J.C.S. 1958, 2010

151. Jones J. G., Poole J. B., Tomkinson J. C. and Williams R. J. P. J.C.S. 1958, 2001

152. Burstall F. H. J.C.S. 1938, 1664

153. Brandt W. W. and Smith G.F. Analyt. Chem. 21, 1313 (1949)

154. Smith G.F. and Richter F. P. Ind. Eng. Chem. 16, 580 (1944)

155. Hale M. N. and Mellon M. G. J.A.C.S. 72, 3217 (1950)

156. Dwyer F. P. J. Proc. Roy. Soc. N.S.W. 83, 134, (1950)

157. James B. R. and Williams R. J. P. J.C.S. 1961, 2007

158. Ewens R. V. G. Nature 155, 398, (1945)

159. Brandt W. W. and Gullstrom D. K. J.A.C.S. 74, 3532, (1952)

160. Schwarzenbach G., Anderegg G., Schneider W. and Senn H. Helv. chim. Acta. 38, 1147, (1955)

161. Uusitalo E. Ann. Acad. Sci. fenn. A (87), 1957

162. Tomkinson J. C. and Williams R. J. P. J.C.S., 1958, 1153

163. Brown H. C. and Mihm X. R. J.A.C.S. 77, 1723, (1955)

164. Pitzer K. S. J.A.C.S. 59, 2365, (1937)

165. Orgel L. E. "An Introduction to Transition Metal Chemistry" Methuen (1960), p. 37

166. Baker J. W. "Hyperconjugation" Clarendon Press (1952) Chapter I

167. Dwyer F. P., McKenzie H. A. and Nyholm R. S. J. Proc. Roy. Soc. N.S.W. 78, 260, (1946)

168. idem ibid 81, 216, (1948)

169. Ahrland S. Chatt J. Quart. Revs. 12, 265, (1958)

170. Leden I. Chatt J. J.C.S. 1955, 2937

171. Williams R. J. P. Proc. Chem. Soc. 20, (1960)

172. Poe A. J. and Vaidya M. S. J.C.S. 1961, 1023

173. Westland A. D. and Westland L. Canad. J.Chem. 39, 324, (1961)

174. Laidler K. and Pegis C. Proc. Roy. Soc. A 241, 80, (1957)

175. Powell R. E. and Latimer W. M. J.Chem. Phys. 19, 1139, (1951)