

REACTIONS OF OXO COMPLEXES OF OSMIUM AND RUTHENIUM

A thesis submitted for the degree of

DOCTOR OF PHILOSOPHY

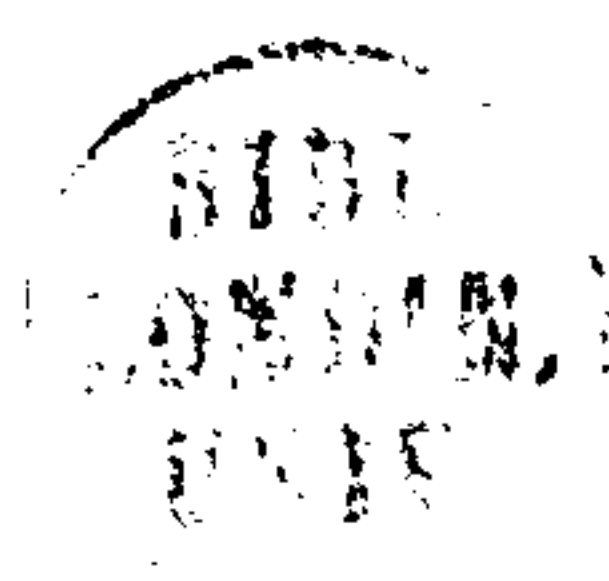
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ABSTRACT

REACTIONS OF OXO COMPLEXES OF OSMIUM AND RUTHENIUM

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The work presented in this thesis is concerned mainly with the reactions of osmium tetroxide, (OsO_4), ruthenium tetroxide, (RuO_4), and potassium ruthenate, ($\text{K}_2[\text{RuO}_4]$), with organic substrates. Particular use has been made of vibrational spectroscopy for the analysis of isolated intermediate ester complexes.

The adducts $\text{OsO}_4 \cdot \text{L}$ (L = tertiary amines) react with alkenes R to give the osmium(VI) ester complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ and $[\text{OsO}_2(\text{O}_2\text{R})\text{L}]_2$. Reaction of OsO_4 with dienes R in the presence of tertiary amines L gives the osmium(VI) ester products $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_4]$, $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_2]_n$, $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ and $[\text{OsO}_2(\text{O}_2\text{R})\text{L}]_2$. With alkynes R , the adducts $\text{OsO}_4 \cdot \text{L}$ react to give the tetrolato osmium(VI) ester complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_4]$ and $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_2]_n$. The vibrational spectra and hydrolyses of these products are discussed. The catalytic oxidation of alkynes by OsO_4 in the presence of potassium chlorate, t -butylhydroperoxide or N -methylmorpholine- N -oxide to give α -diones or carboxylic acids is described.

The ruthenate ion, $[\text{RuO}_4]^{2-}$, in the presence of potassium persulphate, catalytically oxidises a variety of organic substrates; alcohols and aldehydes are oxidised to ketones and carboxylic acids, and primary amines to nitriles and aldehydes. Alkenes, alkynes and tertiary alcohols are unaffected by the catalytic reagent, which can therefore be used for the oxidations of unsaturated alcohols to give the corresponding carboxylic acids. The salts $\text{K} \cdot \text{Ph}_4\text{M}[\text{RuO}_4]$ ($\text{M} = \text{P}$ or As) have also been prepared.

The reactions of RuO_4 with alkenes, alkynes and tertiary amines and the preparation of oxo chloro ruthenium(VI) species from $[\text{RuO}_4]^{2-}$ are

described.

The preparations of trinuclear and binuclear nitrido complexes of osmium and ruthenium have been carried out and their suitability as selective electron microscopic stains tested. Finally the preparation and reactions of the nitrido species $[\text{OsNI}_4]^-$ are discussed.

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TO MY PARENTS
AND ELA

ABBREVIATIONS AND SYMBOLS

A) Vibrational Spectra

Frequencies for infrared (I.R.) and Raman (R) spectra are quoted in wavenumbers, cm^{-1} . Stretching and deformation modes of a particular bond or group are designated by ν and δ respectively. These symbols are qualified by the superscripts s, symmetric or as, asymmetric, referring to the symmetry of the vibration. Infrared absorptions are described as s, strong, m, medium or w, weak.

B) Nuclear Magnetic Resonance Spectra (n.m.r.)

Chemical shift values (δ) are quoted relative to tetramethylsilane (T.M.S., $\delta = 00.00$).

C) Ligands

Me = methyl, CH_3	
Et = ethyl, C_2H_5	Ox = oxalate, $\text{C}_2\text{O}_4^{2-}$
Ph = phenyl, C_6H_5	phen = 1,10-phenanthroline, $\text{C}_{12}\text{H}_{12}\text{N}_2$
py = pyridine, $\text{C}_5\text{H}_5\text{N}$	M = metal
bipy = 2,2'-bipyridyl, $\text{C}_{10}\text{H}_8\text{N}_2$	

D) Miscellaneous

$\text{\AA}$	= Angstrom unit
M.P.	= melting point
B.P.	= boiling point
e.m.	= electron microscopy
M.W.	= molecular weight

CHAPTER ONE

INTRODUCTION : TERMINAL OXO COMPLEXES OF THE GROUP(VIII) METALS - OSMIUM, RUTHENIUM AND IRON

Abstract

The chemistry of the high oxidation state terminal oxo complexes of osmium, ruthenium and iron is described. The bonding and vibrational spectra of these complexes are discussed.

Section 1-A Generalities

The oxo (O^{2-}) ligand is a strong electron donor both in the σ - and π - sense, and is therefore able to stabilise the high oxidation states of transition metals. Both osmium and ruthenium can assume a variety of high oxidation states, particularly (VI) and (VIII), so these metals would be expected to form a range of oxo complexes.

The isoelectronic nitrido (N^{3-}) ligand is also capable of stabilising high oxidation state species, and indeed the formal similarity between the oxo (O^{2-}) and nitrido (N^{3-}) ligands has been illustrated in two definitive reviews.^{1,2}

The formation of oxo and nitrido complexes is generally restricted to the Group(VIII) metals and to the left-hand side of Group(VIII) in the Periodic Table; thus molybdenum, rhenium, osmium and ruthenium all form a wide variety of high oxidation state oxo and nitrido complexes. The most important high oxidation state oxo complex of iron is the Fe(VI) ferrate species $[FeO_4]^{2-}$.³

In general, the stability of high oxidation state oxo complexes of the Group(VIII) metals decreases in the order $Os > Ru > Fe$, as would be expected for moving from the third row to the first row of the transition series. This is reflected in the electrode potentials for osmium and ruthenium tetroxide.⁴ The tetroxide of iron, FeO_4 , is unknown.

$$E^0[RuO_2/RuO_4] = -0.58 \text{ V}$$

$$E^0[OsO_2/OsO_4] = -0.2 \text{ V}$$

Likewise, the reactivity of oxo complexes decreases in the order $Fe > Ru > Os$; thus ferrate, $[FeO_4]^{2-}$, is a stronger oxidant than ruthenate, $[RuO_4]^{2-}$, while the analogous osmium(VI) species $[OsO_2(OH)_4]^{2-}$

is generally much less reactive towards organic substrates.⁵

The remainder of this Chapter consists of a brief survey of the chemistry of the oxo complexes of osmium, ruthenium and iron, with a short discussion of the bonding and vibrational spectra of these complexes.

Section 1-B Summary of the Chemistry of Oxo Complexes of Osmium

1-B-1 Oxo Complexes of Osmium

The chemistry of transition metal oxo complexes has been comprehensively reviewed,¹ and this section gives a brief resumé of the types of oxo complexes formed by osmium.

Osmium tetroxide, (OsO_4), is the commonest complex of osmium and is therefore a convenient starting material for a wide variety of complexes.⁶ Treatment of OsO_4 with aqueous potassium hydroxide yields the corresponding octahedral osmium(VIII) species potassium perosmate, $\text{K}_2[\text{OsO}_4(\text{OH})_2]$, as a highly water soluble, deep red product.^{7,8} Reaction of $\text{K}_2[\text{OsO}_4(\text{OH})_2]$ with aqueous ammonia gives the pale yellow nitrido complex potassium osmiamate, $\text{K}[\text{OsO}_3\text{N}]$,^{9,10} which has been shown to involve tetrahedral osmium(VIII) with a triple $\text{Os} \equiv \text{N}$ bond.¹¹ OsO_4 reacts with a range of nitrogen donors (L) to give adducts $\text{OsO}_4 \cdot \text{L}$ (L = ammonia,^{12,13} pyridine,^{14,15} isoquinoline, phthalazine, quinuclidine or pyridazine¹⁶) and $(\text{OsO}_4)_2 \cdot \text{L}$ (L = hexamethylenetetramine,¹⁶⁻¹⁸ pyrazine, triethylenediamine or 5-methylpyrimidine¹⁶). The fluoro-oxo species $[\text{OsO}_3\text{F}_2]_n$ and $\text{K}[\text{OsO}_3\text{F}_3]$ have been prepared by treatment of OsO_4 with BrF_3 and KBr .¹⁹ More recently, trioxo bis(tert-alkylimido)osmium(VIII) complexes, $\text{C}_{10}\text{H}_{15}\text{N}=\text{OsO}_3$ ²⁰ and $\text{C}_8\text{H}_{16}\text{N}=\text{OsO}_3$,²¹ have been reported, as have the corresponding dioxo and mono-oxo (tert-alkylimido)osmium(VIII)

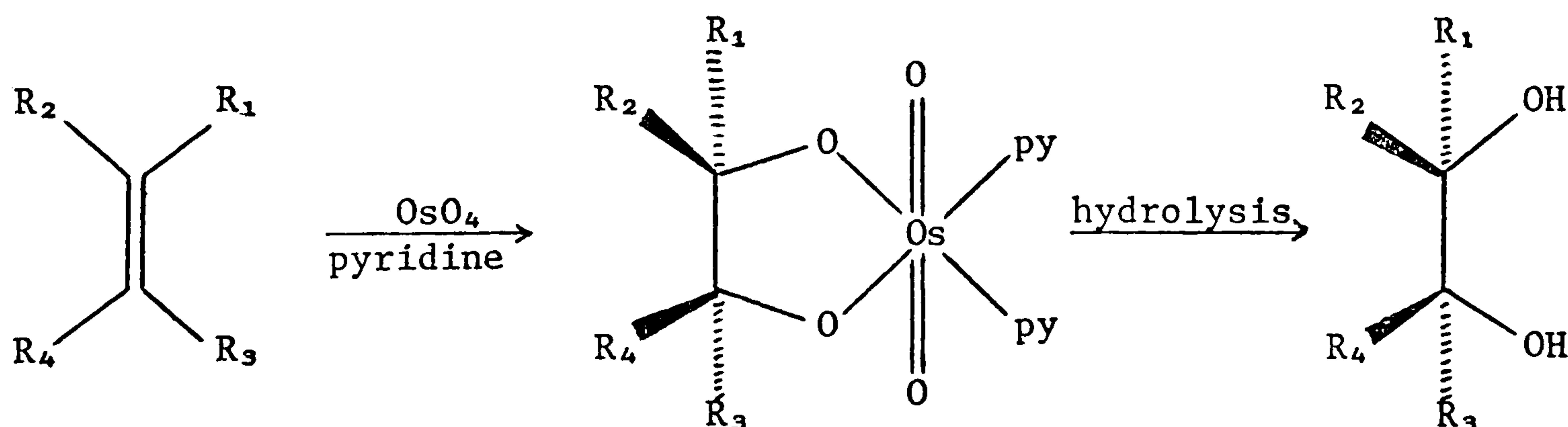
complexes.²²

The only fully characterised oxo osmium(VII) complex is OsOF_5 ,²³ although the species $\text{K}_3[\text{OsO}_5]$ and $\text{Na}_5[\text{OsO}_6]$ have also been reported.²⁴

Reduction of OsO_4 or $[\text{OsO}_4(\text{OH})_2]^{2-}$ under controlled conditions leads to the formation of octahedral trans dioxo complexes $[\text{OsO}_2\text{X}_4]^{2-}$ ($\text{X} = \text{Cl}$,^{25,26} Br ,²⁵ $\frac{1}{2}\text{ox}$,²⁵ OMe ²⁷ or OH ^{28,29}), $[\text{OsO}_2\text{L}_2\text{L}'_2]^{2-}$ ($\text{L} = \text{OH}$, $\text{L}' = \text{Cl}$, Br or $\frac{1}{2}\text{ox}$)²⁵ and $[\text{OsO}_2\text{L}_4]^{2+}$ ($\text{L} = \text{NH}_3$,^{25,30} or $\frac{1}{2}\text{en}$ ³¹). The formation of the osmium(VI) ester complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ ^{14,32} and $[\text{OsO}_2(\text{O}_2\text{R})\text{L}]$ ¹⁶ and the complexes $[\text{Os}_2\text{O}_6\text{L}_4]$ ^{14,27} ($\text{R} = \text{alkene}$, $\text{L} = \text{tertiary amine}$) is discussed in Chapter 2. A number of mono-oxo complexes are also known. The dimeric monoester complexes $[\text{Os}_2\text{O}_4(\text{O}_2\text{R})_2]$ ^{33,34} and the diester complexes $[\text{OsO}(\text{O}_2\text{R})_2]$ ^{35,36} have been prepared by reaction of OsO_4 with alkenes R . The oxotetrahalides OsOF_4 ²³ and OsOCl_4 ,¹⁹ and the complexes $[\text{OsOX}_3(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}$ or Br)³⁷ have also been reported. These latter species have been recently shown to be trans dioxo complexes $[\text{OsO}_2\text{X}_2(\text{PPh}_3)_2]$.³⁸ Rhenium also has an extensive chemistry of mono-oxo complexes, e.g., $[\text{ReOCl}_5]^{2-}$,³⁹ $[\text{ReOCl}_5]^-$,⁴⁰ $[\text{ReOCl}_3(\text{PPh}_3)_2]$,⁴¹ ReOCl_4 ,⁴² ReOCl_2 ⁴³ and binuclear complexes with $\text{Re}=\text{O}$ bonds.⁴⁴⁻⁴⁶

1-B-2 Reactions of Oxo Complexes of Osmium with Organic Substrates

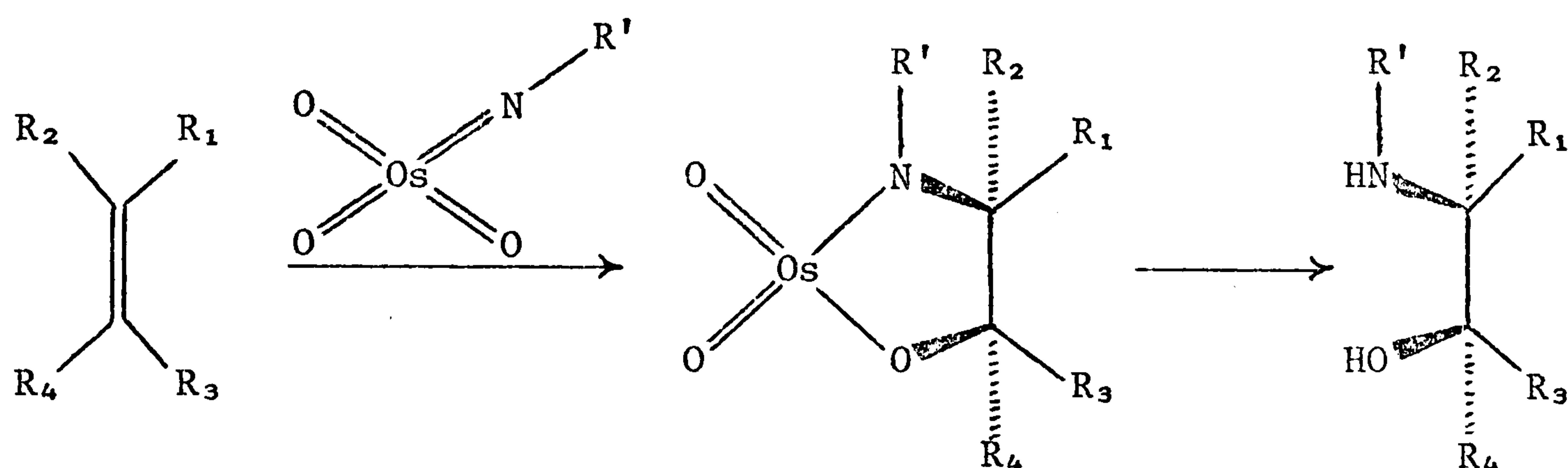
Osmium tetroxide, (OsO_4), is extensively used for the cis-hydroxylation of alkenes to give the corresponding cis-diols⁴⁷⁻⁵⁰ (Scheme 1).



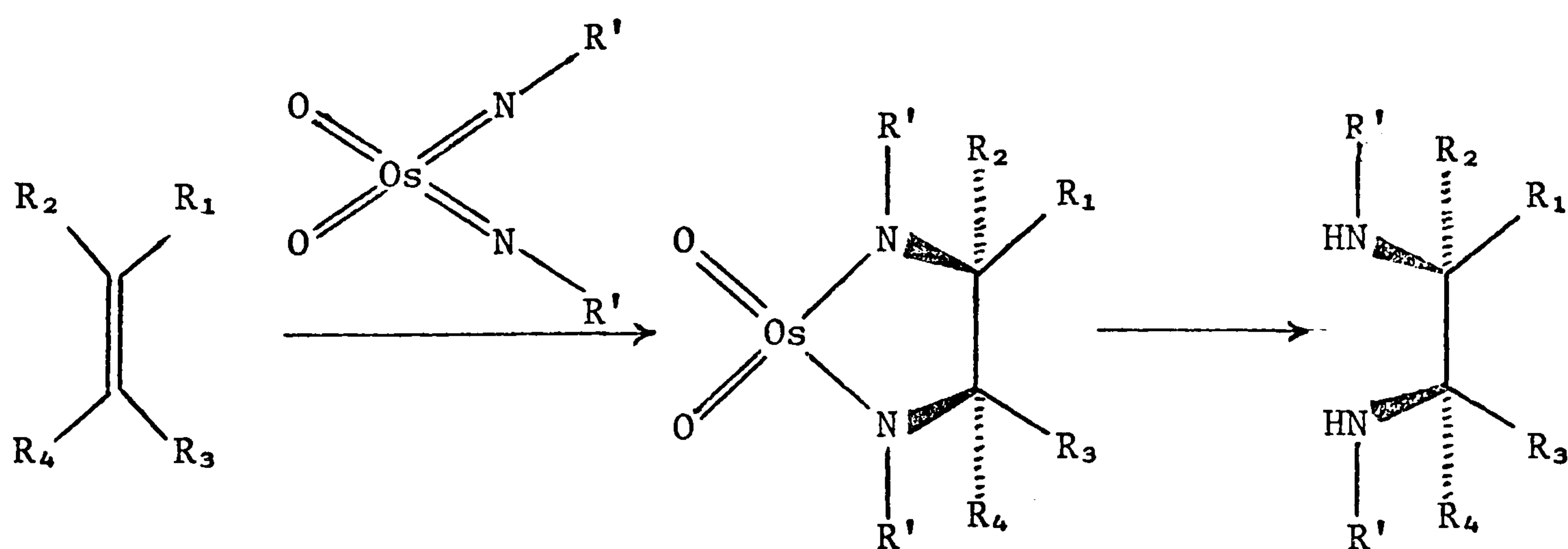
Scheme 1

The reactions of OsO_4 and the adducts $\text{OsO}_4 \cdot \text{L}$ and $(\text{OsO}_4)_2 \cdot \text{L}$ (L = tertiary amines) with alkenes, dienes and alkynes are discussed further in Chapters 2, 3 and 4 respectively.

Alkylimido osmium(VIII) complexes have been used for the vicinal oxyamination^{20,51-53} (Scheme 2) and diamination²² of alkenes (Scheme 3).



Scheme 2



Scheme 3

The vicinal oxyamination of alkenes can also be carried catalytically using OsO_4 in the presence of chloramine T^{51,52} or N-chloro-N-argento-

carbamates.⁵³

The corresponding osmium(VIII) nitrido complex potassium osmiamate, $K[OsO_3N]$, however, reacts with alkenes and alcohols only very slowly at elevated temperatures.⁵⁴

Section 1-C Summary of the Chemistry of Oxo Complexes of Ruthenium

1-C-1 Oxo Complexes of Ruthenium

As for osmium, the highest oxidation state found for ruthenium is (VIII), the tetraoxide RuO_4 being readily prepared by oxidation of RuO_2 with either periodate⁵⁵ or hypochlorite.^{56,57} The only other ruthenium-(VIII) oxo complexes reported are the adducts $RuO_4 \cdot 2py$,⁵⁸ $RuO_4 \cdot bipy \cdot 3H_2O$,^{59,60} $Ru_2O_7 \cdot phen_2$,^{59,60} and the explosive $RuO_4 \cdot L$ ^{12,13} ($L = NH_3$ or PF_3) and $(RuO_4)_2 \cdot PF_3$.^{12,13} The adduct " $RuO_4 \cdot 2py$ " has since been reformulated as $RuO_2(OH)_2 \cdot py_2$,^{15,61} $Ru(OH)_4 \cdot py_2$ ¹⁵ and $Ru_2O_6 \cdot py_4$.⁶² The reaction between RuO_4 and pyridine is discussed further in Chapter 5. The absence of a ruthenium complex analogous to the very stable potassium osmiamate, $K[OsO_3N]$, is striking since osmium and ruthenium are otherwise fairly similar in their high oxidation state chemistry.⁶

The ruthenium(VII) oxo species potassium perruthenate, $K[RuO_4]$, can be prepared by treating potassium ruthenate, $K_2[RuO_4]$, with chlorine gas.⁶³ This is the only known ruthenium(VII) oxo complex although the species $[RuO_4(OH)_2]^{3-}$ and $[RuO_4(OH)_2]^{2-}$ have been postulated to exist in solution.⁶⁴⁻⁶⁶

Reduction of RuO_4 under controlled conditions leads to the formulation of the trans dioxo ruthenium(VI) complexes $[RuO_2X_4]^{2-}$ ($X = Cl, Br$ or $\frac{1}{2}ox$),⁶⁷ $[RuO_2Cl_2L_2]$ ($L = pyridine$ or $\frac{1}{2}$ bipyridyl)⁶⁷ and the cationic species $[RuO_2(NH_3)_4]Cl_2$.⁶⁷

Potassium ruthenate, $K_2[RuO_4]$, is usually prepared by fusion of $RuCl_3$ with potassium nitrate and potassium hydroxide⁶⁸ or by reduction of

RuO_4 with aqueous alkali.⁶⁹ The product is relatively stable in alkaline aqueous solutions but readily disproportionates on acidification to RuO_4 and ruthenium(V) aquo species.⁷⁰ An X-ray study on barium ruthenate has shown it to have the structure $\text{Ba}[\text{RuO}_3(\text{OH})_2]$, involving a trigonal bipyramidal configuration with the three oxo ligands occupying equatorial positions.⁷¹

The only ruthenium complexes containing single $\text{M}=\text{O}$ bonds are the oxotetrahalide RuOF_4 ,⁷² the complex $[\text{RuO}(\text{bipy})_2\text{py}]^{2+}$ ⁷³ and the unusual $\text{Cs}_3[\text{RuO}(\text{CN})_4(\text{NCO})_2]$.⁶⁷

1-C-2 Reactions of Oxo Complexes of Ruthenium with Organic Substrates

RuO_4 is a much more powerful oxidant than OsO_4 ,⁶ as would be expected for a second row transition metal tetraoxo species. RuO_4 is found to oxidise alcohols and aldehydes to carboxylic acids and ketones,⁷⁴⁻⁷⁶ alkenes to aldehydes and acids,⁷⁴⁻⁷⁶ amines to amino acids,^{77,78} lactones to keto acids,^{79,80} glycosides to glyculopyranosides^{81,82} and steroid alcohols to ketones.⁵⁵ The oxidation of substituted biphenyls,⁸³ monoaza analogues of naphthalenes⁸⁴ and alkynes⁸⁵ by RuO_4 have also been reported.

The reaction of RuO_4 with alkenes differs markedly from that observed with OsO_4 ; the oxidations of alkenes by OsO_4 and RuO_4 have been compared^{86,87} and while OsO_4 oxidises alkenes to give the corresponding cis-diols, with RuO_4 carbon-carbon bond cleavage usually occurs, leading to the formation of aldehydes and subsequently carboxylic acids. The reactions of RuO_4 with alkynes and alkenes are discussed further in Chapter 5.

The ruthenium(VI) oxo complex sodium ruthenate, $\text{Na}_2[\text{RuO}_4]$, has been used stoichiometrically for the oxidation of alcohols and aldehydes to

the corresponding ketones or carboxylic acids,^{88,89} the oxidation of alkenes proceeding only very slowly.⁹⁰ The catalytic use of $K_2[RuO_4]$ in the presence of persulphate ion is discussed in Chapter 5.

The oxidation of alkenes by sodium perruthenate, $Na[RuO_4]$, has also been reported.⁹¹

Section 1-D Summary of the Chemistry of Oxo Complexes of Iron

1-D-1 Oxo Complexes of Iron

The Fe(VI) ferrate species, $[FeO_4]^{2-}$, is the best characterised example of a discrete oxo complex of iron.³ It can be prepared by oxidation of Fe_2O_3 with hypochlorite⁹²⁻⁹⁴ or hypobromite,⁹⁵ by anodic oxidation of iron or by oxidation of iron filings with fused KNO_3 .³ The $[FeO_4]^{2-}$ ion, like $[RuO_4]^{2-}$, is paramagnetic with 2 unpaired electrons.³ It is relatively stable under basic conditions but rapidly decomposes on acidification or reduction to give Fe(III) species.^{3,96} Other reported oxo iron species include $[FeO_3]^{2-}$,⁹⁷ $[FeO_4]^{4-}$,^{98,99} and $[FeO_4]^{3-}$.^{95,100}

1-D-2 Reactions of Oxo Complexes of Iron with Organic Substrates

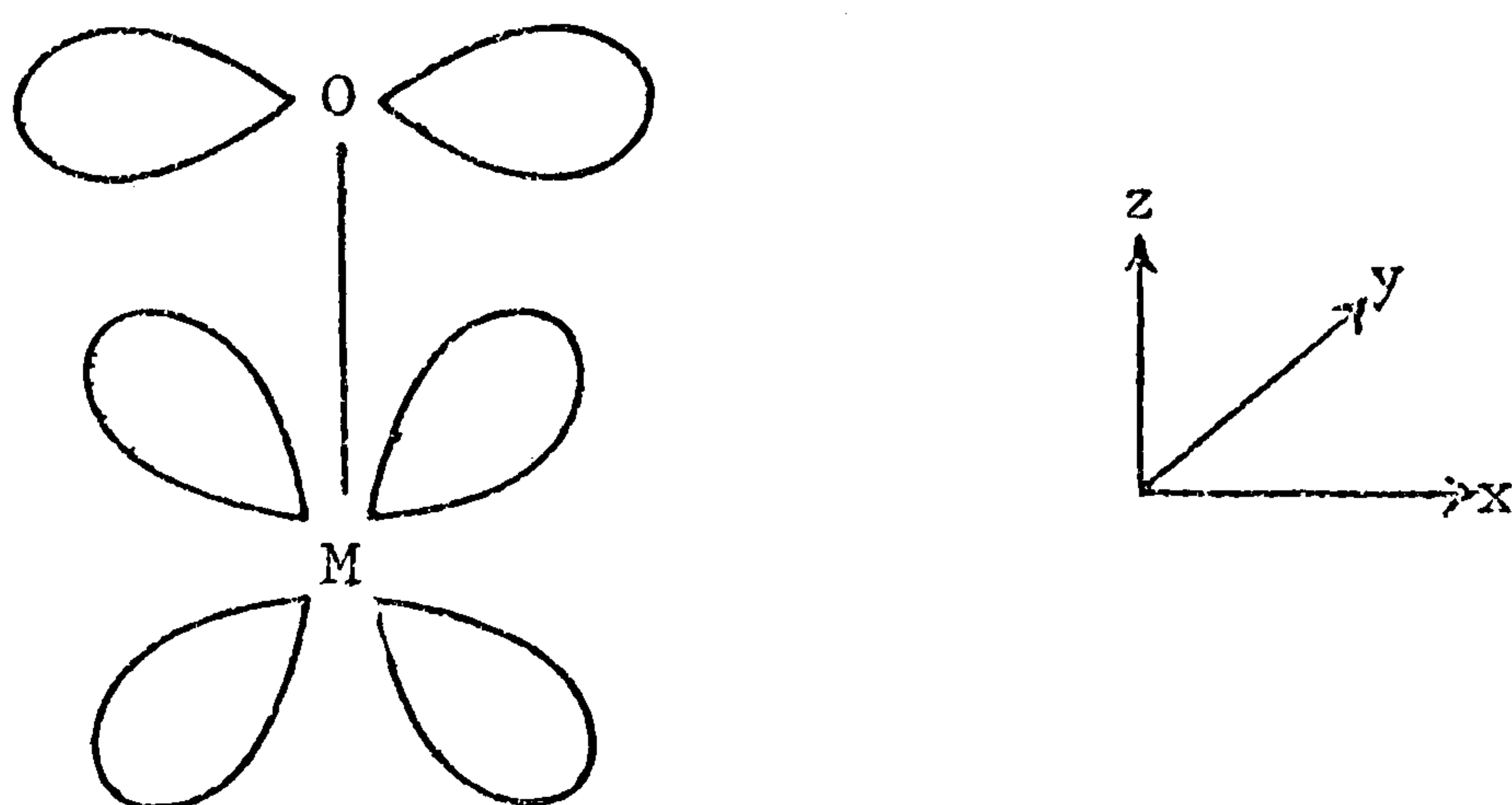
The ferrate ion, $[FeO_4]^{2-}$, is a stronger oxidising agent than permanganate $[MnO_4]^-$ ³ and can oxidise NH_3 to N_2 , Cr(II) to CrO_4^{2-} and arsenite to arsenate.³ The oxidations of alcohols and aldehydes to the corresponding ketones and carboxylic acids by $[FeO_4]^{2-}$ have been reported.¹⁰¹⁻¹⁰³

Section 1-E Bonding in Terminal Oxo Complexes

Although formally denoted by $M=O$, the metal-oxygen bond in octahedral mono-oxo complexes (e.g., $[VO(H_2O)_5]^{2+}$) is in fact a triple bond made up of one σ - and two π - bonds, which may be described by the following orbital overlaps:-¹⁰⁴

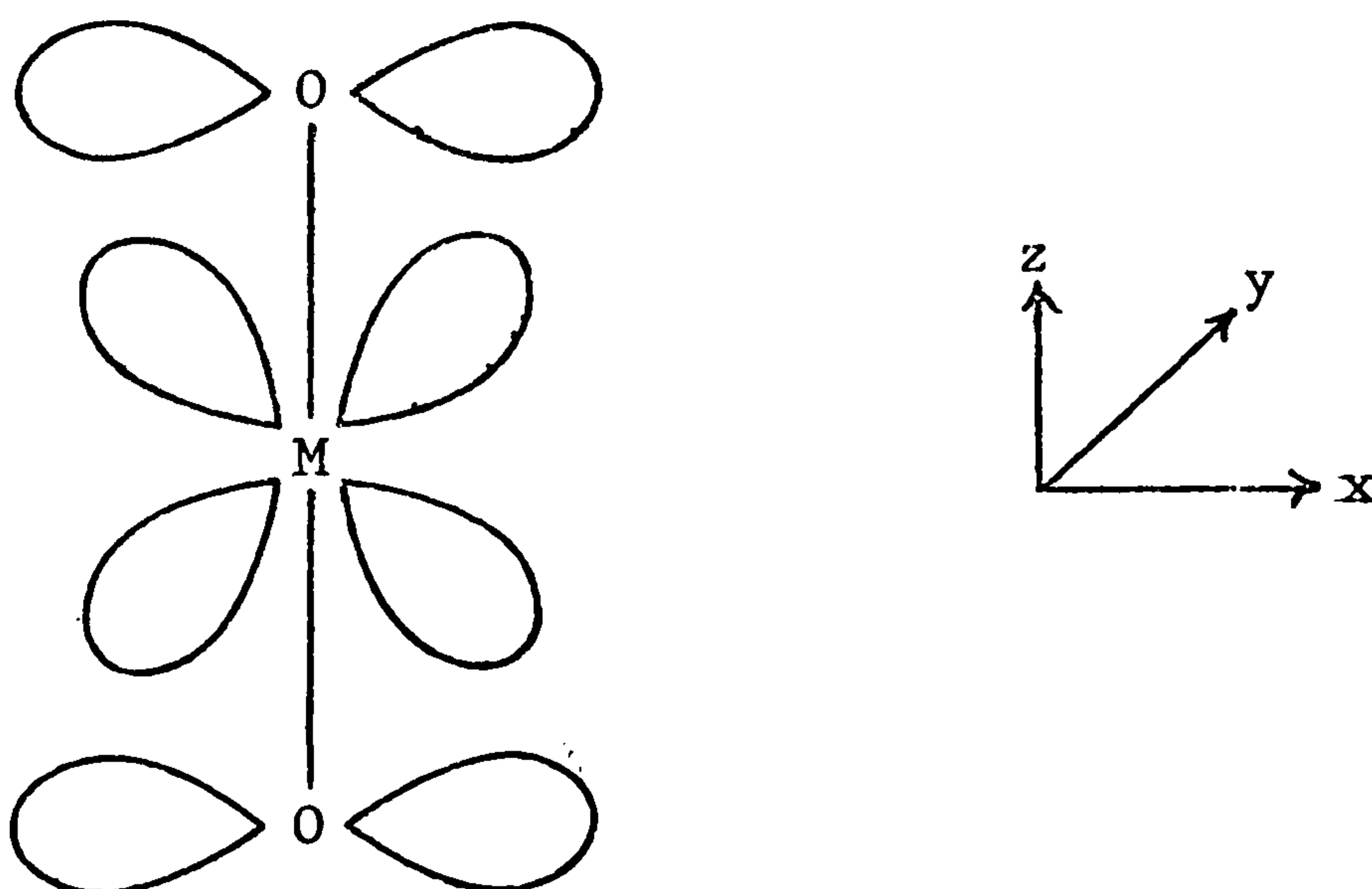
σ bond:- Metal d_{z^2} and s orbitals overlapping with oxygen
 $2sp_\sigma$ orbital

π bonds:- Metal d_{xz} and d_{yz} orbitals overlapping with
 oxygen $2p_x$ and $2p_y$ orbitals respectively.



For octahedral dioxo complexes, cis or trans configurations of oxo ligands are possible.

In trans dioxo complexes, π -bonding occurs between the metal and oxo ligands via overlap between the metal d_{xz} and d_{yz} orbitals with the oxygen $2p_x$ and $2p_y$ orbitals respectively, the metal d_{xz} and d_{yz} orbitals interacting with the p orbitals of both oxo ligands. This leaves the



metal d_{xy} orbital as a non-bonding orbital with significant metal

character;^{105,106} it is this orbital that is occupied by the d-electrons in d^2 trans dioxo complexes, which explains their diamagnetism.¹⁰⁷

For cis dioxo complexes, however, all three metal d_ϵ orbitals, d_{xz} , d_{yz} and d_{xy} , are involved in π -bonding overlap with the p orbitals of the oxo ligands.^{105,106}

In general, d^0 octahedral dioxo complexes (e.g., $[\text{MoO}_2\text{Cl}_4]^{2-}$) assume a cis dioxo configuration since this enables the greatest π -bonding overlap to occur between the metal and oxo ligands, while d^2 octahedral complexes [e.g., $\text{OsO}_2(\text{O}_2\text{R})\text{L}_2$] assume a trans dioxo configuration, with the d-electrons occupying the non-bonding metal d_{xy} orbital.

Section 1-F Vibrational Spectra of Terminal Oxo Complexes

Since vibrational spectroscopy has been extensively used in the work described in this thesis, the essential features of the vibrational spectra of octahedral mono-oxo and dioxo complexes are described (Table 1-1).

For mono-oxo complexes, the metal-oxygen stretching vibration, ν_{MO} , occurs in the range $900\text{--}1020\text{ cm}^{-1}$. Thus, for the monomeric diester complexes $[\text{OsO}(\text{O}_2\text{R})_2]$ and dimeric monoester complexes $[\text{Os}_2\text{O}_4(\text{O}_2\text{R})_2]$ (R = alkene), the stretching vibration, ν_{OsO} , occurs in the infrared near 980 cm^{-1} .³²

For octahedral dioxo complexes, cis or trans configurations of oxo ligands are possible. The vibrational spectra of octahedral dioxo complexes show two metal-oxygen stretching vibrations; a symmetric stretching mode, $\nu_{\text{MO}_2}^{\text{S}}$, and an asymmetric stretching mode, $\nu_{\text{MO}_2}^{\text{as}}$.

For trans dioxo complexes of D_{4h} symmetry, the symmetric stretching mode, $\nu_{\text{MO}_2}^{\text{S}}$, occurs in the Raman near 880 cm^{-1} , with the asymmetric

stretching mode, $\nu_{\text{MO}_2}^{\text{as}}$, occurring in the infrared near 800 cm^{-1} (Table 1-1).

For cis dioxo complexes of C_{2v} symmetry, the symmetric and asymmetric stretching modes, $\nu_{\text{MO}_2}^{\text{s}}$ and $\nu_{\text{MO}_2}^{\text{as}}$, occur near 930 cm^{-1} and 900 cm^{-1} respectively, both vibrations being infrared and Raman active (Table 1-1).

It is of interest to note that the metal-oxygen stretching vibrations for cis dioxo complexes occur at higher frequencies than for the corresponding trans dioxo complexes (Table 1-1). This is due to the greater π -bonding overlap in cis dioxo complexes where all three metal d_{ϵ} orbitals are involved in π -bonding. This is in contrast to trans dioxo complexes in which only two metal d_{ϵ} orbitals (d_{xz} , d_{yz}) are involved in π -bonding (Section 1-E).

Table 1-1
Vibrational Spectra of Terminal Oxo Complexes

a = trans dioxo complexes; b = cis dioxo complex.

		ν_{MO} (cm^{-1})	δ_{MO} (cm^{-1})	
OsO ₄		960	330	
RuO ₄		900	330	
K ₂ [RuO ₄]		836, 810	330	
K ₂ [FeO ₄]		827, 779	339	
K[OsO ₃ N]		880, 860	330	
[Os ₂ O ₄ (O ₂ R) ₂], [OsO(O ₂ R) ₂]		980	300	
		$\nu_{\text{MO}}^{\text{as}}$ (cm^{-1})	$\nu_{\text{MO}}^{\text{s}}$ (cm^{-1})	δ_{MO} (cm^{-1})
[OsO ₂ X ₄] ²⁻ , [OsO ₂ L ₂ L' ₂] ²⁻ , [OsO ₂ (O ₂ R)L ₂] ^a	IR	840	—	300
	R	—	880	—
[RuO ₂ X ₄] ²⁻ , [RuO ₂ L ₂ L' ₂] ²⁻ ^a	IR	800	—	300
	R	—	860	—
[OsO ₂ (O ₂ R)L]	IR	900	—	300
	R	—	910	—
Cs ₂ [MoO ₂ Cl ₄] ^b	IR	882	919	381
	R	887	919	—

CHAPTER TWO

REACTIONS OF OSMIUM TETRAOXIDE WITH ALKENES

Abstract

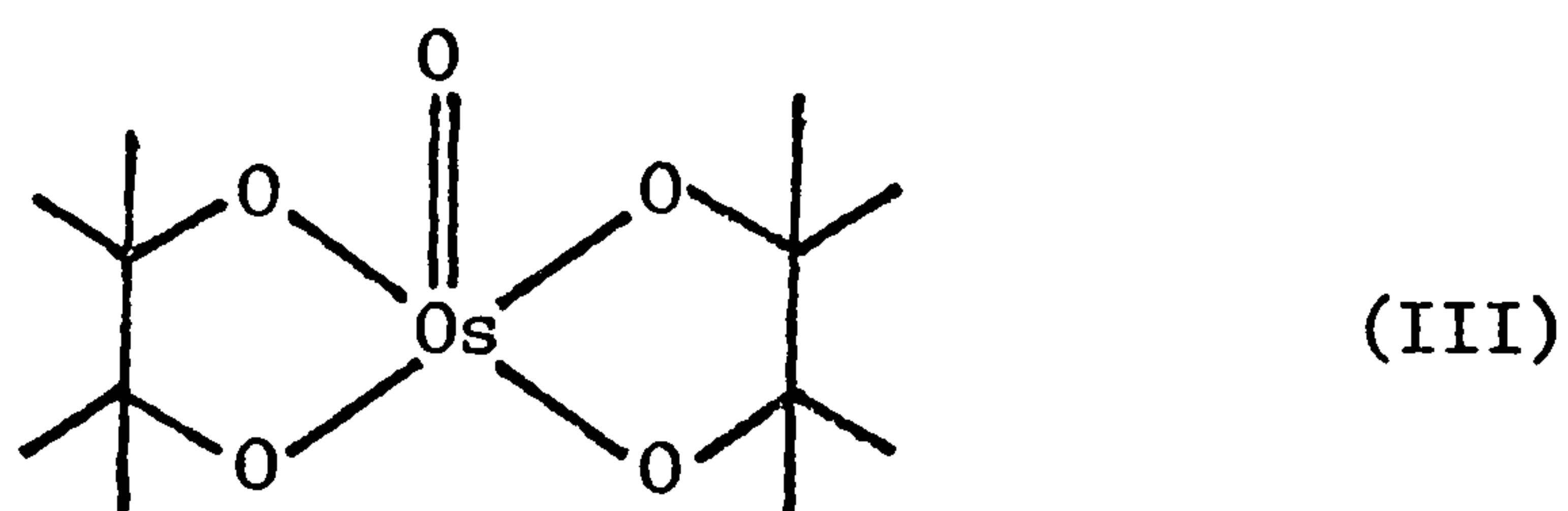
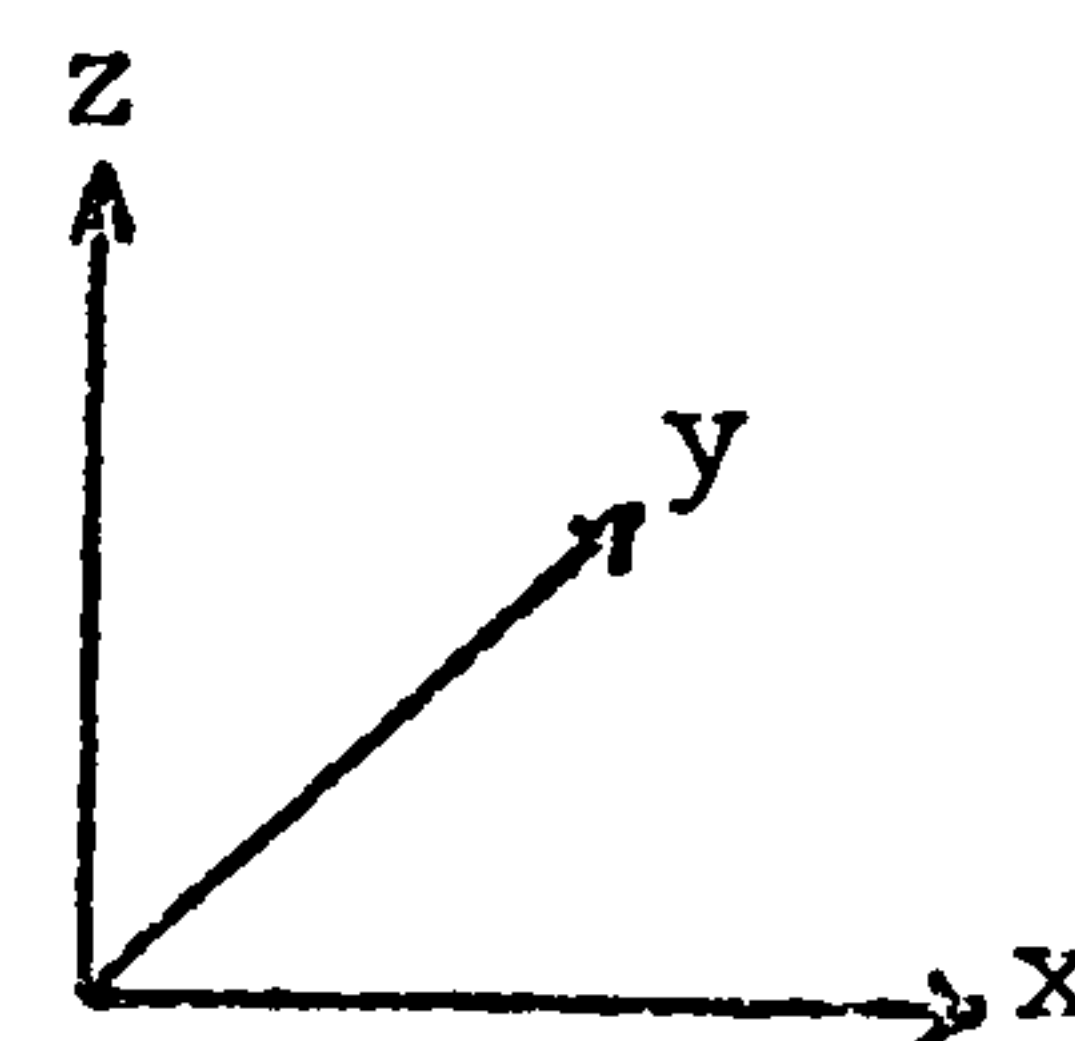
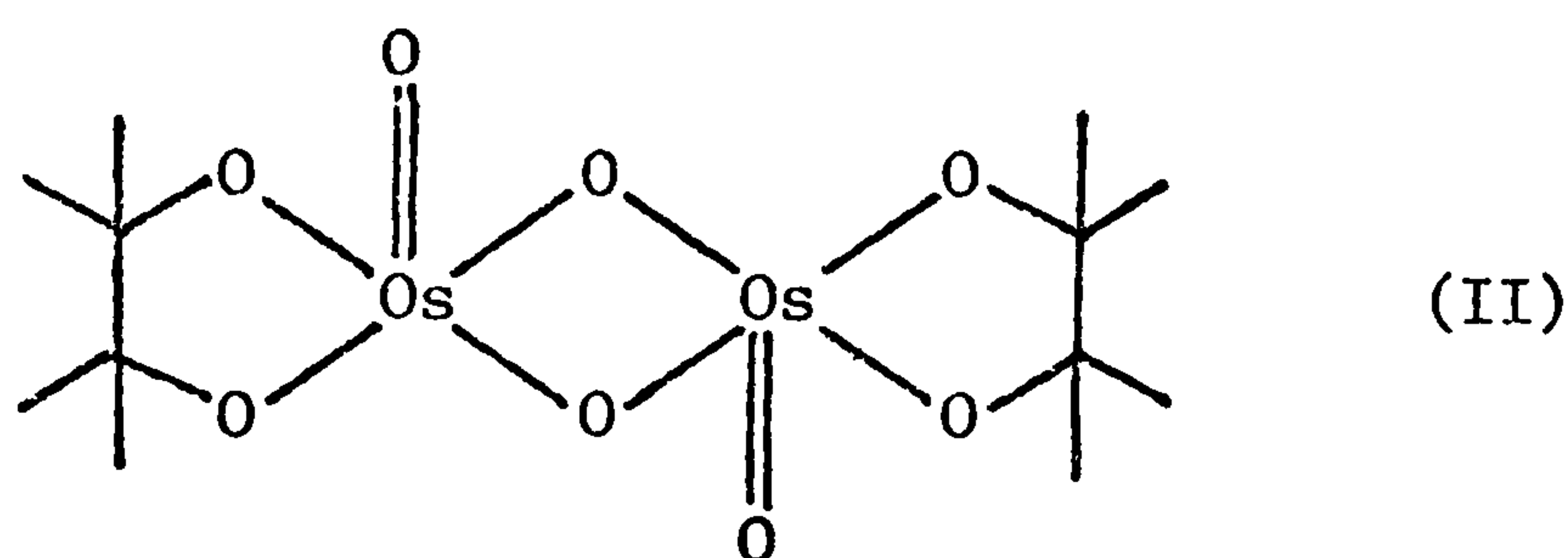
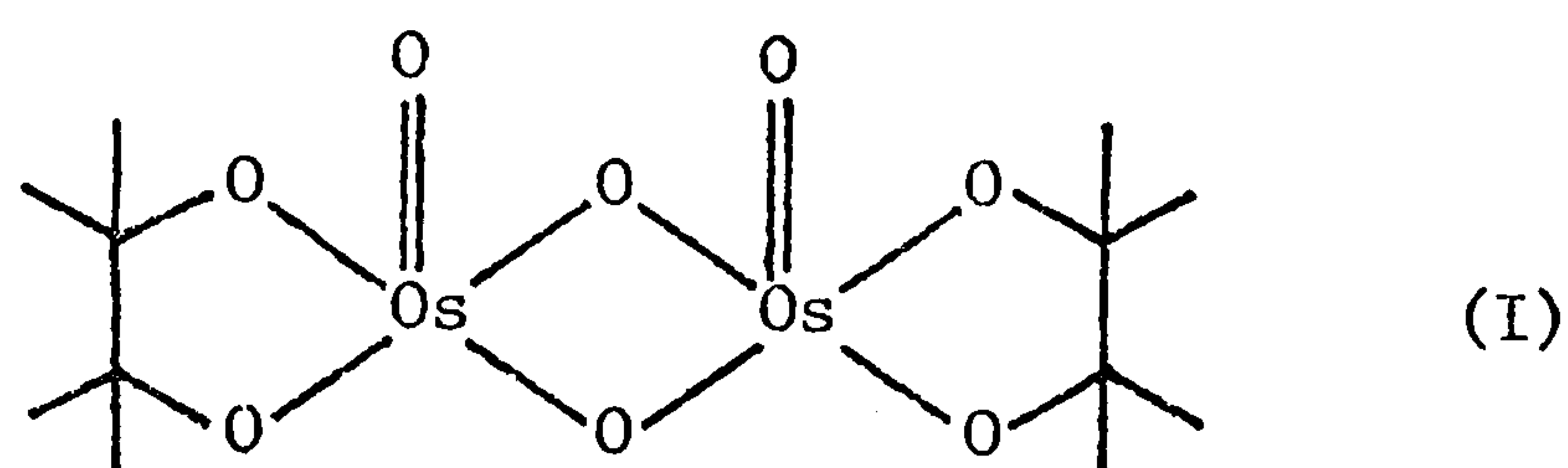
Osmium tetroxide, (OsO_4) , reacts with alkenes R in the presence of tertiary amines L to give oxo amine osmium(VI) ester complexes $[OsO_2(O_2R)L]_2$ and $[OsO_2(O_2R)L_2]$ (L = pyridine, isoquinoline or quinuclidine). The X-ray crystal structure of $[OsO_2(O_2C_6H_{10})C_7H_{13}N]_2$ (C_6H_{10} = cyclohexene, $C_7H_{13}N$ = quinuclidine) is reported.

OsO_4 can be reduced with ethanol in the presence of tertiary amines L to give oxo amine osmium(VI) complexes $[Os_2O_6L_4]$ (L = pyridine or 4-^tbutylpyridine) and $[Os_2O_6L_2]$ (L = quinuclidine or hexamethylene-tetramine), which react with cis-diols to give the corresponding oxo amine osmium(VI) ester complexes $[OsO_2(O_2R)L_2]$ and $[OsO_2(O_2R)L]_2$ respectively.

The structures of all these complexes are discussed on the basis of their vibrational and ^1H n.m.r. spectra. The hydrolysis of the complex $[OsO_2(O_2C_6H_{10})(C_5H_5N)_2]$ (C_6H_{10} = cyclohexene, C_5H_5N = pyridine) is described.

Section 2-A Introduction

Osmium tetroxide, (OsO_4), is a valuable reagent in organic synthesis and is extensively used for the cis-hydroxylation of alkenes to give the corresponding cis-diols.⁴⁷⁻⁵⁰ Reaction of OsO_4 with alkenes R gives the corresponding dimeric monoester complexes syn¹⁰⁸ or anti³² [$\text{Os}_2\text{O}_4(\text{O}_2\text{R})_2$] (I), (II) and, in some cases, the monomeric diester complexes [$\text{OsO}(\text{O}_2\text{R})_2$] (III).^{32,109,110} These diamagnetic products have been shown by X-ray studies to contain square based pyramidal osmium(VI) with cyclic ester rings.³³⁻³⁶



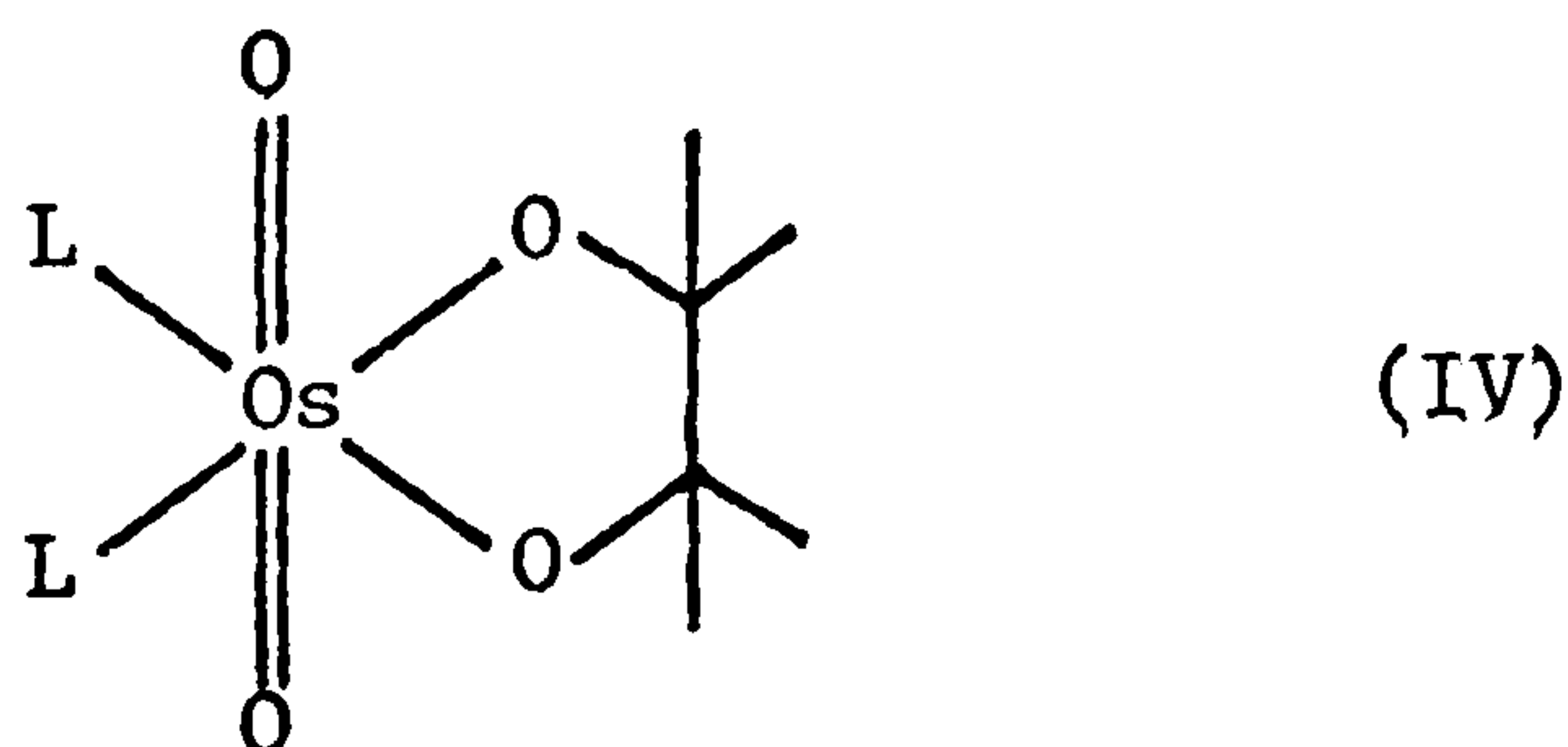
The π -bonding in these complexes probably occurs via overlap between the metal d_{xy} and d_{yz} orbitals and the oxygen p_x and p_y orbitals, the two remaining d-electrons being accommodated by the non-bonding metal d_{xy} orbital, thus explaining their diamagnetism.

These complexes are thought to be the intermediates formed during the cis-hydroxylation of alkenes by OsO_4 ,^{27,32} their hydrolysis leading

to the formation of the corresponding cis-diols.^{27,109,110} The monoester and diester complexes can also be regarded as models for the types of osmium complexes formed when OsO₄ interacts with unsaturated substrates present in biological tissues during staining and fixation for electron microscopy;¹¹¹⁻¹¹⁵ the formation of osmium(VI) species when OsO₄ interacts with certain biological tissues has been demonstrated by X-ray photoelectron spectroscopy.¹¹⁶

For the cis-hydroxylation of alkenes to cis-diols, OsO₄ is usually used catalytically together with a secondary oxidising agent such as potassium chlorate¹¹⁷⁻¹¹⁹ or hydrogen peroxide.¹²⁰⁻¹²² The reaction proceeds via formation of the osmium(VI) ester intermediate which is then hydrolysed to give the corresponding cis-diol, OsO₄ being regenerated by the secondary oxidising agent. In this way, oxidations can be carried out using only catalytic amounts of OsO₄. It was observed, however, that the presence of tertiary amines, such as pyridine, greatly increased the rate of cis-hydroxylation of alkenes by OsO₄,^{14,123-125} presumably by increasing the rate of formation of the osmium(VI) intermediates.¹⁴ This led to the investigation of the osmium(VI) complexes formed by reaction of OsO₄ with alkenes in the presence of tertiary amines.^{14,32,61}

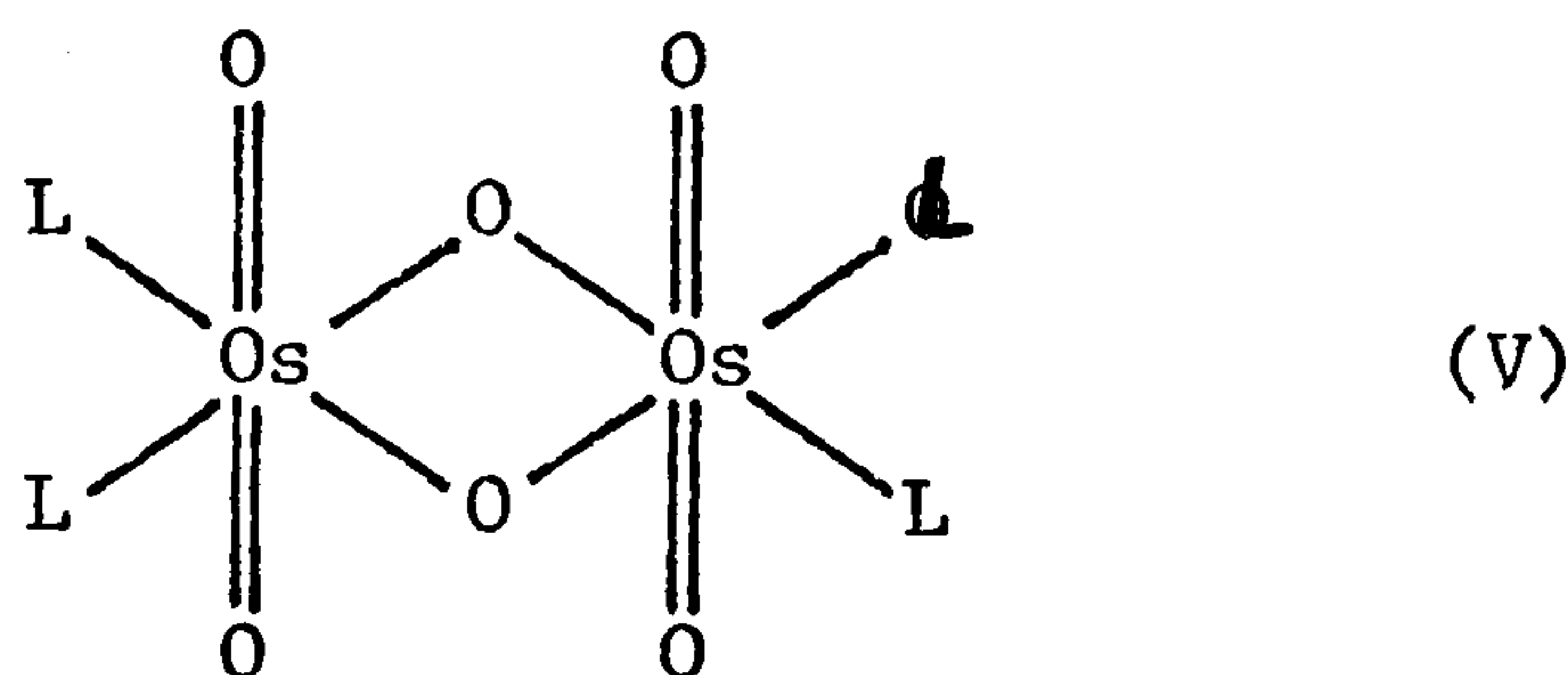
OsO₄ was found to react with alkenes R in the presence of excess of tertiary amines L to give diolato dioxo amine osmium(VI) ester complexes [OsO₂(O₂R)L₂] (IV) (L = pyridine,^{14,32,126-128} isoquinoline,³² quinoline¹⁴ or $\frac{1}{2}$ -bipyridyl^{14,126})



These complexes contain the trans O=Os=O moiety and are diamagnetic, as

expected for trans dioxo osmium(VI) species.¹⁰⁷ They can be readily hydrolysed using alcoholic sodium sulphite^{14,129} to give the corresponding cis-diols.

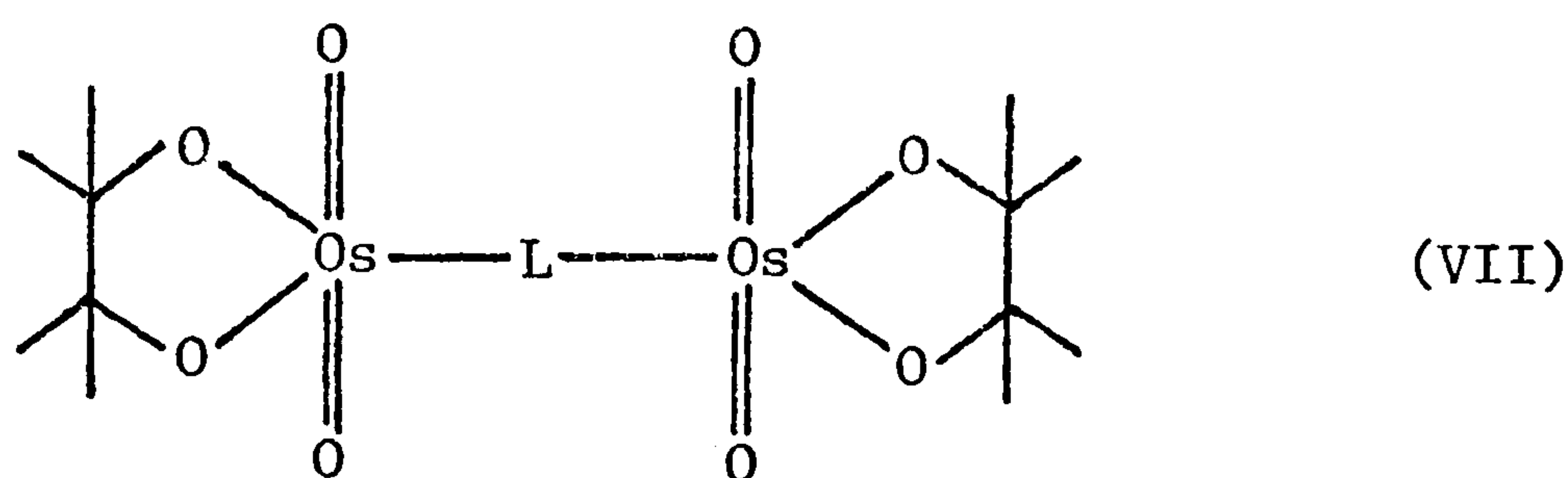
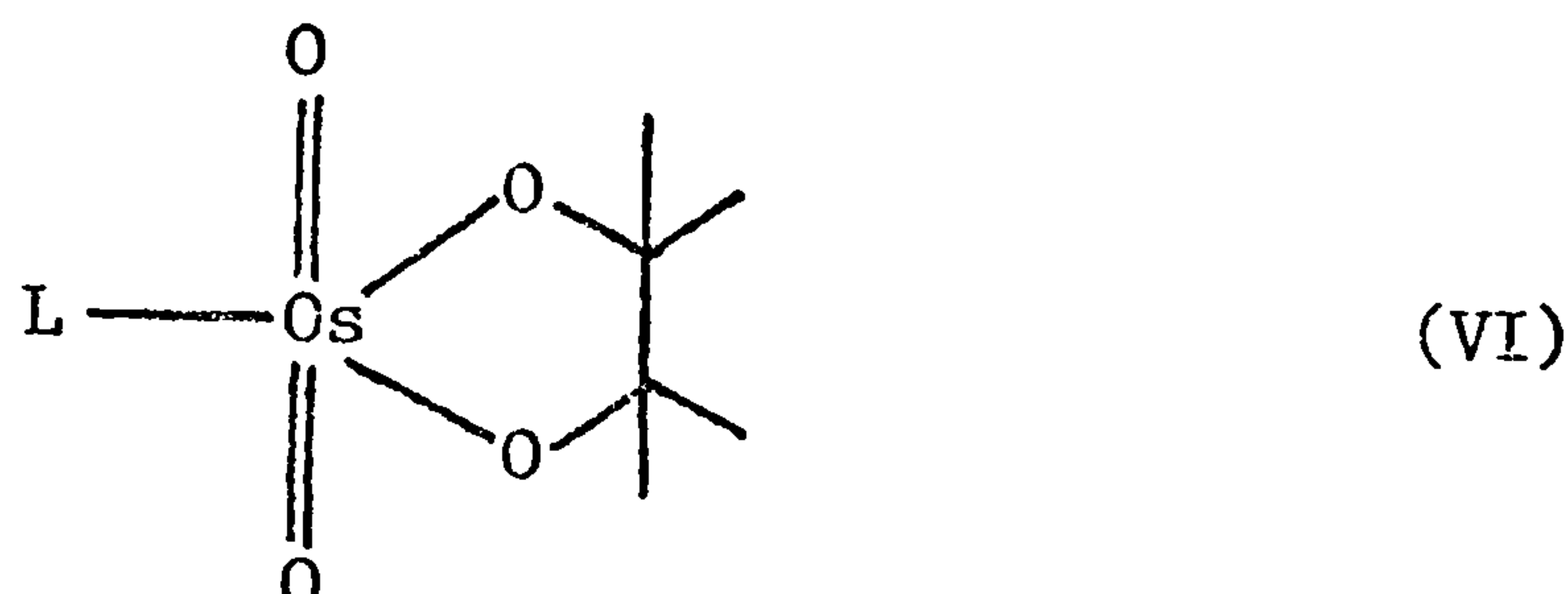
An alternative method of preparing the osmium(VI) ester complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ is by reaction of the oxo amine osmium(VI) complexes $[\text{Os}_2\text{O}_6\text{L}_4]$ with cis-diols.^{14,130} OsO_4 can be reduced with ethanol in the presence of excess of tertiary amine L to give the complexes $[\text{Os}_2\text{O}_6\text{L}_4]$ (V) (L = pyridine,^{61,130} 3-picoline,¹³⁰ 3-chloropyridine¹³⁰ or $\frac{1}{2}$ -bipyridyl¹³¹).



The products are dimeric in the solid state containing the trans dioxo "osmyl" moiety and a symmetric Os_2O_2 bridging system;^{61,130,131} similar bridging systems have been noted for the dimeric monoester complexes $[\text{Os}_2\text{O}_4(\text{O}_2\text{R})_2]$ ³³ and for $\text{K}_4[\text{Os}_2\text{O}_6(\text{NO}_2)_4]$.^{132,133} The complexes $[\text{Os}_2\text{O}_6\text{L}_4]$ react readily with cis-diols $\text{R}(\text{OH})_2$ to give the corresponding oxo amine osmium(VI) ester complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ (IV).^{14,130}

OsO_4 also reacts with polydentate and monodentate tertiary amines, in non-reducing conditions, to give the adducts $\text{OsO}_4 \cdot \text{L}$ (L = pyridine,^{14,15} isoquinoline, phthalazine, quinuclidine or pyridazine¹⁶) and $(\text{OsO}_4)_2 \cdot \text{L}$ (L = pyrazine,¹⁶ hexamethylenetetramine,¹⁶⁻¹⁸ triethylenediamine, or 5-methylpyrimidine¹⁶). These adducts retain the integrity of the $\text{Os}^{\text{VIII}}\text{O}_4$ entity and, in the case of the hexamethylenetetramine complex, can be used as a stabilised, non-volatile form of OsO_4 ,^{18,134,135} the high volatility and toxicity of OsO_4 being considered a great hazard.⁶

Reaction of the adducts with alkenes R gives products formulated as $[\text{OsO}_2(\text{O}_2\text{R})\text{L}]$ (VI)¹⁶ (L = isoquinoline, phthalazine, quinuclidine or hexamethylenetetramine) and $[\text{OsO}_2(\text{O}_2\text{R})]_2\text{L}$ (VII)¹³⁶ (L = triethylenediamine). Structures (VI)¹⁶ and (VII)¹³⁶ involving trigonal bipyramidal osmium(VI) with trans oxo ligands, have been proposed for these complexes respectively.



Spectroscopic data for these latter species however are not fully consistent with the proposed five coordinate structure, the asymmetric stretching vibration, $\nu_{\text{OsO}_2}^{\text{as}}$, for these complexes appearing in the infrared at much higher frequencies than expected.¹⁶

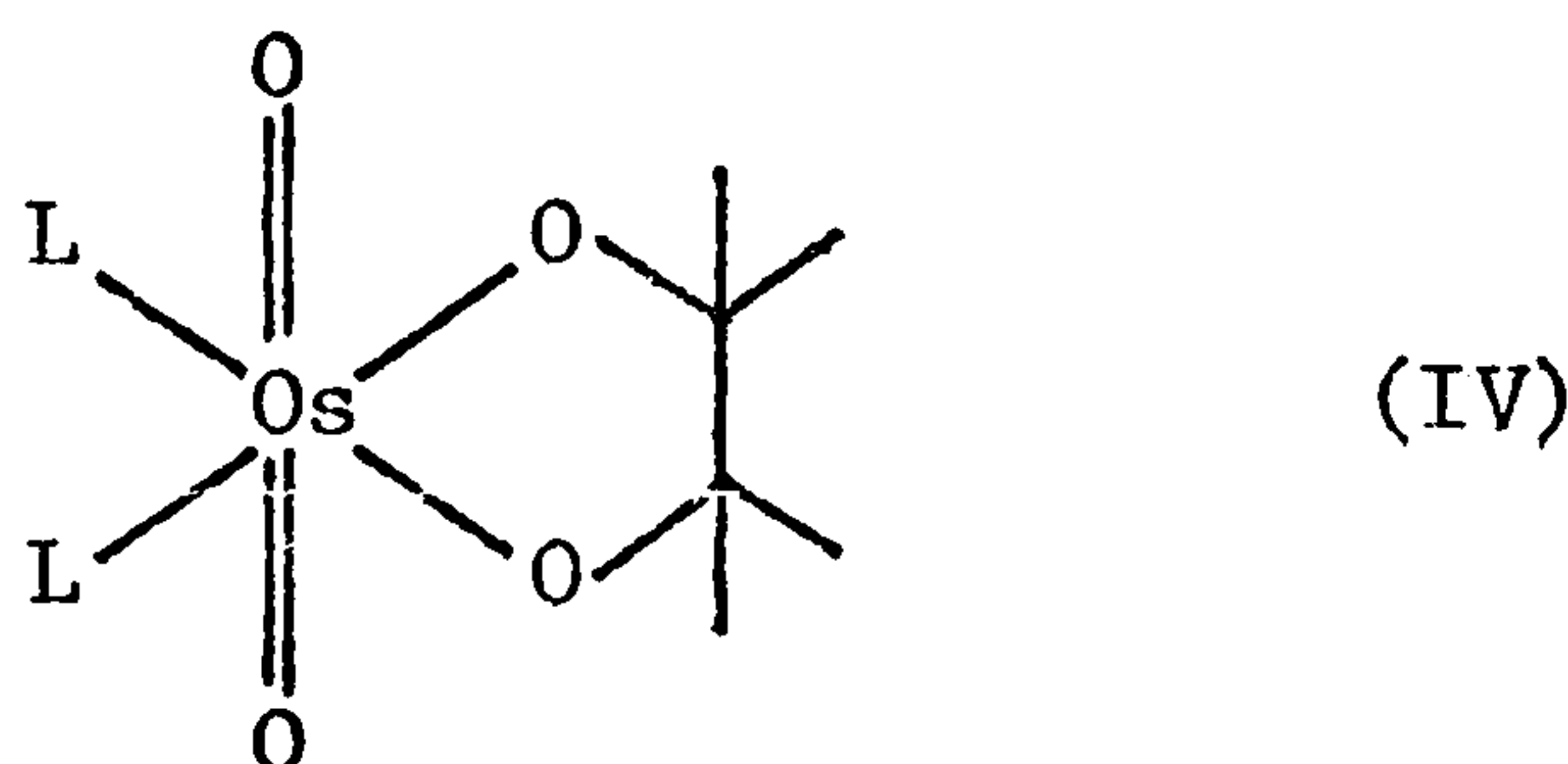
This ambiguity led to the re-investigation of the products formulated as $[\text{OsO}_2(\text{O}_2\text{R})\text{L}]$. Work was also carried out on the formation and reactions of the oxo amine osmium(VI) complexes $[\text{Os}_2\text{O}_6\text{L}_4]$ and $[\text{Os}_2\text{O}_6\text{L}_2]$, and on the hydrolysis of the ester complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$.

Section 2-B Reaction of Adducts $\text{OsO}_4 \cdot \text{L}$ with Alkenes (L = pyridine, isoquinoline, 4-^tbutylpyridine)

The 1 : 1 amine adducts $\text{OsO}_4 \cdot \text{L}$ (L = phthalazine, isoquinoline or

quinuclidine) have been shown to react with alkenes R to give products $[\text{OsO}_2(\text{O}_2\text{R})\text{L}]$.¹⁶ This work was extended and the adducts $\text{OsO}_4\cdot\text{L}$ (L = pyridine $\text{C}_5\text{H}_5\text{N}$, 4-^tbutylpyridine $\text{C}_9\text{H}_{13}\text{N}$ or isoquinoline $\text{C}_9\text{H}_7\text{N}$) were treated in 1 : 1 reacting molar ratios with a range of alkenes R (R = cyclohexene C_6H_{10} , cyclopentene C_5H_8 , ethylene C_2H_4 or 2,3-dimethylbut-2-ene C_6H_{12}). The brown, diamagnetic products obtained, however, did not have the expected stoichiometry $\text{OsO}_4\cdot\text{R}\cdot\text{L}$, but $\text{OsO}_4\cdot\text{R}\cdot\text{L}_2$, and were isolated together with the corresponding dimeric monoesters $[\text{Os}_2\text{O}_4(\text{O}_2\text{R})_2]$ (II).

For the products $\text{OsO}_4\cdot\text{R}\cdot\text{L}_2$, structure (IV) is consistent with the observed stoichiometry, molecular weight measurements and diamagnetism¹⁰⁷ of the complexes, and also by vibrational and ^1H n.m.r. spectroscopic studies (Table 2-1)



In addition to bands due to coordinated ligands, the infrared spectra of the solid complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ in the $800\text{--}950\text{ cm}^{-1}$ range show strong bands near 840 cm^{-1} and weaker bands near 300 cm^{-1} , as observed in other complexes containing the trans $\text{O}=\text{Os}=\text{O}$ "osmyl" unit;^{16, 32, 61} these bands are assigned to the asymmetric stretching vibrations, $\nu_{\text{OsO}_2}^{\text{as}}$, and deformations, δ_{OsO_2} , of the "osmyl" moiety respectively. Raman spectra of the solid complexes, in the $800\text{--}1000\text{ cm}^{-1}$ range, show strong bands near 880 cm^{-1} , polarised in solution, assigned to the symmetric stretch, $\nu_{\text{OsO}_2}^{\text{s}}$, again, as found in other "osmyl" complexes.¹³⁷ Infrared bands near 1000 cm^{-1} and 600 cm^{-1} are tentatively assigned as being predominantly due to C-O and Os-O stretching vibrations respectively on the basis of their shifts on ^{18}O substitution and their absence from the spectra of the parent

Table 2-1

Spectroscopic^a and Molecular Weight Data for Oxo Amine Osmium(VI) Ester Complexes Prepared from Alkenes

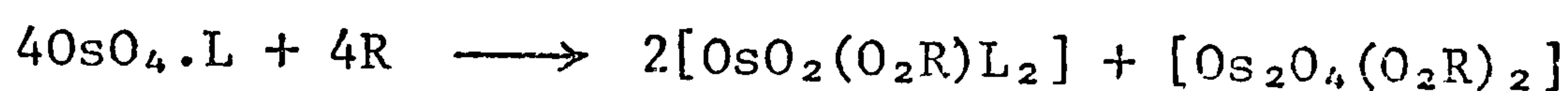
	Alkene	ν_{OsO_2} ^b	δ_{OsO_2}	$\nu_{\text{Os-O}}$	$\nu_{\text{C-O}}$	^1H n.m.r. ^c	M.W. ^d
<u>Pyridine Ester Complexes</u> ^e	$\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_2$	836s, 828s <u>877s</u>	292w	589m	-	4.38 (2H)	481 (494)
	$\text{OsO}_2(\text{O}_2\text{C}_5\text{H}_8)(\text{C}_5\text{H}_5\text{N})_2$	840, 825s <u>879s</u>	300w	615m	1030m	4.85 (2H)	471 (480)
	$\text{OsO}_2(\text{O}_2\text{C}_2\text{H}_4)(\text{C}_5\text{H}_5\text{N})_2$	837, 827s <u>871s</u>	292w	590m	1040m	4.45 (4H)	474 (438)
	$\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_2$	834, 820s	310w	611m	1125m	-	-
	2,3-dimethylbut-2-ene						
<u>Isoquinoline Ester Complexes</u> ^f	$\text{OsO}_2(\text{O}_2\text{C}_5\text{H}_8)(\text{C}_9\text{H}_7\text{N})_2$	830, 820s	300w	598m	1010m	4.84 (2H)	
	$\text{OsO}_2(\text{O}_2\text{C}_2\text{H}_4)(\text{C}_9\text{H}_7\text{N})_2$	848, 840s <u>878s</u>	295, 280w	593m	1030m	4.45 (4H)	576 (541)
	ethylene						
<u>4-^tButylpyridine Ester Complexes</u> ^g	ethylene	845, 835s	278w	595m	1042m	4.43 (4H)	-
	$\text{OsO}_2(\text{O}_2\text{C}_2\text{H}_4)(\text{C}_9\text{H}_{13}\text{N})_2$						
	$\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_9\text{H}_{13}\text{N})_2$	835, 828s	290w	590m	1030m	-	-

^a measured as solids; ^b as ν_{OsO_2} i.r. active; measured as Nujol mulls. ^c ν_{OsO_2} Raman active; measured as KBr discs. Raman modes underlined; ^c δ values for protons adjacent to donor oxygen atoms (ppm relative to TMS; measured in C^2HCl_3); ^d Molecular weights osmotically in dichloromethane (calculated values in parentheses); ^e Prepared from the adduct $\text{OsO}_4 \cdot \text{C}_5\text{H}_5\text{N}$; ^f Prepared from the adduct $\text{OsO}_4 \cdot \text{C}_9\text{H}_7\text{N}$; ^g Prepared from the adduct $\text{OsO}_4 \cdot \text{C}_9\text{H}_{13}\text{N}$ and separately from $\text{Os}_2\text{O}_6(\text{C}_9\text{H}_{13}\text{N})_4$.

alkenes and amines.

The ^1H n.m.r. spectra of the complexes in C^2HCl_3 show resonances due to protons adjacent to the donor oxygen atoms at δ 4.3-4.8 supporting the proposed structure. Integration of the ^1H n.m.r. spectra of the protons adjacent to the donor oxygen atoms against the coordinated amine protons further confirms the stoichiometries of these complexes.

The overall reaction for the formation of the complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ can be written as:-



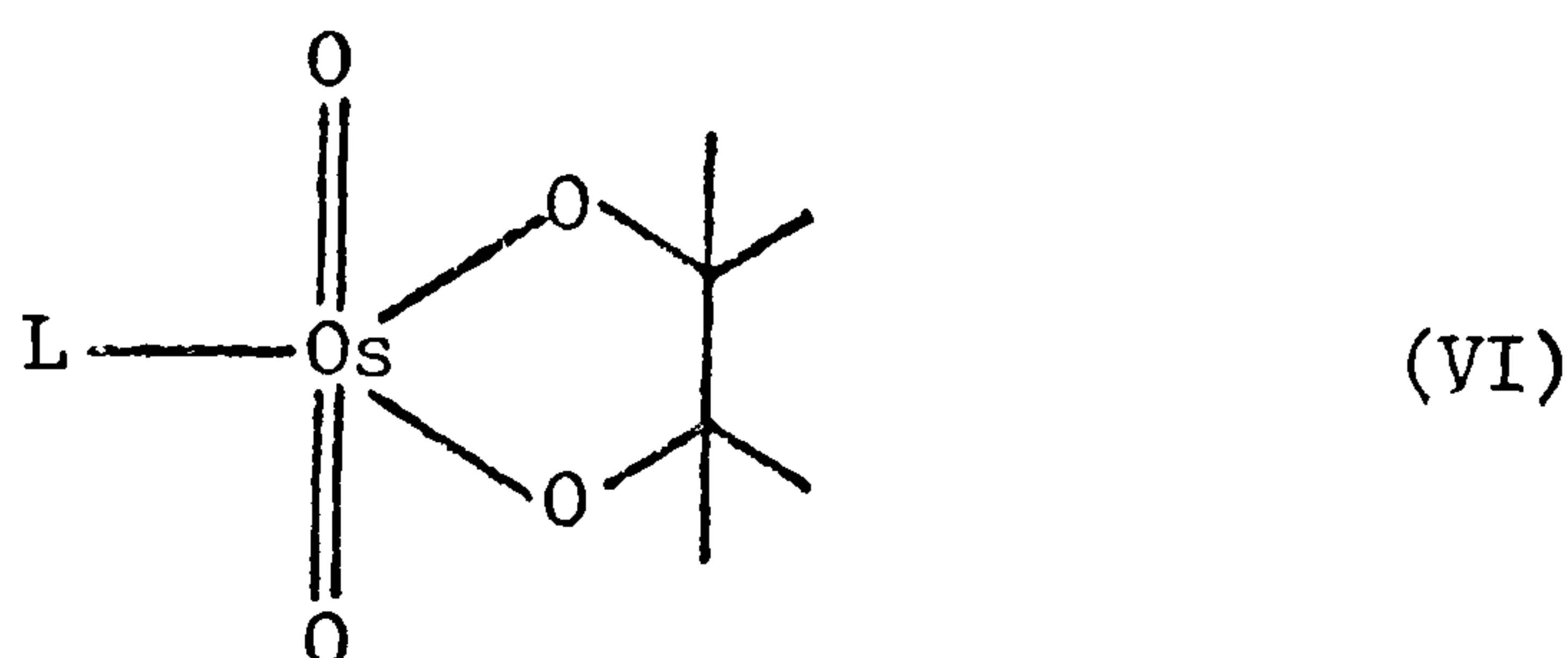
and in the case of $\text{L} = \text{pyridine } (\text{C}_5\text{H}_5\text{N})$ and $\text{R} = 2,3\text{-dimethylbut-2-ene } (\text{C}_6\text{H}_{12})$, the products have been obtained in quantitative yield.

The formation of the products $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ from the adducts $\text{OsO}_4.\text{L}$ is presumably due to the weak osmium-nitrogen bond in the osmium-(VIII) adducts breaking, leading to the formation of the bis-amine ester complex together with free OsO_4 , which reacts further with the alkene to give the corresponding diester $[\text{Os}_2\text{O}_4(\text{O}_2\text{R})_2]$. On one occasion the pyridine complex $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_5\text{H}_5\text{N})]$ was isolated, but this preparation could not be repeated, the major product being the corresponding bis-amine complex $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_2]$.

Section 2-C Reaction of the Adducts $\text{OsO}_4.\text{L}$ with Alkenes ($\text{L} = \text{quinuclidine}$)

The adduct $\text{OsO}_4.\text{C}_7\text{H}_{13}\text{N}$ ($\text{C}_7\text{H}_{13}\text{N} = \text{quinuclidine}$) has been shown to react with alkenes R ($\text{R} = \text{cycloheptene } \text{C}_7\text{H}_{12}$ or $2,3\text{-dimethylbut-2-ene } \text{C}_6\text{H}_{12}$) in a 1 : 1 reacting molar ratio to give products of stoichiometry $\text{OsO}_4.\text{R}.\text{C}_7\text{H}_{13}\text{N}$.^{16, 136} Structure (VI), involving trigonal bipyramidal osmium(VI) with trans oxo ligands, was tentatively proposed for these

products on the basis of analytical and spectroscopic evidence.^{16,136}



However, this structure is unlikely on steric grounds since for the osmium(VI) monoester and diester complexes the O (ester) Os O (ester) angles have been shown, by single-crystal X-ray studies, to be 82° ³³ and 83° ³⁵ respectively. A trigonal bipyramidal configuration (VI) involving trans oxo ligands, however, would invoke an O (ester) Os O (ester) angle of 120° , which would seem intrinsically highly unlikely.¹³⁸ This led to the re-investigation of the products formulated as $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_7\text{H}_{13}\text{N}]$, particularly with respect to their vibrational spectra in the solid state and in solution.

The adduct $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$ was treated with a range of alkenes R (R = cyclohexene C_6H_{10} , cyclopentene C_5H_8 , ethylene C_2H_4 or stilbene $\text{C}_{14}\text{H}_{12}$) in a 1 : 1 reacting molar ratio to give green, diamagnetic products. Molecular weight measurements in dichloromethane and elemental analysis data on the products are in agreement with the stoichiometry $\text{OsO}_4 \cdot \text{R} \cdot \text{C}_7\text{H}_{13}\text{N}$ as previously reported.^{16,136} Infrared spectra of the solid complexes in the $800\text{--}950\text{ cm}^{-1}$ range show bands near 900 cm^{-1} (Figure 2-1) and near 300 cm^{-1} assigned to the asymmetric stretching vibrations, $\nu_{\text{OsO}_2}^{\text{as}}$, and deformations, δ_{OsO_2} , respectively; Raman spectra of the solid complexes in the $800\text{--}1000\text{ cm}^{-1}$ range show bands near 900 cm^{-1} assigned to the symmetric stretching vibrations, $\nu_{\text{OsO}_2}^{\text{s}}$.¹³⁷ Infrared bands near 600 cm^{-1} and 1000 cm^{-1} tentatively assigned to $\nu_{\text{Os-O}}$ and $\nu_{\text{C-O}}$ respectively are given in Table 2-2.

Table 2-2

Spectroscopic ^a and Molecular Weight Data for Oxo Amine Osmium(VI) Ester Complexes Prepared from Alkenes

	Alkene	$\nu_{\text{OsO}_2}^b$	δ_{OsO_2}	$\nu_{\text{Os-O}}$	$\nu_{\text{C-O}}$	$^1\text{H n.m.r.}^c$	M.W. ^d
<u>Quinuclidine Ester Complexes</u>							
[OsO ₂ (O ₂ C ₆ H ₁₀)C ₇ H ₁₃ N] ₂ [OsO ₂ (O ₂ C ₅ H ₈)C ₇ H ₁₃ N] ₂ [OsO ₂ (O ₂ C ₁₄ H ₁₂)C ₇ H ₁₃ N] ₂ [OsO ₂ (O ₂ C ₂ H ₄)C ₇ H ₁₃ N] ₂ OsO ₂ (O ₂ C ₆ H ₁₀)(C ₇ H ₁₃ N) ₂ OsO ₂ (O ₂ C ₂ H ₄)(C ₇ H ₁₃ N) ₂	<u>cyclohexene</u>	903s <u>898s</u>	312w	618m	980m	3.76 (2H)	465 (447)
	<u>cyclopentene</u>	889s	325w	620m	972m		
	stilbene	895s	300w	-	1008m	-	
	ethylene	870s <u>887s</u>	296w	590m	1030m		420 (493)
	<u>cyclohexene</u>	835s <u>882s</u>	315, 295w	587m	978m		e
	ethylene	835s <u>881s</u>	325w	620m	1005m		e

^a Measured as solids

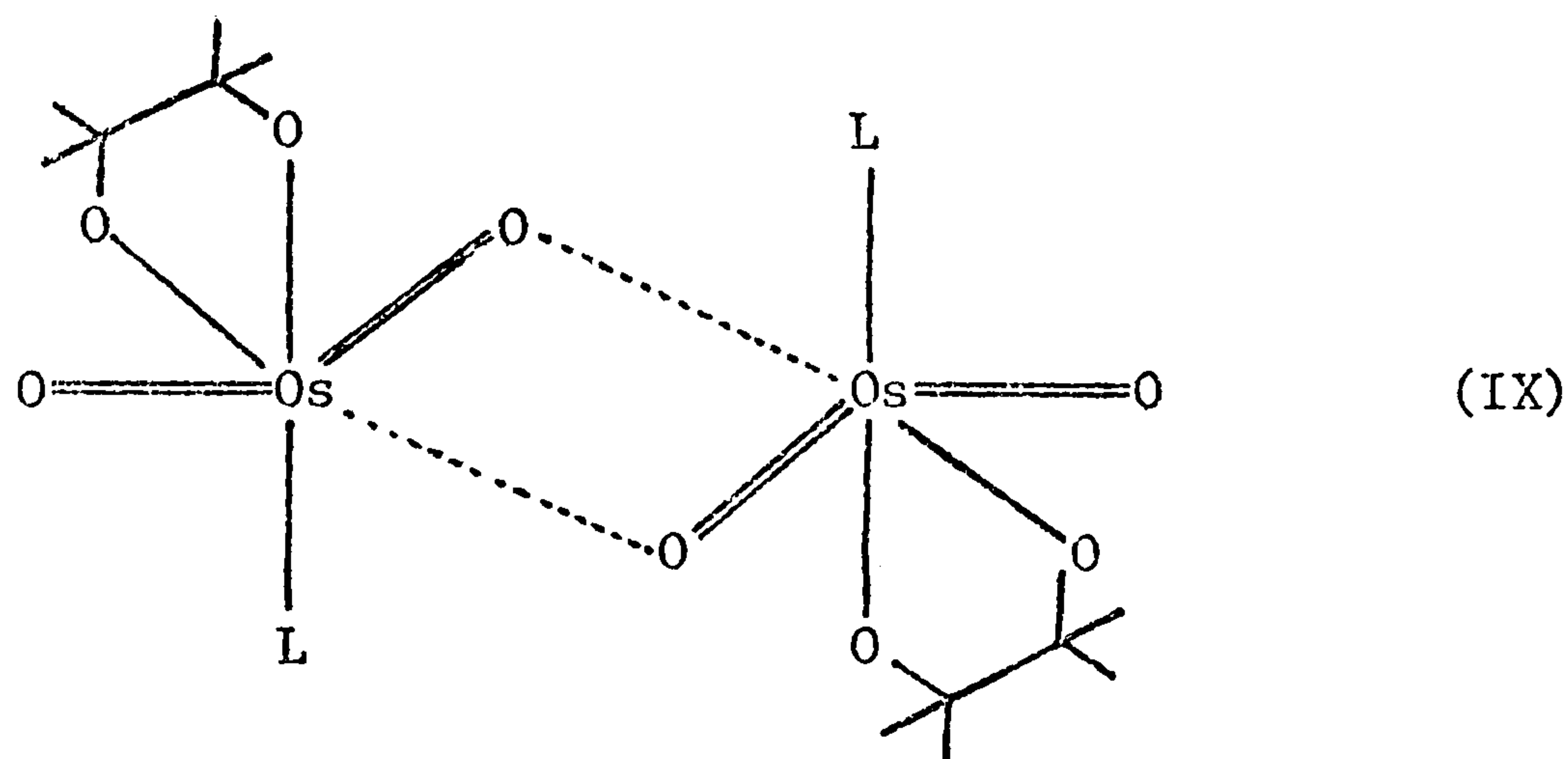
^b $\nu_{\text{OsO}_2}^{\text{as}}$ i.r. active; measured as Nujol mulls. $\nu_{\text{OsO}_2}^{\text{s}}$ Raman active; measured as KBr discs. Raman modes underlined.

^c δ values for protons adjacent to donor oxygen atoms (ppm relative to TMS, measured in C²HCl₃)

^d Measured osmotically in dichloromethane (calculated values in parentheses)

^e Dissociates in solution to give [OsO₂(O₂R)C₇H₁₃N] and free quinuclidine.

A single-crystal X-ray study of the complex $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})\text{C}_7\text{H}_{13}\text{N}]$ (C₆H₁₀ = cyclohexene) has been carried out by B. Cartwright and A. Skapski of this Department. The complex has been found to be dimeric in the solid state, involving an asymmetric Os₂O₂ bridge (IX) (Section 2-D)

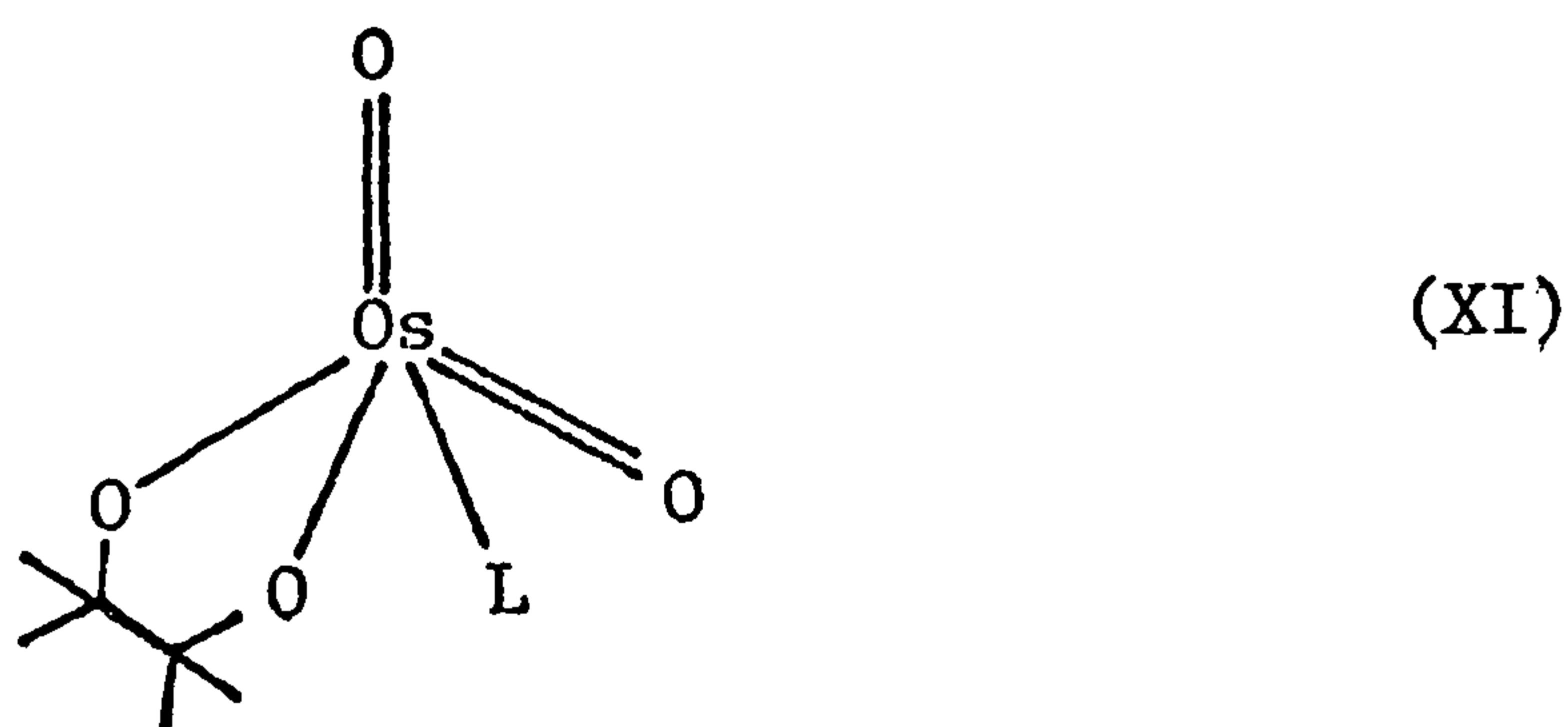
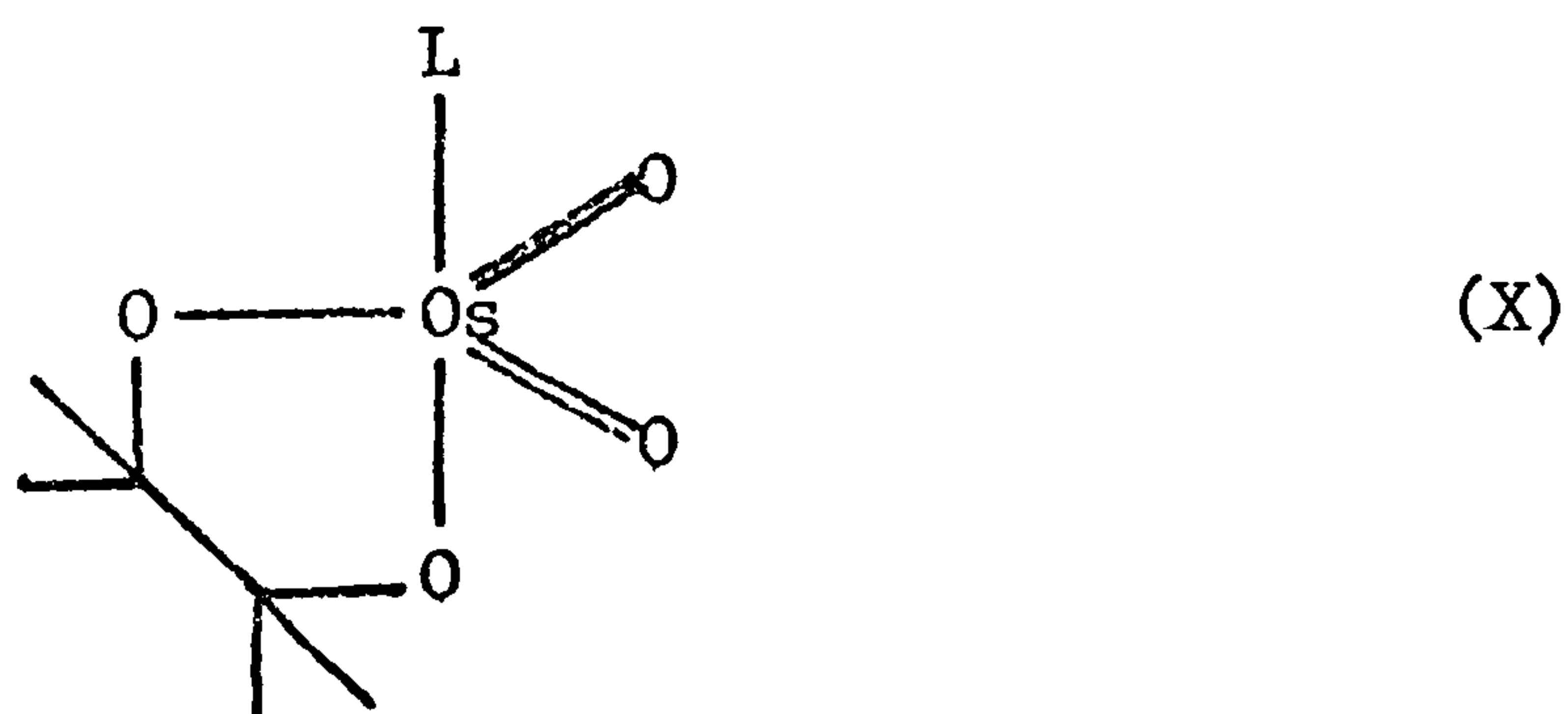


The coordination about the metal atom is distorted octahedral; the angle between the two doubly-bonded oxo ligands is 154° and the O (ester) Os O (ester) angle is 84° .

The distortion of the $\text{O}=\text{Os}=\text{O}$ angle from linearity to 156° would imply that the d_{xy} orbital, non-bonding in purely trans dioxo species, can participate, together with the metal d_{xz} and d_{yz} orbitals, in π -bonding with the p-orbitals of the oxo ligands. This increased π -bonding would explain the shift of the stretching vibration, $\nu_{\text{OsO}_2}^{\text{as}}$, to near 900 cm^{-1} in the infrared for the complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_7\text{H}_{13}\text{N}]_2$, as compared with the analogous trans dioxo complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ (L = pyridine, isoquinoline or quinuclidine) for which $\nu_{\text{OsO}_2}^{\text{as}}$ occurs in the infrared near 840 cm^{-1} (Section 2-B). The ring stretching vibration $\nu_{\text{Os}_2\text{O}_2}$ of the Os_2O_2 bridge, observed near 640 cm^{-1} in the infrared for the species $[\text{Os}_2\text{O}_6\text{L}_4]$ (L = pyridine,^{61,130} 3-picoline,¹³⁰ 3-chloropyridine,¹³⁰ $\frac{1}{2}$ -bipyridyl¹³¹) and for the dimeric monoester complexes $[\text{Os}_2\text{O}_4(\text{O}_2\text{R})_2]$,³² is not observed for the complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_7\text{H}_{13}\text{N}]_2$. This is probably due to the quite different nature of the Os_2O_2 oxygen bridge in these latter complexes.

Vibrational spectra of the complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_7\text{H}_{13}\text{N}]_2$ ($\text{R} =$ cyclohexene or ethylene) in chloroform show two Raman-active and two infrared active vibrations in the $800\text{--}950\text{ cm}^{-1}$ region which may be assigned to $\text{Os}=\text{O}$ stretching modes. The ligands do not have interfering modes in this region. The presence of two rather than one $\text{Os}=\text{O}$ stretching vibration suggests a cis rather than trans configuration of oxo ligands for these complexes in solution.¹⁰⁶ The coincidence in frequency of the strong, polarised Raman mode with the weak infrared band suggests this is the symmetric $\nu_{\text{OsO}_2}^{\text{S}}$ mode, while the weak depolarised Raman shift close to the strong infrared band is assigned to the asymmetric $\nu_{\text{OsO}_2}^{\text{as}}$ mode (Table 2-3, Figure 2-1). Similar behaviour has been noted for octahedral cis-dioxo complexes.¹⁰⁶

Either (X), based on a trigonal bipyramid, or (XI), based on a square-based pyramid, are consistent with the vibrational spectra of the complexes in solution.



Structure (XI) is more likely on the basis that it enables greater π -bonding overlap to occur between the metal and oxo ligands.^{139,140} However, the related d^2 complex $\text{Ba}[\text{RuO}_3(\text{OH})_2]$ has been shown by X-ray studies to involve a trigonal bipyramidal configuration with the three oxo ligands

Table 2-3

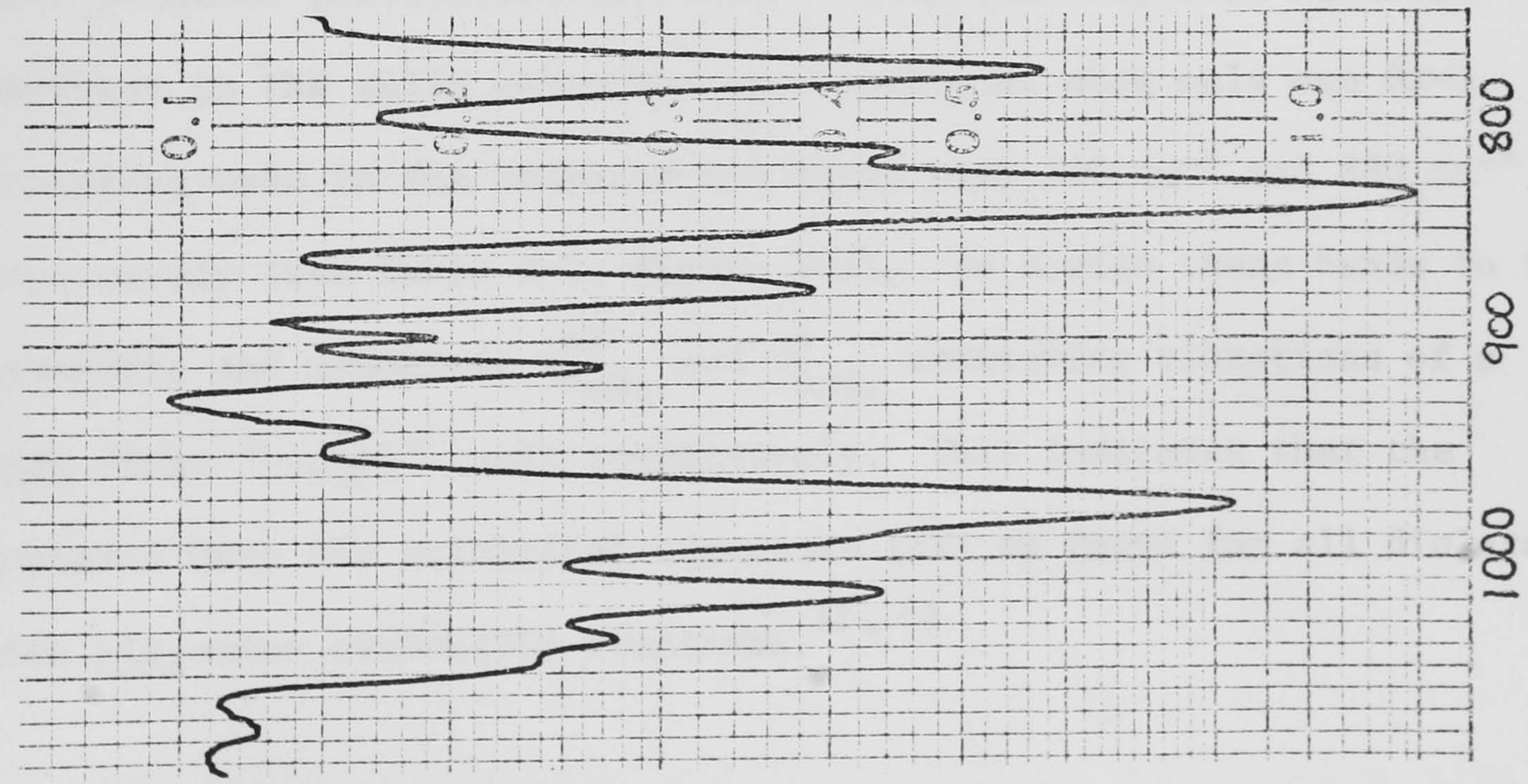
Vibrational Spectra of Oxo Quinuclidine Osmium(VI) Ester Complexes Prepared from Alkenes

		Metal Oxygen Stretching Frequencies (ν_{OsO_2})		
		Solid	Solution ^a	
			$\nu_{\text{OsO}_2}^{\text{s}}$	$\nu_{\text{OsO}_2}^{\text{as}}$
<u>Cyclohexene Ester Complexes</u>				
	$[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})\text{C}_7\text{H}_{13}\text{N}]_2$	Infrared	903s	879s
		Raman	898m	881vw(dp)
	$\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_7\text{H}_{13}\text{N})_2$	Infrared	835s	835s ^b
		Raman	882m	c
<u>Ethylene Ester Complexes</u>				
	$[\text{OsO}_2(\text{O}_2\text{C}_2\text{H}_4)\text{C}_7\text{H}_{13}\text{N}]_2$	Infrared	870s	878s
		Raman	887m	880vw(dp)
	$\text{OsO}_2(\text{O}_2\text{C}_2\text{H}_4)(\text{C}_7\text{H}_{13}\text{N})_2$	Infrared	835s	835s ^b
		Raman	881m	c

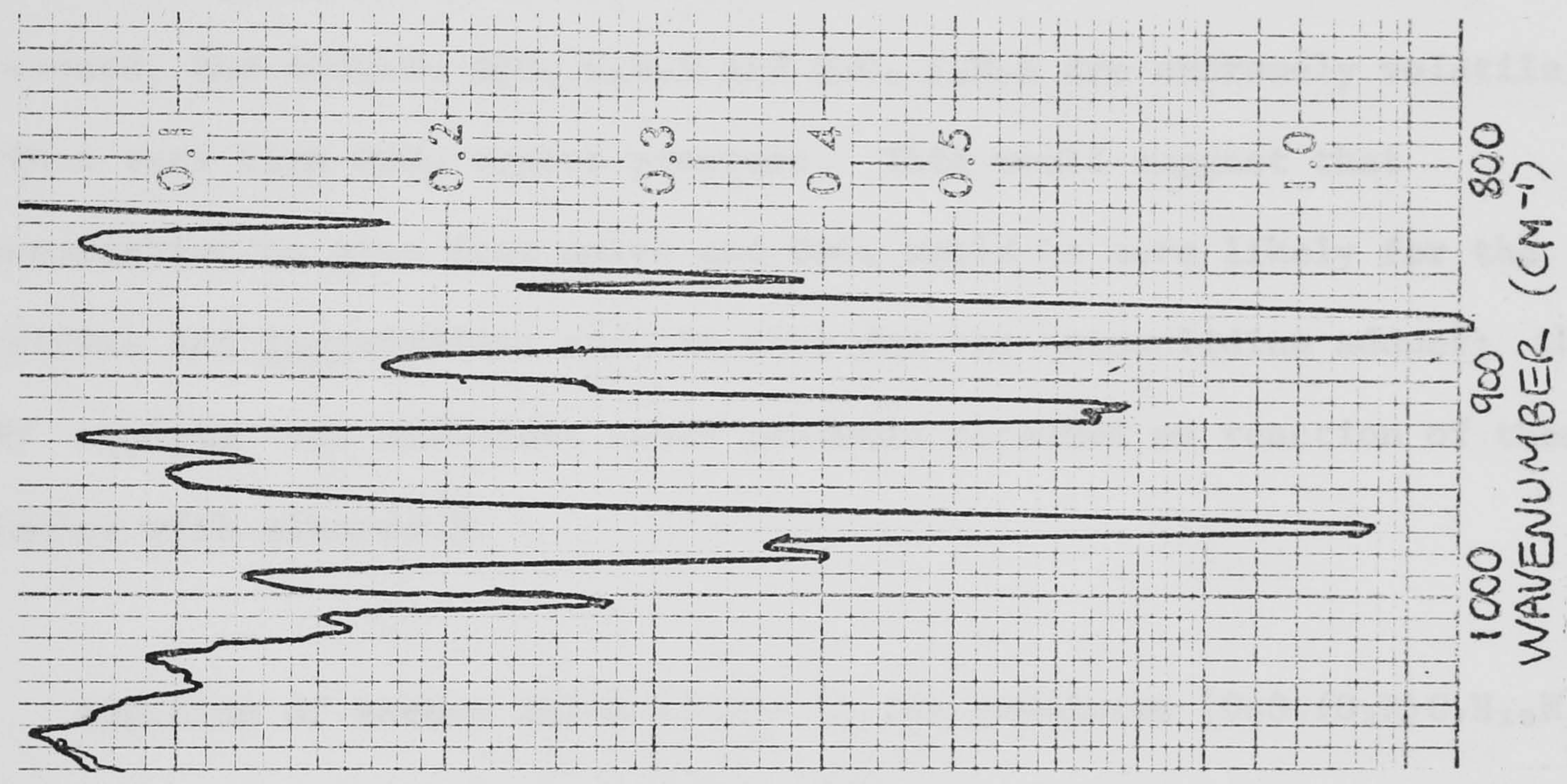
^a Measured in CHCl_3 in KBr and quartz cells.

^b Measured in the presence of excess quinuclidine to prevent dissociation of product.

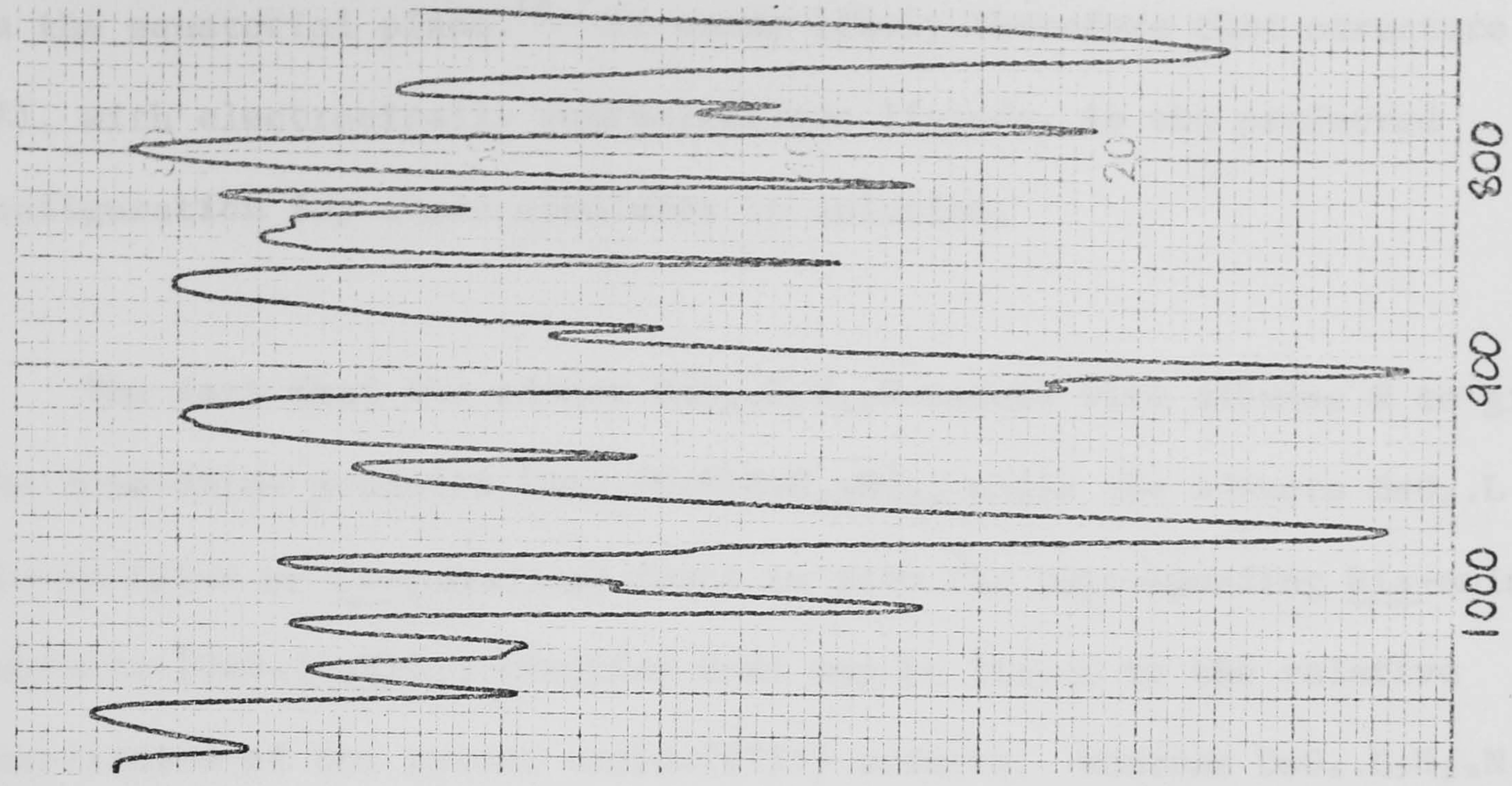
^c Could not be measured due to fluorescence of the sample .



$[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_7\text{H}_{13}\text{N})_2]$
Nujol mull



$[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})\text{C}_7\text{H}_{13}\text{N}]_2$
in CHCl_3



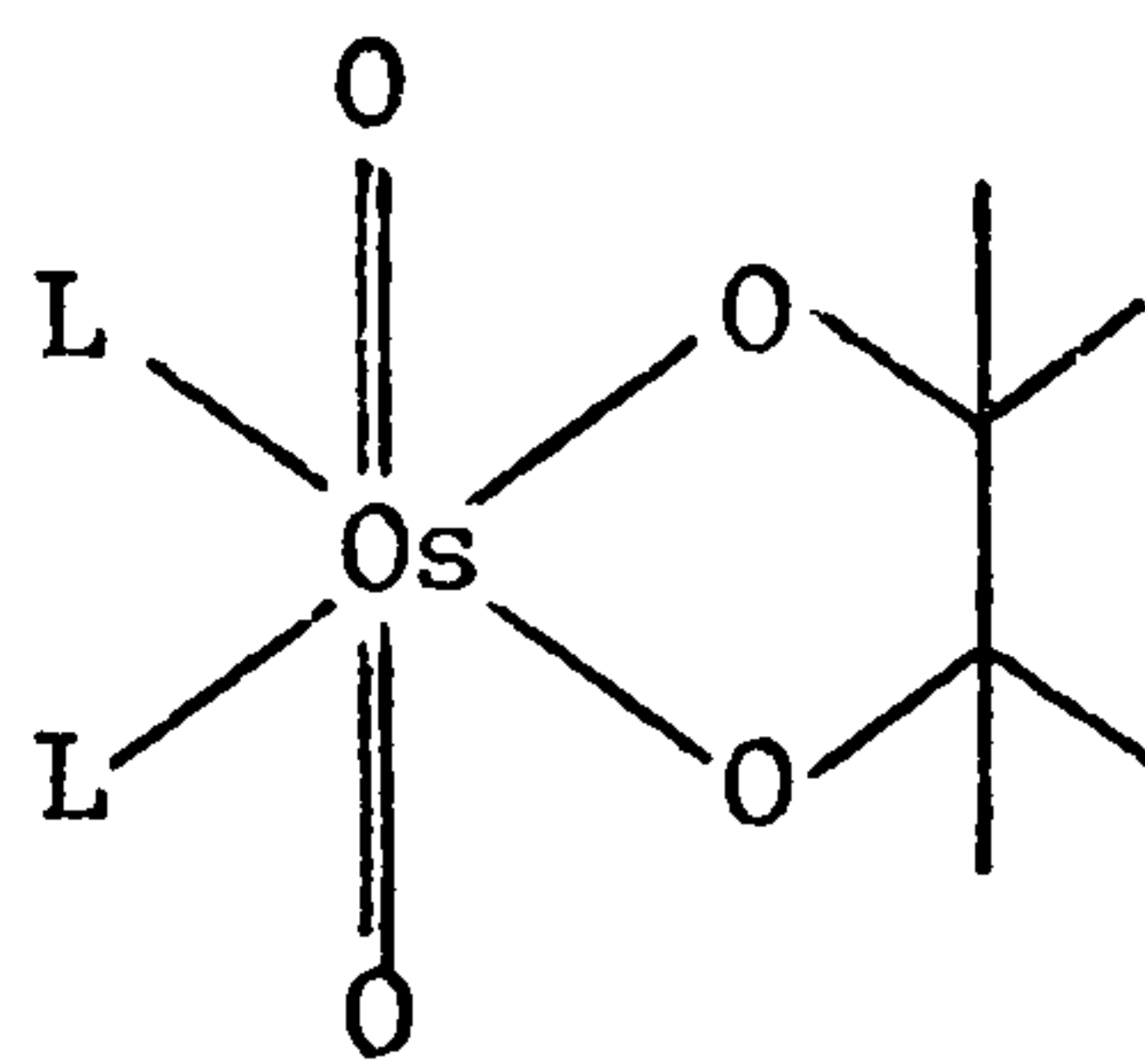
$[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})\text{C}_7\text{H}_{13}\text{N}]_2$
Nujol mull

Figure 2-1. Infrared Spectra of Quinuclidine Osmium(VI) Ester Complexes Derived from Cyclohexene

in the equatorial plane.⁷¹ It seems likely therefore that structure (X), with electronically equivalent oxo ligands, is the preferred configuration for these complexes in solution.

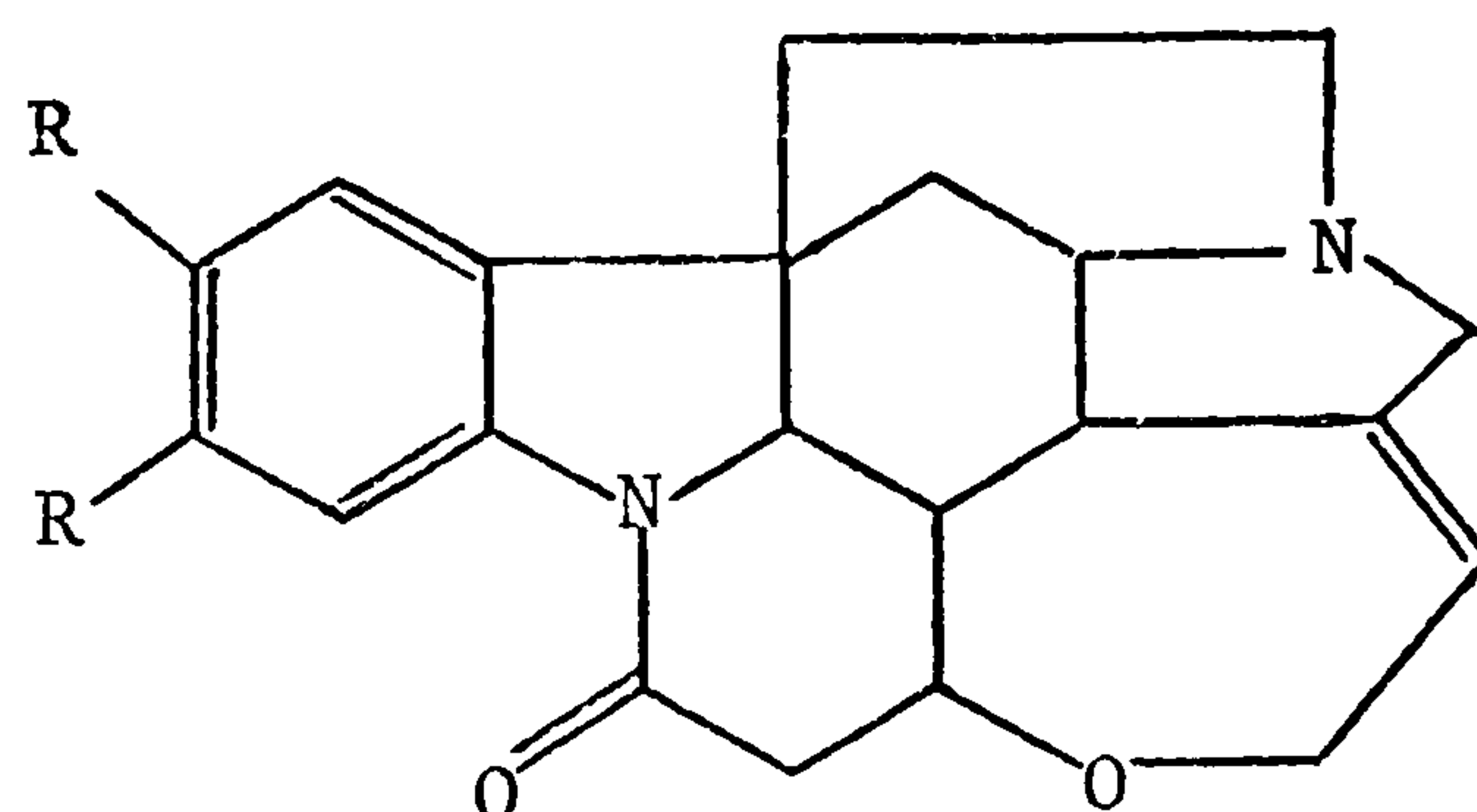
The fact that the adduct $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$ reacts with alkenes R to give the mono-amine products $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_7\text{H}_{13}\text{N}]_2$, while the adducts $\text{OsO}_4 \cdot \text{L}$ (L = pyridine or isoquinoline) react to give the corresponding bis-amine products $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ (Section 2-B) may be linked to the relative stabilities of the parent osmium(VIII) adducts. Whereas $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$ is fairly stable at room temperature with a relatively low OsO_4 vapour pressure, the adducts $\text{OsO}_4 \cdot \text{C}_5\text{H}_5\text{N}$ and $\text{OsO}_4 \cdot \text{C}_9\text{H}_7\text{N}$ are extremely volatile, with a very high OsO_4 vapour pressure. This would suggest that dissociation to give free amine and OsO_4 would be more likely for the pyridine and isoquinoline adducts than for the quinuclidine adduct; this may explain the different ester products obtained on reaction of these adducts with alkenes R.

Addition of excess quinuclidine to the complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_7\text{H}_{13}\text{N}]_2$ in solution leads to the formation of the corresponding bis-quinuclidine ester products $[\text{OsO}_2(\text{O}_2\text{R})(\text{C}_7\text{H}_{13}\text{N})_2]$. Vibrational spectra of these complexes in the solid state and in chloroform, show only one $\text{Os}=\text{O}$ stretching mode in the infrared and Raman near 840 cm^{-1} and 880 cm^{-1} respectively (see Table 2-2, Figure 2-1); we assign these bands to the asymmetric and symmetric $\nu_{\text{OsO}_2}^{\text{as}}$ and $\nu_{\text{OsO}_2}^{\text{s}}$ stretching vibrations of a trans dioxo "osmyl" unit respectively. This indicates that the complexes have the octahedral structure (IV) as found for all diolato dioxo bis-amine osmium(VI) complexes.^{32, 61}



(IV)

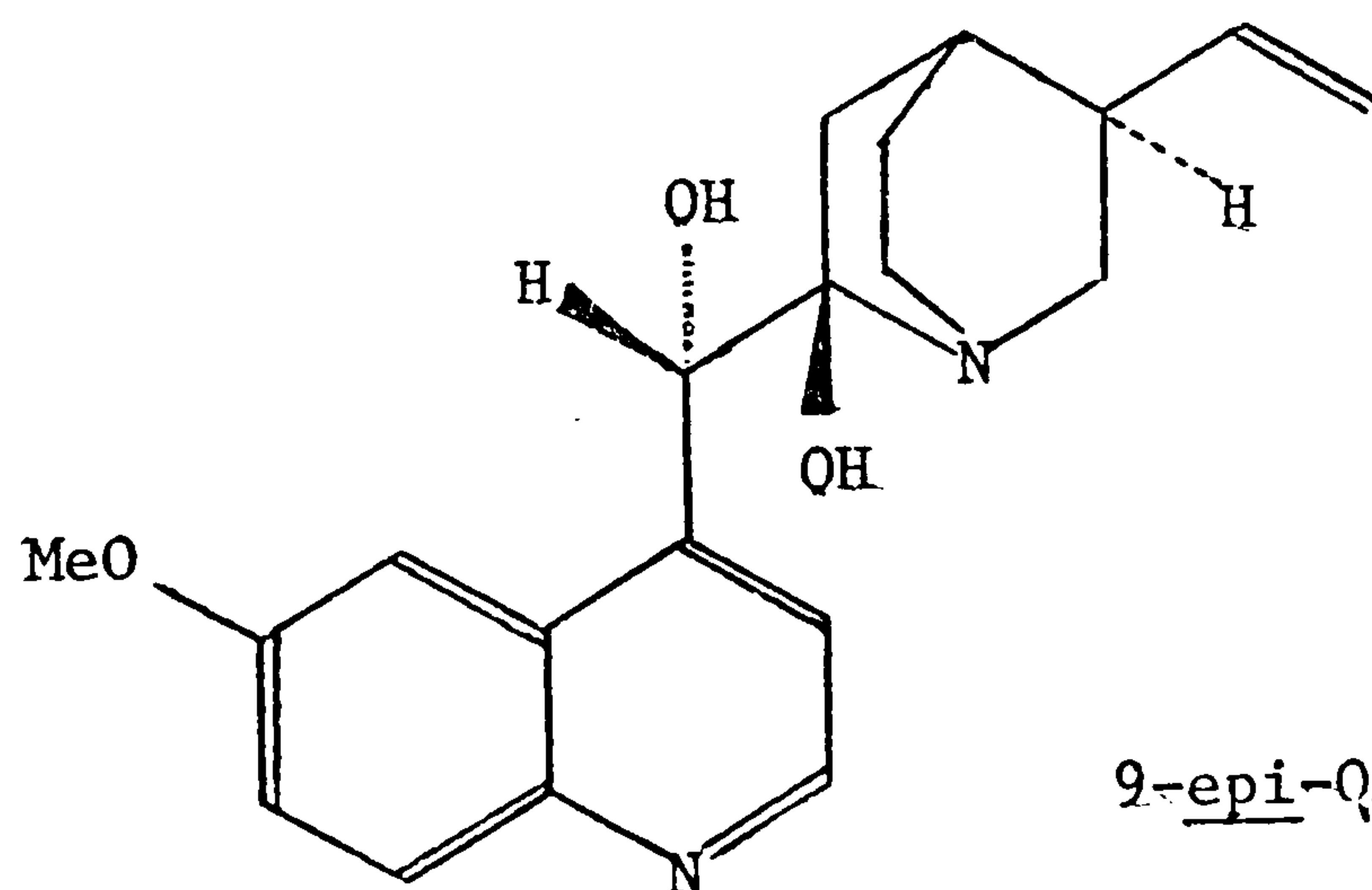
Since tertiary amines when treated with OsO_4 form red or yellow adducts $\text{OsO}_4 \cdot \text{L}$ ¹⁶ which react with alkenes R to give complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ (Section 2-B) or $[\text{OsO}_2(\text{O}_2\text{R})\text{L}]_2$ (Section 2-C), it is possible that alkaloids containing cyclic tertiary amine groups (e.g., strychnine, brucine (XII),¹⁴¹ cocaine or atropine), quinuclidine-type cages (e.g., quinine (XIII))¹⁴² or isoquinoline rings,¹⁴³ could behave in a similar manner.



(XII)

R = H = strychnine

R = OMe = brucine



(XIII)

9-epi-Quinine

OsO_4 reacts with alkaloids R (R = strychnine or brucine) to give red

solutions, however no osmium adducts $\text{OsO}_4 \cdot \text{L}$ could be isolated presumably due to their high solubility in organic solvents. Raman spectra of the solutions showed bands near 930 cm^{-1} assigned to $\nu_{\text{Os}=\text{O}}$ of the adduct complexes $\text{OsO}_4 \cdot \text{L}$.¹⁴⁴ In addition, the red solutions obtained from strychnine and brucine (L) and OsO_4 react with cyclohexene to give products formulated as $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})\text{L}]_2$.¹⁴⁴

If the red $\text{OsO}_4 \cdot \text{strychnine}$ or $\text{OsO}_4 \cdot \text{brucine}$ solutions are allowed to stand, they deposit green products, the stoichiometries of which are consistent with the formulation $[\text{OsO}_2(\text{O}_2\text{L})]_2$ (L = brucine or strychnine). Since both alkaloids contain alkenyl groups, it seems likely that intra-molecular attack of the alkenyl group has occurred. Molecular models show this to be possible, and the infrared spectra of the products are consistent with their having a structure analogous to (IX) (Section 2-C).

It is possible that where such alkaloids occur in plant tissue and are available for coordination, they could react during fixation procedures with OsO_4 to give adducts $\text{OsO}_4 \cdot \text{L}$, which could then react further with the double bonds of unsaturated lipids or other alkaloid substrates.

Section 2-D X-Ray Molecular Structure of $\text{Di}[\mu\text{-oxo-bis(cyclohexane-1,2-diolato)oxo(quinuclidine)osmium(VI)}], [\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})\text{C}_7\text{H}_{13}\text{N}]_2$

The adduct $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$ ($\text{C}_7\text{H}_{13}\text{N}$ = quinuclidine) was treated with cyclohexene (C_6H_{10}) in a 1 : 1 molar ratio in diethyl ether, and the solution allowed to evaporate slowly. Dark green crystals were deposited, which proved to be orthorhombic, with $a = 23.394$, $b = 10.303$, $c = 11.743 \text{ \AA}$, space group Pbca and $z = 4$ dimeric molecules. Intensity data were collected on a Siemens four-circle off-line automatic diffractometer. A total of 1784 independent reflections were observed to

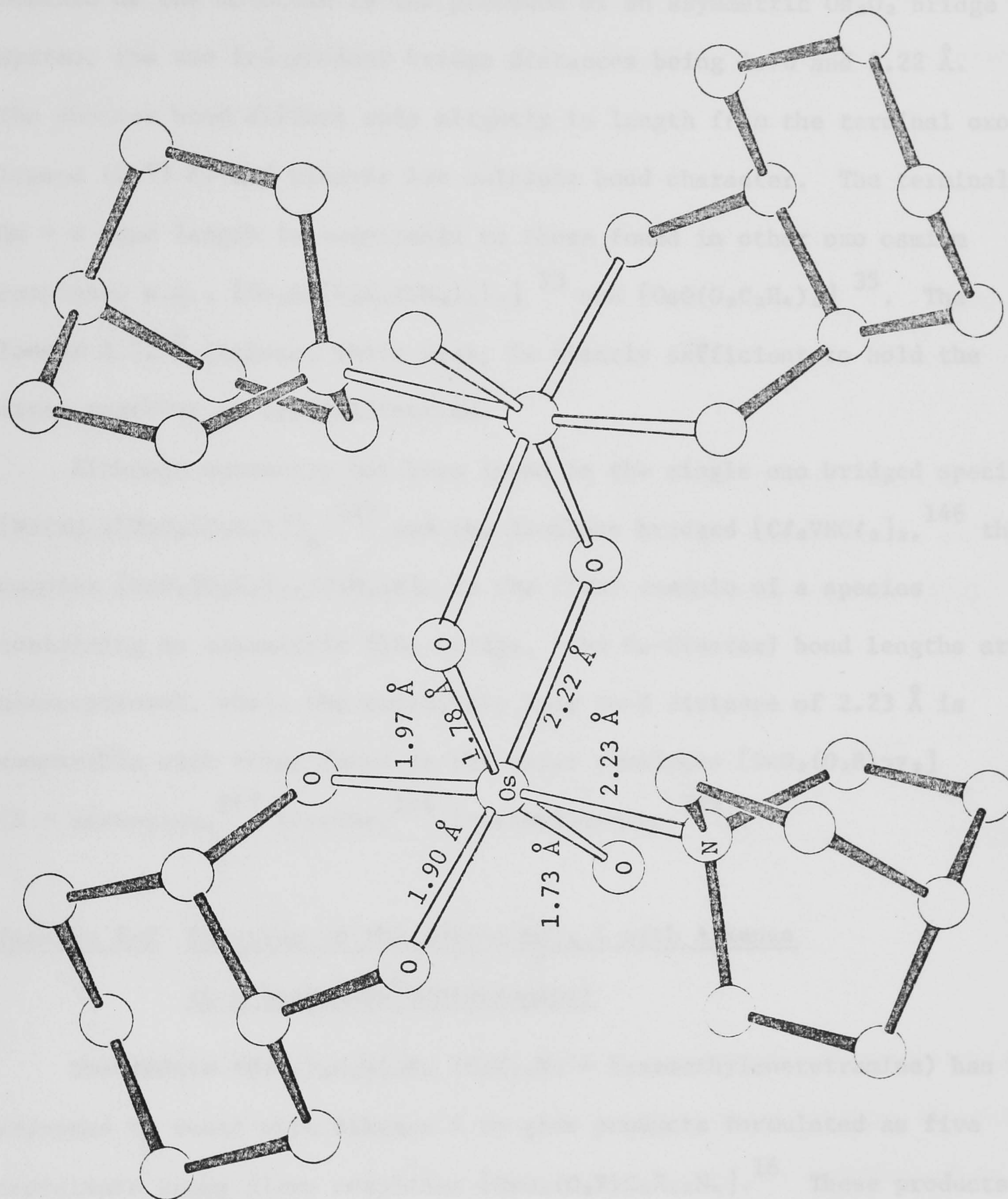


Figure 2-2 X-ray Molecular Structure of $\text{Di}[\mu\text{-oxo-bis(cyclohexane-1,2-diolato)oxo(osmium(VI))}]_2$, $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})\text{C}_7\text{H}_{13}\text{N}]_2$

$\theta = 55^\circ$. The least-squares refinement has reached $R = 0.059$.

Figure 2-2 shows the structure of the dimeric molecule, in which the two halves are related by a centre of symmetry. A notable feature of the molecule is the presence of an asymmetric Os_2O_2 bridge system, the two independent bridge distances being 1.78 and 2.22 Å. The shorter bond differs only slightly in length from the terminal oxo ligand (1.73 Å) and clearly has multiple bond character. The terminal $\text{Os} = \text{O}$ bond length is comparable to those found in other oxo osmium complexes e.g., $[\text{Os}_2\text{O}_4(\text{O}_2\text{C}_2(\text{CH}_3)_4)_2]$ ³³ and $[\text{OsO}(\text{O}_2\text{C}_2\text{H}_4)_2]$ ³⁵. The longer 2.22 Å linkage, while weak, is clearly sufficient to hold the dimer together on crystallisation.

Although asymmetry has been found in the single oxo bridged species $\{\text{Na}(\text{NH}_4)[\text{MoO}_3(\text{C}_2\text{O}_4)]\}_n$ ¹⁴⁵ and the dichloro bridged $[\text{Cl}_3\text{VNCI}_2]_2$,¹⁴⁶ the complex $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})\text{C}_7\text{H}_{13}\text{N}]_2$ is the first example of a species containing an asymmetric M_2O_2 bridge. The $\text{Os}-\text{O}(\text{ester})$ bond lengths are unexceptional, while the relatively long $\text{Os}-\text{N}$ distance of 2.23 Å is comparable with those found in the ester complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{py}_2]$ ($\text{R} = \text{adenosine}$,¹⁴⁷ thymine ,¹⁴⁸ 1-methylthymine ¹⁴⁹).

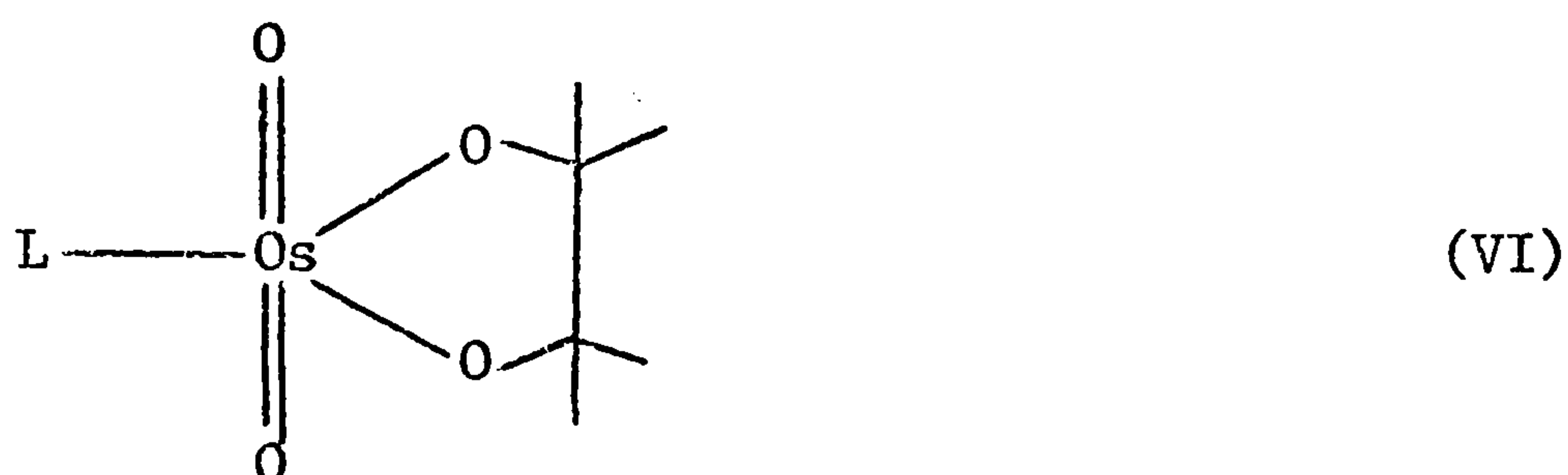
Section 2-E Reaction of the Adduct $\text{OsO}_4 \cdot \text{L}$ with Alkenes

($\text{L} = \text{Hexamethylenetetramine}$)

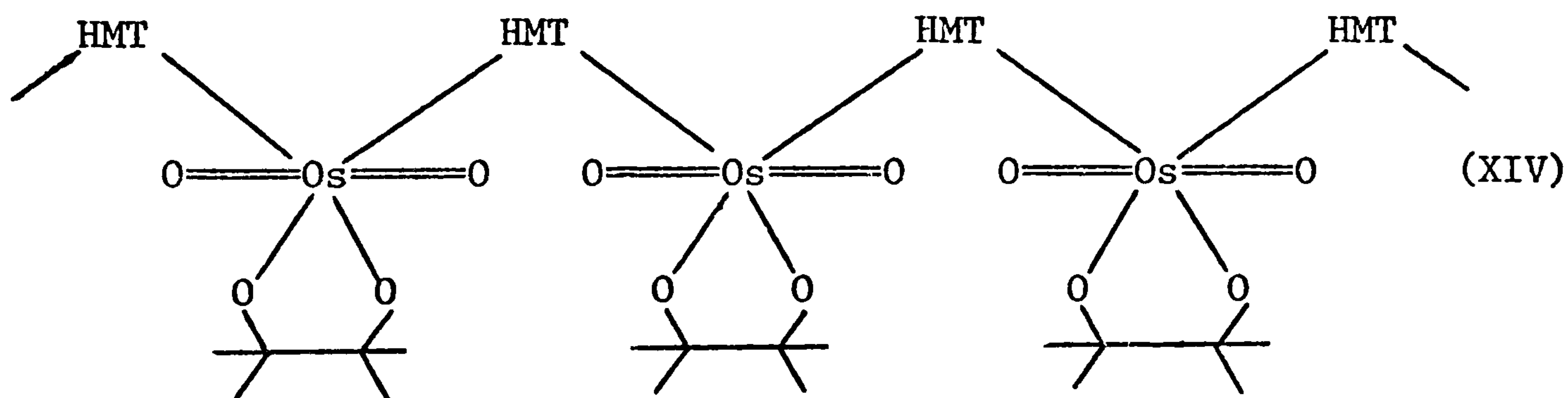
The adduct $(\text{OsO}_4)_2\text{C}_6\text{H}_{12}\text{N}_4$ ($\text{C}_6\text{H}_{12}\text{N}_4 = \text{hexamethylenetetramine}$) has been reported to react with alkenes R to give products formulated as five coordinate trans dioxo complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_6\text{H}_{12}\text{N}_4]$.¹⁶ These products have been reprepared ($\text{R} = \text{cyclopentene } \text{C}_5\text{H}_8$, ethylene C_2H_4 or cyclohexene C_6H_{10}) and compared with the corresponding quinuclidine complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_7\text{H}_{13}\text{N}]_2$ discussed in Section 2-C.

The infrared and Raman spectra of the solid complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_6\text{H}_{12}\text{N}_4]$ in the $800\text{--}950 \text{ cm}^{-1}$ range, unlike the corresponding

quinuclidine complexes, show bands indicative of trans dioxo species, $\nu_{\text{OsO}_2}^{\text{as}}$ and $\nu_{\text{OsO}_2}^{\text{s}}$ appearing at 835 cm^{-1} in the infrared and near 880 cm^{-1} in the Raman respectively (Table 2-4). However, the proposed five coordinate trigonal bipyramidal structure (VI) ¹⁶ is unlikely on steric grounds since the "bite" of the ester ring does not allow it to span 120° ¹³⁸ (Section 2-C).



Since hexamethylenetetramine can also act as a polydentate ligand,¹⁵⁰ the complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_6\text{H}_{12}\text{N}_4]$ may be in fact polymeric in the solid state with octahedral osmium(VI) cross-linked by amine ligands (XIV)



It has been reported that the infrared spectra of these complexes in chloroform show bands assigned to the asymmetric stretching vibration, $\nu_{\text{OsO}_2}^{\text{as}}$, near 870 cm^{-1} , at higher frequencies than for the solids. This, together with molecular weight measurements in chloroform,¹⁶ suggest that, in solution, these complexes may indeed be monomeric, presumably with a trigonal bipyramidal configuration analogous to the solute structure of the quinuclidine complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_7\text{H}_{13}\text{N}]_2$ discussed in Section 2-C. It should be noted, however, that on repeating the solution

Table 2-4

Vibrational Spectra^a of Oxo Amine Osmium(VI) Ester Complexes Prepared from Alkenes

	Alkene	$\nu_{\text{OsO}_2}^b$	δ_{OsO_2}	$\nu_{\text{Os-O}}$	$\nu_{\text{C-O}}$
<u>Hexamethylenetetramine Ester Complexes^c</u> $\text{OsO}_2(\text{O}_2\text{C}_5\text{H}_8)\text{C}_6\text{H}_{12}\text{N}_4$ $\text{OsO}_2(\text{O}_2\text{C}_2\text{H}_4)\text{C}_6\text{H}_{12}\text{N}_4$ $\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})\text{C}_6\text{H}_{12}\text{N}_4$	cyclopentene	835, 822s <u>882s</u>	290w	600m	1030m
	ethylene	835, 825s <u>884s</u>	300w	590m	1030m
	cyclohexene	835, 822s <u>885s</u>	290w	590m	1030m

^a Measured as solids.

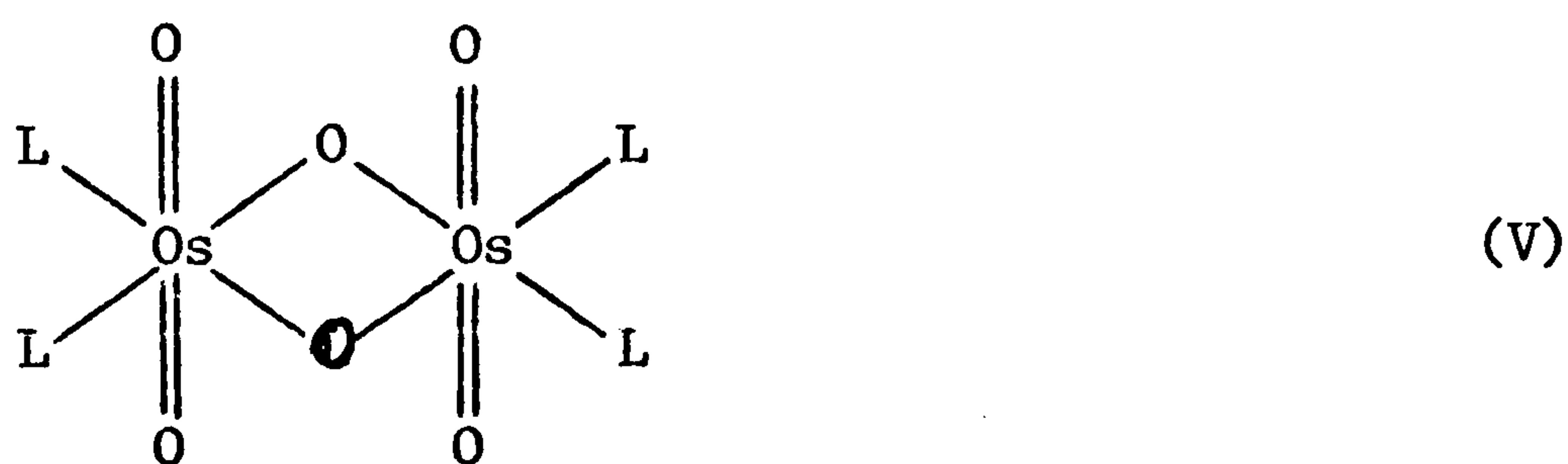
^b $\nu_{\text{OsO}_2}^{\text{as}}$ i.r. active; measured as Nujol mulls. $\nu_{\text{OsO}_2}^{\text{s}}$ Raman active; measured as KBr discs. Raman modes underlined.

^c Prepared from the adduct $(\text{OsO}_4)_2\text{C}_6\text{H}_{12}\text{N}_4$.

infrared measurements on the complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_6\text{H}_{12}\text{N}_4]$, no bands at 870 cm^{-1} were detected, the stretching vibration, $\nu_{\text{OsO}_2}^{\text{as}}$, appearing at 835 cm^{-1} as for the solid complexes.

Section 2-F $\text{Di}[\mu\text{-Oxo-Amine Dioxo Osmium(VI)}] [\text{Os}_2\text{O}_6\text{L}_4]$, $[\text{Os}_2\text{O}_6\text{L}_2]$ and
Their Reactions with *cis*-Diols (L = pyridine, 4-^tbutyl-
pyridine, quinuclidine or hexamethylenetetramine)

OsO_4 can be reduced with ethanol in the presence of excess of tertiary amine L to give the oxo amine osmium(VI) complexes $[\text{Os}_2\text{O}_6\text{L}_4]$ (V) (L = pyridine,^{61,130} 3-picoline,¹³⁰ 3-chloropyridine,¹³⁰ or $\frac{1}{2}$ bipyridyl¹³¹).



Whereas the $\text{Os}^{\text{VIII}}\text{O}_4$ adducts react with *cis*-diols only very slowly,³² these amine osmium(VI) complexes react readily with *cis*-diols to give the corresponding osmium(VI) ester complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$.^{14,130} In an attempt to prepare the unknown five coordinate complexes $[\text{Os}_2\text{O}_6\text{L}_2]$, the adducts $\text{OsO}_4\cdot\text{L}$ (L = pyridine, $\text{C}_5\text{H}_5\text{N}$, 4-^tbutylpyridine, $\text{C}_9\text{H}_{13}\text{N}$, or quinuclidine, $\text{C}_7\text{H}_{13}\text{N}$) and $(\text{OsO}_4)_2\text{L}$ (L = hexamethylenetetramine, $\text{C}_6\text{H}_{12}\text{N}_4$) were treated with ethanol and the reduction products investigated.

Reduction of the adducts $\text{OsO}_4\cdot\text{L}$ (L = pyridine $\text{C}_5\text{H}_5\text{N}$ or 4-^tbutylpyridine $\text{C}_9\text{H}_{13}\text{N}$) with ethanol gave the corresponding six coordinate *bis*-amine complexes $[\text{Os}_2\text{O}_6\text{L}_4]$ (V). Infrared spectra of the solid

complexes in the $800\text{--}950\text{ cm}^{-1}$ range show bands near 840 cm^{-1} and near 300 cm^{-1} assigned to $\nu_{\text{OsO}_2}^{\text{as}}$ and δ_{OsO_2} respectively. Bands due to the stretching vibrations of the Os_2O_2 bridge, $\nu_{\text{Os}_2\text{O}_2}$, and the Os-O(bridge) , $\nu_{\text{Os-O}}$, appear at 642 cm^{-1} and near 590 cm^{-1} respectively (Table 2-5). The formation of the products $[\text{Os}_2\text{O}_6\text{L}_4]$ from the adducts $\text{OsO}_4\cdot\text{L}$ presumably occurs via cleavage of the weak osmium-nitrogen bond in the adduct complexes to give the corresponding bis-amine complexes. The formation of the bis-amine complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ by reaction of the adducts $\text{OsO}_4\cdot\text{L}$ (L = pyridine or isoquinoline) with alkenes R has been noted in Section 2-B.

Reduction of the adduct $\text{OsO}_4\cdot\text{L}$ (L = quinuclidine $\text{C}_7\text{H}_{13}\text{N}$) with ethanol gave a deep green solution, but no amine osmium(VI) complex could be isolated. Addition of ethane-1,2-diol to the green solution, however, gave the corresponding osmium(VI) ester complex $[\text{OsO}_2(\text{O}_2\text{C}_2\text{H}_4)\text{-C}_7\text{H}_{13}\text{N}]_2$, indicating that an amine osmium(VI) species was indeed present in solution. Repeated attempts to isolate this quinuclidine osmium(VI) complex failed, the only isolated product being the starting material $\text{OsO}_4\cdot\text{C}_7\text{H}_{13}\text{N}$.

Reduction of the adduct $(\text{OsO}_4)_2\text{L}$ (L = hexamethylenetetramine $\text{C}_6\text{H}_{12}\text{N}_4$) with ethanol in tetrahydrofuran gave a brown, insoluble product; elemental analysis of the product indicates a stoichiometry of $[\text{Os}_2\text{O}_6(\text{C}_6\text{H}_{12}\text{N}_4)_2]\cdot\text{THF}$. Although the infrared spectrum of the solid complex shows bands assigned to $\nu_{\text{OsO}_2}^{\text{as}}$ and δ_{OsO_2} near 840 cm^{-1} and 280 cm^{-1} respectively, no bands assigned to the stretching mode $\nu_{\text{Os}_2\text{O}_2}$ were observed.

Structure (XV) is tentatively proposed for the osmium(VI) quinuclidine

Table 2-5

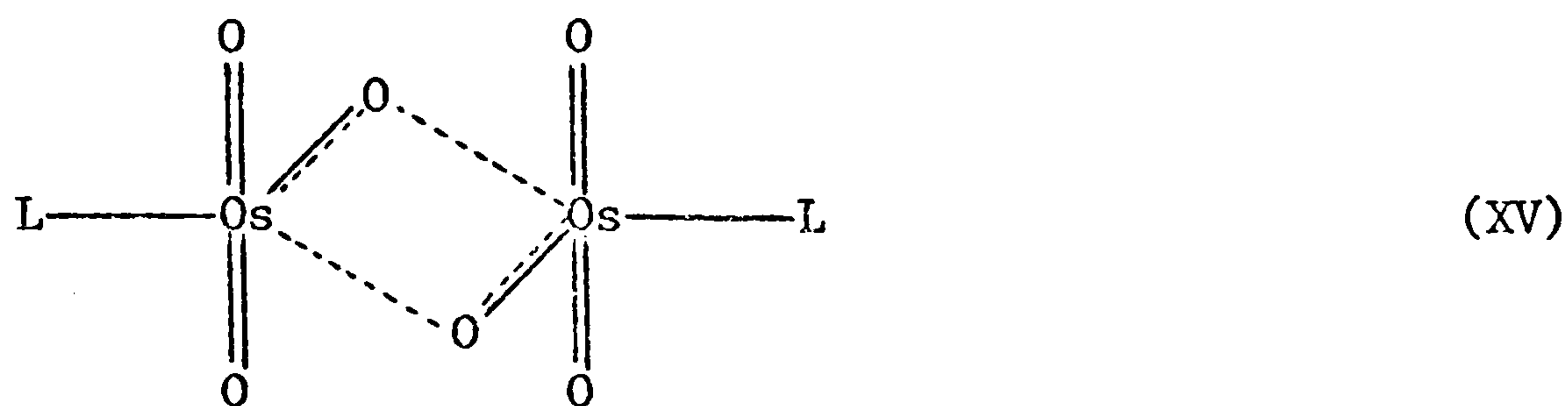
Spectroscopic ^a and Molecular Weight Data for Oxo Amine Osmium(VI) Complexes

Complex	Amine	$\nu_{\text{OsO}_2}^{\text{as}}$	$\nu_{\text{Os}_2\text{O}_2}$	δ_{OsO_2}	ν_{OsO}	M.W. ^b
$\text{Os}_2\text{O}_6(\text{C}_9\text{H}_{19}\text{N})_4$	4- ^t butylpyridine	845, 832s	642m	300w	592m	480 (1017)
$\text{Os}_2\text{O}_6(\text{C}_5\text{H}_5\text{N})_4$	pyridine	838, 830s	642m	300w	582m	-
$\text{Os}_2\text{O}_6(\text{C}_6\text{H}_{12}\text{N}_4)_2 \cdot \text{THF}$	hexamethylenetetramine	845, 835s	-	280, 266w	589m	-

^a ignoring ligand modes; measured as Nujol mulls.

^b molecular weight measured in chloroform.

and hexamethylenetetramine species



This structure, involving five coordinate osmium(VI) with trans oxo ligands and a highly asymmetric Os_2O_2 bridging system, is consistent with the observed vibrational spectra of $[\text{Os}_2\text{O}_5(\text{C}_6\text{H}_{12}\text{N}_4)_2]\cdot\text{THF}$.

Section 2-G Hydrolysis of Oxo Osmium(VI) Ester Complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$

Oxo amine osmium(VI) ester complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ can be hydrolysed using sodium sulphite¹²⁹ or bisulphite,^{151,152} alkaline mannitol,^{14,27} hydrogen sulphide¹⁵³ or catechol¹⁰⁸ to yield the corresponding cis-diol $\text{R}(\text{OH})_2$ in good yield.

The hydrolysis of the ester complex $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_2]$ (C_6H_{10} = cyclohexene, $\text{C}_5\text{H}_5\text{N}$ = pyridine) was carried out using sodium sulphite to give cis-cyclohexan-1,2-diol in 92% yield. The precipitated osmium sulphito complex was isolated and found, by elemental analysis, to be $\text{Na}_4[\text{Os}(\text{SO}_3)_3]\cdot 2\text{H}_2\text{O}$. Criegee et al¹⁴ previously formulated this product as $\text{Na}_4[\text{Os}(\text{SO}_3)_3]\cdot 6\text{H}_2\text{O}$.

The ester complex was also hydrolysed using aqueous neutral mannitol to give cis-cyclohexan-1,2-diol in 72% yield.

Section 2-H Experimental

All manipulations involving osmium tetroxide were carried out in a fume cupboard.

2-H-1 Tetraoxo Amine Osmium(VIII) Adducts; $\text{OsO}_4 \cdot \text{L}$ and $(\text{OsO}_4)_2 \cdot \text{L}$

Tetraoxo(pyridine)osmium(VIII). $\text{OsO}_4 \cdot \text{C}_5\text{H}_5\text{N}$. To a solution of osmium tetroxide (1.0 g, 3.9 mmol) in cyclohexane (5 cm^3) at 0°C was added dropwise with stirring a solution of pyridine (0.31 g, 3.9 mmol) in cyclohexane (2 cm^3). The yellow precipitate was filtered off, washed with cyclohexane (1 cm^3) and dried in air. The product is highly volatile and should not be dried in vacuo. Yield:- 60%.

Tetraoxo(isoquinoline)osmium(VIII). $\text{OsO}_4 \cdot \text{C}_9\text{H}_7\text{N}$. To a solution of osmium tetroxide (1.0 g, 3.9 mmol) in cyclohexane (5 cm^3) at 0°C was added dropwise with stirring a solution of isoquinoline (0.5 g, 3.9 mmol) in cyclohexane (2 cm^3). The yellow precipitate was filtered off, washed with cyclohexane (1 cm^3) and dried in air. The product is highly volatile and should not be dried in vacuo. Yield:- 70%.

Tetraoxo(4-^tbutylpyridine)osmium(VIII). $\text{OsO}_4 \cdot \text{C}_9\text{H}_{13}\text{N}$. To a solution of osmium tetroxide (1.0 g, 3.9 mmol) in cyclohexane (5 cm^3) at 0°C was added dropwise with stirring a solution of 4-^tbutylpyridine (0.53 g, 3.9 mmol) in cyclohexane (2 cm^3). The yellow precipitate was filtered off, washed with cyclohexane (1 cm^3) and dried in air. The product is highly volatile and should not be dried in vacuo. Yield:- 60%.

Tetraoxo(quinuclidine)osmium(VIII). $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$. Osmium tetroxide (1.0 g, 3.9 mmol) was dissolved in water (20 cm^3) and added dropwise with stirring to a solution of quinuclidine hydrochloride (0.57 g, 3.9 mmol) in water (10 cm^3) neutralised with sodium hydroxide. The orange precipitate was filtered off, washed with water (5 cm^3) and dried

in vacuo. Yield:- 75%.

μ -Hexamethylenetetramine bis(tetraoxo osmium(VIII)). $(\text{OsO}_4)_2\text{C}_6\text{H}_{12}\text{N}_4$.

Osmium tetroxide (1.0 g, 3.9 mmol) was dissolved in water (20 cm³) and added dropwise with stirring to a solution of hexamethylenetetramine (0.27 g, 1.9 mmol) in water (10 cm³). The orange precipitate was filtered off, washed with water (5 cm³) and dried in vacuo. Yield:- 80%.

2-H-2 Diolato Dioxo Bis-Amine Osmium(VI) from Alkenes

$[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ (L = pyridine, isoquinoline or 4-^tbutylpyridine).

Elemental analyses are listed in Table 2-6.

Pyridine Complexes $[\text{OsO}_2(\text{O}_2\text{R})(\text{C}_5\text{H}_5\text{N})_2]$

The preparation of $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_2]$ is typical.

To a solution of the adduct $\text{OsO}_4 \cdot \text{C}_5\text{H}_5\text{N}$ (1.0 g, 3.0 mmol) in diethyl ether (10 cm³) was added dropwise with stirring 2,3-dimethylbut-2-ene (0.25 g, 3.0 mmol) in diethyl ether (5 cm³). After five minutes, the brown product $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_2]$ was filtered off, copiously washed with diethyl ether (20 cm³) and dried in vacuo. Yield:- 48%.

The filtrate was concentrated and passed down a silica column eluted with chloroform. Concentration of the eluate gave black crystals of the dimeric monoester complex $[\text{Os}_2\text{O}_4(\text{O}_2\text{C}_6\text{H}_{12})_2]$. Yield:- 45%.

An alternative method of preparation was carried out by treating osmium tetroxide (1.0 g, 3.9 mmol), dissolved in diethyl ether (10 cm³) containing pyridine (0.62 g, 7.8 mmol), with 2,3-dimethylbut-2-ene (0.33 g, 3.9 mmol) in diethyl ether (5 cm³). After five minutes, the brown product was filtered off, copiously washed with diethyl ether (20 cm³) and dried in vacuo. Yield:- 90%.

Table 2-6

Elemental Analyses for Pyridine, Isoquinoline and 4-^tButylpyridine Osmium(VI) Ester Complexes from Alkenes

	% Found			% Required		
	C	H	N	C	H	N
<u>Pyridine Ester Complexes</u>						
OsO ₂ (O ₂ C ₆ H ₁₀)(C ₅ H ₅ N) ₂	38.72	3.89	5.53	38.86	4.08	5.56
OsO ₂ (O ₂ C ₅ H ₈)(C ₅ H ₅ N) ₂	37.78	4.11	6.26	37.49	3.78	5.82
OsO ₂ (O ₂ C ₂ H ₄)(C ₅ H ₅ N) ₂	32.70	3.11	6.43	32.72	3.18	6.36
OsO ₂ (O ₂ C ₆ H ₁₂)(C ₅ H ₅ N) ₂	39.03	4.47	5.44	38.70	4.47	5.64
<u>Isoquinoline Ester Complexes</u>						
OsO ₂ (O ₂ C ₂ H ₄)(C ₉ H ₇ N) ₂	44.77	3.39	5.09	44.44	3.36	5.18
<u>4-^tButylpyridine Ester Complexes</u>						
OsO ₂ (O ₂ C ₂ H ₄)(C ₉ H ₁₃ N) ₂	43.40	5.58	4.76	43.47	5.47	5.07
OsO ₂ (O ₂ C ₆ H ₁₀)(C ₉ H ₁₃ N) ₂	48.02	6.03	4.43	47.51	5.98	4.62

Isoquinoline Complexes $[\text{OsO}_2(\text{O}_2\text{R})(\text{C}_9\text{H}_7\text{N})_2]$

The preparation of $[\text{OsO}_2(\text{O}_2\text{C}_5\text{H}_8)(\text{C}_9\text{H}_7\text{N})_2]$ is typical.

To a solution of the adduct $\text{OsO}_4 \cdot \text{C}_9\text{H}_7\text{N}$ (1.0 g, 2.6 mmol) in diethyl ether (10 cm³) was added dropwise with stirring cyclopentene (0.18 g, 2.6 mmol) in diethyl ether (5 cm³). After five minutes the brown product was filtered off, copiously washed with diethyl ether (20 cm³) and dried in vacuo. Yield:- 40%.

An alternative method of preparation was carried out by treating osmium tetroxide (1.0 g, 3.9 mmol), dissolved in diethyl ether (10 cm³) containing isoquinoline (1.0 g, 7.8 mmol), with cyclopentene (0.26 g, 3.8 mmol) in diethyl ether (5 cm³). After five minutes, the brown product was filtered off, washed with diethyl ether (20 cm³) and dried in vacuo. Yield:- 85%.

4-^tButylpyridine Complexes $[\text{OsO}_2(\text{O}_2\text{R})(\text{C}_9\text{H}_{13}\text{N})_2]$

The preparation of $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_9\text{H}_{13}\text{N})_2]$ is typical.

To a solution of the adduct $\text{OsO}_4 \cdot \text{C}_9\text{H}_{13}\text{N}$ (1.0 g, 2.6 mmol) in diethyl ether (10 cm³) was added dropwise with stirring cyclohexene (0.21 g, 2.6 mmol) in diethyl ether (5 cm³). After five minutes the brown product was filtered off, copiously washed with diethyl ether (20 cm³) and dried in vacuo. Yield:- 30%.

An alternative method of preparation was carried out by treating osmium tetroxide (1.0 g, 3.9 mmol), dissolved in diethyl ether (10 cm³) containing 4-^tbutylpyridine (1.05 g, 7.8 mmol), with cyclohexene (0.32 g, 3.9 mmol) in diethyl ether (5 cm³). After five minutes, the brown product was filtered off, copiously washed with diethyl ether (20 cm³) and dried in vacuo. Yield:- 85%.

2-H-3 Diolato Dioxo Amine Osmium(VI) from Alkenes

$[\text{OsO}_2(\text{O}_2\text{R})\text{L}]_2$, $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ (L = quinuclidine). Elemental analyses

are listed in Table 2-7.

Quinuclidine Complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_7\text{H}_{13}\text{N}]_2$

The preparation of $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})\text{C}_7\text{H}_{13}\text{N}]_2$ is typical.

To a solution of the adduct $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$ (0.5 g, 1.4 mmol) in diethyl ether (10 cm³) was added dropwise with stirring cyclohexene (0.115 g, 1.4 mmol) in diethyl ether (5 cm³). The reaction mixture was cooled to 0° C and the dark green precipitate was filtered off, washed with diethyl ether (10 cm³) and dried in vacuo. Yield:- 65%.

Quinuclidine Complexes $[\text{OsO}_2(\text{O}_2\text{R})(\text{C}_7\text{H}_{13}\text{N})_2]$

The preparation of $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_7\text{H}_{13}\text{N})_2]$ is typical.

To a solution of osmium tetroxide (0.5 g, 2.0 mmol) in diethyl ether (10 cm³) was added dropwise with stirring a solution of quinuclidine (0.44 g, 4.0 mmol) and cyclohexene (0.16 g, 2.0 mmol) in diethyl ether (10 cm³). The reaction mixture was cooled to 0° C and if necessary reduced in volume. The green precipitate was filtered, washed with diethyl ether (5 cm³) and dried in vacuo. Yield:- 50%.

An alternative method of preparation was carried out by treating the complex $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})\text{C}_7\text{H}_{13}\text{N}]_2$ (0.25 g, 0.28 mmol) in dichloromethane (10 cm³) with quinuclidine (0.07 g, 0.63 mmol). The reaction mixture was reduced in volume and the product precipitated by the addition of diethyl ether (30 cm³). The product was filtered, washed with diethyl ether (10 cm³) and dried in vacuo. Yield:- 60%.

2-H-4 Diolato Dioxo Amine Osmium(VI) from Alkenes

$[\text{OsO}_2(\text{O}_2\text{R})\text{L}]$ (L = hexamethylenetetramine.) Elemental analyses are listed in Table 2-7.

Table 2-7

Elemental Analyses for Quinuclidine and Hexamethylenetetramine Osmium(VI) Ester Complexes from Alkenes

	% Found			% Required		
	C	H	N	C	H	N
<u>Quinuclidine Ester Complexes</u>						
$[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})\text{C}_7\text{H}_{13}\text{N}]_2$	35.03	5.26	3.06	34.89	5.18	3.13
$[\text{OsO}_2(\text{O}_2\text{C}_{14}\text{H}_{12})\text{C}_7\text{H}_{13}\text{N}]_2$	46.18	4.89	2.50	46.23	4.62	2.57
$[\text{OsO}_2(\text{O}_2\text{C}_2\text{H}_4)\text{C}_7\text{H}_{13}\text{N}]_2$	27.84	4.30	3.45	27.47	4.36	3.56
$\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_7\text{H}_{13}\text{N})_2$	42.48	6.44	4.76	42.68	6.45	4.98
$\text{OsO}_2(\text{O}_2\text{C}_2\text{H}_4)(\text{C}_7\text{H}_{13}\text{N})_2$	37.88	5.87	5.28	38.08	5.99	5.55
<u>Hexamethylenetetramine Ester Complexes</u>						
$\text{OsO}_2(\text{O}_2\text{C}_5\text{H}_8)\text{C}_6\text{H}_{12}\text{N}_4$	28.95	4.29	11.78	28.6	4.30	12.1
$\text{OsO}_2(\text{O}_2\text{C}_2\text{H}_4)\text{C}_6\text{H}_{12}\text{N}_4$	23.04	3.81	12.86	22.75	3.82	13.26

Hexamethylenetetramine Complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_6\text{H}_{12}\text{N}_4]$

The preparation of $[\text{OsO}_2(\text{O}_2\text{C}_5\text{H}_8)\text{C}_6\text{H}_{12}\text{N}_4]$ is typical.

To a solution of the adduct $(\text{OsO}_4)_2\text{C}_6\text{H}_{12}\text{N}_4$ (0.5 g, 0.77 mmol) in tetrahydrofuran (20 cm^3) was added dropwise with stirring cyclopentene (0.026 g, 0.38 mmol) in tetrahydrofuran (5 cm^3). After three minutes the pale green precipitate was filtered off, copiously washed with diethyl ether (10 cm^3) and dried in vacuo. Yield:- 35%.

2-H-5 Di[μ -Oxo-Amine Dioxo Osmium(VI)]



Di[μ -oxo-bis(pyridine)dioxo osmium(VI)] $[\text{Os}_2\text{O}_6(\text{C}_5\text{H}_5\text{N})_4]$

The adduct $\text{OsO}_4 \cdot \text{C}_5\text{H}_5\text{N}$ (0.5 g, 1.5 mmol) was dissolved in tetrahydrofuran (20 cm^3) containing a little ethanol (1 cm^3). The reaction mixture slowly darkened and after one hour a brown precipitate had formed. The product was filtered off, washed with diethyl ether and dried in vacuo. Yield:- 30%.

An alternative method of preparation was carried out by treating osmium tetroxide (0.5 g, 2.0 mmol) in tetrahydrofuran (10 cm^3) with a solution of pyridine (0.32 g, 4.1 mmol) and ethanol (1 cm^3) in tetrahydrofuran (10 cm^3). After one hour, the product was filtered off, washed with diethyl ether and dried in vacuo. Yield:- 75%.

Elemental analysis Found:- C, 30.81%; H, 2.54%; N, 7.21%

$\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_6\text{Os}_2$ Requires:- C, 30.30%; H, 2.54%; N, 7.07%.

Di[μ -oxo-bis(4-^tbutylpyridine)dioxo osmium(VI)] $[\text{Os}_2\text{O}_6(\text{C}_9\text{H}_{13}\text{N})_4]$

The adduct $\text{OsO}_4 \cdot \text{C}_9\text{H}_{13}\text{N}$ (0.4 g, 1.0 mmol) was dissolved in tetrahydrofuran (10 cm^3) containing a little ethanol (1 cm^3). After one hour, the brown reaction mixture was reduced in bulk and the product

precipitated by the addition of diethyl ether (40 cm³). The product was filtered off, washed with diethyl ether (20 cm³) and dried in vacuo. Yield:- 30%.

An alternative method of preparation was carried out by treating osmium tetroxide (0.5 g, 2.0 mmol) in tetrahydrofuran (10 cm³) with a solution of 4-^tbutylpyridine (0.6 g, 4.4 mmol) and ethanol (1 cm³) in tetrahydrofuran (10 cm³). The product was filtered off, washed with diethyl ether (20 cm³) and dried in vacuo. Yield:- 70%.

Elemental analysis Found:- C, 42.58%; H, 5.24%; N, 5.49%;

M.W. 480 (in CHCl₃)

C₃₆H₅₂N₄O₆Os₂ Requires:- C, 42.51%; H, 5.15%; N, 5.51%;

M.W. 1017.

Diolato dioxo bis(4-^tbutylpyridine)osmium(VI) [OsO₂(O₂R)(C₉H₁₃N)₂]

The complex [Os₂O₆(C₉H₁₃N)₄] (0.5 g, 0.5 mmol) was dissolved in dichloromethane (10 cm³) and treated with cis-cyclohexan-1,2-diol (0.15 g, 1.3 mmol) or ethane-1,2-diol (0.07 g, 1.1 mmol). The reaction mixture was stirred for ten minutes, reduced to low bulk and the product precipitated by the addition of diethyl ether (50 cm³). The product was filtered off, washed with diethyl ether (20 cm³) and dried in vacuo. Yield:- 70-80%. Elemental analyses are listed in Table 2-6.

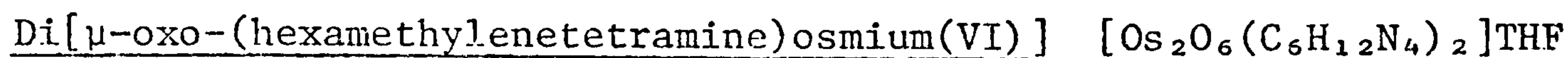
Di[μ-oxo(quinuclidine)osmium(VI)] [Os₂O₆(C₇H₁₃N)₂]

The adduct OsO₄.C₇H₁₃N (0.5 g, 1.4 mmol) was dissolved in diethyl ether (20 cm³) containing a little ethanol (1 cm³). After twenty minutes the reaction mixture had turned deep green, however no osmium(VI) product could be isolated from the reaction mixture.

Diolato dioxo(quinuclidine)osmium(VI)

Ethane-1,2-diol (0.09 g, 1.5 mmol) was added to the green reaction

solution prepared above. After five minutes, the reaction mixture was reduced to low bulk and cooled to 0° C. The precipitated ester complex $[\text{OsO}_2(\text{O}_2\text{C}_2\text{H}_4)\text{C}_7\text{H}_{13}\text{N}]_2$ was filtered off, washed with diethyl ether (10 cm³) and dried in vacuo. The product was characterised by comparison of its infrared spectrum with that of an authentic sample.

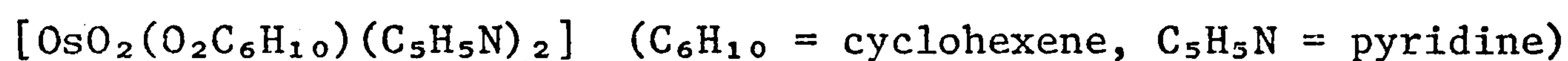


The adduct $(\text{OsO}_4)_2\text{C}_6\text{H}_{12}\text{N}_4$ (0.5 g, 0.8 mmol) was dissolved in tetrahydrofuran (30 cm³) containing a little ethanol (1 cm³). After twenty four hours the resulting brown precipitate was filtered, washed with tetrahydrofuran (5 cm³) and dried in vacuo. Yield:- 50%.

Elemental analysis Found:- C, 22.94%; H, 3.75%; N, 13.43%

$\text{C}_{16}\text{H}_{32}\text{N}_8\text{O}_7\text{Os}_2$ Requires:- C, 23.19%; H, 3.89%; N, 13.52%.

2-H-6 Hydrolysis of Oxo Amine Osmium(VI) Ester Complex



With Na_2SO_3

The complex $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_2]$ (1.0 g, 2.1 mmol) was refluxed for three hours with a solution of sodium sulphite (2.0 g, 16.0 mmol) in water (50 cm³) containing ethanol (10 cm³). The reaction mixture was allowed to cool, the osmium sulphito complex filtered off and the filtrate extracted with diethyl ether (5 x 5 cm³). The ether extract was dried over MgSO_4 and dried in vacuo to give cis-cyclohexan-¹⁴¹-1,2-diol in 92% yield, M.P. 93° C (Lit. 98° C). The product was characterised by its infrared ¹H n.m.r. and mass spectrum (M = 116).

With Mannitol

The complex $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_2]$ (1.0 g, 2.1 mmol) was refluxed for four hours with a solution of mannitol (2.0 g, 21.7 mmol) in water

(50 cm³) containing ethanol (5 cm³) and the reaction mixture extracted with diethyl ether (5 x 25 cm³). The ether extract was dried over MgSO₄ and evaporated in vacuo to give cis-cyclohexan-1,2-diol in 72% yield.

M.P. 94⁰ C (Lit. 98⁰ C). The product was characterised by its infrared, ¹⁴¹
¹H n.m.r. and mass spectrum (M = 116).

CHAPTER THREE

REACTIONS OF OSMIUM TETRAOXIDE WITH DIENES

Abstract

Osmium tetroxide, (OsO_4), reacts with dienes R in the presence of excess of tertiary amines L to give oxo amine osmium(VI) ester complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_4]$ and $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ (L = pyridine or isoquinoline). The adduct $\text{OsO}_4 \cdot \text{L}$ (L = quinuclidine) reacts with dienes R to give the oxo amine osmium(VI) ester complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_2]_n$ and $[\text{OsO}_2(\text{O}_2\text{R})\text{L}]_2$. The structures of these complexes are discussed on the basis of their vibrational and ^1H n.m.r. spectra. Hydrolysis of the product $[\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_2]$, (C_8H_{12} = cycloocta-1,5-diene, $\text{C}_5\text{H}_5\text{N}$ = pyridine) has been carried out and cis-cycloocten-5,6-diol isolated in high yield.

Section 3-A Introduction

Osmium tetroxide, (OsO_4), can be used stoichiometrically^{154,155} or catalytically in the presence of a secondary oxidising agent, such as hydrogen peroxide,¹⁵⁶⁻¹⁵⁸ for the cis-hydroxylation of dienes to give either unsaturated cis-diols^{121,154-156} or tetra-ols.^{120,121,158} Although it has been noted that the presence of tertiary amines such as pyridine greatly^{14,130} increases the rate of diene cis-hydroxylation, very little work has been carried out on the isolation and identification of oxo amine osmium(VI) ester intermediates formed during the reaction of OsO_4 with dienes R. Products of stoichiometry $(\text{OsO}_4)_2 \cdot \text{R} \cdot \text{L}_4$ and $\text{OsO}_4 \cdot \text{R} \cdot \text{L}_2$ (L = pyridine) have been isolated, depending upon the initial OsO_4 : diene reacting molar ratios used, but no structures were suggested and the products were characterised only by osmium analyses.^{14,159}

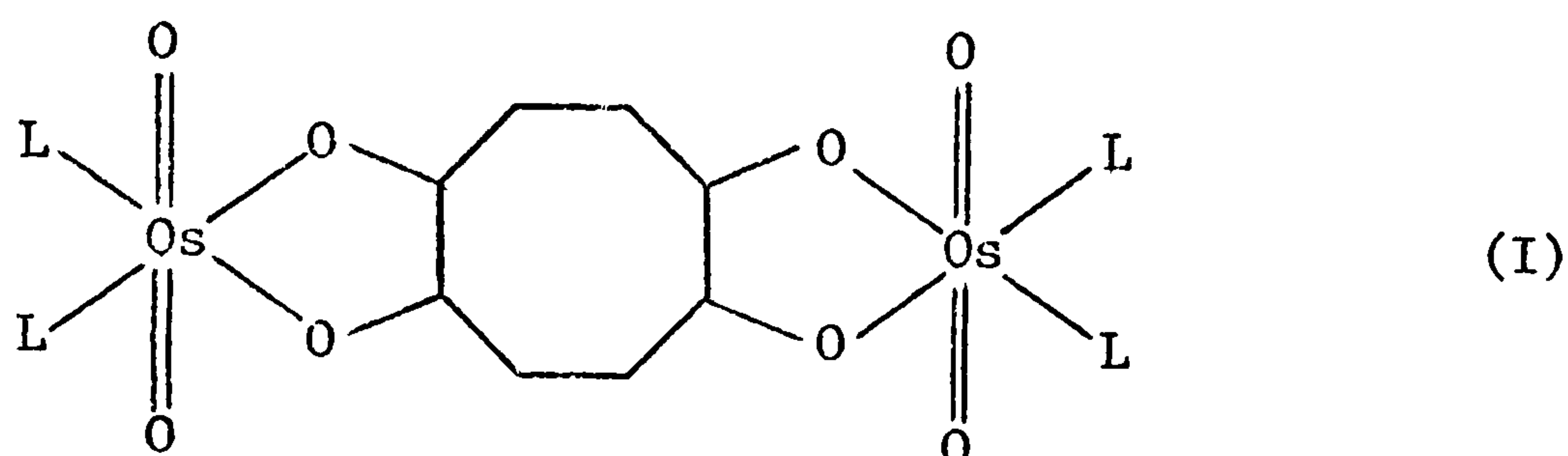
Oxo amine osmium(VI) ester products have been prepared by reaction of OsO_4 with a range of dienes in the presence of tertiary amines; the hydrolysis of the product $[\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_2]$ (C_8H_{12} = cyclo-octa-1,5-diene, $\text{C}_5\text{H}_5\text{N}$ = pyridine) is briefly discussed.

Section 3-B Reaction of Osmium Tetroxide with Dienes in the Presence of Tertiary Amines L (L = pyridine or isoquinoline)

3-B-1 Oxo Amine Osmium(VI) Ester Complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_4]$

OsO_4 was treated with a range of dienes R (R = cyclohexa-1,3-diene C_6H_8 , cycloocta-1,5-diene C_8H_{12} , 4-vinylcyclohex-1-ene C_8H_{12} or 2,3-dimethyl-1,3-butadiene C_6H_{10}) in a 2 : 1 OsO_4 : diene reacting molar ratio in the presence of excess of tertiary amine L (L = pyridine or iso-quinoline), to give brown diamagnetic products of stoichiometry

$(\text{OsO}_4)_2 \cdot \text{R} \cdot \text{L}_4$. On the basis of their diamagnetism,¹⁰⁷ of molecular weight measurements in dichloromethane and spectroscopic evidence, these products are formulated as diolato dioxo amine osmium(VI) complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_4]$ containing trans oxo ligands. Thus, for the product formed from cycloocta-1,5-diene, structure (I) is proposed.



The infrared spectra of the solid complexes, as for the complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ ^{32,61} prepared from alkenes (Section 2-B), show bands near 840 cm^{-1} and 300 cm^{-1} assigned to $\nu_{\text{OsO}_2}^{\text{as}}$ and δ_{OsO_2} of the trans dioxo "osmyl" moiety; Raman spectra of the solid complexes in the $800\text{--}1000\text{ cm}^{-1}$ range show bands near 880 cm^{-1} , polarised in solution, assigned, as for other osmyl complexes,¹³⁷ to $\nu_{\text{OsO}_2}^{\text{s}}$. Infrared bands near 1000 cm^{-1} and 600 cm^{-1} are tentatively assigned to the stretching vibrations $\nu_{\text{C-O}}$ and $\nu_{\text{Os-O}}$ respectively (Table 3-1).

The ^1H n.m.r. spectra of the complexes, in C^2HCl_3 , show resonances due to protons adjacent to the donor oxygen atoms near $\delta\ 4.7$, as found for the complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ derived from alkenes (Section 2-B). Integration of the ^1H n.m.r. spectra of the complexes of the protons adjacent to the donor oxygen atoms against the amine protons confirms the amine : diene ratio as 4 : 1.

3-B-2 Oxo Amine Osmium(VI) Ester Complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$

Reaction of OsO_4 with a five-fold excess of cycloocta-1,5-diene in the presence of excess of tertiary amine L (L = pyridine or isoquinoline)

Table 3-1

Spectroscopic ^a and Molecular Weight Data for Oxo Amine Osmium(VI) Ester Complexes Prepared from Dienes

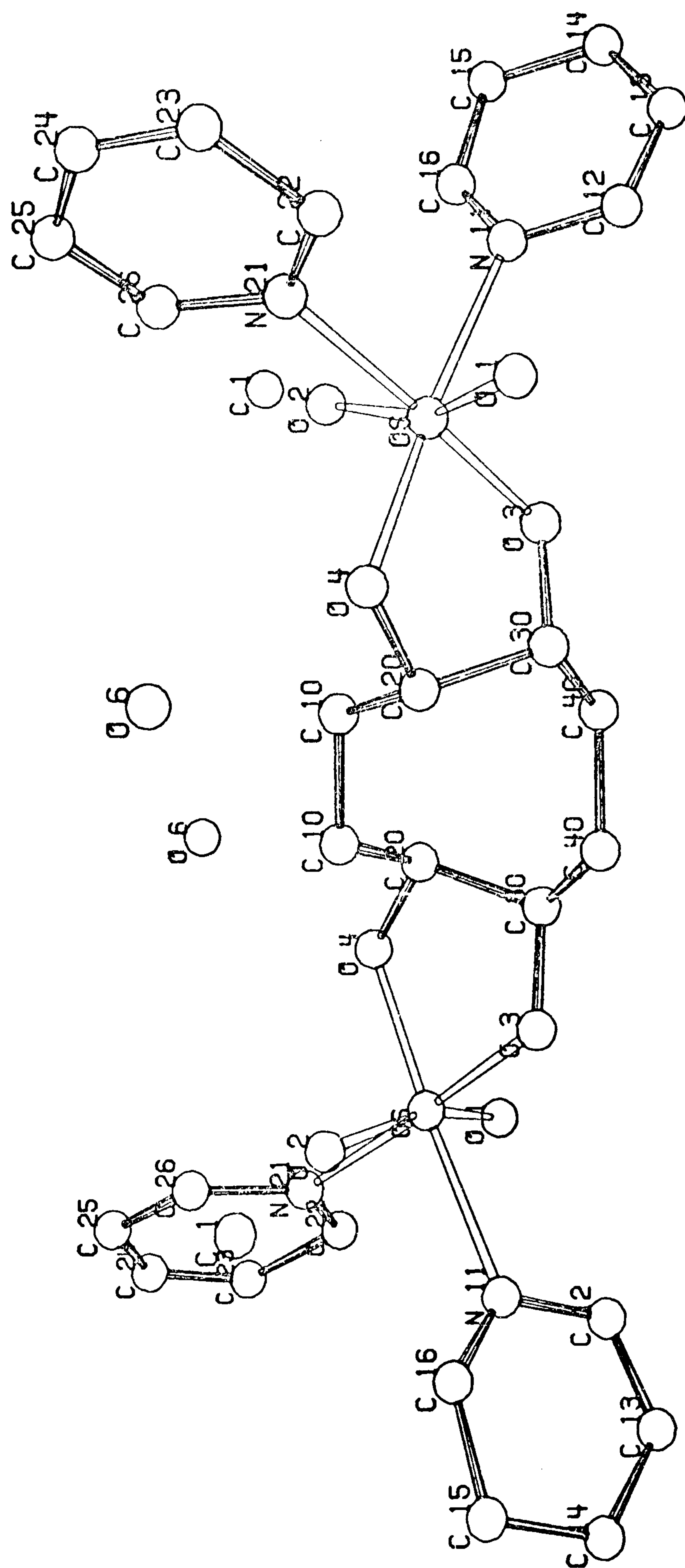
	Diene	$\nu_{\text{OsO}_2}^b$	δ_{OsO_2}	$\nu_{\text{Os-O}}$	$\nu_{\text{C-O}}$	$^1\text{H n.m.r.}^c$	M.W. ^d
<u>Pyridine Ester Complexes</u>	2,3-dimethyl-1,3-butadiene	825s <u>877s</u>	301w	-	998m	-	840 (907)
	4-vinylcyclohex-1-ene	835, 830s <u>879s</u>	290w	592m	990m	3.95 (3H) 4.81 (2H)	969 (933)
	cycloocta-1,5-diene	845, 830s <u>880s</u>	290w	583m	970m	4.75 (4H)	934 (933)
	cycloocta-1,5-diene	840, 835s <u>876s</u>	288w	593m	970m	4.67 (2H)	536 (521)
<u>Isoquinoline Ester Complexes</u>	cycloocta-1,5-diene	832, 820s <u>878s</u>	332w	-	1007m	4.80 (4H)	1177 (1133)
	cyclohexa-1,3-diene	834, 820s	292w	595m	1020m	-	-
	cycloocta-1,5-diene	840, 828s <u>880s</u>	282w	600m	972m	4.70 (2H)	465 (474)

^a Measured as solids.

^b $\nu_{\text{OsO}_2}^{\text{as}}$ i.r. active; measured as Nujol mulls. $\nu_{\text{OsO}_2}^{\text{s}}$ Raman active; measured as KBr discs. Raman modes underlined.

^c δ values for protons adjacent to donor oxygen atoms (ppm relative to TMS, measured in C^2HCl_3).

^d Molecular weights osmotically in dichloromethane. (Calculated values in parentheses).



Supplementary Figure

Preliminary X-Ray Molecular Structure of $[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_4]$

$(\text{C}_8\text{H}_{12} = \text{cycloocta-1,5-diene}, \text{C}_5\text{H}_5\text{N} = \text{pyridine})$

$\underline{a} = 8.363 \text{ \AA}; \underline{b} = 14.441 \text{ \AA}; \underline{c} = 14.546 \text{ \AA}$

$\text{Os}-\text{O}(1) \ 1.58 \text{ \AA}, \text{Os}-\text{O}(2) \ 1.70 \text{ \AA}, \text{Os}-\text{O}(3) \ 1.90 \text{ \AA},$

$\text{Os}-\text{O}(4) \ 1.95 \text{ \AA}, \text{Os}-\text{N}(11) \ 2.24 \text{ \AA}, \text{Os}-\text{N}(21) \ 2.16 \text{ \AA},$

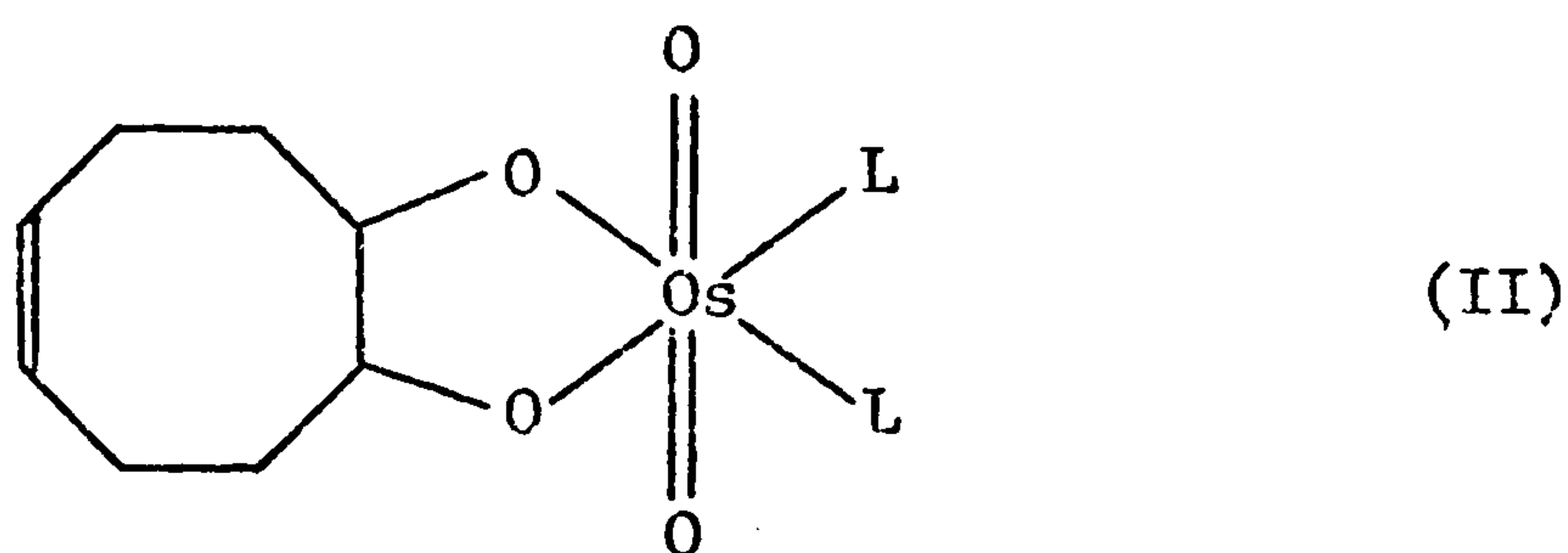
$\text{O}(1)-\text{Os}-\text{O}(2) \ 163^\circ, \text{O}(3)-\text{Os}-\text{O}(4) \ 86^\circ, \text{O}(1)-\text{Os}-\text{O}(3) \ 94^\circ, \text{O}(3)-\text{Os}-\text{N}(21) \ 178^\circ.$

Space group P_{222_1} , orthorhombic, θ to 70° , 1936 reflections.

gave brown, diamagnetic products of stoichiometry $\text{OsO}_4 \cdot \text{R} \cdot \text{L}_2$.

Vibrational spectra of these products are very similar to those of the complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_4]$ discussed in Section 3-B-1, with bands near 840 cm^{-1} and near 300 cm^{-1} in the infrared assigned to $\nu_{\text{OsO}_2}^{\text{as}}$ and δ_{OsO_2} respectively and bands near 880 cm^{-1} in the Raman assigned to $\nu_{\text{OsO}_2}^{\text{s}}$.

The ^1H n.m.r. spectra of the complexes, however, show alkenyl protons at δ 5.58 (2H) and protons adjacent to the donor oxygen atoms near δ 4.7 (2H) (Table 3-1), indicating that only one of the double bonds of the diene substrate has reacted. The products are therefore formulated as diolato dioxo amine osmium(VI) complexes $[\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})\text{L}_2]$ (II) with only one of the double bonds having reacted.



The hydrolysis of this product is discussed in Section 3-D.

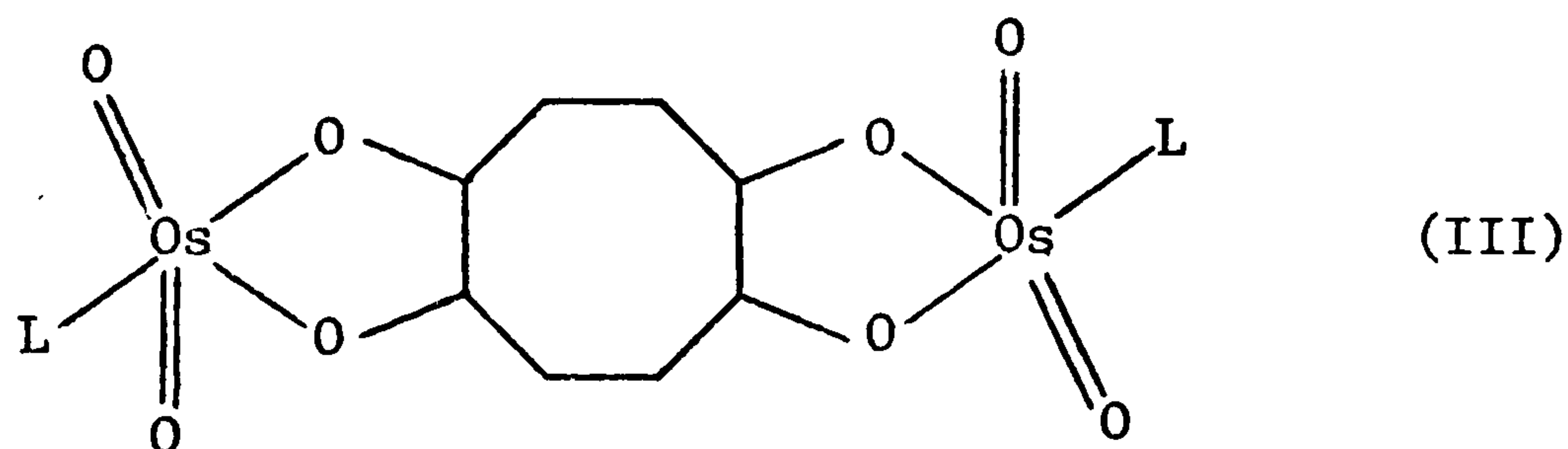
Section 3-C Reaction of the Adduct $\text{OsO}_4 \cdot \text{L}$ with Dienes ($\text{L} = \text{quinuclidine}$)

3-C-1 Oxo Amine Osmium(VI) Ester Complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_2]_n$

The adduct $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$ ($\text{C}_7\text{H}_{13}\text{N} = \text{quinuclidine}$) has been shown to react with alkenes R to give, in solution, the five coordinate osmium(VI) ester complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_7\text{H}_{13}\text{N}]$ (Section 2-C). In an attempt to prepare the corresponding five coordinate ester complexes from dienes, the adduct $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$ was treated with a range of dienes R ($\text{R} = \text{cycloocta-1,5-diene } \text{C}_8\text{H}_{12}$, cyclohexa-1,3-diene C_6H_8 or 2,5-dimethyl-2,4-hexadiene C_8H_{14}) in a 2 : 1 $\text{OsO}_4 \cdot \text{L}$: diene reacting molar ratio. The green, diamagnetic products were found to be of stoichiometry $(\text{OsO}_4)_2 \cdot \text{R} \cdot (\text{C}_7\text{H}_{13}\text{N})_2$.

The infrared spectra of the solid complexes show bands near 900 cm^{-1} and 300 cm^{-1} assigned to stretching vibrations, $\nu_{\text{OsO}_2}^{\text{as}}$, and deformations, δ_{OsO_2} , respectively; the Raman spectra of the solid complexes show bands near 880 cm^{-1} assigned to $\nu_{\text{OsO}_2}^{\text{s}}$ (Table 3-2). These spectral features are very similar to those found for the corresponding mono-alkene complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{C}_7\text{H}_{13}\text{N}]_2$ (Section 2-C) and it seems reasonable to formulate them as $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})(\text{C}_7\text{H}_{13}\text{N})_2]_n$ with an asymmetric bridging system as described previously (Sections 2-C and 2-D). Molecular weight measurements of the complexes in dichloromethane (Table 3-2) suggest that the monomeric species $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})(\text{C}_7\text{H}_{13}\text{N})_2]$ exist in solution, indicating that the asymmetric bridge system has been broken.

For the product derived from cycloocta-1,5-diene, structure (III) is therefore envisaged in solution, with a trigonal bipyramidal coordination about each osmium atom, the oxo ligands occupying equatorial positions. These complexes are presumably polymeric in the solid state.



3-C-2 Oxo Amine Osmium(VI) Ester Complexes $[\text{OsO}_2(\text{O}_2\text{R})\text{L}]_2$

Reaction of the adduct $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$ ($\text{C}_7\text{H}_{13}\text{N}$ = quinuclidine) with a five-fold excess of cycloocta-1,5-diene gave a product of stoichiometry $\text{OsO}_4 \cdot \text{C}_8\text{H}_{12} \cdot \text{C}_7\text{H}_{13}\text{N}$. The infrared spectrum of the solid complex shows strong bands at 904 cm^{-1} and 300 cm^{-1} assigned to $\nu_{\text{OsO}_2}^{\text{as}}$ and δ_{OsO_2} respectively; the Raman spectrum of the solid complex shows $\nu_{\text{OsO}_2}^{\text{s}}$ at 890 cm^{-1} .

Table 3-2

Spectroscopic^a and Molecular Weight Data for Oxo Amine Osmium(VI) Ester Complexes Prepared from Dienes

	Diene	$\nu_{\text{OsO}_2}^b$	δ_{OsO_2}	$\nu_{\text{Os-O}}$	$\nu_{\text{C-O}}$	$^1\text{H n.m.r.}^c$	M.W. ^d
<u>Quinuclidine Ester Complexes^e</u>							
$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_8\text{H}_{12})(\text{C}_7\text{H}_{13}\text{N})_2]_n$	<u>cycloocta-1,5-diene</u>	872s	330w	—	978m	4.00 (4H)	350 (839)
	2,5-dimethyl-1,2,4-hexadiene	875s	320w	625m	1018m		789 (841)
	<u>cyclohexa-1,3-diene</u>	870s	315w	600m	1008m	3.96 (4H)	895 (811)
	<u>cycloocta-1,5-diene</u>	904s <u>890s</u>	300w	—	967m		611 (621)

^a Measured as solids.

^b as ν_{OsO_2} i.r. active; measured as Nujol mulls. $\nu_{\text{OsO}_2}^s$ Raman active; measured as KBr discs. Raman modes underlined.

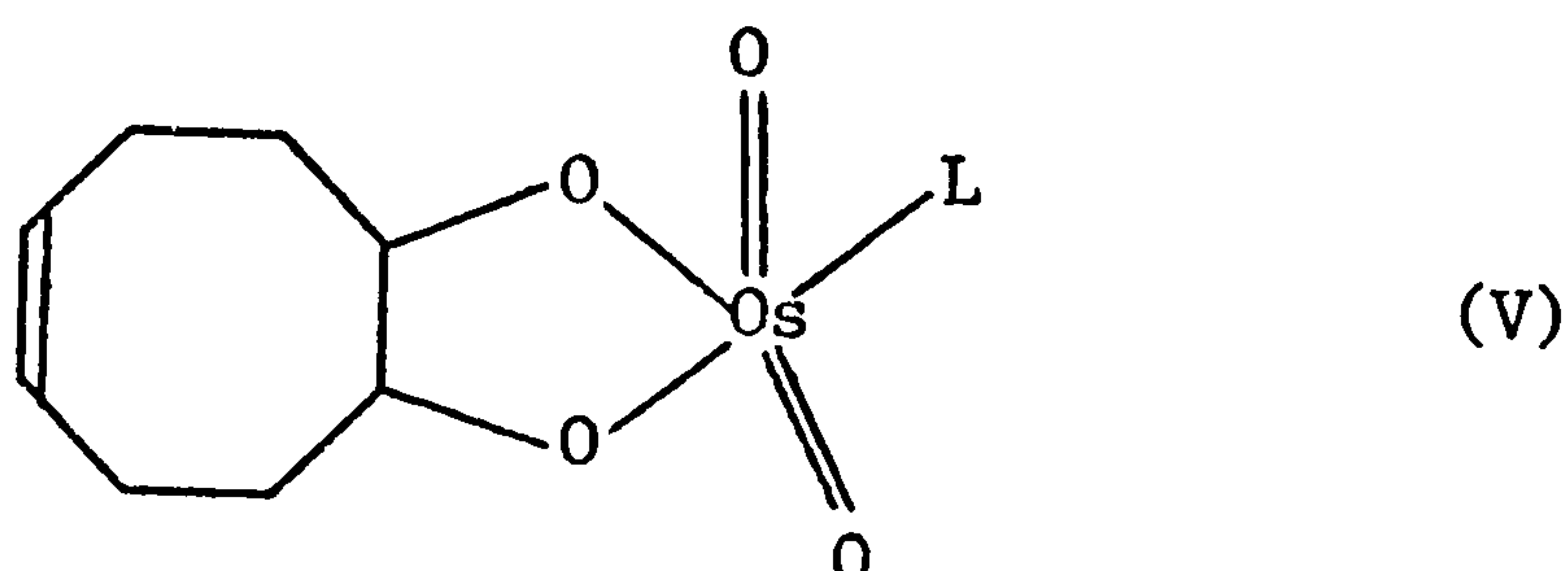
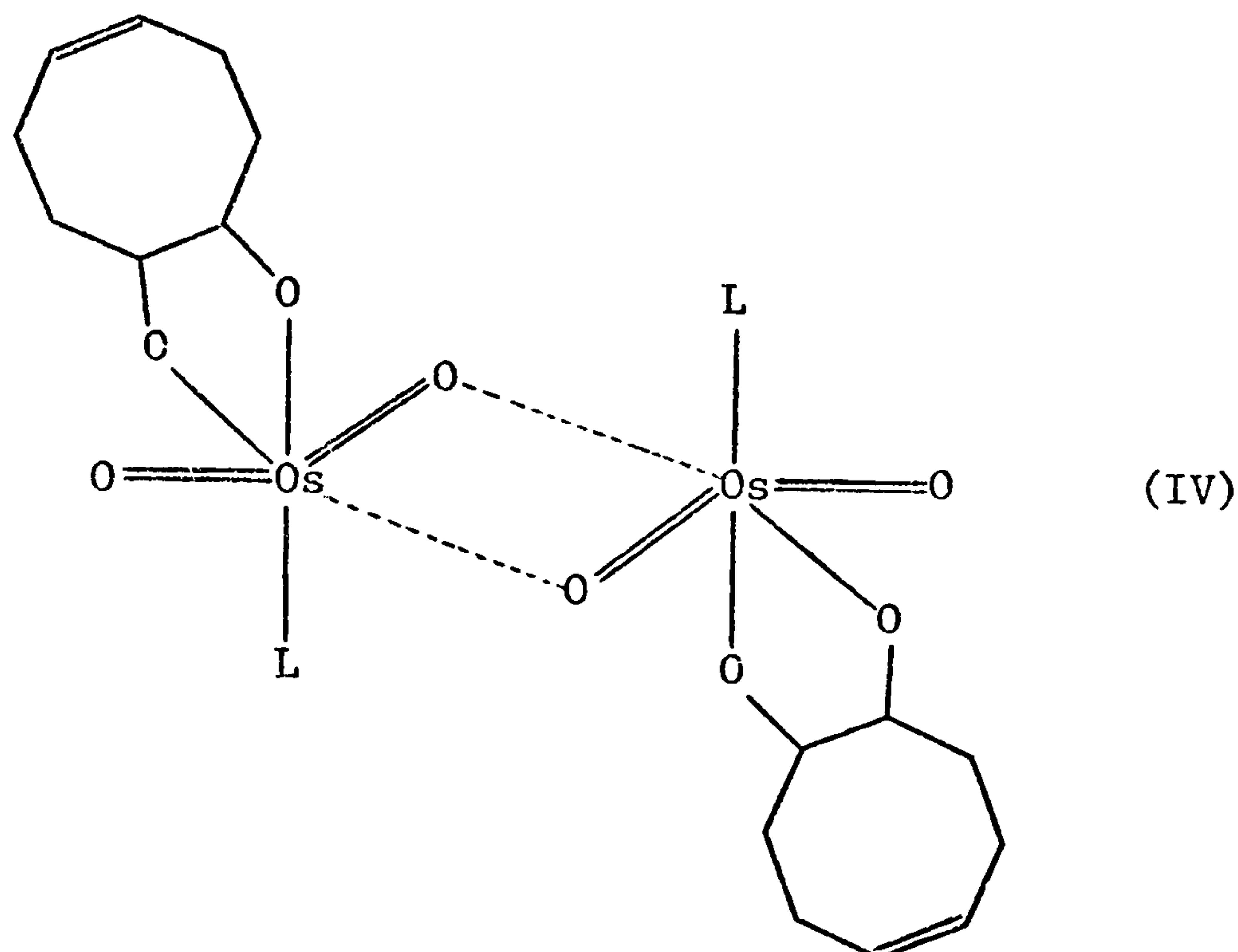
^c δ values for protons adjacent to donor oxygen atoms (ppm relative to TMS; measured in C^2HCl_3).

^d Molecular weight osmotically in dichloromethane (calculated values in parentheses).

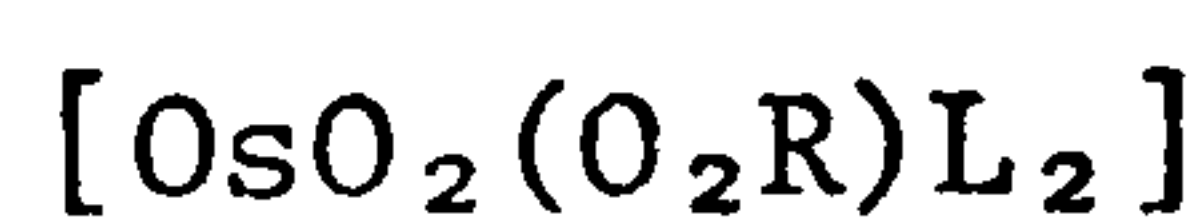
^e Prepared from the adduct $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$.

The ^1H n.m.r. spectrum of the complex in C^2HCl_3 shows resonances due to alkenyl protons at δ 5.55(2H) and protons adjacent to the donor oxygen atoms at δ 3.99 (2H) (Table 3-2), indicating that only one of the double bonds has reacted.

Structures (IV) and (V), involving trigonal bipyramidal coordination, are therefore proposed for the complex in the solid state and in solution respectively.

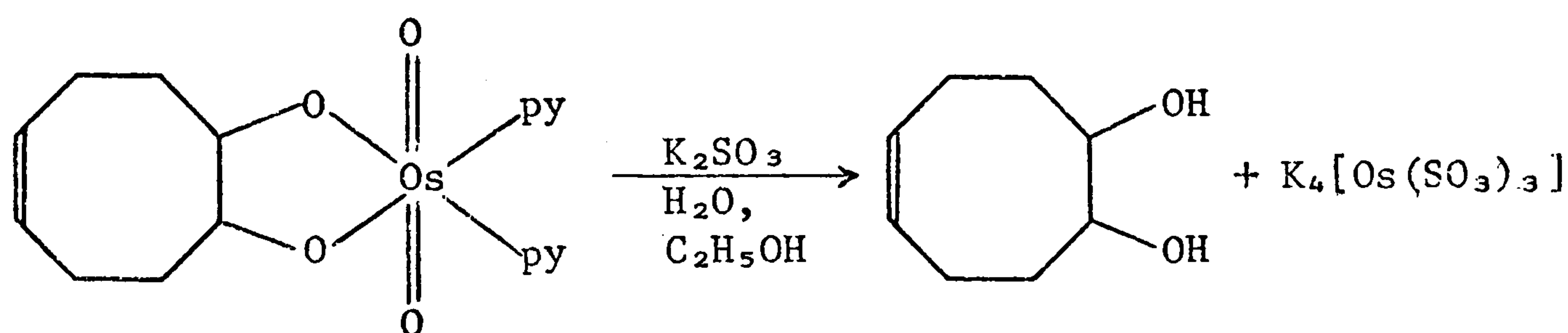


Section 3-D Hydrolysis of Oxo Amine Osmium(VI) Ester Complexes



The hydrolysis of the oxo amine osmium(VI) complex $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_2]$ (C_6H_{10} = cyclohexene, $\text{C}_5\text{H}_5\text{N}$ = pyridine) has been described in Section 2-G. A similar hydrolysis procedure can be carried out on the corresponding osmium(VI) ester complex $[\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_2]$ prepared from cyclo-octa-1,5-diene.

It has been reported that treatment of OsO_4 , pyridine and cycloocta-1,5-diene with hydrogen sulphide gives cis-cycloocten-5,6-diol in 14% yield.¹⁶⁰ This work has been repeated and by isolating the intermediate osmium(VI) ester complex $[\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_2]$ and hydrolysing this with potassium sulphite solution, cis-cycloocten-5,6-diol has been isolated in 76% yield, appreciably higher than the 3% yield reported for the corresponding oxidation using potassium permanganate.¹⁶¹



Section 3-E Experimental

All manipulations involving osmium tetroxide were carried out in a fume cupboard.

3-E-1 Diolato Dioxo Bis-Amine Osmium(VI) from Dienes

$[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_4]$, $[\text{OsO}_2(\text{O}_2\text{R})\text{L}_2]$ (L = pyridine or isoquinoline). The preparations of these complexes were carried out under a dry nitrogen atmosphere since the products were found to be hygroscopic. Elemental analyses are listed in Table 3-3.

Pyridine Complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})(\text{C}_5\text{H}_5\text{N})_4]$

The preparations of these complexes followed similar procedures; the preparation of $[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_6\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_4]$ is typical.

To a solution of OsO_4 (0.4 g, 1.6 mmol) in diethyl ether (10 cm³) containing pyridine (0.3 g, 3.8 mmol) was added dropwise with stirring 2,3-dimethylbuta-1,3-diene (0.06 g, 0.7 mmol) in diethyl ether (10 cm³). After five minutes, the brown precipitate was filtered and copiously washed with diethyl ether (20 cm³). The product was recrystallised from dichloromethane and diethyl ether and dried in vacuo. Yield:- 60%.

Isoquinoline Complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})(\text{C}_9\text{H}_7\text{N})_4]$

The preparations of these complexes followed similar procedures; the preparation of $[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_8\text{H}_{12})(\text{C}_9\text{H}_7\text{N})_4]$ is typical.

To a solution of OsO_4 (0.4 g, 1.6 mmol) in diethyl ether (10 cm³) containing isoquinoline (0.5 g, 3.9 mmol) was added dropwise with stirring cycloocta-1,5-diene (0.08 g, 0.7 mmol) in diethyl ether (10 cm³). After five minutes the brown precipitate was filtered off and copiously washed with diethyl ether (20 cm³). The product was recrystallised from dichloromethane and diethyl ether and dried in vacuo. Yield:- 65%.

Table 3-3

Elemental Analysis for Pyridine and Isoquinoline Osmium(VI) Ester Complexes from Dienes

	% Found			% Required		
	C	H	N	C	H	N
<u>Pyridine Ester Complexes</u>						
$\text{Os}_2\text{O}_4(\text{O}_4\text{C}_6\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_4$	34.15	3.36	5.91	34.43	3.33	6.18
$\text{Os}_2\text{O}_4(\text{O}_4\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_4^a$	36.10	3.54	5.54	36.05	3.46	6.01
$\text{Os}_2\text{O}_4(\text{O}_4\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_4^b$	35.99	3.45	5.57	36.05	3.46	6.01
$\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_2^b$	41.28	4.31	5.27	41.53	4.26	5.38
<u>Isoquinoline Ester Complexes</u>						
$\text{Os}_2\text{O}_4(\text{O}_4\text{C}_8\text{H}_{12})(\text{C}_9\text{H}_7\text{N})_4^b$	46.47	3.66	4.62	46.64	3.56	4.94
$\text{Os}_2\text{O}_4(\text{O}_4\text{C}_6\text{H}_8)(\text{C}_9\text{H}_7\text{N})_4$	45.46	3.55	4.60	45.65	3.28	5.07
$\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})(\text{C}_9\text{H}_7\text{N})_2^b$	50.13	4.24	4.34	50.31	4.22	4.51

^a Derived from 4-vinylcyclohex-1-ene

^b Derived from cycloocta-1,5-diene

Pyridine Complex $[\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_2]$

To a solution of cycloocta-1,5-diene (0.9 g, 8.3 mmol) in diethyl ether (10 cm³) containing pyridine (0.3 g, 3.8 mmol) was added dropwise with stirring a solution of OsO₄ (0.4 g, 1.6 mmol) in diethyl ether (10 cm³). After five minutes the dark brown precipitate was filtered off and washed with diethyl ether (20 cm³). The product was recrystallised from dichloromethane and diethyl ether. Yield:- 60%.

Isoquinoline Complex $[\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})(\text{C}_9\text{H}_7\text{N})_2]$

To a solution of cycloocta-1,5-diene (0.9 g, 8.3 mmol) in diethyl ether (10 cm³) containing isoquinoline (0.5 g, 3.9 mmol) was added dropwise with stirring a solution of OsO₄ (0.4 g, 1.6 mmol) in diethyl ether (10 cm³). After five minutes the dark brown precipitate was filtered off and washed with diethyl ether (20 cm³). The product was recrystallised from dichloromethane and diethyl ether. Yield:- 65%.

3-E-2 Diolato Dioxo Amine Osmium(VI) from Dienes

$[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_2]_n$, $[\text{OsO}_2(\text{O}_2\text{R})\text{L}]_2$ (L = quinuclidine). The preparations of these complexes were carried out under a dry nitrogen atmosphere since the products were found to be hygroscopic. Elemental analyses are listed in Table 3-4.

Quinuclidine Complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})(\text{C}_7\text{H}_{13}\text{N})_2]_n$

The preparations of these complexes followed similar procedures; the preparation of $[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_8\text{H}_{14})(\text{C}_7\text{H}_{13}\text{N})_2]_n$ is typical.

To a solution of the adduct OsO₄.C₇H₁₃N (0.5 g, 1.4 mmol) in diethyl ether (15 cm³) was added dropwise with stirring 2,5-dimethyl-2,4-hexadiene (0.07 g, 0.6 mmol) in diethyl ether (10 cm³). After five minutes the green precipitate was filtered off and washed with diethyl ether (10 cm³). The product was recrystallised from dichloromethane and diethyl ether. Yield:- 55%.

Table 3-4

Elemental Analyses for Quinuclidine Osmium(VI) Ester Complexes from Dienes

	% Found			% Required		
	C	H	N	C	H	N
<u>Quinuclidine Ester Complexes</u>						
$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_8\text{H}_{12})(\text{C}_7\text{H}_{13}\text{N})_2]_n^a$	32.05	4.57	3.03	31.50	4.57	3.34
$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_8\text{H}_{14})(\text{C}_7\text{H}_{13}\text{N})_2]_n$	31.82	4.76	3.28	31.42	4.79	3.33
$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_6\text{H}_8)(\text{C}_7\text{H}_{13}\text{N})_2]_n$	29.31	4.16	3.41	29.62	4.23	3.45
$[\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})\text{C}_7\text{H}_{13}\text{N}]_2^a$	38.28	5.34	2.82	38.04	5.32	2.96

^a Derived from cycloocta-1,5-diene

Quinuclidine Complex $[\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})\text{C}_7\text{H}_{13}\text{N}]_2$

To a solution of cycloocta-1,5-diene (0.8 g, 7.4 mmol) in diethyl ether (15 cm³) was added dropwise with stirring a solution of the adduct $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$ (0.5 g, 1.4 mmol) in diethyl ether (10 cm³). After five minutes the green precipitate was filtered off and washed with diethyl ether (10 cm³). The product was recrystallised from dichloromethane and diethyl ether. Yield:- 50%.

3-E-3

Hydrolysis of Diolato Dioxo Bis-Amine Osmium(VI) $[\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_2]$

To a solution of K_2SO_3 (2.0 g, 13 mmol) in water (40 cm³) and ethanol (5 cm³) was added the complex $[\text{OsO}_2(\text{O}_2\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_2]$ (1.9 g, 3.6 mmol). The solution was refluxed for two hours and allowed to cool. The precipitated osmium sulphito complex was filtered off and the filtrate extracted with diethyl ether (5 x 40 cm³). The diethyl ether extract was dried over MgSO_4 and evaporated in vacuo to give cis-cycloocten-5,6-diol in 76% yield. The product was characterised by its mass spectrum ($M = 142$) and by ^1H n.m.r. (C^2HCl_3); δ 5.73 (2H) alkene, δ 4.04 (2H) protons adjacent to hydroxyl groups.

CHAPTER FOUR

REACTIONS OF OSMIUM TETRAOXIDE WITH ALKYNES

Abstract

The adducts $\text{OsO}_4 \cdot \text{L}$ react with alkynes R to give tetrolato dioxo amine osmium(VI) complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_4]$ (L = pyridine or isoquinoline) and $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_2]_n$ (L = quinuclidine). The structures of these complexes are discussed on the basis of their vibrational and ^1H n.m.r. spectra. Hydrolysis of some of the complexes has been carried out and the organic products isolated and identified. In addition, OsO_4 can be used catalytically in the presence of secondary oxidising agents such as potassium chlorate, ^{t} butylhydroperoxide or N-methylmorpholine-N-oxide for the cis-hydroxylation of alkynes to give the corresponding α -diketones or carboxylic acid derivatives.

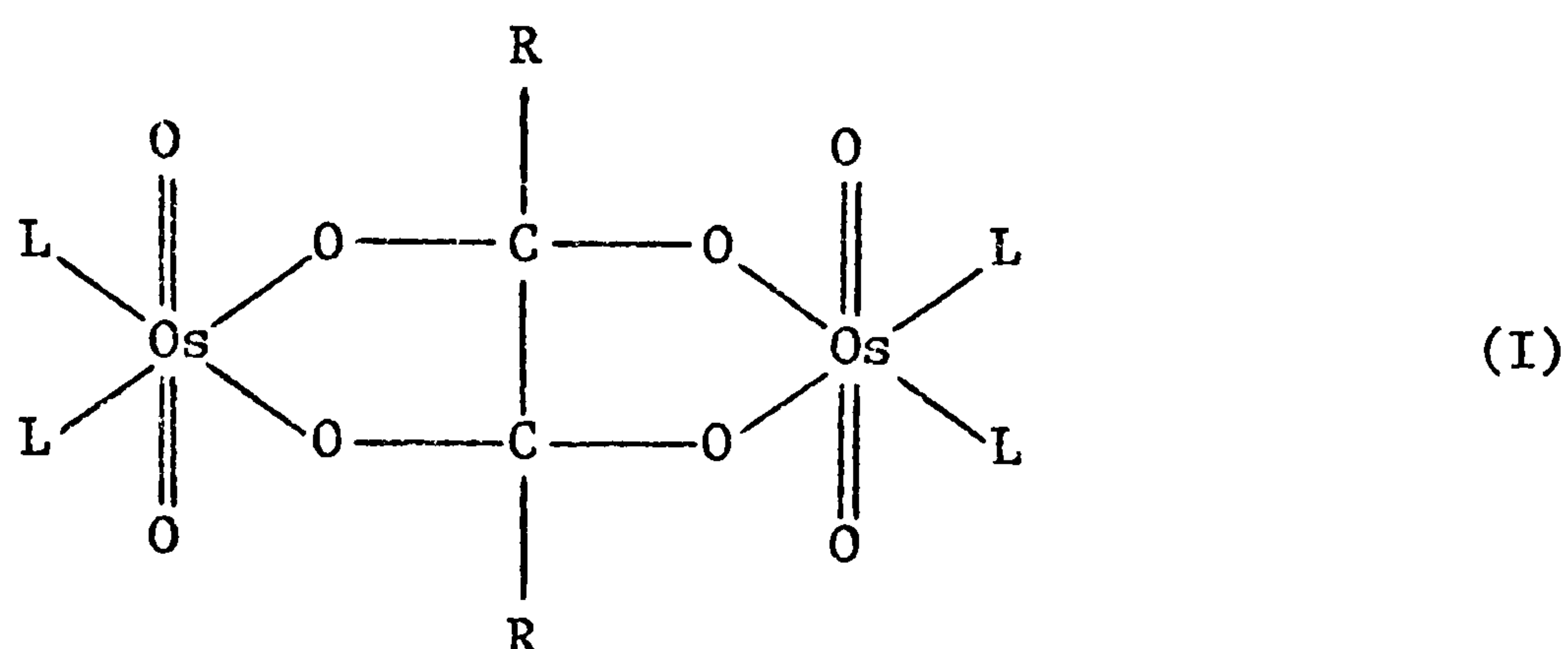
Section 4-A Introduction

Although the cis-hydroxylation of mono-alkenes using OsO_4 is well documented,⁴⁷⁻⁵⁰ very little work has been carried out on the interaction of OsO_4 with alkynes. The reduction of OsO_4 by acetylene gas has been used for the quantitative determination of osmium metal;¹⁶² however no osmium(VI) intermediates were isolated. More recent studies have shown that OsO_4 reacts with acetylene in the presence of excess of tertiary amines L to give products of stoichiometry $(\text{OsO}_4)_2 \cdot \text{L}_4 \cdot \text{C}_2\text{H}_2$ (L = pyridine,³² isoquinoline^{14,32}). This latter work has been extended and a series of tetrolato oxo amine osmium(VI) ester complexes have been isolated. These products can be readily hydrolysed by refluxing with aqueous sodium sulphite to give α -diketones or, in the case of terminal alkynes, the corresponding carboxylic acids. Work has also been carried out on the catalytic cis-hydroxylation of alkynes using OsO_4 in the presence of secondary oxidising agents such as potassium chlorate, ^tbutylhydroperoxide and N-methylmorpholine-N-oxide.

Section 4-B Reaction of the Adducts $\text{OsO}_4 \cdot \text{L}$ with Alkynes (L = pyridine or isoquinoline)

The adducts $\text{OsO}_4 \cdot \text{L}$ (L = pyridine or isoquinoline) were treated with a range of alkynes R (R = diphenylacetylene $\text{C}_{14}\text{H}_{10}$, phenylacetylene C_8H_6 , phenylmethylacetylene C_9H_8 or acetylene C_2H_2) in 2 : 1 adduct : alkyne reacting molar ratios to give brown, crystalline complexes of stoichiometry $(\text{OsO}_4)_2 \cdot \text{R} \cdot \text{L}_4$. Despite the low solubilities of the products in organic solvents, molecular weight measurements were able to be measured in dichloromethane and the results are in close agreement with the above formula weights. The complexes are diamagnetic, in the solid state and in solution, as expected for oxo-osmium(VI) complexes.¹⁰⁷

Structure (I) is proposed for the pyridine and isoquinoline complexes, as has been suggested for the complex $[\text{Os}_2\text{O}_4(\text{O}_2\text{C}_2\text{H}_2)(\text{C}_5\text{H}_5\text{N})_4]$.³² This structure, involving octahedral osmium(VI) with trans oxo ligands, is consistent with the observed stoichiometry and molecular weight measurements, and also by vibrational and ^1H n.m.r. spectroscopic studies (Table 4-1).



In addition to bands due to coordinated ligands, the infrared spectra of the solid complexes in the $800\text{--}950\text{ cm}^{-1}$ range show strong bands near 840 cm^{-1} and weaker bands near 300 cm^{-1} ; as for the bis-amine osmium(VI) ester complexes derived from alkenes and dienes (Chapter 2 and 3), these bands are assigned to asymmetric stretches, $\nu_{\text{OsO}_2}^{\text{as}}$, and deformations, δ_{OsO_2} , of the trans dioxo "osmyl" moiety respectively. Raman spectra of the solid complexes in the $800\text{--}1000\text{ cm}^{-1}$ range show strong bands near 880 cm^{-1} assigned to the symmetric stretch, $\nu_{\text{OsO}_2}^{\text{s}}$, again as found in "osmyl" complexes.¹³⁷ These latter bands are somewhat broader for the tetrolato amine esters than for the analogous monomeric diolato complexes (e.g., $[\text{OsO}_2(\text{O}_2\text{R})(\text{C}_5\text{H}_5\text{N})_2]$) presumably since, for structure (I), two $\nu_{\text{OsO}_2}^{\text{as}}$ and two $\nu_{\text{OsO}_2}^{\text{s}}$ modes are predicted but are likely to be close in frequency. Infrared bands near 950 cm^{-1} and 650 cm^{-1} are tentatively assigned to being predominantly due to C-O and Os-O stretching vibrations respectively since they are present in the corresponding $[\text{OsO}_2(\text{O}_2\text{R})(\text{C}_5\text{H}_5\text{N})_2]$ complexes but are not observed for the parent

Table 4-1

Spectroscopic ^a and Molecular Weight Data for Oxo Amine Osmium(VI) Ester Complexes Prepared from Alkynes

	Alkyne	ν_{OsO_2} ^b	δ_{OsO_2}	$\nu_{\text{C-O}}$	$\nu_{\text{Os-O}}$	¹ H n.m.r. ^c	M.W. ^d
<u>Pyridine Ester Complexes</u> ^e	acetylene	838, 830s <u>883m</u>	292, 282w	1004m	590m	6.02 (2H)	-
	diphenylacetylene	835, 825s <u>881m</u>	307w	985s	-	-	977 (1003)
	phenylacetylene	838, 833s <u>880m</u>	299, 282w	990m	565m	6.22 (1H)	905 (927)
	methylphenylacetylene	829s <u>880m</u>	303w	965m	582m	-	-
	acetylene	834, 823s <u>882m</u>	325w	995m	585m	6.18 (2H)	1082 (1051)
<u>Isoquinoline Ester Complexes</u> ^f	diphenylacetylene	830, 817s	310w	985m	-	-	-
	methylphenylacetylene	832, 820s <u>878m</u>	306, 300w	970m	-	-	-
	Os ₂ O ₄ (O ₄ C ₂ H ₂)(C ₉ H ₇ N) ₄						

^a Measured as solids.

^b ^{as} ν_{OsO_2} i.r. active; measured as Nujol mulls. ^s ν_{OsO_2} Raman active; measured as KBr discs. Raman modes underlined.

^c δ values for protons adjacent to donor oxygen atoms (ppm relative to TMS; measured in C²HCl₃).

^d Molecular weights osmotrically in dichloromethane (calculated values in parentheses).

^e prepared from the adduct OsO₄.C₃H₅N. ^f Prepared from the adduct OsO₄.C₉H₇N.

alkynes or amines. The infrared spectrum of $[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_2\text{H}_2)(\text{C}_5\text{H}_5\text{N})_4]$ shows a band at 2820 cm^{-1} as expected for $\nu_{\text{C-H}}$ in alkanes, while ^1H n.m.r. of the complex in C^2HCl_3 shows a resonance due to protons adjacent to the donor oxygen atoms at $\delta\ 6.02$ (2H), supporting the proposed structure. Integration of the ^1H n.m.r. spectra of the protons adjacent to the donor oxygen atoms against the amine protons confirms the stoichiometries of the products.

A preliminary X-ray study on crystals of $[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_{14}\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_4]$ indicate that they are triclinic.¹³⁸

Section 4-C Reaction of the Adduct $\text{OsO}_4\cdot\text{L}$ with Alkynes ($\text{L} = \text{quinuclidine}$)

In an attempt to prepare the corresponding tetrolato five-coordinate complexes, the adduct $\text{OsO}_4\cdot\text{C}_7\text{H}_{13}\text{N}$ ($\text{C}_7\text{H}_{13}\text{N} = \text{quinuclidine}$) was treated with alkynes R in a 2 : 1 OsO_4 : alkyne reacting molar ratio to give green, diamagnetic, products of stoichiometry $(\text{OsO}_4)_2\cdot\text{R}\cdot(\text{C}_7\text{H}_{13}\text{N})_2\cdot\text{S}$ (R = acetylene C_2H_2 , S = benzene, toluene or carbon tetrachloride) and $(\text{OsO}_4)_2\cdot\text{R}\cdot(\text{C}_7\text{H}_{13}\text{N})_2$ (R = phenylacetylene C_8H_6).

Infrared spectra of the solid complexes show strong bands near 900 cm^{-1} and weaker ones near 300 cm^{-1} assigned, as previously for the quinuclidine complexes derived from alkenes and dienes (Sections 2-C and 3-C), to $\nu_{\text{OsO}_2}^{\text{as}}$ and δ_{OsO_2} . The Raman spectra of the solid complexes show bands near 890 cm^{-1} assigned to $\nu_{\text{OsO}_2}^{\text{s}}$.

The ^1H n.m.r. spectra of the complexes show no resonances due to alkynyl protons but do show protons adjacent to the donor oxygen atoms near $\delta\ 5.3$ (2H) for the products derived from acetylene, as well as resonances due to molecules of solvation.

The vibrational spectra of these complexes are analogous to those described for the quinuclidine complexes derived from alkenes (Section 2-C) and dienes (Section 3-C); the complexes are therefore formulated as

Table 4-2

Spectroscopic^a and Molecular Weight Data for Oxo Amine Osmium(VI) Ester Complexes from Alkynes

	Alkyne	$\nu_{\text{OsO}_2}^b$	δ_{OsO_2}	$\nu_{\text{C-O}}$	$\nu_{\text{Os-O}}$	$^1\text{H n.m.r.}^c$	M.W. ^d
<u>Quinuclidine Ester Complexes^e</u>							
	$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_2\text{H}_2)(\text{C}_7\text{H}_{13}\text{N})_2]_n \text{ nC}_6\text{H}_6$	910s <u>899m</u>	279w	952m	555m	5.31 (2H)	385
	$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_2\text{H}_2)(\text{C}_7\text{H}_{13}\text{N})_2]_n \text{ nC}_7\text{H}_9$	910s <u>899m</u>	280w	952m	560m	5.26 (2H)	
	$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_2\text{H}_2)(\text{C}_7\text{H}_{13}\text{N})_2]_n \text{ nCCl}_4$	908s	277w	952m	540m	-	
	$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_6\text{H}_6)(\text{C}_7\text{H}_{13}\text{N})_2]_n$	872s	310w	978m	555m	-	

^a Measured as solids.

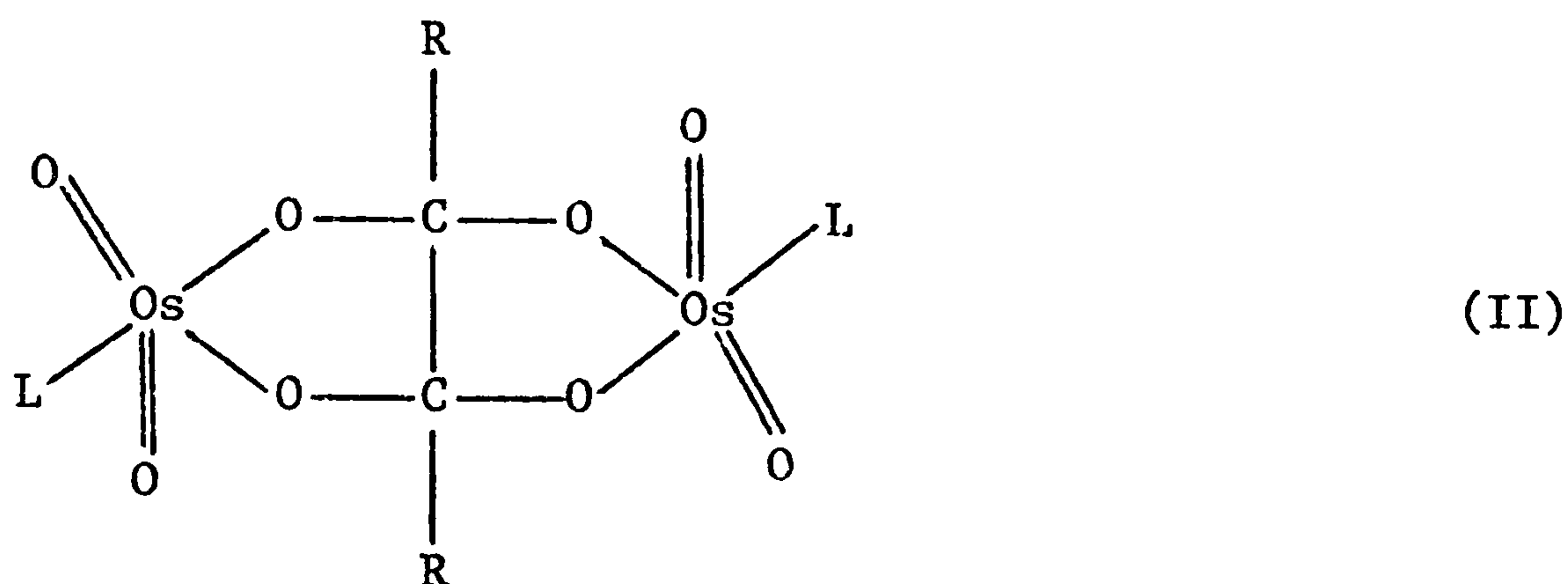
^b $\nu_{\text{OsO}_2}^{\text{as}}$ i.r. active; measured as Nujol mulls. $\nu_{\text{OsO}_2}^{\text{s}}$ Raman active; measured as KBr discs. Raman modes underlined.

^c δ values for protons adjacent to donor oxygen atoms and protons due to solvent of crystallisation (ppm relative to TMS measured in C^2HCl_3).

^d Molecular weight measurements in DMSO.

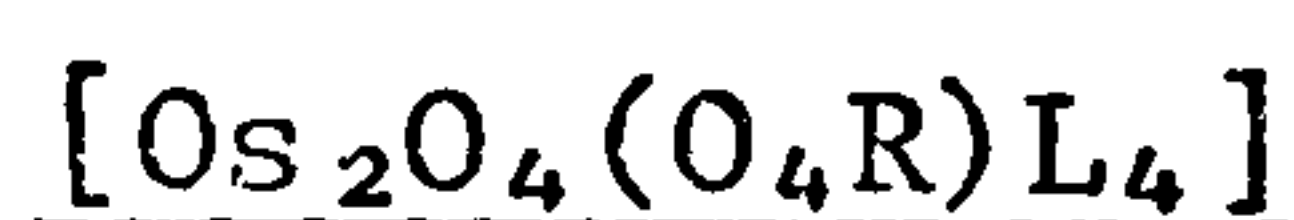
^e Prepared from the adduct $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$.

tetrolato dioxo osmium(VI) species in solution, involving a trigonal bipyramidal configuration (II).



In the solid state, the complexes are probably polymeric with weak asymmetric oxo bridges as described in Section 2-D.

Section 4-D Hydrolysis of Oxo Amine Osmium(VI) Ester Complexes



Since hydrolysis of the osmium(VI) ester complexes formed by reaction of OsO_4 with mono-alkenes is known to give good yields of the corresponding cis-diols,^{14,27} it is of interest to investigate the hydrolysis of the corresponding ester complexes $[Os_2O_4(O_4R)L_4]$ obtained from alkynes. The only hitherto reported hydroxylation of alkynes using OsO_4 appears in the patent literature,¹⁶³ but no osmium containing intermediates were isolated, the hydroxylation being carried out catalytically in the presence of hydrogen peroxide.¹⁶³

The hydrolyses were carried out using the procedure adopted by Criegee¹⁴ for the hydrolysis of mono-alkene esters, modified by using sodium sulphite solution neutralised to prevent possible rearrangement of the expected diketo product.¹⁶⁴ Thus hydrolysis of $[Os_2O_4(O_4C_{14}H_{10})(C_5H_5N)_4]$ gave benzil and benzoic acid, while hydrolysis of $[Os_2O_4(O_4C_8H_6)(C_5H_5N)_4]$ gave benzoic acid, with very little phenyl glyoxal being detected. Hydrolysis of $[Os_2O_4(O_4C_9H_8)(C_5H_5N)_4]$ yielded 1-phenylpropan-1,2-dione (Table 4-3).

Table 4-3

Hydrolysis of Tetralato Oxo Osmium(VI) Ester Complexes

<u>Alkyne</u>	<u>Oxo Osmium(VI) Ester</u>	<u>Hydrolysis Product</u>	<u>Yield</u>
Diphenylacetylene	$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_{14}\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_4]$	Benzil	65%
		Benzoic Acid	19%
Phenylacetylene	$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_8\text{H}_6)(\text{C}_5\text{H}_5\text{N})_4]$	Benzoic Acid	57%
Methylphenyl- acetylene	$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_9\text{H}_8)(\text{C}_5\text{H}_5\text{N})_4]$	1-phenylpropan-1,2- -dione	54%

Benzil and benzoic acid respectively are obtained from the oxidations of diphenylacetylene and phenylacetylene using ruthenium tetraoxide (RuO_4),¹⁶⁵ or potassium permanganate (KMnO_4),¹⁶⁶ no α -diketones being produced by oxidation of terminal alkynes.

Section 4-E Catalytic Oxidation of Alkynes by OsO_4

The catalytic cis-hydroxylation of alkenes by OsO_4 in the presence of excess of hydrogen peroxide,¹²⁰⁻¹²² N-methylmorpholine-N-oxide,¹⁶⁷ *t*-butylhydroperoxide^{168,169} or chlorate ion^{117,170,171} has been reported. However little work has been carried out on the catalytic oxidation of alkynes by OsO_4 , OsO_4 having been used catalytically in the presence of hydrogen peroxide for the oxidation of alkynes to give the corresponding keto aldehydes and hydroxy acids.¹⁶³

Work was therefore carried out on the catalytic oxidation of alkynes by OsO_4 in the presence of excess of N-methylmorpholine-N-oxide, *t*-butylhydroperoxide or potassium chlorate and the results are listed in Table 4-4.

Table 4-4

Catalytic Oxidation of Alkynes by OsO₄

Alkyne	Product	Method	Reaction Time (hours)	Yield ^a
Diphenylacetylene	Benzil	A	24	79%
		B	24	78%
		C	24	74%
Methylphenylacetylene	1-Phenylpropan-1,2-dione	A	4	59%
Phenylacetylene	Benzoic acid	B	4	62%
		A	48	72%
		B	48	82%
		C	48	71%

Method A = potassium chlorate as secondary oxidant

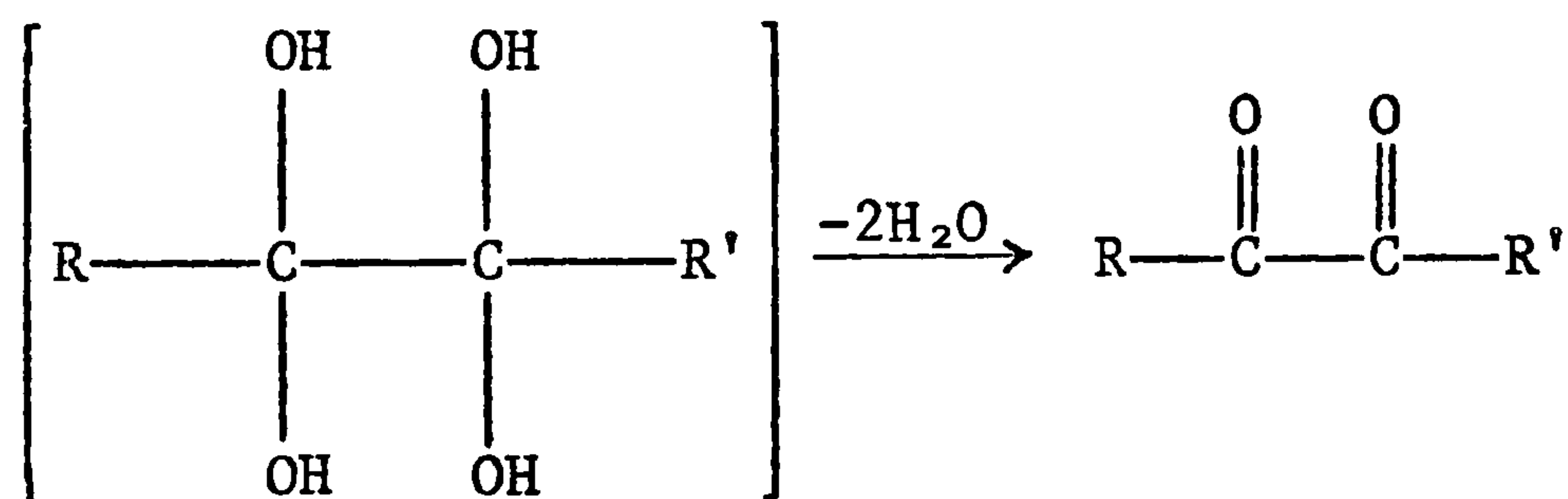
Method B = ^tbutylhydroperoxide as secondary oxidant

Method C = N-methylmorpholine-N-oxide as secondary oxidant

^a Yield of isolated, pure product.

The oxidations were carried out in air, in an acetone/^tbutanol/water solvent system at an elevated temperature (56° C), alkynes being generally more resistant to oxidation than alkenes.¹⁶⁶ As for the hydrolysis of tetrolato osmium(VI) ester complexes derived from alkynes and the oxidation of alkynes by RuO₄,¹⁶⁵ and KMnO₄,¹⁶⁶ the catalytic oxidations of alkynes by OsO₄ yielded α-diones from non-terminal alkynes and carboxylic acids from terminal alkynes. The 3 secondary oxidants were found to be equally effective for regenerating OsO₄ in situ, the yields of products being similar for all 3 reagents. However practically, N-methylmorpholine-N-oxide presented more work-up problems and the use of potassium chlorate or ^tbutylhydroperoxide is therefore preferred.

The formation of α-diones from alkynes presumably occurs via cleavage of the osmium(VI) ester complex to give the intermediate (III) which rapidly re-arranges with loss of water to give the corresponding α-dione.



(III)

For the oxidation of terminal alkynes, carbon-carbon bond cleavage evidently occurs in preference to the loss of two water molecules.

Section 4-F Experimental

All manipulations involving osmium tetroxide were carried out in a fume cupboard.

4-F-1 Tetrolato Dioxo Bis-Amine Osmium(VI) from Alkynes



Elemental analyses are listed in Table 4-5.

Pyridine Complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})(\text{C}_5\text{H}_5\text{N})_4]$ The preparations of these complexes followed similar procedures; the preparation of $[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_{14}\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_4]$ is typical.

To a solution of the adduct $\text{OsO}_4 \cdot \text{C}_5\text{H}_5\text{N}$ (0.5 g, 1.5 mmol) in diethyl ether (10 cm³) was added dropwise with stirring a solution of diphenylacetylene (0.13 g, 0.7 mmol) in diethyl ether (10 cm³). After five minutes the brown product was filtered off, copiously washed with diethyl ether (20 cm³) and dried in vacuo. Yield:- 45%.

An alternative method of preparation was carried out by treating OsO_4 (0.5 g, 2.0 mmol) dissolved in diethyl ether (10 cm³) containing pyridine (0.4 g, 5.1 mmol), with diphenylacetylene (0.18 g, 1.0 mmol) in diethyl ether (10 cm³). After five minutes, the brown product was filtered off, copiously washed with diethyl ether (20 cm³) and dried in vacuo. Yield:- 80%.

Isoquinoline Complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})(\text{C}_9\text{H}_7\text{N})_4]$ The preparation of these complexes followed similar procedures; the preparation of $[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_9\text{H}_8)(\text{C}_9\text{H}_7\text{N})_4]$ is typical.

To a solution of the adduct $\text{OsO}_4 \cdot \text{C}_9\text{H}_7\text{N}$ (0.5 g, 1.3 mmol) in diethyl ether (10 cm³) was added dropwise with stirring methylphenylacetylene (0.07 g, 0.6 mmol) in diethyl ether (10 cm³). After five minutes, the brown product was filtered off, copiously washed with diethyl ether (20 cm³)

Table 4-5

Elemental Analyses for Pyridine and Isoquinoline Osmium(VI) Ester Complexes from Alkynes

	% Found			% Required		
	C	H	N	C	H	N
<u>Pyridine Ester Complexes</u>						
$\text{Os}_2\text{O}_4(\text{O}_4\text{C}_2\text{H}_2)(\text{C}_5\text{H}_5\text{N})_4$	31.65	2.84	6.33	31.06	2.61	6.59
$\text{Os}_2\text{O}_4(\text{O}_4\text{C}_{14}\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_4$	40.69	3.11	5.56	40.72	3.01	5.59
$\text{Os}_2\text{O}_4(\text{O}_4\text{C}_8\text{H}_6)(\text{C}_5\text{H}_5\text{N})_4$	36.48	3.07	5.99	36.28	2.83	6.04
$\text{Os}_2\text{O}_4(\text{O}_4\text{C}_9\text{H}_8)(\text{C}_5\text{H}_5\text{N})_4$	37.32	3.02	5.77	37.02	3.00	5.95
<u>Isoquinoline Ester Complexes</u>						
$\text{Os}_2\text{O}_4(\text{O}_4\text{C}_2\text{H}_2)(\text{C}_9\text{H}_7\text{N})_4$	43.16	2.89	5.17	43.42	2.87	5.33
$\text{Os}_2\text{O}_4(\text{O}_4\text{C}_9\text{H}_8)(\text{C}_9\text{H}_7\text{N})_4$	47.06	3.07	4.91	47.36	3.18	4.91
$\text{Os}_2\text{O}_4(\text{O}_4\text{C}_{14}\text{H}_{10})(\text{C}_9\text{H}_7\text{N})_4$	49.57	3.13	4.61	49.91	3.18	4.66

and dried in vacuo. Yield:- 40%.

An alternative method of preparation was carried out by treating OsO_4 (0.5 g, 2.0 mmol) dissolved in diethyl ether (10 cm^3) containing isoquinoline (0.6 g, 4.7 mmol) with methylphenylacetylene (0.12 g, 1.0 mmol) in diethyl ether (10 cm^3). After five minutes, the brown product was filtered off, copiously washed with diethyl ether (20 cm^3) and dried in vacuo. Yield:- 70%.

4-F-2 Tetrolato Dioxo Amine Osmium(VI) from Alkynes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_2]_n$
(L = quinuclidine)

Elemental analyses are listed in Table 4-6.

Quinuclidine Complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})(\text{C}_7\text{H}_{13}\text{N})_2]_n$ The preparation of these complexes followed similar procedures; the preparation of $[\text{OsO}_4(\text{O}_4\text{C}_8\text{H}_6)(\text{C}_7\text{H}_{13}\text{N})_2]_n$ is typical.

To a solution of the adduct $\text{OsO}_4 \cdot \text{C}_7\text{H}_{13}\text{N}$ (0.5 g, 1.4 mmol) in diethyl ether (10 cm^3) was added dropwise with stirring phenylacetylene (0.07 g, 0.7 mmol) in diethyl ether (10 cm^3). The reaction mixture was cooled to 0°C and the dark green product filtered off, washed with diethyl ether (10 cm^3) and dried in vacuo. Yield:- 40%.

4-F-3 Hydrolysis of Oxo Amine Osmium(VI) Ester Complexes $[\text{Os}_2\text{O}_4(\text{O}_4\text{R})\text{L}_4]$

Hydrolysis of $[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_{14}\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_4]$ To a solution of Na_2SO_3 (1.0 g, 7.9 mmol) in water (50 cm^3), acidified with HCl to pH 7.3, was added ethanol (5 cm^3) and the complex $[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_{14}\text{H}_{10})(\text{C}_5\text{H}_5\text{N})_4]$ (0.6 g, 0.6 mmol). The solution was refluxed for 3 hours and then allowed to cool. The precipitated osmium sulphito complex was filtered off and the filtrate extracted with diethyl ether ($3 \times 30 \text{ cm}^3$). The ethereal extract was dried over MgSO_4 and evaporated in vacuo. Purification of the crude product by preparative thin layer chromatography (silica, chloroform) yielded benzil, PhCOCOPh , in 65% yield. M.P. 95°C (Lit.¹⁴¹ 95°C); the product was characterised by its mass spectrum ($M = 210$) and infrared spectrum.

Table 4-6

Elemental Analyses for Quinuclidine Osmium(VI) Ester Complexes from Alkynes

	% Found			% Required		
	C	H	N	C	H	N
<u>Quinuclidine Ester Complexes</u>						
$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_2\text{H}_2)(\text{C}_7\text{H}_{13}\text{N})_2]_n\text{C}_6\text{H}_6^a$	31.24	4.20	3.27	31.65	4.11	3.36
$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_2\text{H}_2)(\text{C}_7\text{H}_{13}\text{N})_2]_n\text{C}_7\text{H}_9$	32.51	4.15	3.17	32.54	4.27	3.30
$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_2\text{H}_2)(\text{C}_7\text{H}_{13}\text{N})_2]_n\text{CCl}_4$	22.13	3.16	3.14	22.42	3.09	3.07
$[\text{Os}_2\text{O}_4(\text{O}_4\text{C}_6\text{H}_6)(\text{C}_7\text{H}_{13}\text{N})_2]_n$	32.42	3.81	3.15	31.73	3.87	3.36

a O analysis; Found 15.46%, Required 15.33%.

b Cl analysis; Found 17.49%, Required 15.57%.

The aqueous layer was acidified with HCl to pH 2 and extracted with diethyl ether (3 x 30 cm³). The ethereal extract was dried over MgSO₄ and evaporated in vacuo. Purification of the crude product by preparative thin layer chromatography (silica, benzene : methanol : acetic acid 60 : 8 : 4) yield benzoic acid, PhCOOH, in 19% yield. M.P. 120° C (Lit.¹⁴¹ 122° C); the product was characterised by its mass spectrum (M = 122) and infrared spectrum.

Hydrolysis of [Os₂O₄(O₄C₈H₆)(C₅H₅N)₄]

The hydrolysis of

[Os₂O₄(O₄C₈H₆)(C₅H₅N)₄] followed the same procedure as above. No product was obtained by extraction of the alkaline aqueous solution with diethyl ether. On extraction of the acidified aqueous solution with diethyl ether however, benzoic acid, PhCOOH, was obtained in 57% yield. M.P. 117° C (Lit.¹⁴¹ 122° C). The product was characterised by its mass spectrum (M = 122) and infrared spectrum.

Hydrolysis of [Os₂O₄(O₄C₉H₈)(C₅H₅N)₄]

The hydrolysis of

[Os₂O₄(O₄C₉H₈)(C₅H₅N)₄] followed the same procedure as above. The alkaline reaction mixture was extracted with diethyl ether (3 x 30 cm³) and the ethereal layer was dried over MgSO₄ and evaporated in vacuo. The crude product was purified by preparative thin layer chromatography (silica, benzene) to give 1-phenylpropan-1,2-dione (PhCOCOMe) as a yellow oil in 54% yield. The product was characterised by its mass spectrum (M = 148), infrared spectrum and ¹H n.m.r. spectrum. δ 7.93-8.08 (2H), 7.59 (3H) phenyl protons; δ 2.51 (3H) methyl protons.

4-F-4 Catalytic Oxidation of Alkynes by OsO₄

The catalytic oxidations of alkynes by OsO₄ in the presence of potassium chlorate followed similar procedures. The oxidation of methylphenylacetylene is typical.

Methylphenylacetylene (0.85 g, 7.3 mmol) was dissolved in acetone (20 cm³) containing ^tbutanol (10 cm³), water (5 cm³) and OsO₄ (0.04 g,

0.16 mmol). The reaction mixture was treated with KClO_3 (1.8 g, 14.7 mmol), refluxed at 56°C for 4 hours and then treated with a solution of KHSO_3 (1.0 g, 8.3 mmol) in water (10 cm^3). The reaction mixture was acidified to pH 8 with hydroxide and extracted with diethyl ether ($3 \times 20\text{ cm}^3$). The ether extract was dried over MgO_4 and evaporated in vacuo. The crude product was purified by preparative thin layer chromatography (silica, benzene) to give 1-phenylpropan-1,2-dione (0.64 g, 59%). ^1H n.m.r. spectrum:- δ 7.93-8.08 (2H), 7.59 (3H) phenyl protons; δ 2.51 (3H) methyl protons. $M = 148$.

The catalytic oxidations of alkynes by OsO_4 in the presence of t -butylhydroperoxide followed similar procedures. The oxidation of phenylacetylene is typical.

Phenylacetylene (0.95 g, 9.3 mmol) was dissolved in acetone (20 cm^3) containing t -butanol (10 cm^3), water (5 cm^3) and OsO_4 (0.04 g, 0.16 mmol). The reaction mixture was treated with t -butylhydroperoxide (2.5 g, 27.8 mmol), refluxed at 56°C for 48 hours and then treated with a solution of KHSO_3 (1 g, 8.3 mmol) in water (10 cm^3). The reaction mixture was treated with KOH to pH 8 and washed with diethyl ether ($2 \times 20\text{ cm}^3$). The aqueous solution was acidified to pH 2 with sulphuric acid and extracted with diethyl ether ($3 \times 25\text{ cm}^3$). The ether extract was dried over MgSO_4 and evaporated in vacuo. The crude product was purified by preparative thin layer chromatography (silica, benzene : methanol : acetic acid, 60 : 8 : 4) or by recrystallisation from water to give benzoic acid (0.93 g, 82%). M.P. 122°C (Lit. ¹⁴¹ 122°C). $M = 122$.

The catalytic oxidations of alkynes by OsO_4 in the presence of N -methylmorpholine- N -oxide followed similar procedures. The oxidation of diphenylacetylene is typical.

Diphenylacetylene (0.925 g, 5.2 mmol) was dissolved in acetone (20 cm³) containing ^tbutanol (10 cm³), water (5 cm³) and OsO₄ (0.04 g, 0.16 mmol). The reaction mixture was treated with N-methylmorpholine-N-oxide.2H₂O (3.0 g, 22.2 mmol), refluxed at 56° C for 20 hours and then treated with a solution of KHSO₃ (1 g, 8.3 mmol) in water (10 cm³). The reaction mixture was treated with KOH to pH 8 and extracted with diethyl ether (3 x 25 cm³). The ether extract was dried over MgSO₄ and evaporated in vacuo. The crude product was purified by preparative thin layer chromatography (silica, diethyl ether or benzene) to give benzil (0.81 g, 74%). M.P. 95° C (Lit. ¹⁴¹ 95° C).

CHAPTER FIVE

REACTIONS OF OXO COMPLEXES OF RUTHENIUM WITH ORGANIC SUBSTRATES

Abstract

The ruthenate ion $[\text{RuO}_4]^{2-}$ can be used catalytically in the presence of excess of potassium persulphate, $(\text{K}_2\text{S}_2\text{O}_8)$, for the oxidation of organic substrates under mild conditions; alcohols and aldehydes are catalytically oxidised to the corresponding ketones and carboxylic acids, while benzylamine is oxidised to benzonitrile. $[\text{RuO}_4]^{2-}$ does not oxidise tertiary alcohols, alkenes or alkynes under normal conditions and can therefore be used for the catalytic oxidation of unsaturated alcohols and aldehydes to give the corresponding unsaturated carboxylic acids. The preparations of the ruthenate salts $\text{K}.\text{Ph}_4\text{M}.[\text{RuO}_4]$ ($\text{M} = \text{As}$ or P) are described.

Ruthenium tetroxide, (RuO_4) , reacts with alkenes R and alkynes R' to give black, intractable products of stoichiometry $\text{RuO}_4.\text{R}$ and $(\text{RuO}_4)_2.\text{R}'$ respectively. The reactions of RuO_4 with tertiary amines are also discussed. $\text{K}_2[\text{RuO}_4]$ and RuO_4 react with HCl to give the ruthenium(VI) species $[\text{RuO}_2\text{Cl}_3]^-$ and $[\text{RuO}_2\text{Cl}_4]^{2-}$; reaction of $[\text{RuO}_2\text{Cl}_3]^-$ with catechol, $\text{C}_6\text{H}_4(\text{OH})_2$, yields the ruthenium(IV) complex $[\text{RuCl}_3(\text{O}_2\text{C}_6\text{H}_4)]_2^{2-}$.

Section 5-A Introduction

Whereas osmium tetroxide, (OsO_4), used stoichiometrically¹⁴ or catalytically,¹²⁰ acts as a 2-electron oxidising agent towards organic substrates, the isoelectronic ruthenium tetroxide, (RuO_4), is more often reduced to ruthenium(IV),^{74,172} thus acting as a 4-electron oxidant. These properties are reflected in the relative reactivities of these two oxidants towards organic substrates (Chapter 1). OsO_4 oxidises alkenes by a 2-electron process to give the corresponding cis-diols⁴⁷⁻⁵⁰ (Chapter 2), reaction of OsO_4 with alcohols proceeding relatively slowly.³² RuO_4 , however, oxidises both alcohols and alkenes to the corresponding carboxylic acids (Chapter 1),⁷⁶ the oxidation of alkenes to cis-diols by RuO_4 proceeding only in low yields and for alkenes of low reactivity.¹⁶⁸ Thus RuO_4 , used either stoichiometrically or catalytically in the presence of hypochlorite or periodate,¹⁶⁵ is only practically useful for oxidations requiring very high oxidising potentials e.g., oxidation of ethers to lactams.¹⁷³

The related ruthenium(VI) ion, $[\text{RuO}_4]^{2-}$, is a potential two electron oxidising agent of interest, but has not been hitherto employed catalytically, although ruthenates in alkaline solution are known to oxidise alcohols to ketones and acids, and benzylamine to benzaldehyde.^{88,89} Indeed by comparing the electrode potentials for $[\text{RuO}_4]^{2-}$ with those for OsO_4 and RuO_4 ,⁴ one would expect $[\text{RuO}_4]^{2-}$ to be a more powerful oxidant than OsO_4 but a milder oxidant than RuO_4 .

$$E^{\circ} (\text{RuO}_2/\text{RuO}_4) = -0.58 \text{ V}$$

$$E^{\circ} (\text{RuO}_2/[\text{RuO}_4]^{2-}) = -0.4 \text{ V}$$

$$E^{\circ} (\text{OsO}_2/\text{OsO}_4) = -0.2 \text{ V}$$

This chapter describes the work carried out on the catalytic use of

$[\text{RuO}_4]^{2-}$ in the presence of potassium persulphate, $(\text{K}_2\text{S}_2\text{O}_8)$, for the oxidation of organic substrates. The preparation of organic salts of $[\text{RuO}_4]^{2-}$ and the reactions of RuO_4 with alkenes, alkynes, and tertiary amines are also described. In addition, work has been carried out on the reactions of $[\text{RuO}_4]^{2-}$ and RuO_4 with HCl to give the ruthenium(VI) complexes $[\text{RuO}_2\text{Cl}_3]^-$ and $[\text{RuO}_2\text{Cl}_4]^{2-}$.

Section 5-B Catalytic Oxidations of Organic Substrates using Potassium Ruthenate, $\text{K}_2[\text{RuO}_4]$

Aqueous solutions of potassium ruthenate, $(\text{K}_2[\text{RuO}_4])$, can be prepared in several ways:-

- a) fusion of RuCl_3 with potassium nitrate, (KNO_3) , and potassium hydroxide, (KOH) ,⁶⁸
- b) reduction of RuO_4 with aqueous KOH solution,^{69,70}
- c) oxidation of RuO_2 by sodium peroxide,¹⁷⁴
- d) oxidation of RuCl_3 by alkaline persulphate.¹⁷⁵

The oxidation of RuCl_3 by alkaline persulphate was found to be the most convenient method of generating $[\text{RuO}_4]^{2-}$, the persulphate regenerating $[\text{RuO}_4]^{2-}$ if the latter is reduced by organic substrates.

Spectrophotometric measurements on such solutions show that all the ruthenium is present as $[\text{RuO}_4]^{2-}$, no $[\text{RuO}_4]^-$ or RuO_4 being detected.

Oxidants such as hypochlorite or periodate can not be used for the generation of $[\text{RuO}_4]^{2-}$ since the generation of RuO_4 can also occur with these oxidants.^{55,56,165}

Results obtained for the oxidation of organic substrates using catalytic solutions of $[\text{RuO}_4]^{2-}$ (typically 1.7×10^{-4} M in $[\text{RuO}_4]^{2-}$, 3×10^{-2} M in potassium persulphate and 2×10^{-1} M in potassium hydroxide for the oxidation of alcohols) are listed in Table 5-1. The oxidations

Table 5-1

Catalytic Oxidations of Organic Substrates by $[\text{RuO}_4]^{2-}$ in the
Presence of Alkaline Persulphate

<u>Substrate</u>	<u>Product</u>	<u>Reaction Time (hours)</u>	<u>Yield^a</u>
<u>1° Alcohols</u>			
benzyl alcohol	benzoic acid	1½	98%
4-nitrobenzyl alcohol	4-nitrobenzoic acid	1	97%
<u>2° Alcohols</u>			
benzhydrol	benzophenone	5	95%
<u>cyclohexanol</u>	<u>cyclohexanone</u>	2	64%
	adipic acid		7%
<u>cyclopentanol</u>	<u>cyclopentanone</u>	2	71%
1,2,3,4-tetrahydro-1-naphthol	α-tetralone	2	84%
benzoin	benzil ^b	5	26%
	benzoic acid		68%
<u>Aldehydes</u>			
4-nitrobenzaldehyde	4-nitrobenzoic acid	¾	98%
3-chlorobenzaldehyde	3-chlorobenzoic acid	2	99%
benzaldehyde	benzoic acid	1	98%
2-hydroxybenzaldehyde	2-hydroxybenzoic acid	5	71%
4-methoxybenzaldehyde	4-methoxybenzoic acid	2½	96%
<u>Unsaturated Alcohols</u>			
<u>trans-cinnamyl alcohol</u>	<u>trans-cinnamic acid</u>	3	97%
3- <u>cyclohexene</u> -1-methanol	3- <u>cyclohexene</u> -1-carboxylic acid	6	68%
allyl alcohol	acrylic acid	3½	45%
<u>Alkenes</u>			
<u>cyclohexene</u>	no reaction	6	-
<u>cyclohexene</u>	adipic acid	96	20%
<u>Alkynes</u>			
acetylene dicarboxylic acid	no reaction	5	-
<u>Amines</u>			
benzylamine	benzonitrile	24	66%
butylamine	butyric acid	24	34%
N-methylbenzylamine	benzaldehyde ^c	6	40%

Table 5-1 [continued]

<u>Substrate</u>	<u>Product</u>	<u>Reaction Time (hours)</u>	<u>Yield^a</u>
<u>Nitriles</u>			
benzonitrile	benzamide ^d	24	39%
<u>3^o Alcohols</u>			
^t butyl alcohol	no reaction	4	-
phenol	no reaction	4	-

^a Yields of isolated pure products.

^b Two phase reaction diethyl ether : water.

^c Yield of benzaldehyde determined by G.L.C. analysis.

^d Oxidation of benzonitrile by alkaline persulphate alone gave benzamide in 29% yield.

were carried out at room temperature in air, with a substrate : $[\text{RuO}_4]^{2-}$ molar ratio of approximately 45 : 1, reaction being complete within a few hours. Although persulphate is known to oxidise alcohols and aldehydes in the presence of silver(I) ion,^{176,177} alkaline persulphate alone does not oxidise the substrates listed in Table 5-1. It seems therefore that persulphate functions not only as a facile generator of $[\text{RuO}_4]^{2-}$, but also as a secondary oxidising agent for the catalytic oxidation of organic substrates.

5-B-1 Oxidation of Alcohols

$[\text{RuO}_4]^{2-}$ was found to catalytically oxidise primary and secondary alcohols to the corresponding carboxylic acids and ketones. The reaction between $[\text{RuO}_4]^{2-}$ and alcohols and aldehydes was found to be generally very fast and so reacting molar ratios of substrate versus $[\text{RuO}_4]^{2-}$ could be measured for oxidations using $[\text{RuO}_4]^{2-}$ stoichiometrically.

$\text{K}_2[\text{RuO}_4]$ was prepared by alkaline reduction of RuO_4 and the resulting solution titrated against a series organic substrates. Estimation of the $[\text{RuO}_4]^{2-}$ concentration in aqueous solution was carried out spectrophotometrically using the 460 nm band ($\epsilon = 1820$)¹⁷⁸ and the results are listed in Table 5-2.

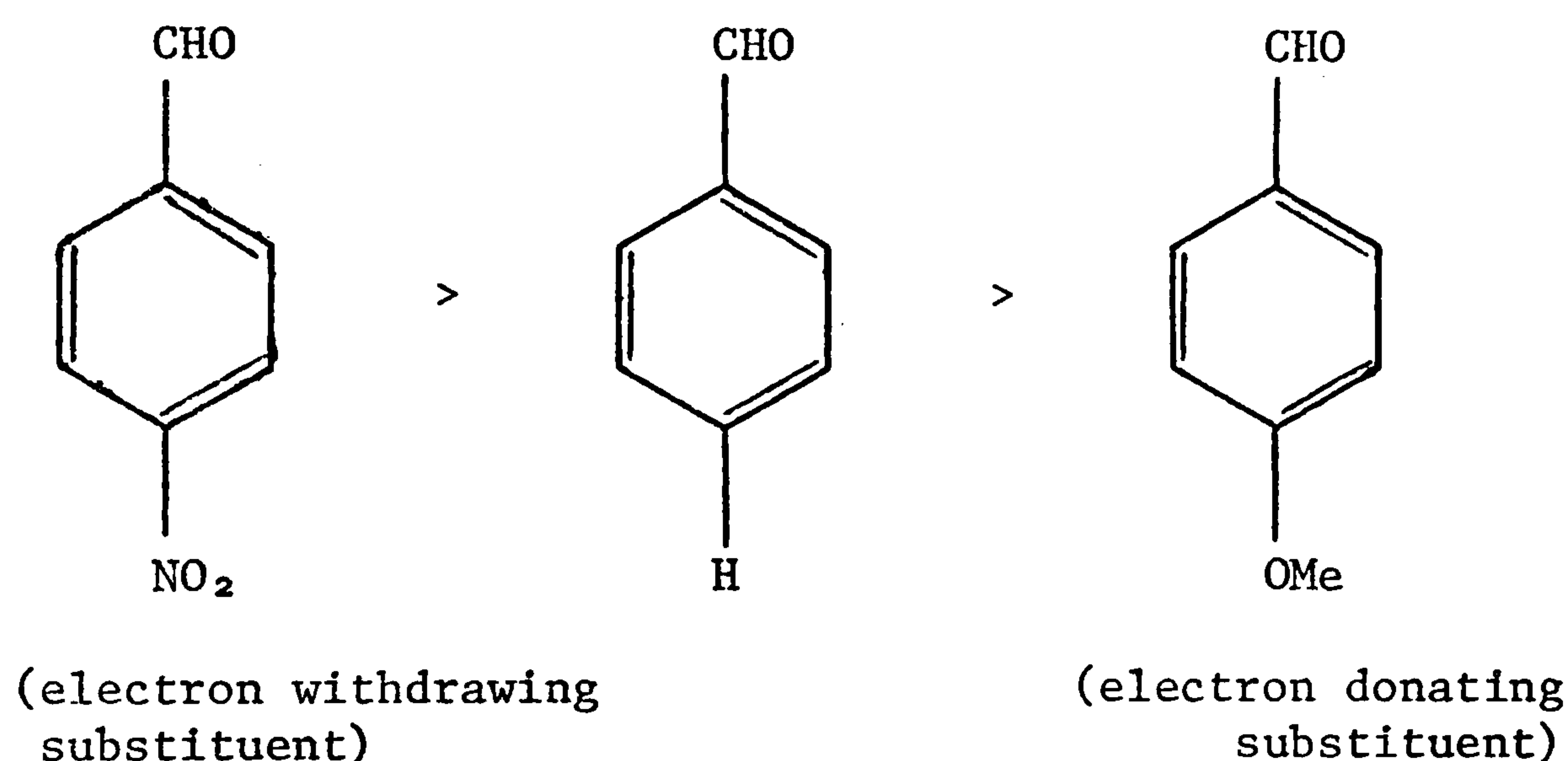
Table 5-2

$[\text{RuO}_4]^{2-}$: Substrate Reacting Molar Ratios for Oxidations
using $[\text{RuO}_4]^{2-}$ Stoichiometrically

<u>Substrate</u>	<u>$[\text{RuO}_4]^{2-}$: Substrate Reacting Molar Ratios</u>
acetaldehyde	1 : 1
benzaldehyde	1 : 1
ethanol	2 : 1
benzyl alcohol	2 : 1
allyl alcohol	2 : 1

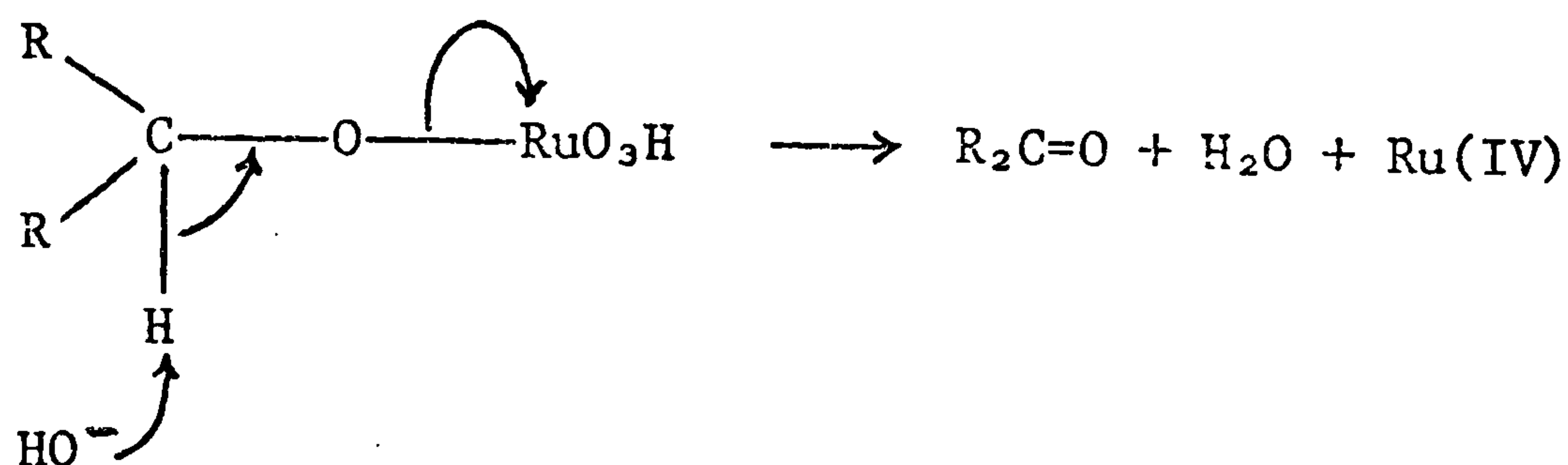
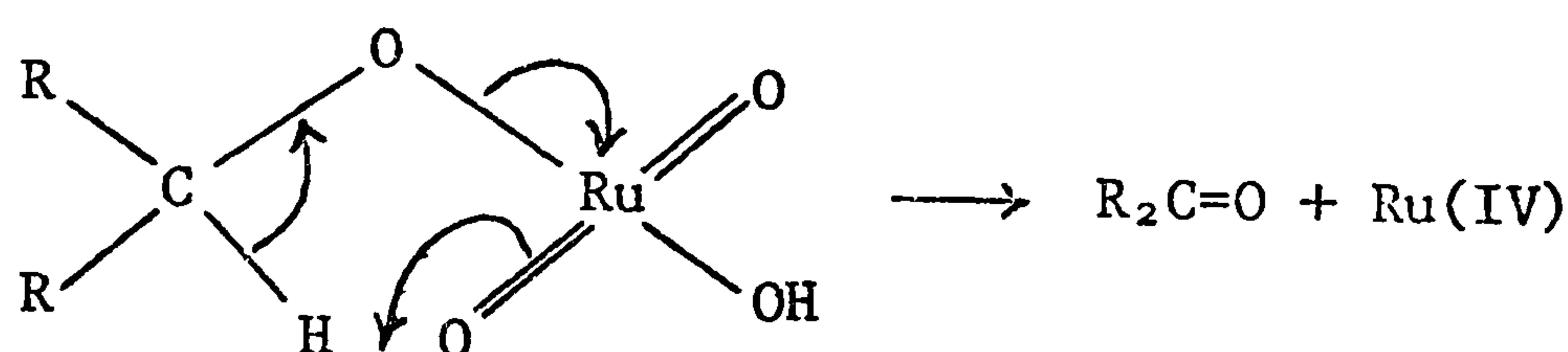
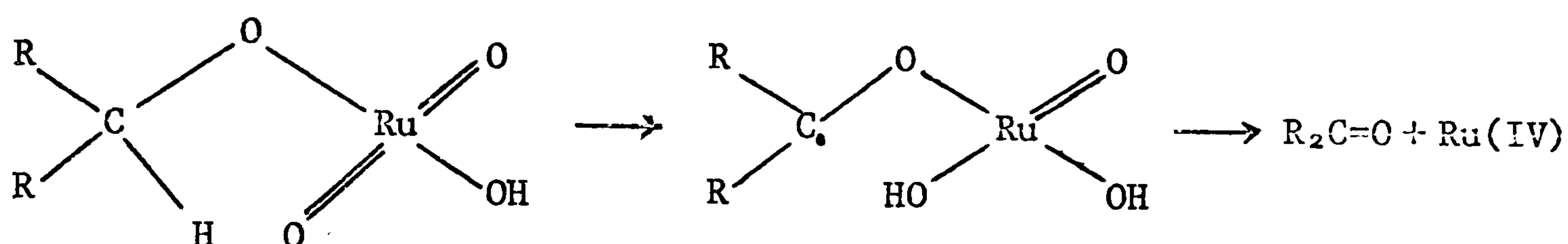
In general, $[\text{RuO}_4]^{2-}$ reacts with aldehydes in a 1 : 1 molar ratio and with alcohols in a 2 : 1 molar ratio, thus confirming that $[\text{RuO}_4]^{2-}$ is indeed acting as a 2-electron oxidant.

It is of interest to note that the rate of oxidation of substituted benzaldehydes by $[\text{RuO}_4]^{2-}$ varies according to the substituent present, the time for oxidation being linked to the electron withdrawing or donating capacity of the substituent. It was found that the time for oxidation of substituted benzaldehydes by $[\text{RuO}_4]^{2-}$ in the presence of persulphate decreased in the order:-



Similar rate effects have been noted for oxidations of substituted benzyl alcohols and benzaldehydes by CrO_3 ¹⁷⁹ and $[\text{FeO}_4]^{2-}$.¹⁰¹

Chromic acid, like $[\text{RuO}_4]^{2-}$, can act as a 2-electron oxidant^{180,181} and several reaction mechanisms have been proposed for the oxidation of alcohols by chromium(VI)^{180,181} which may be applicable to the oxidation of alcohols by $[\text{RuO}_4]^{2-}$. The oxidation of alcohols by Cr(VI) (or by Ru(VI)) may proceed either via proton transfer to a base (Scheme 1),^{182,183} or by unimolecular decomposition of the intermediate ester (Scheme 2)¹⁸⁴⁻¹⁸⁷ or by a radical process (Scheme 3).^{180,188}

Scheme 1Scheme 2Scheme 3

The relative strengths and weaknesses of these mechanisms have been thoroughly discussed elsewhere.^{180,181}

Unlike other 2-electron oxidants such as OsO_4 ,⁴⁷⁻⁵⁰ CrO_3 ,¹⁸⁰ $\text{Ag}^{(\text{II})}\text{O}$ ¹⁸⁹ and silver(II) picolinate,¹⁹⁰ $[\text{RuO}_4]^{2-}$ reacts with alkenes and alkynes only very slowly. Thus acetylene dicarboxylic acid, though very soluble in water, is unaffected by $[\text{RuO}_4]^{2-}$ over a period of several hours. Cyclo-hexene reacts with $[\text{RuO}_4]^{2-}$ only very slowly over a period of several days to give adipic acid in low yield. This property makes $[\text{RuO}_4]^{2-}$ highly effective for the catalytic oxidations of unsaturated alcohols to give the corresponding unsaturated carboxylic acids; thus in the presence of alkaline persulphate trans-cinnamyl alcohol is catalytically oxidised by

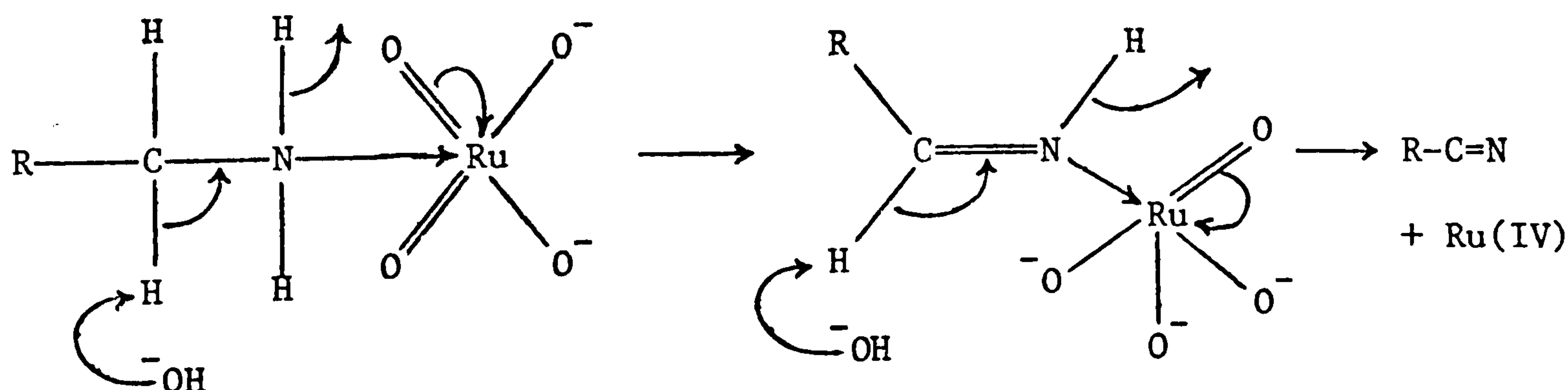
$[\text{RuO}_4]^{2-}$ to trans-cinnamic acid in high yield. Titration of allyl alcohol against $[\text{RuO}_4]^{2-}$ requires a $[\text{RuO}_4]^{2-}$: allyl alcohol reacting molar ratio of 2 : 1 (Table 5-2), the oxidation of allyl alcohol giving acrylic acid in fair yield (Table 5-1).

5-B-2 Oxidation of Amines

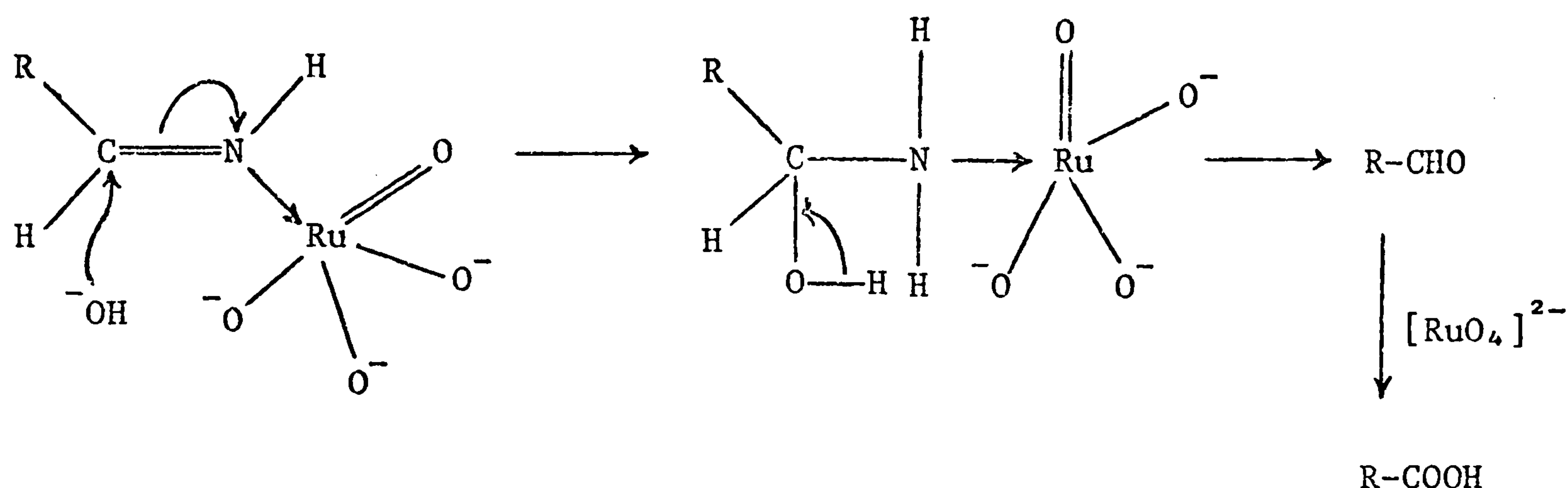
Benzylamine is catalytically oxidised by $[\text{RuO}_4]^{2-}$ in the presence of alkaline persulphate to give benzonitrile as the major product, together with benzaldehyde and benzoic acid. This reaction is complicated by the apparent complexation of the ruthenium(VI) species by benzylamine to give a dark green complex which is not re-oxidised by alkaline persulphate, the resulting poisoning of the catalyst lowering the yield of nitrile obtained. The poisoning of the $[\text{RuO}_4]^{2-}$ catalyst may be greatly diminished by carrying out the oxidation using a lower amine : $[\text{RuO}_4]^{2-}$ molar ratio of 10 : 1 and by very slow addition of the amine to the catalytic solution, thus preventing a large excess of amine building up.

It seems likely that the mechanism of amine oxidation by $[\text{RuO}_4]^{2-}$ proceeds either via base abstraction of the α -protons to give the corresponding nitrile (Scheme 4) or via hydroxyl attack of the imine intermediate to give carboxylic acid or aldehydic products (Scheme 5).

Scheme 4



Scheme 5



Similar mechanisms have been proposed for the oxidation of amines to nitriles and aldehydes by silver(II)picolinate under basic conditions.^{191,192}

In addition to benzonitrile and benzaldehyde, some imine complex $\text{PhCH}=\text{NCH}_2\text{Ph}$ was also obtained from the catalytic oxidation of benzylamine by $[\text{RuO}_4]^{2-}$. It seems likely that this product is formed by condensation of benzaldehyde with unreacted benzylamine; the reaction of $[\text{RuO}_4]^{2-}$ with $\text{PhCH}=\text{NCH}_2\text{Ph}$ was found to be very slow with appreciable hydrolysis of the imine by aqueous alkali taking place.

The catalytic oxidation of other primary amines by $[\text{RuO}_4]^{2-}$ gave lower yields of nitrile product than for the oxidation of benzylamine. This may reflect the greater ease of base abstraction of the α -protons of benzylamine as compared with other primary amines. Thus for the catalytic oxidation of butylamine, Scheme 5 predominates giving butyric acid as the main product with very little butyronitrile ($\sim 10\%$).

Secondary amines are slowly oxidised by $[\text{RuO}_4]^{2-}$ to give the corresponding aldehydes.

Section 5-C Preparation of Organic Salts of $[\text{RuO}_4]^{2-}$

The main problem with the catalytic oxidations described in Section 5-B is that $\text{K}_2[\text{RuO}_4]$ exists in solution in only highly alkaline, aqueous conditions. This restricts the oxidation of organic substrates by $[\text{RuO}_4]^{2-}$ to water soluble species not sensitive to alkali.

Sodium and potassium ruthenate are highly water soluble species and can only be isolated in the solid state by evaporation of aqueous, alkaline solutions; as a result the products obtained are always contaminated with solid hydroxides. Barium ruthenate, $\text{Ba}[\text{RuO}_4]$, can be precipitated by addition of BaCl_2 to a solution of $[\text{RuO}_4]^{2-}$. However, this complex is virtually insoluble in water and organic solvents and therefore can not be used for organic oxidations. A recent X-ray structure determination has shown barium ruthenate to be a five coordinate species $\text{Ba}[\text{RuO}_3(\text{OH})_2]$ with three oxo ligands occupying equatorial positions.⁷¹ The infrared spectrum of barium ruthenate (Figure 5-1) supports this structure, bands assigned to the metal oxygen vibrations, $\nu_{\text{RuO}_2}^{\text{as}}$, and deformations, δ_{RuO_2} , occurring near 820 cm^{-1} and 330 cm^{-1} respectively and bands assigned to the hydroxyl stretching vibrations and deformations, $\nu_{\text{O-H}}$ and $\delta_{\text{O-H}}$, occurring near 3570 cm^{-1} and 920 cm^{-1} respectively.

In an attempt to prepare organic soluble salts of $[\text{RuO}_4]^{2-}$, $\text{K}_2[\text{RuO}_4]$ was treated with $\text{Ph}_4\text{MC}\ell$ ($\text{M} = \text{P}$ or As) and a series of quaternary ammonium salts.

$\text{K}_2[\text{RuO}_4]$, prepared by alkaline reduction of RuO_4 , was treated with a solution of $\text{Ph}_4\text{MC}\ell$ ($\text{M} = \text{P}$ or As). Dark green products were isolated, the infrared spectra of which showed bands near 820 cm^{-1} and 300 cm^{-1} assigned to the asymmetric stretching vibration, $\nu_{\text{RuO}_2}^{\text{as}}$, and to the deformation, δ_{RuO_2} , of the trans $\text{O}=\text{Ru}=\text{O}$ "ruthenyl" moiety respectively (Figure 5-2). Elemental analyses for these products are consistent with

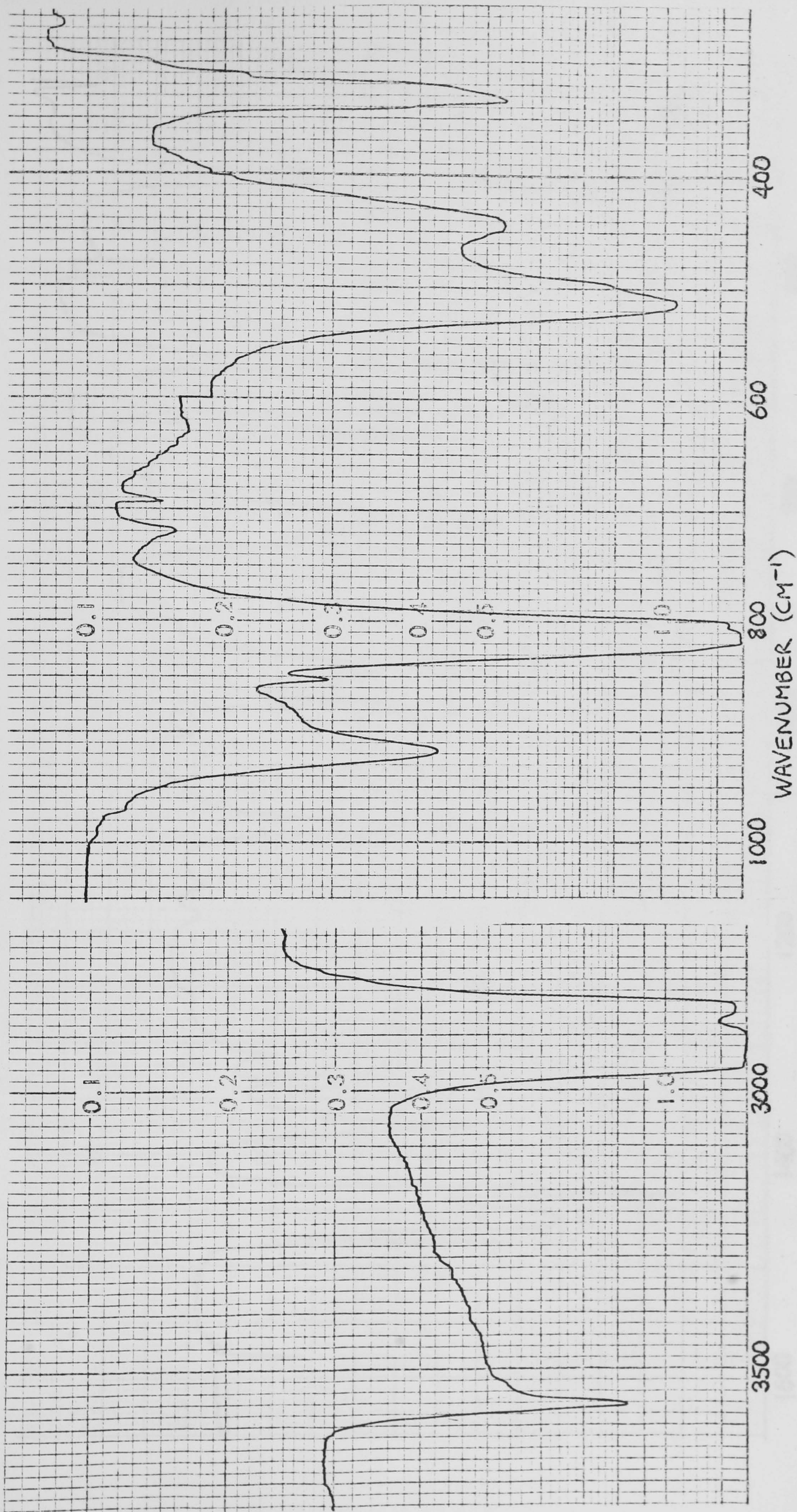


Figure 5-1. Infrared Spectrum of $\text{Ba}[\text{RuO}_3(\text{OH})_2]$

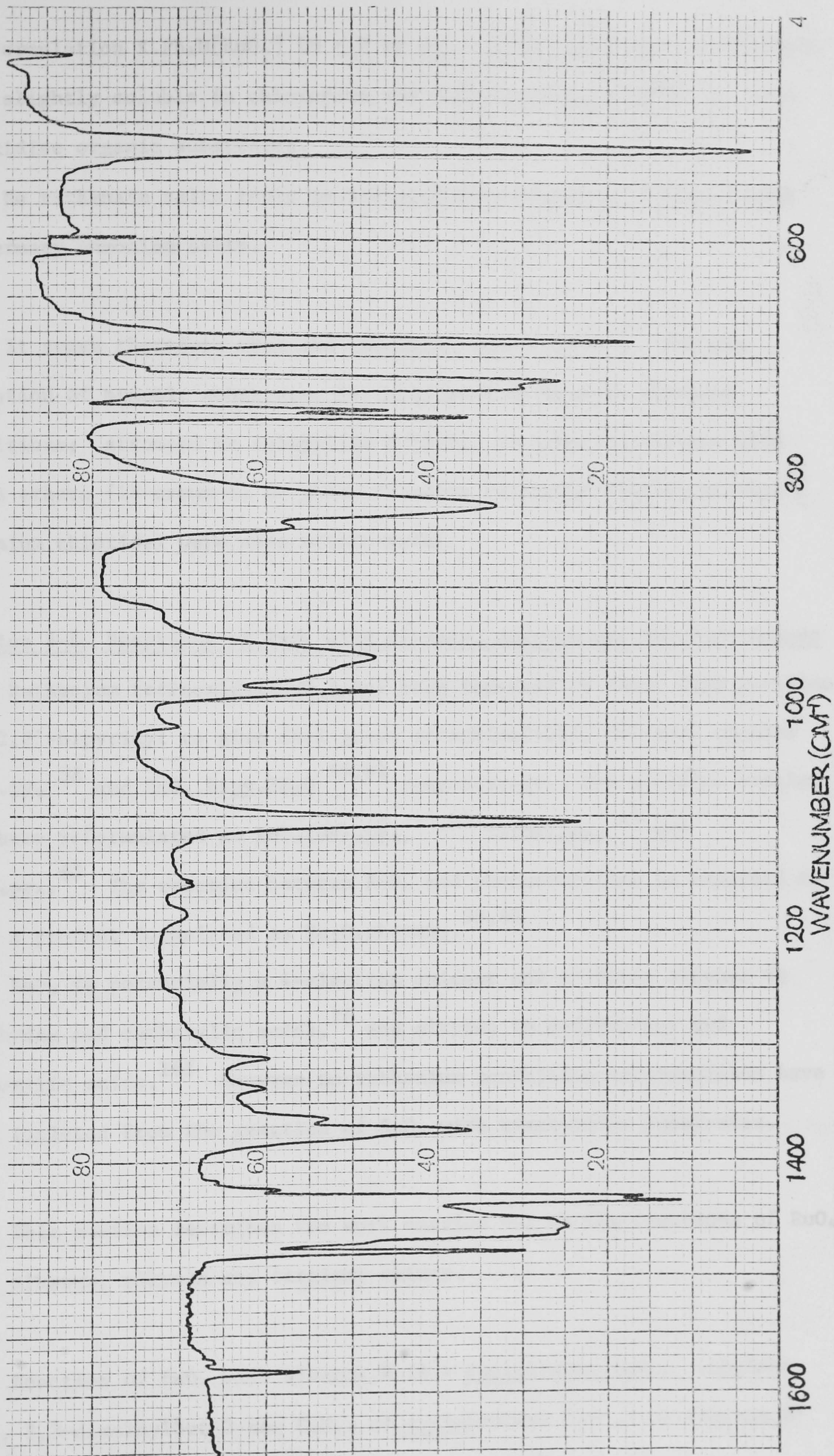


Figure 5-2. Infrared Spectrum of $\text{K}_2\text{P}_2\text{O}_7 \cdot \text{RuO}_4$.

the formulation $K.Ph_4M[RuO_4]$ ($M = P$ or As). These complexes, however, are only slightly soluble in chloroform and methyl cyanide and do not seem to oxidise organic substrates.

No ruthenate salts could be isolated by reaction of $K_2[RuO_4]$ with quaternary ammonium salts.

It seems therefore that the catalytic use of $[RuO_4]^{2-}$ for the oxidation of organic substrates is restricted to aqueous alkaline conditions; attempts to solubilise $K_2[RuO_4]$ in organic solvents with crown ethers (18-crown-6) or phase transfer catalysts (benzyltriethylammonium chloride) were also unsuccessful.

Section 5-D Reactions of RuO_4 with Alkenes, Alkynes and Tertiary Amines

Ruthenium tetraoxide, (RuO_4), has been reported to react with pyridine and 2,2'-bipyridyl to give dark green ruthenium(VIII) tetraoxo species $RuO_4.py_2$ ⁵⁸ and $RuO_4.bipy.3H_2O$ ^{59,60} respectively. The pyridine complex has been reformulated as $RuO_2(OH)_2py_2$,^{15,61} $Ru(OH)_4py_2$ ¹⁵ and $Ru_2O_6py_4$.⁶² The reaction between RuO_4 and phenanthroline is reported to give a product formulated as $Ru_2O_7phenan_2$.^{59,60}

RuO_4 is potentially a 4-electron oxidant and oxidises alkenes to aldehydes and carboxylic acids,⁷⁶ and alkynes to α -diketones and carboxylic acids.¹⁶⁵ However no ruthenium containing intermediates have been isolated from the reaction of RuO_4 with unsaturated substrates.

This section describes the work carried out on the reactions of RuO_4 with alkenes, alkynes and tertiary amines.

Reaction of RuO_4 with alkenes R ($R =$ cyclohexene C_6H_{10} , ethylene C_2H_4 , 2,3-dimethylbut-2-ene C_6H_{12} or cycloheptene C_7H_{14}) or alkynes R'

(R' = acetylene C₂H₂ or diphenylacetylene C₁₄H₁₀) in carbon tetrachloride at -20° C gave black intractable products of stoichiometry RuO₄.R.H₂O and (RuO₄)₂R'(H₂O)₂. If the reactions are carried out under nitrogen, products of stoichiometry RuO₄.R and (RuO₄)₂.R' are isolated. The infrared spectra of the complexes show no bands assignable to Ru=O stretching vibrations, but do show bands near 980 cm⁻¹ and 580 cm⁻¹ assigned to the carbon-oxygen stretching mode, ν_{C-O} , and metal oxygen stretching vibration, ν_{Ru-O} , respectively.

Hydrolysis of the products RuO₄.C₆H₁₀ and (RuO₄)₂.C₁₄H₁₀ using alcoholic Na₂SO₃ solution yielded cyclohexan-1,2-diol (48%) and benzoic acid (52%) respectively.

The above products are the first examples of isolated ruthenium ester complexes and are formulated as polymeric ruthenium(IV) species probably involving a $-\{Ru-O-Ru\}_n$ bridging system.

RuO₄ was treated with a range of tertiary amines L (L = pyridine C₅H₅N, 2,6-lutidine C₇H₉N, 4-picoline C₆H₇N, 2,2'-bipyridyl C₁₀H₈N₂, pyridine-N-oxide C₅H₅NO, 4-^tbutylpyridine C₉H₁₃N, pyridazine C₄H₄N₂ or pyrazine C₄H₄N₂) in carbon tetrachloride at -20° C. The reaction mixture immediately turned bright red, slowly to brown and then a dark green product was precipitated. The infrared spectra of the green complexes show no bands assigned to Ru=O stretching vibrations (Figure 5-3). Molecular weight measurements on the complex derived from 4-^tbutylpyridine in chloroform show it to be polymeric, while determination of the oxidation state of the complex derived from pyridine by the method of Kirschmann and Crowell¹⁹³ show it to be a ruthenium(IV) species. Elemental analyses of these complexes, however, are not in agreement with the stoichiometries RuO₄.L₂ (L = pyridine, 2,6-lutidine, 4-picoline, pyridine-N-oxide, 4-^tbutylpyridine or pyridazine)

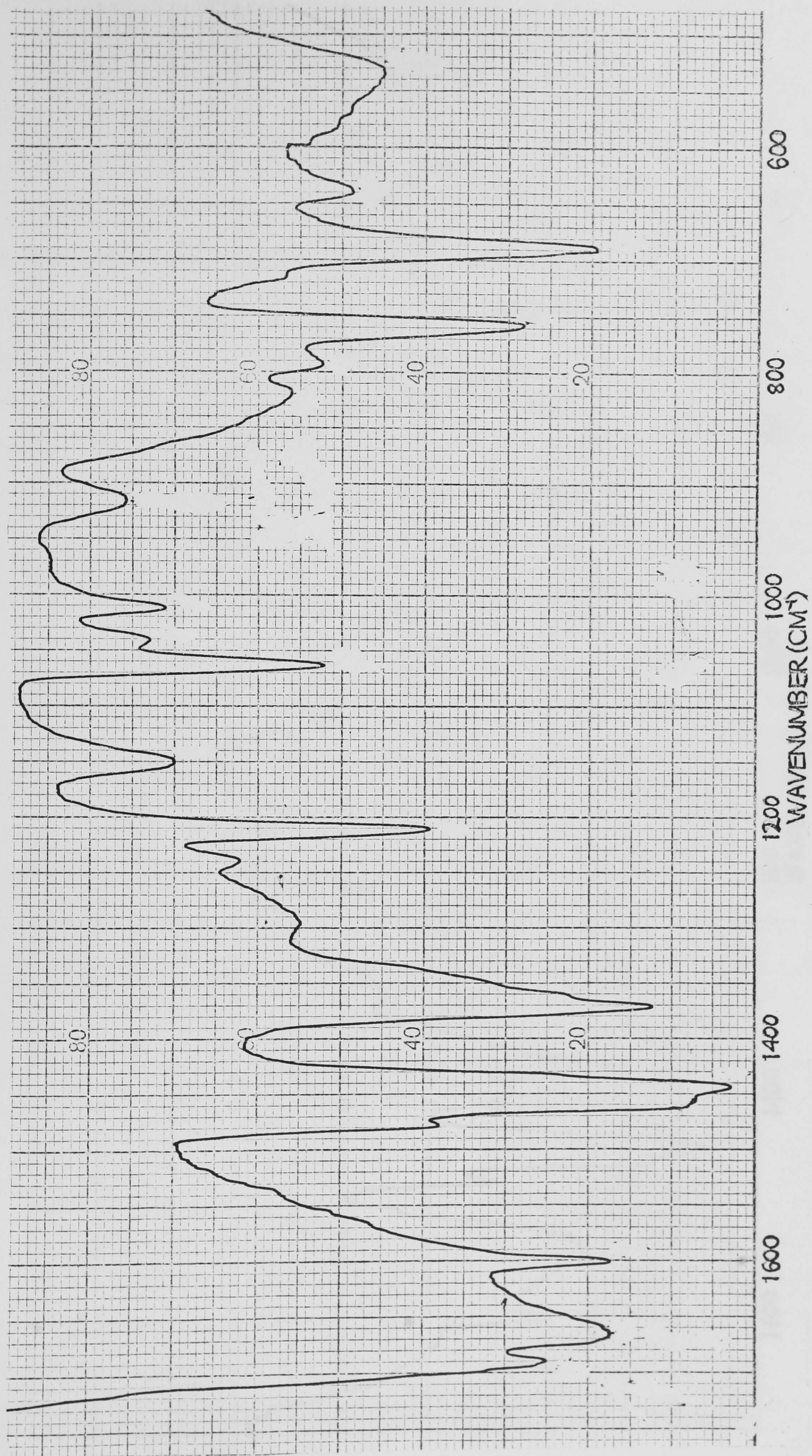


Figure 5-3. Infrared Spectrum of $\text{RuO}_4(\text{C}_5\text{H}_5\text{N})_2$

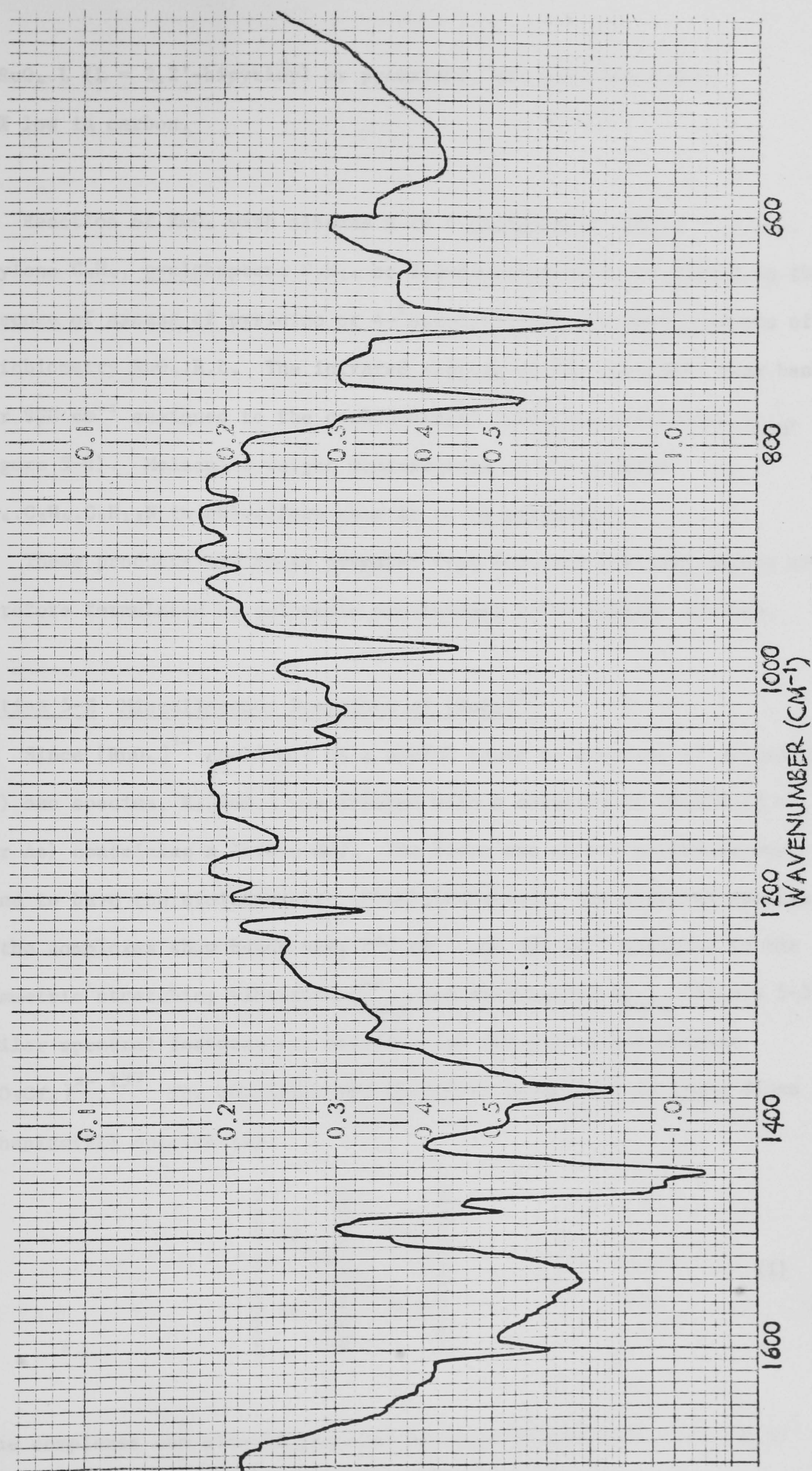


Figure 5-4. Infrared Spectrum of $\text{RuO}_4 \cdot \text{C}_6\text{H}_{10} \cdot \text{C}_5\text{H}_5\text{N}$

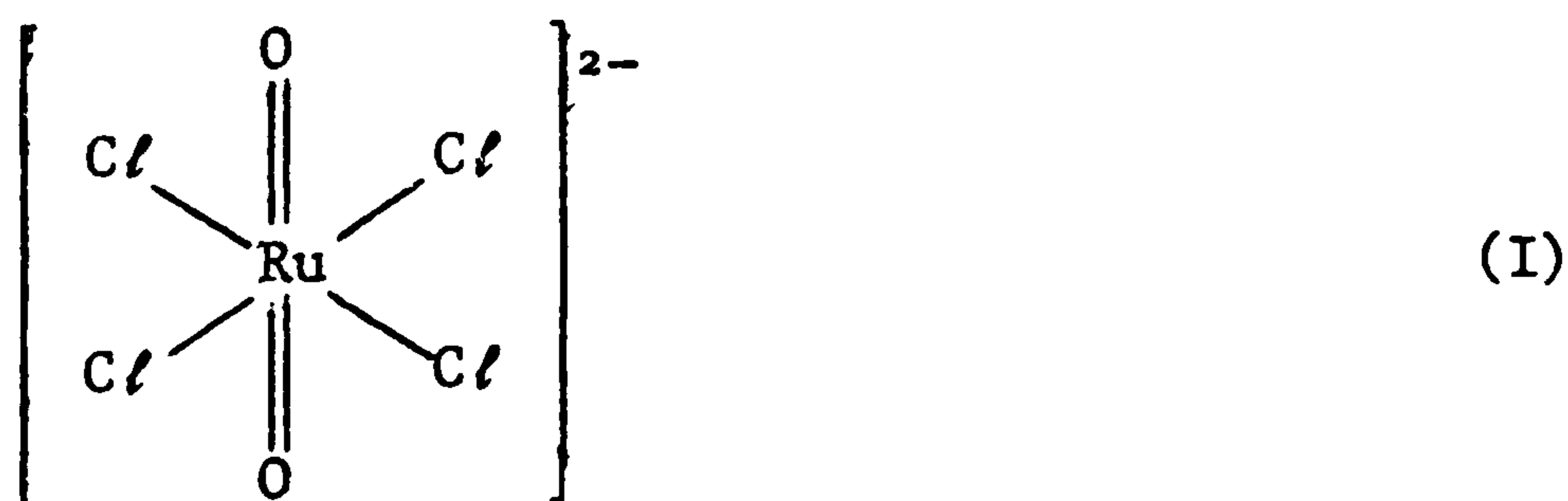
or $\text{RuO}_4 \cdot \text{L}$ ($\text{L} = 2,2'$ -bipyridyl or pyrazine), the analyses being 2-3% low in carbon.

Reaction of RuO_4 with alkenes R ($\text{R} = \text{cyclohexene } \text{C}_6\text{H}_{10}$, ethylene C_2H_4 , cycloheptene C_7H_{14} or 2,3-dimethylbut-2-ene C_6H_{12}) in the presence of excess of pyridine or 4-^tbutylpyridine (L) gave products of stoichiometry $\text{RuO}_4 \cdot \text{R} \cdot \text{L}$. The infrared spectra of the complexes show bands near 980 cm^{-1} assigned to the carbon-oxygen stretching vibration, $\nu_{\text{C-O}}$, (Figure 5-4). Molecular weight measurements on the complex $\text{RuO}_4 \cdot \text{C}_2\text{H}_4 \cdot \text{C}_9\text{H}_{13}\text{N}$ in chloroform show it to be polymeric.

These products and those prepared from RuO_4 and tertiary amines are therefore formulated as polymeric oxo-bridged ruthenium(IV) species.

Section 5-E Miscellaneous Reactions of $[\text{RuO}_4]^{2-}$

Since $[\text{RuO}_4]^{2-}$ could act as a useful route to a series of ruthenium-(VI) oxo species, $\text{K}_2[\text{RuO}_4]$ was treated with a solution of Ph_4MCl ($\text{M} = \text{P}$ or As) containing a little HCl . The brown oxo chloro complexes were found to have the stoichiometry $(\text{Ph}_4\text{M})_2[\text{RuO}_2\text{Cl}_4]$. The infrared spectra of the complexes show bands near 830 cm^{-1} and 300 cm^{-1} assigned to the asymmetric stretching vibration, $\nu_{\text{RuO}_2}^{\text{as}}$, and deformation, δ_{RuO_2} , (Figure 5-5); similar spectral features are observed for the osmium(VI) complex $[\text{OsO}_2\text{Cl}_4]^{2-}$.¹³⁷ The complexes are therefore formulated as trans dioxo ruthenium(VI) species (I).



These complexes can also be prepared by reduction of RuO_4 with HCl in

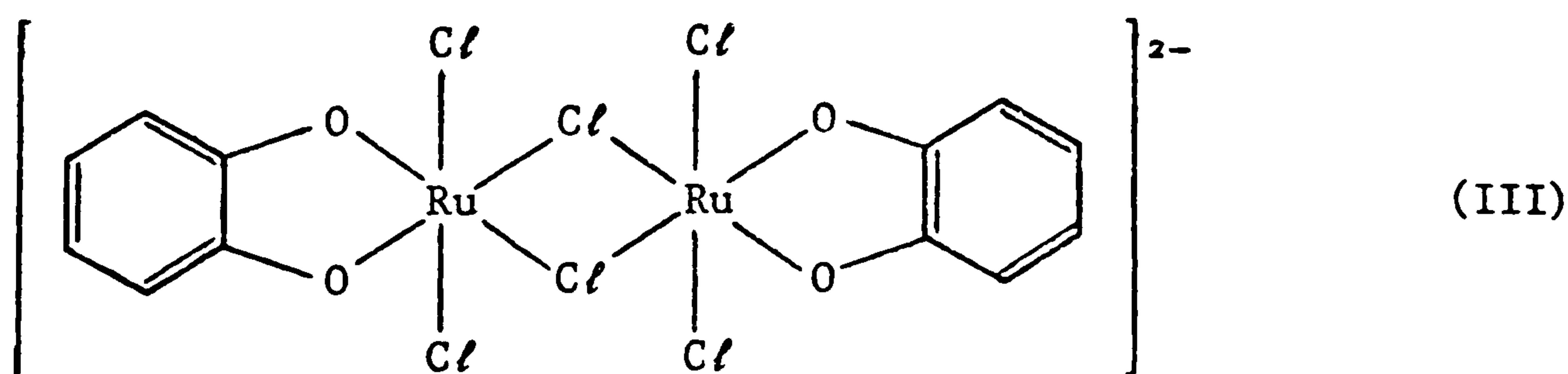
the presence of Ph_4MCl .^{67,136}

Reaction of $\text{K}_2[\text{RuO}_4]$ with a solution of Ph_4MCl ($\text{M} = \text{P}$ or As) containing a lower concentration of HCl , however, gave green oxo chloro species of stoichiometry $\text{Ph}_4\text{M}[\text{RuO}_2\text{Cl}_3]$. The infrared spectra of these complexes show bands at 875 cm^{-1} and 890 cm^{-1} assigned to metal oxygen stretching vibrations, ν_{RuO_2} , and a band near 300 cm^{-1} assigned to the metal oxygen deformation, δ_{RuO_2} . The presence of two $\text{Ru}=\text{O}$ stretching modes in the infrared suggests, as it does for cis-dioxo complexes,^{105,106} a non-linear arrangement of oxo ligands; the bands at 875 cm^{-1} and 890 cm^{-1} are assigned to $\nu_{\text{RuO}_2}^{\text{as}}$ and $\nu_{\text{RuO}_2}^{\text{s}}$ respectively (Figure 5-5). The complexes $[\text{RuO}_2\text{Cl}_3]^-$ are therefore formulated as five coordinate trigonal bipyramidal species with the oxo ligands occupying equatorial positions (II).



An X-ray crystal structure determination on this complex would be desirable to confirm this proposed structure.

Few catechol complexes of the platinum metals are known, the tris-catecholato osmium(VI) complex $\text{Os}(\text{O}_2\text{C}_6\text{H}_4)_3$ having been recently reported.¹⁹⁴⁻¹⁹⁶ Addition of catechol to the ruthenium(VI) complex $(\text{Ph}_4\text{As})_2[\text{RuO}_2\text{Cl}_4]$ yields a dark blue complex of stoichiometry $\text{Ph}_4\text{As}.\text{Ru}.\text{Cl}_3.\text{C}_6\text{H}_4\text{O}_2$. The infrared spectrum of this complex shows no bands assigned to $\text{Ru}=\text{O}$ stretching vibrations or deformations. The complex is probably a dimeric ruthenium(IV) species with structure (III).



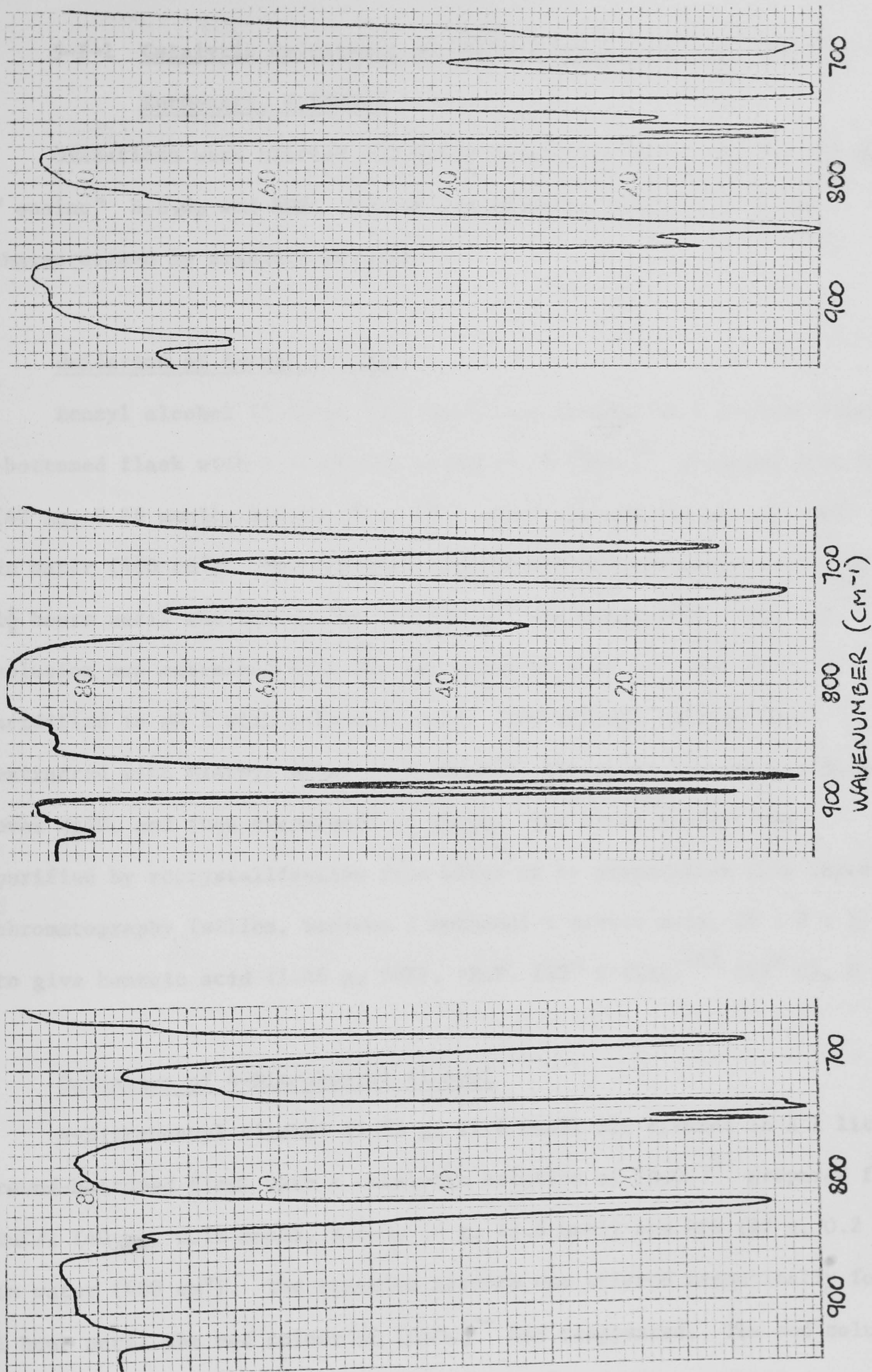


Figure 5-5. Infrared Spectra of Oxo Chloro Ruthenium(VI) and Osmium(VI) Complexes

Section 5-F Experimental

5-F-1 Catalytic Oxidations of Organic Substrates by Potassium Ruthenate, $K_2[RuO_4]$

Oxidations were carried out using commercial $RuCl_3$ (42.76% Ru) and "analar" $K_2S_2O_8$ and KOH. Yields are of pure, isolated products characterised by standard methods.

Oxidation of Benzyl Alcohol

Benzyl alcohol (1.32 g, 12.2 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of $[RuO_4]^{2-}$ prepared from $RuCl_3$ (40 mg, 0.16 mmol), $K_2S_2O_8$ (8 g, 29.6 mmol) and KOH (12 g, 0.2 mol) in water (400 cm³). The reaction mixture was stirred magnetically for 1½ hours until the red colour of $[RuO_4]^{2-}$ had reappeared. The red solution was extracted with diethyl ether (2 x 15 cm³) and then acidified to pH 2 with sulphuric acid. The aqueous solution was extracted with diethyl ether (5 x 20 cm³), the ether extract was dried over $MgSO_4$ and then evaporated in vacuo. The crude product was purified by recrystallisation from water or by preparative thin layer chromatography (silica, benzene : methanol : acetic acid, 15 : 2 : 1) to give benzoic acid (1.46 g, 98%). M.P. 122° C (Lit.¹⁴¹ 122° C), M = 122.

Oxidation of 4-Nitrobenzyl Alcohol

4-Nitrobenzyl alcohol (1.81 g, 11.8 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of $[RuO_4]^{2-}$ prepared from $RuCl_3$ (40 mg, 0.16 mmol), $K_2S_2O_8$ (8 g, 29.6 mmol) and KOH (12 g, 0.2 mol) in water (400 cm³). The reaction mixture was stirred magnetically for 1 hour until the red colour of $[RuO_4]^{2-}$ had reappeared. The red solution was extracted with diethyl ether (2 x 15 cm³) and then acidified to pH 2 with sulphuric acid. The precipitated product was filtered off, washed

with water (2 cm³) and then dried in vacuo to give 4-nitrobenzoic acid (1.92 g, 97%). M.P. 240° C (Lit.¹⁴¹ 242° C), M = 167.

Oxidation of 1,2,3,4-Tetrahydro-1-Naphthol

1,2,3,4-Tetrahydro-1-naphthol (1.28 g, 8.6 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of [RuO₄]²⁻ prepared from RuCl₃ (40 mg, 0.16 mmol), K₂S₂O₈ (3 g, 11 mmol) and KOH (6 g, 0.1 mol) in water (400 cm³). The reaction mixture was stirred magnetically for 2 hours and extracted with diethyl ether (4 x 25 cm³). The ether extract was dried over MgSO₄ and dried in vacuo. The crude product was purified by column chromatography (silica, benzene or diethyl ether) to give α-tetralone (1.06 g, 84%).

Oxidation of Cyclohexanol

Cyclohexanol (1.48 g, 14.8 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of [RuO₄]²⁻ prepared from RuCl₃ (40 mg, 0.16 mmol), K₂S₂O₈ (5 g, 18.5 mmol) and KOH (8 g, 0.14 mol) in water (400 cm⁴). The reaction mixture was stirred magnetically for 2 hours until the red colour of [RuO₄]²⁻ had reappeared. The red solution was extracted with diethyl ether (4 x 25 cm³), the ether extract was dried over MgSO₄ and then evaporated in vacuo. The crude product was purified by column chromatography (silica, diethyl ether) to give cyclohexanone (0.93 g, 64%).

The aqueous solution was acidified to pH 2 with sulphuric acid and then extracted with diethyl ether (4 x 30 cm³). The ether extract was dried over MgSO₄ and evaporated in vacuo to give adipic acid (0.15 g, 7%), M.P. 149° C (Lit.¹⁴¹ 149-150° C).

Oxidation of Cyclopentanol

Cyclopentanol (1.21 g, 14.1 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of $[\text{RuO}_4]^{2-}$ prepared from RuCl_3 (40 mg, 0.16 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (5 g, 18.5 mmol) and KOH (8 g, 0.14 mol) in water (400 cm^3). The reaction mixture was stirred magnetically for 2 hours until the red colour of $[\text{RuO}_4]^{2-}$ had reappeared. The red solution was extracted with diethyl ether (4 x 25 cm^3), the ether extract was dried over MgSO_4 and then evaporated in vacuo. The crude product was purified by column chromatography (silica, diethyl ether) to give cyclopentanone (0.84 g, 71%).

Oxidation of Benzhydrol

Benzhydrol (1.69 g, 9.2 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of $[\text{RuO}_4]^{2-}$ prepared from RuCl_3 (40 mg, 0.16 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (3.5 g, 13.0 mmol) and KOH (5 g, 0.09 mol) in water (600 cm^3). The reaction mixture was stirred magnetically for 5 hours until the red colour of $[\text{RuO}_4]^{2-}$ had reappeared. The red solution was extracted with diethyl ether (4 x 25 cm^3), the ether extract was dried over MgSO_4 and then evaporated in vacuo. The crude product was recrystallised from methanol and water to give benzophenone (1.49 g, 89%). M.P. 48° C (Lit. ¹⁴¹ 49° C).

Oxidation of Benzoin

Benzoin (1.07 g, 5.0 mmol) was dissolved in diethyl ether (150 cm^3) in a 1 litre round-bottomed flask and treated with a catalytic solution of $[\text{RuO}_4]^{2-}$ prepared from RuCl_3 (40 mg, 0.16 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (2.5 g, 9.2 mmol) and KOH (4 g, 0.07 mol) in water (300 cm^3). The reaction mixture was stirred magnetically for 5 hours and the ether layer removed. The aqueous solution was extracted with diethyl ether (2 x 25 cm^3) and

the ethereal extracts were combined, dried over MgSO_4 and evaporated in vacuo. The crude product was purified by preparative thin layer chromatography (silica, benzene) or by recrystallization from methanol and water to give benzil (0.28 g, 26%), M.P. 95°C (Lit. ¹⁴¹ 95°C).

The aqueous solution was acidified to pH 2 with sulphuric acid and extracted with diethyl ether ($4 \times 25 \text{ cm}^3$). The ether extract was dried over MgSO_4 and evaporated in vacuo. The crude product was purified by preparative thin layer chromatography (silica, benzene : methanol : acetic acid, 15 : 2 : 1) to give benzoic acid (0.84 g, 68%), M.P. 121°C (Lit. ¹⁴¹ 122°C).

Oxidation of 4-Nitrobenzaldehyde

4-Nitrobenzaldehyde (1.85 g, 12.3 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of $[\text{RuO}_4]^{2-}$ prepared from RuCl_3 (40 mg, 0.16 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (5 g, 18.5 mmol) and KOH (8 g, 0.14 mol) in water (400 cm^3). The reaction mixture was stirred magnetically for $\frac{3}{4}$ hour until the red colour of $[\text{RuO}_4]^{2-}$ had reappeared. The red solution was extracted with diethyl ether ($2 \times 15 \text{ cm}^3$) and then acidified to pH 2 with sulphuric acid. The precipitated product was filtered off, washed with water (2 cm^3) and then dried in vacuo to give 4-nitrobenzoic acid (2.00 g, 98%). M.P. 240°C (Lit. ¹⁴¹ 242°C), $M = 167$.

Oxidation of 3-Chlorobenzaldehyde

3-Chlorobenzaldehyde (1.25 g, 8.9 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of $[\text{RuO}_4]^{2-}$ prepared from RuCl_3 (40 mg, 0.16 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (3.5 g, 13.0 mmol) and KOH (5 g, 0.09 mol) in water (400 cm^3). The reaction mixture was stirred magnetically for 2 hours until the red colour of $[\text{RuO}_4]^{2-}$ had reappeared. The aqueous solution was extracted with diethyl ether ($2 \times 15 \text{ cm}^3$) and then acidified

to pH 2 with sulphuric acid. The precipitated product was filtered off, washed with water (2 cm³) and then dried in vacuo to give 3-chlorobenzoic acid (1.38 g, 99%). M.P. 155° C (Lit. ¹⁴¹ 158° C), M = 156.

Oxidation of Benzaldehyde

Benzaldehyde (1.30 g, 12.3 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of [RuO₄]²⁻ prepared from RuCl₃ (40 mg, 0.16 mmol), K₂S₂O₈ (5 g, 18.5 mmol) and KOH (8 g, 0.14 mol) in water (400 cm³). The reaction mixture was stirred magnetically for 1 hour until the red colour of [RuO₄]²⁻ had reappeared. The aqueous solution was extracted with diethyl ether (2 x 15 cm³) and then acidified to pH 2 with sulphuric acid. The aqueous solution was extracted with diethyl ether (4 x 25 cm³), the ether extract was dried over MgSO₄ and then evaporated in vacuo. The crude product was purified by preparative thin layer chromatography (silica, benzene : methanol : acetic acid, 15 : 2 : 1) to give benzoic acid (1.46 g, 98%), M.P. 122° C (Lit. ¹⁴¹ 122° C), M = 122.

Oxidation of 2-Hydroxybenzaldehyde

2-Hydroxybenzaldehyde (1.14 g, 9.3 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of [RuO₄]²⁻ prepared from RuCl₃ (40 mg, 0.16 mmol), K₂S₂O₈ (4 g, 14.8 mmol) and KOH (7 g, 0.13 mol) in water (400 cm³). The reaction mixture was stirred magnetically for 5 hours and then extracted with diethyl ether (2 x 15 cm³). The aqueous solution was acidified to pH 2 with sulphuric acid and extracted with diethyl ether (4 x 25 cm³). The ether extract was dried over MgSO₄ and evaporated in vacuo. The crude product was purified by preparative thin layer chromatography (silica, benzene : methanol : acetic acid, 15 : 2 : 1) to give 2-hydroxybenzoic acid (0.91 g, 71%), M.P. 156° C

(Lit. ¹⁴¹ 159° C).

Oxidation of 4-Methoxybenzaldehyde

4-Methoxybenzaldehyde (1.60 g, 11.8 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of $[\text{RuO}_4]^{2-}$ prepared from RuCl_3 (40 mg, 0.16 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (5 g, 18.5 mmol) and KOH (8 g, 0.14 mol) in water (400 cm^3). The reaction mixture was stirred magnetically for $2\frac{1}{2}$ hours until the red colour of $[\text{RuO}_4]^{2-}$ had reappeared. The aqueous solution was extracted with diethyl ether (2 x 15 cm^3) and then acidified to pH 2 with sulphuric acid. The precipitated product was filtered off, washed with water (2 cm^3) and then dried in vacuo to give 4-methoxybenzoic acid (1.72 g, 96%), M.P. 274° C (Lit. ¹⁴¹ 275-280° C), M = 152.

Oxidation of trans-Cinnamyl Alcohol

trans-Cinnamyl alcohol (0.89 g, 6.6 mmol) was treated in 1 litre round-bottomed flask with a catalytic solution of $[\text{RuO}_4]^{2-}$ prepared from RuCl_3 (40 mg, 0.16 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (5 g, 18.5 mmol) and KOH (8 g, 0.14 mol) in water (300 cm^3). The reaction mixture was stirred magnetically for 3 hours until the red colour of $[\text{RuO}_4]^{2-}$ had reappeared. The aqueous solution was extracted with diethyl ether (2 x 15 cm^3) and then acidified to pH 2 with sulphuric acid. The acidified solution was extracted with diethyl ether (4 x 30 cm^3) and the ether extract dried over MgSO_4 and evaporated in vacuo. The crude product was purified by preparative thin layer chromatography (silica, benzene : methanol : acetic acid, 15 : 2 : 1) to give trans-cinnamic acid (0.96 g, 98%), M.P. 133° C (Lit. ¹⁴¹ 133° C), M = 148.

Oxidation of 3-Cyclohexene-1-methanol

3-Cyclohexene-1-methanol (1.66 g, 14.8 mmol) was treated in a 1 litre

round-bottomed flask with a catalytic solution of $[\text{RuO}_4]^{2-}$ prepared from RuCl_3 (40 mg, 0.16 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (9 g, 33.3 mmol) and KOH (12 g, 0.2 mol) in water (600 cm^3). The reaction mixture was stirred magnetically for 6 hours and extracted with diethyl ether (2 x 20 cm^3). The aqueous solution was acidified to pH 2 with sulphuric acid and then extracted with diethyl ether (4 x 30 cm^3). The ether extract was dried over MgSO_4 and evaporated in vacuo. The crude product was purified by preparative thin layer chromatography (silica, benzene : methanol : acetic acid, 15 : 2 : 1) to give 3-cyclohexene-1-carboxylic acid (1.27 g, 68%). ^1H n.m.r. δ 5.51 (2H) alkene, 2.15 (7H).

Oxidation of Allyl Alcohol

Allyl alcohol (1.53 g, 26.4 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of $[\text{RuO}_4]^{2-}$ prepared from RuCl_3 (60 mg, 0.32 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (15 g, 55.5 mmol) and KOH (20 g, 0.36 mol) in water (300 cm^3). The reaction mixture was stirred magnetically for $3\frac{1}{2}$ hours and then washed with diethyl ether (2 x 20 cm^3). The aqueous solution was acidified to pH 2 with sulphuric acid and extracted with diethyl ether (4 x 30 cm^3). The ether extract was dried over MgSO_4 and evaporated in vacuo to yield acrylic acid (0.85 g, 45%).

Oxidation of Cyclohexene

Cyclohexene (2.10 g, 25.6 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of $[\text{RuO}_4]^{2-}$ prepared from RuCl_3 (60 mg, 0.32 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (7 g, 25.9 mmol) and KOH (10 g, 0.18 mol) in water (300 cm^3). The reaction mixture was stirred magnetically for 6 hours and then extracted with diethyl ether to give unreacted cyclohexene in almost quantitative yield.

The oxidation was repeated, the reaction mixture being stirred magnetically for 4 days. The aqueous solution was washed with diethyl ether (3 x 15 cm³), acidified to pH 2 with sulphuric acid and extracted with diethyl ether (4 x 25 cm³). The ether extract was dried over MgSO₄ and evaporated in vacuo to give adipic acid (0.75 g, 20%), M.P. 149° C (Lit.¹⁴¹ 149-150° C).

The same oxidation product is obtained using [RuO₄]²⁻ stoichiometrically.

Oxidation of Acetylene Dicarboxylic Acid

Acetylene dicarboxylic acid (1.51 g, 13.2 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of [RuO₄]²⁻ prepared from RuCl₃ (40 mg, 0.16 mmol), K₂S₂O₈ (3.5 g, 13.0 mmol) and KOH (5 g, 0.09 mol) in water (100 cm³). The reaction mixture was stirred magnetically for 5 hours, acidified to pH 2 with sulphuric acid and extracted with diethyl ether (4 x 25 cm³). The ether extract was dried over MgSO₄ and evaporated in vacuo to give unreacted acetylene dicarboxylic acid in near quantitative yield.

Oxidation of Benzylamine

A solution of benzylamine (6.29 g, 58.8 mmol) in water (100 cm³) in a 250 cm³ dropping-funnel was added dropwise with stirring over a 7 hour period to a catalytic solution of [RuO₄]²⁻ prepared from RuCl₃ (1.0 g, 4.0 mmol), K₂S₂O₈ (31 g, 0.11 mol) and KOH (35 g, 0.63 mol) in water (500 cm³). The reaction mixture was left to stand overnight and then extracted with diethyl ether (4 x 50 cm³). The ether extract was dried over MgSO₄ and evaporated in vacuo. The residue was distilled and the product further purified by column chromatography (silica, diethyl ether) to give benzonitrile (4.01 g, 66%), B.P. 190° C (Lit.¹⁴¹ 190.7° C).

Oxidation of Butylamine

A solution of butylamine (4.32 g, 59.2 mmol) in water (100 cm³) in a 250 cm³ dropping-funnel was added dropwise with stirring over a 6 hour period to a catalytic solution of [RuO₄]²⁻ prepared from RuCl₃ (1 g, 4.0 mmol), K₂S₂O₈ (32 g, 0.12 mol) and KOH (35 g, 0.63 mol) in water (400 cm³). The reaction mixture was left to stand overnight and then extracted with diethyl ether (3 x 50 cm³). The ether extract was dried over MgSO₄ and evaporated in vacuo to give a mixture of butyraldehyde and butyronitrile in very low yield (~ 10%).

The aqueous solution was acidified to pH 2 with H₂SO₄ and then extracted with diethyl ether (5 x 25 cm³). The ether extract was dried over MgSO₄ and evaporated in vacuo to give butyric acid (1.78 g, 34%).

Oxidation of N-Methyl Benzylamine

A solution of N-methyl benzylamine (1.83 g, 15.1 mmol) in water (100 cm³) in a 250 cm³ dropping-funnel was added dropwise with stirring over a 6 hour period to a catalytic solution of [RuO₄]²⁻ prepared from RuCl₃ (0.25 g, 1.0 mmol), K₂S₂O₈ (8 g, 29.6 mmol) and KOH (10 g, 0.18 mol) in water (500 cm³). The reaction mixture was left to stand overnight and then extracted with diethyl ether (4 x 25 cm³). The ether extract was dried over MgSO₄ and evaporated in vacuo to give benzaldehyde (yield:- 40% by G.L.C. analysis).

Oxidation of Benzonitrile

Benzonitrile (0.96 g, 9.3 mmol) was treated in a 1 litre round-bottomed flask with a catalytic solution of [RuO₄]²⁻ prepared from RuCl₃ (40 mg, 0.16 mmol), K₂S₂O₈ (3 g, 11.1 mmol) and KOH (5 g, 0.09 mol) in water (300 cm³). The reaction mixture was stirred magnetically for 24 hours and then extracted with diethyl ether (4 x 30 cm³). The ether

extract was dried over MgSO_4 and evaporated in vacuo. The crude product was purified by preparative thin layer chromatography (silica, methanol : chloroform, 1 : 10) to give benzamide (0.44 g, 39%), M.P. 130°C (Lit.¹⁴¹ 130°C).

Oxidation of benzonitrile occurred using alkaline persulphate alone to give benzamide in 29% yield.

5-F-2 Preparation of Organic Salts of $[\text{RuO}_4]^{2-}$

Ruthenium tetroxide was prepared in CCl_4 solution by the method of Nakata.⁵⁵

RuO_4 (20 cm^3 in CCl_4) was shaken with a solution of potassium hydroxide (1 g, 0.018 mol) in water (20 cm^3). After 3 hours the aqueous solution was separated and treated with a solution of Ph_4MCl (M = P or As) (0.5 g) in water (5 cm^3). The dark green precipitate was filtered off washed with water and dried in vacuo. Yield:- 40%.

Elemental analysis Found:- C, 51.18%; H, 4.24%

$\text{K} \cdot \text{Ph}_4\text{P} \cdot [\text{RuO}_4]$ Required:- C, 53.03%; H, 3.70%

Elemental analysis Found:- C, 48.92%, 49.37%; H, 3.69%, 3.95%

$\text{K} \cdot \text{Ph}_4\text{As} \cdot [\text{RuO}_4]$ Required:- C, 49.07% ; H, 3.43%.

5-F-3 Reactions of RuO_4 with Alkenes, Alkynes and Tertiary Amines

Elemental analyses of the products are given in Table 5-3.

Preparation of Complexes $\text{RuO}_4 \cdot \text{R}$ from Alkenes

The preparation of these complexes followed similar procedures. The preparation of $\text{RuO}_4 \cdot \text{C}_6\text{H}_{10}$ is typical.

To a solution of RuO_4 (20 cm^3 in CCl_4) at -20°C under nitrogen was added dropwise with stirring cyclohexene (1 cm^3) in CCl_4 (10 cm^3). The

reaction mixture was allowed to warm to room temperature, the black product was filtered off, washed with CCl_4 (15 cm^3) and dried in vacuo. Yield:- 70%. (No oxidation products of cyclohexene were detected in the filtrate).

If the reactions are carried out in the presence of atmospheric moisture, products of stoichiometry $\text{RuO}_4 \cdot \text{R} \cdot \text{H}_2\text{O}$ are isolated.

Preparation of Complexes $(\text{RuO}_4)_2 \cdot \text{R}'$ from Alkynes

The preparation of these complexes followed similar procedures. The preparation of $(\text{RuO}_4)_2 \cdot \text{C}_{14}\text{H}_{10}$ is typical.

To a solution of RuO_4 (20 cm^3 in CCl_4) at -20°C under nitrogen was added dropwise with stirring diphenylacetylene (0.5 g, 2.8 mmol) in CCl_4 (20 cm^3). The reaction mixture was allowed to warm to room temperature, the black product was filtered off, washed with CCl_4 (15 cm^3) and dried in vacuo. Yield:- 60%. (No oxidation products of diphenylacetylene were detected in the filtrate).

If the reactions are carried out in the presence of atmospheric moisture, products of stoichiometry $(\text{RuO}_4)_2 \cdot \text{R}' \cdot (\text{H}_2\text{O})_2$ are isolated.

Hydrolysis of the Complex $\text{RuO}_4 \cdot \text{C}_6\text{H}_{10}$

The product $\text{RuO}_4 \cdot \text{C}_6\text{H}_{10}$ (1.41 g, 5.7 mmol) was refluxed with a solution of Na_2SO_3 (3 g, 23.8 mmol) in water (200 cm^3) containing ethanol (15 cm^3) for 3 hours. The reaction mixture was allowed to cool and the ruthenium sulphito complex filtered off. The aqueous solution was extracted with diethyl ether ($4 \times 30 \text{ cm}^3$), the ether extract was dried over MgSO_4 and evaporated in vacuo to give cyclohexan-1,2-diol (0.275 g, 48%). The product was characterised by its infrared spectrum, no aldehydic products being detected.

Hydrolysis of the Complex $(\text{RuO}_4)_2 \cdot \text{C}_{14}\text{H}_{10}$

The product $(\text{RuO}_4)_2 \cdot \text{C}_{14}\text{H}_{10}$ (1.63 g, 3.2 mmol) was refluxed with a solution of Na_2SO_3 (4 g, 31.7 mmol) in water (200 cm^3) containing ethanol (15 cm^3) for 3 hours. The reaction mixture was allowed to cool and the ruthenium sulphito complex filtered off. The aqueous solution was washed with diethyl ether (2 x 15 cm^3) and acidified to pH 2 with sulphuric acid. The acidified solution was extracted with diethyl ether (4 x 25 cm^3), the ether extract was dried over MgSO_4 and evaporated in vacuo to yield benzoic acid (0.41 g, 52%).

Preparation of Complexes $\text{RuO}_4 \cdot \text{L}_2$ from Tertiary Amines

The preparation of these complexes followed similar procedures. The preparation of $\text{RuO}_4 \cdot (\text{C}_5\text{H}_5\text{N})_2$ is typical.

To a solution of RuO_4 (20 cm^3 in CCl_4) at -20°C under nitrogen was added dropwise with stirring pyridine (1 cm^3) in CCl_4 (10 cm^3). The reaction mixture turned bright red and then slowly to brown. On warming to room temperature a dark green precipitate formed. The product was filtered off, washed with CCl_4 (20 cm^3) and dried in vacuo. Yield:- 60%.

Preparation of Complexes $\text{RuO}_4 \cdot \text{R} \cdot \text{L}$ from Alkenes and Tertiary Amines

The preparation of these complexes followed similar procedures. The preparation of $\text{RuO}_4 \cdot \text{C}_6\text{H}_{10} \cdot \text{C}_5\text{H}_5\text{N}$ is typical.

To a solution of RuO_4 (20 cm^3 in CCl_4) at -20°C under nitrogen was added dropwise with stirring a solution of pyridine (0.5 g, 6.3 mmol) and cyclohexene (0.52 g, 6.3 mmol) in CCl_4 (20 cm^3). The reaction mixture was warmed to room temperature and the green precipitate filtered off, washed with CCl_4 (20 cm^3) and dried in vacuo. Yield:- 50%.

Table 5-3

Elemental Analyses of Ruthenium(IV) Ester Complexes

	% Found			% Required		
	C	H	N	C	H	N
$\text{RuO}_4 \cdot \text{C}_6\text{H}_{10}$	29.22	4.18		29.15	4.08	
$\text{RuO}_4 \cdot \text{C}_5\text{H}_8$	26.47	3.74		25.76	3.46	
$\text{RuO}_4 \cdot \text{C}_6\text{H}_{12} \cdot \text{H}_2\text{O}$	26.22	4.56		26.97	5.28	
$\text{RuO}_4 \cdot \text{C}_6\text{H}_{10} \cdot \text{H}_2\text{O}$	27.56	4.68		27.17	4.56	
$\text{RuO}_4 \cdot \text{C}_7\text{H}_{14} \cdot \text{H}_2\text{O}$	29.29	5.41		29.89	5.73	
$\text{RuO}_4 \cdot \text{C}_2\text{H}_4 \cdot \text{H}_2\text{O}$	11.63	2.63		11.38	2.87	
$(\text{RuO}_4)_2 \cdot \text{C}_{14}\text{H}_{10}$	32.44	2.69		33.08	1.98	
$(\text{RuO}_4)_2 \cdot \text{C}_2\text{H}_2 \cdot (\text{H}_2\text{O})_2$	6.34	1.97		6.12	1.54	
$\text{RuO}_4 \cdot \text{C}_6\text{H}_{10} \cdot \text{C}_5\text{H}_5\text{N}$	40.36	4.69	4.33	40.49	4.63	4.29
$\text{RuO}_4 \cdot \text{C}_6\text{H}_{12} \cdot \text{C}_5\text{H}_5\text{N}$	41.22	4.47	6.12	40.24	5.22	4.27
$\text{RuO}_4 \cdot \text{C}_7\text{H}_{14} \cdot \text{C}_5\text{H}_5\text{N}$	42.65	4.88	5.47	42.10	5.59	4.09

5-F-4 Preparation of Oxo Chloro Ruthenium(VI) Complexes

Preparation of $(\text{Ph}_4\text{As})_2[\text{RuO}_2\text{Cl}_4]$

An aqueous solution of $\text{K}_2[\text{RuO}_4]$ (10 cm^3), prepared from alkaline reduction of RuO_4 , was brought to pH 8 with HCl and treated with a solution of Ph_4AsCl (0.5 g) in water (10 cm^3) containing 6 M HCl (1 cm^3). The brown product was filtered off, washed with dilute HCl and dried in vacuo. The complex was recrystallised from acetone and petroleum ether (60/40). Yield:- 50%.

Elemental analysis Found:- C, 55.45%; H, 4.09%; Cl, 14.58%
 $(\text{Ph}_4\text{As})_2[\text{RuO}_2\text{Cl}_4]$ Required:- C, 55.35%; H, 3.87%; Cl, 13.61%.

Preparation of $\text{Ph}_4\text{P}[\text{RuO}_2\text{Cl}_3]$

An aqueous solution of $\text{K}_2[\text{RuO}_4]$ (10 cm^3) was treated with a solution of Ph_4PCl (0.5 g) in water (10 cm^3) acidified with 6 M HCl (1 cm^3). The bright green precipitate was filtered off, washed with dilute HCl and recrystallised from acetone and diethyl ether. Yield:- 50%.

Elemental analysis Found:- C, 49.48%; H, 3.97%; Cl, 18.00%
 $\text{Ph}_4\text{P}[\text{RuO}_2\text{Cl}_3]$ Required:- C, 49.80%; H, 3.48%; Cl, 18.37%.

Preparation of $(\text{Ph}_4\text{As})_2[\text{RuCl}_3(\text{O}_2\text{C}_6\text{H}_4)]_2$

A solution of $(\text{Ph}_4\text{As})_2[\text{RuO}_2\text{Cl}_4]$ (0.5 g) in acetone (10 cm^3) was treated with catechol (0.5 g, 4.5 mmol) in acetone (10 cm^3). The reaction mixture turned dark purple and the product was precipitated by addition of diethyl ether. The complex was recrystallised from acetone and diethyl ether.

Elemental analysis Found:- C, 51.79%; H, 3.83%; Cl, 15.10%
 $(\text{Ph}_4\text{As})_2[\text{RuCl}_3(\text{O}_2\text{C}_6\text{H}_4)]_2$ Required:- C, 51.56%; H, 3.46%; Cl, 15.22%.

CHAPTER SIX

NITRIDO COMPLEXES OF OSMIUM AND RUTHENIUM

Abstract

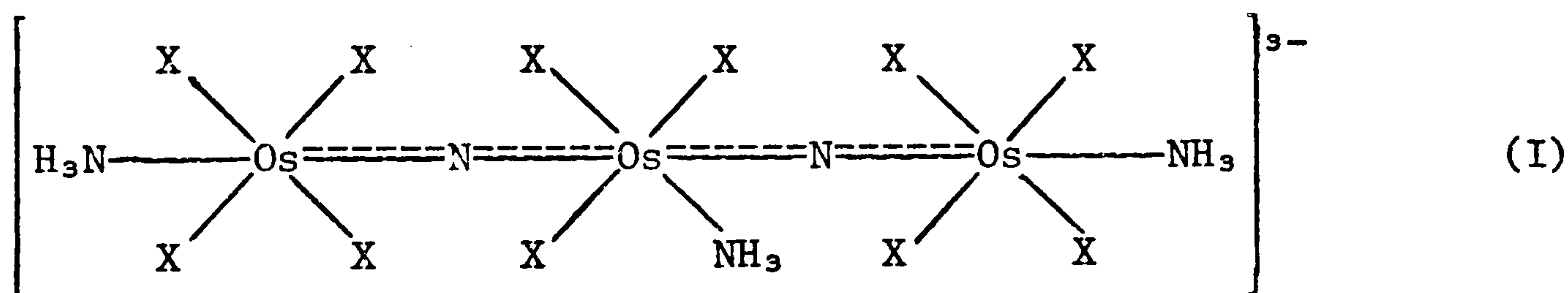
Osmium tetroxide, (OsO_4) , reacts with concentrated aqueous ammonia to give a trinuclear osmium nitrido complex which, when treated in aqueous solution with SO_2 , acts as a selective electron microscopy (e.m.) stain for aldehydic moieties present in biological tissues; the binuclear nitrido complexes $[\text{Os}_2\text{N}(\text{NH}_3)_8\text{X}_2]\text{Y}_3$ and $[\text{Ru}_2\text{N}(\text{NH}_3)_8\text{X}_2]\text{Y}_3$ ($\text{X} = \text{Cl}$, $\text{Y} = \text{NO}_3$) also function in the presence of SO_2 as selective e.m. stains for aldehydic moieties. The possible mechanisms of staining by these species is briefly discussed.

Potassium osmiamate, $\text{K}[\text{OsO}_3\text{N}]$, reacts with HI in the presence of $\text{Ph}_4\text{MCℓ}$ ($\text{M} = \text{P}$ or As) under controlled conditions to give the terminal nitrido complexes $\text{Ph}_4\text{M}[\text{OsNI}_4]$. The reactions of $\text{Ph}_4\text{M}[\text{OsNI}_4]$ with pyridine, isoquinoline and PPh_3 are briefly described.

Section 6-A Introduction

Early work showed that prolonged reaction of osmium tetroxide, (OsO_4), with concentrated aqueous ammonia yielded a black product formulated as $[\text{OsO}_2(\text{NH}_3)_2\text{H}_2\text{O}]$;¹⁹⁷ this complex was later reformulated as a trinuclear nitrido species $[\text{Os}_3\text{N}_2(\text{NH}_3)_4(\text{OH})_8(\text{H}_2\text{O})_2]$.¹⁹⁸ The infrared spectrum of the complex shows two broad bands near 1000 cm^{-1} assigned to the asymmetric stretching vibration of the bridging nitrido ligands, $\nu_{\text{Os}_2\text{N}}^{\text{as}}$,¹⁹⁸ these bands shift by 20 cm^{-1} to lower frequencies on ^{15}N substitution.¹⁹⁸

Reaction of $[\text{Os}_3\text{N}_2(\text{NH}_3)_4(\text{OH})_8(\text{H}_2\text{O})_2]$ with HX ($\text{X} = \text{Cl}$ or Br) in the presence of CsX yields the salts $\text{Cs}_3[\text{Os}_3\text{N}_2\text{X}_{11}(\text{NH}_3)_3] \cdot 2\text{H}_2\text{O}$.^{67,198} The infrared spectra of the complexes again show the same broad bands near 1000 cm^{-1} assigned to the stretching vibration of the bridging nitrido ligands $\nu_{\text{Os}_2\text{N}}^{\text{as}}$.^{67,198} These complexes were thought to have structure (I).^{67,198}



The diamagnetism of this formally $\text{Os}^{\text{V}} - \text{N} - \text{Os}^{\text{VI}} - \text{N} - \text{Os}^{\text{V}}$ species may be rationalised using the bonding scheme applied to ruthenium red $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]^{6+}$,^{199,200} which has an analogous structure with a linear $\text{Ru}^{\text{III}} - \text{O} - \text{Ru}^{\text{IV}} - \text{O} - \text{Ru}^{\text{III}}$ unit.²⁰¹

Reaction of OsO_4 with liquid ammonia yields an apparently related trinuclear nitrido complex of stoichiometry $[\text{Os}_3\text{N}_7\text{O}_9\text{H}_{21}]$,²⁰²⁻²⁰⁴ while RuO_4 reacts with liquid ammonia to give the tetranuclear species $\text{Ru}_4\text{N}_{11}\text{O}_{12}\text{H}_{33}$.²⁰⁵

The preparations of the binuclear nitrido complexes $[\text{Os}_2\text{N}(\text{NH}_3)_8\text{X}_2]^{3+}$, $[\text{Ru}_2\text{N}(\text{NH}_3)_8\text{X}_2]^{3+}$, $[\text{Os}_2\text{NCl}_8(\text{H}_2\text{O})_2]^{3-}$ and $[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]^{3-}$ have been reported.^{202,206-208} Infrared spectra of these complexes show a strong, sharp band in the range 1050-1130 cm^{-1} assigned to the asymmetric stretching vibration of the nitride bridge $\nu_{\text{M}_2\text{N}}^{\text{as}}$; this band is unchanged in frequency on deuteration of the complexes but shifts downwards by 70 cm^{-1} on ^{15}N substitution.^{202,209} The structure of $\text{K}_3[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]$ has been confirmed by a single crystal X-ray study²¹⁰ as a binuclear, centrosymmetric species with a linear $\text{H}_2\text{O}-\text{Ru}-\text{N}-\text{Ru}-\text{OH}_2$ skeleton.

This chapter describes the work carried out on the use of trinuclear and binuclear nitrido complexes of osmium and ruthenium for the selective staining of aldehydic moieties in biological tissues for electron microscopy. The preparation of the tetraiodo nitrido species $[\text{OsNI}_4]^-$ and its reactions with pyridine, isoquinoline and PPh_3 are also reported.

Section 6-B Trinuclear Nitrido Complexes

Gautier et al.^{211,212} have described the preparation of an osmium-ammine complex which, when treated in aqueous solution with SO_2 , acts as a selective stain for aldehydic moieties for electron microscopy. The osmium-ammine complex was prepared by reaction of OsO_4 with HCl followed by the addition of concentrated aqueous ammonia. The solution was left to stand for several hours, heated, treated with oxygen and the product precipitated by addition of ethanol to give a dark brown complex; this complex, when treated with SO_2 , was found to act as an effective e.m. stain for aldehydic functions (See Section 6-E, Experimental). No

structures for the ammine complex, or the product produced by treatment with SO_2 , were proposed.

In an attempt to identify the osmium-ammine product prepared by Gautier et al., the preparation of this complex by the published method ²¹¹ was studied spectrophotometrically. The results are listed in Table 6-1.

Table 6-1

Preparation of Gautier's Osmium-Ammine Complex

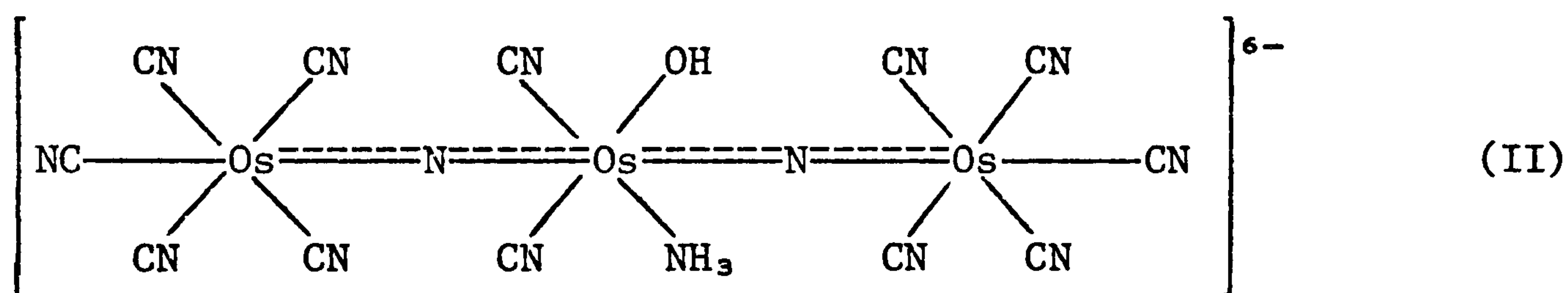
<u>Reaction</u>	<u>Time</u> (hours)	<u>Colour</u>	<u>U.V.</u> <u>Spectrum of</u> <u>Reaction Mixture</u> (n.m.)	<u>Main Species</u> <u>Present</u>
OsO_4	0	pale yellow	250s	OsO_4
$\text{OsO}_4 + \text{HCl}$	24	pale yellow	250s	OsO_4
$\text{OsO}_4 + \text{HCl} + \text{NH}_4\text{OH}$	24	orange	280s, 250s	$[\text{OsO}_4(\text{OH})_2]^{2-}$
	25	yellow	240s, 317m, 357w	$[\text{OsO}_3\text{N}]^-$
	28	brown	245s, 325s	
Addition of EtOH	29	brown precipitate	248s, 329s	osmium-ammine complex

The preparation of the osmium-ammine complex follows a similar procedure to that of ruthenium red except that the starting material is OsO_4 . The results listed in Table 6-1 indicate that the main reaction taking place is between OsO_4 and ammonia via $[\text{OsO}_3\text{N}]^-$ and that HCl has little if any important function.

OsO_4 was treated with concentrated aqueous ammonia and the reaction carried out as for the preparation of Gautiers osmium-ammine complex but excluding the addition of HCl , the heating of the reaction mixture to 90°C and the treatment of the solution with oxygen. A brown product was obtained, the electronic and infrared spectra of which were the same

as for the original osmium-amine complex; the infrared spectrum of the product showed two bands near 1000 cm^{-1} which are assigned to the asymmetric stretching vibration of the nitrido bridge, $\nu_{\text{Os}_2\text{N}}^{\text{as}}$. The complex was found to have the overall stoichiometry $[\text{Os}_3\text{N}_7\text{O}_9\text{H}_{21}]$ but is likely to be a mixture of trinuclear nitrido species with varying hydroxy and ammonia ligands.

The brown nitrido complex was refluxed with KCN solution to give a light brown product of stoichiometry $\text{K}_3[\text{Os}_3\text{N}_2(\text{CN})_{12}(\text{NH}_3)\text{OH}]6\text{H}_2\text{O}$. The infrared spectrum of the complex showed bands near 980 cm^{-1} and 1020 cm^{-1} assigned to the stretching vibration $\nu_{\text{Os}_2\text{N}}^{\text{as}}$ and bands assigned to $\nu_{\text{C}\equiv\text{N}}$ near 2100 cm^{-1} . This complex is therefore tentatively formulated as a trinuclear nitrido bridged species (II).



This suggests that Gautier's osmium-amine complex may also be a trinuclear species. However, since the ammine complex is almost certain to be a mixture of trinuclear species, it was decided to study the characterised analogous binuclear nitrido complexes²⁰² to determine the exact role of SO_2 in the staining of aldehydic functions and to isolate the active intermediates involved.

Section 6-C Binuclear Nitrido Complexes

The binuclear nitrido complexes $[\text{Os}_2\text{N}(\text{NH}_3)_8\text{Cl}_2](\text{NO}_3)_3$ and $[\text{Ru}_2\text{N}(\text{NH}_3)_8\text{Cl}_2](\text{NO}_3)_3$, when treated in aqueous solution with SO_2 , were found to act as stains for aldehydic moieties in the same way as the

trinuclear complexes discussed in Section 6-B; however they were found to be inactive as stains when not treated with SO_2 . In addition, if the tissue section was treated with SO_2 , rinsed with distilled water and then treated with an aqueous solution of the nitride complex, no staining occurred. This suggests that the active species involved in the staining process is formed by reaction of the nitride complex with SO_2 .

The complexes $[\text{Os}_2\text{N}(\text{NH}_3)_8\text{Cl}_2](\text{NO}_3)_3$ and $[\text{Ru}_2\text{N}(\text{NH}_3)_8\text{Cl}_2](\text{NO}_3)_3$ were treated in aqueous solution with SO_2 . Addition of KI to these reaction mixtures however yielded no sulphito complexes but gave only $[\text{Os}_2\text{N}(\text{NH}_3)_8\text{Cl}_2]\text{I}_3$ and $[\text{Ru}_2\text{N}(\text{NH}_3)_8\text{Cl}_2]\text{I}_3$ respectively. Attempts to prepare water soluble binuclear sulphito complexes failed.

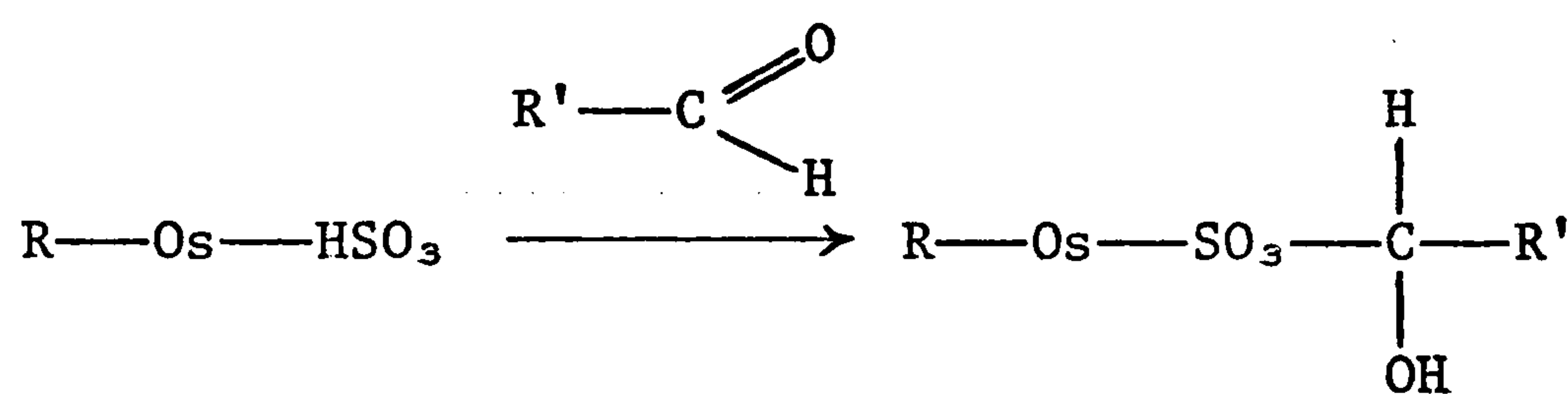
$[\text{Os}_2\text{N}(\text{NH}_3)_8\text{Cl}_2](\text{NO}_3)_3$ was treated in aqueous solution with SO_2 for five minutes and the excess SO_2 removed in vacuo. The resulting pale yellow solution failed to act as a stain. U.V. spectral analysis of this solution indicated that the only species present was in fact the starting material $[\text{Os}_2\text{N}(\text{NH}_3)_8\text{Cl}_2](\text{NO}_3)_3$. However, a positive result was obtained if SO_2 was bubbled through the nitride solution and the staining test carried out in the presence of excess SO_2 . Since it is known that the ligands X trans to the nitrido bridge in the complexes $[\text{M}_2\text{N}(\text{NH}_3)_8\text{X}_2]^{3-}$ tend to be labile and can be readily replaced by other single charged ligands,²⁰² it seems likely that an equilibrium exists in solution, probably:-



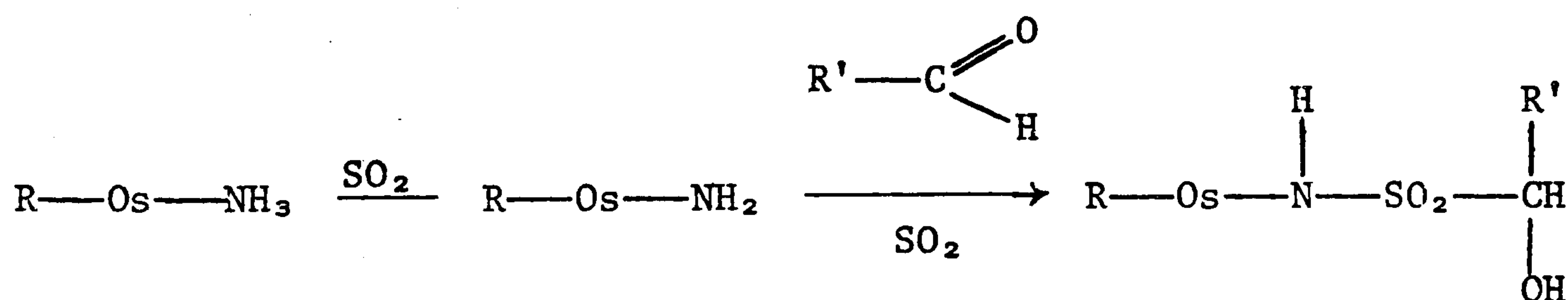
In the presence of excess SO_2 (HSO_3^- in solution) an osmium bisulphite complex, possibly $[\text{Os}_2\text{N}(\text{NH}_3)_8(\text{HSO}_3)_2]^{3+}$, exists in solution and acts as the active staining agent. On removal of excess of SO_2 , however, the equilibrium moves to the left, leading to the reformation of the non-active starting material.

The results of staining tests carried out on a series of osmium and ruthenium complexes are listed in Table 6-2. The sections were either treated with periodic acid to convert glycogen to aldehydic moieties or treated with HCl to hydrolyse DNA fragments. Photographs of sections stained by trinuclear and binuclear nitrido complexes are shown in Fig.6-1.

Two possible mechanisms for the staining of aldehydic moieties by nitrido complexes are illustrated in Schemes 1 and 2; the osmium bisulphite complex may form an addition complex with an aldehyde group (Scheme 1), or reaction of the osmium-ammine complex with SO₂ forms an amide species which reacts with the bisulphite addition complex of the aldehydic moiety (Scheme 2).



Scheme 1



Scheme 2

The formation of an osmium-amide complex by reaction of the ammine with SO₂ has been proposed,²¹¹ but it seems unlikely that a strong reducing agent such as SO₂ would oxidise an ammine to an amide. However, if the formation of an osmium bisulphite addition complex is taking place (Scheme 1), it is difficult to explain why bisulphite complexes such as [Ru(NH₃)₄(HSO₃)₂] do not act as e.m. stains.

Table 6-2

Staining Results Using Ammine and Sulphito Complexes
of Osmium and Ruthenium

[Staining tests carried out by Mr. D. Robinson and Dr. M. Birbeck]

Compound	Treatment		Staining ^a
	Compound	Section ^b	
$[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]\text{Cl}_6$	5 mins SO_2	1% PA 1 hr	5+
	-	1% PA 1 hr	-ve
$[\text{Os}_2\text{N}(\text{NH}_3)_8\text{Cl}_2](\text{NO}_3)_3$	5 mins SO_2	1% PA 1 hr	5+
"	10 mins SO_2 and free SO_2 removed under vacuum	1% PA 1 hr	-ve
"	"	1% PA 1 hr then 30 mins SO_2 and rinsed with water	-ve
"	10 mins SO_2 and free SO_2 removed under vacuum then SO_2 5 mins	1% PA 1 hr	5+
"	"	-	-ve
$[\text{Os}_2\text{N}(\text{NH}_3)_8\text{Cl}_2]\text{Br}_3$	5 mins SO_2	1% PA 1 hr	5+
	-	1% PA 1 hr	-ve
	5 mins SO_2	-	-ve
Gautier Nitrido Complex ^c	5 mins SO_2	1% PA 1 hr	5+
	-	1% PA 1 hr then SO_2 and rinsed with water	-ve
	5 mins SO_2	-	-ve
$\text{Na}_6[\text{OsO}_2(\text{SO}_3)_4]^{\text{d}}$	-	1% PA 1 hr	-ve
$[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)]\text{Cl}^{\text{d}}$	-	1% PA 1 hr	-ve
$[\text{Ru}(\text{NH}_3)_4(\text{HSO}_3)_2]^{\text{d}}$	-	1% PA 1 hr	-ve
$[\text{Ru}(\text{NH}_3)_5(\text{SO}_3)]2\text{H}_2\text{O}^{\text{d}}$	-	1% PA 1 hr	-ve

Table 6-2 [continued]

Compound	Treatment		Staining ^a
	Compound	Section ^b	
$[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ ^d	5 mins SO_2	1% PA 1 hr	2+
	-	1% PA 1 hr then SO_2 and rinsed with water	-ve
$[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ ^d	5 mins SO_2	1% PA 1 hr	3+
	-	1% PA 1 hr then SO_2 and rinsed with water	-ve
$[\text{Os}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ ^d	5 mins SO_2	1% PA 1 hr	1+
	-	1% PA 1 hr then SO_2 and rinsed with water	-ve
$[\text{Os}_2\text{N}(\text{NH}_3)_8\text{Cl}_2](\text{NO}_3)_3$	5 mins SO_2	6N HCl 1 hr	3+

^a Graded from 1+ to 5+; 5+ represents good staining properties.

^b Staining carried out on glycogen treated with PA (Periodic Acid) or on D.N.A. fragments treated with HCl .

^c Prepared by literature method ²¹¹ or by reaction of OsO_4 with aqueous ammonia.

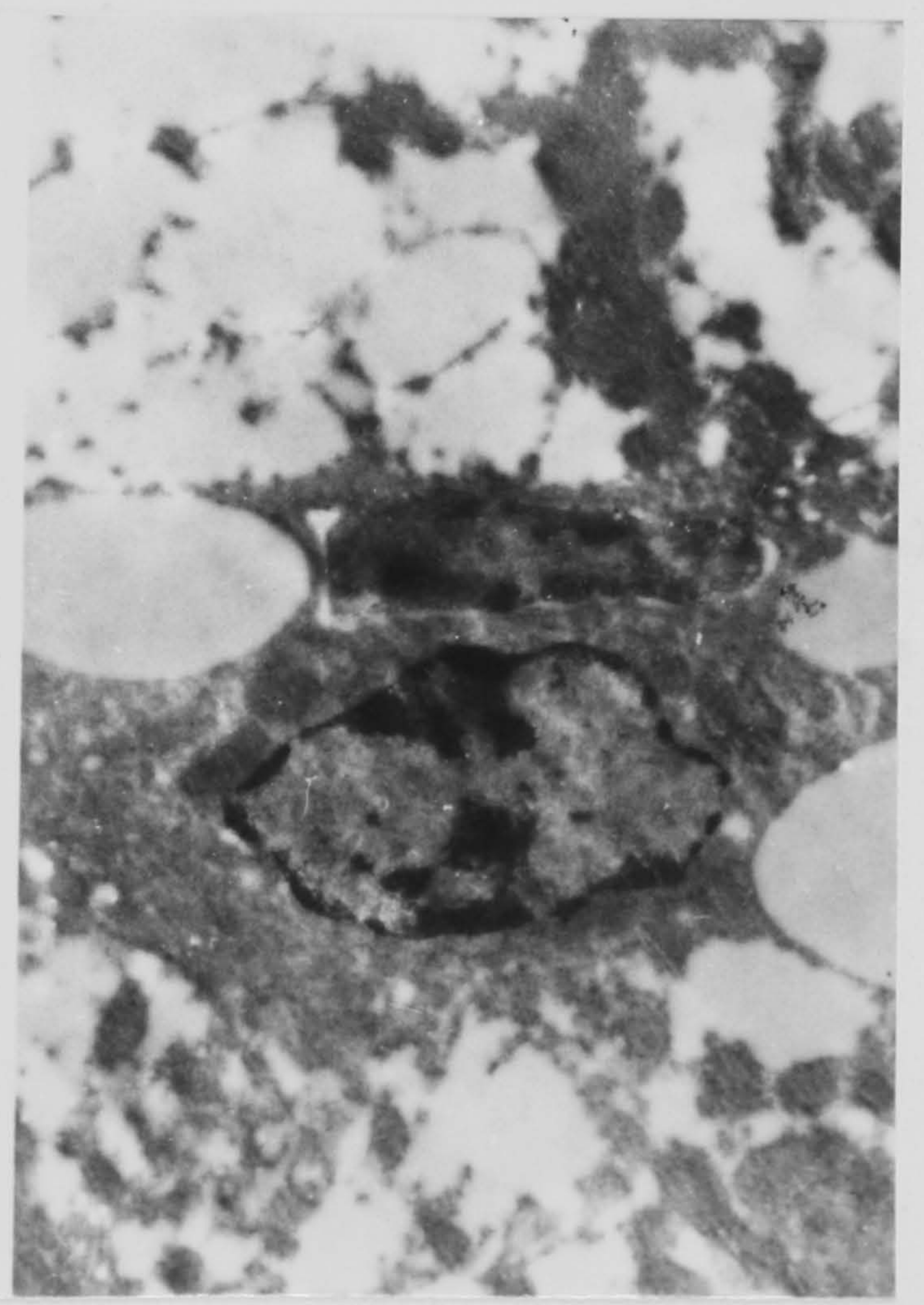
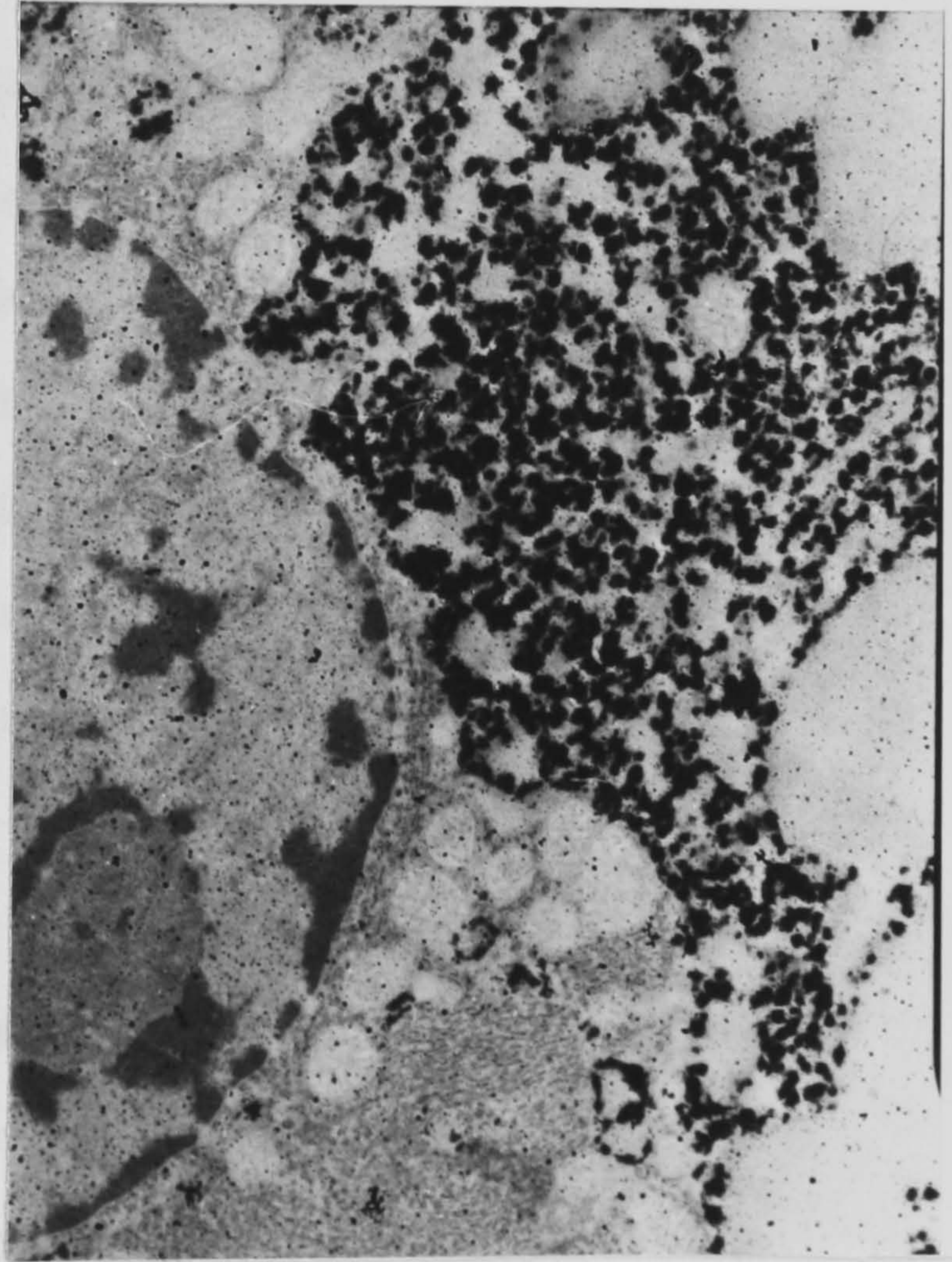
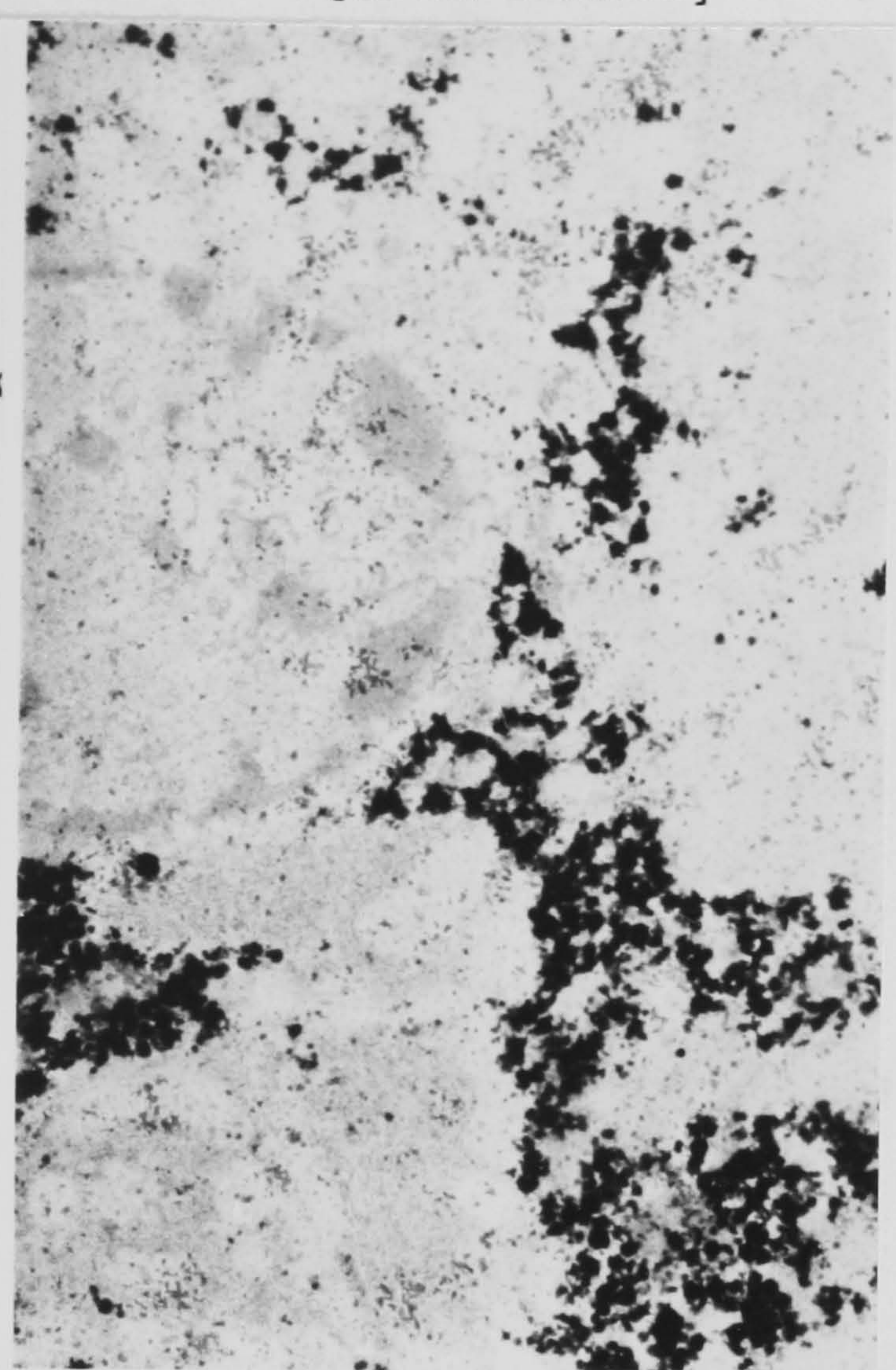
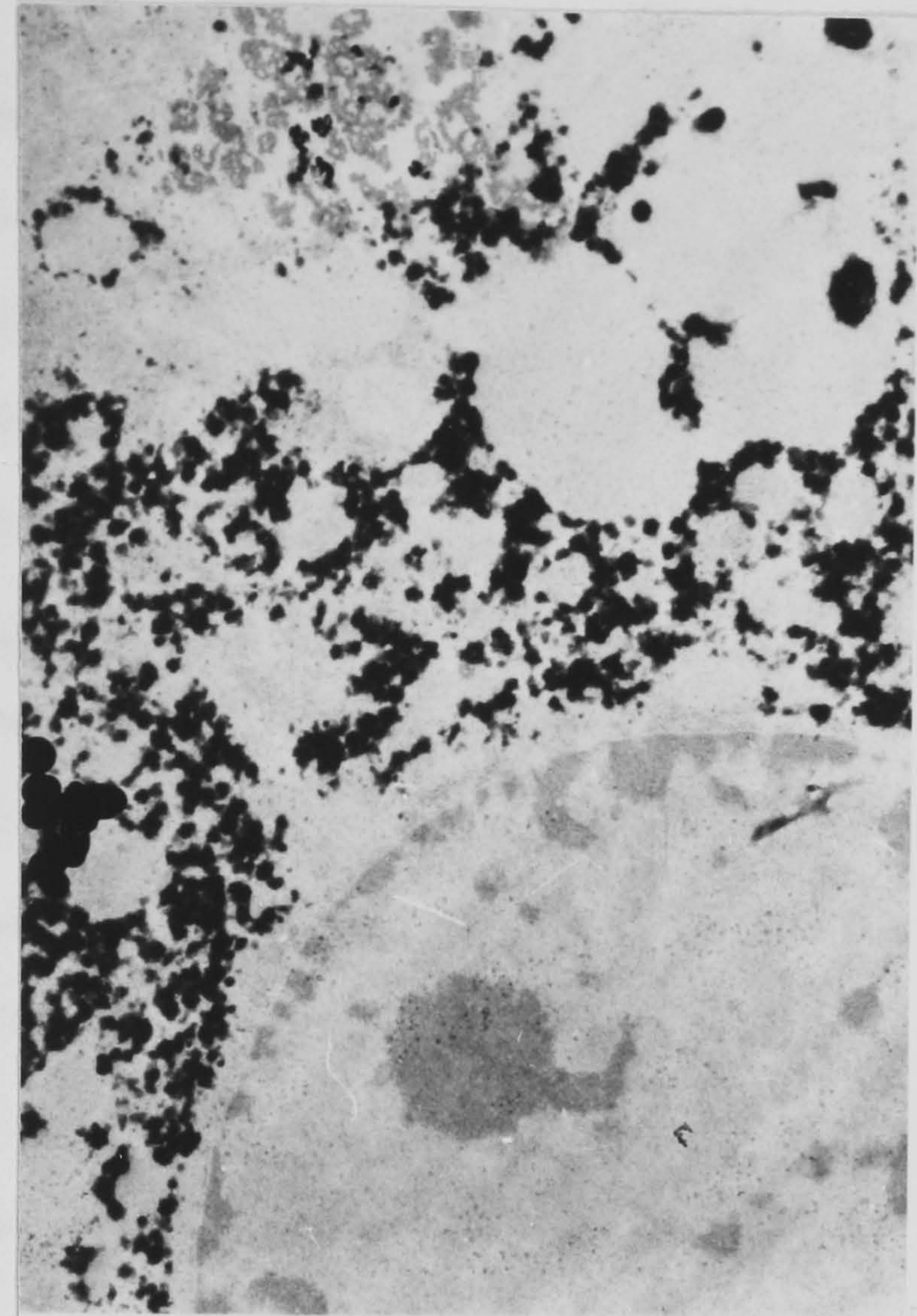
^d Complexes prepared by J. Hall.

Figure 6-1

Electron Microscopy Staining of Biological Tissues by Nitrido
Complexes of Osmium and Ruthenium

a [liver section]

b [liver section]



c [liver section]

d [pancreas section]

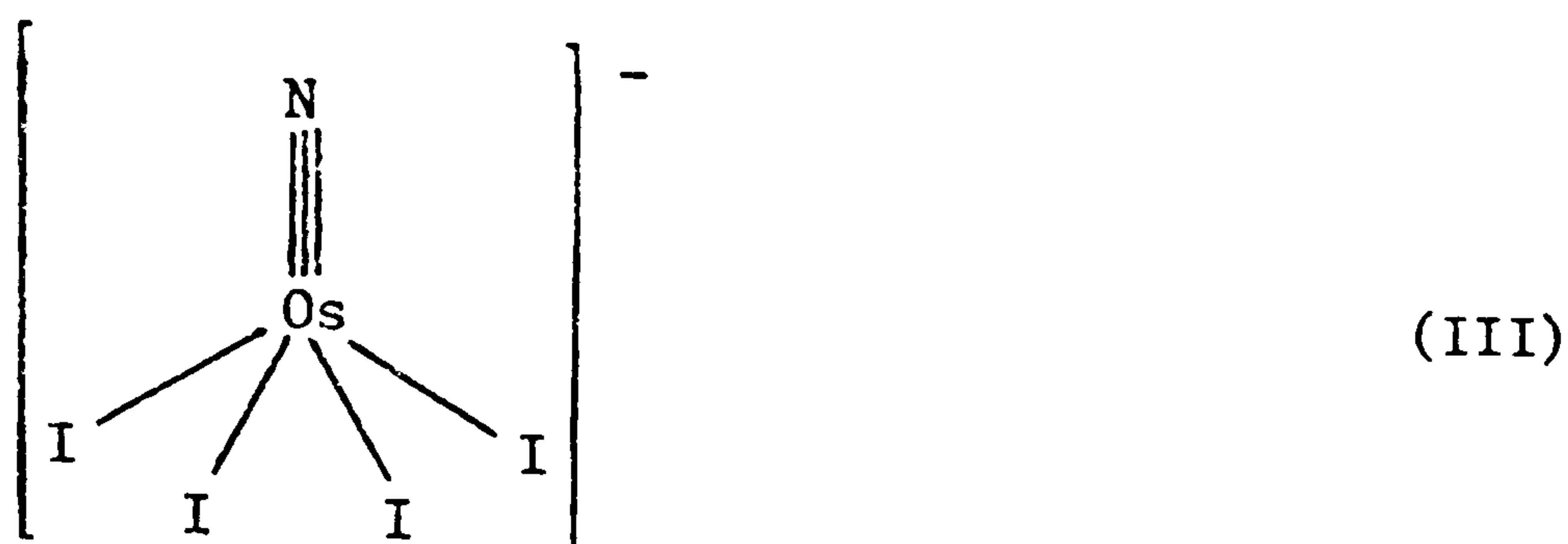
- a glycogen staining by Gautier's osmium-ammine complex.
- b glycogen staining by Gautier's osmium-ammine complex prepared by modified method.
- c glycogen staining by $[\text{Os}_2\text{N}(\text{NH}_3)_8\text{Cl}_2](\text{NO}_3)_3$.
- d DNA staining by $[\text{Os}_2\text{N}(\text{NH}_3)_8\text{Cl}_2](\text{NO}_3)_3$.

Section 6-D Mononuclear Nitrido Complexes

The only known osmium(VIII) mononuclear nitrido complex is the osmiamate $[\text{OsO}_3\text{N}]^-$ anion,^{10,11,213} although many osmium(VI) and ruthenium(VI) mononuclear nitrido complexes are known; e.g., $[\text{OsNX}_4]^-$,^{136,214} $[\text{OsNX}_5]^{2-}$,^{67,198} $[\text{RuNX}_4]^-$ ^{67,198} and $[\text{RuNX}_5]^{2-}$ ^{67,198} (X = Cl or Br). The infrared spectra of these complexes show bands in the region 1020-1120 cm^{-1} assigned to metal-nitride stretching vibration, $\nu_{\text{M}\equiv\text{N}}$. It is of interest to note that the change from six to five coordination in these complexes brings about an increase in the frequency of $\nu_{\text{M}\equiv\text{N}}$. The shorter Os $\equiv$ N distance in $\text{Ph}_4\text{As}[\text{OsNCl}_4]$ as compared with $\text{K}_2[\text{OsNCl}_5]$ has been explained in terms of predominantly electronic effects, rather than steric.²¹⁵ The possible electronic repulsion effects of the very strongly π -donating terminal nitrido ligand have been discussed for the complexes $\text{Ph}_4\text{As}[\text{OsNCl}_4]$ ²¹⁶ and $\text{Ph}_4\text{As}[\text{OsNI}_4]$.²¹⁷

Treatment of the complexes $[\text{MNCI}_4]^-$ with PR_3 or AsPh_3 yield the products $[\text{M}(\text{NPR}_3)\text{Cl}_3(\text{PR}_3)_2]$ and $[\text{MNCI}_3(\text{AsPh}_3)_2]$ respectively.²¹⁸⁻²²¹ The infrared spectra of the complexes $[\text{M}(\text{NPR}_3)\text{Cl}_3(\text{PR}_3)_2]$ show a strong band in the 1050-1200 cm^{-1} region assigned to the P=N stretching vibration, $\nu_{\text{P}=\text{N}}$, while the infrared spectra of the complexes $[\text{MNCI}_3(\text{AsPh}_3)_2]$ and $[\text{MNCI}_3(\text{PR}_3)_2]$, prepared by reaction of $[\text{M}(\text{NPR}_3)\text{Cl}_3(\text{PR}_3)_2]$ with chlorine,²²⁰ show a band near 1060 cm^{-1} assigned to the metal-nitride stretching vibration, $\nu_{\text{M}\equiv\text{N}}$.²²⁰

The tetraiodo nitrido complex $\text{Ph}_4\text{As}[\text{OsNI}_4]$ has been previously prepared^{136,198} and a single-crystal X-ray study of this complex has confirmed the presence of a distorted square-based pyramidal $[\text{OsNI}_4]^-$ ion²¹⁷ (III).



This is an unusual complex for iodine to form in view of the high oxidation state of the osmium. The infrared spectrum of $\text{Ph}_4\text{As}[\text{OsNI}_4]$ shows a strong band at 1106 cm^{-1} assigned to the stretching vibration, $\nu_{\text{Os}\equiv\text{N}}$. In an attempt to prepare other salts of $[\text{OsNI}_4]^{-}$, $\text{K}[\text{OsO}_3\text{N}]$ was treated with HI in the presence of Ph_4PCl . The infrared spectrum of the orange product $\text{Ph}_4\text{P}[\text{OsNI}_4]$ shows a band at 1158 cm^{-1} assigned to the stretching vibration, $\nu_{\text{Os}\equiv\text{N}}$, (Figure 6-2). This shift to higher frequency of the $\nu_{\text{Os}\equiv\text{N}}$ mode for $\text{Ph}_4\text{P}[\text{OsNI}_4]$ as compared for $\text{Ph}_4\text{As}[\text{OsNI}_4]$ is most likely due to the presence of the different cation.

Reaction of the complexes $\text{Ph}_4\text{M}[\text{OsNI}_4]$ with pyridine or isoquinoline (L) leads to the formation of products of stoichiometry $\text{Ph}_4\text{M}[\text{OsNI}_3\text{L}_2]$. These products are tentatively formulated as Os(V) species involving a triple $\text{Os}\equiv\text{N}$ bond, the infrared spectra of the complexes showing bands assigned to $\nu_{\text{Os}\equiv\text{N}}$ near 1070 cm^{-1} . Magnetic susceptibility measurements on these complexes however indicate that they are diamagnetic.

The complexes $\text{Ph}_4\text{M}[\text{OsNI}_4]$ react with PPh_3 to give purple products of stoichiometry $\text{Ph}_4\text{M}[\text{OsN}(\text{PPh}_3)_2\text{I}_4]$. The infrared spectra of the complexes show no bands assigned to $\nu_{\text{Os}\equiv\text{N}}$ or $\nu_{\text{P}=\text{N}}$ and are therefore tentatively formulated as Os(IV) species $[\text{Os}(\text{N}(\text{PPh}_3)_2)\text{I}_4]^{-}$ with two phosphine ligands coordinated to nitrogen.

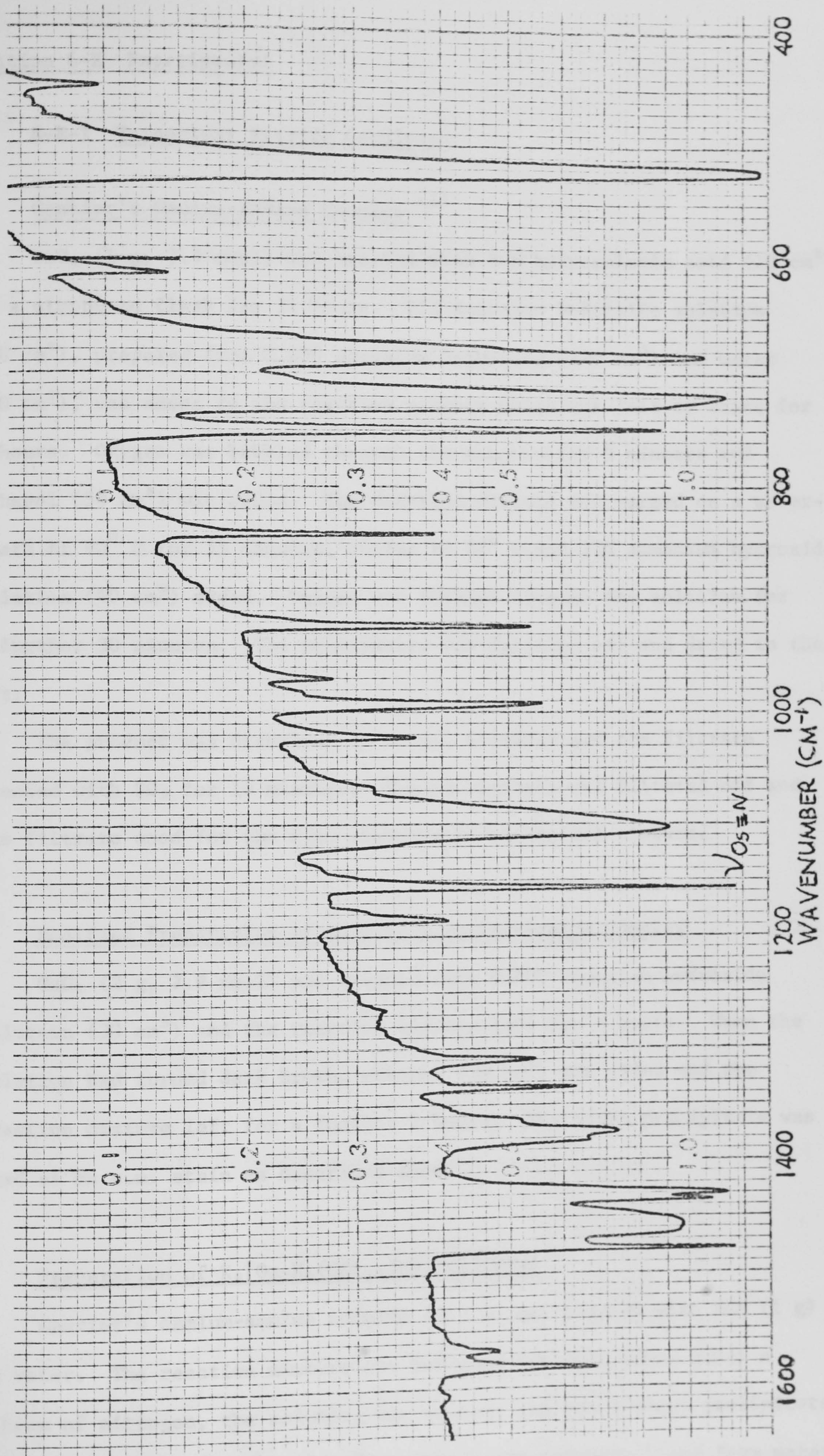


Figure 6-2. Infrared Spectrum of $\text{Ph}_4\text{P}[\text{OsNI}_4]$

Section 6-E Experimental

6-E-1 Trinuclear Nitrido Complexes

Gautier's Osmium-Ammine Complex ²¹¹

OsO_4 (1 g, 3.9 mmol) was treated with 5 M hydrochloric acid (10 cm^3) in a stoppered flask for 24 hours. 25% Ammonium hydroxide solution (30 cm^3), prepared from 0.880 ammonium hydroxide (100 cm^3) and water (40 cm^3), was added to the reaction mixture which was left to stand for 3 hours. Oxygen was bubbled through the solution for 5 minutes and ethanol (50 cm^3) was added. The reaction mixture was warmed on a water-bath at 90°C for 15 minutes, cooled to 60°C and 25% ammonium hydroxide solution (40 cm^3) added. Oxygen was bubbled through the solution for a further 30 minutes. The precipitate was filtered off and dried in the air.

The product was dissolved in water, filtered and the filtrate treated with SO_2 for 10 minutes. The precipitate was filtered off and the filtrate used for the e.m. staining of biological tissues.

Modified Preparation of Gautier's Osmium-Ammine Complex

OsO_4 (2 g, 7.9 mmol) was treated with 0.880 ammonium hydroxide solution (30 cm^3) and the reaction mixture left for 3 hours. When the solution had turned dark brown, ethanol (50 cm^3) was added and the reaction mixture left for a further 2 hours. The brown precipitate was used as an e.m. stain as described above.

Preparation of $\text{K}_6[\text{Os}_3\text{N}_2(\text{CN})_{12}(\text{NH}_3)\text{OH}]\cdot 6\text{H}_2\text{O}$

Gautier's osmium-ammine complex (0.3 g) was treated with KCN (1 g) in water. The reaction mixture was refluxed for five hours under a stream of nitrogen, the solution was cooled, and the product precipitated by fast addition of methanol. The complex was recrystallised from water

and methanol.

Elemental analyses Found:- C, 11.45%; H, 0.88%; N, 16.05%; K, 18.17%; O, 8.43%
 $C_{12}H_{16}N_{15}O_7K_6Os_3$ Requires:- C, 11.19%; H, 1.25%; N, 16.32%; K, 18.22%; O, 8.70%.

6-E-2 Binuclear Nitrido Complexes

The complexes $[Os_2N(NH_3)_8X_2]X_3$ and $[Ru_2N(NH_3)_8X_2]X_3$ ($X = Cl$ or NO_3) were prepared by the published method.²⁰² The complexes were treated with SO_2 for five minutes and the resulting aqueous solutions used as e.m. stains for biological tissues.

6-E-3 Mononuclear Nitrido Complexes

Tetraphenylphosphonium Tetraiodonitrido Osmium(VI) $Ph_4P[OsNI_4]$

$K[OsO_3N]$ (2 g, 6.9 mmol) was stirred with mixture of concentrated HI (s.g. = 1.7 g cm^{-3} , 10 cm^3) and water (10 cm^3) for 5 minutes at 0°C . A solution of tetraphenylphosphonium chloride (3 g, 8.0 mmol) in methanol (10 cm^3) was added to the reaction mixture. After 5 minutes, acetone (40 cm^3) was added and the solution filtered. The precipitate was copiously washed with acetone and recrystallised from methyl cyanide.

Elemental analyses Found:- C, 27.65%; H, 1.83%; N, 1.37%; P, 2.90%

$C_{24}H_{20}NI_4POs$ Requires:- C, 27.42%; H, 1.92%; N, 1.33%; P, 2.95%

Elemental analyses Found:- C, 26.45%; H, 1.70%; N, 1.30%

$C_{24}H_{20}NI_4AsOs$ Requires:- C, 26.32%; H, 1.84%; N, 1.27%.

Preparation of Complexes $Ph_4M[OsNI_3L_2]$ ($M = P$ or As ; $L = \text{pyridine}$ or isoquinoline)

The preparation of $Ph_4As[OsNI_3(C_5H_5N)_2]$ is typical.

$Ph_4As[OsNI_4]$ (0.2 g, 0.18 mmol) in methyl cyanide (40 cm^3) was treated with pyridine (2 cm^3) and the reaction mixture stirred for 1 hour. The solution was reduced in volume, the product precipitated by addition of

diethyl ether and recrystallised from acetone and diethyl ether.

Elemental analyses Found:- C, 36.95%; H, 2.59%; N, 3.46%

$C_{34}H_{30}N_3I_3AsOs$ Requires:- C, 36.25%; H, 2.68%; N, 3.73%

Elemental analyses Found:- C, 37.50%; H, 2.79%; N, 2.45%; P, 3.17%

$C_{34}H_{30}N_3I_3POs$ Requires:- C, 37.97%; H, 2.81%; N, 3.26%; P, 2.77%

Elemental analyses Found:- C, 40.66%; H, 2.87%; N, 3.24%

$C_{42}H_{34}N_3I_3AsOs$ Requires:- C, 41.13%; H, 2.79%; N, 3.43%.

Preparation of Complexes $Ph_4M[Os(N(PPh_3)_2)I_4]$ (M = P or As)

The preparation of $Ph_4P[Os(N(PPh_3)_2)I_4]$ is typical.

$Ph_4P[OsNI_4]$ (0.2 g, 0.19 mmol) in methyl cyanide (40 cm³) was treated with PPh_3 (1 g, 3.8 mmol). The reaction mixture slowly turned purple and after two hours was reduced in volume. The product was precipitated by addition of diethyl ether and recrystallised from acetone and diethyl ether.

Elemental analyses Found:- C, 44.08%; H, 3.43%; N, 2.31%; P, 3.58%

$C_{60}H_{50}NI_4P_2AsOs$ Requires:- C, 44.49%; H, 3.11%; N, 0.86%; P, 3.82%

Elemental analyses Found:- C, 45.30%; H, 3.28%; N, 2.02%; P, 5.26%

$C_{60}H_{50}NI_4P_3Os$ Requires:- C, 45.73%; H, 3.20%; N, 0.89%; P, 5.90%.

PHYSICAL MEASUREMENTS

Microanalyses were performed by the Microanalytical Department, Imperial College, A. Bernhardt (Munich) and F. Pascher (Bonn). Infrared spectra were recorded ($200\text{--}4000\text{ cm}^{-1}$) on Perkin-Elmer 457 and 325 instruments as Nujol mulls between caesium iodide plates, and in various solvents using potassium bromide cells. ^1H n.m.r. spectra were measured on a Perkin-Elmer R-12B instrument operating at 60 MHz. Electronic spectra were obtained using a Perkin-Elmer 402 instrument. Raman spectra were measured on a Spex Ramalog 5 instrument with a DPC-2 detector using a krypton-ion laser; solids were scanned as 5% sample - 95% KBr spun discs and solutions in chloroform in a spinning solution cell. Magnetic susceptibility measurements were made on solids by the Gouy method and on solutions by the Evans' method.²²² Mass spectra were obtained on a VG 7070 instrument and molecular weights were determined osmotically on a Perkin-Elmer-Hitachi 115 instrument.

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