PLATINUM METAL NITRIDO COMPLEXES

AND RELATED SPECIES

A thesis submitted for the degree of

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by

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ABSTRACT

The research described in this thesis is concerned with the preparation, characterisation, and chemical and physical properties of complexes containing a nitrido ligand, N^{3-}. Particular use has been made of vibrational spectroscopy, and ^{15}N and ^{2}D isotopic substitution has helped in the assignment of vibrational modes.

New ruthenium terminal nitrido halide complexes have been prepared from trans-dioxo species by azide decomposition reactions. They are five or six coordinate, $R[RuNX_4]$, or $Cs_2[RuNX_5]$ (X = Cl, Br; R = Ph_4As, Bu^n_4N) according to the cation used as precipitant; osmium nitrido halide complexes showed similar behaviour. Some new ruthenium oxo and dioxo complexes have been prepared as potential precursors for further nitrido species.

The reactions of $R[MNX_4]$ (M = Ru, Os) with tertiary phosphine, arsine, and stibine ligands, LR'_3, have been studied. Substituted nitrido complexes of the type $[MNX_3(LR'_3)_2]$ have been obtained, and also species with phosphinenitride ligands $[M(NPR'_3)Cl_3(PR'_3)_2]$. The nitrene-like behaviour of the nitrido ligand in M(VI) complexes is discussed.

New binuclear nitrido complexes with an Ru-N-Ru unit and attendant π-bonding and chelating ligands are described. Some supposed osmium oxo ammine species have been reformulated as trinuclear complexes with bridging nitrido ligands.

The reaction of sulphamic acid with platinum metal chlorides has been

investigated as a potential route to nitrido complexes. Salts containing an N-bonded sulphamato ligand, $K_3[M'Cl_5(NH_2SO_3)]$, and lattice sulphamic acid, $K_3[M'Cl_6].nNH_3SO_3$, (M' = Rh, Ir, Ru, Os; n = 0.9-1.1) have been isolated.

To my parents and sister.

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Abbreviations and symbols

1. Vibrational spectra

Frequency units for infra - red (i.r.) and Raman spectra are wavenumbers, cm^{-1}. Vibrational modes involved with the stretching, deformation, or rocking of a particular bond or group are designated ν, δ, or ρ respectively. Subscripts to these symbols refer to the bond or group involved in the vibration, or the symmetry of the vibration, sym, symmetrical or asym, asymmetric. I.r. absorptions are described as s, strong, m, medium, or w, weak in intensity, and these descriptions may be qualified by v, very, m, moderately, br, broad, or sh, shoulder.

2. Ligands and radicals

Me,	methyl, CH_3.	Dae,	1,2-diaminoethane.
Et,	ethyl, C_2H_5.	Ox,	oxalate, $C_2O_4^{2-}$.
Bu^n,	n-butyl, C_4H_9.	Dtc,	N,N'-diethyldithiocarbamate.
Ph,	phenyl, C_6H_5.	R,	alkyl or aryl.
Py,	pyridine, C_5H_5N.	L,	ligand.
Bipy,	2,2'-bipyridine.		

3. Miscellaneous

Å,	Ångstrom unit.	χ_g,	gram susceptibility.
B.M.	Bohr magnetons.	μ_{eff}	effective magnetic moment.
m.p.	melting point.		
nm,	nanometres.		
n.m.r.	nuclear magnetic resonance		

CHAPTER 1

INTRODUCTION.

The work presented in this thesis is mainly concerned with the preparation and characterisation of complexes containing a nitrido ligand, N^{3-}, and an investigation of the structures and reactions of complexes of this uncommon ligand. The research has been carried out using the platinum group metals, ruthenium, rhodium, osmium and iridium, but we shall concentrate mainly on ruthenium and osmium, since they both have commonly occurring high oxidation states which are able to stabilise the nitrido ligand. Here we shall discuss the properties of the ligand, its occurrence in metal complexes, the structures and bonding of such, and the application of various physical techniques in characterising nitrido complexes. A discussion of *trans*-effect and *trans*-influence with respect to the nitrido ligand is also included, since it is frequently claimed to exert either or both of these properties. We shall only consider species with discrete molecular units $[MN_xL_y]_z^{n-}$ $(Z \leqslant 4)$

1 - A. GENERAL SURVEY OF NITRIDO COMPLEXES[1]

1 - A - 1. The nitrido ligand.

Transition metal complexes containing a nitrogen atom bonded solely to a metal or metals are normally considered to be complexes of the nitride anion, N^{3-}, and referred to as nitrido complexes[1], a convention and notation which we will adopt here. Pauling has estimated the radius of the N^{3-} ion as 1.71 Å [2], but even in the most 'ionic' nitrides (e.g. Li_3N) there is likely to be significant covalent bonding. In nitrido complexes the short metal-nitrogen distances (1.6 - 1.9 Å) are normally considered indicative of strong

σ- and π- covalent bonding. Since all the available ligand orbitals will be filled, overlap with empty metal orbitals of the appropriate symmetries and energies will give a favourable bonding situation. As a consequence, the nitrido ligand will tend to stabilise (or be stabilised by) metals in high oxidation states. In these respects the nitrido ligand is very similar to the isoelectronic oxo ligand, and indeed many useful comparisons can be made between the two[3].

The presence of extensive multiple covalent bonding between ligand and metal means that little significance can be attached to the formal oxidation state of the metal in nitrido complexes. In a formal sense, they could equally well be regarded as complexes of deprotonated nitrene, N^-, i.e. in valence bond terms we have two canonical forms:

$$\left[M^{x+}(N^{3-})\ L_y\right] \leftrightarrow \left[M^{(x-2)+}\ (N^-)\ L_y\right].$$

The electron distribution in a particular M-N bond will be a function of the suitability of the required metal-ligand orbital overlaps and the electronegativity of the metal.

1 - A - 2. Types of nitrido complexes.

Complexes with nitrido ligands have been established for relatively few transition metals, namely vanadium, molybdenum, tungsten, rhenium, ruthenium, osmium and iridium. The predominance of 2nd and 3rd row elements is noteworthy, and reflects their greater tendency to give high oxidation states. Nitrido complexes normally have highly distorted octahedral structures, and several cases of the distortions producing penta-coordinate complexes are now known. The three substituted oxo anions $\left[MO_3N\right]^{n-}$ (M = Mo, Re, Os) have distorted tetrahedral structures.

Several different structural environments are known for the nitrido ligand, and these are illustrated below:

a) Terminal nitrido complexes

$$L_y M \equiv N \quad \text{e.g.} \quad K_2\left[OsNCl_5\right],^4 \quad Os - N \text{ distance } 1.614\text{Å}.$$

b) Linear, symmetrically bridged nitrido complexes

$$L_y M \overset{x}{-} N \overset{x}{-} ML_y \quad \text{e.g.} \quad K_3\left[Ru_2NCl_8(H_2O)_2\right] \; ; \; x = 1.720\text{Å} \quad \text{(Ref. 5)}$$

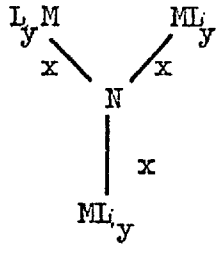
c) Linear, asymmetrically bridged nitrido complexes.

$$L_y M \overset{x}{-} N \overset{x'}{\text{———}} ML_y \quad \text{e.g.} \quad K_{2n}\left[ReN(CN)_4\right]_n \cdot nH_2O \; ; \; \text{(Ref 6)}$$

$$x = 1.53\text{Å}, \; x' = 2.44\text{Å}$$

The two metals here are not necessarily the same and $\sphericalangle$ MNM may vary slightly from 180°. Such a complex is best pictured as a terminal nitrido complex (See (a)) functioning as a weak nitrogen donor ligand to another metal.

d) Trigonal planar nitrido complexes



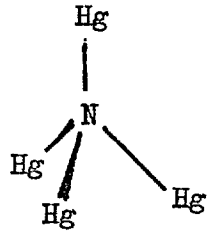
e.g. $(NH_4)_4\left[Ir_3N(SO_4)_6(H_2O)_3\right]$ [7]; x = 1.918Å

A linear trinuclear unit has been proposed for an ill-defined osmium (VI) complex[8]

$$L_y \; Os \text{ —— } N \text{ —— } Os \text{ —— } N \text{ —— } OsL_y$$

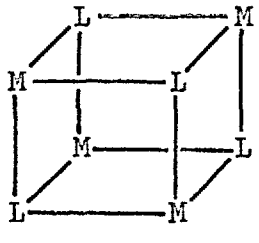
$$L_y$$

A tetrahedral environment for the nitrido ligand has been suggested for the complex $\left[(CH_3Hg)_4 N\right]ClO_4$ [9]



Each of the above types of nitrido complex have well defined oxo analogues, but there are several well known series of oxo complexes (e.g. $[MO_4]^{n-}$, $[MO_2L_4]^{n-}$, $[L_3OM(O)_2MOL_3]^{n-}$) which have no nitrido analogues.[3] There have been fewer investigations on nitrido than oxo complexes, but it is likely that the range of stable nitrido complexes will be more limited than those of oxide because of the more demanding π-bonding requirements of the nitrido ligand, and its greater charge delocalisation.

There are no complexes of the lower Group V congeners of the nitride ion with similar structures to the above nitrido types, but complexes with mononuclear phosphorus[10], arsenic[11] and antimony[12] ligands are known. They have structures similar to the hydrocarbon cubane, with two interpenetrating tetrahedra of metal and ligand atoms.



L = P, As, Sb.

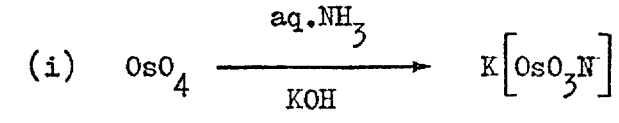
Since there are also oxo[13] and sulphido[14] analogues of these species, it is possible that nitride too will give complexes of this type.

1 - A - 3 Synthesis of nitrido complexes

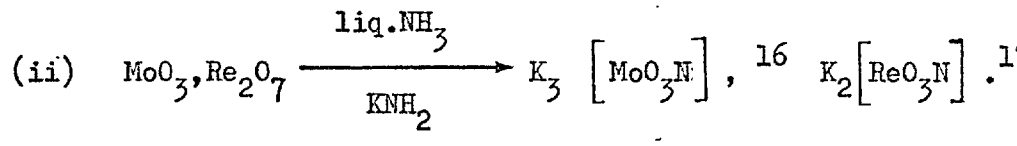
A more detailed discussion of the synthesis of nitrido complexes will

be given at the beginning of the appropriate chapter, but here we give a brief illustrated summary of the methods which have been used. There is no general preparative route, and each of the methods is normally quite specific in its application:

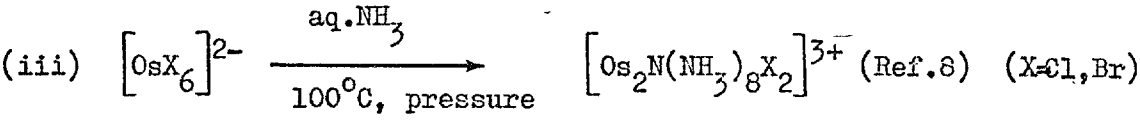
a) Deprotonation of ammonia.



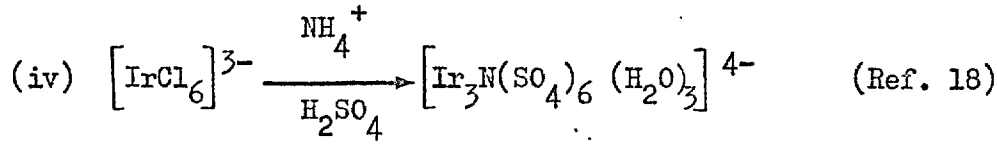
(i) $OsO_4 \xrightarrow[KOH]{aq.NH_3} K[OsO_3N]$ [15]



(ii) $MoO_3, Re_2O_7 \xrightarrow[KNH_2]{liq.NH_3} K_3[MoO_3N]$, [16] $K_2[ReO_3N]$. [17]

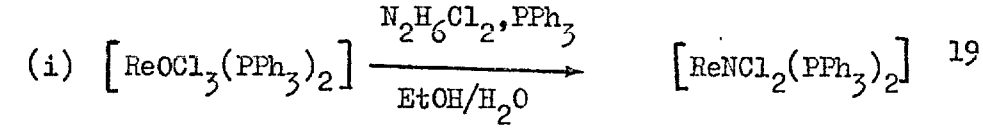


(iii) $[OsX_6]^{2-} \xrightarrow[100^oC,\ pressure]{aq.NH_3} [Os_2N(NH_3)_8X_2]^{3+}$ (Ref.8) (X=Cl,Br)



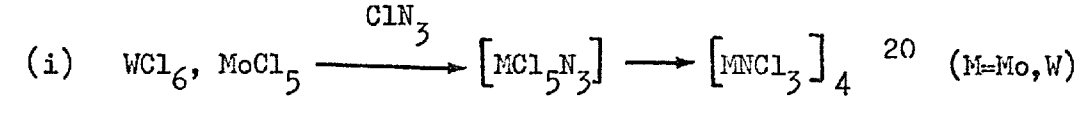
(iv) $[IrCl_6]^{3-} \xrightarrow[H_2SO_4]{NH_4^+} [Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ (Ref. 18)

b) Decomposition of hydrazine

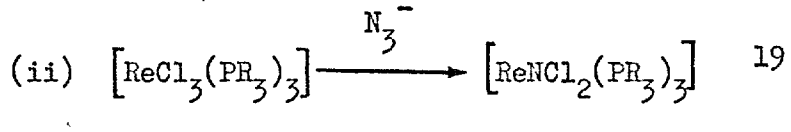


(i) $[ReOCl_3(PPh_3)_2] \xrightarrow[EtOH/H_2O]{N_2H_6Cl_2, PPh_3} [ReNCl_2(PPh_3)_2]$ [19]

c) Decomposition of azide



(i) WCl_6, $MoCl_5 \xrightarrow{ClN_3} [MCl_5N_3] \longrightarrow [MNCl_3]_4$ [20] (M=Mo,W)



(ii) $[ReCl_3(PR_3)_3] \xrightarrow{N_3^-} [ReNCl_2(PR_3)_3]$ [19]

d) Miscellaneous methods

$$\text{(i)}\quad (NH_4)_2[OsCl_6] \xrightarrow[Cl_2]{400^\circ} [Os_2NCl_5]_n \xrightarrow[Cs^+]{\text{aq.HCl,}} Cs_3[Os_2NCl_8(H_2O)_2]^{8}$$

$$\text{(ii)}\quad [Ru(NO)Cl_5]^{2-} \xrightarrow[\text{or HCHO}]{SnCl_2} [Ru_2NCl_8(H_2O)_2]^{3-} \quad \text{(Ref. 8)}$$

$$\text{(iii)}\quad \text{"}RuCl_3\text{"} \xrightarrow[HCl]{NH_3SO_3} (NH_4)_3[Ru_2NCl_8(H_2O)_2]^{21.}$$

1 - A - 4 Bonding in nitrido complexes.

No comprehensive bonding schemes have been proposed for terminal and linear, symmetrically bridged binuclear nitrido complexes, and we therefore use adaptations of the bonding schemes proposed for similar oxo species. The bonding in trigonal planar nitrido and oxo complexes has been discussed by Jørgensen[22].

(a) Terminal nitrido complexes

We use the bonding scheme proposed by Gray for vanadyl[23] and chromium and molybdenum[24] mono-oxo complexes, and apply it to the d^2 Os(VI) complex $[OsNCl_5]^{2-}$.

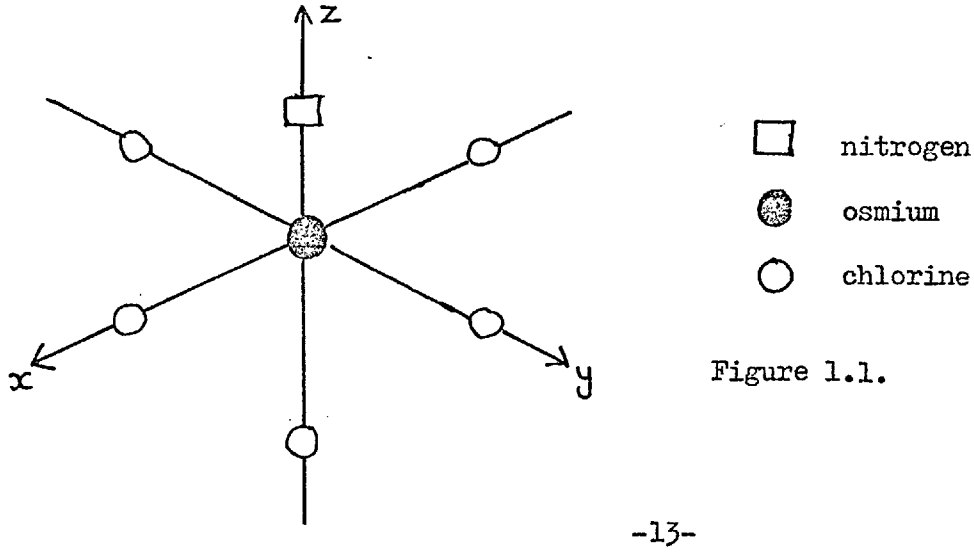


Figure 1.1.

For bonding purposes we use 5d, 6s, and 6p osmium orbitals, sp_σ chlorine orbitals, a nitrogen sp_σ orbital (σ_5),and two nitrogen p orbitals ($2p_x$ and $2p_y$). We assume no π-bonding between the osmium and the chloro ligands. Under C_{4v} symmetry the metal and ligand orbitals transform as shown below, and we set the metal and ligand orbitals which overlap side by side.

Representation	Metal Orbitals	Ligand Orbitals	Bond Description
a_1	$5d_z^2 + 6s$	σ_5	N-Os σ bond
	$6s - 5d_z^2$	$\frac{1}{2}(\sigma_1+\sigma_2+\sigma_3+\sigma_4)$	Cl_{cis} - Os σ bonds
	$6p_z$	σ_6	Cl_{trans} - Os σ bond
e	$5d_{xz}$, $5d_{yz}$	π_5 ($2p_x$, $2p_y$)	Two N - Os π bonds
	$6p_x$, $6p_y$	$\sqrt{\frac{1}{2}}(\sigma_1-\sigma_3)$, $\sqrt{\frac{1}{2}}(\sigma_2-\sigma_4)$	Cl_{cis} - Os σ bonds
b_1	$5d_{x^2-y^2}$	$\frac{1}{2}(\sigma_1-\sigma_2+\sigma_3-\sigma_4)$	Cl_{cis} - Os σ bonds
b_2	$5d_{xy}$		Non-bonding

Gray[23] has calculated the ordering of molecular orbitals so produced for the vanadyl system, and on this basis we show a simplified molecular orbital diagram for $[OsNCl_5]^{2-}$, showing for clarity only the orbitals of the metal-nitrogen bond. (See Figure 1.2.)

The six electrons in the nitrogen sp_σ and $2p_x$ and $2p_y$ orbitals, and the two from the osmium atom fill the bonding a_1 and e_π and non-bonding b_2 orbitals. Since the antibonding orbitals remain unfilled, the Os-N linkage has a bond order of three. We would thus expect that d^2 terminal nitrido

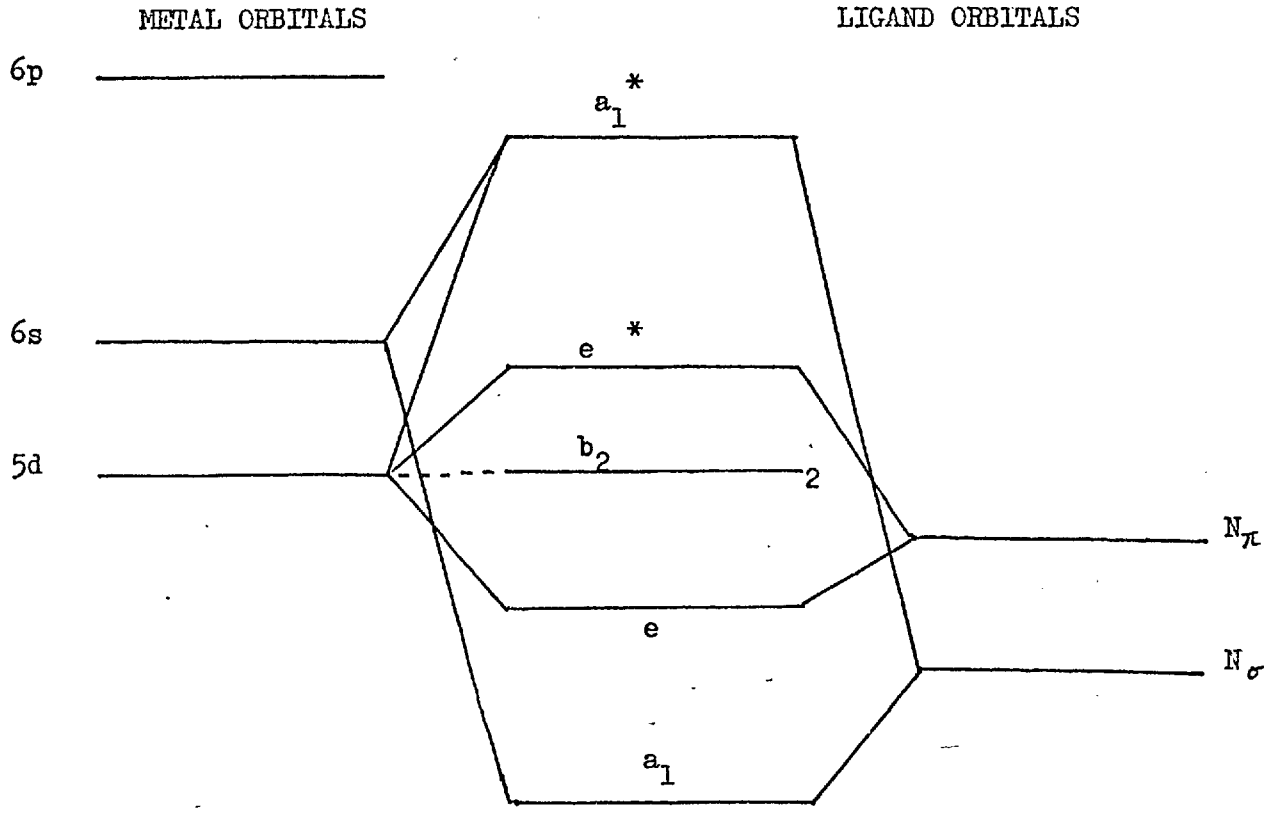


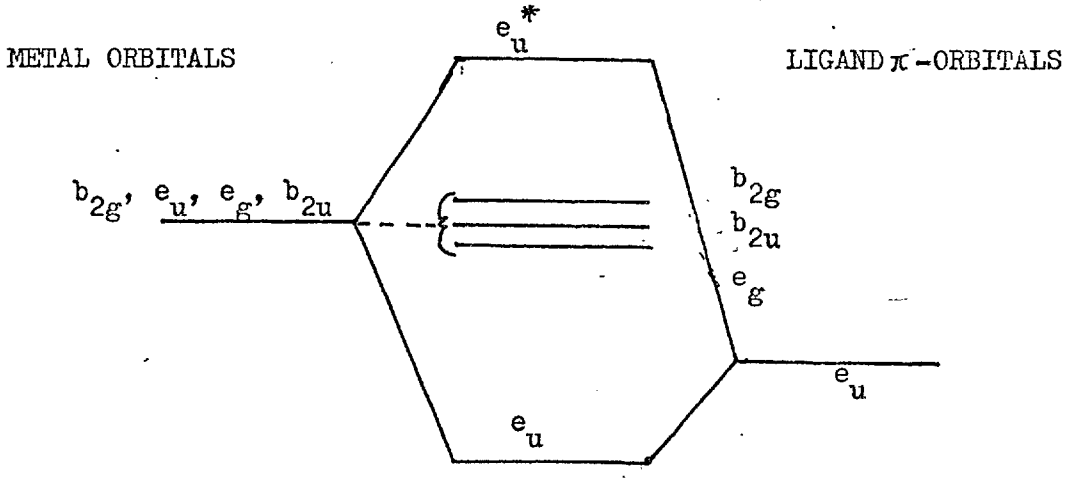
Figure 1.2.

complexes would be diamagnetic. It is interesting to note that under this scheme the ligand trans to the nitrido ligand is more weakly bonded than those cis to it.

(b) Linear symmetrically bridged nitrido complexes

The diamagnetic potassium[5] and ammonium[25] salts $M^{I}_{3}[Ru_2NCl_8(H_2O)_2]$ (M^{I} = K,NH_4) both have a centrosymmetric anion with a linear H_2O-Ru-N-Ru-OH_2 unit and overall D_{4h} symmetry. For these complexes we therefore use the scheme of Dunitz and Orgel[26] for $[Ru_2OCl_{10}]^{4-}$, which has a similar structure. The local symmetry of the ruthenium atom in $[Ru_2NCl_8(H_2O)_2]^{3-}$ is C_{4v}, and to form σ-bonds to the nitrido, chloro and aquo ligands we therefore use the same overlaps as in $[OsNCl_5]^{2-}$, but using ruthenium 4d, 5s and 5p orbitals (See Figure 1.1.). Whereas in $[OsNCl_5]^{2-}$ one sp_σ orbital on the nitrogen was unused, here it is used in σ-bonding to the other ruthenium atom. This

leaves a b_2 orbital (d_{xy}) and e orbitals (d_{xz}, d_{yz}) on each ruthenium atom, and a degenerate pair of p orbitals ($2p_x$, $2p_y$), which transforms as e_u under D_{4h} symmetry, on the nitrogen atom. We combine the remaining atomic orbitals on the ruthenium atoms to give new molecular orbitals, transforming (in the point group D_{4h}) as b_{2g}, b_{2u}, e_g and e_u. The metal and nitrogen e_u orbitals overlap to give a bonding and an antibonding orbital, while the b_{2g}, b_{2u} and e_g orbitals remain non bonding; they have similar energies.

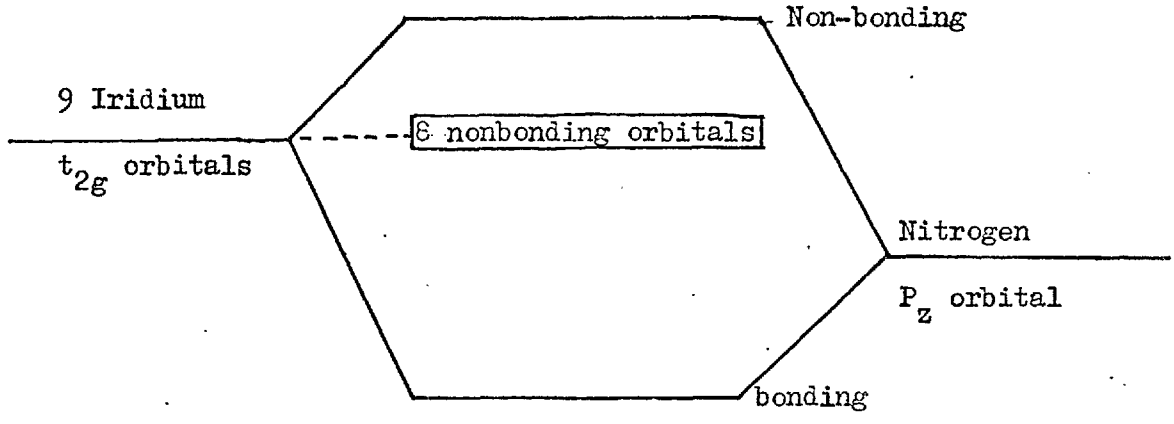


There are twelve electrons to feed into this system, four from each ruthenium atom, and four from the nitrogen e_u orbitals. These pair up in the e_u, e_g, b_{2u} and b_{2g} molecular orbitals, and thus there is a degenerate pair of bonding π-orbitals supplementing the Ru - N - Ru σ bonds. As a consequence of this π-bonding system, the ligands on the two ruthenium atoms will be eclipsed. Furthermore, as is indeed found, the complexes should be diamagnetic and have short Ru - N bonds.

(c) Trigonal planar nitrido complexes

The trinuclear iridium complex anion $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ has a trigonal planar Ir_3N unit, octahedrally coordinated iridium [7] and is diamagnetic[8]. The bonding scheme of Jorgensen[22] requires overlap of the nitrogen $2p_z$ orbital (the z axis is the three fold axis) with a linear combination of

iridium t_{2g} orbitals of appropriate symmetry giving a bonding and an anti-bonding orbital.



The remaining 8 linear combinations of iridium t_{2g} orbitals are non-bonding. The sixteen iridium electrons and the nitrogen pair fill the bonding and non-bonding orbitals. We thus explain the planarity and diamagnetism of the complex.

1 - A - 5 Trans-effect and trans-influence.

The trans-influence of a ligand L in a metal complex has been defined[27] as the extent to which L weakens the bond trans to itself in the equilibrium state of that complex. A ligand is said to exert a trans-effect[28] when the rate of substitution of the ligand trans to it is preferentially accelerated with respect to similar ligands in cis positions. Ligands which have a high trans-effect need not necessarily have a high trans-influence. One might expect that a trans-influencing ligand L would labilise the ligand trans to it in solution, and ^{17}O n.m.r. studies show that the rate of exchange of the aquo ligand trans to the oxo group in $[VO(H_2O)_5]^{2+}$ is at least 10^6 times greater than that of the cis aquo ligands[29]. In view of the likely

nature of trans-influence[30], however, the rate of substitution of the ligand trans to L will probably depend on the nature of the incoming ligand.

A discussion of the trans-effect of the nitrido ligand is premature since there have been no kinetic studies on its complexes. Trans-influence studies on other ligands mainly use data from n.m.r. coupling constants, i.r. spectroscopy and X-ray structural determinations [30]. Data of the latter two types are available for nitrido complexes. The different techniques will have different sensitivities to the two major components of trans-influence, said to be [30] (a) the effect of L on the hybrid orbital used by the metal in its bond to the trans ligand A and (b) the charge transfer ($\sigma_{covalent} \pm \pi$) from L to the metal. A ligand L which has a high trans-influence on the M - A bond will be the one with more demanding overlap requirements for the M - L bond and the one which has a high net charge transfer from itself to the metal.

We have already noted that the nitride ion forms strong covalent bonds to metals and transfers much of its negative charge to the metal. In the bonding schemes for $[OsNCl_5]^{2-}$ and $[Ru_2NCl_8(H_2O)_2]^{3-}$, there is no metal s orbital character in the bond to the ligand trans to the nitride. We would therefore expect the nitrido ligand to exert a high trans-influence. It is however difficult to obtain evidence for trans-influence in nitrido complexes, since the lengthening of the bond trans to the nitride observed in such species can be explained simply by steric factors [4]. In the course of this work however we shall discuss several points of evidence which indicate that the nitrido ligand does indeed have an electronic trans-influence of the type discussed above.

1 - A - 6 Structural characterisation of nitrido complexes.

Several X-ray structural determinations have been carried out on nitrido complexes and the data thus obtained are shown in Table 1. Of particular note are the short metal-nitrogen distances (1.6 - 1.9Å), the rather long bonds trans the nitrido ligand (or the absence of a ligand trans to the nitride), and the rather large N - M - X_{cis} angles. In order to interpret these effects Ibers made a careful study of complexes II, V and VII and also of some related imino complexes $[Re(NPhY)Cl_3(PEt_2Ph)_2]$ (Y = OAc, OMe) [38], and $[Re(NCH_3)Cl_3(PPh_2Et)_2]$ [39] which have meridional chloro ligands and trans phosphine groups. The points of interest are:

(a) The long Re ≡ N bond in V

(b) The long bonds trans to the nitrido ligand in II and V

(c) The Re = N bonds in the imino complexes are short (1.69 - 1.71Å) and insensitive to the nitrogen substituent group.

(d) All the Re - Cl bonds in the imino complexes are of similar length.

(e) In all the complexes the metal is raised above the plane of the cis ligands towards the nitrogen donor.

Ibers rationalised these variations by reference to intramolecular non-bonded interactions between the nitrogen donor and the cis ligands[4]. The N....Cl and N....P distances are never less than 3.0Å, and because of the short M - N distances this requires

(i) Raising the metal above the plane of the cis ligands.

(ii) In some cases lengthening the bonds to the ligands in the cis plane. (If effect (i) alone operated it could cause undue non-bonded interactions between the ligands in the cis plane).

(iii) In the case of V, lengthening the Re ≡ N bond.

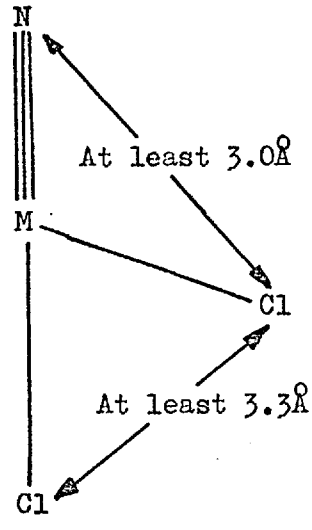
TABLE 1.

Structural data for transition-metal nitrido complexes

		d_{M-N}	Other data (bond lengths in Å)	Space group	[Z]	Ref.
I	$K[OsO_3N]$	1.75(2)	Os-O 1.75(2)	$I4_1/a$	4	31
II	$K_2[OsNCl_5]$	1.614(10)	cisOs-Cl2.362(2) transOs-Cl2.605(4); ∠NOsCl97.5°.	Pnma	4	4
III	$K[OsNCl_4(H_2O)]$	1.74	Os-Cl 2.35			32
IV	trans-$K[OsN(H_2O)Br_4]$	1.61	Os-O 2.07	Cmc	4	33
V	$ReNCl_2(PEt_2Ph)_3$	1.788(10)	cisRe-Cl2.454(4); trans Re-Cl2.563(4) cis Re-P2.442(4)	$P2_1/c$	4	34
VI	$ReN(S_2CNEt_2)_2$	1.687	Re-S 2.381; ∠NReS 108°	$P2_1/c$	4	35
VII	$ReNCl_2(PPh_3)_2$	1.603(9)	cisRe-Cl2.377(2) cis Re-P2.448(2)	I2/a		36
VIII	$K_3[Ru_2NCl_8(H_2O)_2]$	1.720(4)[a]	Ru-Cl2.364(6) ;Ru-O 2.175(20) ∠ClRuN 94.3°	C2/n	2	5
IX	$(NH_4)_3[Ru_2NCl_8(H_2O)_2]$	1.725(5)[a]	Ru-Cl2.370(10);Ru-O 2.20(20);	B2/m	2	25
X	$[MoNCl_3]_4$	1.672[a] 2.143[a]	Mo-Cl2.276 ∠MoNMo 167°, 178°	$P\bar{1}$	4	37
XI	$K_{2n}[ReN(CN)_4]_n \cdot nH_2O$	1.53[a] 2.44[a]	Re-N 2.13,C-N1.31	Imm2	2	6
XII	$(NH_4)_4[Ir_3N(SO_4)_6(H_2O)_3] \cdot 3^3/4H_2O$	1.918[a]	$Ir-OH_2$ 2.059,Ir-O(SO_4) 2.005 to 2.056	$I\bar{4}3d$	8	7

[a]Bridging M-N distances.

As a result of these distortions the M - Cl bond *trans* to the nitrido group in II and V is necessarily long, because of non-bonded repulsions between this ligand and the other ligands *cis* to it.



The small changes in the Re - N bond strength in the imino complexes brought about by changing the nitrogen substituent will be dissipated by increasing or decreasing strain on other ligands. Since effect (ii) operates in these complexes any lengthening of the bond *trans* to the imino group due to *trans*-influence is masked.

These arguments can successfully be applied to explain the distortions in the binuclear nitrido complexes $M^{I}_{3}[Ru_2NCl_8(H_2O)_2]$, [5, 25], and also in the oxo complex $Cs_4[Os_2OCl_{10}]$ [40]. In III and IV the aquo ligand (which has a lower *trans*-influence than chloride)[41] is *trans* to the nitride, and in the five coordinate complexes VI and VII a distorted square based pyramidal configuration with apical nitride is adopted, and the position *trans* to the nitride left vacant. Even here, however, it is difficult to disentangle steric and electronic effects, and we conclude overall that steric factors play a most important part in determining the structures of nitrido complexes.

Apart from X-ray data, the most useful method of identifying nitrido complexes is by their infra-red spectra, which show a strong band in the region 1000 - 1150 cm^{-1} (apart from trigonal planar complexes), due to the stretching of MN bonds. In a complex spectrum this band can be readily identified by ^{15}N isotopic substitution. The high frequency of the vibration and corresponding high bond stretching force constants[42] are further indications of the multiple character of the metal-nitrogen bond. There are several effects which may cause small variations in the frequency of the absorption which we will discuss in later chapters, but it is interesting to note that the complexes V (d_{ReN} = 1.603Å) and VII (d_{ReN} 1.778Å) probably have very similar values for the frequency of ν_{ReN}, near 1050 cm^{-1} (Ref. 19) A similar situation occurs in some isomeric molybdenum oxo complexes[43,44].

CHAPTER TWO

TERMINAL NITRIDO HALIDE COMPLEXES OF RUTHENIUM AND OSMIUM

ABSTRACT

The preparation and physical properties of the new complexes $Cs_2[RuNX_5]$, $R[MNX_4]$ and $Et_4N[MNX_4(H_2O)]$ (X = Cl, Br, M = Ru, Os; R= Ph_4As, Bu^n_4N) are described. The structures of these species and of known osmium nitrido halide species are discussed on the basis of their vibrational spectra and other properties. The X-ray crystal structure of $Ph_4As[OsNCl_4]$ is reported. We also describe some new oxo- and dioxo-complexes of ruthenium.

SECTION 2 - A NITRIDO COMPLEXES OF THE FORM $[MNX_5]^{2-}$, $[MNX_4(H_2O)]^-$ and $[MNX_4]^-$.

2 - A - 1, Introduction.

The first known complex containing an M ≡ N triple bond was potassium osmiamate, $K[OsO_3N]$, prepared by adding aqueous ammonia to a solution of osmium tetraoxide in aqueous potassium hydroxide[15]. Reduction of osmiamate in aqueous HX (X = Cl,Br) gave the terminal nitrido halide salts $M^I_2[OsNX_5]$ and $K[Os NBr_4]\cdot 2H_2O$ (M^I = K, Rb, Cs; X = Cl, Br) [45]. There are no known ruthenium analogues of any of these species.

At the commencement of our work, terminal nitrido halide complexes of vanadium (?)[46] molybdenum and tungsten,[20,47] and rhenium[19,48,49] had also been reported. The vanadium, molybdenum and tungsten complexes are made from the products of the reactions between chloroazide, ClN_3, and VCl_4,[46] $MoCl_5$ and WCl_6 [20]. The reactions are said to proceed via intermediate azido complexes $[VCl_4N_3]$ and $[MCl_5(N_3)]$ (M = Mo,W), which decompose to give $[Cl_3VNCl]$ and $[MNCl_3]_4$. The vanadium imido complex is Lewis amphoteric reacting with $SbCl_5$ to give $[VNCl_3][SbCl_6]$ and with pyridine to give $[py_2Cl][VNCl_3]$.[46]

These vanadium ions have been formulated $[Cl_3V^V = \overset{+}{N}]$ (i.e. coordinated N^-) and $[Cl_3V^V \equiv N]^-$ respectively, although they may be polymeric. The latter is isoelectronic with $[MoNCl_3]_4$ which has asymmetric M ≡ N ....M bridges[37]. The complexes $[MNCl_3]_4$ can be converted into terminal nitrides by treatment with Me_4NCl in dichloromethane which gives $(Me_4N)_2[MNCl_5]$ [47]. Since the completion of this work the synthesis of $Et_4N[MoNCl_4]$ by reacting azide ion with $MoCl_4$ or $MoCl_5$ in dichloromethane has been reported, and similar reactions are said to occur for V(III) and V(IV).[50] The isolation of Re(VI) salts $Cs_2[ReNCl_5]$ and $Ph_4As[ReNCl_4]$ has also been reported[49]. These are made by chlorine oxidation of $[Re^VNCl_2(PPh_3)_2]$, itself made by reacting $[ReCl_3(PPh_3)_3]$ with azide ions[19].

Thus, with the exception of the osmium complexes, terminal nitrido complexes are normally synthesised by reactions involving decomposition of a coordinated azide ligand, although in most cases the intermediate azido complexes are too unstable to be isolated. Two modes of decomposition of coordinated azide involving cleavage of an N-N bond are known[51]. The first type (Type A) is given by metals which are readily reduced by one electron, for example Mn(III)[52], Ce(IV)[53], Co(III)[54] and Ru(III)[55], and here the overall reaction is

$$N_3^- \rightarrow 3/2\ N_2 + e$$

The thermal decomposition of sodium azide is of this type.

The second type of reaction (Type B) produces 1 mole of nitrogen, and the resulting N^- species normally effects a two electron oxidation of the metal. The overall reaction is

$$2e + N_3^- \rightarrow N_2 + N^{3-}$$

$$\text{e.g.}\quad 2M^{2+} + HN_3 \xrightarrow{H^+} 2M^{3+} + N_2 + NH_3\ (M = Cr,V)^{56}$$

The formation of nitrido complexes by azide decomposition are reactions of this type

$$[Re^{III}Cl_3(PR_3)_3] \xrightarrow{N_3^-} [Re^{V}NCl_2(PR_3)_3] + N_2 + Cl^- \quad \text{Ref 19}$$

$$[Mo^{V}Cl_5] \xrightarrow{N_3^-} [Mo^{VI}NCl_4]^- + \tfrac{1}{2}Cl_2 + N_2 \quad \text{Ref 50}$$

In some reactions of this type the formal transfer of electrons from the metal to N^- after the decomposition is not required, since intermediates which show electrophilic nitrene-like behaviour are formed

$$[M^{III}(NH_3)_5(N_3)]^{2+} \xrightarrow{H+ \text{ or } h\nu} [M^{III}(NH_3)_5(NH)]^{3+} + N_2$$

$$[M^{III}(NH_3)_5(NH)]^{3+} \xrightarrow{HCl} [M^{III}(NH_3)_5(NH_2Cl)]^{3+}$$

(M = Rh* [57], Ir [58], * hν only)

2 - A - 2 Preparation of osmium and ruthenium nitrido complexes from azide ion.

The considerable stability of Os(VIII) and Os(VI) nitrido complexes led us to investigate the possibility of preparing similar ruthenium species. We found that the reaction of trans $[RuO_2X_4]^{2-}$ ions (X = Cl,Br) with an excess of azide ions followed by addition of caesium halide gave a simple route to the light brown, diamagnetic nitrido salts $Cs_2[RuNX_5]$. The known osmium complexes $Cs_2[OsNX_5]$ [45] could also be prepared by a similar method using trans $[OsO_2X_4]^{2-}$ ions. During the course of these reactions nitrogen and free halogen were liberated. This is consistent with the formation of an intermediate azido (or hydrazo) [59] complex which undergoes a two electron oxidative decomposition reaction of Type B (see previous section). The resulting complex is then reduced by HX.

$$[M^{VI}O_2X_4]^{2-} + HN_3 + 3HX \rightarrow [M^{VI}NX_5]^{2-} + N_2 + X_2 + 2H_2O, \quad (M = Ru, Os)$$

Although this reaction scheme does not necessarily imply that M(VIII) species (e.g. $[MO_3N]^-$) are intermediates, we isolated $Cs[OsO_3N]$ by reacting a suspension of $K_2[OsO_2(OH)_4]$ with azide and caesium ions in cold dilute aqueous acetic or oxalic acid. Osmiamate is not reduced under these conditions, although it is rapidly reduced by aqueous hydrohalic acids to $[OsNX_5]^{2-}$. The unknown ruthenium analogue of osmiamate, $[Ru^{VIII}O_3N]^-$ could not be prepared using procedures similar to those used here to isolate osmiamate, e.g. the reaction of $Cs_2[RuO_2Cl_4]$ or $K_2[RuO_4]$ in aqueous acetic acid with azide ions.

If large organic cations were used in place of caesium in the preparations of $[MNX_5]^{2-}$, then pink, diamagnetic salts $R[MNX_4]$ ($R = Ph_4As, Bu^n_4N$) were isolated. These species are 1:1 electrolytes in acetone. From solutions of osmiamate in aqueous HI we have similarly isolated the salt $Ph_4As[OsNI_4]$ in low yield. The addition of the cation Et_4N^+ to solutions of $[MNX_5]^{2-}$ gave the purple (osmium) or brown (ruthenium) diamagnetic salts $Et_4N[MNX_4(H_2O)]$. In some cases these were dehydrated to $Et_4N[MNX_4]$. The formation of two types of nitrido salts, $Cs_2[ReNCl_5]$ and $R[ReNCl_4]$, has recently been reported[49], and analogous behaviour is found in complexes of the isoelectronic oxo ligand where, for example $Cs_2[MOX_5]$ and $R[MOX_4]$, or in some cases $R[MOX_4(L)]$ (M = Mo, Re; X = Cl, Br; L = solvent molecule) have been isolated[3]. We have already noted the weak binding of the ligand <u>trans</u> to a strongly σand π donating nitrido or oxo ligand (Sections 1 - A - 4 and 1 - A - 6) and it is presumably this ligand which is lost in our 1:1 salts. This process may be favourable because of lattice-energy effects with these large cations.

2 - A - 3 X-ray crystal structure of $Ph_4As[OsNCl_4]$

An X-ray diffraction study of the nitrido complex $K_2[OsNCl_5]$ has been made, and the distortions of its coordination polyhedron rationalised in terms of intra-molecular non-bonded interactions[4]. (See 1 - A - 6). Dr. Skapski of this department has kindly made a similar study of $Ph_4As[OsNCl_4]$ in order to compare the dimensions of its anion with those of its six-coordinate counterpart[60]. In the tetraphenylarsonium salt, the large non-interacting cation allows the anion to adopt its optimum shape.

Crystals of $Ph_4As[OsNCl_4]$ (A) were grown from methyl cyanide solutions. They are wine-red tetragonal prisms with unit-cell dimensions a = 12.667Å, c = 7.820Å and U = 1254.7Å^3, space group $P_{4/n}$ and z = 2. Single crystal photographs of $Ph_4As[RuNCl_4]$ showed that it was isostructural with $Ph_4As[OsNCl_4]$. The square-based pyramidal anion $[OsNCl_4]^-$ is illustrated in Figure 1 and its principal bond lengths and angles are listed in Table 1 and compared with those of $K_2[OsNCl_5]$ (B).

The structure of (A) differs from that of (B) in three main respects

(a) There is no ligand trans to the nitride in (A)

(b) All the metal-ligand distances are shorter in (A) than (B)

(c) The N ≡ Os-Cl_{cis} angle is larger in (A) than in (B)

The decrease in the mean Os-Cl distance in (A) is comparable with decreases observed in similar closely related five and six-coordinate systems, e.g. Re-S in $[ReN(dtc)_2]$ (2.39Å)[35] and $[Re_2O_3(dtc)_4]$ (2.44Å)[61] and Re-Cl in $[ReNCl_2(PPh_3)_2]$ (2.38Å)[36] and $[ReNCl_2(PEt_2Ph)_3]$ (2.45Å)[34]. These reductions in bond length may be due to

(i) The enhanced electronegativity of the metal atom caused by the removal

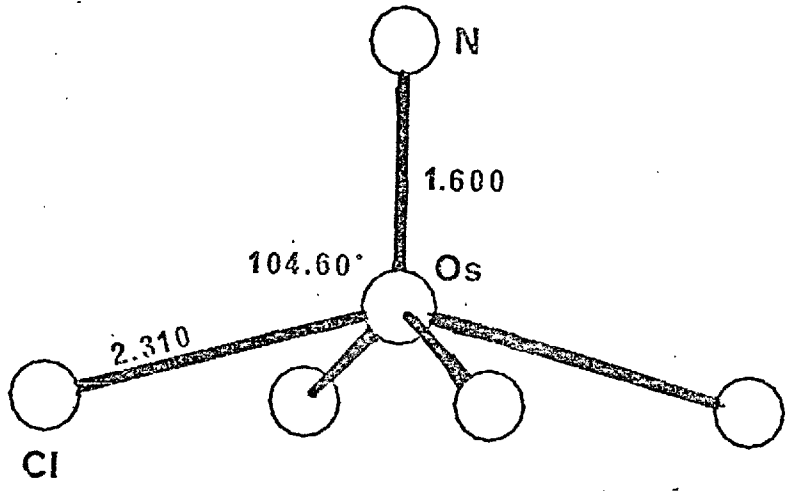


FIGURE 1.

Structure of $[OsNCl_4]^-$. Standard deviations are: Os-N, 0.011; Os-Cl, 0.002Å; ∠N-Os-Cl, 0.06°.

TABLE 1.

Interatomic distances (Å) and bond angles (°).

	$[OsNCl_4]^-$, (A)	$[OsNCl_5]^{2-}$, (B) (See Ref.4)
Os-N	1.600	1.614
Os-Cl(cis)	2.310	2.362 (mean)
Os-Cl(trans)	-	2.605
N-Os-Cl(cis)	104.60	96.2 (mean)
N...Cl(cis)	3.12	3.00 (mean)
Cl(cis)...Cl(cis)	3.16	3.32 (mean)
Cl(cis)...Cl(trans)	-	3.31 (mean)

of one donor atom.

(ii) Electronic effects, e.g. change in metal ion hybridisation and better overlap between metal and ligand orbitals in the less strained system.

(iii) Removal of non-bonded interactions which would cause bond lengthening. This latter effect is thought to account in part for the long Re-Cl bonds in $[ReNCl_2(PEt_2Ph)_3]$ (2.45Å) [34] and $[Re(NPhY)Cl_3(PEt_2Ph)_2]$ (2.40Å, Y=OAc,OMe)[38], although it is probably not important in (B). The increase in Cl-Os ≡ N bond angle in (A) is similar to the increase in Cl-Re ≡ O angle in $[ReOCl_4]$ (105°) [62] compared with $[ReOCl_4(H_2O)]$ (98°) [63].

These changes in coordination geometry in (A) do however produce an unexpected effect. The basal chloride ligands here (and in $[ReOCl_4]$) are moved to within 3.16Å of each other, a much closer Cl....Cl contact than found in (B) or any of the similar rhenium complexes discussed in Sec. 1 - A - 6, where such inter-ligand distances are said to dictate bond angles and lengths. Furthermore, the N...Cl distance in (A) (3.12Å) is greater than in (B) (3.00A)where it is said to be the main factor in determining the coordination geometry [4]. This would seem to indicate that electronic rather than steric effects cause the distortions of the square pyramid in (A). It must however be noted that the steric interactions we are discussing are not between hard, charged spheres but rather between both bonding and non bonding electron pairs within the anions. Thus, if we consider the Os≡N bond, whose $\sigma+\pi$ electron density is likely to be greatly polarised towards the electronegative osmium (VI) ion, these bonding electrons will repel (a) the Os-Cl bonding electrons and (b) the non-bonding electron pair in the d_{xy} orbital (Sec 1 - A - 4). Factor (b) is probably less important than (a) since there is a close correspondence between the bond parameters of (A) and the d^1

system $[ReOCl_4]$ [62]. If, as is likely, the polarisation of the Os ≡ N bonding electrons towards the metal is greater in (A) than in (B), we would expect a greater repulsion between them and the Os-Cl electrons in (A) and hence an increase in N ≡ Os-Cl angle and distance. Similarly, removal of more electron density from the chloride ligands in (A) might permit closer mutual contact. However, data from other similar square pyramidal systems show that the apical-cis ligand angles are as large as basal interactions will permit ($\measuredangle$ NReS = 108° in $[ReN(dtc)_2]$ [35] and $\measuredangle$ O=OsO = 111° in $[Os_2O_4(O_2C_2Me_4)_2]$ [64]. We therefore conclude that there is an electronic rather than steric effect causing the distortions in the structure of (A).

2 - A - 4 Vibrational spectra.

The main features of the vibrational spectra of $Cs_2[MNX_5]$, $R[MNX_4]$, $Et_4N[MNX_4(H_2O)]$ and $K[OsNBr_4(H_2O)]H_2O$ are presented in Table 2; (M = Os, Ru; X = Cl,Br; R = Ph_4As, Bu^n_4N).

(a) Complexes of the type $[MNX_5]^{2-}$, $[MNX_4]^-$

The skeletal symmetry of the anions in both $K_2[OsNCl_5]$ [4] and $Ph_4As[OsNCl_4]$ [60] is approximately C_{4v}, and for these two anions we expect eleven ($4A_1 + 2B_1 + B_2 + E$) and nine ($3A_1 + 2B_1 + B_2 + 3E$) normal vibrational modes respectively. All the modes are Raman active with the A_1 modes polarised, and the A_1 and E modes are also infra-red active. The Raman spectra of most of the salts of these types were rather poor, and most of the ensuing discussion relates to their i.r. spectra. The spectra are consistent with C_{4v} symmetry.

The M-N stretching frequency, γ_{MN}, an A_1 mode, is readily identified by its characteristic absorption frequency and shift on ^{15}N substitution. It

T A B L E 2.

Vibrational Spectra of metal nitrido complexes (200 - 4000 cm^{-1})

	$\nu_{MN}(A_1)$	$\nu^{s}_{MX_4}$ (A_1)*	$\nu^{as}_{MX_4}$ (E)	δ_{XMN} (E)	Other strong bands
$Cs_2[RuNCl_5]$	1045 s	318 (10)*	(340 s (338 s	235 m	307 (1),* 284 (3),* 233 (5)*
$Et_4N[RuNCl_4(H_2O)]$	1084 s		342 s	263 w	3478 m, 1610s, 555m,b.
$Ph_4As[RuNCl_4]$	1092 s	346 (10)	378 s	267 m	304 (4), * 266 (5)*
$Cs_2[RuNBr_5]$	1045 s	207 (5)	257 s	206 m	201 (1) *
$Ph_4As[RuNBr_4]$	1088 s		302 s	230 m	
$Cs_2[OsNCl_5]$	1073 s (1040)		(331 s (330) (325 s (324)	243 m (238)	208 m.
$Rb_2[OsNCl_5]$	1079 s		331 s 326 s	252 m 244 m	205 m
$K_2[OsNCl_5]$	1084 s 1106 w+	348 (10)+	(336 s (329 s	262 m 250 w	334 (2)+, 324 (4)+ 264 (4)+, 210 s
$Et_4N[OsNCl_4(H_2O)]$	1116 m		328 s	276 w	3465 m, 1612 s, 585 m,b.
$Ph_4As[OsNCl_4]$	1123 m (1085)	358 (10)	365 s (362)	271 w (262)	352 (1) *
$Cs_2[OsNBr_5]$	1073 s (1040)	198 (10)+	234 s (232)	216 m (210)	
$Et_4N[OsNBr_4(H_2O)]$	1114 m		232 s	253 m	3425 m, 1608 s, 595 m,b.
$Ph_4As[OsNBr_4]$	1120 m (1082)	229 (10)	274 s (269)	233 m (228)	
$K[OsNBr_4(H_2O)].H_2O$	1109 m 1105 w **		232 s	(261 m (250 m	3580s, 3500s, 3400s,b, 1605s, 1597s, 618 s,b, 536s,b, 300s,b
$Ph_4As[OsNI_4]$	1108 m				

Key to Table 2.

Bands due to cation not quoted. All spectra from infra-red studies on solids except where indicated. Frequencies in parentheses refer to ^{15}N substituted species.

* Raman data on solids;

† Spectra on complex in D_2O solution with excess X^- ion, ** in D_2O solution.

falls in the range 1045-1090 cm^{-1} for the ruthenium complexes and 1070-1120 cm^{-1} for the osmium complexes. Force constant studies[65] show that the M-N stretching force constant k_{MN} is some 10% lower for ruthenium than osmium in corresponding complexes. We attribute this effect to less effective π- orbital overlap in the ruthenium-nitrogen bond. For the osmium chloro complexes ν_{OsN} varies in frequency $Cs_2[OsNCl_5]$ (1073 cm^{-1}) < $Rb_2[OsNCl_5]$ (1079 cm^{-1}) < $K_2[OsNCl_5]$ (1084 cm^{-1}) < $[OsNCl_5]^{2-}$ in aqueous DCl (1106 cm^{-1}) < $R[OsNCl_4]$ (1123 cm^{-1}). Similar trends obtain for the osmium bromides and also the ruthenium complexes. The difference in ν_{MN} between the solid penta- and tetra-halo salts may be attributed chiefly to interaction between the polarisable alkali-metal cations and the M≡N bond rather than a coordination number effect. A similar effect is seen in some rhenium oxo complexes: ν_{ReO} is at 955 cm^{-1} in Cs $[ReOBr_4]$, whereas in Ph_4As $[ReOBr_4]$ it is at 1000 cm^{-1} [66]. The addition of a weakly bound <u>trans</u> ligand to this latter complex to give Ph_4As $[ReOBr_4(MeCN)]$ causes only a small decrease ($\sim 5 cm^{-1}$) in ν_{ReO}.[67] It is likely that in all our penta-halo complexes the ligand <u>trans</u> to the nitride is weakly bound. A situation where the ligand <u>trans</u> to the nitride is likely to be strongly bound is in $[ReN(CN)_5]^{3-}$, and here ν_{ReN} is some 45 cm^{-1} lower in frequency than in $[ReN(CN)_4(H_2O)]^{2-}$.[48]

In the $R[MNX_4]$ species, the i.r. absorption due to ν_{MN} occurs as a moderately strong, very sharp band, and we therefore conclude that they are all monomeric, as is the case with Ph_4As $[OsNCl_4]$ (Sec 2 - A - 3). If substantial linear M ≡ N....M ≡ N... chain bonding were present in these species, we would expect ν_{MN} to occur as a broad absorption at lower frequencies than in $Cs_2[MNX_5]$. Such effects are observed in the i.r. spectra of $K_{2n}[ReN(CN)_4]_n nH_2O$ [6,48] and $[WOCl_4]_n$ [68] which contain such chains in

the solid state, when compared with their monomeric counterparts $K_3[ReN(CN)_5]$ [48] and gaseous $[WOCl_4]$.[69] The X - M ≡ N deformation mode has been identified for the first time in nitrido complexes. It is near 250 cm^{-1}, and changes in sympathy with γ_{MN}.

In contrast to γ_{MN}, the i.r. active metal-halogen stretching E modes γ_{MX} (1 for $[MNX_4]^-$, and for $[MNX_5]^{2-}$) show marked changes in frequency with coordination number. The higher frequency M-X stretching absorption in $[MNX_5]^{2-}$ increases sharply in frequency in the corresponding $[MNX_4]^-$ species, and it has been shown that there is an attendant increase in the M-X stretching force constant[65]. This is consistent with the shortening in Os-Cl distance from $K_2[OsNCl_5]$ to $Ph_4As[OsNCl_4]$. The spectra of the six-coordinate salts $M^I_2[OsNCl_5]$ (M^I = K,Rb,Cs) show a low frequency band near 210 cm^{-1} which does not appear in the bromo complexes, nor does it shift on ^{15}N substitution of the complex. This is probably the M-X stretching A_1 mode, associated mainly with the vibration of the weakly bonded chloride *trans* to the nitride. Similar low frequency bands have been tentatively assigned to $\gamma_{Re-Cl\ trans}$ in $[ReNCl_2(PR_3)_3]$ [19], where the weakening of *trans* bond has been attributed to steric effects, as in $K_2[OsNCl_5]$ [4]. It is interesting to note that low frequency bands have been assigned to γ_{IrCl} in some iridium complexes with a chloride ligand *trans* to a strongly *trans*-influencing acyl group[70].

(b) *Complexes of the type $Et_4N[MNX_4(H_2O)]$ and $K[OsNBr_4(H_2O)].H_2O$.*

We now assign structures to salts containing $[MNX_4(H_2O)]^-$ anions by reference to the discussion on γ_{MN} and γ_{MX} in the preceding section. The spectra of these species are best interpreted on the basis of distorted square-based pyramidal anions with a weakly bonded aquo ligand *trans* to the

apical nitride. We assign a strong, sharp band near 1100 cm^{-1} in the i.r. spectra of the Et_4N^+ salts to ν_{MN}. Its frequency is 5 - 10 cm^{-1} lower than in $R[MNX_4]$, and we therefore rule out structures containing M ≡ N...M ≡ N chains. There is one band in the M-X stretching region, which we assign to the E stretching mode. It has a frequency characteristic of a six-coordinate complex, which indicates that the water molecule in these complexes is indeed coordinated. Only three bands due to the aquo ligand are seen in the spectra of these salts, at ~3450 cm^{-1}, 1610 cm^{-1} and ~580 cm^{-1}. Similar bands have been observed in $Et_4N[ReOBr_4(H_2O)]$ [66], which has a structure of the type we propose for $Et_4N[MNX_4(H_2O)]$. The position and shape of the i.r. bands due to water in these Et_4N^+ salts are rather different to those in $Ph_4As[MoOX_4(H_2O)]$, where two O-H stretching bands are seen at ~3600 cm^{-1} and 3525 cm^{-1}, and the δH_2O mode is at 1575 cm^{-1} [71]. These differences can be attributed to hydrogen bonding of the water in the Et_4N^+ salts, probably to another anion. There are rather different crystal lattices for $Et_4N[ReOBr_4(H_2O)]$ [66] and $Ph_4As[MoOBr_4(H_2O)]$ [72], with little possibility of hydrogen bonding in the latter. The six coordinate $Et_4N[MNX_4(H_2O)]$ configuration may be preferred to the five coordinate $Et_4N[MNX_4]$ arrangement in these salts because of this hydrogen bonding.

The complex $K[OsNBr_4]\,2H_2O$ was first reported by Werner [45]. The i.r. spectrum of '$K[OsNBr_4(H_2O)]$' has been discussed[73]. We find that from solutions of osmiamate in hydrobromic acid two complexes can be isolated whose i.r. spectra differ. One complex has an i.r. spectrum similar to that already reported for '$K[OsNBr_4(H_2O)]$'. The other complex, probably the one isolated by Werner, has a rather different i.r. spectrum with a sharp band at 1109 cm^{-1} and a strong band at 232 cm^{-1} which we assign to ν_{OsN} and ν_{OsBr} respectively. The frequency of ν_{OsBr} suggests the anion has a six-

coordinate structure. The rest of the spectrum is rather complex with bands which can be assigned to lattice and coordinated water. We therefore propose Werner's salt should be formulated $K[OsNBr_4(H_2O)]. H_2O$.

SECTION 2B SOME RUTHENIUM OXO COMPLEXES

2 - B - 1 Introduction.

The formation of $[RuNCl_5]^{2-}$ from azide and *trans* $[RuO_2Cl_4]^{2-}$ ions prompted a further investigation of ruthenium dioxo complexes as possible precursors for nitrido species. Only *trans* $[RuO_2Br_4]^{2-}$ ions were useful in this respect, but we have isolated a number of other ruthenium oxo species in the course of this work. The only firmly established 'ruthenyl' species are those of *trans* $Cs_2[RuO_2Cl_4]$ [74] and *trans* $[RuO_2(OH)_2 py_2]$[75]: although spectroscopic data have been reported for salts of the anions $[RuO_2Br_4]^{2-}$, and $[RuO_2(SO_4)_2]^{2-}$, no preparative details were given.[76] Octahedral complexes containing an MO_2 unit are also known for vanadium, molybdenum, tungsten, rhenium and osmium[3], a list which correlates well with that of metals known to form terminal nitrido complexes[1]. Such complexes normally have d^0 or d^2 electron configurations with *cis* and *trans* oxo ligands respectively. This structural feature has been rationalised in terms of competition between the metal electrons and the ligand π-electrons for the metal t_{2g} orbitals[77]. The oxo ligand is a good σ- and π- donor, but in *trans* complexes it is competing with another oxo ligand for both σ+π orbitals on the metal. X-ray structural and M-O stretching force constant studies show that M-O bonds are consequently weaker in *trans* than *cis* complexes, although comparisons between *cis* and *trans* complexes in the same oxidation state with the same attendant ligands are not yet possible.

2 - B - 2 Preparation and properties of oxo complexes.

The complex $Cs_2[RuO_2Cl_4]$ was originally prepared by dissolving ruthenium tetraoxide in concentrated HCl containing caesium chloride[74]. We have shown that by reacting solutions of ruthenium tetraoxide in carbon tetrachloride with ice-cold aqueous solutions of HX and CsX (X = Br, $\frac{1}{2}C_2O_4$), the salts $Cs_2[RuO_2X_4]$ can be isolated. The ammine complex $[RuO_2(NH_3)_4]Cl_2$ was prepared by treating a similar solution of RuO_4 with a mildly alkaline solution of ammonium chloride. The amine chlorides pyHCl and bipyHCl also react with RuO_4 in mildly alkaline solutions to form $[RuO_2py_2Cl_2]$ and $[RuO_2(bipy)Cl_2]$.

All these complexes are diamagnetic, as expected for Ru(VI) complexes with a trans dioxo group[78]. They show the characteristic i.r. absorption of such a group due to ν_{as} RuO_2 near 830 cm^{-1}. For those complexes whose Raman spectra could be measured, ν_s RuO_2 occurred as an intense sharp band in the same region. Using these two frequencies, approximate stretching force constants for the RuO_2 system were calculated using the equations of Cotton and Wing[79]. They were some 10% lower than in the corresponding Os(VI) complexes[77], probably a result of less effective overlap in the O→M π-bonds for the second row element. The i.r. active metal halogen stretching frequencies in $Cs_2[RuO_2X'_4]$ (X' = Cl,Br) are at lower frequency $\nu_{MX'}$ vibration, in $Cs_2[RuNX'_5]$. This could reflect the lower positive charge on the metal in the dioxo complexes, or indicate Ru-Cl bond weakening due to non-bonded Cl...O interactions in the dioxo complexes.

The reaction of ruthenium tetraoxide with an ice-cold solution of sodium cyanide in the presence of caesium ion did not, surprisingly, yield $Cs_2[RuO_2(CN)_4]$. A green paramagnetic salt (μ_{eff} = 3.0BM), which showed i.r. bands characteristic of coordinated cyano and isocyanato[80] groups was formed.

The complex also has a strong i.r. absorption in the Ru = O stretching region at 787 cm^{-1} which also appeared in its Raman spectrum. We formulate this complex $Cs_3[RuO(CN)_4(NCO)_2]$, although its magnetic moment is rather high for Ru(V) (it is a typical Ru(IV) value), and seven coordinate ruthenium is unusual. Another ill-characterised oxo-cyano species was made by adding sodium cyanide to an ice-cold solution of $Na_2[RuO_4]$ in concentrated sodium hydroxide. A plum red solution was formed, which slowly turned yellow, and caesium carbonate precipitated a yellow paramagnetic salt, $Cs_5[Ru_2O_5(CN)_9]$. The i.r. spectrum of this salt shows peaks typical of co-ordinated cyanide, and also two bands at 690 and 758 cm^{-1} which may be due to oxo ligands. A possible formulation is $Cs_5[(CN)_4ORu\ ORu(CN)_5].3H_2O$.

SECTION 2 - C EXPERIMENTAL

Di-caesium pentachloronitridoruthenate (VI), $Cs_2[RuNCl_5]$

A solution of ruthenium tetraoxide in carbon tetrachloride (10 ml) (vide infra) was stirred rapidly with 8M hydrochloric acid (7 ml), and the red solution cooled to 0°C. Sodium azide (0.24 g) was added to the reaction mixture and the solution stirred at room temperature until the effervescence had ceased (~15 mins). Caesium chloride (0.8 g) was added and the light brown precipitate (80%) was filtered, washed with ice cold concentrated hydrochloric acid (2 ml), then acetone, and finally dried at 110°C. (Found: Cl, 31.4; Cs, 47.5; N, 2.6. Cl_5Cs_2NRu requires Cl, 31.8; Cs, 47.6; N, 2.5%).

Tetraphenylarsonium tetrachloronitridoruthenate (VI), $Ph_4As[RuNCl_4]$

A solution of tetraphenylarsonium chloride (0.8 g) in methanol (5 ml) was added to the previous reaction mixutre in place of caesium chloride.

The pink precipitate (80%) was filtered, washed with water and methanol, and recrystallised from acetonitrile. (Found: C, 45.0; H, 3.2; Cl, 22.9; N, 2.1. $C_{24}H_{20}AsCl_4NRu$ requires C, 45.0; H, 3.1; Cl, 22.2; N = 2.2%).

Tetra-n-butylammonium tetrachloronitridoruthenate (VI), $Bu^n_4N[RuNCl_4]$

Tetra-n-butylammonium hydroxide solution (40%, 2 ml) replaced tetraphenylarsonium chloride solution in the preceding preparation. The pale pink precipitate (80%) was filtered, washed with water and diethyl ether and recrystallised from acetone to give brown crystals of the product. (Found: C, 38.4; H, 7.0; Cl, 28.9; N, 5.2. $C_{16}H_{36}Cl_4N_2Ru$ requires C, 38.5; H, 7.2; Cl, 28.4; N, 5.6%). Infra red (excluding cation bands) 1095(m), 376(s), 265(m). Molar conductance in acetone 121 mho cm^{-2} in 10^{-3} M solution.

Tetraethylammonium aquotetrachloronitridoruthenate (VI), $Et_4N[RuNCl_4(H_2O)]$

Tetraethylammonium chloride (1.0 g) replaced the cations in the preceding preparations and gave brown crystals (50%) of the product which were filtered off and washed with ice cold concentrated hyrdochloric acid. (Found: C, 24.1; H, 5.3: N, 6.9. $C_8H_{22}Cl_4N_2ORu$ requires C, 23.7; H, 5.4; N, 6.9%).

Dicaesium pentabromonitridoruthenate (VI), $Cs_2[RuNBr_5]$

Sodium azide (0.24 g) was dissolved in an ice-cold solution of water (2 ml) and concentrated hydrobromic acid (5 ml). Ruthenium tetraoxide solution (10 ml, vide infra) was added to the solution and the mixture stirred vigorously at 0°C for five minutes. Caesium bromide (0.9 g) was added to the solution and the light brown product (40%) was filtered off, washed with acetone and dried at 110°C. (Found: Br, 50.3; Cs, 34.2; N, 1.9.

Br_5Cs_2NRu requires Br, 51.2; Cs, 34.1; N, 1.8%).

Tetraphenylarsonium tetrabromonitridoruthenate (VI), $Ph_4As[RuNBr_4]$

A solution of tetraphenylarsonium chloride (0.5 g) was dissolved in methanol (5 ml) and added to the previous reaction mixture in place of caesium bromide. The bulky yellow precipitate was filtered off and washed with methanol to leave the light pink precipitate (40%).
(Found: C, 35.2; H, 2.6; Br, 38.9; N, 1.6. $C_{24}H_{20}AsBr_4NRu$ requires C, 35.2; H, 2.4; Br, 39.1; N, 1.7%).

Dicaesium pentahalogenonitrido-osmates (VI), $Cs_2[OsNX_5]$

The chloro and bromo complexes were prepared by the literature methods[45]; an alternative procedure which eliminates contamination with the corresponding osmium (VI) dioxo complex is as follows

a) Chloro complex. Potassium osmate (0.08 g) was dissolved in concentrated hydrochloric acid (3 ml) and sodium azide solution (0.03 g in 1 ml water) added. The solution was stirred for 20 minutes and caesium chloride (0.05 g) precipitated the purple product.

b) Bromo complex. The procedure follows that for the chloro complex but using hydrobromic acid and caesium bromide, giving the purple product.

The tetra-halo organic cation salts were precipitated from solutions of $[OsNX_5]^{2-}$ in HX (X = Cl, Br) using the procedures described for the ruthenium salts.

Tetraphenylarsonium tetrachloronitrido-osmate (VI) $Ph_4As[OsNCl_4]$

Pink crystals (90%). (Found: C, 39.5; H, 2.9; Cl, 19.2; N, 2.0. $C_{24}H_{20}AsCl_4NOs$ requires C, 39.5; H, 2.7; Cl, 19.5; N. 1.9%).

Molar conductance in acetone 113 mho cm^{-2}. in 10^{-3}M solution.

Tetra-n-butylammonium tetrachloronitrido-osmate (VI), $Bu^n_4[OsNCl_4]$

Red complex (90%). (Found: Cl, 23.8; N, 5.5. $C_{16}H_{36}Cl_4N_2Os$ requires Cl, 24.1; N, 4.8%). Infra-red bands (excluding cation absorptions) 1125m, 353s, 262w. Molar conductance in acetone 124 mho cm^{-2} in 10^{-3}M solution.

Tetraethylammonium aquotetrachloronitrido-osmate (VI), $Et_4N[OsNCl_4(H_2O)]$

Purple crystals (65%): (Found: C, 28.4; N, 6.0. $C_8H_{22}Cl_4N_2OOs$ requires C, 28.7; N, 5.7%)

Tetraphenylarsonium tetrabromonitrido-osmate (VI), $Ph_4As[OsNBr_4]$

Pink crystals (90%). (Found: C, 32.0; H, 2.0; Br, 35.5; N, 1.7. $C_{24}H_{20}AsBr_4NOs$ requires C, 31.8; H, 2.2; Br, 35.3; N, 1.5%).

Tetra-n-butylammonium tetrabromonitrido-osmate (VI), $Bu^n_4[OsNBr_4]$

Deep red crystals (90%). (Found: Br, 40.8; N, 3.5. $C_{16}H_{36}Br_4N_2Os$ requires Br, 41.7; N, 3.7%). Infra-red bands (excluding cation absorptions) 1120m, 270s, 232m. Molar conductance in acetone 124 mho cm^{-2}. in 10^{-3} M solution.

Tetraethylammonium aquotetrabromonitrido-osmate (VI), $Et_4N[OsNBr_4(H_2O)]$

Purple salt (80%). (Found: Br, 46.8; N, 4.4. $C_8H_{22}Br_4N_2OOs$ requires Br, 47.5; N, 4.2%). Weight loss on dehydration 2.9%; calculated for $Et_4N[OsNBr_4(OH_2)]$, 2.7%.

Tetraphenylarsonium tetraiodonitrido-osmate (VI), $Ph_4As[OsNI_4]$

Potassium osmiamate (0.5g) was added to concentrated HI solution (5ml), and to the resulting dark brown solution a solution of tetraphenylarsonium chloride (0.5g) in methanol (2ml). The voluminous yellow-brown precipitate was filtered off and washed freely with acetone, leaving the light pink product (20%). (Found: C, 26.2; H, 1.9; I, 46.1; N, 1.4. $C_{24}H_{20}AsI_4NOs$ requires C, 26.3; H, 1.8; I, 46.4; N, 1.3%).

trans-Dicaesium tetrabromodioxoruthenate (VI), $Cs_2[RuO_2Br_4]$

A saturated solution of caesium bromide in a solution of hydrobromic acid (5 ml) and water (2 ml) was cooled to 0°C and ice-cooled ruthenium tetraoxide solution (5 ml) was stirred into it. The light-brown precipitate (40%) was quickly filtered off, sucked dry on the frit and washed with acetone. (Found: Br, 43.9; Cs, 37.6. $Br_4Cs_2O_2Ru$ requires Br, 44.5; Cs, 37.0%). Infra-red spectrum: 825s*, 821ssh*, 230s, 226ssh cm^{-1}.

trans-Dicaesium bisoxalatodioxoruthenate (VI), $Cs_2[RuO_2ox_2]$

Oxalic acid (0.45 g) and caesium carbonate dihydrate (0.90 g) were dissolved in water (4 ml) and the solution ice-cooled. Ruthenium tetraoxide solution (6 ml) was stirred into the solution and the light green precipitate (30%) filtered off after 5 minutes. It was washed with carbon tetrachloride and ethanol. (Found C, 8.0; Cs, 45.8. $C_4Cs_2O_{10}Ru$ requires C, 8.4; Cs, 46.2%). Infra-red spectrum 1710s,b, 1680s, 1335s, 1192m, 910w, 878m, 838s*, 810s, 549m, 460m, 385w, 361ssh, 350s cm^{-1}.

trans-Tetraamminodioxoruthenate (VI)dichloride, $[RuO_2(NH_3)_4]Cl_2$

Ammonium chloride (1.0 g) and sodium carbonate (0.1 g) were dissolved

in 4 ml ice-cold water and ruthenium tetraoxide solution (6 ml) stirred into the reaction mixture. After 15 minutes the yellow microcrystalline precipitate was filtered off, and washed with carbon tetrachloride and ethanol. (Found: H, 4.7; Cl, 26.4; N, 20.7; O, 12.1. $H_{12}Cl_2N_4O_2Ru$ requires H, 4.4; Cl, 26.1; N, 20.6; O, 11.8%). Infra-red spectrum (deuteriated sample in brackets). 3360vsb (2420) 3070vsb (2280), 1660m, 1623m (1148), 1583m 1540msh (1080), 1322s (1018) 1304s(1008), 870s (650), 845*s, 782s, (622), 478m (440), 278s,b (250), 215s cm^{-1}. Raman: 841 (10).

trans-Dichlorodioxodipyridinoruthenate(VI), $[RuO_2py_2Cl_2]$.

A solution of pyridine (1 ml) in water (2 ml) was neutralised by hydrochloric acid and the solution made alkaline with sodium carbonate (0.1 g). Ruthenium tetraoxide solution (6 ml) was stirred into the ice-cooled solution and after 5 minutes the yellow microcrystalline product was filtered off and washed with carbon tetrachloride, water and ethanol. (Found: C, 34.0; H, 2.9; Cl, 18.8; N, 7.9. $C_{10}H_{10}Cl_2N_2O_2Ru$ requires C, 33.1; H, 2.8; Cl, 19.6; N, 7.7%). Infra-red spectrum (neglecting bands due to pyridine). 825*s, 325 cm^{-1}.

trans-2,2'bipyridinodichlorodioxoruthenate(VI), $[RuO_2bipyCl_2]$.

2,2'bipyridyl (0.3 g) was stirred into water (3 ml) and 2M hydrochloric acid added until it was completely dissolved. Sodium carbonate (0.1 g) was added to the ice-cooled solution, and then ruthenium tetraoxide solution (6 ml). The yellow crystalline product was filtered off after 5 minutes and washed with water and acetone. (Found: C, 33.6; H, 2.4; Cl, 19.6; N, 7.9. $C_{10}H_8Cl_2N_2O_2Ru$ requires C, 33.3; H, 2.2; Cl, 19.7; N, 7.8%). Infra-red spectrum 839*s, 325s, 319ssh cm^{-1}.

(* For dioxo complexes indicates $\nu_{as}MO_2$)

Caesium tetracyanobisisocyanatooxoruthenate(V), $Cs_3[RuO(CN)_4(CNO)_2]$

Ruthenium tetraoxide solution (5 ml) was stirred with an ice-cold saturated aqueous solution of sodium cyanide (5 ml) which contained caesium chloride (1.09). The green precipitate was filtered off after 5 minutes and washed with methanol. (Found: C, 10.2; Cs, 56.7; N, 12.3; O, 6.7. $C_6Cs_3N_6O_3Ru$ requires C, 10.2; Cs, 56.4; N. 11.9; O, 6.8%). Infra-red spectrum 3600w, 3515w, 2195vs, 2125s, 2060w, 1630w, 1335w, 787s, 690w, 609w, 450, 388m,s, 370m,s, 328m cm^{-1}. Raman spectrum, 2200(1), 2149(5), 787(10) cm^{-1}.

$$\chi_g = 5.57 \times 10^{-6} \text{ c.g.s.u.}$$

$$\mu_{eff} = 3.00 \text{B.M.}$$

Ruthenium Tetraoxide solution.

The solution of ruthenium tetraoxide in carbon tetrachloride was made by an adaptation of Nakata's method[81], with commercial ruthenium trichloride (10 g) being converted to the hydrated hydroxide and this material being oxidised by sodium metaperiodate (45 g in 400 ml ice-cold water). The resulting aqueous solution of RuO_4 was divided into three and each portion extracted with 3 x 30 ml of carbon tetrachloride, the final solution being made up to 300 ml to give a concentration of ~22 g/l ruthenium tetraoxide. The solution was stored at $-5^{\circ}C$ in the presence of sodium metaperiodate.

All the complexes are diamagnetic unless otherwise stated. $K_2[OsNCl_5]$, $Rb_2[OsNCl_5]$ and $K[OsNBr_4(H_2O)]$ H_2O were prepared by the literature method.[45] The ^{15}N substituted osmium complexes were prepared from $K[OsO_3{}^{15}N]$, obtained

from isotopically enriched (95%) ammonium chloride and osmium tetraoxide in potassium hydroxide solution.

CHAPTER 3

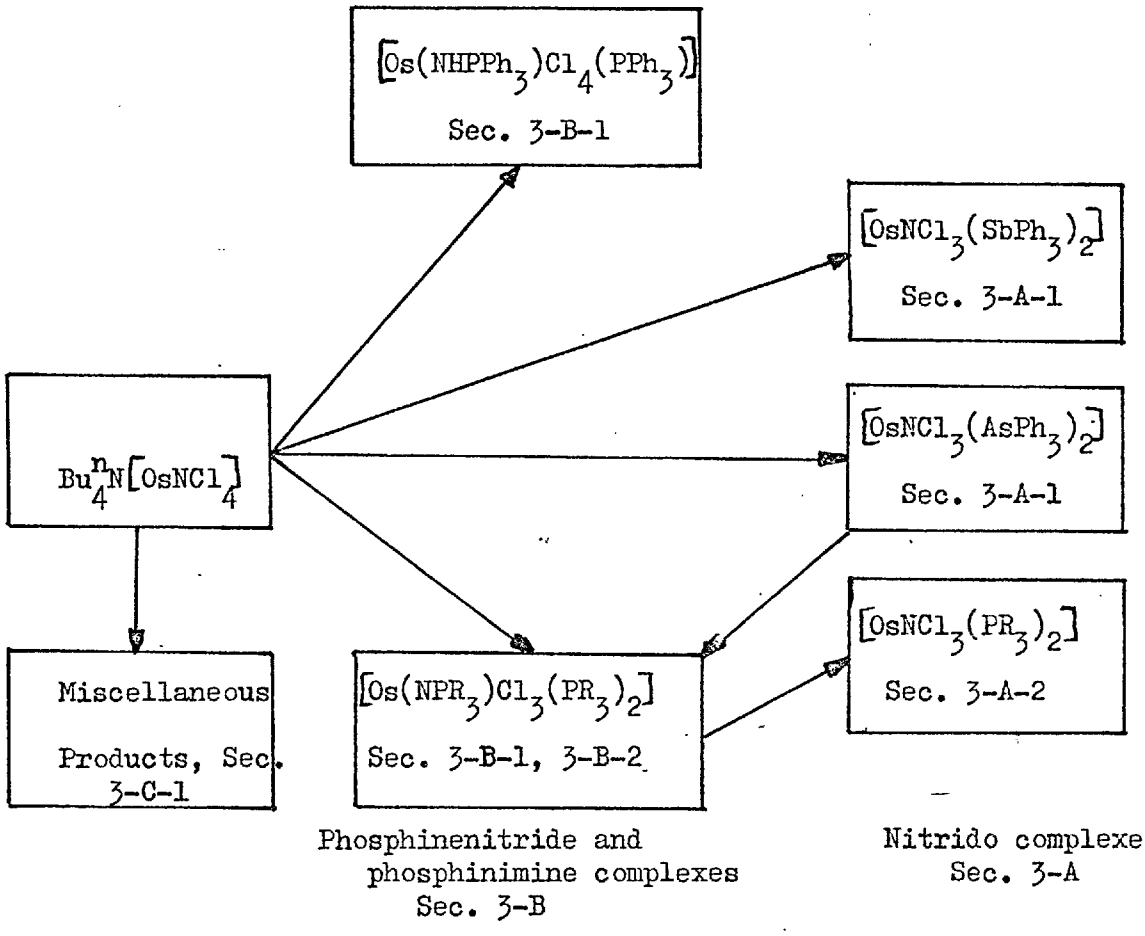
OSMIUM AND RUTHENIUM NITRIDO COMPLEXES WITH GROUP V LIGANDS AND THEIR REACTIONS.

ABSTRACT.

The reactions of the nitrido halide anions $[OsNX_4]^-$ and $[RuNCl_4]^-$ (X = Cl, Br) with amine, and tertiary phosphine, arsine and stibine ligands have been studied. The new complexes thus obtained are of two main types, (a) nitrido complexes $[OsNX_3(L'Ph_3)_2]$, $[RuNCl_3(L'Ph_3)_2]$, $[OsNCl_3(AsEt_3)_2]$, $[OsNX_3(bipy)]$ and $[OsNCl_3(PR_3)_2]$, and (b) complexes with phosphinenitride ligands $[M(NPR_3)Cl_3(PR_3)_2]$, $[Os(NPR'_3)Br_3(PR'_3)_2]$ and $[M(NPMe_2Ph)Cl_3(AsPh_3)_2]$ (X = Cl, Br; L' = As, Sb; PR_3 = PPh_3, PPh_2Et, PEt_2Ph, PEt_3, PPh_2Me, PMe_2Ph; PR'_3 = PPh_3, PPh_2Et, PEt_2Ph; M = Os, Ru). Other new products obtained include the phosphinimine complex $[Os(NHPPh_3)Cl_4(PPh_3)]$, and $[OsCl_4(PPh_3)_2]$, $Ph_4As[OsCl_5(PPh_3)]$, $[Os(OMe)_2Cl_2(PPh_3)_2]$ and $Ph_4As[OsX_4(PR''_3)_2]$ (PR''_3 = PPh_3, PEt_2Ph). The formation and reactions of these complexes, and their characterisation by chemical and physical methods are discussed.

ARRANGEMENT OF MATERIAL.

The order in which these complexes and their interconversion will be discussed is shown in the following diagram for $[OsNCl_4]^-$. Where similar reactions and products have been obtained for $[OsNBr_4]^-$ and $[RuNCl_4]^-$, they will beconsidered in the same section as their osmium-chloro analogues. For clarity, the nitrido phosphine complexes $[OsNCl_3(PR_3)_2]$ will be dealt with in Sec. 3 - A - 2, before the discussion of the formation and structures of the phosphinenitride complexes (Sec. 3 - B - 2) from which they are made.



INTRODUCTION.

A number of stable Os(VI) complexes containing Os ≡ N bonds are known (Sec. 2 - A - 2), but although the isoelectronic Re(V) ion forms a wide range of stable nitrido complexes with tertiary phosphine ligands,[19] all previous attempts to prepare their Os(VI) analogues have failed. The methods which have been tried are:

1) Reaction of $K[Os^{VIII}O_3N]$ or $K_2[Os^{VI}NCl_5]$ with PR_3 in EtOH/HX (X = Cl,Br). This gave $[Os^{IV}X_4(PR_3)_2]$, then $[Os^{III}X_3(PR_3)_3]$ and finally $[Os^{II}_2X_3(PR_3)_6]X$ [82].

2) Reaction of $[Os^{III}X_3(PR_3)_3]$ with ammonia. This gave $[Os^{II}(NH_3)X_2(PR_3)_3]$.[83]

3) Reaction of $[Os^{V}OCl_3(PPh_3)_2]$ with $N_2H_6Cl_2$ in EtOH/HCl.

$[Os^{III}(NH_3)Cl_3(PPh_3)_2]$ was obtained.[19] $[Re^{V}OCl_3(PPh_3)_2]$ reacts with $N_2H_6Cl_2$ in wet ethanol to give $[Re^{V}NCl_2(PPh_3)_2]$.[19]

4) Thermal and photochemical decomposition of azido complexes, (a) $[Os^{II}(N_3)_2(PMe_2Ph)_4]$ which did not react and (b) $[Os^{III}Cl_2(N_3)(PR_3)_3]$ which gave unpurifiable mixtures which may have contained a nitrido complex [84].

5) Reaction of azide ion with $[Os^{IV}Cl_4(PR_3)_2]$, which gave unpurifiable mixtures which possibly contain a nitrido complex [84]. $[Re^{III}Cl_3(PR_3)_3]$ reacts with azide ion to form $[Re^{V}NCl_2(PR_3)_3]$.[19]

The stability of the Re(V) nitrido phosphine complexes and the difficulty in preparing their Os(VI) analogues suggested that these latter complexes might be much more reactive, and unstable under the reaction conditions previously used. We have isolated the complexes $Bu^n_4N[OsNX_4]$ and $Bu^n_4N[RuNCl_4]$ (Sec. 2 - A - 2), which are readily soluble in a variety of polar organic solvents at room temperature, and have thus been able to attempt to substitute them with tertiary phosphine ligands under very mild conditions. For comparison we have also studied the reactions of these salts under similar mild conditions with less nucleophilic, less reducing arsine and stibine ligands, and also the more nucleophilic non-reducing amine 2,2'-bipyridine. There are no known nitrido arsine or stibine complexes of any metal.

3 - A OSMIUM AND RUTHENIUM NITRIDO COMPLEXES WITH GROUP V LIGANDS.

3 - A - 1. Complexes with arsine, stibine and amine ligands.

The reaction of concentrated solutions of $L'Ph_3$ (L' = As,Sb) in acetone with warm solutions of $Bu^n_4N[OsNX_4]$ or $Bu^n_4[RuNCl_4]$ (X = Cl, Br) in methanol gave an immediate precipitate of the diamagnetic nitrido complexes

$[OsNX_3(L'Ph_3)_2]$ and $[RuNCl_3(L'Ph_3)_2]$ in 80 - 90% yield. If these preparations were carried out in acetone alone, then the reactions proceeded much more slowly, taking up to 36 hours for completion. This is presumably because acetone is less able than methanol to solvate the displaced chloride ion, since the reactions in acetone can be expedited by addition of water or aqueous HX.

$$[OsNX_4]^- + 2L'Ph_3 \rightarrow [OsNX_3(L'Ph_3)_2] + X^-$$

The complex $[OsNCl_3(AsEt_3)_2]$ was made by rapid evaporation of the solvent from a solution of $Bu^n_4N[OsNCl_4]$ and $AsEt_3$ in acetone. A second isomer of $[OsNBr_3(AsPh_3)_2]$ (Isomer B) was made by slow evaporation (~48 hours) of solutions of $[OsNBr_4]^-$ and $AsPh_3$ in acetone. The other isomer, (Isomer A) was obtained when any of the more rapid methods outlined above were employed. Slow evaporation of solvent from solutions of $Bu^n_4N[OsNX_4]$ and 2,2'-bipyridine (bipy) in acetone gave microcrystalline precipitates of $[OsNX_3(bipy)]$.

3 - A - 2. Complexes with phosphine ligands.

Reactions similar to those outlined in the previous section between the tertiary phosphine ligands PPh_3 and PEt_2Ph, and $Bu^n_4N[OsNX_4]$ or $Bu^n_4N[RuNCl_4]$ in acetone or methanol did not yield nitrido complexes. These reactions and their products will be discussed fully in Sections 3 - B - 1, and 3 - C - 1. The diamagnetic tertiary phosphine nitrido complexes $[Os^{VI}NCl_3(PR_3)_2]$ (PR_3 = PPh_3, PPh_2Et, PEt_2Ph, PEt_3, PPh_2Me, PMe_2Ph) were made however by oxidising a suspension of $[Os^{IV}(NPR_3)Cl_3(PR_3)_2]$ in methanol with chlorine. (The preparation and structures of these starting materials will be discussed in Sec. 3 - B). We could not isolate pure samples of $[Os^{VI}NBr_3(PR_3)_2]$ by bromine oxidation of $[Os^{IV}(NPR_3)Br_3(PR_3)_2]$ (Sec. 3 - B), nor pure samples of $[Ru^{VI}NCl_3(PPh_3)_2]$ by chlorine oxidation of $[Ru^{IV}(NPPh_3)Cl_3(PPh_3)_2]$ (Sec. 3 - B).

In this latter case products which showed an i.r. band characteristic of ν_{RuN} have been obtained, but the products were always contaminated with a large proportion of starting material.

3 - A - 3 Solution properties.

Solution measurements on these complexes must be interpreted with caution. There are two main reasons for this. Firstly, the i.r. and n.m.r. solution spectra of the phosphine complexes $[OsNCl_3(PR_3)_2]$ showed that decomposition occurred, in some cases (e.g. $PR_3 = PPh_3$) very quickly. Secondly, the complexes $[OsNX_3(L'Ph_3)_2]$ and $[RuNCl_3(L'Ph_3)_2]$ are only slightly soluble in common organic solvents. Apparent molecular weights in benzene solution for the $L'Ph_3$ complexes were approximately half their formula weights, but similar measurements on some of the more stable PR_3 complexes showed that they were essentially undissociated. Neither the $L'Ph_3$ complexes nor the PR_3 complexes were electrolytes in acetone or dichloromethane. The $L'Ph_3$ complexes presumably lose an $L'Ph_3$ ligand in solution, and it is easy to appreciate why dissociation occurs in such a crowded coordination sphere. If a similar dissociation of the PR_3 complexes did occur then it is likely that further decomposition would follow (Sec. 3 - B - 8).

3 - A - 4 Infra-red spectra.

The i.r. absorptions of these complexes from 4000 - 200 cm^{-1} assigned to vibrations of the nitrido and halide ligands are presented in Table 3.1. The presence of a strong sharp band near 1060 cm^{-1} for all the osmium complexes, and near 1030 cm^{-1} for the two ruthenium complexes, which shifts some 30 cm^{-1} to lower frequencies on ^{15}N substitution, confirms the presence of an M ≡ N unit in these species [1]. The shape, position, and shift on isotopic substitution of this absorption are quite characteristic of the metal-

T A B L E 3.1.

Infra-red amd ^1H n.m.r. spectra of osmium and ruthenium nitrido complexes with Group V ligands

	m.p., t^0C.	ν_{OsN}, cm^{-1}	ν_{OsX}, cm^{-1}	δ_{NOsX}; cm^{-1}	n,m.r. spectra, (τ), in $CDCl_3$, 0^0C.
$[OsNCl_3(PPh_3)_2]$	145(decomp)	1058 s	327 s 252 ms	226w	≠
$[Os^{15}NCl_3(PPH_3)_2]$	≠	1026 ms	329 s 251 ms	223w	≠
$[OsNCl_3(PPh_2Et)_2]$	176	1062 ms	321 s 240 ms	230w	8.36(1.4.6.4.1 quintet), methylene; 6.95(methyl); 2.46, 2.07(phenyl).
$[OsNCl_3(PEt_2Ph)_2]$	129	1070 s 1063 ssh	325 s	*	8.72(1.4.6.4.1 quintet), methylene; 7.02(methyl); 2.49. 2.18, phenyl.
$[OsNCl_3(PEt_3)_2]$	≠	1070 ms	330 ssh 319 s. 245 ms	*	≠
$[OsNCl_3(PPh_2Me)_2]$	160	1072 ms 1063 ms	330 s 244 ms	220 w	7.53(1.2.1 triplet), methyl; 2.56, 2.25, phenyl.
$[OsNCl_3(PMe_2Ph)_2]$	158	1068 ms	325 s 238 ms	*	7.86(1.2.1. triplet), methyl; 7.25(1.2.1. triplet)meth (Two isomers?); 2.72, 2.32, 1.72 (phenyl).
$[OsNCl_3(AsEt_3)_2]$	Decomp. 135-145	1070 s	340 sh 328 s 302 sh 230 s	*	8.66(1.2.1. triplet), methyl; 7.68(quintet),methylene
$[OsNCl_3(AsPh_3)_2]$	257	1059 s	325 s 251 ms 243 sh	219 w	≠

TABLE 3.1. contd.

$[OsNCl_3(SbPh_3)_2]$	170	1065 s 1032 **	327 s 306 ms 237 ms	223 w	≠
$[OsNBr_3(AsPh_3)_2]$ (Isomer A)	221	1068 s 1035 **	202 s	231 mw	≠
$[OsNBr_3(AsPh_3)_2]$ (Isomer B)		1062 s 1030 **	200 s	230 mw	≠
$[OsNBr_3(SbPh_3)_2]$	171	1061 s	*	210 m	≠
$[OsNCl_3(bipy)]$	355	1086 s	340 s 326 s 240 m	*	≠
$[OsNBr_3(bipy)]$		1090 s	*	*	≠
$[RuNCl_3(AsPh_3)_2]$	169	1023 s	335 s 323 s 240 ms	215 w	≠
$[RuNCl_3(SbPh_3)_2]$	165	1029 s	338 s 286 s 239 s	*	≠

* Not assigned: ≠ Not measured ** ^{15}N substituted.

nitrogen stretching vibration, ν_{MN}, in a complex with a terminal nitrido ligand. The frequency of ν_{MN} is some 30 - 40 cm^{-1} lower than in the corresponding penta-halo complexes $[MNX_5]^{2-}$ (M = Os, Ru, X = Cl,Br) [86]. There is no large variation in ν_{MN} for amine, phosphine, arsine and stibine complexes of the same metal. In general, the more alkylated the phosphine or arsine, the higher the value of ν_{MN}. These small variations in ν_{MN}, with higher frequencies for more basic ligands with correspondingly lower steric requirements, are similar to the small variations of ν_{ReN} observed in $[ReNCl_2(PR_3)_3]$ [19]. The two isomers of $[OsNBr_3(AsPh_3)_2]$ have ν_{OsN} at 1068cm^{-1} (Isomer A) and 1064 cm^{-1} (Isomer B). There are similar small differences in ν_{ReO} for the three isomers of $[ReOCl_3(PPh_3)_2]$ [87]. Isomer B also had two additional i.r. bands at 695 cm^{-1} and 455 cm^{-1}, and a rather different spectrum near 330 cm^{-1} to Isomer A. These latter modifications to the i.r. spectrum of Isomer B are probably associated with arsine vibrations, and are not seen in the spectra of any of our other triphenylarsine complexes.

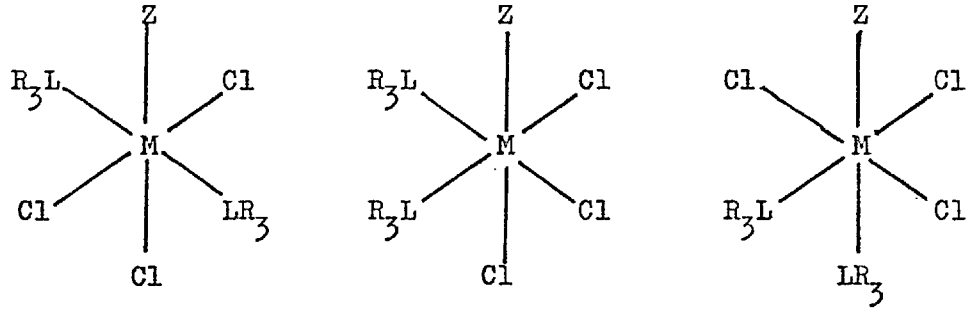
The number of M - Cl stretching absorptions in the i.r. spectra of complexes such as these is not normally a good criterion for determining their stereochemistries. Thus, for each of the three possible geometrical isomers of $[MNCl_3(LR_3)_2]$ (Sec. 3 - A - 6), we would expect three such absorptions. We normally see two, sometimes three bands which we assign to ν_{MCl}, but one of these is some 70 - 80 cm^{-1} lower in frequency than the others. These low frequency bands are not present in the bromo complexes, nor do they shift on ^{15}N substitution, and are probably due to the stretching vibration of a chloro ligand weakly bonded <u>trans</u> to the nitride. Such bands have been similarly assigned in $[ReNCl_2(PR_3)_3]$ [19]. They probably obscure the M ≡ N deformation absorptions in most of the chloro complexes, but in some cases weak bands near 220 cm^{-1} may be due to this mode.

3 - A - 5 ^{1}H n.m.r. spectra.

The ^{1}H n.m.r. spectra of the more stable osmium nitrido phosphine complexes and $[OsNCl_3(AsEt_3)_2]$ are listed in Table 3.1. The chemical shifts of the ligand protons are typical for diamagnetic complexes. The spectra of $[OsNCl_3(PEt_2Ph)_2]$ and $[OsNCl_3(PPh_2Et)_2]$ show quintet 1.4.6.4.1 resonances near τ 8.5 which are assigned to methylene protons. That of $[OsNCl_3(PPh_2Me)_2]$ has a triplet centred on τ 7.51 which is assigned to methyl protons. These splitting patterns probably arise because of 'virtual coupling' [88] of the two phosphorus nuclei , a phenomenon which normally, though not exclusively[89] occurs when the two phosphorus donors are trans to each other. The patterns provide further evidence that the phosphine ligands do not dissociate from the metal in solution. It must however be noted that the methylene resonance in $[OsNCl_3(AsEt_3)_2]$ is also a quintet, although ^{75}As has no nuclear spin. The presence here of a quintet may be due to the overlapping of the two quartet resonances of methylene protons sterically restrained in non-equivalent positions.[98]

3 - A - 6 Structures.

There are three possible geometrical isomers for complexes of the type $[MZCl_3(LR_3)_2]$ (L = P,As,Sb).

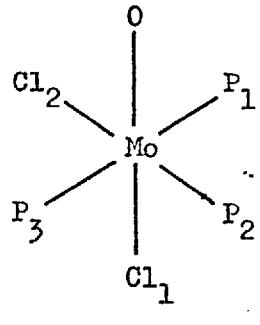


skeletal symmetry C_{2v} C_s C_s

I II III

The evidence that we have presented in the previous two sections suggests that in our nitrido complexes (Z = N), there is a chloride (or, presumably, bromide) ligand trans to the nitride, and that in the phosphine complexes at least, the LR_3 groups are trans to each other, i.e. there is configuration I. In X-ray structural determinations on similar compounds. (Z = O, [90] NR [38,39]) configuration I has been found. One might predict such a structure on steric, electronic (ligand of lower trans-influence trans to the nitride) and kinetic (trans directing influence of LR_3 groups in substitution reactions) grounds. Configuration II is much rarer, but it has been proposed for one of the three isomers of $[ReOCl_3(PEt_2Ph)_2]$ [91] which has a high dipole moment, and also for some ruthenium nitrosyl complexes [92]. Our 2,2'-bipyridine complexes probably have this structure. Complexes with configuration III are not known.

There is however the possibility of another type of isomerism in these extremely crowded systems. There are two isomers of $[MoOCl_2(PR_2Ph)_3]$ [43] (R = Me, Et), one blue and one green, having molybdenum-oxygen stretching frequencies γ_{MoO} differing by 10 cm^{-1}. The blue isomer of $[MoOCl_2(PMe_2Ph)_3]$(A)[93] and the green isomer of $[MoOCl_2(PEt_2Ph)_3]$(B)[94], both have very distorted octahedral structures with mer phosphine ligands and a chloro ligand trans to the oxo group, that is configuration IV.



IV

There are however some important differences between the structures. The Mo-O distance in (A) is 1.676Å and that in (B) is 1.801Å, despite the fact that ν_{MoO} for the two complexes are very similar. The corresponding Mo-Cl_1 distances are 2.551Å and 2.424Å respectively. Furthermore, in (A) there is a mirror plane defined by the atoms O,Cl_2,Cl_1 and P_2, but in (B) the substituent groups on the phosphine atoms adopt a different mutual orientation in order to relieve intra-molecular overcrowding, and hence the mirror plane is not present. This has been called 'distortional isomerism'.[44]

An isomerism of this type is an attractive possibility in $[OsNBr_3(AsPh_3)_2]$ in view of the extreme congestion of its coordination polyhedron, and the modified i.r. spectrum of the arsine ligands in Isomer B. It may also be present in some of our osmium nitrido phosphine complexes which show two bands in their i.r. spectra due to ν_{OsN} (Table 3.1). The ^1H n.m.r. spectrum of $[OsNCl_3(PEt_2Ph)_2]$ (which has two such i.r. bands) shows that only one isomer is present in solution. The green and blue distortional isomers of $[MoOCl_2(PMe_2Ph)_3]$ show similar behaviour [43]. This type of isomerism may be quite common; it is a possibility for one of the three isomers of $[ReOCl_3(PR_3)_2]$ (PR_3 = PPh_3 [87], PEt_2Ph[91]) and also two of the isomers of $[Ru(NO)Cl_3(AsEt_2Ph)_2]$[92].

3 - B NITRENE-LIKE BEHAVIOUR OF THE NITRIDO LIGAND IN SOME OSMIUM AND RUTHENIUM NITRIDO COMPLEXES: COMPLEXES WITH PHOSPHINENITRIDE $(NPR_3)^-$ AND PHOSPHINIMINE LIGANDS.

The reactions discussed in Secs. 3 - B - 1 and 3 - B - 2 are illustrated in Figure 3.1.

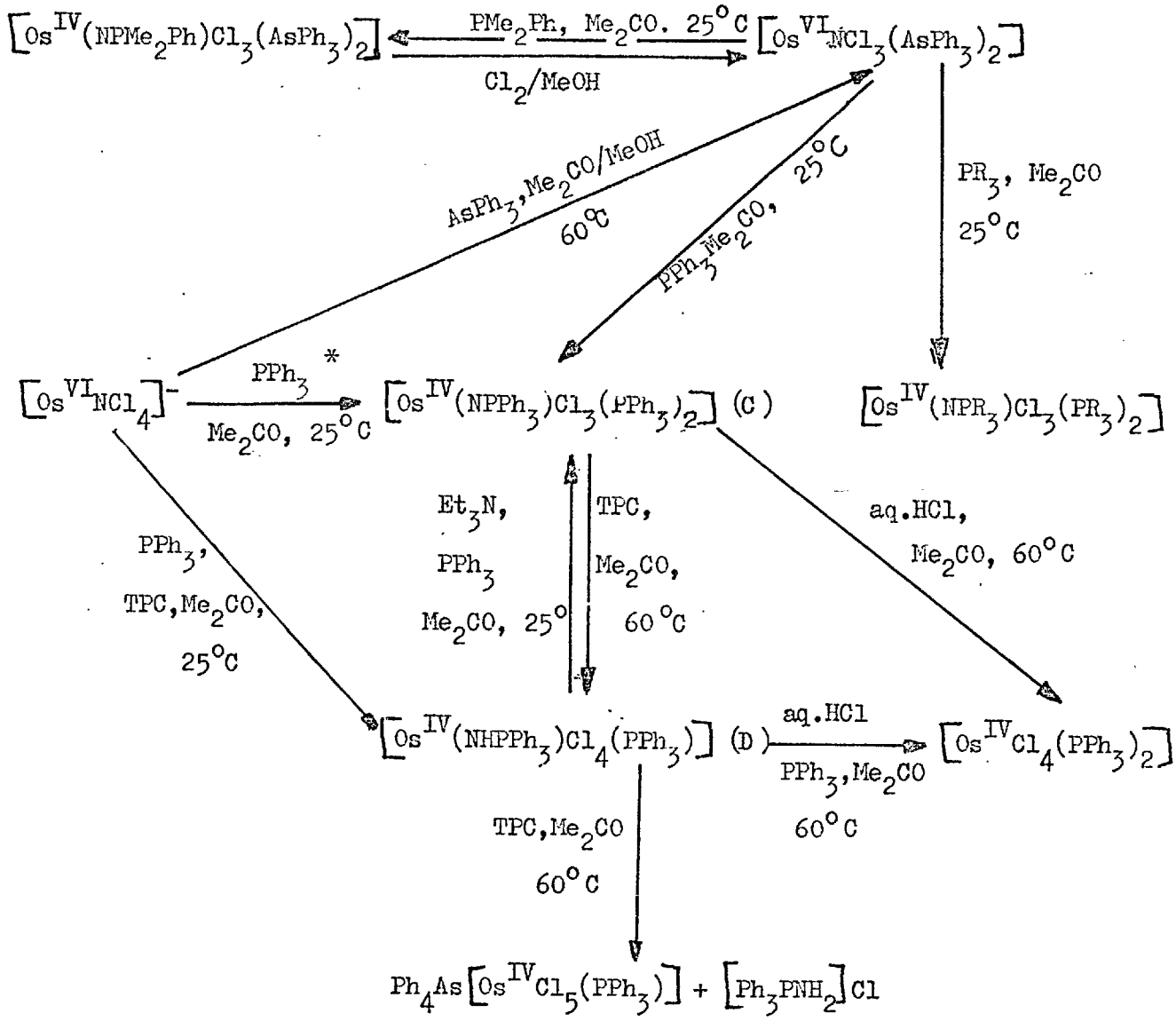
3 - B - 1. Preparation and characterisation of osmium complexes with triphenylphosphinimine and triphenylphosphinenitride ligands

We have already reported (Sec. 3 - A - 2) that even under the mildest substitution conditions, viz. the reaction of PPh_3 with $Bu^n_4N[OsNX_4]$ (X = Cl,Br) in acetone at room temperature, we could not isolate osmium nitrido phosphine complexes. These reactions gave paramagnetic species $[OsNCl_3(PPh_3)_3].Me_2CO$ (μ_{eff} 1.8 B.M.), (C) and $[OsNBr_3(PPh_3)_3].Me_2CO$. Complex (C) was also formed when the nitrido complexes $[OsNCl_3(PPh_3)_2]$ and $[OsNCl_3(AsPh_3)_2]$ were reacted with PPh_3 under similar mild conditions, which suggested that all these Os(VI) nitrido complexes had a similar reactivity towards PPh_3. A protonated derivative of (C), $[Os(NH)Cl_4(PPh_3)_2].Me_2CO$ (μ_{eff} 1.6 B.M.) (D), was made by reacting PPh_3 with $[OsNCl_4]^-$ in the presence of 1 mole of 'tetraphenylarsonium chloride', TPC. ('TPC' is in fact $Ph_4As[H_5O_2]Cl_2$, [95] and therefore a convenient source of HCl in readily controlled small quantities). Complexes (C) and (D) are interconvertible. Complex (C) was protonated to give (D) by treating it in acetone suspension with TPC, and the deprotonation of (D) to give (C) was accomplished by triethylamine in acetone in the presence of excess PPh_3

$$[OsNCl_3(PPh_3)_3] \underset{Et_3N,\ PPh_3}{\overset{HCl}{\rightleftharpoons}} [Os(NH)Cl_4(PPh_3)_2]$$

(C) (D)

FIGURE 3.1.



* Also for PMe_2Ph

TPC; tetraphenylarsonium chloride, $Ph_4As[H_5O_2]Cl_2$.

PR_3: PPh_3, PPh_2Et, PEt_2Ph, PEt_3, PPh_2Me

We propose that these complexes are Os(IV) derivatives of triphenylphosphine-nitride, $[Os(NPPh_3)Cl_3(PPh_3)_2].Me_2CO$, (C), and triphenylphosphinimine, $[Os(NHPPh_3)Cl_4(PPh_3)].Me_2CO$, (D), formed by nucleophilic attack of the phosphine on the nitrido ligand, on the basis of the following chemical and physical properties.

1. When complex (D) was heated with 1 mole of TPC in acetone, a mixture of aminotriphenylphosphonium chloride, $[Ph_3PNH_2]Cl.H_2O$ and the red salt $Ph_4As[OsCl_5(PPh_3)]$ was produced. The phosphonium chloride was removed by washing with methanol. The yields were 80 - 90% based on the equation

$$[Os(NHPPh_3)Cl_4(PPh_3)] + Ph_4As[H_5O_2]Cl_2 \rightarrow Ph_4As[OsCl_5(PPh_3)] + [PPh_3NH_2]ClH_2O + H_2O.$$

Triphenylphosphinimine is known to react with hydrogen chloride to give $[Ph_3PNH_2]Cl$. [96]. The phosphonium salt had an i.r. spectrum identical with that of a sample prepared by a published method [97]. When it was prepared from ^{15}N substituted (D), the strong band in its i.r. spectrum assigned to the P-N stretching vibration, ν_{PN}, showed a characteristic low frequency shift of 20 cm^{-1}. In contrast, the spectrum of $Ph_4As[OsCl_5(PPh_3)]$ (a 1:1 electrolyte in acetone solution) had no band which shifted when prepared from ^{15}N substituted (D). It showed two bands in the Os-Cl stretching region however, and we assign the lower frequency one to the stretching vibration of the chloride ligand <u>trans</u> to the phosphine.

2. Complexes (C) and (D) were readily converted into $[OsCl_4(PPh_3)_2]$ in 85 - 95% yield by treatment in acetone with an excess of aqueous HCl. Complex (D) required 1 mole of PPh_3 to complete the reaction.

$$[Os(NPPh_3)Cl_3(PPh_3)_2] + 2HCl \rightarrow [OsCl_4(PPh_3)_2] + [Ph_3PNH_2]Cl$$

$$[Os(NHPPh_3)Cl_4(PPh_3)] + HCl + PPh_3 \rightarrow [OsCl_4(PPh_3)_2] + [Ph_3PNH_2]Cl$$

3. A triethylphosphine analogue of (C), $[Os(NPEt_3)Cl_3(PEt_3)_2]$ was made. We therefore rule out schemes which involve attack of the nitrido ligand on a phenyl ring.

4. Although (D) is paramagnetic, it had a sharp ^1H n.m.r. spectrum, which showed chemical shifts characteristic of an Os(IV) complex [98,99]. In particular, the resonance assigned to the ortho protons of the phosphine ligand was seen at τ- 2.5; its intensity was one quarter of the total intensity of the resonances due to the remaining protons*. We could not measure the ^1H n.m.r. spectrum of (C) since it was insufficiently soluble, and in any case decomposed in solution (i.r. measurements). We have however measured the ^1H n.m.r. spectra of more stable alkyl-aryl phosphine analogues of (C), and they showed sharp, shifted spectra similar to that of (D) (Sec. 3 - B - 6).

5. The infra-red spectra of (C) and (D) showed strong, broad bands at 1127 cm^{-1} and 924 cm^{-1} respectively, which shifted some 20 cm^{-1} to lower frequencies on ^{15}N substitution. Similar bands with small shifts have been assigned to P-N stretching vibrations, ν_{PN}, in Ph_3PNH, [100] Ph_3PNR, [101] and Ph_3PNH complexes [100]. The spectrum of (D) also had bands at 3299 (N-H stretch), 1243 (N-H deformation) and 586 cm^{-1} (Os-N stretch), which shifted slightly on ^{15}N substitution (to 3291, 1240 and 579 cm^{-1} respectively) and markedly on deuteriation. Deuteriation shifted the high and low frequency bands to 2445 and 572 cm^{-1}, but the sharp band of moderate intensity at 1243 cm^{-1} shifted to the same place as the shifted very broad, very strong band due to ν_{PN}. This resulted in the appearance of two bands at 979 and 865 cm^{-1}, both moderately strong and fairly broad. This effect may be due to Fermi resonance between ν_{PN} and the N-D deformation mode.

* The shifts decrease, however, with increasing temperature.

6. The effective magnetic moments at room temperature of (C) (1.8 B.M.) and (D) (1.6 B.M.) are typical values for Os(IV) complexes [99].

3 - B - 2 Osmium and ruthenium complexes with tertiary phosphinenitride ligands $(NPR_3)^-$.

The reaction of $Bu^n_4N[RuNCl_4]$ with PPh_3, and $Bu^n_4N[OsNX_4]$ (X = Cl,Br) with PEt_2Ph in cold acetone did not give analogues of the triphenylphosphinenitride complex $[Os(NPPh_3)Cl_3(PPh_3)_2]$, (C). These reactions and their products are discussed in Sec. 3 - C. Analogues of (C) were however readily prepared by reacting dry, deoxygenated acetone suspensions of the nitrido complexes $[MNCl_3(AsPh_3)_2]$ (M = Os,Ru) with a variety of tertiary phosphines at room temperature, which gave the paramagnetic species $[M(NPR_3)Cl_3(PR_3)_2]$ (PR_3 = PPh_3, PPh_2Et, PEt_2Ph, PEt_3, PPh_2Me). Using $[OsNBr_3(AsPh_3)_2]$ as starting material we isolated $[Os(NPPh_2Et)Br_3(PPh_2Et)_2]$ and $[Os(NPEt_2Ph)Br_3(PEt_2Ph)_2]$. The magnetic moments at room temperature of these products are ~1.8 B.M. for osmium complexes and ~2.9 B.M. for ruthenium complexes, which are typical values for Os(IV) and Ru(IV) species [102].

Dimethylphenylphosphine reacted differently with $[MNCl_3(AsPh_3)_2]$ under similar conditions, giving the intermediate species $[M(NPMe_2Ph)Cl_3(AsPh_3)_2]$. The osmium complex was oxidised back to the starting material in 90% yield by chlorine (Sec. 3 - A - 2), confirming that the phosphine had attached itself to the nitrogen in these complexes, rather than partially substituting the arsine. We suceeded in preparing $[Os(NPMe_2Ph)Cl_3(PMe_2Ph)_2]$ by reacting the phosphine directly with $Bu^n_4[OsNCl_4]$ in ice-cold acetone, after the manner of the preparation of (C), probably because the complex is rather insoluble and can be quickly filtered off. The general unsuitability of this method for preparing phosphinenitride complexes can be attributed to the

presence of a displaced, poorly solvated, nucleophilic chloride ion in the reaction mixture, which in turn displaces the phosphinenitride ligand.

$$3PR_3 + [OsNCl_4]^- \rightarrow [Os(NPR_3)Cl_3(PR_3)_2] + Cl^-$$

$$3PR_3 + [OsNCl_3(AsPh_3)_2] \rightarrow [Os(NPR_3)Cl_3(PR_3)_2] + 2AsPh_3.$$

The triphenylphosphinenitride ligand in $[Ru(NPPh_3)Cl_3(PPh_3)_2]$ was recovered as aminotriphenylphosphonium chloride, $[Ph_3PNH_2]Cl$ by treating an acetone suspension of the complex with $Ph_4As[H_5O_2]Cl_2$, thus confirming that this ligand is indeed present, as in the osmium complex $[Os(NPPh_3)Cl_3(PPh_3)_2]$ (Sec. 3 - B - 1). Attempts to prepare a ruthenium analogue of $[Os(NHPPh_3)Cl_4(PPh_3)]$ by reacting $[RuNCl_3(AsPh_3)_2]$ in acetone with triphenylphosphine in the presence of $Ph_4As[H_5O_2]Cl_2$ gave only $Ph_4As[RuCl_4(PPh_3)_2]$ and $[Ph_3PNH_2]Cl$.

3 - B - 3 Solution properties of $[M(NPR_3)Cl_3(PR_3)_2]$.

The i.r. and n.m.r. spectra of chloroform solutions of these complexes show that they decompose in solution, in some cases very quickly. Where we have been able to obtain solution data it appears that these complexes are non-conductors in acetone, and have molecular weights of approximately 85% of their formula weights in benzene. These rather low values may indicate that slight dissociation of the complexes occurs, or, more likely, that some decomposition occurs during the time taken for the measurement.

3 - B - 4 Infra-red spectra of $[M(NPR_3)Cl_3(PR_3)_2]$.

Selected bands from the i.r. spectra of these complexes are presented in Table 3.2. The main feature of the spectra is a very strong, broad absorption near 1125 cm^{-1} which we assign to the P-N stretching vibration,

T A B L E 3.2.

Osmium and Ruthenium Phosphinenitride complexes.

	m.p.T°C.	ν_{PN} cm^{-1}	ν_{OsX} cm^{-1}	n.m.r. spectra, (τ) in $CDCl_3$
$[Os(NPPh_3)Cl_3(PPh_3)_2].Me_2CO$	136	1127s,br	309s 294s 285msh	⊀
$[Os(^{15}NPPh_3)Cl_3(PPh_3)_2].Me_2CO$		1104s,br	309s 293 s 284msh	⊀
$[Os(NPPh_2Et)Cl_3(PPh_2Et)_2].Me_2CO$	132	1085s,br	309s 285s 269s	⊀
$[Os(NPEt_2Ph)Cl_3(PEt_2Ph)_2]$	134	1204s	300ssh 290s 276ms	9.42, 8.12(triplet): 4.08,3.60(doublet of quartets); 1.72; 1.32; 0.02(v.complex);-2.92(triplet); -11.8(doublet): T = 0°C
$[Os(NPEt_3)Cl_3(PEt_3)_2]$	⊀	1125,s,br	292s 269ms	12.36(CH_2 of Et_3PN^-); 4.38(CH_2 of PEt_3): 3.50 (CH_3 of PEt_3) -0.08(CH_2 of Et_3PN^-): T = -50°C
$[Os(NPPh_2Me)Cl_3(PPh_2Me)_2]$	165 (decomp)	1128s,br	309s 296s	9.00: 8.10: 7.86: 6.64: 4.64: 3.64: -0.42(triplet) -8.92: -15.65: T = 0°C
$[Os(NPMe_2Ph)Cl_3(PMe_2Ph)_2]$	95-102 (decomp)	1165vs,br	299s 286s 270s	11.40: 8.50: 7.65: 5.35: 4.00: 2.20: 0.00(triplet), -12.65(doublet), -17.30: (T = 0°C)
$[Os(NPMe_2Ph)Cl_3(AsPh_3)_2]$	156	1081vs	323s 294m	⊀
$[Os(NPPh_3)Br_3(PPh_3)_2].Me_2CO$	122	1125s,br	212s	⊀

TABLE 3.2. contd.

$[Os(NPPh_2Et)Br_3(PPh_2Et)_2].Me_2CO$	154 (decomp)	1090s,br	213s	≠
$[Os(NPEt_2Ph)Br_3(PEt_2Ph)_2]$		1160s	205s	≠
$[Ru(NPPh_3)Cl_3(PPh_3)_2].Me_2CO$	150 decomp	1108s,br	325s 301s 280m	≠
$[Ru(NPPh_2Et)Cl_3(PPh_2Et)_2].Me_2CO$	114	1063s,br	317s 290s 269s	≠
$[Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2]$	134 decomp	1165,s,br	320msh 302s 290s	≠
$[Ru(NPEt_3)Cl_3(PEt_3)_2]$	≠	1099s,br	311s 291ms	≠
$[Ru(NPPh_2Me)Cl_3(PPh_2Me)_2]$	145	1114s,br	317s 297ms	≠
$[Ru(NPMe_2Ph)Cl_3(AsPh_3)_2]$	≠	1055vs	325s 310ms 286m	≠

≠ Not measured.

ν_{PN}, since it shifts from 1127 to 1104 cm^{-1} on ^{15}N substitution of $[Os(NPPh_3)Cl_3(PPh_3)_2]$. The frequencies of ν_{PN} here are rather lower than in $R_3P = NY$ (Y = alkyl, aryl, p-substituted tosyl), where this frequency has been correlated with the electronegativity of Y and R [101]. As the electronegativity of Y increases, so the frequency of ν_{PN} falls, and a comparison of ν_{PN} for ruthenium and osmium complexes of the same phosphine would seem to indicate that Ru(IV) is here more electronegative than Os(IV), although mass effects might complicate the relationship. A comparison of ν_{PN} in $[Os(NPMe_2Ph)Cl_3(PMe_2Ph)_2]$ (1165 cm^{-1}) and $[Os(NPMe_2Ph)Cl_3(AsPh_3)_2]$ (1081 cm^{-1}) shows that, as one might expect, the ligand PMe_2Ph renders the Os(IV) ion less electronegative than does $AsPh_3$. In contrast, as the electronegativity of R increases, so does ν_{PN} [101]. Such changes in ν_{PN} caused by changing the R groups of the phosphinenitride ligand in these complexes are obscured by the change in the electronegativity of Y (i.e. the metal) caused by the corresponding change in the phosphine ligands.

We have not been able to identify ν_{MN} in the i.r. spectra of these complexes, nor can we deduce their configuration from the number of i.r. active metal-halogen stretching modes, since for each of the three possible isomers three such i.r. absorptions are expected (See Sec. 3 - A - 6). Two or sometimes three bands are seen, and the absorption profiles vary as the phosphine is varied, although the profiles are similar for complexes of the same phosphine with different metals. From steric and electronic considerations, however, we might expect that these complexes had <u>trans</u> phosphine and meridianal chloride ligands.

3 - B - 5 <u>Infra-red spectrum of $[Os(NHPPh_3)Cl_4(PPh_3)].Me_2CO$, (Table 3.3.)</u>

The P-N and N-H vibrations of this complex are discussed in Sec. 3 - B - 1.

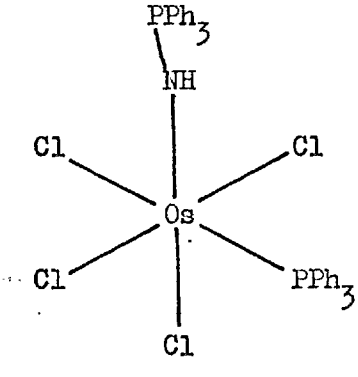
TABLE 3.3.

Infra-red spectrum of $[Os(NHPPh_3)_4Cl_4(PPh_3)].Me_2CO$, cm^{-1}. (M.p. 163° C)

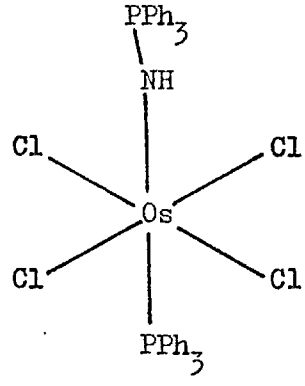
	γ_{NH}	NH	γ_{PN}	γ_{OsN}	γ_{OsCl}
$[Os(NHPPh_3)Cl_4(PPh_3)].(CH_3)_2CO$	3299ms	1243ms	924vs	586s	333s, 320s, 303s, 289s,
$[Os(NDPPh_3)Cl_4(PPh_3)].(CD_3)_2CO$	2445ms	979ms+	865ms+	572s	334s, 319s 302s, 290s
$[Os(^{15}NHPPh_3)Cl_4(PPh_3)].(CH_3)_2CO$	3291ms	1240ms	906vs	579s	334s, 320s 301s, 290s

+ See text.

For its two possible geometrical isomers, V and VI we would expect four ($3A' + A''$) and two ($1A + 1E$) i.r. active osmium-chlorine stretching modes respectively.



V



VI

Skeletal symmetry: Cs C_{4v}

We see four bands near 300 cm^{-1} which do not shift on deuteriation or ^{15}N substitution of the complex, and therefore conclude that it has configuration V.

3 - B - 6 ^{1}H n.m.r. spectra of $[M(NPR_3)Cl_3(PR_3)_2]$.

We have made preliminary studies of the ^{1}H n.m.r. spectra of these species, and find that all show sharp resonances with chemical shifts greater than those observed in diamagnetic complexes. Sharp, shifted ^{1}H n.m.r. spectra have been reported for paramagnetic tertiary phosphine complexes of Os(IV) and Re(III) (d^4) [98,99] and W(IV)(d^2) [103], though there are several differences in direction, magnitude and temperature dependence of the chemical shifts between the d^4 and d^2 systems. Os(IV) and Re(III) complexes which exhibit temperature independent paramagnetism are said to have a diamagnetic ground

state with moments caused by mixing in of a triplet state of only slightly higher energy [102,104]. The abnormal temperature dependence of the spectra of Os(IV) complexes has been related to this effect [98,99]. The low room temperature moments of W(IV) complexes are due to a high spin-orbit coupling constant.

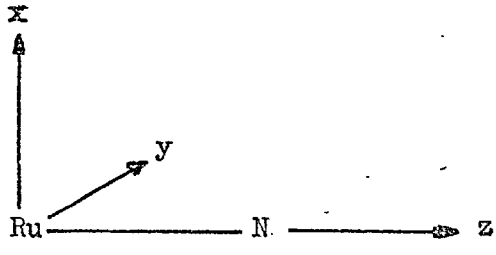
The spectra of our Os(IV) and Ru(IV) complexes are listed in Table 3.2., although only for $[Os(NPEt_3)Cl_3(PEt_3)_2]$ have assignments been made. The spectra of the Os(IV) complexes differ from those which have been reported[98], principally in that the temperature dependence of the chemical shifts is an inverse function of temperature, and that upfield and downfield shifts over a range of 35 p.p.m. (τ = -20 to τ = 15) are seen. The spectra of our Ru(IV) complexes show similar shifted spectra, with rather broader lines, even though they have moments of c.2.9 B.M. A thorough study of the ^1H and ^{31}P n.m.r spectra of our Ru(IV) and Os(IV) phosphinenitride complexes, coupled with studies on the temperature dependence of their magnetic moments would clearly be of considerable interest.

3 - B - 7 Structure and bonding in phosphinenitride complexes.

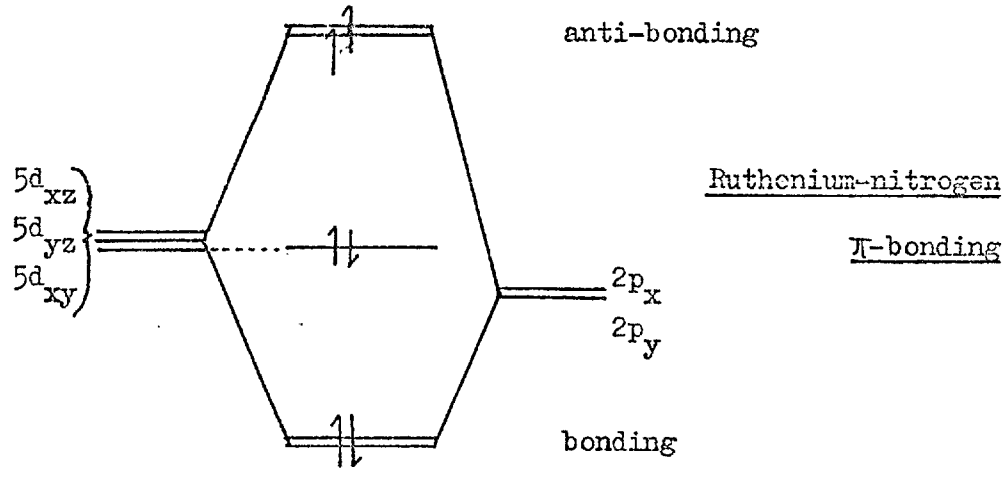
Preliminary X-ray data for the complex $[Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2]$, (E) are in agreement with our proposed structure for the $[M(NPR_3)Cl_3(PR_3)_2]$ complexes. There is distorted octahedral coordination about the ruthenium atom with trans phosphine and meridional chloride ligands, and Ru-Cl bonds rather longer than in $[Ru_2NCl_8(H_2O)_2]^{3-}$. In these respects the complex (E) is similar to the rhenium imido complexes $[Re(NR)Cl_3(PR'_3)_2]$ (R = PhOAc, [38] PhOMe, [38] CH_3 [39]). The important structural feature of (E) is the presence of a slightly non-linear, Ru-N-P_A system ($\sphericalangle RuNP_A \sim 165^\circ$), with an overall Ru-$P_A$ distance of 3.45Å. Phosphorus-nitrogen single and

double covalent bond lengths have been estimated at 1.78Å and 1.64Å respectively [2], and so there is likely to be considerable multiple bonding between the nitrogen and ruthenium and/or phosphorus atoms.

A possible bonding scheme involves multiple Ru-N bonding and a polar $=N-\overset{+}{P}\lesssim$ bond. We take the Ru-N bond as the z axis and choose x and y axes along the Ru-Cl and Ru-P bonds.



If there is sp hybridisation on the nitrogen, then overlap between nitrogen $2p_x$ and $2p_y$ orbitals and ruthenium $5d_{xz}$ and $5d_{yz}$ orbitals is possible



The four nitrogen p electrons fill the two bonding orbitals, two of the four ruthenium electrons pair up in the non-bonding $5d_{xy}$ orbital with the two others remaining unpaired in antibonding orbitals. This scheme gives a total Ru-N bond order of two and a $\gtrsim\overset{+}{P}-N=$ single bond. There may of course

also be $N_{p_\pi} - P_{d_\pi}$ bonding but overlap of a $p_\pi - d_\pi$ type is probably more favourable for N-Ru than N-P bonds. In the anion $[(H_2O)Cl_4Ru\text{-}N\text{-}RuCl_4(OH_2)]^{3-}$ there is a linear Ru-N-Ru system [5], and this has been attributed to such Ru-N-Ru $d_\pi - p_\pi - d_\pi$ bonding (Sec. 1 - A - 4). In $[Ph_3P\text{-}N\text{-}PPh_3]^+$, however, $\measuredangle$ PNP is near 140°, and could be smaller but for steric interactions [110]. In $FPh_2P = NMe$ the nitrogen adopts sp^2 hybridisation and only one of the nitrogen lone pairs is involved in N-P $p_\pi - d_\pi$ bonding [111].

A consequence of our bonding scheme for phosphinenitrides is that the energy of the metal d_{xz} and d_{yz} orbitals is raised above that of the d_{xy} orbital. Thus in the osmium (IV) phosphinenitride complexes it is possible that the normal ordering of singlet ground state and low lying triplet excited state is reversed. If such an effect occurs, we would still expect rather low room temperature magnetic moments because of a high spin-orbit coupling constant, but these should be temperature dependent. Furthermore a normal temperature dependence for ^1H n.m.r. chemical shifts for these complexes might be expected.

3 - B - 8 Nitrene-like behaviour of the nitrido ligand in osmium (VI) and ruthenium (VI) complexes.

The reaction of M(VI) nitrido complexes (M = Os,Ru) with tertiary phosphines to give M(IV) phosphinenitride species $[M(NPR_3)Cl_3(PR_3)_2]$ is unusual. We propose that the highly electronegative M(VI) ion renders the nitrido ligand susceptible to nucleophilic attack, i.e. the nitride is showing electrophilic nitrene-like behaviour:

$$: M^{VI} : : : N : \longleftrightarrow : \underset{\cdot\cdot}{M^{IV}} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}$$

$$: \underset{\cdot\cdot}{M^{IV}} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{N}} : PR_3 \longrightarrow : \underset{\cdot\cdot}{M^{IV}} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{N}} : \overset{+}{P}R_3 \longleftrightarrow : \underset{\cdot\cdot}{M^{IV}} : \overset{\cdot\cdot}{N} : : PR_3$$

This is in contrast to Re(V) nitrido complexes, where the nitrido ligand shows weak nucleophilic properties [85].

There has been considerable recent interest in the stabilisation of the radical nitrene (NH) by coordination to a metal. Nitrene is an intermediate in the decomposition of hydrazoic acid [105], and the decomposition of azido complexes has been shown to give electrophilic intermediates which probably contain coordinated nitrene [55,57,58]. One might expect nitrene to be stabilised by metals in low oxidation states <u>via</u> $M_{d_\pi} \rightarrow N_{p_\pi}$ bonding, and indeed stable complexes of alkylnitrenes RN are known for Fe(0) [106] and Ir (I) [107]. Some Re(V) organo-imido complexes could also be formulated as Re(III) organo-nitrene species [108], and one of them shows some evidence for nitrene-like behaviour [109].

In our reactions, we have shown that stable nitrido complexes probably undergo nucleophilic attack at the nitrogen atom by a phosphine ligand and thus might be better described as complexes of deprotonated nitrene, N^-. Other nucleophiles e.g. Cl^-, 2,2'-bipyridine, triethyl- and triphenyl- arsine and triphenylstibine do not however give similar reactions. The formation of complexes of phosphinenitride may perhaps be related to the ability of phosphorus to form stronger π-bonds to nitrogen in this situation than any of these other nucleophiles.

3 - C. MISCELLANEOUS REACTIONS OF OSMIUM AND RUTHENIUM NITRIDO COMPLEXES WITH PPh_3 AND PEt_2Ph.

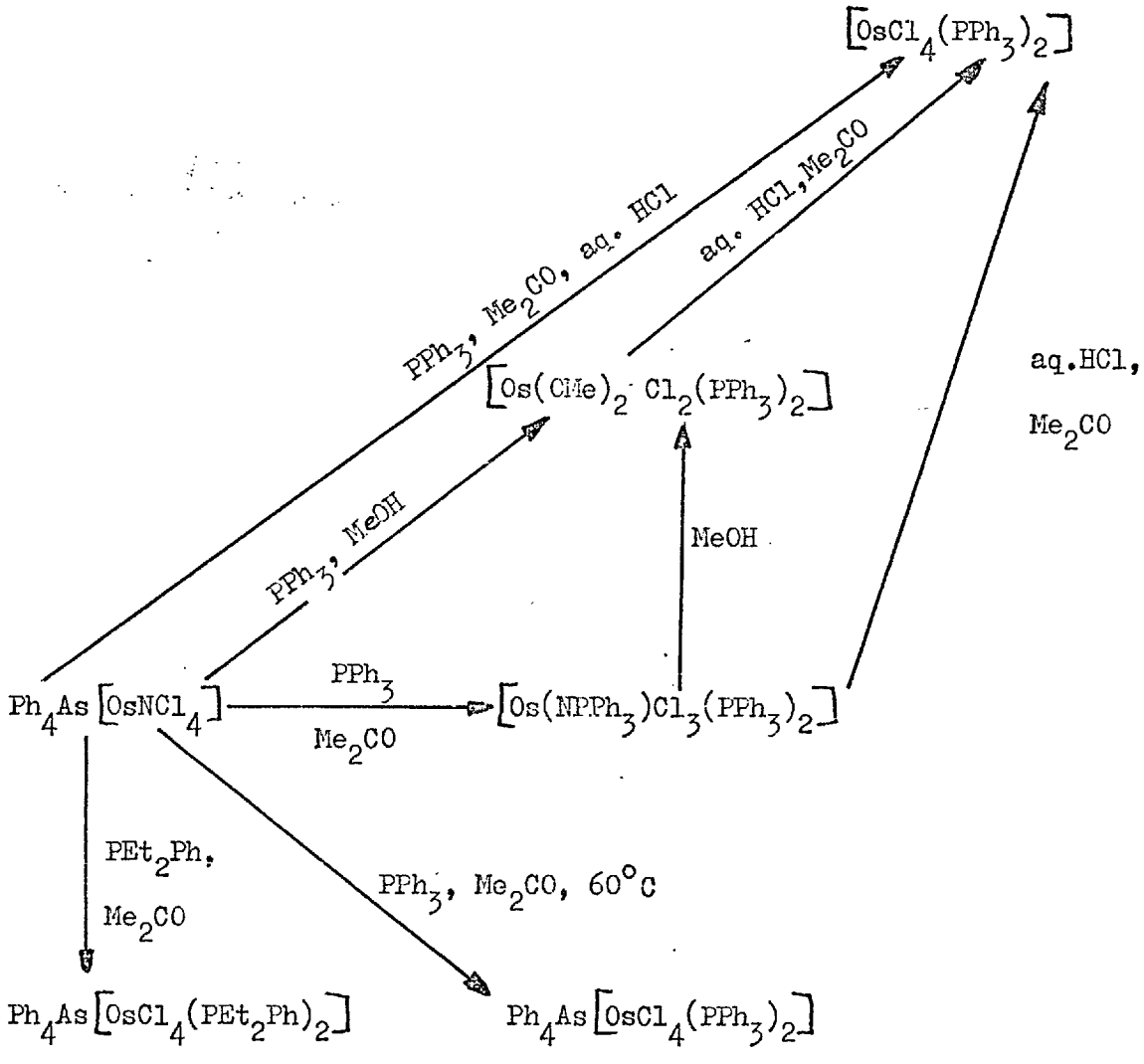
These reactions are illustrated in Figure 3.2. for $[OsNCl_4]^-$.

3 - C - 1. Reactions.

We have shown (Sec. 3 - B - 1) that the reaction of PPh_3 with $R[OsNX_4]$ ($R = Ph_4As$, Bu^n_4N; $X = Cl$, Br) in cold acetone gave the phosphinenitride complexes $[Os(NPPh_3)X_3(PPh_3)_2].Me_2CO$. Similar reactions using other tertiary phosphines and $[OsNX_4]^-$ or any phosphine and $[RuNCl_4]^-$ did not give phosphinenitrides. From the reaction of PEt_2Ph with $Ph_4As[OsNX_4]$ and PPh_3 with $Ph_4As[RuNCl_4]$ in cold acetone we obtained $Ph_4As[OsX_4(PEt_2Ph)_2]$ and $Ph_4As[RuCl_4(PPh_3)_2]$. These products are analogues of $Ph_4As[OsCl_4(PPh_3)_2]$ which is produced when PPh_3 is reacted with $Ph_4As[OsNCl_4]$ in hot acetone. The similarity of all these products suggests that the reactions all proceed *via* intermediate phosphinenitride species, which are unstable under these conditions. The products are 1:1 electrolytes in acetone or dichloromethane and have typical magnetic moments for Os(III) or Ru(III) species.

The phosphinenitride complex $[Os(NPPh_3)Cl_3(PPh_3)_2]$ (C) was not obtained if the reaction between PPh_3 and $[OsNCl_4]^-$ was carried out in some solvents other than cold acetone. If acetone-aqueous HCl was used then $[OsCl_4(PPh_3)_2]$ was obtained, and if methanol was used then a red product, probably $[Os(OMe)_2Cl_2(PPh_3)_2]$ was formed. It is likely that the phoshinenitride (C) is an intermediate in these two reactions, since it reacts with these two solvents to give the same two products. A solution in dichloromethane of $[Os(OMe)_2Cl_2(PPh_3)_2]$ gives $[OsCl_4(PPh_3)_2]$ when shaken with aqueous HCl. For this reason we prefer its given formulation to $[OsO(OMe)Cl_2(PPh_3)_2]$ (which

FIGURE 3.2.


[OsCl4(PPh3)2]
PPh3, Me2CO, aq. HCl
aq. HCl, Me2CO
[Os(CMe)2 Cl2(PPh3)2]
aq.HCl,
Me2CO
PPh3, MeOH
MeOH
Ph4As [OsNCl4]
PPh3
Me2CO
[Os(NPPh3)Cl3(PPh3)2]
PEt2Ph,
Me2CO
PPh3, Me2CO, 60°C
Ph4As[OsCl4(PEt2Ph)2]
Ph4As[OsCl4(PPh3)2]

would have virtually the same analyses), since one would expect such an oxo complex to give the stable $[OsOCl_3(PPh_3)_2]$ [19] under these conditions.

3 - C - 2 Structures.

We assign trans structures to the bis-phosphine tetra-halo complexes $[OsCl_4(PPh_3)_2]$ and $[OsX_4(PR''_3)_2]^-$ (X = Cl, Br, PR''_3 = PPh_3, PEt_2Ph), since the i.r. spectra of the chloro complexes show only one strong Os-Cl stretching absorption (sometimes split by solid state effects). We would expect one such band for a centrosymmetric D_{4h} complex with trans configuration, whereas for a cis configuration (C_{2v}), four i.r. active M-Cl stretching modes are expected. A similar trans structure has been found for $[OsCl_4(PMe_2Ph)_2]$ [112], and assigned to $Ph_4As[RuCl_4(PPh_3)_2]$ [113].

The i.r. spectra of $[Os(OCH_3)_2Cl_2(PPh_3)_2]$ and $[Os(OCD_3)_2Cl_2(PPh_3)_2]$ show that a methoxo ligand [114] is present in these complexes. There is a strong, low frequency C-H stretching vibration $\gamma_{as}CH_3$ at 2799 cm^{-1}, ($\gamma_{as}CD_3$ 2038cm^{-1}) and a band assigned to γ_{O-CH_3} at 1022 cm^{-1} (γ_{O-CD_3} 995 cm^{-1}). Inconsistent analyses preclude positive indentification of this compound, but we exclude the possibility of $[OsO(OMe)Cl_2(PPh_3)_2]$ on chemical grounds (Sec. 3 - C - 1), and also since there is no strong i.r. band near 850 cm^{-1} where one would expect γ_{OsO}.

3 - D. EXPERIMENTAL.

All manipulations involving air-sensitive tertiary phosphine ligands were carried out in dried, deoxygenated solvents under an atmosphere of nitrogen.

3 - D - 1. Complexes of the type $[MNX_3(L'Ph_3)_2]$: M = Ru, Os, X - Cl, Br, L' = As, Sb.

To a rapidly stirred solution of $L'Ph_3$ (1 g) in boiling methanol (6 ml) was added $Bu^n_4N[MNX_4]$ (0.1 g). The immediate precipitate of the product was filtered off, washed with acetone and air dried on the filter.

a) Trichloronitridobis(triphenylarsine)osmium (VI), $[OsNCl_3(AsPh_3)_2]$.

Pink-brown diamagnetic precipitate, (90%). (Found: C, 47.0; H, 3.4; Cl, 11.4; N, 1.7. $C_{36}H_{30}As_2Cl_3NOs$ requires C, 46.9; H, 3.3; Cl, 11.5; N, 1.5%).

b) Trichloronitridobis(triphenylstibine)osmium (VI), $[OsNCl_3(SbPh_3)_2]$.

Orange diamagnetic precipitate, 85%. (Found: C, 42.6; H, 2.9; Cl, 10.4; N, 1.5. $C_{36}H_{30}Cl_3NOsSb_2$ requires C, 42.5; H, 3.0; Cl, 10.5; N, 1.4%).

c) Tribromonitridobis(triphenylarsine)osmium (VI), Isomer A, $[OsNBr_3(AsPh_3)_2]$.

Brown diamagnetic precipitate, 85%. (Found: C, 40.9; H, 2.9; Br, 22.8; N, 1.5. $C_{36}H_{30}As_2Br_3NOs$ requires C, 40.9; H, 2.9; Br, 22.7; N, 1.3%).

d) Tribromonitridobis(triphenyl stibine)osmium (VI), $[OsNBr_3(SbPh_3)_2]$.

Orange diamagnetic precipitate, 85%. (Found: C, 37.4; H, 2.6; Br, 20.7; N, 1.4. $C_{36}H_{30}Br_3NOsSb_2$ requires C, 37.6; H, 2.6; Br, 20.8; N, 1.2%).

e) Trichloronitridobis(triphenylarsine)ruthenium (VI), $[RuNCl_3(AsPh_3)_2]$

Brown-yellow diamagnetic precipitate, 80%. (Found: C, 51.5; H, 3.8; Cl, 12.5; N, 1.7. $C_{36}H_{30}As_2Cl_3NRu$ requires C, 51.9; H, 3.6; Cl, 12.8; N, 1.7%).

f) Trichloronitridobis(triphenylstibine)ruthenium (VI), $[RuNCl_3(SbPh_3)_2]$

Orange diamagnetic precipitate, 90%. (Found: C, 47.3; H, 3.3; Cl, 11.8; N, 1.4. $C_{36}H_{30}Cl_3NRuSb_2$ requires C, 46.6; H, 3.3; Cl, 11.5; N, 1.5%).

3 - D - 2 Tribromonitridobis(triphenylarsine)osmium (VI), Isomer B, $[OsNBr_3(AsPh_3)_2]$

A solution of triphenylarsine (1.0 g) and $Bu^n_4N[OsNBr_4]$ (0.15 g) in cold acetone (12 ml) was set aside for 48 hours. The brown microcrystalline precipitate (50%) was filtered off, washed with acetone and air-dried. (Found: C, 41.1; H, 3.0; Br, 22.7; N, 1.5. $C_{36}H_{30}As_2Br_3NOs$ requires C, 40.9; H, 2.9; Br, 22.7; N, 1.3%).

3 - D - 3 Trichloronitridobis(triethylarsine)osmium (VI), $[OsNCl_3(AsEt_3)_2]$

Triethylarsine (1 ml) was added to a solution of $Bu^n_4N[OsNCl_4]$ (0.5 g) in de-oxygenated acetone (2 ml). The mixture was poured onto a watch glass and the solvent allowed to evaporate, until a sticky mass of red microcrystalline precipitate remained. The precipitate was washed onto a sinter with the minimum amount of acetone (1 ml), filtered off, triturated with a further portion of acetone (1 ml) and air dried on the filter, to give a red microcrystalline solid (50%). (Found C, 22.4; H, 4.9; N, 2.0. $C_{12}H_{30}As_2Cl_3NOs$ requires C, 22.7; H, 4.8; N, 2.2%).

3 - D - 4 (2,2'- bipyridine) trihalo nitrido-osmium (VI), $[OsNX_3(bipy)]$, (X = Cl, Br)

Solutions of 2,2' bipyridine (1.0 g) and $Bu^n_4N[OsNX_4]$ (0.2 g) in acetone (5 ml) were set aside for 24 hours and the microcrystalline precipitates filtered off and washed with a small amount of cold acetone.

a) (2,2'- bipyridine)trichloronitrido-osmium (VI) $[OsNCl_3(bipy)]$.

Deep red microcrystals, 60%. (Found: C, 25.8; H, 2.1; Cl, 22.7, N, 8.9. $C_{10}H_8Cl_3N_3Os$ requires C, 25.7; H, 1.7; Cl, 22.8; N, 9.0%).

b) (2,2'-bipyridine)tribromonitrido-osmium (VI), $[OsNBr_3(bipy)]$.

Purple micro-crystals, 50%. (Found:Br, 39.0; N, 6.9. $C_{10}H_8Br_3N_3Os$ requiresBr, 40.0; N, 7.0%).

3 - D - 5 Trichloronitridobis(tertiaryphosphine)osmium (VI), $[OsNCl_3(PR_3)_2]$ (PR_3 = PPh_3, PPh_2Et, PEt_3, PPh_2Me, PMe_2Ph.

Finely ground $[Os(NPR_3)Cl_3(PR_3)_2]$ (0.2 g), (see below) was suspended in methanol (2 ml), and chlorine gas passed through the solution until all the starting complex had reacted (5-30 sec). The brown to yellow complexes precipitated from the solution within one minute and were filtered off and washed with 1 ml cold methanol. The yields were 50 - 70%.

a) Trichloronitridobis(triphenylphosphine)osmium (VI), $[OsNCl_3(PPh_3)_2]$

Brown complex (60%). (Found: C, 51.6; H, 3.8; Cl, 12.9; N, 1.8. $C_{36}H_{30}Cl_3NOsP_2$ requires C, 51.8; H, 3.6; Cl, 12.7; N, 1.7%).

b) Trichlorobis(ethyldiphenylphosphine)nitrido-osmium (VI), $[OsNCl_3(PPh_2Et)_2]$.

Light brown complex (60%). (Found: C, 45.2; H, 4.0; Cl, 14.7; N, 1.8. $C_{28}H_{30}Cl_3NOsP_2$ requires C, 45.5; H, 4.1; Cl, 14.4; N, 1.9%).

c) Trichlorobis(diethylphenylphosphine)nitrido-osmium (VI), $[OsNCl_3(PEt_2Ph)_2]$.

Yellow-brown complex (70%). (Found: C, 37.5; H, 4.7; Cl, 16.7; N, 2.1. $C_{20}H_{30}Cl_3NOsP_2$ requires C, 37.4; H, 4.7; Cl, 16.6; N, 2.2%). M.W. 633; req. 643.

d) Trichloronitridobis(triethylphosphine)osmium (VI), $[OsNCl_3(PEt_3)_2]$

Brown complex (50%). (Found: C, 26.4; H, 5.4; Cl,20.2; N, 2.5. $C_{12}H_{30}Cl_3NOsP_2$ requires C, 26.3; H, 5.5; Cl, 19.4; N, 2.6%).

e) Trichlorobis(methyldiphenylphosphine)nitrido-osmium (VI), $[OsNCl_3(PPh_2Me)_2]$.

Light brown complex, (70%). (Found: C, 43.6; H, 3.8; Cl, 14.9; N, 1.9. $C_{26}H_{26}Cl_3NOsP_2$ requires C, 43.9; H, 3.7; Cl, 15.0; N, 2.0%). M.W. 671; req. 711.

f) Trichlorobis(dimethylphenylphosphine)nitrido-osmium (VI), $[OsNCl_3(PMe_2Ph)_2]$.

Yellow brown complex, (65%). (Found: C, 32.9; H, 4.0; Cl, 19.1; N, 2.3. $C_{16}H_{22}Cl_3NOsP_2$ requires C, 32.7; H, 3.8; Cl, 18.1; N, 2.4%).

3 - D - 6 Trans-trichlorobis(triphenylphosphine)(triphenylphosphine-nitride)osmium(IV)acetonate, $[Os(NPPh_3)Cl_3(PPh_3)_2]Me_2CO$.

To a stirred solution of triphenylphosphine (0.2 g) in dry, cold acetone (4 ml) was added $Bu^n_4N[OsNCl_4]$ (0.1 g). Orange crystals (90%) precipitated from the solution after one minute and were filtered off and washed with acetone. (Found: C, 59.4; H, 4.2; Cl, 9.0; N, 1.3; O, 1.6; P, 8.0. $C_{57}H_{51}Cl_3NOOsP_3$ requires C, 59.3; H, 4.5; Cl, 9.2; N, 1.2; O, 1.4; P, 8.0%).

3 - D - 7 Cis-tetrachloro(triphenylphosphine)(triphenylphosphinimine) osmium(IV) acetonate, $[Os(NHPPh_3)Cl_4(PPh_3)]Me_2CO$.

To a rapidly stirred solution of triphenylphosphine (0.25 g) in acetone (4 ml) was addedan intimate mixture of $Ph_4As[H_5O_2]Cl_2$ (0.2 g) and $Bu^n_4N[OsNCl_4]$ (0.1 g). The bright red precipitate (75%) was filtered off after two minutes stirring and washed with acetone, then methanol,and air-dried. (Found: C, 50.5; H, 4.1; Cl, 15.1; N, 1.8; P, 7.2. $C_{39}H_{37}Cl_4NOOsP_2$ requires C, 50.4; H, 4.0; Cl, 15.3; N, 1.5; P, 6.7%).

3 - D - 8 Complexes of the type $[M(NPR_3)X_3(PR_3)_2]$, (M = Ru, Os; PR_3 = PPh_3, PPh_2Et, PEt_2Ph, PEt_3, PPh_2Me; X = Cl, Br).

The preparation of all these complexes followed the same outline. We report below the method with the generally used quantities of reagents. In some cases the method was varied slightly because of the particular solubilities of the complexes concerned. These modifications will be listed under the appropriate complex.

To a suspension of $[MNX_3(AsPh_3)_2]$ (0.3 g) in cold, dried deoxygenated acetone (5 ml) in a reaction vessel sealed under nitrogen, was added PR_3 (0.7 g, 0.6 ml) and the solution stirred until all the starting material had dissolved. This gave an orange (M = Os) or dark brown (M = Ru) solution (30 sec). This solution was injected into ice-cold, deoxygenated 60/80 petroleum ether, (100 ml), also sealed under nitrogen. The mixture was set aside at 0°C for up to 1 hour, and the orange (M = Os) or dark brown (M = Ru) precipitate filtered off and air dried. The yields were 60 - 90%. If a fluffy yellow precipitate is formed when the reaction mixture is injected into the 60/80 petroleum ether, dry acetone (up to 10 ml) must be added to redissolve it.

a) Trans-trichlorobis(ethyldiphenylphosphine)(ethyldiphenylphosphine-nitride)osmium(IV) acetonate, $[Os(NPPh_2Et)Cl_3(PPh_2Et)_2].Me_2CO$.

Orange crystals, 80%. The complex may begin to precipitate from acetone solution. It can be filtered off from the 60/80 pet. ether solution after 5 minutes. (Found: C, 53.6; H, 5.3; Cl, 10.7; N, 1.4. $C_{45}H_{51}Cl_3NOOsP_3$ requires C, 53.4; H, 5.6; Cl, 10.5; N, 1.4%).

b) Trans-trichlorobis(diethylphenylphosphine)(diethylphenylphosphine-nitride)osmium(IV), $[Os(NPEt_2Ph)Cl_3(PEt_2Ph)_2]$.

Orange crystals; filtered off after 1 hour (50%). (Found: C, 44.5; H, 5.8; Cl, 13.5; N, 1.8. $C_{30}H_{45}Cl_3NOsP_3$ requires C, 44.5; H, 5.6; Cl, 13.1; N, 1.7%). Molecular weight in benzene, 682; requires 809.

This complex is particularly sensitive to water in the reaction solution; it readily gives an uncharacterised protonated species (ν_{PN} = 962, ν_{NH} = 3335 cm^{-1}).

c) Trans-trichlorobis(triethylphosphine)(triethylphosphinenitride) osmium(IV), $[Os(NPEt_3)Cl_3(PEt_3)_2]$.

Triethylphosphine is pyrophoric, and all the reaction solutions must be carefully deoxygenated. $[OsNCl_3(AsPh_3)_2]$ (1.0 g), acetone (2 ml), PEt_3 (1.5 ml) and 60/80 pet. ether, 250 ml, were used to prepare this complex, which gave orange crystals (50%). The complex is extremely soluble, and air and moisture sensitive. (Found: C, 32.7; H, 6.9; Cl, 16.1, N, 2.1. $C_{18}H_{45}Cl_3NOsP_3$ requires C, 32.5; H, 6.8; Cl, 16.0; N, 2.1%).

d) Trans-trichlorobis(methyldiphenylphosphine)(methyldi phenylphosphine-nitride)osmium(IV), $[Os(NPPh_2Me)Cl_3(PPh_2Me)_2]$.

Orange crystals filtered off after 10 minutes, 80%. (Found: C, 51.5;

H, 4.4; Cl, 11.5; N, 1.7. $C_{39}H_{39}Cl_3NP_3Os$ requires C, 51.4; H, 4.3; Cl, 11.7; N, 1.5%). Molecular weight in benzene, 761; requires 911.

e) Trans-tribromobis(ethyldiphenylphosphine)(ethyldiphenylphosphine-nitride)osmium(IV) acetonate, $[Os(NPPh_2Et)Br_3(PPh_2Et)_2]Me_2CO$.

Orange crystals filtered off after 1 hour, 50%. (Found: Br, 21.3; $C_{45}H_{51}Br_3NOOsP_3$ requires Br, 20.9%).

f) Trans-tribromobis(diethylphenylphosphine)(diethylphenylphosphine-nitride) osmium (IV), $[Os(NPEt_2Ph)Br_3(PEt_2Ph)_2]$.

In this preparation, 200 ml 60/80 petroleum ether were used and the resultant solution cooled for two hours at -10°C. Orange crystals (25%). Very soluble in acetone. (Found: Br, 25.3. $C_{30}H_{45}Br_3NOsP_3$ requires Br, 25.4%).

g) Trans-trichlorobis(triphenylphosphine)(triphenylphosphinenitride) ruthenium(IV) acetonate, $[Ru(NPPh_3)Cl_3(PPh_3)_2]Me_2CO$.

The complex is rather insoluble and did not require precipitation by 60/80 petroleum ether. Dark brown microcrystals (90%). (Found: C, 63.9; H, 4.7; Cl, 10.0; N, 1.3. $C_{57}H_{51}Cl_3NOP_3Ru$ requires C, 64.2; H, 4.8; Cl, 10.0; N, 1.3%).

h) Trans-trichlorobis(ethyldiphenylphosphine)(ethyldiphenylphosphine-nitride)ruthenium (IV) acetonate, $[Ru(NPPh_2Et)Cl_3(PPh_2Et)_2].Me_2CO$.

Dark brown complex (85%). (Found: C, 58.8; H, 5.4; Cl, 12.0; N, 1.5. $C_{45}H_{51}Cl_3NOP_3Ru$ requires C, 58.7; H, 5.6; Cl, 11.5; N, 1.5%).

i) Trans-trichlorobis(diethylphenylphosphine)(diethylphenylphosphine-nitride)ruthenium (IV), $[Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2]$.

Brown complex (80%). (Found: C, 50.7; H, 6.6; Cl, 14.6; N, 1.5. $C_{30}H_{45}Cl_3NP_3Ru$ requires C, 50.0; H, 6.3; Cl, 14.8; N, 1.9%).

j) Trans-trichlorobis(triethylphosphine)(triethylphosphinenitride) ruthenium (IV), $[Ru(NPEt_3)Cl_3(PEt_3)_2]$.

The quantities used for this very soluble complex were $[RuNCl_3(AsPh_3)_2]$, 0.5 g, PEt_3, 0.7 ml, Me_2CO, 2ml and 60/80 pet.ether 250 ml. The brown air and moisture sensitive precipitate (50%) was filtered off under nitrogen and sealed in an inert, dry atmosphere. For other comments see complex 3-D-8(c). (Found: C, 36.9; H, 7.3; Cl, 18.8; N, 2.2. $C_{18}H_{45}Cl_3NP_3Ru$ requires C, 37.5; H, 7.9; Cl, 18.5; N, 2.4%).

k) Trans-trichlorobis(methyldiphenylphosphine)(methyldiphenylphosphinenitride)ruthenium (IV), $[Ru(NPPh_2Me)Cl_3(PPh_2Me)_2]$.

Brown complex (70%). (Found: C, 57.2; H, 4.7; Cl, 12.6; N, 1.9. $C_{39}H_{39}Cl_3NP_3Ru$ requires C, 57.0; H, 4.8; Cl, 12.9; N, 1.7%).

3 - D - 9 Complexes of the type $[M(NPMe_2Ph)Cl_3(AsPh_3)_2]$ (M = Os,Ru

To a rapidly stirred solution of $[MNCl_3(AsPh_3)_2]$ (0.5 g) in cold, dried, deoxygenated acetone (5 ml) was added PMe_2Ph (0.5 ml). The pink (osmium) or green (ruthenium) complex (90%) was filtered off after 30 sec.

a) Trans-trichloro(dimethylphenylphosphinenitride)bistriphenylarsine-osmium (IV), $[Os(NPMe_2Ph)Cl_3(AsPh_3)_2]$.

Pink microcrystalline precipitate. (Found: C, 49.8; H, 3.9; Cl, 10.0; N, 1.4. $C_{44}H_{41}As_2Cl_3NOsP$ requires C, 50.2; H, 3.9; Cl, 10.1; N, 1.3%).

b) Trans-trichloro(dimethylphenylphosphinenitride)bistriphenylarsine-ruthenium (IV), $[Ru(NPMe_2Ph)Cl_3(AsPh_3)_2]$.

Green microcrystalline precipitate. (Found: C, 54.5; H, 4.4; Cl, 10.7; N, 1.3. $C_{44}H_{41}As_2Cl_3NPRu$ requires C, 54.8; H, 4.3; Cl, 11.0; N, 1.5%).

3 - D - 10 Trans-trichlorobis(dimethylphenylphosphine)(dimethylphenylphosphinenitride)osmium (IV), $[Os(NPMe_2Ph)Cl_3(PMe_2Ph)_2]$.

Dimethylphenylphosphine (0.5 ml) was added to a solution of $Bu^n_4N[OsNCl_4]$ (0.5 g) in ice-cold, dried, deoxygenated acetone (2 ml). The orange microcrystalline precipitate was filtered off after two minutes, and washed with a small amount of ice-cold acetone. (Found: C, 39.0; H, 4.7; Cl, 14.8; N, 1.7. $C_{24}H_{33}Cl_3NOsP_3$ requires C, 39.8; H, 4.6; Cl, 14.7; N, 1.9%).

3 - D - 11 Recovery of aminotriphenylphosphonium chloride from $[Os(NHPPh_3)Cl_4(PPh_3)].Me_2CO$.

A suspension of $[Os(NHPPh_3)Cl_4(PPh_3)].Me_2CO$ (0.186 g) in acetone (5 ml) was heated under reflux for ten minutes in the presence of tetraphenylarsonium chloride, $Ph_4As[H_5O_2]Cl_2$ (0.091 g). The solution was cooled and the resultant precipitate filtered off. The precipitate was triturated on the glass sinter with methanol (2 ml), and the methanol then collected and evaporated on a watch glass. This left a white residue of aminotriphenylphosphonium chloride hydrate, $[Ph_3PNH_2]Cl.H_2O$ (85%). (Found: C, 64.9; H, 5.3; Cl, 11.7; N, 4.1. $C_{18}H_{19}ClNO$ requires C, 65.1; H, 5.8; Cl, 10.7; N, 4.2%).

A red product (80%) was left on the sinter which was tetraphenylarsonium pentachlorotriphenylphosphine-osmate (IV), $Ph_4As[OsCl_5(PPh_3)]$ (Found: C, 50.4; H, 3.5; Cl, 17.5. $C_{42}H_{35}AsCl_5OsP$ requires C, 49.8; H, 3.5; Cl, 17.5%). Infra-red bands assigned to ν_{OsCl}, 318s, 270m.

3 - D - 13 Miscellaneous Products.

a) Tetraphenylarsonium tetrachlorobis(triphenylphosphine)osmate (III) acetonate, $Ph_4As[OsCl_4(PPh_3)_2]Me_2CO$.

To a hot solution of triphenylphosphine (0.2 g) in acetone (4 ml) was

added $Ph_4As[OsNCl_4]$ (0.1 g). The solution was stirred rapidly for two minutes giving a yellow, microcrystalline precipitate (60%), which was filtered off, washed with acetone and air dried. (Found: C, 57.1; H, 4.7; Cl, 11.2. $C_{63}H_{56}AsCl_4OsP_2$ requires C, 58.3; H, 4.4; Cl, 10.9%). Molar conductance (in acetone) 62 $\Omega^{-1}cm^{-2}$ in 10^{-3}M solution. Os-Cl stretching frequency: 298cm^{-1}(vs).

b) Tetraphenylarsonium tetrachlorobis(diethylphenylphosphine)osmate (III), $Ph_4As[OsCl_4(PEt_2Ph)_2]$.

$Ph_4As[OsNCl_4]$ (0.1 g) was added to a solution of diethylphenylphosphine (0.5 ml) in acetone (2 ml). The solution was stirred for two minutes giving a yellow microcrystalline precipitate (50%), which was filtered off, washed with acetone and air dried. (Found: C, 51.0; H, 4.8; Cl, 13.2. $C_{44}H_{50}AsCl_4OsP_2$ requires C, 50.4; H, 4.8; Cl, 13.5%). Molar conductance (in acetone) 62 Ω^{-1} cm^{-2} in 10^{-3}M solution. Os-Cl stretching frequency: 298vs.

c) Tetra-n-butylammonium tetrabromobis(diethylphenylphosphine)osmate (III), $Bu^n_4N[OsBr_4(PEt_2Ph)_2]$.

As the previous preparation, but using $Bu^n_4N[OsNBr_4]$ (0.1 g); yellow brown microcrystals (60%). (Found: Br, 15.3; N, 1.6. $C_{36}H_{66}Br_4NOsP_2$ requires Br, 15.7; N, 1.5%).

d) Tetrachlorobis(triphenylphosphine)osmium (IV), $[OsCl_4(PPh_3)_2]$.

$Ph_4As[OsNCl_4]$ (0.1 g) was added to a solution of triphenylphosphine (0.2 g) in acetone (4 ml) and concentrated hydrochloric acid (1 ml). The light brown precipitate (90%) was filtered off, washed with acetone and air dried. (Found: C, 50.3; H, 3.9; Cl, 16.6. $C_{36}H_{30}Cl_4OsP_2$ requires C, 50.5; H, 3.5; Cl, 16.6%). Os-Cl stretching frequencies: 330s, 323ssh, cm^{-1}.

e) trans-Dichlorodimethoxobis(triphenylphosphine)osmium (IV), $[Os(OMe)_2Cl_2(PPh_3)_2]$

A solution of $Bu^n_4[OsNCl_4]$ (0.1 g) in methanol (2 ml) was added to a warm solution of triphenylphosphine (0.2 g) in acetone (2 ml). A red microcrystalline precipitate was formed which was filtered off, washed with acetone and air dried. (Found: C, 53.5; H, 4.3; Cl, 8.5. $C_{38}H_{36}Cl_2O_2OsP_2$ requires C, 53.8; H, 4.3; Cl, 8.4%). Os-Cl stretching frequencies: 324s, 313ssh, cm^{-1}.

CHAPTER 4.

POLYNUCLEAR NITRIDO COMPLEXES

ABSTRACT

The reactions of $K_3[Ru_2NCl_8(H_2O)_2]$ with chelating and π-bonding ligands have been studied and a number of new substitution products obtained. The product from the prolonged reaction of osmium tetraoxide and aqueous ammonia has been reformulated as a trimer with a linear Os-N-Os-N-Os unit. From solutions of this complex in aqueous HX, similar trimers $Cs_3[Os_3N_2X_{11}(NH_3)_3].2H_2O$ (X = Cl,Br) can be isolated. The polymeric nitrido complex $K_n[OsNBr_4]_n$ is described.

INTRODUCTION.

The nitride ion [1], like the isoelectronic oxide ion [3] can act as a terminal ligand, and also bridge two [5], three [7] or four [9] metal atoms in linear, triangular or tetrahedral arrays.

The best known binuclear nitrido complexes are those with M^{IV}——N——M^{IV} units (M = Os,Ru) [8]. One of these complexes, $K_3[Ru_2NCl_8(H_2O)_2]$ has been studied by X-ray diffraction: it has a linear Ru-N-Ru unit, short, equivalent Ru-N distances (1.720Å) and considerable intra-anionic strain [5]. An extensive series of diamagnetic complexes containing this unit with a wide variety of attendant ligands (e.g. Cl,Br, NH_3, NCS^-,NO_2^-) have been characterised [8]. These normally have the stoichiometry $[M_2NX_8Y_2]^{n-}$, and it is assumed that the two Y groups are *trans* to the nitride as are the aquo ligands in $K_3[Ru_2NCl_8(H_2O)_2]$. In several of the compounds the attendant ligands are not normally found in mononuclear M^{IV} complexes,

e.g. $[M^{IV}(NH_3)_5Cl]^{3+}$ are unknown.

The existence of nitrido bridged trinuclear complexes was firmly established by an X-ray structure determination of $(NH_4)_4[Ir_3N(SO_4)_6(H_2O)_3]$ [7]. This has a planar, triangular Ir_3N unit with fairly short, equivalent Ir-N distances (1.918Å). The prolonged reaction of osmium tetraoxide and liquid ammonia gives the trinuclear Os(VI) complex $Os_3N_7O_9H_{21}$ [127], for which a nitrido bridged structure with a linear Os-N-Os(N)-N-Os unit has been proposed [8]. The corresponding reaction between ruthenium tetraoxide and liquid ammonia gives $Ru_4N_{11}O_{12}H_{33}$ which may also contain bridging nitrido ligands. It has a similar i.r. spectrum to $Os_3N_7O_9H_{21}$ [115].

Complexes in which a nitrido ligand asymmetrically bridges two metal atoms are also known. For example the tetramer $[MoNCl_3]_4$ has Mo ≡ N.....Mo ≡ N... bridges [37], and the polymer $K_{2n}[ReN(CN)_4]_n.nH_2O$ has infinite ...Re ≡ N....Re ≡ N... chains [6]. The terminal nitrido complex $[ReNCl_2(PEt_2Ph)_3]$ acts as a weak nitrogen donor and forms a presumably asymmetric Re ≡ N...Pt bridge in the heterometallic compound $[(PEt_2Ph)_3Cl_2Re \equiv N \rightarrow PtCl_2(PEt_3)]$ [85].

SECTION 4 - A <u>BINUCLEAR RUTHENIUM NITRIDO COMPLEXES</u>.

In order to test the hypothesis that the binuclear nitrido complex $K_3[Ru_2NCl_8(H_2O)_2]$ behaves in its substitution reactions as if it had a lower oxidation state than its formal Ru(IV), we have attempted to substitute this complex with ligands not normally found with Ru(IV). A more convenient starting material than the chloro anion is often the hydroxide $Ru_2N(OH)_5.nH_2O$, made by adding sodium hydroxide to aqueous solutions of $K_3[Ru_2NCl_8(H_2O)_2]$ [8]. We have attempted to produce a suitable starting

material for substitution reactions in organic solvents by evaporating to dryness solutions of $Ru_2N(OH)_5.nH_2O$ in aqueous HCl. This gives a brown material which shows two bands in its i.r. spectrum due to $\gamma_{as}M_2N$, and is probably $[Ru_2NCl_5]_n\ xH_2O$.

This complex is quite soluble in methanol, but less soluble in acetone and other mild organic solvents. Unfortunately, reactions in alcoholic solvents with $[Ru_2NCl_5]_n.xH_2O$ readily give reduction rather than substitution products.

4 - A - 1. Carbonyl complexes.

Solutions of $Ru_2N(OH)_5.nH_2O$ in concentrated aqueous HX (X = Cl, Br) (effectively $[Ru_2NX_8(H_2O)_2]^{3-}$) when heated under reflux, slowly took up carbon monoxide, and from the resulting solutions $Cs_3[Ru_2NX_8(CO)_2]$ w isolated. The reactions only took place in concentrated acid solutions; no carbonyl complex was isolated from a similar reaction in 2M HCl. These reactions are similar to that between CO and $[RuCl_6]^{3-}$ in aqueous HCl which gives $[Ru(CO)Cl_5]^{2-}$ [116]; here too an increase in the rate of CO uptake with decreasing pH has been observed. It is also possible to prepare $[Ru_2NCl_8(CO)_2]^{3-}$ by heating under reflux a solution of $Ru_2N(OH)_5.nH_2O$ in a 2:1 mixture of concentrated formic and hydrochloric acids. Again, $[RuCl_6]^{3-}$ reacts under similar conditions to give $[Ru(CO)Cl_5]^{2-}$ [117].

The i.r. spectra of $Cs_3[Ru_2NX_8(CO)_2]$ show bands which we assign to C-O stretching frequencies, γ_{CO} at 2038 cm^{-1} (X = Cl) and 2022 and 1970 cm^{-1} (X = Br) which are similar in frequency to those in $[Ru(CO)X_5]^{2-}$. The nitrido complexes also have bands at 1016 (X = Cl) and 984 cm^{-1} (X = Br) which we assign to $\gamma_{as}M_2N$; these are some 50 cm^{-1} lower in frequency than

$\gamma_{as}M_2N$ in the corresponding diaquo octahalo parent complexes. We have not been able to obtain Raman spectra for the carbonyl complexes because of their poor colours, but the i.r. spectra of $Cs_3[Ru_2NCl_8(H_2O)_2]$ and $Cs_3[Ru_2NCl_8(CO)_2]$ have similar profiles in the Ru-Cl stretching region, and we therefore propose that our two carbonyl complexes contain a linear OC-Ru-N-Ru-CO unit.

If this is indeed the case, then a strong π-donor ligand is <u>trans</u> to a π-accepting ligand, a situation rather similar to that of $[Ru(NO)(NH_3)_4(NH_2)]^{2+}$ [118], where the rare π-donating terminal amide ligand is stabilised by the presence of a <u>trans</u> π-accepting nitrosyl ligand. The N-O stretching frequency in the amido complex is some 50 cm^{-1} lower than in $[Ru(NO)(NH_3)_5]^{3+}$, and this has been attributed to less Ru-NO σ bonding and more Ru→NO back π-bonding in the amide. We would therefore expect γ_{CO} in our complexes to be subject to two influences. Firstly, γ_{CO} should be higher than in $[Ru(CO)X_5]^{2-}$ because of the increase in oxidation state, and secondly the influence of the <u>trans</u>π-donating nitrido group should lower the frequency. The similarity in γ_{CO} for $[Ru^{III}(CO)X_5]^{2-}$ and $[Ru_2{}^{IV}NX_8(CO)_2]^{3-}$ suggests that the effective electron density on the metal experienced by the carbonyl ligand is approximately the same in these complexes. The lowering of $\gamma_{as}Ru_2N$ in the carbonyl complexes probably reflects the competition of the nitrido and carbonyl ligands for the same metal t_{2g} π-orbitals.

4 - A - 2. <u>Cyano complex</u>.

By dissolving $[Ru_2N(OH)_5].nH_2O$ in a hot concentrated aqueous solution of potassium cyanide we obtained the very stable yellow cyano complex $K_5[Ru_2N(CN)_{10}].3H_2O$. The water molecules of crystallisation were quantitatively removed by heating the complex to 110°C, and thesewere taken up again

quantitatively when the complex was set aside in the atmosphere. The i.r. and Raman solution and solid state spectra of the complex are presented in Table 4.1.

The i.r. spectrum of $K_5[Ru_2N(CN)_{10}].3H_2O$ was very complex in the C-N stretching region near 2000 cm^{-1}, and also showed high frequency (3500 - 3650 cm^{-1}) bands due to crystal water. On dehydration the band structure near 2000 cm^{-1} became much simpler. This behaviour is similar to that observed in $Na_2[Fe(CN)_5NO].2H_2O$ whose i.r. spectrum [119] near 2000 cm^{-1} is similarly more complex than that of $Na_2[Fe(CN)_5(NO)]$. X-ray studies [120] show that the water molecules in $Na_2[Fe(CN)_5(NO)].2H_2O$ have equivalent positions in the lattice and along with nitrogen atoms from some cyano ligands are weakly bonded to the cations. There may also be weak hydrogen bonding from the water molecules to the complex anion.

The Raman and i.r. spectra of $K_5[Ru_2N(CN)_{10}]$ are very similar in the solid state and in solution, which suggests that there is no change of coordination geometry in solution. In all, seven bands due to ν_{CN} are seen in the solution spectra, three i.r. bands and four Raman bands, with two of the latter polarised. However, for both the likely configurations of $[Ru_2N(CN)_{10}]^{5-}$ with either eclipsed cyano ligands (D_{4h}, c.f. $[Ru_2NCl_8(H_2O)_2]^{3-}$ [5] or staggered cyano ligands (D_{4d}, c.f. $[Co_2(CN)_{10}]^{6-}$ [121] and $[Mn_2(CO)_{10}]$ [122]) we would expect this number of bands. We cannot therefore distinguish between these two configurations on the basis of this study, but the difference in band profiles in the 2000 cm^{-1} region for $[Ru_2N(CN)_{10}]^{5-}$ and $[Mn_2(CO)_{10}]$ [123] suggests that as expected the symmetry of this anion in solution is D_{4h}.

We provisionally assign the highest polarised Raman active band near

T A B L E 4.1.

Vibrational spectrum of $K_5[Ru_2N(CN)_{10}]$, cm^{-1}

		γ_{OH}	γ_{CN}	H_2O	$\gamma_{as}Ru_2N$	$\gamma_{S}Ru_2N$
$K_5[Ru_2N(CN)_{10}]$	I.r. solid	-	2150m, 2140s, 2138ssh 2120s, 2088m, 2078m 2055m, 2040m	-	1017sb	-
	I.r. aqueous solution	-	2142m, 2121vs, 2044m	-	1006s	-
	Raman solid	-	2155(7), 2142(6) 2134(7), 2123(1)	-	-	262(4)
	Raman aqueous solution	-	2156(7)+, 2142(6), 2130(3), 2116(1)+	-	-	264(7)+
$K_5[Ru_2N(CN)_{10}].3H_2O$	I.r. solid	3625ms, 3590s	2143s, 2138s, 2130s, 2122s, 2110s, 2095w, 2080mw, 2055ms, 2040ms	1635s, 1620s 1610s	1010s 985s	-

+ Polarised

2000 cm^{-1} to the symmetric stretch of the cyano ligands, and the lower frequency, weaker, polarised band to that of the cyano ligands trans to the nitride. This lower frequency probably occurs because the axial cyanide is trans to a strongly trans-influencing nitrido ligand. One might therefore expect a weaker Ru-C_{axial} bond and possibly greater Ru→C π-back bonding and both these effects would lower γ_{CN}.

This competition for σ-orbitals between nitride and cyanide may also be reflected in the symmetric and asymmetric Ru_2N stretching vibrations $\gamma_S Ru_2N$ and $\gamma_{as} Ru_2N$ which are both some 60 cm^{-1} lower than in $[Ru_2NCl_8(H_2O)_2]^{3-}$. A similar fall in the frequency of γ_{ReN} is observed in the solution spectrum of $[Re(N)(CN)_5]^{3-}$ compared with $[Re(N)(CN)_4(H_2O)]^{2-}$ [48], to which the penta-cyano complex is readily hydrolysed. Careful Raman studies of solutions of $[Ru_2N(CN)_{10}]^{5-}$ show no free cyanide is present in the solution even after setting the solution aside for several days at room temperature.

4 - A - 3 Complexes with chelating ligands

The 'chelate effect' leads to greater stability constants for complexes with chelating ligands compared with similar monodentate donors, due to a favourable entropy effect. In the Ru-N-Ru system the increased steric requirements of chelating ligands could well produce a correspondingly unfavourable enthalpy effect in view of the steric constraints resulting from the short Ru-N bonds. We have accordingly attempted substitution reactions of $[Ru_2NCl_8(H_2O)_2]^{3-}$ with chelating ligands.

The 1,2-diaminoethane (dae) complex $[Ru_2N(dae)_4Cl_2]Cl_3.H_2O$ was readily

prepared by heating an aqueous solution of $K_3[Ru_2NCl_8(H_2O)_2]$ under reflux with 50% dae. The 2,2'- bipyridine (bipy) complex $[Ru_2N(bipy)_4Cl_2](PF_6)_3$ was similarly made by heating under reflux an aqueous solution of $K_3[Ru_2NCl_8(H_2O)_2]$ with an acetone solution of the amine. If methanol was used to dissolve the amine, and the reaction carried out under similar conditions, reduction to the red salt $[Ru(bipy)_3]Cl_2$ occurred. Because of steric interactions a trans arrangement of bipy ligands is uncommon [124], and hence in our binuclear complex it is likely that the chloro-ligands are cis rather than trans to the nitrido ligand.

The reaction of sodium diethyldithiocarbamate, Na(dtc) with an aqueous solution of $K_3[Ru_2NCl_8(H_2O)_2]$ gave $[Ru_2N(dtc)_4Cl]$, which is a non-electrolyte in acetone. This may be polymeric in the solid state with -Ru-Cl-Ru-N-Ru-Cl-Ru chains. One might expect considerable steric repulsions in this complex, since X-ray studies on $[Re_2O_3(dtc)_4]$ [61] show that such repulsions cause a staggered configuration of dtc ligands on adjacent metal atoms, presumably at the expense of π-bonding in the Re-O-Re system. The complex $[ReN(dtc)_2]$ [35] has a five-coordinate structure with an N-Re-S angle of 108°.

4 - A - 4 Miscellaneous reactions.

We have made several attempts to prepare phosphine derivatives of $[Ru_2NCl_8(H_2O)_2]^{3-}$, but the anion has a marked inertness towards these ligands. An acetone/water solution of PPh_3 and $K_3[Ru_2NCl_8(H_2O)_2]$ when heated gave a small yield of a diamagnetic complex whose i.r. spectrum showed a band due to ν_{as} Ru_2N and had a chlorine to phosphine ratio of 2:1. The analyses were consistent with its formulation as $K_2[Ru_2NCl_6(PPh_3)_2(OH)]$, and this rather odd structure supported by the presence of a band near

3600 cm^{-1} in the i.r. spectrum which we assign to γ_{OH}. If ethanol/water was used as a solvent for this reaction, then reduction occurred giving $[RuCl_3(PPh_3)_2]$.

Attempts to prepare nitric oxide analogues of the carbon monoxide complexes described in 4 - A - 1 were made by passing NO gas through a solution of $[Ru_2NCl_8(H_2O)_2]^{3-}$ in concentrated HCl heated under reflux. Caesium ion precipitated a soluble yellow salt from this solution with γ_{NO} at 1850 cm^{-1} and $\gamma_{as}Ru_2N$ at 1020 cm^{-1}, but no pure products were ever isolated. Prolonged reaction times gave $Cs_2[Ru(NO)Cl_5]$ and this material normally contaminated the yellow salts. An aqueous solution of $[Ru_2NCl_8(H_2O)_2]^{3-}$ was reacted with hydrazine hydrate in an attempt to prepare a nitrido complex. A vigorous reaction took place, and from the reaction mixture salts of the $[Ru(NH_3)_5N_2]^{2+}$ cation were isolated.

Attempts to reduce $[Ru_2NCl_8(H_2O)_2]^{3-}$ were made using a variety of reducing agents (e.g. SO_3^{2-}, $S_2O_4^{2-}$, $SnCl_2$, BH_4^-, Na/Hg amalgum), but in no case did we isolate products suitable for analysis. The more vigorous reducing agents (e.g. BH_4^-) often produce metallic ruthenium. The yellow solutions of the cyano complex $[Ru_2N(CN)_{10}]^{5-}$ were not reduced to the metal by BH_4^-. Red solutions were formed from which yellow solutions could be regenerated by passing air or adding hydroxide ion to them. Whereas the ions $[Ru_2NX_8(H_2O)_2]^{3-}$ (X = Cl,Br) give excellent baths for electrodeposition of ruthenium from aqueous solution [125], the cyanide anion gives no deposit of metal under similar conditions. Refluxing solutions of $[Ru_2NCl_8(H_2O)_2]^{3-}$ in formic acid/hydrochloric acid (19:1) gave red solutions from which caesium ion precipitated red salts which had i.r. bands characteristic of carbonyl, chloride and formate ligands, but no bands due to $\gamma_{as}Ru_2N$. Dissolution of these salts in dilute

aqueous HCl led to reformation of $[Ru_2NCl_8(H_2O)_2]^{3-}$.

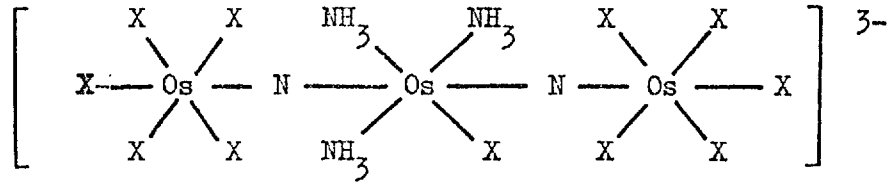
SECTION 4 - B POLYNUCLEAR OSMIUM NITRIDO COMPLEXES.

4 - B - 1. Trinuclear osmium nitrido complexes.

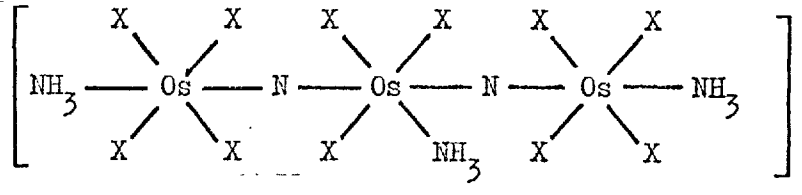
Some early work by Claus [126] showed that the prolonged reaction of osmium tetraoxide with aqueous ammonia yielded a black, diamagnetic, amorp hous precipitate said to be $[OsO_2(NH_3)_2(H_2O)]$. The reaction proceeds via yellow solutions which contain the nitrido anion $[OsO_3N]^-$. When the black material was dissolved in concentrated HCl, $[OsCl_4(NH_3)_2]$ was said to be formed [126]. We examined the i.r. spectrum of the black material and found that it was rather similar to that of $Os_3N_7O_9H_{21}$, the black, diamagnetic material produced by prolonged reaction of osmium tetraoxide and liquid ammonia [127]. The spectrum had two broad bands near 1000cm^{-1}, which we assign to the vibration of bridging nitrido ligands. A ^{15}N substituted sample of this material was prepared by dissolving $K[OsO_3{}^{15}N]$ in aqueous $^{14}NH_3$, and these bands near 1000 cm^{-1} shifted some 20 cm^{-1} to lower frequencies. This strongly supports the presence of nitrido ligands in this complex. The ligands whose vibrations shift must be derived from the nitride in osmiamate, since no ^{14}N peaks were seen on the spectrum. We therefore reformulate the complex $[Os_3N_2(NH_3)_4(OH)_8(H_2O)_2]$. This black material dissolved in concentrated aqueous HX, (X = Cl,Br) and from the yellow-brown solutions, diamagnetic salts $Cs_3[Os_3N_2X_{11}(NH_3)_3].2H_2O$ were precipitated by caesium ion. The i.r. spectra of these salts showed the same two strong absorptions near 1000 cm^{-1} as the black starting material. These are lower in frequency for the bromide than the chloride salt, and shift some 20 cm^{-1} to lower frequencies in a ^{15}N substituted sample of the chloride. Characteristic ammine bands were identified by their shifts ondeuteriation of the chloride complex, which caused only a small shift in the bands near 1000 cm^{-1}.

We propose that these complexes have structure I or II, and assign the

i.r. bands near 1000 cm^{-1} to vibrations of the bridging nitridoligands.



Structure I



Structure II

(X = Cl,Br)

These species contain osmium in an average oxidation state of $+4\frac{2}{3}$ i.e. $Os^{V} - Os^{IV} - Os^{V}$ or $Os^{IV} - Os^{VI} - Os^{IV}$, and we rationalise their diamagnetism using the bonding scheme applied to 'ruthenium red' [129], $[Ru_3O_2(NH_3)_{14}]^{6+}$, which has a similar structure with a linear $Ru^{III} - O - Ru^{IV} - O - Ru^{III}$ [128] unit. In our complex there are four fewer electrons to feed into the multicentre π-bonding system which covers the Os-N-Os-N-Os unit. It has been proposed [129] that in ruthenium red, the three filled orbitals of highest energy are non-bonding orbitals, two from a combination of the d_{xy} orbitals on the terminal ruthenium atoms, and another from the $d_{x^2-y^2}$ orbital on the central ruthenium atom; they have similar energies. Thus in our complex the four fewer electrons are missing either from the combination of terminal osmium d_{xy} orbitals giving $Os^{V} - Os^{IV} - Os^{V}$, or two from the central osmium $d_{x^2-y^2}$ orbitals, and two from the higher energy molecular orbital of the two formed from the terminal osmium d_{xy} orbitals giving $Os^{IV} - Os^{VI} - Os^{IV}$.

4 - B - 2 Polymeric osmium nitrido complex.

Dehydration of the red terminal nitrido salt $K[Os(N)Br_4(H_2O)].H_2O$ (Sec. 2 - A - 4) at 110°C gave a green substance $K_n[OsNBr_4]_n$ which quickly

reverted to the starting material on setting aside in the atmosphere. The loss and uptake of the two molecules of water occurred quantitatively. A comparison of the i.r. spectra of $K[OsNBr_4(H_2O)].H_2O$ and $K_n[OsNBr_4]_n$ shows that, whereas in the former the Os ≡ N stretching frequency is seen as a very sharp moderate intensity band at 1109 cm^{-1}, in the latter it is very much broader and stronger and is at 1002 cm^{-1}. There is a similar difference in W ≡ O stretching frequencies in monomeric $[WOCl_4(L)]$ [130] and the polymer $[WOCl_4]_n$ [68] and in Re ≡ N stretching frequencies in $K_3[ReN(CN)_5]$ and the polymer $K_{2n}[ReN(CN)_4].nH_2O$ [44]. We propose therefore that in $K_n[Os(N)Br_4]_n$ there are infinite linear Os ≡ N....Os ≡ N.... chains.

SECTION 4 - C, EXPERIMENTAL.

Tricaesium Dicarbonyloctachloro-μ-nitrido-diruthenate (IV)

$Cs_3[Ru_2NCl_8(CO)_2]$.

Method (a) The complex $K_3[Ru_2NCl_8(H_2O)_2]$ (2.5 g) was heated under reflux in concentrated hydrochloric acid (25 cm^3) under a stream of carbon monoxide (15 h). The solution was cooled, hydrochloric acid (10 cm^3) added, and the resulting solution set aside under the gas stream (1 h). The solution was then filtered to remove starting material and caesium chloride (2.0 g) added to precipitate the light brown product (30%), which was filtered off and washed with acetone (Found: C, 1.9; Cl, 30.3; Cs, 41.2; N, 1.3. $C_2Cl_8Cs_3NO_2Ru_2$ requires C, 2.5; Cl, 29.7; Cs, 41.7; N, 1.5%).

Method (b) The complex $K_3[Ru_2NCl_8(H_2O)_2]$ (2.0 g) was dissolved in boiling water and the insoluble precipitate $Ru_2N(OH)_5nH_2O$ formed by the addition of sodium hydroxide. The precipitate was filtered off, washed with boiling water, and dissolved in formic acid-hydrochloric acid (2:1, 20 cm^3). The resulting solution was heated under reflux (90 min) and on cooling caesium chloride (2.0 g) was added to give a yellow-brown precipitate, which was mainly the caesium salt of the starting material. The precipitate was filtered off and acetone (50 cm^3) added to the filtrate to precipitate the light brown product (10%); the latter was filtered off and washed with acetone. (Found: C, 2.0; Cl, 30.1; Cs, 42.1; N, 1.5%). I.r. spectrum: 2038s; 1016s; 590w; 470m; 321m; 300m; and 264m cm^{-1}.

Tricaesium Octabromodicarbonyl-μ-nitrido-diruthenate (IV),

$Cs_3[Ru_2NBr_8(CO)_2]$

An adaption of method (a) for the chloro-complex was used with

$K_3[Ru_2NBr_8(H_2O)_2]$, hydrobromic acid, caesium bromide and a reflux time of 6h. The complex is yellow-brown. (Found: C, 1.7; Br, 49.3; Cs, 31.2; N, 1.3. $C_2Br_8Cs_3NO_2Ru_2$ requires C, 1.8; Br, 48.5; Cs, 30.4; N, 1.1%). I.r. spectrum: 2022s; 1970m; 984s; 570w; 457m; 432w; 245s; and 210m cm^{-1}.

Potassium Decacyano-μ-nitrido-diruthenate (IV), $K_5[Ru_2N(CN)_{10}],3H_2O$.

The complex $K_3[Ru_2NCl_8(H_2O)_2]$ (1.0 g) was dissolved in boiling water and the insoluble precipitate $Ru_2N(OH)_5,nH_2O$ formed by the addition of sodium hydroxide. The precipitate was washed with boiling water and stirred (20 min) in a boiling aqueous solution of potassium cyanide (4 g in 10 cm^3). The cooled yellow solution was poured into methanol (40 cm^3) and the yellow precipitate (80%) which formed was filtered off and washed with boiling methanol (200 cm^3). (Found (for the trihydrate): C, 16.3; K, 26.7; N, 20.9. $C_{10}H_6K_5N_{11}O_3Ru_2$ requires C, 16.5; K, 26.9; N, 21.2%).

Dichlorotetrakis (1,2-diaminoethane)-μ-nitrido-diruthenium (IV) Trichloride, $[Ru_2N(dae)_4Cl_2]Cl_3$.

A solution of the complex $K_3[Ru_2NCl_8(H_2O)_2]$ (1 g) in boiling water (10 cm^3) was added to boiling aqueous 1,2-diamincethane (50%, 20 cm^3) and the solution heated under reflux (3 h). Hydrochloric acid (2 cm^3) was added to the cooled orange solution to precipitate orange crystals of the complex. (Found: C, 14.9; H, 5.3; Cl, 27.2; N, 19.7. $C_8H_{32}Cl_5N_9Ru_2$ required C, 15.2; H, 5.1; Cl, 28.0; N, 19.9%). I.r. spectrum (neglecting bands due to 1,2-diaminoethane): 1052s and 315m cm^{-1}. Raman spectrum: 359(6); 353(5); 260(7); 202(3); and 174(1) cm^{-1}.

Tetrakis (2,2'-bipyridine)dichloro-μ-nitrido-diruthenium (IV) Trishexafluorophosphate, $[Ru_2N(bipy)_4Cl_2](PF_6)_3$.

Warmed solutions of the complex $K_3[Ru_2NCl_8(H_2O)_2]$ (1.0 g in 20 cm^3 water) and 2,2'-bipyridine (4.0 g in 30 cm^3 acetone) were mixed and heated under reflux (4 h). The resulting mixture was filtered, cooled, and a solution of ammonium hexafluorophosphate (4 g in 10 cm^3 water) was added to precipitate the brown complex (80%), which was filtered off and recrystallised from acetone. (Found: C, 36.1; H, 2.4; Cl, 5.0; N, 9.1; P, 6.4. $C_{40}H_{32}Cl_2F_{18}N_9P_3Ru_2$ requires C, 35.6; H, 2.4; Cl, 5.2; N, 9.4; P, 6.9%). I.r. spectrum (neglecting bands due to 2,2'-bipyridine and PF_6^-): 1054m and 340m cm^{-1}.

Chlorotetrakis(diethyldithiocarbamato)-μ-nitrido-diruthenium (IV), $[Ru_2NS_2CNEt_2)_4Cl]$. Hot solutions of the complex $K_3[Ru_2NCl_8(H_2O)_2]$ (1.0 g in 10 cm^3 water) and sodium diethyldithiocarbamate (4.0 g in 10 cm^3 water) were mixed and warmed on a steam-bath (2 min). The brown precipitate which formed was filtered off and dissolved in acetone. This solution was filtered and evaporated to dryness to give the brown product (60%). (Found: C, 29.6; H, 4.9; Cl, 3.3; N, 8.6; S, 30.2. $C_{20}H_{40}ClN_5Ru_2S_8$ requires C, 28.4; H, 4.7; Cl, 4.2; N, 8.3; S, 30.3%). ν_{M_2N}(asym) 1030 cm^{-1}.

Potassium hexachlorohydroxotris(triphenylphosphine)-μ-nitrido-diruthenium (IV) $[Ru_2NCl_6(PPh_3)_3(OH)]$.

$K_3[Ru_2NCl_8(H_2O)_2]$ (2 g) was dissolved in 40 ml boiling water, and PPh_3 (6 g) dissolved in acetone (100 ml). The hot solutions were mixed and warmed on a steam bath for 15 minutes. The solution was then made up to 140 ml with acetone, and the precipitate collected on a warmed filter to remove $K_3[Ru_2NCl_8(H_2O)_2]$ and reprecipitated with 80/100 petroleum ether.

(Found: C, 48.1; H, 3.4; Cl, 15.9; N, 1.1; P. 7.5. $C_{54}H_{46}Cl_6K_2NOP_3Ru_2$ requires C, 49.4; H, 3.4; Cl, 16.2; N, 1.1; P. 7.1%). I.r. spectrum (neglecting bands due to triphenylphosphine) 3545m; 983s; 848m; 342m; 314w cm^{-1}.

Ruthenium nitrido nitrosyl complex.

In a typical reaction, nitric oxide gas, freed from nitrogen dioxide was passed through a solution of $K_3[Ru_2NCl_8(H_2O)_2]$ (2 g) in concentrated hydrochloric acid (50 ml) heated under reflux. 5 ml portions of the solution were extracted at the hourly intervals and their contents precipitated with caesium chloride. The yellow products obtained after up to three hours refluxing showed i.r. bands at 1850 cm^{-1} (ν_{NO}) and 1020 cm^{-1} ($\nu_{as}Ru_2N$); after six hours refluxing, $Cs_2[Ru(NO)Cl_5]$ was obtained.

Tricaesium Di-μ-nitrido-bis(amminetetrachloro-osmate (V) amminetrichloro-osmate (IV)) Dihydrate, $Cs_3[Os_3N_2Cl_{11}(NH_3)_3].2H_2O$.

The method of Claus [126] was used to prepare the complex $[OsO_2(NH_3)_2H_2O]$ which we reformulate $[Os_3N_2(NH_3)_4(OH)_8(H_2O)_2]$. The black complex (1.0 g) was heated under reflux in concentrated hydrochloric acid (30 min) and the solution then filtered. To the filtrate was added caesium chloride (2.0 g) to precipitate the brown product (40%). The latter was filtered off, washed with concentrated hydrochloric acid and acetone, and dried at 110°C. (Found: Cl, 26.7; Cs, 26.0; N, 5.2. $C_{11}H_{13}Cs_3N_5O_2Os_3$ requires Cl, 26.4; Cs, 27.0; N, 4.8%). I.r. spectrum (figures in parentheses refer to deuteriated sample): 3540sb (2430); 3260s (2300); 3200s (2260); 1620s (1225); 1565msh (1140); 1335s(obc.); 1025ms, 1004$^+$; 970s, 948$^+$; 550m; 450m; and 320s cm^{-1}.
$^+$$^{15}N$ substituted sample.

Potassium catena-μ-Nitrido-tetrabromo-osmate (VI), $K_n[OsNBr_4]_n$.

A sample of the complex $K[OsNBr_4(H_2O)],H_2O$, prepared by a literature method,[11] was heated to 110°C (15 min) and the green product sealed in an ampoule. (Found: Br, 56.7. Br_4KNOs requires Br, 56.8%). Weight loss on dehydration: 6.5. Calc. for $2H_2O$: 6.0%.

CHAPTER 5.

SULPHAMIC ACID AND SULPHAMATO COMPLEXES AS SOURCES OF PLATINUM-METAL NITRIDO COMPLEXES.

ABSTRACT

The new complexes $K_3[MCl_5(NH_2SO_3)]$ (M = Rh, Ir, Ru, Os) and $K_2[PdCl_2(NH_2SO_3)_2]$ have been characterised and their chemical reactions studied. Spectroscopic data suggest that sulphamate is bonded *via* the nitrogen atom in these salts and also in $K_2[PtX_2(NH_2SO_3)_2]$ (X = Cl,Br,I) and the imido sulphonate $Cs_4[PtCl_2(NHSO_3)_2]$. The complexes $K_3[MCl_6].nNH_3SO_3$(n = 0.9-1.1) are also described.

5 - A - 1 Introduction.

A recent report has described the preparation of the nitrido complex $(NH_4)_3[Ru_2NCl_8(H_2O)_2]$ by heating together under reflux aqueous solutions of sulphamic acid and ruthenium trichloride [21]. We have therefore examined the reactions of this and other platinum-metal chloro complexes with sulphamic acid, to see if other nitrido complexes can be made by this route, and to identify the intermediate species present in such reactions. In order to interpret the vibrational spectra of the intermediate species we have studied the i.r. and Raman spectra of sulphamic acid, potassium sulphamate, and their respective deuteriates.

Sulphamic acid is a white, crystalline solid (m.p.205°C) and a strong monobasic acid in aqueous solution. Although its aqueous solutions are quite stable at room temperature, it is hydrolysed at higher temperatures to ammonium bisulphate (40% in 6hr. at 80°C) [105]. Baumgarten proposed a zwitterionic structure for the molecule [132] and this suggestion has been

verified by a neutron diffraction study [133]. The $-NH_3$ protons are staggered with respect to the $-SO_3$ oxygen atoms and there is extensive N-H....O intermolecular hydrogen bonding. A neutron diffraction study of potassium sulphamate has also been made [134], and the anion has the same atomic framework as the acid with one proton removed. The tetrahedral co-ordination at the nitrogen atom in this salt indicates that there is no N-S P_π-d_π bonding, although the N-S distance (1.67Å) is somewhat shorter than in the free acid (1.76Å).

Few complexes of sulphamate ion have been reported. There are the platinum complexes $K_2[PtX_2(NH_2SO_3)_2]$ (X = Cl, (cis, trans), Br, I, NH_2SO_3) [135], and also the ammine species $[M(NH_3)_5(NH_2SO_3)]^{2+}$ (M = Co,[136,137] Ru [138]). The complexes $[M(NH_3)_5(NHSO_3)]^{+}$ [137,138] and $K_4[PtCl_2(NHSO_3)_2]$ [135] are also known; the acidity of coordinated sulphamate in aqueous solutions of $[Co(NH_3)_5(NH_2SO_3)]^{2+}$(pKa = 5.8) [137] and $[Ru(NH_3)_5(NH_2SO_3)]^{2+}$ (pKa = 2.6) [138] is at least 10^{10} times greater than that of the free ion.

5 - A - 2. Preparation of sulphamato and sulphamic acid containing complexes.

The reaction of hot aqueous solutions of $[MCl_6]^{3-}$ (M = Rh, Ir, Ru, Os) with sulphamic acid in the presence of potassium chloride gave the sulphamato complexes $K_3[MCl_5(NH_2SO_3)]$ in good yield. A palladium complex, $K_2[PdCl_2(NH_2SO_3)_2]$ was prepared by warming together aqueous solutions of $K_2[PdCl_4]$ and sulphamic acid, a method similar to that used to prepare trans-$K_2[PtCl_2(NH_2SO_3)_2]$ [135]. From this latter complex were made $K_2[PtX'_2(NH_2SO_3)_2]$ (X' = Br, I, NH_2SO_3) and $Cs_4[PtCl_2(NHSO_3)_2]$ [135].

If aqueous solutions of potassium chloride and sulphamic acid were

added to solutions of $[MCl_6]^{3-}$ in warm 6M hydrochloric acid, then another series of complexes, $K_3[MCl_6].nNH_3SO_3$ (n = 0.9 to 1.1) were precipitated as shiny platelets from the cooled reaction mixture. Similar reactions using $K_2[M'Cl_4]$ (M' = Pd,Pt) did not give complexes containing sulphamic acid.

Attempts to prepare sulphamato or sulphamic acid complexes using the tetravalent chlorides $[M''Cl_6]^{2-}$ (M'' = Os,Ir) were not successful. The reaction of $[OsCl_6]^{2-}$ with sulphamic acid gave an immediate precipitate of $(NH_4)_2[OsCl_6]$ which indicates that this anion readily catalyses the hydrolysis of sulphamic acid.

The magnetic moments of all the new rhodium, iridium, ruthenium and osmium complexes were consistent with the presence of trivalent metals. The palladium complex was diamagnetic. X-ray powder photographs of the two rhodium salts showed none of the lines characteristic of NH_3SO_3, KNH_2SO_3, KCl, $K_2[RhCl_5(H_2O)]$ or $K_3[RhCl_6]$. On the basis of the following spectroscopic data, we propose that the sulphamato complexes have a N-bonded sulphamato ligand, and those containing sulphamic acid have this zwitterion hosted in a lattice of $[MCl_6]^{3-}$ ions. This is in accord with previous chemical ecidence for N-bonding in sulphamato complexes [137,138]. Also, we have been unable to prepare analogues of these species by reacting $K_3[RhCl_6]$ with methanesulphonic acid(CH_3SO_3H) or its potassium salt, KCH_3SO_3 (the anion of which is iso-electronic with $NH_2SO_3^-$) using a variety of reaction conditions. This suggests N- rather than O-bonding in sulphamato complexes, and that the zwitterion nature of sulphamic acid is important in $K_3[MCl_6].nNH_3SO_3$.

5 - A - 3 Vibrational spectra.

a) Potassium sulphamate and sulphamato complexes.

Incomplete data on the Raman [139] and i.r. [140], spectra of potassium sulphamate and its deutero-analogue have been reported. In Table 5.1. we present the i.r. and Raman spectra of these two species from 200 to 4000 cm^{-1}; we use the notation of Katiyar [141].

The symmetry of the sulphamate ion is C_s [134], and fifteen normal modes of vibration are expected (9A' + 6A"), all of which are i.r. and Raman active. The $-NH_2$ vibrations (3A' + 2A") were readily identified by their shifts on deuteriation. We reassign γ_{NS} in KND_2SO_3 to the band near 800 cm^{-1} in view of the relative intensities of the two Raman lines at 809 and 728 cm^{-1}; this mode is mixed with $\delta^{S}_{ND_2}$, (ν_6) [141].

The i.r. spectra of $[MCl_5(NH_2SO_3)]^{3-}$ (M = Rh,Ir,Ru,Os) are compared with that of KNH_2SO_3 in Table 5.2. They are consistent with N-bonding of the sulphamato ligand. The $-NH_2$ vibrations of complexed sulphamate, identified by preparing deuteriated samples of the rhodium and iridium complexes, are affected more than the $-SO_3$ vibrations by coordination, and vary slightly from metal to metal. The asymmetric $-NH_2$ rocking mode (γ_{12}) is particularly affected; its frequency falls to the region in which the corresponding vibration occurs in mercury (II) amides [9] and platinum-methylamine [142] complexes. The N-S stretching frequency is lower in the complexes than the free ion. The small changes in the $-SO_3$ vibrations brought about by coordination are similar to those seen in S-bonded thiosulphate complexes [143], that is a small increase in $-SO_3$ stretching frequencies and a corresponding small decrease in $-SO_3$ deformation frequencies. The $-SO_3$ rocking frequencies were not identified in our complexes; they are possibly obscured by the M-Cl stretching bands.

T A B L E 5.1.

Vibrational spectra of potassium sulphamate and potassium sulphamate-d_2, cm^{-1}.

	KNH_2SO_3		KND_2SO_3	
	IR	Raman	IR	Raman
γ_9(A') sym. SO_3 rock	359s	367(3)	292s 324m	302(1)
γ_{14}(A'') asym. SO_3 rock	403m	406(6)	365w 383m	388(5)
γ_5(A') sym. SO_3 def.	502m	494(1)	432m	432(1)
γ_{13}(A'') asym. SO_3 def.	562vs	562(5)	543s	544(4)
γ_8(A') sym. SO_3 def.	586 595 vs	583(3)	578 587 s	580(3)
γ_7(A') sym. N-S stretch	807s	803(5)	806s	809(5)
γ_{12}(A'') asym, NH_2 rock	956w	952(1)	718m	728(1)
γ_3(A') sym. SO_3 str.	1054s	1046(20)	1040ssh 1047s	1041(20)
γ_6(A') sym.NH_2 wag	1127m	1141(1)	819ssh	obsc. by γ_7 ?
γ_4(A') sym. SO_3 str.	1197vs	1192(3)	1195vs	1196(1)
γ_{11}(A'') asym. SO_3 str.	1225vs	1251($^1/_2$)	1210vs	1228($^1/_2$)
γ_2(A') sym. NH_2 bend	1545m	1549(1)	1156m	1156(1)
γ_1(A') sym. NH_2 atretch	3265s	3262(7)	2391s	2396(6)
γ_{10}(A'') asym. NH_2 stretch	3315vs	3324(2)	2473m	2489(3)

TABLE 5.2.

Infra-red spectra of N-bonded sulphamato complexes; for description of modes see Table 5.1.

(i) Proton vibrations.

	γ_{10}	γ_1	γ_2	γ_6	γ_{12}	γ_7
KNH_2SO_3	3315vs	3265s	1545m	1127m	956w	807s
$K_3[RhCl_5(NH_2SO_3)]$	3248m	3143m	1516m	1151m 1128m	676w 604w	724s
$K_3[RhCl_5(ND_2SO_3)]$	2424w	2315w	1122m	903m	516w 478w	708s
$K_3[IrCl_5(NH_2SO_3)]$	3234m	3133m	1519m	1169m 1146m	700w 612w	723s
$K_3[IrCl_5(ND_2SO_3)]$	2410m	2309m	1125m	921m	560w 519w	706s
$K_3[RuCl_5(NH_2SO_3)]$	3248m	3153m	1515m	1150w 1122m	658m 595w	726s
$K_3[OsCl_5(NH_2SO_3)]$	3230m	3138m	1517m	1156m 1139m	674w 598w	721s
$K_2[PdCl_2(NH_2SO_3)_2]$	3180s	3112s	1533m	1168m 1143m	758s 626m	736s
trans$K_2[PtCl_2(NH_2SO_3)_2]$	3168s	3110s	1534m	1193m 1153m	781m 634m	738s
trans$K_2[PtCl_2(ND_2SO_3)_2]$	2368s	2297s	1134m	948m 861m	595m	725s
cis $K_2[PtCl_2(NH_2SO_3)_2]$	3206s	3115s	1540m	1185m 1146m	742ssh	730s
$K_2[PtBr_2(NH_2SO_3)_2]$	3148s	3119s	1550m 1524m	1194m 1168w	626m	727s

TABLE 5.2. contd.

$K_2[PtI_2(NH_2SO_3)_2]$	3141m	3120m	1538m 1525sh	1188m	622w	719s
$Cs_4[PtCl_2(NHSO_3)_2]^{++}$	3244s			1270m		883s
$Cs_4[PtCl_2(NDSO_3)_2]^{++}$	2401s			960m		839s

++ γ_{10}; N-H or N-D stretch: γ_6; N-H or N-D deformation: γ_7 N-S stretch

(ii) <u>$-SO_3$ and other low frequency vibrations</u>.

	γ_{11}	γ_4	γ_3	γ_8	γ_{13}	γ_{15}	Other absorptions
KNH_2SO_3	1225vs	1197vs	1054s	595s 586s	562vs	502m	
$K_3[RhCl_5(NH_2SO_3)]$	1293vs	1252s	1058s	575m	538m	492m	330vs, 310m, 302m, 257w
$K_3[RHCl_5(ND_2SO_3)]$	1277vs	1246vs	1057s	574m	536w	478w	324vs, 310ssh, 297msh
$K_3[IrCl_5(NH_2SO_3)]$	1290vs	1259vs	1058s	575m	538m	498m	313vs, 297vs, 259mw
$K_3[IrCl_5(ND_2SO_3)]$	1278s	1248s	1058s	580m	538m	485m	312vs, 295s, 255mw
$K_3[RuCl_5(NH_2SO_3)]$	1290s	1252s	1057s	573m	537m	486m	323vs, 308vs, 285ms
$K_3[OsCl_5(NH_2SO_3)]$	1293vs	1256vs	1058s	571m	536m	490m	319vs, 306s, 297s, 274m
$K_2[PdCl_2(NH_2SO_3)_2]$	1265vs	1240vs	1054s	585m	541m	508s	not measured
<u>trans</u>-$K_2[PtCl_2(NH_2SO_3)_2]$	1263vs	1245vs	1051s	582ms	541ms	512ms	373s, 343s, 280m, 225m
<u>trans</u>-$K_2[PtCl_2(ND_2SO_3)_2]$	1260vs	1240vs	1056s	563ms	528ms	505ms	345s, 282m, 210m

Table 5.2. contd. (ii)

cis-$K_2[PtCl_2(NH_2SO_3)_2]$	1268vs	1238vs	1052s	581m	543m	500m	373m, 359m, 335s, 278w
$K_2[PtBr_2(NH_2SO_3)_2]$	1313vs 1295vs	1265vs 1244vs	1056s	578s	545m	520m 505m	382s, 286m, 220vs
$K_2[PtI_2(NH_2SO_3)_2]$	1310vs 1293s	1260s 1237s	1051s	575s	548m	513m 501m	378s, 280m, 235w

The spectra of the known platinum sulphamato complexes $K_2[PtX_2(NH_2SO_3)_2]$ (X = Cl (cis,trans), Br,I) [135] were measured for comparison and are presented in Table 5.2., along with that of $K_2[PdCl_2(NH_2SO_3)_2]$. They show the same features as the penta-halo complexes, but the $-NH_2$ and $-SO_3$ stretching frequencies are somewhat lower, and the corresponding deformation frequencies rather higher than in the six-coordinate complexes. This may indicate that there is a stronger interaction between the sulphamate ligand and the metal in the square-planar complexes. The spectra of the platinum and palladium complexes show two absorptions other than those due to γ_{MX} in the region 400 - 200 cm^{-1}, at 370 and 280 cm^{-1}. The higher frequency band is shifted in trans $K_2[PtCl_2(ND_2SO_3)_2]$, probably to under the γ_{PtCl} absorption at 343 cm^{-1}, and we therefore assign this to γ_{MN}, and the lower frequency band to an $-SO_3$ rocking vibration. We assign a trans configuration to $K_2[PdCl_2(NH_2SO_3)_2]$ since the Pd-N and Pd-Cl stretching absorptions are single bands in the i.r. spectrum; for a cis (C_{2V}) configuration, two bands of each type would be expected.

The i.r. spectrum of the deprotonated species $Cs_4[Pt(NHSO_3)_2Cl_2]$ has just one N-H stretching absorption, and one high frequency N-H deformation mode. The N-S frequency is some 150 cm^{-1} higher than in $K_2[Pt(NH_2SO_3)_2Cl_2]$, and this may indicate some N-S $p_\pi - d_\pi$ bonding is present.

b) Sulphamic acid and complexes containing sulphamic acid.

Incomplete data on the i.r. [140,144] and Raman [145] spectra of sulphamic acid and sulphamic acid-d_3 have been reported. In Table 5.3. we present the i.r. and Raman spectra of these two species from 200 - 4000 cm^{-1}. We use the notation of Vuagnat and Wagner [140], noting their misassignment of $\gamma^{sym}_{SO_3}$

TABLE 5.3.

Vibrational spectra of Sulphamic acid and Sulphamic acid-d_3

	NH_3SO_3		ND_3SO_3	
	IR	Raman	IR	Raman
γ_{11} (E) degen. SO_3 rock	352 m 370	357(5) 364(5)	343 s 367	336(7)
$\gamma_4(A_1)$ sym. SO_3 def.	538ssh	539(7)	507 s 516	517(8)
γ_{10}(E) degen. SO_3 def.	544 s 552	558(5)	531 s 539	542(5)
$\gamma_5(A_1)$ N-S stretch	690 vs 706	683(3) 702(1)	670 vs 685	665(1) 688(3)
γ_9(E) degen. NH_3 rock	1002 m 1014	1024(1)	792 m 802	808(1)
$\gamma_3(A_1)$ sym. SO_3 stretch	1068 s 1070	1061(20)	1056 1061 vs 1065	1057(20)
γ_8(E) degen. SO_3 stretch	1260, 1275, 1290 1305, 1320, vs	1282(1) 1308(1) 1320(2)	1255 vs 1315	1292(1) 1314(1)
$\gamma_2(A_1)$ sym. NH_3 def.	1437 1443 m 1450	1440(1)	1095m	-
γ_7(E) degen. NH_3 def.	1536 m 1568	1542(1) 1573(1/2)	1114 m 1142	1108(2)
$\gamma_1(A_1)$ sym. NH_3 stretch	3200- 2900	3044(3)	2269m	2280(3)
ν_6(E) degen NH_3 stretch	vs,b	3130(2)	2345 m 2370	2371(2)

(ν_3,A_1) and $\delta_{SO_3}^{sym}$ (ν_4,A_1) [144].

The symmetry of the sulphamic acid zwitterion is approximately C_{3v}, the slight solid-state distortions being due to extensive inter-molecular hydrogen bonding within the unit cell [133]. Twelve fundamental modes of vibration are expected belonging to the classes $5A_1 + A_2 + 6E$. The A_1 and E modes should be both i.r. and Raman active, and the A_2 mode (N-S torsion) active in neither. Of these vibrations, five involve the $-NH_3$ group ($2A_1 + 3E$), and these, along with ν_{N-S} (A_1) were readily identified by their shifts on deuteriation. Several of the absorption bands showed extensive splitting, and this has been attributed to the low site symmetry in the crystal (C_1) and the coupling of modes within the unit cell [140].

The i.r. spectra of $K_3[MCl_6].nNH_3SO_3$ (M = Rh,Ir,Ru,Os) are all very similar, and these are presented in Table 5.4 along with that of $K_3[RhCl_6].nND_3SO_3$ and, for comparison, sulphamic acid. The spectra are consistent with the presence of molecules of sulphamic acid hosted in the lattice of $[MCl_6]^{3-}$ ions, with N-H....Cl_{anion} hydrogen bonds.

The bands which are shifted on deuteriation of the rhodium complex have positions and profiles characteristic of an $-NH_3$ rather than an $-NH_2$ group. The positions of these bands are shifted from those of the corresponding bands in sulphamic acid, but the strong N-H...O hydrogen bonds of the acid will not be present here. The $-NH_3$ stretching vibrations still occur at rather low frequencies in the complexes, however, which indicates that here too there is hydrogen bonding. In this case, however N-H....Cl_{anion} bonds are more likely.

T A B L E 5.4.

Sulphamic acid containing complexes, infra-red spectra 4000-200 cm^{-1}

For descriptions of modes, see Table 5.3.

(i) Proton vibrations.

	γ_6	γ_1	γ_7	γ_2	γ_9	γ_5
NH_3SO_3	3200s	3140s	1568m 1536m	1450m 1443m 1437m	1014m 1002m	706s 690s
$K_3[RhCl_6]\ NH_3SO_3$	3075s	2990vs	1550m 1527m	1389m	999m	692s
$K_3[RhCl_6]\ ND_2SO_3$	2279s	2210s.	1124w	1071w	791w	678s
$K_3[IrCl_6].NH_3SO_3$	3080s	2995vs	1547m 1525m	1385m	995m	691s
$K_3[RuCl_6].NH_3SO_3$	3078s	2995vs	1547m 1525m	1387m	996m	689s
$K_3[OsCl_6].NH_3SO_3$	3075s	2998vs	1550m 1527mw	1387m	996m	689s

TABLE 5.4. cont.

(ii) -SO_3 and low frequency vibrations.

	γ_8	γ_3	γ_{10}	γ_4	γ_{11}	Other absorptions
NH_3SO_3	1320vs 1305vs 1290vs 1275vs 1260vs	1070s 1068s	582s 544s	538ssh	370m 352m	
$K_3[RhCl_6].NH_3SO_3$	1293vs 1279ssh	1071vs	542s	518m	343s	330ssh, 315s, 285w
$K_3[RhCl_6].ND_3SO_3$	1291vs 1277sh	1094vs	532m	495m	-	320vs,b, 288w
$K_3[IrCl_6].NH_3SO_3$	1293vs 1278ssh	1068s	542s	517m	344s	322ssh, 305s, 295ssh,
$K_3[RuCl_6].NH_3SO_3$	1292vs 1280ssh	1071vs	542s	518m	343s	320m, 304vs
$K_3[OsCl_6].NH_3SO_3$	1295vs 1280ssh	1071vs	542s	516m	343s	304msh, 290s, 275wsh

Apart from the N-H stretching region, the spectra of the complexes are extremely simple, showing only the nine absorptions anticipated for a sulphamic acid molecule with C_{3v} configuration, and only two of these absorptions ($\gamma_7(E)$, and $\gamma_8(E)$) show any splitting. If oxygen-coordinated sulphamic acid were present, then we would expect considerable changes in the $-SO_3$ group frequencies, and splitting of the E modes due to the lowering of the local symmetry of the molecule to C_s.

For an octahedral $[MCl_6]^{3-}$ ion we expect one i.r. and two Raman active M-Cl stretching modes. The Raman spectra of the rhodium and iridium complexes show two such bands, but in general the i.r. stretching absorption is split into two, probably a result of solid state effects.

5 - A - 4 Electronic spectra.

In view of the similarities between the i.r. spectra of all the sulphamate complexes, and the similarity of the i.r. spectra of those complexes containing sulphamic acid, we only measured the electronic spectra of the two types of rhodium and iridium complex since their spectra are easier to interpret.

The ground state of low spin octahedral d^6 complexes is a $^1A_{1g}$ state; excitation of an electron to give the configuration to $t_{2g}^{\ 5}e_g^{\ 1}$ produces the states $^3T_{1g} + {}^1T_{1g} + {}^1T_{2g} + {}^3T_{2g}$ [146]. The singlet excited states have higher energies than the triplets. The spectra of $K_3[MCl_6]$ [147] and $K_2[MCl_5(H_2O)]$ [148](M = Rh,Ir) have been interpreted on this basis (despite the lower symmetry of the latter complexes), and the singlet-singlet transitions assigned. The wavelengths of the singlet-singlet absorptions in $K_3[MCl_6]$ and $K_2[MCl_5(H_2O)]$ are compared in Table 5.5. with those of the corresponding absorptions in $K_3[MCl_5(NH_2SO_3)]$ and $K_3[MCl_6].nNH_3SO_3$.

T A B L E 5.5.

Electronic Spectra of Sulphamate and Sulphamic-acid containing complexes, 700 - 200 nm.

(i) Rhodium complexes.

		Singlet-Singlet transitions		Others
$K_3[RhCl_6].nNH_3SO_3$	Aq. Solution	508(105)+	380(100)+	
	Reflectance	528m	422m	321m
$K_3[RhCl_6]$	Aq. solution[147]	518(102)	412(82)	
$K_2[RhCl_5(H_2O)]$	Aq. solution[148]	507(99)	402(99)	
	Reflectance	520m	417m	342m
$K_3[RhCl_5(NH_2SO_3)]$	Aq. Solution	475(80)	382(80)	
	Reflectance	475m	395m	306m
$(NH_4)_2[RhCl_5(NH_3)]$	Reflectance	470m	390m	330m

+ Absorptions due to $[RhCl_5(OH_2)]^{2-}$

Table 5.5. Contd.

(ii) Iridium complexes.

		Singlet-Triplet transitions	Singlet-Singlet transitions		Others
$K_3[IrCl_6]nNH_3SO_3$	Reflectance	562(m)	479m	370m	313w
$K_3[IrCl_6]$	Aq. Solution[147]	615(8) 560(10)	415(76)		
$K_2[IrCl_5(H_2O)]$	Aq. Solution[148]	550(12)	405(110)	347(110)	
$K_3[IrCl_5(NH_2SO_3)]$	Aq. Solution	530(10)	365(100)	330(115)	
	Reflectance	503m	387m	343m	298w

Figures in parentheses are molar extinction coefficients,

It can be seen that the absorption maxima in solutions of $K_3[MCl_5(NH_2SO_3)]$ are at shorter wavelengths than the corresponding aquo complexes, as would be expected for a nitrogen donor. Furthermore the maxima in the complex $K_3[RhCl_5(NH_2SO_3)]$ have similar wavelengths to those in $(NH_4)_2[RhCl_5(NH_3)]$. The reflectance spectra of $K_3[MCl_6].nNH_3SO_3$ show absorptions due to the same two transitions at much longer wavelengths, and near the maxima reported for $K_3[MCl_6]$ [147]. The solution spectrum of $K_3[RhCl_6].nNH_3SO_3$ shows that the species present is almost certainly $[RhCl_5(H_2O)]^{2-}$; the $[RhCl_6]^{3-}$ ion is rapidly aquated in solution.

5 - A - 5 Reactions of N-bonded sulphamato complexes.

When aqueous solutions of $K_3[RuCl_5(NH_2SO_3)]$ were heated under reflux in a nitrogen atmosphere, then the binuclear nitrido anion $[Ru_2NCl_8(H_2O)_2]^{3-}$ was formed. It was precipitated as the caesium salt in 80% yield. Sulphite ion is also produced by this reaction. Similar reactions using $K_3[OsCl_5(NH_2SO_3)]$ gave products which contained only small amounts of $Cs_3[Os_2NCl_8(H_2O)_2]$, which was identified by its characteristic i.r. absorption at 1135 cm^{-1}. Similar impure products were obtained when $Na_3[OsCl_6]$ was heated under reflux with an excess of sulphamic acid. The mechanism of these solution reactions is not clear. A possibility in the ruthenium reaction is a two-electron oxidative decomposition reaction to give a Ru(V) imido (Ru(III) nitrene) complex [55] in a similar manner to the proposed decomposition of Re(III) azido and hydrazinium complexes to give Re(V) nitrido species [19].

$$[Cl_5Ru^{III}-NH_2SO_3]^{3-} \rightarrow [Cl_5Ru^{V}(NH)]^{2-} + HSO_3^-$$

This intermediate could then react with another Ru(III) species to form the

bridging nitrido linkage.

$$[Cl_5Ru^{V}(NH)]^{2-} + [Cl_5Ru^{III} - NH_2SO_3]^{3-} \rightarrow [Cl_5Ru\text{-}N\text{-}RuCl_5]^{5-} + NH_3SO_3$$

The decachloro complex is then aquated [8] to give $[Ru_2NCl_8(H_2O)_2]^{3-}$. Some Ru(III) complexes have been shown to undergo disproportionation to Ru(II) and Ru(IV) [149], and such a process could also be involved. The course of the sulphamato complex decomposition will obviously depend on the rate of the $M\text{-}NH_2SO_3$ bond-breaking process and the stability of the intermediates involved; either or both of these factors must not be favourable in the osmium case. Pyrolysis of $K_3[RuCl_5(NH_2SO_3)]$ at 250° also gave a nitrido complex. When the productwas dissolved in dilute aqueous HCl which contained caesium chloride, $Cs_3[Ru_2NCl_8(H_2O)_2]$ was formed.

No evidence for the formation of nitrido complexes was obtained by heating aqueous solutions of $K_3[M'Cl_5(NH_2SO_3)]$ (M' = Rh, Ir) under reflux. The iridium salt was recovered unchanged after reaction for two days, whereas the rhodium salt was converted into $K_2[RhCl_5(NH_3)]$ after one day. This ammine complex was also formed by heating aqueous solutions of rhodium trichloride and sulphamic acid together for two days.

SECTION 5 - B EXPERIMENTAL

Potassium Sulphamatopentachlororhodate (III), $K_3[Rh(NH_2SO_3)Cl_5].H_2O$.

Hydrated sodium hexachlororhodate (III) (1.5 g) and potassium chloride (1.5 g) were dissolved in water (10 ml) and a saturated solution of sulphamic acid (1.2 g) added. The mixture was warmed for 2 min, cooled, and the light orange microcrystalline solid filtered off and washed with water and acetone (yield 80%). (Found: Cl, 34.4; K, 22.6; N, 3.4; S, 6.4. $H_4Cl_5K_3NO_4RhS$ requires Cl, 34.7; K, 22.9; N, 2.7; S, 6.3%). The complex is diamagnetic.

Potassium Sulphamatopentachloroiridate (III), $K_3[Ir(NH_2SO_3)Cl_5],2H_2O$.

This was prepared in a similar manner to the rhodium salt but using hydrated sodium hexachloroiridate (III). The product is salmon-pink (yield 75%). (Found: Cl, 28.9; K. 19.0; N, 2.4; S, 4.8. $H_6Cl_5K_3IrNO_5S$ requires Cl, 28.7; K, 18.9; N, 2.3; S, 5.2%). The complex is diamagnetic. Raman spectrum of normal salt: 326(10), 305(6), 258(2), 169(1) cm^{-1}; of deuteriate the same.

Potassium Sulphamatopentachlororuthenate (III) $K_3[Ru(NH_2SO_3)Cl_5]$.

Potassium hexachlororuthenate (III) (1 g) and sulphamic acid (1.2 g) were refluxed together in water (10 ml) for 15 min, and potassium chloride (1 g) then added to the mixture which was filtered while still hot. On cooling, the brown microcrystalline salt separated out; it was washed with water (5 ml) and then with acetone (yield 50%). (Found: Cl, 35.6; K, 23.3; N. 3.0; S, 6.6. $H_2Cl_5K_3NO_3SRu$ requires Cl, 36.1; K,23.9; N, 2.9; S, 6.5%). Gram susceptibility (χ_g) 3.74 x 10^{-6} c.g.s.u. (25°C) (μ_{eff} 2.18 B.M.).

Potassium Sulphamatopentachloro-osmate (III), $K_3[Os(NH_2SO_3)Cl_5]$.

This was made by reaction of sodium hexachloro-osmate (IV) (0.9 g) and stannous chloride (0.49 g) in 25% hydrochloric acid (7 ml). This mixture was warmed with sulphamic acid (1 g) and potassium chloride (1.2 g); on cooling, yellow platelets of $K_3[OsCl_6],1.1(NH_3SO_3)$ separated out. This (0.7 g) was warmed with sulphamic acid (1 g) and potassium chloride (1.2 g) in water (5 ml) under a nitrogen atmosphere. After 2 min. yellow crystals of the product were formed and were filtered off (yield 40%). (Found: Cl, 31.1; K, 19.6; N, 2.4. $H_2Cl_5K_3NO_3SOs$ requires Cl, 30.5; K, 20.2; N, 2.4%). Gram susceptibility χ_g 3.27 x 10^{-6} c.g.s.u. (μ_{eff} 2.21 B.M.).

trans-Potassium Bis(sulphamato-N)-dichloropalladate (II), $K_2[Pd(NH_2SO_3)_2Cl_2]$.

Sulphamic acid (2 g) was added to a hot solution (10 ml) of potassium tetrachloropalladate (II) (2 g). The yellow precipitate was formed immediately (yield 80%). (Found: Cl, 15.6; N, 6.4. $H_4Cl_2K_2N_2O_6PdS_2$ requires Cl, 15.9; N, 6.0%). Raman spectrum: 3182(½), 3125(1), 1534(½), 1272(1), 1248(2), 1165(1), 1066(3), 768(1), 708(1), 623(1), 578(½), 548(½), 496(2), 312(9), 269(1) cm^{-1}.

cis-Potassium Bis(sulphamato-N)-dichloroplatinate (II), $K_2[Pt(NH_2SO_3)_2Cl_2],2H_2O$.

This was made by the literature method [135]. (Found: Cl, 12.5; N, 5.1; S, 10.6. $H_8Cl_2K_2N_2O_8S_2Pt$ requires Cl, 12.6; N, 5.0; S, 11.4%). Raman spectrum: 3202(½), 3155(½), 1290(1), 1265(1), 1245(3), 1176(1), 1150(1), 1050(10), 1024(1), 1010(10), 792(1), 745(5), 622(3), 584(4), 545(1), 503(3), 376(1), 329(2), 325(10), 274(1) cm^{-1}.

trans-Potassium Bis(sulphamato-N)-dichloroplatinate (II), $K_2[Pt(NH_2SO_3)_2Cl_2]$.

This was made by the literature method [135]. (Found: Cl, 13.2; N, 5.6. $H_4Cl_2K_2N_2O_6PtS_2$ requires Cl, 13.2; N, 5.2%). Raman spectrum: 3176(1); 3119(1); 1538(1); 1277($\frac{1}{2}$), 1252(1), 1191(1), 1156(1), 1066(10), 764(4), 739(3), 648(1), 580(2), 544($\frac{1}{2}$), 506(3), 366(1) cm^{-1}.

Potassium Bis(sulphamato-N)-dibromoplatinate (II), $K_2[Pt(NH_2SO_3)_2Br_2]$.

This was made by Kirmreuther's method [135]. (Found: Br, 25.6; N, 4.6; S, 9.6. $H_4Br_2K_2N_2O_6PtS_2$ requires Br, 25.6; N, 4.5; S, 10.2%). Raman spectrum: 1280(1), 1250(1), 1070(10), 756(2), 743(10), 600(3), 577(2), 547(1), 500(5), 375(1), 283(3), 200(10) cm^{-1}.

Potassium Bis(sulphamato-N)-di-iodoplatinate (II), $K_2[Pt(NH_2SO_3)_2I_2]$.

This was made by the literature method [135]. (Found: N, 4.1; S,8.4. $H_4I_2K_2N_2O_6PtS_2$ requires N, 3.9; S, 8.9.)

Potassium Hexachlororhodate (III)-Sulphamic Acid, $K_3[RhCl_6].1.1NH_3SO_3$.

Rhodium trichloride (hydrated; 1 g) was dissolved in hot concentrated hydrochloric acid and potassium chloride (1.5 g) and sulphamic acid (1.2 g) added. Shiny pink platelets of the salt were precipitated upon cooling the solution; they were washed in ethanol and acetone (yield 70%). Similar complexes of iridium, ruthenium and osmium (III) may be prepared in like manner using $Na_3[IrCl_6].2H_2O$ (green shiny platelets, 80%), $K_3[RuCl_6]$ (brown shiny platelets, 75%) and $Na_3[OsCl_6]$ (yellow shiny platelets, 80%).

Caesium Bis(imidosulphamato)dichloroplatinate (II), $Cs_4[Pt(NHSO_3)_2Cl_2]$.

This was made by the literature method [135]. I.r. spectrum; 3244s, 1270m, 1140s, 1120s, 1008s, 886s, 770m, 720m, 635m, 580m, 510s, 311s, 280m cm^{-1}.

Potassium μ-Nitrido-octachlorodiaquodiruthenate (IV), $K_3[Ru_2NCl_8(H_2O)_2]$.

An aqueous solution of $K_3[Ru(NH_2SO_3)Cl_5]$ (0.5 g in 2 ml) was refluxed for two days; Potassium chloride (2 g) was added to the solution and the brown crystals of the product filtered off (yield 80%).

Ammonium Amminopentachlororhodate(III), $(NH_4)_2[RhCl_5(NH_3)]$.

An aqueous solution of sulphamic acid (7 g) and of hydrated rhodium trichloride (3 g) were refluxed in water (30 ml) for two days. The solution was then evaporated to low bulk and conc. hydrochloric acid (5 ml) added. The brown crystals were filtered off and washed with water to remove $(NH_4)_3[RhCl_6]$. (Found: Cl, 51.4; N, 11.8. $H_{11}Cl_5N_3Rh$ requires Cl, 53.5; N, 12.6%).

Physical Measurements.

Infra - red spectra were measured as nujol mulls between caesium iodide plates on a Perkin-Elmer 325 instrument (4000 - 200 cm^{-1}), and Raman spectra (4000 - 40 cm^{-1}) on a Cary 81 instrument with a CRL52 Kr laser using excitation at 647.1, 568.2, and 530.8 nm. ^{1}H n.m.r. spectra were measured over a temperature range from 223 to 308°K on a Perkin-Elmer R - 12B instrument, which operates at 60MHz. Electronic spectra were obtained from a Cary 14 machine.

Microanalyses were performed by the Microanalytical Department at Imperial College, Alfred Bernhardt, and F. Pascher. Potassium, ammonium, and caesium were determined as tetra-phenylboronates.

X - ray powder diffraction studies were made by Miss J. Osborne of this department.

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Sulphamato-complexes of the Platinum Metals

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Sulphamato-complexes of the Platinum Metals

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The new complexes $K_3[M(NH_2SO_3)Cl_5]$ (M = Rh, Ir, Ru, or Os) and $K_2[Pd(NH_2SO_3)_2Cl_2]$ have been characterised and their chemical reactions studied. Spectroscopic data suggest that sulphamate is nitrogen-bonded to the metal in these salts, in $K_2[Pt(NH_2SO_3)_2X_2]$ and in the imido-sulphonate $Cs_4[Pt(NHSO_3)_2Cl_2]$.

We have recently described the properties and structure of the nitrido-bridged species $K_3[Ru_2NCl_8(H_2O)_2]$,[1] first made [2] by reduction of $K_2[Ru(NO)Cl_5]$. Another recent publication has shown that $(NH_4)_3[Ru_2NCl_8(H_2O)_2]$ can be made from ruthenium trichloride and sulphamic acid in the presence of chloride ion.[3] As part of a general study of platinum metal nitrido-complexes we have studied the reaction between the metal halogeno-complexes and sulphamate ion in order to establish the nature of the intermediate species involved, and to investigate the possibility of making nitrido-complexes from them. There are few fully characterised sulphamato-complexes in the literature: those previously reported are of platinum(II) [4,5] and $[M(NH_2SO_3)(NH_3)_5]^{2+}$ (M = Co [6,7] and Ru [8]).

We find that reaction of hexachloro-complexes of trivalent rhodium, iridium, ruthenium, and osmium with sulphamic acid in the presence of potassium chloride yields $K_3[M(NH_2SO_3)Cl_5]$ in good yield, and a similar method with $K_2[PdCl_4]$ gives $K_2[Pd(NH_2SO_3)_2Cl_2]$. The magnetic moments of the four pentachloro-species indicate that the metal is in the trivalent state, and, in the case of the rhodium complex, *X*-ray powder photographs show that the complex contains no free $K_3[RhCl_6]$, potassium sulphamate or sulphamic acid.

Several properties suggest that the sulphamato-ligand is bonded to the metal *via* its nitrogen atom rather than oxygen in these new complexes as well as in the platinum(II) species $K_2[Pt(NH_2SO_3)_2X_2]$ (X = Cl, Br, or I). I.r. (and, where obtainable, Raman spectra) of the solids when compared with those of potassium sulphamate show that it is the $-NH_2$ modes (easily identified by their shifts on deuteriation) rather than the $-SO_3$ modes which are affected by co-ordination (see Table and Experimental section). The large shifts in the $-NH_2$ modes are similar to those found in mercury(II) amides,[9] while the much smaller shifts in $-SO_3$ modes are similar to those found in *S*-bonded thiosulphato-complexes.[10] A drop in the N–S stretching frequency from free to

I.r. spectra of sulphamate derivatives in the N–H and N–S regions (cm^{-1})

	ν_{NH_n}[a,c]	ν_{NH_n}[b]	δ_{NH_n}[a,c]	δ_{NH_n}[b]	NH_nrock	ν_{S-N}
$K(NH_2SO_3)$ [a]	3328s	3250s	1546m	1128m	956m	805vs
$K(ND_2SO_3)$	2508s	2417s	1160m	803m	718m	712vs
$K_3[Rh(NH_2SO_3)Cl_5]$	3248m	3143m	1516m	1151m	676w	724vs
$K_3[Rh(ND_2SO_3)Cl_5]$	2424m	2315m	1122m	903m	516w	708vs
$K_3[RhCl_6],1{\cdot}1NH_3SO_3$	3075s	2990vs	1550s	1389m	999m	692s
$K_3[RhCl_6],1{\cdot}1ND_3SO_3$	2279s	2210s	1124s	1071m	791m	678s
NH_3SO_3 [b]	3200s	3140s	1570m	1446m	1015m	695s
ND_3SO_3	2370s	2299s	1143m	1102m	801m	683s
$Cs_4[Pt(NHSO_3)_2Cl_2]$	3244s				1270m	883s
$Cs_4[Pt(NDSO_3)_2Cl_2]$	2401s				960m	839s

[a] Using the assignments of L. Kaityar, *Indian J. Pure Appl. Phys.*, 1968, **6**, 686. [b] Using the assignments of A. M. Vaugnat and B. L. Wagner, *J. Chem. Phys.*, 1957, **26**, 77.

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co-ordinated sulphamate is observed and would be expected for nitrogen co-ordination. In the imidosulphonate complex $Cs_4[Pt(NHSO_3)_2Cl_2]$ (made [4] by deprotonation of $[Pt(NH_2SO_3)_2Cl_2]^{2-}$), the N–S frequency rises to 886 cm^{-1} due presumably to the greater degree of N–S π-bonding attendant on the removal of a proton from the sulphamate amide group. The electronic spectrum of the rhodium complex $K_3[Rh(NH_2SO_3)Cl_5]$ is very similar to that of $K_2[Rh(NH_3)Cl_5]$, and indeed the latter complex may be made from the former by refluxing in aqueous solution, which again suggests *N*- rather than *O*-bonding of the $(NH_2SO_3)^-$ ligand. Attempts to prepare complexes of $CH_3SO_3^-$ from platinum metal halogeno-complexes and methanesulphonic acid or its salts were not successful, which again suggests that the isoelectronic $(NH_2SO_3)^-$ group probably co-ordinates *via* nitrogen; on chemical grounds one would expect the more basic nitrogen centre to co-ordinate preferentially.[7,8]

A curious feature of the reaction system sulphamic acid–platinum group halogeno-complexes is the formation, in very acid solutions, of plate-like crystals of $K_3[MCl_6],nNH_3SO_3$ ($n = 0{\cdot}9$—$1{\cdot}1$). The spectra of all four species (M = Rh, Ir, Ru, and Os) are very similar to each other and that of sulphamic acid in solution (*i.e.* the spectrum of sulphamic acid in the solid state is more complex than that of the solid 'complex'). *X*-Ray powder photographs for $K_3[RhCl_6],1{\cdot}1NH_3SO_3$ are quite different from those of $K_3[RhCl_6]$, solid sulphamic acid, potassium sulphamate, or potassium chloride; moreover the colour of $K_3[OsCl_6],NH_3SO_3$ (yellow) is quite different from that of $K_3[OsCl_6]$ (red). It seems probable that the zwitter-ion structure of sulphamic acid may be responsible, the lattice of the 'complex' containing distorted molecules of $[RhCl_6]^{3-}$ and $NH_3^+SO_3^-$ held together by dipole–dipole interaction or by N–H · · · Cl hydrogen bonds. A similar situation may exist in the double salt $K_2SO_4,2NH_3SO_3$ recently reported.[11] The failure to prepare analogous species with $K_3[MCl_6]$ and methanesulphonic acid also suggests that the zwitter-ion nature of sulphamic acid may be involved.

Prolonged refluxing of $K_3[Ru(NH_2SO_3)Cl_5]$ in aqueous solution gives $K_3[Ru_2NCl_8(H_2O)_2]$ and sulphite ion (simple pyrolysis of the ruthenium sulphamato-complex at 250° also gives the nitride). No such reaction is observed for the rhodium or iridium salts, but $K_3[Os(NH_2SO_3)Cl_5]$ gives a very low yield of a mixture of $K_3[Os_2NCl_8(H_2O)_2]$ and another nitrido-species, probably $K_5[Os_2NCl_{10}]$. The mechanism of the reaction with the ruthenium system is not clear; perhaps there is an oxidative two-electron process [*via* ruthenium(V)] of the type suggested by Chatt for formation of rhenium(V) nitrido-complexes with hydrazinium ion,[12] or possibly a disproportionation of ruthenium(III) to ruthenium(II) and (IV).[13]

EXPERIMENTAL

Potassium Sulphamatopentachlororhodate(III), $K_3[Rh(NH_2SO_3)Cl_5],H_2O$.—Hydrated sodium hexachlororhodate(III) (1·5 g) and potassium chloride (1·5 g) were dissolved in water (10 ml) and a saturated solution of sulphamic acid (1·2 g) added. The mixture was warmed for 2 min, cooled, and the light orange microcrystalline solid filtered off and washed with water and acetone (yield 80%) (Found: Cl, 34·3; K, 22·6; N, 3·4; S, 6·4. $H_4Cl_5K_3NO_4RhS$ requires Cl, 34·7; K, 22·9; N, 2·7; S, 6·3%). The complex is diamagnetic. Electronic spectrum (nm) reflectance: 475m, 395m; aqueous solution 475 ($\varepsilon = 80$), 382 ($\varepsilon = 80$). I.r. spectrum of normal salt: 3248m, 3143m, 1516m, 1293vs, 1252vs, 1151m, 1128m, 1058vs, 724s, 676w, 604w, 575m, 538m, 492m cm^{-1}.

Potassium Sulphamatopentachloroiridate(III), $K_3[Ir(NH_2SO_3)Cl_5],2H_2O$.—This was prepared in a similar manner to the rhodium salt but using hydrated sodium hexachloroiridate(III). The product is salmon-pink (yield 75%) (Found: Cl, 28·9; K, 19·0; N, 2·4; S, 4·8. $H_6Cl_5K_3IrNO_5S$ requires Cl, 28·7; K, 18·9; N, 2·3; S, 5·2%). The complex is diamagnetic. Electronic spectrum (nm) reflectance: 503m, 387m, 343m; solution 530w, 365vs, 330vs. I.r. spectrum of normal salt: 3234m, 3133m, 3013w, 1519m, 1290vs, 1259vs, 1169m, 1146m, 1058s, 723s, 700w, 612w, 575m, 538w, 498m, 309s, 295m, 255w cm^{-1}. Raman spectrum of normal salt: 326(10), 305(6), 258(2), 169(1) cm^{-1}; of deuteriate the same.

Potassium Sulphamatopentachlororuthenate(III) $K_3[Ru(NH_2SO_3)Cl_5]$.—Potassium hexachlororuthenate(III) (1 g) and sulphamic acid (1·2 g) were refluxed together in water (10 ml) for 15 min, and potassium chloride (1 g) then added to the mixture which was filtered while still hot. On cooling, the brown microcrystalline salt separated out; it was washed with water (5 ml) and then with acetone (yield 50%) (Found: Cl, 35·6; K, 23·3; N, 3·0; S, 6·6. $H_2Cl_5K_3NO_3SRu$ requires Cl, 36·1; K, 23·9; N, 2·9; S, 6·5%). Gram susceptibility (χ_g) $3{\cdot}74 \times 10^{-6}$ c.g.s.u. (25 °C) ($\mu_{eff.}$ 2·18 B.M.). I.r. spectrum: 3245m, 3143m, 3010w, 2289w, 1515m, 1290s, 1252s, 1150w, 1122m, 1057s, 726s, 658w, 595m, 573m, 537m, 486m, 323s, 306s, 284s, 272w cm^{-1}.

Potassium Sulphamatopentachloro-osmate(III), $K_3[Os(NH_2SO_3)Cl_5]$.—This was made by reaction of sodium hexachloro-osmate(IV) (0·9 g) and stannous chloride (0·49 g) in 25% hydrochloric acid (7 ml). This mixture was warmed with sulphamic acid (1 g) and potassium chloride (1·2 g); on cooling, yellow platelets of $K_3[OsCl_6],1{\cdot}1(NH_3SO_3)$ separated out. This (0·7 g) was warmed with sulphamic acid (1 g) and potassium chloride (1·2 g) in water (5 ml) under a nitrogen atmosphere. After 2 min yellow crystals of the product were formed and were filtered off (yield 40%) (Found: Cl, 31·1; K, 19·6; N, 2·4. $H_2Cl_5K_3NO_3SOs$ requires Cl, 30·5; K, 20·2; N, 2·4%). Gram susceptibility χ_g $3{\cdot}27 \times 10^{-6}$ c.g.s.u. ($\mu_{eff.}$ 2·21 B.M.). I.r. spectrum: 3230m, 3138m, 1517m, 1293vs, 1256vs, 1156m, 1139m, 1058vs, 721s, 674w, 598w, 511m cm^{-1}.

trans-*Potassium Bis*(*sulphamato*-N)-*dichloropalladate*(II), $K_2[Pd(NH_2SO_3)_2Cl_2]$.—Sulphamic acid (2 g) was added to a hot solution (10 ml) of potassium tetrachloropalladate(II) (2 g). The yellow precipitate was formed immediately (yield 80%) (Found: Cl, 15·6; N, 6·4. $H_4Cl_2K_2N_2O_6PdS_2$ requires Cl, 15·9; N, 6·0%). I.r. spectrum: 3180s, 3112s, 3040m, 1533m, 1265vs, 1240vs, 1168m, 1143m, 1054s, 758s, 734s, 626m, 585s, 541s, 508s cm^{-1}. Raman spectrum: 3182($\frac{1}{2}$), 3125(1), 1534($\frac{1}{2}$), 1272(1), 1248(2), 1165(1), 1066(3),

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768(1), 708(1), 623(1), 578(½), 548(½), 496(2), 312(9), 269(1) cm^{-1}.

cis-*Potassium Bis(sulphamato*-N)-*dichloroplatinate*(II), $K_2[Pt(NH_2SO_3)_2Cl_2],2H_2O$.—This was made by the literature method [4] (Found: Cl, 12·5; N, 5·1; S, 10·6. $H_8Cl_2K_2N_2O_8S_2Pt$ requires Cl, 12·6; N, 5·0; S, 11·4%). I.r. spectrum: 3600s, 3498s, 3149s, 3115s, 3040m, 1614s, 1586s, 1551m, 1522m, 1295vs, 1266m, 1245m, 1180m, 1146m, 1123m, 1067vs, 1064s, 1055s, 1046s, 792m, 748s, 724s, 625m, 619m, 576s, 543m, 503m, 345w cm^{-1}. Raman spectrum: 3202(½), 3155(½), 1290(1), 1265(1), 1245(3), 1176(1), 1150(1), 1050(10), 1024(1), 1010(10), 792(1), 745(5), 622(3), 584(4), 545(1), 503(3), 376(1), 329(2), 325(10), 274(1) cm^{-1}.

trans-*Potassium Bis(sulphamato*-N)-*dichloroplatinate*(II), $K_2[Pt(NH_2SO_3)_2Cl_2]$.—This was made by the literature method [4] (Found: Cl, 13·2; N, 5·6. $H_4Cl_2K_2N_2O_6PtS_2$ requires Cl, 13·2; N, 5·2%). I.r. spectrum: 3168s, 3110s, 1534m, 1263vs, 1245vs, 1193m, 1153m, 1051s, 781w, 738s, 634w, 582s, 541m, 512s, 373m cm^{-1}. Raman spectrum: 3176(1), 3119(1), 1538(1), 1277(½), 1252(1), 1191(1), 1156(1), 1066(10), 764(4), 739(3), 648(1), 580(2), 544(½), 506(3), 366(1) cm^{-1}.

Potassium Bis(sulphamato-N)-*dibromoplatinate*(II), $K_2[Pt(NH_2SO_3)_2Br_2]$.—This was made by Kirmreuther's method [4] (Found: Br, 25·6; N, 4·6; S, 9·6. $H_4Br_2K_2N_2O_6PtS_2$ requires Br, 25·6; N, 4·5; S, 10·2%). I.r. spectrum: 3148s, 3129s, 3052m, 2420w, 1550m, 1524m, 1313vs, 1295vs, 1265vs, 1244s, 1194m, 1168w, 1065s, 727s, 626m, 578s, 545m, 520m, 505m, 382w, 287w cm^{-1}. Raman spectrum: 1280(1), 1250(1), 1070(10), 756(2), 743(10), 600(3), 577(2), 547(1), 500(5), 375(1), 283(3), 200(10) cm^{-1}.

Potassium Bis(sulphamato-N)-*di-iodoplatinate*(II), $K_2[Pt(NH_2SO_3)_2I_2]$.—This was made by the literature method [4] (Found: N, 4·1; S, 8·4. $H_4I_2K_2N_2O_6PtS_2$ requires N, 3·9; S, 8·9). I.r. spectrum: 3141m, 3120m, 3030m, 1538m, 1525m, 1310s, 1293s, 1260s, 1237s, 1188m, 1051s, 719s, 622w, 575s, 543m, 513m, 501m, 376w, 279m cm^{-1}.

Potassium Hexachlororhodate(III)–*Sulphamic Acid*, $K_3[RhCl_6],1{\cdot}1NH_3SO_3$.—Rhodium trichloride (hydrated; 1 g) was dissolved in hot concentrated hydrochloric acid and potassium chloride (1·5 g) and sulphamic acid (1·2 g) added. Shiny pink platelets of the salt were precipitated upon cooling the solution; they were washed in ethanol and acetone (yield 70%). Electronic spectrum, reflectance: 522m, 422m nm. I.r. spectrum: 3075s, 2955vs, 1547s, 1525s, 1389m, 1293s, 1279s, 1071vs, 999m, 692s, 542s, 518m, 343m cm^{-1}. Similar complexes of iridium, ruthenium, and osmium(III) may be prepared in like manner.

Caesium Bis(imidosulphamato)dichloroplatinate(II), $Cs_4[Pt(NHSO_3)_2Cl_2]$.—This was made by the literature method.[4] I.r. spectrum: 3244s, 1270m, 1140s, 1120s, 1008s, 886s, 770m, 720m, 635m, 580m, 510s, 311s, 280m cm^{-1}.

Potassium μ-*Nitrido-octachlorodiaquodiruthenate*(IV), $K_3[Ru_2NCl_8(H_2O)_2]$.—An aqueous solution of $K_3[Ru(NH_2SO_3)Cl_5]$ (0·5 g in 2 ml) was refluxed for two days; potassium chloride (2 g) was added to the solution and the brown crystals of the product filtered off (yield 80%).

Ammonium Amminopentachlororhodate(III), $(NH_4)_2[RhCl_5(NH_3)]$.—An aqueous solution of sulphamic acid (7 g) and of hydrated rhodium trichloride (3 g) were refluxed in water (30 ml) for two days. The solution was then evaporated to low bulk and conc. hydrochloric acid (5 ml) added. The brown crystals were filtered off and washed with water to remove $(NH_4)_3[RhCl_6]$ (Found: Cl, 51·4; N, 11·8. $H_{11}Cl_5N_3Rh$ requires Cl, 53·5; N, 12·6%). Electronic spectrum: reflectance 470m, 390m nm.

Electronic spectra were measured on a Cary 14 instrument (700—200 nm); i.r. spectra on a Perkin-Elmer 325 (4000—200 cm^{-1}) as Nujol mulls in caesium iodide plates. Raman spectra were measured (4000—160 cm^{-1} or, for weak scatterers, 400—160 cm^{-1}) on a Cary 81 instrument with a CRL 52MG laser (argon–krypton), using excitation at 6471 and at 5682 Å. Microanalyses were performed by the Microanalytical Department at Imperial College and by Alfred Bernhardt, Munich; potassium and ammonium were estimated as the tetraphenylborates.

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Metal Nitrido- and Oxo-complexes. Part I. Complexes of Ruthenium and Osmium

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The preparation and physical properties of the new complexes $Cs_2[Ru(N)X_5]$ and $R[M(N)X_4]$ (M = Ru or Os; R = Ph_4As or Bu^n_4N; X = Cl or Br) are described. New binuclear nitrido-bridged complexes of ruthenium(IV) with carbonyl, cyanide, and chelate ligands, the polymeric nitrido-bridged species $[Os(N)Br_4]_n^{n-}$ and $[Os_3(N)_2X_{11}(NH_3)_3]^{3-}$ (X = Cl or Br), and oxo- and dioxo-complexes of ruthenium are also reported. The structures of the species are discussed on the basis of vibrational spectra and other properties.

THE nitride ion (N^{3-}), like the isoelectronic oxide ion (O^{2-}), can function as a terminal ligand [1] or, less commonly, bridges two,[2] three,[3] or four [4] metal atoms in linear, triangular, or tetrahedral arrays. Recently we briefly described the preparation of ruthenium(VI) terminal nitrido-salts $Cs_2[Ru(N)X_5]$ (X = Cl or Br) and related dioxo-species,[5] and here we give fuller details of these and of other terminal nitrido-complexes. We also report an extension of our previous work on binuclear and polynuclear nitrido-bridged complexes of ruthenium and osmium.[6]

RESULTS AND DISCUSSION

Terminal Nitrido-complexes.—Mononuclear species containing M≡N groups have been established for very few metals, *viz.* vanadium,[7] molybdenum and tungsten,[8] rhenium,[9] and osmium.[10] In general the M≡N distance is short (*ca.* 1·7 Å), and the metal is in a high oxidation state due to the very effective σ- and π-donor properties of the nitrido-ligand.[1]

Despite the considerable stability of nitrido-complexes of osmium(VI) and osmium(VIII), the only ruthenium nitrido-complexes hitherto established are binuclear with symmetric Ru–N–Ru units.[6] We found that reaction of the complexes *trans*-$[Ru(O)_2X_4]^{2-}$ (X = Cl or Br) in ice-cold HX solution with an excess of azide ions and caesium halide gave the light brown diamagnetic salts $Cs_2[Ru(N)X_5]$, and the known osmium complexes $Cs_2[Os(N)X_5]$ [11] could be prepared by similar methods using *trans*-$[Os(O)_2X_4]^{2-}$. Liberation of free halogen and nitrogen during these reactions is consistent with the formation of a ruthenium(VI) or osmium(VI) azido-complex which undergoes oxidative decomposition to the nitrido-complex. Furthermore, from the reaction of the complex *trans*-$[Os^{VI}(O)_2(OH)_4]^{2-}$ with azide and caesium ions in dilute acetic acid, the complex $Cs[Os^{VIII}(O)_3N]$ could be isolated (the 'osmiamate' ions do not react with acetic acid). Such a mechanism has been proposed for the formation of rhenium(V) nitrido-complexes from rhenium(III) species and azide ions,[9] and of molybdenum(VI) nitrido-complexes from $MoCl_5$ and azide ions.[12]

The use of large organic cations as precipitants in place of caesium in the preparations of the $[M(N)X_5]^{2-}$ ions gave pink diamagnetic salts $R[M(N)X_4]$ (M = Ru or Os; R = Ph_4As or Bu^n_4N; X = Cl or Br), which were 1 : 1 electrolytes in acetone. It has been shown that the addition of $[Ph_4As]^+$ and $[Bu^n_4N]^+$ ions to solutions of $[Re(N)Cl_5]^{2-}$ precipitates $R[Re(N)Cl_4]$,[13] and mono-oxo-complexes $Cs_2[M(O)X_5]$, $R[M(O)X_4]$ (M = Mo or Re; R = Ph_4As or Bu^n_4N; X = Cl or Br), and $R[M(O)X_4L]$ (L = solvent molecule) can be isolated.[14,15] The considerable repulsion between the axial π-donor and the equatorial halide ligands in $[M(N)X_5]^{2-}$ or

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$[M(O)X_4L]^-$ tends to weaken the *trans*-axial ligand [16] as shown by *X*-ray studies of the complexes $K_2[Os(N)Cl_5]$,[16] *trans*-$[Re(O)Br_4L]^-$ (L = MeCN or H_2O),[14] $[Re(O)Cl_4(H_2O)]$,[17] and $[Ph_4As][Mo(O)Br_4(H_2O)]$.[18] Lattice-energy considerations may also be important.

Vibrational spectra. The main features and assignments of the vibrational spectra of the terminal nitrido-complexes are summarised in the Table. We find that the M≡N stretching frequency ν_{MN} is higher for the solid salts $R[M(N)X_4]$ and $[Os(N)X_5]^{2-}$ than for the corresponding $Cs_2[M(N)X_5]$ species (M = Ru or Os; X = Cl or Br; R = Ph_4As or Bu^n_4N). This may be due to interaction between the polarisable Cs^+ ion and the nitrido-ligand; an analogous effect has been noted for rhenium(v) oxo-species.[14] This frequency is also higher for osmium than those for ruthenium in corresponding complexes and the stretching force constant k_{MN} has been shown to be some 10% higher for osmium than that for ruthenium.[19] The X–M≡N bending mode has been identified for the first time in nitrido-complexes by ^{15}N substitution; it is *ca.* 250 cm^{-1} and changes in sympathy with ν_{MN}.

The spectra of the $R[M(N)X_4]$ salts are consistent with the C_{4v} symmetry of the square-based pyramid.* The presence of substantial · · · M≡N · · · M≡N · · · linear chain bonding seems unlikely; it has been shown that the complexes $K_{2n}[Re(N)(CN)_4]_n$ [20] and $[W(O)Cl_4]_n$ [21] contain such chains and their i.r. spectra in the 850—1100 cm^{-1} region, as compared with those of $K_3[Re(N)(CN)_5]$ and monomeric $[W(O)Cl_4]$ respectively, show a lowering and considerable broadening of the stretching modes. No such effect is observed with the $R[M(N)X_4]$ salts as compared with those of $Cs_2[M(N)X_5]$.

The M–X stretching modes in the $R[M(N)X_4]$ complexes are some 10% higher than those in the corresponding $Cs_2[M(N)X_5]$ salts. This remarkable increase may be due to the four halide ligands in solid $R[M(N)X_4]$ adopting a position which gives better σ- and π-overlap with the appropriate metal orbitals, steric constraints imposed by the sixth *trans*-ligand being removed. Such an effect has been observed in *X*-ray studies of the complexes *trans*-$[Re(O)Cl_4(H_2O)]$ [17] and monomeric $[Re(O)Cl_4]$;[22] in the latter the Cl–Re–O angle of 105° is some 7° greater than in the former, and the Re–Cl distance is shorter.

Binuclear Nitrido-complexes.—The anion in $K_3[Ru_2(N)Cl_8(H_2O)_2]$ is centrosymmetric (D_{4h} with a linear Ru–N–Ru unit).[2,6] Here we describe complexes containing such a Ru–N–Ru unit with ligands not normally found with ruthenium(IV).

Solutions of the complex $K_3[Ru_2(N)Cl_8(H_2O)_2]$, when heated under reflux in concentrated aqueous HX (X = Cl or Br), slowly take up carbon monoxide, and from the resulting solutions the complexes $Cs_3[Ru_2(N)X_8(CO)_2]$ could be obtained. The reaction only occurs in strong acid; analogous reactions are found for solutions of $[RuCl_6]^{3-}$ in HCl.[23] It is also possible to obtain chlorocarbonyl species by reaction of the complex $K_3[Ru_2(N)Cl_8(H_2O)_2]$ in formic acid–hydrochloric acid (2 : 1) (again, $[RuCl_6]^{3-}$ undergoes an analogous reaction with HCO_2H–HCl).[23] Although we were unable to obtain the Raman spectra of the $Cs_3[Ru_2(N)X_8(CO)_2]$ complexes because of their colours, the i.r. spectra in the metal–halogen stretching regions are very similar in profile to those of the complexes $K_3[Ru_2(N)X_8(H_2O)_2]$, which suggests that the carbonyl groups are *trans* to the

Vibrational spectra of metal nitrido-complexes (200—1200 cm^{-1})

Complex	$\nu_{MN}(A_1)$	ν_{MX_4}(sym)(A_1) *	ν_{MX_4}(asym)(E)	$\delta_{XMN}(E)$	Other strong bands
$Cs_2[Ru(N)Cl_5]$	1045s	318 (10)	340s, 338s	235m	307 (1),* 284 (3),* 233 (5) *
$[Ph_4As][Ru(N)Cl_4]$	1092s	346 (10)	378s	267m	304 (4),* 266 (5) *
$Cs_2[Ru(N)Br_5]$	1045s	207 (5)	257s	206m	201 (1) *
$[Ph_4As][Ru(N)Br_4]$	1088s		302s	230m	
$Cs_2[Os(N)Cl_5]$	1073s (1040)		331s (330), 325s (324)	243m (238)	
$K_2[Os(N)Cl_5]$	1084s	348 (10) †	336s, 329s	262m	334 (2),†, 324 (4),† 264 (4) †
	1106w †				
$[Ph_4As][Os(N)Cl_4]$	1123m (1085)	358 (10)	365s (362)	271w (262)	352 (1) *
$Cs_2[Os(N)Br_5]$	1073s (1040)	198 (10) †	234s (232)	216m (210)	
$[Ph_4As][Os(N)Br_4]$	1120m (1082)	229 (10)	274s (269)	233m (228)	
$K[Os(N)Br_4(H_2O)],H_2O$	1109m		232s	261m, 250m	619sb, 535sb, 300s
	1105w ‡				
$K_n[Os(N)Br_4]_n$	1002sb		241s		

Bands due to the cation are not quoted. All spectra from i.r. studies on solids, except where indicated. Frequencies in parentheses refer to ^{15}N substituted species.

* Raman data on the solid. † Spectra on complex in D_2O solution with an excess of the X^- ion. ‡ In D_2O solution.

* *Note added in proof:* Single-crystal *X*-ray studies on the salt $[Ph_4As][OsNCl_4]$ confirm that the anion has C_{4v} symmetry (F. Phillips and A. C. Skapski, unpublished work).

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nitrido-group as are the water ligands in the parent species. The asymmetric Ru_2N stretching frequency of the carbonyl complexes is some 40 cm^{-1} lower than those of the corresponding aquo-species; if the carbonyl groups are indeed *trans* to the nitrido-group, this drop in frequency may well arise from competition of CO and N^{3-} ligands for the same metal t_{2g} orbitals. A related situation is that in the complex *trans*-$[Ru^{II}(NO)(NH_2)(NH_3)_4]^{2+}$, where the terminal π-donor amide ligand is stabilised by the strongly π-accepting nitrosyl group.[24]

The reaction of $[Ru_2(N)Cl_8(H_2O)_2]^{3-}$ with potassium cyanide gave the very stable species $K_5[Ru_2(N)(CN)_{10}],3H_2O$. The i.r. spectrum of the solid was very complex in the C≡N stretching region and also showed sharp high-frequency water bands; on dehydration the C≡N band structure became much simpler. This behaviour is similar to that observed for the complex $Na_2[Fe(CN)_5NO],2H_2O$, where *X*-ray and careful i.r. studies have shown that the water molecules occupy equivalent sites in the lattice and have low site symmetry with very weak hydrogen bonding.[25] The nitrido-species is stable in aqueous solution and there is no evidence that aquation occurs. The Raman spectrum of the dehydrated solid was similar to that of the solution, suggesting that there is no change of configuration in the latter. In solution we observed four Raman modes (two polarised, one an intense band at 2156 cm^{-1}, and a weaker band at 2116 cm^{-1}) and three i.r. bands with no coincidences between the two sets. However, for both the probable symmetries D_{4h} (equatorial ligands eclipsed), as found in $K_3[Ru_2(N)Cl_8(H_2O)_2]$,[2] and D_{4d} (equatorial ligands staggered), as in $[Mn_2(CO)_{10}]$,[26] we expect this behaviour. Although no distinction can be drawn between these two symmetries on the basis of our study, the difference in band profiles in the 2000 cm^{-1} region for $[Ru_2(N)(CN)_{10}]^{5-}$ compared with $[Mn_2(CO)_{10}]$ and $[Co_2(CN)_{10}]^{6-}$ (ref. 26) suggests that the complex has the expected D_{4h} symmetry in solution. We provisionally assign the strongest polarised band to the symmetric stretch of the cyano-ligands, and the weaker band to that of the axial ligands. The symmetric Ru_2N stretch occurs as a strong, polarised band at 264 cm^{-1} in the Raman spectrum of the solution.

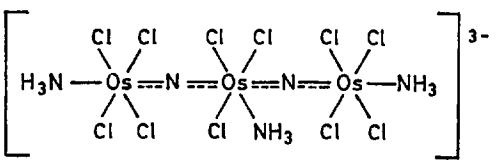
The existence of carbonyl and cyano-complexes of ruthenium(IV) is unusual; it appears that ruthenium in these binuclear species is behaving more as ruthenium(III) or even ruthenium(II). This is probably due to the strong π-donor effect of the nitrido-ligand which, in effect, fills the t_{2g} orbitals of each metal atom which then behaves as a pseudo-d^6 system, ready to delocalise electron density on to π-acceptor ligands. There is also evidence for the formation of phosphine and nitrosyl complexes containing the Ru_2N system.

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Despite the steric constraints imposed by the short ruthenium–nitrido-group bonds {Ru–N = 1·718 Å in $K_3[Ru_2(N)Cl_8(H_2O)_2]$[2]}, it is possible to isolate stable complexes containing the Ru_2N system with chelating ligands, *e.g.* $[Ru_2(N)(dae)_4Cl_2]Cl_3$ and $[Ru_2(N)(bipy)_4Cl_2](PF_6)_3$ (dae = 1,2-diaminoethane, bipy = 2,2′-bipyridine); in the latter case the 2,2′-bipyridine ligands are presumably not in a plane about each ruthenium atom [27] so that the chloro-ligands are likely to be *cis* to the nitrido-ligand. A diethyldithiocarbamate complex, $[Ru_2(N)(S_2CNEt_2)_4Cl]$ has also been prepared; this is a non-electrolyte in acetone solution and may be polymeric in the solid state with ··· Ru–Cl–Ru–N–Ru–Cl ··· chains.

Polynuclear Nitrido-complexes of Osmium.—Dehydration of the red salt $K[Os(N)Br_4(H_2O)],H_2O$ at 110 °C gave a green substance, $K_n[Os(N)Br_4]_n$, which quickly reverted to the starting material on setting aside in the atmosphere. Comparison of the i.r. spectra of $K[Os(N)Br_4(H_2O)],H_2O$ and $K_n[Os(N)Br_4]_n$ shows that, whereas the Os≡N stretching frequency in the former is sharp and intense at 1109 cm^{-1}, in the latter it is much broader and drops to 1002 cm^{-1}; the N≡Os–Br bending mode drops below 200 cm^{-1}. We propose that in this complex $K_n[Os(N)Br_4]_n$, as in that of $K_{2n}[Re(N)(CN)_4]_n$,[20] there are linear ··· M≡N ··· M≡N ··· chains.

The reaction of osmium tetraoxide with concentrated aqueous ammonia yields a black, diamagnetic material originally formulated as $[OsO_2(NH_3)_2(H_2O)]$; with hydrochloric acid, $[OsCl_4(NH_3)_2]$ is said to be formed.[28] We found that, from solutions of the black material in HX, the caesium salts $Cs_3[Os_3(N)_2X_{11}(NH_3)_3],2H_2O$ (X = Cl or Br) could be precipitated; the salts are brown and diamagnetic. The i.r. spectra of the normal and deuteriated salts showed bands due to co-ordinated NH_3 or ND_3; two strong bands in the 950—1100 cm^{-1} region were, however, barely shifted by deuteriation, and these we assign to bridging nitrido-ligands. We propose that these complexes have the structure (I)



(I)

and the diamagnetism of this formally Os^{V}–Os^{IV}–Os^{V} species may then be rationalised using the bonding scheme applied to ruthenium red, $[Ru_3(O)_2(NH_3)_{14}]^{6+}$,[29] which has an analogous structure.[30] A similar structural unit has been proposed for the product obtained from the prolonged reaction of osmium tetraoxide and liquid ammonia.[6,31]

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Ruthenium Oxo-complexes.—The formation of $[Ru(N)Cl_5]^{2-}$ from azide and *trans*-$[Ru(O)_2Cl_4]^{2-}$ ions prompted a further investigation of ruthenium oxo-complexes as possible precursors for nitrido-species. Only *trans*-$[Ru(O)_2Br_4]^{2-}$ ions were useful in this respect, but we have isolated a number of other oxo-species in the course of this work. The only firmly established 'ruthenyl' species are those of *trans*-$Cs_2[Ru(O)_2Cl_4]$ [32] and *trans*-$[Ru(O)_2(OH)_2(py)_2]$ (py = pyridine);[33] although spectroscopic data have been reported on salts of the anions $[Ru(O)_2Br_4]^{2-}$ and $[Ru(O)_2(SO_4)_2]^{2-}$, no preparative details were given.[34]

From solutions of ruthenium tetraoxide in carbon tetrachloride with ice-cold solutions of HX and CsX (X = Br or $\frac{1}{2}C_2O_4$), the salts $Cs_2[Ru(O)_2X_4]$ were obtained; from mildly alkaline solutions of RCl (R = NH_4, Hbipy, or Hpy), the species $[Ru(O)_2(NH_3)_4]Cl_2$, $[Ru(O)_2(bipy)Cl_2]$, and $[Ru(O)_2(py)_2Cl_2]$ were similarly obtained. All the complexes are diamagnetic, consistent with there being a *trans*-RuO_2 unit, as in the corresponding osmium dioxo-species.[35] The complexes all showed a characteristic strong band in the i.r. *ca.* 830 cm^{-1} which we assign to the asymmetric RuO_2 stretch, while for those complexes whose Raman spectra could be measured the symmetric RuO_2 stretch appeared in the same region. The stretching force constants for the RuO_2 systems, calculated from the equations of Cotton and Wing,[36] are some 10% lower than those for the corresponding osmium species.[37]

The reaction of ruthenium tetraoxide with an ice-cold solution of sodium cyanide in the presence of caesium ion did not, surprisingly, yield the complex $Cs_2[Ru(O)_2(CN)_4]$; a green paramagnetic salt, which showed i.r. bands characteristic of co-ordinated cyano- and *iso*-cyanato-groups, was formed. We formulate this complex as $Cs_3[Ru(O)(CN)_4(CNO)_2]$; a strong band at 787 cm^{-1} in the i.r. spectrum, which also appeared in the Raman spectrum of the solid, is assigned to the Ru=O stretch. The magnetic moment of 3·0 B.M. is similar to that recently reported for arylimido-complexes of osmium(V).[38] The reaction of potassium tetraoxoruthenate(VI) with sodium cyanide in the presence of caesium ions yielded a yellow paramagnetic material $Cs_5[Ru_2(O)_5(CN)_9]$, the structure of which is still under investigation.

EXPERIMENTAL

Dicaesium Pentachloronitridoruthenate(VI), $Cs_2[Ru(N)Cl_5]$.—A solution of ruthenium tetraoxide in carbon tetrachloride (10 cm^3) (*vide infra*) was stirred rapidly with 8M-hydrochloric acid (7 cm^3), and the resulting red solution cooled to 0 °C. Sodium azide (0·24 g) was added to the reaction mixture and the solution stirred at room temperature until effervescence had ceased (*ca.* 15 min). Caesium chloride (0·8 g) was added and the light brown *precipitate* (80%) was filtered off, washed with ice-cold concentrated hydrochloric acid (2 cm^3), then acetone, and finally dried at 110 °C [Found: Cl, 31·4; Cs, 47·5; N, 2·6. Cl_5Cs_2NRu requires Cl, 31·8; Cs, 47·6; N, 2·5%].

Tetraphenylarsonium Tetrachloronitridoruthenate(VI), $[Ph_4As][Ru(N)Cl_4]$.—A solution of tetraphenylarsonium chloride (0·8 g) in methanol (5 cm^3) was added to the above reaction mixture in the place of caesium chloride. The pink *precipitate* (80%) which formed was filtered off, washed with water and methanol, and recrystallised from acetonitrile [Found: C, 45·0; H, 3·2; Cl, 22·9; N, 2·1. $C_{24}H_{20}AsCl_4NRu$ requires C, 45·0; H, 3·1; Cl, 22·2; N, 2·2%].

Tetra-n-butylammonium Tetrachloronitridoruthenate(VI), $[Bu^n_4N][Ru(N)Cl_4]$.—Tetra-n-butylammonium hydroxide solution (40%, 2 cm^3) replaced tetraphenylarsonium chloride solution in the preceding preparation. The pale pink precipitate (80%) which formed was filtered off, washed with water and diethyl ether, and recrystallised from acetone to give brown *crystals* of the product [Found: C, 38·4; H, 7·0; Cl, 28·9; N, 5·2. $C_{16}H_{36}Cl_4N_2Ru$ requires C, 38·5; H, 7·2; Cl, 28·4; N, 5·6%]. I.r. spectrum (excluding cation bands): 1095m; 376s; and 265m cm^{-1}. Molar conductance (in acetone) 121 Ω^{-1} cm^{-2} in 10^{-3}M-solution.

Dicaesium Pentabromonitridoruthenate(VI), $Cs_2[Ru(N)Br_5]$.—Sodium azide (0·24 g) was dissolved in an ice-cold solution of water (2 cm^3) and concentrated hydrobromic acid (5 cm^3). Ruthenium tetraoxide solution (10 cm^3, *vide infra*) was added to the solution and the mixture stirred vigorously at 0 °C (5 min). Caesium bromide (0·9 g) was added to the solution and the light brown *product* (40%) was filtered off, washed with acetone, and dried at 110 °C [Found: Br, 50·3; Cs, 34·2; N, 1·9. Br_5Cs_2NRu requires Br, 51·2; Cs, 34·1; N, 1·8%].

Tetraphenylarsonium Tetrabromonitridoruthenate(VI) $[Ph_4As][RuNBr_4]$.—A solution of tetraphenylarsonium chloride (0·5 g) in methanol (5 cm^3) was added to the above reaction mixture in the place of caesium bromide. The bulky yellow precipitate which formed was filtered off and washed with methanol to leave a light pink *precipitate* (40%) [Found: C, 35·2; H, 2·6; Br, 38·9; N, 1·6. $C_{24}H_{20}AsBr_4NRu$ requires C, 35·2; H, 2·4; Br, 39·1; N, 1·7%].

Dicaesium Pentahalogenonitrido-osmate(VI), $Cs_2[Os(N)X_5]$ (X = Cl *or* Br).—The chloro- and bromo-complexes were prepared by literature methods;[11] an alternative procedure which eliminates contamination with the corresponding osmium(VI) dioxo-complex is as follows.

Chloro-complex.—Potassium osmate (0·08 g) was dissolved in concentrated hydrochloric acid (3 cm^3) and sodium azide solution (0·03 g in 1 cm^3 water) added. The solution was stirred (20 min) and caesium chloride (0·05 g) was added to precipitate the purple product.

Bromo-complex. The procedure was similar to that used for the chloro-complex but hydrobromic acid and caesium bromide were used to give the purple product.

Organic cation salts of the tetrahalogeno-osmate(VI) complexes were precipitated from solutions of $[Os(N)X_5]^{2-}$ in HX (X = Cl or Br) using the procedures described for the ruthenium salts. *Tetraphenylarsonium tetrachloronitrido-osmate*(VI), $[Ph_4As][Os(N)Cl_4]$. Pink crystals (90%) [Found: C, 39·5; H, 2·9; Cl, 19·2; N, 2·0. $C_{24}H_{20}AsCl_4NOs$ requires

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C, 39·5; H, 2·7; Cl, 19·5; N, 1·9%]. Molar conductance (in acetone) 113 Ω^{-1} cm^{-2} in 10^{-3}M-solution. *Tetra-n-butylammonium tetrachloronitrido-osmate*(VI), $[Bu^n_4N][Os(N)Cl_4]$. Red (90%) [Found: Cl, 23·8; N, 5·5. $C_{16}H_{36}Cl_4N_2Os$ requires Cl, 24·1; N, 4·8%]. I.r. bands (excluding cation absorptions): 1125m; 353s; and 262w cm^{-1}. Molar conductance (in acetone) 124 Ω^{-1} cm^{-2} in 10^{-3}M-solution. *Tetraphenylarsonium tetrabromonitrido-osmate*(VI), $[Ph_4As][Os(N)Br_4]$. Pink crystals (90%) [Found: C, 32·0; H, 2·0; Br, 35·5; N, 1·7. $C_{24}H_{20}AsBr_4NOs$ requires C, 31·8; H, 2·2; Br, 35·3; N, 1·5%]. *Tetra-n-butylammonium tetrabromonitrido-osmate*(VI), $[Bu^n_4N][Os(N)Br_4]$. Deep red crystals (90%) [Found: Br, 40·8; N, 3·5. $C_{16}H_{36}Br_4N_2Os$ requires Br, 41·7; N, 3·7%]. I.r. bands (excluding cation absorptions): 1120m; 270s; and 232m cm^{-1}. Molar conductance (in acetone) 124 Ω^{-1} cm^{-2} in 10^{-3}M-solution.

Tricaesium Dicarbonyloctachloro-μ-nitrido-diruthenate(IV), $Cs_3[Ru_2(N)Cl_8(CO)_2]$.—*Method* (*a*). The complex $K_3[Ru_2(N)Cl_8(H_2O)_2]$ (2·5 g) was heated under reflux in concentrated hydrochloric acid (25 cm^3) under a stream of carbon monoxide (15 h). The solution was cooled, hydrochloric acid (10 cm^3) added, and the resulting solution set aside under the gas stream (1 h). The solution was then filtered to remove starting material, and caesium chloride (2·0 g) added to precipitate the light brown *product* (30%), which was filtered off and washed with acetone [Found: C, 1·9; Cl, 30·3; Cs, 41·2; N, 1·3. $C_2Cl_8Cs_3NO_2Ru_2$ requires C, 2·5; Cl, 29·7; Cs, 41·7; N, 1·5%].

Method (*b*). The complex $K_3[Ru_2(N)Cl_8(H_2O)_2]$ (2·0 g) was dissolved in boiling water and the insoluble precipitate $Ru_2(N)(OH)_5,nH_2O$ formed by the addition of sodium hydroxide. The precipitate was filtered off, washed with boiling water, and dissolved in formic acid–hydrochloric acid (2 : 1, 20 cm^3). The resulting solution was heated under reflux (90 min) and on cooling caesium chloride (2·0 g) was added to give a yellow-brown precipitate, which was mainly the caesium salt of the starting material. The precipitate was filtered off and acetone (50 cm^3) added to the filtrate to precipitate the light brown *product* (10%); the latter was filtered off and washed with acetone [Found: C, 2·0; Cl, 30·1; Cs, 42·1; N, 1·5%]. I.r. spectrum: 2038s; 1016s; 590w; 520w; 470m; 321s; 300m; and 264m cm^{-1}.

Tricaesium Octabromodicarbonyl-μ-nitrido-diruthenate(IV), $Cs_3[Ru_2(N)Br_8(CO)_2]$.—An adaption of method (*a*) for the chloro-complex was used, with $K_3[Ru_2(N)Br_8(H_2O)_2]$, hydrobromic acid, caesium bromide, and a reflux time of 6 h. The *complex* is yellow-brown [Found: C, 1·7; Br, 49·3; Cs, 31·2; N, 1·3. $C_2Br_8Cs_3NO_2Ru_2$ requires C, 1·8; Br, 48·5; Cs, 30·4; N, 1·1%]. I.r. spectrum: 2022s; 1970m; 984s; 570w; 538w; 500w; 457m; 432w; 245s; and 210m cm^{-1}.

Potassium Decacyano-μ-nitrido-diruthenate(IV), $K_5[Ru_2(N)(CN)_{10}],3H_2O$.—The complex $K_3[Ru_2(N)Cl_8(H_2O)_2]$ (1·0 g) was dissolved in boiling water and the insoluble precipitate $Ru_2(N)(OH)_5,nH_2O$ formed by the addition of sodium hydroxide. The precipitate was washed with boiling water and stirred (20 min) in a boiling aqueous solution of potassium cyanide (4 g in 10 cm^3). The cooled yellow solution was poured into methanol (40 cm^3) and the yellow precipitate (80%) which formed was filtered off and washed with boiling methanol (200 cm^3) [Found (for the trihydrate): C, 16·3; K, 26·7; N, 20·9. $C_{10}H_6K_5N_{11}O_3Ru_2$ requires C, 16·5; K, 26·9; N, 21·2%]. I.r.: (dehydrated solid) 2150m; 2140s; 2138ssh; 2120s; 2088m; 2078m; 2055m; 2040m, 1017sb; 632w; 462m; 437w; 420w; 405w; 378msh; 370m; 360msh; (aqueous solution) 2142m; 2121s; 2044m; and 1006s cm^{-1}. Raman spectrum: (dehydrated solid) 2155(7); 2142(6); 2134(7); 2123(1); 493(4); 262(4); (aqueous solution) 2156(7); † 2142(6); 2130(3); 2116(1); † 493(5); 369(1); and 264(7) † cm^{-1}.

Dichlorotetrakis(1,2-*diaminoethane*)-μ-*nitrido-diruthenium*-(IV) *Trichloride*, $[Ru_2(N)(dae)_4Cl_2]Cl_3$.—A solution of the complex $K_3[Ru_2(N)Cl_8(H_2O)_2]$ (1 g) in boiling water (10 cm^3) was added to boiling aqueous 1,2-diaminoethane (50%, 20 cm^3) and the solution heated under reflux (3 h). Hydrochloric acid (2 cm^3) was added to the cooled orange solution to precipitate orange crystals of the *complex* [Found: C, 14·9; H, 5·3; Cl, 27·2; N, 19·7. $C_8H_{32}Cl_5N_9Ru_2$ requires C, 15·2; H, 5·1; Cl, 28·0; N, 19·9%]. I.r. spectrum (neglecting bands due to 1,2-diaminoethane): 1052s and 315m cm^{-1}. Raman spectrum; 359(6); 353(5); 260(7); 202(3); and 174(1) cm^{-1}.

Tetrakis(2,2′-*bipyridine*)*dichloro-μ-nitrido-diruthenium*(IV) *Trishexafluorophosphate*, $[Ru_2(N)(bipy)_4Cl_2](PF_6)_3$.—Warmed solutions of the complex $K_3[Ru_2(N)Cl_8(H_2O)_2]$ (1·0 g in 20 cm^3 water) and 2,2′-bipyridine (4·0 g in 30 cm^3 acetone) were mixed and heated under reflux (4 h). The resulting mixture was filtered, cooled, and a solution of ammonium hexafluorophosphate (4 g in 10 cm^3 water) was added to precipitate the brown *complex* (80%), which was filtered off and recrystallised from acetone [Found: C, 36·1; H, 2·4; Cl, 5·0; N, 9·1; P, 6·4. $C_{40}H_{32}Cl_2F_{18}N_9P_3Ru_2$ requires C, 35·6; H, 2·4; Cl, 5·2; N, 9·4; P, 6·9%]. I.r. spectrum (neglecting bands due to 2,2′-bipyridine and PF_6^-): 1054m and 340m cm^{-1}.

Chlorotetrakis(*diethyldithiocarbamato*)-μ-*nitrido-diruthenium*(IV), $[Ru_2(N)(S_2CNEt_2)_4Cl]$. Hot solutions of the complex $K_3[Ru_2(N)Cl_8(H_2O)_2]$ (1·0 g in 10 cm^3 water) and sodium diethyldithiocarbamate (4·0 g in 10 cm^3 water) were mixed and warmed on a steam-bath (2 min). The brown precipitate which formed was filtered off and dissolved in acetone. This solution was filtered and evaporated to dryness to give the brown *product* (60%) [Found: C, 29·6; H, 4·9; Cl, 3·3; N, 8·6; S, 30·2. $C_{20}H_{40}ClN_5Ru_2S_8$ requires C, 28·4; H, 4·7; Cl, 4·2; N, 8·3; S, 30·3%]. ν_{M_2N}(asym) 1030 cm^{-1}.

Potassium catena-μ-*Nitrido-tetrabromo-osmate*(VI), $K_n[Os(N)Br_4]_n$.—A sample of the complex $K[Os(N)Br_4(H_2O)],H_2O$, prepared by a literature method,[11] was heated to 110 °C (15 min) and the green *product* sealed in an ampoule [Found: Br, 56·7. Br_4KNOs requires Br, 56·8%]. Weight loss on dehydration: 6·5. Calc. for $2H_2O$: 6·0%.

Tricaesium Di-μ-nitrido-bis[*ammine-tetrachloro-osmate*(V)]-[*ammine-trichloro-osmate*(IV)] *Dihydrate*, $Cs_3[Os_3(N)_2Cl_{11}(NH_3)_3],2H_2O$.—The method of Claus [28] was used to prepare the complex $[Os(O)_2(NH_3)_2H_2O]$ which we reformulate $[Os_3(N)_2(OH)_8(NH_3)_3],H_2O$. The black complex (1·0 g) was heated under reflux in concentrated hydrochloric acid (30 min) and the solution then filtered. To the filtrate was added caesium chloride (2·0 g) to precipitate the brown *product* (40%). The latter was filtered off, washed with concentrated hydrochloric acid and acetone, and dried at 110 °C [Found: Cl, 26·7; Cs, 26·0; N, 5·2. $C_{11}H_{13}Cs_3N_5O_2Os_3$ requires Cl, 26·4; Cs, 27·0; N, 4·8%]. I.r. spectrum (figures in parentheses refer to deuteriated sample): 3540sb (2430); 3260s (2300); 3200s (2260); 1620s (1225); 1565msh (1140); 1335s(obsc.); 1025ms; 970s; 550m; 450m; and 320s cm^{-1}.

† Band polarised.

Tricaesium Di-μ-nitrido-bis[amminetetrabromo-osmate(v)]-[*amminetribromo-osmate*(IV)] *Dihydrate*, $Cs_3[Os_3(N)_2Br_{11}(NH_3)_3],2H_2O$.—The method used was similar to that used from the chloro-complex except that hydrobromic acid and caesium bromide (40%) were employed [Found: Br, 44·8; Cs, 19·3; N, 4·4. $H_{13}Br_{11}Cs_3N_5O_2Os_3$ requires Br, 44·8; Cs, 20·3; N, 3·6%]. I.r. spectrum: 3510sb; 3200s; 3120s; 1610s; 1550msh; 1322m; 1115w; 1015ms; 957s; and 230s cm^{-1}.

Dicaesium trans-*Tetrabromodioxoruthenate*(VI), $Cs_2[Ru(O)_2Br_4]$.—A saturated solution of caesium bromide in hydrobromic acid (5 cm^3) and water (2 cm^3) was cooled to 0 °C and ice-cool ruthenium tetraoxide solution (5 cm^3) was stirred into it. The light brown *precipitate* (40%) which formed was quickly filtered off, sucked dry on a frit, and washed with acetone [Found: Br, 43·9; Cs, 37·6. $Br_4Cs_2O_2Ru$ requires Br, 44·5; Cs, 37·0%]. I.r. spectrum: 825s; * 821ssh; * 230s; and 226ssh cm^{-1}.

Dicaesium trans-*Bisoxalatodioxoruthenate*(VI), $Cs_2[Ru(O)_2(ox)_2]$.—Oxalic acid (0·45 g) and caesium carbonate dihydrate (0·90 g) were dissolved in water (4 cm^3) and the solution cooled in ice. Ruthenium tetraoxide solution (6 cm^3) was stirred into this solution and the light green *precipitate* (30%) which formed was filtered off after 5 min, and washed with carbon tetrachloride and ethanol [Found: C, 8·0; Cs, 45·8. $C_4Cs_2O_{10}Ru$ requires C, 8·4; Cs, 46·2%]. I.r. spectrum: 1710sb; 1680s; 1668s; 1335s; 1192m; 910w; 878m; 838s; * 810s; 549m; 460m; 385w; 361ssh; and 350s cm^{-1}.

trans-*Tetra-amminedioxoruthenium*(VI) *Dichloride*, $[Ru(O)_2(NH_3)_4]Cl_2$.—Ammonium chloride (1·0 g) and sodium carbonate (0·1 g) were dissolved in ice-cold water (4 cm^3) and ruthenium tetraoxide solution (6 cm^3) was stirred into the resulting mixture. After 15 min the yellow microcrystalline *precipitate* was filtered off and washed with carbon tetrachloride and ethanol [Found: H, 4·7; Cl, 26·4; N, 20·7; O, 12·1. $H_{12}Cl_2N_4O_2Ru$ requires H, 4·4; Cl, 26·1; N, 20·6; O, 11·8%]. I.r. spectrum (deuteriated sample in parentheses): 3360vsb (2420); 3070vsb (2280); 1660m; 1623m (1148); 1583m; 1540msh (1080); 1322s (1018); 1304s (1008); 870s (650); 845s; * 782s (622); 478m (440); 278sb (250); and 215s cm^{-1}. Raman spectrum: 841 (10) cm^{-1}.

trans-*Dichlorodioxodipyridineruthenium*(VI), $[Ru(O)_2(py)_2Cl_2]$.—A solution of pyridine (1 cm^3) in water (2 cm^3) was neutralised with hydrochloric acid and the solution made alkaline with sodium carbonate (0·1 g). Ruthenium tetraoxide solution (6 cm^3) was stirred into the ice-cool solution and, after 5 min, the yellow microcrystalline *product* was filtered off and washed with carbon tetrachloride, water, and ethanol [Found: C, 34·0; H, 2·9; Cl, 18·8; N, 7·9. $C_{10}H_{10}Cl_2N_2O_2Ru$ requires C, 33·1; H, 2·8; Cl, 19·6; N, 7·7%]. I.r. spectrum (neglecting bands due to pyridine): 825s * and 325 cm^{-1}.

trans-(2,2′-*Bipyridine*)*dichlorodioxoruthenium*(VI), $[Ru(O)_2(bipy)Cl_2]$.—2,2′-Bipyridine (0·3 g) was stirred into water (3 cm^3) and 2M-hydrochloric acid added until the ligand was completely dissolved. Sodium carbonate (0·1 g) was added to the ice-cool solution, and then ruthenium tetraoxide solution (6 cm^3). The yellow crystalline *product* was filtered off after 5 min and washed with water and acetone [Found: C, 33·6; H, 2·4; Cl, 19·6; N, 7·9. $C_{10}H_8Cl_2N_2O_2Ru$ requires C, 33·3; H, 2·2; Cl, 19·7; N, 7·8%]. I.r. spectrum: 839s; * 325s; and 319ssh cm^{-1}.

Tricaesium Tetracyanodi-isocyanato-oxoruthenate(V), $Cs_3[Ru(O)(CN)_4(CNO)_2]$.—Ruthenium tetraoxide solution (5 cm^3) was stirred with an ice-cold saturated aqueous solution of sodium cyanide (5 cm^3) which contained caesium chloride (1·09 g). The green precipitate which formed was filtered off after 5 min and washed with methanol [Found: C, 10·2; Cs, 56·7; N, 12·3; O, 6·7. $C_6Cs_3N_6O_3Ru$ requires C, 10·2; Cs, 56·4; N, 11·9; O, 6·8%]. I.r. spectrum: 3600w; 3315w; 3440w; 2195vs; 2125s; 2060w; 1630w; 1335w; 787s; 690w; 640w; 609w; 450w; 388ms; 370ms; and 328m cm^{-1}. Raman spectrum: 2200(1); 2149(5); and 787(10) cm^{-1}. χ_g $5·57 \times 10^{-6}$ c.g.s.u., μ_{eff} = 3·00 B.M.

Ruthenium Tetraoxide Solution.—The solution of ruthenium tetraoxide in carbon tetrachloride was prepared by an adaptation of Nakata's method,[39] commercial ruthenium trichloride (10 g) being converted to the hydrated hydroxide which was then oxidised by sodium periodate (45 g in 400 cm^3 ice-cold water). The resulting aqueous solution of RuO_4 was divided into three portions and each portion was extracted with 3 × 30 cm^3 of carbon tetrachloride, the final solution being made up to 300 cm^3 to give a ruthenium tetraoxide concentration of *ca.* 22 g l^{-1}. The solution was stored at −5 °C in the presence of sodium periodate.

All the complexes are diamagnetic unless otherwise stated. The complex $K_2[Os(N)Cl_5]$ was prepared by the literature method.[11] The ^{15}N substituted osmium complexes were prepared from $K[Os(O)_3{}^{15}N]$ obtained from isotopically enriched ammonium chloride (95%) and osmium tetraoxide in potassium hydroxide solution. I.r. spectra were measured as Nujol mulls between caesium iodide plates on a Perkin-Elmer 325 instrument (4000—200 cm^{-1}) and Raman spectra (1200—140 cm^{-1}) on a Cary 81 instrument with a CRL52 Kr laser using excitation at 6471, 5682, and 5308 Å. Microanalyses were performed by the Microanalytical Department at Imperial College and Alfred Bernhardt, Munich; caesium and potassium were determined as the tetraphenylborates.

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* ν_{MO_3}(asym).

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Osmium Nitrido-complexes with Triphenyl-phosphine, -arsine, and -stibine, with Evidence for Nitrene-like Behaviour of the Phosphine Complex

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Osmium Nitrido-complexes with Triphenyl-phosphine, -arsine, and -stibine, with Evidence for Nitrene-like Behaviour of the Phosphine Complex

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Summary The new complexes $[OsNX_3(AsPh_3)_2]$ and $[OsNCl_3(LPh_3)_2]$ (X = Cl or Br, L = P or Sb) have been made; we propose that nucleophilic attack of the nitrogen atom by triphenylphosphine occurs in some of these complexes to give derivatives of triphenylphosphine imine.

ALTHOUGH osmium imido tertiary phosphine complexes are known[1] there are no nitrido-analogues, and no arsine or stibine nitrido-complexes of any metal. We find that the salts $Bu^n_4N[OsNX_4]$, made by addition of Bu^n_4NX to solutions of $[OsNX_5]^{2-}$ in HX (X = Cl or Br),[2] react quickly in methanol at 70° with an excess of triphenylarsine or triphenylstibine to give $[OsNX_3(AsPh_3)_2]$ or $[OsNCl_3(SbPh_3)_2]$. With triphenylphosphine, however, a suspension of $Ph_4As[OsNCl_4]$ in acetone at room temperature yields a paramagnetic species of empirical formula $[OsNCl_3(PPh_3)_3],Me_2CO$ (I) (μ_{eff} 1·8 B.M.); a suspension of this in methanol reacts with chlorine to give $[OsNCl_3(PPh_3)_2]$. The bromo-analogue of (I) has also been prepared. The complexes $[OsNX_3(LPh_3)_2]$ are non-conductors in acetone and have properties typical of osmium(VI) nitrido-species:[2] they are diamagnetic and have sharp Os≡N stretching i.r. bands near 1060 cm^{-1} the frequencies of which decrease by *ca.* 30 cm^{-1} on ^{15}N substitution.

Addition of an equimolar quantity of $Ph_4As[H_5O_2]Cl_2$, to $Ph_4As[OsNCl_4]$ with triphenylphosphine in acetone yields a second paramagnetic product of empirical formula $[OsNHCl_4(PPh_3)_2],Me_2CO$ (II) (μ_{eff} 1·6 B.M.); this may also be made directly from (I) and $Ph_4As[H_5O_2]Cl_2$ in acetone. If aqueous HCl is used for these two reactions, $[OsCl_4(PPh_3)_2]$ is formed. Deprotonation of (II) to give (I) may be accomplished with strong bases, *e.g.* triethylamine, in the presence of triphenylphosphine. We formulate (I) and (II) as Os^{IV} derivatives of triphenylphosphine imine, *i.e.* [Os

TABLE

	Colour	ν(M≡^{14}N)/cm^{-1}	ν(M≡^{15}N)/cm^{-1}	M.p. (*t*/°C)
$OsNCl_3(PPh_3)_2$	Brown	1058	1027	145 (decomp.)
$OsNCl_3(AsPh_3)_2$	Brown	1059		257
$OsNBr_3(AsPh_3)_2$	Brown	1068	1035	221
$OsNCl_3(SbPh_3)_2$	Orange	1065	1032	170
$Os(NPPh_3)Cl_2(PPh_3)_2,Me_2CO$ (I)	Orange	1127[a]	1104[a]	136
$Os(NPPh_3)Br_2(PPh_3)_2,Me_2CO$	Brown	1123[a]		122
$Os(NHPPh_3)Cl_4(PPh_3),Me_2CO$ (II)	Red	924[a]	906[a]	163 (decomp.)

[a] P–N stretching frequency.

Elemental analyses for all complexes (C, H, N, O, halogen) are in satisfactory agreement with the quoted formulae.

$(NPPh_3)Cl_3(PPh_3)_2]$,Me_2CO (I) and $[Os(NHPPh_3)Cl_4(PPh_3)]$,-Me_2CO (II) for the following reasons. Prolonged treatment of (II) with an equimolar quantity of $Ph_4As[H_5O_2]Cl_2$ gives $[Ph_3PNH_2]Cl$ and $Ph_4As[OsCl_5(PPh_3)]$ in high yields. Triphenylphosphineimine is known to react quantitatively with hydrogen chloride to give $[Ph_3PNH_2]Cl$.[3] The i.r. spectra of (I) and (II) have strong bands at 1127 and 924 cm^{-1} respectively, which shift downwards some 20 cm^{-1} on ^{15}N substitution, and we assign these to P–N stretching modes (similar bands and shifts have been observed in Ph_3PNH and its complexes and in Ph_3PNR [4]). Complex (II) has additional strong bands at 3299 and 1243 cm^{-1} which we assign to the N–H stretching and deformation modes respectively. There is no evidence from the i.r. data that the acetone molecule is co-ordinated in either complex. The ^1H n.m.r. spectrum of (I) could not be measured owing to the low solubility of the compound, but that of (II) gave a sharp resonance centred at τ — 2·5 which we assign to the *ortho*-protons on the Ph_3P group directly co-ordinated to osmium; its intensity relative to the remaining phenyl protons is consistent with this assignment. Shifts of this magnitude, together with sharp resonances, are characteristic of osmium(IV) complexes which exhibit temperature-independent paramagnetism.[5]†

Since (I) and (II) are obtained from $[OsNCl_4]^-$, and (I) can also be made by reaction of triphenylphosphine with $[OsNCl_3(LPh_3)_2]$ (L = P or As), we propose that their formation proceeds by nucleophilic attack of the phosphine on the co-ordinated nitrogen, which is here behaving as an electrophilic nitrene. This is in contrast to the nucleophilic behaviour of Re≡N in $[ReNCl_2(PEt_2Ph)_3]$,[6] although nitrene-like behaviour has been observed for rhenium[7] and iridium[8] imido-complexes.

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