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TRANSITION METAL NITRIDO COMPLEXES

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CONTENTS

A INTRODUCTION

This review is concerned with the chemistry of transition metal complexes of the nitride ligand, N^{3-}. It has been written to complement the author's earlier review on metal oxo complexes[1], and the general arrangement of material in that article will be followed here. The complementary nature (or intention) of the two reviews is emphasised because the ligands N^{3-} and O^{2-} are isoelectronic and their chemistries are in many respects quite similar.

In order to keep the material within bounds we consider only those complexes which may reasonably be considered to involve discrete molecular units, i e. those of the form $[MN_xX_y]_z^{n-}$ (where $z \leqslant 4$), so that high-polymer and interstitial nitrides are not covered.

There is a fairly recent review on the binary nitrides of first-row transition elements[2], and both these and other nitrides not mentioned here are adequately covered in the standard texts of Mellor, Gmelin and Pascal. It may be added here that for the purposes of this review mercury is considered as an honorary member of the transition metal group since it has a particularly interesting nitride chemistry

(i) Arrangement of material

This follows the pattern of the oxo ligand review[1]. In Sect. B we survey the general chemistry of nitrido complexes, the nature of the metal–nitride bond, and summarise the principal physico-chemical measurements which have been made on nitrides. Finally, in Sect C, we consider individual complexes by the Periodic group to which their metals belong.

(ii) Nomenclature

The only term which seems to be consistently used in the literature for the (N^{3-}) ligand is nitride, and its complexes are indiscriminately referred to as "nitride" or "nitrido" species, we shall use the latter term.

(iii) Reviews

There are no other comprehensive reviews on nitrido complexes, the author gave a short account of the subject some years ago[3], and it was very briefly reviewed in the course of an article on the activation of molecular nitrogen[4]

B GENERAL SURVEY

(i) Occurrence

In Table 1 we summarise the known complexes of the type $[MN_xX_y]_z{}^{n-}$ for each Periodic group, only reasonably well characterised complexes are listed It will be observed that, as is the case with most transition-metal oxo complexes, monomeric nitrido species are formed by metals in their higher oxidation states only, the d^0 and d^2 electron configurations being the most common (hence the predominance of complexes from the left-hand part of the Periodic Table). A striking difference from the chemistry of oxo complexes is that most nitrido species are formed with second- or third-row elements; this may be a reflection of the very effective high-oxidation-state stabilisation brought about by nitride, a factor which will favour heavier elements since these are more prone to formation of high oxidation states For binuclear nitrido complexes the d^4 configuration is found, while for trinuclear systems where there is a much reduced capacity on the part of the bridging nitride for π-donation, near-normal oxidation states are found.

TABLE 1

General types of nitrido complex

		IVa		Va	VIa	VIIa	VIII	
		(M = Ti)		(M = V)	(M = Mo, W)	(M = Re)	(M = Ru, Os)	(M = Ir)
(a)	$[MO_3N]^{n-}$	d^0			$[MO_3N]^{3-}$	$[ReO_3N]^{2-}$	$[MO_3N]^-$	
(b)	$[MNX_x]^{n-}$	d^0	$[TiNCl]_n$?	$[VNCl_3]^-$ $[VNCl_3]_4$	$[MNCl_3]_4$ $[MNCl_5]^{2-}$			
(c)	$MNX_x(PR_3)_y$	d^2				$ReNX_2(PR_3)_3$ $ReNX_2(PR_3)_2$	$[MNX_5]^{2-}$ $[MN(H_2O)X_4]^-$	
(d)	$[MN(CN)_5]^{n-}$	d^2				$[ReN(CN)_5]^{3-}$		
(e)	$[M_2NX_8(H_2O)_2]^{3-}$	d^4					$[M_2NX_8(H_2O)_2]^{3-}$	
(f)	$[M_3NX_{12}(H_2O)_3]^{n-}$	d^5, d^6					?$[Ru_3NX_{12}(H_2O)_3]^{7-}$	$[Ir_3NX_{12}(H_2O)_3]^{4-}$

(ii) Stereochemistry

Most nitrido complexes have octahedral coordination, albeit with strong axial compression brought about by the shortness of the M≡N bond, the oxo species $[MO_3N]^{n-}$ (Mo^{VI}, Re^{VII}, Os^{VIII}) are distorted tetrahedra (both oxo and nitrido ligands are such strong π-donors that it is unlikely that the two together could sustain octahedral coordination of a metal) and pentacoordination occurs for a few nitrido phosphines, e g. $ReNCl_2(PPh_3)_2$, probably for steric reasons*. Heptacoordination may possibly occur in $MNCl_3(py)_3$ (M = Mo, W, see p. 385).

(iii) Modes of bonding

Most nitrido complexes involve a terminal N^{3-} group, M≡N, as indeed most oxo complexes involve terminal, "triple"-bonded oxide. In (a)–(d) we illustrate the other types of bonding which have been established for nitrido complexes with examples of typical bond parameters, where these are obtainable

$M \overset{x}{—} N \overset{x}{—} M$

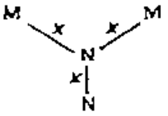
(a)

Linear symmetrical, as in $K_3[Ru_2NCl_8(H_2O)_2]$, $x = 1.720$ Å

$M \overset{x}{—} N \overset{y}{---} M$

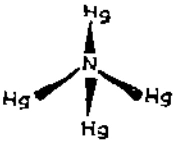
(b)

Linear asymmetric, as in $K_{2n}[ReN(CN)_4]_n$, $x = 1\ 53$, $y = 2\ 44$ Å



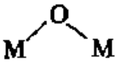
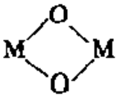
(c)

Trigonal planar, as in $(NH_4)_4[Ir_3N(SO_4)_6(H_2O)_3]$; $x = 1\ 918$ Å



(d)

Tetrahedral, as in $[(H_3CHg)_4N](ClO_4)$ (no structural data available)

Comparison of each type of bridge with corresponding oxo systems is of interest. For binuclear nitrides, only linear bridges (symmetric or asymmetric as in (a) or (b)) have been established, whereas for oxo species bridges of the types  and  are quite common, in addition to the linear bridge found in nitrides. It is true that a di-nitrido bridge

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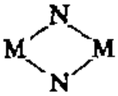
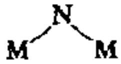
*The halogeno complexes $[MNX_4]^-$ (M = Mo, Re, Ru, Os, X = Cl or Br) have recently been isolated (Sect. C), and may also be pentacoordinate.

of the  type has been proposed for a series of polymeric complexes[5], but this structure has not been established and is in the author's opinion unlikely to be correct; an osmium complex has been claimed in which a bent  bridge was supposed to feature, but doubt must be cast on this also (see p. 392 below). There are a number of oxo analogues of type (c), in which the M_3N or M_3O triangles are coplanar (there are also examples in oxo chemistry of pyramidal M_3O groups, though coplanarity of all four atoms is much more common), and there are oxo analogues for the tetrahedral type (d)*

Only one nitrido cluster compound has been claimed, $Ba_9Os_3N_{10}$ (see p 392 below); the structure is not known

(iv) Similarities between nitride and other ligands

The most important property of (N^{3-}) is its very strong π-donor capability, and so it is best compared with other ligands which also have such properties, it is particularly relevant to consider the isoelectronic oxo and pseudo-isoelectronic sulphido ligands. From bond-length data, force constants and *trans*-effect studies it is apparent that (N^{3-}) is by far the strongest π-donor ligand known, its only rival in this respect being the oxo ligand. The fact that, whereas poly-oxo species are common, only mono-nitrides have been characterised is also indicative of its very effective π-donor character. Comparisons between it and other ligands such as F^-, S^{2-} and $(O_2)^{2-}$ have also been made[1]

(v) Preparation of nitrido complexes

(a) Deprotonation of ammonia

This is used under aqueous solution conditions for preparation of $[OsO_3N]^-$ from OsO_4, and for the formation of "mixed valence" iridium complexes containing the Ir_3N unit It is also possible to prepare binuclear osmium and ruthenium nitrido species in this manner Liquid ammonia or solutions of potassium or potassium amide in liquid ammonia have been used for preparation of $[MO_3N]^{3-}$ (M = Mo, W), $[ReO_3N]^{2-}$, and complexes of Group Ib metals

(b) Deprotonation of hydrazine

This is potentially a very useful method, though so far it has been used for rhenium(V) nitrido complexes only.

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* No examples of (d) are yet known with transition metals, although there are transition metal oxo analogues.

(c) Decomposition of azides

The thermal decomposition of azides has been used for preparation of nitrido species of vanadium(V), molybdenum and tungsten(VI), ruthenium(VI) and some rhenium(V) phosphine complexes

(d) Miscellaneous methods

These include the thermal decomposition of ammonium hexahalogenoosmates (for osmium binuclear nitrides), the reaction of coordinated nitrosyl groups with reducing agents (ruthenium nitrides), and the decomposition of coordinated sulphamate groups.

It is one of the problems of nitride chemistry that no one of these methods seems to be really general, the azide method has so far proved to have the widest range of applicability, but even this is severely limited by the few suitable azides which have been synthesised There is no doubt that many more nitrido complexes remain to be discovered, and it is likely that the best method of making new species would be to use a suitably designed deprotonation technique (or to use azide ion as a nitrogenating agent).

(vi) Properties of nitrido complexes

The physico-chemical properties of the complexes are summarised in the sections below and in Sect. C. The most remarkable general chemical property is the stability of the metal–nitrogen bond, particularly noticeable in the platinum group elements and in rhenium(V) (the chemical stability of the M≡N bond in Group Va and VIa elements seems to be of a much lower order). This extends not only to addition and substitution reactions but in some cases to chemical reduction as well. Thus, the osmiamate ion $[OsO_3N]^-$ is a much more stable chemical entity than the isoelectronic OsO_4, and when it is attacked, for example by mild reducing agents, it is the Os=O rather than the Os≡N bonds which are broken. Treatment of $[OsO_3N]^-$ with HX (X = F, Cl, Br, CN, ½ ox, etc) yields $[Os^{VI}NX_5]^{n-}$ or *trans*-$[Os^{VI}N(H_2O)X_4]^{n-}$, in which there is still an Os≡N triple bond, while the use of strong reducing agents like stannous chloride does not break the metal–nitrogen bond but reduces it to a coordinated ammine. The same stability is found in the M_2N groups in such species as $[M_2NX_8(H_2O)_2]^{3-}$ (X = Cl, Br, I, M = Os, Ru) and $[M_2N(NH_3)_8(H_2O)_2]^{3+}$, which will undergo a wide range of substitution reactions of all the outer ligands without affecting the M_2N unit. In iridium complexes containing the coplanar Ir_3N unit, substitution, oxidation or reduction reactions may be carried out in aqueous solution without destroying the metal–nitrogen triangle.

(vii) Structure and bonding

There have as yet been no theoretical calculations on metal–nitrido bonding in complexes. The structural data are so far rather scattered although a careful study has been made on rhenium(V) nitrides; all the reputable studies which have been made are summarised in Table 2. It is clear from the following compilation that the metal–nitrogen

TABLE 2

Structural data for transition metal nitrido complexes

	d_{M-N}	Other data (bond lengths in A)	Space group	[Z]	Ref
$K[OsO_3N]$	1 75(2)	Os–O 1.75(2)	$I4_1/a$	4	74
$K_2[OsNCl_5]$	1 614(10)	*cis* Os–Cl 2.362(2) *trans* Os–Cl 2 605(4), ∠ NOsCl 97 5°	*Pnma*	4	7
trans-$K[OsN(H_2O)Br_4]$	1 61	Os–O 2.07	*Cmc*	4	77
$ReNCl_2(PEt_2Ph)_3$	1 788(10)	*cis* Re–Cl 2 454(4), *trans* Re–Cl 2 563(4) *cis* Re–P 2.442(4)	$P2_1/c$	4	15
$ReN(S_2CNEt_2)_2$	1 687	Re–S 2 381, ∠ NReS 108°	$P2_1/c$	4	52a
$ReNCl_2(PPh_3)_2$	1 603(9)	*cis* Re–Cl 2 377(2) *cis* Re–P 2 448(2)	$I2/a$		12
$K_3[Ru_2NCl_8(H_2O)_2]$	1 720(4) [a]	Ru–Cl 2 364(60), Ru–O 2 175(20) ∠ ClRuN 94.3°	$C2/n$	2	9
$(NH_4)_3[Ru_2NCl_8(H_2O)_2]$	1 725(5) [a]	Ru–Cl 2 370(10), Ru–O 2.20(20), ∠ ClRuN 94.1°	$B2/m$	2	19
$[MoNCl_3]_4$	1 672 [a] 2.143 [a]	Mo–Cl 2 276 ∠ MoNMo 167°, 178°	$P\bar{1}$	4	48
$K_{2n}[ReN(CN)_4]_n\ nH_2O$	1 53 [a] 2 44 [a]	Re–N 2 13, C–N 1 31	*Imm*2	2	10
$(NH_4)_4[Ir_3N(SO_4)_6(H_2O)_3]\ 3\frac{3}{4}H_2O$	1 918 [a]	Ir–OH$_2$ 2 059, Ir–O(SO$_4$) 2 005 to 2 056	$I\bar{4}3d$	8	13

[a] Bridging M–N distances

distance in nitrides is considerably less than that of a "normal" σ-bond.

Complex	d_{M-N} (Å)	Ref
$Os(NH_3)Cl_3(PPh_3)_2$	2 136(9)	6
$K_2[OsNCl_5]$	1 614(10)	7
trans-$[Ru(NH_3)_4(SO_2)Cl]Cl$	2 127(6)	8
$K_3[Ru_2NCl_8(H_2O)_2]$	1 725(5)^a	9
$K_{2n}[ReN(CN)_4]_n\ nH_2O$	1 53, 2 44^a	10
$Re(N_2)Cl(PMe_2Ph)_4$	1 966(20)	11
$ReNCl_2(PPh_3)_2$	1 603(9)	12
$(NH_4)_4[Ir_3N(SO_4)_6H_2O)_3]$	1 918(2)^a	13

^{a} M–N (bridge) distance

Thus, in nitrido complexes, the metal–nitrogen bond always has some multiple bond character, in terminal nitrides it is, of course, a valence requirement that the bond should be triple The situation is to some extent mirrored in the nitrogeno complex $Re^I(N_2)Cl(PMe_2Ph)_4$, where the Re–N distance is also short, but in this instance the shortening arises from the π-bond component in the metal-to-ligand sense, rather than the ligand-to-metal π-donation which is such a dominant feature in metal nitrido complexes

(a) Bonding in mononuclear nitrido complexes

Although no comprehensive bonding scheme has yet been proposed we may borrow that of Gray and co-workers for vanadyl and related mono-oxo complexes, in which there is effectively a metal–oxygen triple bond (one σ, two π-bonds)[14]. The osmium(VI), d^2 complex $K_2[OsNCl_5]$ is taken as an example If the nitride ligand is placed on the vertical z Cartesian axis with the equatorial ligands on the x and y axes, the metal–nitrogen orbital overlaps will be

$$N\text{–}M\ \sigma\text{-}bond\quad sp_\sigma \text{ to } 5d_{z^2} + 6s \quad (a_1)$$

$$\left.\begin{array}{l} N\text{–}M\ \pi\text{-}bond\ (1)\quad 2p_x \text{ to } 5d_{xz} \\ N\text{–}M\ \pi\text{-}bond\ (2)\quad 2p_y \text{ to } 5d_{yz} \end{array}\right\} \quad (e)$$

For the M–X bonds, *cis* (four ligands) and *trans* (one), the overlaps would be

$$X_4\text{–}M \text{ cis } \sigma\text{-}bonds\quad p_\sigma \text{ to } 6s - 5d_{z^2}\ (a), \text{ to } 6p_x \text{ and } 6p_y\ (e), \text{ to } 5d_{x^2-y^2}\ (b_1)$$

$$X\text{–}M \text{ trans } \sigma\text{-}bonds\quad p_\sigma \text{ to } 6p_z\ (a_1)$$

It is implicit in this scheme that the ligand bound *trans* to the nitride group will be less strongly held to the metal atom than those *cis* to it, and although there is some structural and other evidence of such a *trans* weakening effect in many nitrido complexes, it is difficult to disentangle structural from steric factors (see below).

The metal–nitrogen distances in terminal nitrido species have been the subject of careful study in rhenium(V) and osmium(VI) complexes. In the case of $K_2[OsNCl_5]$, the chloride ligand *trans* to the nitride is 2.605 Å distant from the osmium atom[7] while the *cis* chloride ligands are at 2 363 Å. Although this might, on the face of it, appear to constitute good evidence for the sort of *trans* weakening influence discussed above, the parameters may equally well be explained by simple steric hindrance effects. In $K_2[OsNCl_5]$ the (*cis*) Cl–Os–N angle is not 90° as would be expected for an undistorted octahedron, but 97 5° – that is, the osmium atom is shifted out of the (Cl_4) plane towards the nitride ligand (a similar effect has been found in a number of mono-oxo complexes) By so distorting the octahedron the (*cis*) chlorine-to-nitrogen distance becomes greater than the sum of van der Waals radii of nitrogen and chlorine so that steric hindrance is minimised, and as a consequence the *trans* Os–Cl distance is lengthened[7] (earlier, erroneous X-ray data on the salt had suggested that the *trans* chloride was *closer* to the metal than the *cis* ligands – see below, p. 391).

Comparisons have been made between the Re–N distances in rhenium(V) imido complexes, based on very accurate X-ray studies

Complex	d_{M-N} (Å)	Ref
I $ReNCl_2(PEt_2Ph)_3$	1 788(10)	15
II $Re(N-PhOMe)Cl_3(PEt_2Ph)_2$	1 709	16
III $Re(N-PhCOMe)Cl_3(PEt_2Ph)_2$	1 690	16
IV $Re(N-Me)Cl_2(PPh_2Et)_2$	1 685	17
V $ReNCl_2(PPh_3)_2$	1 603	12

It appears from these data that the Re–N bond lengths in the nitrides (formally a triple bond) and in the imides (formally a double bond) are quite close, and indeed in the case of I the Re–N distance is longer than in any of the others The reasons for the differences in Re–N bond lengths between I and V appear to be basically steric (in I the long metal–nitrogen distance is attributed to repulsion between the nitrogen atom and the very bulky triphenylphosphine groups, whereas in V there are only two such groups[7]), an alternative explanation based on electronic bonding considerations has been adduced[16], but the steric factors are now considered to be of overriding importance[7]. It is of interest in this connection to note that all attempts to make the triphenylphosphine analogue of I lead always to V. In the imino complexes steric factors again play some part in dictating the observed metal–nitrogen distances[7], but here electronic factors are probably more important in explaining the shortness of these lengths and their comparability with those in the nitrido complex, V. It has been argued by Chatt et al [18] that the nitrogen in the imides has more *s*-orbital character to impart to its Re–N σ-bond, which would lead to a strengthening, and hence shortening, of that bond Spectroscopic evidence has also been brought forward as evidence for this, the Re–N stretching frequency in the imide IV is higher than that in the nitrides[18]

(b) Bonding in binuclear nitrido-bridged species

The structures of both the potassium and ammonium salts of the $[Ru_2NCl_8(H_2O)_2]^{3-}$

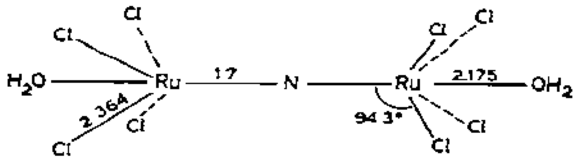

Fig. 1 Structure of the $[Ru_2NCl_8(H_2O)_2]^{3-}$ ion.

ion have been studied by accurate X-ray analysis. The anion is centrosymmetric (D_{4h} skeletal symmetry) with a metal—nitrogen distance of 1.720 Å (Fig 1)[9,19]; the shortness of this symmetric bridge is clearly indicative of considerable metal—nitrogen multiple bonding. The ion is isoelectronic (after due allowance has been made for the replacement of the two water ligands by two chloride ions) with $K_4[Ru_2OCl_{10}]$ which similarly[20] has D_{4h} symmetry and a linear, symmetric M—O—M bridge (Ru—O = 1 80 Å) For the nitrido complex, then, we may justifiably use the bonding scheme of Dunitz and Orgel[21] which has been applied to $[Ru_2OCl_{10}]^{4-}$ The nitrido bridge uses its sp_σ orbitals to overlap with the metal $d_{x^2-y^2}$ orbitals, while its filled $2p_x$ and $2p_y$ orbitals interact with the d_{xz} and d_{xy} of the two ruthenium(IV) atoms. These each accommodate one electron so there are under D_{4h} symmetry, two sets of bonding, two of non-bonding and two of antibonding MO's. The eight electrons (four from nitrogen in its p_x and p_y orbitals, four from the metal atoms) fill all but the antibonding molecular orbitals. The remaining "metal" electrons (two per ruthenium atom) then pair up in the remaining t_{2g} orbital, the d_{yz}, so that overall diamagnetism results

(c) Bonding in trinuclear complexes

In $(NH_4)_4[Ir_3N(SO_4)_6(H_2O)_3]\cdot3\frac{3}{4}H_2O$ there is a coplanar Ir_3N unit (Ir—N = 1 918 Å) and octahedral coordination about each metal atom from the bridging sulphate groups with

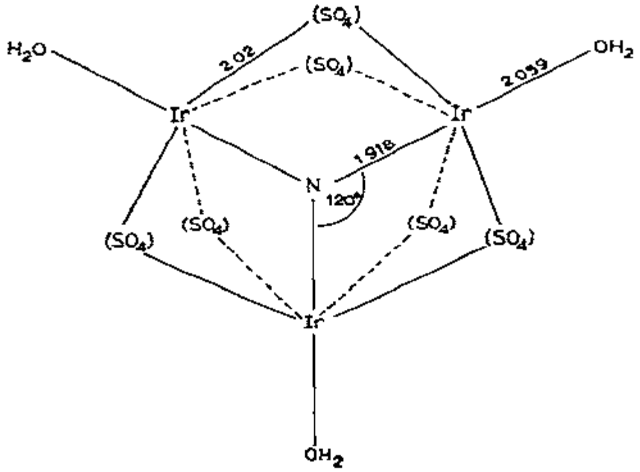

Fig 2. Structure of the $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ ion.

TABLE 3

Vibrational spectra and force constant data for nitrido–oxo complexes

Frequency	Assignment		Position (cm^{-1})		Force constant[c]	Value of force constant (mdyne/Å)	
			$[ReO_3N]^{2-}$ (ref. 23)[a]	$[OsO_3N]^-$ (ref. 24)[b]		$[ReO_3N]^{2-}$ (ref. 23)	$[OsO_3N]^-$ (ref. 24)
ν_1	ν_{MN}	(A_1)	1022	1021[d]	k_{MN}	7.95	7.95
ν_2	ν_{MO_3}	(A_1)	878	897	k_{MO_3}	6.74	6.76
ν_3	δ_{MO_3}	(A_1)	315	309	$lk_{MO/MO}$	0.44	0.34
ν_4	ν_{MO_3}	(E)	830	871	δ_{MO_3}	0.31	0.34
ν_5	δ_{NMO}	(E)	380	372	$l\delta_{MO/MO}$	0.07	−0.007
ν_6	δ_{MO_3}	(E)	273	309	δ_{OMN}	0.44	0.43

[a] Infrared data

[b] Raman data

[c] k = stretching force constant, δ = deformation force constant, l = interaction force constant

[d] Shifts from 1023 to 992 cm^{-1} in the infrared[26].

one water molecule per metal atom coordinated *trans* to the nitride bridge[13]. There is effectively, according to the formula, an average oxidation state of $3^2/_3$, or two iridium(IV) plus one iridium(III) atom. The crystal structure suggests that, within the errors of the analysis, the three Ir–N distances are the same, but preliminary Mossbauer studies (see below) favour an inequivalence of the iridium atoms. A bonding scheme for the anion has been proposed in which the diamagnetism of the species is accounted for by assuming equivalence of the three metal atoms and a four-centre molecular orbital encompassing the planar Ir_3N unit[22]. The $2p_z$ filled orbital of (N^{3-}) – assuming the z-axis to be perpendicular to the Ir_3N plane – has the correct symmetry to overlap with one of the t_{2g} orbitals of each metal atom, assuming a low-spin configuration, there are sixteen electrons in the metal t_{2g} orbitals and these, together with the $2p_z$ nitride pair, give a bonding and an antibonding molecular orbital If the latter remains unoccupied then the resulting system will be diamagnetic, as observed[22]. Reduction and oxidation of the species will then be possible without destruction of the Ir_3N entity if electrons are put in the antibonding level (in the case of reduction to a $3 \times Ir^{III}$ state) or if an electron is removed from the bonding level (giving $3 \times Ir^{IV}$) (see below, p. 392).

(viii) Physical measurements on nitrido complexes

We have already reviewed the structural data (see above and Table 2), further reference to these, when appropriate, is made in Sect C.

(a) Vibrational spectra

(1) Mononuclear species Complete assignments of the vibrational spectra of the $[ReO_3N]^{2-}$ (ref 23) and $[OsO_3N]^-$ (ref 24) anions have been given on the basis of C_{3v} symmetry (Table 3), force constants have been calculated from these data and are remarkably similar for the two species It is of interest to note that these force constants do support the hypothesis that the nitride ligand is a more effective π-donor than (O^{2-}), at least on the basis of the greater strength of M≡N bonds than M=O Thus, in the species $[Re^{VII}O_3X]^{n-}$, the Re=O stretching force constant for the (ReO_3) unit is 6.24 mdyne/Å when X = N, but rises[23] to 7 50 when X = S and to 7.54 when X = O, similarly, in $[OsO_3X]^{n-}$, the Os=O stretching force constant for the (OsO_3) unit is[24] 6.76 mdyne/Å for X = O.

Partial assignments have been given[25] for $[OsNCl_5]^{2-}$ (the Os–N stretching band 1073 cm^{-1} shifts to 1041 cm^{-1} on ^{15}N-substitution, thus confirming the correctness of the assignment[26]), for $[MoNCl_5]^{2-}$ and $[WNCl_5]^{2-}$ (ref. 27), $[MoNCl_3]_n$ and $[WNCl_3]_n$ (ref. 28), $[VNCl_3]^+$ and $[VNCl_3]^-$ (ref. 29) (Table 4) There are also a considerable number of data on the M≡N stretching frequencies in a wide range of rhenium(V) phosphine nitrido complexes[18,30,31] of osmium(VI) species[25], and of a few molybdenum and tungsten(VI) complexes[27]. Most M≡N stretches fall in the comparatively narrow range of 1020–1150 cm^{-1}, there is far less information on the position of the deformation mode,

TABLE 4

Vibrational spectra of nitrido–halo complexes

	$K_2[OsNCl_5]$ (ref. 25)	$(NMe_4)_2[MoNCl_5]$ (ref 27)	$(NMe_4)_2[WNCl_5]$ (ref 27)	$[MoNCl_3]_4$ (ref 28)	$[WNCl_3]_n$ (ref. 28)	$[VNCl_3]^+$ (ref. 29)	$[VNCl_3]^-$ (ref. 29)
ν_{MN}	1073[a]	1023	1035	1045	1084 1068	1038	1208
$\nu^{as}_{MCl_n}$	328	317	338	424 403	380 360	504 485	495
$\nu^{s}_{MCl_n}$	336	355 334	324 311	364	337	417	423
δ_{NMCl}				317			
δ_{MCl_n}				272	273		292

[a] Shifts to 1041 cm^{-1} on ^{15}N substitution[26]

but this is probably to be found in the 300–380 cm^{-1} range for most complexes.

(2) Polynuclear species There are studies[32,33] on the Raman and infrared spectra of ruthenium and osmium binuclear nitrido-bridged complexes of the form $[M_2NX_8(H_2O)_2]^{3-}$ and $[M_2N(NH_3)_8Y_2]^{3+}$ (X = Cl, Br, Y = Cl, Br, NCS, N_3). In these the asymmetric M_2N stretch appears near 1050 cm^{-1} for the ruthenium compounds and near 1120 cm^{-1} for osmium, the symmetric (Raman-active) M_2N stretching modes are near 350 cm^{-1} (ruthenium) and 280 cm^{-1} (osmium)[32], while the infrared-active M_2N deformations fall[33] near 120 cm^{-1} In trinuclear complexes containing Ir_3N units the asymmetric M_3N stretch is found[32] near 770 cm^{-1} and the symmetric mode near 220 cm^{-1}, while in the only established complex containing a M_4N unit the mercuric complex $[(H_3CHg)_4N](ClO_4)$, the asymmetric stretch is seen in the infrared at 590 cm^{-1} and the symmetric mode is inferred[34] to lie near 141 cm^{-1}

We may summarise the information on positions of stretching and deformation modes, making comparison with the corresponding bands in analogous oxo complexes; despite the greater mass of oxygen compared with nitrogen, it is clear that the M≡N bonds are stronger than M=O, and this result is also obtained from force-constant data[23,24,32]

Comparison of the vibrational spectra of nitrido and oxo complexes

		$\nu^{asym}_{M_xX}$	$\nu^{sym}_{M_xX}$	δ_{M_xX}
$[MO_3X]^{n-}$	X = N	~ 1020		~ 380
	X = O	760–980	770–970	260–430
$[MXY_y]^{n-}$	X = N	1000–1120		300–370
	X = O	850–1040		300–360
$[M_2XY_y]^{n-}$	X = N	1040–1130	240–370	~ 120
	X = O	750–900	200–260	~ 110
$[M_3XY_y]^{n-}$	X = N	~ 770	~ 220	~ 130
	X = O	~ 660	~ 200	~ 110
$[M_4XY_y]^{n-}$	X = N	~ 600	~ 140	
	X = O	~ 580	180	~ 100

(b) Electronic spectra

The electronic spectroscopy of nitrido complexes and interpretation of the results is a wide-open field for investigation, no doubt one of the reasons for its neglect is that most of the complexes available for study are from the second- and third-row transition elements. The electronic spectrum of the osmiamate ion, $[OsO_3N]^-$, has been studied both in aqueous solution and in its solution in liquid ammonia, and tentative band assignments proposed[35]. The spectra of a number of binuclear ruthenium(IV) and osmium(IV) complexes have been recorded[32,36] and the results qualitatively interpreted on the model used to explain the spectra of the analogous oxo-bridged species[22], on this basis it appears from the shifts of the nitrido complex bands to higher energies that the metal–nitride bond is stronger than the metal–oxo bond[32,36]. Finally, the spectrum of $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ has been interpreted satisfactorily on the basis of the molecular orbital bonding model outlined above (see p 378)[22,37,38].

(c) Dipole moment data

Systematic studies on the dipole moments of a number of rhenium(V) nitrido phosphine complexes have been made[30] and suggest that the Re≡N bond has approximately the same moment as the Re–Cl bond (ca 1.5–2 0 debye); the results were compared and contrasted with those obtained for rhenium(V) imido phosphine species[18,30].

(d) Mossbauer spectra

Preliminary studies on salts of the $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ ion at 4°K suggest[38] that two iridium atoms are equivalent and the third non-equivalent, presumably as 2 × Ir^{IV} and one Ir^{III}. This conflicts with the molecular orbital approach to this ion given above (see p 378) and clearly a more complete discussion of the results would be of interest.

C DESCRIPTIVE CHEMISTRY

The arrangement of material is based on the Periodic group of the metal atom.

(i) Groups IVa and Va

No established nitrido complexes of Group IVa are known; $[TiNCl]_n$ can be made[39,40] by thermal decomposition of the azide $TiCl_3(N_3)$, but the species is probably a polymer. No zirconium or hafnium analogues are known

Treatment of vanadium tetrachloride with ClN_3 gives an azido complex $Cl_4V(N_3)$ which may be thermally decomposed to $Cl_3V{=}NCl$ This is, in the Lewis sense, amphoteric, and will react with antimony pentachloride to give $[VNCl_3]^+[SbCl_6]^-$ and with pyridine to give $[VNCl_3]^-[Cl(py)_2]^+$. In the former case the bonding has been represented as $[Cl_3V{=}\overset{+}{N}]$ while in the latter, anionic species it is $[Cl_3V^V{\equiv}N]^-$; the V–N stretching frequencies are at 1038 and 1208 cm^{-1} respectively[29]. The X-ray crystal structures of these species have not been obtained and the ionic formulations above are based on spectroscopic and analytical data, but the structure of the parent species, $Cl_3V{=}NCl$, has been established by X-ray methods (Fig. 3) The complex is basically dimeric with approximate square-based pyramidal coordination for the vanadium atoms, these dimer units are, however, linked by weakly bound chloride bridges (V–Cl (terminal) 2.204 Å, V–Cl (bridge) 2.600 Å), so that the vanadium may be thought of as having distorted octahedral coordination. The V=N–Cl group[41] is linear (V=N 1.642(9) Å, N–Cl 1.59 Å); the shortness of the V–N linkage is remarkable since there is formally a double rather than a triple bond in the compound. The reason is probably similar to that which has been suggested for rhenium imido complexes (see above, p. 377); one may compare this distance of 1.642 Å for V=N with that[42] of 1.62 Å for a V=O bond in $(NH_4)_2[VO(NCS)_4(H_2O)]$.

Apart from these, the only other vanadium nitrido species reported is the rather ill-defined $K_3[(VO)_2N(NH)_2]$, obtained from "vanadyl amide", $VO(NH_2)_2$, and potassium

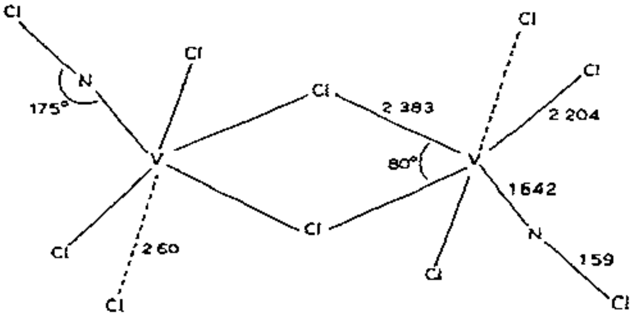

Fig 3 Structure of the dimer unit, $(Cl_3VNCl)_2$ The dashed lines indicate the positions of chloride bridge atoms linking dimer units

in liquid ammonia[43], and $[VON]_x$, made[39] by heating $VOCl_2(N_3)$

(ii) Group VIa

It is surprising that no chromium nitrido species have been established or even claimed, though it is possible that the rather ill-defined products of the reaction between chromium trioxide and liquid ammonia[44] could contain such a complex.

The only oxo–nitrido complex established for this group is the molybdenum species $[MoO_3N]^{3-}$, of which potassium, lead and silver salts have been isolated Anhydrous molybdenum trioxide is allowed to react with liquid ammonia at room temperature in a sealed system to give a product which is either $(NH_4)_2[Mo(NH)O_3]$ or $(NH_4)_2[MoN(OH)O_2]$, reaction of this with potassium in liquid ammonia yields the very unstable potassium salt, $K_3[MoO_3N]$, which is instantly hydrolysed by water. The lead and silver salts may be prepared by metathetical procedures and are more stable than the potassium salt[45] The action of potassium in liquid ammonia on MoO_2Cl_2 is also said[46] to give $K_3[MoO_3N]$, though the ammonia–MoO_2Cl_2 reaction is said by other workers to yield a complex mixture of molybdenum(VI) amido compounds[47]. A tungsten complex, formulated[46] as WO_3 $3NH_3$ or as $(NH_4)_2[W(NH)O_3]$, might perhaps contain the $[WO_3N]^{3-}$ ion, one would certainly expect a tungsten(VI) nitrido species to be more stable than its molybdenum analogue.

Nitrido–chloro complexes of both molybdenum and tungsten are well characterised, however The species $[MNCl_3]_n$ (M = Mo, W) are made by thermal decomposition of the azides $M(N_3)Cl_5$ (which in their turn are made by the action of chlorine azide on $MoCl_5$ or WCl_6). The molybdenum complex is deep violet (sublimes in vacuo at 130°) and the tungsten species is ochre-coloured (sublimes in vacuo at 80°)[27,28]. Powder X-ray data for both species have been reported[28]. The X-ray crystal structure of $[MoNCl_3]_4$ has been established (Fig. 4). There are tetrameric $[MoNCl_3]_4$ units which are themselves loosely held together by weak chloro bridges (Mo–Cl (terminal) 2 276 Å, Mo–Cl (bridge) 2 822 Å)

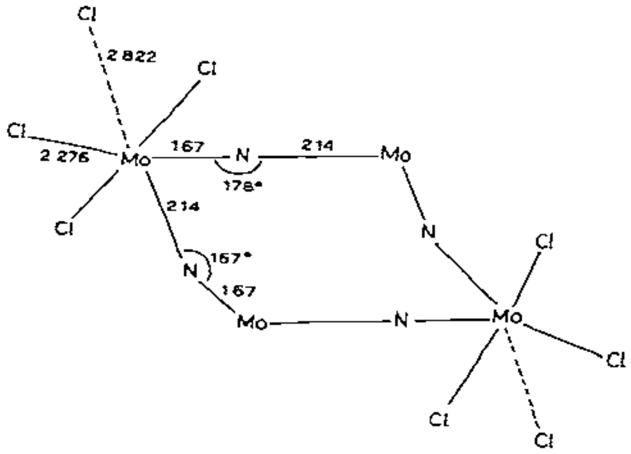

Fig 4 Structure of the tetramer unit, $(MoNCl_3)_4$ For simplicity, chloride ligands are shown for only two of the metal atoms. Dashed lines indicate chloro bridges linking tetramer units

The tetramer units have approximate C_{4h} symmetry, and each unit contains two pairs of Mo—N—Mo bridges, differing only in the Mo—N—Mo angles (178° and 167°) Each bridge is asymmetric, the two Mo—N distances being 1.67 and 2 14 Å The coordination about each metal atom is square based pyramidal or, if the weakly bridging chloride ligands are taken into account, distorted octahedral[48] The infrared and Raman spectra of both the molybdenum and tungsten species have been measured (Table 4)[28] and a number of the fundamental modes assigned, it is said that the M≡N stretching force constants are some 0 5 mdyne/Å higher for the tungsten than the molybdenum complexes, and that this is also true for the other nitrido—chloro complexes of these metals described below[27,28]

Reaction of $[MNCl_3]_n$ (M = Mo, W) with tetramethylammonium chloride yields the pentachloro complexes $(NMe_4)_2[MNCl_5]$, and the infrared spectra of these have been measured (Table 4)[27] With pyridine, $[MNCl_3]_n$ yields the adducts $MNCl_3$ 3py (M = Mo, W)[27] which appear to be heptacoordinated on the basis of their formulae; with triphenylphosphine, $MNCl_3$ yields[27] $MNCl_3(PPh_3)$ Infrared spectra of the pyridine and triphenylphosphine complexes have been measured[27]*.

(iii) Group VIIa

No nitrido complexes of manganese or technetium have been established (the so-called[49] "TcNF" is almost certainly $(NH_4)_2[TcF_6]$). In view, however, of the considerable stability of rhenium(V) nitrido complexes it is likely that technetium nitrido species could be made, and probably manganese complexes also.

The oxo—nitrido salt $K_2[ReO_3N]$ can be prepared by the reaction of rhenium heptoxide with potassium amide in liquid ammonia[50], viz.

$$Re_2O_7 + 3\ KNH_2 \rightarrow K_2[ReO_3N] + K[ReO_4] + 2\ NH_3$$

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*Reaction of azide ion with $MoCl_5$ yields salts[49a] of $[MoNCl_4]^-$.

It is the salt of a weak dibasic acid, and like its molybdenum analogue is excessively unstable, being instantly decomposed by water with the evolution of ammonia We may note here that the stabilities of the three known oxo–nitrido complexes fall in the sequence

$$[OsO_3N]^- \gg [ReO_3N]^{2-} > [MoO_3N]^{3-}$$

The infrared spectrum of the potassium salt has been measured and all the fundamentals assigned on the basis of C_{3v} symmetry for the anion, the frequencies and force constants are remarkably similar to those for $[OsO_3N]^-$ (Table 3)[23]

The nitrido–halides $(Ph_4As)[ReNCl_4]$ and $Cs_2[ReNCl_5]$ have recently been made[48a] by chlorination of $ReNCl_2(PPh_3)_2$ The so-called "ReNF" has been shown to be ammonium perrhenate[49].

Two nitrido–cyanide complexes of rhenium(V) are known (with the exception of $[ReO_3N]^{2-}$, $[ReNCl_5]^{2-}$ and $[ReNCl_4]^-$ all rhenium nitrido species so far isolated involve the metal in the pentavalent state) Reaction of a solution of potassium cyanide in methanol with $ReNCl_2(PPh_3)_2$ yields the yellow pentacyano complex $K_3[ReN(CN)_5]$ if the potassium cyanide is present in excess, if it is not, then the polymeric species $K_{2n}[ReN(CN)_4]_n\ nH_2O$ is formed Caesium and sodium salts were also prepared, and the electronic and infrared spectra measured[51] The tetracyano complex can also be made by treating a mixture of potassium cyanide and potassium perrhenate with hydrazine[52] The infrared spectra of penta- and tetra-cyano species are quite different in the Re≡N stretching region, the stretch being at 1035 cm^{-1} in the former and at 980 cm^{-1} in the latter complex[51]

An X-ray crystal structure analysis of $K_{2n}[ReN(CN)_4]_n\ nH_2O$ shows that this contains linear Re–N $\cdots$ Re chains, the alternating rhenium–nitrogen distances[10] being 1 53 and 2.44 Å.

There are many nitrido–phosphine complexes of rhenium(V), and these have been the subject of particularly detailed studies by Chatt et al [18,30,31] and, in respect of their structures, by Ibers et al [7,12,15] The compounds fall into two main classes, six- and five-coordinate The octahedral species are $ReNX_2(PR_2Ph)_3$ (X = Cl, Br, R = Me, Et, Pr^n, Bu^n), $ReNX_2(PEt_2Ph)_3$ (X = Cl, Br, I) (refs 30, 31) and $ReNCl_2(PRPh_2)_3$ (R = Me, Et, Pr^n) (ref 18) They are made by the reaction of the oxo-complex $ReOCl_3(PR_3)_2$ with hydrazine in the presence of ethanol, a less convenient method of preparation involves the treatment of $Re^{III}Cl_3(PR_3)_3$ with azide followed by decomposition of the product to the nitride[18]. The mechanism of formation of the complexes by the hydrazine reaction, it has been suggested, involves the prior formation of an oxo–ethoxo–dichloro rhenium(V) complex, protonation of the ethoxo group and its replacement by the positively charged hydrazinium group, $N_2H_5^+$ This highly electronegative ligand increases the electrophilic character of the oxo ligand which is removed with the encouragement of the nucleophilic phosphine A rhenium(III) complex is formed which then de-protonates and reduces the hydrazine giving the rhenium(V) nitride[18] The pentacoordinate complexes are $ReNX_2(PPh_3)_2$

(X = Cl, Br, I) and $ReNCl_2(PEtPh_2)_2$, and these are prepared in similar fashion to the octahedral species[18,30*].

Dipole moments have been measured for many of these complexes and the results[30,31] suggest that the moment of the Re≡N bond is roughly equivalent to that of the Re–Cl bond (ca 1 5–2.0 Å). Infrared studies on the compounds in the Re≡N and Re–Cl stretching regions have been carried out; the former are lower than the Re≡N stretches in imido rhenium(V) analogues (see p. 377 above). There is some evidence for the existence of a *trans* weakening effect brought about by the nitride group on the chloride ligand opposite it in $ReNCl_2(PEt_2Ph)_3$ (Fig 5), since the two Re–Cl infrared stretches are so far apart[18] at 285 and 217 cm^{-1}.

The crystal structures of $ReNCl_2(PEt_2Ph)_3$ (Fig 5)[15] and of $ReNCl_2(PPh_3)_2$ (Fig. 6)[12] have been mentioned above (p 377 and Table 2). In the former case the rhenium has distorted octahedral coordination with the chloride *trans* to the nitride 0 01 Å further from the metal atom than the *cis* chloride. In the second complex there is approximately square-based pyramidal coordination of the rhenium with the nitride in the axial position[12], the two phosphorus atoms being drawn out of the basal plane towards the metal atom (∠ ClReN 110°, ∠ PReN 98°).

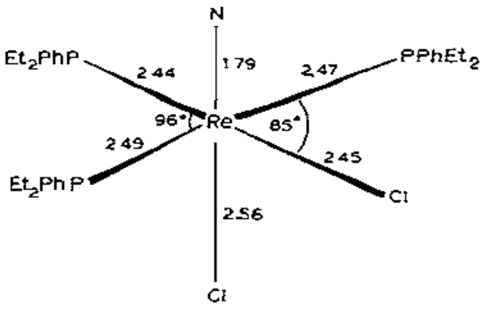

Fig 5 Structure of $ReNCl_2(PEt_2Ph)_3$

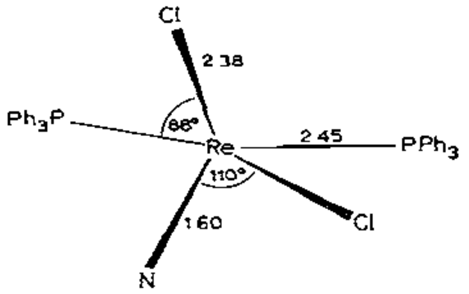

Fig 6 Structure of $ReNCl_2(PPh_3)_2$

Rhenium nitrido complexes as ligands It has been shown[53] that $ReNX_2(PEt_2Ph)_3$ (X = Cl, Br) can function as Lewis bases, the nitride being the donor atom, giving species of the form $(PEt_2Ph)_3Cl_2Re{\equiv}N{\rightarrow}L$ (L = BF_3, BCl_3, BBr_3, $PtCl_2(PEt_3)$), and $(PEt_2Ph)_3Br_2Re{\equiv}N{\rightarrow}L$ (L = BCl_3, BBr_3) These are prepared from the acceptor and the nitride in benzene solution, and the adducts often contain benzene molecules in the lattice The Re≡N stretching frequency increases on such coordination by some 100 cm^{-1} for boron trihalide acceptors, although the increase is only 20 cm^{-1} in the "heterometallic" rhenium nitrido platinum complex The increase has been attributed to a strengthening of

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*The rhenium(VI) species $ReNCl_3(PPh_3)$ has also been isolated[49a] the rhenium–nitrogen bond brought about by an increase in the *s*-orbital contribution to the Re–N δ-bond (a similar explanation has been used to account for high Re–N stretching frequencies in rhenium(V) imido complexes, cf. p 377 above)[18,53].

It is also of interest to note that, whereas in $ReNCl_2(PEt_2Ph)_3$ the two infrared Re–Cl stretches are well separated at 285 and 217 cm^{-1}, suggesting a possible *trans* weakening for the chloride opposite the nitride (vide supra), in the donor–acceptor complexes these two frequencies draw closer to each other (e g 285 and 265 cm^{-1} in $(PEt_2Ph)_3Cl_2Re{\equiv}N{\rightarrow}BCl_3$), which suggests that formation of the N→L bond weakens the *trans* effect of the nitride ligand[53]

(iv) Group VIII

(a) Iron–cobalt–nickel triad

$Li_3[FeN_2]$ and $Li_3[Fe_2N_2]$ have been reported, but are almost certainly polymeric or interstitial compounds[54] The reaction between cobalt(III) amide, $Co(NH_2)_3$ and potassium amide yields[55] $K_3[Co_2N_3]$.

(b) Platinum group metals

There is a short review on nitrido complexes of the platinum group metals[36], and the author's book on four of the metals also treats the subject[56]

(i) Ruthenium–rhodium–palladium triad. No nitrido complexes of rhodium or palladium have yet been established, and most of those so far obtained for ruthenium are polymeric and probably involve the metal in the tetravalent (d^4) state

Mononuclear ruthenium nitrido complexes. Few of these are known as yet, since reduction to the ruthenium(IV) binuclear species is very easy. Reaction of ruthenium tetroxide with HX (X = Cl, Br) and azide under carefully controlled conditions leads[56a] to $[RuNX_5]^{2-}$ and to *trans*-$[RuN(H_2O)X_4]^{-\star}$. It would be expected, by analogy with the osmium systems, that ruthenium(VIII) or -(VI) complexes should be obtainable by deprotonation of ammonia by ruthenium tetroxide, but such reactions lead in the first instance[57] to $RuO_4(NH_3)$ and then to a polymer formulated as a ruthenium(VI) tetramer[58], $Ru_4N_{11}O_{12}H_{33}$.

Binuclear ruthenium(IV) complexes. Several of these are known, the typical member of the series being $K_3[Ru_2NCl_8(H_2O)_2]$, which can be made by reaction of $K_2[Ru(NO)Cl_5]$ with formaldehyde[32,59] or stannous chloride[32,59]; it was thought to be a nitrosyl hydride[59] or an amido bridged species[60] by the original workers Its present formulation followed spectroscopic[32,61] and X-ray studies[9]. Other methods of preparation have been reported[61–66] using ruthenium trichloride and sulphamate or potassium ruthenate and ammonia followed by treatment with ammonia; the intermediate in the latter process was thought to be an oxo complex of ruthenium(VIII) (ref. 63) or ruthenium(VI) (ref. 64), but is in fact a

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[*] The complexes $(Ph_4As)[RuNX_4]^-$ (X = Cl, Br) have recently been isolated (see also p. 391)[66]

ruthenium(IV) nitrido complex[32], $Ru_2N(OH)_5.nH_2O$. There are crystal structure data on both the potassium[9] and ammonium[19] salts, both giving very similar parameters for the complex anion (Table 2 and Fig. 2) It is noteworthy that the ruthenium atoms are displaced some 0.19 Å out of the Cl_4 planes towards the bridging nitrogen atom, an effect which is almost certainly to be attributed more to steric factors[9,32] than to bonding considerations. By undergoing such a displacement the distance between the bridging nitrogen atom and the chloride ligands becomes approximately that of the sum of the van der Waals radii of these atoms, whereas a strict "octahedral" angle for Cl–Ru–N of 90° would involve considerable nitrogen–chlorine repulsion As a consequence the ruthenium–oxygen distance for the coordinated water molecules is apparently unduly long (2.180 Å) (a similar effect[7] is observed in $K_2[OsNCl_5]$), so this long Ru–O distance may not justifiably be used as evidence of a *trans* weakening effect of the bridging nitride ligand Nevertheless, the difficulty of substituting these water molecules by π-bonding ligands does suggest that there is a *trans* weakening effect, although such species as $[Ru_2NCl_{10}]^{5-}$, $[Ru_2NCl_9(H_2O)]^{4-}$ (ref 32), $[Ru_2N(CN)_{10}]^{5-}$, $[Ru_2NCl_8(NO)(H_2O)]^{3-}$, and $[Ru_2NCl_8(CO)(H_2O)]^{3-}$ have now been obtained[66] Vibrational spectra of $[Ru_2NCl_8(H_2O)_2]^{3-}$ salts have been obtained together with their ^{15}N-substituted analogues and are consistent with the known structure[32,33,61] The electronic spectrum of the anion suggests that the Ru–N interaction is stronger in $[Ru_2NCl_8(H_2O)_2]^{3-}$ than the Ru–O interaction in the "pseudo-isoelectronic" $[Ru_2OCl_{10}]^{4-}$ ion[32] (see p 382).

Apart from the anionic species mentioned above metathetical reactions have been used to isolate[32] salts of $[Ru_2NX_8(H_2O)_2]^{3-}$ (X = Br, NCS), and $[Ru_2N(NO_2)_6(OH)_2(H_2O)_2]^{3-}$ Spectra of these species suggest that the linear Ru–N–Ru unit is present in all of them, and this is also the case for the cationic complexes $[Ru_2N(NH_3)_8X_2]^{3+}$ (X = Cl, Br, NO_3) and $[Ru_2N(NH_3)_6(H_2O)Y_3]^{2+}$ (Y = NCS, N_3)[32]

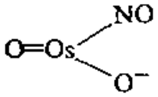
The polynuclear complex $Ru_4N_{11}O_{12}H_{33}$ is said to be the final product of reaction of ruthenium tetroxide with liquid ammonia[67], and the structure is thought to be related to that[68] of $Os_3N_7O_9H_{21}$ It is believed to decompose to the nitride, RuN There is also evidence[67] for the existence of a red trinuclear species $[Ru_3N(SO_4)_6(H_2O)_3]^{7-}$, analogous to the iridium trinuclear sulphato complexes (p. 392).

(2) Osmium–iridium–platinum triad No platinum nitrido complexes are known, and all those as yet established for iridium are trinuclear. Osmium, however, has a very extensive nitride chemistry, the (VIII), (VI) and (IV) oxidation states being involved. It is probably true to say that osmium has the most extensive nitride chemistry of all elements.

(a) Osmium nitrido complexes

(1) Mononuclear. The first nitrido complex to be prepared[70] was the oxo–nitrido complex $K[OsO_3N]$, by long usage, salts containing the $[OsO_3N]^-$ ion are known as *osmiamates*. They are made by addition of aqueous ammonia to a solution of osmium tetroxide in an alkali-metal hydroxide; potassium hydroxide is most commonly used, giving the sparingly

soluble yellow, crystalline $K[OsO_3N]$ Although the structure originally proposed for the complex anion was



Werner and Dinklage showed that the nitrido formulation was much more likely[72], chiefly on the grounds that the salt evolved nitrogen rather than oxides of nitrogen when heated, and with hydrochloric acid gave an oxygen-free product[72], $K_2[OsNCl_5]$

Free osmiamic acid can be obtained by the action of liquid ammonia on osmium tetroxide, a complicated reaction which also yields[57] OsO_4 NH_3 and, ultimately, a polynuclear species[67,68] Infrared studies on the free acid (which is apparently anhydrous) indicate that the proton is attached to an oxygen rather than a nitrogen atom, so that it is best formulated[25] as $OsN(OH)O_2$.

Although potassium osmiamate is an exceedingly useful starting material for osmium complexes and has long been known there is still no fully adequate structural study of it, though two attempts have been made The first, that of Jaeger and Zanstra, showed that Werner and Dinklage's structure for the anion was correct, there being three oxo and one nitrido ligand about the metal atom (the tetrahedron is slightly distorted to give a tetragonal bisphenoid), the Os=O and Os≡N distances were both given[73] as 1 56 Å A more recent study, while in agreement with the unit cell data of the earlier workers, gave both the Os=O and Os≡N distances[74] as 1.75±0 02 Å There have been X-ray powder diffraction studies on a number of heavy metal osmiamates in which the unit cell dimensions were measured[75], and a careful study of the Raman spectrum of $[OsO_3N]^-$ in aqueous solution in which all the fundamental modes were assigned (Table 3) (the frequencies and force constants[24] are remarkably similar to those observed for $[ReO_3N]^{2-}$) There is an infrared study[26] on osmiamate substituted with nitrogen-15 and studies on the infrared spectra of a number of osmiamates with factor group analyses of the results[75,75a] It is interesting to note that the Os≡N stretching frequency in $K[OsO_3N]$, 1021 cm^{-1}, is lower than that ascribed[71] to the (formally doubly bonded) Os=N stretch in $Me_3CN{=}OsO_3$ (1184 cm^{-1}), the reason is presumably similar to that suggested for the corresponding phenomenon in rhenium(V) imido and nitrido complexes (cf p. 377 above). The electronic spectrum of $[OsO_3N]^-$ has been measured in aqueous and liquid ammonia solutions[35].

Osmiamates are stable in the solid state and fairly stable in aqueous solution, they are slowly decomposed photochemically, and on heating to 200° decomposition to nitrogen, osmium dioxide and potassium osmate occurs With acids HX, salts of $[OsNX_5]^{2-}$ or $[OsNX_4(H_2O)]^-$ form (X = Cl, Br, CN, ½ ox) (see below). All these are osmium(VI) complexes, and it is surprising that no osmium(VIII) nitrido complexes other than $[OsO_3N]^-$ are known. Certainly an osmium(VIII) nitrido oxofluoro complex might be expected. but reaction of hydrofluoric acid with $K[OsO_3N]$ is said to yield $K[OsN(H_2O)F_2(OH)_2]$

Nitrido- halo complexes of osmium(VI) are formed from the osmiamate ion and the appropriate halogen acid (binuclear osmium(IV) nitrido halides are considered below,

p. 391). The best known salt is $K_2[OsNCl_5]$, made by the action of hydrochloric acid on $K[OsO_3N]$ in the presence of potassium chloride[71], recrystallisation from water yields[72] *trans*-$K[OsN(H_2O)Cl_4]$. Both are red, crystalline solids. The bromo complex *trans*-$K[OsN(H_2O)Br_4]$ is formed by the action of hydrobromic acid on potassium osmiamate, the pentabromo salt $(NH_4)_2[OsNBr_5]$ may similarly be prepared[76]. Finally, hydrofluoric acid and potassium osmiamate yield[25] $K[OsN(H_2O)F_2(OH)_2]$.

There has been a very careful X-ray crystal structure analysis of $K_2[OsNCl_5]$ (Table 2 and p. 376)[7]. It shows that the octahedron is very distorted, the Os≡N distance being 1.614 Å, the Os–Cl (*cis*) distance being 2.362 Å with the chloride *trans* to the nitride at 2.605 Å. In an earlier and now discredited X-ray analysis of $K_2[OsNCl_5]$, it was suggested that the Os≡N distance was 1.61 Å, the *cis* Os–Cl bond length 2.40 Å and the *trans* Os–Cl distance had the extraordinarily short value[77] of 2.16 Å. It now appears very likely that the substance actually examined was $K[OsN(H_2O)Cl_4]$ or an impure form of this[7], although elaborate theories involving δ-bonding between the metal and the *trans* chloride ligand were put forward at the time to explain its apparent shortness[78], a recent publication also suggests that the complex examined may have been the aquated tetrachloro salt[79]. Another early X-ray study, this time on $K[OsN(H_2O)Br_4]$, may also be of dubious value according to Bright and Ibers[7]. In this study, a *trans* configuration for the anion with an Os≡N distance of 1.61 Å and an Os–O distance of 2.07 Å was reported[77].

There has been an infrared study[25] on $K_2[OsNCl_5]$ and its ^{15}N-substituted form[26] (Table 4), and the Os≡N stretching frequencies for the bromo and fluoro complexes (and their deuterated forms) have been measured[25][*].

Miscellaneous mononuclear osmium complexes. A nitrido cyanide, *trans*-$K[OsN(H_2O)(CN)_4]$, can be obtained by the action of liquid hydrocyanic acid on potassium osmiamate, and the use of oxalic acid with the latter leads to *trans*-$K[OsN(H_2O)(ox)_2]$ and -$K[OsN(H_2O)(OH)_2ox]$. The infrared spectra of these species were measured[25].

The absence of osmium(VI) nitrido–phosphines is puzzling, a number of methods have been tried in order to prepare these compounds, but none has been produced[18]. They are expected to be stable since the isoelectronic rhenium(V) species are easily made and are very stable.

(2) Polynuclear complexes. Reaction of ammonium hexachloroosmate, $(NH_4)_2[OsCl_6]$ with chlorine at 400–500°C gives an ill-defined polymeric species which has been formulated[80] as Os_2NCl_n, where n varies from 5 to 7, since it is diamagnetic, $[Os_2NCl_5]_n$ is probably the best formulation[32]. Infrared spectra suggest that a linear Os–N–Os unit is present[32]. Reaction of the material with hydrochloric acid and potassium chloride yields deep red crystals of $K_3[Os_2NCl_8(H_2O)_2]$, the vibrational spectrum of which suggests that the anion has a centrosymmetric structure similar to that of the analogous ruthenium complex[32]. A bromo analogue, $K_3[Os_2NBr_8(H_2O)_2]$, can be made by the action of bromine on $(NH_4)_2[OsBr_6]$ at 450°, followed by treatment of the product with potassium

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[*] Tetraphenylarsonium and tetrabutylammonium salts of $[OsNX_4]^-$ (X = Cl, Br) have recently been isolated; as yet it is uncertain whether these have nitrido-bridged octahedral or truly pentacoordinate structures[66].

bromide and hydrobromic acid[32].

As with ruthenium, binuclear octa-ammines with nitrido bridges can be made for osmium. Reaction of $K_3[Os_2NCl_8(H_2O)_2]$ with ammonia yields $[Os_2N(NH_3)_8Cl_2]Cl_3$, and metathetical reactions with this lead to[32] $[Os_2N(NH_3)_8X_2]^{3+}$ ($X = Br, I, NO_3, NCS, N_3$). The chloro and bromo species can also be made by the reaction of salts of $[OsX_6]^{2-}$ with aqueous ammonia in a sealed tube[81—83]. The original workers suggested a nitride-bridged structure for the complexes[81], and this was later confirmed by the study of the infrared spectrum of the bromo complex, with its normal and nitrogen-15-enriched forms[84]. Studies have been made of the Raman, infrared and electronic spectra of some osmium octa-ammine nitrido complexes, and the results are consistent with the presence of a centrosymmetric structure[32] analogous to that established for $[Ru_2NCl_8(H_2O)_2]^{3-}$. No osmium species analogous to binuclear ruthenium hexammines, $[Ru_2N(NH_3)_6(H_2O)X_3]^{2+}$, have been found[32].

The reaction between liquid ammonia and osmium tetroxide gives free osmiamic acid and $OsO_4.NH_3$ in the first instance[57], but prolonged reaction leads to a polymeric species formulated as an osmium(VI) complex[32,68], $Os_3N_7O_9H_{21}$.

A nitride cluster compound, $Ba_9Os_3N_{10}$, has been made by heating barium nitride with osmium metal at 750°. The magnetic moment is 1.76 B.M., but the structure is unknown[85]. It is possible that the explosive black compound obtained by treatment of an ammonium osmiamate with ammonia under pressure contains $Os_2N(OH)_5\ nH_2O$ or an ammoniated form of this, the original workers[86] formulated it as $OsO(NH_3)_2(OH)_2$.

(b) Iridium nitrido complexes

All the iridium nitrido species so far reported involve the trinuclear Ir_3N unit. The series of nitrido—sulphate complexes, made by boiling $(NH_4)_2[IrCl_6]$ with sulphuric acid, have long been known as Delepine's green salts, and they were formulated long after their original discovery at the turn of this century as containing the $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ ion[87]. A structure was proposed in which there is a coplanar Ir_3N unit, with coordinated water molecules *trans* to each of the three Ir—N bonds, the octahedral coordination for iridium being made up by bridging sulphato ligands (Fig. 2)[22,37]. This predicted structure was shown to be correct by a recent X-ray crystal structure study of the green ammonium salt[13], the Ir—N distance of 1.918 Å is shorter than that expected for an iridium—nitrogen single bond and is thus consistent with the proposal that a delocalised four-centre molecular orbital encompasses the iridium and nitrogen atoms[22] (cf. p. 378). The *trans* iridium—oxygen (water) distance and *cis* iridium—oxygen (sulphate) distances of 2.059 and 2.005 Å respectively are not exceptional[13]. The vibrational[32], Mossbauer[38] and electronic[22,37,38] spectra of the ion have been measured.

Treatment of salts of $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ with alkali leads to a hydroxo complex $[Ir_3N(SO_4)_6(OH)]^{7-}$ and finally to an insoluble material, presumably $Ir_3N(OH)_8\ nH_2O$. Treatment of the latter with hydrochloric acid gives salts of the $[Ir_3NCl_{12}(H_2O)_3]^{4-}$ ion[87], vibrational spectra of these species were measured[32]. It is also possible to replace the three coordinated water molecules in $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ by pyridine, ammonia or β-picoline[37,88].

Studies on the redox behaviour of $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ have been made; there is some evidence that there may be oxidation to an iridium(IV) species, presumably $[Ir_3N(SO_4)_6(H_2O)_3]^{3-}$. It appears that the nitride is unlike the somewhat analogous oxo system, $[Ir_3O(SO_4)_9]^{10-}$, which may readily be oxidised or reduced[38]. It is possible to reduce the nitride chemically, however, by means of zinc in sulphuric acid or by using vanadium(II) solutions, the product is straw-yellow (in solution), and may be re-oxidised to the original green salt with hydrogen peroxide[37] This implies that the Ir_3N system is not destroyed, a remarkable circumstance because there can be no metal—nitrogen π-bonding to stabilise the presumed iridium(III) reduction product, $[Ir_3N(SO_4)_6(H_2O)_3]^{6-}$

(v) Groups Ib and IIb

(a) Copper–silver–gold triad

There has been little systematic investigation of the nitrido chemistry of these elements. Copper nitride, Cu_3N, can be made by heating cupric fluoride and ammonium fluoride in nitrogen[89], the complexes $Cu_3N\ nNH_3$ and $K_2[CuN(NH_3)_n]$ ($n = 1, 2$ or 3) have been isolated from the reaction between cupric nitrate, potassium amide and liquid ammonia[90] It seems possible that $K_2[CuN(NH_3)_3]$ could contain the nitride ligand in a tetrahedral environment (p. 372). The explosive silver nitride, Ag_3N, can be obtained from silver oxide and aqueous ammonia; it is soluble in ammonia to give complexes of unknown constitution[91] The iodo complex $AgNI_2$ has also been reported[92] There do not appear to be any gold nitrides

(b) Mercury

Although it is not a transition metal, mercury forms nitrido complexes of an unusual nature and of a type which could well exist for transition metals There are two reviews on mercury–nitrogen complexes, one, the more recent, dealing with the general chemistry[93] and the other with structural studies[94]. The metal has considerable affinity for nitrogen and many of the complexes it forms with it are polymeric

(1) Monomeric nitrido complexes The complex $[(CH_3Hg)_4N](ClO_4)$ can be obtained[95] by deprotonation of mercury amides (eqn. (1)) or by disproportionation of a mercury imide (eqn. (2))

$$2\,CH_3HgOH + [(CH_3Hg)_2NH_2](ClO_4) \rightarrow [(CH_3Hg)_4N](ClO_4) + 2\,H_2O \qquad (1)$$

$$2\,[(CH_3Hg)_3NH](ClO_4) \rightarrow [(CH_3Hg)_2NH_2](ClO_4) + [(CH_3Hg)_4N](ClO_4) \qquad (2)$$

An infrared study[34] showed that the asymmetric mercury—nitride stretch is at 590 cm^{-1} and the Raman symmetric stretch, though not directly measured, was calculated to lie near 141 cm^{-1}. This complex is, so far, the only example of a system in which the nitride ligand forms four bonds to metal atoms (it is presumed that it lies at the centre of a tetrahedron of mercury atoms)[95].

Although $(ClHg)_3N$ has been reported (it is said to be formed by the reaction between mercuric chloride and ammonium chloride)[96] it appears[69] that the product is $HgCl_2(NH_3)_2$. One might however expect such a trinuclear compound to exist since the corresponding oxo species $[(ClHg)_3O)]Cl$, is well known and very stable

(2) Polymeric complexes The nitride Hg_3N_2 can be made by the action of potassium amide in liquid ammonia on mercuric chloride; it is soluble in ammonia to give complexes of unknown constitution[97]. Millon's base, $NHg_2OH.2H_2O$, is made by the action of aqueous ammonia on yellow mercuric oxide, and a number of derivatives, e.g the halides NHg_2X ($X = Br, I$) can be prepared. Millon's base itself has a cubic structure analogous to that of cristoballite (nitrogen replacing silicon, mercury replacing oxygen)[98] while the halides have a denser hexagonal lattice of the tridymite type[99] In all cases the lattices are made up of tetrahedra of mercury atoms joined at the vertices, there being nitride ions at the centre of each tetrahedron (Hg–N distances lie between 2 04 and 2.09 Å)[94]. Infrared spectral studies show that the mercury–nitrogen stretching frequencies in Millon's base and its derivatives lie in the 620–700 cm^{-1} region[100]

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