

## 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  $\text{Cs}_2[\text{Ru}(\text{N})\text{X}_5]$  and  $\text{R}[\text{M}(\text{N})\text{X}_4]$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ;  $\text{R} = \text{Ph}_4\text{As}$  or  $\text{Bu}^n_4\text{N}$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) are described. New binuclear nitrido-bridged complexes of ruthenium(IV) with carbonyl, cyanide, and chelate ligands, the polymeric nitrido-bridged species  $[\text{Os}(\text{N})\text{Br}_4]_n^{n-}$  and  $[\text{Os}_3(\text{N})_2\text{X}_{11}(\text{NH}_3)_3]^{3-}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ), 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 ( $\text{N}^{3-}$ ), like the isoelectronic oxide ion ( $\text{O}^{2-}$ ), can function as a terminal ligand<sup>1</sup> or, less commonly, bridges two,<sup>2</sup> three,<sup>3</sup> or four<sup>4</sup> metal atoms in linear, triangular, or tetrahedral arrays. Recently we briefly described the preparation of ruthenium(VI) terminal nitrido-salts  $\text{Cs}_2[\text{Ru}(\text{N})\text{X}_5]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) and related dioxo-species,<sup>5</sup> 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.<sup>6</sup>

### RESULTS AND DISCUSSION

*Terminal Nitrido-complexes.*—Mononuclear species containing  $\text{M}\equiv\text{N}$  groups have been established for very few metals, viz. vanadium,<sup>7</sup> molybdenum and tungsten,<sup>8</sup> rhenium,<sup>9</sup> and osmium.<sup>10</sup> In general the  $\text{M}\equiv\text{N}$  distance is short (ca. 1.7 Å), and the metal is in a high oxidation state due to the very effective  $\sigma$ - and  $\pi$ -donor properties of the nitrido-ligand.<sup>1</sup>

Despite the considerable stability of nitrido-complexes of osmium(VI) and osmium(VIII), the only ruthenium nitrido-complexes hitherto established are binuclear with symmetric  $\text{Ru}-\text{N}-\text{Ru}$  units.<sup>6</sup> We found that reaction of the complexes  $\text{trans}[\text{Ru}(\text{O})_2\text{X}_4]^{2-}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) in ice-cold  $\text{HX}$  solution with an excess of azide ions

and caesium halide gave the light brown diamagnetic salts  $\text{Cs}_2[\text{Ru}(\text{N})\text{X}_5]$ , and the known osmium complexes  $\text{Cs}_2[\text{Os}(\text{N})\text{X}_5]$ <sup>11</sup> could be prepared by similar methods using  $\text{trans}[\text{Os}(\text{O})_2\text{X}_4]^{2-}$ . 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  $\text{trans}[\text{Os}^{\text{VI}}(\text{O})_2(\text{OH})_4]^{2-}$  with azide and caesium ions in dilute acetic acid, the complex  $\text{Cs}[\text{Os}^{\text{VIII}}(\text{O})_3\text{N}]$  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,<sup>9</sup> and of molybdenum(VI) nitrido-complexes from  $\text{MoCl}_5$  and azide ions.<sup>12</sup>

The use of large organic cations as precipitants in place of caesium in the preparations of the  $[\text{M}(\text{N})\text{X}_5]^{2-}$  ions gave pink diamagnetic salts  $\text{R}[\text{M}(\text{N})\text{X}_4]$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ;  $\text{R} = \text{Ph}_4\text{As}$  or  $\text{Bu}^n_4\text{N}$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ ), which were 1 : 1 electrolytes in acetone. It has been shown that the addition of  $[\text{Ph}_4\text{As}]^+$  and  $[\text{Bu}^n_4\text{N}]^+$  ions to solutions of  $[\text{Re}(\text{N})\text{Cl}_5]^{2-}$  precipitates  $\text{R}[\text{Re}(\text{N})\text{Cl}_4]$ ,<sup>13</sup> and mono-oxo-complexes  $\text{Cs}_2[\text{M}(\text{O})\text{X}_5]$ ,  $\text{R}[\text{M}(\text{O})\text{X}_4]$  ( $\text{M} = \text{Mo}$  or  $\text{Re}$ ;  $\text{R} = \text{Ph}_4\text{As}$  or  $\text{Bu}^n_4\text{N}$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ ), and  $\text{R}[\text{M}(\text{O})\text{X}_4\text{L}]$  ( $\text{L} = \text{solvent molecule}$ ) can be isolated.<sup>14,15</sup> The considerable repulsion between the axial  $\pi$ -donor and the equatorial halide ligands in  $[\text{M}(\text{N})\text{X}_5]^{2-}$  or

<sup>1</sup> W. P. Griffith, *Co-ordination Chem. Rev.*, 1972, **8**, 369.

<sup>2</sup> M. Ciechanowicz and A. C. Skapski, *J. Chem. Soc. (A)*, 1971, 1792.

<sup>3</sup> M. Ciechanowicz, M. J. Cleare, W. P. Griffith, D. Pawson, and A. C. Skapski, *Chem. Comm.*, 1971, 876.

<sup>4</sup> N. Q. Dao and D. Breitinger, *Spectrochim. Acta*, 1971, **27A**, 905.

<sup>5</sup> W. P. Griffith and D. Pawson, *Chem. and Ind.*, 1972, 609.

<sup>6</sup> M. J. Cleare and W. P. Griffith, *J. Chem. Soc. (A)*, 1970, 1117.

<sup>7</sup> J. Strähle and K. Dehnicke, *Z. anorg. Chem.*, 1965, **338**, 287.

<sup>8</sup> J. Strähle, *Z. anorg. Chem.*, 1970, **375**, 238; 1971, **380**, 96; W. Kolitsch and K. Dehnicke, *Z. Naturforsch.*, 1970, **25B**, 1080.

<sup>9</sup> J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, *J. Chem. Soc. (A)*, 1969, 2288.

<sup>10</sup> J. Fritsche and H. Struve, *J. prakt. Chem.*, 1847, **41**, 97.

<sup>11</sup> A. Werner and K. Dinklage, *Ber.*, 1906, **39**, 499; 1901, **34**, 2698.

<sup>12</sup> R. D. Bereman, *Inorg. Chem.*, 1972, **11**, 1149.

<sup>13</sup> N. P. Johnson, *Proc. 14th Internat. Conf. Co-ordination Chem.*, Toronto, 1972, 657.

<sup>14</sup> F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1966, **5**, 9, 416; 1965, **4**, 1621.

<sup>15</sup> J. G. Scane, *Proc. Phys. Soc.*, 1967, **92**, 833; A. Sabatini and I. Bertini, *Inorg. Chem.*, 1966, **5**, 207.

$[M(O)X_4L]^-$  tends to weaken the *trans*-axial ligand<sup>16</sup> as shown by X-ray studies of the complexes  $K_2[Os(N)Cl_5]$ ,<sup>16</sup> *trans*- $[Re(O)Br_4L]^-$  ( $L = MeCN$  or  $H_2O$ ),<sup>14</sup>  $[Re(O)Cl_4(H_2O)]$ ,<sup>17</sup> and  $[Ph_4As][Mo(O)Br_4(H_2O)]$ .<sup>18</sup> 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  $M\equiv N$  stretching frequency  $\nu_{MN}$  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  $Bu^+_4N$ ). This may be due to interaction between the polarisable  $Cs^+$  ion and

plexes 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  $\sigma$ - and  $\pi$ -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*- $[Re(O)Cl_4(H_2O)]$ <sup>17</sup> and monomeric  $[Re(O)Cl_4]$ ;<sup>22</sup> in the latter the  $Cl-Re-O$  angle of  $105^\circ$  is some  $7^\circ$  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

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

Complex	$\nu_{MN}(A_1)$	$\nu_{MX_4}(\text{sym})(A_1) *$	$\nu_{MX_4}(\text{asym})(E)$	$\delta_{XMN}(E)$	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)	
$K[Os(N)Br_4(H_2O)] \cdot H_2O$	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.

the nitrido-ligand; an analogous effect has been noted for rhenium(v) oxo-species.<sup>14</sup> 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.<sup>19</sup> The  $X-M\equiv N$  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  $\nu_{MN}$ .

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  $\cdots M\equiv N \cdots M\equiv N \cdots$  linear chain bonding seems unlikely; it has been shown that the complexes  $K_{2n}[Re(N)(CN)_4]_n$ <sup>20</sup> and  $[W(O)Cl_4]_n$ <sup>21</sup> 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  $R[M(N)X_4]$  com-

\* 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).

<sup>16</sup> D. A. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 709.

<sup>17</sup> P. W. Fraiss and C. J. L. Lock, *Canad. J. Chem.*, 1972, **50**, 1811.

<sup>18</sup> J. G. Scane, *Acta Cryst.*, 1967, **23**, 85.

$Ru-N-Ru$  unit).<sup>2,6</sup> 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  $HCl$ .<sup>23</sup> It is also possible to obtain chloro-carbonyl 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  $HCO_2H-HCl$ ).<sup>23</sup> 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

<sup>19</sup> R. J. Collin, W. P. Griffith, and D. Pawson, *J. Mol. Spectroscopy*, in the press.

<sup>20</sup> N. P. Johnson, *J. Chem. Soc. (A)*, 1969, 1843.

<sup>21</sup> D. M. Adams and R. G. Churchill, *J. Chem. Soc. (A)*, 1968, 2310; M. Hess and M. Hartung, *Z. anorg. Chem.*, 1966, **344**, 157; B. G. Ward and F. E. Stafford, *Inorg. Chem.*, 1968, **7**, 2569.

<sup>22</sup> A. J. Edwards, *J.C.S. Dalton*, 1972, 582.

<sup>23</sup> M. J. Cleare and W. P. Griffith, *J. Chem. Soc. (A)*, 1969, 372; J. Halpern, B. R. James, and A. W. Kemp, *J. Amer. Chem. Soc.*, 1966, **88**, 5142.

nitrido-group as are the water ligands in the parent species. The asymmetric  $\text{Ru}_2\text{N}$  stretching frequency of the carbonyl complexes is some  $40\text{ cm}^{-1}$  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  $\text{N}^{3-}$  ligands for the same metal  $t_{2g}$  orbitals. A related situation is that in the complex *trans*- $[\text{Ru}^{\text{II}}(\text{NO})(\text{NH}_2)(\text{NH}_3)_4]^{2+}$ , where the terminal  $\pi$ -donor amide ligand is stabilised by the strongly  $\pi$ -accepting nitrosyl group.<sup>24</sup>

The reaction of  $[\text{Ru}_2(\text{N})\text{Cl}_3(\text{H}_2\text{O})_2]^{3-}$  with potassium cyanide gave the very stable species  $\text{K}_5[\text{Ru}_2(\text{N})(\text{CN})_{10}]\cdot 3\text{H}_2\text{O}$ . The i.r. spectrum of the solid was very complex in the  $\text{C}\equiv\text{N}$  stretching region and also showed sharp high-frequency water bands; on dehydration the  $\text{C}\equiv\text{N}$  band structure became much simpler. This behaviour is similar to that observed for the complex  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ , 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.<sup>25</sup> 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  $2156\text{ cm}^{-1}$ , and a weaker band at  $2116\text{ cm}^{-1}$ ) 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  $\text{K}_3[\text{Ru}_2(\text{N})\text{Cl}_3(\text{H}_2\text{O})_2]$ ,<sup>2</sup> and  $D_{4d}$  (equatorial ligands staggered), as in  $[\text{Mn}_2(\text{CO})_{10}]$ ,<sup>26</sup> 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  $2000\text{ cm}^{-1}$  region for  $[\text{Ru}_2(\text{N})(\text{CN})_{10}]^{5-}$  compared with  $[\text{Mn}_2(\text{CO})_{10}]$  and  $[\text{Co}_2(\text{CN})_{10}]^{6-}$  (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  $\text{Ru}_2\text{N}$  stretch occurs as a strong, polarised band at  $264\text{ cm}^{-1}$  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  $\pi$ -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  $\pi$ -acceptor ligands. There is also evidence for the formation of phosphine and nitrosyl complexes containing the  $\text{Ru}_2\text{N}$  system.

<sup>24</sup> F. Bottomley and J. R. Crawford, *J.C.S. Dalton*, 1972, 2145.  
<sup>25</sup> M. Holzbecher, O. Knop, and M. Falk, *Canad. J. Chem.*, 1971, **49**, 1413; P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, 1963, **2**, 1043.

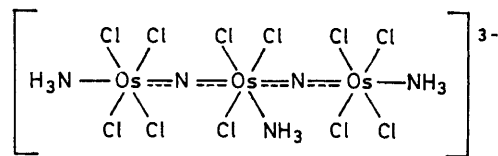
<sup>26</sup> D. M. Adams, M. A. Hooper, and A. Squire, *J. Chem. Soc. (A)*, 1971, 71; G. L. Simon, A. W. Adamson, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1972, **94**, 7654.

<sup>27</sup> E. D. McKenzie, *Co-ordination Chem. Rev.*, 1971, **6**, 187.

Despite the steric constraints imposed by the short ruthenium-nitrido-group bonds  $\{\text{Ru}-\text{N} = 1.718\text{ \AA}$  in  $\text{K}_3[\text{Ru}_2(\text{N})\text{Cl}_3(\text{H}_2\text{O})_2]^{3-}$ , it is possible to isolate stable complexes containing the  $\text{Ru}_2\text{N}$  system with chelating ligands, e.g.  $[\text{Ru}_2(\text{N})(\text{dae})_4\text{Cl}_2]\text{Cl}_3$  and  $[\text{Ru}_2(\text{N})(\text{bipy})_4\text{Cl}_2](\text{PF}_6)_3$  (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<sup>27</sup> so that the chloro-ligands are likely to be *cis* to the nitrido-ligand. A diethyldithiocarbamate complex,  $[\text{Ru}_2(\text{N})(\text{S}_2\text{CNET}_2)_4\text{Cl}]$  has also been prepared; this is a non-electrolyte in acetone solution and may be polymeric in the solid state with  $\cdots\text{Ru}-\text{Cl}-\text{Ru}-\text{N}-\text{Ru}-\text{Cl}\cdots$  chains.

*Polynuclear Nitrido-complexes of Osmium.*—Dehydration of the red salt  $\text{K}[\text{Os}(\text{N})\text{Br}_4(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$  at  $110^\circ\text{C}$  gave a green substance,  $\text{K}_n[\text{Os}(\text{N})\text{Br}_4]_n$ , which quickly reverted to the starting material on setting aside in the atmosphere. Comparison of the i.r. spectra of  $\text{K}[\text{Os}(\text{N})\text{Br}_4(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$  and  $\text{K}_n[\text{Os}(\text{N})\text{Br}_4]_n$  shows that, whereas the  $\text{Os}\equiv\text{N}$  stretching frequency in the former is sharp and intense at  $1109\text{ cm}^{-1}$ , in the latter it is much broader and drops to  $1002\text{ cm}^{-1}$ ; the  $\text{N}=\text{Os}-\text{Br}$  bending mode drops below  $200\text{ cm}^{-1}$ . We propose that in this complex  $\text{K}_n[\text{Os}(\text{N})\text{Br}_4]_n$ , as in that of  $\text{K}_{2n}[\text{Re}(\text{N})(\text{CN})_4]_n$ ,<sup>20</sup> there are linear  $\cdots\text{M}\equiv\text{N}\cdots\text{M}\equiv\text{N}\cdots$  chains.

The reaction of osmium tetroxide with concentrated aqueous ammonia yields a black, diamagnetic material originally formulated as  $[\text{OsO}_2(\text{NH}_3)_2(\text{H}_2\text{O})]$ ; with hydrochloric acid,  $[\text{OsCl}_4(\text{NH}_3)_2]$  is said to be formed.<sup>28</sup> We found that, from solutions of the black material in HX, the caesium salts  $\text{Cs}_3[\text{Os}_3(\text{N})_2\text{X}_{11}(\text{NH}_3)_3]\cdot 2\text{H}_2\text{O}$  (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  $\text{NH}_3$  or  $\text{ND}_3$ ; two strong bands in the  $950\text{--}1100\text{ cm}^{-1}$  region were, however, barely shifted by deuteration, and these we assign to bridging nitrido-ligands. We propose that these complexes have the structure (I)



(I)

and the diamagnetism of this formally  $\text{Os}^{\text{V}}-\text{Os}^{\text{IV}}-\text{Os}^{\text{V}}$  species may then be rationalised using the bonding scheme applied to ruthenium red,  $[\text{Ru}_3(\text{O})_2(\text{NH}_3)_{14}]^{6+}$ ,<sup>29</sup> which has an analogous structure.<sup>30</sup> A similar structural unit has been proposed for the product obtained from the prolonged reaction of osmium tetroxide and liquid ammonia.<sup>6,31</sup>

<sup>28</sup> C. Claus, *J. prakt. Chem.*, 1863, **90**, 97.

<sup>29</sup> C. K. Jorgensen and L. E. Orgel, *Mol. Phys.*, 1961, **4**, 215; L. E. Orgel, *Nature*, 1960, **187**, 504.

<sup>30</sup> P. M. Smith, T. Fealey, J. E. Earley, and J. V. Silverton, *Inorg. Chem.*, 1971, **10**, 1943.

<sup>31</sup> G. W. Watt and W. C. McCordie, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2013.

**Ruthenium Oxo-complexes.**—The formation of  $[\text{Ru}(\text{N})\text{Cl}_5]^{2-}$  from azide and  $\text{trans}-[\text{Ru}(\text{O})_2\text{Cl}_4]^{2-}$  ions prompted a further investigation of ruthenium oxo-complexes as possible precursors for nitrido-species. Only  $\text{trans}-[\text{Ru}(\text{O})_2\text{Br}_4]^{2-}$  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  $\text{trans}-\text{Cs}_2[\text{Ru}(\text{O})_2\text{Cl}_4]$ <sup>32</sup> and  $\text{trans}-[\text{Ru}(\text{O})_2(\text{OH})_2(\text{py})_2]$  (py = pyridine);<sup>33</sup> although spectroscopic data have been reported on salts of the anions  $[\text{Ru}(\text{O})_2\text{Br}_4]^{2-}$  and  $[\text{Ru}(\text{O})_2(\text{SO}_4)_2]^{2-}$ , no preparative details were given.<sup>34</sup>

From solutions of ruthenium tetraoxide in carbon tetrachloride with ice-cold solutions of HX and CsX (X = Br or  $\frac{1}{2}\text{C}_2\text{O}_4$ ), the salts  $\text{Cs}_2[\text{Ru}(\text{O})_2\text{X}_4]$  were obtained; from mildly alkaline solutions of RCl (R =  $\text{NH}_4$ , Hbipy, or Hpy), the species  $[\text{Ru}(\text{O})_2(\text{NH}_3)_4]\text{Cl}_2$ ,  $[\text{Ru}(\text{O})_2(\text{bipy})\text{Cl}_2]$ , and  $[\text{Ru}(\text{O})_2(\text{py})_2\text{Cl}_2]$  were similarly obtained. All the complexes are diamagnetic, consistent with there being a  $\text{trans}-\text{RuO}_2$  unit, as in the corresponding osmium dioxo-species.<sup>35</sup> The complexes all showed a characteristic strong band in the i.r. ca.  $830\text{ cm}^{-1}$  which we assign to the asymmetric  $\text{RuO}_2$  stretch, while for those complexes whose Raman spectra could be measured the symmetric  $\text{RuO}_2$  stretch appeared in the same region. The stretching force constants for the  $\text{RuO}_2$  systems, calculated from the equations of Cotton and Wing,<sup>36</sup> are some 10% lower than those for the corresponding osmium species.<sup>37</sup>

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  $\text{Cs}_2[\text{Ru}(\text{O})_2(\text{CN})_4]$ ; a green paramagnetic salt, which showed i.r. bands characteristic of co-ordinated cyano- and isocyanato-groups, was formed. We formulate this complex as  $\text{Cs}_3[\text{Ru}(\text{O})(\text{CN})_4(\text{CNO})_2]$ ; a strong band at  $787\text{ cm}^{-1}$  in the i.r. spectrum, which also appeared in the Raman spectrum of the solid, is assigned to the  $\text{Ru}=\text{O}$  stretch. The magnetic moment of 3.0 B.M. is similar to that recently reported for arylimido-complexes of osmium(v).<sup>38</sup> The reaction of potassium tetraoxoruthenate(vi) with sodium cyanide in the presence of caesium ions yielded a yellow paramagnetic material  $\text{Cs}_5[\text{Ru}_2(\text{O})_5(\text{CN})_9]$ , the structure of which is still under investigation.

#### EXPERIMENTAL

**Dicaesium Pentachloronitridoruthenate(vi)**,  $\text{Cs}_2[\text{Ru}(\text{N})\text{Cl}_5]$ .—A solution of ruthenium tetraoxide in carbon tetrachloride (10 cm<sup>3</sup>) (*vide infra*) was stirred rapidly with 8M-hydrochloric acid (7 cm<sup>3</sup>), 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<sup>3</sup>), then acetone, and finally dried at 110 °C [Found: Cl, 31.4; Cs, 47.5; N, 2.6.  $\text{Cl}_5\text{Cs}_2\text{NRu}$  requires Cl, 31.8; Cs, 47.6; N, 2.5%].

**Tetraphenylarsonium Tetrachloronitridoruthenate(vi)**,  $[\text{Ph}_4\text{As}][\text{Ru}(\text{N})\text{Cl}_4]$ .—A solution of tetraphenylarsonium chloride (0.8 g) in methanol (5 cm<sup>3</sup>) 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.  $\text{C}_{24}\text{H}_{20}\text{AsCl}_4\text{NRu}$  requires C, 45.0; H, 3.1; Cl, 22.2; N, 2.2%].

**Tetra-n-butylammonium Tetrachloronitridoruthenate(vi)**,  $[\text{Bu}^n_4\text{N}][\text{Ru}(\text{N})\text{Cl}_4]$ .—Tetra-n-butylammonium hydroxide solution (40%, 2 cm<sup>3</sup>) 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.  $\text{C}_{16}\text{H}_{36}\text{Cl}_4\text{N}_2\text{Ru}$  requires C, 38.5; H, 7.2; Cl, 28.4; N, 5.6%]. I.r. spectrum (excluding cation bands): 1095m; 376s; and 265m  $\text{cm}^{-1}$ . Molar conductance (in acetone) 121  $\Omega^{-1}\text{ cm}^{-2}$  in  $10^{-3}\text{M}$ -solution.

**Dicaesium Pentabromonitridoruthenate(vi)**,  $\text{Cs}_2[\text{Ru}(\text{N})\text{Br}_5]$ .—Sodium azide (0.24 g) was dissolved in an ice-cold solution of water (2 cm<sup>3</sup>) and concentrated hydrobromic acid (5 cm<sup>3</sup>). Ruthenium tetraoxide solution (10 cm<sup>3</sup>, *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.  $\text{Br}_5\text{Cs}_2\text{NRu}$  requires Br, 51.2; Cs, 34.1; N, 1.8%].

**Tetraphenylarsonium Tetrabromonitridoruthenate(vi)**  $[\text{Ph}_4\text{As}][\text{RuNBr}_4]$ .—A solution of tetraphenylarsonium chloride (0.5 g) in methanol (5 cm<sup>3</sup>) 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.  $\text{C}_{24}\text{H}_{20}\text{AsBr}_4\text{NRu}$  requires C, 35.2; H, 2.4; Br, 39.1; N, 1.7%].

**Dicaesium Pentahalogenonitrido-osmate(vi)**,  $\text{Cs}_2[\text{Os}(\text{N})\text{X}_5]$  (X = Cl or Br).—The chloro- and bromo-complexes were prepared by literature methods;<sup>11</sup> 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<sup>3</sup>) and sodium azide solution (0.03 g in 1 cm<sup>3</sup> 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  $[\text{Os}(\text{N})\text{X}_5]^{2-}$  in HX (X = Cl or Br) using the procedures described for the ruthenium salts. **Tetraphenylarsonium tetrachloronitrido-osmate(vi)**,  $[\text{Ph}_4\text{As}][\text{Os}(\text{N})\text{Cl}_4]$ . Pink crystals (90%) [Found: C, 39.5; H, 2.9; Cl, 19.2; N, 2.0.  $\text{C}_{24}\text{H}_{20}\text{AsCl}_4\text{NOs}$  requires

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C, 39.5; H, 2.7; Cl, 19.5; N, 1.9%]. Molar conductance (in acetone)  $113 \Omega^{-1} \text{cm}^{-2}$  in  $10^{-3}\text{M}$ -solution. *Tetra-n-butylammonium tetrachloronitrido-osmate*(vi),  $[\text{Bu}^n_4\text{N}][\text{Os}(\text{N})\text{Cl}_4]$ . Red (90%) [Found: Cl, 23.8; N, 5.5.  $\text{C}_{16}\text{H}_{36}\text{Cl}_4\text{N}_2\text{Os}$  requires Cl, 24.1; N, 4.8%]. I.r. bands (excluding cation absorptions): 1125m; 353s; and 262w  $\text{cm}^{-1}$ . Molar conductance (in acetone)  $124 \Omega^{-1} \text{cm}^{-2}$  in  $10^{-3}\text{M}$ -solution. *Tetraphenylarsonium tetrabromonitrido-osmate*(vi),  $[\text{Ph}_4\text{As}][\text{Os}(\text{N})\text{Br}_4]$ . Pink crystals (90%) [Found: C, 32.0; H, 2.0; Br, 35.5; N, 1.7.  $\text{C}_{24}\text{H}_{20}\text{AsBr}_4\text{NO}$  requires C, 31.8; H, 2.2; Br, 35.3; N, 1.5%]. *Tetra-n-butylammonium tetrabromonitrido-osmate*(vi),  $[\text{Bu}^n_4\text{N}][\text{Os}(\text{N})\text{Br}_4]$ . Deep red crystals (90%) [Found: Br, 40.8; N, 3.5.  $\text{C}_{16}\text{H}_{36}\text{Br}_4\text{N}_2\text{Os}$  requires Br, 41.7; N, 3.7%]. I.r. bands (excluding cation absorptions): 1120m; 270s; and 232m  $\text{cm}^{-1}$ . Molar conductance (in acetone)  $124 \Omega^{-1} \text{cm}^{-2}$  in  $10^{-3}\text{M}$ -solution.

*Tricaesium Dicarboxyloctachloro- $\mu$ -nitrido-diruthenate*(iv),  $\text{Cs}_3[\text{Ru}_2(\text{N})\text{Cl}_8(\text{CO})_2]$ .—*Method (a)*. The complex  $\text{K}_3[\text{Ru}_2(\text{N})\text{Cl}_8(\text{H}_2\text{O})_2]$  (2.5 g) was heated under reflux in concentrated hydrochloric acid (25  $\text{cm}^3$ ) under a stream of carbon monoxide (15 h). The solution was cooled, hydrochloric acid (10  $\text{cm}^3$ ) 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.  $\text{C}_2\text{Cl}_8\text{Cs}_3\text{NO}_2\text{Ru}_2$  requires C, 2.5; Cl, 29.7; Cs, 41.7; N, 1.5%].

*Method (b)*. The complex  $\text{K}_3[\text{Ru}_2(\text{N})\text{Cl}_8(\text{H}_2\text{O})_2]$  (2.0 g) was dissolved in boiling water and the insoluble precipitate  $\text{Ru}_2(\text{N})(\text{OH})_5 \cdot n\text{H}_2\text{O}$  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  $\text{cm}^3$ ). 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  $\text{cm}^3$ ) 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  $\text{cm}^{-1}$ .

*Tricaesium Octabromodicarbonyl- $\mu$ -nitrido-diruthenate*(iv),  $\text{Cs}_3[\text{Ru}_2(\text{N})\text{Br}_8(\text{CO})_2]$ .—An adaption of method (a) for the chloro-complex was used, with  $\text{K}_3[\text{Ru}_2(\text{N})\text{Br}_8(\text{H}_2\text{O})_2]$ , 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.  $\text{C}_2\text{Br}_8\text{Cs}_3\text{NO}_2\text{Ru}_2$  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  $\text{cm}^{-1}$ .

*Potassium Decacyano- $\mu$ -nitrido-diruthenate*(iv),  $\text{K}_5[\text{Ru}_2(\text{N})(\text{CN})_{10}] \cdot 3\text{H}_2\text{O}$ .—The complex  $\text{K}_3[\text{Ru}_2(\text{N})\text{Cl}_8(\text{H}_2\text{O})_2]$  (1.0 g) was dissolved in boiling water and the insoluble precipitate  $\text{Ru}_2(\text{N})(\text{OH})_5 \cdot n\text{H}_2\text{O}$  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  $\text{cm}^3$ ). The cooled yellow solution was poured into methanol (40  $\text{cm}^3$ ) and the yellow precipitate (80%) which formed was filtered off and washed with boiling methanol (200  $\text{cm}^3$ ) [Found (for the trihydrate): C, 16.3; K, 26.7; N, 20.9.  $\text{C}_{10}\text{H}_6\text{K}_5\text{N}_{11}\text{O}_3\text{Ru}_2$  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  $\text{cm}^{-1}$ . 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) †  $\text{cm}^{-1}$ .

*Dichlorotetrakis(1,2-diaminoethane)- $\mu$ -nitrido-diruthenium*(iv) *Trichloride*,  $[\text{Ru}_2(\text{N})(\text{dae})_4\text{Cl}_2]\text{Cl}_3$ .—A solution of the complex  $\text{K}_3[\text{Ru}_2(\text{N})\text{Cl}_8(\text{H}_2\text{O})_2]$  (1 g) in boiling water (10  $\text{cm}^3$ ) was added to boiling aqueous 1,2-diaminoethane (50%, 20  $\text{cm}^3$ ) and the solution heated under reflux (3 h). Hydrochloric acid (2  $\text{cm}^3$ ) 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.  $\text{C}_8\text{H}_{32}\text{Cl}_5\text{N}_9\text{Ru}_2$  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  $\text{cm}^{-1}$ . Raman spectrum: 359(6); 353(5); 260(7); 202(3); and 174(1)  $\text{cm}^{-1}$ .

*Tetrakis(2,2'-bipyridine)dichloro- $\mu$ -nitrido-diruthenium*(iv) *Trisheptafluorophosphate*,  $[\text{Ru}_2(\text{N})(\text{bipy})_4\text{Cl}_2](\text{PF}_6)_3$ .—Warmed solutions of the complex  $\text{K}_3[\text{Ru}_2(\text{N})\text{Cl}_8(\text{H}_2\text{O})_2]$  (1.0 g in 20  $\text{cm}^3$  water) and 2,2'-bipyridine (4.0 g in 30  $\text{cm}^3$  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  $\text{cm}^3$  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.  $\text{C}_{40}\text{H}_{32}\text{Cl}_2\text{F}_{18}\text{N}_9\text{P}_3\text{Ru}_2$  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  $\text{PF}_6^-$ ): 1054m and 340m  $\text{cm}^{-1}$ .

*Chlorotetrakis(diethyldithiocarbamate)- $\mu$ -nitrido-diruthenium*(iv),  $[\text{Ru}_2(\text{N})(\text{S}_2\text{CNET}_2)_4\text{Cl}]$ . Hot solutions of the complex  $\text{K}_3[\text{Ru}_2(\text{N})\text{Cl}_8(\text{H}_2\text{O})_2]$  (1.0 g in 10  $\text{cm}^3$  water) and sodium diethyldithiocarbamate (4.0 g in 10  $\text{cm}^3$  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.  $\text{C}_{20}\text{H}_{40}\text{ClN}_5\text{Ru}_2\text{S}_8$  requires C, 28.4; H, 4.7; Cl, 4.2; N, 8.3; S, 30.3%].  $\nu_{\text{M}_2\text{N}}$ (asym) 1030  $\text{cm}^{-1}$ .

*Potassium catena- $\mu$ -Nitrido-tetrabromo-osmate*(vi),  $\text{K}_n[\text{Os}(\text{N})\text{Br}_4]_n$ .—A sample of the complex  $\text{K}[\text{Os}(\text{N})\text{Br}_4(\text{H}_2\text{O})]$ ,  $\text{H}_2\text{O}$ , prepared by a literature method,<sup>11</sup> was heated to 110 °C (15 min) and the green *product* sealed in an ampoule [Found: Br, 56.7.  $\text{Br}_4\text{KNO}$  requires Br, 56.8%]. Weight loss on dehydration: 6.5. Calc. for  $2\text{H}_2\text{O}$ : 6.0%.

*Tricaesium Di- $\mu$ -nitrido-bis[amminetetrachloro-osmate(v)]-amminetrichloro-osmate(iv)] Dihydrate*,  $\text{Cs}_3[\text{Os}_3(\text{N})_2\text{Cl}_{11}(\text{NH}_3)_3] \cdot 2\text{H}_2\text{O}$ .—The method of Claus<sup>28</sup> was used to prepare the complex  $[\text{Os}(\text{O})_2(\text{NH}_3)_2\text{H}_2\text{O}]$  which we reformulate  $[\text{Os}_3(\text{N})_2(\text{OH})_8(\text{NH}_3)_3] \cdot \text{H}_2\text{O}$ . 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.  $\text{C}_{11}\text{H}_{13}\text{Cs}_3\text{N}_5\text{O}_2\text{Os}_3$  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(obs.); 1025ms; 970s; 550m; 450m; and 320s  $\text{cm}^{-1}$ .

† Band polarised.

*Tricaesium Di-μ-nitrido-bis[amminetetra-bromo-osmate(v)]-[amminetribromo-osmate(IV)] Dihydrate*,  $\text{Cs}_3[\text{Os}_3(\text{N})_2\text{Br}_{11}(\text{NH}_3)_3]_2 \cdot 2\text{H}_2\text{O}$ .—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.  $\text{H}_{13}\text{Br}_{11}\text{Cs}_3\text{N}_5\text{O}_2\text{Os}_3$  requires Br, 44.8; Cs, 20.3; N, 3.6%]. I.r. spectrum: 3510sb; 3200s; 3120s; 1610s; 1550msh; 1322m; 1115w; 1015ms; 957s; and 230s  $\text{cm}^{-1}$ .

*Dicaesium trans-Tetrabromodioxoruthenate(vI)*,  $\text{Cs}_2[\text{Ru}(\text{O})_2\text{Br}_4]$ .—A saturated solution of caesium bromide in hydrobromic acid (5  $\text{cm}^3$ ) and water (2  $\text{cm}^3$ ) was cooled to 0 °C and ice-cool ruthenium tetroxide solution (5  $\text{cm}^3$ ) 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.  $\text{Br}_4\text{Cs}_2\text{O}_2\text{Ru}$  requires Br, 44.5; Cs, 37.0%]. I.r. spectrum: 825s; \* 821ssh; \* 230s; and 226ssh  $\text{cm}^{-1}$ .

*Dicaesium trans-Bisoxalatodioxoruthenate(vI)*,  $\text{Cs}_2[\text{Ru}(\text{O})_2(\text{ox})_2]$ .—Oxalic acid (0.45 g) and caesium carbonate dihydrate (0.90 g) were dissolved in water (4  $\text{cm}^3$ ) and the solution cooled in ice. Ruthenium tetroxide solution (6  $\text{cm}^3$ ) 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.  $\text{C}_4\text{Cs}_2\text{O}_{10}\text{Ru}$  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  $\text{cm}^{-1}$ .

*trans-Tetra-amminedioxoruthenium(vI) Dichloride*,  $[\text{Ru}(\text{O})_2(\text{NH}_3)_4]\text{Cl}_2$ .—Ammonium chloride (1.0 g) and sodium carbonate (0.1 g) were dissolved in ice-cold water (4  $\text{cm}^3$ ) and ruthenium tetroxide solution (6  $\text{cm}^3$ ) 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.  $\text{H}_{12}\text{Cl}_2\text{N}_4\text{O}_2\text{Ru}$  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  $\text{cm}^{-1}$ . Raman spectrum: 841 (10)  $\text{cm}^{-1}$ .

*trans-Dichlorodioxodipyridineruthenium(vI)*,  $[\text{Ru}(\text{O})_2(\text{py})_2\text{Cl}_2]$ .—A solution of pyridine (1  $\text{cm}^3$ ) in water (2  $\text{cm}^3$ ) was neutralised with hydrochloric acid and the solution made alkaline with sodium carbonate (0.1 g). Ruthenium tetroxide solution (6  $\text{cm}^3$ ) 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.  $\text{C}_{10}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2\text{Ru}$  requires C, 33.1; H, 2.8; Cl, 19.6; N, 7.7%]. I.r. spectrum (neglecting bands due to pyridine): 825s \* and 325  $\text{cm}^{-1}$ .

*trans-(2,2'-Bipyridine)dichlorodioxoruthenium(vI)*,  $[\text{Ru}(\text{O})_2(\text{bipy})\text{Cl}_2]$ .—2,2'-Bipyridine (0.3 g) was stirred into water (3  $\text{cm}^3$ ) 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 tetroxide solution (6  $\text{cm}^3$ ). 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.  $\text{C}_{10}\text{H}_8\text{Cl}_2\text{N}_2\text{O}_2\text{Ru}$  requires C, 33.3; H, 2.2; Cl, 19.7; N, 7.8%]. I.r. spectrum: 839s; \* 325s; and 319ssh  $\text{cm}^{-1}$ .

*Tricaesium Tetracyanodi-isocyanato-oxoruthenate(v)*,  $\text{Cs}_3[\text{Ru}(\text{O})(\text{CN})_4(\text{CNO})_2]$ .—Ruthenium tetroxide solution (5  $\text{cm}^3$ ) was stirred with an ice-cold saturated aqueous solution of sodium cyanide (5  $\text{cm}^3$ ) 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.  $\text{C}_6\text{Cs}_3\text{N}_6\text{O}_3\text{Ru}$  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  $\text{cm}^{-1}$ . Raman spectrum: 2200(1); 2149(5); and 787(10)  $\text{cm}^{-1}$ .  $\chi_g$   $5.57 \times 10^{-6}$  c.g.s.u.,  $\mu_{\text{eff}} = 3.00$  B.M.

*Ruthenium Tetraoxide Solution*.—The solution of ruthenium tetroxide in carbon tetrachloride was prepared by an adaptation of Nakata's method,<sup>39</sup> commercial ruthenium trichloride (10 g) being converted to the hydrated hydroxide which was then oxidised by sodium periodate (45 g in 400  $\text{cm}^3$  ice-cold water). The resulting aqueous solution of  $\text{RuO}_4$  was divided into three portions and each portion was extracted with  $3 \times 30$   $\text{cm}^3$  of carbon tetrachloride, the final solution being made up to 300  $\text{cm}^3$  to give a ruthenium tetroxide concentration of ca. 22 g  $\text{l}^{-1}$ . The solution was stored at -5 °C in the presence of sodium periodate.

All the complexes are diamagnetic unless otherwise stated. The complex  $\text{K}_2[\text{Os}(\text{N})\text{Cl}_5]$  was prepared by the literature method.<sup>11</sup> The  $^{15}\text{N}$  substituted osmium complexes were prepared from  $\text{K}[\text{Os}(\text{O})_3^{15}\text{N}]$  obtained from isotopically enriched ammonium chloride (95%) and osmium tetroxide in potassium hydroxide solution. I.r. spectra were measured as Nujol mulls between caesium iodide plates on a Perkin-Elmer 325 instrument (4000—200  $\text{cm}^{-1}$ ) and Raman spectra (1200—140  $\text{cm}^{-1}$ ) 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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\*  $\nu_{\text{MO}_2}$  (asym).

<sup>39</sup> H. Nakata, *Tetrahedron*, 1963, 19, 1959.