676. *Infrared Spectra and Structures of Osmium Nitrido-complexes*

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The infrared spectra of a number of normal and deuterated diamagnetic nitrido-complexes of osmium-(VIII), -(VI), and -(IV) have been studied and band assignments suggested. The structures of $[Os^{VIII}(OH)O_2N]$, $[Os^{VI}N(H_2O)X_4]^{2-}$, and $[Os_2{}^{IV}N(NH_3)_8Br_2]Br_3$ are discussed on the basis of these results.

(a) *Osmium*(VIII) *Nitrido-complexes*.—The commonest nitrido-complex is potassium osmiamate, $K(OsO_3N)$. *X*-Ray studies show that the anion has a C_{3v} configuration [1] and this is confirmed by a recent infrared and Raman study [2] and by infrared nitrogen-15 substitution work.[3]

The preparation of free anhydrous osmiamic acid by the action of liquid ammonia on osmium tetroxide has been reported,[4] and its infrared spectrum is given in the Table. The very strong bands at 1021, 889, and 863 cm.$^{-1}$ are not shifted by deuteration and in view of their close similarity to assigned bands in potassium osmiamate are likely to arise from osmium–nitrogen (1021) and osmium–oxygen (889, 863) stretching modes. The band at 3120 cm.$^{-1}$ shifts to 2380 cm.$^{-1}$ on deuteration and is clearly an O–H (or possibly N–H) stretch, while the weaker peaks at 1176 and 479 cm.$^{-1}$ probably arise from an Os–O–H bend and Os–(OH) stretch, respectively, being close to the frequencies of these modes observed in osmium oxy-hydroxy-complexes.[5] Although osmiamic acid is generally considered to be strong, water may be removed from its solutions to give the anhydrous acid, though with some decomposition.

The infrared spectrum is fully consistent with the structure $[OsN(OH)O_2]$ (distorted tetrahedron, point group C_s). The possibility that the hydrogen atom is attached to the nitrogen rather than the oxygen giving an imide ($OsNHO_3$) is eliminated by the spectra, since the Os–N stretch is not shifted by deuteration and moreover has the same frequency as in the osmiamate ion; the appearance of the 1176 and 479 cm.$^{-1}$ bands is additional evidence for this structure. For the same reasons a polymeric structure based on nitrogen, hydroxy, or oxygen bridging is unlikely.

(b) *Osmium*(VI) *Complexes*.—The octahedral complexes $K_2(OsNCl_5)$ and $K[OsN(H_2O)Br_4]$ are known and *X*-ray studies have been briefly reported; in the former complex the chlorine group *trans* to the nitrogen is stated to be 0·3 Å closer to the metal than the equatorial chlorine atoms, and in the bromo-salt the water is *trans* to the nitrogen.[6] It has been suggested that there is a metal–chlorine δ-bond in $K_2(OsNCl_5)$.[7]

The new complexes $K[OsN(H_2O)X_4]$ ($X = CN^-$, $\frac{1}{2}C_2O_4{}^{2-}$) and $K[OsN(H_2O)(OH)_2X_2]$ ($X = F^-$, $\frac{1}{2}C_2O_4{}^{2-}$) were made by the action of the appropriate acid on potassium osmiamate, and their spectra are given in the Table together with those of $K[OsN(H_2O)Br_4]$ and $K[OsN(D_2O)Br_4]$. All of them are diamagnetic and are likely to contain osmium(VI).

For the chloro- and bromo-complexes the skeletal symmetry is known to be C_{4v} [6] and the simplicity of the spectrum of $K[OsN(H_2O)(CN)_4]$ indicates that this, and probably $Cs[OsN(H_2O)(C_2O_4)_2]$, has the same symmetry also. For these molecules, eleven (skeletal) normal modes ($4A_1 + 2B_1 + B_2 + 4E$) are expected, of which eight (A_1 and E) should be active in the infrared spectrum. The osmium–nitrogen stretch ν_1 is easily located in all the spectra as a very sharp and intense line in the 1000—1100 cm.$^{-1}$ region; previous work with nitrogen-15 has located this at 1073 cm.$^{-1}$ for $K_2(OsN^{14}Cl_5)$.[3] The variation in

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[1] F. M. Jaeger and Z. E. Zanstra, *Proc. Acad. Amsterdam*, 1932, **35**, 610.
[2] L. A. Woodward, J. A. Creighton, and K. A. Taylor, *Trans. Faraday Soc.*, 1960, **56**, 1267.
[3] J. Lewis and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **6**, 12.
[4] M. L. Hair and P. L. Robinson, *J.*, 1960, 2775.
[5] W. P. Griffith, *J.*, 1964, 245.
[6] L. A. Atovyman and G. B. Bokii, *J. Struct. Chem., U.S.S.R.*, 1960, **1**, 461.
[7] V. M. Volkov and M. E. Dyatkina, *Dokl. Akad. Nauk S.S.S.R.*, 1960, **134**, 351.

frequency for ν_1 with the nature of the other ligands present follows a sequence similar to that observed for osmyl[5] and vanadyl[8] complexes—thus highly electronegative ligands such as fluoride and oxalate produce a low Os–N stretching frequency while the reverse is true for ligands of lower electronegativity. Spectra of $K_2(OsNCl_5)$ show no absorption between 320 and 1020 cm.$^{-1}$ so that ν_4, the Os–N bending mode, must lie below this range, and similarly no band above 300 cm.$^{-1}$ can be assigned to ν_4 in $K[OsN(H_2O)Br_4]$; the two bands at 336 and 328 cm.$^{-1}$ in $K_2(OsNCl_5)$ are probably the metal–chlorine stretches, ν_3 and ν_8.

Deuteration Studies.—These were carried out to help in the assignment of bands and particularly to locate the metal–water stretch (ν_2) in the bromo-complex, which is the simplest one to study for this purpose. Between 300 and 1200 cm.$^{-1}$ $K[OsN(H_2O)Br_4]$ has bands at 1087 (ν_1), 611, and 509 cm.$^{-1}$ while $K[OsN(D_2O)Br_4]$ has only two bands at 1085 (ν_1) and 471 cm.$^{-1}$. It seems likely that the 611 cm.$^{-1}$ band in the aquo-complex is a water-rocking mode, as found for similar compounds,[9] and the 509 cm.$^{-1}$ band is the metal–water stretch ν_2, shifting to 471 cm.$^{-1}$ in the deutero-form [the ratio ν_2 (aquo)/ν_2 (deutero) is 1·076 as against a calculated ratio of $(20/18)^{\frac{1}{2}} = 1{\cdot}054$, taking the water and deuterium oxide groups as single masses]. Recent work has shown that metal–water stretches in tetra- and hexa-co-ordinated aquo-complexes[9] and in $(CH_3{\cdot}HgOH_2)$[10] occur in the 350—500 cm.$^{-1}$ region. Taking these values for ν_1 and ν_2 and following the procedure used for osmyl

Infrared spectra of osmium nitrido-complexes

Complex	ν_{O-H} (O–D)	δ_{H-O-H} co-ord. (D–O–D)	$\nu_{Os\equiv N}$	δ_{Os-O-H} (Os–O–D)	ν_{Os-OH_2} or ν_{Os-OH} ($Os-OD_2$ or Os–OD)	Other strong bands and assignments
$[Os^{VIII}N(OH)O_2]$	3120vs	—	1021vs	?1176w	479m	889vs ($\nu_{Os=O}$); 863vs ($\nu_{Os=O}$)
$[Os^{VIII}N(OD)O_2]$	2398vs 2358vs	—	1067m, 1020s		455w	
$K[Os^{VIII}O_3N]$[a]	—	—	1021vs	—	—	897vs ($\nu_{Os=O}$); 871vs ($\nu_{Os=O}$)
$K_2[Os^{VI}NCl_5]$	—	—	1081vs	—	—	336vs (ν_{Os-Cl}); 328vs (ν_{Os-Cl})
$K(Os^{VI}N(H_2O)Br_4]$	3367vs	1581s	1087vs		509s	966w, 611 (H_2O rock)
$K[Os^{VI}N(D_2O)Br_4]$	2347m	1166, 1151w	1085vs		471s	
$K[Os^{VI}N(H_2O)(CN)_4]$	3367s	1603m	1085s		526m	2155w ($\nu_{C\equiv N}$); 2070vs ($\nu_{C\equiv N}$)
$K[Os^{VI}N(D_2O)(CN)_4]$	2320s	1158w	1085s		500m	
$K_2[Re^{V}N(H_2O)(CN)_4]$[b] ...	3625m	1620m	997 + 974s			2160s ($\nu_{C\equiv N}$)
$K[Os^{VI}N(H_2O)(OH)_2C_2O_4]$	3410s	1635m	1025s	1150w	550w	1715s, 1680s, 1405s, 1250s, 893s, 868s ($C_2O_4^{2-}$ vibs.)
$K(Os^{VI}N(D_2O)(OD)_2C_2O_4]$	2420, 2380m		1025s	818w	540w	
$Cs[Os^{VI}N(H_2O)(C_2O_4)_2]$ ...	3344s	1605m	1025m		546m	1664s, 1433s, 1222s, 892s, 802s ($C_2O_4^{2-}$ vibs.); 617b (H_2O rock)
$K[Os^{VI}N(H_2O)(OH)_2F_2]$ ...	3145s	1603s	1020s	971w		568b (ν_{Os-F})
$[Os^{IV}N(NH_3)_8Br_2]Br_3$	3125b		1098s			1592s, 1335s, 823vs, 573m (NH_3 vibs.)
$[Os_2^{IV}N(ND)_3)_8Br_2]Br_3$	2404, 2283s		1095s			1025s, 625vs, 500w (ND_3 vibs.)
$[Os^{IV})NH_3)_6][Os^{IV}Br_6]$	3120					1605m, 1339s, 790vs (NH_3 vibs.); 450s (ν_{Os-N})

[a] L. A. Woodward, J. A. Creighton, and K. A. Taylor, *Trans. Faraday Soc.*, 1960, **56**, 1267.
[b] C. J. L. Lock and G. Wilkinson, *J.*, 1964, 2281.

Spectra were taken in Nujol mulls using potassium bromide windows from 400—4000 cm.$^{-1}$ {also from 200—400 cm.$^{-1}$ in the cases of $K_2[OsNCl_5]$ and $K[OsN(H_2O)Br_4]$}.

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[8] J. Selbin, L. H. Holmes, and S. P. McGlynn, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1359; J. Selbin, H. R. Manning, and G. Cessac, *ibid.*, p. 1235.

[9] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1964, **20**, 429; R. E. Hester and R. A. Plane, *Inorg. Chem.*, 1964, **3**, 769.

[10] P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 1962, **58**, 1495.

complexes[5] (*i.e.*, neglecting the effect of equatorial ligands) use of the potential function

$$V = \tfrac{1}{2}k_1r_1^2 + k_{12}r_1r_2 + \tfrac{1}{2}k_2r_2^2$$

gives values of 9·4 mdyne/Å for k_1 (Os–N stretch force constant) and 2·5 mdyne/Å for k_2 (Os–OH_2 stretch force constant) when k_{12} (interaction constant) = 0 (or, since in osmyl complexes $k_{12} \sim 0{\cdot}3$, $k_1 = 9{\cdot}5$, and $k_2 = 2{\cdot}5$, when $k_{12} = 0{\cdot}5$, and for the deutero-complex with $k_{12} = 0{\cdot}5$, $k_1 = 9{\cdot}4$, and $k_2 = 2{\cdot}4$); these are reasonable values for Os–N triple[2] and Os–O single bonds {thus in $[OsO_2(OH)_4]^{2-}$, the Os–OH stretch constant is 2·5 mdyne/Å},[5] so it appears that, in the case of $K[OsN(H_2O)Br_4]$, the bonding of the water group *trans* to the nitrogen atom is not markedly weaker than normal. The fact that complexes of the form $(OsNBr_5)^{2-}$ and $[OsN(CN)_5]^{2-}$ are not formed may, however, indicate that the nitride group does have a strong *trans*-effect on π-bonding groups. It is interesting to note that although $[ReN(H_2O)(CN)_4]^{2-}$ is known and has a rather similar spectrum[11] to the iso-electronic osmium complex, $[ReN(CN)_5]^{3-}$ has not been made.

(c) *Osmium*(IV) *Nitrido-complexes*.—Binuclear compounds of the form $[Os_2N(NH_3)_8X_2]X_3$ (X = Cl or Br) have been reported.[12] The infrared spectra of the bromide and its deutero-form are given in the Table, together with that of $[Os(NH_3)_6](OsBr_6)$. The only band which does not appear in the ammine spectrum and does not shift on deuteration is at 1098 cm.$^{-1}$ and is therefore likely to be an osmium–nitrogen stretching mode. If the complex is indeed binuclear, as seems clear from the work of Dwyer and Hogarth,[12] the most likely structures consistent with the overall stoicheiometry are $[Os_2{}^{IV}N(NH_3)_8Br_2]Br_3$, $[Os_2{}^{III,IV}NH(NH_3)_8Br_2]Br_3$, and $[Os_2{}^{III}NH_2(NH_3)_8Br_2]Br_3$. The latter two are unlikely, however, since none of the characteristic absorptions of bridging $>NH_2$[13] or $>NH$[14] groups is observed. The spectrum is fully consistent with the presence of a linear Os–N–Os grouping, the asymmetric vibration of which (ν_3) would be little affected by deuteration. The complex would then be fully analogous to the linear $(Ru_2{}^{IV}OCl_{10})^{4-}$ ion, in which ν_3 for the linear Ru–O–Ru group is at 885 cm.$^{-1}$;[15] the higher frequency for the Os–N–Os system would be consistent with the lower mass of the nitrogen atom.

EXPERIMENTAL

Potassium Nitridopentachloro-osmate(VI), $K_2(OsNCl_5)$.—This salt was made by the action of hydrochloric acid on potassium osmiamate[16] (Found: K, 16·8. Calc. for Cl_5K_2NOs: K, 17·0%).

Potassium Nitridotetrabromo-osmate(VI), $K[OsN(H_2O)Br_4]$.—This bromo-salt was made by the careful addition of hydrobromic acid to potassium osmiamate[16] (Found: K, 7·0; Br, 56·7. Calc. for Br_4H_2KNOOs: K, 6·7; Br, 55·0%). The deutero-form was made by using deutero-bromic acid in heavy water with potassium osmiamate.

Potassium Nitridotetracyanoaquo-osmate(VI), $K[OsN(H_2O)(CN)_4],2H_2O$.—This *salt* was prepared by suspending potassium osmiamate (5 g.) in a mixture of water (20 ml.) and liquid hydrocyanic acid (20 ml.) and stirring the mixture overnight. The solution was filtered and the filtrate evaporated to the point where black crystals appeared. A partially deuterated form was made by using heavy water in the above preparation and increasing the water : acid ratio (Found: K, 9·0; Os, 47·1; CN, 24·8; H_2O of crystallisation, 9·0. $C_4H_6KN_5O_3Os$ requires K, 9·7; Os, 47·4; CN, 25·9; H_2O, 8·0%).

Potassium Dihydroxynitrido-oxalatoaquo-osmate(VI), $K[OsN(H_2O)(OH)_2(C_2O_4)],2H_2O$.—Potassium osmiamate was added to an excess of a saturated solution of potassium tetraoxalate and the solution set aside for a week. The deep brown crystals of *product* were filtered off, washed with small portions of iced water, alcohol, and ether, and dried (Found: K, 9·0; C, 5·2; H, 1·4. $C_2H_8KNO_9Os$ requires K, 9·3; C, 5·7; H, 1·9%).

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[11] C. J. L. Lock and G. Wilkinson, *J.*, 1964, 2281.

[12] G. W. Watt and L. Vaska, *J. Inorg. Nuclear Chem.*, 1958, **6**, 246; F. P. Dwyer and J. W. Hogarth, *J. Proc. Roy. Soc. New South Wales*, 1950, **84**, 117; V. I. Belova and Ya. K. Syrkin, *J. Inorg. Chem., U.S.S.R.*, 1958, **3**, 2016.

[13] N. Vannerberg, *Arkiv Kemi*, 1964, **20**, 245.

[14] W. Hieber and H. Beutner, *Z. anorg. Chem.*, 1962, **317**, 63.

[15] J. L. Woodhead and J. M. Fletcher, U.K. Atomic Energy Authority, AERE R-4123.

[16] A. Werner and K. Dinklage, *Ber.*, 1901, **31**, 2698; 1906, **39**, 500.

Cæsium Nitridobisoxalatoaquo-osmate(VI), $Cs[OsN(H_2O)(C_2O_4)_2],4H_2O$.—This was made by dissolving potassium osmiamate in an excess of a saturated solution of oxalic acid at 40° and adding the filtrate to cæsium chloride solution. The deep brown crystals of the *salt* were washed with iced water, alcohol, and ether (Found: Cs, 21·4; C, 8·6; H, 1·6. $C_4H_{10}C_5NO_{13}Os$ requires Cs, 22·0; C, 8·0; H, 1·7%).

Potassium Dihydroxynitridodifluoroaquo-osmate(VI), $K[OsN(H_2O)(OH)_2F_2],5H_2O$.—This was made by the addition of potassium osmiamate to an excess of 40% hydrofluoric acid at room temperature. The dark brown *salt* was filtered off, washed with water, and dried (Found: K, 9·4; F, 8·3. $H_{14}F_2KNO_8Os$ requires K, 9·3; F, 9·0%).

Anhydrous Osmiamic Acid, $HOsO_3N$.—This was made by Hair and Robinson's method [4] (Found: Os, 74·7. Calc. for $HOsO_3N$: Os, 75·1%). Deutero-osmiamic acid was made from osmium tetroxide and liquid deuteroammonia.

Hexammineosmium(III) *Hexabromo-osmate*(III), $[Os(NH_3)_6][OsBr_6]$.—This was made by Watt and Vaska's [17] method (Found: Os, 40·3. Calc. for $H_{18}Br_6N_6Os_2$: Os, 39·6%), and dibromo-octa-ammine-μ-nitridodiosmium(IV) tribromide, $[Os_2N(NH_3)_8Br_2]Br_3$ was made by the same procedure [12,17] (Found: Br, 43·6. Calc. for $H_{24}Br_5N_9Os_2$: Br, 43·0%).

Analyses.—Analyses for carbon, hydrogen, and cyanide were done by the Microanalytical Laboratory, Imperial College; osmium was determined as the thiorea complex [18] and potassium and cæsium were determined as the sulphates after repeatedly evaporating the compounds with concentrated nitric acid to remove osmium.

Infrared Spectra.—These were taken on a Grubb-Parsons Spectromaster and on a Grubb-Parsons DM-2 far-infrared instrument; permission to use the latter was kindly granted by the Chemistry Department of University College.

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[17] G. W. Watt and L. Vaska, *J. Inorg. Nuclear Chem.*, 1958, **5**, 308.

[18] G. H. Ayres and W. N. Wells, *Analyt. Chem.*, 1950, **22**, 317.