

40. *Infrared Spectra and Structures of Osmium Oxy-complexes.*

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The structures of a number of osmyl complexes of the form $[\text{Os}^{\text{VI}}\text{O}_2\text{X}_2\text{X}'_2]^{2-}$ have been investigated by infrared spectroscopy; from these and chemical results the "perosmates" are formulated as $[\text{Os}^{\text{VII}}\text{O}_4\text{X}_2]^{2-}$ and the "oxy-osmyl" salts as $[\text{Os}^{\text{VI}}\text{O}_2(\text{OH})_2\text{X}_2]^{2-}$.

A WIDE range of very stable osmyl complexes has been known for some time. Recent X-ray studies have shown that the oxygen atoms are *trans* in potassium osmate¹ $\text{K}_2[\text{Os}^{\text{VI}}\text{O}_2(\text{OH})_4]$ and in the salt $\text{K}_2(\text{OsO}_2\text{Cl}_4)$.² A less-known series is that of the "oxy-osmyl" salts, so-called by Wintrebert³ who regarded them as containing apparently five co-ordinated ions, $(\text{Os}^{\text{VI}}\text{O}_3\text{X}_2)^{2-}$ ($\text{X} = \text{Cl}^-$, Br^- , NO_2^- , or $\frac{1}{2}\text{C}_2\text{O}_4^{2-}$); in a previous Note,⁴ it was suggested that the nitro-complex was better represented as $[\text{Os}^{\text{VI}}\text{O}_2(\text{OH})_2(\text{NO}_2)_2]^{2-}$. The present paper is concerned chiefly with the structures of other members of this series and also with those of the "perosmates" of osmium(VIII), which are usually regarded as being salts of an acid H_2OsO_5 .

Osmates and Perosmates (or "Osmenates").—Osmium tetroxide dissolves in concentrated aqueous potassium hydroxide to give a solution from which deep red crystals of potassium perosmate, $2\text{KOH}\cdot\text{OsO}_4$, may be isolated;⁵ it has been shown by polarography

TABLE I.

Hydroxyl frequencies in the infrared spectra of osmium oxy-complexes.

Complex	$\text{K}_2[\text{OsO}_4(\text{OH})_2]$	$\text{K}_2[\text{OsO}_2(\text{OH})_4]$	$\text{K}_2[\text{OsO}_2(\text{OH})_2\text{C}_2\text{O}_4]$	$\text{K}_2[\text{OsO}_2(\text{OH})_4(\text{NO}_2)_2]$
$\nu(\text{O-H})$	3200s, b	3260s	3440s	3310s
$\nu(\text{O-D})$	2400s, b	2425, 2340s	2460s, 2380s	2360s
$\nu(\text{O-H})/\nu(\text{O-D})$	1.33	1.37	1.42	1.40
$\delta(\text{O-H})$	1090s (1087)	1090s (1090)	1050w	1070w
$\delta(\text{O-D})$	790s	780s	770w	790w
$\delta(\text{O-H})/\delta(\text{O-D})$	1.38	1.40	1.36	1.36
$\nu(\text{Os-OH})$	520m	527m	526m	504w
$\nu(\text{Os-OD})$	505m	510m	514m	492w
$\nu(\text{Os-OH})/\nu(\text{Os-OD})$	1.03	1.03	1.02	1.02

Frequencies from spectra of Nujol mulls, except for those in parentheses which refer to bands observed for aqueous solutions of the complex.

and by controlled-potential reduction that this is a complex of osmium(VIII).⁶ This perosmate may be reduced with ethanol to potassium osmate, $\text{K}_2[\text{OsO}_2(\text{OH})_4]$.⁷ The infrared and far-infrared spectra of these complexes and of their deuterated forms have now been measured and are reported in Tables 1 and 2. Potassium osmate is known to have a *trans*-octahedral configuration¹ for which one infrared-active $\text{O}=\text{Os}=\text{O}$ and $\text{Os}-(\text{OH})$ stretching mode would be expected. The bands at 800 and 520 cm^{-1} are assigned to these modes. The former band is not affected by deuteration of the potassium osmate and arises in the region where *trans*-metal-dioxy-groups normally give bands in the infrared spectrum,⁸ but the latter is shifted by deuteration to 505 cm^{-1} . On the assumption that the OH and OD groups move as units against the osmium atoms (*i.e.*, that the degree of vibrational coupling between the Os-O and O-H stretching modes is small, an assumption which has been shown to be valid for the metal-carbon stretching vibrations in normal and deuterated platinum-methyl compounds) the ratio

¹ Porai-Koshits, Atovymán, and Adrianov, *J. Struct. Chem. (U.S.S.R.)*, 1960, **2**, 686.

² Kruse, *Acta Cryst.*, 1961, **14**, 1035.

³ Wintrebert, *Ann. Chim. phys.*, 1903, **28**, 54, 102.

⁴ Griffith, *J.*, 1962, 3248.

⁵ Kraus and Wilken, *Z. anorg. Chem.*, 1925, **145**, 156.

⁶ Meites, *J. Amer. Chem. Soc.*, 1957, **79**, 4931; Crowell, Heyrovsky, and Engelmeier, *ibid.*, 1941, **63**, 2888.

⁷ Muller, *Z. Elektrochem.*, 1922, **28**, 307.

⁸ Johnson, Lock, and Wilkinson, *Chem. and Ind.*, 1963, 333; and personal communication.

$\nu(\text{Os-OH}) : \nu(\text{Os-OD})$ should be $(18/17)^{1/2} = 1.03$, as observed in this case and in other instances cited in Table 1; metal-oxygen single-bond stretches are found near 500 cm.^{-1} in metal alkoxide complexes.^{9,10} The band at 1090 cm.^{-1} for potassium osmate is shifted to 780 cm.^{-1} on deuteration, and may reasonably be assigned to a deformation mode of the co-ordinated hydroxyl group: bands in this region are found for $[\text{Sn}(\text{OH})_6]^{2-}$ ¹¹ and certain ruthenium hydroxy-complexes.¹² The ratio of 1.40 for $\nu(\text{O-H}) : \nu(\text{O-D})$ is reasonable for a system in which there is little hydrogen bonding.¹³ As expected, no band is found in the 1100 or 500 cm.^{-1} region for the salt $\text{K}_2(\text{OsO}_2\text{Cl}_4)$. The single strong band in the far-infrared region, at 302 cm.^{-1} , probably arises from the O=Os=O deformation mode.

On the basis of these assignments, the spectra of potassium perosmate and its deuterated form may be explained as in Table 1; then the ion is likely to have D_{4h} symmetry and should be formulated as *trans*- $\text{K}_2[\text{OsO}_4(\text{OH})_2]$, which is in accordance with the chemical and polarographic results (formulations such as $\text{K}_2[\text{OsO}_5(\text{H}_2\text{O})]$ and $\text{K}_2\text{H}_2[\text{OsO}_6]$ may be excluded since the spectra show that co-ordinated hydroxyl groups are present and water groups absent). The analogous fluoro-complex ${}^5\text{Cs}_2[\text{OsO}_4\text{F}_2]$ could not be obtained pure in the solid state.

TABLE 2.
Skeletal modes of osmyl complexes.

Complex	Assumed point group	ν_3	$(\nu_1 + \nu_3)^*$	ν_9	ν_{10}	Other strong bands and assignments
$\text{K}_2[\text{OsO}_4(\text{OH})_2]$	D_{4h}	815vs (812)	1595m	520m	303	See Table 1
$\text{K}_2[\text{OsO}_2(\text{OH})_4]$	"	800vs (800)	1575m	527m	302vs	" "
$\text{K}_2[\text{OsO}_2\text{Cl}_4]$	"	837vs (840)	1645w	325s	308s	
$\text{K}_2[\text{OsO}_2(\text{CN})_4]$	"	830vs (832)	1635w			2152vs (C≡N stretch)
$\text{K}_2[\text{OsO}_2(\text{C}_2\text{O}_4)_2]$	"	824vs	1625m			1710, 1690, 1665, 1355, 1207, 893, 865 †
$[\text{OsO}_2(\text{NH}_3)_4]\text{Cl}_2$	"	808vs	1605w			1558, 1350, 1334, 867, 849 ‡
$\text{K}_2[\text{OsO}_2(\text{OCH}_3)_4]$	"	840vs	1657	518m		3300, 1630, 1350, 1045, 1021, 961, 818
$\text{K}_2[\text{OsO}_2(\text{NO}_3)_2(\text{NO}_2)_2]$	D_{2h}	871	1663			1540, 1490, 1340, 990, 955, 840, 820 §
		(O=Os=O) stretches	Combination band			
$\text{K}_2[\text{OsO}_2(\text{OH})_2(\text{NO}_2)_2]$	C_{2v}	840vs, 883m	1720w			1640, 1340, 1320, 831, 825
$\text{K}_2[\text{OsO}_2(\text{OH})_2\text{C}_2\text{O}_4]$...	C_{2v}	796	1570w			1710, 1695, 1660, 1440, 1257, 885, 830 †

Frequencies in parentheses were those observed in films of solutions of the complexes in heavy water.

* These bands did not shift on deuteration of the complex; the assignment for the combination band in the case of the oxalato-complexes is tentative owing to the presence of bands in this region due to the ligands. † Bands due to co-ordinated oxalate groups. ‡ Bands due to co-ordinated ammonia groups. § Bands due to co-ordinated nitrate- and nitro-groups.

Similar assignments can be made for the other hydroxy-complexes of osmium as given in Table 1. In compounds which are extensively hydrogen-bonded, the O-H stretching frequency is normally far below 3500 cm.^{-1} and the M-O-H deformation modes appear near 1650 cm.^{-1} ; ¹⁴ in these cases such shifts are not observed and it seems clear that hydrogen bonding is not an important factor. The crystallographic studies of potassium osmate have also shown that there is little hydrogen bonding in this compound.¹

"*Oxy-osmyl*" Salts.—Samples of the chloro- and bromo-salts could not be obtained free from the corresponding osmyl salts, $[\text{OsO}_2\text{X}_4]^{2-}$. However, the oxalato-complex

⁹ Chatt and Rowe, *J.*, 1962, 4023.

¹⁰ Barraclough, Bradley, Lewis, and Thomas, *J.*, 1961, 2601.

¹¹ Williams and Pace, *J.*, 1957, 4143.

¹² Scargill, *J.*, 1961, 4444.

¹³ Stuart and Sutherland, *J. Chem. Phys.*, 1956, 24, 559.

¹⁴ Braunholtz, Hall, Mann, and Sheppard, *J.*, 1959, 868; Hadzi and Sheppard, *Proc. Roy. Soc.*, 1953, A, 216, 247.

was easily prepared by reaction between potassium tetroxalate and osmium tetroxide or potassium osmate. The analytical results and infrared spectra are consistent with the formulation $[\text{OsO}_2(\text{OH})_2\text{C}_2\text{O}_4]^{2-}$, but not with $[\text{OsO}_3\text{C}_2\text{O}_4]^{2-}$; the infrared spectrum of anhydrous material has bands which, from observation of their behaviour on deuteration, may be assigned to O-H stretching and deformation modes (Tables 1 and 2).

The complexity of the infrared spectrum of the complex $\text{K}_2[\text{OsO}_2(\text{OH})_2(\text{NO}_2)_2]$ indicates that the two nitro-groups are *cis* to each other; it has been shown that *cis*-dinitro-complexes have an extra band near 1350 cm^{-1} (attributed to an out-of-phase symmetrical vibration of the two nitro-groups) and split bands in the 800 cm^{-1} region (due to both the in-phase and out-of-phase vibrations' being infrared-active),¹⁵ and such bands are also found in the spectrum of this complex. Their absence, however, for the compound reported previously as $\text{K}_2[\text{OsO}_2(\text{NO}_3)(\text{NO}_2)_3]$,⁴ together with a more accurate determination of the osmium content of the substance, make it likely that this would be better formulated as $\text{K}_2[\text{OsO}_2(\text{NO}_3)_2(\text{NO}_2)_2]$; there is no splitting of the bands due to the co-ordinated nitrate groups (such splitting has been observed with *cis*-dinitrato-complexes¹⁶), so that in this case the two oxygen groups are probably *trans* to each other as are the nitro- and nitrato-groups (giving the ion a skeletal symmetry of D_{2h}). The spectrum is quite different from that recently reported for a salt $\text{K}_2[\text{UO}_2(\text{NO}_3)_2(\text{NO}_2)_2]$, in which, however, it appears that the two nitrate groups are bidentate, so that the uranium atom has eight co-ordination.¹⁷

Osmium-Oxygen Stretching Vibrations.—The spectra of complexes of the form $(\text{OsO}_2\text{X}_4)^{2-}$ comply with the selection rules for an ion of skeletal symmetry D_{4h} . From the appropriate character tables¹⁸ for this point group it may be deduced that there will be eleven normal vibrations of the ion, of species $2A_{1g} + 2A_{2u} + B_{1g} + B_{2g} + B_{2u} + E_g + 3E_u$; of these, only the A_{2u} and E_u modes will be infrared active. In the conventional notation, the antisymmetric (infrared-active) O=Os=O stretching vibration will have species A_{2u} and is designated ν_3 , while the infrared-active Os-X stretching mode, ν_9 will have the species E_u . Although the symmetric O=Os=O stretch (ν_1) should be active in the Raman effect only, the combination frequency ($\nu_1 + \nu_3$) has an infrared-active sub-level and may be observed as a band of weak to moderate intensity (Table 2). This combination band has also been observed for a number of uranyl complexes.¹⁹ The values obtained for ν_1 and ν_3 for the osmyl complexes listed in Table 2 conform closely to the equation, $\nu_1 = 16 + 0.95\nu_3$, which is in fair agreement, in view of the fact that anharmonicity terms have been neglected, with the expression derived for a linear XY_2 system where a simple valence-force field (SVFF) approximation is assumed:^{17,18}

$$\nu_1 = \nu_3[1 + 2M_{\text{O}}/M_{\text{Os}}]^{-\frac{1}{2}} = 0.93\nu_3,$$

M_{O} and M_{Os} being the atomic masses of oxygen and osmium.

Using a more general quadratic function for the osmyl system, and again neglecting both anharmonicity terms and the interaction of the equatorial ligands X with the O=Os=O group in *trans*- $[\text{OsO}_2\text{X}_4]^{2-}$, we find the expressions relating F_{MO} , the metal-oxygen stretching force constant, with ν_3 and $(\nu_1 + \nu_3)$ derived by Jones¹⁹ for uranyl complexes to give values of 5.8 and 5.4 mdynes/Å for F_{OsO} in the salts $\text{K}_2[\text{OsO}_2\text{Cl}_4]$ and $\text{K}_2[\text{OsO}_2(\text{OH})_4]$, respectively (the corresponding mean values given by the SVFF approximation are 5.9 and 5.4 mdynes/Å). Substitution of these values into Badger's relation,^{17,19,20} $R_{\text{OsO}} = 1.08[F_{\text{OsO}}]^{-1/3} + 1.17$, gives the values of 1.78 and 1.79 Å for R_{OsO} , the osmium-oxygen bond length, in the salts $\text{K}_2[\text{OsO}_2\text{Cl}_4]$ and $\text{K}_2[\text{OsO}_2(\text{OH})_4]$, respectively; the results from the X-ray studies were 1.75 ± 0.02 and 1.77 Å.^{1,2}

¹⁵ Chatt, Duncanson, Gatehouse, Lewis, Nyholm, Tobe, Todd, and Venanzi, *J.*, 1959, 4073.

¹⁶ Gatehouse and Comyns, *J.*, 1958, 3965.

¹⁷ McGlynn, Smith, and Neely, *J. Chem. Phys.*, 1961, 35, 105.

¹⁸ Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, van Nostrand, New York, 1945.

¹⁹ Jones, *Spectrochim. Acta*, 1958, 10, 395; 1959, 11, 409.

²⁰ Badger, *J. Chem. Phys.*, 1935, 3, 710.

Values of ν_9 , the Os-X stretching frequency, are given in Table 2. These have already been discussed for the salt $K_2[OsO_2(OH)_4]$; for the complex $K_2(OsO_2Cl_4)$ the two bands observed in the far-infrared region at 325 and 308 cm^{-1} are probably to be assigned to the Os-Cl (ν_9) stretching and O=Os=O (ν_{10}) deformation frequencies [bands are also found in this region for a salt $K_2(OsCl_6)^{21}$]. In the osmyl complexes $[OsO_2(OH)_2Y_2]^{2-}$, where the two hydroxyl groups are probably *cis* to each other and the two doubly-bonded oxygen groups *trans*, the likely symmetry is C_{2v} , for which two infrared-active O=Os=O stretching modes ($A_1 + B_2$) are expected; however, the dipole change for the A_1 vibration will be low, so only one strong Os=O stretching frequency is expected, and tentative assignments of these are given in Table 2. Weak bands near 500 cm^{-1} in the spectra of salts $K_2[OsO_2(NO_3)_2(NO_2)_2]$ and $K_2[OsO_2(OH)_2(NO_2)_2]$ may be associated with osmium-oxygen and osmium-nitrogen stretching modes; a platinum nitro-complex also has a band in this region.²²

EXPERIMENTAL

All the complexes prepared were diamagnetic at room temperature.

Potassium Tetroxydihydroxyosmate(VIII), $K_2[OsO_4(OH)_2]$.—This was prepared by dissolving osmium tetroxide in a slight excess of cooled, concentrated potassium hydroxide solution. The solution was evaporated *in vacuo* over phosphorus pentoxide until it was almost dry, and the product was then recrystallised from water (Found: K, 21.5; Os, 51.1. $H_2K_2OsO_6$ requires K, 21.3; Os, 51.9%).

Potassium Dioxytetrahydroxyosmate(VI), $K_2[OsO_2(OH)_4]$.—This salt was made by adding a solution of osmium tetroxide in potassium hydroxide to ethanol⁷ (Found: K, 21.0; Os, 50.9. $H_4K_2OsO_6$ requires K, 21.2; Os, 51.6%).

Potassium Dioxydihydroxyoxalato-osmate(VI), $K_2[OsO_2(OH)_2C_2O_4] \cdot 5H_2O$.—This complex was prepared by reaction of osmium tetroxide with potassium tetroxalate solution³ (which requires nine months) and by addition of potassium osmate to an excess of potassium tetroxalate solution (Found: C, 5.1; H, 2.6; K, 14.4; Os, 37.6. $H_{12}C_2K_2OsO_{13}$ requires C, 4.7; H, 2.3; K, 15.3; Os, 37.1%).

Potassium Dioxydihydroxydinitro-osmate(VI), $K_2[OsO_2(OH)_2(NO_2)_2]$.—This salt was prepared by Wintrebert's method³ (Found: K, 18.5; Os, 44.6; N, 6.3. $H_2K_2N_2OsO_8$ requires K, 18.3; Os, 44.6; N, 6.6%).

Deuterated samples of all the above products were made in each case by using deuterium oxide as solvent.

Potassium Dioxynitratodinitro-osmate(VI), $K_2[OsO_2(NO_3)_2(NO_2)_2]$.—This salt was prepared by Wintrebert's method³ (Found: K, 15.7; Os, 36.2; N, 10.8. $K_2OsN_4O_{12}$ requires K, 15.1; Os, 36.8; N, 10.8%).

Other osmium complexes were prepared by standard methods.²³

Physical Measurements.—Infrared spectra were measured on a Perkin-Elmer model 21 recording instrument (450—4000 cm^{-1}) with sodium chloride and potassium bromide optics, by the Nujol and hexachlorobutadiene mull method and also in aqueous or deuterium oxide films, with silver chloride and arsenic trisulphide plates (800—1300 cm^{-1}). Far-infrared spectra were measured on a Grubb-Parsons grating Spectromaster (200—450 cm^{-1}) for Nujol mulls between Polythene plates. Magnetic measurements were made at room temperatures in a field of 7000 gauss by the Gouy method.

Analyses.—Carbon, hydrogen, and nitrogen, were determined by the Microanalytical Laboratory, Imperial College; potassium was determined as potassium hexachloroplatinate and as potassium nitrate (in the latter determinations osmium was removed by repeated evaporation of the complexes with concentrated nitric acid). Osmium was determined spectrophotometrically as the thiourea complex.²⁴

²¹ Adams, Chatt, Davidson, and Gerratt, *J.*, 1963, 2189.

²² Adams, Chatt, and Shaw, *J.*, 1960, 2047.

²³ Pascal, "Nouveau Traité de Chimie Minérale," Vol. XIX, Masson et Cie., Paris, 1958.

²⁴ Ayres and Wells, *Anal. Chem.*, 1930, 22, 317.

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