

203. Structure and Reactivity of the Oxyanions of Transition Metals. Part X.* Sexivalent Ruthenium and Osmium.

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Osmate(vi) is shown to exist as the octahedrally bonded ion $\text{OsO}_2(\text{OH})_4^{2-}$ both in solid potassium osmate and in aqueous solution. The diamagnetism of this ion is discussed in terms of ligand field theory. Visible and ultraviolet spectra of solid potassium osmate and its solutions in aqueous alkali and methanol are presented and discussed. Attempts to prepare osmate(vi) as the tetrahedral ion OsO_4^{2-} have failed. In contrast, ruthenate is tetrahedrally bonded, having two unpaired electrons.

It has been stated that potassium osmate, formulated as K_2OsO_4 , is diamagnetic.¹ The ion, OsO_4^{2-} , should contain two electrons outside the closed-shell of osmium tetroxide. Since the two "outer" electrons in hypomanganate and ferrate are unpaired in an orbital doublet,² and since ruthenate, RuO_4^{2-} , probably contains two unpaired electrons,³ it seemed most improbable that osmate, provided it exists as a regular tetrahedral ion, should be diamagnetic.

Our attempts to prepare this ion have been unsuccessful. We have, however, prepared a pink solid, $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$, which is shown to contain the ion $\text{OsO}_2(\text{OH})_4^{2-}$ and to be diamagnetic. Ultraviolet and visible absorption spectra of its solution in aqueous alkali and methanol are shown in Fig. 1, and a diffuse reflectance spectrum of the potassium salt is given in Fig. 2.

EXPERIMENTAL AND RESULTS

Water was doubly distilled from concentrated alkaline permanganate. Metallic ruthenium and osmium were supplied by Johnson, Matthey & Co.; other reagents were of "AnalaR" grade.

Potassium osmate was prepared by reducing alkaline solutions of purified osmium tetroxide (obtained from the metal by a standard procedure) with absolute ethyl alcohol. The resulting violet precipitate of potassium osmate was washed with ethyl alcohol and stored *in vacuo*.

* Part IX, *J.*, 1960, 889.

¹ Earnshaw, Figgis, Lewis, and Nyholm, *Nature*, 1957, **179**, 1121.

² Carrington and Symons, *J.*, 1960, 889; cf. Hrowstowski and Scott, *J. Chem. Phys.*, 1950, **18**, 106.

³ Carrington, Ingram, Schonland, and Symons, *J.*, 1956, 4710.

Potassium ruthenate was obtained by alkaline reduction of ruthenium tetroxide. Metallic ruthenium in molten potassium hydroxide was oxidised with sodium peroxide, and the aqueous extract treated with acidified potassium permanganate. The resulting ruthenium tetroxide was distilled into concentrated aqueous potassium hydroxide and thereby reduced to ruthenate. The purity and concentration of these solutions were estimated spectrophotometrically.⁴

Cæsium tetrachloro-osmate, $\text{Cs}_2\text{OsO}_2\text{Cl}_4$, was prepared as a buff powder⁵ by addition of concentrated aqueous cæsium chloride to a solution of potassium osmate in 4*N*-hydrochloric acid.

Analysis of Potassium Osmate.—The valency state of osmium in alkaline solutions of osmium tetroxide is known to be eight.⁶ Comparison of solutions containing identical concentrations of osmium as alkaline osmium tetroxide and potassium osmate, by the iodometric procedure outlined previously,⁷ showed the valency state in potassium osmate to be six.

FIG. 1. Spectra of osmium(VI) in (a) aqueous alkali and (b) methanol.

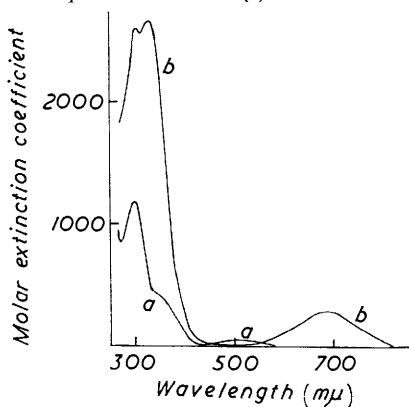
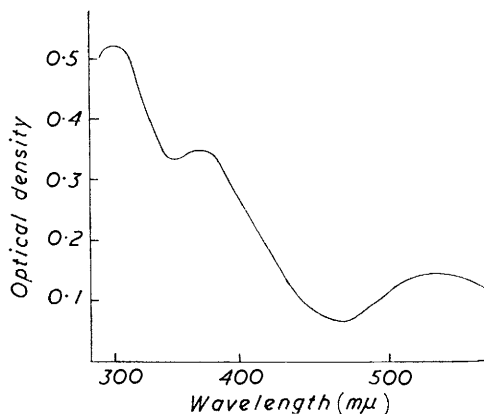


FIG. 2. Diffuse reflectance spectrum of potassium osmate diluted with lithium fluoride.



It has been stated⁸ that solid potassium osmate prepared as described is $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$. To check this, molar extinction coefficients were obtained at 300 μ for solutions of potassium osmate prepared quantitatively from known weights of osmium tetroxide. By comparison with spectra obtained from weighed amounts of solid potassium osmate, the formula of this compound was found to be $\text{K}_2\text{OsO}_4 \cdot (2 \pm 0.3)\text{H}_2\text{O}$.

Spectrophotometric Measurements.—These were made with either a Unicam SP.600 glass or SP.500 quartz spectrophotometer, the latter having a photomultiplier attachment.

Solutions of potassium osmate in water or aqueous alkali were pink (Fig. 1*a*), but methanolic solutions were blue (Fig. 1*b*). The original spectrum (1*a*) was restored quantitatively by addition of excess of alkali.

Diffuse reflectance spectra (Fig. 2) were measured by using a Unicam SP.540 attachment, with lithium fluoride as diluent and reference surface, suitable precautions being observed.⁹

The spectrum of $\text{Cs}_2\text{OsO}_2\text{Cl}_4$ in aqueous hydrochloric acid resembled that of potassium osmate, having a shoulder of low intensity at 500 μ and more intense bands at 350 and 270 μ .

We confirmed the statement¹⁰ that the spectrum of osmium tetroxide in water is almost identical with that in hexane. Addition of alkali, to give H_3OsO_6^- or $\text{H}_2\text{OsO}_6^{2-}$, causes a marked spectral change. These observations strongly support the theory that osmium tetroxide in aqueous solution is largely unhydrated.¹¹

⁴ Connick and Hurley, *J. Amer. Chem. Soc.*, 1952, **74**, 5012.

⁵ Hepworth and Robinson, *J. Inorg. Nuclear Chem.*, 1957, **4**, 24.

⁶ Kraus and Wilken, *Z. anorg. Chem.*, 1924, **137**, 349.

⁷ Lott and Symons, *J.*, 1959, 829.

⁸ Crowell, Yost, and Roberts, *J. Amer. Chem. Soc.*, 1940, **62**, 2176.

⁹ Griffiths, Lott, and Symons, *Analyt. Chem.*, 1959, **31**, 1338.

¹⁰ Langseth and Qviller, *Z. phys. Chem.*, 1934, *B*, **27**, 79.

¹¹ Sauerbrunn and Sandell, *J. Amer. Chem. Soc.*, 1953, **75**, 4170.

Infrared Measurements.—These were made with the Unicam SP.100 instrument, the spectrum of potassium osmate being measured in a Nujol mull. A broad band at about 3550 cm^{-1} was observed but there was no absorption in the 1600 cm^{-1} region. This is consistent with the formulation $\text{K}_2\text{OsO}_2(\text{OH})_4$, and rules out the possibility of water of crystallisation.¹²

Magnetic-susceptibility Measurements.—These were made as described previously.¹³ The concentrations (0.1—0.01M) were estimated spectrophotometrically and by weight for ruthenate and osmate respectively. The magnetic moment of ruthenate was calculated to be 2.75 B.M. which is close to the free spin value of 2.83 B.M. for two unpaired electrons. In contrast, osmate was found to have zero moment.

Summary.—The experimental results show that potassium osmate, in which osmium is hexivalent, can be formulated as $\text{K}_2\text{OsO}_2(\text{OH})_4$. Since the diffuse reflectance spectra and the spectra of aqueous and alkaline solutions of potassium osmate are similar, it is assumed that the solid dissolves unchanged in water and dilute alkali. The spectrum of the blue solution in methanol is similar and also contains hexivalent osmium: the spectral change is thought to be too large for a simple solvent shift and is tentatively ascribed to the formation of a methyl ester, possibly $\text{K}_2\text{OsO}_2(\text{OMe})_4$.

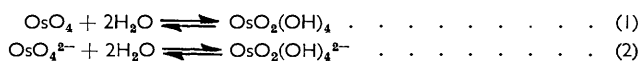
DISCUSSION

We conclude that solid potassium osmate, $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$, contains osmium octahedrally bonded to two oxide and four hydroxide ligands, and that the resultant ion is essentially unchanged in aqueous solution. The original aim, to study the magnetic properties of tetrahedral osmate, has therefore not been realised. Since, however, ruthenate has two unpaired electrons, and electron-spin resonance studies on hypomanganate and ferrate show that zero-field splitting of the doublet level containing these electrons is very small,¹⁴ it is considered most improbable that OsO_4^{2-} would be diamagnetic.

On the other hand, that $\text{OsO}_2(\text{OH})_4^{2-}$ is diamagnetic is to be expected both on theoretical grounds and by analogy with compounds of similar symmetry. Thus, although osmium hexafluoride, OsF_6 , is paramagnetic with two unpaired electrons,¹⁵ Hepworth and Robinson⁵ have shown that both $\text{OsO}_2\text{Cl}_4^{2-}$ and $\text{RuO}_2\text{Cl}_4^{2-}$ are diamagnetic, although they offered no explanation.

Structure.—Writing osmate as $\text{OsO}_2(\text{OH})_4^{2-}$, and assuming a *trans*-configuration with the *z* axis passing through the two oxide ligands and the *x* and *y* axes through the hydroxides, one can see that the familiar splitting of the *d*-orbitals into an upper doublet (e_g) and lower triplet (t_{2g}) will be accompanied by a further splitting of the e_g level into two singlets ($d_{x^2-y^2}$ and d_{z^2}), and of the t_{2g} level into a singlet (d_{xy}) and a doublet (d_{xz} , d_{yz}). Our problem is to decide upon the relative stabilities of the two lower levels. Since the d_{xy} orbital lies in the plane of the four hydroxide ligands, π -interaction will be with p - π -electrons on hydroxide only, whereas π -bonding with the (d_{xz} , d_{yz}) orbitals will be with electrons on the oxide ligands as well as hydroxide. One may therefore expect d_{xy} to lie below (d_{xz} , d_{yz}) because such π -interaction, which will destabilise these *d*-orbitals, should be greater for oxide than hydroxide ligands. This effect will be enhanced if, as seems reasonable, the metal-oxide distance is less than the metal-hydroxide distance. Similar remarks can be applied to tetrachloro-osmate(VI) and tetrachlororuthenate(VI) ions, and we conclude that, provided the splitting between d_{xy} and (d_{xz} , d_{yz}) is fairly large, these ions should be diamagnetic. This conclusion is in accord with experiment.

Ease of Hydration.—Since osmium tetroxide is largely unhydrated in neutral solution, equilibrium (1) must lie largely to the left, but equilibrium (2) lies to the right:



¹² Williams and Pace, *J.*, 1957, 4143.

¹³ Symons, *J.*, 1957, 387.

¹⁴ Carrington, Ingram, Lott, Schonland, and Symons, *Proc. Roy. Soc.*, in the press.

¹⁵ Hargreaves and Peacock, *Proc. Chem. Soc.*, 1959, 85.

It is probable that the generalisation can be made that "closed-shell" tetrahedral oxyanions will have a smaller tendency for hydration than the corresponding ions with one or two "outer" electrons. This can be understood in terms of the relative importance of bonding in the tetrahedral and the octahedral ion. If we start with the approximation that the two "outer" electrons are fed into the d_{z^2} - and $d_{x^2-y^2}$ -orbitals in OsO_4^{2-} , and into the d_{xy} -orbital of $\text{OsO}_2(\text{OH})_4^{2-}$, then, as π -overlap between oxide or hydroxide p - π -orbitals and the metal d -orbitals increases, so those containing the "outer" electrons will be increasingly destabilised. Since π -overlap should be considerably stronger with oxide than with hydroxide ligands, it will be smallest for the d_{xy} -orbital in $\text{OsO}_2(\text{OH})_4^{2-}$, and therefore this orbital will be of lowest energy, and diamagnetic $\text{OsO}_2(\text{OH})_4^{2-}$ will be favoured energetically.

One reason why π -interaction should be more important in OsO_4^{2-} than in $\text{OsO}_2(\text{OH})_4^{2-}$ is that Pauling's electroneutrality principle^{16,17} is satisfied almost completely by σ -bonding in the latter, but cannot thus be satisfied in the former. Although π -bonding in tetrahedral oxyanions of the transition metals is thought to be less extensive² than was postulated by Wolfsberg and Helmholtz¹⁸ it seems to play an important rôle in the chemistry of these ions (cf. ref. 19).

Spectra.—If, as has been assumed, the ion $\text{OsO}_2(\text{OH})_4^{2-}$ has a *trans*-configuration, one would expect to find a broad band (or doublet) of low intensity close to the visible region, corresponding to the forbidden $e_g \leftarrow t_{2g}$ transitions of octahedral complexes. The broad band of low intensity found in the 500 $m\mu$ region is thought to correspond to these transitions, and is further evidence for the proposed octahedral structure for osmate. A similar band has also been found for $\text{OsO}_2\text{Cl}_4^{2-}$, but would not be expected either theoretically or by analogy for the tetrahedral ion OsO_4^{2-} . Thus no weak band of this sort has been found for hypomanganate, ferrate,²⁰ or ruthenate.⁴

The more intense bands in the near-ultraviolet region are probably charge-transfer bands from p - π or p - σ levels on oxide and hydroxide to vacant d -orbitals.

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¹⁶ Pauling, *J.*, 1948, 1461.

¹⁷ Dunn, *J.*, 1949, 623.

¹⁸ Wolfsberg and Helmholtz, *J. Chem. Phys.*, 1952, 20, 837.

¹⁹ Bailey, Carrington, Lott, and Symons, *J.*, 1960, 290.

²⁰ Carrington, Schonland, and Symons, *J.*, 1957, 659.