

SIMPLE AND COMPLEX OXYHALIDES OF RUTHENIUM AND OSMIUM

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Abstract—Attempts to prepare simple and complex oxyfluorides of ruthenium have failed. Osmium is shown to form an octavalent oxyfluoride, OsO_3F_3 , the parent of the trifluoroperperosmates, $\text{M}^{\text{I}}\text{OsO}_3\text{F}_3$ ($\text{M}^{\text{I}} = \text{K}, \text{Cs}, \text{Ag}$). The preparation of an oxychloride of hexavalent osmium, OsOCl_4 , is also described together with its reaction with hydrochloric acid under varying conditions. Structural and magnetic data are presented for compounds of the type $\text{Cs}_2\text{MO}_2\text{Cl}_4$ ($\text{M} = \text{Ru}, \text{Os}$).

ALTHOUGH all the six platinum metals form well-characterized binary and complex compounds with the halogens, ruthenium and osmium alone show a readiness to combine with oxygen to form stable oxides. This feature suggests that these two elements should be able to form compounds containing both oxygen and a halogen and this premise is borne out by a survey of the rather scanty literature on the subject.

Complex oxyhalides of both ruthenium and osmium are known. These include the hexavalent tetrachlororuthenates $\text{M}_2^{\text{I}}\text{RuO}_2\text{Cl}_4$ ($\text{M}^{\text{I}} = \text{Rb}, \text{Cs}$,⁽¹⁾ and H ⁽²⁾) and the corresponding tetrachloro- and tetrabromo-osmates $\text{M}_2^{\text{I}}\text{OsO}_2\text{X}_4$ ($\text{M}^{\text{I}} = \text{K}, \text{NH}_4$; $\text{X} = \text{Cl}, \text{Br}$)⁽³⁾; more recent work has disclosed that the compound " $\text{K}_2\text{RuCl}_5\text{OH}$ " is to be regarded as a complex oxyhalide of tetravalent ruthenium with the constitution $\text{K}_4\text{Ru}_2\text{OCl}_{10}\cdot\text{H}_2\text{O}$.⁽⁴⁾ No true simple oxyhalides have been reported, however, beyond some separated from aqueous solutions which contain hydrogen in addition, either as hydroxyl or water of constitution. Reactions which might conceivably have led to the formation of an oxyhalide failed; for example, the chlorination of ruthenium dioxide⁽⁵⁾ gave only the binary chloride. In this connection it may be noted that the claim of RUFF⁽⁶⁾ to have produced an oxyfluoride of iridium, IrOF_4 , has recently been shown to be ill-founded.⁽⁷⁾

EXPERIMENTAL

Two general experimental approaches have been employed: (1) the fluorination, using both elementary fluorine and liquid fluorides, of oxygenated derivatives of the elements, and (2) the action of gaseous halogen/oxygen mixtures on the metal.

Oxyhalides of ruthenium

(1) *Reaction of ruthenium dioxide with elementary fluorine.* Anhydrous ruthenium dioxide was prepared by igniting metallic sponge in a current of oxygen at 1000° . The product, in a nickel boat, was transferred to a silica reaction tube and heated to 150° in a stream of fluorine (4 litres/hr), freed from hydrogen fluoride, and suitably diluted with nitrogen. Bright green droplets of ruthenium pentafluoride distilled from the reaction zone as the sole product of the reaction.

(2) *The action of bromine pentafluoride on ruthenium tetroxide.* Bromine pentafluoride was

⁽¹⁾ J. L. HOWE *J. Amer. Chem. Soc.* **23**, 779 (1901).

⁽²⁾ S. AOYAMA *Z. anorg. Chem.* **138**, 252 (1924).

⁽³⁾ L. WINTREBERT *Ann. Chim. Phys.* [vii] **28**, 54, 86 (1903).

⁽⁴⁾ A. McL. MATHIESON, D. P. MELLOR, and N. C. STEPHENSON *Acta Cryst.* **5**, 185 (1952).

⁽⁵⁾ H. REMY and T. WAGNER *Z. anorg. Chem.* **157**, 344 (1926).

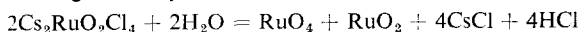
⁽⁶⁾ O. RUFF and J. FISCHER *Z. anorg. Chem.* **179**, 161 (1929).

⁽⁷⁾ P. L. ROBINSON and G. J. WESTLAND *J. Chem. Soc.* (in press).

prepared by passing a mixture of bromine vapour and fluorine through a nickel tube heated to 200°, and the crude product purified by trap-to-trap distillation from solid potassium fluoride (to retain any bromine trifluoride) in a stream of dilute fluorine. Ruthenium tetroxide (0.5 g), prepared according to MARTIN,⁽⁸⁾ was dried over phosphoric oxide and transferred in a vacuum to a Pyrex-glass reaction bulb containing 20 ml of bromine pentafluoride. At temperatures below 0° the tetroxide dissolved to a clear yellow solution in the pentafluoride, but, as the temperature rose, a deep green colour developed which changed, through blue, finally to brown and meanwhile oxygen was copiously evolved. Removal of the excess reagent in a vacuum at room temperature left a pale pink solid which, on heating to 114° in a vacuum, melted and evolved bromine pentafluoride together with a vapour which formed green droplets of ruthenium pentafluoride. Evidently, the solid consisted of an addition compound between ruthenium pentafluoride and bromine pentafluoride, possibly of the type $\text{RuF}_5 \cdot \text{BrF}_5$ and similar to the one formed with bromine trifluoride.⁽⁹⁾

(3) *Potassium perruthenate and bromine trifluoride*. Excess bromine trifluoride, prepared as described previously,⁽⁹⁾ was condensed in a vacuum on to 0.2 g of potassium perruthenate. A smooth evolution of oxygen took place on warming to room temperature and a white precipitate appeared in the pale yellow liquid. Excess reagent was removed in a vacuum and the product dried at 100°. A partial analysis for fluorine only, and a qualitative examination of its X-ray photograph, established the material to be potassium hexafluororuthenate(V), KRuF_6 . Found: F = 45.0%; calc. for KRuF_6 , F = 44.9%.

(4) *Caesium tetrachlororuthenate(VI)*. This salt was prepared according to HOWE.⁽¹¹⁾ Found: Cl = 26.1%; calc. for $\text{Cs}_2\text{RuO}_2\text{Cl}_4$; Cl = 26.2%. An X-ray powder photograph of it taken in a 19-cm camera using $\text{FeK}\alpha$ radiation, established a cubic structure with $a = 10.07 \text{ \AA}$. A measurement of the magnetic moment, using the Gouy method, showed it to be diamagnetic. Water produced instant hydrolysis according to the equation



but the crystals can be recovered unchanged from dilute hydrochloric-acid solution. Boiling 10 N hydrochloric acid brings about reduction with precipitation of black, crystalline caesium hexachlororuthenate(IV), Cs_2RuCl_6 . This also is cubic with $a = 10.22 \text{ \AA}$.

Elementary fluorine reacted vigorously at about 150° with $\text{Cs}_2\text{RuO}_2\text{Cl}_4$ to give a pale blue solid which X-ray examination showed to contain caesium hexafluororuthenate(V), CsRuF_6 , as the main constituent. When treated with liquid, anhydrous hydrofluoric acid, $\text{Cs}_2\text{RuO}_2\text{Cl}_4$ turned black but no hydrogen chloride was evolved.

Oxyhalides of osmium

(1) *Osmium oxytetrachloride*. Osmium metal powder (0.3 g) was spread in a shallow layer along the length of a glass reaction vessel and heated to 400° in a stream of dry chlorine and oxygen in which the gases were present in the volume ratio 8 : 1, respectively. Volatile products were collected in a U-tube cooled to -10°. When all the metal had been consumed, the contents of the U-tube were allowed to come to room temperature and the osmium tetroxide present was removed under a pressure of 10^{-2} mm. The dark brown residue of crude osmium oxytetrachloride was then purified by distillation in a vacuum. The yield, based on osmium taken, was 70%. Found: Cl = 41.0%. OsOCl_4 requires Cl = 40.8%.

Osmium oxytetrachloride is a dark brown diamagnetic solid which, on careful heating in a vacuum, sublimes as long, needle-shaped crystals, m.p. 32°. The liquid boils above 200° and produces a deep yellow vapour.

(2) *Caesium tetrachloro-osmate(VI)*. Osmium oxytetrachloride was dissolved in excess 10 N hydrochloric acid cooled to -20° and a concentrated solution of caesium chloride was added to the deep green solution. The dark green precipitate was separated on a sintered glass disk and washed with cold 10 N hydrochloric acid. Found: Cl = 26.0, 25.4, 24.8%. $\text{Cs}_2\text{OsO}_2\text{Cl}_4$ requires Cl = 22.5%, $\text{Cs}_2\text{OsOCl}_6$ requires Cl = 31.1%. The specimen containing 26.0% chlorine was cubic with $a = 10.12 \text{ \AA}$. On warming the crystals with excess 2 N hydrochloric acid, they dissolved to an orange solution which, on cooling, deposited pure caesium tetrachloro-osmate(VI) as a buff powder. Found: Cl = 22.4%. The cubic lattice is iso-dimensional with $\text{Cs}_2\text{RuO}_2\text{Cl}_4$. A measurement of the magnetic moment of this material showed it to be diamagnetic. Boiling with 10 N

⁽⁸⁾ F. S. MARTIN *J. Chem. Soc.* 3055 (1952).

⁽⁹⁾ M. A. HEPWORTH, R. D. PEACOCK, and P. L. ROBINSON *J. Chem. Soc.* 1197 (1954).

hydrochloric acid brings about reduction to the red caesium hexachloro-osmate(IV), Cs_2OsCl_6 . Found: Cl = 31.5%. Cs_2OsCl_6 requires Cl = 31.8%. Cs_2OsCl_6 is cubic and iso-dimensional with Cs_2RuCl_6 .

(3) *Potassium, caesium, and silver trifluoroperperosmates*. A known weight of osmium metal was quantitatively converted to the tetroxide by burning in pure dry oxygen and transferring the product in a vacuum to a break-seal vessel. This, in turn, was attached to a train of traps which allowed the tetroxide, together with an excess of bromine trifluoride, to be condensed in a vacuum into a bulb containing an equivalent of potassium or caesium bromide or, in the case of silver, of silver iodate. In all the reactions there was a smooth evolution of oxygen on warming to room temperature. Those involving alkali metals formed salts which gave orange solutions in the excess of bromine trifluoride. The silver salt proved to be less soluble, and separated as deep orange crystals. The excess solvent was removed in a vacuum at room temperature and the orange salts were dried at 40–50° for several hours. Found: F = 20.0%, E = 317. KOsO_3F_3 requires F = 17.0%, E = 334. Iodometric titration showed that 3.9 equivalents of iodine were liberated per the equivalent of osmium, indicating that the valency of osmium in the salt was $4 + 3.9 = 8$. Found: F = 15.1%, E = 454. CsOsO_3F_3 requires F = 13.3%, E = 428. 4.2 equivalents of iodine were liberated per equivalent of osmium. Found: F = 13.8, Ag = 26.7%. AgOsO_3F_3 requires F = 14.1, Ag = 26.8%. An X-ray powder photograph of the silver salt revealed a complex pattern which could not be indexed.

(4) *Osmium trioxydifluoride*. (a) When two equivalents of osmium tetroxide were allowed to react with one of potassium bromide under the conditions just described, an orange residue remained in the reaction bulb after the removal of the excess of bromine trifluoride at room temperature. This, on heating to 100° in a vacuum, produced an orange sublimate which by a suitable application of heat was driven into a collecting arm of the apparatus. Found: F = 13.5, 14.2%. OsO_3F_2 requires F = 13.8%. 4 equivalents of iodine were liberated per equivalent of osmium, hence the valency of the osmium is $4 + 4 = 8$.

A little of the preparation was introduced, by tapping, into a melting-point tube attached to the main apparatus, and the melting-point, taken in the usual way, at atmospheric pressure was found to be 170–172°. The material melted to a red liquid; the vapour pressure at the melting-point was appreciable, since, at that temperature, a quantity of it sublimed on to the cooler surfaces of the apparatus. The material appears to be identical with the orange sublimate formed during the heating of the product from the action of bromine trifluoride on osmium tetrabromide,⁽¹⁰⁾ which probably arises from either a trace of moisture or some oxy-compound in the bromide.

(b) Osmium-metal sponge was fluorinated in an alumina apparatus of the kind which has been described previously,⁽¹⁰⁾ using oxygen as carrier gas in the volume ratio oxygen : fluorine of 2 : 1. Under these conditions, OsO_3F_2 was almost the sole product of the reaction. Higher oxygen concentrations lead to the production of some osmium tetroxide, b.p. 130°, and, conversely, higher fluorine concentrations lead to the formation of some octafluoride, b.p. 47°; incidentally, both of these materials, by reason of their greater volatility, may be easily removed from the oxyfluoride by distillation.

DISCUSSION

In contrast to oxygen, with which ruthenium forms a tetroxide, fluorine is unable to excite the octavalent state of the element, the highest known fluorides being the pentafluoride, RuF_5 , and its derivatives the hexafluororuthenates(V). However, since the intermediate valencies six and seven are so well characterized in the ruthenates and their derivatives and the perruthenate, respectively, it might be expected that either simple or complex oxyfluorides of Ru(VI), Ru(VII), or perhaps even of Ru(VIII) could be prepared. Many analogies exist which support this view. Thus, chromium forms a pentafluoride, CrF_5 , and also forms the hexavalent oxyfluoride CrO_2F_2 ;⁽¹¹⁾ manganese forms a trifluoride, MnF_3 , and the heptavalent oxyfluoride, MnO_3F , recently observed;⁽¹²⁾ and rhenium the hexafluoride ReF_6 and all three possible heptavalent oxyfluorides ReOF_5 , ReO_2F_3 ,⁽¹³⁾ and ReO_3F .⁽¹²⁾

⁽¹⁰⁾ M. A. HEPWORTH, P. L. ROBINSON, and G. J. WESTLAND *J. Chem. Soc.* 4269 (1954).

⁽¹¹⁾ A. ENGBRECHT and A. V. GROSSE *J. Amer. Chem. Soc.* 74, 5262 (1952).

⁽¹²⁾ A. ENGBRECHT and A. V. GROSSE *J. Amer. Chem. Soc.* 76, 2042 (1954).

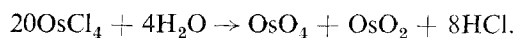
Nevertheless, a comprehensive search involving many reactions which might have been expected to produce oxyfluorides of ruthenium resulted, in every instance, in the formation of the pentafluoride. Attempts to stabilize the expected oxyfluoride as part of a co-ordination compound by fluorinating potassium perruthenate and caesium tetrachlororuthenate led in each case to the complete elimination of oxygen and the formation of the corresponding hexafluororuthenate(V). These two observations accord with those of WEISE and KLEMM,⁽¹⁴⁾ who found that the fluorination of "K₂RuCl₅OH," or more properly K₄Ru₂OCl₁₀, H₂O, gave "K₂RuF₈," that is KRuF₆ + KF₂. Milder fluorinating conditions, secured by using anhydrous hydrogen fluoride, proved no more effective, and it must be concluded that oxyfluorides of ruthenium, if they exist, are very unstable substances.

The facts about ruthenium just disclosed do little to suggest that osmium, the element immediately below it in the Periodic Table, should yield oxyhalides. But the evidence from the horizontally placed rhenium is more encouraging. Both rhenium and osmium have a great affinity for oxygen, exemplified by the extremely stable perrhenate ion and the tetroxide of osmium, and, in addition, each forms a set of well characterized halides. Furthermore, oxychlorides and oxyfluorides are both established in rhenium chemistry. Clearly there is a high probability that osmium could be made to furnish similar compounds.

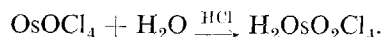
Chlorination of osmium metal by the halogen itself produces the tetrachloride, OsCl₄,⁽¹⁵⁾ but introduction of a little oxygen into the chlorine stream causes the reaction to take place at a much lower temperature and changes the product to osmium oxytetrachloride, OsOCl₄. This compound bears a remarkable resemblance to the corresponding rhenium compound, ReOCl₄,⁽¹⁶⁾ as shown by the properties of both summarized below.

Property	ReOCl ₄	OsOCl ₄
Colour of solid	Brown	Brown
Colour of vapour	Deep yellow	Deep yellow
m.p.	29°	32°
b.p.	223°	above 200°
Reaction with water	Hydrolyses; black ppt	Hydrolyses; black ppt
Organic solvents	Soluble	Soluble

Osmium oxytetrachloride is hydrolysed by water with the appearance of a black precipitate of hydrated osmium dioxide,



With warm, dilute hydrochloric acid, on the other hand, an orange solution of tetrachloro-osmic acid results,



Starting with osmium metal, these reactions furnish a new and rapid synthesis of this acid and its salts. WINTREBERT,⁽³⁾ starting from the tetroxide and proceeding through

⁽¹³⁾ E. E. AYNLEY, R. D. PEACOCK, and P. L. ROBINSON *J. Chem. Soc.* 1622 (1950).

⁽¹⁴⁾ E. WEISE and W. KLEMM *Z. anorg. Chem.* **279**, 74 (1955).

⁽¹⁵⁾ O. RUFF and F. BORNEMANN *Z. anorg. Chem.* **65**, 446 (1910).

⁽¹⁶⁾ A. BRÜL and K. ZIEGLER, *Ber.* **65**, 916 (1932).

the complex nitrite, has succeeded in preparing the very soluble potassium and ammonium tetrachloro-osmates. The former of these was shown by HOARD⁽¹⁷⁾ to have a tetragonal structure. Caesium tetrachloro-osmate(VI) is by contrast sparingly soluble in water and is isostructural with caesium hexachloro-osmate(IV), Cs_2OsCl_6 , which possesses the cubic antiferroite structure. Such a difference in structure between a potassium and a caesium salt is not very common in this type of compound⁽¹⁸⁾ and implies that in the potassium salt the $\text{OsO}_2\text{Cl}_4^{2-}$ groups are oriented in one direction, whilst in the caesium salt orientation is random.

The behaviour of osmium oxytetrachloride in cooled 10 N hydrochloric acid is quite different; it dissolves to form an intensely green solution from which the addition of caesium chloride precipitates a dark green salt. The green colour is fugitive, and keeping, diluting, or warming the solution causes it to change to the yellow-orange tetrachloro-osmic acid. Its lability has hindered any spectral or other investigation of the solution. However, an examination of the dark green caesium salt showed that it (1) contains more chlorine than is required for the formula $\text{Cs}_2\text{OsO}_2\text{Cl}_4$, (2) varies slightly in composition, and (3) has a cubic structure of the antiferroite type with a unit cell slightly larger than that of $\text{Cs}_2\text{OsO}_2\text{Cl}_4$ and increasing in size with increasing chlorine content. On the basis of this evidence, it is tentatively suggested, first, that the colour of the solution is due to the green ionic species OsOCl_6^{2-} which results from the following reaction



and, secondly, that the caesium salt consists of $\text{Cs}_2\text{OsO}_2\text{Cl}_4$, though it is mixed with greater or lesser amounts of $\text{Cs}_2\text{OsOCl}_6$. An attempt to isolate pure $\text{Cs}_2\text{OsOCl}_6$ by conducting the reaction in cooled glacial acetic acid saturated with hydrogen chloride failed; only pure $\text{Cs}_2\text{OsO}_2\text{Cl}_4$ was obtained. SIDGWICK,⁽¹⁹⁾ quoting I. and W. NODDACK, reports the preparation of the rhenium compound K_2ReOCl_6 by adding potassium chloride to what is described as the brown solution of ReOCl_4 in hydrochloric acid at -10° . This experiment has been repeated here, but in the first place ReOCl_4 did not give a brown colour even when the hydrochloric acid was cooled to -40° , a transient deep purple being all that was noticed; and, secondly, the addition of caesium chloride to the stable pale green solution which was formed gave an obviously heterogeneous mixture of white caesium perrhenate and pale yellow caesium hexachlororhenate(IV).

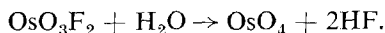
Osmium tetroxide is not attacked by fluorine at the ordinary temperature; actually, it is always formed during the fluorination of an osmium compound when moisture happens to be present; the fluorine then acts in its capacity as an oxidizing agent. However, when bromine trifluoride is used as a solvent and fluorinating agent, orange osmium trioxydifluoride, OsO_3F_2 , has been isolated together with a series of complex oxyfluoride salts of the general formula $\text{M}^1\text{OsO}_3\text{F}_3$ ($\text{M}^1 = \text{K}, \text{Cs}, \text{Ag}$) to which it gives rise. Alternatively, the new oxyfluoride may be prepared by the direct fluorination of the metal in the presence of oxygen. It is unique among the volatile fluorine compounds of osmium in that it does not attack dry Pyrex glass

⁽¹⁷⁾ J. L. HOARD and J. D. GRENKO *Z. Krist.* **87**, 100 (1934).

⁽¹⁸⁾ Cf. WYCKOFF *Crystal Structures* Vol II. Interscience, New York.

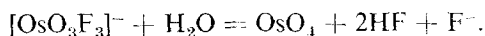
⁽¹⁹⁾ N. V. SIDGWICK *Chemical Elements and their Compounds* Vol. II p. 1302. Oxford University Press (1950).

and can be conveniently manipulated in an apparatus of this material. Moisture hydrolyses it rapidly,



Osmium trioxydifluoride may be regarded as derived from osmium tetroxide by the replacement of one oxygen by two fluorine atoms. Surprisingly, it is much less volatile than the parent oxide. A point of interest is that in both its simple oxyhalides, OsOCl_4 and OsO_3F_2 , osmium displays the unusual co-ordination number of 5.

The trifluoroperperosmates of which only the silver compound could be obtained pure, are orange salts, unaffected by dry air. Their solubilities in bromine trifluoride are in the reverse order of those found in the corresponding members of hexafluoro-osmate(V) series, ⁽¹⁰⁾ but are similar in this respect to those found by SHARPE⁽²⁰⁾ for the tetrafluoroaurates. Cold water dissolves them to form orange-yellow solutions which, on heating to just below the boiling-point, decolorise, liberating osmium tetroxide of which the liquid now smells strongly.



The formation and behaviour of these salts are not unlike those of a corresponding series of compounds derived from Re(VII) which have been prepared by PEACOCK⁽²¹⁾ and shown by him to have the general formula $\text{M}^1\text{ReO}_2\text{F}_4$ ($\text{M}^1 = \text{K}, \text{Rb}, \text{Cs}, \text{Ag}$).

MAGNETOCHEMISTRY OF Ru(VI) AND Os(VI)

The scanty literature on this subject is limited to the observations of MELLOR,⁽²²⁾ who found the complex nitrite $\text{K}_2[\text{OsO}_3(\text{NO}_2)_2] \cdot 3\text{H}_2\text{O}$ to be diamagnetic, and those of DWYER and HOGARTH,⁽²³⁾ who found the complex $[\text{Os}(\text{en-H})_3]_2 \cdot 3\text{H}_2\text{O}$ also to be diamagnetic. The character of these moments is surprising and in marked contrast to the paramagnetism expected for the presence of $2d_5$ electrons. The implication of the first of the measurements, as MELLOR pointed out, is open to question, since, the structure of the compound being unknown, the possibility of spin quenching by metal-metal interaction either directly, or through an oxygen bridge, cannot be ruled out.

On the other hand, the formulae $\text{Cs}_2\text{RuO}_2\text{Cl}_4$ and $\text{Cs}_2\text{OsO}_2\text{Cl}_4$ represent compounds of established structure in which the magnetic moment manifested might be expected to be a maximum one. In the event, both these compounds and also osmium oxytetrachloride were found to be diamagnetic, and it seems clear that the $2d_5$ electrons in Ru(VI) and Os(VI) compounds pair and cause the materials to be diamagnetic.

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This with other work has been carried out during the tenure of a British Titan Products Fellowship (M. A. H.).

⁽²⁰⁾ A. G. SHARPE *J. Chem. Soc.* 2901 (1949).

⁽²¹⁾ R. D. PEACOCK *J. Chem. Soc.* 602 (1955).

⁽²²⁾ D. P. MELLOR *J. Proc. Roy. Soc. N.S.W.* 77, 145 (1943).

⁽²³⁾ F. P. DWYER and J. W. HOGARTH *J. Amer. Chem. Soc.* 75, 1008 (1953).