Complex Fluorides of Iridium and Osmium.

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Complex fluorides of the general formula $M(\text{I})M(\text{V})F_6$, where $M(\text{I})$ = Li, Na, K, Rb, Cs, Ag, and $M(\text{V})$ = Ir, Os, involving quinquevalent iridium and osmium have been prepared and characterised. Further, the preparation of complexes of the formula $M(\text{I})_2M(\text{IV})F_6$, where $M(\text{I})$ = K, Cs, and $M(\text{IV})$ = Ir, Os, is also described. Evidence is presented to show that complexes of the types $M(\text{I})IrF_7$ and $M(\text{I})OsF_9$, where $M(\text{I})$ = Na, K, do not exist.

Hitherto the known complex halides of iridium and osmium were the chloride and bromide, and, for osmium only, the iodide. Those of iridium, derived from the sexacovalent element in the ter- and quadri-valent conditions, had the formulæ $M(\text{I})_3Ir(\text{III})Cl_6$ and $M(\text{I})_2Ir(\text{IV})Cl_6$ respectively; those of osmium included the isomorphous chloro-osmates $M(\text{I})_2Os(\text{IV})Cl_6$ and also a sexavalent series containing the osmyl, OsO_2, grouping.

Attempts to obtain complex fluorides from the chloroiridates and aqueous hydrogen fluoride were not successful (cf. Sharpe, *J.*, 1950, 3444). Schlesinger and Tapley (*J. Amer. Chem. Soc.*, 1924, **46**, 276), however, claim to have prepared K_2IrF_6 and $PbIrF_6$ from powdered iridium and potassium plumbifluoride, K_3HPbF_8. The classic work of Ruff and his collaborators (1913—1930), although mainly directed to the making of simple fluorides, *e.g.*, IrF_6, IrF_4, OsF_8, OsF_6, and OsF_4, included the observations that fluorination of metallic iridium or osmium intimately mixed with an alkali-metal fluoride, yielded white, salt-like substances. No analyses or further information about these compounds was given and the present communication describes a reopening of the subject in which, by using bromine trifluoride as the fluorinating agent, we have been able to prepare new complex fluorides. These compounds are of special interest in that they are the first in which the metals osmium and iridium have been shown to exhibit a valency of five.

Experimental

Complex Fluorides of Quinquevalent Iridium.—The bromine trifluoride was prepared as previously described (*J.*, 1954, 1197). As the reagent does not react at room temperature with metallic iridium and only slowly and very incompletely at its boiling point, a bromide was substituted for the element and proved ideal for the preparations. The iridium bromide was prepared by dissolving good-quality sodium chloroiridate (Found: Ir, 34·1. Calc. for $Na_2IrCl_6,6H_2O$: Ir, 34·4%) in 10% hydrochloric acid and heating the solution to 70—80° with a slight excess of "AnalaR" ammonium chloride. After 12 hr. the black crystals of ammonium chloroiridate were collected on a fritted-glass filter, well washed under suction with dilute hydrochloric acid, with 50% aqueous alcohol, both cooled to 0°, and, finally, with absolute alcohol [Found: Ir, 43·3. Calc. for $(NH_4)_2IrCl_6$: Ir, 43·6%]. The dried salt was warmed with aqua regia until it dissolved and the ammonium ion was destroyed; afterwards the solution was reduced to small bulk and twice evaporated to dryness following additions of 48% "AnalaR" hydrobromic acid. Gentle heating for 2 hr. in a platinum dish removed the remaining acid and left a black crystalline mass with a composition approximating to $IrBr_{3\cdot5}$ (Found: Ir, 40·9, 40·7, 39·8. Calc. for $IrBr_{3\cdot5}$: Ir, 40·8%). The temperature employed is critical; overheating gives material which reacts with bromine trifluoride only with difficulty.

(1) *Reaction of bromine trifluoride with iridium bromide.* Reaction occurred on warming and was rapidly completed on boiling. Evaporation of the red solution gave a buff residue: this, at 125° in a vacuum, evolved a vapour which condensed to a yellowish-brown, oily liquid and left behind a second, buff solid. A similar liquid was described by Ruff (*Z. anorg. Chem.*, 1929, **179**, 161) as iridium tetrafluoride, IrF_4, but the exact nature of both liquid and solid is still uncertain and is being investigated.

(2) *Reactions of bromine trifluoride with mixtures of potassium and iridium bromides.* (*a*) Mixture $KBr : IrBr_{3\cdot5} = 1 : 1$. Warmed together these produced *potassium hexafluoroiridate* (V), $KIrF_6$, a white solid sparingly soluble in bromine trifluoride and readily freed from bromine

by heating in a vacuum at 180° for 30 min. (Found: K, 11·5; Ir, 56·4; F, 34·0%; equiv., 354; loss on reduction in hydrogen, 26·7%. $KIrF_6$ requires K, 11·3; Ir, 55·8; F, 32·9%; equiv., 346; loss on reduction in hydrogen, 27·4%). The valency of the iridium was established by allowing a known weight of the compound to react with potassium iodide (2%) in 2N-sulphuric acid and titrating the iodine released; 2 equiv. of iodine were liberated per equiv. of iridium which was itself thereby reduced to the tervalent state, indicating that the metal in the complex had a valency of $3 + 2 = 5$. Potassium hexafluoroiridate(v) is stable in dry air but rapidly turns from white to reddish-violet in a moist atmosphere owing to formation of colloidal iridium hydroxide. With hydrochloric acid it liberates chlorine; its significant behaviour with water is described in detail below. Debye *X*-ray powder photographs showed that it is isostructural with potassium hexafluororuthenate(v), $KRuF_6$; it has a rhombohedral lattice with $a = 4{\cdot}98$ Å and $\alpha = 97{\cdot}4°$.

(*b*) Mixture KBr : $IrBr_{3\cdot5}$ = 2 : 1 and 3 : 1. Again the products were sparingly soluble in bromine trifluoride, the excess of which was readily removed under reduced pressure at room temperature, to leave pink residues which, on heating to 180° for 30 min. in a vacuum, left cream solids. *X*-Ray examination of both preparations indicated that they were largely potassium hexafluoroiridate(v); other lines present showed the solids contained respectively 1 and 2 equiv. of partially decomposed $KBrF_4$, *i.e.*, $KF,0{\cdot}5BrF_3$ (Found: Ir, 40·1%; equiv., 486. $KIrF_6,KF,0{\cdot}5BrF_3$ requires Ir, 40·9%; equiv., 472).

(3) *Cæsium, rubidium, and silver hexafluoroiridates*(v). Treatment of a 1 : 1 mixture of cæsium and iridium bromides with bromine trifluoride yielded *cæsium hexafluoroiridate*(v), a white solid almost insoluble in bromine trifluoride (Found: Ir, 44·0; F, 26·6%; equiv., 454. $CsIrF_6$ requires Ir, 43·9; F, 25·9%; equiv., 440). The quinquevalency of the iridium was clear since 2 equiv. of iodine were liberated; and *X*-ray examination, giving $a = 5{\cdot}26$ Å, $\alpha = 96{\cdot}2°$, showed it to be isostructural with the potassium salt which it closely resembles. In a like manner *rubidium hexafluoroiridate*(v), also a white powder, was obtained (Found: Ir, 48·4; F, 29·6%; equiv., 409. $RbIrF_6$ requires Ir, 49·2; F, 29·0%; equiv., 393). Similarly a 1 : 1 mixture of silver bromide and iridium bromide yielded *silver hexafluoroiridate*(v) (Found: Ir, 45·6; Ag, 26·3; F, 28·0%; equiv., 430. $AgIrF_6$ requires Ir, 46·5; Ag, 26·0; F, 27·5%; equiv., 415). This salt bears a remarkable resemblance to the corresponding silver hexafluororuthenate(v) in being soluble in warm bromine trifluoride and in possessing a deep orange colour the intensity of which increases on heating and diminishes on cooling.

(4) *Lithium and sodium hexafluoroiridates*(v). Starting with a 1 : 1 mixture of lithium or sodium bromides with the iridium bromide, the corresponding *hexafluoroiridates* were prepared. Whereas, however, the sodium and other salts here described were stable when heated to 180°, the lithium salts seemed to decompose slightly with, as would appear from the analysis, the loss of some iridium (Found: Ir, 53·8; F, 41·3%; equiv., 298. $LiIrF_6$ requires Ir, 61·5; F, 36·3%; equiv., 314. Found: Ir, 58·5; F, 34·8%; equiv., 356. $NaIrF_6$ requires Ir, 58·5; F, 34·5%; equiv., 330). Both the lithium and the sodium salt are white solids, insoluble in bromine trifluoride, and extremely sensitive to moisture which immediately darkens the surface.

(5) *Barium hexafluoroiridate*(v). A 1 : 2 mixture of barium bromate and iridium bromide gave white *barium hexafluoroiridate*(v). It is slightly soluble in bromine trifluoride, and is rapidly attacked by moisture with formation of superficial, reddish-violet iridium hydroxide [Found: Ir, 50·8; F, 30·9%; equiv., 741. $Ba(IrF_6)_2$ requires Ir, 51·4; F, 30·3%; equiv., 751].

Complex Fluorides of Quadrivalent Iridium.—(1) *Potassium hexafluoroiridate*(iv). Potassium hexafluoroiridate(v) (see above) was treated with the minimum amount of distilled water required to bring it into solution. Oxygen was immediately and rapidly evolved in the cold, and afterwards the solution was gently heated (not above 70°) to complete the reaction. After separation of a small quantity of iridium hydroxide, it was allowed to crystallise. Different specimens of potassium hexafluoroiridate(v) gave preparations which differed slightly: one, for example, left a pale yellow solution when the evolution of oxygen had ceased, which yielded very pale yellow crystals; another sample left a pale pink solution from which pale pink plates separated. The latter appear to correspond with crystals prepared by Schlesinger and Tapley (*loc. cit.*). Undoubtedly these were both *potassium hexafluoroiridate*(iv) (Found: Ir, 49·5; F, 30·4. K_2IrF_6 requires Ir, 50·1; F, 29·6%). Further crops of less pure crystals were obtained by adding concentrated potassium fluoride solution to either of the mother-liquors. Potassium hexafluoroiridate(iv) is slightly soluble in cold water to give an almost colourless solution which shows no hydrolysis after several days. In this respect the compound is more stable than the corresponding potassium fluororuthenate(IV), from which it also differs in its resistance to attack by chloride ions: even boiling with concentrated hydrochloric acid for some time leads to no trace of the characteristically coloured $IrCl_6^{--}$ ion. It is, however, reduced to the tervalent state by 48% hydrobromic acid and the solution turns green.

(2) *Cæsium hexafluoroiridate*(IV). Exactly analogous results were obtained when cæsium hexafluoroiridate(V) was treated with water. Oxygen was evolved, and pale pink or yellow solutions gave correspondingly coloured crystals of *cæsium hexafluoroiridate*(IV) [Found: Ir, 33·4 (pink), 34·4 (yellow); F, 20·4 (pink), 20·4 (yellow); Cs, 46·6 (yellow). Cs_2IrF_6 requires Ir, 33·7; F, 19·9; Cs, 46·4%], whose properties closely resemble those of the potassium salt.

(3) *Barium hexafluoroiridate*(IV). When barium hexafluoroiridate(V) was warmed with water, oxygen was evolved and a pale pink precipitate remained. The mother-liquor yielded more of the same precipitate when barium nitrate was added. The latter was pure *barium hexafluoroiridate*(IV) (Found: Ir, 43·1; F, 25·9. $BaIrF_6$ requires Ir, 43·5; F, 25·7%). The salt is almost insoluble in water. *X*-Ray examination shows it to have a rhombohedral lattice with $a = 4{\cdot}90$ Å, $\alpha = 97{\cdot}8°$.

(4) Both iridium and silver hexafluoroiridates(V) were tried but the reddish-violet solutions contained much colloidal iridium oxide from which crystals were difficult to isolate.

Possible Sexavalent Complex Fluorides of Iridium.—Ruff (*loc. cit.*) demonstrated the extreme reactivity of iridium hexafluoride, and, to get it in a pure form, fluorinated metallic iridium in a fluorite tube and subsequently manipulated the product in silica apparatus. In these laboratories it has been found that many reactive materials can be conveniently prepared in alumina tubes and we have found them completely satisfactory for this preparation. Fluorine, freed from hydrogen fluoride by passage over sodium fluoride pellets followed by a trap at −180°, and diluted with nitrogen, was passed over iridium. The metal was in the active, finely divided condition resulting from the reduction of ammonium chloroiridate in hydrogen at a low temperature. The operation was carried out in an alumina boat in a 0·75-in. alumina tube, the temperature of which was slowly raised until, at about 300°, the iridium reacted with great vigour. The bright yellow hexafluoride vapour was collected at −65° in a silica train, whence, after purification by trap-to-trap distillation in a vacuum, it was condensed on to well-dried potassium fluoride in a silica bulb. No evidence of reaction was observed when the mixture was heated to the boiling point of the iridium hexafluoride and, furthermore, all the iridium hexafluoride was easily removed by maintaining a vacuum at room temperature. These careful observations agree with those of Ruff (*loc. cit.*) and establish the absence of sexavalent iridium complexes.

Complex Fluorides of Quinquevalent Osmium.—(1) The extent to which osmium reacts with bromine trifluoride and the ease with which this takes place depend markedly on the state of the metal. Some samples reacted quietly and completely at about 30°; others even prolonged boiling in the bromine trifluoride failed to bring completely into solution. Hence recourse was had to a material consisting essentially of osmium tetrabromide, $OsBr_4$. Metallic osmium (3 g.) was burnt in a porcelain boat in a current of oxygen, and the volatile tetroxide carried forward was collected in a trap cooled with liquid air; the further arm of the trap was attached by a " Quickfit " joint to a vertical water-cooled condenser. The trap and its contents were sealed off from the reaction tube, and a mixture of " AnalaR " 48% hydrobromic acid (50 c.c.) and absolute alcohol (3 c.c.) was poured through the condenser on to the osmium tetroxide where it was vigorously refluxed for 8 hr., by which time the liquid was an intense deep red. It was first evaporated gently in a platinum dish to remove free hydrobromic acid, and then heated over a small flame for 2 hr. to convert the sticky mass into black, friable, crystalline *osmium tetrabromide* (Found: Os, 37·7; Br, 63·1. $OsBr_4$ requires Os, 37·4; Br, 62·6%).

This osmium tetrabromide dissolved in bromine trifluoride, even below room temperature; it gave a pale red solution which left a pale buff residue after the solvent had been removed in a vacuum at room temperature. Heated, still under vacuum, to 110°, this turned pale violet and later evolved (i) a more readily volatile material which froze to a brown solid in a liquid-air-cooled trap, and (ii) a smaller quantity of a less volatile substance which formed an orange sublimate on the upper surface of the reaction vessel. Both these products retained bromine with tenacity and are still under investigation.

(2) *Potassium bromide–osmium tetrabromide* (1 : 1). This reacted readily with bromine trifluoride at room temperature, completion being marked by the appearance of a white precipitate. Removal of excess of bromine trifluoride in a vacuum at room temperature followed by heating the residue to 190° for 30 min. left *potassium hexafluoro-osmate* as a white

powder (Found: Os, 54·6; F, 33·4%; equiv., 347. $KOsF_6$ requires Os, 55·5; F, 33·1%; equiv., 343). By titration after an appropriate amount of the complex had been added to approximately 1 g. of potassium iodide in 50 ml. of 2N-sulphuric acid, it was shown that one equiv. of iodine was liberated. Hence the valency of the osmium is $4 + 1 = 5$. *X*-Ray examination showed it to be isostructural with $KRuF_6$ and $KIrF_6$; the rhombohedral lattice has $a = 4{\cdot}99$ Å, $\alpha = 97{\cdot}2°$. Potassium hexafluoro-osmate(V) is stable in dry air; in the presence of moisture it soon smells of osmium tetroxide and eventually turns black. This hydrolytic decomposition is much slower, however, than that of the corresponding hexafluororuthenate(V) and hexafluoroiridate(V) in a similar environment; these deliquesce very rapidly. This characteristic is reflected in the reaction with water described below.

(3) *Cæsium bromide–osmium tetrabromide* (1 : 1). Similarly *cæsium hexafluoro-osmate*(V) was obtained as a white powder insoluble in bromine trifluoride (Found: Cs, 30·8; F, 25·8. $CsOsF_6$ requires Cs, 30·4; F, 26·0%). It liberated one equiv. of iodine, hence the osmium is again quinquevalent; furthermore, it closely resembles the potassium salt. *X*-Ray examination showed it to be isostructural with the corresponding cæsium hexafluoroiridate(V), the lattice being rhombohedral with $a = 5{\cdot}28$ Å, $\alpha = 96{\cdot}13°$.

(4) *Sodium and silver hexafluoro-osmates*(V). Fluorination of 1 : 1 mixtures of osmium tetrabromide with sodium and silver bromides respectively yielded the hexafluoro-osmates(V). *Sodium hexafluoro-osmate*(V) is white, slightly soluble in bromine trifluoride, and very like the potassium salt (Found: Os, 58·5; F, 35·2. $NaOsF_6$ requires Os, 58·0; F, 34·8%). *Silver hexafluoro-osmate*(V) is pale orange and notably soluble in bromine trifluoride; in these respects it resembles the corresponding hexafluoro-ruthenate and -iridate though the colour is lighter (Found: Ag, 25·7; F, 27·4. $AgOsF_6$ requires Ag, 26·1; F, 27·6%).

Complex Fluorides of Quadrivalent Osmium.—(1) *Potassium hexafluoro-osmate*(IV). Potassium hexafluoro-osmate(V) dissolved in water to form a colourless solution which, at first odourless, through a slow hydrolysis shortly smelt of osmium tetroxide. On the addition of 1 equiv. of potassium hydroxide to a freshly prepared solution, an orange colour immediately developed, oxygen was copiously evolved, and crystals began to form. The preparation was kept in the refrigerator for 12 hr., and the pale yellow crystals of *potassium hexafluoro-osmate*(IV) were separated on a glass filter (suction), and well washed with successive quantities of ice-cold water and finally with absolute alcohol (Found: Os, 49·0; F, 30·2. K_2OsF_6 requires Os, 49·7; F, 29·6%). These crystals, though much less sensitive to hydrolysis, resemble the corresponding potassium hexafluororuthenate(IV) very closely. They are sparingly soluble in cold water and the solution appears to be stable for several days at least; indeed, their mode of preparation shows a resistance to hydrolysis even by alkalis. In the presence of hydrogen ions exchange with chloride ions readily takes place: $OsF_6^{--} + 6Cl^- \xrightarrow{H^+} OsCl_6^{--} + 6F^-$, shown by the fact that warming with dilute hydrochloric acid slowly produced the readily recognisable yellow colour of the $OsCl_6^{--}$ ion. This change is accelerated by increasing the temperature and the concentration of the acid; it does not occur in the absence of hydrogen ions. With sulphuric acid an intense brown colour develops slowly which is very similar to that of a ruthenium(IV) sulphate solution; it is probably due to the analogous osmium(IV) sulphate.

(2) *Cæsium hexafluoro-osmate*(IV). Cæsium hexafluoro-osmate(V) was dissolved in water and formed a colourless solution which rapidly developed a smell of tetroxide. The addition of an equal volume of alcohol to the freshly made solution precipitated pale yellow crystals of *cæsium hexafluoro-osmate*(IV) (Found: Os, 32·5; F, 20·7. Cs_2OsF_6 requires Os, 33·3; F, 20·0%). It closely resembles the potassium salt, and on warming with concentrated hydrochloric acid turns yellow and precipitates orange Cs_2OsCl_6. Attempts to prepare the silver salt, Ag_2OsF_6, by this method were not successful, probably owing to its higher solubility in water

The Absence of Complex Fluorides of Octavalent Osmium.—Fluorine (10 g. per hr.), free from hydrogen fluoride and diluted with nitrogen, was passed over metallic osmium (1 g.) in a nickel boat in an electrically heated alumina tube. Reaction began at 180° and was complete at 200°; the osmium octafluoride carried by the gas stream separated in a trap cooled in liquid air. The yield was almost theoretical; a slight blackening at the outlet when the temperature was raised to 300° to remove lower fluorides showed a trace of these, but no residue remained in the nickel boat (cf. Ruff and Tschirch, *Ber.*, 1913, **46**, 929). The octafluoride was purified by trap-to-trap distillation and finally frozen in an evacuated bulb containing sodium or potassium fluorides. It was melted and then boiled for about 30 min.

but the white, alkali-metal fluorides simply remained suspended in the boiling, pale red octafluoride. When the latter was subsequently removed under a vacuum at room temperature, the weight increases of the solids showed little retention of osmium: 0·387 g. of sodium fluoride increased by 0·133 g., and 0·191 g. of potassium fluoride by 0·048 g., in conformity with an unpublished observation by Peacock, who found that 0·030 g. of potassium fluoride increased by 0·010 g. Both residues were white, smelt of osmium tetroxide, and gave a yellow colour with alkali, but combination, if it occurred, was less than 4—5%, certainly not enough to justify an assumption of the existence of $NaOsF_9$ or $KOsF_9$. Ruff's statement that osmium octafluoride combines with alkali-metal fluorides with " unusual ease " to form salt-like addition products which can also be obtained by passing fluorine over a heated mixture of osmium powder and the alkaline fluoride, though quoted in recent texts, is clearly incorrect. The first reaction does not take place, and the second yields a hexafluoro-osmate(v).

Analysis.—Iridium. Attempts to precipitate the oxide by hydrolysis in aqueous solution proved, as Sharpe and Emeléus (*J.*, 1948, 2135) found for platinum in corresponding complexes, incomplete in a fluoride solution (*e.g.*, Ir, 51·6 in place of 55·8%). Satisfactory results were obtained only by heating the complex with fusion mixture in a platinum dish, leaching the melt with water, and collecting the oxide on a Whatman 541 paper. The precipitate was well washed with hot 2% ammonium sulphate solution, ignited in a platinum crucible, reduced in hydrogen, and weighed as metal.

Osmium. Fusing the complexes in a platinum dish with fusion mixture in an atmosphere of hydrogen with a view to securing the metal in one stage was tried, but gave low results (*e.g.*, Os, 52·6 in place of 55·5%). Thereafter quinquevalent osmium was determined simply by titrating the iodine liberated from potassium iodide in 2N-sulphuric acid with sodium thiosulphate. On the other hand, quadrivalent osmium complexes were treated with sulphuric acid to remove fluorine as fluosilicic acid, the resulting brown osmium(IV) sulphate was diluted with water, and the element determined in this solution by titration with 0·1N-potassium permanganate, 4 equiv. of which are required to oxidise it to the octavalent state.

Fluorine. This was determined as lead chlorofluoride, either directly in the filtrate after the removal of the " platinum " metal, or in the fluosilicic acid distillate produced by heating the compound with sulphuric acid.

Alkali metals and silver. The complex was reduced in hydrogen, the residue extracted with water, and the resulting solution evaporated with sulphuric acid in a platinum dish. After ignition to a dull red heat the alkali metal was weighed as sulphate. Silver was determined as the chloride.

X-*Ray Photographs.*—A 0·5-mm. capillary was charged with the complex fluoride, the dry-box technique being employed. Photographs were taken by using a 19-cm. camera and Fe-K_α radiation in conjunction with a lithium fluoride monochromator.

DISCUSSION

Table 1, covering only the potassium salts, shows our present view of the relationship between the complex fluorides of the platinum metals. With one exception, namely K_3RhF_7, the complexes are of two types: (i) $KM(v)F_6$ restricted to ruthenium, osmium, and iridium which are able to exhibit valencies higher than four, and (ii) $K_2M(IV)F_6$ common to all six metals.

TABLE 1

$KRuF_6$ (1)	K_2RhF_6 (3)	K_2PdF_6 (5) (6)
K_2RuF_6 (1)	K_3RhF_7 (4)	
$KOsF_6$ (2)	$KIrF_6$ (2)	K_2PtF_6 (4)
K_2OsF_6 (2)	K_2IrF_6 (2)	

References: (1) Hepworth, Peacock, and Robinson, *J.*, 1954, 1197. (2) Present work. (3) Weise and Klemm, *Z. anorg. Chem.*, 1953, **272**, 211. (4) Sharpe, *J.*, 1950, 3444. (5) *Idem, J.*, 1953, 197. (6) Hoppe and Klemm, *Z. anorg. Chem.*, 1952, **268**, 364.

(i) *Type* $KM(v)F_6$.—This type is unique in the series of metals in that ruthenium, osmium, and iridium exhibit the unusual valency of five, for previously only one compound containing quinquevalent osmium had been prepared (Dwyer and Hogarth, *J. Amer. Chem. Soc.*, 1953, **75**, 1008) and none containing quinquevalent iridium. No simple pentafluorides of either osmium or iridium corresponding with this series of complexes are known, but work proceeding in these laboratories gives promise of leading to their isolation.

Magnetic measurements kindly made for us on these complexes by Dr. J. K. Dawson and by Professor R. S. Nyholm are summarised in Table 2.

TABLE 2

$KRuF_6$, 3·6 B.M. *	$KOsF_6$, 3·2 B.M. *	$KIrF_6$, 1·18 B.M. †
$CsRuF_6$, 3·83 B.M. †	$NaOsF_6$, 3·05 B.M. †	$NaIrF_6$, 1·23 B.M. †
$AgRuF_6$, 3·70 B.M. †	$AgOsF_6$, 2·95 B.M. †	$AgIrF_6$, 1·24 B.M. †
Cs_2RuF_6, 2·98 B.M. †	K_2OsF_6, 1·35 B.M. †	

* Dawson † Nyholm

The moments of the hexafluororuthenates(v) definitely show the presence of three unpaired electrons on the ruthenium atom. These moments have the highest values so far found among the relatively few magnetic measurements as yet made on the platinum metals. The moment of cæsium hexafluororuthenate(iv), however, corresponds to that required for two unpaired electrons. The bonding in these ruthenium complexes is clearly of the d^2sp^3 type, the six fluorine atoms being at the corners of an octahedron centred on the heavy metal atom. A study of the structure of these compounds at present being made confirms this view.

The moments of the hexfluoro-osmates(v) thus far measured leave little doubt that the osmium atoms also have three unpaired electrons. The values are all less than that calculated for the postulated electronic condition, but a similar discrepancy between calculated and determined moments is found in other osmium compounds (*e.g.*, K_2OsCl_6 where μ calc. is 2·83 B.M. and μ found only 1·44 B.M.); indeed it happens in the case of K_2OsF_6 shown above, where the depression is of the same order as that found in the chloro-complex just instanced.

TABLE 3

		Outer electron configuration			
Element	Bonding	$(n-1)\ d$	*ns*	*np*	μ, calc., B.M.
Ru(v)	$4d^25sp^3$	[↓][↓][↓][↓↑][↓↑]	[↓↑]	[↓↑][↓↑][↓↑]	3·88
Ru(iv)	$4d^25sp^3$	[↓][↓][↓↑][↓↑][↓↑]	[↓↑]	[↓↑][↓↑][↓↑]	2·83
Os(v)	$5d^26sp^3$	[↓][↓][↓][↓↑][↓↑]	[↓↑]	[↓↑][↓↑][↓↑]	3·88
Os(iv)	$5d^26sp^3$	[↓][↓][↓↑][↓↑][↓↑]	[↓↑]	[↓↑][↓↑][↓↑]	2·83
Ir(v)	$5d^26sp^3$	[↓][↓][↓↑][↓↑][↓↑]	[↓↑]	[↓↑][↓↑][↓↑]	2·83

In the hexafluoroiridates(v) the moments are of the same order as that of the Os(iv) complex, and the respective co-ordinating atoms possess the same outer electronic configuration. It may reasonably be supposed, as Nyholm (personal communication) suggested, that in the iridates there has been a break-down of Hund's rule of maximum multiplicity, and that the iridium atoms, despite the low moments observed, possess two unpaired electrons.

The alkali-metal salts are nearly all insoluble in bromine trifluoride; in this respect they are analogous to the isostructural barium fluorosilicate(iv) and fluorogermanate(iv) which are insoluble in water. A peculiarity of the ruthenium series is an apparent, possibly a real, inability to form a sodium salt; this suggested there was a limit to the size of the alkali-metal cation below which salts of this type were not formed (Hepworth, Peacock, and Robinson, *loc. cit.*). The present work has shown, however, that both sodium hexafluoro-osmate(v) and hexafluoroiridate(v) can be readily prepared and that even lithium hexafluoroiridate(V) can be obtained, although it is evidently less stable since it suffered some thermal decomposition at the temperature of preparation. As the dimensions of the RuF_6^-, OsF_6^-, and IrF_6^- ions are very similar, some explanation, other than that depending solely on the effect of size of the positive ion, must be sought for the absence of a sodium hexafluororuthenate(V). A knowledge of the relative strengths of the hypothetical " acids " $(BrF_2)RuF_6$, $(BrF_2)OsF_6$, and $(BrF_2)IrF_6$ might well explain the anomaly.

Sharpe (*J.*, 1950, 3444) has pointed out the need for choosing correct proportions of " acid " and " base " in preparing a complex by means of bromine trifluoride, and the possibility of subsequent solvolysis leading to an impure preparation. The main products of thermal decomposition of the " acids " mentioned above, when they are heated in a vacuum, are, however, volatile and, unlike those of other " acids " such as $(BrF_2)_2PtF_6$ and $(BrF_2)_2PdF_6$, can be readily removed by evaporation. Excess of " acid " may thus be safely employed in preparations involving the use of the first kind, the advantage being two-fold: (*a*) visual evidence is afforded of the extent to which salt formation has proceeded when the residue is heated above 120° in a vacuum; (*b*) solvolysis is reduced to a minimum and the purity of the resulting complex is assured. In practice only very small excesses of " acid " are found to be necessary to ensure satisfactory preparations.

With water the various MF_6^- ions undergo a complicated change of which the essentials may be represented thus: $4MF_6^- + 2H_2O \longrightarrow 4MF_6^{--} + 4H^+ + O_2$. This reaction occurs readily with the RuF_6^- and IrF_6^- ions even in the cold. The OsF_6^- ion is different; initially it appears to dissolve in water without obvious change, and the above reaction only takes place after the pH has been raised above 7 by the addition of alkali. The ion can, however, oxidise aqueous alcohol as is illustrated in the preparation of Cs_2OsF_6 (p. 4272). Furthermore, both the ruthenium and osmium complexes disproportionate with the formation of small amounts of their respective tetroxides. Disproportionation reactions are not feasible in the iridium complexes owing to the instability of the element's higher valency states in aqueous solution; a little quadrivalent oxide is found to separate as a black precipitate or to remain in a colloidal suspension.

(ii) *Type* $K_2M(IV)F_6$.—In general, these complexes are similar in physical and chemical properties to K_2PtF_6, first described in detail by Sharpe (*loc. cit.*). Qualitatively their resistance to hydrolysis appears to increase in the following order: $PdF_6^{--} < RhF_6^{--} < RuF_6^{--} < PtF_6^{--} < IrF_6^{--}$, OsF_6^{--}. In the presence of hydrogen ions ready interchange with simple halide ions takes place according to the scheme: $6MF_6^{--} + 6Cl^- \xrightarrow{H^+} 6MCl_6^{--} + 6F^-$. Iridium is something of an exception in that the reaction is exceptionally slow with chloride ions but faster with bromide owing, presumably, to the accompanying reduction which they cause.

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