Complex Fluorides of Quadri- and Quinque-valent Ruthenium.

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[Reprint Order No. 4835.]

Work on the complex fluorides of ruthenium has been continued; those involving the metal in the quadri- and quinque-valent states are described. Ability to prepare fluororuthenates of the type $M(\textsc{i})RuF_6$ and $N(\textsc{ii})(RuF_6)_2$ depends upon the ionic radius of M(I) and N(II) and appears to be restricted to ions with values of 0·99 Å and above.

Before the subject was studied in these laboratories, the known halide complexes of quadrivalent ruthenium were restricted to those involving only chlorine or bromine. They had a co-ordination number of 6 and were of the types M_2RuCl_6 and $M_2RuCl_5(OH)$. Furthermore, the only quinquevalent compound of ruthenium described in the literature was the simple pentafluoride. The series of new compounds formulated below and now described show that this view of the fluorine chemistry of ruthenium calls for extensive revision.

Quadrivalent ruthenium : K_2RuF_6, Cs_2RuF_6.

Quinquevalent ruthenium : $KRuF_6$, $CsRuF_6$, $AgRuF_6$, $TlRuF_6$, $Ca(RuF_6)_2$, $Sr(RuF_6)_2$, $Ba(RuF_6)_2$.

Since the complexes of quadrivalent are derived from those of quinquevalent ruthenium, it is convenient to begin with the latter.

Complex Fluorides of Quinquevalent Ruthenium.—Recently it was shown (Aynsley, Peacock, and Robinson, *Chem. and Ind.*, 1952, 1002) that a white substance having a composition corresponding to K_2RuF_8 could be obtained by the action of elementary fluorine on potassium chlororuthenate at 200°. At the time, this was assumed to be a true complex fluoride of sexavalent ruthenium, principally on the evidence of *X*-ray photographs in which the accompanying presence of potassium fluoride or other potassium salt was not disclosed. Klemm (personal communication) has pointed out, however, that the magnetic behaviour of this material suggests that it is more probably a mixture of a new quinquevalent complex fluoride, potassium hexafluororuthenate(V), $KRuF_6$, and Bode and Wendt's potassium difluoride, KF_2 (*Naturwiss.*, 1950, **37**, 477). The preparation of the pure potassium hexafluororuthenate(V), described below, and its *X*-ray examination leave little doubt as to the correctness of this view.

In the course of a further investigation of these complexes we have used bromine trifluoride as the fluorinating agent (cf. Sharpe, *J.*, 1950, 3444). Metallic ruthenium reacts violently at room temperature with this reagent, forming a brownish solution which, after removal of the solvent in a vacuum at room temperature, yields a pale cream solid bromofluoride with the composition $RuBrF_8$. When heated to 120° in a vacuum, this compound melts with decomposition forming emerald-green droplets of ruthenium pentafluoride, RuF_5, and bromine trifluoride which volatilises easily: $RuBrF_8 \longrightarrow RuF_5 + BrF_3$. Prepared in this manner, ruthenium pentafluoride can be readily purified by a simple vacuum-distillation into a side-arm receiver where it condenses and sets to a pale green crystalline mass. Under the rigorously dry conditions of this preparation, ruthenium pentafluoride can be conveniently handled in glass apparatus with very little evidence of attack. Indeed, this operation probably constitutes the easiest method of obtaining in a pure form the highly reactive and deliquescent pentafluoride.

Of special interest is the reaction of bromine trifluoride with a mixture of potassium bromide and ruthenium metal in the ratio KBr : Ru = 1 : 1. This leads to the formation of a new complex fluoride, potassium hexafluororuthenate(V), $KRuF_6$, which had an *X*-ray pattern identical with that of the material previously reported as K_2RuF_8. That the former is the true complex fluoride of ruthenium was demonstrated in the course of an examination of the products resulting from the action of bromine trifluoride on mixtures of potassium bromide and ruthenium metal in the ratios KBr : Ru = 1 : 2, 2 : 1, and 3 : 1. The residue from the ruthenium-rich mixture, on being heated to 120° in a vacuum, evolved ruthenium pentafluoride and left $KRuF_6$ behind; the products from the other two mixtures, after being heated at 180° in a vacuum, contained, respectively, 1 and 2 equivs. of potassium fluorobromite, $KBrF_4$. Assuming the compound $RuBrF_8$ to be formulated as $(BrF_2)^+(RuF_6)^-$, we may postulate the following reaction as leading to the formation of $KRuF_6$:

$$KBrF_4 + (BrF_2)^+(RuF_6)^- \longrightarrow KRuF_6 + 2BrF_3$$

Similar reactions involving cæsium chloride and silver bromide lead to the formation of the cæsium and silver salts, $CsRuF_6$ and $AgRuF_6$, respectively. The corresponding salts of the bivalent alkaline earth barium, strontium, and calcium metals, which have the general formula $N(RuF_6)_2$ may also be prepared by using the bromate of the particular metal along with its equivalent of ruthenium.

On the other hand, attempts to obtain the sodium salt by treating 1 : 1 or 2 : 1 equivalent mixtures of sodium bromide and ruthenium failed. Presumably the salt $NaRuF_6$ is completely solvolysed in bromine trifluoride to $NaBrF_4$ and $RuBrF_8$. The residues when heated above 120° in a vacuum lost the whole of their ruthenium as the volatile pentafluoride, RuF_5. A similar result attends the heating of the product from the action of bromine trifluoride on a 1 : 1 equivalent mixture of thallous bromide and ruthenium; in this instance, however, the issue is complicated by the fact that 80—90% of the thallium is oxidised to the thallic form when dissolved in bromine trifluoride (Emeléus and Sharpe, *J.*, 1948, 2135). These results accord well with the behaviour of iron. We find that the action of elementary fluorine at 300° on an intimate mixture of iron and ruthenium, both in the metallic form, leads to the separate formation of ruthenium pentafluoride, which distils as it is produced, and of ferric fluoride, which remains behind. It is not obvious why certain metallic ions, *e.g.*, Na^+, fail to form salts with the RuF_6^- ion; but it seems fairly certain that the radius of the cation is involved. This is clearly demonstrated by the behaviour of the metal thallium which, as pointed out above, fails entirely to form a thallic salt, and yet can, given suitable conditions, yield the thallous salt, $Tl(I)RuF_6$. These conditions we have realised by using the hitherto unexploited fact that thallous fluoride is soluble in selenium tetrafluoride to form thallous selenofluorite, $Tl(I)SeF_5$ (Aynsley, Peacock, and Robinson, *J.*, 1952, 1231). By mixing solutions of ruthenium pentafluoride and thallous fluoride, each in selenium tetrafluoride, the thallous hexafluororuthenate(V), $TlRuF_6$, is formed. When this series of complex fluorides is tabulated against the values for the ionic radius of the respective cations (data from Wells, "Structural Inorganic Chemistry," Oxford Univ. Press, 1945, p. 93), the influence of this factor on the ability of the cation to form a ruthenium(V) salt is clearly displayed. Cations with a radius below about 0·99 Å appear to be ineffective.

Cation	Ionic radius (Å)	Salt	Cation	Ionic radius (Å)	Salt	Cation	Ionic radius (Å)	Salt
K^+	1·33	$KRuF_6$	Ba^{++}	1·35	$Ba(RuF_6)_2$	Na^+	0·95	None
Cs^+	1·69	$CsRuF_6$	Sr^{++}	1·12	$Sr(RuF_6)_2$	Tl^{+++}	0·95	None
Ag^+	1·26	$AgRuF_6$	Ca^{++}	0·99	$Ca(RuF_6)_2$	Fe^{+++}	0·60	None
Tl^+	1·44	$TlRuF_6$						

The complex salts just mentioned are cream-coloured solids, with the exception of those of silver and thallium(I), which are orange. They are all stable in dry air. The barium salt did not commence to decompose in a vacuum below 400°: it evolved a fume of ruthenium pentafluoride. In moist air the salts are rapidly attacked; they blacken on the surface and have the odour of ruthenium tetroxide, RuO_4. Their behaviour with water, which decomposes them rapidly, is complicated: it has been studied in detail and is described below.

Complex Fluorides of Quadrivalent Ruthenium.—When warmed with a small quantity of water, potassium and cæsium hexafluororuthenate(V) both slowly dissolve to give pale yellow solutions. The solutions evolve oxygen and have a decided smell of ruthenium tetroxide. When cooled they deposit crystals of potassium hexafluororuthenate(IV), K_2RuF_6, and the corresponding cæsium salt, respectively, as pale yellow plates. Further crops of less pure crystals may be obtained by adding concentrated solutions of potassium or cæsium fluoride to the respective mother-liquors. The evidence leads us to believe that reaction may be represented by equation (1), but the fact that ruthenium tetroxide is

$$4RuF_6^- + 2H_2O \longrightarrow 4RuF_6^{--} + 4H^+ + O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

produced at the same time as the oxygen must indicate a certain degree of concurrent disproportionation, most probably according to (2). The amount of Ru(VIII) (*i.e.*, Ru as RuO_4) produced is, however, very small, and the disproportionation shown in (2) probably involves less than 10% of the material which originally reacted with water.

$$4Ru(v) \longrightarrow Ru(viii) + 3Ru(iv) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Potassium hexafluororuthenate(IV) is slightly soluble in water, giving a colourless solution in which the compound is not immediately hydrolysed, but which decomposes in 1—2 hr. with precipitation of black, hydrated ruthenium dioxide. Exactly as has been found by Sharpe (*J.*, 1950, 3444) for the corresponding platinum salt, K_2PtF_6, there is no interaction with chloride ions in the absence of hydrogen ions. In the presence of these, however, as when hydrochloric acid is used, the reaction

$$RuF_6^{--} + 6Cl^- \xrightarrow{H^+} RuCl_6^{--} + 6F^-$$

proceeds; its course is shown by the development of an intense red-brown colour in the solution, readily recognisable as due to the chlororuthenate ion. The rate is accelerated by warming of the solution and by increase in the concentration of the acid.

EXPERIMENTAL

Reagents.—Bromine trifluoride was prepared from bromine which had been dried (P_2O_5) and distilled in a vacuum. Over this was passed, at the rate of 6 g./hr., hydrogen fluoride-free fluorine diluted with nitrogen, the reaction taking place in a Pyrex vessel cooled in a bath of cold water. The product was distilled in a vacuum, and the middle fraction employed by condensing it on the reactants. Ruthenium metal, in the form of a fine powder, was dried in a vacuum along with the other solids before use. Because chlorides were found to give products of a somewhat different colour and generally of a less reactive character, bromides were selected in the case of the alkali metals; and because of the deliquescence of the simple halide, bromates in that of the alkaline-earth metals.

Fluorides of Quinquevalent Ruthenium.—Ruthenium with bromine trifluoride. The reaction began at 10—15° with liberation of bromine and of sufficient heat to raise the metal rapidly to incandescence; but the action was readily controlled by appropriate cooling with liquid oxygen. Care was required, however, when the quantities used reached the order of 1 g. The removal of excess of bromine trifluoride in a vacuum at room temperature left a cream-coloured solid, $RuBrF_8$, (Found: Ru, 30·8%; equiv., 326. $RuBrF_8$ requires R, 30·5%; equiv., 333·7); this new *ruthenium bromo-octafluoride* reacts vigorously with water, giving a black precipitate of hydrated ruthenium dioxide, some ruthenium tetroxide, and hydrolysis products of bromine trifluoride. When heated to 120° in a vacuum, it melts with decomposition, forming ruthenium pentafluoride and bromine fluorides. By raising the temperature to 150—160° and maintaining the vacuum, the ruthenium pentafluoride can be readily distilled into a side-arm receiver where it condenses to a pale green crystalline mass (Found: Ru : F = 1 : 4·95).

Mixtures of ruthenium and potassium bromide with bromine trifluoride. (*a*) Mixture, Ru : KBr = 1 : 1. Reaction occurred at room temperature with formation of a cream precipitate insoluble in excess of bromine trifluoride. When this excess had been removed in a vacuum, the product was heated to 180° for 30 min. and yielded *potassium hexafluororuthenate*(V), a cream-coloured powder (Found: Ru, 39·4; K, 15·3; F, 44·5. $KRuF_6$ requires Ru, 39·9; K, 15·2; F, 44·9%). The quinquevalency was established by liberation of iodine from potassium iodide using Crowell and Yost's method (*J. Amer. Chem. Soc.*, 1928, **50**, 37).

(*b*) Mixture, Ru : KBr = 2 : 1. The product, after the excess of bromine trifluoride had been removed in a vacuum, evolved, on further heating to 120° in a vacuum, half the ruthenium present as ruthenium pentafluoride. Clearly it was a mixture of potassium hexafluororuthenate(V) and ruthenium bromo-octafluoride, $RuBrF_8$.

(*c*) Mixtures, Ru : KBr = 1 : 2 and 1 : 3. Again the products were mixtures. After being heated at 180° in a vacuum for 1 hr. the residue consisted of *complexes* of $KRuF_6$ with respectively 1 and 2 equivs. of potassium tetrafluorobromite, $KBrF_4$ (Found: equiv., 440.

$KRuF_6,KBrF_4$ requires equiv., 449. Found: equiv., 625. $KRuF_6,2KBrF_4$ requires equiv., 644).

Preparation of cæsium, silver, barium, calcium, and strontium salts. The fluorination by bromine trifluoride of a 1 : 1 mixture of cæsium chloride and ruthenium metal yielded *cæsium hexafluororuthenate*(V) as a creamy-white solid, sparingly soluble in bromine trifluoride (Found: Ru, 28·4; Cs, 38·0. $CsRuF_6$ requires Ru, 29·2; Cs, 38·2%). In a similar manner, the *silver* salt is formed, as an orange powder soluble in bromine trifluoride, on use of a 1 : 1 mixture of silver bromide and ruthenium metal (Found: Ru, 32·0; Ag, 32·7. $AgRuF_6$ requires Ru, 31·3; Ag, 33·4%). For the corresponding salts of the alkaline earths, mixtures of their bromates and ruthenium metal in the molecular proportions 1 : 2 were treated with bromine trifluoride. The products, which were slightly soluble in bromine trifluoride, could be heated to 200° in a vacuum without evolving any ruthenium pentafluoride, and left as residues a cream-coloured powder in every case [Found: Ru, 42·7; F, 47·6. $Ca(RuF_6)_2$ requires Ru, 43·1; F, 48·4. Found: Ru, 38·6; F, 44·4. $Sr(RuF_6)_2$ requires Ru, 39·1; F, 44·0. Found: Ru, 34·1; F, 39·5%; Ba equiv., 561. $Ba(RuF_6)_2$ requires Ru, 35·6; F, 40·0%; Ba equiv., 568]. In order to ascertain approximately the stability of these *compounds*, the barium salt was heated in a vacuum, through a rising range of temperature; decomposition was first observed at 400° owing to evolution of a green fume (probably ruthenium pentafluoride). At higher temperatures ruthenium pentafluoride was released in some quantity with the expected marked attack on, and blackening of, the apparatus.

Preparation of thallous salt, $TlRuF_6$. Ruthenium pentafluoride was prepared as described above by the action of bromine trifluoride on ruthenium metal followed by heating of the product to 140° in a vacuum, the excess of bromine trifluoride having been removed from the apparatus by sealing off the trap in which it had been condensed. Selenium tetrafluoride, prepared according to Aynsley, Peacock, and Robinson (*loc. cit.*), was distilled on to the ruthenium pentafluoride in an evacuated apparatus, and simultaneously on to the calculated quantity of thallous fluoride in a bulb attached to the main apparatus by a " Quickfit " joint, lubricated with C.F.L.4 Fluorolube. Both bulbs were warmed to dissolve the respective solids in the selenium tetrafluoride. The ruthenium pentafluoride dissolved readily to give a clear, yellowish-green liquid. The solution of thallous pentafluoroselenate, $TlSeF_5$, was frozen and the ruthenium pentafluoride solution poured over the solid; on warming, a yellow to buff-coloured precipitate formed at the liquid–solid interface and spread throughout as liquefaction took place and the solutions mixed. The excess of selenium tetrafluoride was removed under a vacuum, and the residue, after being heated to 160°, proved to be *thallous hexafluororuthenate*(V), a pale orange powder (Found: Tl, 48·0; Ru, 23·4; F, 28·0; Se, trace. $TlRuF_6$ requires Tl, 48·7; Ru, 24·2; F, 27·1%).

Potassium Hexafluororuthenate(IV).—$KRuF_6$ was treated with the minimum amount of water (15 ml. per g. of $KRuF_6$) and gently warmed until effervescence ceased and it had completely dissolved. The solution was kept below 80°, since boiling caused an irreversible hydrolysis to set in with the deposition of black, hydrated ruthenium dioxide. Immediately dissolution was complete the liquid was cooled to 0°; pale yellow plates of *potassium hexafluororuthenate*(IV) crystallised. These were collected on a sintered-glass filter, washed well with ice-cold water, then with carbon tetrachloride to remove any adhering traces of ruthenium tetroxide, and finally dried in a vacuum-desiccator (P_2O_5). A further crop of less pure crystals was obtained by adding a concentrated solution of potassium fluoride to the filtered mother-liquor, and was separated in exactly the same way (Found: Ru, 34·6; K, 26·3; F, 38·3. K_2RuF_6 requires Ru, 34·5; K, 26·6; F, 38·9%). The valency of the ruthenium was fixed by heating the compound to 90° for 1 hr. with a known excess of ceric ammonium sulphate solution, removing the ruthenium tetroxide thus formed by bubbling nitrogen through the solution, and determining the excess of ceric salt by titration with standard ferrous ammonium sulphate solution. 4 Equivs. of ceric salt were required per equiv. of ruthenium present in order to oxidise the latter to the octavalent state: *i.e.*, the valency of the ruthenium is $8 - 4 = 4$.

Potassium hexafluororuthenate(IV) is sparingly soluble in water to a colourless solution; immediately on warming this solution, or on keeping it at room temperature for upwards of an hour, black, hydrated ruthenium dioxide was precipitated. With hydrochloric acid the distinctive red-brown colour of the chlororuthenate ion, $RuCl_6^{2-}$, develop, the exchange being markedly catalysed by hydrogen ions. Thus both an increase in concentration of the acid and an increase in temperature were found to promote this change. In a similar manner, dilute sulphuric acid leads to the particular brown colour typical of a Ru(IV) sulphate solution.

Cæsium Hexafluororuthenate(IV).—By starting with $CsRuF_6$ and proceeding as just described, this *cæsium* salt is obtained as pale yellow plates (Found: Ru, 20·4; Cs, 55·1; F, 24·1. Cs_2RuF_6 requires Ru, 21·0; Cs, 55·3; F, 23·7%). In physical and chemical properties it closely resembles the corresponding potassium salt.

Analyses.—Ruthenium. (*a*) In the absence of interfering elements, ruthenium was determined by hydrolytic precipitation, by sodium hydrogen carbonate from hydrochloric acid solution, of the hydrated dioxide, followed by ignition of the oxide and its reduction to the metal in hydrogen. (*b*) In other cases, *e.g.*, when alkaline-earth salts were present, the compound was dissolved in cold 10% hydrogen peroxide–sulphuric acid mixture; the fluorine was then removed by distillation as fluorosilicic acid, and the ruthenium remaining in the sulphate solution was distilled out as the tetroxide, after addition of potassium bromate. The distillate was received in ice-cold, 3% hydrogen peroxide, and the ruthenium recovered by addition of thionalide. The precipitated complex was ignited in air and reduced in hydrogen to the metal (Rogers, Beamish, and Russell, *Ind. Eng. Chem. Anal.*, 1940, **12**, 561).

Fluorine. This was determined as lead chlorofluoride either directly in the filtrate after removal of ruthenium, or, after the addition of concentrated sulphuric acid, in the distillate containing it as fluorosilicic acid.

Alkali metals. These were weighed as sulphates after reduction of the complex fluoride in hydrogen, extraction of the alkali fluoride from the residue in hot water, evaporation with sulphuric acid in a platinum dish, and ignition to dull red heat. Silver was determined as chloride.

The authors acknowledge grants for material and maintenance (M. A. H.) from the Ministry of Supply; they thank Imperial Chemical Industries Limited, General Chemicals Division, Widnes, for the use of the necessary fluorine cell, and Johnson, Matthey, and Co. Ltd. for the loan of ruthenium.

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