263. *The Quadrivalent Fluororhenates.*

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Complex fluorides of rhenium involving the quadrivalent ReF_6^{2-} ion have been obtained and characterised, and the acid H_2ReF_6 has been prepared in solution.

IN an earlier communication [1] the preparation of the hitherto unknown potassium fluororhenate(IV) K_2ReF_6 from the interaction of anhydrous potassium hydrogen fluoride and ammonium iodorhenate(IV) was described.

A representative selection of fluororhenates has now been prepared and some of their individual properties have been investigated. Table 1 shows the solubilities of these, along with those of the fluoroplatinates. Most of them are as unreactive towards water as the potassium salt, but the apparently very soluble silver and calcium salts decompose when their solutions are evaporated to dryness. From potassium fluororhenate, by using a suitable ion-exchange resin, a solution of fluororhenic acid has been prepared, but, unlike fluoroplatinic acid,[2] it cannot be isolated as a solid. Attempts to do this, even by careful evaporation at 25°, have only resulted in decomposition, with formation of the hydrated dioxide ReO_2,nH_2O : $H_2ReF_6 + 2H_2O \longrightarrow ReO_2 + 6HF\uparrow$. The solution, however, is stable for several weeks in the cold; it behaves as a strong acid and can be titrated in the ordinary way with alkalis.

Neither its salts nor the free acid is easily attacked by alkalis; indeed, to effect the breakdown of potassium fluororhenate quantitatively it must be fused with alkali carbonate or hydroxide. The behaviour shown by these compounds towards hydrochloric acid is again unexpected; most of the salts are unaffected even by hot, concentrated acid, and fluororhenic acid itself is attacked only after its solution has been completely evaporated to dryness, *i.e.*, under conditions when the ReF_6^{2-} ion has already been destroyed. By contrast, the neighbouring fluoro-osmates react with even dilute hydrochloric acid at 25° to give $OsCl_6^{2-}$ ion. The ReF_6^{2-} ion is attacked only slowly by alkali and hydrogen peroxide, but in acid solution is easily reduced electrolytically to the metal. This reduction to the

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[1] Peacock, *Chem. and Ind.*, 1955, 1453.

[2] Clarke and Perros, *J. Amer. Chem. Soc.*, 1953, **75**, 5734.

element is not surprising, since fluorine complexes of tervalent rhenium are probably unstable, a view which receives confirmation from the fact that rhenium tri-iodide[3] breaks down to rhenium metal when fused with potassium hydrogen difluoride.

Crystallographically the fluororhenates resemble the complex fluorides of manganese and the platinum metals (Table 2). The alkali salts (except sodium) are trigonal; ammonium fluororhenate resembles most other ammonium complex metal fluorides in having a unit-cell size comparable with that of the rubidium rather than the potassium salt. Barium fluororhenate is isomorphous with the corresponding fluoro-osmate and fluoroiridate.

The available experimental data indicate that sodium fluororhenate, unlike the corresponding fluoroplatinate, could be indexed on a pseudo-cubic tetragonal cell, but more evidence is required before its structure can be definitely settled.

TABLE 1.

	Fluororhenates		Fluoroplatinates
	Colour	Solubility	Solubility[4] *
Na_2ReF_6	White	Very soluble hot and cold	20·49
$(NH_4)_2ReF_6$	,,	,, ,,	7·32
K_2ReF_6	,,	Very soluble hot; soluble cold	0·750
Rb_2ReF_6	,,	Soluble hot; slightly soluble cold	0·278
Cs_2ReF_6	,,	,, ,,	0·484
$BaReF_6$	White	Soluble only when freshly pptd.	—
$[Ni(NH_3)_6]ReF_6$	Purple	Slightly soluble	—
$[Co(NH_3)_6]_2(ReF_6)_3$	Red-brown	,, ,,	—

* In g./100 ml. of solution at 25°.

TABLE 2. *Crystal structures of the fluororhenates.*

		Unit-cell size (Å)	
		Fluororhenates	Fluoroplatinates[5, 6]
Na_2ReF_6	Tetragonal	a_0 = 10·02; c_0 = 10·14	a_0 = 9·41; c_0 = 5·16 (trigonal)
K_2ReF_6	Trigonal	a_0 = 5·86; c_0 = 4·60	a_0 = 5·76; c_0 = 4·64
Rb_2ReF_6	,,	a_0 = 6·01; c_0 = 4·77	a_0 = 5·96; c_0 = 4·83
$(NH_4)_2ReF_6$	,,	a_0 = 6·06; c_0 = 4·77	—
Cs_2ReF_6	,,	a_0 = 6·32; c_0 = 4·99	a_0 = 6·22; c_0 = 5·01
$BaReF_6$	Rhombohedral	a_0 = 4·92; α = 97·25°	a_0 = 4·90; α = 97·8° ($BaIrF_6$)
$[Ni(NH_3)_6]ReF_6$	,,	—	—
$[Co(NH_3)_6]_2(ReF_6)_3$	?Orthorhombic	—	—

Professor R. S. Nyholm has very kindly made magnetic measurements on the potassium and barium salts. For potassium fluororhenate(IV) $\mu = 3{\cdot}3_2$ B.M. and for barium fluororhenate(IV) $\mu = 3{\cdot}4_1$ B.M., both at 20°. The calculated spin-only value for the expected 3 unpaired electrons is $\mu = 3{\cdot}88$ B.M.

EXPERIMENTAL

Reagents.—Potassium hydrogen difluoride was prepared from " AnalaR " potassium carbonate and " AnalaR " hydrofluoric acid (40%) in slight excess. The rubidium and cæsium salts were made similarly from their carbonates. Immediately before use the acid fluorides were dried at 150°. *Ammonium iodorhenate* was obtained by reduction of recrystallised ammonium per-rhenate, NH_4ReO_4, with hot " AnalaR " hydriodic acid (*d* 1·7) in the presence of recrystallised ammonium iodide. The crude product was recrystallised from hot hydriodic acid [Found: I, 77·0. $(NH_4)_2ReI_6$ requires I, 77·4%].

Potassium, Rubidium, and Cæsium Fluororhenates.—The potassium salt was prepared by slowly heating ammonium iodorhenate with potassium hydrogen difluoride to 250°. After the characteristic purple colour of the ReI_6^{2-} ion had disappeared, the temperature was gradually raised until all the ammonium salts had been driven off together with most of the hydrogen

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[3] Peacock, unpublished work.
[4] Wheeler, Perros, and Naeser, *J. Amer. Chem. Soc.*, 1955, **77**, 3489.
[5] Cox, *J.*, 1954, 3251.
[6] Cox and Sharpe, *J.*, 1953, 1783.

fluoride so that a solid cake remained. After cooling, this was leached with cold water to remove most of the potassium iodide and fluoride, and the crude *potassium fluororhenate* was twice recrystallised from a little hot water (Found: Re, 49·9; F, 29·2. K_2ReF_6 requires Re, 49·2; F, 30·1%). Usually a small amount of an unidentified soluble brown material was formed during the fusion, but rapidly decomposed in the hot water to hydrated rhenium dioxide ReO_2,nH_2O, which was filtered off. *Rubidium* and *cæsium fluororhenates* were similarly prepared by using the corresponding acid fluorides (Found: Re, 39·1; F, 23·7. Rb_2ReF_6 requires Re, 39·5; F, 24·2%. Found: Re, 32·3; F, 21·0. Cs_2ReF_6 requires Re, 32·9; F, 20·1%).

Barium, Hexamminonickel, and Hexamminocobaltic Fluororhenates.—To hot aqueous potassium fluororhenate (1 g. in 50 ml.) was added excess of barium chloride solution. After filtering, an equal volume of absolute alcohol was added; *barium fluororhenate* soon separated. The solid had to be immediately recrystallised from hot water, as on ageing the precipitate soon became almost completely insoluble (Found: Ba, 31·7; Re, 42·0; F, 26·2. $BaReF_6$ requires Ba, 31·4; Re, 42·6; F, 26·0%). To a hot solution of potassium fluororhenate was added a strongly ammoniacal nickel sulphate solution. On stirring, purple *hexamminonickel fluororhenate* crystallised in needles and rhombohedral plates [Found: Ni, 12·0. $Ni(NH_3)_6ReF_6$ requires Ni, 12·7%]. *Hexamminocobaltic fluororhenate* was prepared by interaction of hot solutions of potassium fluororhenate and hexamminocobaltic chloride (Found: Co, 10·0. $[Co(NH_3)_6]_2[ReF_6]_3$ requires Co, 10·4%).

Fluororhenic Acid.—Warm, dilute, potassium fluororhenate solution was poured through a column of Zeo-Carb 225, and the colourless solution of H_2ReF_6 collected at the lower end. A N/100-solution of the acid had pH 2·6 at the glass electrode, and showed the ordinary characteristics of a strong acid when titrated with N/10-potassium hydroxide, the equivalence point being at pH 7—8.

Ammonium and Sodium Fluororhenates.—A slight excess of ammonium carbonate solution was added to fluororhenic acid solution; when the solution was evaporated nearly to dryness, crystals of *ammonium fluororhenate* appeared [Found: Re, 54·8; F, 33·6. $(NH_4)_2ReF_6$ requires Re, 55·4; F, 33·9%]. For the *sodium* compound sodium hydrogen carbonate was used. The very soluble crude salt, which sometimes appeared bluish instead of white, was recrystallised from cold water (Found: Re, 52·0; F, 32·0. Na_2ReF_6 requires Re, 53·8; F, 32·9%).

Attempted Preparation of Silver and Calcium Fluororhenates.—Solutions of these salts could be obtained by shaking freshly prepared silver or calcium carbonate in a hot fluororhenic acid solution and filtering off residual carbonate. In neither case, however, could the solid salts be obtained either by evaporating the solution to dryness or by addition of a large excess of absolute alcohol.

Attempted Direct Preparation of Ammonium Fluororhenate.—Ammonium iodorhenate was added to fused, carefully dried ammonium hydrogen difluoride, and the product dissolved in water. Owing to its high solubility, ammonium fluororhenate could not be separated from the ammonium hydrogen difluoride, but the presence of the fluororhenate ion was shown by the addition of potassium carbonate, which precipitated crystals of potassium fluororhenate.

Analysis.—The compounds were broken down by heating with fusion mixture together with a little sodium peroxide to ensure oxidation of the rhenium to the septavalent state. Rhenium was determined, after removal of interfering elements, as nitron per-rhenate; fluorine as lead chlorofluoride; barium as sulphate; cobalt as the pyridine thiocyanate complex, and nickel as dimethylglyoxime complex.

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