Complex Fluorides. Part II.* Studies on Fluoroferrates and on Hydrogen Bonding in Complex Fluorides.

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There is at present no evidence for hydrogen bonding as an important factor in complex fluorides containing the ammonium ion. Infra-red spectroscopy shows no more than slight variation in the position of the 1400 cm.$^{-1}$ N–H vibration in such compounds, and more detailed work on the analytical composition and structures of the fluoroferrates appears to refute the hitherto accepted evidence for strong hydrogen bonding in ammonium fluoroferrate. In connection with this investigation an electrolytic method has been developed for the preparation of complex fluorides of manganese(IV).

In Part I * we drew attention to a possible connection between the Fe–F bond type in the $FeF_6{}^{3-}$ ion (deduced from the magnetic properties to be " outer orbital " in character) and the evidence cited by Pauling (" Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N.Y., 1940, p. 300) for strong hydrogen bonding in ammonium hexafluoroferrate (namely, the relative sizes of the cubic or pseudo-cubic unit cells of the alkali-metal and ammonium hexafluoroferrates). Lattice constants reported for these substances are : Li_3FeF_6, $a = 8\cdot88$ (Minder, *Z. Krist.*, 1937, **96**, 15); $(NH_4)_3FeF_6$, $a = 9\cdot17$ (*idem, ibid.*), $9\cdot10$ (Pauling, *J. Amer. Chem. Soc.*, 1924, **46**, 2738; Rice, Turner, and Brydon, *Nature*, 1952, **169**, 749; Steward and Rooksby, *Acta Cryst.*, 1953, **6**, 49); Na_3FeF_6, $a = 9\cdot26$; K_3FeF_6, $a = 9\cdot93$; Rb_3FeF_6, $a = 10\cdot23$; Cs_3FeF_6, $a = 10\cdot46$ Å (Minder, *loc. cit.*).

* Part I, *J.*, 1953, 1783.

A knowledge of the structure and magnetic properties of ammonium hexafluoro-cobaltate, $(NH_4)_3CoF_6$, would shed light on this problem, but attempts to make this substance by the method used by Mitchell (Thesis, Univ. Buffalo, 1940) for the preparation of the corresponding potassium salt have failed. This may be due to the extreme insolubility of the hydrated fluoride, $Co_2F_6,7H_2O$ (Barbieri and Calzolari, *Atti R. Accad. Lincei*, 1905, **14**, 464; *Z. anorg. Chem.*, 1928, **170**, 109), an intermediate product, compared with that of the desired ammonium salt. Although among complex chlorides and bromides the lattice dimensions of ammonium and rubidium salts of the same acid are almost identical, and their solubilities are of the same order of magnitude, yet among complex fluorides ammonium salts are invariably considerably more soluble than the corresponding potassium or rubidium salts. The solubilities (in g. per 100 g. of water) of potassium, ammonium, and rubidium fluoroborates, for example, are: KBF_4, 0·6[17] (de Boer and van Liempt, *Rec. Trav. chim.*, 1927, **46**, 124); $RbBF_4$, 0·6[17] (*idem, ibid.*); NH_4BF_4, 25[16] (Stolba, *Centr. Ges. chem. Grossind.*, 1890, **7**, 459). Those of the fluorosilicates (in the same units) are: K_2SiF_6, 0·132[16] (Carter, *Ind. Eng. Chem.*, 1930, **22**, 886); Rb_2SiF_6, 0·160[20] (Stolba, *J. pr. Chem.*, 1870, **103**, 396); $(NH_4)_2SiF_6$, 18·58[17·5] (*idem, Chem. Zentr.*, 1877, **8**, 418). For the fluorotitanates the values reported (in the same units) are: $(NH_4)_2TiF_6$, 25[20] (Ginsberg, *Z. anorg. Chem.*, 1932, **204**, 225); Rb_2TiF_6, 0·8[20] (*idem, ibid.*). Quantitative data for other complex fluorides are lacking, but similar relationships have been reported for the fluoro-beryllates, -germanates, and -aluminates.

A probable explanation is that the differences in solubility arise from small differences in the lattice energies of the compounds. To a first approximation we may regard solubility as determined by the relative magnitudes of lattice energy and ionic solvation energies. Because of the exponential nature of the relation between an equilibrium constant (in this instance, a solubility product) and the corresponding change in free energy (in this instance, the lattice energy), solubility should be very much affected by even small changes in lattice energy. Accordingly, we have compared the molecular volumes (as determined from X-ray data) of potassium, ammonium, and rubidium salts of complex fluoro-acids having the same structure type with those of analogous complex chloro- and bromo-acids. The results are given in the following table.

Molecular volume, cm.³ × 10⁻²⁴

	PdCl₆″	PdBr₆″	PtCl₆″	PtBr₆″	TeCl₆″	SeCl₆″	SnBr₆″	SnCl₆″	PbCl₆″	SiF₆″
K⁺	231·3[4]	269·3[4]	229·8[3]	270·8[4]	261·0[3]	—	290·2[3]	248·7[3]	—	135·0[7]
NH₄⁺	239·0[4]	276·5[4]	238·0[3]	279·8[4]	263·8[3]	245·0[3]	297·0[5]	253·7[3]	260·3[3]	148·0[8,1]
Rb⁺	241·0[4]	280·3[4]	241·5[3]	282·0[4]	267·7[3]	248·5[3]	301·5[5]	257·0[3]	264·7[3]	150·4[7,1]

	GeF₆″	TiF₆″	MnF₆″	BF₄′	SbF₆′	SbF₅″	Sb₄F₁₃′	BeF₄″	AlF₄′
K⁺	127·3[9]	130·2[2,11]	131·6[12]	82·15[13]	—	138·7[16]	256·0[17]	101·1[18]	77·5[6]
NH₄⁺	141·5[10]	147·9[2]	144·1[1]	92·35[14]	131·5[15]	153·3[16]	263·8[17]	114·7[18]	81·6[6]
Rb⁺	140·5[10]	143·5[2]	140·7[12]	91·85[14]	132·0[15]	149·9[16]	263·6[17]	113·2[18]	81·8[6]

References. [1] Present work. [2] Cox and Sharpe, *J.*, 1953, 1783. [3] Engel, *Z. Krist.*, 1935, **90**, 341. [4] Sharpe, *J.*, 1953, 4177. [5] Markstein and Nowotny, *Z. Krist.*, 1938, **100**, 265. [6] Brosset, *Z. anorg. Chem.*, 1938, **239**, 301. [7] Ketelaar, *Z. Krist.*, 1935, **92**, 155. [8] Bozorth, *J. Amer. Chem. Soc.*, 1922, **44**, 1066. [9] Hoard and Vincent, *ibid.*, 1939, **61**, 2849. [10] Vincent and Hoard, *ibid.*, 1942, **64**, 1233. [11] Siegel, *Acta Cryst.*, 1952, **5**, 683. [12] Bode and Wendt, *Z. anorg. Chem.*, 1952, **269**, 165. [13] Pesce, *Gazzetta*, 1930, **60**, 936. [14] Hoard and Blair, *J. Amer. Chem. Soc.*, 1935, **57**, 1985. [15] Schrewelius, *Arkiv Kemi, Min., Geol.*, 1942, B, **16**, No. 7. [16] Byström and Wilhelmi, *Arkiv Kemi*, 1952, **3**, 461. [17] *Idem, ibid.*, p. 17. [18] Mukherjee, *Indian J. Physics*, 1944, **18**, 148.

We find that, whereas in the case of salts of complex chloro- and bromo-acids the molecular volume of the ammonium salt lies between those of the potassium and rubidium salts, yet in all the reported examples of complex fluorides (except the hexafluorosilicates) the molecular volume of the ammonium salt is approximately equal to or greater than that of the rubidium salt. We have confirmed that the fluorosilicates do constitute an exception by redetermining their unit-cell sizes, and obtaining values $a = 8·39$ and $a = 8·44$ Å, respectively, for ammonium and rubidium fluorosilicates. These are in close agreement with those previously reported for the ammonium salt [$a = 8·34$ (Ketelaar, *Z. Krist.*, 1935, **92**, 155), 8·38 (Bozorth, *J. Amer. Chem. Soc.*, 1922, **44**, 1066)] and the rubidium salt [$a = 8·45$ Å (Ketelaar, *loc. cit.*)]. The correlation we suggest must, therefore, be regarded as probable but not proved.

As we failed to prepare ammonium hexafluorocobaltate, we studied the application of the electrolytic method to the preparation of complex fluorides of other transition metals in their higher oxidation states. By electrolytic oxidation of a suspension of manganous fluoride in aqueous hydrofluoric acid an oxidation state, in solution, of slightly greater than 3 was attained. When a saturated solution of potassium hydrogen difluoride in aqueous hydrofluoric acid was added to this solution and the electrolysis was continued, a deposit of yellow crystals of potassium hexafluoromanganate(IV) was obtained. A sample of the hitherto unknown ammonium hexafluoromanganate(IV) was obtained in the same manner but in smaller yield. *X*-Ray powder photography shows the potassium (hexagonal, $a = 5.70$, $c = 9.33$) and ammonium (hexagonal, $a = 5.91$, $c = 9.55$ Å) salts to be isomorphous. The values obtained for the potassium salt agree well with those reported by Bode and Wendt (*loc. cit.*) and tabulated in Part I (*loc. cit.*).

Complex salts of manganese(III) can be obtained by omitting the second stage of electrolysis and allowing crystallisation to take place. Electrolysis of a suspension of plumbous fluoride or nickel fluoride in aqueous hydrofluoric acid did not give a solution of higher oxidation state than 2.

Since we were unable to investigate the structure of ammonium hexafluorocobaltate we re-examined the structural chemistry of the fluoroferrates. In a recent paper by Steward and Rooksby (*loc. cit.*) values are given for the lattice constants of sodium, potassium, and ammonium hexafluoroaluminates. These values are widely different from Minder's values (*loc. cit.*) for the fluoroferrates, despite the similarity in the tervalent radii of iron and aluminium.

From the Na^+–Fe^{3+}–F^- system in aqueous solution we find that only one phase can be isolated, and that this phase is isomorphous with cryolite, the unit cell sizes being respectively $a = 5.51$, $b = 5.74$, $c = 7.94$, β approx. $90°$, and $a = 5.46$, $b = 5.61$, $c = 7.80$ Å, $\beta = 90°\ 10'$ (Naray-Szabo and Sasvari, *Z. Krist.*, 1938, **99**, 27). Analysis, however, establishes that the composition of this phase corresponds closely to $Na_{2.0}FeF_{5.0},1.0H_2O$; the conclusion that " sodium hexafluoroferrate " does not have an analytical composition corresponding to Na_3FeF_6 was reached much earlier by Nicklès (*Rev. Scient.*, 1868, **5**, 391), Welo (*Phil. Mag.*, 1928, **6**, 496), and Röder (" Über kristallisierte wasserfreie Fluor Verbindungen," Göttingen, 1863), but their conclusions appear to have been ignored by most later workers on the fluoroferrates, Minder included. It should be noted that natural and synthetic cryolite also show departures from the ideal composition Na_3AlF_6 (Tananaev and Lel'chuk, *Doklady Akad. Nauk S.S.S.R.*, 1943, **41**, 118).

In the system NH_4^+–Fe^{3+}–F^-, the only product obtained when the concentration ratio $NH_4^+ : Fe^{3+}$ exceeds $3 : 1$ is a cubic phase with $a = 9.10$ Å; this phase can be recrystallised from very dilute hydrofluoric acid without change, and its composition corresponds approximately to $(NH_4)_{2.6}FeF_{5.6},0.4H_2O$. Since our value for the unit-cell size agrees well with all earlier determinations (for none of which chemical analyses are given) it seems impossible to avoid the conclusion that earlier investigations have been made, not on $(NH_4)_3FeF_6$, but on products of composition similar to that described above. The sample of the isomorphous ammonium fluoroaluminate investigated by Menzer (*Z. Krist.*, 1930, **73**, 113) had an analytical composition agreeing well with that calculated for $(NH_4)_3AlF_6$; however, Baud (*Compt. rend.*, 1902, **135**, 1337) has reported the formation of a compound with the $NH_4F : AlF_3$ ratio less than $3 : 1$.

We have been unable to identify a phase K_3FeF_6 among the products obtained by varying the $K^+ : Fe^{3+}$ ratio in the solutions used, and none of the powder photographs of our preparations has shown lines corresponding to the cubic phase reported by Minder (*loc. cit.*). With low potassium concentrations the product was found to be cubic ($a = 8.21$ Å) and corresponded to $K_{1.8}FeF_{4.8},1.5H_2O$. A non-cubic phase of approximate composition $K_2FeF_5,0.5H_2O$ was obtained from solutions of higher potassium concentration. Attempts to interpret the *X*-ray powder pattern of this phase by analogy with Tl_2AlF_5 and K_2AlF_5,H_2O (Brosset, *Z. anorg. Chem.*, 1937, **235**, 139; " Electrokemisk och rontgenkristallographisk undersökning av complexa aluminiumfluorider," Stockholm, 1942) were not successful.

Comparison of cell dimensions for these compounds does not confirm the hitherto

accepted sequence for the lattice constants among the fluoroferrates, but it does show the order of difference to be expected from the conventional ionic radii of Na^+, K^+, and NH_4^+. The unit-cell sizes thus afford no evidence for the presence of strong hydrogen bonds in the fluoroferrates.

We therefore sought independent evidence of the presence or absence of hydrogen bonds by investigating the infra-red spectra of a large number of ammonium salts. The position of the N–H vibration at about 1400 cm.$^{-1}$ has been used as diagnostic of the presence of hydrogen bonding in ammonium fluoride (Bovey, *J. Chem. Physics*, 1950, **18**, 684); the frequency of this vibration is 1397 cm.$^{-1}$ in ammonium iodide, 1407 cm.$^{-1}$ in ammonium bromide, 1397 cm.$^{-1}$ in the chloride, and 1484 cm.$^{-1}$ in the fluoride. (We should mention, however, that in ammonium hydrogen difluoride the frequency is 1406 cm.$^{-1}$.) Among a wide range of ammonium oxy-salts (Miller and Wilkins, *Ind. Eng. Chem. Anal.*, 1952, **24**, 1253) and ammonium salts of chloro- and fluoro-complex acids the values for this N–H vibration frequency lie in the range 1390—1420 cm.$^{-1}$. Only in the fluoro-beryllate (1426 cm.$^{-1}$), fluoroferrate and fluoroaluminate (1428 cm.$^{-1}$), and fluoroborate (1430 cm.$^{-1}$) is the frequency outside this range and is then only just so. Furthermore, in the fluoroborate the hydrogen bonding is insufficiently strong to affect the B–F vibration frequency, which is identical with that in the other alkali-metal fluoroborates (Coté and Thompson, *Proc. Roy. Soc.*, 1951, *A*, **210**, 217). We therefore conclude that there is no evidence for hydrogen bonding's being an important factor in the determination of the structure of any complex fluoride so far investigated.

Finally, it is of interest to consider what effect hydrogen bonding has on the interionic distance in ammonium fluoride, which, unlike the other halides, crystallises with the wurtzite structure. From the ionic radii of the fluoride and ammonium ions (1·33 and 1·48 Å, respectively) derived from halides having the sodium chloride type structure, the equilibrium interionic distance in the hypothetical sodium chloride type modification of ammonium fluoride should be 2·81 Å. From Madelung's constants for the sodium chloride ($A_{r_0} = 1·7476$) and wurtzite ($A_{r_0} = 1·641$) structures, the Born exponents being assumed to be the same in each case, r_0 for the wurtzite form of ammonium fluoride, no allowance being made for hydrogen bonding, should be $2·81 \times 1·641/1·748 = 2·64$ Å. An alternative calculation, based on Pauling's method (*op. cit.*, pp. 354, 367), leads to a value of 2·70 Å. The observed distance is 2·66 Å (Zachariasen, *Z. physikal. Chem.*, 1927, **127**, 218). In view of evidence from the unusual co-ordination number and infra-red spectrum in favour of the presence of strong hydrogen bonding, we can only conclude that interionic distance (as distinct from unusually close approach of non-bonded atoms) is unlikely to have any diagnostic value in this connection.

EXPERIMENTAL

Cobalt(III).—A saturated solution of cobaltous fluoride in 40% aqueous hydrofluoric acid was electrolysed at a potential of 2—3 v, the resistance of the cell being such that a current of 0·5—0·75 a was maintained. After 1—2 hours' electrolysis the blue hydrated fluoride, $Co_2F_6,7H_2O$, was deposited; this was filtered off by use of a pump, and washed first with a little 40% aqueous hydrofluoric acid, then immediately with several portions of absolute alcohol, and finally with dry ether. The solid was immediately transferred to a platinum crucible and stored in a vacuum-desiccator. After the initial drying period was passed, the solid could be stored almost indefinitely in a desiccator without decomposition. The hydrated fluoride was analysed for tervalent cobalt by adding a weighed quantity slowly, with vigorous stirring, to acidified potassium iodide solution. The iodine liberated was determined with thiosulphate (Found : Co, 32·8. Calc. for $Co_2F_6,7H_2O$: Co, 32·9%).

Ammonium hydrogen difluoride was added to the hydrated fluoride, before this was filtered off, either as the solid or as a saturated solution in aqueous hydrofluoric acid, and the electrolysis was continued. No evidence was obtained for complex formation having taken place, and when solid ammonium hydrogen difluoride had been added the product appeared to be a mixture of the hydrated fluoride with undissolved ammonium hydrogen difluoride.

Manganese(IV).—Manganous carbonate was added to 40% aqueous hydrofluoric acid until a white suspension of manganous fluoride was obtained; this was electrolysed with a potential of 2—3 v and a current of about 0·75 a until a clear red-brown solution containing manganese(III) was obtained. Solid potassium hydrogen difluoride or a saturated solution of this in 40%

aqueous hydrofluoric acid was added to the liquid and the electrolysis was continued. Any deposit of crystals of manganese(III) complexes, formed on the addition of the alkali-metal salt, dissolved on further electrolysis, and was replaced by yellow crystals of the hexafluoro-manganate(IV). The liquid was decanted from these crystals and they were washed first with a little 40% hydrofluoric acid and then with alcohol and ether; they were stored in a desiccator.

The *ammonium* salt was prepared in an analogous manner; owing to its greater solubility, however, the initial washing with hydrofluoric acid was omitted [Found, for K_2MnF_6: Mn, 21·95. Calc.: Mn, 22·25. Found, for $(NH_4)_2MnF_6$: Mn, 26·4. $(NH_4)_2MnF_6$ requires Mn, 26·8%].

Manganese(III).—The oxidation state of the solution obtained by the electrolysis of a suspension of manganous fluoride in 40% aqueous hydrofluoric acid was determined by commencing with a weighed quantity of manganous carbonate, and determining the iodine liberated when the resulting solution containing manganese(III) was added to acidified potassium iodide. Several such estimations all gave values slightly higher than 3, with a mean of 3·06, for the oxidation state of the manganese. Red-brown crystals of manganese(III) complexes were obtained by adding excess of a saturated solution of potassium hydrogen difluoride in hydrofluoric acid to this solution. The supernatant liquid having been drained off, the crystals were washed with acetone and ether. Their *X*-ray powder photograph did not resemble that given by a sample of the salt K_2MnF_5,H_2O prepared by Müller and Koppe's method (*Z. anorg. Chem.*, 1910, **68**, 160), although many of the lines did occur on both, suggesting that the product was a mixture. After a sample of these crystals had been washed carefully with a saturated solution of potassium hydrogen difluoride in aqueous hydrofluoric acid, a pink residue resembling the K_2MnF_5,H_2O preparation and giving an identical *X*-ray powder pattern was obtained.

Lead(IV).—Use of the simple electrolytic cell employed for the manganese and cobalt preparations resulted in deposition of lead on the cathode when a suspension of plumbous fluoride in aqueous hydrofluoric acid was electrolysed. On use of a cell in which the anode compartment was connected to the cathode compartment by a bridge consisting of a rolled filter-paper soaked in hydrofluoric acid, and electrolysis at a potential of 30—40 v with a current of 0·24 A, owing to the high resistance of the cell, the solution remaining did not liberate iodine from acidified potassium iodide and contained only a very small quantity of lead in solution. The only evidence for any oxidation's having taken place after the current had been passed for several hours was a brown stain of PbO_2 above the liquid level in the anode compartment.

Nickel(IV).—Electrolysis of a solution of nickel(II) fluoride in 40% aqueous hydrofluoric acid gave no evidence of oxidation after several hours.

Iron(III).—Fluoroferrates were prepared by mixing a saturated solution of the alkali-metal fluoride, or ammonium fluoride, in aqueous hydrofluoric acid with a solution of either ferric chloride or ferric hydroxide in hydrofluoric acid. The molecular proportions in which these were present were varied in an attempt to obtain different phases in the product.

Sodium fluoroferrate was the only product obtained from sodium fluoride and ferric hydroxide solutions over the whole range of Na⁻Fe concentrations up to the point where considerable quantities of sodium hydrogen difluoride were co-precipitated. Analysis were consistent with a formula of Na_2FeF_5,H_2O for the sodium fluoroferrate. The presence of water in the compound was confirmed by infra-red spectroscopy (Found: Fe, 26·1; F, 44·5. Calc. for Na_2FeF_5,H_2O: Fe, 26·0; F, 44·1%).

With NH_4:Fe ratios greater than 3 : 1 a white precipitate was formed immediately; the *X*-ray powder diagram was the same in all cases, but the products showed a slight variation about a mean composition $(NH_4)_{2·6}FeF_{5·6},0·4H_2O$ [Found, in a typical preparation: NH_4, 23·3; Fe, 26·2; F, 48·7. Calc. for $(NH_4)_{2·6}FeF_{5·6},0·4H_2O$: NH_4, 21·9; Fe, 26·2; F, 49·7%]. When the NH_4 : Fe ratio was less than 3 : 1 no precipitate was formed on mixing of the solutions, and when the bulk of the solution was reduced a crop of pale green crystals was obtained. Analysis showed this to have consisted almost entirely of ferric fluoride.

For the potassium salt, when the K : Fe ratio was 3—4 : 1 the product was a cubic phase which corresponded approximately to K_2FeF_5,H_2O. With higher concentrations of potassium, however, the water content of the product diminished, and a non-cubic phase corresponding approximately to K_2FeF_5 was obtained. Throughout the series of preparations *X*-ray powder photography failed to reveal the existence of any cubic phase corresponding either to Minder's reported value for K_3FeF_6 or to a cell size which might be expected for K_3FeF_6 from the values obtained for the sodium and ammonium salts (Found: K, 29·2; Fe, 22·7; F, 36·7. Calc. for K_2FeF_5,H_2O: K, 31·6; Fe, 22·7; F, 38·5. Found: K, 33·8; Fe, 24·8; F, 37·2. Calc. for K_2FeF_5: K, 34·0; Fe, 24·4; F, 41·4%).

Analytical Methods.—Potassium was determined gravimetrically as chloroplatinate, and ammonium ion by distillation from alkali into saturated boric acid solution, followed by titration with standard hydrochloric acid. Iron was determined gravimetrically as ferric oxide, fluorine as calcium fluoride (Grant, " Clowes and Coleman's Quantitative Chemical Analysis," Churchill, London, 15th Edn., 1944, p. 101). Methods used for the determination of cobalt(III), manganese(III), and manganese(IV) are described above. The presence of water as distinct from OH groups in the compounds was confirmed by infra-red spectroscopy.

Infra-red Spectroscopy.—The infra-red spectra of the ammonium salts were measured in suspension in Nujol and hexachlorobutadiene on a Perkin–Elmer Model 21 Spectrometer with rock-salt optics. The frequencies (in cm.$^{-1}$) of the N–H vibrations are tabulated below.

$(NH_4)_2SiF_6$	1405	—	—	3060	3150	—
$(NH_4)_2TiF_6$	1408	—	2870	—	—	3280
$(NH_4)_2GeF_6$	1408	—	2870	—	—	3280
$(NH_4)_2BeF_4$	1426	—	2925	—	3125	—
$(NH_4)_3CrF_6$	1418	—	2870	3030	—	3240
$(NH_4)_{2\cdot6}FeF_{5\cdot6},0\cdot4H_2O$	1428	—	2880	—	—	3250
$(NH_4)_3AlF_6$	1428	—	—	3060	—	3250
NH_4BF_4	1430	—	2930	—	—	—
$(NH_4)_2PbCl_6$	1408	—	—	—	—	3225
$(NH_4)_2PtCl_6$	1406	2770	2925	—	—	3221
$(NH_4)_2PtBr_6$	1403	—	2860	3050	3150	—
$(NH_4)_2SnCl_6$	1407	—	—	—	—	3220
NH_4HF_2	1406	—	—	3070	3140	—

X-Ray Photography.—X-Ray powder photographs were taken by means of Cu-K_α radiation and a 19-cm. camera; samples were filled into Pyrex capillaries, a " dry-box " being used when necessary, and were sealed with warm picein wax. Lattice constants were evaluated by the methods of Henry, Lipson, and Wooster (" The Interpretation of X-ray Diffraction Photographs," Macmillan, 1951). The lines of the sodium fluoroferrate photograph were indexed by analogy with those found by Naray-Szabo and Sasvari (*loc. cit.*) for sodium fluoroaluminate. The corresponding " calculated " and " found " values for sin^2 θ are :

Sodium fluoroaluminate				Sodiumfluoroferrate		
$\sin^2\theta$ (Mo-K_α)	Int.	$\sin^2\theta$ (converted into Cu-K_α)	Indices	$\sin^2\theta$, found	Int.	$\sin^2\theta$, calc.
0·0061	s	0·0286	011	0·0271	s	0·0274
0·0064	vs	0·0301	101	0·0291	vs	0·0289
0·00827	s	0·0389	{002 110}	0·0375	s	0·0375
0·0161	s	0·0756	020	0·0721	w	0·0720
0·0166	vs	0·0780	112	0·0749	s	0·0750
0·01715	s	0·0806	200	0·0776	w	0·0781
0·02125	s	0·0998	210	0·0961	w	0·0961
0·0225	s	0·1058	121	0·1009	w	0·1010
0·0231	vs	0·1086	103	0·1045	m	0·1040
0·0234	s	0·1097	211	—	—	—
0·0256	vs	0·1203	202	—	—	—
0·0272	s	0·1278	113	0·1223	w	0·1220
0·0288	s	0·1353	122	0·1290	w	0·1291
0·0331	vs	0·1556	004 220	0·1502	s	0·1502
0·0334	vs	0·1570				
0·0383	vw	0·1800	031	0·1759	vw	0·1717
0·0403	m	0·1897	130	0·1820	w	0·1818
0·0415	m	0·1953	{114 222}	0·1877	m	0·1877
0·0423	w	0·1990	131	0·1915	w	0·1912
0·0492	s	0·2315	024	0·2207	m	0·2223
0·0506	s	0·2380	204	0·2310	m	0·2283
			224	0·2990	vw	0·3004
			304	0·3257	vw	0·3258
			332	0·3740	vw	0·3754