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Synthesis of Fluorometallates in Methanol. Some Structure Relationships[1a]

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Methanol solutions of nine representative metal bromides were treated with methanol solutions of potassium, rubidium and cesium fluorides. The products obtained were identified by chemical analysis and X-ray diffraction and are discussed in relation to the alkali metal involved and the corresponding ammonium compounds. From X-ray powder patterns the ammonium, potassium and rubidium complexes of cobalt, manganese and zinc are shown to be cubic and isostructural, the copper complexes to be tetragonal. Hydrogen bonding is indicated in $(NH_4)_2NiF_4$, $(NH_4)_2CuF_4$, NH_4CdF_3 and possibly in NH_4NiF_3. Infrared spectra suggest that the ammonium ions in $(NH_4)_2NiF_4$ and $(NH_4)_2CuF_4$ do not occupy equivalent positions and support the contention that isomorphous substitution of hydroxyl ion for fluoride ion can occur in some fluorometallates.

Introduction

In an earlier paper[2] a method for the preparation of ammonium fluorometallates in methanol was introduced, and the formation of seventeen fluorometallate complexes reported. Because of the similarity in solubility of potassium, rubidium and cesium fluorides in methanol to that of ammonium fluoride, the reaction was extended to include these alkali fluorides as well. Rather than duplicate all the reactions carried out with ammonium fluoride, the metal bromides were selected to represent the various stoichiometric combinations found among the ammonium fluorometallates and to offer comparisons of significant structural interest. In general, the potassium fluorometallates are fairly well known and have been the subject of several recent investigations,[3,4] thus offering a basis for comparison with the product obtained by synthesis in methanol. The compounds of rubidium and cesium provide additional interest because of their novelty.

There has been much general discussion concerning the structures of the fluorometallates. In only a few cases have crystals of unquestioned identity been studied; more often the structures have been based on fragmentary evidence. Cox and Sharpe,[5] for example, have shown that in the case of $(NH_4)_3FeF_6$, earlier workers had actually prepared $(NH_4)_{2.6}FeF_{5.6}\cdot 0.4H_2O$. A color anomaly in copper(II) fluoride formed by the thermal decomposition of ammonium trifluorocuprate(II) has led to the conclusion that isomorphous substitution of hydroxyl ion for fluoride can occur if water is present. It is probable that a similar situation exists with many other complexes when prepared in aqueous solution. The preparation of the fluorometallates in methanol has made it possible to secure these compounds without danger of hydration or hydrolysis and in certain instances to prepare compounds not previously reported.

Knox[3] has reported recently the potassium trifluorometallates of cobalt(II), manganese(II), iron(II), nickel(II) and zinc(II) to be cubic and isostructural, in contrast to the pseudo-cubic structures of Martin, Nyholm and Stephenson[4] and to earlier more complicated structures. From X-ray powder photographs it has been possible to show the isostructural nature of the ammonium, potassium and rubidium fluorometallates of zinc, cobalt and manganese, assuming free rotation, or complete disorder, of the ammonium ion. On the basis of the structures of the potassium complexes, as reported by Knox, they are seen to be cubic. It has also been shown that the trifluorocuprates(II) are tetragonal, in accord with Knox's reported structure for $KCuF_3$.

The possibility of hydrogen bonding in the ammonium fluorometallates has been considered, using infrared spectral data and structural comparisons of the analogous potassium and rubidium complexes as the criterion. Waddington[6] successfully used this approach for other ammonium complex salts. Hydrogen bonding is indicated in NH_4CdF_3, $(NH_4)_2CuF_4$ and $(NH_4)_2NiF_4$, while in NH_4CoF_3, NH_4CuF_3, NH_4MnF_3, NH_4ZnF_3 and $(NH_4)_3FeF_6$ we find no evidence for hydrogen bonding. The unique character of the infrared spectra of $(NH_4)_2CuF_4$ and $(NH_4)_2NiF_4$ suggests that the two ammonium ions in these compounds do not occupy equivalent lattice sites.

I. The Synthesis of Potassium, Rubidium and Cesium Fluorometallates in Methanol

Experimental

Preparation of the Metal Bromides.—The metal bromides were prepared by the addition of bromine to the metal shot, powder or metal foil suspended in methanol. Approximately 0.1 mole of the metal was used in 100 milliliters of methanol, with an excess of bromine. A small amount of unreacted bromine has no apparent effect in the subsequent complex formation. Any residue was removed by filtration, and the bromide solution diluted to an approximate molarity. The methanol solutions of the metal bromides remained clear indefinitely with the exception of copper and iron (III). In these two cases a residue formed on standing. If the solutions were refiltered and the filtrate mixed with metal bromides, anomalous results were obtained.

Preparation of the Compounds.—In all cases the potassium, rubidium and cesium compounds were prepared by the addition of a methanol solution of the metal bromide to a concentrated solution of the alkali fluoride in methanol. The amount of metal bromide added to the alkali fluoride solution was estimated so that an excess of the alkali fluoride remained at completion of the reaction. The filtrates were checked for the presence of alkali fluoride. The products were washed several times by decantation with a dilute

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(2) H. M. Haendler, F. A. Johnson and D. S. Crocket, THIS JOURNAL, **80**, 2662 (1958).

(3) K. Knox, American Crystallographic Association Meeting, Ithaca, N. Y., July 19–24, 1959, Paper J-11, Abstracts, p. 39.

(4) R. L. Martin, R. S. Nyholm and N. C. Stephenson, *Chem. & Ind. (London)*, 83 (1956).

(5) B. Cox and A. C. Sharpe, *J. Chem. Soc.*, 1798 (1954).

(6) T. C. Waddington, *ibid.*, 4340 (1958).

TABLE I

POTASSIUM FLUOROMETALLATES

Formula	*Anal.* calcd., %	*Anal.* found, %	Metal method	Color	Ref.
$KBiF_4$	Bi, 64.49	Bi, 65.00, 64.65	Phosphate	White	.....
	F, 23.45	F, 23.39, 23.51			
$KCdF_3$	Cd, 53.91	Cd, 53.65, 53.58	Anthranilate	White	4
	F, 27.34	F, 27.23, 27.16			
$KCoF_3$	Co, 38.02	Co, 37.20, 37.45	Electrolysis	Pink	3, 4
	F, 36.76	F, 36.30, 36.39			
$KCuF_3$	Cu, 39.80	Cu, 39.32, 39.49	Anthranilate	Light blue	3, 4
	F, 35.70	F, 35.66, 35.66			
$KMnF_3$	Mn, 36.37	Mn, 35.85, 35.90	Oxide	Pale pink	3, 4
	F, 37.74	F, 37.73, 37.61			
$KNiF_3$	....	[a]	....	Yellow	3, 4
$KZnF_3$	Zn, 40.49	Zn, 39.55, 39.45	Anthranilate	White	3, 4, 11
	F, 35.30	F, 35.20, 35.20			
K_3FeF_6	....	[a]	....	White	12
K_2ZrF_6	Zr, 32.19	Zr, 32.25, 32.38	Oxide	White	13
	F, 40.22	F, 40.29, 40.36			

[a] Identified by X-ray powder pattern.

solution of alkali fluoride in methanol and finally with pure methanol, filtered by suction, washed on the filter paper with methanol and dried at 110°. Regrinding of the product and digestion in dilute methanol solution of the alkali fluoride was necessary, particularly in the case of potassium. The gelatinous nature of the products caused considerable entrapment of potassium bromide which could not be removed by washing on the filter. In some cases several successive grindings and digestions were necessary to remove all of the contaminating potassium bromide. As in the case of the ammonium fluorometallates, prolonged digestion of the complex in a dilute solution of the alkali fluoride in methanol greatly improved the quality of the X-ray powder pattern obtained. The quantitative nature of the precipitation was indicated by negative tests for metal ion in the filtrates during preparation.

Analytical.—Cesium was determined by precipitation with sodium tetraphenylboron at a *p*H of four to six, and a temperature of about 40°, drying at 110° and weighing as the cesium tetraphenylboron.[7] In cases where the heavy metal ion would precipitate as the hydroxide at this *p*H, it was first removed by the addition of a small quantity of sodium hydroxide, and the *p*H readjusted with acetic acid after filtration.

Fluorine was determined by distillation of fluorosilicic acid from sulfuric acid solution and then titration with thorium nitrate using the oscillometric method of Grant and Haendler.[8]

The determination of the heavy metal was carried out by a standard analytical procedure as indicated in the tables.

Discussion of Results

The products of the reactions of various metal bromides with potassium, rubidium and cesium are listed in Tables I, II and III, together with analytical data, color and references to other work concerning the compound. A comparison of the products shown in these tables with the corresponding product of the reaction with ammonium fluoride[2] discloses several interesting points. Several anomalies can be seen when the ammonium, potassium and rubidium compounds are compared. Nickel forms $(NH_4)_2NiF_4$, $KNiF_3$ and $RbNiF_3$, while zirconium forms $(NH_4)_2ZrF_7$, K_2ZrF_6 and Rb_3ZrF_7, and copper forms $(NH_4)_2CuF_4$, $(NH_4)CuF_3$, $KCuF_3$ and $RbCuF_3$. In all other cases the stoichiometric ratios of the ammonium, potassium and rubidium compounds are the same for each heavy metal considered. This cannot be explained on the basis of size of the alkali or ammonium ion involved since the ionic radii are $K = 1.33$, $NH_4 = 1.43$ and Rb = 1.48 Å. In the packing of ions in a crystal it would be expected that the smaller size of the potassium ion would permit the association of more potassium ions with the heavy metal ion. This would be reflected in the stoichiometry by a higher potassium ion to heavy metal ion ratio. Such is not the case. A large excess of the alkali fluoride was used in all reactions, thus favoring the formation of the complex of high ammonium or alkali metal ratio. Since K_2NiF_4[9] and K_2CuF_4[10] are both known, on the basis of the concentrations used, it would be expected that these would be formed. Except for the ammonium–copper and rubidium–bismuth compounds, there was no evidence either from X-ray powder patterns or from analytical data for the existence of more than one potassium, rubidium or ammonium compound of any given metal under these conditions. Considering those metals which form compounds whose proportions are identical for potassium, ammonium and rubidium, it is interesting to note that the iron(III), cobalt, manganese and zinc compounds all have simple cubic structures. This would tend to indicate the importance of the crystal structure on the relative stabilities of possible complexes in equilibrium, the product obtained being that which has the most favorable structure.

The reactions of cesium fluoride with various metal bromides, as seen in Table III, present a completely different situation from that found with ammonium, potassium or rubidium fluoride. The large size of the cesium ion, 1.65 Å., seems to be a definite factor as to the complex formed. In each case where a single compound was isolated, the cesium ion to metal ion ratio has been less than for the corresponding ammonium, potassium or rubidium compounds. Of special interest is the cobalt complex $CsCo_2F_5$, for in this case the cesium to cobalt ratio is less than one. It is likely that a similar

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(7) W. Geilmann and W. Gebauhr, *Z. Anal. Chem.*, **139**, 161 (1953).

(8) C. L. Grant and H. M. Haendler, *Anal. Chem.*, **28**, 415 (1956).

(9) G. Wagner and D. Balz, *Z. Elektrochem.*, **56**, 574 (1952).

(10) K. Knox, *J. Chem. Phys.*, **30**, 991 (1959).

TABLE II

RUBIDIUM FLUOROMETALLATES

Formula	*Anal.* calcd., %	*Anal.* found, %	Metal method	Color	Ref.
$RbBiF_4$	....	[a]	Phosphate	White	..
$RbCdF_3$	Cd, 44.10	Cd, 43.50, 43.75	Anthranilate	White	..
	F, 22.36	F, 22.03, 22.16			
$RbCoF_3$	Co, 29.26	Co, 29.40, 29.29	Electrolysis	Pink	..
	F, 28.30	F, 27.94, 27.98			
$RbCuF_3$	Cu, 30.84	Cu, 30.37, 30.52	Anthranilate	Pale blue	14
	F, 27.67	F, 26.74, 26.96			
$RbMnF_3$	Mn, 27.83	Mn, 27.60, 27.37	Oxide	Light pink	..
	F, 28.87	F, 28.37, 28.50			
$RbNiF_3$	Ni, 29.20	Ni, 28.50, 28.65	Electrolysis	Yellow	.
	F, 28.35	F, 27.70, 27.90			
$RbZnF_3$	Zn, 31.45	Zn, 30.83, 30.77	Anthranilate	White	11
	F, 27.42	F, 27.34, 27.52			
Rb_3FeF_6	Fe, 13.10	Fe, 12.35, 13.53	Oxide	White	12
	F, 26.74	F, 26.54, 16.04			
Rb_3ZrF_7	Zr, 18.98	Zr, 18.34, 18.40	Oxide	White	..
	F, 27.67	F, 27.40, 27.27			

[a] Analysis indicates a mixture of $RbBiF_4$ and $RbBi_2F_7$.

TABLE III

CESIUM FLUOROMETALLATES

Formula	*Anal.* calcd., %	*Anal.* found, %	Metal method	Color	Ref.
$CsBi_2F_7$	Cs, 19.43	Cs, 18.39, 18.68	....	White	..
	Bi, 61.12	Bi, 60.83, 61.18	Phosphate		
	F, 19.45	F, 19.20, 19.05			
CdF_2	......	[a]	....	...	..
$CsCo_2F_5$	Cs, 38.44	Cs, 39.45, 38.15	....	Pink	..
	Co, 34.09	Co, 33.70, 34.10	Electrolysis		
	F, 27.47	F, 26.73, 26.99			
CuOHF	......	[a]	....	...	..
$Cs_xMn_yF_z$	......	[b]	....	...	..
$Cs_xNi_yF_z$	......	[b]	....	...	..
$Cs_xZn_yF_z$	......	[b]	....	...	..
Cs_3FeF_6	Cs, 63.18	Cs, 62.20, 62.70	....	White	..
	Fe, 13.47	Fe, 12.80, 12.68	Oxide		
	F, 22.73	F, 22.64, 22.81			
Cs_2ZrF_6	Cs, 56.45	Cs, 56.37, 56.10	....	White	13
	Zr, 19.36	Zr, 19.85, 19.74	Oxide		
	F, 24.20	F, 24.90, 24.60			

[a] Identified by X-ray powder patterns. [b] Analysis and X-ray powder patterns indicate several compounds present.

situation exists with zinc and manganese as well, for powder pattern evidence indicates the existence of more than one compound, and analysis indicates low cesium content in some of the mixtures. Schmitz-DuMont[11] has shown the existence of $CsZn_2F_5$ in the fused system CsF–ZnF. However, powder patterns taken of the products of the reactions of various concentrations of cesium fluoride and zinc fluoride in methanol have not corresponded to the powder patterns taken by Schmitz-DuMont. The bismuth complex $CsBi_2F_7$ also has a cesium to metal ratio of less than one. In the case of bismuth, however, this tendency first appears in the rubidium reaction which has a product that is a mixture of $RbBiF_4$ and $RbBi_2F_7$. That bismuth should do this is somewhat unusual, in that bismuth is the largest of the heavy metal cations considered. Again the answer probably lies in the relative stabilities of crystal structures involved, which in this case are not known. The failure of both cadmium and copper to form cesium complexes is also rather interesting. In the case of cadmium a possible explanation lies in the low relative affinity that cadmium(II) shows for the fluoride ion. This has been pointed out recently by Ahrland, Chatt and Davies,[15] and would tend to give cadmium a mediocre ability to form a complex fluoride anion. This, coupled with the rather large size of the cesium ion, results in the precipitation of cadmium fluoride. There is no obvious explanation for the behavior of the copper.

In considering the course of the reaction taking place in methanol solution between the alkali fluoride and the metal bromide, little can be concluded. The foremost unknown factor is the species of the metal bromide present in the methanol solutions. Color changes on dilution, heating and upon the addition of small quantities of water seem to indicate in some cases, at least, that there is methanolation of the metal ion. That the formation of the compound itself is not strictly an ionic reaction is indicated by the slowness of some of the reactions, especially those of cobalt bromide and nickel bromide with ammonium fluoride. Heating of the solution increases the reaction rate considerably. From the reaction of ferric bromide with sodium fluoride in methanol, the immediate decolorization of the ferric bromide solution indicates the formation of a colorless anion, probably the hexafluoroferrate(III) ion. In the case of reaction with sodium fluoride, however, no insoluble product is formed, probably due to the small size of the sodium ion. Similarly cobalt, manganese and cadmium fail to form a precipitate with sodium fluoride. This would tend to indicate that the first step in these reactions is the formation of a soluble complex

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[11] O. Schmitz-DuMont and H. Bornefeld, *Z. anorg. Chem.*, **287**, 120 (1956).

[12] W. Minder, *Z. Krist.* **96**, 15 (1937).

[13] H. Bode and G. Teufer, *Z. anorg. Chem.*, **283**, 18 (1956).

[14] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, Longmans, Green and Company, London, p. 157.

[15] S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev.*, **12**, 265 (1958).

anion and that in some cases, at least, the first step is considerably faster than the subsequent ones. It should be noted that the presence of fluorocomplexes in solution does not imply that similar or related complex ions exist as such in the solid products obtained. Structural results show that some of the compounds are mixed salts and should not be classified as complexes. Thus, $RbMnF_3$ should not be envisioned as containing discrete MnF_3^- and Rb^+ ions but as composed of Rb^+, Mn^{++} and F^- ions and named as rubidium manganese(II) fluoride. We have used the term fluorometallate as a convenience. The nature of the metal bromide species in methanol, and possible complex formation are being investigated further.

II. Some Structural Relationships in the Fluorometallates of Ammonium, Potassium and Rubidium

Experimental

Infrared Spectra.—All infrared spectra were taken on a Perkin–Elmer model 21 spectrophotometer, with sodium chloride optics. The samples were run as mulls prepared with halocarbon oil (series 11–14), as described by Crocket and Haendler,[16] or with Nujol.

X-Ray Powder Photographs.—All powder patterns were taken using 57.3 and 114.56 mm. Philips cameras. Copper and iron radiation were used, and samples were mounted in 0.3 mm. glass capillaries. Intensities were estimated visually and with the aid of a densitometer (Welch Densichron). Unit cell parameters were calculated from the powder data.[17]

Discussion of Results

The manganese(II), cobalt(II) and zinc(II), trifluorometallates of ammonium, potassium and rubidium are isostructural. The powder patterns are readily indexed as cubic, with the unit cell parameters as listed in Table IV. For comparison, the unit cell values of Knox,[3] from single crystal data, and of Nyholm and co-workers[4] are also listed. The latter assigned a pseudo-cubic structure to these compounds on the basis of several faint lines observed in the powder patterns of samples prepared from aqueous solution. Long exposure of samples prepared from methanol gave no indication of any lines other than those of cubic index, and interplanar spacings of these lines agree with values calculated from unit cell data given by Knox. Copper(II), as would be expected from considerations of the ligand field theory, exhibits a distortion of the normally symmetrical crystallographic coördination of six fluorides about the central metal atom, resulting in a lower symmetry for the copper(II) complexes of ammonium, potassium and rubidium. The three compounds remain isostructural, however, as shown from the powder patterns, and can be indexed as tetragonal. Knox has shown $KCuF_3$ to be tetragonal with $a = 8.280$ and $c = 7.844$, $c/a = 0.947$. The $KCuF_3$ prepared from methanol gives the same interplanar spacings as the single crystal used by Knox. The approximate corresponding parameters for NH_4CuF_3 are $a = 8.62$, $c = 7.78$, $c/a = 0.90$ and for $RbCuF_3$, $a = 8.48$, $c = 7.88$, $c/a = 0.93$.

TABLE IV

COMPARISON OF UNIT CELL PARAMETERS, a

Compound	This work	Knox[3]	Nyholm[4]
$KMnF_3$	4.192	4.182	4.19
$KCoF_3$	4.078	4.071	4.07
$KZnF_3$	4.057	4.063	4.05
NH_4MnF_3	4.238	...	..
NH_4CoF_3	4.129	...	..
NH_4ZnF_3	4.115	...	..
$RbMnF_3$	4.243	...	..
$RbCoF_3$	4.141	...	..
$RbZnF_3$	4.116	...	..

Table V lists the infrared absorption bands for the ammonium fluorometallates considered in this work, along with comparisons of the structures of the analogous potassium and rubidium compounds. According to Waddington,[6] the presence of hydrogen bonding in ammonium compounds is indicated by the appearance of a $\nu_4 + \nu_6$ band at about 1600 cm.$^{-1}$ and by the failure of the ammonium compound to be isostructural with the corresponding potassium and rubidium compounds. These are indications of interference in the free rotation of the ammonium ion. Of the ammonium complexes included in this work, NH_4CuF_3, NH_4MnF_3, NH_4CoF_3, NH_4ZnF_3 and $(NH_4)_3FeF_6$ indicate an absence of hydrogen bonding, both from the absence of an absorption band in the region 1600 cm.$^{-1}$ and from the isostructural nature of the respective ammonium, potassium and rubidium complexes. The diammonium complexes $(NH_4)_2NiF_4$ and $(NH_4)_2CuF_4$, in contrast, appear to have hydrogen bonding, both from infrared data and X-ray powder pattern comparisons. In this case, since the rubidium complexes are not known, structural evidence is based on the comparison of the powder patterns of $(NH_4)_2CuF_4$ and $(NH_4)_2NiF_4$ with K_2CuF_4 and K_2NiF_4, which in both cases show the ammonium and potassium complexes not to be isostructural. NH_4CdF_3 exhibits a pronounced absorption band at 1790 cm.$^{-1}$ and from the powder patterns appears to be of lower symmetry than the corresponding potassium and rubidium complexes, which can be indexed as cubic. That NH_4CdF_3 should exhibit hydrogen bonding is particularly interesting since $KCdF_3$ and $RbCdF_3$ appear isostructural with those complexes listed in Table V. A possible explanation lies in the low affinity displayed by cadmium for the fluoride ion, as recently pointed out by Ahrland, Chatt and Davies.[15] This enhances the attraction between hydrogen in the ammonium ion and fluoride ion, resulting in a noticeable degree of hydrogen bonding in this case. NH_4NiF_3 presents an anomalous situation in that the infrared spectrum shows a weak band at 1640 cm.$^{-1}$, while the powder pattern data indicates $KNiF_3$ and NH_4NiF_3 to be isostructural. The relative magnitude of the absorption peak at 1640 cm.$^{-1}$, however, is not comparable to that of either NH_4CdF_3 or $(NH_4)_2CuF_4$ and $(NH_4)_2NiF_4$. If there is a tendency toward hydrogen bonding in NH_4NiF_3, it is presumably not of sufficient proportion to cause a distortion of the crystal structure from that found in $KNiF_3$.

The infrared spectra of diammonium tetrafluoronickelate(II) and diammonium tetrafluorocuprate (II) give evidence of some interesting structural characteristics. In both cases two widely separated

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[16] D. S. Crocket and H. M. Haendler, *Anal. Chem.*, **31**, 626 (1959).

[17] N. F. M. Henry, H. Lipson and W. A. Wooster, "The Interpretation of X-Ray Diffraction Photographs," D. Van Nostrand Co., New York, N. Y., 1951, p. 192.

TABLE V

INFRARED SPECTRA

Compound	ν_4	$\nu_4 + \nu_6$	$2\nu_4$	$\nu_2 + \nu_4$	ν_3	K complex	Rb complex
NH_4CuF_3	1435	..	2880	3080	3260	Isostruct.	Isostruct.
NH_4CoF_3	1445	..	..	..	3240	Isostruct.	Isostruct.
NH_4CdF_3	1425	1790	2840	3020	3200	Not isostruct.	Not isostruct.
NH_4MnF_3	1437	..	2845(sh)[e]	3078(sh)	3260	Isostruct.	Isostruct.
NH_4NiF_3	1425	1640 (slight)	2860(sh)	3120(sh)	3290	[a]	[b]
NH_4ZnF_3	1435	..	2880(sh)	3090(sh)	3260	Isostruct.	Isostruct.
$(NH_4)_2CuF_4$	1430, 1473	1677	2890	3070	3240	Not isostruct.	[c]
$(NH_4)_2NiF_4$	1415, 1470	1717	2860	3140(sh)	3270	Not isostruct.	[c]
$(NH_4)_3FeF_6$	1432	..	2865(sh)	3035	3240	Isostruct.	[d]

[a] Powder pattern from sample prepared by thermal decomposition of $(NH_4)_2NiF_4$ appears isostructural. [b] Poor powder pattern, appears isostructural. [c] Compounds not known. [d] Powder pattern not good enough for positive identification. Cox and Sharpe[5] indicate no hydrogen bonding. [e] sh = shoulder.

peaks of approximately equal magnitude appear in the 1400–1500 cm.$^{-1}$ region, connected with the ν_4 deformation frequency. This compares to one well defined peak for the other compounds, irrespective of the stoichiometric ratio of the ammonium ions to central metal ion. The position of this ν_4 absorption band varies with the compound, ranging from about 1425 cm.$^{-1}$ for most of the complexes to about 1480 cm.$^{-1}$ for highly hydrogen-bonded ammonium fluoride. In those fluorometallates whose structure is known, the position of every ammonium ion in the crystal is identical as to its environment.

The dual peaks observed in $(NH_4)_2CuF_4$ and $(NH_4)_2NiF_4$ are probably not due merely to a splitting of the ν_4 absorption band caused by distortion of the ammonium ion, as shown by Wagner and Hornig[18] in the infrared spectra of NH_4Br and NH_4Cl. If the distortion of the ammonium ion were sufficient in $(NH_4)_2CuF_4$ and $(NH_4)_2NiF_4$ to produce ν_4 splitting of the magnitude observed, it would be expected that the $\nu_4 + \nu_6$ band would be more pronounced and sharper than is observed. It is suggested, therefore, that in the case of $(NH_4)_2NiF_4$ and $(NH_4)_2CuF_4$ the ammonium ions occupy two unequivalent lattice positions, resulting in two distinct ν_4 bands. The higher one in each case, 1475 cm.$^{-1}$ for $(NH_4)_2CuF_4$ and 1470 cm.$^{-1}$ for $(NH_4)_2NiF_4$, would be associated with ammonium ions which more closely approximate the environment of ammonium ions in NH_4F.

Reflections have been cast upon the identity of some fluorometallates when prepared from aqueous solutions.[5] These are further supported by some data obtained as the result of an observed color anomaly in the thermal decomposition of ammonium trifluorocuprate(II). The color of the complex varies from white to blue, depending on the age of the copper(II) bromide solution in methanol. There is a direct relationship between the formation of a brown thermal decomposition product and the intensity of blue color in the original complex. The powder patterns for the complexes are identical, as are those of the products which show only copper(II) fluoride. Copper(II) oxide is not present, and hydrolysis leads to CuOHF, without contamination.

A similar situation occurs in the preparation of $KCuF_3$, and it has been possible to establish a connection between the blue color of the sample and the replacement of fluoride ion by hydroxyl ion. The bluest of the potassium complexes produced was shown by analysis to be the extreme case $KCuOHF_2$.

Anal. Calcd. for $KCu(OH)F_3$: Cu, 40.31; F, 24.10. Found: Cu, 39.12, 39.64; F, 24.01, 24.13.

The presence of the hydroxyl group was confirmed with infrared spectra by the appearance of a band in the region 3400 cm.$^{-1}$. Direct addition of a small amount of water to the copper(II) bromide solution, results in formation of CuOHF. It is suggested that the brown color of the decomposition product as well as the blue color of the complex is due to the variable and random replacement of fluoride ions by hydroxyl ions. Since the X-ray powder patterns are identical regardless of color, it appears that the fluoride ions are replaced without disturbing the crystal structure of the compound. That this is possible can be seen by comparing the crystal structures of copper(II) fluoride as determined by Billy and Haendler[19] with the structure of copper fluoride dihydrate as determined by Geller and Bond.[20] In the dihydrate two of the four fluorides nearest to the copper have been replaced by water molecules. The copper–oxygen distance remains quite similar to the original copper–fluorine distance, however, being 1.89 and 1.93 Å., respectively. The difference between the copper–oxygen distance of a hydroxide ion and a water molecule is not considered as being significant.

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(18) E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296, 305 (1950).

(19) C. Billy and H. M. Haendler, THIS JOURNAL, **79**, 1049 (1957).

(20) S. Geller and W. L. Bond, *J. Chem. Phys.*, **29**, 925 (1958).