oxygen sheets in the $BaTi_4O_9$ structure,[6] but the stacking of these sheets is quite different. We know of no other substance with a structure which resembles the entire arrangement.

The layers are bonded together only by weak forces. The I–I contacts between layers (Table VI) all exceed 4.07 Å. The orientation of these layers conforms to the platy $\{10\bar{1}\}$ habit of the crystals.

TABLE VI

IODINE–IODINE DISTANCES BETWEEN LAYERS

Atoms	Distance,[a] Å.
I(1)–I(2)	4.155
I(1)–I(3)	4.252
I(2)–I(3)	4.125
I(2)–I(4)	4.079

[a] Standard deviations are 0.006 Å. or less.

[6] D. H. Templeton and C. H. Dauben, *J. Chem. Phys.*, **32**, 1515 (1960).

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The Interaction between Ammonium Fluoride and Metal Fluorides as Compressed Powders

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Finely powdered mixtures of metal fluorides interact with NH_4F to form double salts of the type NH_4MF_3 (where M = Co^{+2}, Cu^{+2}, Mn^{+2}, Cd^{+2}, Ni^{+2}, or Zn^{+2}) at pressures of 100,000 p.s.i. at 25°. In the case of Co, Cu, Ni, and Zn compounds heating to 110° caused the formation of $(NH_4)_2MF_4$ type compounds which are isostructural with K_2NiF_4.

Introduction

The interchange of anions in powdered mixtures subjected to pressure has been shown by Meloche and Kalbus,[1] Ketelaar,[2] and others. Nonnenmacher and Merke[3] have also shown that complex ions can be formed under pressure in the formation of KBr disks used in infrared spectral determinations.

With this in mind it was decided to investigate a series of known fluoride double salts as to the interaction of powdered mixtures of their components under various conditions of temperature and pressure.

Experimental

Reagents.—The NH_4F used throughout was J. T. Baker or Mallinckrodt analytical grade reagent. It was further purified by dissolving in methyl alcohol and reprecipitating by the addition of ether. Cobalt(II) fluoride and manganese(II) fluoride were prepared by the reaction of the carbonates with HF followed by oven heating to remove water. The infrared spectra of these compounds showed them to be anhydrous. Copper(II) fluoride and nickel fluoride were formed by reaction of the metal bromide with ClF_3 at 250–300°.[4] X-Ray diffraction patterns gave lines attributable only to the fluorides.

Complex Fluorides.—The known fluoride complexes NH_4ZnF_3, NH_4CoF_3, NH_4CuF_3, NH_4CdF_3, and NH_4MnF_3 for comparison purposes were prepared by reaction of the metal bromides with ammonium fluoride in methyl alcohol as fully described by Haendler, *et al.*[5]

Analytical.—Copper, zinc, nickel, and cobalt were determined using standard EDTA titrations.

Ammonia was determined by distillation from strongly alkaline solutions into cold boric acid solution, followed by titration with hydrochloric acid, using brom cresol green indicator.

Fluorine was determined by distillation from sulfuric acid solution[6] followed by titration of aliquots of distillate with cerium(III) chloride, using murexide indicator.[7]

Infrared spectra were determined using a Beckman IR-5 spectrophotometer with sodium chloride optics. Samples were run as Halocarbon mulls[8] on calcium fluoride plates.

X-Ray diffraction patterns were taken using a G.E. RDX-5 diffractometer with filtered copper Kα and iron Kα radiation.

Procedure for Determination of Complex Formation in the Mixtures of NH_4F and Metal Fluorides.—The particular metal fluoride involved was well ground with a large excess of ammonium fluoride in an agate mortar and pestle. The mixture was then placed in a die constructed of a 0.5-in. i.d. steel bushing[9] and two hardened steel pins, one 0.5 in. long, the other 2.5 in. long; the diameter was such as just to allow passage through the bushing. The mixture was then pressed into a pellet by subjecting it to a pressure of about 100,000 p.s.i. in a Carver 10-ton bench press. Depending upon the circumstances the pellet was held at this pressure for a certain length of time or removed immediately. Again depending upon the purpose of the particular run the pellet might or might not be heated. The pellet was then reground, leached with methyl alcohol to remove the unchanged ammonium fluoride, and dried with anhydrous ether. Since the complex fluorides are very insoluble in methyl alcohol, and the metal fluorides are for the most part insoluble in methyl alcohol also, these remained as a residue. The formation of any complex was then shown from a comparison of the infrared spectrum or X-ray powder pattern of the residue with that of an authentic sample, and the amount of complex formed could be determined from an ammonia analysis, since the only ammonium ion remaining in the residue was tied up in the complex.

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[1] V. W. Meloche and G. E. Kalbus, *J. Inorg. Nucl. Chem.*, **6**, 104 (1958).

[2] J. A. A. Ketelaar, C. Haas, and J. van der Elshen, *J. Chem. Phys.*, **24**, 624 (1956).

[3] W. Nonnenmacher and R. Merke, *Chem. Ber.*, **93**, 1279 (1960).

[4] J. Parcher, B.S. Thesis, Lafayette College, Easton, Pa., 1962.

[5] (a) H. M. Haendler, F. A. Johnson, and D. S. Crocket, *J. Am. Chem. Soc.*, **80**, 2662 (1958); (b) D. S. Crocket and H. M. Haendler, *ibid.*, **82**, 4158 (1960); (c) A. E. Baker and H. M. Haendler, *Inorg. Chem.*, **1**, 127 (1962).

[6] W. B. Huckabay, E. T. Welch, and A. V. Metter, *Ind. Eng. Chem., Anal. Ed.*, **19**, 154 (1947).

[7] C. Brunisholz and J. Michod, *Helv. Chim. Acta*, **37**, 598, 1546 (1954).

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

[9] Accurate Bushing Co., Garwood, N. J.

TABLE I

THE EFFECT OF CONDITIONS ON THE PERCENTAGE OF COMPLEX FORMATION IN MIXTURES OF METAL FLUORIDE AND AMMONIUM FLUORIDE[a]

	Simple mixture not pressed			Mixture pressed into pellet at 100,000 p.s.i.[b]			
Metal fluoride	Analyzed immediately	1 hr. in desiccator at 25°	1 hr. at 110°	Analyzed immediately	1 hr. in desiccator at 25°	Under pressure 1 hr. at 25°	1 hr. at 110°
CoF_2	4.3	4.2	50	5.5	35.6	44.8	65
MnF_2[c]	13	14	27	19	21	22	56
NiF_2	4.2	4.5	37	15	5.5	6.1	41
ZnF_2[c]	14.7	25.7	93	23	51.0	69	[d]

[a] Based on formation of the 1:1 complex; average value for three runs from the ammonia present in residue after leaching with methanol. [b] Pellet under pressure only during its formation (2–3 min.) except for column under pressure 1 hr. [c] Some degree of formation of 1:1 complex during leaching step due to slight solubility of metal fluoride; formamide unsuccessfully tried as solvent (see W. Rudorf, J. Kandler, and D. Babel, *Z. anorg. allgem. Chem.*, **317**, 261 (1962)). [d] Formation of $(NH_4)_2ZnF_4$ in excess of 75%.

Formation of the 2:1 Complexes.—The preceding experimental method was used with a few modifications, adopted in an attempt to get the most complete reaction possible. The 2:1 complexes were formed by pressing the 1:1 complex prepared by other means with an excess of ammonium fluoride and then heating the pellet at 110° for 2 hr. in an oven at 1 atm. The pellet was then usually left in a desiccator overnight before leaching with methyl alcohol.

Anal. Calcd. for $(NH_4)_2CuF_4$: NH_3, 20.5; Cu, 36.2; F, 43.3. Found: NH_3, 20.6; Cu, 36.7; F, 42.7.

Anal. Calcd. for $(NH_4)_2ZnF_4$: NH_3, 20.3; Zn, 36.9; F, 42.8. Found: NH_3, 19.1; Zn, 38.4; F, 42.5.

Results and Discussion

When MF_2 (where M = Cd, Co, Mn, Ni, or Zn) was mixed with powdered NH_4F and pressed into pellets at room temperature at *ca.* 100,000 p.s.i., a NH_4MF_3 type complex was formed. This was indicated by comparing the X-ray diffraction patterns and the infrared spectra of authentic samples with the residue that was left after the pellets had been leached with methyl alcohol. In X-ray powder patterns of the *unwashed* mixture it was also possible to identify the lines attributable to the complex fluoride.

An indication of the amount of complex formation taking place was measured for M = Co, Mn, Ni, or Zn, by analysis for residual ammonia on mixtures washed with methanol. In every case a small degree of interaction takes place in the mixing and washing process itself.

From Table I it is concluded that the effect of pressure on these mixtures appears to be that of a concentration effect in that the particles are placed in closer proximity when formed into a pellet. This is concluded from (1) the small difference in complex formation between a pellet held at 100,000 p.s.i. and a pellet kept in a desiccator; (2) in almost every instance a thin pellet (proportionately large surface) gave much lower yields than a thicker pellet. It is also noted that, as in the case of anion exchange both on salt plates[10] and in KBr disks,[1,2] surface moisture greatly enhances interaction. This was found to be especially true in mixtures at room temperature. No attempt was made to exclude all moisture; however, samples were oven dried and experiments carried out in a dehumidified room with relative humidity less than 45%.

The effect of temperature on these mixtures is also indicated in Table I. The temperature chosen, 110°, gave the maximum amount of interaction in all cases. At higher temperatures loss of NH_4F occurs, causing break-up of the pellets, and also, as will be discussed later, the decomposition of the 2:1 complexes which form in some instances. At 110° there is no sintering or fusing of the pellets, so the reaction remains a solid–solid interaction. Although NH_4F would exhibit a considerable vapor pressure at this temperature it is not felt that this is a solid–vapor interaction since: (1) preliminary investigation with the KF–metal fluoride system gave the same results, (2) at slightly higher temperatures where the vapor pressure of NH_4F is higher, and where considerable pitting of the surface of the pellets occurs due to loss of NH_4F, there is less reaction.

Formation of the 2:1 Complex Fluorides.—The formation of the $(NH_4)_2MF_4$ complexes (M = Co, Cu, Ni, or Zn) was first noticed in the infrared spectra of their washed residues from a splitting in the ν_4 ammonium band which occurs at about 1400 cm.$^{-1}$. The infrared spectra have been reported for the compounds $(NH_4)_2NiF_4$ and $(NH_4)_2CuF_4$[5b] prepared in methyl alcohol. The formation of the higher complex was confirmed from X-ray diffraction patterns for the washed residues which contained lines attributable to the 1:1 complex, no lines attributable to the metal fluoride, and a set of lines for a compound isostructural with K_2NiF_4.

This also indicated that in each case the formation of the 2:1 complex takes place in a stepwise fashion; for example

$$ZnF_2 + NH_4F \longrightarrow NH_4ZnF_3$$

$$NH_4ZnF_3 + NH_4F \longrightarrow (NH_4)_2ZnF_4$$

This is further suggested from the greatly increased yield of $(NH_4)_2MF_4$ attained by starting with NH_4MF_3.

Failure to find $(NH_4)_2MnF_4$ is compatible with the results of Hoppe, *et al.*,[11] and with the fact that K_2MnF_4 and Rb_2MnF_4 have not been reported. There also is no evidence for the formation of $(NH_4)_2CdF_4$. This is not surprising since cadmium shows inhibitions concerning its complexing with fluorine as seen in its failure to form Cs_xCdF_y complexes.[5b] NH_4CdF_3 is

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(10) D. S. Crocket and R. Grossman, *Anal. Chem.*, **34**, 1505 (1962).

(11) R. Hoppe, W. Liebe, and W. Dahne, *Z. anorg. allgem. Chem.*, **307**, 276 (1961).

Table II

X-Ray Diffraction Data for $(NH_4)_2ZnF_4$

a = 4.14 Å. c = 13.97 Å.

d, Å.	I/I_0[a]	hkl	10^4Q obsd.	10^4Q calcd.[b]
7.02	90	002	203	205
4.13[c]	11			
3.99	100	101	629	634
3.48	5	004	828	820
3.09	45	103	1048	1045
2.94[c]	60	110	1159	1167
2.30	40	105	1186	1865
2.24	2	114	1986	1986
2.07	55	200	2331	2333
1.98	20	202	2541	2538
1.84	25	211	2963	2968
1.81	12	107	3059	3095
1.78	15	204	3160	3153
1.72	15	213	3351	3379
1.68[c]	...			
1.54	10	215	4155	4199
1.48	...			
1.46	10	220	4680	4667
1.43	5	222	4872	4872
1.37	3	301	5312	5301

[a] Estimated from diffractometer chart. [b] $Q = 1/d^2$. [c] Corresponds with a line in pattern for NH_4ZnF_3.

also not the simple perovskite structure as are the other 1:1 complexes used in this work. When starting from the zinc fluoride there was always an appreciable amount of NH_4ZnF_3 indicated in the X-ray pattern, and generally no residual zinc fluoride. By starting with the 1:1 complex and ammonium fluoride it was possible in the zinc and copper systems to synthesize the pure phases of $(NH_4)_2ZnF_4$ and $(NH_4)_2CuF_4$ (see Experimental section).

Properties of the 2:1 Complex Fluorides.—From the X-ray data in Tables II and III it can be seen that $(NH_4)_2ZnF_4$ and $(NH_4)_2CoF_4$ are of the K_2NiF_4 type. This is as was expected since the 1:1 complexes NH_4ZnF_3 and NH_4CoF_3 have perovskite structures and are isostructural with the potassium and rubidium analogs.[12]

Balz and Plieth[13] in their discussion of the structure of K_2NiF_4 have aptly pointed out the structural relationship between the rutile structure of certain metal fluorides, the perovskite structure of the corresponding 1:1 complex fluoride, and the 2:1 complex fluoride in terms of maintenance of the octahedral metal–fluorine bonding and the "adding on" of, in that case, KF. In the structure of K_2NiF_4, the $KNiF_3$ entity can be seen to remain intact.[14] In view of the structural relationships this stepwise buildup, as well as the stepwise thermal decomposition of $(NH_4)_2ZnF_4$, is not surprising. The thermogravimetric analysis of $(NH_4)_2ZnF_4$ shows that $(NH_4)_2ZnF_4$ begins to evolve NH_4F above 55°, decomposing rapidly above 125°; between 160 and 180° NH_4ZnF_3 remains stable, then rapidly evolves another mole of NH_4F, giving ZnF_2 above 235°. The thermal decomposition of $(NH_4)_2NiF_4$ and $(NH_4)_2CuF_4$ has been reported previously.[5b]

The inability to form the 2:1 complexes $(NH_4)_2ZnF_4$ and $(NH_4)_2CoF_3$ by the reaction of NH_4F with $CoBr_2$ or $ZnBr_2$ in methyl alcohol lies in the almost complete insolubility of the 1:1 complexes.[5a,b] Samples of NH_4ZnF_3 or NH_4CoF_3 suspended in a saturated NH_4F solution over a long period of time have given no indication of forming the 2:1 complex. Recently Rudorf, Lincke, and Babel[15] have reported failure to find $(NH_4)_2CoF_4$ in the system NH_4HF_2 and CoF_2. Since they were working at temperatures above 130° in molten NH_4HF_2 they were above the decomposition temperature of the 2:1 complex. In this same paper the complex copper compounds are also discussed; however, no mention is made of the CuF_2–NH_4HF_2 system. $(NH_4)_2CuF_4$ should exist in this system since preliminary work in this laboratory on the interaction of $CuCO_3$ with NH_4HF_2 has shown its existence in an instance where the melt was brought to 170°. Again in the fused system $NH_4HF_2 + ZnF_2$ one would not expect to isolate $(NH_4)_2ZnF_4$ due to its low decomposition temperature.

Table III

X-Ray Diffraction Data for $(NH_4)_2CoF_4$

$NH_4F + NH_4CoF_3$

d, Å.	I/I_0[a]	hkl[b]
6.89	100	002
4.37	4	?
4.14[c]	12	
3.98	100	101
3.45		004
3.23[d]		
3.08	40	103
2.93	60	110
2.30	45	006 105
2.23		114
2.07	60	200
1.98	15	202
1.84	20	211
1.81	6	116
1.78	12	107
1.72	12	213
1.64[d]	2	
1.54	25	206 215
1.46	12	118
1.43	2	220
1.37	2	301

[a] Estimated from diffraction chart. [b] Indexed by analogy to $(NH_4)_2ZnF_4$. [c] Lines attributable to NH_4CoF_3. [d] Lines attributable to CoF_2.

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(12) In a private communication Dr. H. M. Haendler has pointed out that $(NH_4)_2CuF_4$ is isostructural with K_2NiF_4. This work is soon to be published by him.

(13) D. Balz and K. Plieth, *Z. Elektrochem.*, **59**, 545 (1955).

(14) See structure of K_2NiF_4 in ref. 14, Fig. 4.

(15) W. Rudorf, G. Lincke, and D. Babel, *Z. anorg. allgem. Chem.*, **320**, 150 (1963).