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Synthesis of Fluorometallates in Methanol. The Solid Solution NH_4MnF_3 - NH_4ZnF_3 [1]

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Solid solutions of anhydrous ammonium fluorometallates can be prepared from methanol solution by reaction of ammonium fluoride with a solution of mixed bromides, prepared by direct bromination of the metal mixture in methanol. Solid solutions in the series NH_4MnF_3 - NH_4ZnF_3 have been prepared and characterized. X-Ray diffraction, magnetic susceptibility, thermal decomposition, and infrared spectra have been studied as functions of composition.

Introduction

In previous work,[4,5,6] we have shown that anhydrous, unhydrolyzed fluorometallates can be prepared by reaction of alkali and ammonium fluorides with metal bromide solutions in methanol. Interaction with the solvent has been detected only with the Group V metals.[6] The present study demonstrates that this technique is applicable to the preparation of solid solutions of fluorometallates. A few studies of solid solutions of alkali fluorometallates have been reported.[7,8] In these instances the most satisfactory method of preparation involved fusion of alkali hydrogen fluoride with the two metal fluorides in an argon-hydrogen fluoride atmosphere at 800°. This procedure is not applicable to the preparation of solid solutions containing ammonium fluorometallates, as these decompose at relatively low temperatures. Solid solutions of composition $NH_4(Me_xMe'_{1-x})F_3$ can readily be prepared by precipitation with ammonium fluoride from solutions of the mixed bromides in methanol. The solid solutions decompose to solid solutions of the metal fluorides on heating, suggesting several interesting applications to the study of solid state kinetics.

Ammonium trifluoromanganate(II), NH_4MnF_3, and trifluorozincate, NH_4ZnF_3, are isostructural, based upon the x-ray powder patterns.[5] They have been indexed as cubic, with unit cell parameters of 4.242 Å and 4.120 Å, respectively. The simple fluorides, MnF_2 and ZnF_2, are also isostructural, with the rutile structure. This, and the distinct difference in magnetic susceptibility of Mn^{2+} and Zn^{2+}, suggested the system NH_4MnF_3 - NH_4ZnF_3 as an effective model on which to test this method of synthesis.

Experimental Section

Preparation of the Solid Solutions. The reactions were done in a nitrogen atmosphere. Appropriate quantities of manganese and zinc were suspended in methanol and bromine slowly added to excess, keeping the mixture under gentle reflux. Solutions were thus prepared with selected mole ratios of manganese/zinc. The solutions were filtered to remove any traces of insoluble material and added to warm saturated ammonium fluoride in methanol. After digestion, the precipitate was removed by filtration, washed with methanol until free of bromide, and dried in an Abderhalden drying apparatus over boiling acetone to avoid the slow decomposition which can occur at higher temperature. Tests for bromide in the solid, and for manganese and zinc in the filtrate, were negative. Ammonium fluoride and hydroxyl groups were shown to be absent by infrared spectral measurement. Since precipitation was shown to be complete, and since infrared analysis and chemical tests confirmed the absence of contamination, complete analyses of the products were not carried out. The solids were checked for zinc content by atomic absorption analysis and, in the case of samples of high zinc content, by gravimetric analysis with anthranilic acid, in order to detect any gross error in preparation. These data are summarized in Table I.

X-Ray Powder Photographs. Powder patterns were taken with a 114.56 mm Philips camera, with filtered copper and iron radiation. Samples were screened through 325-mesh silk and mounted in 0.3 mm glass capillaries.

Magnetic Measurements. These were made by the Gouy method, using a Varian V-4004 magnet system, at a field strength of 8000 gauss. $Hg[Co(SCN)_4]$ was used for calibration. Measurements were in duplicate with a precision of 0.03 B.M.

Thermogravimetric Analysis. Weight loss as a function of temperature was measured on a thermobalance constructed by Kingston.[9] Samples (50-70 mg)

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[9] D. W. Kingston, M. S. Thesis, University of New Hampshire, 1962.

Table I. Summary of results.

Mole % NH_4MnF_3	Unit cell parameter, *a*, Å	Magnetic Moment B.M.	Decomposition temperature, °C	Weight % Zn(Calc)	Weight % Zn(Found)
0.0	4.120	0.00	210	46.6	46.2[a]
1.0	—	0.60	—	—	—
12.5	4.134	1.90	—	41.1	41.3[a]
25.0	4.158	2.62	215	35.5	34.7
50.0	4.178	3.77	225	24.2	23.5
75.0	4.219	4.37	233	12.3	12.0
87.5	4.232	4.69	—	6.2	6.3
100.0	4.242	5.00	240	—	—

[a] Average of atomic absorption and gravimetric determinations.

of the solid solutions were decomposed at a heating rate of approximately 3°/min in an atmosphere of nitrogen.

Infrared Spectra. Spectra were taken of mulls in Halocarbon oil, using a Perkin-Elmer Model 337 spectrophotometer in the range 4000-1200 cm^{-1}.

Discussion of Results

X-Ray Measurements. Comparison of the x-ray powder patterns of the products shows clearly the existence of solid solutions over the entire range of composition. The lattice parameters vary linearly with composition, in accord with Vegard's Law. The lattice parameters were calculated using the method of Henry, Lipson, and Wooster,[10] using the higher order reflections. The cubic unit cell dimension is calculated from each line of known index, and each value is plotted against the error function of Nelson and Riley.[11] Extrapolation to zero error function gives the best value for the cell parameter, *a*. A representative plot is shown in Figure 1, and the final results for the system are summarized in Table I and Figure 2.

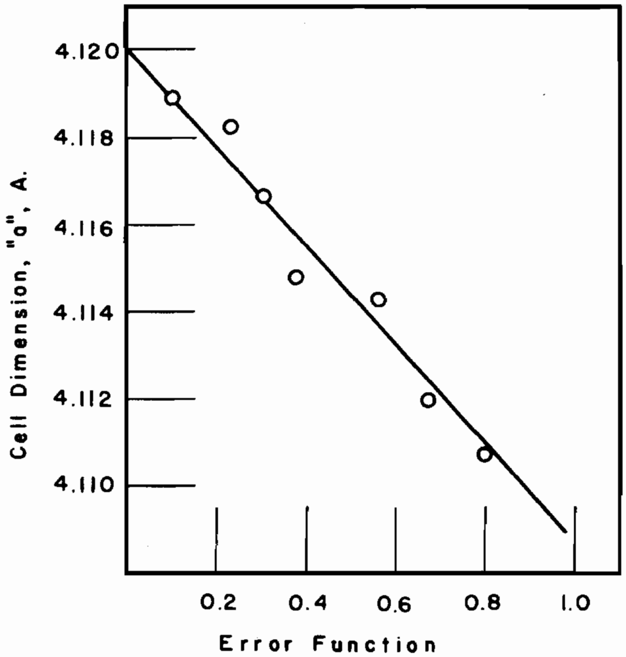

Figure 1. Determination of unit cell dimension using error function of Nelson and Riley, $\frac{1}{2}(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta})$.

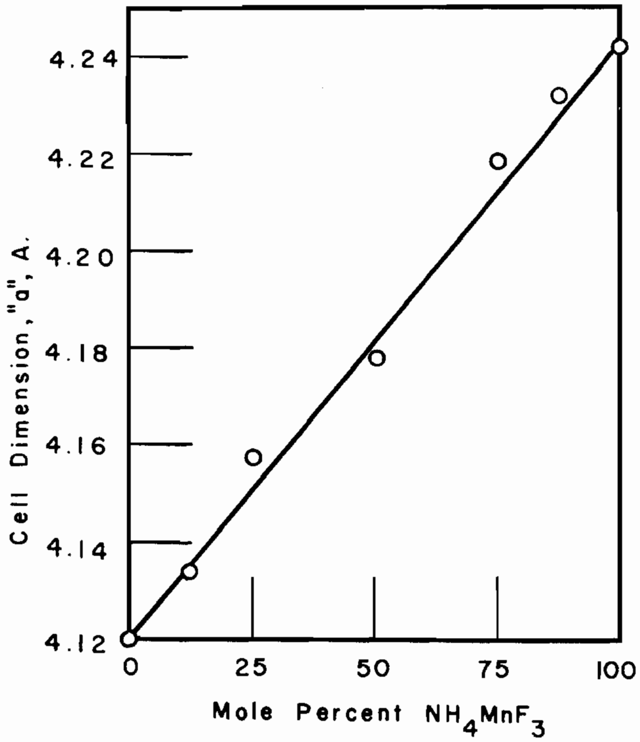

Figure 2. Unit cell dimensions as a function of NH_4MnF_3 concentration.

Magnetic Measurements. Deviation from linearity in the plot of susceptibility vs. composition would be expected over the continuous range of these solid solutions, in which the paramagnetic manganese(II) ion is progressively replacing non-paramagnetic zinc. Deviations usually occur in the direction corresponding to the composition of lower paramagnetism.[12] The magnetic moments (B.M.), determined from the gram magnetic susceptibility of the total sample and corrected for diamagnetism of the ligand, are shown in Table I and in Figure 3. The effective magnetic susceptibility of the manganese(II) ion in each com-

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(10) N. F. M. Henry, H. Lipson, and W. A. Wooster, «The Interpretation of X-Ray Diffraction Photographs», 2nd Ed., Macmillan & Co., Ltd., London, 1960, p. 191.

(11) J. B. Nelson and D. P. Riley, *Proc. Roy. Soc. London, A.* 57. 160 (1945).

(12) E. C. Stoner, «Magnetism and Matter», Methuen, London, 1934, p. 520.

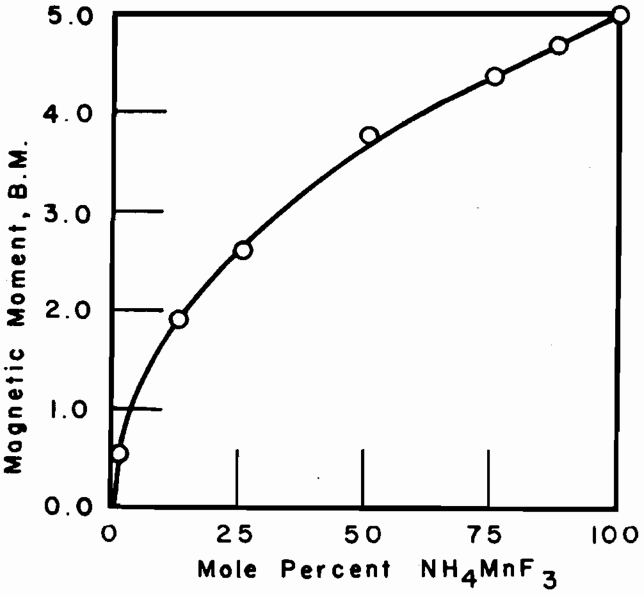

Figure 3. Magnetic moment (B.M.) as a function of NH_4MnF_3 concentration.

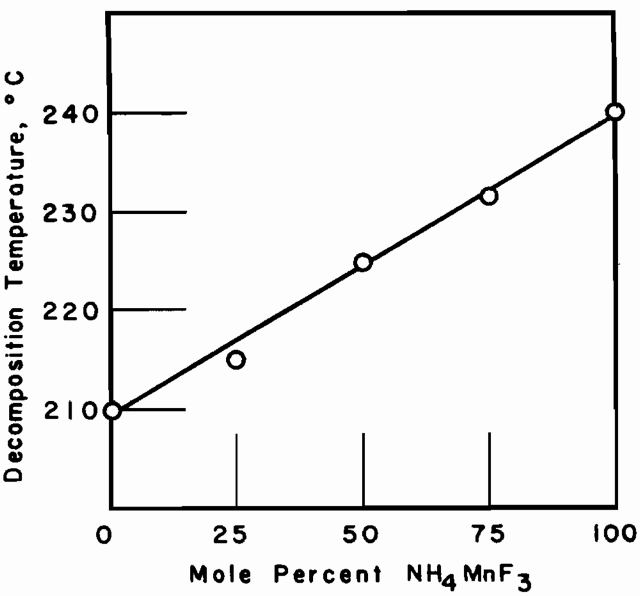

Figure 4. Decomposition temperature as a function of NH_4MnF_3 concentration.

position was determined by considering only the weight of NH_4MnF_3 in the sample. Isomorphous substitution of zinc for manganese should decrease antiferromagnetic interactions between manganese ions, and the effective susceptibility should increase to correspond to the spin only value of the magnetic moment, 5.92 B.M.[13] The effective B.M. number for all samples, including the most dilute one, was close to 5.00, suggesting that under these conditions NH_4MnF_3 is only paramagnetic.

Thermal Decomposition. Thermogravimetric analyses were made of five compositions, the percent weight loss being measured as a function of temperature. The temperature at which decomposition begins was taken as the intersection of the tangents drawn on each side of the slope change occurring at decomposition. Weight loss calculations were made on a similar basis. Values thus obtained agreed with the theoretical weight loss of ammonium fluoride to ± 0.1%. The initial decomposition temperatures are listed in Table I and shown in Figure 4.

The products of decomposition of pure NH_4MnF_3 and NH_4ZnF_3 were confirmed as the corresponding fluorides by x-ray diffraction. The products resulting from decomposition of the solid solutions were themselves solid solutions of composition $Mn_xZn_{1-x}F_2$. Lattice parameters for the tetragonal rutile structure were calculated for the decomposition solid solutions, assuming no change in Mn/Zn ratio from the original solid solution, and these indicate that Vegard's Law is followed in this case also.

Infrared Spectra. The infrared spectra of NH_4MnF_3 and NH_4ZnF_3 are similar, with the major absorption in the 4000 - 1200 cm^{-1} range at about 3250 cm^{-1} for the manganese compound and 3300 cm^{-1} for the zinc compound. There is a progressive shift of the band with change in solid solution composition, and a 1 : 1 mixture of the two pure components shows the two individual bands. Additional infrared studies would be advisable before an attempt is made to assess the significance of such spectral shifts.

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(13) J. Lewis and R. G. Wilkins, «Modern Coordination Chemistry», Interscience Publishers, Inc., New York, N. Y., 1960, p. 441.