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AMMONIUM FLUOROLANTHANATES

by

ROSEMARIE C. RUSSO

B.S., University of Minnesota, Duluth, 1964

A THESIS

Submitted to the University of New Hampshire

In Partial Fulfillment of

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ABSTRACT

AMMONIUM FLUOROLANTHANATES

by

ROSEMARIE C. RUSSO

Many different pathways to the synthesis of ammonium fluorolanthanates were investigated. The attempted routes met with varying degrees of success, depending upon factors such as metal used, molar ratios of reactants, concentrations of reactants, solvent used, and method of isolation and drying of products obtained. Only through careful control of reaction conditions can pure compounds be obtained reproducibly.

Of the various synthetic routes examined and the many products obtained, three methods proved most useful and a series of new compounds was prepared using each method. These methods and the types of products obtained from each are:

The compounds prepared by each method were studied by

differential thermal analysis, thermogravimetric analysis, X-ray diffraction, and infrared spectroscopy.

Computer programs were written to expedite the comparison of X-ray diffraction data and to calculate per cent compositions of ammonium fluorolanthanates and ammonium fluorolanthanate hydrates.

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Rosemarie G. Russo

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I. INTRODUCTION

Complexes of transition metal fluorides have been widely studied and amply reviewed.¹⁻⁴ However, fluorocomplexes of the lanthanide metals have come under much less extensive investigation. The lanthanide fluorocomplexes studied have been almost exclusively of the types $A^I Ln^{III} F_4$ ($A = Li, Na, K$) and $A^I_3 Ln^{III} F_6$ ($A = K, Rb, Cs, NH_4$).* Not all of the possible compounds of these two types have been prepared for every lanthanide metal with each of the monopositive cations listed, and almost all of the reported work has dealt with the alkali metal cations.

Most of the complexes have been prepared in studies of phase equilibria in molten $AF-LnF_3$ ($A =$ alkali metal) mixtures⁵⁻¹² or by melting together stoichiometric amounts of the metal fluorides.¹³⁻¹⁶ A small number have been prepared by the action of fluorine on mixtures of fluorides or chlorides at 400°¹⁷ or by heating Na_2CO_3 or NaF with Ln_2O_3 in hydrogen fluoride.¹⁵

Successful attempts to prepare lanthanide fluorocomplexes in aqueous solution have been extremely limited in number. The complexes $(NH_4)_3ScF_6$ and NH_4ScF_4 have been prepared in aqueous solution.^{18,19} Shevchenko²⁰ reported isolation of $KSm_2F_7 \cdot H_2O$ and $RbSm_5F_{16}$ from aqueous solution. Ivanov-Emin and coworkers,²¹ in work published while the

*In this thesis, the symbol Ln has been used as a general representation for any lanthanide.

present study was in progress, did solubility, optical density, and electrical conductivity studies on the systems $\text{LnCl}_3\text{-AF-H}_2\text{O}$ where Ln is Er, Yb, or Lu and A is Na, K, Rb, or Cs. They reported obtaining the complexes $\text{NaEr}_2\text{F}_7 \cdot 0.5 \text{ H}_2\text{O}$, $\text{NaYb}_2\text{F}_7 \cdot 0.5 \text{ H}_2\text{O}$, $\text{A}_2\text{Ln}_3\text{F}_{11} \cdot 1.5 \text{ H}_2\text{O}$ ($\text{A} = \text{K, Rb; Ln} = \text{Er, Yb}$), $\text{Cs}_2\text{Ln}_3\text{F}_{11} \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Er, Yb, Lu}$), and $\text{K}_2\text{Lu}_3\text{F}_{11} \cdot 1.5 \text{ H}_2\text{O}$.

Isolation of ammonium complexes of the lanthanide fluorides in aqueous solution was attempted by Batsanova.²² He treated lanthanide chlorides with ammonium fluoride solutions and reported obtaining the compounds $0.5 \text{ NH}_4\text{F} \cdot \text{LaF}_3 \cdot 0.5 \text{ H}_2\text{O}$; $0.7 \text{ NH}_4\text{F} \cdot \text{LaF}_3 \cdot 0.4 \text{ H}_2\text{O}$; $0.3 \text{ NH}_4\text{F} \cdot \text{NdF}_3 \cdot 0.4 \text{ H}_2\text{O}$; $0.7 \text{ NH}_4\text{F} \cdot \text{SmF}_3 \cdot 0.4 \text{ H}_2\text{O}$; $0.7 \text{ NH}_4\text{F} \cdot \text{SmF}_3 \cdot 0.8 \text{ H}_2\text{O}$; $1.1 \text{ NH}_4\text{F} \cdot \text{EuF}_3$; $1.2 \text{ NH}_4\text{F} \cdot \text{GdF}_3$; $0.8 \text{ NH}_4\text{F} \cdot \text{DyF}_3$; $0.6 \text{ NH}_4\text{F} \cdot \text{HoF}_3 \cdot 0.1 \text{ H}_2\text{O}$; $0.7 \text{ NH}_4\text{F} \cdot \text{ErF}_3 \cdot 0.1 \text{ H}_2\text{O}$; $0.7 \text{ NH}_4\text{F} \cdot \text{YbF}_3 \cdot 0.1 \text{ H}_2\text{O}$; $0.8 \text{ NH}_4\text{F} \cdot \text{YbF}_3 \cdot 0.2 \text{ H}_2\text{O}$; and $1.1 \text{ NH}_4\text{F} \cdot \text{YF}_3$.

The present investigation was therefore undertaken in order to investigate the preparation of ammonium fluorolanthanates in both aqueous and nonaqueous solutions. The synthesis of ammonium fluorolanthanates in nonaqueous media was of particular interest since it offered the potentiality of preparing anhydrous complexes.

While the present work was in progress, a report on the reaction of potassium, rubidium, and cesium fluorides with lanthanide chlorides in methanol solutions appeared.²³ Preparation of the compounds K_3LnF_6 ($\text{Ln} = \text{La, Sm, Er, Yb, Lu}$), RbLnF_4 ($\text{Ln} = \text{La, Er, Yb}$) and CsLnF_4 ($\text{Ln} = \text{La, Sm, Er, Yb}$) was described.

In addition to synthesizing new ammonium fluorolan-

thanate compounds, the present work also had as its objective the characterization of these new compounds by means of thermal decomposition studies, X-ray diffraction, and infrared spectroscopy. Even for known fluorolanthanates there is a paucity of experimental data available, and almost no thermal studies have been done.

II. EXPERIMENTAL

A. Starting Materials.

Reagent grade methanol (Fisher or Mallinckrodt) was purified by distillation from magnesium activated with iodine.²⁴ Practical grade 2,2-dimethoxypropane (Baker) and 1,2-dimethoxyethane (Eastman) were used without further purification. Rare earth metals used were nuclear grade (99.9+ %) ingots, metal sponge, or powders, and were obtained from Lunex Co.* All other chemicals used were reagent grade and were used without further purification; these included: 48% hydrofluoric acid (Baker & Adamson), bromine (Fisher), acetonitrile (Fisher), anhydrous diethyl ether (Fisher), anhydrous erbium fluoride (99.9%, Apache Chemicals**), ammonium fluoride (Fisher or Mallinckrodt), ammonium bifluoride (Fisher), scandium oxide (A. D. Mackay), and other rare earth oxides (99.9%, American Potash & Chemical Corp.).

B. Bromination of Erbium in Various Solvents.

Erbium metal was brominated in several different solvents in order to determine a generally suitable solvent for lanthanide bromination reactions. Table I lists the quantities of reactants used for the reactions and includes some observations.

The same general procedure was employed for all of the reactions. The metal was suspended in 50-100 ml of solvent in a 100- or 250-ml round-bottomed flask. This mixture

*Pleasant Valley, Iowa.

**Rockford, Illinois 61105.

TABLE I

Experimental Conditions and Observations for Erbium Bromination Reactions

<u>Solvent</u>	<u>Quantity of Erbium (mmol)</u>	<u>Quantity of Bromine (mmol)</u>	<u>Color of Residue</u>	<u>Remarks</u>
Methanol	5.9	17.6	yellow- brown	Vigorous reaction at 0°, Refluxed 1.5 hr.
Water	6.0	18.3	white	No reaction at 0°, heated 3 hr at just below reflux temp.
1,2-dimethoxy- ethane	6.3	19.0	brown	No reaction at 0°, refluxed 26 hr, incomplete reaction.
2,2-dimethoxy- propane	13.8	36.6	yellow- brown	Vigorous reaction at 0°, re- fluxed 24 hr, incomplete reaction.
Acetonitrile	10.5	55.0	dark brown	No reaction at 0°, heated 14 hr at just below reflux temp.

was cooled in an ice-water bath before addition of a solution of the specified amount of bromine in 10 ml of the solvent. The bromine solution was added dropwise with stirring. After all of the bromine solution had been added and any initial vigorous reaction at 0° had subsided, the reaction mixture was heated: to reflux temperature if the reaction was proceeding slowly or to just below reflux temperature if reaction was proceeding readily. In all cases, a small amount of solid residue which did not contain metal was left. For the solvents 1,2-dimethoxyethane and 2,2-dimethoxypropane, complete reaction of the metal was not effected for the conditions shown in the table; a small amount of unchanged metal was left.

The bromination reaction went most smoothly and rapidly in the solvents methanol and water; therefore, the products of these reactions were isolated and identified.

1. Isolation of $\text{ErBr}_3 \cdot 4\text{CH}_3\text{OH}$.

Erbium (0.98 g, 5.87 mmol) was allowed to react with bromine (0.48 ml, 17.6 mmol) in 100 ml of methanol according to the procedure described above. The reaction mixture was filtered to remove a small amount of yellow-brown residue. To 50 ml of the filtrate was added 100 ml of 2,2-dimethoxypropane; this solution was reduced in volume to about 5-10 ml on a rotary evaporator. Two liquid phases separated; a viscous dark red-brown layer and a less viscous pale yellow-brown layer. Crystals, tan-pink in color, separated from the solution. The hygroscopic solid product was dried over

silica gel.

Anal. Calcd for $\text{ErBr}_3 \cdot 4\text{CH}_3\text{OH}$: Br, 44.80; Er, 31.25.
Found: Br, 45.09; Er, 33.8.

2. Isolation of $\text{ErBr}_3 \cdot 6\text{H}_2\text{O}$.

Erbium metal (0.61 g, 3.65 mmol) was allowed to react with 0.30 ml (11 mmol) of bromine in water. The bromination reaction was carried out as described above. A small amount of a white residue was removed by filtration. The pale pink filtrate was evaporated to dryness at 50° , leaving the hygroscopic pink solid, $\text{ErBr}_3 \cdot 6\text{H}_2\text{O}$.

Anal. Calcd for $\text{ErBr}_3 \cdot 6\text{H}_2\text{O}$: Br, 46.54. Found: Br, 46.11.

C. Preliminary Investigation of the Reaction of Methanolic Lanthanide Bromide Solutions with Ammonia.

Lanthanide bromide solutions of erbium, samarium, and lanthanum were prepared by bromination of the metals in methanol, as described previously. Ammonia gas was bubbled through the metal bromide solutions, resulting in formation of white precipitates from the samarium and lanthanum solutions and a pink precipitate from the erbium solution. When precipitation was complete, the solid products were collected by filtration, washed with a dilute solution of ammonia in methanol and then methanol, and dried over silica gel.

In the case of samarium and lanthanum, the white products originally precipitated changed color upon drying to chartreuse and yellow, respectively. However, if the

product were recovered by evaporation to dryness, the coloration change did not occur.

Analytical results, although incomplete, suggest the composition $\text{SmBr}_3 \cdot \text{NH}_3$ for the samarium compound collected by filtration and washed with ammonia/methanol and methanol. Calcd for $\text{SmBr}_3 \cdot \text{NH}_3$: N, 3.44%; found: 3.01. The product obtained by evaporation of the solvent had a higher nitrogen content (7.63%) which falls between the calculated %N values for the di- and triammine (6.60 and 9.52, respectively).

Nitrogen analyses on the lanthanum and erbium products recovered by filtration gave results of 5.80 for lanthanum (calcd for $\text{LaBr}_3 \cdot \text{NH}_3 = 3.54$, for $\text{LaBr}_3 \cdot 2\text{NH}_3 = 7.08$) and 2.26 for erbium (calcd for $\text{ErBr}_3 \cdot \text{NH}_3 = 3.30$).

D. Preparation of the Compounds $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11} \cdot \text{H}_2\text{O}$.

1. Preparation of $(\text{NH}_4)_2\text{Er}_3\text{F}_{11} \cdot \text{H}_2\text{O}$.

Granular erbium metal (1.01 g, 6.01 mmol) was placed in a 250-ml round-bottomed flask; to this was added 90 ml of dry methanol. Bromine (0.5 ml, 18.3 mmol) was pipetted into an addition funnel containing 10 ml of dry methanol. The bromine-methanol solution was added dropwise with stirring, at room temperature, to the erbium-methanol mixture. After all of the bromine solution had been added, the reaction mixture was heated at reflux temperature for 5 hr and then stirred at room temperature overnight.

The reaction mixture was filtered to remove a small amount of brown residue. The yellow filtrate was added dropwise, with stirring and heating, to 120 ml of a saturated

solution of NH_4F (60 mmol) in dry methanol. A finely divided, gelatinous pink precipitate formed immediately. The reaction mixture was stirred at 30° overnight. The pink product was collected by filtration through a fine sintered glass crucible; it was washed repeatedly with small portions of methanol and dried over silica gel.

Anal. Calcd for $(\text{NH}_4)_2\text{Er}_3\text{F}_{11}\cdot\text{H}_2\text{O}$: N, 3.66; H, 1.32; Er, 65.60; F, 27.32. Found: N, 3.61; H, 1.30; Er, 65.06; F, 27.47.

Ten ml of a similarly prepared solution of ErBr_3 (1.0 mmol) in methanol was allowed to react with 50 ml of a 0.2 M solution of NH_4HF_2 (10.0 mmol) in methanol. The product was collected and dried as above. The identity of the product as $(\text{NH}_4)_2\text{Er}_3\text{F}_{11}\cdot\text{H}_2\text{O}$ was confirmed by X-ray.

2. Preparation of $(\text{NH}_4)_2\text{Y}_3\text{F}_{11}\cdot\text{H}_2\text{O}$.

Yttrium metal sponge (3.01 g, 33.86 mmol) was suspended in 150 ml of dry methanol; bromine (4.0 ml, 146.6 mmol) dissolved in a small amount of dry methanol was added dropwise with stirring and gentle heating. After all of the bromine had been added, the reaction mixture was heated at reflux temperature for 3 hr. After cooling, a small amount of yellow residue was removed by filtration.

The filtrate was added dropwise with stirring and heating to 500 ml of a saturated solution of NH_4F (250 mmol) in dry methanol. After addition of all of the metal bromide solution, the reaction mixture was stirred and heated gently for ca. 1 hr; the white precipitate was allowed to settle and

the supernatant was decanted. The gelatinous precipitate was digested in 0.1 M NH_4F in methanol at 50° for 2 days. It was then collected by filtration, washed several times with ether, and dried in a drying pistol using P_2O_5 and acetone (bp 56.1°).

Anal. Calcd for $(\text{NH}_4)_2\text{Y}_3\text{F}_{11}\cdot\text{H}_2\text{O}$: N, 5.29; H, 1.90; F, 39.45. Found: N, 5.34; H, 1.80; F, 39.16.

3. Preparation of $(\text{NH}_4)_2\text{Dy}_3\text{F}_{11}\cdot\text{H}_2\text{O}$.

Powdered dysprosium metal (2.00 g, 12.31 mmol) was suspended in 100 ml of dry methanol. Bromine (1.0 ml, 36.6 mmol) was added dropwise with stirring at room temperature. The reaction mixture was heated at reflux temperature for 2 hr and then was allowed to cool to room temperature and was stirred for an additional 3.5 hr. The mixture was filtered to remove a yellow-brown residue. The filtrate was added with stirring to 246 ml of a saturated solution of NH_4F (123 mmol) in dry methanol. A white precipitate formed immediately. The reaction mixture was stirred overnight at room temperature. It was then filtered and the gelatinous precipitate was washed with methanol, then ether, and dried over $\text{Mg}(\text{ClO}_4)_2$. The dried product was ground thoroughly in methanol, filtered, washed with ether, and dried first over $\text{Mg}(\text{ClO}_4)_2$ and then under vacuum.

Anal. Calcd for $(\text{NH}_4)_2\text{Dy}_3\text{F}_{11}\cdot\text{H}_2\text{O}$: N, 3.73; H, 1.34; Dy, 64.95. Found: N, 4.71; H, 1.86; Dy, 65.00.

4. Preparation of $(\text{NH}_4)_2\text{Ho}_3\text{F}_{11}\cdot\text{H}_2\text{O}$.

Holmium (1.17 g, 7.09 mmol) was suspended in 100 ml

of methanol; bromine (0.6 ml, 22.0 mmol) was added dropwise with stirring at room temperature. The mixture was heated gently for 3 hr, then at reflux temperature for 2 hr. The mixture was cooled, and an additional 0.4 ml of bromine was added (total amount Br_2 added = 36.6 mmol). The mixture was heated at reflux temperature for 0.5 hr, then stirred at room temperature overnight. The mixture was filtered to remove a small amount of yellow residue. The filtrate was added, with stirring, to 142 ml of a saturated solution of NH_4F (70.9 mmol) in methanol. A peach-colored precipitate formed immediately. The reaction mixture was stirred at room temperature overnight, then was filtered. The gelatinous precipitate collected was washed with methanol, then ether, and dried over $\text{Mg}(\text{ClO}_4)_2$. The dried product was ground thoroughly in methanol, filtered, again washed with ether, and dried first over $\text{Mg}(\text{ClO}_4)_2$ and then under vacuum.

Anal. Calcd for $(\text{NH}_4)_2\text{Ho}_3\text{F}_{11} \cdot \text{H}_2\text{O}$: N, 3.70; H, 1.33; Ho, 65.29. Found: N, 4.78; H, 1.63; Ho, 64.6.

E. Preparation of the Compounds $(\text{NH}_4)_3\text{Ln}_2\text{F}_9 \cdot \text{H}_2\text{O}$.

1. Preparation of $(\text{NH}_4)_3\text{Er}_2\text{F}_9 \cdot \text{H}_2\text{O}$.

Granular erbium metal (0.45 g, 2.69 mmol) was placed in a 30-ml beaker. A small amount of concd nitric acid was added to dissolve the metal and form the nitrate. The solution was evaporated to dryness; a few ml of water were added and the evaporation was repeated.

The product nitrate was dissolved in 5 ml of water. To this solution was added 15 ml of a 30% (w/v) aqueous NH_4F

solution. A pink precipitate formed immediately. The reaction mixture was stirred, then allowed to stand at room temperature overnight. The reaction mixture was filtered; the gelatinous pink precipitate collected was washed with methanol and then ether and dried over silica gel.

Anal. Calcd for $(\text{NH}_4)_3\text{Er}_2\text{F}_9 \cdot \text{H}_2\text{O}$: N, 7.27; H, 2.44; Er, 57.91. Found: N, 6.72; H, 1.82; Er, 58.88.

2. Preparation of $(\text{NH}_4)_3\text{Sm}_2\text{F}_9 \cdot \text{H}_2\text{O}$.

Samarium metal cast (0.36 g, 2.39 mmol) was placed in a 30-ml beaker; concd nitric acid was added and the solution was evaporated to dryness. A few ml of water were added and the evaporation was repeated. The product was dissolved in 5 ml of water; to this solution was added 15 ml of a 30% (w/v) aqueous NH_4F solution. An off-white precipitate formed immediately. The reaction mixture was stirred, then allowed to stand at room temperature overnight. The gelatinous precipitate was collected by filtration, washed with methanol, then with ether, and dried over silica gel.

Anal. Calcd for $(\text{NH}_4)_3\text{Sm}_2\text{F}_9 \cdot \text{H}_2\text{O}$: N, 7.73; H, 2.60; Sm, 55.29; F, 31.44. Found: N, 7.62; H, 2.59; Sm, 55.72; F, 31.12.

$(\text{NH}_4)_3\text{Sm}_2\text{F}_9 \cdot \text{H}_2\text{O}$ was also prepared in methanol solution. Samarium was brominated as described in the general procedure on p 4 to give a 0.1 M solution. Addition of 10 ml of this solution (1.0 mmol SmBr_3) to 50 ml of a 0.2 M solution of NH_4HF_2 in methanol yielded the product, which was collected by filtration, washed with methanol, and dried over

$\text{Mg}(\text{ClO}_4)_2$. The identity of the product as $(\text{NH}_4)_3\text{Sm}_2\text{F}_9 \cdot \text{H}_2\text{O}$ was confirmed by X-ray and nitrogen analysis (%N found = 7.55).

3. Preparation of $(\text{NH}_4)_3\text{Y}_2\text{F}_9 \cdot \text{H}_2\text{O}$.

Yttrium metal sponge (0.27 g, 3.04 mmol) was placed in a 30-ml beaker. Concd nitric acid was added to dissolve the metal, and the solution was evaporated to dryness. A small amount of water was added to redissolve the product, and the solution was again evaporated to dryness. The product was dissolved in 5 ml of water; to this solution was added 15 ml of a 30% (w/v) aqueous NH_4F solution. A white precipitate formed immediately. The reaction mixture was stirred, then allowed to stand at room temperature overnight. The gelatinous precipitate was collected by filtration, washed with methanol, then with ether, and dried over silica gel.

Anal. Calcd for $(\text{NH}_4)_3\text{Y}_2\text{F}_9 \cdot \text{H}_2\text{O}$: N, 9.98; H, 3.35; F, 40.62. Found: N, 9.75; H, 2.95; F, 40.92.

4. Preparation of $(\text{NH}_4)_3\text{Pr}_2\text{F}_9 \cdot \text{H}_2\text{O}$.

Praseodymium metal, stored under oil, was washed with CCl_4 and acetone to remove the oil; 3.65 g (25.92 mmol) of the metal was placed in a 50-ml beaker. Enough concd nitric acid was added to dissolve the metal. The solution was evaporated to dryness; a few ml of water were added and the evaporation was repeated. The metal nitrate was dissolved, with heating, in 55 ml of water; 25 ml of the solution (11.78 mmol Pr) was allowed to react with 74 ml of a 30% aqueous

NH_4F solution. A curdy green precipitate formed immediately. The reaction mixture was stirred overnight at room temperature. The gelatinous precipitate was allowed to settle, then was collected by filtration, washed with methanol followed by a washing with ether, and dried over silica gel. The product was digested in a 0.1 N solution of NH_4F in methanol at 50° overnight, filtered, washed with methanol, with copious amounts of ether, and dried over $\text{Mg}(\text{ClO}_4)_2$. To remove NH_4F contaminant, the product was shaken for 1.5 hr with 20 ml of methanol; this mixture was allowed to stand overnight, then the precipitate was again collected by filtration, washed with methanol and ether, and dried over $\text{Mg}(\text{ClO}_4)_2$.

Anal. Calcd for $(\text{NH}_4)_3\text{Pr}_2\text{F}_9 \cdot \text{H}_2\text{O}$: N, 8.00; H, 2.69; F, 32.57. Found: N, 8.17; H, 2.13; F, 32.98.

5. Preparation of $(\text{NH}_4)_3\text{La}_2\text{F}_9 \cdot \text{H}_2\text{O}$.

Lanthanum nitrate hydrate, 2.42 g, was prepared in an identical manner to the preparation described above for praseodymium. This product was dissolved in 20 ml of water and to this solution was added 46.7 ml of a 30% aqueous NH_4F solution. A white precipitate formed immediately. The reaction mixture was stirred, then allowed to stand overnight at room temperature. The gelatinous precipitate was collected by filtration, washed with methanol and then ether, and dried over $\text{Mg}(\text{ClO}_4)_2$.

Anal. Calcd for $(\text{NH}_4)_3\text{La}_2\text{F}_9 \cdot \text{H}_2\text{O}$: N, 8.07; H, 2.71; F, 32.82. Found: N, 8.09; H, 2.36; F, 33.0.

F. Preparation of the Compounds NH_4LnF_4 .

1. Preparation of NH_4ErF_4 from $\text{ErF}_3 \cdot x\text{H}_2\text{O}$.

$\text{ErF}_3 \cdot x\text{H}_2\text{O}$ ($x = 0.5$ to 1) was prepared as described in the literature.^{25,26} Erbium metal (0.8 g, 4.8 mmol) was dissolved in a minimum amount of concd hydrochloric acid; the solution was evaporated to dryness. The solid was dissolved in 0.1 M hydrochloric acid and diluted to 100 ml with water. The solution was heated to near boiling and transferred to a polyethylene beaker. To this solution was added 100 ml of 48% hydrofluoric acid. The mixture was allowed to stand for 3 hr. The pink product was collected by filtration, washed with 2% (v/v) hydrofluoric acid, and dried under vacuum.

A 1.02 -g sample of the erbium fluoride hydrate was allowed to react with 100 ml of a 20% (w/v) aqueous NH_4F solution. The reaction mixture was stirred vigorously at room temperature overnight. The pink product was collected by filtration, washed with methanol, and dried over $\text{Mg}(\text{ClO}_4)_2$.

Anal. Calcd for NH_4ErF_4 : N, 5.36 ; H, 1.54 ; Er, 64.01 ; F, 29.08 . Found: N, 4.94 ; H, 1.37 ; Er, 63.66 ; F, 29.30 .

2. Preparation of NH_4GdF_4 from $\text{GdF}_3 \cdot x\text{H}_2\text{O}$.

$\text{GdF}_3 \cdot x\text{H}_2\text{O}$ ($x = 0.5$ to 1) was prepared as described in the literature.^{25,26} Gadolinium metal (0.5 g, 3.2 mmol) was dissolved in a minimum amount of concd hydrochloric acid. The solution was evaporated to near dryness, then diluted to 100 ml with water. The solution was heated to near boiling, then transferred to a polyethylene beaker. To this hot metal chloride solution was slowly added 100 ml of 48% hydrofluoric

acid, and the mixture was allowed to stand overnight. The white product was collected by filtration, washed with several portions of 2% (v/v) hydrofluoric acid, and dried over $\text{Mg}(\text{ClO}_4)_2$.

The $\text{GdF}_3 \cdot x\text{H}_2\text{O}$ (0.63 g) prepared in this manner was allowed to react with a solution of 20 g of NH_4F in 80 ml of water. The mixture was stirred vigorously at room temperature overnight. It was then filtered, and the white crystalline solid collected was washed with methanol and then with ether. The product was dried over $\text{Mg}(\text{ClO}_4)_2$.

Anal. Calcd for NH_4GdF_4 : N, 5.57; H, 1.60; Gd, 62.58. Found: N, 5.60; H, 1.74; Gd, 62.32.

3. Preparation of NH_4GdF_4 from Gd_2O_3 .

Gd_2O_3 (0.10 g, 0.28 mmol) was dissolved in concd nitric acid. The solution was evaporated to near dryness. Water (5 ml) was added to redissolve the solid, and the evaporation was repeated. The gadolinium nitrate was again dissolved in 5 ml of water and was transferred to a 50-ml Erlenmeyer flask using another 5 ml of water. To this solution was added a solution prepared by dissolving 4.1 g NH_4F in 9.6 ml water. A white precipitate formed immediately. The reaction mixture was allowed to stand for 2 days. It was then filtered and a finely divided white precipitate was collected. The precipitate was washed with methanol and dried over silica gel.

Anal. Calcd for NH_4GdF_4 : N, 5.57; H, 1.60; Gd, 62.58. Found: N, 5.42; H, 1.70; Gd, 62.46.

4. Preparation of NH_4ScF_4 from $(\text{NH}_4)_3\text{ScF}_6$.

$(\text{NH}_4)_3\text{ScF}_6$ was prepared from Sc_2O_3 according to the procedure of Ivanov-Emin *et al.*¹⁹ Sc_2O_3 was converted to the nitrate with nitric acid. An aqueous solution of the nitrate was allowed to react with a 30% (w/v) aqueous NH_4F solution to yield white $(\text{NH}_4)_3\text{ScF}_6$.

Anal. Calcd for $(\text{NH}_4)_3\text{ScF}_6$: N, 19.72; H, 5.68; F, 53.50. Found: N, 19.80; H, 5.66; F, 52.69.

NH_4ScF_4 was prepared¹⁸ by dissolving the $(\text{NH}_4)_3\text{ScF}_6$ in water and stirring the solution at room temperature for 3 days, during which time white NH_4ScF_4 crystallized out of solution.

Anal. Calcd for NH_4ScF_4 : N, 10.08; H, 2.90. Found: N, 9.68; H, 2.81.

Both products were further confirmed by comparison of their X-ray powder patterns with those reported in the literature.¹⁸

5. Preparation of NH_4YF_4 from $\text{YF}_3 \cdot x\text{H}_2\text{O}$.

$\text{YF}_3 \cdot x\text{H}_2\text{O}$ ($x = 0.5$ to 1) was prepared as described in the literature.^{25,26} Yttrium metal (0.50 g, 5.6 mmol) was dissolved in a minimum amount of concd hydrochloric acid. The solution was evaporated nearly to dryness, then diluted to 100 ml with water. The dilute solution was heated to near boiling, then transferred to a polyethylene beaker prior to addition of 100 ml of 48% hydrofluoric acid. The mixture was allowed to stand overnight; it was filtered and the white precipitate was washed with 2% (v/v) hydrofluoric acid

solution and dried at 120° .

The yttrium fluoride hydrate (0.57 g) was allowed to react with a solution prepared by dissolving 20 g of NH_4F in 80 ml of water. The mixture was stirred vigorously at room temperature overnight. The reaction mixture was filtered; the white precipitate collected was washed with methanol and then with ether and dried under vacuum.

Anal. Calcd for NH_4YF_4 : N, 7.66; H, 2.20; F, 41.54.
Found: N, 8.10; H, 2.64; F, 41.01.

G. Study of the System $\text{NH}_4\text{F}-\text{ErF}_3-\text{H}_2\text{O}$ at 25° .

Of the methods employed in studying three-component systems, the most accurate is the synthetic complex method.^{27,28} If a straight line is drawn from the composition of the liquid phase, obtained by direct analysis, through a point representing the synthetic composition of the whole system, this line must pass through the composition of the pure solid phase. If several of these tie-lines intersect, the composition of the solid becomes known. The synthetic composition point is determined by use of a simple proportion between the differences in the amounts of the same two components at one of those points and at the composition of the solid phase. Thus the synthetic composition point represents the composition of the anhydrous solid phase.

The complexes used for the ternary system were made up from weighed amounts of ammonium fluoride, anhydrous erbium fluoride, and water. These samples, of a total weight of approximately 10 g, were placed in small polyethylene

bottles. The samples were shaken for a minimum of 12 hr, then immersed in a constant-temperature bath at 25° for a minimum of 8 hr. These minimum times were those found necessary for attainment of equilibrium by analysis of samples at various times. Weighed samples of the liquid phase at equilibrium were removed and analyzed for erbium and nitrogen content. In some cases, the identity of the solid phase was confirmed by obtaining X-ray powder patterns of the dried residue.

Table II gives the composition of the original complex, the composition of the saturated solution, and the composition of the dry residue. Figure 1 is a graph of the curves obtained by drawing tie-lines between the solution points and the synthetic composition points.

H. Analytical Procedures.

1. Determination of Nitrogen.

Nitrogen analyses on solid samples were performed on a Coleman Model 29 Nitrogen Analyzer.

Nitrogen analyses on samples in aqueous solution were performed on a micro Kjeldahl apparatus made by Robert Anderson. The procedure used was adapted from Steyermark²⁹ and Kemmerer and Hallett.³⁰ The aqueous sample was steam-distilled from a 15 M sodium hydroxide solution and the distillate was collected into a 4% boric acid solution containing a mixed indicator of 5:1 bromcresol green:methyl red, both 0.2% solutions in 95% ethanol. The boric acid solution of ammonia was titrated with 0.1 N HCl to a red end point.

Table II
 $\text{NH}_4\text{F}-\text{ErF}_3-\text{H}_2\text{O}$ System at 25°

Original Complex		Saturated Solution		Dry Residue	
Wt.% NH_4F	Wt.% ErF_3	Wt.% NH_4F	Wt.% ErF_3	Wt.% NH_4F	Wt.% ErF_3
39.51	2.74	38.47	0.00	55.37	44.63
33.55	3.69	32.63	0.00	46.05	53.95
29.27	1.51	28.93	0.00	41.92	58.08
27.36	6.40	28.03	0.00	18.47	81.53
22.55	11.17	24.80	0.00	5.82	94.18
20.98	9.30	22.63	0.00	5.97	94.03
20.40	9.05	22.18	0.00	3.10	96.90
18.00	8.58	19.14	0.00	6.74	93.26
11.52	8.77	12.27	0.00	4.05	95.95
9.43	11.10	10.39	0.00	1.94	98.06
8.72	3.57	8.88	0.00	4.55	95.45
5.00	8.58	5.40	0.00	0.81	99.19
3.51	1.90	3.51	0.00	3.55	96.45
1.28	6.40	1.32	0.00	0.78	99.22

2. Determination of Rare Earth Metals.³¹

Samples were dissolved in concd sulfuric acid or hydrochloric acid; the solutions were evaporated to near dryness, then diluted with water to give a pH of approximately 1. The metals were precipitated as the oxalates with saturated oxalic acid and were ignited to the oxides at 850-900°.

3. Determination of Fluoride.³²

The samples were steam-distilled, with collection of the fluoride as fluorosilicic acid followed by titration of the distillate with thorium nitrate solution, using a high frequency oscilometer for end point detection.

4. Carbon, Hydrogen, Nitrogen Analyses.

Samples were analyzed for carbon, hydrogen, and nitrogen with an F&M Corporation Model 185 Carbon, Hydrogen, Nitrogen Analyzer. In two cases carbon, hydrogen, nitrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

5. Determination of Bromide.³³

Bromide was determined by dissolving the sample in water and titrating aliquots of the solution with 0.1 N silver nitrate. Dichlorofluorescein (0.1% in 70% alcohol) was used as indicator and formation of a reddish silver bromide sol was taken as end point.

I. Differential Thermal Analyses.

Differential thermal analyses (dta) were carried out

with a DuPont Differential Thermal Analyzer Model 900 employing a Differential Scanning Calorimeter cell. All dta runs were made under a 2-mm helium atmosphere with a heating rate of $15^{\circ}/\text{min}$. A temperature (T) scale of 2 mv/in. and a differential temperature (ΔT) scale of either 0.02 or 0.08 mv/in. were used. Temperature was measured using a chromel-alumel thermocouple, and all temperature readings were corrected for chromel-alumel thermocouples using a correction table³⁴ furnished by DuPont for the Model 900 instrument. The thermocouple reference junction was immersed in an ice-water bath.

The differential thermograms obtained for the compounds $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11} \cdot \text{H}_2\text{O}$ are shown in Figure 2; those for the compounds $(\text{NH}_4)_3\text{Ln}_2\text{F}_9 \cdot \text{H}_2\text{O}$ are shown in Figure 3, and those for the compounds NH_4LnF_4 in Figure 4. A ΔT scale of 0.02 mv/in. was used except where noted otherwise, in which cases a scale of 0.08 mv/in. was used. Temperatures of the dta peaks observed are summarized in the corresponding Tables III-V, which include the temperature range investigated for each compound. The temperatures reported in the tables were obtained from the thermograms according to the following scheme: (a) onset temperature was taken as the temperature at which the thermogram starts to depart from the base line; (b) peak temperature was taken as the temperature of reversal, or peak maximum; (c) recovery temperature was taken as the temperature at which the thermogram returns to either the same or a different base line. All peaks were endothermic except where noted otherwise.

Figure 2

Differential Thermograms of $(\text{NH}_4)_2\text{LnF}_{11} \cdot \text{H}_2\text{O}$ Compounds

Table III

Differential Thermal Analysis Data for $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11}\cdot\text{H}_2\text{O}$ Compounds

<u>Compound</u>	<u>Peak Temperatures, °C</u>			<u>Temp. Range Investigated</u>
	<u>Onset</u>	<u>Peak</u>	<u>Recovery</u>	
$(\text{NH}_4)_2\text{Y}_3\text{F}_{11}\cdot\text{H}_2\text{O}$	56	119	141	18-386°
	151	180	211	
	226	311	338	
$(\text{NH}_4)_2\text{Er}_3\text{F}_{11}\cdot\text{H}_2\text{O}$	75	115	146	24-471°
	290	316	334	
$(\text{NH}_4)_2\text{Dy}_3\text{F}_{11}\cdot\text{H}_2\text{O}$	37	69	98	18-429°
	105	159	219	
	316 ^a	332 ^a	337 ^a	
$(\text{NH}_4)_2\text{Ho}_3\text{F}_{11}\cdot\text{H}_2\text{O}$	40	61	84	17-471°
	129	204	235	
	253	286, ^b 304 ^b	326	

^aExotherm^bShoulder

Table IV

Differential Thermal Analysis Data for $(\text{NH}_4)_3\text{Ln}_2\text{F}_9 \cdot \text{H}_2\text{O}$ Compounds

<u>Compound</u>	<u>Peak Temperatures, °C</u>			<u>Temp. Range Investigated</u>
	<u>Onset</u>	<u>Peak</u>	<u>Recovery</u>	
$(\text{NH}_4)_3\text{Er}_2\text{F}_9 \cdot \text{H}_2\text{O}$	57	94	99	28-429°
	114	207	288	
	310	316	325	
	325	331	341	
$(\text{NH}_4)_3\text{Y}_2\text{F}_9 \cdot \text{H}_2\text{O}$	62	92	109	16-432°
	124	214	290	
	290	302	313	
	313	323	333	
$(\text{NH}_4)_3\text{Pr}_2\text{F}_9 \cdot \text{H}_2\text{O}$	75	109	124	25-414°
	134	174	186	
	186	211	252	
$(\text{NH}_4)_3\text{La}_2\text{F}_9 \cdot \text{H}_2\text{O}$	42	100	107	14-428°
	107	132	170	
	170	190	301	
$(\text{NH}_4)_3\text{Sm}_2\text{F}_9 \cdot \text{H}_2\text{O}$	91	206	247	26-422°
	251	265	285	

Figure 4
Differential Thermograms of NH_4LnF_4 Compounds

Table V
Differential Thermal Analysis Data for NH_4LnF_4 Compounds

<u>Compound</u>	<u>Peak Temperatures, °C</u>			<u>Temp. Range Investigated</u>
	<u>Onset</u>	<u>Peak</u>	<u>Recovery</u>	
NH_4ScF_4	156	257	355	26-383 ^o
NH_4YF_4	116	195	205	19-434 ^o
	205	210	236	
	274	297	338	
NH_4GdF_4	134	235	302	30-456 ^o
NH_4ErF_4	131	221	259	29-422 ^o
	269	296	350	

J. Thermogravimetric Analyses.

Thermogravimetric analyses (tga) were carried out using a DuPont Thermogravimetric Analyzer, Model 950. All tga runs were made under a helium atmosphere of 2 mm pressure. The heating rate for all runs was $15^{\circ}/\text{min}$, with a time constant of 1 sec. Temperature was measured with a chromel-alumel thermocouple and was corrected by usage of chart paper embodying corrections for thermocouple response. The thermocouple reference junction was immersed in an ice-water bath. Sample sizes ranged from about 10 to 22 mg; the weight scale used was either 0.4, 1, or 2 mg/in.

The data obtained from the tga analyses are given in Table VI for the compounds $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11}\cdot\text{H}_2\text{O}$, in Table VII for the compounds $(\text{NH}_4)_3\text{Ln}_2\text{F}_9\cdot\text{H}_2\text{O}$, and in Table VIII for the compounds NH_4LnF_4 .

K. X-Ray Powder Diffraction Photographs.

Powder patterns were obtained with either a 57.3 or 114.6 mm Philips camera using copper ($\lambda=1.5418 \text{ \AA}$) or iron ($\lambda=1.9373 \text{ \AA}$) radiation. Finely ground samples were mounted in 0.3 mm glass capillaries. All powder films were corrected for shrinkage. Values for the interplanar spacings were obtained from the corrected 2θ values using the X-ray diffraction tables of Fang and Bloss.³⁵ Relative intensities were estimated visually. Powder patterns for the $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11}\cdot\text{H}_2\text{O}$, $(\text{NH}_4)_3\text{Ln}_2\text{F}_9\cdot\text{H}_2\text{O}$, and NH_4LnF_4 compounds are given in Part A of the Appendix.

Table VI

Thermogravimetric Analysis Data for $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11} \cdot \text{H}_2\text{O}$ Compounds

<u>Compound</u>	<u>Decomposition Temperature</u>	<u>Per Cent Weight Loss</u>	
		<u>Obsd</u>	<u>Calcd</u>
$(\text{NH}_4)_2\text{Y}_3\text{F}_{11} \cdot \text{H}_2\text{O}$	55-163 ^o	3.60	H ₂ O, 3.40
	163-306 ^o	7.00	NH ₄ F, 6.99
	306-325 ^o	8.20	NH ₄ F, 6.99
$(\text{NH}_4)_2\text{Er}_3\text{F}_{11} \cdot \text{H}_2\text{O}$	77-176 ^o	2.20	H ₂ O, 2.36
	187-338 ^o	9.20	2NH ₄ F, 9.68
$(\text{NH}_4)_2\text{Dy}_3\text{F}_{11} \cdot \text{H}_2\text{O}$	56-113 ^o	3.01	H ₂ O, 2.40
	126-207 ^o	11.33	2NH ₄ F, 9.86
	330-337 ^o	0.30	?
$(\text{NH}_4)_2\text{Ho}_3\text{F}_{11} \cdot \text{H}_2\text{O}$	50-140 ^o	2.36	H ₂ O, 2.38
	178-226 ^o	4.57	NH ₄ F, 4.89
	226-300 ^o		
	300-327 ^o	5.70	NH ₄ F, 4.89

Table VII
Thermogravimetric Analysis Data for $(\text{NH}_4)_3\text{Ln}_2\text{F}_9 \cdot \text{H}_2\text{O}$ Compounds

<u>Compound</u>	<u>Decomposition Temperature</u>	<u>Per Cent Weight Loss</u>	
		<u>Obsd</u>	<u>Calcd</u>
$(\text{NH}_4)_3\text{Er}_2\text{F}_9 \cdot \text{H}_2\text{O}$	45-175°	2.43	H_2O , 3.12
	200-238°	11.46	$2\text{NH}_4\text{F}$, 12.82
	238-312°	4.08	HF , 3.46
	312-328°	2.23	NH_3 , 2.95
$(\text{NH}_4)_3\text{Y}_2\text{F}_9 \cdot \text{H}_2\text{O}$	86-145°	4.48	H_2O , 4.28
	198-233°	15.12	$2\text{NH}_4\text{F}$, 17.60
	233-302°	5.77	HF , 4.75
	302-317°	2.99	NH_3 , 4.04
$(\text{NH}_4)_3\text{Pr}_2\text{F}_9 \cdot \text{H}_2\text{O}$	90-141°	2.86	H_2O , 3.43
	145-173°	7.20	NH_4F , 7.06
	206-238°	14.48	$2\text{NH}_4\text{F}$, 14.11
$(\text{NH}_4)_3\text{La}_2\text{F}_9 \cdot \text{H}_2\text{O}$	40-147°	11.95	$\text{H}_2\text{O} + \text{NH}_4\text{F}$, 10.57
	147-205°	7.16	NH_4F , 7.11
	205-345°	6.00	NH_4F , 7.11
$(\text{NH}_4)_3\text{Sm}_2\text{F}_9 \cdot \text{H}_2\text{O}$	38-261°	16.77	$\text{H}_2\text{O} + 2\text{NH}_4\text{F}$, 16.93
	261-405°	3.23	NH_4F , 6.81

Table VIII
Thermogravimetric Analysis Data for NH_4LnF_4 Compounds

<u>Compound</u>	<u>Decomposition Temperature</u>	<u>Per Cent Weight Loss</u>	
		<u>Obsd</u>	<u>Calcd</u>
NH_4ScF_4	237-321°	26.27	NH_4F , 26.65
NH_4YF_4	155-242°	14.15	HF, 10.94
	242-326°	9.27	NH_3 , 9.31
NH_4GdF_4	215-259°	16.59	NH_4F , 14.74
NH_4ErF_4	199-245°	7.48	HF, 7.66
	283-342°	6.45	NH_3 , 6.52

L. Infrared Spectra.

Infrared spectra in the $4000\text{--}200\text{ cm}^{-1}$ range were obtained with a Beckman IR-12 spectrophotometer. Nujol and halocarbon mulls with cesium iodide and potassium bromide windows or cesium iodide and potassium bromide pellets were used.

Tables IX, X, and XI list the infrared absorptions for the $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11}\cdot\text{H}_2\text{O}$, $(\text{NH}_4)_3\text{Ln}_2\text{F}_9\cdot\text{H}_2\text{O}$, and NH_4LnF_4 compounds, respectively.

M. Raman Spectra.

Raman spectra of NH_4YF_4 , NH_4ErF_4 and NH_4GdF_4 were obtained by Dr. Charles V. Berney, University of New Hampshire, through the courtesy of Dr. Richard E. Miller, Michigan State University. An Ar^+ (5145 Å) laser source was used; the spectrometer has been described previously.³⁶ Raman data of these compounds are included with the infrared data in Table XI.

Table IX
Infrared Spectra of $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11}\cdot\text{H}_2\text{O}$ Compounds^{a,b}

<u>$(\text{NH}_4)_2\text{Y}_3\text{F}_{11}\cdot\text{H}_2\text{O}$</u>	<u>$(\text{NH}_4)_2\text{Dy}_3\text{F}_{11}\cdot\text{H}_2\text{O}$</u>	<u>$(\text{NH}_4)_2\text{Ho}_3\text{F}_{11}\cdot\text{H}_2\text{O}$</u>	<u>$(\text{NH}_4)_2\text{Er}_3\text{F}_{11}\cdot\text{H}_2\text{O}$</u>
3260 s,b	3225 ms	3250 s,b	3260 s
1665 vw,vb	3090 m,sh	3095 s,b	3080 m,sh
1430 s	2900 w,sh	2920 m,sh	2862 w,sh
520 m	1648 w	1670 w	1668 w
380 s	1425 s	1435 s	1428 s
321 m,sh	368 s	1025 w	520 m
		728 w	365 s
		370 s	280 s
		295 s	

^aValues given in cm^{-1} .

^bAbbreviations used: s, strong; ms, medium-strong; m, medium;
w, weak; vw, very weak; sh, shoulder;
b, broad; vb, very broad.

Table X
Infrared Spectra of $(\text{NH}_4)_3\text{Ln}_2\text{F}_9 \cdot \text{H}_2\text{O}$ Compounds^{a,b}

<u>$(\text{NH}_4)_3\text{Y}_2\text{F}_9 \cdot \text{H}_2\text{O}$</u>	<u>$(\text{NH}_4)_3\text{La}_2\text{F}_9 \cdot \text{H}_2\text{O}$</u>	<u>$(\text{NH}_4)_3\text{Pr}_2\text{F}_9 \cdot \text{H}_2\text{O}$</u>	<u>$(\text{NH}_4)_3\text{Sm}_2\text{F}_9 \cdot \text{H}_2\text{O}$</u>	<u>$(\text{NH}_4)_3\text{Er}_2\text{F}_9 \cdot \text{H}_2\text{O}$</u>
3200 ms	3167 s	3190 ms	3150 s, vb	3250 s
3100 s	3032 s	3040 s	1665 w	3120 s
2920 m, sh	2848 s	2890 m, sh	1480 m	2942 m, sh
1430 s	1497 s	1685 w, sp	1410 s	1655 w
1405 s	1465 ms, sh	1488 m, sp, sh	490 w	1488 s } db
325 s	1413 s, sp	1475 s, sp	328 s	1470 s }
	749 ms, sh	1420 s, sp	288 s	1438 s
	729 s	480 m, sp	255 s	1415 sh
	480 ms, sp	322 s		485 w
	346 ms, sh	265 s		415 w
	262 s, b	225 s		330 s
				295 s
				215 s

^aValues given in cm^{-1} .

^bAbbreviations used: s, strong; ms, medium-strong; m, medium; w, weak; sh, shoulder; b, broad; vb, very broad; sp, sharp; db, doublet.

Table XI
Infrared Spectra of NH_4LnF_4 Compounds^{a,b,c}

<u>NH_4ScF_4</u>	<u>NH_4YF_4</u>	<u>NH_4GdF_4</u>	<u>NH_4ErF_4</u>
3220 s	3100 s	3200 s	3215 s
3110 s, sh	2900 s, sh	3040 s	3062 s
2870 m, sh	2180 m	2885 s, sh	3012 s, sh
2335 w	1889 m	2135 w, b	2900 ms, sh
1430 s	1476 s	1883 w, b	1494 s
597 s	1430 s	1720 vw	1447 s, sp
491 s	446 s	1680 w	1425 s, sp
230 s	345 s	1482 s, sp	419 s
	296 s	1442 s, sp	341 s
	233 s	1422 s, sp } db	300 s
	(2814)	1410 s, sp }	234 s
		401 s	(2815)
		336 s	
		290 s	
		238 s	
		(2816)	

^aValues given in cm^{-1} .

^bAbbreviations used: s, strong; ms, medium-strong; m, medium; w, weak; vw, very weak; sh, shoulder; sp, sharp; b, broad; db, doublet.

^cNumbers in parentheses are Raman bands.

III. RESULTS AND DISCUSSION

A. Bromination of Rare Earth Metals in Various Solvents;
Reaction of Bromination Solutions with Ammonium Fluoride.

The initial approach to synthesizing compounds of the type $\text{NH}_4\text{-Ln-F}$ involved preparation of the metal bromides. Methods of preparation of the tribromides of the rare earth metals have been reviewed by Brown;³⁷ the tribromides are generally obtained as the hydrates from aqueous hydrobromic acid, the oxides, or the trichlorides. In order to obtain anhydrous tribromides, carefully controlled vacuum thermal decomposition of the hydrates is required.

In this study the metal bromides were prepared by reaction of the metal with bromine in a suitable solvent. Subsequent reaction of the metal bromide solutions with solutions of ammonium fluoride in the same solvent was investigated as a potential route to preparation of ammonium fluorolanthanates. Acetonitrile, 1,2-dimethoxyethane, 2,2-dimethoxypropane, water, and methanol were surveyed to ascertain their potential usefulness for the above synthetic route. Preparation of a compound of the type $\text{NH}_4\text{-Er-F}$ was used for the survey of these solvents.

Acetonitrile has found wide application as a solvent for synthetic inorganic reactions.³⁸ Reactions of some transition metals with bromine in acetonitrile have been reported.³⁹⁻⁴¹ In the present case, using erbium metal, the bromination reaction proceeded smoothly, although fairly slowly, at reflux temperature. Reaction of the solution of

metal bromide in acetonitrile with a saturated solution of ammonium fluoride in acetonitrile was not fruitful, however, since no solid $\text{NH}_4\text{-Er-F}$ product could be isolated.

1,2-Dimethoxyethane also proved to be a poor solvent for these reactions. The bromination of erbium proceeded very slowly at reflux temperature, and a large excess of bromine was required for even incomplete reaction of the metal. The attempted reaction of the metal bromide solution with a saturated solution of ammonium fluoride in 1,2-dimethoxyethane yielded no isolable product.

2,2-Dimethoxypropane proved similarly unsuccessful; incomplete reaction of the metal resulted after prolonged heating at reflux temperature, and the erbium/bromine/2,2-dimethoxypropane reaction mixture, upon standing, deposited a yellow residue containing Er^{3+} . A very small amount of a yellow-brown solid was isolated from the reaction between the bromination reaction mixture and a saturated solution of ammonium fluoride in 2,2-dimethoxypropane. This solid, however, was shown by qualitative tests to contain only fluoride and erbium ions; no ammonium fluoroerbate product was collected.

The bromination reaction went very smoothly in water; heating at a temperature slightly below reflux effected complete reaction of the metal in a relatively short time. Reaction of the metal bromide solution with a 2 M aqueous ammonium fluoride solution produced a very finely divided pale pink precipitate which could not be collected by filtration, but was separated from the mother liquor by centrifugation.

This synthetic method was abandoned due to difficulties encountered in separating the product from the reaction mixture. Also, it was thought that by refraining from the use of water as a solvent, probable hydrate formation would be avoided. However, it was subsequently found that the product obtained by this method was identical to the $(\text{NH}_4)_2\text{Er}_3\text{F}_{11}\cdot\text{H}_2\text{O}$ prepared by the method which was eventually pursued, as shall be described. Confirmation of the product's identity was accomplished through comparison of its X-ray powder pattern with that of a genuine sample.

A brief investigation was conducted of the reaction mixture obtained from bromination of the metal in water. The small amount of white residue always obtained after bromination of the metal in water was removed by filtration, and careful evaporation of the filtrate to dryness produced pink, extremely hygroscopic $\text{ErBr}_3\cdot 6\text{H}_2\text{O}$.

The bromination of erbium proceeded quite readily in methanol; a vigorous reaction ensued at 0° , and heating at reflux temperature for a relatively short time effected complete reaction of the metal. The bromination of metals other than the rare earths in methanol has been investigated^{39,42-44} by earlier workers in this laboratory; the mechanism of the bromination process is not yet thoroughly understood.

The bromination reaction in methanol was successfully extended to other rare earth metals: yttrium, lanthanum, praseodymium, samarium, gadolinium, dysprosium, and holmium. In all of these bromination reactions, it was found that at

least a twofold excess of bromine from that calculated for stoichiometric reaction to produce LnBr_3 was required for complete reaction of the metal; further, a small amount of yellow to yellow-brown residue, containing bromide ion, was always present after all of the metal had reacted. After filtration to remove this residue, erbium bromide solutions were found to remain clear upon being allowed to stand at room temperature for periods of up to four weeks. Presumably, these solutions would be stable for even longer periods of time. Generally, however, the solutions were used within a day or two after their preparation.

In the case of erbium the compound $\text{ErBr}_3 \cdot 4\text{CH}_3\text{OH}$ was isolated by treatment of the filtered bromination reaction mixture with 2,2-dimethoxypropane which removed any water in the solution and served to protect the solution from moisture. The usefulness of 2,2-dimethoxypropane as a dehydrating agent is well known,⁴⁵ particularly for hydrated metal nitrates,⁴⁶ chlorides,⁴⁶ and perchlorates.^{47,48} Its use in this instance is particularly apt since the products of its reaction with water are methanol and acetone, which neither complicate the system nor cause side reactions. Acetone and any excess 2,2-dimethoxypropane are volatile and easily removed during condensation of the solution to smaller volume. Sometimes, however, difficulty due to polymerization is encountered. But with careful control of reaction conditions, pink crystals of $\text{ErBr}_3 \cdot 4\text{CH}_3\text{OH}$ separate out of solution. The compound is extremely hygroscopic.

Compounds of the type $\text{LnBr}_3 \cdot 4\text{CH}_3\text{OH}$ have not been reported previously, although Quill and Clink⁴⁹ have reported the preparation of compounds $\text{LnCl}_3 \cdot 4\text{CH}_3\text{OH}$ ($\text{Ln} = \text{La, Pr, Nd, Gd, Ho, Tb}$) from solutions of the metal chloride hydrates in methanol and 2,2-dimethoxypropane.

Methanolated erbium bromide can also be obtained by careful evaporation of the bromination reaction mixture to dryness; however, the number of moles of solvated methanol per mole of erbium bromide is fewer than four. This partial loss of the coordinately bound methanol is probably due to replacement of some of the solvated methanol by water.

Since bromination of the rare earth metals in methanol provides a simple method of preparing solutions of the tetramethanolated bromides, this reaction can serve as a means of preparing lanthanide complexes which are difficult to obtain in aqueous solution. Further, characterization of the lanthanide bromide methanolates themselves is worthy of further study, since alcoholates of lanthanide halides have not been studied in detail.

Methanol was selected as the solvent of preference for this synthetic method, for several reasons. The bromination reaction went very smoothly, rapidly, and to completion in methanol; and, the solubility of ammonium fluoride in methanol exceeded that in the other solvents except for water (saturated ammonium fluoride in methanol is about $0.5 \text{ } \underline{m}$ ⁴⁴). The difficulty encountered in isolation of products was far less pronounced in methanol than in water; moreover, it was

hoped that hydrated products could be avoided by carrying out the syntheses in a nonaqueous medium. A detailed discussion of the reaction of methanolic solutions of lanthanide bromides and ammonium fluoride is relegated to a separate section; some remarks on the reaction of the lanthanide bromide solutions with ammonia will also be presented separately.

B. Preliminary Investigation of the Synthesis of Lanthanide Bromide Ammines.

The reactions between ammonia and methanolic lanthanide bromide solutions were investigated in a preliminary way, in order to evaluate the potential of this synthetic route as a method of preparation of lanthanide bromide ammines.

Lanthanide halide ammines have been little investigated. Most of the reported work has dealt with the reaction of scandium halides with ammonia at elevated pressure.

$\text{ScF}_3 \cdot 0.4 \text{ NH}_3$ has been prepared in this manner from $\text{ScF}_3 \cdot 0.25\text{H}_2\text{O}$,⁵⁰ and $\text{ScCl}_3 \cdot (7.49-7.63)\text{NH}_3$,⁵¹ $\text{ScBr}_3 \cdot 7.5\text{NH}_3$,⁵¹ and $\text{ScX}_3 \cdot n\text{NH}_3$ ($\text{X} = \text{Cl}, \text{Br}; n = 2, 4, 5$)^{52, 53} have been similarly prepared from anhydrous scandium chloride and bromide. The scandium fluoride ammine cannot be prepared from anhydrous scandium fluoride,⁵¹ and the scandium chloride ammines cannot be prepared from hydrated scandium chloride.⁵² $\text{ScI}_3 \cdot n\text{NH}_3$ ($n = 2, 4, 8$) has also been reported.⁵³

A small number of lanthanide halide ammines for metals other than scandium have been reported: $\text{YF}_3 \cdot 0.35\text{NH}_3$ ⁵⁰ and $\text{LnCl}_3 \cdot n\text{NH}_3$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}; n = \text{variously } 1-20$).⁵⁴

Since addition of ammonia to an aqueous solution of lanthanide chlorides precipitates the metal hydroxides,⁵⁵ it was deemed worthwhile to attempt the preparation of lanthanide bromide amines in nonaqueous solution, i.e., methanol. In the cases examined (erbium, lanthanum, samarium) it was possible to obtain lanthanide bromide amines through reaction of methanolic lanthanide bromide solutions with ammonia. Composition of the product ammine obtained by this method varies depending upon which metal is used and upon how the solid product is recovered from the reaction mixture.

Preliminary results indicate that samarium bromide monoammine can be prepared by this method, and that lanthanum and erbium bromide amines of ammonia:lanthanide bromide molar ratios greater than and less than one, respectively, are formed.

This method of preparation of lanthanide bromide amines thus appears promising and could provide a much more convenient synthesis than the gas-solid reactions generally employed. However, any further discussion of these reactions would be premature at this point, because a thorough investigation of the effect of various reaction conditions on the composition of products obtained should be undertaken.

C. Computer Programs.

Three programs were written to circumvent the need for laborious and time-consuming calculations and comparisons of powder data. These programs are described below.

1. Program for Comparison of X-Ray Powder Patterns.

X-Ray powder patterns were taken routinely of all products prepared during the course of this investigation. Comparison of powder patterns of products prepared by different synthetic methods was a useful means of determining whether various products obtained were the same or different compounds. In order to expedite comparison of compounds from their powder patterns, a program was written so that this could be done by computer.

The program compares d values and intensities of powder patterns and determines whether films match. In addition to providing a rapid comparison of compounds prepared in the course of the research, the program can also be used to compare compounds with published powder pattern data.

Using the program, one or more films can be compared with a library of films or with a designated set of films within the library; or, of a set of films, all can be compared with each other. The procedure followed for the comparison is described below. The program is written in Fortran IV, Level G, and is designed for use on any computer with a Fortran IV compiler and 85K bytes of core available, such as an IBM 360.

The comparison between any two films is made on the basis of both d values and their corresponding intensities. This comparison is made by scanning through d values on the film with the greater number of lines to find a match for each d value on the film with fewer lines. The d values on the

two films being compared are divided into three sections: $d \geq 4$, $4 > d > 2$, and $d \leq 2$. Limits are placed on the amounts by which two d values within a given section can differ in order to be considered matched. The limits are least strict for the largest d values and most strict for the smallest d values. Two sets of limits are incorporated into the program itself; these are given below:

<u>Section</u>	<u>Difference in Value of d</u>	
	Limit Set 1	Limit Set 2
$d \geq 4$	± 0.10	± 0.30
$4 > d > 2$	± 0.05	± 0.15
$d \leq 2$	± 0.01	± 0.10

Either of these sets can be chosen for the comparison of d values, or the operator can read in any limits desired. Thus, great latitude is permitted in the stringency of the d value comparison.

To consider the section of largest d values as matched, all but one of the d values on the film with fewer lines must agree with those on the other film within the limits selected. To consider the other two sections as matched, at least 80% of the d values on the film with fewer lines must agree with lines on the other film, again within the limits selected.

If the d values in a given section do not match according to the criteria used, the two films are considered not to match and comparison of those two films is discontinued.

If the d values in a given section do agree, comparison is then made of the intensities of the paired d values in that section.

Intensities are assigned numerical values on a scale from 1 to 100. Any two intensities must agree within ± 15 in order to be considered matched. If intensities for a given film have been estimated visually (i.e., vvs , vs , ... vvw), a subroutine converts these intensities to the 1 to 100 scale. Additionally, if the strongest line on a film whose intensities are estimated visually is found to be less than 90 when converted, a scale factor is employed to set that intensity to 90 and all other intensities for that film are correspondingly scaled upwards.

If at any time the intensities of two paired d values do not agree within the ± 15 limit, the two films are considered not matched. If all intensities for a particular section do agree within this limit, this section is considered matched and the computer goes on to compare d values for the next section.

Required input for each film consists merely of (1) an information card identifying the film number and compound, together with any additional information the user deems desirable; (2) instructions designating which of the program options are desired; and (3) data cards listing all d values and their corresponding intensities.

For two films that are found to match, output consists of the numbers and identifying information for the two films

followed by a table listing the line numbers, d values, and intensities on the first film with their matched counterparts on the second. For films that do not match, the computer prints out only that fact, followed by the numbers and identifying information for the films.

A complete listing of the program is provided in Section B of the Appendix.

2. Programs for Calculation of Per Cent Compositions of Ammonium Fluorolanthanates and Ammonium Fluorolanthanate Hydrates.

In order to have a relatively complete list of possible compounds and their theoretical per cent compositions for reference in using the experimental analytical data obtained, programs were written to have these calculations done by computer. Two separate programs were written.

The first of these was a program designed to calculate the molecular weights and per cent compositions of all compounds of the type $(\text{NH}_4)_x\text{Ln}_y\text{F}_z$ where x varied from 1 to 15, y from 1 to 5, and z from 4 to 30. The lanthanide metals used in the calculations were yttrium, lanthanum, gadolinium, erbium, samarium, praseodymium, and europium. The only data required for the program were the atomic weights of all of the elements involved; these were included directly in the program. The program output was in table form; each compound's formula was listed, and beneath this was printed the molecular weight and the theoretical per cent of each element in the compound. A complete listing of the program is provided in

Part C of the Appendix.

The second program calculated the molecular weights and per cent compositions of compounds of the type $(\text{NH}_4)_x\text{Ln}_y\text{F}_z \cdot n\text{H}_2\text{O}$. Again x varied from 1 to 15, y from 1 to 5, and z from 4 to 30; n had the values 0.5, 1, 1.5, and 2. The lanthanide metals for which the calculations were made were the same as those listed above. All necessary atomic weight data were included directly in the program itself. The output was a tabulated listing of each compound's formula, molecular weight, and theoretical per cent composition. A complete listing of the program is given in Part D of the Appendix.

D. Reactions of Methanolic Solutions of Rare Earth Bromides and Ammonium Fluoride.

Reactions of solutions obtained from bromination of the rare earth metals in methanol with saturated solutions of ammonium fluoride in methanol afforded different products for different molar ratios of the reactants and for different metals used. The method by which the products were recovered from the reaction mixture was also an important factor in the obtaining of pure products.

Reactions using ammonium fluoride:erbium bromide molar ratios of 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 10:1, and 25:1 were carried out. It was found that no solid product is precipitated from the reaction mixture when the ratio is less than 4:1, and at least a 6:1 ratio is necessary in order to obtain a good crystalline product. A progressive increase

in nitrogen content is observed as the ratio is increased from 4:1 to 6:1; a further increase in the ratio does not change the composition of the solid. In regard to these findings, it is pertinent to note the results of Ivanov-Emin et al.,²¹ who studied the systems $\text{LnCl}_3\text{-AF-H}_2\text{O}$ ($\text{Ln} = \text{Er, Y, Lu}$; $\text{A} = \text{Na, K, Rb, Cs}$). They found that reaction in the systems depended upon the components and on their ratios $\text{AF}:\text{LnCl}_3$; also, the appearance of the solid phase was crystalline at ratios $\geq 5:1$, whereas at lower ratios the solid phase was amorphous. Increasing the ratio up to 10:1 did not significantly alter the composition of the solid phase.

Reactions of lanthanide bromide/methanol solutions with saturated ammonium fluoride/methanol solutions for the metals yttrium, lanthanum, praseodymium, samarium, gadolinium, dysprosium, holmium, and erbium were carried out; ammonium fluoride:lanthanide bromide molar ratios used were 6-10:1. In all cases solid products were isolated; however, products of different stoichiometric composition were obtained depending upon the metal used. The metals of smaller ionic radius (see Table XII, p 51) formed compounds which were more stable to decomposition in water or methanol. Indeed, with lanthanum, the largest ion in the series, it was impossible to obtain an ammonium fluorolanthanate by this synthetic method. Reaction of methanolic solutions of lanthanum bromide and ammonium fluoride merely resulted in the precipitation of lanthanum trifluoride. This is in line with the general observations that the tendency towards complex formation

Table XII
Effective Ionic Radii of Ln^{3+} Ions (in Å)⁵⁶

Sc	0.73
Y	0.89
La	1.06
Pr	1.01
Sm	0.96
Gd	0.94
Dy	0.91
Ho	0.89
Er	0.88

risers with increase in the atomic number of the lanthanide metal,²¹ and that there is an increase in complex stability with decreasing size of Ln^{3+} .⁵⁷ For the metals of smaller ionic radius (yttrium, dysprosium, holmium, erbium for this particular type of reaction), it was possible to prepare compounds of the composition $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11} \cdot \text{H}_2\text{O}$. For the larger cations, excluding lanthanum (praseodymium, samarium, gadolinium in this study), compounds of different stoichiometries were obtained.

On the basis of differences in the solubilities of many specific lanthanide salts, the lanthanide series is commonly subdivided into two groups, the cerium group comprising elements of atomic numbers 57-62 and the yttrium group comprising elements of atomic numbers 39, 63-71. In regard to

the above findings, it is apparent that this subdividing is also appropriate in the case of the ammonium fluorolanthanates. However, it must be pointed out that differences between the two groups are not completely clear-cut; one group gradually shades into the other.

It must be noted that size of lanthanide ion alone is probably not the only factor in determining stabilities and types of stoichiometries and structures found for $A^I-Ln^{III}-F$ compounds in general. Babel,⁵⁸ in a review of the structural chemistry of transition metal fluorocomplexes, notes that compounds having the same formula type never adopt the same structure type or at least the same coordination number for A-ions at the extremes of the size range. Kemmitt et al.⁵⁹ have also suggested, for complex fluorides of the general formula $A^I M^V F_6$, that the major factor controlling the structure of the complex is the ionic radius of the cation A. They found that variation in the size of M had only a very small effect. However, the ions M in the compounds included in their study are generally small, whereas tripositive lanthanide ions are comparatively quite large and would thus be expected to have a much more significant effect on the structure of their complex fluorides. In the present study, the cation A was the same for all compounds, so differences in stoichiometry of the complexes were due to the differences in lanthanide metal ions. However, for complexes containing the same lanthanide ion but different A ions, it might be of interest to note an observation made during the course of this

work. An attempt was made to synthesize potassium and sodium fluorolanthanates by substituting sodium fluoride and potassium fluoride for ammonium fluoride in the reaction with methanolic erbium bromide. Ionic radii of the three cations are in the order $\text{Na}^+ < \text{K}^+ < \text{NH}_4^+$. It was found that no solid fluoroerbate could be obtained with sodium ion, but a complex was isolated with potassium. This potassium compound was shown by its X-ray powder pattern to be structurally different from the ammonium fluoroerbate prepared similarly. The effect of changing the monopositive ion while holding the lanthanide ion constant was examined in only a cursory way, but preliminary results seem to indicate that both of the metal ions in alkali fluorolanthanate compounds have an effect upon stability and structure.

In this respect, it is consequently more valid to look upon the ratio of the radii of the ions A and M in alkali fluorometallates as being the important factor. This ratio has been concluded⁶⁰ to be a determining factor in the types of stoichiometry found for alkali fluorometallates of transition metals of oxidation states II to V. For the compounds prepared in the present work, the radius ratio changes solely due to changes in lanthanide ion; however, the fact that different stoichiometries are found for different values of this ratio is in agreement with this general observation.

Recovery of the ammonium fluorolanthanate products from the reaction mixtures also was a factor in obtaining pure compounds. The ammonium fluorolanthanates, as originally

precipitated, were all very gelatinous solids, thus making filtration difficult. Bromide ion from the reaction of the excess bromine present with ammonium ion⁶¹ and any ammonium bromide produced from the reaction of ammonium ion (in excess of that used to form the complex) with the bromide ion present in the mixture had to be removed from the desired ammonium fluorolanthanate. This was accomplished by repeated washings with small amounts of methanol. Prolonged washing or use of copious amounts of methanol was avoided, because the ammonium fluorolanthanates decomposed in a great excess of methanol. After all bromide had been removed from the products, they were washed with anhydrous ether and dried at room temperature over a suitable desiccant, generally silica gel or magnesium perchlorate. Drying at elevated temperatures was also avoided, inasmuch as the products lost ammonium fluoride upon heating.

All of the ammonium fluorolanthanates prepared by this method were stable in air over long periods of time. The compounds were of the color characteristic of the tripositive lanthanide ions; compounds of colorless lanthanide ions were white. The compounds decomposed in water and were virtually insoluble in common organic solvents and dilute acids. The compounds were difficultly soluble in concentrated hydrochloric or sulfuric acids and were moderately soluble in a mixture of nitric acid and boric acid.

Elemental analyses of the ammonium fluorolanthanates proved to be a difficult task. Accurate metal analyses could

not be obtained by atomic absorption, flame emission, EDTA titration, or ashing. It was possible to determine the metals by a gravimetric procedure³¹ involving dissolution of sample in sulfuric or hydrochloric acid, dilution to a pH of 1, precipitation as the oxalate, and ignition to the oxide. This method gave accurate results, so long as dissolution of all of the lanthanide metal was accomplished, in light of the compounds' being difficultly soluble. Analysis for fluoride was not successful using a fluoride-ion electrode, or either oxygen flask combustion or pyrohydrolysis with a volumetric finish. Fluoride analyses were performed successfully by steam distillation of fluorosilicic acid from the sample followed by oscillometric titration with thorium nitrate solution.³² The problems encountered with the metal and fluoride analyses were largely due to the difficulty involved in decomposing the fluorolanthanate portion of the compounds so that lanthanide(III) and fluoride could be separately determined. Nitrogen and hydrogen analyses presented no great difficulties; nitrogen analyses were easily performed by use of either a Coleman Nitrogen Analyzer or the Kjeldahl method;⁶² hydrogen analyses were carried out with an F&M Carbon-Hydrogen-Nitrogen Analyzer.

Of the ammonium fluorolanthanates prepared by the method under discussion, the yttrium, dysprosium, holmium, and erbium compounds were determined by elemental analysis to be $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11} \cdot \text{H}_2\text{O}$. The hydrated composition was further confirmed by the presence of infrared absorptions in the

mid-1600 cm^{-1} region. The HOH bending mode of water of hydration generally absorbs in this region.⁶³ The same hydrated composition is obtained even if all phases of the synthesis are carried out under dry nitrogen. Treatment of the metal bromide solutions with 2,2-dimethoxypropane after their initial preparation also did not result in anhydrous products' being obtained. Since the methanol used in the syntheses was carefully dried,²⁴ it is assumed that the water present to form the hydrate is produced during the course of the bromination reaction.

The mechanism of the reaction between metals and bromine in methanol is still not well understood. It has been suggested⁶⁴ that bromination of metals in polar organic solvents first involves the reaction of bromine with the solvent to form hydrogen bromide. Baker,⁴² in a study of the bromination of uranium in methanol, questioned this hypothesis and postulated reaction of bromine with the metal as the first step in the reaction mechanism. However, hydrogen bromide was shown to be formed by reaction of methanol with the uranium bromides formed initially. If hydrogen bromide is formed, then water would be produced by reaction of hydrogen bromide with methanol.⁶⁵

Several approaches to inhibiting the reaction of hydrogen bromide with methanol to form water were successfully employed in the brominations of niobium and tantalum in methanol;⁴² the use of excess bromine, rapid addition of the bromine to the reaction mixture, and the immediate use of the

bromination solution in subsequent reactions. These approaches did not result in anhydrous ammonium fluorometallates when applied to the preparation of the lanthanide compounds.

Formation of hydrated lanthanide complexes from non-aqueous media has also been found by L. J. Basile *et al.*,⁶⁶ who reported the synthesis of tetrahydrated 8-aminoquinoline complexes of neodymium and gadolinium. The complexes were prepared from the reaction of anhydrous metal bromides with the ligand in absolute ethanol. No explanation was offered as to the source of the water of hydration; however, Basile has suggested⁶⁷ that the absolute ethanol picked up water from the air, since no precautions were taken to keep the ethanol anhydrous.

X-Ray diffraction data, thermal decomposition studies, and infrared spectra of the $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11}\cdot\text{H}_2\text{O}$ compounds of yttrium, dysprosium, holmium, and erbium, prepared by the above synthetic method, are presented in the following section.

E. Ammonium Undecafluorotrilanthanate(III) Monohydrates.

Ammonium undecafluorotrilanthanate(III) monohydrates, $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11}\cdot\text{H}_2\text{O}$, were prepared for the metals yttrium, dysprosium, holmium, and erbium.

These compounds were all prepared by the synthetic method discussed in the previous section (pp 50-51), and specific preparations of each compound have also been described earlier (Section II.D.). The yttrium and dysprosium compounds are white, the holmium compound is peach-colored,

and the erbium compound is pink. All of these compounds are stable in air but decompose in water and excess methanol and upon heating. They are insoluble in most solvents, with the exception of concentrated sulfuric and hydrochloric acids or a mixture of nitric and boric acids.

X-Ray powder patterns were obtained for the four compounds. The powder data are presented in Tables XIII-XVI in Section A of the Appendix. The powder patterns showed that the four compounds are all isostructural, i.e., have similar arrangements of atoms within their particular unit cells. Fluorocomplexes having cations of similar size quite often are found to be isostructural, and these are no exception. The metal ions in these compounds are of nearly equal size, with a difference in ionic radius of only 0.03 Å between the largest and the smallest (see Table XII, p 51).

The characteristic infrared absorptions of the four compounds are reported in Table IX, p 35.

The thermal decomposition of these compounds in a helium atmosphere was studied by both differential thermal analysis (dta) and thermogravimetric analysis (tga). The differential thermograms for the compounds are shown in Figure 2, p 24; peak temperatures and the temperature ranges investigated are tabulated in Table III, p 25.

In any discussion of dta studies, it is important to bear in mind the fact that, unlike that from many physical methods, dta data are not standardized; many factors affect the differential curves. Some of these factors are^{68,69} size

and shape of the furnace, furnace atmosphere, nature of the sample holder, sample packing and preparation, heating rate, sample particle size, and speed and response of the recording device. Standardization of these variables has not been accomplished, thus dta results are generally not very reproducible from one laboratory to another. Even when dta data for a series of compounds are obtained from the same instrument, comparisons between dta results for compounds in the series are valid only when operating condition variables such as furnace atmosphere, heating rate, etc., are identical.

In studying the thermal decomposition of the $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11} \cdot \text{H}_2\text{O}$ compounds, the operating conditions were the same for all runs (with one minor exception which will be noted), and it is therefore possible to compare directly their dta curves with respect to peak temperatures and relative sizes and shapes of curves. On each thermogram, any change in dta base line after a peak is due to a change in thermal conductivity of the sample after the transformation has occurred. Temperatures mentioned in the following discussion are those of the peak maxima.

As with dta, tga results are also affected by a number of factors.⁷⁰ These include both instrumental factors and sample characteristics. Some of the former are heating rate, chart speed, furnace atmosphere, geometry of the sample holder, and recorder sensitivity; some of the latter are amount of sample, particle size, heat of reaction, nature of the sample, and thermal conductivity. In the present study

many of the above factors are fixed merely through use of the same instrument for all runs and because of the fact that the compounds studied are very similar to one another. Other factors which are variable were controlled as much as possible so that the tga results for the series of compounds could be validly compared. The tga data for the $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11}\cdot\text{H}_2\text{O}$ compounds are reported in Table VI, p 31.

Correlation of dta and tga results is very useful since it permits identification of what is involved in each step of a thermal decomposition. Correspondence between number of breaks in the tga curve and number of peaks in the dta curve is more important than close agreement with respect to temperature. There is always some discrepancy in temperature between a break in a tga curve and its corresponding dta peak, due to differences in experimental conditions. Figure 5 of the yttrium compound's decomposition exemplifies the kind of correlation found between the curves obtained by dta and tga for these compounds.

Some general observations can be made regarding the thermal decompositions of the four compounds. There is a decrease in the coordination number on heating, an observation which has also been made by Ivanov-Emin et al.¹⁸ for the thermal decomposition of ammonium fluoroscandates. Comparison of the initial decomposition temperatures given in Table III with the ionic radii of the lanthanide ions given in Table XII shows that the thermal stability of these compounds increases with decreasing ionic radius of the metal. Also,

Figure 5

DTA and TGA Curves for $(\text{NH}_4)_2\text{Y}_3\text{F}_{11} \cdot \text{H}_2\text{O}$

for all of these compounds the initial decomposition step is dehydration. This elimination of water is commonly the first effect for crystal hydrates.⁷¹ The final decomposition product under helium is the metal trifluoride in all cases. Presumably the intermediate compounds formed during the course of the thermal decompositions could be isolated with careful control of temperature, inasmuch as the compounds' decompositions occurred in a stepwise manner.

The thermal decomposition of $(\text{NH}_4)_2\text{Y}_3\text{F}_{11} \cdot \text{H}_2\text{O}$ occurs in three steps. The dta curve for this compound shows an initial broad endotherm at 119° . The tga curve shows a gradual weight loss beginning at 55° and culminating in a break at 163° , corresponding to the loss of one mole of water. Thus the first step in the decomposition is dehydration, leaving anhydrous $(\text{NH}_4)_2\text{Y}_3\text{F}_{11}$. A second dta endotherm appears at 180° , corresponding to a second gradual weight loss in the tga curve over the temperature range 163 - 306° . This results from the loss of one mole of ammonium fluoride, which leaves a compound of stoichiometry $\text{NH}_4\text{Y}_3\text{F}_{10}$. The third dta endotherm occurs at 311° ; this correlates with the third break in the tga curve at 305° , followed by a sharp drop, corresponding to the loss of the second mole of ammonium fluoride. Thus the final product of the decomposition is yttrium trifluoride.

The first effect in the dta curve of $(\text{NH}_4)_2\text{Dy}_3\text{F}_{11} \cdot \text{H}_2\text{O}$ is an endotherm at 69° ; this corresponds with a break in the tga curve beginning at 56° and indicates the loss of one mole

of water. The second dta endotherm occurs at 159° and is due to the gradual loss of two moles of ammonium fluoride in a single step, as shown from the tga curve where the corresponding break occurs at 126° . This leaves DyF_3 , which was confirmed by an X-ray powder pattern of the cooled decomposition residue. After this decline, there is a very gradual and slight decline on the tga curve with a miniscule drop from $330\text{--}337^{\circ}$. This drop at 330° , corresponding to a weight loss of 0.3%, seems too small to be of any significance. However, the dta thermogram surprisingly shows a sharp exotherm at 332° , so the tga drop may correlate to some exothermic process.

Of all the compounds examined in this study, this was the only time an exotherm was observed. Dehydration and decomposition generally produce endothermic heat effects,⁷² and these were thought to be the only reactions which would occur. Since by the time this exotherm occurs, the trifluoride has already been formed, the exotherm must reflect some change in or reaction involving dysprosium trifluoride.

Some processes known to produce exothermic effects are crystallographic transitions and oxidation reactions.^{72,73} Crystallographic transition in the end-product can involve conversion from an amorphous to a crystalline phase or conversion from a low-temperature phase to a high-temperature phase.⁷¹ In the present case the sample was scanned in an inert atmosphere, so it is highly unlikely that the exotherm is due to oxidation. A possible explanation for the exothermic

effect could be a conversion from a low- to high-temperature phase. Yttrium trifluoride and the trifluorides of samarium to lutetium inclusive are known to be dimorphic.⁷⁴ At room temperature dysprosium trifluoride is orthorhombic; the high-temperature modification possesses hexagonal symmetry.⁷⁴ The transition temperature, orthorhombic $\rightleftharpoons$ hexagonal, is reported to be 1030°, ⁷⁵ the transition temperatures for the other three metal trifluorides involved here are higher than this. The great discrepancy between the literature transition temperature and the dta exotherm observed in the present study casts doubt on this explanation. In the present study the sample was under helium and in the other⁷⁵ the sample was in vacuum; possibly the difference in furnace atmosphere has some effect. It is well known⁷⁶ that furnace atmosphere has a marked effect on dta curves for certain thermal reactions (oxidation, those in which a gas is involved); whether the difference in atmosphere could result in such a pronounced temperature difference in the present case is rather doubtful.

The decomposition of $(\text{NH}_4)_2\text{Ho}_3\text{F}_{11} \cdot \text{H}_2\text{O}$ occurs in four steps. The first step is again the loss of a mole of water, leaving anhydrous $(\text{NH}_4)_2\text{Ho}_3\text{F}_{11}$. The dta endotherm for this effect occurs at 61° and corresponds to a break in the tga curve at 50°. The second dta endotherm has its maximum at 204° and correlates with a weight loss in the tga curve at 178° corresponding to the loss of one mole of ammonium fluoride, leaving a compound of stoichiometry $\text{NH}_4\text{Ho}_3\text{F}_{10}$. The formation of $\text{NH}_4\text{Ho}_3\text{F}_{10}$ has been suggested by Zalkin and

Templeton⁷⁷ in a report on the structure determination of yttrium trifluoride and other lanthanide trifluorides. When preparing holmium trifluoride by reaction of holmium oxide, dissolved in dilute hydrochloric acid and neutralized with ammonium hydroxide, with concentrated hydrofluoric acid, a cubic phase was recovered initially; it was tentatively identified as $\text{NH}_4\text{Ho}_3\text{F}_{10}$.

A third dta peak in the $(\text{NH}_4)_2\text{Ho}_3\text{F}_{11} \cdot \text{H}_2\text{O}$ decomposition has its maximum at 286° with a shoulder at 304° . This feature has its tga counterpart as a gradual weight loss beginning at 226° followed by a break in the curve at 300° with a second weight loss culminating in a plateau at 327° . Apparently ammonia and hydrogen fluoride are lost in separate steps; the theoretical weight losses for ammonia and hydrogen fluoride are quite similar, and the two observed weight losses are of nearly equal magnitude, so it is impossible to say with certainty which substance correlates with which weight loss. The two weight losses taken together are equivalent to the loss of a mole of ammonium fluoride. The final product is holmium trifluoride.

The decomposition of $(\text{NH}_4)_2\text{Er}_3\text{F}_{11} \cdot \text{H}_2\text{O}$ initially involves the loss of one mole of water, leaving $(\text{NH}_4)_2\text{Er}_3\text{F}_{11}$. The dta endotherm for this has its peak maximum at 115° ; the corresponding break in the tga curve is very slight and begins at 77° . In the second and final decomposition step, two moles of ammonium fluoride are lost simultaneously; the tga curve shows this loss to be gradual over the temperature range

187-317°, then rapid from 317-338°. The dta temperature for this step is 316°. The decomposition residue is erbium trifluoride. Thus no intermediate compound of composition $\text{NH}_4\text{Er}_3\text{F}_{10}$ is indicated by these data. In this regard, it is of interest to note that a phase tentatively identified as $\text{NH}_4\text{Er}_3\text{F}_{10}$ was reported by Zalkin and Templeton⁷⁷ to have been synthesized en route to erbium trifluoride.

It should be noted here that, in visual comparison of the Figure 2 dta curves for $(\text{NH}_4)_2\text{Er}_3\text{F}_{11}\cdot\text{H}_2\text{O}$ with those of the analogous yttrium, dysprosium, and holmium compounds, the erbium compound's dta curve was obtained using a different ΔT scale than that for the others ($\Delta T = 0.08$ mv/in. for the erbium compound, 0.02 mv/in. for the others). Thus the sizes of the erbium compound's endotherms are smaller relative to the others' peaks. However, this size difference is undoubtedly very slight, since comparison of the erbium compound's dta curve for $\Delta T = 0.08$ mv/in. with one run at $\Delta T = 0.2$ mv/in. showed only an almost imperceptible difference in peak size.

The thermal decomposition schemes for the compounds $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11}\cdot\text{H}_2\text{O}$ are summarized in Figure 6.

F. Reaction of Lanthanide Nitrate Hydrates with Ammonium Fluoride.

Dergunov⁵ has reported using compounds of the type $(\text{NH}_4)_3\text{LnF}_6$ as intermediates in the preparation of lanthanide trifluorides of erbium, samarium, and praseodymium. Reaction of hydrogen fluoride, ammonium carbonate, and lanthanide nitrate reportedly yielded the compounds $(\text{NH}_4)_3\text{LnF}_6$, which

Figure 6

Thermal Decomposition of $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11} \cdot \text{H}_2\text{O}$ Compounds*

*Temperatures given are dta peak maxima.

were then heated to obtain the trifluorides. Composition of the hexafluorolanthanates was not confirmed experimentally.

Unsuccessful attempts were made to reproduce Dergunov's results. Reaction of hydrogen fluoride, ammonium carbonate, and lanthanide nitrate, and reaction of ammonium fluoride with erbium nitrate both were attempted. In no case was a compound of composition $(\text{NH}_4)_3\text{LnF}_6$ obtained.

$(\text{NH}_4)_3\text{ScF}_6$ has been prepared¹⁹ by dissolving scandium oxide in nitric acid to form the nitrate, followed by reaction with a 30% aqueous ammonium fluoride solution. A similar reaction using the lanthanides yttrium, lanthanum, praseodymium, europium, gadolinium, and erbium did not produce $(\text{NH}_4)_3\text{LnF}_6$. This is not unexpected in that scandium generally differs from the rare earths in its property of forming complex fluorides.⁷⁸

A series of reactions was run, using 30% (w/v) aqueous ammonium fluoride solutions and lanthanide nitrate prepared variously from the metal or the metal oxide. Use of the metal oxide as starting material generally yielded compounds of relatively high nitrogen content, indicative of ammonium fluoride contamination of the ammonium fluorolanthanate produced. However, when the lanthanide nitrate hydrate was prepared from the metal and nitric acid, subsequent reaction of the nitrate with a 30% aqueous ammonium fluoride solution yielded $(\text{NH}_4)_3\text{Ln}_2\text{F}_9 \cdot \text{H}_2\text{O}$ for the metals for which this method was used (yttrium, lanthanum, praseodymium, samarium, and erbium).

Many of the general remarks made in Section III.E. about the $(\text{NH}_4)_2\text{Ln}_3\text{F}_{11}\cdot\text{H}_2\text{O}$ compounds are also applicable here. Specifically, the observations about solubility, stability in air, analyses, and presence of infrared HOH bending absorptions are all equally pertinent to the $(\text{NH}_4)_3\text{Ln}_2\text{F}_9\cdot\text{H}_2\text{O}$ compounds, so these comments will not be repeated here. Specific mention of various properties of each compound will be included in the following section which deals with the X-ray diffraction data, thermal decomposition studies, and infrared spectra of the $(\text{NH}_4)_3\text{Ln}_2\text{F}_9\cdot\text{H}_2\text{O}$ compounds.

G. Ammonium Nonafluorodilanthanate(III) Monohydrates.

Ammonium nonafluorodilanthanate(III) monohydrates, $(\text{NH}_4)_3\text{Ln}_2\text{F}_9\cdot\text{H}_2\text{O}$, were prepared by the synthetic method described above (p 68) for the metals yttrium, lanthanum, praseodymium, samarium, and erbium. Specific preparations of each compound have also been described earlier (Section II.E.).

The yttrium, lanthanum, and samarium compounds are all white; the praseodymium compound is light green, and the erbium compound is pink. The lanthanum compound is appreciably hygroscopic. All of the compounds are difficultly soluble in concentrated sulfuric and hydrochloric acids.

X-Ray powder patterns were obtained for the five compounds. The powder data are presented in Tables XVII-XXI in Section A of the Appendix. The powder patterns showed that the samarium and praseodymium compounds are isostructural and different from the isostructural erbium and yttrium

compounds. The lanthanum compound is structurally different from all of the others. That the erbium and yttrium compounds are isostructural would be expected, because the ionic radii of the metals (see Table XII, p 51) differ by only 0.01 Å. From the ionic radii of lanthanum (1.06 Å), praseodymium (1.01 Å) and samarium (0.96 Å) it is seen that praseodymium is intermediate in size between lanthanum and samarium. The lanthanum and samarium compounds would not be expected to be isostructural, and the data show that the praseodymium compound adopts the same structure as that of the samarium compound, rather than that of the lanthanum compound.

The characteristic infrared absorptions of the five compounds are reported in Table X, p 36.

The thermal decomposition of these compounds in a helium atmosphere was studied by both differential thermal analysis and thermogravimetric analysis. The differential thermograms for the compounds are shown in Figure 3, p 26; peak temperatures and the temperature ranges investigated are listed in Table IV, p 27. The tga data are reported in Table VII, p 32. A representative comparison of the dta and tga curves is provided in Figure 7, which illustrates the thermal decomposition of $(\text{NH}_4)_3\text{Y}_2\text{F}_9 \cdot \text{H}_2\text{O}$. The general comments in Section III.E. regarding thermal studies should be kept in mind during the following discussion of the $(\text{NH}_4)_3\text{Ln}_2\text{F}_9 \cdot \text{H}_2\text{O}$ decompositions.

Certain general observations can be made from the thermal decomposition data of the series of compounds. There

Figure 7

DTA and TGA Curves for $(\text{NH}_4)_3\text{Y}_2\text{F}_9 \cdot \text{H}_2\text{O}$

is a decrease in coordination number upon heating. The final decomposition product is the metal trifluoride in all cases. The first step in the decomposition of the yttrium, praseodymium, and erbium compounds is the loss of a mole of water, leaving anhydrous $(\text{NH}_4)_3\text{Ln}_2\text{F}_9$. In this regard it is interesting to note that Sterba-Böhm,⁷⁸ from qualitative observations, suggested the possibility of the formation of this type of compound with scandium. He reported that $(\text{NH}_4)_3\text{Sc}_2\text{F}_9$ was formed as an intermediate compound in the stepwise decomposition of $(\text{NH}_4)_3\text{ScF}_6$ in aqueous solution. However, Ivanov-Emin and coworkers,¹⁸ in a later study, stated that the reported $(\text{NH}_4)_3\text{Sc}_2\text{F}_9$ formation was erroneous.

The samarium and lanthanum compounds lose water and some ammonium fluoride in one step, the samarium compound gradually and the lanthanum compound rapidly. Their thermograms do not show a tga plateau nor a dta return to base line indicative of the presence of $(\text{NH}_4)_3\text{Ln}_2\text{F}_9$. There is a slight decline in the dta curve of the samarium compound, over the range 91-152°, which occurs prior to the sizable endotherm for ammonium fluoride loss. This has a counterpart in a scarcely perceptible break in the tga curve at ca. 75° and would seem to indicate that the samarium compound does dehydrate initially, but the loss of ammonium fluoride begins just as the last of the water is lost. The lanthanum compound's thermograms show that it is the least stable of all of these compounds. Disregarding the dehydration temperatures, which vary randomly, the ammonium fluorolanthanate compounds

themselves decompose, through loss of ammonium fluoride, in an order related to ionic radius of the metal. That is, the smaller the metal, the more stable the compound is to heat. This can best be seen by examination of Figure 3.

$(\text{NH}_4)_3\text{Y}_2\text{F}_9 \cdot \text{H}_2\text{O}$ decomposes in four steps. The peak temperature for the first, weak dta endotherm is 92° ; this corresponds to a break in the tga curve commencing at 86° and representing the loss of one mole of water. The second, strong dta endotherm occurs at 214° . The corresponding break in the tga curve occurs at 198° and correlates with the loss of two moles of ammonium fluoride, leaving $\text{NH}_4\text{Y}_2\text{F}_7$. The third mole of ammonium fluoride appears to be lost in two steps, as hydrogen fluoride and ammonia. The two weak dta peaks for this effect occur at 302° and 323° ; the corresponding tga temperatures are 233° and 302° . The theoretical weight losses for hydrogen fluoride and ammonia are not very different, so it is difficult to say with certainty which is lost first. The data suggest, however, that loss of a mole of hydrogen fluoride occurs first, followed by the loss of ammonia. The final decomposition product is yttrium trifluoride.

The thermal decomposition of $(\text{NH}_4)_3\text{La}_2\text{F}_9 \cdot \text{H}_2\text{O}$ occurs in three steps. The compound begins to decompose almost immediately upon heating; the first dta endotherm begins at 42° and has its maximum at 100° . This correlates with the loss of a mole of water and one mole of ammonium fluoride as evidenced by the tga curve, where the temperature at which

this decomposition step begins is 40° . This leaves two moles of NH_4LaF_4 , which rapidly lose a mole of ammonium fluoride to form $\text{NH}_4\text{La}_2\text{F}_7$. The dta endotherm for this step has its maximum at 132° , and the corresponding break in the tga curve commences at 147° . The final dta endotherm, representing the loss of the final mole of NH_4F , has its maximum at 190° , correlating with a very gradual weight loss commencing at 205° on the tga curve. The final decomposition product is lanthanum trifluoride.

$(\text{NH}_4)_3\text{Pr}_2\text{F}_9 \cdot \text{H}_2\text{O}$ decomposes in three steps. The first effect is dehydration, shown by a dta endotherm at 109° and the corresponding break at 90° in the tga curve. $(\text{NH}_4)_3\text{Pr}_2\text{F}_9$ then loses one mole of ammonium fluoride; this process is shown as a dta endotherm having its maximum at 174° . The corresponding break in the tga curve begins at 145° . The final effect is the loss of two moles of ammonium fluoride in one step. The dta curve for this effect is a strong endotherm having its maximum at 211° ; the break in the tga curve occurs at 206° . The final decomposition product is praseodymium trifluoride.

The thermal data for $(\text{NH}_4)_3\text{Sm}_2\text{F}_9 \cdot \text{H}_2\text{O}$, as mentioned earlier, give some indication that the initial step is dehydration. However, the first actually measurable effect on the tga curve is a gradual weight loss beginning at 38° and corresponding to the loss of both a mole of water and two moles of ammonium fluoride, resulting in $\text{NH}_4\text{Sm}_2\text{F}_7$. The feature on the dta curve corresponding to this is an unsymmetrical

endotherm having its maximum at 206° . The dta curve first begins to deviate from the base line at 91° and undergoes a gradual decline before tracing out the 206° endotherm. A second, weak dta endotherm occurs at 265° . This correlates with an observed gradual weight loss on the tga curve with the break in the curve occurring at 261° . This weight loss was attributed to the loss of the final mole of NH_4F . The observed weight loss was slightly low; it may be that complete loss of the remaining NH_4F requires a longer heating time than was provided during the tga scan. The break in the tga curve occurs at 264° . The final decomposition product is samarium trifluoride.

$(\text{NH}_4)_3\text{Er}_2\text{F}_9 \cdot \text{H}_2\text{O}$ decomposes in a manner similar to the decomposition of the yttrium compound. The thermograms for the two compounds are nearly identical (see Figure 3). The first feature on the dta curve is a very weak endotherm at 94° ; the corresponding weight loss on the tga curve begins at 45° and correlates with the loss of one mole of water. The dta curve next exhibits a strong endotherm having its maximum at 207° . The tga curve exhibits a corresponding weight loss which correlates with the loss of two moles of ammonium fluoride, leaving $\text{NH}_4\text{Er}_2\text{F}_7$. The break in the tga curve for this decomposition step occurs at 200° . The last two features on the dta curve are two weak endotherms at 316° and 331° . The corresponding features on the tga curve are a gradual decline beginning at 238° and an abrupt decline beginning at 312° . These data indicate that the remaining mole of ammonium

fluoride is lost in two steps, as hydrogen fluoride and ammonia. Again the theoretical weight losses for hydrogen fluoride and ammonia are quite similar. However, the data indicate that hydrogen fluoride is lost first, followed by the loss of ammonia. The final decomposition product is erbium trifluoride.

The thermal decomposition schemes for the $(\text{NH}_4)_3\text{Ln}_2\text{F}_9 \cdot \text{H}_2\text{O}$ compounds are summarized in Figure 8.

H. The System Ammonium Fluoride - Erbium Fluoride - Water.

The three-component system consisting of erbium fluoride, ammonium fluoride, and water was studied at 25° . The purpose of this study was to ascertain what solid fluoro-complexes, if any, are formed between erbium fluoride and ammonium fluoride in aqueous solution.

The synthetic complex method as described by Purdon and Slater²⁸ was employed. Ammonium fluoride:erbium fluoride mixtures varying from $\sim 95:5$ to $\sim 10:90$ were used to give a wide range of component concentrations. Table II, p 20, contains the data obtained for the system; the results are plotted in Figure 1, p 21. The calculated positions of NH_4ErF_4 and $(\text{NH}_4)_3\text{ErF}_6$ are also shown in Figure 1.

Examination of Figure 1 shows that no tie-lines pass through the NH_4ErF_4 and $(\text{NH}_4)_3\text{ErF}_6$ points. Further, there is no intersection of a number of tie-lines to indicate the formation of a distinct compound. Also, the X-ray powder data obtained for a few of the residues confirmed that these solids were merely mixtures of ammonium fluoride and erbium

Figure 8

Thermal Decomposition of $(\text{NH}_4)_3\text{Ln}_2\text{F}_9 \cdot \text{H}_2\text{O}$ Compounds*

Figure 8, continued

*Temperatures given are those of dta peak maxima.

fluoride.

The mixture containing the highest ammonium fluoride:erbium fluoride ratio approaches a saturated ammonium fluoride solution in concentration. The solubility of ammonium fluoride in water at 25° has been reported variously as 45.9, 45.12, 45.50, and 45.31 grams of ammonium fluoride per 100 grams of saturated solution.⁷⁹ Thus no tie-lines lie in the lower left third (ammonium fluoride section) of Figure 1. The extremely low solubility of erbium fluoride accounts for the heavy concentration of tie-line dry residue points in the region of high erbium fluoride concentration.

Ivanov-Emin and Zaitseva⁸⁰ have obtained solubility isotherms at 25° for erbium, ytterbium, and lutetium fluorides in aqueous ammonium fluoride solutions. They also were unable to isolate solid fluorocomplexes, although they did conclude that the solubility of the metal fluoride in ammonium fluoride solutions increased with the ammonium fluoride concentration. A similar result was not found in the present study. However, the metal fluorides used in the Russian study were not anhydrous, but were assumed to have the composition $\text{LnF}_3 \cdot 0.5\text{H}_2\text{O}$. This would make a significant difference in the solubility of the metal fluoride.

I. Reactions of Lanthanide Fluorides with Ammonium Fluoride.

A number of reactions between lanthanide fluorides and ammonium fluoride were investigated to determine their potential as a means of preparing ammonium fluorolanthanates. It was found that different products are obtained from these

reactions, depending upon certain factors such as whether the metal fluoride is anhydrous or a hydrate, the concentration of the ammonium fluoride solution, the metal used, and the solvent used.

The products obtained from the series of reactions of this type were in most cases not identified beyond the determination of nitrogen content and the obtaining of an X-ray powder pattern. These data were used to give a preliminary suggestion of composition and to ascertain whether the product was the same as any prepared by a different method. Only those products whose preliminary characterization indicated that further work was desirable were investigated more fully.

Besse and Capestan,⁸¹ in a study of the reaction of $\text{CeF}_4 \cdot x\text{H}_2\text{O}$ with saturated aqueous ammonium fluoride solutions, reported the preparation of $(\text{NH}_4)_3\text{CeF}_7$, $(\text{NH}_4)_2\text{CeF}_6$, and NH_4CeF_5 . The product obtained depended upon the ratio ammonium fluoride:cerium tetrafluoride of the reactants. Peneman and Rosenzweig⁸² later found that the complex in the cerium tetrafluoride - ammonium fluoride - water system having the highest ammonium fluoride:cerium tetrafluoride ratio was $(\text{NH}_4)_4\text{CeF}_8$. They prepared this compound using saturated ammonium fluoride solutions containing some solid ammonium fluoride.

In an attempt to prepare the complex having the highest ammonium fluoride:erbium trifluoride ratio by an analogous reaction, $\text{ErF}_3 \cdot x\text{H}_2\text{O}$ was allowed to react with a saturated

(40 wt %) aqueous ammonium fluoride solution containing a small amount of solid ammonium fluoride. The $\text{ErF}_3 \cdot x\text{H}_2\text{O}$ used in the reaction was prepared from the metal by dissolving it in hydrochloric acid and then treating the acid solution with 48% hydrofluoric acid. The pink product obtained from this reaction gave elemental analysis results corresponding to the composition $(\text{NH}_4)_8\text{ErF}_{11}$. X-Ray powder data for this compound, however, subsequently showed that the product was a mixture of ammonium fluoride and some unidentified $\text{NH}_4\text{-Er-F}$ complex. Attempts to remove the ammonium fluoride by washing with water resulted in decomposition of the $\text{NH}_4\text{-Er-F}$ compound. Washing with methanol yielded a compound shown by its powder pattern to be the same as that prepared using a 20% aqueous ammonium fluoride solution, i.e., NH_4ErF_4 .

When $\text{LaF}_3 \cdot x\text{H}_2\text{O}$ and $\text{PrF}_3 \cdot x\text{H}_2\text{O}$ were used in a similar reaction with nearly saturated aqueous ammonium fluoride solutions, compounds of very low nitrogen content (less than 2%) were obtained. This corroborated the observation, made earlier, that size of the tripositive lanthanide ion is a determining factor regarding the types of compounds formed. Lanthanum (1.06 Å) and praseodymium (1.01 Å) have significantly larger ionic radii than does erbium (0.88 Å).

When anhydrous erbium fluoride was used instead of the hydrated material in reaction with saturated aqueous ammonium fluoride, $\text{NH}_4\text{-Ln-F}$ compounds of very small nitrogen content (less than 1%) were obtained. When anhydrous erbium fluoride was allowed to react with ammonium fluoride using

methanol as the solvent, again compounds with fairly low nitrogen content were obtained. Also, the less concentrated the methanolic ammonium fluoride solutions, the lower the nitrogen content of the products obtained. The anhydrous fluoride thus appears to be relatively unreactive. The same has been found to be true for scandium and yttrium.⁵⁰ In a study of reactions of scandium and yttrium trifluorides with ammonia, Orlovskii⁵⁰ has commented on the higher reactivity of metal fluoride hydrates compared with anhydrous metal fluorides.

A similar reaction was carried out using $\text{ErF}_3 \cdot x\text{H}_2\text{O}$ and a 15 wt % aqueous ammonium fluoride solution, instead of a saturated solution, at 80° . In this case the product obtained was shown by X-ray to be $(\text{NH}_4)_2\text{Er}_3\text{F}_{11} \cdot \text{H}_2\text{O}$, which had already been prepared by a different method, described earlier.

Erbium fluoride hydrate was then allowed to react with a 20% (w/v) aqueous ammonium fluoride solution. The product in this case was found by elemental analysis to be ammonium tetrafluoroerbate(III), NH_4ErF_4 . On the basis of this result, attempts were made to prepare the analogous tetrafluorolanthanates of other rare earth metals. These attempts were unsuccessful for samarium, lanthanum, and praseodymium. Reaction of these metal fluoride hydrates with 20% aqueous ammonium fluoride solutions yielded products of fairly low nitrogen content (less than 2%). However, ammonium tetrafluorogadolate(III) and ammonium tetrafluoroyttrate(III)

were successfully prepared by this method, which was not unexpected because gadolinium and yttrium have smaller ionic radii than do the other three metals.

To this series of three tetrafluorolanthanates was added, for purposes of comparison, ammonium tetrafluoroscandate which was prepared by a literature method.¹⁸ X-Ray diffraction data, thermal decomposition studies, and infrared spectra of these four ammonium tetrafluorolanthanates are presented in the following section.

J. Ammonium Tetrafluorolanthanate(III) Compounds.

Ammonium tetrafluorolanthanate(III) compounds, NH_4LnF_4 , were prepared for the metals scandium, yttrium, gadolinium, and erbium; specific preparations of these compounds have been described earlier (Section II.F.). The scandium, yttrium, and gadolinium compounds are white, and the erbium compound is pink. All of the compounds are stable in air.

X-Ray powder patterns were obtained for the four compounds; the powder data are presented in Tables XXII-XXV in Section A of the Appendix. The powder patterns showed that erbium and yttrium again form isostructural compounds; the scandium and gadolinium compounds adopt structures different from each other and from those of erbium and yttrium. The scandium compound's powder pattern agrees with that reported by Ivanov-Emin et al.¹⁸ It is included in the Appendix since the earlier workers' data were presented as a line diagram rather than as tabulated d values and intensities.

The characteristic infrared absorptions of the four

compounds are reported in Table XI, p 37; the Raman data obtained for the yttrium, gadolinium, and erbium compounds are also included in this table.

The thermal decomposition of these compounds in a helium atmosphere was studied by both differential thermal analysis and thermogravimetric analysis. The differential thermograms for the compounds are shown in Figure 4, p 28; peak temperatures and the temperature range investigated are given in Table V, p 29. The tga data are reported in Table VIII, p 33. A representative comparison of the dta and tga curves is provided in Figure 9, which illustrates the thermal decomposition of NH_4GdF_4 . Again the general comments made previously regarding thermal studies should be borne in mind during the ensuing discussion of the ammonium tetrafluorolanthanate decompositions.

The thermal decomposition of NH_4ScF_4 has been studied by Ivanov-Emin et al.¹⁸ The atmosphere in which their thermal studies were carried out was not specified; presumably it was air. Their data showed that NH_4ScF_4 decomposes in one step, with the dta endotherm for this effect starting at $220-230^\circ$ and reaching a maximum at 320° . The decomposition product is scandium trifluoride.

Thermal data from the present study are in agreement with the previous work, except for the expected discrepancy in temperatures due to the difference in furnace atmosphere. The single endotherm observed during the decomposition began at 156° and reached a maximum at 257° . This correlates with

Figure 9

DTA and TGA Curves for NH_4GdF_4

the weight loss observed on the tga curve beginning at 237° and corresponding to the loss of one mole of ammonium fluoride, leaving scandium trifluoride as the decomposition product.

The thermograms of NH_4YF_4 are more difficult to interpret. The dta curve shows a strong endotherm having its maximum at 195° ; this endotherm has a shoulder at 210° . A weak dta endotherm occurs at 297° . The tga curve shows that initial weight loss begins at 155° ; there is a break in the curve at 242° followed by first a gradual and slight weight loss until approximately 290° when this drop in the curve becomes more pronounced. The weight loss prior to the break in the curve at 242° can be correlated with the loss of one mole of hydrogen fluoride. The fact that the dta curve shows this to be a two-step process (i.e., the shoulder at 210°) is puzzling. The tga curve does have a scarcely perceptible inflection at 220° , but it is not a significant enough feature to consider the weight loss as two distinctly separate steps. It is, therefore, concluded that the first step in the decomposition of NH_4YF_4 is the loss of one mole of hydrogen fluoride, apparently by a two-step process not readily subject to interpretation. The remaining feature on the tga curve, the final weight loss, correlates with the loss of one mole of ammonia. The final decomposition product is yttrium trifluoride.

The thermal decomposition of NH_4GdF_4 is similar to that of the scandium compound. The dta curve consists of a

single strong endotherm having its maximum at 235° . This correlates with a sharp drop on the tga curve which corresponds to the loss of a mole of ammonium fluoride. The break in the tga curve occurs at 215° . The final decomposition product is gadolinium trifluoride.

The differential thermogram for NH_4ErF_4 has a strong endotherm at 221° and a medium endotherm at 296° . The first endotherm correlates with a weight loss on the tga curve at 199° . This corresponds to the loss of one mole of hydrogen fluoride, leaving $\text{ErF}_3 \cdot \text{NH}_3$. The second dta endotherm has its counterpart in a break in the tga curve beginning at 283° and showing a weight loss corresponding to the loss of ammonia. The final decomposition product is thus erbium trifluoride.

The thermal decomposition schemes of the ammonium tetrafluorolanthanates are summarized in Figure 10.

K. Miscellaneous Attempted Preparations of Ammonium Fluorolanthanates.

In addition to the synthetic approaches previously described for preparation of ammonium fluorolanthanates, a number of other synthetic routes were attempted. None of the reactions yielded products warranting further work.

These other synthetic routes included the reaction of erbium fluoride with ammonium fluoride in trifluoroacetic acid, the reaction of erbium oxide with ammonium fluoride in trifluoroacetic acid, the reaction of erbium fluoride with ammonium fluoride in aqueous hydrofluoric acid, and the reaction of erbium oxide with saturated aqueous ammonium fluoride.

Figure 10

Thermal Decomposition of NH_4LnF_4 Compounds*

*Temperatures given are dta peak maxima.

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V. APPENDIX

A. X-Ray Powder Diffraction Data

Table XIII
X-Ray Powder Diffraction Data for
Ammonium Undecafluorotriyttrate(III) Monohydrate
 $(\text{NH}_4)_2\text{Y}_3\text{F}_{11}\cdot\text{H}_2\text{O}$

<u>d_{hkl}, Å</u>	<u>Intensity</u>	<u>d_{hkl}, Å</u>	<u>Intensity</u>
6.9211	m	1.5046	vw
5.9060	vs	1.4376	w
4.5706	w	1.3825	w
3.4997	w	1.3560	vw
3.2596	vs	1.2868	vvw
3.0000	m	1.2691	vvw
2.7557	vw	1.2519	vvw
2.6069	m	1.2352	w
2.5142	vvw	1.2180	w
2.2362	w	1.1840	w
2.1250	m	1.1296	w
1.9462	vs	1.1099	vw
1.8668	m	1.0799	w
1.7975	w	1.0653	vw
1.7747	w	1.0539	vw
1.7157	vw	1.0438	w
1.6805	vw	1.0173	vw
1.6388	m	1.0009	vw
1.5918	vvw	.98667	vvw
1.5552	vw	.97516	vvw

Table XIII, continued

<u>d_{hkl}, Å</u>	<u>Intensity</u>
.96475	vvw
.95475	vw
.93823	vvw
.92655	vw
.91388	vw
.89869	vvw
.85697	vw
.82671	vw
.79751	vw
.79446	vw

Table XIV
X-Ray Powder Diffraction Data for
Ammonium Undecafluorotridysprosate(III) Monohydrate
 $(\text{NH}_4)_2\text{Dy}_3\text{F}_{11}\cdot\text{H}_2\text{O}$

<u>d_{hkl}, Å</u>	<u>Intensity</u>	<u>d_{hkl}, Å</u>	<u>Intensity</u>
8.1450	w	2.2324	vw
6.7221	m	2.1177	m
5.9716	vvs	1.9565	vs
5.6115	vvw	1.8632	w
4.4613	m	1.8013	w
4.1358	vw	1.7176	vw
3.6133	vw	1.6790	vw
3.4307	w	1.6426	m
3.2757	vvs	1.5615	vw
3.1095	m	1.5296	vw
2.9520	s	1.5010	vw
2.7397	vw	1.4422	vw
2.5791	m	1.3844	vvw
2.3946	vvw	1.2932	vvw

Table XV
X-Ray Powder Diffraction Data for
Ammonium Undecafluorotriholmate(III) Monohydrate
 $(\text{NH}_4)_2\text{Ho}_3\text{F}_{11}\cdot\text{H}_2\text{O}$

<u>d_{hkl}, Å</u>	<u>Intensity</u>	<u>d_{hkl}, Å</u>	<u>Intensity</u>
7.1923	vw	1.6337	m
6.5610	s	1.5924	vvw
5.9058	vvs	1.5570	vvw
5.0583	vw	1.5369	vvw
4.4613	m	1.5238	vvw
3.4115	w	1.4985	w
3.2491	vvs	1.4387	w
3.1346	vvw	1.3826	w
2.9752	m	1.3540	vw
2.9307	m	1.2888	vw
2.7277	vw	1.2714	vvw
2.5581	s	1.2512	vvw
2.2053	w	1.2321	vvw
2.1517	vw	1.2156	vvw
2.1009	m	1.1863	m
1.9974	vvw	1.1255	m
1.9455	vvs	1.1125	vvw
1.8533	m	1.0931	vvw
1.7804	m	1.0782	w
1.7160	w	1.0654	vvw
1.6715	w	1.0555	vvw
		1.0443	vw

Table XVI
X-Ray Powder Diffraction Data for
Ammonium Undecafluorotri-erbate(III) Monohydrate
 $(\text{NH}_4)_2\text{Er}_3\text{F}_{11}\cdot\text{H}_2\text{O}$

<u>d_{hkl}, Å</u>	<u>Intensity</u>	<u>d_{hkl}, Å</u>	<u>Intensity</u>
6.6819	s	1.5829	vvw
5.8865	vvs	1.5538	w
4.4482	m	1.5214	w
3.8733	vvw	1.4905	w
3.4063	w	1.4291	w
3.2364	vvs	1.3770	w
2.9535	s	1.3423	vvw
2.7167	w	1.2824	vw
2.5586	s	1.2795	vw
2.2020	w	1.2466	vvw
2.0955	m	1.2250	vw
1.9379	vvs	1.2107	vw
1.8420	m	1.1822	w
1.7719	m	1.1229	w
1.7133	w	1.1066	vvw
1.6645	w	1.0725	vw
1.6266	s		

Table XVII
X-Ray Powder Diffraction Data for
Ammonium Nonafluorodiyttrate(III) Monohydrate
 $(\text{NH}_4)_3\text{Y}_2\text{F}_9 \cdot \text{H}_2\text{O}$

<u>d_{hkl}, Å</u>	<u>Intensity</u>	<u>d_{hkl}, Å</u>	<u>Intensity</u>
7.4119	vs	1.7800	w
6.4393	w	1.7452	w
5.9247	m	1.7060	w
5.1689	s	1.6545	w
3.4176	w	1.6383	vvw
3.2935	vs	1.6093	vvw
3.1563	m	1.5596	w
2.9995	m	1.5269	vw
2.7725	w	1.4957	vvw
2.6758	vvw	1.4679	w
2.5931	w	1.4355	vvw
2.5020	vvw	1.3757	w
2.4174	w	1.3446	w
2.3092	m	1.2887	vvw
2.2010	w	1.1774	vvw
2.1459	m	1.1611	vvw
2.0575	w	1.0900	vvw
1.9844	m	1.0487	vvw
1.9481	vvw	.97171	vvw
1.8370	m	.95604	vvw

Table XVIII
X-Ray Powder Diffraction Data for
Ammonium Nonafluorodilanthanate(III) Monohydrate
 $(\text{NH}_4)_3\text{La}_2\text{F}_9 \cdot \text{H}_2\text{O}$

<u>d_{hkl}, Å</u>	<u>Intensity</u>	<u>d_{hkl}, Å</u>	<u>Intensity</u>
6.4869	w	1.9171	vw
5.4846	m	1.8795	vw
4.9662	m	1.7962	s
4.1009	m	1.7356	m
3.9567	vw	1.6250*	vw
3.7744	vw	1.4868	vw
3.5366	s	1.4515*	w
3.1776	vs	1.3668	w
2.8947	vw	1.3311	s
2.8321	vw	1.2724	vw
2.5495	w	1.2211	vw
2.4487	vw	1.1906*	m
2.3921	vw	1.1366	m
2.2426	m	1.0547	vw
2.2007	vw	1.0363	vw
2.0659	vs	.99876	vw
2.0051	s	.98612	w

*broad

Table XIX
X-Ray Powder Diffraction Data for
Ammonium Nonafluorodipraseodymate(III) Monohydrate
 $(\text{NH}_4)_3\text{Pr}_2\text{F}_9 \cdot \text{H}_2\text{O}$

<u>d_{hkl}, Å</u>	<u>Intensity</u>	<u>d_{hkl}, Å</u>	<u>Intensity</u>
8.2910	s	1.7773	w
5.5807	m	1.7274	w
4.8268	w	1.5997	w
4.2542	s	1.5275	w
3.6956	s	1.5007	w
3.2215	vs	1.4423	vw
2.9892	s	1.3961	w
2.4747	m	1.3571	w
2.4044	m	1.2835	w
2.1365	s	1.2127	w
2.0144	s	1.1734	vvw
1.8621	s	1.0794	vw
1.8272	m	1.0511	vw
1.7903	s		

Table XX
X-Ray Powder Diffraction Data for
Ammonium Nonafluorodisamarate(III) Monohydrate
 $(\text{NH}_4)_3\text{Sm}_2\text{F}_9 \cdot \text{H}_2\text{O}$

<u>d_{hkl}, Å</u>	<u>Intensity</u>
8.4489	vvw
5.6874	m
4.2542	m
3.6791	m
3.2329	s
2.9592	m
2.4487	vw
2.3672	vvw
2.1123	w
2.0014	w
1.8337	w
1.7642	vw
1.5794	vvw

Table XXI
X-Ray Powder Diffraction Data for
Ammonium Nonafluorodierbate(III) Monohydrate
 $(\text{NH}_4)_3\text{Er}_2\text{F}_9 \cdot \text{H}_2\text{O}$

<u>d_{hkl}, Å</u>	<u>Intensity</u>	<u>d_{hkl}, Å</u>	<u>Intensity</u>
7.3996	vs	1.9473	m
6.8779	vw	1.8398	s
6.5244	vw	1.7794	w
6.0785	vs	1.7446	w
5.2541	vs	1.7083	w
4.5576	vw	1.6567	w
3.7093	vw	1.6297	w
3.4807	m	1.6037	w
3.3031	vs	1.5616	vw
3.1432	m	1.5287	vw
2.9975	m	1.4931	vw
2.8841	vw	1.4654	w
2.7792	m	1.4332	vw
2.6820	vvw	1.3771	w
2.5844	m	1.3476	w
2.4099	m	1.3261	vw
2.3138	m	1.2884	vvw
2.2051	vw	1.2606	vvw
2.1401	m	1.2396	vvw
2.0566	w	1.1795	w
1.9877	m	1.1586	vw

Table XXI, continued

<u>d_{hkl}, Å</u>	<u>Intensity</u>
1.1332	vvw
1.1035	vvw
1.0869	vw
1.0730	vw
1.0426	w
1.0201	vvw
1.0065	vvw
.96785	vw
.95470	vvw
.91237	vvw
.89404	vvw
.87818	vvw
.86802	vvw
.86072	vvw
.85233	vvw
.84185	vvw

Table XXII
X-Ray Powder Diffraction Data for
Ammonium Tetrafluoroscandate(III)
 NH_4ScF_4

<u>d_{hkl}, Å</u>	<u>Intensity</u>	<u>d_{hkl}, Å</u>	<u>Intensity</u>
6.8360	vs	1.8042	m
5.9854	vw	1.7652	m
5.1702	vw	1.7386	s
4.3322	vvw	1.7071	m
3.9497	vs	1.6765	w
3.5188	vw	1.6515	w
3.4256	vs	1.5888	m
3.3374	w	1.5655	w
3.1361	w	1.5638	m
3.0883	w	1.5033	m
2.7782	m	1.4815	m
2.4571	m	1.4171	m
2.3933	m	1.4021	m
2.2632	m	1.3847	m
2.2362	m	1.3430	w
2.1870	m	1.3199	vw
2.1496	m	1.3057	m
2.0260	s	1.2919	m
1.9819	s	1.2792	vvw
1.9473	s	1.2726	vvw
1.9013	m	1.2273	w

Table XXII, continued

<u>d_{hkl}, Å</u>	<u>Intensity</u>
1.2077	VVW
1.1952	W
1.1359	VW
1.1113	VW
1.0917	VW
1.0818	W
1.0628	VVW
1.0495	VW
1.0115	VW
1.0005	VW
.99020	VW
.97995	VW
.97162	VW
.95862	VW
.94951	VW
.94103	VW
.93311	VVW
.92275	VVW
.88191	VVW
.85998	VW
.85505	VW
.84822	VVW
.80852	VVW
.79872	VVW
.78736	VVW

TABLE XXIII
X-Ray Powder Diffraction Data for
Ammonium Tetrafluoroyttrate(III)
 NH_4YF_4

<u>d_{hkl}, Å</u>	<u>Intensity</u>	<u>d_{hkl}, Å</u>	<u>Intensity</u>
8.0870	m	1.9893	s
7.0585	vs	1.9294	w
6.1763	w	1.8806	vvw
4.7350	w	1.8378	s
5.4544	s	1.8002	s
5.0819	s	1.7551	vs
4.1216	s	1.6919	vw
3.6538	vs	1.6609	vw
3.3936	w	1.5747	vw
3.2820	s	1.5602	vw
3.1242	vvs	1.5344	w
3.0010	w	1.4898	w
2.9242	m	1.4706	w
2.7993	vw	1.4322	vvw
2.6011	vw	1.4092	vvw
2.5095	vw	1.3708	w
2.4181	w	1.3501	vw
2.3630	s	1.3318	vw
2.2874	m	1.2848	vw
2.1457	m	1.2528	vw
2.0808	m	1.2336	vw

Table XXIII, continued

<u>d_{hkl}, Å</u>	<u>Intensity</u>
1.1767	vw
1.1639	vw
1.1110	vw
1.0914	vvw
1.0638	vvw
1.0466	vw
1.0287	w
.96589	vw
.95591	vvw

TABLE XXIV
X-Ray Powder Diffraction Data for
Ammonium Tetrafluorogadolate(III)
 NH_4GdF_4

<u>d_{hkl}, Å</u>	<u>Intensity</u>
8.4212	vs
5.4912	s
4.1298	m
3.6545	s
3.1388	vs
2.9336	s
2.7240	vw
2.6453	vw
2.5435	vw
2.3965*	w
2.1754	vw
2.1231	vw
2.0946	m
1.9948	w
1.9521	vw
1.8100	m
1.7664	m
1.7032	w
1.5711	w
1.5470	w

*broad

TABLE XXV
X-Ray Powder Diffraction Data for
Ammonium Tetrafluoroerbate(III)
 NH_4ErF_4

<u>$d_{hkl}, \text{\AA}$</u>	<u>Intensity</u>	<u>$d_{hkl}, \text{\AA}$</u>	<u>Intensity</u>
8.4489	vvs	2.0936*	m
6.7223	m	1.9972	m
5.9178	s	1.9665	m
5.4644	s	1.9387	m
4.4570	w	1.8445	vw
4.0916	s	1.8237	vw
3.6303	vs	1.7903	s
3.4192	w	1.7473	vs
3.2422	s	1.7274	vw
3.1146	vs	1.6891	w
2.9824	w	1.6245	w
2.9159	s	1.5738	vvw
2.7015	w	1.5509	w
2.6210	w	1.5277	w
2.5594	w	1.4836	w
2.4973	w	1.4648	vvw
2.4100	w	1.4258	vw
2.3583	s	1.4058	vw
2.2863	vw	1.3652	w
2.2033	vw	1.3472	vvw
2.1555	vw	1.3298	vw

TABLE XXV, contd

<u>d_{hkl}, Å</u>	<u>Intensity</u>
1.2838	W
1.2473	W
1.2283	W
1.1852	VVW
1.1727	W
1.1611	VVW
1.1432	VVW
1.1209	VVW
1.1082	VW
1.0614	VVW
1.0443	VVW
1.0261*	VW

*broad

8. Program for Comparison of X-Ray Powder Patterns

Input Instructions

Card No. 1

NCLASS in columns 1-3

[This number indicates the number of "classes" of films; i.e., Er class, Pr class, etc.]

Card No. 2

NPERM, NUMB in columns 1-3 and 4-6, respectively

[If NPERM $\neq$ 0, films submitted will all be compared with each other.

If NPERM = 0, "NUMB" films at end of deck will be compared with the first (I-NUMB) films in data deck, where I is the total number of films.]

Card No. 3

Information about the compound in columns 1-72

[This includes such things as compound number, film number, description of compound, etc.]

INCH in columns 73-76

[If INCH = 0, then the program will convert visually estimated intensities (according to the scheme $vvs=7$, $vs=6$, $s=5$, $m=4$, $w=3$, $vw=2$, $vvw=1$) to a scaled 1-100 representation.

If INCH $\neq$ 0, then intensity data is read in on a 1-100 scale.]

NOLINE in columns 77-78

[NOLINE = number of d values in a given film.]

Card No. 3, continued

LIMIT in columns 79-80

[If $LIMIT > 0$, then the limits on d value differences permissible for a match are the strict limits included in the program (see p 46).

If $LIMIT = 0$, the less stringent of the two limit sets (p 46) is used.

If $LIMIT < 0$, a limit set of the user's choice is read into the program.

(Note: If two films being compared have different designations for LIMIT, the rank of LIMIT is:

$LIMIT < 0$ takes precedence over $LIMIT = 0$ which takes precedence over $LIMIT > 0$. For example, if one film has $LIMIT > 0$ and a second has $LIMIT = 0$, the two films will be compared on the basis of the less stringent limits.)]

Card No. 4

ALIM1, ALIM2, ALIM3 in columns 1-10, 11-20, and 21-30,
respectively

[If the user wants to read in a different limit set from either of those provided in the program, the desired limits are read in here.]

Cards No. 5, 6, . . . n

DVAL(I) and INTEN(I) in columns 1-7 and 8-10, 11-17 and
18-20, etc.

[These are the d values and corresponding intensities for each film.]

```

      DIMENSION DVAL(60,100),INTEN(60,100),NOLINE(60),NCOMP(60),NOFILM
      1(100),RECORD(19,100),LIMIT(100),ALIM1(100),ALIM2(100),
      2ALIM3(100)
      WRITE(6,203)
203  FORMAT('1  THIS PROGRAM COMPARES D VALUES AND INTENSITIES OF POWDE
      IR PATTERNS',//)
      READ(5,1) NCLASS
      1  FORMAT(5I3)
      2  DO 66 IJ=1,NCLASS
      READ(5,1) NPERM,NUMB
      I=0
      3  I=I+1
      NOFILM(I)=1
      READ(5,4) (RECORD(KI,I),KI=1,18),INCH,NOLINE(I),LIMIT(I)
      IF(NOLINE(I).LT.0) GO TO 6
      IF(LIMIT(I).GE.0) GO TO 8
      READ(5,11) ALIM1(I),ALIM2(I),ALIM3(I)
      11  FORMAT(3F10.5)
      4  FORMAT(16A4,14,2I2)
      5  NI=1
      READ(5,5) (DVAL(L,I),INTEN(L,I),L=1,NI)
      5  FORMAT(8(F7.3,I3))
      IF(INCH.NE.0) GO TO 3
      CALL CHANGE (INTEN,I,NI)
      GO TO 3
      6  CONTINUE
      WRITE(6,611)
611  FORMAT('1, ' WE ARE PAST THE DATA',//)
      I=I-1
      IZ=I
      IF(NPERM) 500,7,500
      7  IJ=I-NUMB
      MQ=1
      NUMB1=IJ+1
      DO 110 JIJ=NUMB1,IZ
      MR=MQ
      DO 110 K=1,IJ
      IF(NOLINE(JIJ)-NOLINE(K))10,10,20
      10  NO1=NOFILM(K)
      NO2=NOFILM(JIJ)
      GO TO 21
      20  NO1=NOFILM(JIJ)
      NO2=NOFILM(K)
      21  CONTINUE
      IF(LIMIT(NO1).LT.0) GO TO 22
      GO TO 23
      22  ALIM1=ALIM1(NO1)
      ALIM2=ALIM2(NO1)
      ALIM3=ALIM3(NO1)
      GO TO 24
      23  IF(LIMIT(NO2).LT.0) GO TO 25
      GO TO 24
      25  ALIM1=ALIM1(NO2)

```

```

    ALIM2=ALIM22(NO2)
    ALIM3=ALIM33(NO2)
24  CONTINUE
    CALL COMPO (NO1,NO2,DVAL,INTEN,NOLINE,NCOMP,NFLAG,LIMIT,ALIM1,
    1ALIM2,ALIM3)
    IF(NFLAG.EQ.0) GO TO 30
    IF(MR.GT.MQ) GO TO 113
    WRITE(6,35) RECORD(1,J1J)
    WRITE(6,112) (RECORD(11,J1J),11=1,18)
113 WRITE(6,111) (RECORD(12,K),12=1,18)
    MR=MR+1
111 FORMAT(20X,18A4)
112 FORMAT(20X,18A4,/)
35 FORMAT(/'  FILM',2X,A4,2X,'DOES NOT MATCH THE FOLLOWING FILMS',/)
    GO TO 110
30 WRITE(6,31) RECORD(1,J1J),RECORD(1,K)
31 FORMAT(////,'  FILM',2X,A4,2X,'MATCHES FILM',2X,A4,2X,62('*'),/)
    WRITE(6,111) (RECORD(13,J1J),13=1,18)
    WRITE(6,112) (RECORD(14,K),14=1,18)
    WRITE(6,32) RECORD(1,NC2),RECORD(1,NO1)
32 FORMAT(20X,'LISTING OF D VALUES AND CORRESPONDING INTENSITIES THAT
1 MATCHED',///20X,'FILM WITH FEWER D VALUES.',12X,'FILM WITH MORE D
1 VALUES.',//27X,'FILM ',A4,25X,'FILM ',A4,//20X,'NO.  D VALUE  I
INTENSITY',12X,'NO.  D VALUE  INTENSITY',/20X,62('*'),/20X,62('*')
1,/)
    JKL=NOLINE(NO2)
    DVAL(60,NO1)=0.0
    INTEN(60,NO1)=1000
    DO 60 I=1,JKL
    NC=NCOMP(I)
    IF(NC.GT.0) GO TO 67
    NC=60
67  WRITE(6,61)I,DVAL(I,NO2),INTEN(I,NO2),NCOMP(I),DVAL(NC,NO1),
1INTEN(NC,NO1)
61  FORMAT(20X,13,3X,F7.4,5X,14,15X,13,3X,F7.4,5X,14)
    WRITE(6,62)
62  FORMAT(20X,62('*'),1X)
60  CONTINUE
    MR=MQ
110  CONTINUE
    GO TO 66
500  CONTINUE
    MQ=1
    GO 510 IN=1,I
    MR=MQ
    IIN=IN+1
    IF(IIN.GT.I) GO TO 510
    DO 510 JN=IIN,I
    IF(NOLINE(IN).GT.NOLINE(JN)) GO TO 515
    NO1=JN
    NO2=IN
    GO TO 520
515  NO1=IN

```



```

      NO2=JN
520 CONTINUE
      IF(LIMIT(NO1).LT.0) GO TO 540
      GO TO 541
540 ALIM1=ALIM11(NO1)
      ALIM2=ALIM22(NO1)
      ALIM3=ALIM33(NO1)
541 IF(LIMIT(NO2).LT.0) GO TO 542
      GO TO 543
542 ALIM1=ALIM11(NO2)
      ALIM2=ALIM22(NO2)
      ALIM3=ALIM33(NO2)
543 CONTINUE
      CALL COMPD(NO1,NO2,DVAL,INTEN,NOLINE,NCOMP,NFLAG,LIMIT,ALIM1,
1 ALIM2,ALIM3)
      IF(NFLAG.EQ.0) GO TO 530
      IF(MR.GT.MQ) GO TO 114
      WRITE(6,35) RECORD(1,IN)
      WRITE(6,112) (RECORD(11,IN),11=1,18)
114 WRITE(6,111) (RECORD(12,JN),12=1,18)
      MR=MR+1
      GO TO 510
530 WRITE(6,31) RECORD(1,IN),RECORD(1,JN)
      WRITE(6,111) (RECORD(11,IN),11=1,18)
      WRITE(6,112) (RECORD(12,JN),12=1,18)
      WRITE(6,32) RECORD(1,NO2),RECORD(1,NO1)
      JKL=NOLINE(NO2)
      DVAL(60,NO1)=0.0
      INTEN(60,NO1)=1000
      DO 535 IA=1,JKL
      NC=NCOMP(IA)
      IF(NC.GT.0) GO TO 531
      NC=60
531 WRITE(6,61) IA,DVAL(IA,NO2),INTEN(IA,NO2),NCOMP(IA),DVAL(NC,NO1),
      INTEN(NC,NO1)
      WRITE(6,62)
535 CONTINUE
      MR=MQ
510 CONTINUE
60 CONTINUE
      CALL EXIT
      END
      SUBROUTINE COMPD(NO1,NO2,DVAL,INTEN,NOLINE,NCOMP,NFLAG,LIMIT,ALIM1
1,ALIM2,ALIM3)
      DIMENSION DVAL(60,100),INTEN(60,100),NOLINE(60),NCOMP(60)
      DIMENSION LIMIT(100)
      MIN=0
      MAX=0
      IF(LIMIT(NO1)) 603,602,601
601 IF(LIMIT(NO2)) 603,602,600
600 ALIM1=0.10
      ALIM2=0.05
      ALIM3=0.01

```

```

15 CONTINUE
   NQ=NQ+1
   DO 300 I=NN1,NN2
   DO 301 JIJ=1,NM
      IF(NCOMP(JIJ).EQ.1) GO TO 300
301 CONTINUE
      IF(ABS(ABS(DVAL(I,NQ1)-DVAL(IJ,NQ2))) 300,310,310
310 IF(ABS(ABS(INTER(I,NQ2)-INTER(I,NQ1)).GT.15) GO TO 300
      NCOMP(IJ)=1
      NQ1=NQ1+1
      GO TO 315
300 CONTINUE
315 CONTINUE
      IJ=IJ+1
      IF(DVAL(IJ,NQ2).GT.2.00) GO TO 5
      DNUM=FLOAT(NQ1)
      DNOM=FLOAT(NQ)
      PER=DNUM/DNOM
      IF(0.799-PER) 325,325,320
320 NFLAG=1
      RETURN
325 NFLAG=0
      GO TO 6
20 CONTINUE
   NQ=NQ+1
   DO 400 I=NN3,NN4
   DO 401 JIJ=1,NM
      IF(NCOMP(JIJ).EQ.1) GO TO 400
401 CONTINUE
      IF(ABS(ABS(DVAL(I,NQ1)-DVAL(IJ,NQ2))) 400,410,410
410 IF(ABS(ABS(INTER(I,NQ2)-INTER(I,NQ1)).GT.15) GO TO 400
      NCOMP(IJ)=1
      NQ1=NQ1+1
      GO TO 415
400 CONTINUE
415 CONTINUE
      IF(IJ.LT.NM) GO TO 5
      IF(IJ.GT.1) GO TO 5
      DNUM=FLOAT(NQ1)
      DNOM=FLOAT(NQ)
      PER=DNUM/DNOM
      IF(0.799-PER) 425,425,420
420 NFLAG=1
      RETURN
425 NFLAG=0
6   NQ=0
   NQ1=0
5   CONTINUE
7   RETURN
END
SUBROUTINE CHANGE(INTER,IJ,NI1)
  DIMENSION INTER(60,100)
  NUM = INTER(1,IJ)

```

```

      GO TO 603
602 ALIM1=0.30
   ALIM2=0.15
   ALIM3=0.10
603 NM=NOLINE(NO2)
   MN=NOLINE(NO1)
   DO 40 J=1,MN
40  NCOMP(J)=0
   NQ=0
   NQ1=0
   NS1=0
   NS2=0
   NS3=0
   DO 4 I=1,MN
   IF(DVAL(I,NO1).GE.4.00)GO TO 105
   IF(DVAL(I,NO1).LT.4.00.AND.DVAL(I,NO1).GT.2.00)GO TO 110
   IF(DVAL(I,NO1).LE.2.00)GO TO 115
105 NS1=NS1+1
   GO TO 4
110 NS2=NS2+1
   GO TO 4
115 NS3=NS3+1
   4 CONTINUE
   NN1=NS1+1
   NN2=NS1+NS2
   NN3=NN2+1
   NN4=NS1+NS2+NS3
   DO 5 II=1,NM
   IF(DVAL(II,NO2).GE.4.00) GO TO 10
   IF(DVAL(II,NO2).LT.4.00.AND.DVAL(II,NO2).GT.2.00) GO TO 15
   IF(DVAL(II,NO2).LE.2.00) GO TO 20
10 CONTINUE
   NQ=NQ+1
   DO 200 I=1,NS1
   DO 201 JIJ=1,NM
   IF(NCOMP(JIJ).EQ.1) GO TO 200
201 CONTINUE
   IF(ABS(ABS(DVAL(I,NO1)-DVAL(II,NO2))) 200,210,210
210 IF(ABS(INTER(II,NO2)-INTER(I,NO1)).GT.15) GO TO 200
   NCOMP(II)=1
   NQ1=NQ1+1
   GO TO 215
200 CONTINUE
215 CONTINUE
   IJ=NO+1
   IF(DVAL(IJ,NO2).GE.4.00) GO TO 5
   NO2=NQ-1
   IF(NQ1.LT.NQ2) GO TO 220
   GO TO 225
220 NFLAG=1
   RETURN
225 NFLAG=0
   GO TO 6

```

```
DO 5 I=1,N11
  IF(NUM.LT.INTEN(I,IJ)) NUM = INTEN(I,IJ)
5 CONTINUE
  IF(NUM.EQ.7) GO TO 16
  IF(NUM.EQ.6) GO TO 12
  DO 10 I=1,N11
    INTEN(I,IJ)=INTEN(I,IJ)*18
    IF(INTEN(I,IJ).EQ.18) INTEN(I,IJ)=15
10 CONTINUE
  RETURN
12 DO 15 I=1,N11
  15 INTEN(I,IJ)=INTEN(I,IJ)*15
  RETURN
16 DO 18 I=1,N11
  18 INTEN(I,IJ)=INTEN(I,IJ)*13
  RETURN
END
```

C. Program for Calculation of Per Cent Composition
of Ammonium Fluorolanthanates

```

      INTEGER *2LN
      DIMENSION IQ(15,5)
      DIMENSION LN(7),X1(15,5),X2(15,5),Y(15,5),FLU(15,5),FLUR(15,5)
      DIMENSION COMB(15,5),WTMOL(15,5)
      DIMENSION ALN1(7)
      DATA LN/' Y','LA','GD','ER','SM','PR','EU'/
      ALN1(1)=88.905
      ALN1(2)=138.91
      ALN1(3)=157.25
      ALN1(4)=167.26
      ALN1(5)=150.35
      ALN1(6)=140.907
      ALN1(7)=151.96
      DO 10 IJK=1,7
      WRITE(6,600)
600  FORMAT('1')
      DO 20 I=1,15
      DO 20 J=1,5
      X1(I,J)=I*14.0067
      X2(I,J)=I*4.032
      Y(I,J)=J*ALN1(IJK)
      FLU(I,J)=(I+3.0*J)*18.9984
      COMB(I,J)=X1(I,J)+X2(I,J)+Y(I,J)+FLU(I,J)
      WTMOL(I,J)=COMB(I,J)/100.0
      X1(I,J)=X1(I,J)/WTMOL(I,J)
      X2(I,J)=X2(I,J)/WTMOL(I,J)
      Y(I,J)=Y(I,J)/WTMOL(I,J)
      IQ(I,J)=3*J + I
      FLUR(I,J)=FLU(I,J)/WTMOL(I,J)
      DO 30 I=1,15
      WRITE(6,601) (I,LN(IJK),J,IQ(I,J),J=1,5)
601  FORMAT('1',10X,'(NH4)',12,A2,11,'F',12,4(11X,'(NH4)',12,A2,11,'F',
      112)/5(11X,13('1'))//)
      30  WRITE(6,602) (COMB(I,J),J=1,5),(X1(I,J),J=1,5),(X2(I,J),J=1,5),
      1  (LN(IJK),Y(I,J),J=1,5),(FLUR(I,J),J=1,5)
602  FORMAT(5(7X,'MOL. WT.=',F8.3)/5(6X,'PERCENT N =',F7.3)/5(6X,'PERCENT
      1 H =',F7.3)/5(6X,'PERCENT ',A2,'=',F7.3)/5(6X,'PERCENT F =',F7.3))
      10  CONTINUE
      CALL EXIT
      END

```

D. Program for Calculation of Per Cent Composition
of Ammonium Fluorolanthanate Hydrates

```

      INTEGER *2LN
      DIMENSION AQ(4)
      DIMENSION IQ(15,5),LQ(7),X1(15,5,4),X2(15,5,4),X3(15,5,4)
      DIMENSION Y(15,5,4),FLU(15,5,4),CCMB(15,5,4),WTMCL(15,5,4),
      1 ALN1(7)
      DATA LN/' Y', 'LA', 'GC', 'ER', 'SM', 'PR', 'ED'/
      ALN1(1)=88.905
      ALN1(2)=138.91
      ALN1(3)=157.25
      ALN1(4)=167.26
      ALN1(5)=150.35
      ALN1(6)=143.907
      ALN1(7)=151.96
      DO 10 IJK=1,7
      WRITE(6,600)
600  FORMAT('1')
      AQ(1)=0.5
      AQ(2)=1.0
      AQ(3)=1.5
      AQ(4)=2.0
      DO 21 I=1,15
      DO 21 J=1,5
      DO 20 K=1,4
      X1(I,J,K)=I*14.0067
      FLU(I,J,K)=(I+3*J)*18.9934
      Y(I,J,K)=J*ALN1(IJK)
      X2(I,J,K)=(4.0*I+2.0*AQ(K))*1.008
      X3(I,J,K)=AQ(K)*15.9994
      CCMB(I,J,K)=X1(I,J,K)+FLU(I,J,K)+Y(I,J,K)+X2(I,J,K)+X3(I,J,K)
      WTMCL(I,J,K)=CCMB(I,J,K)/100.0
      X1(I,J,K)=X1(I,J,K)/WTMCL(I,J,K)
      FLU(I,J,K)=FLU(I,J,K)/WTMCL(I,J,K)
      Y(I,J,K)=Y(I,J,K)/WTMCL(I,J,K)
      X2(I,J,K)=X2(I,J,K)/WTMCL(I,J,K)
20  X3(I,J,K)=X3(I,J,K)/WTMCL(I,J,K)
21  IQ(I,J)=I+3*J
      DO 30 I=1,15
      DO 30 J=1,5
      WRITE(6,601) (I,LN(IJK),J,IQ(I,J),AQ(K),K=1,4)
601  FORMAT('1',12X,'(NH4)',12,A2,11,'F',12,'.(P20)',F3.1,3( 8X,'(NH4)'
      1 ,12,A2,11,'F',12,'.(P20)',F3.1)/5X,4( 5X,A2('1')/1)
      30  WRITE(6,602) (CCMB(I,J,K),K=1,4),(X1(I,J,K),K=1,4),(X2(I,J,K),
      1 K=1,4),(LN(IJK),Y(I,J,K),K=1,4),(FLU(I,J,K),K=1,4),(X3(I,J,K),
      2 K=1,4)
602  FORMAT(5X,4(10X,'MCL. WT.=',F7.3)/5X,4(1X,'PERCENT N =',F7.3)
      1 /5X,4(10X,'PERCENT H =',F7.3)/5X,4(10X,'PERCENT ',A2,'=',F7.3)
      2 /5X,4(10X,'PERCENT F =',F7.3)/5X,4(10X,'PERCENT D =',F7.3))
      10 CONTINUE
      CALL EXIT
      END

```