J. inorg. nucl. Chem., 1974, Vol. 36, pp. 763–770. Pergamon Press. Printed in Great Britain.

AMMONIUM FLUOROLANTHANATES*

ROSEMARIE C. RUSSO† and HELMUT M. HAENDLER‡

Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824

(*Received* 2 *May* 1973)

Abstract—Ammonium nonafluorodilanthanate(III) monohydrates, $(NH_4)_3Ln_2F_9 . H_2O$, where Ln is yttrium, lanthanum, praseodymium, samarium, and erbium, have been prepared by the reaction of the metal nitrates with ammonium fluoride in aqueous solution. Ammonium undecafluorotrilanthanate(III) monohydrates, $(NH_4)_2Ln_3F_{11} . H_2O$, where Ln is yttrium, dysprosium, holmium, and erbium, have been prepared by the reaction of the lanthanide bromide with ammonium fluoride in methanol. The effect of solvent on the bromination of the metals and subsequent reaction with ammonium fluoride is discussed.

Results of the thermal decomposition of these compounds, as studied by differential thermal analysis and thermogravimetric analysis, are discussed. I.R. spectral and X-ray diffraction data are presented.

INTRODUCTION

Complexes of transition metal fluorides have been widely studied and reviewed[1–4]. Fluoride complexes of the lanthanide (Ln) metals have been less extensively investigated. The synthesis of lanthanide fluorocomplexes in solution, in particular, has received little attention, and most of this work has dealt with alkali metal cations rather than with the ammonium ion [5–6].

Batsanova[7] has reported the synthesis of some non-stoichiometric ammonium fluorolanthanates. Even for known fluorolanthanates there is a paucity of experimental data, and almost no thermal studies have been done. In an attempt to prepare anhydrous fluorolanthanates, syntheses in non-aqueous media were investigated. Synthesis of the compounds K_3LnF_6 (Ln = La, Sm, Er, Yb, Lu), $RbLnF_4$ (Ln = La, Er, Yb), and $CsLnF_4$ (Ln = La, Sm, Er, Yb) in methanol was reported[6] while the present work was in progress. In this paper, we report on the synthesis of ammonium fluorolanthanates in aqueous and in methanol solution and on some of their properties.

EXPERIMENTAL

Reagents

Nuclear grade (99·9+ %) rare earth metals were obtained from Lunex Co., Pleasant Valley, Iowa. Reagent grade ammonium fluoride was used without further purification. Reagent grade methanol was purified by distillation from magnesium activated with iodine.

Preparation of complexes

$(NH_4)_3Ln_2F_9 . H_2O$ *compounds*. The metal (2–12 m-mole) was first converted to the nitrate by dissolving it in 15 M nitric acid and evaporating the solution to dryness. A few ml of water were added, and the evaporation was repeated. The nitrate was dissolved in a small amount of water, and to this solution was added a 30 % (w/v) aqueous ammonium fluoride solution in a volume such that the molar ratio NH_4F:Ln was about 5:1. A gelatinous precipitate formed immediately. The reaction mixture was stirred, then allowed to stand at room temperature overnight. The precipitate was collected by filtration, washed thoroughly with methanol and then with anhydrous ether, and dried over silica gel or magnesium perchlorate.

$(NH_4)_2Ln_3F_{11} . H_2O$ *compounds*. The complexes were prepared by brominating the finely divided metal suspended in methanol. The bromide solution was added to a saturated solution of ammonium fluoride in methanol. The precipitate was filtered, washed, and dried. There were slight variations in procedure, but the details of the preparation of the dysprosium complex will serve as a representative example.

$(NH_4)_2Dy_3F_{11} . H_2O$. Powdered dysprosium metal (2·00 g, 12·3 m-mole) was suspended in 100 ml of dry methanol. Bromine (1·0 ml, 36·3 m-mole) was added dropwise, with stirring, at room temperature. The reaction mixture was then heated at reflux temperature for 2 hr, cooled to room temperature, and stirred for an additional 3·5 hr. The mixture was filtered to remove a small amount of yellow-brown residue. The filtrate was added, with stirring, to 246 ml of a saturated solution of ammonium fluoride (123 m-mole) in methanol. A white precipitate formed immediately. The reaction mixture was stirred overnight at room temperature. It was filtered, and the gelatinous precipitate was washed with methanol, then with ether, and was

---

* Taken in part from the Ph.D. thesis of R. C. Russo. Supported in part by the U.S. Atomic Energy Commission.

† Present address: Department of Chemistry, Montana State University, Bozeman, Montana 59715.

‡ To whom communications should be addressed.

Table 1. Analytical results

Compound	Element determined	% Calcd	% Found	Color
$(NH_4)_3Y_2F_9 . H_2O$	N	9·98	9·75	white
	H	3·35	2·95	
	F	40·62	40·92	
$(NH_4)_3La_2F_9 . H_2O$	N	8·07	8·09	white
	H	2·71	2·36	
	F	32·82	33·0	
$(NH_4)_3Pr_2F_9 . H_2O$	N	8·00	8·17	green
	H	2·69	2·13	
	F	32·57	32·98	
$(NH_4)_3Sm_2F_9 . H_2O$	N	7·73	7·62	off-white
	H	2·60	2·59	
	Sm	55·29	55·72	
	F	31·44	31·12	
$(NH_4)_3Er_2F_9 . H_2O$	N	7·27	6·72	pink
	H	2·44	1·82	
	Er	57·91	58·88	
$(NH_4)_2Er_3F_{11} . H_2O$	N	3·66	3·61	pink
	H	1·32	1·30	
	Er	65·60	65·06	
	F	27·32	27·47	
$(NH_4)_2Y_3F_{11} . H_2O$	N	5·29	5·34	white
	H	1·90	1·80	
	F	39·45	39·16	
$(NH_4)_2Dy_3F_{11} . H_2O$	N	3·73	4·71	white
	H	1·34	1·86	
	Dy	64·95	65·00	
$(NH_4)_2Ho_3F_{11} . H_2O$	N	3·70	4·78	peach
	H	1·33	1·63	
	Ho	65·29	64·6	

dried over magnesium perchlorate. The dried product was ground under methanol, filtered, washed with ether, and dried, first over magnesium perchlorate and then in a vacuum desiccator.

The erbium complex was also prepared by the reaction of ammonium hydrogen fluoride with the bromide (10:1 molar ratio) in methanol.

Analyses

Nitrogen was determined with a Coleman Model 29 Nitrogen Analyzer. Hydrogen was determined with an F & M Corp. Model 185 CHN Analyzer. Metals were determined by dissolution of the sample in 18 M sulfuric acid or in 12 M hydrochloric acid, evaporation to near dryness, dilution with water to a pH of *ca.* 1, precipitation as the oxalate, and ignition to the oxide at 850–900°[8]. Fluorine was determined by oscillometric titration with thorium nitrate solution after steam distillation of the samples[9]. The results are shown in Table 1.

Thermal analyses

Differential thermal analyses (dta) were carried out with a duPont Model 900 Differential Thermal Analyzer using a Differential Scanning Calorimeter Cell. Runs were made under a helium atmosphere, at 2 mm positive pressure, with a heating rate of 15°/min. Thermogravimetric analyses (tga) were done on a duPont Model 950 Analyzer, using the same conditions as for the differential analyses.

X-ray powder photographs

Powder patterns were obtained with a 57·3 mm Philips camera using copper $- K_\alpha$ (λ = 1·5418 Å) radiation. Finely ground samples were mounted in 0·3 mm glass capillaries. Relative intensities were estimated visually.

Infrared spectra

I.R. spectra (4000–200 cm^{-1}) were obtained with a Beckman IR-12 spectrophotometer. Nujol and halocarbon mulls on cesium iodide and potassium bromide windows, or cesium iodide and potassium bromide pellets, were used.

RESULTS

The $(NH_4)_3Ln_2F_9 . H_2O$ compounds are stable in air except for the lanthanum compound, which is hygroscopic. The compounds are insoluble in common organic solvents but can be dissolved in concentrated sulfuric or hydrochloric acids. X-ray diffraction data indicate that the samarium and praseodymium compounds are isotypes, but of different structure than the isotypic erbium and yttrium compounds. The lanthanum compound differs structurally from the others. The X-ray diffraction data are given in Table 2.

The $(NH_4)_2Ln_3F_{11} . H_2O$ compounds decompose in water and excess methanol. They are insoluble in common organic solvents, but dissolve in concentrated sulfuric and hydrochloric acids or a mixture of nitric and boric acids. X-ray diffraction data (Table 2) indicate that the four complexes are isotypes.

The characteristic i.r. absorption bands for the complexes are given in Table 3. The differential thermal and thermogravimetric analyses are interconsistent, and the results of the thermogravimetric analyses are tabulated in Table 4.

DISCUSSION

Preparation

$(NH_4)_3Ln_2F_9 . H_2O$ *compounds.* Dergunov[10] has reported synthesis of ammonium hexafluorolanthanate (III) complexes of erbium, samarium, and praseodymium by reaction of hydrogen fluoride, ammonium carbonate, and lanthanide nitrate. Prior to the present work, the reaction of lanthanide nitrates with ammonium fluoride in aqueous solution had not been studied, although reaction of scandium nitrate with aqueous ammonium fluoride is known to produce ammonium hexafluoroscandate[11]. Lanthanide nitrate solutions were prepared from both metal and oxide and reacted with ammonium fluoride in aqueous solution. Use of the oxide as starting material generally resulted in fluorocomplexes with high nitrogen content.

$(NH_4)_2Ln_3F_{11} . H_2O$ *compounds.* Methanol, 1,2-dimethoxyethane, 2,2-dimethoxypropane, and acetonitrile were tested as solvents for the two reactions. The reaction of metal with bromine proceeded smoothly and completely at reflux temperature in acetonitrile and methanol, fairly rapidly in methanol but somewhat slowly in acetonitrile. 1,2-Dimethoxyethane and 2,2-dimethoxypropane were poor solvents for this reaction, which was slow and incomplete. Subsequent reaction of the metal bromide solutions with saturated ammonium fluoride solutions in the same solvent yielded isolable products only in methanol.

Yttrium, lanthanum, praseodymium, samarium, gadolinium, dysprosium, holmium, and erbium were brominated successfully in methanol. At least a twofold stoichiometric excess of bromine was required for complete reaction, assuming tribromide formation. A small amount of yellowish residue, containing bromide, was present after the metal had reacted. After filtration, erbium bromide solutions remained clear for at least four weeks, and presumably solutions of the other bromides would also be stable. Solutions were generally used within a day or two of preparation.

The product of the reaction of erbium metal with bromine in methanol was isolated by addition of 2,2-dimethoxypropane to the filtered solution. The hygroscopic product was determined by analysis to be $ErBr_3 . 4CH_3OH$. Compounds of this type have not been reported before, although Quill and Clink[12] have reported the preparation of $LnCl_3 . 4CH_3OH$ compounds from solutions of the metal chloride hydrates in methanol and 2,2-dimethoxypropane. Evaporation of an erbium bromide–methanol solution resulted in an adduct with fewer than 4 moles of solvated methanol.

Products obtained upon addition of bromide solutions to ammonium fluoride solution in methanol varied with molar ratios used and with the metal. Tests with erbium bromide gave no solid product when the ratio of ammonium fluoride to erbium bromide was less than 4:1. At least a 6:1 ratio was necessary to obtain a good crystalline product, and an increase to 10:1 did not significantly alter the product. The nitrogen content of the complex increases as the ratio is increased from 4:1 to 6:1, and then remains stable. This is consistent with the observations in the lanthanide chloride–alkali fluoride–water systems[6], in which crystalline solids were only obtained at ratios of 5:1 or greater.

Solid products were isolated from yttrium, lanthanum, praseodymium, samarium, gadolinium, dysprosium, holmium, and erbium bromide solutions, at molar ratios of 6–10:1. With lanthanum, the largest ion in this series, it was not possible to obtain an ammonium fluorolanthanate by this method, the product being lanthanum trifluoride. The tendency towards complex formation increases with increasing atomic number of the lanthanide metal[6], and there is an increase in complex stability with decreasing size of Ln^{3+}[13]. The metals of smaller ionic radius (yttrium, dysprosium, holmium, and erbium) form compounds with the composition $(NH_4)_2Ln_3F_{11} . H_2O$. For the larger cations (praseodymium, samarium, gadolinium), compounds of different, and as yet unknown, stoichiometry were obtained.

Size of lanthanide ion alone is probably not the only factor affecting stabilities, stoichiometries, and structures of $A^ILn^{III}F_x$ compounds. Babel[14a] notes that compounds of the same formula type do not adopt the same structure type or at least the same coordination number for A-ions at the extremes of the size range. Kemmit *et al.*[15] have also suggested, for $A^IM^VF_6$ compounds, that the major factor is the radius of the cation A^I, with variation in the size of M^V having a very small effect. However, tripositive lanthanide ions are comparatively large and would be expected to have a more significant effect on structure. In the present study, the cation A was the same for all compounds, so differences can be related to the size of the lanthanide ion. An attempt was made to synthesize a sodium and potassium fluorolanthanate from methanol. No solid sodium fluoroerbate was found, and a potassium complex was shown by X-ray diffraction to be structurally different from the ammonium compound. Indications are that both metal ions affect stability and structure, and that it is better to consider the ratio of the radii of the ions A and M in alkali fluorometallates[14b]. See Table 5[16].

The presence of water of hydration was confirmed by the presence of infrared absorption in the mid-1600 cm^{-1} region. Synthesis under nitrogen and treatment of the bromide solutions with 2,2-dimethoxypropane did not result in anhydrous products. It is assumed

Table 2. X-ray

$(NH_4)_3La_2F_9 . H_2O$ d(Å) I	$(NH_4)_3Pr_2F_9 . H_2O$ d(Å) I	$(NH_4)_3Sm_2F_9 . H_2O$ d(Å) I	$(NH_4)_3Er_2F_9 . H_2O$ d(Å) I	$(NH_4)_3Y_2F_9 . H_2O$ d(Å) I
6·49 w	8·29 s	8·45 m	7·40 vs	7·41 vs
5·48 m	5·58 m	5·69 m	6·52 vw	6·44 w
4·97 m	4·83 w	4·25 m	6·08 vs	5·92 m
4·10 m	4·25 s	3·68 m	5·25 vs	5·17 s
3·54 s	3·70 s	3·23 s	3·48 m	3·42 w
3·18 vs	3·22 vs	2·96 m	3·30 vs	3·29 vs
2·90 vs	2·99 s	2·45 vw	3·14 m	3·16 m
2·55 w	2·48 m	2·37 vw	3·00 m	3·00 m
2·45 vw	2·40 m	2·11 w	2·78 m	2·77 w
2·39 vw	2·14 s	2·001 w	2·58 m	2·59 w
2·24 m	2·014 s	1·834 w	2·41 m	2·42 w
2·066 vs	1·862 s	1·764 vw	2·31 m	2·31 m
2·005 s	1·827 m		2·20 vw	2·20 w
1·796 s	1·790 s		2·14 m	2·15 m
1·736 m	1·777 w		2·057 w	2·058 w
	1·727 w		1·988 m	1·984 m
			1·947 m	1·837 m
			1·840 s	1·780 w
			1·779 w	1·745 w
			1·745 w	1·706 w
			1·708 w	

Table 3.

$(NH_4)_3Y_2F_9 . H_2O$	$(NH_4)_3La_2F_9 . H_2O$	$(NH_4)_3Pr_2F_9 . H_2O$	$(NH_4)_3Sm_2F_9 . H_2O$	$(NH_4)_3Er_2F_9 . H_2O$
3188 m,b	3167 s	3190 ms	3150 s,vb	3192 ms,b
3062 s	3032 s	3040 s	3036 sh	3080 s
2900 m	2848 s	2890 m,sh		2918 ms
		1685 w,sp	1665 w	1655 w
1471 m	1497 s	1488 m,sp,sh	1480 m	1482 ms
1463 m	1465 ms,sh	1475 s,sp		1465 ms
1427 s	1413 s,sp	1420 s,sp	1410 s	1430 s
1403 s				1406 s
	749 ms,sh			
	729 s			
451 w	480 ms,sp	480 m,sp	490 w	485 w
422 w	346 ms,sh	322 s	328 s	415 w
354 s	262 s,b	265 s	288 s	311 s
321 s		255 s	255 s	286 s
292 s			212 s	209 s
204 s				

*Values given in cm^{-1}.

†Abbreviations used: s, strong; ms, medium-strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad;

that the water present is formed during the bromination reaction, in a manner similar to that proposed in the bromination of uranium in methanol[17]. Formation of hydrated lanthanide complexes from anhydrous metal bromides in absolute ethanol has been reported by Basile[18].

Thermal decompositions: Correlation of dta and tga results permitted identification of the probable course of decomposition. There is a decrease in coordination number on heating, an observation also reported[19] for the thermal decomposition of ammonium fluoroscandates. The final product is the metal trifluoride.

$(NH_4)_3Ln_2F_9 . H_2O$ *compounds.* The first step in the decomposition of the yttrium, erbium, and praseodymium compounds is dehydration, leaving $(NH_4)_3Ln_2F_9$. It is of interest to note that Sterba-Böhm[20], from qualitative observations, suggested the possibility that $(NH_4)_3Sc_2F_9$ was formed as an intermediate in the decomposition of $(NH_4)_3ScF_6$ in aqueous solution, although Ivanov-Emin[19] later stated the report was erroneous. After dehydration, the yttrium and erbium compounds lose two moles of ammonium fluoride, forming $NH_4Ln_2F_7$. The third mole of diffraction data

$(NH_4)_2Y_3F_{11}.H_2O$ d(Å)	I	$(NH_4)_2Dy_3F_{11}.H_2O$ d(Å)	I	$(NH_4)_2Ho_3F_{11}.H_2O$ d(Å)	I	$(NH_4)_2Er_3F_{11}.H_2O$ d(Å)	I
6·92	m	6·72	m	6·56	s	6·68	s
5·91	vs	5·97	vs	5·90	vs	5·89	vs
4·57	w	4·46	m	4·46	m	4·45	m
3·50	w	3·43	w	3·41	w	3·41	w
3·26	vs	3·28	vs	3·25	vs	3·24	vs
3·00	m	2·95	s	2·98	m	2·95	s
2·756	vw	2·740	vw	2·728	vw	2·717	w
2·607	m	2·579	m	2·558	s	2·559	s
2·236	w	2·232	vw	2·205	w	2·203	w
2·125	m	2·118	m	2·101	m	2·096	m
1·946	vs	1·956	vs	1·946	vs	1·938	vs
1·867	m	1·863	w	1·853	m	1·842	m
1·798	w	1·801	w	1·780	m	1·772	m
1·716	vw	1·718	vw	1·716	w	1·713	w
1·680	vw	1·679	vw	1·672	w	1·664	w
1·639	m	1·643	m	1·634	m	1·627	s

Infrared spectra*†

$(NH_4)_2Y_3F_{11}.H_2O$	$(NH_4)_2Dy_3F_{11}.H_2O$	$(NH_4)_2Ho_3F_{11}.H_2O$	$(NH_4)_2Er_3F_{11}.H_2O$
3260 s,b	3220 s	3250 s,b	3260 s
3096 ms,sh	3082 ms,sh	3095 s,b	3080 m,sh
2894 m,sh	2900 m,sh	2920 m,sh	2862 w,sh
1665 vw,b	1658 w,b	1670 w,b	1668 w,b
1430 s	1435 s	1435 s	1428 s
520 m	368 s	1025 w	520 m
380 s		728 w	365 s
321 m,sh		370 s	280 s
		295 s	

vb, very broad; sp, sharp; db, doublet.

ammonium fluoride appears to be lost in two steps, as hydrogen fluoride and ammonia, as indicated by two weak endotherms. The $(NH_4)_3Pr_2F_9$ formed by dehydration loses one mole of ammonium fluoride initially, and this is followed by the loss of the remaining two moles simultaneously.

The lanthanum compound begins to decompose almost immediately upon heating. The thermal data correlate with the initial loss of a mole of water and a mole of ammonium fluoride, the loss of fluoride beginning before all the water is removed. The NH_4LaF_4 remaining rapidly decomposes to $NH_4La_2F_7$ and subsequently to LaF_3. The samarium compound, $(NH_4)_3Sm_2F_9.H_2O$, appears to lose water and two moles of ammonium fluoride simultaneously over a wide range of temperature, resulting in $NH_4Sm_2F_7$, which then slowly decomposes to SmF_3 at a somewhat higher temperature.

The thermal decomposition schemes for the $(NH_4)_3Ln_2F_9.H_2O$ compounds are summarized in Fig. 1, in which the decomposition temperatures are those of the corresponding dta peaks. The lanthanum compound is the least stable. Disregarding the dehydration temperatures, which vary randomly, the ammonium

Table 4. Thermogravimetric analysis data

Compound	Decomposition temperature, (°C)	% Weight loss Obsd	Calcd
$(NH_4)_3Er_2F_9 . H_2O$	45–175	2·43	H_2O, 3·12
	200–238	11·46	$2NH_4F$, 12·82
	238–312	4·08	HF, 3·46
	312–328	2·23	NH_3, 2·95
$(NH_4)_3Y_2F_9 . H_2O$	86–145	4·48	H_2O, 4·28
	198–233	15·12	$2NH_4F$, 17·60
	233–302	5·77	HF, 4·75
	302–317	2·99	NH_3, 4·04
$(NH_4)_3Pr_2F_9 . H_2O$	90–141	2·86	H_2O, 3·43
	145–173	7·20	NH_4F, 7·06
	206–238	14·48	$2NH_4F$, 14·11
$(NH_4)_3La_2F_9 . H_2O$	40–147	11·95	$H_2O + NH_4F$, 10·57
	147–205	7·16	NH_4F, 7·11
	205–345	6·00	NH_4F, 7·11
$(NH_4)_3Sm_2F_9 . H_2O$	38–261	16·77	$H_2O + 2NH_4F$, 16·93
	261–405	3·23	NH_4F· 6·81
$(NH_4)_2Y_3F_{11} . H_2O$	55–163	3·60	H_2O, 3·40
	163–306	7·00	NH_4F, 6·99
	306–325	8·20	NH_4F, 6·99
$(NH_4)(NH_4)_2Er_3F_{11} . H_2O$	77–176	2·20	H_2O, 2·36
	187–338	9·20	$2NH_4F$, 9·68
$(NH_4)(NH_4)_2Dy_3F_{11} . H_2O$	56–113	3·01	H_2O, 2·40
	126–207	11·33	$2NH_4F$, 9·86
	330–337	0·30	?
$(NH_4)_2Ho_3F_{11} . H_2O$	50–140	2·36	H_2O, 2·38
	178–226	4·57	NH_4F, 4·89
	226–300 300–327	5·70	NH_4F 4·89

fluorolanthanates decomposed in an order related to the ionic radius of the metal. The smaller the ionic radius of the element, the more stable the compound is to heat. It is probable that all intermediate compounds are possible, depending upon experimental control of kinetic and thermodynamic conditions. It should also be noted that not all intermediate compounds have been completely characterized, and that the outline in Fig. 1 indicates results consistent with the thermal data.

$(NH_4)_2Ln_3F_{11} . H_2O$ *compounds.* After dehydration to $(NH_4)_2Ln_3F_{11}$, the yttrium and holmium compounds lose one mole of ammonium fluoride, forming $NH_4Ln_3F_{10}$, followed by loss of a second ammonium fluoride in a separate step. There is no distinct break in the decomposition of the dysprosium and erbium complexes, two moles of ammonium fluoride being lost in a single step. The formation of $NH_4Ho_3F_{10}$ has been suggested by Zalkin and Templeton[21]. The dysprosium compound shows a sharp exotherm in the dta curve at 332°, suggesting the possible existence of low temperature forms of the trifluorides, similar to those observed with aluminium, gallium, and indium [22]. Thermal decomposition schemes consistent with the thermal data are suggested in outline form in Fig. 2.

Table 5. Effective ionic radii (Å)

Sc	0·73	Pr	1·01	Dy	0·91
Y	0·89	Sm	0·96	Ho	0·89
La	1·06	Gd	0·94	Er	0·88

Infrared spectra and postulated structures

Because the structures of these compounds are not known, an unequivocal assignment of i.r. vibrations cannot be made. Some tentative band assignments have been made, however, based on literature data for fluorometallates. These assignments are consistent with the structures proposed below.

Lattice water in general absorbs at 3550–3200 cm^{-1} (antisymmetric and symmetric O–H stretches) and at 1650–1620 cm^{-1} (H–O–H bending mode)[23–24]. The broad bands in the mid-3200 cm^{-1} and in the mid-1600 cm^{-1} region in the spectra of the complexes are thus probably due to the water of hydration. The bands at ~2900 cm^{-1} may be due to lattice water, but may also be the first harmonic of the ammonium ion deformation, $2\nu_4$.

In an i.r. study of bound water in hydrates, Lucceshi and Glasson[25] reported an absorption band at around 2915 cm^{-1}.

The ammonium ion has two fundamentals active in the i.r.: ν_3, the N–H stretching mode, and ν_4, a deformation frequency[26]. The effect of hydration on

$$(NH_4)_3Y_2F_9\,.\,H_2O \xrightarrow[92^\circ]{-H_2O} (NH_4)_3Y_2F_9 \xrightarrow[214^\circ]{-2NH_4F} NH_4Y_2F_7 \xrightarrow[302^\circ]{-HF} 2YF_3\,.\,0{\cdot}5NH_3 \xrightarrow[323^\circ]{-NH_3} 2YF_3$$

$$(NH_4)_3La_2F_9\,.\,H_2O \xrightarrow[100^\circ]{\substack{-H_2O\\ -NH_4F}} 2NH_4LaF_4 \xrightarrow[132^\circ]{-NH_4F} NH_4La_2F_7 \xrightarrow[190^\circ]{-NH_4F} 2LaF_3$$

$$(NH_4)_3Pr_2F_9\,.\,H_2O \xrightarrow[109^\circ]{-H_2O} (NH_4)_3Pr_2F_9 \xrightarrow[174^\circ]{-NH_4F} 2NH_4PrF_4 \xrightarrow[211^\circ]{-2NH_4F} 2PrF_3$$

$$(NH_4)_3Sm_2F_9\,.\,H_2O \xrightarrow[206^\circ]{\substack{-H_2O\\ -2NH_4F}} NH_4Sm_2F_7 \xrightarrow[265^\circ]{-NH_4F} 2SmF_3$$

$$(NH_4)_3Er_2F_9\,.\,H_2O \xrightarrow[94^\circ]{-H_2O} (NH_4)_3Er_2F_9 \xrightarrow[207^\circ]{-2NH_4F} NH_4Er_2F_7 \xrightarrow[316^\circ]{-HF} 2ErF_3\,.\,0{\cdot}5NH_3 \xrightarrow[331^\circ]{-NH_3} 2ErF_3$$

Fig. 1. Thermal decomposition of $(NH_4)_3Ln_2F_9\,.\,H_2O$ compounds. Temperatures given are dta peak maxima.

the position of the N–H absorption may be considerable, particularly if the O–H stretching frequency occurs at the lower end of the 3550–3200 cm^{-1} range[27]. Hydrogen bonding also results in a decrease in the frequency of the N–H stretch and an increase in the frequency of the NH_4 deformation mode. In the present case both hydration and hydrogen bonding are expected to affect the vibrations of the ammonium ion. Thus, the N–H stretching vibration, which generally is observed at about 3200 cm^{-1}, is found at 3032–3096 cm^{-1} in these ammonium fluorolanthanates. Both ν_3 and ν_4 are triply degenerate in the freely rotating ammonium ion. When the ion is not free to rotate, due to hydrogen bonding, the degeneracy is removed and splitting of the band will occur. Thus, ν_4, which is generally found at about 1400 cm^{-1}, would be expected to split and to occur at somewhat higher frequencies. Consequently, the bands at 1497–1403 cm^{-1} are assigned to ν_4 of NH_4^+.

If the $(NH_4)_3Ln_2F_9\,.\,H_2O$ compounds are considered to consist of NH_4^+ ions and $[Ln_2F_9\,.\,H_2O]^{3-}$ ions, a possible structure for the anion could involve two octahedral LnX_6 units sharing an edge, joined by fluorine bridging atoms, and with a water molecule replacing what would normally be a terminal fluorine. A possible structure for the anion, $[Ln_3F_{11}\,.\,H_2O]^{2-}$, could incorporate three octahedral LnF_6 units sharing two faces with one terminal fluorine replaced by water.

Octahedral MF_6^{n-} ions should have two i.r.-active vibrations, ν_3 and ν_4. Metal–fluorine stretching frequencies, ν_3, for octahedral molecules with tervalent metals occur in the range 400–600 cm^{-1} [28]. In general, bridging metal–halogen stretching frequencies are lower than terminal metal–halogen frequencies ([24], p. 216), and distortion of the regular octahedral configuration due to a shared edge could cause splitting of vibrational frequencies. The deformation mode, ν_4, generally absorbs in the range 315–220 cm^{-1} and is also frequently split in solid state spectra.

The bands found from 520–451 cm^{-1} have been designated as the terminal metal–fluorine stretching vibrations, ν_t(Ln–F). The lower bands in the yttrium and erbium compounds (422 and 415 cm^{-1}, respectively) could possibly be bridging metal–fluorine absorptions, but the absence of corresponding bands in the other compounds, and their relatively weak intensities seem to indicate that they are due to splitting of the ν_t(Ln–F). The next lower bands are fairly strong and are probably the metal–fluorine bridging bands, ν_b(Ln–F). The remaining bands may be ascribed to ν_4.

REFERENCES

1. D. Babel, In *Structure and Bonding*, Vol. 3, pp. 1–87. Springer, Berlin (1967).
2. A. G. Sharpe, *Adv. Fluorine Chem.* **1**, 29 (1960).
3. R. D. Peacock, *Progr. Inorg. Chem.* **2**, 193 (1960).
4. D. Brown, *Halides of the Lanthanides and Actinides*, Chapter 2. Wiley, New York (1968).
5. G. V. Shevchenko, Candidate's Thesis, Institute of General and Inorganic Chemistry, Moscow, 1965;

$$(NH_4)_2Y_3F_{11}\,.\,H_2O \xrightarrow[119^\circ]{-H_2O} (NH_4)_2Y_3F_{11} \xrightarrow[180^\circ]{-NH_4F} NH_4Y_3F_{10} \xrightarrow[311^\circ]{-NH_4F} 3YF_3$$

$$(NH_4)_2Dy_3F_{11}\,.\,H_2O \xrightarrow[69^\circ]{-H_2O} (NH_4)_2Dy_3F_{11} \xrightarrow[159^\circ]{-2NH_4F} 3DyF_3$$

$$(NH_4)_2Ho_3F_{11}\,.\,H_2O \xrightarrow[61^\circ]{-H_2O} (NH_4)_2Ho_3F_{11} \xrightarrow[204^\circ]{-NH_4F} NH_4Ho_3F_{10} \xrightarrow[286^\circ,\,304^\circ]{-NH_3,\,HF} 3HoF_3$$

$$(NH_4)_2Er_3F_{11}\,.\,H_2O \xrightarrow[115^\circ]{-H_2O} (NH_4)_2Er_3F_{11} \xrightarrow[316^\circ]{-2NH_4F} 3ErF_3$$

Fig. 2. Thermal decomposition of $(NH_4)_2Ln_3F_{11}\,.\,H_2O$ compounds. Temperatures given are dta peak maxima.

according to B. N. Ivanov-Emin, V. A. Zaitseva and A. I. Ezhov, *Russ. J. inorg. Chem.* **13**, 1253 (1968); *Zh. neorg. Khim.* **13**, 2428 (1968).

6. B. N. Ivanov-Emin, V. A. Zaitseva and A. I. Ezhov, *Russ. J. inorg. Chem.* **12**, 710 (1967); *Zh. neorg. Khim.* **12**, 1343 (1967). *Russ. J. inorg. Chem.* **13**, 1253 (1968); *Zh. neorg. Khim.* **13**, 2428 (1968).
7. L. R. Batsanova, *Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* 83 (1963); *Chem. Abstr.* **59**, 13578 (1963).
8. M. L. Salutsky, In *Comprehensive Analytical Chemistry* (Edited by C. L. Wilson and D. W. Wilson) Vol. 1(C), Chapter X, Part 3c, pp. 450, 453. Elsevier, New York (1962).
9. C. L. Grant and H. M. Haendler, *Analyt. Chem.* **28**, 415 (1956).
10. E. P. Dergunov, *Dokl. Akad. Nauk SSSR* **85**, 1025 (1952); *Chem. Abstr.* **47**, 1524 (1953).
11. B. N. Ivanov-Emin, T. N. Susanina, and L. A. Ogorodnikova, *Russ. J. inorg. Chem.* **11**, 274 (1966); *Zh. neorg. Khim.* **11**, 504 (1966).
12. L. L. Quill and G. L. Clink, *Inorg. Chem.* **6**, 1433 (1967).
13. T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel and W. J. Randall, *Chem. Rev.* **65**, 1 (1965).
14. D. Babel, In *Structure and Bonding*, Vol. 3. Springer, New York (1967); (a) p. 57; (b) p. 59.
15. R. D. W. Kemmitt, D. R. Russell and D. W. A. Sharp, *J. chem. Soc.* 4408 (1963).
16. R. D. Shannon and C. T. Prewitt, *Acta crystallogr.* **B25**, 925 (1969).
17. A. E. Baker and H. M. Haendler, *Inorg. Chem.* **1**, 127 (1962).
18. L. J. Basile, D. L. Kovacic and J. R. Ferraro, *Inorg. Chem.* **6**, 406 (1967).
19. B. N. Ivanov-Emin, T. N. Susanina and A. I. Ezhov, *Russ. J. inorg. Chem.* **12**, 11 (1967); *Zh. neorg. Khim.* **12**, 23 (1967).
20. J. Sterba-Böhm, *Bull. Soc. chim. Fr.* **27**, 185 (1920).
21. A. Zalkin and D. H. Templeton, *J. Am. chem. Soc.* **75**, 2453 (1953).
22. D. B. Shinn, D. S. Crocket and H. M. Haendler, *Inorg. Chem.* **5**, 1927 (1965); L. K. Beck, B. L. Kugler and H. M. Haendler, *J. Solid St. Chem.* In press.
23. K. Kuo and S. K. Madan, *Inorg. Chem.* **8**, 1580 (1969).
24. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd Edn, p. 166. Wiley–Interscience, New York (1970).
25. P. J. Lucchesi and W. A. Glasson, *J. Am. chem. Soc.* **78**, 1347 (1956).
26. T. C. Waddington, *J. chem. Soc.* 4340 (1958).
27. G. F. Svatos, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.* **77**, 6159 (1955).
28. R. J. H. Clark, In *Halogen Chemistry* (Edited by V. Gutmann) Vol. 3, pp. 85–121. Academic Press, London (1967).