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The Thermal Decomposition of Ammonium Hexafluorogallate and Ammonium Hexafluoroindate. New Crystalline Forms of Gallium Fluoride and Indium Fluoride*

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Ammonium hexafluorogallate, $(NH_4)_3GaF_6$, and ammonium hexafluoroindate, $(NH_4)_3InF_6$, occur in two polymorphic forms, a low temperature tetragonal and a high temperature cubic form, which transform reversibly. They decompose on heating with an initial loss of 2 moles of ammonium fluoride, forming ammonium tetrafluorogallate, NH_4GaF_4, and ammonium tetrafluoroindate, NH_4InF_4. Further heating results in the gradual loss of ammonium fluoride; the final decomposition products are γ-gallium fluoride and γ-indium fluoride, new crystalline forms. These convert on further heating to the common hexagonal forms of the trifluorides. The structural relationship of the compounds are discussed and compared with those of the aluminum analogs.

Introduction

In 1936 Hannebohn and Klemm (*1*) reported the synthesis of ammonium hexafluorogallate and ammonium hexafluoroindate and their thermal decomposition to gallium trifluoride and indium trifluoride. More recently, Brewer, Garton, and Goodgame (*2*) suggested this decomposition sequence for ammonium hexafluorogallate:

$$(NH_4)_3GaF_6 \rightarrow (NH_4)_2GaF_5 \rightarrow NH_4GaF_4 \rightarrow GaF_3.$$

Mermant, Belinski, and Lalau-Keraly (*3*) reported that ammonium hexafluoroindate decomposes in two stages:

$$(NH_4)_3InF_6 \rightarrow NH_4InF_4 \rightarrow InF_3.$$

The aluminum analog, ammonium hexafluoroaluminate, was studied by Shinn, Crocket, and Haendler (*4*) in its room temperature form. Steward and Rooksby (*5*) had observed a low temperature form of the hexafluoro compound, and these two studies show the reaction sequence to be

$$\beta\text{-}(NH_4)_3AlF_6 \rightarrow \alpha\text{-}(NH_4)_3AlF_6 \rightarrow NH_4AlF_4 \rightarrow \gamma\text{-}AlF_3 \rightarrow \alpha\text{-}AlF_3.$$

Schwarzmann (*6*) subsequently reported that ammonium hexafluoroaluminate, -gallate, and -indate are present at atmospheric pressure, and at temperatures above –100°C, in two forms, which are rapidly and reversibly changed into each other at –49, –25, and 82°C, respectively. Structures of room temperature forms of ammonium hexafluorogallate (*7*) (cubic) and hexafluoroindate [tetragonal (*8*) or monoclinic (*6*)] have been reported, as have those of gallium (*2*) and indium (*9*) fluorides (hexagonal). Preliminary work on ammonium tetrafluorogallate has been reported (*2*), and there is a report of two different forms of gallium fluoride, one obtained by thermal decomposition of ammonium hexafluorogallate and one by fluorination of gallium oxide at 600°C (*9*).

The incomplete knowledge of the thermal behavior of ammonium hexafluorogallate and -indate, the obvious differences in the reported decomposition sequences for analogous compounds, and the opportunity to speculate on the

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topochemistry of the related aluminum, gallium, and indium compounds prompted a closer study of the latter two systems. Differential thermal analysis, thermogravimetry, X-ray diffraction, and infrared spectroscopy were utilized.

Materials and Equipment

Ammonium hexafluorogallate and hexafluoroindate were prepared by the reaction of the metal bromide with ammonium fluoride in methanol (*10*). Identity was checked by X-ray diffraction. Intermediate compounds were prepared by controlled thermal decompositions, monitoring the corresponding weight losses. Analytical checks were made on the intermediate indium compounds.

Anal: calcd for NH_4InF_4: NH_4^+, 8.64; F, 36.39; found: NH_4^+, 8.43; F, 36.35.

Anal: calcd for γ-InF_3: In, 66.83 found: In, 66.63.

Ammonium was determined by distillation from alkaline solution into boric acid, followed by titration with standard hydrochloric acid. Fluoride was determined oscillometrically, by titration with thorium nitrate after distillation. Indium was determined gravimetrically as the oxide.

X-Ray powder diffraction photographs were made with 57.3 and 114.56 Philips cameras. Samples were mounted in sealed 0.3 mm glass capillaries. Intensities were estimated visually. Diffractometer patterns were also recorded on a Norelco wide-range diffractometer equipped with a Materials Research Corp. environmental chamber and proportional temperature controller. Low temperatures were obtained by cooling the specimen holder with ethanol passed through a solid carbon dioxide–acetone mixture. Nickel filtered copper radiation (1.54178 Å) was used. A silicon standard was used for calibration.

Infrared spectra were run on a Beckman IR-12 spectrophotometer, using cesium iodide pellets, and were checked against spectra made with Nujol mulls on polyethylene windows.

Thermogravimetric analyses were carried out on a duPont thermogravimetric analyzer Model 950, and differential thermal analyses on a duPont Model 900 analyzer equipped with a differential scanning calorimeter cell. All samples in dynamic analyses were heated at the rate of 15°C/min. An X–Y recorder was used. The system was flushed continuously with argon or helium at a rate of 2.5 std ft^3/hr. Flow rate changes in this range did not affect temperature readings. Temperature was checked periodically against known melting points. The ice point was used as the reference temperature.

Results

Hexafluorometallate Transitions

A compound with the general formula $(NH_4)_3MeF_6$ which has cubic structure will be referred to as the α-form, and one which has tetragonal structure will be referred to as the β-form. X-Ray data for $(NH_4)_3GaF_6$, recorded at room temperature, agreed with values calculated from Schwarzmann's parameters (*7*) for a cubic cell. The pattern recorded at approximately −40°C differed appreciably from the room temperature pattern and was completely indexed on the basis of a tetragonal cell. The reversibility of the transition was checked by warming the sample to room temperature and repeating the original cubic pattern. The transition is completely and rapidly reversible.

The X-ray data for $(NH_4)_3InF_6$, recorded at room temperature, agreed with values calculated from the tetragonal parameters of Bode and Voss (*8*). A series of diffraction patterns taken at 5°C intervals between 80 and 120°C showed a gradual change from the tetragonal pattern to the cubic pattern, with most pairs of adjacent reflections degenerating into a single reflection. No intermediate structure was observed. The high temperature form appeared to be isostructural with α-$(NH_4)_3GaF_6$, and the pattern was indexed on a cubic basis. The transition was again observed to be reversible and rapid.

Thermal Analyses

The differential thermal analysis (DTA) curve for α-$(NH_4)_3GaF_6$ shows an initial broad endotherm at 235°C. The corresponding thermogravimetric analysis (TGA) curve shows a gradual weight loss beginning at 125°C and changing slope at 294°C. Isothermal analysis at 210°C gives a weight loss of 29.9%, consistent with the theoretical weight loss of 31.6% for the loss of 2 moles of NH_4F. The X-ray powder data for the product agreed with that reported for NH_4GaF_4 (*2*). A second DTA endotherm appears at 345°C, corresponding to a second gradual weight loss in the TGA curve over the range 300–500°C. Isothermal analysis at 335°C gives a constant weight loss of 46.1%, based on the original hexafluoro compound. The theoretical weight loss for the formation of GaF_3, with loss

TABLE I

INFRARED ABSORPTION SPECTRA[a]

	Ammonium vibrations				Metal fluorine vibrations	
Compound	ν_3	$\nu_2 + \nu_4$	$2\nu_4$	ν_4	ν_3	ν_4
α-$(NH_4)_3AlF_6$[b]	3250	3060	—	1428	570	—
NH_4AlF_4	3230	3120	2905	1435	610	573w
γ-AlF_3	—	—	—	—	665	605sh
α-AlF_3	—	—	—	—	675	566s
α-$(NH_4)_3GaF_6$	3200	3031	2872sh, 2806s	1431, 1413s	481	297
NH_4GaF_4	3237	3115	2925	1433	569, 541	259br
γ-GaF_3	—	—	—	—	568	239br
α-GaF_3	—	—	—	—	587	244
β-$(NH_4)_3InF_6$	3113br	3031	2913, 2806	1440br,[c] 1405s	450	245br
NH_4InF_4	3213br	3100	2906sh	1433	497	209br
γ-InF_3[d]	—	—	—	—	514	281br
α-InF_3	—	—	—	—	541	298

[a] CsI pellets were used between 200 and 3400 cm^{-1}; w, weak; sh, shoulder; br, broad; s, sharp.

[b] Reported by Shinn, Crocket and Haendler (*4*).

[c] Split by coupling.

[d] Shows a trace of ammonium vibration.

of 1 mole of NH_4F, is 46.7%. The powder data for this product did not match that reported for GaF_3 by Hebecker and Hoppe (*9*), and which they had termed β-GaF_3. The film could be indexed, however, on a tetragonal basis, suggesting that the compound was isostructural with γ-AlF_3 (*4*). At 455°C the DTA curve shows a small exotherm without an accompanying weight change in the TGA curve, indicating a polymorphic transition from γ-GaF_3 to the normal high temperature form, here referred to as α-GaF_3. X-Ray data for the final product matches that reported for the hexagonal α-GaF_3.

The differential thermal analysis curve for the tetragonal, low temperature, β-form of $(NH_4)_3InF_6$ shows two small endotherms at 57 and 95°C, but there is no weight change. Repeated cycling indicates that both peaks represent reversible transitions associated with the polymorphic transition reported by Schwarzmann. A broad DTA endotherm appears at 227°C, and the TGA shows a gradual weight loss beginning at 100°C and a change in slope at 230°C. Isothermal analysis at 168°C gives a constant weight loss of 27.0%; the theoretical value for the loss of 2 moles of NH_4F is 26.2%. The powder data indicated that the product was isostructural with NH_4GaF_4 and NH_4AlF_4, and the pattern could be indexed on the tetragonal basis. The last DTA endotherm appears at 273°C, with a gradual weight loss in the range 230–275°C. Isothermal analysis at 243°C gives a weight loss of 40.0%, compared to the theoretical weight loss of 39.3% for formation of InF_3. This product is

TABLE II

UNIT CELL DATA (Å)

	Al	Ga	In
M^{3+} radius	0.50	0.62	0.81
β-$(NH_4)_3MF_6$[a]	—	$a = 6.36$ $c = 9.14$	$a = 6.53$ $c = 9.49$
α-$(NH_4)_3MF_6$[b]	$a = 8.93$	$a = 9.04$	$a = 9.32$
NH_4MF_4[a]	$a = 3.59$ $c = 6.35$	$a = 3.71$ $c = 6.39$	$a = 4.00$ $c = 6.40$
γ-MF_3[a]	$a = 3.54$ $c = 6.00$	$a = 3.65$ $c = 6.30$	$a = 3.97$ $c = 6.74$
α-MF_3[c]	$a = 4.91$ $c = 12.45$	$a = 5.00$ $c = 12.97$	$a = 5.42$ $c = 14.43$

[a] Tetragonal.

[b] Cubic.

[c] Rhombohedral, hexagonal axes listed.

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR β-$(NH_4)_3GaF_6$ AND γ-GaF_3

β-$(NH_4)_3GaF_6$				γ-GaF_3			
d_{obs} (Å)[a]	I/I_0	$h\,k\,l$[b]	d_{calcd} (Å)	d_{obs} (Å)[c]	I/I_0[d]	$h\,k\,l$[e]	d_{calcd} (Å)
5.22	100	1 0 1	5.22	6.30	s	0 0 1	6.30
4.57	25	0 0 2	4.57	3.65	vs	1 0 0	3.65
4.51	39	1 1 0	4.50	3.16	s	0 0 2	3.15
3.20	41	1 1 2	3.20	2.583	m	1 1 0	2.584
2.75	8	1 0 3	2.75	2.392	w	1 1 1	2.391
2.715	11	1 2 1	2.716	1.826	s	2 0 0	1.827
2.280	10	0 0 4	2.285	1.754	w	2 0 1	1.755
2.252	20	2 2 0	2.249	1.634	m	1 2 0	1.634
2.086	30	1 2 3	2.079	1.582	m	1 2 1	1.582
2.036	5	1 1 4	2.037	1.292	m	2 2 0	1.292
2.016	8	2 2 2	2.018				
1.858	5	2 0 4	1.856				
1.840	10	1 3 2	1.841				

[a] Diffractometer measurement at about −40°C.
[b] Based on a tetragonal cell, $a = 6.36$, $c = 9.14$ Å.
[c] Film measurement using Philips 114 mm camera.
[d] Visual estimation.
[e] Based on a tetragonal cell, $a = 3.654$, $c = 6.305$ Å.

TABLE IV

X-RAY POWDER DIFFRACTION DATA FOR α-$(NH_4)_3InF_6$, NH_4InF_4, AND γ-InF_3

α-$(NH_4)_3InF_6$				NH_4InF_4				γ-InF_3			
d_{obs} (Å)[a]	I/I_0	$h\,k\,l$[b]	d_{calcd} (Å)	d_{obs} (Å)[c]	I/I_0[d]	$h\,k\,l$[e]	d_{calcd} (Å)	d_{obs} (Å)	I/I_0[d]	$h\,k\,l$[f]	d_{calcd} (Å)
5.38	100	1 1 1	5.38	6.40	vs	0 0 1	6.40	6.74	m	0 0 1	6.74
4.66	48	2 0 0	4.66	4.00	vs	1 0 0	4.00	3.97	vs	1 0 0	3.97
3.29	65	2 2 0	3.29	3.39	vs	1 0 1	3.39	3.38	s	0 0 2	3.37
2.81	34	3 1 1	2.81	3.17	w	0 0 2	3.20	2.79	vw	1 1 0	2.81
2.33	21	4 0 0	2.33	2.81	m	1 1 0	2.83	2.58	m	1 0 2	2.57
2.139	13	3 3 1	2.138	2.58	w	1 1 1	2.59	1.988	vw	2 0 0	1.985
2.034	22	4 2 0	2.084	2.49	w	1 0 2	2.49	1.955	vw	1 0 3	1.955
1.903	25	4 2 2	1.902	2.113	w	1 1 2	2.113	1.757	w	1 1 3	1.754
1.793	17	5 1 1, 3 3 3	1.794	1.994	w	2 0 0	2.000	1.711	m	2 0 2	1.710
				1.905	m	2 0 1	1.909	1.566	w	1 2 2	1.565
				1.875	m	1 0 3	1.882	1.392	vw	1 2 3	1.393
				1.779	w	1 2 0	1.789				
				1.720	m	1 2 1	1.723				
				1.694	m	2 0 2	1.696				
				1.595	vw	0 0 4	1.600				
				1.559	vw	1 2 2	1.561				
				1.483	vw	1 0 4	1.486				
				1.456	vw	2 0 3	1.459				
				1.369	vw	1 2 3	1.371				

[a] Diffractometer measurement at about 125°C.
[b] Based on a cubic cell, $a = 9.32$ Å.
[c] Film measurement using Philips 114 mm camera.
[d] Visual estimation.
[e] Based on a tetragonal cell, $a = 4.00$, $c = 6.40$ Å.
[f] Based on a tetragonal cell, $a = 3.97$, $c = 6.74$ Å. Film showed traces of contaminant lines.

TABLE V

TRANSITION TEMPERATURE RANGES

	Al[a]	Ga	In
β-$(NH_4)_3MF_6 \rightarrow \alpha$-$(NH_4)_3MF_6$[b]	−49	−25	82
α-$(NH_4)_3MF_6 \rightarrow NH_4MF_4$	170–240 (205)[c]	125–294 (210)	100–230 (168)
$NH_4MF_4 \rightarrow \gamma$-$MF_3$	240–365 (400)	294–395 (335)	230–275 (243)
γ-$MF_3 \rightarrow \alpha$-MF_3	720	455	375

[a] Ref. (*4*).

[b] Ref. (*6*).

[c] Values in parentheses are the isothermal reaction temperatures used to determine weight loss.

also in the γ-form. At 376°C the DTA curve shows a sharp exotherm, while the TGA curve indicates a slight weight loss, This is consistent with the collapse of the γ-structure to the α-form, and the weight loss might result from small amounts of trapped ammonium fluoride or other contaminant. The final product is α-InF_3.

Infrared Spectra

The infrared data are listed in Table I. The major absorptions in the metal–fluorine vibration region have been assigned to ν_3 and ν_4. Peacock and Sharpe (*11*) have discussed shifts in ν_3 vibration frequencies in octahedrally-bound metal–fluorine systems in cryolites. Observed frequencies decrease as the effective ionic radius of the metal increases, a decrease which is apparent when corresponding aluminum, gallium, and indium compounds are compared. There is also a trend towards higher frequencies as sharing of octahedral corners increases. The ν_4 ammonium vibration of $(NH_4)_3MF_6$ is split in the gallium and indium compounds, indicative of two crystallographically distinct types of ammonium ions.

X-Ray Diffraction

The available unit cell data for the compounds discussed are summarized in Table II, and the powder diffraction data for the new compounds are listed in Tables III and IV.

Discussion

The decomposition sequences of the three hexafluorometallates are represented by the equations

$$\beta\text{-}(NH_4)_3MF_6 \rightarrow \alpha\text{-}(NH_4)_3MF_6,$$
$$\alpha\text{-}(NH_4)_3MF_6 \rightarrow NH_4MF_4 + 2NH_4F,$$
$$NH_4MF_4 \rightarrow \gamma\text{-}MF_3,$$
$$\gamma\text{-}MF_3 \rightarrow \alpha\text{-}MF_3.$$

The transition temperature ranges are summarized in Table V. Kinetic and thermodynamic factors are both significant in reporting transition temperatures in reaction series such as these.

The metal–metal distances in the compounds are listed in Table VI. Structural changes in the gallium and indium compounds are comparable to those in the aluminum system (*4*), and most of that discussion is not repeated here.

The idealized structure of the cubic cryolites, with the general formula A_3MF_6, is characteristic of space group *Fm3m*, $Z = 4$. This ideal structure is sometimes distorted to structures of lower symmetry. Disorientations existing at

TABLE VI

METAL–METAL DISTANCES (Å)

	Al	Ga	In
β-$(NH_4)_3MF_6$	—	6.36(4)[b]	6.53(4)
α-$(NH_4)_3MF_6$	6.31(12)[a]	6.39(12)	6.59(12)
NH_4MF_4	6.35(2)	6.39(2)	6.40(2)
	5.07(4)	5.25(4)	5.66(4)
	3.59(4)	3.71(4)	4.00(4)
γ-MF_3[b]	6.03(2)	6.31(2)	6.74(2)
	5.02(4)	5.17(4)	5.61(4)
	3.55(4)	3.65(4)	3.97(4)
α-MF_3	3.52(6)	3.61(6)	3.92(6)

[a] Number of equivalent distances in parentheses.

[b] Based on an assumed structure.

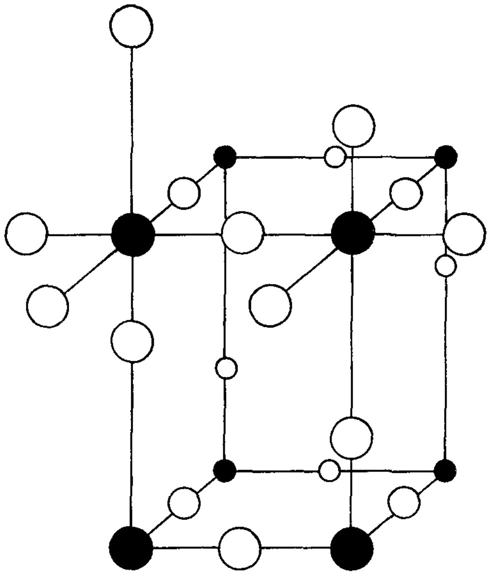

FIG. 1. Proposed structure of γ-AlF_3, γ-GaF_3, and γ-InF_3. Open circles represent fluorine atoms.

room temperature may be removed by thermal expansion, or introduced into a room temperature cubic form by contraction.

The temperature of deformation is influenced by the radius of the alkali or ammonium ion, but is also related to the radius of the metal ion.

This distortion of the idealized cubic structure can be visualized in terms of the polymorphic transitions referred to above. As the temperature decreases, the [100] and the [010] directions of the cube contract, with a slight accompanying increase in the [001] direction. The [110] direction becomes [100] of the tetragonal structure. The contracted $a = 6.36$ Å parameter of tetragonal β-$(NH_4)_3GaF_6$ is comparable to the 6.39 Å metal–metal distance in the [110] direction of cubic α-$(NH_4)_3GaF_6$. The [001] parameter increases at the same time from 9.04 to 9.14 Å. Corresponding shifts are noted with the indium compounds. If the true structure of β-$(NH_4)_3InF_6$ is monoclinic, as Schwarzmann (*6*) suggested, the first stage in the two-step polymorphic transition indicated by differential thermal analysis may be the transition from a monoclinic structure to a slightly different tetragonal structure, which then converts to the cubic form.

The structural changes involved in the first step of the thermal decomposition have been discussed (*4*). The a-parameter of NH_4MF_4 increases in the order aluminum, gallium, indium, but there is not a corresponding increase in the c-parameter. The layers of ammonium ions, interpolated between the octahedral metal–fluorine layers, serve as a restraint on the expansion of the c-axis, which remains at about 6.38 Å throughout the series. Removal of the remaining ammonium fluoride leads to the proposed open structure for the γ-form of the trifluoride, shown in Fig. 1, in which the size of the metal ion affects both a- and c-parameters. The final transition is the collapse to the normal, hexagonal form of the trifluoride, with the parametral relationships shown in Table II.

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