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Compounds in the Cerium Tetrafluoride–Ammonium Fluoride–Water System[1]

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In the CeF_4–NH_4F–H_2O system, $(NH_4)_4CeF_8$ is the solid phase in equilibrium at 25° with NH_4F solutions over the concentration range 28.9–45 wt % NH_4F (saturated solution). It is monoclinic, C2/c, $a = 13.02$, $b = 6.66$, $c = 13.61$ Å, $\beta = 121° 18'$, $Z = 4$, and is isostructural with $(NH_4)_4UF_8$. Thermogravimetric analysis and differential thermal analysis establish that $(NH_4)_4CeF_8$ decomposes to $(NH_4)_2CeF_6$ without indication of a transition to an anhydrous compound of stoichiometry $(NH_4)_3CeF_7$. However, the monohydrate $(NH_4)_3CeF_7 \cdot H_2O$ can be obtained from $\sim$28 wt % NH_4F solutions. It is monoclinic, $P2_1/n$, $a = 11.09$, $b = 12.10$, $c = 7.13$ Å, $\beta = 95° 55'$, $Z = 4$. $(NH_4)_2CeF_6$ is orthorhombic and isostructural with α-$(NH_4)_2UF_6$. $7NH_4F \cdot 6CeF_4$ is rhombohedral, $a = 9.50$ Å, $\alpha = 106° 42'$, and is obtained from 1% NH_4F solution. NH_4CeF_5 is formed from $7NH_4F \cdot 6CeF_4$ on thermal decomposition and is isostructural with β-NH_4UF_5.

Introduction

The tetravalent actinide fluorides, protactinium(IV) through americium(IV), form with ammonium fluoride an isostructural series of composition $(NH_4)_4XF_8$.[2] To data, anhydrous compounds of composition $(NH_4)_3XF_7$ have not been made for the tetravalent actinides although the rubidium compound Rb_3XF_7 is well known for a number of them.[3] Since the radii of the above actinide(IV) ions span that of Ce(IV), it was surprising to read that $(NH_4)_3CeF_7$ was reported to be the complex with the highest $NH_4F:CeF_4$ ratio in the CeF_4–NH_4F–H_2O system.[4] Lattice dimensions for this tetragonal compound were given as $a = 10.0$ Å, $c = 11.95$ Å, $Z = 8$, yielding a volume of 149 Å^3/molecule of $(NH_4)_3CeF_7$. It is useful to recall a study by Zachariasen which showed that the volume per fluoride in complex compounds of the tetravalent actinides is about 18 Å^3/F.[5] If we subtract from the molecular volume of putative "$(NH_4)_3CeF_7$" Zachariasen's value of 78 Å^3 for three ammonium ions, this leaves but 71 Å^3 for seven fluorides. This value of 10 Å^3/F is clearly far too low. Indeed, even in the octahedrally coordinated group(V) hexafluorides, the volume per fluoride is 16–17 Å^3.[6] Also the reported assignment of $(NH_4)_2CeF_6$ to the cubic system was surprising; it gives a higher calculated density and lower volume per fluoride than anticipated on the basis of known actinide compounds of analogous composition, none of which is isometric. In addition, the ubiquitous rhombohedral $7NH_4F \cdot 6XF_4$ type of compound which might have been anticipated was not reported. These anomalies prompted us to reinvestigate the CeF_4–NH_4F–H_2O system.

Experimental Section

Technique.—The complex in the CeF_4–NH_4F–H_2O system having the highest $NH_4F:CeF_4$ ratio would be formed in equilibrium with a saturated solution containing some solid NH_4F. Since excess NH_4F floats in saturated NH_4F solution while the much denser ammonium cerium fluoride complex sinks, centrifugation is conveniently used to separate the two solid phases. This obviates the water wash recommended by the French workers to dissolve excess ammonium fluoride, a step which we find alters the product. Solid phases were equilibrated with aqueous NH_4F in plastic bottles by rotating them end-over-end for periods of several days. Identity of solid phases was established by examination under a petrographic microscope and by single-crystal (precession) and powder diffraction X-ray techniques. In the case of crystallographically pure phases, ammonia was determined by the Kjeldahl method, cerium was determined by ignition to CeO_2, and fluoride was determined in the distillate from pyrohydrolysis by titration with thorium nitrate.

Preparation of $(NH_4)_4CeF_8$.—Reagent $(NH_4)_2Ce(NO_3)_6$ was dissolved in water and 48% HF was added until precipitation ceased. The washed precipitate (later shown to be $7NH_4F \cdot 6CeF_4$) was equilibrated with concentrated NH_4F solutions. Alternatively, $Ce(HSO_4)_4$ was used, as well as $CeF_4 \cdot xH_2O$ obtained from $Ce(OH)_4$. To ensure saturation, solid NH_4F was added until crystals of NH_4F were observed floating on the surface of the solution. Overnight at room temperature (or in a few hours on cooling a warmed slurry), dense, colorless crystals were obtained which were separated by centrifugation. At 25° this same crystalline phase was found over the range of NH_4F concentration from 45 to 28.9 wt %. Examination under the petrographic microscope showed well-formed, biaxial crystals that could be washed with CH_3OH without alteration. Water, however, decomposed the surfaces immediately, giving them a mottled, translucent appearance. *Anal.* Calcd for $(NH_4)_4CeF_8$: NH_3, 18.7; Ce, 38.47; F, 41.72. Found: NH_3, 18.5; Ce, 38.2; F, 41.9.

Crystallographic Properties of $(NH_4)_4CeF_8$. (a) X-Ray Data.—Precession photographs of single crystals of $(NH_4)_4CeF_8$ show that it and $(NH_4)_4UF_8$ are isostructural. A complete single-crystal study of $(NH_4)_4UF_8$ has been published and the data will not be repeated here.[7] $(NH_4)_4CeF_8$ belongs to the monoclinic space group, C2/c, with cell parameters determined by a least-

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] R. A. Penneman, F. H. Kruse, R. S. George, and J. S. Coleman, *Inorg. Chem.*, **3**, 309(1964).

[3] E. M. Levin, C. R. Robbins, and H. F. McMurdee, "Phase Diagrams for Ceramists," American Ceramic Society, Inc., Columbus, Ohio, 1964. See also G. D. Brunton, H. Insley, T. N. McVay, and R. E. Thoma, ORNL Report 3761, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

[4] J.-P. Besse and M. Capestan, *Bull. Soc. Chim. France*, 577 (1966).

[5] W. H. Zachariasen, *J. Am. Chem. Soc.*, **70**, 2147 (1948).

[6] R. A. Penneman, *Inorg. Chem.*, **6**, 431 (1967).

[7] A. Rosenzweig and D. T. Cromer, *Acta Cryst.*, in press.

squares fit of our precession data: $a = 13.02$, $b = 6.66$, $c = 13.61$ Å, $\beta = 121°\ 18'$, $Z = 4$. The calculated density is 2.40 g/cm^3. The density measured using bromobenzene is 2.396 g/cm^3. The indexed partial X-ray powder pattern is tabulated in a following section.

(b) **Optical Data.**—For comparison, the properties of the prototype $(NH_4)_4UF_8$ are given together with those of $(NH_4)_4CeF_8$. Both compounds form diamond-shaped, monoclinic plates parallel to (001) which is also the twin plane and cleavage direction. Other forms present are $\{11\bar{1}\}$ (prominent), $\{110\}$ and $\{100\}$ (small).

The optical properties of the two compounds are given in Table I (indices and extinction are for Na light (~590 mμ) unless otherwise noted).

Table I

N_z	N_y	N_x	$2V$	Orientation	Molar refractivity
		$(NH_4)_4CeF_8$			
1.485 (Colorless)	1.475 (Colorless)	1.468 (Colorless)	~+80°	$X = b$ $\angle Za = 44°$ (dispersion slight)	42.8
		$(NH_4)_4UF_8$			
1.464 (Blue-green)	1.459 (Green)	1.454 (Pale yellow-green)	~+85°	$X = b$ $\angle Za = 45°$ (530 mμ) $\angle Za = 42°$ (623 mμ)	42.4

Preparation of $(NH_4)_2CeF_6$.—Dissolution of $(NH_4)_4CeF_8$ (or CeF_4) in a 5–20 wt % NH_4F solution at 80° yields crystals of $(NH_4)_2CeF_6$ on cooling. The crystals are orthorhombic, Pbcn, and isostructural with α-$(NH_4)_2UF_6$.[2] They can be washed with CH_3OH without decomposition but water causes decomposition. A single-crystal X-ray study of $(NH_4)_2CeF_6$ has just been completed,[8] giving $a = 7.026$, $b = 12.098$, $c = 7.44$ Å; the indexed partial powder pattern is listed in a later section. Thermogravimetric analysis of $(NH_4)_2CeF_6$ shows halts at the compositions $7NH_4F \cdot 6CeF_4$ and $NH_4F \cdot CeF_4$ (Figure 1). *Anal.* Calcd for $(NH_4)_2CeF_6$: NH_3, 11.74; Ce, 48.29; F, 39.28. Found: NH_3, 11.7; Ce, 48.0; F, 39.1.

Optical Properties of $(NH_4)_2CeF_6$.—These data are as follows: biaxial, $+2V = 73°$ (calcd); $N_x = 1.496$, $N_y = 1.505$, $N_z = 1.521$; prismatic habit: $Z = a =$ elongation, $Y = b$, $X = c$; molar refractivity = 28.4.

Preparation of $(NH_4)_3CeF_7 \cdot H_2O$.—At aqueous NH_4F concentrations greater than 29%, $(NH_4)_4CeF_8$ is obtained, while $(NH_4)_2CeF_6$ is found at concentrations lower than ~24%. Before discovery of $(NH_4)_3CeF_7 \cdot H_2O$ an attempt was made to find the invariant solution composition where both $(NH_4)_2CeF_6$ and $(NH_4)_4CeF_8$ would be present as solid phases. $(NH_4)_2CeF_6$ or $(NH_4)_4CeF_8$ was equilibrated with solutions near 28%. On overnight equilibration well-formed crystals of a new phase appeared. The X-ray powder pattern of this new phase matched neither that of $(NH_4)_2CeF_6$ nor that of $(NH_4)_4CeF_8$. Differential thermal analysis of the new phase shows a sharp endothermic peak at about 85°, a temperature much lower than that for any previously noted NH_4F loss (Figure 1). It was assumed that this represented dehydration; this is supported by the chemical analysis. *Anal.* Calcd for $(NH_4)_3CeF_7 \cdot H_2O$: NH_3, 14.76; Ce, 40.59; F, 38.52. Found: NH_3, 14.58; Ce, 40.49; F, 38.8. $(NH_4)_3CeF_7 \cdot H_2O$ is formed only slowly from $(NH_4)_2CeF_6$, yielding excellent single crystals showing cleanly beveled edges and 2/m symmetry. The conversion of the hydrate into anhydrous $(NH_4)_2CeF_6$ and $(NH_4)_4CeF_8$ was followed by equilibrating the hydrate with different NH_4F solutions. The limits of stability of the hydrate are ~24 and 28.9 wt % NH_4F.

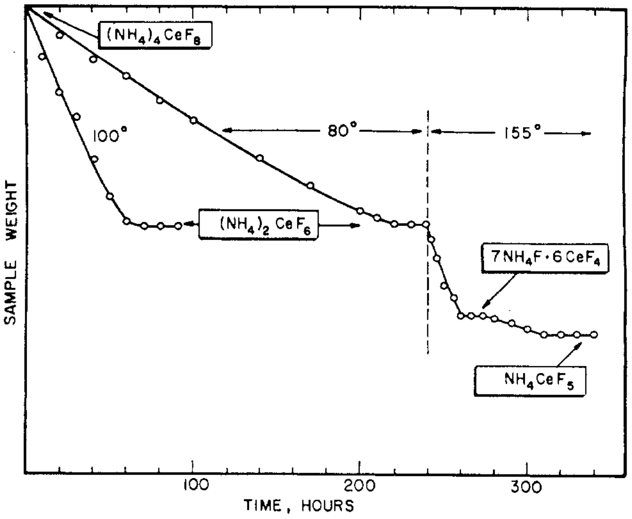

Figure 1.—Thermal decomposition of $(NH_4)_4CeF_8$. The runs were made at the constant temperatures indicated; after 240 hr, the temperature was increased from 80 to 155°, to increase the decomposition rate of $(NH_4)_2CeF_6$.

Crystallographic Properties of $(NH_4)_3CeF_7 \cdot H_2O$. (a) **X-Ray Data.**—Precession photographs of single crystals (coated with Fluorocarbon oil to retard decomposition) were indexed so as to correspond with a simple indexing of the morphology. The crystals are monoclinic, with systematic extinctions establishing the space group as $P2_1/n$. The cell constants are $a = 11.09$, $b = 12.10$, $c = 7.13$ Å, and $\beta = 95°\ 55'$. There are four formula units per cell. The calculated density is 2.41 g/cm^3; the measured density is 2.38 g/cm^3.

(b) **Optical Data.**—The crystals are short prisms, $\{110\}$, terminated by prominent faces, $\{011\}$, and small faces, $\{\bar{1}01\}$. The refractive indices and orientation for sodium light are: $N_x = 1.461$, $N_y = 1.463$, $N_z = 1.472$; $+2V = 51°$; $X = b$, $\angle Zc = 67°$; molar refractivity = 39.6. The optic axes show strong symmetrical dispersion with $v > r$. Inclined dispersion is very slight.

Attempted Preparation of Anhydrous $(NH_4)_3CeF_7$.—A Cahn electrobalance with recorder was used in the thermogravimetric analysis of $(NH_4)_4CeF_8$. $(NH_4)_4CeF_8$ was placed in a platinum basket which was suspended by a thin nickel wire in an oven at controlled temperature. In air at 100° a slow, steady loss in weight was observed until a plateau at $(NH_4)_2CeF_6$ was reached (Figure 1). Since there was no indication of an arrest at composition $(NH_4)_3CeF_7$, a run was made at a lower temperature (80°); it gave similar results (Figure 1). An anhydrous preparation then was attempted using NH_4F and CeF_4 in a 3:1 mole ratio. The ground mixture was heated in a Teflon bomb at 100° for 2 days. The X-ray powder pattern of the product showed only the strong lines of $(NH_4)_4CeF_8$ and $(NH_4)_2CeF_6$. On differential thermal analysis, the decomposition of $(NH_4)_4CeF_8$ yields $(NH_4)_2CeF_6$ (Figure 2). After the hydrate $(NH_4)_2CeF_7 \cdot H_2O$ was found, dehydration was attempted. It was dried over $Mg(ClO_4)_2$ and also *in vacuo* at 25°. Loss of H_2O and NH_4F both occurred and the X-ray powder pattern of the product showed primarily the presence of $(NH_4)_2CeF_6$. At temperatures above 85°, disproportionation into $(NH_4)_4CeF_8$ and $(NH_4)_2CeF_6$ follows water loss (Figure 2).

Preparation of $7NH_4F \cdot 6CeF_4$.—Concentrated (48%) HF was added to a solution of $(NH_4)_4Ce(SO_4)_4$ until precipitation was nearly complete (the solution still retained a slight yellow color). The precipitate was $7NH_4F \cdot 6CeF_4$, identified by chemical analysis and by comparison of its characteristic X-ray pattern with

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[8] R. R. Ryan, A. C. Larson, and F. H. Kruse, *Inorg. Chem.*, **8**, 33 (1969).

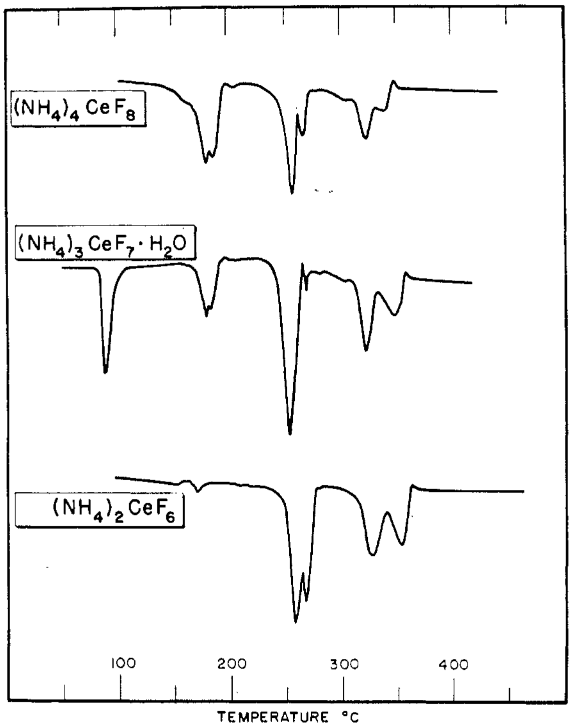

Figure 2.—Differential thermal analysis of $(NH_4)_4CeF_8$, $(NH_4)_3CeF_7\cdot H_2O$, and $(NH_4)_2CeF_6$. Heating rate is 15°/min, in a low pressure of 18 in., using a Du Pont 900 differential thermal analyzer.

TABLE II

$(NH_4)_4CeF_8$

a = 13.02, b = 6.66, c = 13.61,

β = 121°18' Space group C2/c (C_{2h}^6)

h k ℓ	d_{obsd}
1 1 $\bar{1}$	5.78 VS
2 0 0	5.57 M
1 1 1	4.66 S
1 1 $\bar{3}$	3.70 M
3 1 $\bar{1}$	3.56 M
4 0 $\bar{2}$	3.25 W
3 1 0	
1 1 3	2.874 W
2 2 1	2.620 M
2 2 $\bar{5}$	2.093 M
2 2 3	2.053 M

$(NH_4)_3CeF_7\cdot H_2O$

a = 11.09, b = 12.10, c = 7.13,

β = 95°55', Z = 4. Space group $P2_1/n$

d_{obsd}	I_{est}
8.16	VS
6.28	MS
6.07	VS
5.72	M
5.54	M
5.31	S
5.17	W
5.01	S
3.43	MS

$(NH_4)_2CeF_6$

a = 7.026, b = 12.098, c = 7.44,

Space group Pbcn (D_{2h}^{14})

h k ℓ	d_{obsd}
1 1 0	6.07 VS
1 1 1	4.71 W
0 0 2	3.75 W
2 0 0	3.50 W
1 1 2	3.18 M
2 4 1	2.190 W

β-NH_4CeF_5

d_{obsd}	I_{est}
6.88	VS
3.94	M
3.80	S
3.44	S
3.20	S
2.03	M
1.99	MS

$7NH_4F\cdot 6CeF_4$

a = 15.24, c = 10.73, (rhombohedral cell: a = 9.50, α = 106°42'

Space group R$\bar{3}$ (C_{3i}^2)

h k $\ell_{(hex)}$	d_{obsd}
1 0 1	8.33 S
0 1 2	4.97 M
2 1 1	4.52 M
1 3 1	3.47 VS
3 1 2	3.02 W
1 5 2	2.163 MS
1 3 4	
0 1 5	2.113 MS
5 2 0	

that of the isostructural, rhombohedral $7NH_4F\cdot 6UF_4$.[9] Single crystals of $7NH_4F\cdot 6CeF_4$ were obtained on cooling a 1% NH_4F solution saturated with $(NH_4)_2CeF_6$ at 90°. Precession photos gave a = 9.50 Å and α = 106° 42', The partial X-ray powder pattern is given in Table II. *Anal.* Calcd for $7NH_4F\cdot 6CeF_4$: NH_3, 7.66; Ce, 54.03; F, 37.85. Found: NH_3, 7.6; Ce, 53.7; F, 36.7.

Optical Properties.—These data are as follows: uniaxial positive, N_e = 1.556, N_o = 1.551; habit: rhombohedra.

Preparation of NH_4CeF_5.—This compound was prepared by thermal decomposition of $(NH_4)_2CeF_6$ as shown in Figure 1. The X-ray properties showed this phase to be isostructural with β-NH_4UF_5.

Discussion

The valuable aid given by examination of solids using a petrographic microscope should be mentioned with respect to phase studies and compound preparation in general. Assignment to one of three main classes—cubic; tetragonal or hexagonal; orthorhombic, monoclinic, or triclinic—is easily indicated. It is important to examine crystals while they are still in the mother liquor. Subsequently they can be washed while on the microscope stage and changes (which frequently occur) can be noted. Refractive index measurements taken during the course of such observations allow calculation of the rarely used but useful quantity, the molar refractivity.

$(NH_4)_4CeF_8$.—$(NH_4)_4CeF_8$ is clearly isostructural with $(NH_4)_4UF_8$ since the crystallographic properties (as evidenced by both X-ray powder diffraction and precession data) are nearly identical. The crystal morphologies are identical and the molar refractivities are nearly so. With regard to the latter, the values of the refractive indices of $(NH_4)_4CeF_8$ seem high when compared to those of $(NH_4)_4UF_8$ until the value of the molar refractivity is calculated. The value R_m = 42.8 clearly shows that the compound cannot have the formula $(NH_4)_3CeF_7$, which would have an expected molar refractivity in the middle 30's. Chemical analysis confirms the formula $(NH_4)_4CeF_8$, which is the complex in the CeF_4–NH_4F–H_2O system having the highest NH_4F:CeF_4 ratio, contrary to the results reported in ref 4. It is formed over the NH_4F concentration range 28.9–45 wt %.

$(NH_4)_3CeF_7\cdot H_2O$.—This compound is the first hydrate as well as the first compound of a 3:1 NH_4F:MF_4 composition to be found in the aqueous ammonium fluoride–actinide (or lanthanide)–tetrafluoride systems. It is unstable on removal of hydrate water, with respect to $(NH_4)_2CeF_6$ and $(NH_4)_4CeF_8$. This is clearly shown by dta, since the decomposition next after H_2O loss is that of $(NH_4)_4CeF_8$, followed by an $(NH_4)_2CeF_6$ decomposition endotherm clearly relatively greater than that from 4:1 to 2:1 alone (Figure 2). Thus

$$2(NH_4)_3CeF_7\cdot H_2O \xrightarrow{\Delta} 2H_2O + (NH_4)_4CeF_8 + (NH_4)_2CeF_6$$

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(9) R. Benz, R. M. Douglass, F. H. Kruse, and R. A. Penneman, *Inorg. Chem.*, **2**, 799 (1963).

Chemical analyses, optical measurements, and single-crystal X-ray studies establish that the compound is $(NH_4)_3CeF_7 \cdot H_2O$ and not a mixture of $(NH_4)_4CeF_8$ and $(NH_4)_2CeF_6$. The difference in the molar refractivities of $(NH_4)_4CeF_8$ (42.8) and $(NH_4)_2CeF_6$ (28.4) is 14.4, or 7.2/mol of NH_4F. Thus, adding 7.2 to the value for $(NH_4)_2CeF_6$ (28.4) plus Fajans' value for H_2O (3.8) gives 39.4 as the molar refractivity expected for $(NH_4)_3CeF_7 \cdot H_2O$. The experimental value is 39.6

$(NH_4)_3CeF_7$.—We were not successful in preparing this compound from aqueous NH_4F solution, in the thermal decomposition of $(NH_4)_4CeF_8$, nor on dehydration of $(NH_4)_3CeF_7 \cdot H_2O$.

$(NH_4)_2CeF_6$.—This compound, isostructural with α-$(NH_4)_2UF_6$, is optically biaxial and, thus, cannot have symmetry higher than orthorhombic. Since the strong X-ray lines of orthorhombic $(NH_4)_2CeF_6$ were indexed as cubic in the earlier work on this material,[4] it is of interest to mention how this could occur. The cell dimensions of orthorhombic $(NH_4)_2CeF_6$, a = 7.026, b = 12.098, c = 7.440 Å, have nearly exactly the required ratio to permit indexing on the basis of a pseudo-cubic cell.[8] Specifically, $a'/a = {}^3/_2$, $a'/b = \sqrt{3}/2$, and $a'/c = \sqrt{2}$. Our data would give values for a' of 10.54, 10.48, and 10.52; Besse and Capestan reported 10.52 ± 0.04 Å for their cubic indexing.[4] Our measured and calculated densities are 3.02 *vs.* 3.05. The cubic phase reported previously would have a density of 3.3 and, thus, an abnormally small volume per fluorine.[4]

$7NH_4F \cdot 6CeF_4$.—This rhombohedral compound, which was not reported in the earlier work,[4] is isostructural with $7NH_4F \cdot 6UF_4$; its structure type is $7NaF \cdot 6ZrF_4$.[10] However, the compound is very stable and, indeed, it rather than $CeF_4 \cdot xH_2O$ precipitated on addition of HF to a dilute solution of an ammonium salt of Ce(IV). NH_4F is extracted very slowly from it, even by hot water, but it is converted into complexes containing a greater $NH_4F:CeF_4$ ratio by equilibration with more concentrated NH_4F solutions.

NH_4CeF_5.—Evidence for NH_4CeF_5 was obtained as a halt in the composition *vs.* temperature curve (Figure 1), showing the steps $(NH_4)_4CeF_8 \rightarrow (NH_4)_2CeF_6 \rightarrow 7NH_4F \cdot 6CeF_4 \rightarrow NH_4CeF_5$. The X-ray powder diffraction data for NH_4CeF_5 (obtained by thermal decomposition at 100°) showed that it is isostructural with β-NH_4UF_5.[9] We did not prepare NH_4CeF_5 from aqueous solution since treatment of higher phases with hot water removed ammonium fluoride readily, only until the composition $7NH_4F \cdot 6CeF_4$ was reached, as mentioned above.

Acknowledgments.—The authors thank Ivan K. Kressin for the chemical analyses and some preparation work and Robert R. Ryan for his single-crystal data on $(NH_4)_2CeF_6$ which was used to index its powder pattern.

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(10) J. H. Burns, R. D. Ellison, and H. A. Levy, *Acta Cryst.*, **B24**, 230 (1968).