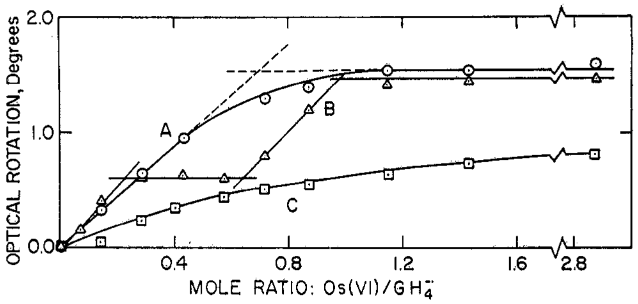

Fig. 4.—Mole-ratio study of the osmium(VI)-gluconate system using optical rotation as the measured variable. All solutions contained 2×10^{-3} *F* sodium gluconate and were adjusted to pH 14. The measurements were made in a 40-cm. polarimeter tube. Curve A is for 2-hr. old solutions, curve B for 2-day old solutions, and curve C for 24-day old solutions.

Osmium(IV) to osmium(III); pH 13 to 14

$$\mathrm{Os(GH_4)_2(OH)}_{x-3}{}^{5-x} + \mathrm{e}^- \longrightarrow \mathrm{Os(GH_4)_2(OH)}_{x-3}{}^{4-x} \quad (4)$$

pH 11 to 13

$$\mathrm{Os(GH_4)_2(OH)}_{x-3}{}^{5-x} + \mathrm{e}^- \longrightarrow \mathrm{Os(GH_4)_2(OH)}_{x-4}{}^{5-x} + \mathrm{OH}^- \quad (5)$$

pH 8 to 11

$$\mathrm{Os(GH_4)_2(OH)}_{y-1}{}^{3-y} + \mathrm{e}^- \longrightarrow \mathrm{Os(GH_4)_2(OH)}_{y-1.5}{}^{2.5-y} + 0.5\mathrm{OH}^- \quad (6)$$

Consideration of these five equations indicates that $x \geqq 4$; $y \geqq 1$; $y \leqq x$.

Under basic conditions it is probable that the osmium complexes would all carry negative charges. Thus, reference to eq. 2 indicates that assuming $x = 6$ gives a consistent set of equations. Also, these same conditions indicate that it is consistent to assume $y = 5$.

In summary gluconate ion forms strong complexes with osmium(VI, IV, III) in alkaline solutions. Advantage can be taken of these complexes as a means for stabilizing the ions in solution and also as a polarographic method of analysis. The use of sodium gluconate plus NaOH as a supporting electrolyte has the advantage that osmium(VIII) is spontaneously and quickly reduced to osmium(VI) by the gluconate. The resulting osmium(VI) gives a well defined and analytically useful reduction wave over a wide concentration range.

Acknowledgment.—We wish to thank the United States Atomic Energy Commission for support of this work under Contract No. AT(11-1)-34, Project No. 45. Appreciation is expressed to the National Science Foundation for an Undergraduate Summer Fellowship which was awarded to D. S. T.

CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
UNIVERSITY OF CALIFORNIA, LOS ALAMOS, NEW MEXICO

Preparation and Properties of Several Ammonium Uranium(IV) and Ammonium Plutonium(IV) Fluorides[1]

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A series of anhydrous fluoride complexes is formed between NH_4F and actinide tetrafluorides. Compounds with $NH_4F:MF_4$ (M = U or Pu) mole ratios of 4:1, 2:1, 7:6, 1:1, and 1:3 were prepared by reaction of stoichiometric quantities in sealed tubes or by gravimetric arrests during NH_4F distillation. X-Ray powder diffraction data are presented. Corresponding U(IV) and Pu(IV) compounds are isostructural. The $7NH_4F \cdot 6MF_4$ compounds are rhombohedral, $a_0 = 9.55$ and 9.42 Å., $\alpha = 107.4°$ and 107.4° for M = U and Pu, respectively. A method of chemical analysis for NH_4, U, and F on a single sample was developed using pyrohydrolysis, ion exchange, and volumetric techniques.

Introduction

The extensive studies of compounds formed in melts containing UF_4 and the alkali fluorides have been reviewed by Thoma,[2] who noted that several compound types are common: $3MF \cdot UF_4$, $2MF \cdot UF_4$, $7MF \cdot 6UF_4$, and $MF \cdot UF_4$. Only one corresponding compound in the NH_4F–UF_4 and NH_4F–PuF_4 systems has been reported, "NH_4PuF_5"; the occurrence of $NH_4F \cdot PuF_4$ and $7NH_4F \cdot 6PuF_4$ as separate compounds was not noted.[3–8] Prior work with ammonium fluoride complexes of U(IV) and Pu(IV) obtained by precipitation from aqueous solution or by treatment of the dioxide with NH_4HF_2 often has contained errors, primarily from the lack of recognition that "drying" can result in loss of NH_4F. Furthermore, NH_4F loss has been confused with loss of hydrate water (note the near coincidence of the formula weights of NH_4F, 37, and $2H_2O$, 36).

The direct reaction of actinide tetrafluorides with NH_4F under anhydrous conditions has not been re-

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] R. E. Thoma, *Inorg. Chem.*, **1**, 220 (1962).

[3] (a) H. A. Bernhardt, R. A. Gustison, and J. C. Posey, K-410 (June 1, 1949); (b) W. B. Tolley, HW-31211 (Mar. 16, 1954); (c) W. B. Tolley, HW-35814 (Feb. 1, 1955); (d) M. D. Alford, HW-41713 (Mar. 1, 1956). Obtainable from Office of Technical Services, Department of Commerce Washington 25, D. C.

[4] J. Van Impe, *Chem. Eng. Progr.*, **50**, 230 (1954).

[5] W. B. Tolley and R. C. Smith, U. S. Pat. 2,917,360 (Dec. 15, 1959).

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[8] N. P. Galkin, B. N. Sudarikov, and V. A. Zaitsev, *At. Energy*, **11**, 554 (1961).

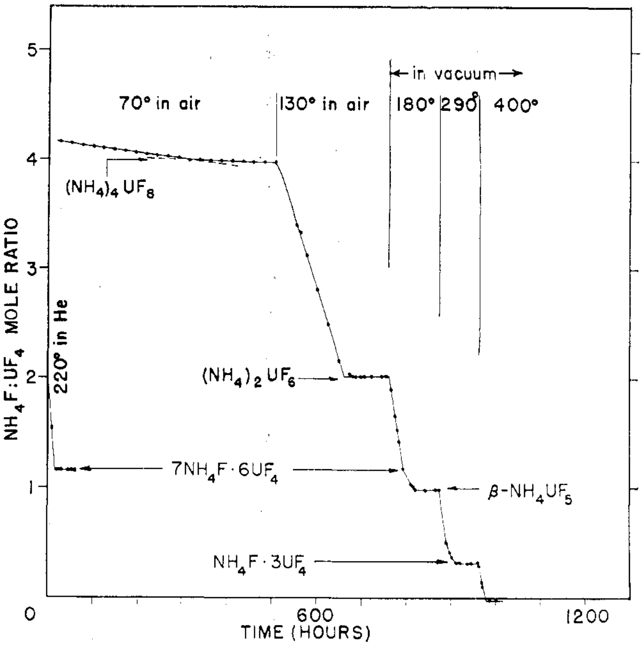

Fig. 1.—Thermal decomposition of compounds in the NH_4F–UF_4 system.

ported. Two difficulties in the direct reaction are that certain proportions reach equilibrium only sluggishly at temperatures as high as 300° and that above 400° NH_4F reduces PuF_4. These difficulties are avoided by *first* treating the tetrafluoride with sufficient NH_4F to form $(NH_4)_4UF_8$ and $(NH_4)_4PuF_8$; equilibrium is reached rapidly even at *ca.* 100°. This product then is easily converted to other compounds by distillation of the excess NH_4F.

Using this technique we have prepared a series of NH_4F–UF_4 and NH_4F–PuF_4 compounds. The compounds were characterized by thermogravimetric, X-ray powder diffraction, and chemical analysis.

Experimental

Materials.—Finely divided UF_4 (99.9%) and PuF_4 (99.9%) were used. Baker and Adamson Reagent NH_4F was dried 1 hr. at 130° in a partially covered platinum crucible and then ground to a fine powder. Argon (99.99%), helium (99.7%), and oxygen (99.5%) were dried in a −80° cold trap. Dry gases were used in order to avoid hydration and hydrolysis of the tetrafluorides.

General Procedure for Compound Preparation.—The reaction of NH_4F with UF_4 to yield complex fluorides proceeds readily at 80–130° at all mole ratios from 1:1 to 4:1. With PuF_4 the reaction did not proceed rapidly when the NH_4F:PuF_4 ratio was below 2:1. In most cases, however, equilibrium was reached from both directions, the identical compound being prepared by direct reaction ($NH_4F + MF_4$) as well as by decomposition of a phase richer in NH_4F. For the preparations at 80°, tightly closed polyethylene or Teflon bottles were used. At 130° and above, screw-cap containers of Dural were satisfactory.

Typical Procedure for Thermogravimetric Analysis.—For the preparation of the 4:1 compound, 10 g. of MF_4 was weighed into a platinum or nickel crucible. Five g. of NH_4F (a slight excess over 4:1) then was added and the two fine powders were mixed thoroughly. Weighing was done in a glove box provided with recirculated and dried air. The crucible was covered and placed in a horizontal 2-in. diameter nickel tube closed at one end and surrounded by a tube furnace provided with automatic temperature control. Temperature readings were taken with a thermocouple located on the nickel tube. The covered crucible was heated 1 hr. at 130° (1 hr. at 130° or 6 hr. at 70° was sufficient to form the 4:1 compound). After cooling, the product was weighed, reground, and mixed thoroughly. When a starting mole ratio of 2:1 was used, the mole ratio was adjusted to exactly 2:1.

During the thermogravimetric runs, the sample was maintained at a constant temperature under vacuum or in a stream of dry argon, helium, oxygen, or air at atmospheric pressure. The crucible was cooled and weighed periodically. After each weighing, the sample was mixed thoroughly. At arrests, a portion was taken for X-ray diffraction and chemical analysis.

Compounds in the NH_4F–UF_4 System.—Typical decomposition curves for compounds in the NH_4F-UF_4 system are illustrated in Fig. 1. Arrests in the decomposition curves were reproducible within 0.3% of the stoichiometric weight independent of whether NH_4F removal was effected under vacuum, argon, helium, or air. Five complex compounds forming seven distinct phases were found.

$(NH_4)_4UF_8$.—Non-stationary arrests were obtained for this compound in a partially covered crucible in air at 60–90°. For preparative purposes, formation proceeds readily at 80–130° in a sealed plastic tube containing a mixture of NH_4F and UF_4 in 4:1 mole ratio. After heating the mixture for 3–6 hr., the container is cooled to room temperature before opening to avoid loss of NH_4F. Fine-grain crystals are pea green; large crystals are emerald green.[9]

$(NH_4)_2UF_6$.—Stationary arrests were obtained for this compound in air at 110–130°. Decomposition (loss of NH_4F) becomes appreciable under vacuum at 150–170°. The compound is readily formed from NH_4F and UF_4 by heating 2:1 mixtures at 80–130° for 3–6 hr. in a sealed tube. Fine-grain crystals are blue-green.

$7NH_4F \cdot 6UF_4$.—Stationary arrests were obtained for this compound in helium at 200–220°; a non-stationary arrest was obtained under vacuum at 180°. This compound also is obtained on heating NH_4F and UF_4 in 7:6 mole ratio at 80–100° in a sealed tube for 3–6 hr. Prepared in this way, no NH_4F loss was detected from a 10-g. sample on subsequent heating for 24 hr. at 92° under vacuum (1 μ) over a liquid nitrogen trap. Fine-grain crystals are light green.

α-NH_4UF_5.—This phase may be regarded as an NH_4F-*deficient* form of the 7:6 compound from which it was not distinguishable by X-ray powder techniques. This 1:1 phase invariably was produced on direct reaction of NH_4F with UF_4 in 1:1 mole ratio at 80–200°. Annealing in a sealed capsule at 190° for 30 days produced partial conversion to β-1:1. It is likely that a single phase of variable composition exists between the 7:6 and 1:1 stoichiometries. However, at 150° the 1:1 composition has a special stability with respect to compositions slightly richer or poorer in NH_4F: removal of NH_4F under vacuum from the 7:6 phase proceeds smoothly until the 1:1 composition (α form) is reached at which point the rate of NH_4F loss becomes very slow. At higher temperatures, removal of NH_4F from the 7:6 phase gives either the β or γ form of 1:1 or gives no stationary arrest at the 1:1 composition. Fine-grain crystals are light green.

β-NH_4UF_5.—Stationary arrests were obtained for this phase under vacuum at 180–210° starting with either the 4:1 or 2:1 compound. Fine-grain crystals are green to blue-green.

γ-NH_4UF_5.—Stationary arrests were obtained for this phase on decomposition under vacuum at 150° of the 2:1 compound (prepared at 80°). Fine-grain crystals are light blue-green.

$NH_4F \cdot 3UF_4$.—Arrests were obtained for this compound under vacuum at 270–290°. This compound decomposes to pure UF_4 under vacuum at 300–400° as shown by weight changes and X-ray powder patterns of the product. An attempt was made to produce the 1:3 compound by direct reaction of NH_4F and UF_4 at 270° for 40 hr. in a sealed Dural container, but the product

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(9) In a study (to be published) of the NH_4F–UF_4–H_2O system, we find that large crystals, giving the same X-ray powder pattern and chemical analysis as the anhydrous 4:1 preparation, are readily obtained by equilibration of 2.5 wt. % UF_4 with 40% aqueous NH_4F at 25°.

gave an X-ray powder pattern showing only lines of UF_4 and α-1:1. Fine-grain crystals are green.

Compounds in the NH_4F–PuF_4 System.—Typical decomposition curves for compounds in the NH_4F–PuF_4 system are illustrated in Fig. 2. Arrests in the decomposition curves were reproducible within 0.3% of the stoichiometric weight independent of whether NH_4F removal was effected under vacuum, argon, helium, oxygen, or air. (Results in helium and argon are essentially the same as in air and are not shown.) Five complex compounds forming seven distinct phases were found.

$(NH_4)_4PuF_8$.—Non-stationary arrests were obtained for this compound in air at 70–100°. It is not hygroscopic at 70° in water-saturated helium. For preparative purposes, a 4:1 mixture of NH_4F and PuF_4 reacts to form this compound in a sealed tube at 80–130° in 6 hr. Crystals vary in color from light red to pink, depending on crystal size.

$(NH_4)_2PuF_6$.—Stationary arrests were obtained for this compound in air at 130–160° and under vacuum at 130°. It is not hygroscopic at 70°. The 2:1 compound also is formed by reaction of NH_4F and PuF_4 in 2:1 mole ratio in a sealed tube at 80–130° for 6 hr. Fine-grain crystals are green. Coarse crystals are prismatic and optically biaxial negative with optic axial angle *ca.* 60°. They exhibit parallel extinction, positive elongation, and strong pleochroism with X and Y colorless, Z green; extreme refractive indices are 1.484 ± 0.005, 1.500 ± 0.005. Polysynthetic twinning is common.

$7NH_4F \cdot 6PuF_4$.—Stationary arrests were obtained for this compound in air or under vacuum at 200–230° starting with either the 4:1 or 2:1 compound. Direct reaction of NH_4F and PuF_4 in 7:6 mole ratio is sluggish and did not produce the 7:6 phase after 6 hr. at 80°. Fine-grain crystals are light brown to orange.

α-NH_4PuF_5.—This phase may be regarded as an NH_4F-*deficient* form of the 7:6 compound from which it is indistinguishable by X-ray powder techniques. It is formed by annealing 1:1 mixtures of NH_4F and PuF_4 in a sealed tube for 1 day at 220°. Partial conversion of β-1:1 to α-1:1 was observed at 220° in 2 weeks. Partial conversion of α-1:1 to β-1:1 was observed at 270° in 1 week. Fine-grain crystals are light brown to orange.

β-NH_4PuF_5.—Crystals were obtained in nine different runs involving thermal decomposition of the 2:1 compound in oxygen at 180–200°. The compound is not hygroscopic at 70°. Fine-grain crystals are yellow-green to light green.

γ-NH_4PuF_5.—Stationary arrests were obtained for this compound in air, oxygen, or under vacuum at 190–230°. Decomposition of 4:1 or 2:1 compounds usually gave γ-1:1 rather than β-1:1. Fine-grain crystals are orange to light brown. The crystals are optically biaxial positive with large optic axial angle, and strongly pleochroic with X colorless, Z olive drab.

$NH_4F \cdot 3PuF_4$.—A stationary arrest was obtained from β-1:1 in oxygen at 220°. Starting with γ-1:1, non-stationary arrests usually were obtained at the 1:3 composition at 280–290°. X-Ray powder patterns from these samples confirmed the presence of the 1:3 phase by comparison with the corresponding uranium compound. Crystals decompose slowly under vacuum at 300–330° to very nearly pure PuF_4 as shown by weight changes and X-ray powder patterns. A small fraction of the PuF_4 was consumed in a slow, unidentified side reaction at these temperatures. Fine-grain crystals are pink.

Chemical Analysis of Phases.—Plutonium was determined by titration with cerium. Ammonia was determined by the Kjeldahl method.

For most of the uranium samples, we extended a pyrohydrolysis method to allow determination of NH_4, U, and F on a single sample. A sample containing 3–4 mequiv. of total fluoride was weighed into a platinum boat and heated progressively to 1000° in a stream of superheated steam in a pyrohydrolysis apparatus.[10] The residue in the boat was weighed as U_3O_8. The condensate containing NH_4F and HF was caught in a plastic beaker and titrated to the methyl red end point with 0.1 M NaOH. This procedure gives only fluoride equivalent to UF_4 as found by Alford.[3d] Our extension of his procedure was to pass the solution, after titration, through Dowex-50 resin (100–200 mesh) contained in plastic tubing. The H^+-form resin converted the NH_4F and the NaF (resulting from the first titration) into HF. A second titration was made to the phenolphthalein end point, giving total fluoride. The difference between the first and second titrations gave NH_4 (*e.g.*, in the case of $(NH_4)_4UF_8$ the second titer is twice the first). To check the combined method, we used crystallographically pure $(NH_4)_3UO_2F_5$ and obtained: first titration, F/U = 2.04 (theoretical, 2); second titration, F/U = 5.00 (theoretical, 5); (second titration − first titration) = NH_4/U = 2.96 (theoretical, 3).

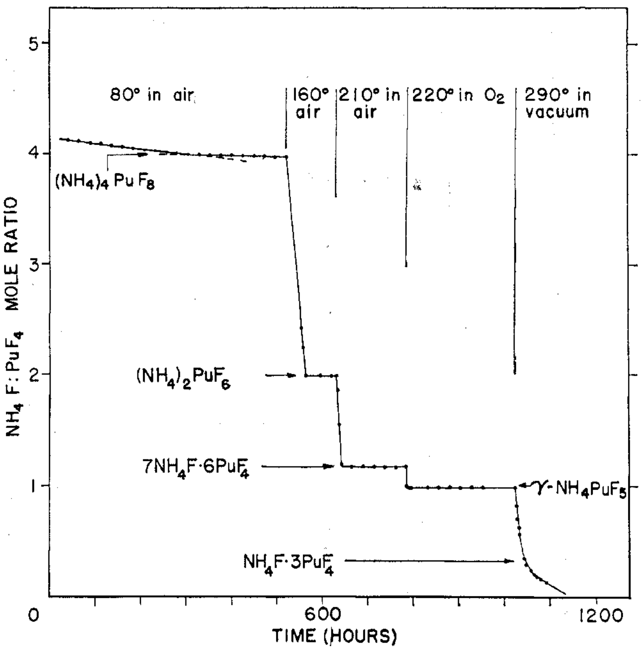

Fig. 2.—Thermal decomposition of compounds in the NH_4F–PuF_4 system.

Typical data for $NH_4F:MF_4$ (M = U or Pu) mole ratios in the various phases as determined by thermogravimetric and chemical analyses are compared in Table I. Data from X-ray powder diffraction studies of the pure phases are listed in Tables II, III, and IV.

TABLE I

COMPOSITION OF COMPLEX COMPOUNDS IN THE NH_4F–UF_4 AND NH_4F–PuF_4 SYSTEMS

Chemical formula	$NH_4F:MF_4$ (M = U or Pu) mole ratio From dec. curves[a]	From chem. anal.
$(NH_4)_4UF_8$	3.99	3.94–4.01
$(NH_4)_4PuF_8$	3.99	3.69–4.00
$(NH_4)_2UF_6$	2.02	1.97–2.01
$(NH_4)_2PuF_6$	1.99	1.90
$7NH_4F \cdot 6UF_4$	1.15	1.16–1.17
$7NH_4F \cdot 6PuF_4$	1.17	1.28
α-NH_4UF_5	1.00	1.00–1.01
α-NH_4PuF_5	(1.01)[b]	. . .
β-NH_4UF_5	0.98	1.00
β-NH_4PuF_5	0.98	0.97
γ-NH_4UF_5	0.98	. . .
γ-NH_4PuF_5	1.00	1.00
$NH_4F \cdot 3UF_4$	0.32	0.43
$NH_4F \cdot 3PuF_4$	0.34	0.34

[a] Computed from the total weight at the arrest in the decomposition curve and the initial weight of the tetrafluoride. [b] Formed only by direct reaction, $NH_4F + PuF_4$.

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[10] J. C. Warf, W. D. Cline, and R. Tevebaugh. *Anal. Chem.*, **26**, 342 (1954).

Table II

Partial X-Ray Powder Patterns of 7:6 and α-1:1 Phases

	7$NH_4F \cdot 6UF_4$ and α-$NH_4F \cdot UF_4$			7$NH_4F \cdot 6PuF_4$ and α-$NH_4F \cdot PuF_4$		
hkl[a]	d_{calcd}	d_{obsd}	I[b]	d_{calcd}	d_{obsd}	I[c]
101	8.25	8.4	80	8.13	8.3	s
110	7.69	7.7	14	7.60	7.6	mw
201	5.63	5.67	20	5.55	5.59	m
102	4.88	5.00	28	4.82	4.95	m
211	4.54	4.55	30	4.48	4.50	m
300	4.44	4.44	23	4.38	4.37	m
202	4.12	4.19	11	4.07	4.14	w
220	3.85	3.85	13	3.79	3.78	mw
212	3.63	3.68	17	3.59	3.58	m
221	3.61	3.60	20[d]	...	...	...
003	3.50	3.49	100	3.46	3.45	s
311	3.49			3.44		
400	3.33	3.26	10[d]	...	...	...
113	3.18	3.18	10	3.14	3.14	w
401	3.17			3.13		
312	3.02	3.03	40	2.98	3.02	ms
321	2.94	2.94	7	2.89	2.90	w
410	2.91	2.90	8	2.87	2.86	w
402	2.82	2.83	3	2.77	2.78	vw
303	2.75	2.79	8	...	...	...
322	2.64	2.64	8	2.61	2.62	w
330	2.56	2.56	2	2.53	2.53	vw
420	2.52	2.51	2[d]	...	...	...
421	2.45	2.45	3	2.42	2.42	vw
502	2.38	2.38	3	2.34	2.35	vw
511	2.33	2.33	6	2.30	2.30	w
214	2.33			2.30		
422	2.27	2.27	10	2.24	2.24	w
512	2.18	2.18	35	2.15	2.16	ms
520	2.13	2.13	40	2.10	2.11	ms
333	2.07	2.08	3	2.04	2.06	vw
432	2.02	2.02	6	1.99	2.00	w

[a] Hexagonal indices. [b] Relative uncorrected intensities from diffractometer scan; Cu Kα radiation, λ = 1.5418 Å. [c] Intensities estimated visually; Cu Kα radiation. [d] These lines appear in typical films but do not index in R$\bar{3}$. They can be either indexed in P$\bar{3}$ or ascribed to minor contaminant phases.

Table III

Partial X-Ray Powder Patterns of 4:1 and 2:1 Phases

$4NH_4F \cdot UF_4$		$4NH_4F \cdot PuF_4$		$2NH_4F \cdot UF_4$		$2NH_4F \cdot PuF_4$	
d_{obsd}	I[a]	d_{obsd}	I[a]	d_{obsd}	I[a]	d_{obsd}	I[a]
5.80	vs	5.80	vs	6.00	vs	5.98	vs
5.54	m	5.54	m	5.81	ms	5.80	ms
4.74	mw	4.67	s-b	4.03	m	3.97	m
4.64	s			3.51	m	3.49	m
3.70	ms	3.70	m	3.41	m	3.39	m
3.60	w	3.57	ms-b	3.35	s	3.30	s
3.56	ms			3.00	m	2.99	m
3.40	mw	3.40	mw	2.92	w	2.91	w
3.34	mw	3.33	mw	2.65	mw	2.63	mw
3.25	m	3.24	m	2.61	m	2.58	m
3.19	mw	3.19	w	2.41	ms	2.39	ms
2.95	vw	2.89	m-b	2.36	m	2.35	m
2.92	w			2.29	m	2.28	m
2.87	m			2.24	w	2.23	w
2.79	w-b	2.79	w-b	2.22	w	2.21	w
2.67	mw	2.67	mw	2.01	w	1.985	ms
2.62	m	2.62	m	1.995	ms		
2.52	w	2.52	w	1.962	m	1.950	m
2.43	mw	2.42	mw	1.942	m	1.930	m
2.39	m	2.39	mw	1.910	ms	1.885	ms
2.33	w	2.33	w	1.795	m	1.787	m
2.29	mw	2.28	mw-b				
2.27	w						
2.23	w	2.22	w				
2.19	m	2.19	m				
2.16	w	2.15	w				
2.11	m-b	2.11	m				
2.06	mw	2.06	mw				
2.03	w	2.03	w				
2.00	vw	2.00	vw				
1.97	ms	1.97	ms				
1.94	w	1.94	vw				
1.91	m	1.91	m				

[a] Intensities estimated visually; Cu Kα radiation, λ = 1.5418 Å.

Discussion

We have shown that the direct reaction of NH_4F with UF_4 or PuF_4 yields a series of complex fluorides. Analogous reactions between UF_5 and NH_4F also have been reported recently.[11] In contrast, no compound consisting of NH_4F and PuF_3 could be detected using techniques described above. The 4:1 compounds, $(NH_4)_4UF_8$ and $(NH_4)_4PuF_8$, are the least stable in the NH_4F–UF_4 and NH_4F–PuF_4 systems. Nevertheless, in the NH_4F–UF_4–H_2O system[9] anhydrous $(NH_4)_4UF_8$ is the stable crystalline phase over wide ranges of NH_4F concentration.

In the NH_4F–UF_4 system, the 4:1 compound is the highest complex formed, whereas in the alkali fluoride–UF_4 series[2] it is found only between LiF and UF_4.[12] Loss of NH_4F from the 4:1 compounds yields the 2:1 compounds without evidence for 3:1 or other intermediate compounds. As the ionic radii of NH_4^+ and Rb^+ are nearly the same,[13] it is of particular interest to compare the series of compounds in the RbF–UF_4[14] and NH_4F–UF_4 systems: $3RbF \cdot UF_4$, $2RbF \cdot UF_4$, $7RbF \cdot 6UF_4$, $RbF \cdot UF_4$, and $RbF \cdot 3UF_4$ *vs.* $4NH_4F \cdot UF_4$, $2NH_4F \cdot UF_4$, $7NH_4F \cdot 6UF_4$, $NH_4F \cdot UF_4$, and $NH_4F \cdot 3UF_4$. The 4:1 compound occurs in the NH_4F–UF_4, NH_4F–PuF_4, and NH_4F–AmF_4 systems,[15] whereas the 3:1 compound is missing. The 2:1 compound occurs in both the rubidium and ammonium systems but the compounds are not isostructural.[16] However, corresponding ammonium and rubidium uranium(IV) fluoride compounds are isostructural in the case of $7NH_4F \cdot 6UF_4$ and $7RbF \cdot 6UF_4$.

In earlier work, a pink NH_4F–PuF_4 compound was assigned the formula $(NH_4)_2PuF_6$ by Alenchikova, *et al.*,[6] based on analysis of "dried" material. However, this pink compound is undoubtedly $(NH_4)_4PuF_8$, which readily loses two molecules of NH_4F forming green $(NH_4)_2PuF_6$. Alenchikova, *et al.*,[6] also prepared a green NH_4F–PuF_4 compound which, although it was not analyzed, they stated "probably" had the formula NH_4PuF_5. Their X-ray powder data for this phase correspond with our data for $(NH_4)_2PuF_6$.

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Galkin, Sudarikov, and Zaitsev[8] concluded that solid NH_4F–UF_4 mixtures decompose in three steps: NH_4UF_5 (10% excess NH_4F) $\xrightarrow{220-280°}$ NH_4UF_5 $\xrightarrow{320-360°}$ HUF_5 $\xrightarrow{420-450°}$ UF_4 when heated at a linear rate up to *ca.* 600°. They found percentage-weight losses which correspond very nearly to the values which we obtained for the series: $(NH_4)_2UF_6 \xrightarrow{180°} NH_4UF_5 \xrightarrow{290°} NH_4F \cdot 3UF_4 \xrightarrow{400°} UF_4$ illustrated in Fig. 1. The decomposition scheme is probably the same in both cases. We found no evidence for the existence of their suggested compound "HUF_5."

Maly, *et al.*,[7] have carried out thermogravimetric analyses on very small (mg.) quantities of products obtained by reaction of PuO_2 with NH_4HF_2. Our results suggest that the arrest which they attribute to "dark green $NH_4PuF_5 \cdot 2H_2O$" was due instead to the green compound $(NH_4)_2PuF_6$. Their decomposition curve also indicates an arrest at the weight near that of $NH_4F \cdot 3PuF_4$ that they did not point out.

The X-ray powder patterns of the 7:6 and α-1:1 phases could be indexed in the $R\overline{3}$ space group assigned to similar members of the alkali fluoride–UF_4 series. The lattice dimensions derived are: $7NH_4F \cdot 6UF_4$ and α-$NH_4F \cdot UF_4$, $a_0 = 9.55$ Å., $\alpha = 107.4°$ (hexagonal dimensions $a_0 = 15.40$, $c_0 = 10.49$ Å.); $7NH_4F \cdot 6PuF_4$ and α-$NH_4F \cdot PuF_4$, $a_0 = 9.42$ Å., $\alpha = 107.4°$ (hexagonal dimensions $a_0 = 15.18$, $c_0 = 10.36$ Å.). The preparations were too fine-grained to permit confirmation of symmetry by optical-microscopic methods.

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TABLE IV

PARTIAL X-RAY POWDER PATTERNS OF β-1:1, γ-1:1, AND 1:3 PHASES

β-$NH_4F \cdot UF_4$		β-$NH_4F \cdot PuF_4$		$NH_4F \cdot 3UF_4$		$NH_4F \cdot 3PuF_4$	
d_{obsd}	I^a	d_{obsd}	I^a	d_{obsd}	I^a	d_{obsd}	I^a
6.97	vs	6.95	vs	8.2	vw	8.2	vw
5.50	vw	...	...	7.9	m	7.8	m
4.55	vw	...	...	7.2	mw-b	7.2	mw-b
4.19	vw	4.10	vw	5.50	m	5.47	m
4.01	ms	3.94	ms	5.37	w	5.35	vw
3.79	m	3.74	m	4.51	mw	4.49	mw
3.66	vw	...	...	4.19	m	4.15	m
3.48	s	3.44	s-b	3.98	w	3.95	vw
3.35	vw	...	...	3.70	w	3.67	vw
3.24	ms	3.20	ms	3.63	ms	3.60	ms
3.18	mw	3.15	w	3.50	ms	3.46	ms
3.00	vw	2.99	vw	3.34	ms	3.31	ms
2.90	mw	2.86	w	3.23	ms	3.19	ms
2.71	mw	2.69	mw	3.09	mw	3.06	vw
2.62	m-b	2.61	mw-b	3.04	vw	3.00	vw
2.32	m-b	2.32	m	2.89	ms	2.86	ms
		2.28	w	2.69	m	2.66	mw
2.14	w	2.13	w	2.62	mw	2.58	w
2.02	ms-b	2.01	ms	2.56	m	2.54	mw
		1.985	ms	2.40	vw	2.36	vw
1.95	m	1.935	vw	2.34	mw	2.32	w
				2.25	mw-b	2.22	w-b
				2.15	mw	2.15	mw
γ-$NH_4F \cdot UF_4$		γ-$NH_4F \cdot PuF_4$		2.11	w	2.11	w-b
d_{obsd}	I^a	d_{obsd}	I^a	2.08	mw	2.06	mw
4.15	m	4.10	m	2.02	s	2.00	s
3.49	s-b	3.48	s-b	1.995	m	1.975	m
2.68	mw-b	2.66	mw-b	1.945	s	1.925	s
2.08	w	2.06	w				
2.02	vw	2.00	vw				
1.80	vw	1.81	vw				
		1.77	w				
...	...	1.60	vw				

[a] Intensities estimated visually; Cu Kα radiation, λ = 1.5418 Å.

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The Effect of Pressure upon the Optical Activity of Crystalline Inorganic Compounds

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Extreme pressures of 10,000 to 40,000 atmospheres were found to increase the rate of racemization of potassium trioxalatocobaltate(III) in the solid state. The volume of activation, ΔV^*, for the racemization process was determined experimentally and found to be -1.44 ± 0.23 and 1.80 ± 0.28 cm.^{3}/mole for two independent experiments. These data are consistent with an intramolecular mechanism. An intramolecular process that does not include metal–oxygen bond rupture and re-formation is preferred. The mechanism is discussed in terms of the possible structures for the transition state and the relationship of structure to ΔV^*. Approximate values of $4.7 \pm 1.1 \times 10^{-4}$ and $2.11 \pm 0.93 \times 10^{-4}$ hr.$^{-1}$ for the specific rate constant for racemization of $K_3[Co(C_2O_4)_3]$ at zero pressure were obtained.

Introduction

Despite the observation that the optically active salts, potassium trioxalatocobaltate(III) and potassium trioxalatochromate(III), undergo slow racemization in the solid state,[1] there has been little experimental work centered on this phenomenon and the theoretical implications arising from it. The study of isotope exchange in aqueous solution for the systems $Co(C_2O_4)_3^{3-}$–$*C_2O_4^{2-}$ [2a] and $Cr(C_2O_4)_3^{3-}$–$*C_2O_4^{2-}$ [2b] showed no interchange under conditions that lead to racemization. These results immediately suggest an intramolecular rearrangement that may or may not involve bond

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