SYNTHESIS, THERMAL DECOMPOSITION AND POWDER DIFFRACTION DATA OF AMMONIUM DECAFLUOROURANATE(VI), (NH₄)₄UF₁₀

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Abstract—The synthesis of $(NH_4)_4 UF_{10}$ is described. Thermal decomposition proceeds through four steps giving $(NH_4)_3 UF_8$ at 200°C, $(NH_4)UF_6$ at 280°C, $(NH_4)U_3F_{13}$ at 380°C and finally UF₄ at 600°C. $(NH_4)UF_6$ decomposes through an intermediate to UF₄ and not directly. Powder data of $(NH_4)_4 UF_{10}$ were indexed on the basis of a monoclinic cell $[a = 12.87(2), b = 8.36(2), c = 13.60(7) \text{ Å}, \beta = 121.5(3)^\circ].$

In 1984 we reported the synthesis and vibrational spectra of $(NH_4)_4 UF_{10}$.¹ This is, as far as we are aware, the first monomeric hexavalent uranium compound with so high a coordination number (larger than eight). There were reports² of attempted syntheses of such a species, but in our case the Raman spectrum of a definitely stoichiometric diamagnetic compound clearly indicates a coordination number larger than eight, and the broad IR N-H stretching absorption showing moderate hydrogen bonding suggests a distorted UF_{10}^{4-} ion, with one of the fluorine atoms having significant ionic character. The radius of hexavalent uranium³ should be comparable for higher coordination numbers with the intramolecular nonbonded atomic radius of fluorine,⁴ allowing space for even more than 10 fluorine atoms. Nevertheless, it is an unexpected result (see also the discussion on the unlikeliness of nonacoordination in isolated anions of actinide fluorides in ref. 5). We report more details of the synthesis, the thermal behaviour and the powder diffraction data of the compound. Attempts to prepare a single crystal suitable for X-ray structure determination were unsuccessful.

EXPERIMENTAL

Synthesis

White $(NH_4)_4 UF_{10}$ was synthesized by the procedure, described previously.1 The results were better if the argon arc-welded copper vessel equipped with a Teflon packed nickel valve containing $(NH_4)_4UF_8$ and XeF_2 in excess (added by sublimation) was held at 55°C for a prolonged time, even for a few days. For reliable synthesis, one should start from very active UF₄, with a large specific surface (obtained by thermal decomposition⁶ of $(N_2H_5)UF_5$, from which $(NH_4)_4UF_8$ is prepared.⁷ More coarse UF₄, prepared by the usual hydrofluorination⁸ of UO₂, results in $(NH_4)_4 UF_8$ of insufficient purity, giving, at the end, impure and very unstable $(NH_4)_4 UF_{10}$. $(NH_4)_4 UF_{10}$ decomposes rapidly in air, changing colour to green. Found: U, 47.9; (NH₄)⁺, 13.9; F, 37.7. Calc. for $(NH_4)_4 UF_{10}$: U, 47.6; $(NH_4)^+$, 14.4; F, 38.0%.

Thermoanalysis

A 100 mg sample was referenced on a Mettler TA-1 thermoanalyser against a 100 mg sample of α -Al₂O₃. The heating rate was 4°C min⁻¹ in a

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(NH ₄) ₄ UF ⁷ ₈	((NH	₄)₄UF10	(NH ₄) ₃ UF ¹⁰		₃ UF ¹⁰	Product at 200°C	
d (Å) I	$d_{(obs)}$	Ι	$d_{(\text{calc})}$	hkl	d (Å)	Ι	d (Å)	Ι
	8.39	w	8.36	010				
	6.97	w	6.78	011				
	6.01	w	5.80	002				
5.80 vs							5.61	w
5.54 m					5.56	100	5.49	vs
	5.45	vs	5.48	200				
	5.05	w	5.11	111				
4.74 mw	4.76	vs	4.76	012	4.77	40	4.74	m
4.64 s								
	4.15	m	4.18	020				
3.70 ms								
3.60 w	3.64	w	3.66	300				
3.56 ms								
3.40 mw	3.38	S	3.39	022	3.37	60	3.37	S
3.34 mw								
3.25 m								
3.19 mw	3.16	w	3.16	103				
	3.05	w	3.06	301				
2.95 vw				004	• • •	-0	• • • •	
2.92 w	2.897	m	2.899	004	2.90	50	2.88	ms
2.87 m	0.754		0.750	220				
2.79 w-b	2.756	w	2.752	320				
2.67 mw	2 (20		2 (20	22.4				
2.62 m	2.630	w	2.638	22-4				
2.52 W	2.514	w	2.512	032				
2.43 mw	2 404		2 402	401	2.41	15	2 20	
2.39 m	2.404	m 	2.402	401	2.41	15	2.39	III (
2 22	2.303	w	2.301	15-5				
2.33 w	2 205		2 203	420				
2.23 IIIw	2.295	**	4.475	420				
2.27 w								
2.19 m	2.197	m	2,199	223	2.21	20	2.19	m
2.16 w	2.137		2.177			20	,	
2.11 m-b	2.143	m	2.142	204	2.15	20	2.07	w
2.06 mw	2.089	m	2.090	040				
2.03 w	2.025	w	2.029	412				
2.00 vw	1.976	w	1.967	042				
1.97 ms	1.956	m	1.955	430	1.96	40	1.96	m
1.94 w								
1.91 m	1.898	m	1.896	233				
	1.856	m	1.860	134	1.86	30b	1.85	ms
	1.770	w	1.768	502				
	1.628	m	1.628	522	1.63	15	1.63	m
	1.608	m	1.607	052	1.61	10	1.60	mw
	1.525	m	1.525	235				

Table 1. Powder diffraction data of $(NH_4)_4 UF_{10}$, of its first decomposition product at 200°C, of $(NH_4)_4 UF_8$ and of $(NH_4)_3 UF_8$

Unit cell⁹ of $(NH_4)_4UF_8$: monoclinic, a = 13.126, b = 6.692, c = 13.717 Å, $\beta = 121.32^\circ$, V = 1029 Å³; unit cell of $(NH_4)_4UF_{10}$ (this paper): monoclinic, a = 12.87(2), b = 8.36(2), c = 13.60(7) Å, $\beta = 121.5(3)^\circ$; V = 1248 Å³.

Intensities of $(NH_4)_4 UF_{10}$ and of the decomposition product are estimated visually.

stream of dried argon (5 dm³ h⁻¹). The DTA range was 10 μ V and the DTG range was 10 mg min⁻¹.

Thermal decomposition was also followed, confirming the results of the Mettler thermoanalyser, by weighing 2 g of $(NH_4)_4UF_{10}$ into a Ni crucible (100 cm^3) in an Ar dry-box. The crucible was held at successive temperatures for 1 h at each step (starting at 60°C, with steps of 10°C). Volatile products were pumped off in a dynamic vacuum. At each stage it was cooled down and samples were taken for powder data and chemical analysis.

Powder data

Debye–Scherrer X-ray diffraction patterns were obtained from a sample sealed in a quartz capillary using graphite monochromatized Cu- K_{α} radiation

on an Enraf-Delft instrument. Intensities were estimated visually.

RESULTS AND DISCUSSION

In the series of known ammonium fluorouranates, $(NH_4)_4UF_{10}$ has the highest $NH_4:U$ mol ratio and the highest valency state of uranium. Of the possible $NH_4:U$ mol ratios for uranium in IV, V and VI valency states, only the lowest two (1:1 and 2:1) are fully represented by six compounds.^{7,9,10} Within the higher ratios (3:1 and 4:1) there are, except for $(NH_4)_4UF_{10}$, only two compounds known; $(NH_4)_3UF_8^9$ and $(NH_4)_4$ $UF_{8,}^7$ both synthesized by heating NH_4F and the fluoride of uranium in the proper valency state. This is not surprising since higher $NH_4:F$

Table 2. Powder diffraction data of decomposition products of $(NH_4)_4 UF_{10}$ at 280, 380 and 600°C

Product at 280°C (NH ₄)UF ¹⁰ ₆			Product				Produ		uct UF		
		at 380°C		$(NH_{4})U_{3}F_{13}^{7}$		at 600°C		(ASTM data)			
d (Å)	Ι	$d(\mathbf{A})$	Ι	d (Å)	Ι	d (Å)	Ι	d (Å)	Ι	d (Å)	Ι
5.76	s	5.81	100b			8.2	vw	4.19	s	4.213	10
4.12	vs	4.13	80	7.88	vw	7.9	m	4.16	m	4.183	6
4.06	m	3.99	30	7.28	w	7.2	mw-b	3.92	m	3.957	6
3.22	S	3.30	80	6.55	w			3.70	m	3.728	8
		2.96	10	5.53	w	5.50	m	3.52	m	3.555	6
2.91	m	2.88	50			5.37	w	3.39	w	3.374	4
2.65	w	2.64	20	4.54	vw	4.51	mw			3.299	6
		2.62	20	4.20	m	4.19	m	3.26	m	3.276	5
2.40	w	2.38	10	3.94	m	3.98	w			2.798	5
		2.35	10	3.71	S	3.70	w			2.782	1
2.22	s	2.20	70Ь			3.63	ms			2.705	3
2.10	m	2.07	30	3.55	m	3.50	ms	2.68	w	2.689	4
1.98	w	2.00	10	3.35	vw	3.34	ms			2.666	2
1.91	m	1.90	30	3.28	8	3.23	ms			2.580	1
		1.87	10	3.13	w	3.09	mw	2.47	vw	2.471	2
1.86	m	1.85	35			3.04	vw			2.454	1
1.82	m	1.81	30	2.82	w	2.89	ms	2.11	w	2.121	3
		1.77	10	2.69	m	2.68	m			2.109	2
1.71	w	1.75	10			2.62	mw			2.095	4
				2.59	w	2.56	m	2.06	m	2.068	7
				2.47	wd			2.00	m	2.001	6
						2.40	vw	1.94	m	1.977	4
						2.34	mw	1.87	m		
						2.25	mw-b				
				2.17	w	2.15	mw				
				2.12	w	2.11	w				
				2.07	m	2.08	mw				
				2.00	m	2.02	s				
				1.990	w	1.995	m				
				1.946	m	1.945	s				

Intensities of the decomposition products are estimated visually.

380°C

600°C



Fig. 1. TG and DTA curves of $(NH_4)_4 UF_{10}$, as determined by a Mettler TA-1 thermoanalyser.

ratios and higher valency states tend to make these compounds increasingly less stable. The synthesis of $(NH_4)_4UF_{10}$ by oxidizing $(NH_4)_4UF_8$ with XeF₂ under very mild conditions is a new approach in the chemistry of these compounds, which in this case, using the proper starting compounds, overcame the problem of stability.

The powder diffraction data of $(NH_4)_4 UF_8$ from which $(NH_4)_4UF_{10}$ was prepared, of $(NH_4)_4UF_{10}$ itself and of its first proved decomposition product at 200°C, identified as $(NH_4)_3UF_8$, are of a similar kind (Table 1). Such a degree of similarity was already observed in some potassium, and also in sodium fluorouranates. It was suggested that variations in valency and coordination of the actinide ions may leave their positions virtually unchanged.⁵ Probably this is also happening in our case, particularly as the synthesis of $(NH_4)_4UF_{10}$ from $(NH_4)_4 UF_8$ occurs through a relatively mild fluorinating agent under mild conditions. Powder data of $(NH_4)_4 UF_{10}$ were indexed on the basis of a monoclinic unit cell. Its dimensions are similar to those⁹ of $(NH_4)_4 UF_8$ (Table 1), with the b axis significantly enlarged (by more than 25%).

 $(NH_4)_4 UF_{10}$ decomposes through three steps (at 200, 280 and 380°C) (Fig. 1) in which we could clearly identify the intermediate products by weight loss and powder data (Tables 1 and 2) and through a fourth at 600°C to UF₄. Additionally, we always noticed on the Mettler thermoanalyser an endothermic effect at ca 110°C, accompanied with a small weight loss, and the powder data at 110°C showed a mixture of $(NH_4)_4 UF_{10}$ and an unknown compound. Nevertheless, we were not able to isolate this intermediate, even by slowly decomposing $(NH_4)_4 UF_{10}$ in bulk. The actual decomposition path is not surprising. Uranium is reduced in the first step to a valency of V and in the third to IV. The N:U ratio diminishes from 4:1 to 3:1, 1:1 and in the last intermediate to 1:3. The 3:1 com-

		Calculated weight loss in %	Measured weight ^a loss in %		
	(NH ₄) ₄ UF ₁₀				
200°C	(NH₄)₃UF8	11.2	11.9		
280°C		26.0	27.5		

34.7

37.2

36.2

38.0

Table 3. Thermal decomposition of $(NH_4)_4 UF_{10}$

"Results of a Mettler TA-1 thermoanalyser.

 $(NH_4)U_3F_{13}$

ŬF₄

pound, $(NH_4)_3UF_8$, is known, and although its thermal decomposition was not investigated in detail, it has been observed⁹ that on heating it under certain conditions, $(NH_4)UF_6$ was obtained. This is in accordance with our decomposition path. But it has not yet been observed that $(NH_4)UF_6$ decomposes through an intermediate to UF_4 .¹² This last intermediate, $(NH_4)U_3F_{13}$, is identical with the last intermediate in the decomposition of $(NH_4)_4$ UF_{83} ⁷ where it was obtained from $(NH_4)UF_5$.

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