Synthesis and Characterization of a New Uranium(VI) Compound with a Co-ordination Number Larger than Eight, Ammonium Decafluorouranate(VI)

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Oxidation of $[NH_4]_4UF_8$ by XeF_2 gave a new compound, $[NH_4]_4UF_{10}$, for which Raman spectra indicate a co-ordination number larger than eight, and infrared spectra show moderate hydrogen bonding.

During our investigations of the reactions between xenon fluorides and hydrazinium or ammonium fluorometallates[1] we have synthesized a new compound which is, so far as we know, the first proven example of a compound of hexavalent uranium with a co-ordination number larger than eight (see for instance ref. 2).

$$[NH_4]_4UF_8 + nXeF_2 \xrightarrow[\text{Several hours}]{55\ ^\circ C} [NH_4]_4UF_{10} + Xe + n-1\ XeF_2 \quad (1)$$

Reaction (1) was carried out in an argon arc welded copper vessel equipped with a Teflon packed nickel valve. $[NH_4]_4UF_8$[3] was weighed (3—6 mmol) into the vessel and XeF_2[4] was added by sublimation. The volatile components pumped off after the reaction were pure xenon (pumped off at −80 °C), as shown by mass spectrometry, and XeF_2 (pumped off at room temperature), as shown by i.r. spectroscopy. The amount of xenon evolved was equivalent to the oxidation of U^{4+} to U^{6+} by XeF_2. No F_2 was evolved during the preparation. The white powdery solid product had analytical data in agreement with the formula $[NH_4]_4UF_{10}$ ($[NH_4]_4UF_8$ is green). It decomposes readily in air, changing its colour to green. All operations had to be performed in an argon flushed dry box. The compound is diamagnetic. Raman spectra of the samples in quartz capillary tubes were recorded in reflection geometry on a SPEX-1401 double monochromator with the 5682 Å exciting line of a Kr^+ laser, Coherent Radiation model CR-500 K. The spectra (Table 1) are different from the spectra of UF_6[5] and of known fluorouranates(VI)[6] (MUF_7 and M_2UF_8, M = Na^+, K^+, Rb^+, Cs^+, NH_4^+, and NO^+). The band assigned to the totally symmetric stretching vibration of the U–F bonds is the strongest band in the Raman spectra for all these compounds. Its position depends on the counter ion, oxidation state of the central atom, and on the co-ordination number.[7] Cation influence, which could be observed in both types of fluorouranates(VI)[6] (order of shifts is 10—25 cm^{-1}), is smaller than the bathochromic shifts caused by increasing co-ordination numbers, oxidation state being the same. Such a

Table 1. I.r. and Raman spectra[a] of $[NH_4]_4UF_{10}$, in cm^{-1}.

I.r.	Raman	Assignment	
	3230 (5)		NH_4^+
3180 vs,br.		ν_3	
	3106 (10)	ν_1	
3065 vs,br.		ν_3	
	2859 (3)	H-bond	
2870 s,br.			
	2855 (3)		
2362 vw		Overtone and combination bands	
2346 vw			
2105 w			
2000 w			
1810 vw			
	1697 (6)	ν_3	
1545 w—m			
1438 s			
	1417 (3)	ν_4	
	558 (100)	ν_s UF[b]	UF_{10}^{4-}
	494 (3)		
425 m,br.	428 (2)		
	325 (4)		
	270 (38)		

[a] Intensities of Raman bands are given in parentheses. Intensities of i.r. bands: s = strong, m = medium, w = weak, v = very, br. = broad.
[b] ν_s = totally symmetric stretching.

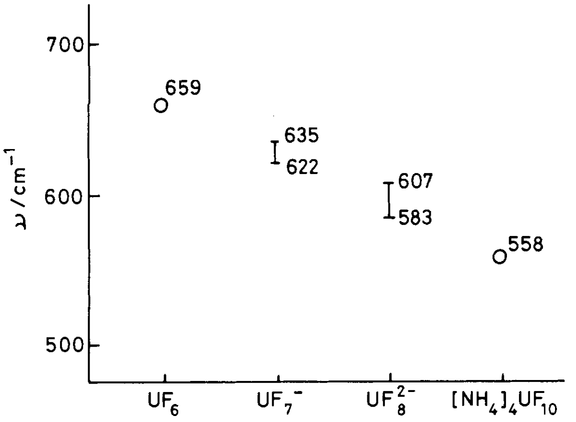

Figure 1. Position of the strongest Raman band, assigned to the totally symmetric stretching vibration of the U–F bonds in UF_6,[5] in the known fluorouranates MUF_7 and M_2UF_8,[6] and in $[NH_4]_4UF_{10}$.

distinct shift (Figure 1) can be understood only as the consequence of an increase in co-ordination number. We conclude, therefore, that the co-ordination number in this compound must be larger than eight.

I.r. spectra were obtained on Perkin-Elmer 521 (250—4000 cm^{-1}) and K. Zeiss UR-20 (400—4000 cm^{-1}) spectrophotometers with polyethylene and with AgCl windows in a leak tight brass holder. The sample was dusted in the dry-box on the windows or perfluorobutadiene mulls were prepared (paraffin oil rapidly reacted with the sample). Ammonium compounds show weak hydrogen bonds[8] with frequencies of the corresponding N–H stretching modes well above 3000 cm^{-1}. Only with fluoride ion does NH_4^+ seem able to form a moderately strong hydrogen bond which shifts the N–H absorption below 3000 cm^{-1} (NH_4F, $\nu_1 = 2970$ cm^{-1}, $\nu_3 = 2810\,cm^{-1}$).[9] The i.r. spectrum of $[NH_4]_4UF_{10}$ shows, besides very strong absorptions which are recognised as split ν_3, a strong band at 2870 cm^{-1}. The line width at half height of the N–H stretching absorption is 290 cm^{-1} in contrast to *ca.* 110 cm^{-1} for various halides,[9] which could be explained by disordering at room temperature. We may conclude, therefore, that polarization effects comparable to those in UF_7^- and UF_8^{2-} ions[6] take place, causing a distorted UF_{10}^{4-} ion with one of the fluorine atoms having significant ionic character.

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References

1 J. Slivnik, B. Žemva, M. Bohinc, D. Hanžel, J. Grannec, and P. Hagenmuller, *J. Inorg. Nucl. Chem.*, 1976, **38**, 997; B. Žemva, S. Milićev, and J. Silvnik, *J. Fluorine Chem.*, 1977, **9**, 251; 1978, **11**, 519, 545; B. Žemva and J. Slivnik, *ibid.*, 1981, **17**, 375; J. Slivnik, B. Družina, and B. Žemva, *Z. Naturforsch., Teil B*, 1981, **36**, 1457.

2 Gmelin Handbuch der Anorganischen Chemie, 'Uran,' Ergänzungsband C8, System-Nummer 55, Springer, 1980.

3 Synthesis of $[NH_4]_4UF_8$: R. Benz, R. M. Douglas, F. M. Kruse, and R. A. Penneman, *Inorg. Chem.*, 1963, **2**, 799.

4 Synthesis of XeF_2: A. Šmalc, K. Lutar, and J. Slivnik, *J. Fluorine Chem.*, 1975, **6**, 287.

5 J. Shamir and J. G. Malm, *J. Inorg. Nucl. Chem., Supplement*, 1976, 107.

6 R. Bougon, P. Charpin, J. P. Desmoulin, and J. G. Malm, *Inorg. Chem.*, 1976, **15**, 2532.

7 For example: A. Finch, P. N. Gates, K. Radcliffe, F. N. Dickson, and F. F. Bentley, 'Chemical Applications of Far Infrared Spectroscopy,' Academic Press, London, New York, 1970.

8 T. C. Waddington, *J. Chem. Soc.*, 1958, 4340; E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, 1950, **18**, 296, 305; G. L. Cote and H. W. Thompson, *Proc. R. Soc. London, Ser. A*, 1951, **210**, 217; P. Mathieu and H. Poulet, *Spectrochim. Acta*, 1960, **16**, 696.

9 R. C. Plumb and D. F. Hornig, *J. Chem. Phys.*, 1955, **23**, 947.