CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY,
ARGONNE, ILLINOIS

Fluoride Complexes of Uranium (IV). The Preparation of Fluorouranium(IV) Sulfates[1]

BY LAWRENCE STEIN, CLAYTON W. WILLIAMS, IRENE M. FOX, AND ELIZABETH GEBERT

Received October 20, 1965

Uranium(IV) is strongly complexed by fluoride in aqueous solutions, forming the cations UF^{3+}, UF_2^{2+}, UF_3^+. Spectral bands at 430, 485, 494, 549, 652, and 1130 mμ diminish greatly in intensity on the addition of HF to solutions of $U(SO_4)_2$; other bands are affected to a lesser degree. Perchlorate and sulfate solutions containing chiefly UF_2^{2+} exhibit spectra with vibrational fine structure in the region 400–650 mμ analogous to spectra of the oxygenated ions UO_2^{2+}, NpO_2^{2+}, NpO_2^+, PuO_2^{2+}. Intervals of approximately 400 cm^{-1} between several bands are ascribed to the symmetric uranium–fluorine vibration of UF_2^{2+} in excited electronic states. The complex salts $UFSO_4(HSO_4)\cdot 2H_2O$, $UF_2SO_4\cdot 2H_2O$, and $(UF_3)_2SO_4\cdot 4H_2O$ have been obtained by precipitation from aqueous and mixed aqueous–organic solutions. Infrared spectra and X-ray powder patterns of several phases are reported.

Introduction

When hydrofluoric acid is added to a solution of uranium(IV) sulfate, the color changes from dull green to bright blue-green. Previously this was ascribed[2,3] to the formation of the acid complex $H_2U(SO_4)_2F_2$ and its anion $U(SO_4)_2F_2^{2-}$. However, the same color change occurs in solutions of UCl_4, $U(NO_3)_4$, and $U(ClO_4)_4$ although chloride, nitrate, and perchlorate are much weaker complexing agents than sulfate for uranium(IV). It was suggested by workers at the Metallurgical Laboratory and the Clinton Laboratories[4] during the Manhattan Project that the blue-green species in solution was the UF_2^{2+} ion since it was known that two moles of hydrofluoric acid could be added per mole of uranium before a precipitate appeared and since evidence had been obtained for similar complex cations of thorium(IV) and plutonium(IV). Equilibrium constants for the formation or dissociation of UF^{3+}, UF_2^{2+}, UF_3^+, ThF^{3+}, ThF_2^{2+}, ThF_3^+, and PuF^{3+} have now been published.[5–10] Savage and Browne[5] report evidence for the existence of UF_5^- and UF_6^{2-} as well as cationic complexes. Recently Tananaev and Savchenko[11] prepared two uranium oxalates, $(UF)_2(C_2O_4)_3$ and $UF_2C_2O_4\cdot 1.5H_2O$, which probably contain the ions UF^{3+} and UF_2^{2+}, respectively. In the present article we describe the preparation of monofluoro-, difluoro-, and trifluorouranium(IV) sulfates. We also describe spectral changes produced by fluoride complexing of U(IV) in H_2SO_4 and $HClO_4$ solutions.

Experimental Section

Stock solutions of UO_2SO_4 were prepared by dissolving reactor grade uranium metal in 3 *M* H_2SO_4 containing small amounts of H_2O_2. The solutions were reduced electrolytically or with zinc amalgam and aerated to oxidize U(III) to U(IV).

Absorption Spectra.—Spectra of U(IV) complexed by fluoride in 1.0 *M* H_2SO_4 were obtained from 300 to 1300 mμ with a Cary Model 14 spectrophotometer. Dilute solutions were examined in a 1.00-cm nickel cell with sapphire windows; concentrated solutions were examined in a 2.0-mm Teflon cell with thin Kel-F windows. Similar cells containng 1.0 *M* H_2SO_4 were used in the reference beam. Figure 1 shows a series of curves obtained for solutions of constant uranium concentration (0.23 *M*) and increasing HF concentration.

Since sulfate complexes U(IV) to a moderate extent, the spectral changes were also studied in 1.0 *M* $HClO_4$ solutions, in which complexing by perchlorate is known to be negligible. Uranium(IV) hydroxide was precipitated from a sulfate solution with ammonia, washed thoroughly, and redissolved in 1.0 *M* $HClO_4$ to obtain a stock solution of $U(ClO_4)_4$. Figure 2 shows spectra of U(IV) complexed by increasing amounts of fluoride in perchloric acid solutions (1.0 *M* $HClO_4$ in the reference beam). The absorption bands are narrower and more intense, and the fine structure is more distinct than in the corresponding spectra in sulfate solutions.

Preparation of Compounds.—The difluorouranium salt $UF_2SO_4\cdot 2H_2O$ was prepared initially by adding 3 *M* HF slowly, with shaking, to a water–acetone or water–alcohol solution of 0.15 *M* $U(SO_4)_2$, 1.0 *M* H_2SO_4. (The organic component, 30 to 45% of the solution by volume, reduced the solubility of the complex salt.) A flocculent, pale green precipitate appeared with each addition of HF and coalesced into a dark green solid, which was collected, washed with acetone, and dried under vacuum at 200°. The compound prepared in this manner was amorphous (no structure discernible in X-ray power photographs). *Anal.* Calcd for $UF_2SO_4\cdot 2H_2O$: U, 58.32; F, 9.31; SO_4, 23.54; H_2O, 8.83. Found: U, 59.0, 59.2, 58.7; F, 10.0, 9.5, 9.3; SO_4, 23.8, 24.1, 25.2.

Attempts to prepare crystalline $UF_2SO_4\cdot 2H_2O$ by evaporation of aqueous solutions of low or moderate acidity were unsuccessful. Solutions of 0.45 *M* $U(SO_4)_2$, 1 to 3 *M* H_2SO_4, 0.9 *M* HF generally yielded mixtures of $U(SO_4)_2$ hydrate and complex salts when heated to 95°. On removal of the initial precipitate by centrifugation and on continued evaporation of the supernate at 95°, a second phase consisting of $UF_4\cdot H_2O$ was frequently obtained.

---

[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] G. O. Morris, U. S. Atomic Energy Commission Report BR-454A, June 1944.

[3] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," National Nuclear Energy Series, Division VIII, Vol. 5, Part 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp 358, 359.

[4] F. W. Schuler, F. L. Steahly, and R. W. Stoughton, U. S. Atomic Energy Commission Reports CC-3576, Aug. 1946, and TID-5223, 1952, Part 1, pp 307–317.

[5] A. W. Savage, Jr., and J. C. Browne, *J. Am. Chem. Soc.*, **82**, 4817 (1960).

[6] Yu. A. Luk'yanchev and N. S. Nikolaev, *At. Energ.* (U.S.S.R.), **13**, 179 (1962).

[7] H. W. Dodgen and G. K. Rollefson, *J. Am. Chem. Soc.*, **71**, 2600 (1949).

[8] R. A. Day, Jr., and R. W. Stoughton, *ibid.*, **72**, 5662 (1950).

[9] I. V. Tananaev and L. Chzao-Da, *Zh. Neorgan. Khim.*, **4**, 2122 (1959).

[10] J. C. Hindman, "The Actinide Elements," National Nuclear Energy Series, Division IV, Vol. 14A, G. T. Seaborg and J. J. Katz, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1954, pp 342–344.

[11] I. V. Tananaev and G. S. Savchenko, *At. Energ.* (U.S.S.R.), **12**, 392 (1962).

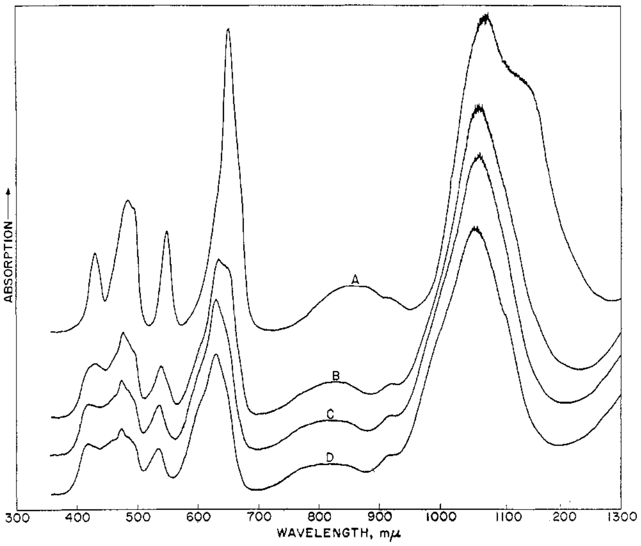


Figure 1.—Effect of fluoride complexing on absorption spectrum of 0.23 M U(IV) in 1.0 M H_2SO_4 (2.0-mm cell): A = 0.00; B = 0.20; C = 0.33; D = 0.40 M HF.

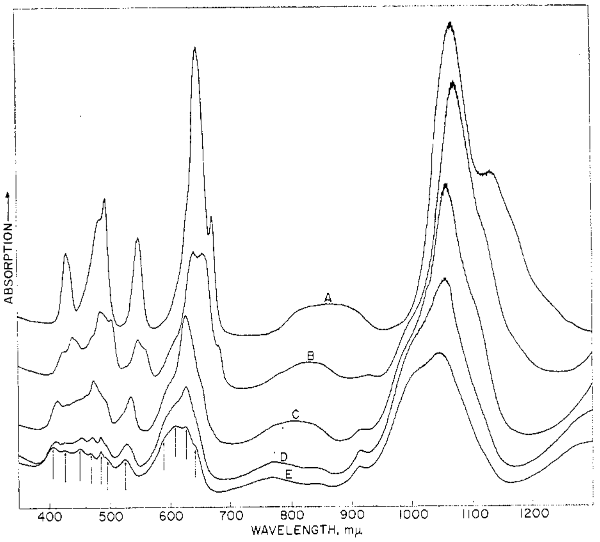


Figure 2.—Effect of fluoride complexing on absorption spectrum of 0.030 M U(IV) in 1.0 M $HClO_4$ (1.00-cm cell). Arrows indicate bands listed in Table III: A = 0.000; B = 0.020; C = 0.033; D = 0.053; E = 0.080 M HF.

Anal. Calcd for $UF_4{\cdot}H_2O$: U, 71.68; F, 22.89; H_2O, 5.43. Found: U, 71.4, 71.8, 71.6; F, 22.5, 22.8, 22.7.

The sulfuric acid concentration was increased to approximately 6 M and the solutions were allowed to stand at room temperature for several days. Microcrystalline $UF_2SO_4{\cdot}2H_2O$ was then obtained. The bright green salt was washed with acetone and dried at 110°. *Anal.* Found: U, 58.0; F, 8.4; SO_4, 24.1.

The monofluorouranium salt $UFSO_4(HSO_4){\cdot}2H_2O$ was prepared by cooling a hot solution of 0.044 M $U(SO_4)_2$, 9 M H_2SO_4, and 0.2 M HF. Iridescent green crystals which separated were washed with acetone and dried at 110°. *Anal.* Calcd for $UFSO_4(HSO_4){\cdot}2H_2O$: U, 48.96; F, 3.91; SO_4, 39.52, H, 0.21; H_2O, 7.41. Found: U, 48.8; F, 3.3, 3.4; SO_4, 39.4, 39.2.

Amorphous $(UF_3)_2SO_4{\cdot}4H_2O$ was prepared by adding 3 M HF to a solution of 0.2 M $U(SO_4)_2$ and 3 M H_2SO_4, to the appearance of a precipitate. This was washed with acetone and dried at 110°. Blue-green crystals of the salt were also obtained by slowly evaporating at room temperature a solution of 0.2 M $U(SO_4)_2$ and 3 M H_2SO_4, saturated with HF. The crystals were blotted on filter paper and dried at 110°. *Anal.* Calcd for $(UF_3)_2SO_4{\cdot}4H_2O$: U, 62.79; F, 15.04; SO_4, 12.67; H_2O, 9.50. Found: U, 62.5, 62.5, 62.6; F, 14.2, 15.5, 15.5; SO_4, 11.9, 12.2, 12.2.

TABLE I

X-RAY POWDER PATTERNS

$UFSO_4(HSO_4){\cdot}2H_2O$		$UF_2SO_4{\cdot}2H_2O$		$(UF_3)_2SO_4{\cdot}4H_2O$		$UF_4{\cdot}H_2O$	
d, A	I_0	*d*, A	I_0	*d*, A	I_0	*d*, A	I_0
5.6590	vvw	8.1160	s	3.8525	s	4.4001	vvw
5.2968	ft	7.8643	m	3.5062	m	4.2288	m
4.9264	ft	5.7904	vvw	3.0443	ft	4.0589	w
4.6890	m	5.1998	vvw	2.9297	ft	3.6513	mw
4.5022	ft	4.9548	mw	2.7938	ft	3.5422	vw
4.2776	ft	4.6703	vvw	2.7078	ft	3.4562	ft
4.1280	vw	4.3848	w	2.6152	ft	3.3272	vvw
3.9118	vvw	4.0580	vvw	2.4631	ft	3.0605	vvw
3.8275	vvw	3.8830	m	2.2959	ft	2.8570	ft
3.6461	ft	3.7615	mw	2.0509	m	2.8152	w
3.3160	m	3.6329	ms	1.9860	m	2.6996	ft
3.2337	ft	3.3631	w	1.9502	m	2.2967	ft
2.9668	ft	3.2258	vw	1.8814	w	2.1179	ft
2.7036	s	3.1048	vvw	1.8484	ft	2.0810	w
2.6138	w	3.0027	ft	1.7448	ft	2.0072	m
2.4765	ft	2.9073	vvw	1.4453	ft	1.9770	ft
2.4055	ft	2.8709	vvw	1.3954	ft	1.9295	vw
2.3461	ft	2.7838	ft	1.3172	ft	1.8906	vvw
2.0420	ft	2.7342	ft			1.8674	vvw
1.9803	ft	2.5957	m			1.8121	ft
1.9397	w	2.3587	ft			1.7644	ft
1.9093	ft	2.2728	w			1.7232	ft
1.8593	ft	2.1009	m			1.6804	ft
1.7889	ft	2.0164	vvw				
1.7300	vw	1.9933	vvw				
1.7054	vvw	1.9428	w				
1.5870	ft	1.9273	vvw				
1.4941	vvw	1.8877	vvw				
1.4284	w	1.8412	vvw				
1.3960	ft	1.8087	ft				
1.3715	ft	1.7397	w				
1.3501	ft	1.6778	w				
		1.6500	ft				
		1.6103	ft				
		1.5849	ft				
		1.5570	ft				
		1.4999	ft				
		1.4546	ft				
		1.4386	ft				
		1.4030	vw				
		1.3678	ft				
		1.3364	ft				

With the exception of uranium, all chemicals were of reagent grade. Vessels used to contain fluoride solutions or solid products were made of polyethylene, polypropylene, or platinum.

Analytical Methods.—Uranium in the complex salts was determined gravimetrically as the oxide. Uranium(IV) hydroxide was precipitated from solutions of the salts with ammonia, washed, and ignited to U_3O_8. The percentage of uranium was also determined in several instances by passing solutions through a lead reductor and titrating U(IV) to U(IV) with ceric sulfate. Sulfate was determined gravimetrically as $BaSO_4$ or by a compleximetric method with ethylenediaminetetraacetic acid.[12] Fluoride was precipitated and weighed as PbClF or separated from interfering ions by Willard–Winters distillation and titrated with $Th(NO_3)_4$, using alizarin red indicator.

The $UF_4{\cdot}H_2O$ samples were analyzed by pyrohydrolysis.[13] Distillate was collected in a polyethylene flask and titrated with standard base. Uranium was determined by weighing the U_3O_8 residue.

Crystallographic Data.—Table I lists lines and intensities of

---

(12) K. F. Sporek, *Anal. Chem.*, **30**, 1032 (1958).

(13) J. C. Warf, "Analytical Chemistry of the Manhattan Project," National Nuclear Energy Series, Division VIII, Vol. 1, C. J. Rodden, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp 728–731.

X-ray powder patterns which were obtained for $UFSO_4(HSO_4)\cdot 2H_2O$, $UF_2SO_4\cdot 2H_2O$ (from 6 *M* sulfuric acid), $(UF_3)_2SO_4\cdot 4H_2O$, and $UF_4\cdot H_2O$. Photographs were taken with a 9-cm Bradley-Jay camera, using copper $K\alpha$ radiation. Thus far, we have indexed only the pattern of $UFSO_4(HSO_4)\cdot 2H_2O$, which is orthorhombic, $a_0 = 17.11 \pm 0.10$ A, $b_0 = 9.38 \pm 0.03$ A, $c_0 = 9.91 \pm 0.03$ A. Our films for $UF_4\cdot H_2O$ have been compared with those of Zachariasen[14] and appear to be the same. Dawson, D'Eye, and Truswell[15] report that the structure is pseudo-cubic, with $a = 5.69$ kX. However, we observe several low-angle reflections which cannot be indexed for this unit cell.

Infrared Spectra.—The compounds were pressed into disks with KBr powder and examined from 300 to 4000 cm^{-1} with a Beckman IR-10 spectrophotometer. Several samples were also examined as Nujol and fluorocarbon mulls, with no significant changes in the spectra. The absorption bands and probable assignments are given in Table II. (Vibration modes for sulfate groups are designated for T_d symmetry; actual symmetry may be lower.)

TABLE II

INFRARED SPECTRA OF SOLIDS[a]

	$UFSO_4(HSO_4)\cdot 2H_2O$	$UF_2SO_4\cdot 2H_2O$	$(UF_3)_2SO_4\cdot 4H_2O$	$UF_4\cdot H_2O$
H_2O stretch	3400 s, b	3400 s, b	3400 s, b	3400 s, b
H_2O bend	1625 m	1625 m	1625 m	1625 m
SO_4, ν_3	1070 vs, b	1100 vs, b	1130 s	. . .
	1200 sh			
SO_4, ν_4	640 sh	640 sh	650 sh	. . .
	625 m	. . .	. . .	. . .
	585 m	590 m	600 m	. . .
SO_4, ν_2	440 w	. . .	. . .	. . .
U–F stretch	340 w	380 m	390 s, b	400 vs, b

[a] vs, very strong; s, strong; m, medium; w, weak; b, broad; sh, shoulder.

Discussion

Fluoride complexing of U(IV) in 1 *M* H_2SO_4 causes bands at 430, 485, 495, 549, 652, and 1130 mμ to drop sharply in intensity (Figure 1). Bands at 870 and 1075 mμ decline more slowly, and a weak band at 915 mμ grows in intensity.

Tananaev and Savchenko[16] report an initial increase in the optical density of a band at 620 mμ and a decrease in the optical density of a band at 520 mμ. Probably these correspond to our 652- and 549-mμ bands, respectively, which decrease continuously with increasing fluoride concentration.

The initial spectrum which we observe for U(IV) in 1 *M* $HClO_4$ is very similar to that observed by Cohen and Carnall[17] in 1 *M* $DClO_4$. Fluoride complexing causes bands at 430, 485, 495, 549, 648, 670, and 1132 mμ to drop rapidly (Figure 2). Bands at 870 and 1070 mμ decrease more slowly, and new bands appear at 915 and 1005 mμ. In both 1 *M* H_2SO_4 and 1 *M* $HClO_4$ the final spectrum (before appearance of a precipitate) can be assumed to be chiefly that of the UF_2^{2+} ion; UF^{3+} and UF_3^+ ions are also present, but at much lower concentrations.

A striking feature of the UF_2^{2+} spectrum in both acids, but particularly in $HClO_4$, is the fine structure of the bands between 400 and 650 mμ. Oxygenated ions, such as UO_2^{2+}, NpO_2^+, NpO_2^{2+}, and PuO_2^{2+}, exhibit spectra with similar fine structure produced by metal–oxygen vibrations.[18–22] The average spacing between bands ranges from 657 to 753 cm^{-1} for the oxygenated ions, corresponding to symmetric vibrations of the ions in excited electronic states. In Table III, we list the differences in wavenumbers of successive bands of UF_2^{2+} in 1 *M* $HClO_4$ from 405 to 642 mμ. Three intervals of approximately 400 cm^{-1} and two of approximately 800 cm^{-1} may be noted. It is highly probable that these are fundamental and second harmonic frequencies produced by the symmetric uranium–fluorine vibration of UF_2^{2+} in excited electronic states. In the infrared spectrum of solid $UF_2SO_4\cdot 2H_2O$, the asymmetric vibration is observed (for the ground state) at approximately 380 cm^{-1}.

TABLE III

FINE STRUCTURE IN ABSORPTION BANDS OF UF_2^{2+} IN 1 *M* $HClO_4$

λ, mμ	Wavenumber, cm^{-1}	Δ(wavenumber), cm^{-1}
405	24,690	
426	23,470	1220
452	22,120	1350
469	21,320	800
486	20,580	740
495	20,200	380
525	19,050	1150
590	16,950	2100
610	16,400	550
626	16,000	400
642	15,600	400

Since fluoride is labile in the complexes and transformations occur among UF^{3+}, UF_2^{2+}, and UF_3^+, the analogy of these to the more stable oxygenated ions is not perfect. However, it can be noted that the spectrum of UF_2^{2+} (Figure 2) resembles the spectra of NpO_2^+ and PuO_2^{2+} more closely than does that of uncomplexed U^{4+}. The species U(IV), Np(V), and Pu(VI) all have $5f^2$ electron configurations. The enhanced resemblance of the UF_2^{2+} spectrum to spectra of NpO_2^+ and PuO_2^{2+} is attributed both to the vibrational fine structure and to perturbations of the 5f energy levels by the fluoride ligands.

The infrared spectra of all of the solid compounds have bands due to lattice water at 3200–3600 and 1625 cm^{-1}. The sulfate ν_3 band at approximately 1100 cm^{-1} is very broad in $UFSO_4(HSO_4)\cdot 2H_2O$ and becomes progressively narrower in $UF_2SO_4\cdot 2H_2O$ and $(UF_3)_2SO_4\cdot 4H_2O$. The shoulder at 1200 cm^{-1} and the ν_2 band at 440 cm^{-1} in the spectrum of $UFSO_4(HSO_4)\cdot 2H_2O$ are probably due to the presence of the bisulfate group.[23]

---

(14) W. H. Zachariasen, U. S. Atomic Energy Commission Report ANL-4166, 1948.

(15) J. K. Dawson, R. W. M. D'Eye, and A. E. Truswell, *J. Chem. Soc.*, 3922 (1954).

(16) I. V. Tananaev and G. S. Savchenko, *At. Energ.* (U.S.S.R.), **12**, 397 (1962).

(17) D. Cohen and W. T. Carnall, *J. Phys. Chem.*, **64**, 1933 (1960).

(18) E. Rabinowitch and R. L. Belford, "Spectroscopy and Photochemistry of Uranyl Compounds," The Macmillan Co., New York, N. Y., 1964, pp 1–183.

(19) M. Kasha, *J. Chem. Phys.*, **17**, 349 (1949).

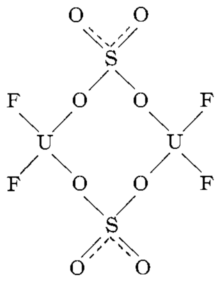
(20) R. E. Connick, M. Kasha, W. H. McVey, and G. E. Sheline, "The Transuranium Elements," National Nuclear Energy Series, Division IV, Vol. 14B, Part 1, G. T. Seaborg, J. J. Katz, and W. M. Manning, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1949, pp 590, 591.

(21) R. Sjoblom and J. C. Hindman, *J. Am. Chem. Soc.*, **73**, 1744 (1951).

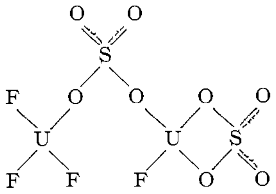
(22) R. H. Betts and B. G. Harvey, *J. Chem. Phys.*, **16**, 1089 (1948).

(23) G. E. Walrafen, D. E. Irish, and T. F. Young, *ibid.*, **37**, 662 (1962).

Evidence for coordination of sulfate to uranium has been obtained in several spectra of $UF_2SO_4 \cdot 2H_2O$ and $(UF_3)_2SO_4 \cdot 4H_2O$. The difluorouranium salt obtained from acetone–water solutions has the spectrum shown in Table II, in which the sulfate appears to be present as the free ion (T_d symmetry). However, the salt of composition $UF_2SO_4 \cdot 2H_2O$ obtained from 6 M H_2SO_4 has a more complex spectrum with the following features: lattice water bands at 3400 and 1625 cm^{-1}; a band of medium intensity at 1680 cm^{-1}, origin unknown; ν_3 split into multiplets at 1270, 1180, 1065, 1020, and 965 cm^{-1} (the last band may be ν_1, normally forbidden); ν_4 at 640 and 590 cm^{-1}; ν_2 at 440 cm^{-1}; U–F stretching band at 340 cm^{-1}. Two simple structures can be postulated for coordinated salts which might exhibit this spectrum. The most probable is a cyclic dimer with two bridging sulfate groups

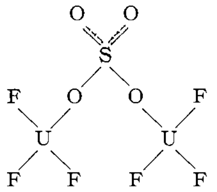


It is also possible that monofluorouranium and trifluorouranium groups are present rather than two difluorouranium groups in a molecule containing a bridging sulfate and a second bidentate sulfate



Although the chemical equilibria do not permit UF^{3+} and UF_3^+ to coexist at high concentrations simultaneously in solution, each of the ions may be much less soluble than UF_2^{2+} in 6 M H_2SO_4 and may well appear in the solid phase. However, a molecule of this type should have different U–F stretching frequencies for the monofluorouranium and trifluorouranium groups. Since only one band is observed at 340 cm^{-1}, this structure is less probable than the first structure.

In addition to the normal spectrum of $(UF_3)_2SO_4 \cdot 4H_2O$ shown in Table II, we have obtained spectra for this compound in which ν_3 is split into a prominent doublet, 1100 and 1150 cm^{-1}, with a weak shoulder at approximately 1220 cm^{-1}. Forbidden frequency ν_1 then appears as a sharp spike at 990 cm^{-1}. We ascribe this spectrum to a coordinated compound with a bridging sulfate group



Previous investigators seem to have encountered at least two of the compounds which we describe here without recognizing their complex nature. Morris[2] reports analyses corresponding to $UF_2SO_4 \cdot 2H_2O$ which are attributed to an equimolar mixture of $UF_4 \cdot H_2O$ and $U(SO_4)_2 \cdot 4H_2O$. Tananaev and Savchenko[16] state that the addition of excess HF to a solution of $U(SO_4)_2$ produces only $UF_4 \cdot 2.5H_2O$, whereas we note that the initial precipitate always contains sulfate which is not removed by washing with acetone. Frequently, a mixture of $(UF_3)_2SO_4 \cdot 4H_2O$ and UF_4 hydrate is obtained. The complex trifluorouranium salt is indistinguishable from UF_4 hydrate in appearance but is much more soluble in water and dilute acids. If such a mixture is washed with water or acid, the $(UF_3)_2SO_4 \cdot 4H_2O$ dissolves, leaving only UF_4 hydrate as a residue.

All three complex salts are soluble in dilute H_2SO_4, HCl, HNO_3, and $HClO_4$, insoluble in acetone or alcohol. The range of solution composition in which each salt is stable in the quaternary system $U(SO_4)_2$–H_2SO_4–HF–H_2O is very small. In this respect the compounds resemble double salts which decompose readily to simple salts on dilution of the supernatant solutions.[24] We have examined the solid phases in only a small range of $U(SO_4)_2$, H_2SO_4, and HF concentrations. Probably a number of other compounds exists in the system.

In several preliminary experiments, sulfates of fluoride-complexed thorium(IV) and protactinium(IV) have also been prepared. These appear to be analogs of the uranium compounds. The similarity of the fluoride complexes of quadrivalent thorium, protactinium, uranium, neptunium, and plutonium leads us to expect each of these to form a series of compounds, not only with sulfate, but with chloride, bromide, iodide, nitrate, perchlorate, and other anions, in appropriate solvent systems.

Acknowledgment.—We are greatly indebted to D. Cohen for a supply of redistilled perchloric acid and to W. H. Zachariasen and A. Plettinger for allowing us to examine many X-ray powder patterns of uranium fluorides in their files.

---

(24) A. Findlay and A. N. Campbell, "The Phase Rule and Its Applications," 8th ed, Dover Publications, New York, N. Y., 1945, pp 249–255.