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Crystal Structures of α-UF_5 and U_2F_9 and Spectral Characterization of U_2F_9

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Crystals of α-UF_5 and the mixed-valence compound U_2F_9 have been obtained from the reaction of sulfur dioxide and uranium hexafluoride at 160 °C. The structures have been refined by single crystal X-ray methods. In accordance with conclusions of previous powder determinations, we find a six-coordinate chain structure for α-UF_5 (U–F (bridging) = 2.235(1), U–F (non-bridging) = 1.995(7) Å) and a nine-coordinate, three-dimensionally bridged structure for U_2F_9 (U–F = 2.19(2)–2.40(2) Å). Absorption spectral studies of U_2F_9 indicate no unusual oxidation state for uranium; U(IV) and U(V) are present. The principal structural disparity between earlier structure determinations and our study is the finding of a U–F (non-bridging) distance of 1.995(7) Å for α-UF_5, more than 0.2 Å shorter than the earlier estimate but in good accord with recent bond length–bond strength considerations. Cell data: α-UF_5, I4/m, Z = 2, a = 6.518(4), c = 4.470(1) Å, R = 0.022 for 161 reflections with $I \geqslant 2\sigma(I)$; U_2F_9, $I\bar{4}3m$, Z = 4, a = 8.462(2) Å, R = 0.032 for 104 reflections with $I \geqslant 2\sigma(I)$.

Introduction

The binary uranium–fluorine system is one of surprising complexity. Presently five single-valence (oxidation states +3 to +6, including two forms of UF_5) [1–5] and four mixed-valence (oxidation states +4.25 to +4.50 [6–11] uranium fluoride crystal structures are reported. These are summarized in Table I. Although uranium fluorides have been studied intensively for more than thirty years because of their great industrial importance, many important physicochemical questions remain unanswered, and the field is still a very active research area [12–15].

TABLE I. Known Uranium Fluorides and their Structures.

	Structure	Ref.
UF_3	9-coordinate, three dimensionally bridged	1
UF_4	8-coordinate, three dimensionally bridged	2
α-UF_5	6-coordinate, chain structure	^{a}
β-UF_5	8-coordinate, three dimensionally bridged	3, 4
UF_6	6-coordinate, monomeric	5
U_2F_9	9-coordinate, three dimensionally bridged	^{b}
U_3F_{13}	? ^{c}	9
U_4F_{17}	? ^{c}	11
U_5F_{22}	?	10

^{a}Present study. See also Ref. 3. ^{b}Present study. See also Refs. 6, 7, and 17. ^{c}'U_4F_{17}' may, in fact, be U_3F_{13}. Ref. 9.

Recently we investigated the known redox reaction of uranium hexafluoride and sulfur dioxide [16], and fortuitously obtained excellent single crystals of α-UF_5 and U_2F_9. Structures of both fluorides were deduced by X-ray powder methods in the 1940s by W. H. Zachariasen, and later U_2F_9 was determined by neutron powder methods with further structural interpretation by Taylor [3, 6, 7, 17]. However, single crystals of sufficient quality for X-ray single crystal measurements apparently have not been obtained before, and thus details of the structures have remained in doubt. Because of the availability of suitable crystals and the continuing interest in uranium–fluorine chemistry, we considered the structures of α-UF_5 and U_2F_9 to be of sufficient interest to warrant their refinement by single-crystal methods. Our structural results for α-UF_5 and U_2F_9 are reported herein, together with a spectral characterization of U_2F_9.

Experimental

Synthesis of α-UF_5 and U_2F_9 Single Crystals

The method follows the procedure used by Moncelon *et al.* [16] to reduce UF_6 with SO_2. A 500

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TABLE II. X-ray Data Collection Description.

Formula	*α-UF_5*	*U_2F_9*
Systematic Absences	h + k + l = 2n + 1	h + k + l = 2n + 1
Space Group	I4/m	I$\bar{4}$3m
ρ_{calc} (g/cm^3)	5.823	7.091
a (Å)	6.518(4)	8.462(2)
c (Å)	4.470(1)	–
λ (Å)	0.70930	0.7930
Z	2	4
Temperature (°C)	22 ± 3	22 ± 3
Base scan width (°)	2.0	2.0
θ_{min}, θ_{max} (°)	2, 60	2, 60
Take-off Angle (°)	3.0	3.0
Transmission Coefficients	0.124–0.191	0.050–0.140
No. Reflections Collected	617 in the hemisphere (+h, ±k, ±l)	1865 in the hemisphere (±h, ±k, +l)
No. Reflections with $I \geqslant 2\sigma(I)$	161	104
R Factor on Averaging Equivalent Reflections	0.047	0.170
μ(cm^{-1})	523	802
Crystal Dimensions (mm)	0.040 × 0.040 × 0.280	0.050 × 0.050 × 0.050
Crystal Faces	{110}, {001}	(100), ($\bar{1}$00), (010), (0$\bar{1}$0), (00$\bar{1}$), (015)
Cell Parameter Refinement Data	12 reflections with $40° \leqslant 2\theta \leqslant 49°$	12 reflections with $40° \leqslant 2\theta \leqslant 41°$
Diffractometer	Computer controlled Picker FACS I equipped with graphite monochromater	Computer controller Picker FACS I equipped with graphite monochromater
R, R_w	0.022, 0.021	0.032, 0.031

mL flask was evacuated and then filled with 160 torr of SO_2 and 80 torr of UF_6. The flask was sealed and heated in an oven at 150–160 °C for 8.5 hr. On cooling, the flask wall was found to be coated by a mixture of a white, sugary powder (shown by X-ray powder photographs to be principally α-UF_5) and a smaller yield of black, cubic crystals of U_2F_9 (up to 100 μm on an edge). Also, a mass of blue-white needles (up to 3 cm in length) of α-UF_5 was present (0.50 g, 70% yield). A small amount of unreacted UF_6 was also present in the flask, indicating the reaction had not gone entirely to completion during the time of reaction. Powdered U_2F_9 was prepared by heating an intimate 1:1 molar ratio of UF_4:UF_5 at 190 °C for 48 hours.

X-Ray Data Collection

Details of the data collection procedure are given in Table II and previous publications [18]. The U_2F_9 crystals were stable in dry air for at least several months and were simply mounted on a glass fiber with Epoxy cement. The α-UF_5 crystals were too reactive to be handled in air or under mineral oil, but they could be handled and examined briefly under carefully dried fluorolube oil. A single crystal was selected and sealed in a nitrogen-filled, thin-walled glass capillary.

Preliminary ω-scans were examined for both data crystals to ensure the presence of high-quality single crystals. Crystal decomposition during data collection amounted to less than 3% for U_2F_9 and to about 25% for the reactive α-UF_5. Appropriate corrections were applied by a least-squares polynomial procedure as previously described [18]. A limited 2θ hemisphere of data, with each cell dimension doubled, was collected for each crystal to verify the lattice-type deduced from powder patterns. For each crystal, a full hemisphere of data was collected and redundant reflections were averaged in order to verify the cell symmetry and systematic absences and to minimize errors in the large absorption corrections.

Structure Refinement

Refinement procedure details were generally as described previously [18]. Patterson functions were computed for both U_2F_9 and α-UF_5 to check consistency with the previously proposed structures, and then least-squares refinement was carried out to convergence. Final difference Fourier syntheses were computed, and no features were found that were indicative of misplaced (or missing) atoms in the structures. The occurrence of some highly anisotropic thermal ellipsoids is probably due to inaccuracies in absorption corrections for these highly absorbing crystals. Refined atomic parameters are given in Table III.

Spectral Characterization of U_2F_9

Over the spectral range 300 to 1100 nm, absorption spectra of small U_2F_9 crystals, prepared as

TABLE III. Positional and Thermal Parameters.

α-UF_5	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0.0000	0.0000	0.0000	0.0115(2)	0.0115(2)	0.0069(3)	0.0000	0.0000	0.0000
F1	0.0000	0.0000	0.5000	0.015(2)	0.015(2)	0.009(4)	0.0000	0.0000	0.0000
F2	0.285(1)	0.113(1)	0.0000	0.015(1)	0.019(1)	0.032(3)	–0.006(2)	0.0000	0.0000

U_2F_9	x	y	z	β_{11} or β	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0.1877(2)	0.1877(2)	0.1877(2)	0.0018(1)	0.0018(1)	0.0018(1)	–0.0003(3)	–0.0003(3)	–0.0003(3)
F1	0.2087(18)	0.2087(18)	0.4447(29)	0.008(3)	0.008(3)	0.015(4)	0.000(6)	0.004(4)	0.004(4)
F2	0.00000	0.00000	0.2216(5)	0.003(2)	0.003(2)	0.013(5)	0.005(5)	0.0000	0.0000

described above, were obtained by the use of a microscope-spectrophotometer [19]. For spectral studies over a wider range, 200 to 2000 nm, reflectance spectral measurements of powdered U_2F_9 were made using a reflectance attachment and vacuum-tight sample holder of local design [20] which was used with a Cary Model 14 Recording Spectrophotometer.

Discussion

The structures of α-UF_5 and U_2F_9 are illustrated in Figs. 1 and 2, and selected interatomic distances and angles are given in Table IV.

The structure of α-UF_5 consists of UF_6 octahedra bridged by *trans*-fluorides [U–F = 2.235(1) Å] to give an infinite linear chain parallel to the *c*-axis. The remaining four fluorines in each octahedron are bound to only one uranium (U–F = 1.995(7) Å). The F–U–F angles within each octahedron are specified to be exactly 90° by the 4/m crystallographic symmetry, and the UF_6 octahedra are separated by normal non-bonding F–F separations of 2.8–3.7 Å.

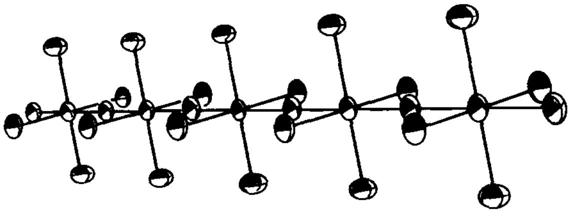

Fig. 1. A view of the structure of α-UF_5. The tetragonal axis is along the chain.

The overall structure agrees with that inferred by Zachariasen by X-ray powder methods in 1949, except for placement of the non-bridging fluorine. Our refined value of 1.995(7) Å is much shorter than Zachariasen's value of 2.18 Å and is much more in line with modern, accurately determined fluoride structures [12]. The observed U–F distances are in excellent agreement with values calculated, 1.988 (bond strength 1.00) and 2.265 (bond strength 0.50) using recent bond length-bond strength correlations [21].

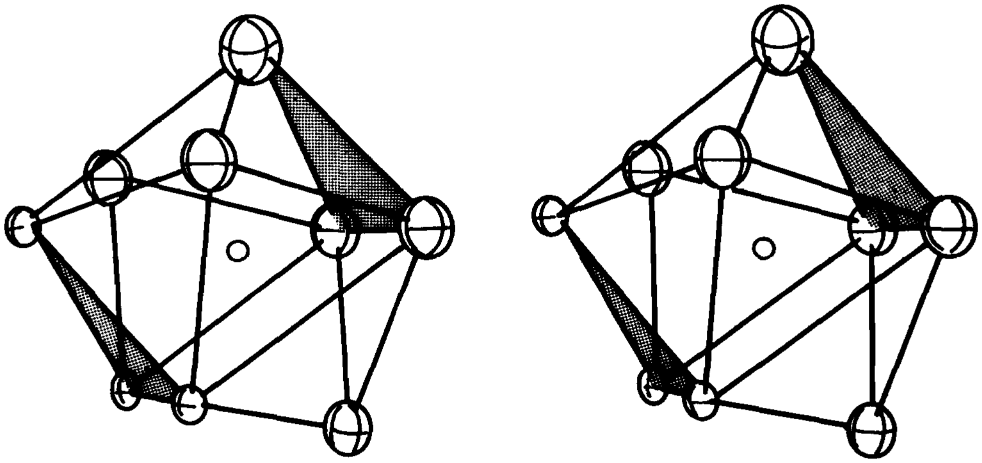

Fig. 2. A stereoview of the central coordination unit of U_2F_9. The three-fold axis passes through the shaded end faces of the tricapped trigonal prism.

TABLE IV. Interatomic Distances (Å) and Angles (°).

α-UF_5			
U–F1	2.235(1)		
U–F2	1.995(7)		
F1–F2	2.888(7), 2.996(4)		
F2–F2	2.82(1), 2.897(8), 3.166(9), 3.171(2)		
U_2F_9			
U–F1	2.37(2), 2.21(2)	F1–U–F1	119.5(1), 71.2(3)
U–F2	2.266(3)		
F1–F1	2.67(3), 2.85(4)	F1–U–F2	67.0(5), 128.4(9)
F1–F2	2.57(2), 3.15(3)		

The transformation from the low temperature phase of uranium pentafluoride, β-UF_5, to α-UF_5 is reported to occur at about 120 °C [22], but the α-form clearly has considerable kinetic stability since our samples can be stored for months (at least) and cooled to liquid nitrogen temperature with no noticeable change. However, in our hands, α-UF_5 is notably more reactive to air and other agents than the β-form, consistent with the more open structure and reduced coordination number at uranium of the α-form (α-UF_5 is some 10% less dense than β-UF_5 and β-UF_5 has a three-dimensionally bridged eight-coordinate structure).

The structure of U_2F_9 consists of a three-dimensionally bridged polymer composed of tricapped trigonal prismatic UF_9 units, as previously described [17]. The coordination units are aligned along body diagonals of the unit cell, with 3m symmetry at uranium. All fluorides in the structure are involved in bridging, with U–F distances [2.19–2.40 Å (avg. 2.28 Å)] intermediate to the range reported in the X-ray and neutron powder studies [3, 6, 7].

Since all the uraniums in the structure are crystallographically identical, U_2F_9 is either an intervalence material, or it has a statistical distribution of equal numbers of U(IV) and U(V) throughout the lattice. According to Zachariasen's bond length–bond strength formalism, with the assumption of nine equivalently bonded fluorides, the U(IV)–F and U(V)–F bond distances should be 2.326 and 2.223 Å, respectively, *i.e.*, bracketing the average value (2.28 Å) found in the present structure. The average U–F distance observed in KU_2F_9, which also has a tricapped trigonal prismatic coordination, is 2.322 Å, in excellent agreement with the U(IV)–F value [23]. Alternatively, one may calculate individual bond strengths (from the nine observed bond lengths), sum to give the overall valence, and compare with the average valence, *i.e.*, 4.5. The values thus obtained are 4.374 for U(IV) and 4.533 for U(V), and here again the range of U–F distances indicates a compromise of values expected for U(IV) or U(V). However, a shift in the average U–F distances of only a few hundredths of an angstrom (nearly the resolution of the present structure) would suffice for good agreement with either the expected U(IV)–F or U(V)–F distances. The structure determination, therefore, does not positively discriminate between the intervalence and disorder possibilities for U_2F_9.

A more definitive description of U_2F_9 is obtained from optical spectroscopy. The reflectance spectra of U_2F_9 and a physical mixture of equal parts of UF_4 and β-UF_5 are shown in Fig. 3. Over the spectral range where comparisons could be made, identical spectra were obtained for the transmission spectrum of a U_2F_9 crystal and the reflectance spectrum of U_2F_9 powder. It can be seen from Fig. 3 that, except for minor shifts of absorption peaks probably due to differences in coordination (U in both UF_4 and β-UF_5 is 8-coordinate, whereas in U_2F_9 it is 9-coordinate), the spectrum of U_2F_9 is as would be expected for a mixture of U(IV) and U(V). No spectral characteristics ascribable to any unusual oxidation state of uranium are seen. One can postulate that the different crystal structure seen for U_2F_9 is not the result of any intermediate oxidation state of uranium.

Although air stability is noted for U_2F_9 single crystals, the powdered U_2F_9 product reacts with air and/or water vapor within 24 hrs at humidity levels greater than 50%. This reaction caused the dark U_2F_9 to change color to green, ultimately yielding a spectrum attributable to U(IV), possibly UOF_2.

A comment is in order regarding the procedure used to prepare the crystals used in this study. We carried out the reaction because we were surprised at reports that SO_3, normally considered a good oxidizing agent, reduces UF_6 within seconds, while the reduction of UF_6 with SO_2, normally a good reducing agent, fails to go to completion even after many hours at 200 °C [8, 16]. Our studies have verified these observations, and we conjecture that the Lewis-acidity of the reductant (SO_3 or SO_2) is a more important factor than its reduction potential in determining the rate of reaction. A preliminary step

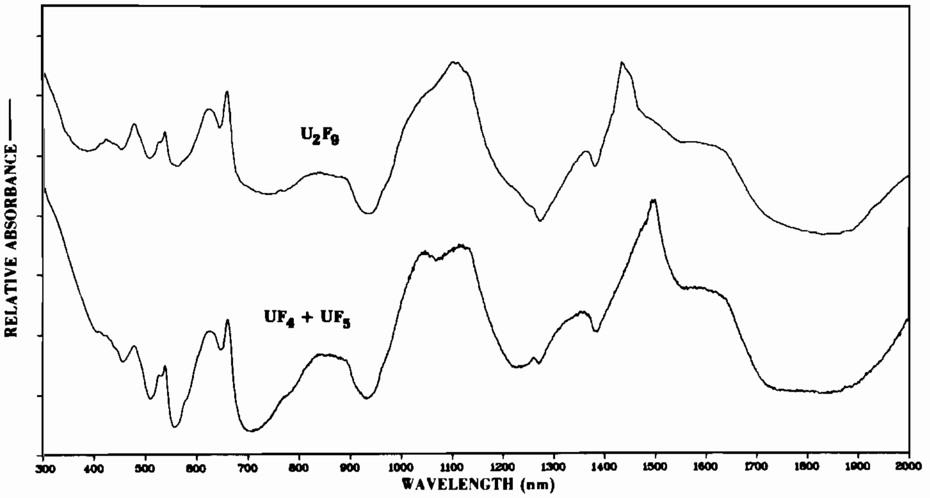

Fig. 3. The reflectance spectra of U_2F_9 powder and of an intimate UF_4/β-UF_5 mixture (equal parts).

to the actual metal reduction might be acid–base reaction with a uranium-coordinated fluoride, a reaction which should be more favored for SO_3 than the poorer Lewis-acid SO_2.

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