Hydrothermal Synthesis of $(C_6N_2H_{14})_2(U^{VI}_2U^{IV}O_4F_{12})$, a Mixed-Valent One-Dimensional Uranium Oxyfluoride

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A new hybrid organic−inorganic mixed-valent uranium oxyfluoride, $(C_6N_2H_{14})_2(U_3O_4F_{12})$, UFO-17, has been synthesized under hydrothermal conditions using uranium dioxide as the uranium source, hydrofluoric acid as mineralizer, and 1,4-diazabicyclo[2.2.2]octane as template. The single-crystal X-ray structure was determined. Crystals of UFO-17 belonged to the orthorhombic space group *Cmcm* (no. 63), with $a = 14.2660(15)$ Å, $b = 24.5130(10)$ Å, $c = 7.201(2)$ Å, and $Z = 4$. The structure reveals parallel uranium-containing chains of two types: one type is composed of edge-sharing UO_2F_5 units; the other has a backbone of edge-sharing UF_8 units, each sharing an edge with a pendant UO_2F_5 unit. Bond-valence calculations suggest the UF_8 groups contain U^{IV}, while the UO_2F_5 groups contain U^{VI}. EXAFS data give results consistent with the single-crystal X-ray structure determination, while comparison of the uranium L_{III}-edge XANES of UFO-17 with that of related U^{IV} and U^{VI} compounds supports the oxidation-state assignment. Variable-temperature magnetic susceptibility measurements on UFO-17 and a range of related hybrid organic−inorganic uranium(IV) and uranium(VI) fluorides and oxyfluorides further support the formulation of UFO-17 as a mixed-valent U^{IV}/U^{VI} compound.

Introduction

Hydrothermal chemistry has been used in recent years for the synthesis of a large number of novel inorganic solids.[1,2] Solution-mediated reactions in sealed reaction vessels under autogenous pressure, generated when temperatures of up to 200 °C are applied, offer completely different conditions from those of the traditional high-temperature ceramic methods employed in solid-state inorganic chemistry. Under these milder regimes new phases are accessed with often previously unseen compositions and topologies. Aluminosilicate zeolites are perhaps the best known group of materials prepared using the hydrothermal method, but more recently other zeolitic frameworks have been synthesized incorporating a huge variety of elements; metal phosphates containing transition elements and main-group metals, and metal sulfide frameworks, are well-known families.[1,2] Another group of compounds prepared by hydrothermal methods, and that have received much attention, are low-dimensional hybrid inorganic−organic phases, for example, transition-metal oxo clusters linked by organoamine groups which have been discussed as models for the rational modification of the properties of inorganic oxides.[3]

Our group has recently been investigating the use of hydrothermal chemistry with the aim of preparing open-framework uranium compounds. As well as some layered uranium(VI) phosphates[4] and molybdates,[5] we have discovered a family of uranium fluorides and oxyfluorides that exhibit a huge structural diversity.[6−10] The latter compounds are designated UFO-*n* (uranium fluoride from Oxford), and all consist of an anionic uranium fluoride component with charge-balancing protonated amine cations. The uranium(IV) fluorides are constructed from edge-sharing $[UF_8]$ polyhedra to give (one-dimensional) chain or (two-dimensional) layered structures. The uranium(VI) oxyfluorides are all constructed from $[UO_2F_5]$ units with short axial U−O distances and longer equatorial U−F bonds. Linking of these basic building units through fluoride sharing produces a wide range of topologies. For example, using piperazine and by varying the composition of the initial reaction mixture, a series of uranium (oxy)fluorides with (zero-dimensional) molecular, (one-dimensional) chain, (two-dimensional) layer, and (three-dimensional) open-framework structures have been prepared.[9,10] The anionic inorganic framework of the three-dimensional phase resembles the open framework of an aluminosilicate zeolite, having intersecting channels (the largest has dimensions 5.5 × 12.2 Å), and is named MUF-1 (microporous uranium fluoride 1).

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(1) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3268.

(2) Weller, M. T.; Dann, S. E. *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 137.

(3) Hagrman, D.; Hagrman, P. J.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 3165.

(4) Francis, R. J.; Drewitt, M. J.; Halasyamani, P. S.; Ranganathachar, C.; O'Hare, D.; Clegg, W.; Teat, S. J. *Chem. Commun.* **1998**, 279.

(5) Halasyamani, P. S.; Francis, R. J.; Walker, S. M.; O'Hare, D. *Inorg. Chem.* **1999**, *38*, 271.

(6) Francis, R. J.; Halasyamani, P. S.; O'Hare, D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2214.

(7) Francis, R. J.; Halasyamani, P. S.; O'Hare, D. *Chem. Mater.* **1998**, *10*, 3131.

(8) Francis, R. J.; Halasyamani, P. S.; Bee, J. S.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 1609.

(9) Halasyamani, P. S.; Walker, S. M.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 7415.

(10) Walker, S. M.; Halasyamani, P. S.; Allen, S.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 10513.

10.1021/ic000193r CCC: $19.00

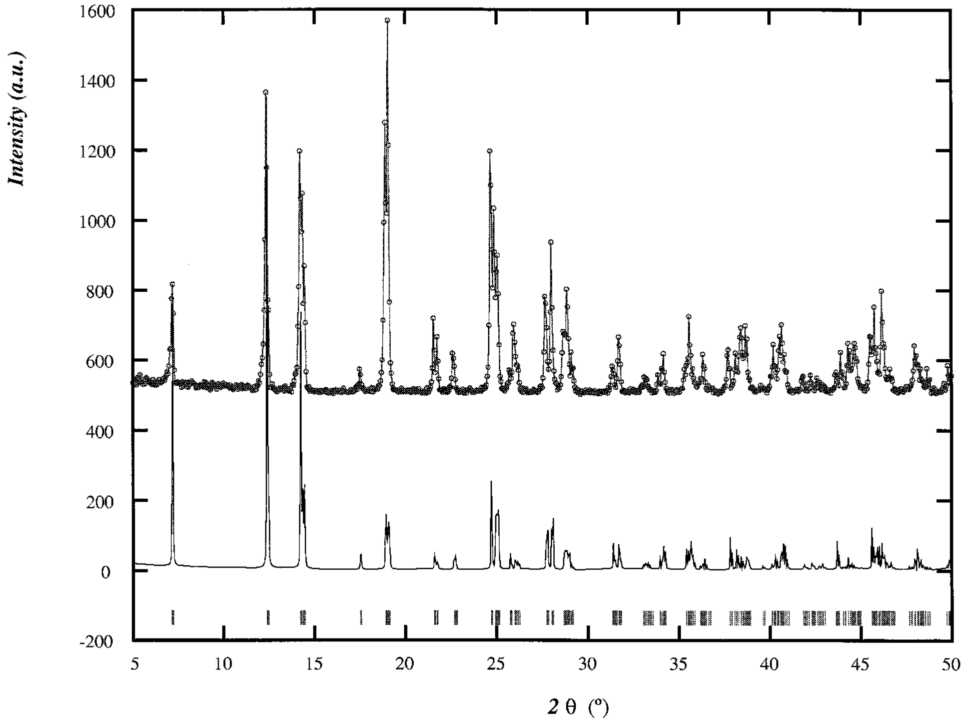

Figure 1. Comparison of the experimental powder X-ray diffraction pattern of UFO-17 with the pattern calculated from single-crystal data.

In this paper we describe the hydrothermal synthesis and characterization of a mixed-valent uranium(IV)/uranium(VI) oxyfluoride, designated UFO-17. The material was synthesized phase-pure in high yield using 1,4-diazabicyclo[2.2.2]octane (DABCO) in the reaction mixture; this is the first uranium fluorine compound we have prepared using this amine. The material has been fully characterized using single-crystal X-ray diffraction, infrared and Raman spectroscopies, X-ray absorption fine spectroscopy, (XAFS) spectroscopy, and solid-state magnetic susceptibility measurements.

Experimental Section

Synthesis of UFO-17. The title compound was prepared by heating reagents in a Teflon pouch, made from FEP Teflon film (type A), 0.005 in. thick. A 0.270 g (1×10^{-3} mol) sample of uranium dioxide (used as supplied, Testbourne), 0.785 g (7×10^{-3} mol) of DABCO (98%, supplied by Aldrich), 5 g (280×10^{-3} mol) of demineralized water, and 0.850 g (1.7×10^{-2} mol) of aqueous hydrofluoric acid (40%, BDH) were sealed in the pouch, and placed in a 1 L capacity stainless steel autoclave, with 300 mL of tap water. The autoclave was heated to 180 °C for 24 h at a heating rate of 60 °C h^{-1}, followed by controlled cooling at a rate of 6.7 °C h^{-1}. The solid product was separated from the liquor by suction filtration and washed with demineralized water and acetone. A 79% yield (based on uranium) of pure light green needlelike crystals of up to 2.5 mm in length was obtained from a supernatant of pH 4.5. Figure 1 shows the experimentally observed powder X-ray pattern and that simulated from the single-crystal structural data. Elemental microanalysis for $(C_6N_2H_{14})_2(U_3O_4F_{12})$, obsd (calcd): C, 11.71 (11.68); N, 4.48 (4.54); H, 2.57 (2.29); F, 17.87 (18.47), U, 60.24 (57.85).

Synthesis of Model Compounds. UFO-6 $[(C_5N_2H_{14})_2(U_2F_{12})\cdot 2H_2O]$, UFO-7 $[(C_5N_2H_{14})(H_3O)(U_2F_{11})]$, UFO-8a $[(C_4N_2H_{12})(UO_2F_4)\cdot 3H_2O]$, UFO-9 $[(C_4N_2H_{12})_2(U_2F_{12})\cdot H_2O]$, MUF-1 $[(C_4N_2H_{12})_2(U_2O_4F_6)]$, uranyl acetate, and $(NH_4)_7U_6F_{31}$ were synthesized using procedures described elsewhere.[8,10] $UO_2(HPO_4)$ was supplied by BDH.

Single-Crystal Diffraction. Single-crystal data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) on an Enraf-Nonius DIP 2000 image-plate diffractometer with a step of 2 deg/frame ($\theta_{max} = 26°$). Each frame was collected, processed, and indexed using the program DENZO,[11] and the files were scaled together using the program SCALEPACK[11] to give an *hkl* file. SIR92[12] was used to determine the positions of heavy atoms in space group *Cmcm* (no. 63), while refinements were completed by SHELXL-93.[13] Fourier-difference syntheses indicated the locations of the remaining non-hydrogen atoms. All atoms were refined with anisotropic thermal parameters using full-matrix least-squares procedures on F^2. Corrections were made for Lorentz and polarization effects. All crystallographic calculations were carried out within the WinGX-98 crystallographic software suite.[14] Crystallographic data are summarized in Tables 1–3.

Table 1. Summary of Single-Crystal Diffraction Data for UFO-17

empricial formula	$(C_6N_2H_{14})_2(U_3O_4F_{12})$	fw	1234.45
a (Å)	14.2660(15)	space group	*Cmcm* (no. 63)
b (Å)	24.5130(10)	temp (K)	150
c (Å)	7.201(2)	λ (Å)	0.710 73
V (Å^3)	2518.2(8)	ρ_{calcd} (g cm^{-1})	3.256
Z	4	μ (cm^{-1}), Mo Kα	19.360
$R_{obsd}(F)^a$	5.88		
$R_{w,\ obsd}(F^2)^b$	13.56		

[a] $R = \sum||F_o||F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o{}^2| - |F_c{}^2|)^2/\sum w(F_o{}^2)^2]^{1/2}$.

Thermogravimetric Analysis. Measurements were carried out on a Rheometric Scientific STA 1500H thermal analyzer. The samples of mass ca. 20 mg were loaded onto platinum crucibles and heated at a rate of 5 °C min^{-1} from room temperature to 700 °C under static air.

Elemental Analysis. Nitrogen, carbon, hydrogen, and all metal analyses were carried out in-house by the analytical services department of the Inorganic Chemistry Laboratory, Oxford. Fluorine analysis was performed by Medac Ltd.

Vibrational Spectroscopy. Infrared spectra were collected on a Mattson Instruments POLARIS FT-IR spectrometer using Nujol mulls

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(11) Otwinowski, Z. *Data Collection and Processing*; Daresbury Laboratory: Warrington, U.K., 1993.

(12) Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(13) Sheldrick, G. M. *SHELXL-93—A program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1993.

(14) Farrugia, L. J. *WinGX—An integrated system of publically available windows programs for the solution, refinement, and analysis of single-crystal X-ray diffraction data*; University of Glasgow: Glasgow, 1998.

Table 2. Atomic Parameters for UFO-17

	fractional coordinates			
atom	*x*	*y*	*z*	$U_{iso}{}^{a}$ (Å^2)
U(1)	0.5	0.696 39(5)	0.75	0.0139(3)
U(2)	0.5	0.533 42(4)	0.75	0.0120(3)
U(3)	0	0.530 62(5)	0.75	0.0227(3)
O(1)	0	0.5	0.6955(7)	0.027(4)
O(2)	0	−0.122 7(16)	0.5281(11)	0.055(7)
F(1)	0.5	0.786 0(7)	0.75	0.016(4)
F(2)	0.5875(9)	0.612 4(5)	0.75	0.020(3)
F(3)	0.6468(9)	0.507 7(6)	0.75	0.032(4)
F(4)	0.6548(9)	0.717 9(5)	0.75	0.029(4)
F(5)	0	0.548 t1(5)	1.0661(23)	0.029(4)
F(6)^b	−0.0301(29)	0.619 2(12)	0.75	0.052(16)
F(7)	0.5	0.548 0(5)	1.0605(22)	0.024(3)

^{a} U_{iso} = one-third of the trace of the orthogonalized U_{ij} tensor. ^{b} F(6) has an occupancy of 0.5.

between KBr disks over the range 600−4000 cm^{-1}. Raman spectra were recorded on a Dilor Labram Fourier transform laser spectrometer over the range 200−2000 cm^{-1} with a fundamental frequency of 632.8 nm, using single-crystal samples mounted on glass microscope slides.

X-ray Absorption Studies. XAS measurements were made on Station 16.5 of the SRS, Daresbury Laboratory, U.K., at the uranium L_{III}-edge (~17 165 eV). The synchrotron operates with an average beam current of 200 mA and a typical energy of 2 GeV. Station 16.5 receives X-rays from a 6 T superconducting wiggler with energies in the range 9−37 keV. XAFS measurements were performed in transmission mode from samples of UFO-17 and other uranium-containing compounds. Around 50 mg of each sample was finely ground and thoroughly mixed with a similar mass of polyethylene powder (spectrophotometric grade, Aldrich). Data were collected using standard procedures[15] with the incident X-ray wavelength selected using a Si(311) double-crystal monochromator which was calibrated using the Zr K-edge (~17 998 eV) of a ~20 μm zirconium foil. Data in the near-edge region were collected in angular steps equivalent to less than 0.7 eV with resolution on the order of 0.2 eV. The Daresbury Laboratory data analysis programs EXCALIB, EXBROOK, and EXCURV92 were used to normalize the XAFS data, determine E_0, perform background subtractions, and model the EXAFS spectrum.[16] EXAFS spectra were Fourier transformed to produce a one-dimensional radial distribution function, using phase shifts calculated for the first atomic shell. Least-squares refinements of structural parameters to the experimental data were performed to minimize the fit index, defined as $\sum_i(k^3(\chi_i^{calc}(k) - \chi_i^{exptl}(k)))^2$. The goodness of fit was also reported as the *R* factor, $(\int|\chi_i^{calcd}(k) - \chi_i^{exptl}(k)|k^3\,dk/\int|\chi_i^{exptl}(k)|k^3\,dk) \times 100\%$.

Magnetic Measurements. Solid-state magnetic susceptibility data were measured on a Quantum design MPMS SQUID magnetometer. An accurately weighed powdered sample of ca. 50 mg weight was loaded in a gelatin capsule, which was packed in a drinking straw between additional gelatin capsules; samples are therefore mounted in a uniform weakly diamagnetic medium, and no correction need be made for sample-holder magnetism. Samples were checked for ferromagnetic impurities by measuring the magnetization vs field over a field range of ±5 T at 40 and 300 K. For UFO-6, UFO-7, UFO-9, and UFO-17, no such impurities were revealed, and variable-temperature data were then acquired on warming a zero-field-cooled sample in a field of 0.1 T. The data were corrected for the inherent diamagnetism of the core electrons using Pascal constants.[17] No attempt was made to correct the UFO-17 data for the temperature-independent paramagnetism (TIP) associated with the uranyl moieties. MUF-1 was shown to contain a small amount of an unidentified ferromagnetic impurity (which, if iron, would correspond to 10^{-4}% of the sample by weight); zero-field-cooled magnetization data were therefore acquired in fields of 2.0 and 2.5 T (both above the saturation field of the impurity), and the difference data divided by the difference field (0.5 T) to afford susceptibility data showing net TIP. We did not regard the data as of sufficient quality to use to estimate the TIP per uranyl and, hence, to apply a TIP correction to the UFO-17 data.

Ion-Exchange Reactions. The possibility of removal of the occluded protonated DABCO cation in UFO-17 by ion exchange was investigated. Experiments were carried out using 5 mL of 2 M aqueous solutions of alkali-metal or alkaline-earth-metal cations (M = Na, K, Rb, Cs, Mg, Ca, Sr, Ba) added to individual vials each containing 0.2 g of UFO-17. The mixtures were stirred at room temperature for 24 h and the solid products recovered by filtration. In all these cases, rather than undergoing ion exchange with solutions of alkali-metal and alkali-earth-metal cations, UFO-17 dissolves, and known dense metal uranium fluorides crystallize from the solution.

Results

Synthesis and Characterization of UFO-17. Hydrothermal reaction of UO_2 and aqueous HF in the presence of DABCO at 180 °C produces phase-pure UFO-17 in the form of large green single crystals. The elemental analysis is consistent with the formulation $(C_6N_2H_{14})_2(U_3O_4F_{12})$. Thermogravimetric analysis of UFO-17 shows a mass loss of 15.8% over the range 290−350 °C, attributable to the expulsion of the DABCO template from the structure (calculated loss 18.5%). Combustion of the uranium oxyfluoride chains occurs over the range 350−700 °C, as a further 16.1% mass of the material is lost (the calculated loss if pure U_3O_8 forms is 13.3%). U_3O_8 was the only observable phase in an X-ray powder pattern of the product of calcination of UFO-17 at 700 °C. IR spectral data of UFO-17 revealed a broad, strong band at 2650 cm^{-1} characteristic of an R_3NH^+ group, assigned to the protonated DABCO template N−H stretch. The corresponding N−H bending vibration was weakly observed at 1640 cm^{-1}, while a sharp template C−H deformation band was apparent at 1390 cm^{-1}, as a shoulder of a paraffin vibration. Two very sharp and intense bands at 920 and 890 cm^{-1} are due to the asymmetric uranyl stretch. Band splitting is possibly due to the lower symmetry of the uranyl environments in the solid state compared to in solution. Weaker bands at 840 and 810 cm^{-1} are a result of the symmetric uranyl stretches. Corresponding U−F stretches are present at 470 and 420 cm^{-1}. The Raman spectrum of UFO-17 showed DABCO N−H bending bands at 1660 and 1700 cm^{-1}, C−H bends at 1390 cm^{-1}, an intense $UO_2{}^{2+}$ symmetric stretching band at 830 cm^{-1}, and finally U−F stretches at 430 cm^{-1}. Vibrational spectroscopy thus confirms the presence of the uranyl(VI) group in UFO-17, and that DABCO is incorporated.

Crystal Structure of UFO-17. The crystal structure of UFO-17 reveals the presence of two unique uranyl fluoride polyhedra and one uranium fluoride polyhedron, as shown in Figure 2. U(1) and U(3) are found in slightly distorted pentagonal bipyramidal geometries, showing coordination to two axial uranyl oxygens and five equatorial fluorines. The O═U═O bond angles are 178.5(12)° and 176.0(18)°, while the U═O bond lengths are 1.78(2) and 1.75(2) Å, for U(1) and U(3), respectively. These values are in excellent agreement with those seen in other members of the UFO-*n* family; for example, in UFO-8a, U═O = 1.799(5) Å and O═U═O = 178.8(2)°,[10] and in UFO-10, U═O = 1.788(7) Å (average value) and O═U═O = 178.85(5)° (average value).[10] Average equatorial U(1)−F distances are 2.31(8) Å, and average U(3)−F distances are 2.31(7) Å. U(2) is coordinated in a distorted square antiprismatic arrangement of eight F atoms, with a mean bond distance of 2.29(8) Å. Similar $[UF_8]$ coordination polyhedra have previously been observed in UFOs that have 8-coordinate uranium such

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(15) Teo, B. K. *EXAFS: Basic Principles and Data Analysis*; Springer-Verlag: New York, 1986.

(16) Binsted, N.; Campbell, J. W.; Gurman, S. J.; Stephenson, P. C. *EXAFS data analysis program*: Daresbury Laboratory: Warrington, U.K., 1991.

(17) Conner, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

Table 3. Relevant Bond Lengths and Angles for UFO-17

atoms	bond length (Å)	atoms	bond length (Å)	atoms	bond angle (deg)
U(1)−O(1)	1.78(2)	U(1)−U(2)	3.995(2)	O(1)−U(1)−O(2)	178.1(8)
U(3)−O(2)	1.75(2)	U(2)−U(2)	3.9559(13)	O(3)−U(3)−O(3)	176.0(10)
U(1)−F(1)	2.20(2)	U(3)−U(3)	3.9010(14)		
U(1)−F(2)	2.407(12)	av U(1)−F	2.311(8)		
U(1)−F(4)	2.270(13)	av U(2)−F	2.292(83)		
U(2)−F(2)	2.304(13)	av U(3)−F	2.306(76)		
U(2)−F(3)	2.187 (12)				
U(2)−F(7)	2.26(2)				
U(2)−F(7)′	2.417(13)				
U(3)−F(5)	2.32(2)				
U(3)−F(5)′	2.341(14)				
U(3)−F(6)	2.21(3)				

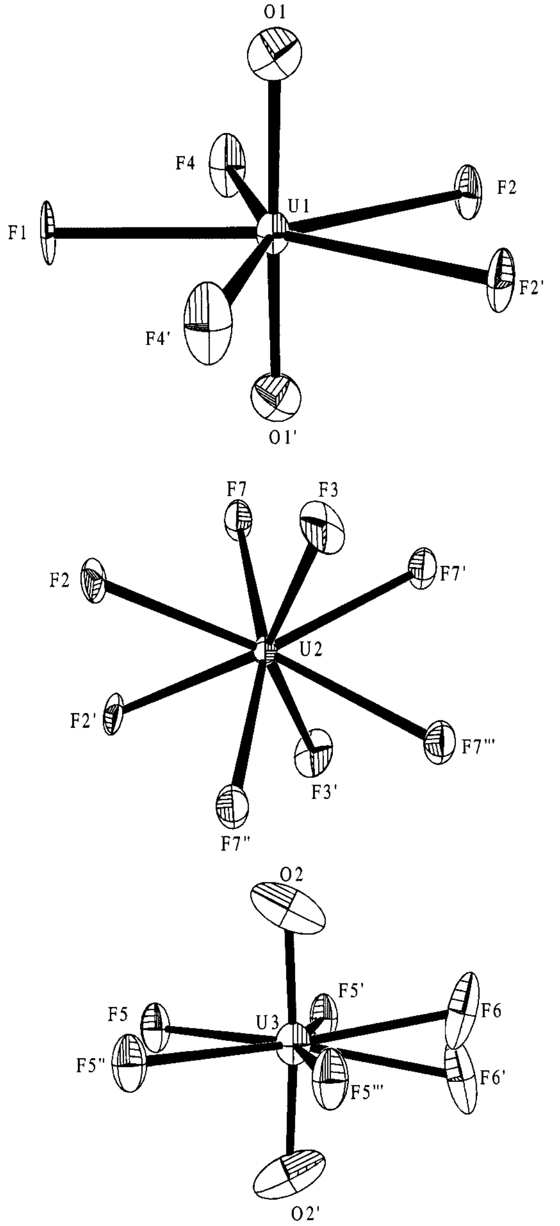

Figure 2. ORTEP diagrams (probability ellipsoids 50%) showing the local environments of the uranium atoms in UFO-17: (a, top) [UO_2F_5] environment of U(1); (b, middle) The [UF_8] environment of U(2); (c, bottom) [UO_2F_5] environment of U(3) including the half-occupied sites F6 and F6′.

as UFO-9[10] and also in some recently reported zirconium fluoride compounds.[18]

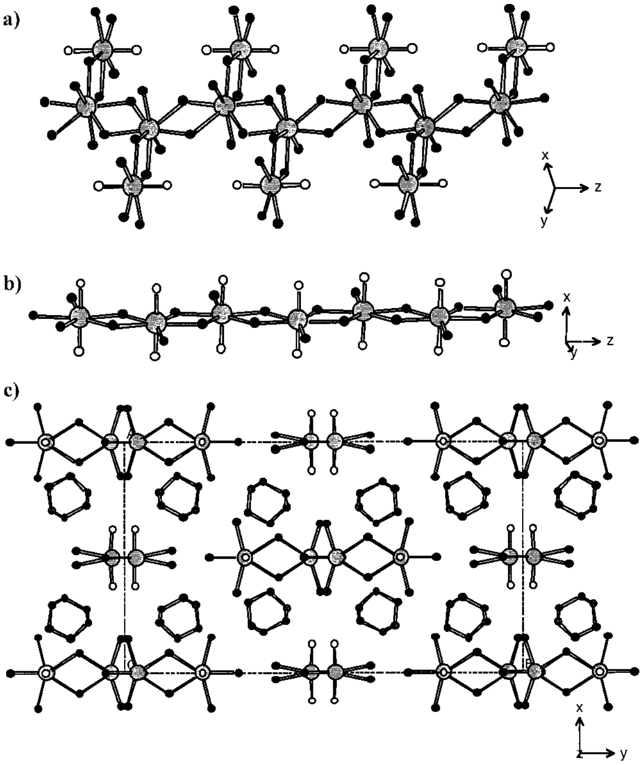

Figure 3. Three views of the structure of UFO-17: (a) chain A showing the backbone of U(2) polyhedra and pendant U(1) polyhedra; (b) chain B (only one of the sites for the disordered F6 is shown for clarity); (c) along *c* showing both types of chains and their relative orientations. In all cases, O is shown as a white circle, F as a black circle, and U as a gray larger circle.

Within the structure of UFO-17 there are two types of chains (see Figure 3a,b). The first, type A, comprises both [UF_8] and [UO_2F_5] units, while the second, type B, is formed purely from [UO_2F_5] units. In the type A chains, the [UF_8] polyhedra share two edges with other [UF_8] units to form the backbone of the chain and a further edge with a [UO_2F_5] unit, leaving the remaining two fluorine atoms terminal. The [UO_2F_5] units are found on alternate sides of the [UF_8] backbone as seen in Figure 3a. The closest intrachain uranium separations are 3.9558(13) Å between two U(2) atoms, and 3.995(2) Å between a U(1) and U(2) pair. Type B chains are formed solely from [U(3)-O_2F_5] units sharing two edges with other [UO_2F_5] units, leaving one terminal fluorine as seen in Figure 3b. The intrachain uranium distance in this case is 3.9010(14) Å. One-dimensional chains of [UO_2F_5] are otherwise only observed in $M_3(UO_2)_2F_7$·$6H_2O$, (M = Na or K),[19] although these chains are formed from [UO_2F_5] linked alternately by edges and vertexes.

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(18) Bauer, M. R.; Ross, C. R.; Neilson, R. M.; Abrahams, S. C. *Inorg. Chem.* **1999**, *38*, 1028.

(19) Dao, N. Q.; Chourou, S.; Heckly, J. *Inorg. Nucl. Chem.* **1981**, *44*, 1835.

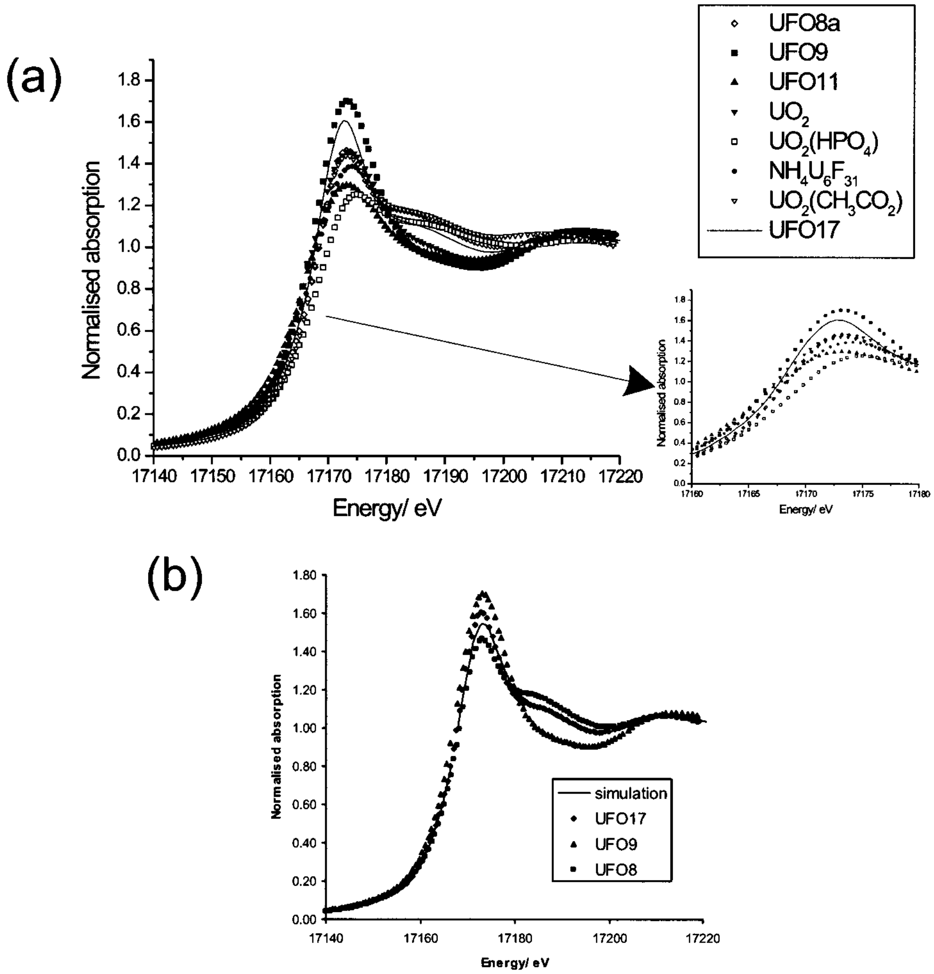

Figure 4. (a) Uranium L_{III}-edge XANES of the model compounds and UFO-17. The inset shows an expanded region, illustrating the difference in edge position of U^{IV}- and U^{VI}-containing compounds. Open symbols are used for U^{VI} materials, and filled symbols for U^{IV} materials. (b) Simulated U L_{III} XANES (see the text) spectra of UFO-9, UFO-8a, and UFO-17.

Both types of chains run parallel to the crystallographic *c* axis, as shown in Figure 3c, and the chains are separated by doubly protonated DABCO cations, which participate in substantial ionic and hydrogen-bonding interactions with the uranium chains. Each NH group of the template has one strong N−H···F interaction within a 3 Å range; N(1)···F(3) is 2.61(2) Å, and N(2)···F(4) is 2.59(2) Å. The evidence for hydrogen-bonding in the structure suggests that the DABCO is fully protonated, and thus for charge to balance the material must be formulated as $[C_6N_2H_{14}{}^{2+}]_2[U^{VI}{}_2U^{IV}O_2F_{12}]^{4-}$. The possibility that the material contains U^V and each DABCO is only singly protonated, giving a formulation of $[C_6N_2H_{13}{}^{+}]_2[U^VU^{IV}O_2F_{12}]^{4-}$, is unlikely given the length of the U═O bond of the uranyl group. In U^V uranyl compounds the bond length of the uranyl anion has previously been shown by both single-crystal studies of solids and EXAFS studies of solutions to be ca. 1.90 Å,[20] significantly longer than the ca. 1.8 Å U═O distance we observe in UFO-17. Bond valence calculations[21−23] using the crystallographic data give the valencies of U(1), U(2), and U(3) to be 5.39, 4.12, and 5.67, close to the assigned values of +6, +4, and +6, respectively.

X-ray Absorption Fine Structure Studies. The X-ray absorption studies were performed to provide independent evidence for the occurrence of two distinct oxidation states of uranium in the compound. Figure 4a shows the uranium L_{III}-edge XANES for UFO-17 and a number of U^{IV}- and U^{VI}-containing compounds. These data were normalized to the background fitted to the postedge region of the spectrum. Uranium L_{III}-edge XANES has been studied in some detail previously, and it is established that the fine structure of this region of the X-ray absorption spectrum can provide a fingerprint, allowing different uranium oxidation states to be distinguished qualitatively.[24,25] The edge shift between the two oxidation states is very small (maximum ca. 2 eV), although the materials containing U^{VI} all have edge positions of higher energy if the edge position is defined as the value of the energy when normalized absorption equals 0.5, as shown in the inset of Figure 4a. The most obvious difference in the spectra, however, is that the compounds containing U^{VI} exhibit a feature at ca. 15 eV above the absorption edge which is absent in the U^{IV}-containing compounds. This is well-known and has been attributed to strong multiple scattering in the near-linear atomic arrangement of the uranyl group.[25] The "white line", the first strong feature of the absorption edge, varies in intensity from compound to compound and has no obvious dependence on

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[20] Docrat, T. I.; Mosselmans, J. F. W.; Charnock, J. M.; Whiteley, M. W.; Collison, D.; Livens, F. R.; Jones, C.; Edmiston, M. J. *Inorg. Chem.* **1999**, *38*, 1879.

[21] Brese, N. E.; O'Keeffe, M. *Acta Crystallogr., B* **1991**, *47*, 192.

[22] Brown, I. D.; Altermatt, D. *Acta Crystallogr., B* **1985**, *41*, 244.

[23] Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. *Can. Mineral.* **1997**, *35*, 1551.

[24] Bertram, S.; Kaindl, G.; Jové, J.; Pagès, M.; Gal, J. *Phys. Rev. Lett.* **1989**, *63*, 2680.

[25] Hudson, E. A.; Rehr, J. J.; Bucher, J. J. *Phys. Rev. B* **1995**, 13815.

oxidation state; this is most likely due to its sensitivity to the local environment, and the fact that here we are comparing uranium oxides and fluorides with uranium in a range of different coordination geometries. To understand better the uranium L$_{III}$-edge XANES of UFO-17, the spectra of the two most similar compounds in terms of the local environment were considered. The method of summing XANES spectra, which has been used with some success previously in other systems when two or more distinct atomic environments are expected,[26] was used to simulate a spectrum for UFO-17. Figure 4b shows the simulated uranium L$_{III}$-edge XANES of a spectrum produced by summing the spectra of UFO-8a (containing U^{VI} in [UO$_2$F$_5$] units) and UFO-9 (containing U^{IV} in [UF$_8$] units) weighted to the expected proportions of uranium type in UFO-17 (2/3 and 1/3, respectively) along with the three pertinent experimental spectra. The experimental spectrum of UFO-17 matches very closely the simulated spectrum, thus providing clear evidence that UFO-17 contains two distinct types of uranium, and corroborating the crystal structure data.

Analysis of the uranium L$_{III}$ EXAFS data of UFO-8a, UFO-9, and UFO-17 was performed to provide further evidence that the new phase contains a mixture of uranium sites. Figure 5 shows the three EXAFS spectra and their Fourier transform along with spectra generated from fitted models. A simple single-scattering model approach proved adequate to model the data satisfactorily and allow the data from the three compounds to be compared. It is well-known that multiple scattering due to the linear nature of the $O{=}U{=}O$ group manifests itself in the uranium L$_{III}$-edge EXAFS of uranyl-containing compounds,[20] but the only discernible feature attributable to this is in our data is a very small feature at ca. 3.6 Å in the Fourier transform, and the directly bonded shells are not affected by this. For UFO-8a and UFO-9 the coordination numbers of the first two atomic shells were fixed at the values found by crystallography and all other parameters allowed to vary in least-squares refinements to minimize the fit index. Excellent agreement was found between the interatomic distance thus derived and those from the crystal structure (Table 4). As well as the directly bonded fluorine shell in UFO-9, it was found that the expected nonbonded uranium shell at ca. 4 Å significantly improved the fit of the model. For UFO-17, initially the same approach was taken for data analysis. Since the EXAFS experiment probes the *average* local environment of a uranium atom, in UFO-17 we expect a uranium atom to have $2/3 \times 2 = 1.3$ oxygen neighbors at ca. 1.8 Å and $2/3 \times 5 + 1/3 \times 8 = 6$ fluorine neighbors at $2/3 \times 2.29$ Å $+ 1/3 \times 2.31$ Å $= 2.30$ Å. The coordination numbers were fixed and all other parameters allowed to vary in least-squares refinements, giving the results shown in Table 4. The interatomic distances show excellent agreement with the crystallographic values, and the $U{=}O$ distance determined by EXAFS provides further evidence that UFO-17 contains $U^{VI}{=}O$ and not $U^{V}{=}O$, as discussed above. An important parameter to also consider is the Debye−Waller factor of the oxygen shell in the uranyl-containing compounds. With the coordination number (N_O) fixed at 1.3 as expected for the crystal structure, the Debye−Waller factor shows good agreement with that seen in UFO-8a in which the uranyl anion is found in a very similar environment, but if the coordination number is fixed at higher or lower values, physically unreasonable Debye−Waller factors result on least-squares refinements. For example, if N_O was fixed at 2, to simulate a larger proportion of uranyl in UFO-17, a Debye−Waller factor of 0.007 Å^2 was produced, considerably higher than the expected value, and if N_O was set at 0.3, an impossible negative Debye−Waller factor resulted. In both cases significantly poorer fits of the model to

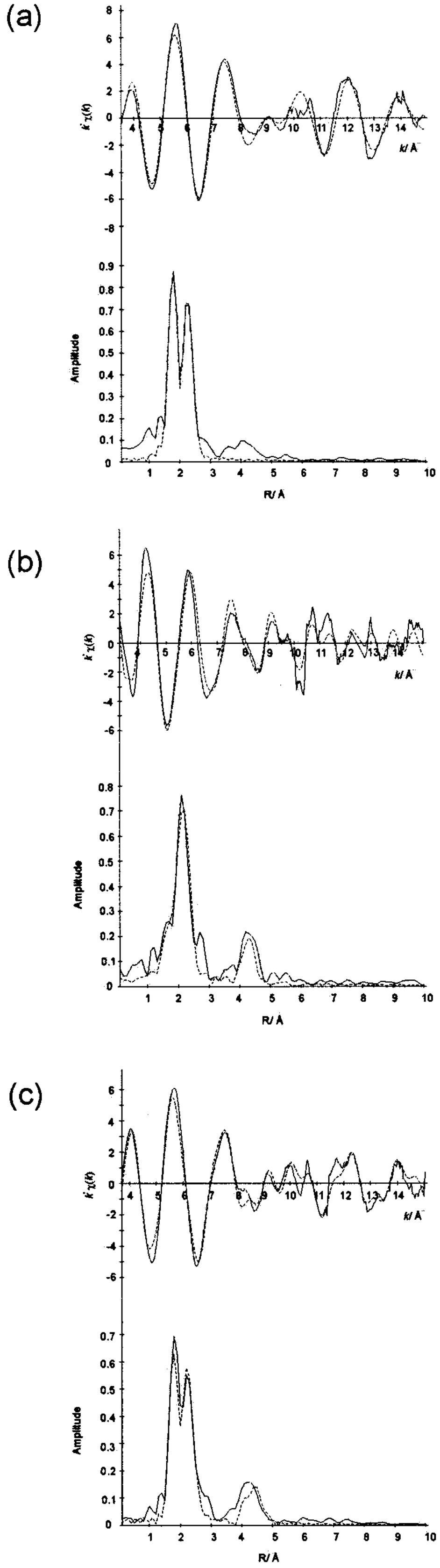

Figure 5. Uranium L$_{III}$-edge EXAFS spectra (top) and their Fourier transforms (bottom) for (a) UFO-9, (b) UFO-8a, and (c) UFO-17. Full lines are the experimental data and broken lines spectra generated from fitted models (see Table 4).

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[26] Resasco, D. E.; Webber, R. S.; S.Sakellson; McMillan, M.; Haller, G. L. *J. Phys. Chem.* **1988**, *92*, 189.

Table 4. Structural Parameters Determined by the U L_{III}-Edge EXAFS Study of UFO-8, UFO-9, and UFO-17

compd	shell	occupation number	radial distance (Å)	Debye−Waller factor ($=2\sigma^2$) (Å^2)	*R* factor (%)	crystallographic distance (Å)
UFO-9	F	8	2.227(4)	0.0202(6)	38.40	2.32
U	2	4.025(5)	0.0090(8)	4.05		
UFO-8a	O	2	1.791(2)	0.0036(4)	24.91	1.78
F	5	2.291(25)	0.0107(4)	2.28		
UFO-17	O	1.3	1.778(2)	0.0032(3)	25.91	1.76
F	6	2.265(3)	0.0178(5)	2.30		
U	2	4.021(5)	0.0122(9)	4.00		

[a] Estimated errors are those derived from least-squares refinements; experimental error limits the true accuracy of the interatomic distances to ±0.02 Å, and of the Debye−Waller factor to ±20%. Coordination numbers were fixed at the given values as described in the text.

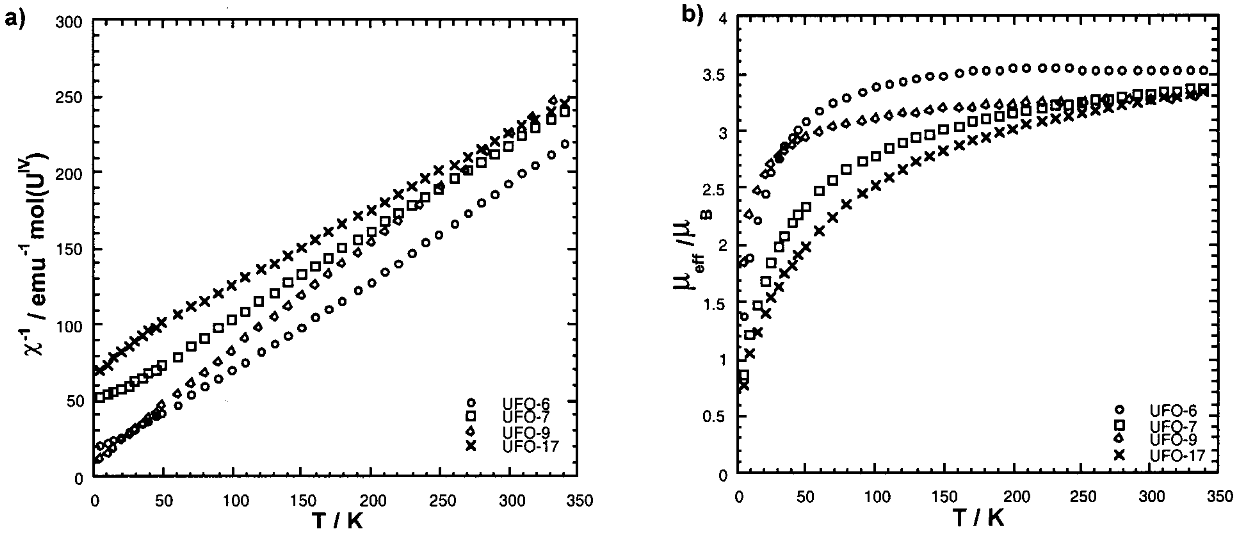

Figure 6. Magnetic data from UFO-6, -7, -9, and -17: (a) $1/\chi$ vs *T* and (b) μ_{eff} vs *T*. In each case data are scaled per mole of U^{IV} present in the structure. χ was corrected for sample diamagnetism using Pascal's constants.

the data resulted, as evidenced by the large values of the *R* factor and fit index. Thus, the EXAFS data confirm the crystallographically determined average local environment of UFO-17 and provide extra evidence for the occurrence of two uranium oxidation states.

Magnetic Susceptibility Measurements. To gain further support for our formulation of UFO-17 as a U^{IV}/U^{VI} mixed-valence compound, we performed variable-temperature magnetic susceptibility measurements on UFO-17. We also studied the magnetism of several model compounds for comparison: UFO-6 and UFO-9 contain $U^{IV}F_8$ polyhedra similar to those in UFO-17, UFO-7 contains 9-coordinate U^{IV}, and MUF-1 contains $U^{VI}O_2F_5$ polyhedra similar to those of UFO-17. Susceptibility data for UFO-17, corrected for sample diamagnetism using Pascal's constants,[17,27] are presented in Figure 6, together with the effective magnetic moment, defined by $\mu_{eff} = (8\chi T)^{0.5}$. Table 5 compares data for UFO-17 with those for the U^{IV} compounds UFO-6, UFO-7, and UFO-9. The uranyl(VI) ion shows TIP.[28] Samples of the U^{VI} compound MUF-1 were found to contain small amounts of an unidentified ferromagnetic impurity; however, once this was corrected for (see the Experimental Section), the data indicated net TIP of ca. 5×10^{-6} emu mol^{-1}.

Table 5. Magnetic Data for UFO-6, UFO-7, UFO-9, and UFO-17 per Mole of Uranium(IV)

compd	C_{40-350}[a] (emu [mol of U^{IV}]$^{-1}$)	μ_{eff}[b] (μ_B)	Θ_{40-350} (K)	$\mu_{eff}^{[300]}$[c] (μ_B)
UFO-6	1.62[d]	3.59[d]	14.7[d]	3.53
UFO-7	1.73	3.72	78.8	3.32
UFO-9	1.41	3.35	15.7	3.21
UFO-17[e]	2.01	4.01	153.6	3.26

[a] Constants obtained by fitting susceptibility data (corrected for diamagnetism using Pascal's constant) to the Curie−Weiss law, $\chi = C/(T - \theta)$, over the temperature range 40−350 K. [b] Effective magnetic moment obtained using $\mu_{eff} = (8C_{40-350})^{1/2}$. [c] Room-temperature magnetic moment derived using $\mu_{eff} = (8\chi T)^{1/2}$. [d] The plot of $1/\chi$ is strongly nonlinear over the temperature range 40−350 K. Thus, values are strongly dependent on the exact temperature range fitted. For example, in the range 200−350 K the values of *C*, μ_{eff}, and Θ are 1.52 emu mol^{-1}, 1.75 μ_B, and 5.85 K, respectively. [e] Assuming the formula is correct when assigned as $(C_6N_2H_{14})_2(UO_2F_2)_2UF_8$.

Evidently the diamagnetism of the fluorides, the organics, and the water molecules is insufficient to dominate over the TIP of the uranyl group.

The effective magnetic moments per uranium atom for UFO-6, UFO-7, and UFO-9 (Table 5) are typical for U^{IV} ions. Previously reported moments for a number of U^{IV} compounds have fallen in the range 2.7−3.6 μ_B.[29−31] The previously studied hybrid organic−inorganic uranium(IV) fluorides UFO-1, UFO-2, and UFO-3 showed moments corresponding to between 3.5

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(27) Correction using Pascal's constants does not correct for the temperature-indepedant paramagnetism associated with the uranyl(VI) group; correction using extrapolation of the raw χ data to infinite temperature results in lower values of μ_{eff}. However, the extrapolation method is only valid when the susceptibility data vary linearly with $1/T$; this is not the case for some of the compounds under consideration here. Moreover, studies of MUF-1 show that the TIP term is small relative to the diamagnetism in this type of compound.

(28) Edelstein, N. M.; Goffart, J. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman & Hall: London, 1986; Vol. 2.

(29) Dawson, J. K. *J. Chem. Soc.* **1951**, 429.

(30) Gamp, E.; Edelstein, N.; Malek, C. K.; Hubert, S.; Genet, M. *J. Chem. Phys.* **1983**, 79.

(31) Tam, D. L.; Aldred, A. T. In *The Actinides: Electronic structure and related properties*; Freeman, A. J., Darby, J. B., Eds.; Academic Press: New York, 1974; Vol. 1.

and 4.0 μ_B per $\mathrm{U^{IV}}$ center.[7] Some of this variation may arise from the magnetic anisotropy of $\mathrm{U^{IV}}$ ions, leading to possible complications arising from preferred orientation effects in powders or even field-induced realignment.[30] Indeed, measurement of a second sample of UFO-17 gave a room-temperature moment of ca. 4.0 μ_B. However, variations in the exact coordination geometry and in any interionic magnetic interactions may also play a role. Some of the compounds in Table 5, UFO-17 in particular, have rather large Weiss constants; however, comparably large values of −146 K[32] and −116 K[29] have been reported for UF_4 (which contains $\mathrm{U^{IV}F_8}$ polyhedra).

The magnetic data are clearly consistent with the presence of one $\mathrm{U^{IV}}$ ion and two $\mathrm{U^{VI}}$ ions per formula unit of UFO-17 when comparisons with the model compounds are made. Moreover, the data are less consistent with other possible formulations. For example, the molecular formula of UFO-17 does not rule out the possibility of two $\mathrm{U^{V}}$ ions and one $\mathrm{U^{VI}}$ ion per formula unit. However, $\mathrm{U^{V}}$, and other f^1 actinide, compounds typically have effective magnetic moments of ca. 1 μ_B; for example, values in the range 0.6−1.2 μ_B have been reported for a range of uranates(V),[33] and a high-temperature moment of 1.04 μ_B has been reported for $PaCl_4$.[34] Thus, for a $\mathrm{U^{V}{}_2U^{VI}}$ compound, one would expect a moment of ca. 1.4 μ_B per formula unit. Other possibilities arise if the amine template molecules are not fully protonated; this would require either one $\mathrm{U^{V}}$ ion and two $\mathrm{U^{VI}}$ ions per formula unit (expected moment ∼1.0 μ_B), or three $\mathrm{U^{VI}}$ ions (diamagnetic). Thus, the observed data are in agreement with the local structure suggested by the diffraction and XAFS results.

Discussion

We have previously prepared uranium(IV) fluorides from both uranium(IV)[7,8] and uranium(VI)[10] starting materials under hydrothermal conditions, as well as from U_3O_8.[7] Although the hybrid organic−inorganic uranium(VI) fluorides we have reported are best synthesized from uranyl(VI) acetate,[10] MUF-1, UFO-8a, and UFO-9 have also been formed from UO_2.[35] Thus, it appears the two oxidation states are rather close in energy under our reaction conditions, and the formation of a mixed $\mathrm{U^{IV}/U^{VI}}$ material is not surprising.

A range of uranium mixed-valence compounds have previously been reported with a variety of oxidation states and of positions in the Robin and Day class I/II/III classification.[36] $\mathrm{U^{IV}/U^{VI}}$ compounds generally fall toward the class I end of the spectrum due to large structural differences between $\mathrm{U^{IV}}$ and $\mathrm{U^{VI}}$ sites. These include molecular compounds with completely separated $\mathrm{U^{IV}}$ and $\mathrm{U^{VI}}$ ions such as $\mathrm{[U^{IV}Cl_3(trien)]^{+}{}_2[U^{VI}O_2Cl_4(trien)]^{2-}}$ {trien = triethylenetetramine}[37] and $\mathrm{[U^{IV}Cl(dmf)_7]^{3+}{}_2[U^{VI}O_2Cl_4]^{2-}{}_3}$ {dmf = *N*,*N*-dimethylformamide},[38] and extended structures such as $\mathrm{U^{IV}(U^{VI}O_2)(PO_4)_2}$[39] (although U_3O_8 could be described as $\mathrm{U^{IV}U^{VI}{}_2}$, a $\mathrm{U^{V}{}_2U^{VI}}$ formulation is probably more appropriate[40]). Thus, the observed structure of UFO-17 is consistent with that of a class I $\mathrm{U^{IV}/U^{VI}}$ compound.

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Supporting Information Available: X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[32] Elliott, N. *Phys. Rev.* **1949**, *76*, 489.

[33] Kanellakopulos, B.; Heinrich, E.; Keller, C.; Baumgärtner, F.; König, E.; Desai, V. P. *Chem. Phys.* **1980**, *53*, 197.

[34] Hendricks, M. E.; Jones, E. R.; Stone, J. A.; Karraker, D. G. *J. Chem. Phys.* **1971**, *55*, 29937.

[35] Walker, S. M. Unpublished results, 1999.

[36] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

[37] Kokare, M. B.; Kesavadas, T. *Ind. J. Chem.* **1987**, *26A*, 516.

[38] Kepert, D. L.; Patrick, J. M.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 381.

[39] Bénard, P.; Louër, D.; Dacheux, N.; Brandel, V.; Genet, M. *Chem. Mater.* **1994**, *6*, 1049.

[40] Ahrland, S.; Bagnall, K. W.; Brown, D.; Dell, R. M.; Eberle, S. H.; Keller, C.; Lee, J. A.; Liljenzin, J. O.; Mardon, P. G.; Marples, J. A. C.; Milner, G. W. C.; Phillips, G.; Potter, P. E.; Rydberg, J. *The Chemistry of the Actinides*; Pergamon Press: Oxford, 1975.