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$[N(CH_2CH_2NH_3)_3][U_3O_2F_{13}]\cdot 2H_2O$: A Novel Organically Templated Mixed-Valent Uranium Oxyfluoride with a Hybrid Network Structure

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The synthesis and characterization of a novel mixed-valent uranium oxyfluoride is described; the inorganic network consists of 2-D $[U_2F_{10}]^{2-}$ sheets constructed from corner- and edge-sharing $U^{IV}F_9$ tricapped trigonal prisms and 1-D $[UO_2F_3]^-$ chains constructed from edge-sharing $U^{VI}O_2F_5$ pentagonal bipyramids with the organic cations and water molecules between the sheets. This is the first example with a hybrid network structure in the system of uranium fluoride or oxyfluoride. The variable-temperature magnetic susceptibility confirms the oxidation state of the uranium ions. Crystal data follow: $C_6H_{25}N_4O_4F_{13}U_3$, monoclinic, space group $P2_1$ (No. 4); $a = 8.6876(4)$ Å, $b = 7.3158(4)$ Å, $c = 16.3376(8)$ Å, $\beta = 93.7285(9)°$, $V = 1036.2(2)$ Å^3, and $Z = 2$.

Hydrothermal synthesis of open-framework transition metal phosphates and silicates has been the subject of intense research owing to their interesting structural chemistry and potential applications as ion-exchangers, catalysts, and adsorbents.[1–3] Recently, the synthesis of uranium-containing compounds with open-framework structures has also been the focus of considerable interest.[4,5] In addition to phosphates and silicates, a family of uranium fluorides and oxyfluorides with wide variety of structures has recently been reported.[6–17]

An organically templated uranium oxyfluoride, $[(C_2H_5)_4N][(UO_2)_2F_5(H_2O)]\cdot H_2O$, was reported by Mikhailov et al. as early as 1979.[18] As compared with transition metals, the large actinide metal cation has higher coordination numbers. A compound built from UX_7, UX_8, or even UX_9 units may have a completely new and distinct crystal structure. Uranium-containing materials, such as uranium oxides, are also known to be effective catalysts.[19] In addition, the existence of more than one stable oxidation state of uranium offers the possibility of synthesizing materials with interesting magnetic properties. In this paper, we report the synthesis and structural characterization of an organically templated mixed-valent uranium(IV)/uranium(VI) oxyfluoride, $[N(CH_2CH_2NH_3)_3][U_3O_2F_{13}]\cdot 2H_2O$ (denoted as **1**), with a hybrid network structure. To date, we are not aware of any example whose anionic network consists of 1-D chains of uranium oxyfluoride and 2-D layers of uranium fluoride. Magnetic susceptibility confirms the oxidation state of uranium ions.

Compound **1** was synthesized by heating a mixture of 1 mmol of $UO_2(CH_3COO)_2\cdot 2H_2O$ (Emsdiasum, 99.6%), 7 mmol of HF(aq) (Merck, 40% solution), 0.334 mmol of $N(CH_2CH_2NH_2)_3$ (tris(2-aminoethyl)amine, Aldrich, 96%), and H_2O (10 mL) in a Teflon-lined, 23-mL autoclave at 180 °C for 3 days followed by slow cooling at 5 °C h^{-1} to room temperature. After reaction, the product was recovered by filtration, washed with water, and allowed to dry in air. This procedure yielded pure, monophasic green crystals of **1** in a yield of 9% based on uranium acetate. The powder X-ray

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diffraction pattern of the bulk product is in good agreement with the calculated pattern on the basis of the results from single-crystal X-ray diffraction (see Figure S1 in the Supporting Information). The optimum reaction conditions for a higher yield have not been found. The CHN and fluorine elemental analysis (ion chromatography) results are consistent with the formula (Anal. Found/Calcd: C, 6.11/6.12; H, 2.10/2.14; N, 4.62/4.76; F, 21.1/20.96). To confirm the amount of lattice water, thermogravimetric analysis (TGA) was performed by heating a sample from 40 to 900 °C at 5 °C/min in flowing air. The TGA curve shows a number of overlapping weight losses, indicating a complex process of decomposition (Figure S2). The first step of weight loss between 50 and about 230 °C is 2.96%, which is close to that calculated for the loss of 2 mol of water molecules (3.06%). Infrared spectroscopy on **1** (KBr method) revealed bands at 3569 (strong), 3120 (strong and broad), and 910 cm^{-1} (strong and sharp) consistent with H_2O, RNH_3^+, and uranyl groups, respectively (Figure S3). The two strong and sharp bands at 1509 and 1618 cm^{-1} can be attributed to bending modes of ammonium groups. To confirm the oxidation state of uranium, magnetic data were measured on a powder sample of 28.6 mg using a dc SQUID system between 2 and 300 K in a magnetic field of 0.2 T. Susceptibility values were corrected for the sample diamagnetic contribution according to Pascal's constants (-358×10^{-6} emu/formula unit).[20] To determine the thermal stability of **1**, a sample was heated in air to 200, 250, and 300 °C and kept there for 1 h for each temperature, followed by powder X-ray diffraction study. The results showed that **1** retained its structure at 250 °C and decomposed at 300 °C.

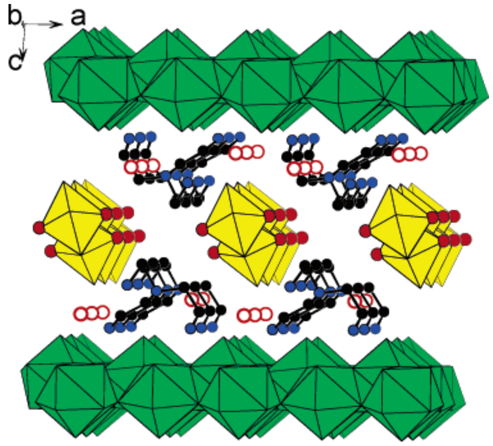

Figure 1. The structure of **1** viewed approximately parallel to the *b*-axis. The anionic $[U_2F_{10}]^{2-}$ sheets and $[UO_2F_3]^-$ chains are shown in green and yellow, respectively. Black solid circles, C atoms; red solid circles, O atoms; red open circles, water O atoms; blue solid circles, N atoms.

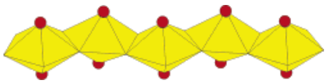

Figure 2. Section of a $[UO_2F_3]^-$ chain in **1**. Red solid circles, O atoms.

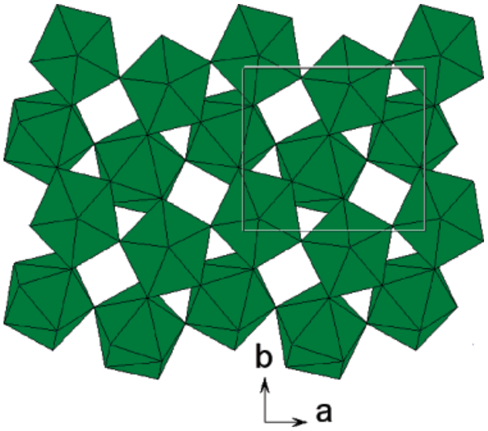

Figure 3. Section of a $[U_2F_{10}]^{2-}$ sheet in **1**.

As revealed by single-crystal X-ray crystallography,[21] the structure of **1** is composed of anionic $[U_2F_{10}]^{2-}$ sheets separated by triprotonated tris(2-aminoethyl)amine cations, anionic $[UO_2F_3]^-$ chains, and occluded water molecules (Figure 1). Although it is difficult to distinguish oxygen from fluorine by X-ray diffraction alone, the atoms were assigned with the help of elemental analysis results, bond-valence calculation, and a comparison of the bond lengths in the structural units of **1** with those in the literature. There are three unique uranium atoms. The bond-valence sums for U(1), U(2), and U(3) are 6.24, 4.02, and 3.98, respectively, indicating that U(1) is hexavalent and the other two U atoms are tetravalent.[22] The structural formula of **1** can be written as $[N(CH_2CH_2NH_3)_3][U^{VI}O_2F_3][U^{IV}{}_2F_{10}]\cdot 2H_2O$. U(1) is axially bonded to two oxygen atoms, forming a uranyl unit (d(U═O) = 1.80(1) Å (×2)) with an O═U═O bond angle of 177.6(8)°. Equatorially, U(1) is bonded to five fluorine atoms, four of which bridge to adjacent U(1) atoms, with U─F bonds ranging from 2.32(1) to 2.33(1) Å, whereas the fifth fluorine is singly bonded (U─F, 2.192(9) Å). As shown in Figure 2, UO_2F_5 pentagonal bipyramids share two edges to form linear chains with the composition $UO_2F_{4/2}F_{1/1}$, i.e., UO_2F_3. This type of chain was observed in several 1-D uranium(VI) oxyfluorides.[11,14] Their U═O and U─F bond lengths are comparable.

In contrast, both U(2) and U(3) are coordinated solely by fluoride ligands, producing UF_9 tricapped trigonal prisms. Each UF_9 polyhedron shares three edges with three adjacent polyhedra and shares two corners with two additional polyhedra to form a $[U_2F_{10}]^{2-}$ layer as shown in Figure 3. The ninth fluorine atom of each prism is unshared and extends from one side of the layer into the interlamellar region. The U─F bond involving the terminal fluorine atom is significantly shorter than the other U─F bonds. The U─F distances for terminal fluorines are U(2)─F(5) = 2.165(9) Å and U(3)─F(10) = 2.177(8) Å, whereas for the bridging fluorines, the mean U(2)─F and U(3)─F distances are 2.362 and 2.367 Å, respectively. Similar layers were also observed

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(21) Crystal data for **1**: $C_6H_{25}N_4O_4F_{13}U_3$, green tablet crystal of dimensions $0.3 \times 0.1 \times 0.1$ mm^3, $T = 298$ K, monoclinic, space group $P2_1$ (No. 4); $a = 8.6876(4)$ Å, $b = 7.3158(4)$ Å, $c = 16.3376(8)$ Å, $\beta = 93.7285(9)°$, $V = 1036.2(2)$ $Å^3$, $Z = 2$, $\rho_{calcd} = 3.777$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu = 23.52$ cm^{-1}, 7640 reflections measured, 4809 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 56.6°$, $R_{int} = 0.0603$), GOF = 1.052, R1 = 0.0463, wR2 = 0.1239. The Flack x parameter was 0.025(17), indicative of a correct absolute structure. The H atoms were not located. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all atoms.

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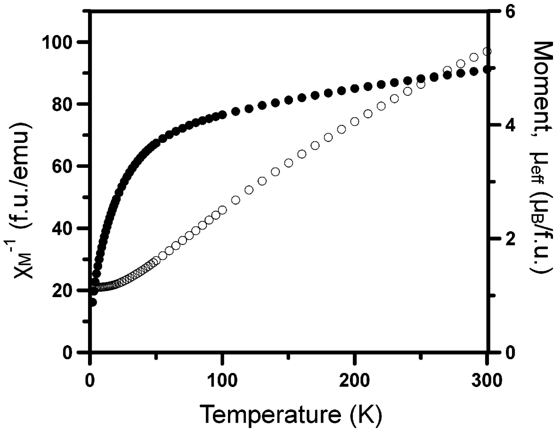

Figure 4. μ_{eff} versus T (●) and $1/\chi_M$ versus T (○) for **1**.

in a few layered uranium(IV) fluorides.[6,7,13] Their U−F distances are similar. Each ammonium nitrogen atom of the organic cation is within 3 Å of one to three network F atoms; this distance is indicative of N−H···F hydrogen bonding. The water molecules also participate in hydrogen bonding with the networks, as indicated from short O···F and O···O distances. The extensive hydrogen bonding network likely plays an important role in determining precisely which species is least soluble under the given hydrothermal conditions.

The temperature dependence of μ_{eff} and $1/\chi_M$ curves is shown in Figure 4. The effective magnetic moment at 300 K is 4.97 μ_B/formula unit as compared with the theoretical value of $(3.58 \times 2)^{1/2} = 5.06$ μ_B/formula unit, which is in good agreement with the presence of 1 U^{6+} and 2 U^{4+} ions considering that the magnetic moment of 1 U^{4+} ion is 3.58 μ_B expected according to Russell−Saunders coupling ($g_J = {}^4/_5$ and $J = 4$) for a $^3H_4$ ground state. The μ_{eff} value decreases smoothly upon cooling and rapidly below ~50 K. The magnetic susceptibilities above about 100 K follow the Curie−Weiss law with a negative value of the Weiss constant. A fit of the data from 100 to 300 K to the equation $\chi_M = C/(T - \theta)$ results in $C = 3.90$ cm^3·K/mol and $\theta = -87$ K. Although the rapid decrease of the effective moment below ~50 K and a large negative Weiss constant may result from antiferromagnetic interactions between layers, the tendency of the susceptibility to a temperature-independent value of about 0.047 emu/formula unit below 15 K may indicate that the ground state of the U^{4+} ion is nonmagnetic. An organically templated uranium(IV) fluoride with a 2-D layer structure shows a similar temperature dependence of reciprocal magnetic susceptibility.[13]

A large number of organically templated uranium fluorides and oxyfluorides have been reported. Most of them adopt either 1-D chain or 2-D layer structures, while only a few have 3-D framework structures. Although the anionic $[UO_2F_3]^-$ chains and $[U_2F_{10}]^{2-}$ layers have already been observed in several 1-D uranium oxyfluorides and 2-D uranium fluorides, respectively, compound **1** is the first example which consists of the two types of inorganic networks within the same structure. The title compound should be a member of the class I system in the Robin−Day scheme because the tetravalent and hexavalent uranium atoms are in very different coordination environments, the compound is green, and the observed magnetism can be explained by localized and separate redox centers. One 2-D uranium fluoride which was also prepared using tris(2-aminoethyl)amine as the structure-directing agent has been reported.[7] It contains negatively charged uranium fluoride layers constructed from linked UF_8 and UF_9 polyhedra separated by the organic cations, which is quite different from the structure of **1**. Uranium fluorides and oxyfluorides have shown a rich structural chemistry. Given the large variety of organic templates that could be used in the hydrothermal synthesis, the scope for the synthesis of further novel compounds in this system appears to be very large.

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Supporting Information Available: Crystallographic data for **1** in CIF format, X-ray powder patterns, TGA curve, and IR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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