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$UF_3(H_2O)(C_2O_4)_{0.5}$: A Fluorooxalate of Tetravalent Uranium with a Three-Dimensional Framework Structure

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A new uranium(IV) fluorooxalate, $UF_3(H_2O)(C_2O_4)_{0.5}$, has been synthesized by a hydrothermal method and structurally characterized by single-crystal X-ray diffraction, infrared spectroscopy, and thermogravimetric analysis. The structure consists of two-dimensional layers of corner- and edge-sharing tricapped trigonal prisms with the composition $UF_{4/2}F_{2/2}O_3$ linked by bisbidentate oxalate ligands to form a three-dimensional framework. Magnetic susceptibilities were measured to confirm the tetravalent state of uranium. Crystal data: monoclinic, space group *C*2/*c*, $a = 17.246(3)$ Å, $b = 6.088(1)$ Å, $c = 8.589(2)$ Å, $\beta = 95.43(3)°$, and $Z = 8$.

A large number of organically templated uranium fluorides and oxyfluorides with a wide variety of structures have recently been reported.[1−13] Most of them adopt either one-dimensional chain or two-dimensional (2-D) layer structures, while only a few have three-dimensional (3-D) framework structures. In contrast, few uranium fluoride (or oxyfluoride)−organic framework solids in which organic molecules are directly incorporated into the extended structures of the metal fluorides or oxyfluorides are known. Such organic−inorganic hybrid compounds can combine the characteristics of each component to produce a novel structural type. Recently, we synthesized a mixed-metal uranyl oxyfluoride incorporating an organic ligand, $[(UO_2)_2F_8(H_2O)_2Zn_2(4,4'\text{-bpy})_2]\cdot(4,4'\text{-bpy})$ (bpy = bipyridine).[14] The bpy molecule is coordinated to two Zn atoms in adjacent layers to produce a 3-D framework. Bimetallic compounds are highly interesting because the second metal provides the possibility of incorporating neutral organic ligands with N-donor groups into the extended structures. The metal cations (U^{4+} and UO_2^{2+}) are hard acids, and the strength of the base (bpy) is insufficient to replace the hard base F^-. In order for an organic ligand to coordinate to a U atom, one may choose a difunctional carboxylate ligand such as oxalate because carboxylate is considered to be a hard base. Uranyl dicarboxylates have been synthesized by polymerizing U−O polyhedra through difunctional carboxylate ligands. For example, several uranyl dicarboxylates, in which mononuclear or dinuclear uranyl building units are connected by bidentate anions such as succinate, glutarate, isophthalate, adipate, and 3,5-pyrazoledicarbonate, were reported.[15−17] Uranium(IV) dicarboxylate to date has not been reported. Previously, the compositions of two fluorooxalates of tetravalent uranium, $UF_2(C_2O_4)\cdot 1.5H_2O$ and $(UF)_2(C_2O_4)_3$, with unknown crystal structures were obtained by the reaction of oxalic acid and UF_4.[18] Several alkali-metal fluorooxalates of Sn^{IV}, Zr^{IV}, and Hf^{IV} were reported, but they adopt considerably different structures.[19,20] We report in this paper the synthesis and structural characterization of a new

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uranium(IV) fluorooxalate, $UF_3(H_2O)(C_2O_4)_{0.5}$ (denoted as **1**), in which oxalate ligands show bisbidentate coordination to the U atoms acting as pillars between adjacent uranium fluoride layers to produce an extended 3-D network. Variable-temperature magnetic susceptibility data confirm the tetravalent state of uranium.

Light-green tablet crystals of **1** were obtained as the only solid product by heating a mixture of UO_2 (0.25 mmol), HF(aq) (4 mmol, 40% solution), oxalic acid dihydrate (1 mmol), and H_2O (2.5 mL) in a Teflon-lined, 23-mL autoclave at 120 °C for 3 days, followed by slow cooling at 6 °C/h to room temperature. The yield was 50% based on U. A suitable crystal of **1** was selected for single-crystal X-ray diffraction study.[21] The X-ray powder pattern of the bulk product is in good agreement with the calculated pattern based on the results from single-crystal X-ray diffraction (see Figure S1 in the Supporting Information). Energy-dispersive X-ray fluorescence spectroscopic analysis of several crystals confirms the presence of U and F. Elemental analysis results are consistent with the formula [Anal. Found (calcd): C, 3.22 (3.36); H, 0.74 (0.56)]. The infrared spectrum (KBr method) reveals the bands characteristic of a H_2O molecule [ν(O−H) ~ 3370 cm^{-1}] and an oxalate ligand [ν(C−O) ~ 1670, 1350, 1310 cm^{-1}] (Figure S2 in the Supporting Information). Thermogravimetric analysis measurements in flowing air show a weight loss of 22.3% in several overlapping steps between 40 and 900 °C (Figure S3 in the Supporting Information). The final decomposition product was determined to be U_3O_8 by powder X-ray diffraction. The observed total weight loss of 22.3% is close to the calculated value of 21.38% for H_2O, $1.5F_2$, CO, and CO_2. An abrupt weight loss commences at about 300 °C because of the decomposition of the oxalate ligand. To confirm the oxidation state of U, magnetic susceptibility data were measured on a powder sample of 23.2 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 (-94×10^{-6} emu/formula unit).

There is only one unique U atom in the structure, which is coordinated by six F atoms, one bidentate oxalate chelate, and one H_2O molecule. The bond-valence sum for this nine-coordinate U(1), calculated by using the bond-valence parameters for U^{4+}−F and U^{4+}−O from Brese and O'Keeffe,[22] is 4.08 valence units, in accordance with the occurrence of U^{4+} in this site. The UF_6O_3 unit approximates to a tricapped trigonal prism, formed by placing one oxalate O atom, one H_2O molecule, and one F atom above the three rectangular faces of the trigonal prism. Each prism shares an edge with an adjacent prism and shares four corners with four additional prisms to form a $[UF_{2/2}F_{4/2}(H_2O)_{1/1}(C_2O_4)_{1/2}]$ layer in the *bc* plane, as shown in Figure 1. The fractional numbers in the chemical formula denote coordination number 9 for the U atom (=2 + 4 + 1 + 2 = sum of the numerators), coordination number 2 for two different kinds of F atoms, and coordination number 1 for the water O atom, and the oxalate ligand is coordinated to two U atoms. All of the shared atoms are F atoms, and the remaining three corners of each polyhedra include one water O atom and two oxalate O atoms. Several layered organically templated uranium(IV) fluorides that consist of U-centered tricapped trigonal prisms have been reported.[1,2,8,10] However, the polyhedra in these layered compounds are linked in different ways. The oxalate anion in **1** shows bisbidentate coordination to two U(1) atoms, acting as pillars between adjacent layers to produce the extended 3-D network (Figure 2). The bisbidentate coordination is very common and is seen in 90% of the structures of metal oxalatophosphates. Many of these phosphates can be described by metal phosphate layers pillared by oxalate anions.[23]

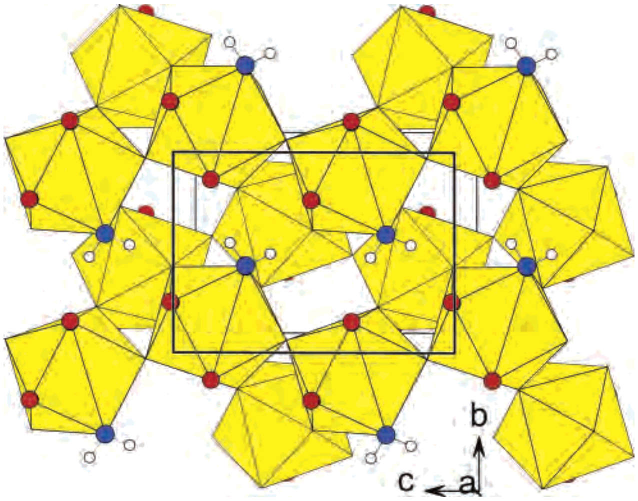

Figure 1. Section of a $[UF_{2/2}F_{4/2}(H_2O)_{1/1}(C_2O_4)_{1/2}]$ sheet in **1**: red circles, oxalate O atoms; blue circles, water O atoms; small open circles, H atoms. The other corners of each U-centered tricapped trigonal prism are F atoms. C atoms are not shown for clarity.

The temperature dependence of μ_{eff} and $1/\chi_M$ curves is shown in Figure 3. The effective magnetic moment at 300 K is 2.89 μ_B/formula unit, which is consistent with U^{4+} ions. Previously reported moments for a number of U^{IV} compounds have fallen in the range of 2.7−3.6 μ_B.[6] The previously studied uranium(IV) fluorides showed room-temperature moments corresponding to between 3 and 4 μ_B per U^{IV} center.[2,6,12,13] The large variation of the moments may arise from magnetic anisotropy of the U^{4+} ions.[24] The magnetic

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(21) Crystallographic data for **1**: light-green crystals of dimensions 0.1 × 0.075 × 0.025 mm, $T = 100$ K, monoclinic, space group *C*2/*c* (No. 15); $a = 17.246(3)$ Å, $b = 6.088(1)$ Å, $c = 8.589(2)$ Å, $\beta = 95.43(3)°$, $V = 897.8(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 5.283$ g cm^{-3}, $\lambda = 0.710\,73$ Å, $\mu = 361.5$ mm^{-1}, 6382 reflections measured, 938 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 54.99°$, $R_{int} = 0.0504$), GOF = 1.081, R1 = 0.0187, wR2 = 0.0497. The H atoms of the coordinated water were located with the difference Fourier maps. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The atomic coordinates and isotropic thermal parameters for H atoms were fixed. The final difference maps were featureless, and the highest peak and deepest hole were 1.89 and −2.08 e/Å^3, respectively. All calculations were performed using *SHELXTL*, version 5.1, software package.

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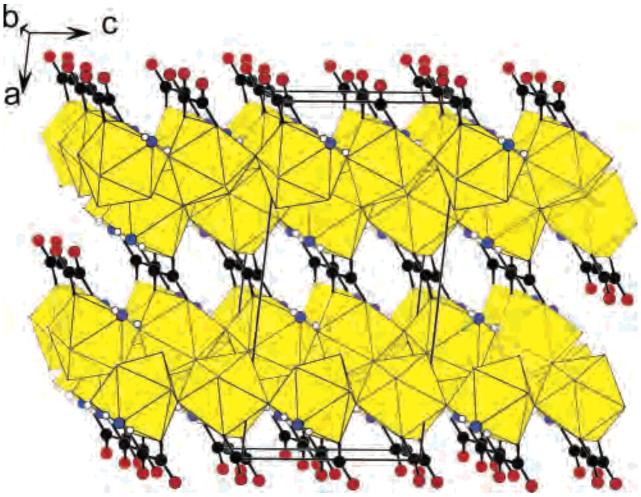

Figure 2. Structure of **1** viewed approximately parallel to the *b* axis: black circles, C atoms; red circles, oxalate O atoms; blue circles, water O atoms; small open circles, H atoms.

moment decreases rapidly upon cooling, which indicates the presence of antiferromagnetic interactions between the U ions. The magnetic susceptibilities above about 50 K follow the Curie−Weiss law with a negative value of the Weiss constant. A fit of the data from 60 to 300 K to the equation $\chi_M = C/(T - \theta)$ results in $C = 1.47$ cm^3·K/mol and $\theta = -123$ K. The effective magnetic moment obtained using $\mu_{eff} = (8C_{60-300})^{1/2}$ is 3.43 μ_B.

In summary, we have synthesized and structurally characterized a new uranium(IV) fluoride incorporating an oxalate ligand. The structure consists of 2-D layers of uranium fluoride, which are pillared through oxalate ligands to form a 3-D framework. Its structure is featured by the presence of both inorganic fluoride and organic oxalate anions in the same framework. It is a new example of an interesting class of inorganic−organic hybrid compounds. The title compound has the potential for further exploration. For example, it would be interesting to synthesize organically templated uranium fluoride−oxalates and to replace oxalate with extended analogues such as squarate and 1,4-benzenedicarboxylate. Further work on this theme is in progress.

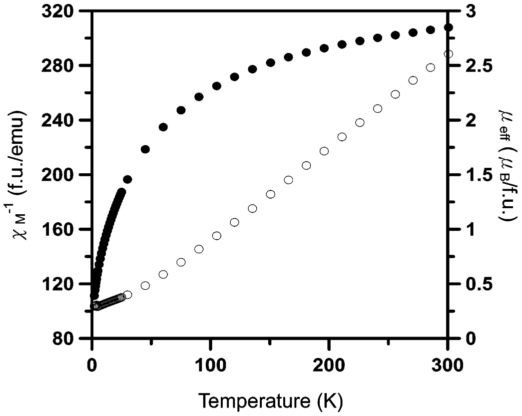

Figure 3. μ_{eff} vs T (solid circles) and $1/\chi_M$ vs T (open circles) for **1**.

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

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