Hydrothermal Syntheses of Layered Uranium Oxyfluorides: Illustrations of Dimensional Reduction

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Rationalizing and predicting changes in the architecture of crystalline solids can be accomplished in many cases through the application of the dimensional reduction formalism.[1−5] Long and co-workers have recently compiled a database demonstrating that the structures of numerous low-dimensional transition metal halides can be interconnected through this theory.[6] While the majority of these compounds have been derived from solid-state reactions, hydrothermal syntheses also provide access to inorganic materials with reduced dimensionality, particularly when structure-directing agents are employed.[7−19] While many main group and transition metal systems have been explored over the past 15 years, employment of these methods in the preparation of low-dimensional actinides is quite novel, being first reported by O'Hare and co-workers in 1998.[20−26] Actinide-based materials possess exploitable chemical and physical properties, including use as oxidation catalysts[29] and as luminescent[28] and magnetic materials.[20,27]

Our studies of the hydrothermal preparation and characterization of uranium-containing materials has led to the discovery of a large number of low-dimensional U(IV) fluorides and U(VI) oxyfluorides.[27,28] Thus far, all of the U(VI) compounds that we have isolated contain $[UO_2F_5]$ pentagonal bipyramids. The use of these polyhedra as building blocks for low-dimensional[26] and open-framework materials[25] has recently yielded two striking examples of dimensional reduction that demonstrate both the strengths and weaknesses of this theory. Specifically, the reactions of $UO_2(C_2H_3O_2)_2$ or UO_3 with aqueous HF in the presence of pyridine or pyrazole at 180 °C for 72 h have resulted in the isolation of one-dimensional $(C_5H_6N)UO_2F_3$ (**AU1-4**)[28] and $(C_3H_5N_2)UO_2F_3$ (**AU1-5**)[28] and two-dimensional $(C_5H_6N)U_2O_4F_5$ (**AU2-4**) and $(C_3H_5N_2)U_2O_4F_5 \cdot 1.75H_2O$ (**AU2-5**). Hydrothermal methods are particularly advantageous in these syntheses because the products are isolated in high yield as large single crystals. All of these compounds luminesce brightly at room temperature when irradiated with long-wavelength UV light (365 nm). The observed emission, as measured using a fluorescence microscope on single crystals, is characteristic of the uranyl units contained in these materials.[28,30,31]

In both the pyridinium[32] and pyrazolium[33] systems, we have been able to isolate and determine the conditions necessary for preparing pure phases through the use of compositional space diagrams.[23,24,26,34−36] One of the difficulties in establishing systems

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(32) $(C_5H_6N)U_2O_4F_5$ (**AU2-4**). $UO_2(C_2H_3O_2)_2$ (1.060 g, 2.5 mmol) and pyridine (0.04 mL, 0.5 mmol) were loaded in a 23 mL PTFE lined autoclave. Water (1 mL) was then added to the solids followed by the dropwise addition of HF (0.25 mL, 7 mmol). The autoclave was sealed and placed in a box furnace that had been preheated to 180 °C. After 72 h the furnace was cooled at 9 °C/h to 23 °C. The product consisted of a light-yellow liquid over pale-yellow prisms. The mother liquor was decanted from the crystals, which were then washed with methanol and allowed to dry; yield, 698 mg (78% yield). Anal. Calcd for C_5H_6-$NF_5O_4U_2$: C, 8.40; H, 0.85; N, 1.96. Found: C, 8.27; H, 0.92; N, 1.83.
(33) $(C_3H_5N_2)U_2O_4F_5 \cdot 1.75H_2O$ (**AU2-5**). UO_3 (1.430 g, 5 mmol) and pyrazole (136 mg, 2 mmol) were loaded in a 23 mL PTFE lined autoclave. Water (1 mL) was then added to the solids followed by the dropwise addition of HF (0.65 mL, 18 mmol). The autoclave was sealed and placed in a box furnace that had been preheated to 180 °C. After 72 h the furnace was cooled at 9 °C/h to 23 °C. The product consisted of a yellow liquid over pale-yellow rectangular plates. The mother liquor was decanted from the crystals, which were then washed with methanol and allowed to dry; yield, 1.270 g (73% yield). Anal. Calcd for $C_3H_5N_2F_5O_4U_2 \cdot 1.75H_2O$: C, 4.90; H, 1.16; N, 3.81. Found: C, 4.92; H, 0.92; N, 3.65.
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where stepwise transformation of a structure can be observed is that these reactions often involve complex redox processes yielding U(IV) products.[20,22,24,26,27] While previous reports have enumerated the isolation of zero-, one-, two-, and three-dimensional uranium fluorides and oxyfluorides, the fundamental building blocks in these compounds typically vary drastically.[24,26] We have been able to greatly reduce, but not eliminate, reduction of the U(VI) centers through the employment of aromatic amines as templates. These structure-directing agents are far more stable and less reducing under mild hydrothermal conditions than saturated amines such as homopiperazine.[27]

The structure of $(C_5H_6N)U_2O_4F_5$ (**AU2-4**)[37] consists of two-dimensional sheets formed from edge- and corner-sharing $[UO_2F_5]$ pentagonal bipyramids, as shown in Figure 1. These sheets can be sectioned into one-dimensional chains that are linked by the bridging F(1) anions. As the $[UO_2F_5]$ pentagonal bipyramid translates, this fluoride anion alternates between sides of the chain. This results in the chains joining at every other uranium center, creating channels that run down [001]. The pyridinium cations are located above and beneath these channels, forming hydrogen bonds with the fluoride ligands, and further serve to separate the $[U_2O_4F_5]^{1-}$ layers. U−F bond distances, all of which are bridging, range from 2.291(1) to 2.328(5) Å. The uranyl, UO_2^{2+}, moiety is within expected ranges, being essentially linear with a O(1)−U(1)−O(2) bond angle of 179.5(5)° and U=O bonds distances of 1.751(1) and 1.762(1) Å.

Using dimensional reduction, we can predict that the addition of 1 equiv of pyridinium fluoride to **AU2-4** will result in the transformation of the bridging F(1) fluoride ligand into a terminal group, thereby yielding one-dimensional chains, as depicted in Figure 1. In fact, **AU1-4** contains such linear, one-dimensional $[UO_2F_3]^{1-}$ chains formed through edge-sharing $[UO_2F_5]$ pentagonal bipyramids.[28] This is a particularly spectacular transformation because there are virtually no other changes in the inorganic architecture.

In contrast to **AU2-4**, the two-dimensional sheets in **AU2-5**[37] are formed solely through corner-sharing of the $[UO_2F_5]$ polyhedra. The pyrazolium cations lie perpendicular to these layers and form hydrogen-bonding networks between layers. The structural arrangement of $[U_2O_4F_5]^{1-}$ layers in **AU2-5** was also
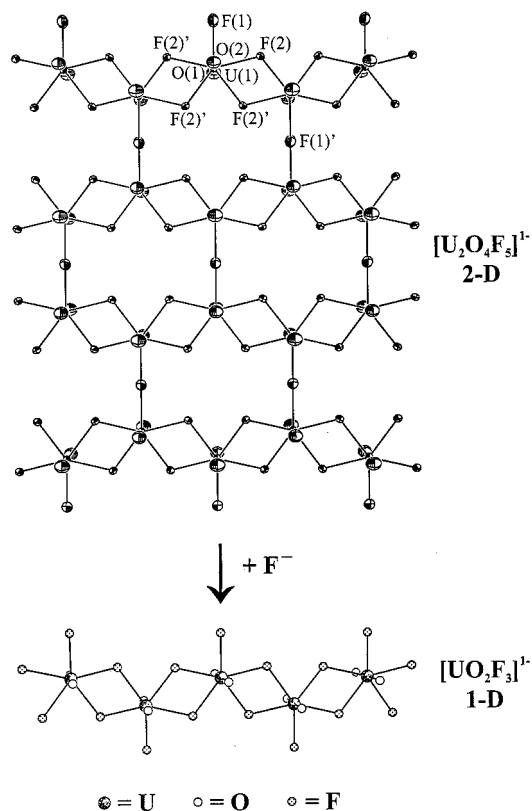
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(37) Crystallographic data: **AU2-4** (295 K), monoclinic, space group $C2/m$, $a = 11.802(6)$ Å, $b = 7.323(3)$ Å, $c = 7.018(4)$ Å, $\beta = 102.34(4)°$, $V = 592.5(5)$ Å^3, $Z = 2$, Mo Kα, $\lambda = 0.710$ 73, R1 = 0.0399, wR2 = 0.0958 for 540 independent reflections with $I > 2\sigma$ and 48 parameters; **AU2-5** (crystals are of marginal quality, and the pyrazolium cations are not well-resolved), orthorhombic, space group $Pnnm$, $a = 17.32(1)$ Å, $b = 12.034(5)$ Å, $c = 12.172(5)$ Å, $V = 2537(2)$ Å^3, $Z = 8$, Mo Kα, $\lambda = 0.710$ 73, R1 = 0.0494, wR2 = 0.1296 for 1549 independent reflections with $I > 2\sigma$ and 176 parameters.

Figure 1. Conversion of two-dimensional $[U_2O_4F_5]^{1-}$ sheets in **AU2-4** to $[UO_2F_3]^{1-}$ linear, one-dimensional chains in **AU1-4**. Ellipsoids for 50% displacement are shown for **AU2-4**. The pyridinium cations have been omitted for clarity.

observed in $(C_4H_{12}N_2)_2(U_2O_4F_5)_4 \cdot 11H_2O$.[26] As found in the pyridinium system, increased concentrations of pyrazolium fluoride also leads to dimensional reduction, yielding **AU1-5**, which contains the same one-dimensional chains as found in **AU1-4**. Considerable structural rearrangement is required in order to form these chains. As indicted by Holm and co-workers,[2] herein lies the weakness of dimensional reduction theory in that isomerization cannot be predicted at each step of the transformation.

Supporting Information Available: X-ray crystallographic files for **AU2-4** and **AU2-5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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