$[N_2C_6H_{14}]_2[(UO_2)_6(H_2O)_2F_2(PO_4)_2(HPO_4)_4]\cdot 4H_2O$: A New Microporous Uranium Phosphate Fluoride

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Microporous solids have attracted considerable attention owing to optical, catalytic, or sorption properties.[1] The incorporation of metal centers into microporous materials has been extensively studied toward the goal of preparing compounds with the chemical and thermal stability and selectivity of zeolites.[2] Many chemical reactions can be facilitated by transition metal centers such as free-radical chemistry, redox chemistry, and photochemical reactions.

The hydrothermal chemistry of uranium has been the subject of attention in recent years[3−7] owing to the potential structural diversity resulting from the high coordination numbers available to U^{6+} and the existence of several desirable physical properties.[8] Despite this, few organically templated open-framework uranium materials are known; one phosphate,[4] one oxide,[5b] one molybdate,[5c] one fluoride,[6c] one sulfate,[6i] one phosphite,[6r] and one silicate.[7] We report the phase-pure synthesis, crystal structure, and thermal stability analysis of the first microporous uranium phosphate fluoride, $[N_2C_6H_{14}]_2[(UO_2)_6(H_2O)_2F_2(PO_4)_2(HPO_4)_4]\cdot 4H_2O$ (MUPF-1).[9,10]

Six distinct uranium sites are observed in MUPF-1, each of which is seven-coordinate in a pentagonal bipyramidal geometry. Each uranium(VI) cation is bound to two oxide ligands through short "uranyl" bonds. The $[UO_2]^{2+}$ bonds exhibit distances ranging between 1.765(8) and 1.795(8) Å, and O−U−O angles that range between 177.5(4) and 179.0(4)°. These values are near to the average reported values.[11] The five equatorial coordination sites around each uranium center differ. U(1), U(2), U(5), and U(6) are each bound to two oxide ligands that are shared between one UO_7 polyhedron and one PO_4 tetrahedron each, and three oxides that are shared between two UO_7 polyhedra and one PO_4 tetrahedron each. The equatorial coordination environment around U(3) and U(4) contains bonds to three oxides that are shared with PO_4 tetrahedra, one water molecule and one fluoride anion. The assignment of bound water molecules and fluoride anions was based upon bond length (2.299(8) and 2.306(8) Å versus 2.490(9) and 2.452(9) Å for U−F and $U-O_{water}$ bonds, respectively) and hydrogen-bonding interactions (see Figure 1), which are aligned along the *a* axis. Bond valence calculations[12,13] on MUPF-1, using uranium parameters from Burns et al.,[11] resulted in values between 5.939 and 6.071 for the uranium centers. Six distinct phosphate sites exist in MUPF-1, each of which resides in the center of one of two types of phosphate tetrahedra. P(1) and P(6) are each bound to four oxide ligands that bridge to uranium centers, while P(2), P(3), P(4), and P(5) are each bound to three bridging and one protonated oxide.

Three analogous $[U_2O_{12}]$ dimers, consisting of two edge-shared UO_7 polyhedra, are observed in MUPF-1. Each dimer contains either one U(1) and one U(2) site,

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(9) MUPF-1 (microporous uranium phosphate fluoride number 1) was synthesized by combining $UO_2(CH_3CO_2)_2\cdot 2H_2O$ (0.3190 g, 7.52×10^{-4} mol), dabco (0.0143 g, 1.28×10^{-4} mol), $H_4P_2O_7$ (0.2892 g, 1.66×10^{-3} mol), water (9.0143 g, 5.01×10^{-1} mol), and $HF_{(aq)}$ (40%, 5 drops) in a Teflon lined stainless steel autoclave, and heating to 180 °C for 24 h, before cooling to 157 °C at 0.6 °C h^{-1}, then from 157 °C to room temperature at 6 °C h^{-1}. A monophasic yellow crystalline product was recovered by filtration. A yield of 63% (based upon uranium) was observed. IR data: 520 cm^{-1}, U−F; 922 cm^{-1}, U = O; 1070 cm^{-1}, P − O; 1500 cm^{-1}, N − H; 3070 cm^{-1}, N − H.

(10) Crystal data: crystal size $0.08 \times 0.08 \times 0.18$ mm, monoclinic, space group $P2_1/n$ (No. 14) with $a = 13.4487(2)$ Å, $b = 17.9210(2)$ Å, $c = 19.9026(3)$ Å, $\beta = 90.9833(7)°$, $V = 4796.1(1)$ Å^3, $Z = 4$, $\rho_{calc} = 3.557$ g cm^{-1}, $2\theta_{max} = 55.0°$, $\lambda = 0.71069$ Å, $T = 150$ K, total data 20627, unique data 10871, observed data ($I > 3\sigma(I)$) 7499, $\mu = 20.514$ mm^{-1}, 650 parameters, $R/R_w = 0.0399/0.0988$ on $|F^2|$.

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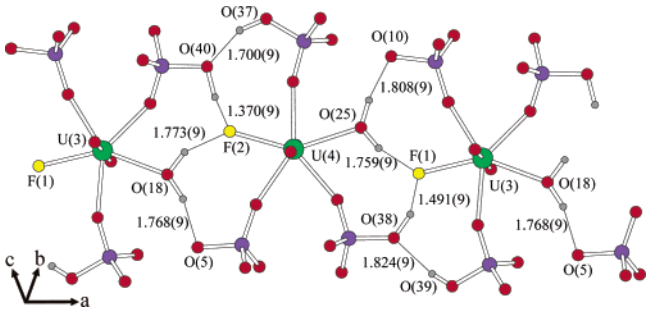

Figure 1. Intraframework hydrogen bonding in MUPF-1. Participating atomic sites are labeled. Selected distances are shown in angstroms (Å). Hydrogen bonds are shown as solid lines with corresponding distances (Å).

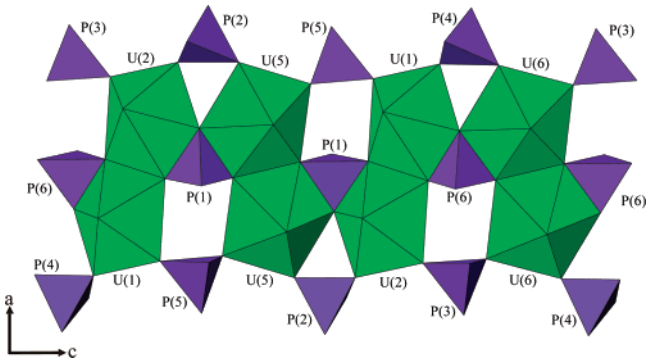

Figure 2. $[(UO_2)_2(PO_4)_3]^{5-}$ chains in MUPF-1. UO_7 pentagonal bipyramids are green and phosphate tetrahedra are purple. The central atom in each coordination polyhedron is labeled.

two symmetry-related U(5) sites, or two symmetry-related U(6) sites. These dimers are connected by bridging phosphate tetrahedra. See Figure 2. The tetrahedra containing P(1) and P(6) bridge between adjacent dimers, through two shared edges, while the tetrahedra containing P(2), P(3), P(4), and P(5) connect neighboring dimers through shared corners. The resulting chains run along the *c* axis and lie next to one another in the *ac* plane.

The directions of the $[(UO_2)_2(PO_4)_3]^{5-}$ chains and the intraframework hydrogen bonding are perpendicular to one another. Layers of adjoining chains are bound to one another through the $[UO_5F(H_2O)]$ polyhedra, which act as pillars. The result is a three-dimensional open framework. See Figure 3.

The channels present in the structure are occupied by $[dabcoH_2]^{2+}$ ($dabcoH_2 = N_2C_6H_{14}$) cations and occluded water molecules. Two distinct $[dabcoH_2]^{2+}$ cations and four occluded water molecules are observed in MUPF-1. Each $[dabcoH_2]^{2+}$ cation donates two hydrogen bonds to adjacent occluded waters, which in turn donate hydrogen bonds to the inorganic framework. The primary channels run along the *a* axis and have approximate dimensions of 6.5 × 7.5 Å. Smaller secondary channels run along the [2 2 1], [2 −2 1], [2 2 −1], and [2 −2 −1] directions, with approximate dimensions of 4.5 × 6 Å. A view of the interconnected channels in MUPF-1, as calculated using ATOMS v.6.0,[14] is shown in Figure 4. The spaces occupied by the chains, which run along the *c* axis, are clearly visible.

The powder X-ray diffraction pattern of the bulk sample is in agreement with the predicted pattern based

(14) Dowty, E. *ATOMS v.6.0*; Shape Software: TN.

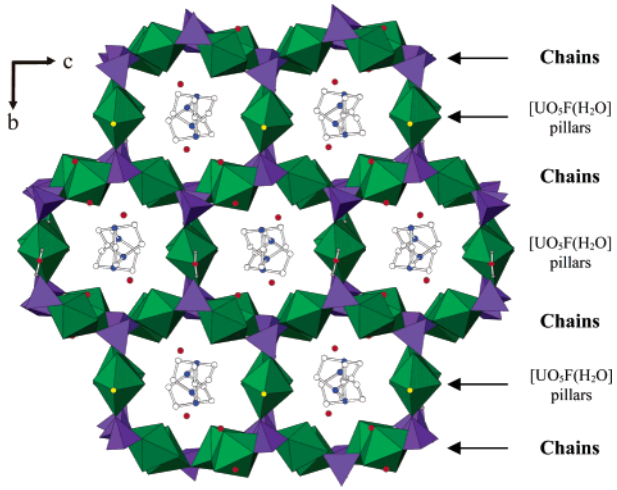

Figure 3. MUPF-1 as viewed along the [1 0 0] direction. UO_7 pentagonal bipyramids are green and phosphate tetrahedra are purple. Fluorides and water molecules are shown as yellow and red spheres, respectively. Template and occluded water hydrogens have been removed for clarity.

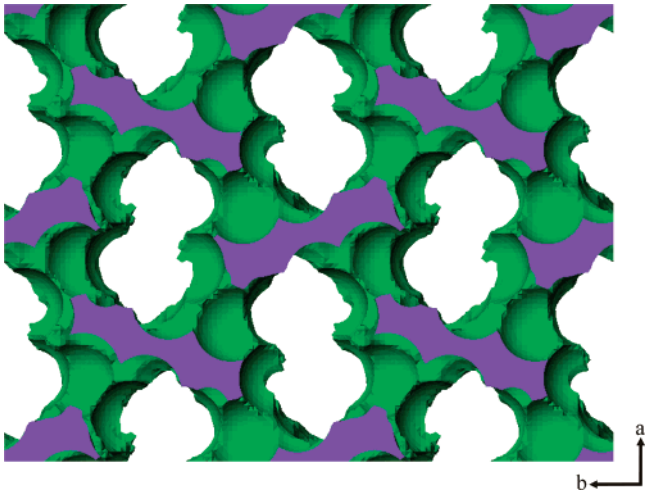

Figure 4. Three-dimensional pore space in MUPF-1.

upon the single-crystal model. Thermogravimetric measurements show loss of bound and occluded water molecules, and loss of HF, between 40 and 290 °C. Template decomposition is observed between 300 and 420 °C. The structure completely collapses to $U_2O(PO_4)_2$ by 800 °C, as determined using powder X-ray diffraction.

The promise of new microporous materials containing uranium is supported by the discovery of this three-dimensional uranium phosphate fluoride. The combination of both fluoride anions and phosphate tetrahedra bound to uranium(VI) centers resulted in a new compound with a novel three-dimensional framework. Additional experiments using alternate organic templating agents are ongoing.

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Supporting Information Available: Complete lists of crystallographic details, atomic coordinates, and bond lengths and angles are available in an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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