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Controlled Structural Variations in Templated Uranium Sulfates

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A series of experiments in the $UO_2(CH_3CO_2)_2 \cdot 2H_2O/H_2SO_4$/1-(2-aminoethyl)piperazine/H_2O system were conducted to determine the effects of variation in initial reactant concentrations on the reaction products. Several reaction gels were produced, in which the composition varied from 16:80:4:500 $UO_2(CH_3CO_2)_2 \cdot 2H_2O/H_2SO_4$/1-(2-aminoethyl)-piperazine/H_2O to 4:92:4:500 $UO_2(CH_3CO_2)_2 \cdot 2H_2O/H_2SO_4$/1-(2-aminoethyl)piperazine/H_2O. Single crystals of two new organically templated uranium sulfates, $[N_3C_6H_{18}]_2[(UO_2)_5(H_2O)(SO_4)_8] \cdot 5H_2O$ and $[N_3C_6H_{18}][(UO_2)_2(H_2O)(SO_4)_3(HSO_4)] \cdot 4.5H_2O$, were isolated. Both compounds exhibit structures in which the inorganic frameworks are two-dimensional and the protonated amines reside between layers, participating in extensive hydrogen bonding. The composition and structure of each compound is dependent on the nature of the starting concentrations. Crystal data: for $[N_3C_6H_{18}]_2[(UO_2)_5(H_2O)(SO_4)_8] \cdot 5H_2O$, monoclinic, space group $P2_1/n$ (No. 14), $a = 21.5597(3)$ Å, $b = 10.2901(2)$ Å, $c = 22.8403(3)$ Å, $\beta = 96.7436(7)°$, and $Z = 4$; for $[N_3C_6H_{18}][(UO_2)_2(H_2O)(SO_4)_3(HSO_4)] \cdot 4.5H_2O$, monoclinic, space group $P2_1/a$ (No. 14), $a = 15.7673(4)$ Å, $b = 10.5813(3)$ Å, $c = 16.7710(5)$ Å, $\beta = 99.9216(9)°$, and $Z = 4$.

Introduction

The synthesis of new materials under hydrothermal conditions using amine structure-directing agents and aqueous acids has been employed to produce a multitude of new materials.[1–8] A host of compounds containing the phosphate tetrahedron have been prepared in this manner. Despite this rich chemistry, the incorporation of the sulfate tetrahedron into an analogous family of compounds is in its infancy. We have recently reported several uranium sulfates;[9] Rao et al. have reported organically templated cadmium,[10] iron,[11] and vanadium sulfates;[12] Louër et al.[13] and Pang et al.[14] have reported lanthanum sulfates; Takano et al. and Wright et al. have reported phosphate sulfates containing cerium[15] and scandium[16] respectively; Khan et al. reported a vanadium sulfate;[17] and Lingafelter et al. reported a zinc sulfate.[18]

Organically templated metal sulfates hold vast promise of desirable physical properties despite the small number of reported compounds. These compounds exhibit great structural diversity, with reported compounds containing molecular anions to three-dimensional microporous frameworks. However, little is understood about crystallization mechanisms and the formation of tailored materials is not yet

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possible. Composition space,[19] a method of reaction variable isolation, has been used to elucidate the controlling factors in the synthesis of templated uranium materials,[9c,20] which comprise a well-known family of compounds.[21] Uranium was chosen for study because of its potential use in catalytic applications and ability to exhibit coordination numbers higher than 6. A similar approach to composition space is detailed in this study. A series of reactions, in which variations are carefully introduced, was conducted to demonstrate the dependence of composition and structure on initial reactant concentrations. The synthesis, structure and characterization of two new organically templated uranium sulfates are reported. They are designated USO-15 and USO-16 (uranium sulfate from Oxford).

Experimental Section

Caution! *Although all uranium materials used in these experiments are depleted, extra care should always be taken when handling uranium containing materials.*

Materials. 1-(2-aminoethyl)piperazine (99%, Aldrich) and sulfuric acid (98%, Aldrich) were used as received. Deionized water was also used in these syntheses. $UO_2(CH_3CO_2)_2{\cdot}2H_2O$ was prepared[21d] from UO_3 (99.8%, Strem).

Synthesis. All reactions were conducted in poly(fluoroethylenepropylene)-lined 23 mL autoclaves. The autoclaves were heated to 180 °C at 10 °C min^{-1}, where the temperature was held constant for 24 h. The reactions were cooled to room temperature at 6 °C h^{-1}. The autoclaves were opened in air. The solid products were collected using filtration and washed with deionized water and acetone.

Synthesis of $[N_3C_6H_{18}]_2[(UO_2)_5(H_2O)(SO_4)_8]{\cdot}5H_2O$ (USO-15) and $[N_3C_6H_{18}][(UO_2)_2(H_2O)(SO_4)_3(HSO_4)]{\cdot}4.5H_2O$ (USO-16). USO-15 was synthesized through the reaction of 0.6772 g (1.40×10^{-3} mol) of $UO_2Ac_2{\cdot}2H_2O$ (Ac = $CH_3CO_2^-$), 0.0257 g (1.99×10^{-4} mol) of aep (1-(2-aminoethyl)piperazine), 0.3296 g (3.36×10^{-3} mol) of H_2SO_4, and 0.9936 g (5.52×10^{-2} mol) of deionized water. Yellow plates were isolated after reaction in 10% yield. The remaining uranium remains in solution. No other solid products were observed. USO-16 was synthesized through the reaction of 0.1712 g (3.54×10^{-4} mol) of $UO_2Ac_2{\cdot}2H_2O$, 0.0578 g (4.48×10^{-4} mol) of aep, 0.9695 g (9.89×10^{-3} mol) of H_2SO_4, and 1.0293 g (5.72×10^{-2} mol) of deionized water. Yellow blocks were isolated after reaction in 58% yield. Anal. Obsd for USO-15 (calcd): N, 3.46 (3.37); C, 5.86 (5.79); H, 1.53 (1.94); S, 10.05 (10.30); U, 46.90 (47.77). Obsd for USO-16 (calcd): N, 3.61 (3.63); C, 6.20 (6.23); H, 2.45 (2.60); S, 11.08 (11.07); U, 39.98 (41.16). Powder X-ray diffraction patterns of each respective bulk sample matched patterns generated from the single-crystal X-ray structure data.

Table 1. Crystallographic Data for USO-15 and USO-16

param	USO-15	USO-16
formula	$[N_3C_6H_{18}]_2[(UO_2)_5$-$(H_2O)(SO_4)_8]{\cdot}5H_2O$	$[N_3C_6H_{18}][(UO_2)_2(H_2O)(SO_4)_3$-$(HSO_4)]{\cdot}4.5H_2O$
fw	2481.12	1147.56
space group	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)
a/Å	21.5597(3)	15.7673(4)
b/Å	10.2901(2)	10.5813(3)
c/Å	22.8403(3)	16.7710(5)
β/°	96.7436(7)	99.9216(9)
V/Å^3	5032.1	2756.2
Z	4	4
D_c/g cm^{-3}	3.275	2.765
λ/Å	0.710 69	0.710 69
T/°C	−123	−123
μ/mm^{-1}	16.502	12.147
R_1[a]	0.0443	0.0310
wR_2[b]	0.1141	0.0725

[a] $R_1 = \Sigma|F_o| - F_c|/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/[\Sigma w(F_o^2)^2]^{1/2}$.

X-ray Crystallographic Analysis. Single crystals of dimension $0.08 \times 0.20 \times 0.30$ mm for USO-15 and $0.04 \times 0.06 \times 0.10$ mm for USO-16 were used for structural determination. Data were collected using an Enraf Nonius FR 590 Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystals were mounted on a glass fiber using N-Paratone oil and cooled in-situ using an Oxford Cryostream 600 Series to 150 K for data collection. Frames were collected, indexed, and processed using Denzo SMN and the files scaled together using HKL GUI within Denzo SMN.[22] The heavy atom positions were determined using SIR97[23] and other non-hydrogen atoms refined using Crystals.[24] All non-hydrogen sites were refined using anisotropic thermal parameters using full-matrix least-squares procedures on F_o^2 with $I > 3\sigma(I)$. Hydrogen atoms were placed in geometrically idealized positions. All calculations were performed using Crystals[24] and Cameron.[25] Relevant crystallographic data are listed in Table 1, and selected bond lengths are listed in Tables 2 and 3.

Infrared Spectroscopy. All infrared measurements were obtained using a Perkin-Elmer 1600 FT spectrometer. Samples were diluted with spectroscopic KBr and pressed into a pellet. Scans were run over the range 400−4000 cm^{-1}.

Thermogravimetric Analysis. TGA measurements were conducted using a Rheometric Scientific STA 1500H thermal analyzer. Samples were loaded into a platinum crucible and heated from ambient temperature to 800 °C at 10 °C min^{-1} under flowing argon. The structures of the calcination products were determined using powder X-ray diffraction.

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Table 2. Selected Bond Lengths (Å) for USO-15

U(1)−O(1)	1.758(8)	U(3)−O(19)	2.411(7)
U(1)−O(2)	1.767(8)	U(3)−O(20)	2.374(7)
U(1)−O(3)	2.366(7)	U(3)−O(21)	2.416(7)
U(1)−O(4)	2.348(8)	U(4)−O(22)	1.763(8)
U(1)−O(5)	2.375(7)	U(4)−O(23)	1.777(8)
U(1)−O(6)	2.432(7)	U(4)−O(24)	2.425(7)
U(1)−O(7)	2.439(7)	U(4)−O(25)	2.384(7)
U(2)−O(8)	1.772(7)	U(4)−O(26)	2.481(7)
U(2)−O(9)	1.757(7)	U(4)−O(27)	2.378(7)
U(2)−O(10)	2.358(7)	U(4)−O(28)	2.346(8)
U(2)−O(11)	2.378(7)	U(5)−O(29)	1.773(8)
U(2)−O(12)	2.347(7)	U(5)−O(30)	1.763(6)
U(2)−O(13)	2.392(7)	U(5)−O(31)	2.389(7)
U(2)−O(14)	2.441(7)	U(5)−O(32)	2.375(7)
U(3)−O(15)	1.795(7)	U(5)−O(33)	2.381(7)
U(3)−O(16)	1.767(8)	U(5)−O(34)	2.398(7)
U(3)−O(17)	2.387(7)	U(5)−O(35)	2.356(7)
U(3)−O(18)	2.337(7)		
S(1)−O(7)	1.488(7)	S(5)−O(6)	1.482(7)
S(1)−O(25)	1.501(7)	S(5)−O(14)	1.499(8)
S(1)−O(34)	1.466(7)	S(5)−O(21)	1.469(8)
S(1)−O(36)	1.420(8)	S(5)−O(40)	1.456(7)
S(2)−O(3)	1.475(7)	S(6)−O(13)	1.491(8)
S(2)−O(28)	1.485(8)	S(6)−O(20)	1.494(7)
S(2)−O(33)	1.472(7)	S(6)−O(31)	1.471(7)
S(2)−O(37)	1.463(8)	S(6)−O(41)	1.439(8)
S(3)−O(4)	1.492(8)	S(7)−O(19)	1.501(8)
S(3)−O(10)	1.498(8)	S(7)−O(24)	1.518(7)
S(3)−O(27)	1.487(8)	S(7)−O(35)	1.480(8)
S(3)−O(38)	1.439(8)	S(7)−O(42)	1.434(8)
S(4)−O(5)	1.495(7)	S(8)−O(12)	1.486(8)
S(4)−O(11)	1.490(7)	S(8)−O(18)	1.486(7)
S(4)−O(17)	1.476(7)	S(8)−O(32)	1.475(8)
S(4)−O(39)	1.453(8)	S(8)−O(43)	1.457(8)

Table 3. Selected Bond Lengths (Å) for USO-16

U(1)−O(1)	1.768(7)	U(2)−O(8)	1.763(6)
U(1)−O(2)	1.774(6)	U(2)−O(9)	1.783(6)
U(1)−O(3)	2.343(6)	U(2)−O(10)	2.427(6)
U(1)−O(4)	2.342(6)	U(2)−O(11)	2.355(6)
U(1)−O(5)	2.367(7)	U(2)−O(12)	2.382(6)
U(1)−O(6)	2.333(7)	U(2)−O(13)	2.368(6)
U(1)−O(7)	2.438(7)	U(2)−O(14)	2.366(6)
S(1)−O(3)	1.499(6)	S(3)−O(5)	1.486(8)
S(1)−O(11)	1.481(6)	S(3)−O(6)	1.492(7)
S(1)−O(13)	1.481(6)	S(3)−O(18)	1.456(8)
S(1)−O(15)	1.449(6)	S(3)−O(19)	1.447(9)
S(2)−O(4)	1.493(6)	S(4)−O(12)	1.498(6)
S(2)−O(10)	1.479(6)	S(4)−O(14)	1.492(6)
S(2)−O(16)	1.472(6)	S(4)−O(20)	1.472(6)
S(2)−O(17)	1.457(7)	S(4)−O(21)	1.463(6)

Elemental Analysis. C, H, and N analyses were conducted using an Elementar Vario EL analyzer. S and U compositions were determined by ICP using a Thermo Jarrell Ash Scan 16 instrument.

Results

USO-15. Five distinct uranium sites are observed in USO-15. Each U^{6+} cation is seven coordinate, in a pentagonal bipyramidal geometry. All five metal centers are bound to two oxide ligands through short "uranyl" bonds with lengths ranging from 1.757(7) to 1.795(7) Å. These values are close to the reported average uranyl bond length of 1.758(4) Å.[26] The five equatorial coordination sites around four of the five $[UO_2]^{2+}$ centers (U(1), U(2), U(3), and U(5)) are occupied by five oxide ligands that are part of sulfate tetrahedra. The five equatorial coordination sites around U(4) are occupied by four sulfate oxides and one bound water molecule. The $U-O_{water}$ bond distance is significantly longer than the $U-O_{sulfate}$ distances in this structure. The $U-O_{water}$ distance is 2.481(7) Å compared to $U-O_{sulfate}$ distances ranging from 2.337(7) to 2.441(7) Å. Bond valence calculations[27,28] on USO-15, using uranium parameters from Burns et al.,[26] resulted in values of 6.08, 6.11, 6.00, 5.98, and 6.10 for U(1)−U(5), respectively.

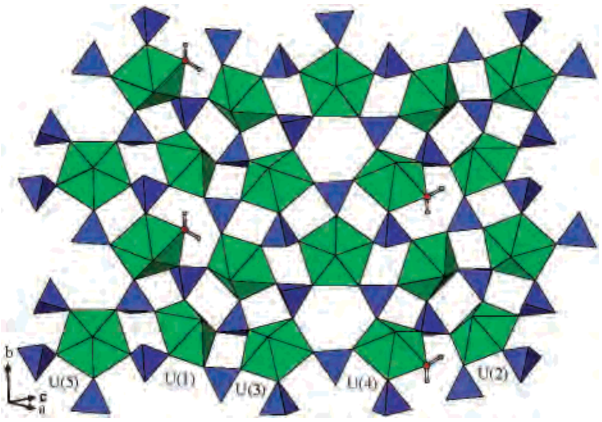

Figure 1. Two-dimensional $[(UO_2)_5(H_2O)(SO_4)_8]^{6-}$ layers in USO-15. Green and blue polyhedra represent $[UO_7]$ and $[SO_4]$, respectively. Distinct uranium sites are labeled, and bound water molecules are shown.

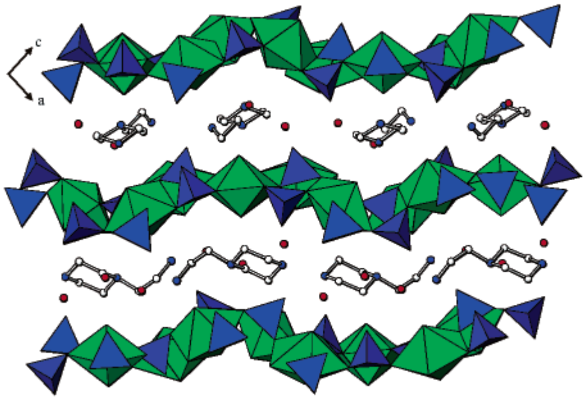

Figure 2. Three-dimensional packing of USO-15. Green and blue polyhedra represent $[UO_7]$ and $[SO_4]$, respectively. Hydrogen atoms have been removed for clarity.

Eight discrete sulfur environments exist in USO-15. The S−O bonds range in length from 1.420(8) to 1.518(7) Å. Each sulfate tetrahedron bridges between three adjacent uranium centers, creating two-dimensional layers in which the layer topology is unprecedented in uranium chemistry. See Figure 1. The $[(UO_2)_5(H_2O)(SO_4)_8]^{6-}$ layers lie in the $[10\bar{1}]$ plane. Successive layers pack in an *aba* arrangement with protonated templates and occluded waters residing in the interlayer spaces. See Figure 2.

The packing of the inorganic frameworks creates two distinct interlayer spaces, each of which is occupied by $[aepH_3]^{3+}$ cations that adopt one of two orientations. The two orientations of the $[aepH_3]^{3+}$ cations can be differentiated by the torsion angle between the aminoethyl amine and the piperazine amine to which it is attached. The N(2)−N(3)

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torsion angle is 78.5(3)°, while the N(5)−N(6) torsion angle is 161.8(4)°. Despite the structural differences between the templates, they both donate hydrogen bonds to the two adjacent inorganic layers, stabilizing the structure. Several occluded water molecules also reside in the interlayer spacings and participate in hydrogen bonding.

The presence of the organic template was confirmed using infrared spectroscopy. N−H bands were observed between 3000 and 3500 cm^{-1} and at 1595 cm^{-1}. The asymmetric uranyl stretch and S−O bands were observed at 926 and 1100 cm^{-1}, respectively.

The thermal stability of USO-15 was investigated using thermogravimetric analysis. A weight loss of 3.0% between 100 and 195 °C corresponds to the loss of five occluded molecules/formula unit (3.6%). Another weight loss of 0.8% between 195 and 205 °C represents the loss of a single bound water molecule/formula unit (0.7%). Concurrent decomposition of the organic templates and calcination to UO_2, as confirmed using powder X-ray diffraction, occurs between 320 and 480 °C. The experimental weight loss, 45%, is in agreement with the calculated value of 46%.

USO-16. Two discrete uranium centers are observed in USO-16. Both U(1) and U(2) are seven coordinate, in a pentagonal bipyramidal geometry. The two uranyl bonds to U(1) have lengths of 1.768(7) and 1.774(6) Å. Four oxides that are bound to sulfur centers and one bound water molecule occupy the five equatorial coordination sites. The $U{-}O_{sulfate}$ distances range between 2.333(7) and 2.367(7) Å, while the $U{-}O_{water}$ bond length is 2.438(7) Å. Sulfate oxides occupy all five equatorial coordination sites around U(2) through bond distances ranging from 2.355(6) to 2.427(6) Å. Bond valence calculations[26−28] on USO-16 resulted in values of 6.17 and 6.07 for U(1) and U(2), respectively.

Four distinct sulfur environments are observed crystallographically in USO-16. Each sulfur center is bound to four oxides in a tetrahedral geometry. The coordination around each type of tetrahedron differs. The sulfate tetrahedra containing S(1) bridge between three adjacent uranium centers, U(1) and U(2) × 2. Those containing S(2) bridge between two neighboring $[UO_2]^{2+}$ cations, U(1) and U(2). One oxide ligand bound to S(2) is protonated, O(16). The assignment of the protonated oxide was based upon charge balance, bond length, and the absence of $[H_3O]^{3+}$ modes using infrared spectroscopy. The S(3) sulfates each bridge two U(1) uranium sites. The sulfate tetrahedra containing S(4) are coordinated to two adjacent U(2) centers. One-dimensional chains containing only U(2) centers connected by S(1) and S(4) sulfates run along the *b* axis. These chains are linked to one another by $(UO_2)_2(H_2O)_2(SO_4)_4$ bridges attached through the S(1) and S(2) tetrahedra. Each linking unit contains two U(1) centers connected by two S(3) tetrahedra. The resultant two-dimensional layers, which form in the *bc* plane, are shown in Figure 3. This layer topology is unprecedented in uranium chemistry. Pores are observed within each layer, which are occupied by occluded water molecules. The approximate dimensions of these pores are 4.8 × 12.8 Å.

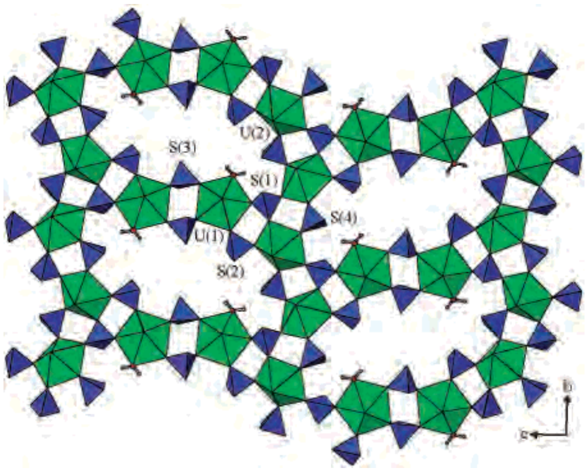

Figure 3. Two-dimensional $[(UO)_2(H_2O)(SO_4)_3(HSO_4)]^{3-}$ layers in USO-16. Green and blue polyhedra represent represent $[UO_7]$ and $[SO_4]$, respectively. Distinct uranium and sulfur sites are labeled, and bound water molecules are shown.

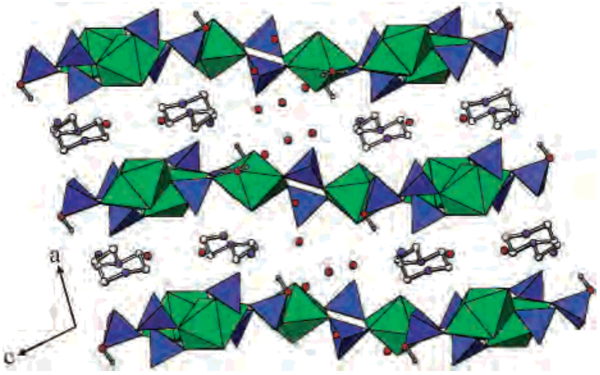

Figure 4. Three-dimensional packing of USO-16. Green and blue polyhedra represent $[UO_7]$ and $[SO_4]$, respectively. Template and occluded water hydrogen atoms have been removed for clarity.

The $[aepH_3]^{3+}$ cations reside between inorganic layers, balancing charge and donating hydrogen bonds to the layers. Each protonated amine donates hydrogen bonds to both the layer above and below. N(1) donates hydrogen bonds to O(15) and O(20) through distances of 2.744(7) and 2.696(7) Å, respectively. The tertiary amine N(2) donates one hydrogen bond to O(17) through a distance of 2.708(7) Å. N(3) donates two hydrogen bonds, one to each of O(10) and O(22) through distances of 2.968(7) and 2.801(7) Å, respectively. The three-dimensional packing of USO-16 is shown in Figure 4.

In the infrared spectrum a sharp stretch at 1620 cm^{-1}, a very wide stretch between 3000 and 3700 cm^{-1}, and a sharp band at 1400 cm^{-1} correspond to N−H, O−H, and C−H modes, respectively. The asymmetric uranyl stretch is located at 924 cm^{-1}, while the S−O band is observed between 1000 and 1200 cm^{-1}.

A distinct weight loss between 80 and 150 °C is observed using TGA. This 6.8% loss corresponds to 4.5 occluded water molecules (7.0% calcd). A further loss of 1.2% is observed between 150 and 200 °C, which corresponds to the loss of the bound water molecules (1.6% calcd). A larger loss between 280 and 650 °C represents the decomposition of the organic template and the simultaneous calcination of

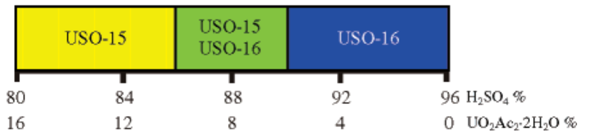

Figure 5. Plot of product composition as a function of both UO_2Ac_2·$2H_2O$ and H_2SO_4 concentration in the UO_2Ac_2·$2H_2O/H_2SO_4$/aep system. The yellow region represents USO-15, the green region represents a mixture of USO-15 and USO-16, and the blue region represents USO-16 as the reaction product.

the inorganic framework to UO_2, as confirmed using powder X-ray diffraction. The final mass loss of 48.0% corresponds well with the calculated value of 46.7%.

Reaction Gel Variation

A series of experiments were conducted in the UO_2Ac_2·$2H_2O/H_2SO_4$/aep/H_2O system. The reaction gel compositions were varied over several reactions between 16:80:4:500 UO_2Ac_2·$2H_2O/H_2SO_4$/aep/H_2O to 4:92:4:500 UO_2Ac_2·$2H_2O/H_2SO_4$/aep/H_2O. The aep and H_2O concentrations remain constant throughout the series of experiments; only the UO_2Ac_2·$2H_2O/H_2SO_4$ ratio was varied. Constant amounts of aep and solvent water were added to each experiment. These reactions form a line that is similar to a binary phase diagram. However, only the crystalline products are analyzed and any soluble species after reaction are neglected. The reactant and product compositions are not necessarily the same. Therefore, this "line" does not obey the phase rule and is not a binary phase diagram. The experimental results are shown in Figure 5.

Three regions are observed. Reactions conducted with H_2SO_4 mole percents between 80 and 86% result in the formation of USO-15 in phase purity. When the H_2SO_4 mole percent falls between 86 and 90% mixtures of USO-15 and USO-16 are observed. USO-16 is the only crystalline product when the H_2SO_4 mole percent is above 90%.

Discussion

The variations in reactant concentrations are reflected in the composition of the reaction products. Three relationships can be examined to show this dependence. First, as the U:SO_4 ratio decreases from 1:5 to 1:23, a shift in reaction product is observed. USO-15, the sulfate deficient phase, is observed when this ratio is 1:5, while a mixture of USO-15 and the sulfate-rich phase, USO-16, is observed as the U:SO_4 ratio decreases. Finally, USO-16 is the only reaction product when the U:SO_4 ratio reaches its lowest values.

Second, the ratio of aep to U in this series of reactions increases from 1:4 to 1:1. This shift can be observed in the compositions of USO-15, $[aepH_3]_2[(UO_2)_5(H_2O)(SO_4)_8]$·$5H_2O$, and USO-16, $[aepH_3][(UO_2)_2(H_2O)(SO_4)_3(HSO_4)]$·$4.5H_2O$. The aep:U ratios in USO-15 and USO-16 are 1:2.5 and 1:2, respectively. As the aep:UO_2Ac_2·$2H_2O$ ratio increases in the reaction gels, a shift is observed from USO-15, the compound in which the higher concentration of uranium is observed, to USO-16, the compound with the lower concentration of uranium. This shift is gradual, with a mixture of the two phases cocrystallizing when the H_2SO_4 mole fraction is near 88%.

Third, as the amount of H_2SO_4 relative to the amount of aep increases, a change in the sulfate tetrahedra is observed. Despite a constant aep:SO_4 ratio of 1:2 in both USO-15 and USO-16, one obvious difference is present. None of the oxide ligands on the eight unique sulfate tetrahedra in USO-15 are protonated. However, an oxide ligand on one of the four distinct sulfates is protonated in USO-16. This change reflects the increased acidity as the aep:SO_4 ratio of the reaction gel decreases from 1:20 to 1:23. The solution pH is sufficiently low to force the protonation of this oxide ligand.

The U:SO_4 ratios in USO-15 and USO-16 are reflected in the coordination environments of their respective sulfate tetrahedra. All eight distinct sulfate tetrahedra in USO-15 bridge between three adjacent uranium centers, while three of four sulfate tetrahedra in USO-16 bridge between only two $[UO_2]^{2+}$ cations. The USO-15 sulfates are bound to more uranium centers on average than those in USO-16 because the U:SO_4 ratio is higher, 5:8 versus 5:10. Each sulfate tetrahedra in USO-15 is required to bond to three uranium sites to satisfy the coordination preference of each uranium site. The increase in the number of sulfates/uranium in conjunction with more bound water molecules/uranium in USO-16 (1 for every 2 in USO-16 versus 1 for every 5 in USO-15) results in 75% of the sulfate tetrahedra in USO-16 coordinating to only two uranium centers. The effects on the layer topology are marked. Each uranium center in USO-15 is surrounded by six others within a 7 Å radius, while the two distinct uranium sites in USO-16 have only three neighboring uranium sites within 7 Å.

Conclusion

Two new organically templated uranium sulfates were synthesized under hydrothermal conditions, both of which contain novel layer topologies. A series of reactions were conducted in which subtle variations in the reactant concentrations were introduced. The compositions of the reaction products are highly dependent on these variations, resulting in structural variations. This suggests that compositions may be targeted in an attempt to control structure.

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Supporting Information Available: Two crystallographic information files in CIF format containing complete tables of atomic coordinates, bond length, and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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