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Synthesis of Cyclical Diamine Templated Uranium Sulfates

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The hydrothermal synthesis of uranium sulfates in the presence of a series of structurally related organic templating agents has been investigated. Piperazine, 2-methylpiperazine, and 1,4-diazabicyclo[2.2.2]octane, each of which is based upon the same six-membered cyclical diamine, exhibit different point symmetries and hydrogen-bonding characteristics. Small changes in the template structure result in marked differences in the reaction product. Three new compounds were synthesized and structurally characterized, $[N_2C_4H_{12}][UO_2(H_2O)(SO_4)_2]$, $[N_2C_5H_{14}][UO_2(H_2O)(SO_4)_2]$, and $[N_2C_6H_{14}][UO_2(H_2O)(SO_4)_2]$. The inorganic framework of each compound was found to be dependent on the template structure. $[N_2C_4H_{12}][UO_2(H_2O)(SO_4)_2]$ consists of one-dimensional $[UO_2(H_2O)(SO_4)_{4/2}]_\infty^{2-}$ chains, which hydrogen bond to one another to form quasi two-dimensional layers. One-dimensional chains are observed in $[N_2C_5H_{14}]$-$[UO_2(H_2O)(SO_4)_2]$. These chains, which have the formula $[UO_2(H_2O)(SO_4)_{4/2}(UO_2(H_2O)(SO_4)_2)]_\infty^{4-}$ are unprecedented in uranium chemistry. Two-dimensional layers are observed in $[N_2C_4H_{12}]$-$[UO_2(H_2O)(SO_4)_2]$. Each uranyl $[UO_2]^{2+}$ unit is bound to one water molecule and four bridging sulfate tetrahedra.

Introduction

A host of new materials has been produced under hydrothermal conditions in the presence of aqueous acids and amines.[1−8] The ability of organic molecules to act as templates or structure directors is well-known.[9−11] However, the role of the "template" is not completely understood.[12,13] Several groups have studied the synthesis of new materials using series-related amines to determine how structural changes affect the three-dimensional structure. It has been shown that the introduction of small changes into the template structure can have profound effects on the products in similar reactions. For example, Davis and co-workers have studied the synthesis of zeolites using a series of sparteine cations,[14] 1,4-diazabicyclo[2.2.2]octane derivatives,[15] and alkylammonium polycations.[16] Férey and co-workers and O'Hare and co-workers have synthesized several gallium fluorophosphates[17−19] and uranium fluorides,[20] respectively, using linear diamines of differing lengths. In each of these examples, the inorganic structure was found to be dependent on the amine used.

In this paper we report on how the structures of uranium sulfates are affected by structural changes in the organic component during the hydrothermal synthesis. The chemistry of organically template U^{4+} and U^{6+} compounds is well-developed. Albrecht-Schmitt and co-workers prepared several organically templated uranium fluorides,[21] Danis et al. reported a three-dimensional uranium phosphate,[22] Cahill and Burns reported two organically template uranium fluorides,[23] and O'Hare and co-workers have reported several uranium fluorides,[24] molybdates,[25] phosphates,[26] and phosphites.[27] The effects of using three related diamines, piperazine

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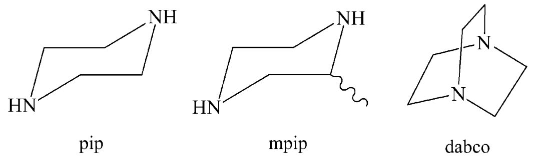

Figure 1. Structures of the cyclic diamines: pip, mpip, and dabco.

(pip), 2-methylpiperazine (mpip), and 1,4-diazabicyclo[2.2.2]octane (dabco) (Figure 1), each of which is based upon the piperazine ring, have been explored. The chemistry of organically templated inorganic sulfates is underdeveloped,[28−31] despite the breadth of templated zeolite, metal phosphate, and fluoride chemistry. The synthesis and structure of three new uranium sulfates are reported and are designated USO-3, USO-4, and USO-5 (Uranium Sulfate from Oxford).

Experimental Section

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

Materials. Piperazine (99%, Aldrich), 2-methylpiperazine (95%, Aldrich), 1,4-diazabicyclo[2.2.2]octane (98%, 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[25] from UO_3 (99.8%, Strem).

Synthesis. All reactions were conducted in poly(fluoroethylene-propylene)-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 $[N_2C_4H_{12}][UO_2(H_2O)(SO_4)_2]$ (USO-3), $[N_2C_5H_{14}][UO_2(H_2O)(SO_4)_2]$ (USO-4), and $[N_2C_6H_{14}][UO_2(H_2O)(SO_4)_2]$ (USO-5). USO-3 was synthesized through the reaction of 0.0845 g (1.99×10^{-4} mol) of $UO_2Ac_2 \cdot 2H_2O$ (ac = $CH_3CO_2^-$), 0.0190 g (2.21×10^{-4} mol) of pip, 0.4754 g (4.85×10^{-3} mol) of H_2SO_4, and 4.9937 g (2.77×10^{-1} mol) of deionized water. Yellow rods were isolated after reaction in 71% yield. USO-4 was synthesized through the reaction of 0.6783 g (1.60×10^{-3} mol) of $UO_2Ac_2 \cdot 2H_2O$, 0.0220 g (2.89×10^{-4} mol) of mpip, 0.3307 g (3.37×10^{-3} mol) of H_2SO_4, and 0.9926 g (5.51×10^{-2} mol) of deionized water. Yellow rods were isolated in 19% yield after 6 days. The remaining uranium remains in solution. USO-5 was synthesized through the reaction of 0.0852 g (2.01×10^{-4} mol) of $UO_2Ac_2 \cdot 2H_2O$, 0.0246 g (2.20×10^{-4} mol) of dabco, 0.4774 g (4.87×10^{-3} mol) of H_2SO_4, and 0.9940 g (5.52×10^{-2} mol) of deionized water. Yellow rods were isolated in 79% yield after 6 days. Elemental microanalysis for USO-3, obsd (calc): N, 4.97 (4.93); C, 8.53 (8.45); H, 2.75 (2.48); S, 10.85 (11.28); U, 41.86 (41.88). For USO-4, obsd (calc): N, 4.81 (4.81); C, 10.39 (10.31); H, 2.82 (2.77); S, 11.31 (11.01); U, 41.16 (40.87). For USO-5, obsd (calc): N, 4.74 (4.72); C, 12.21 (12.15); H, 2.64 (2.55); S, 11.31 (10.81); U, 39.17 (40.12). Powder X-ray diffraction patterns of each respective bulk sample matched patterns generated from the single-crystal X-ray structure data.

X-ray Crystallographic Analysis. Single crystals of dimensions 0.08 × 0.16 × 0.40 mm for USO-3, 0.14 × 0.14 × 0.14 mm for USO-4, and 0.20 × 0.25 × 0.25 mm for USO-5 were used for structural determination. Data were collected using an Enraf Nonius FR 590 Kappa CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ 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.[32] The heavy atom positions were determined using SIR97[33] and other non-hydrogen atoms refined using Crystals.[34] All non-hydrogen atom were located from Fourier difference maps and refined with anisotropic thermal parameters using full-matrix least-squares procedures on F_o^2 with $I > 3\sigma(I)$. Hydrogen atoms attached to bound water molecules were located from Fourier difference maps; all others were placed in geometrically idealized positions. All calculations were performed using Crystals[34] and Cameron.[35] Relevant crystallographic data are listed in Table 1.

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 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.

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-3. One crystallography unique uranium site is observed in the crystal structure determination of USO-3. U(1) is seven-coordinate, in a pentagonal bipyramidal geometry. The uranyl bond length is 1.776(2) Å. This is close to the average reported uranyl bond in pentagonal bipyramidal coordination, which is 1.758(4) Å.[36] Four of the five equatorial oxide ligands are part of $[SO_4]^{2-}$ tetrahedra; the fifth is a bound water molecule. The average $U-O_{Sulfate}$ bond length is 2.370 Å. The uranium−water bond distance is 2.444(3) Å. Bond valence calculations[37,38] on USO-1, using uranium parameters from Burns et al.,[36] resulted in a value of 6.10 for U(1). Two

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Table 1. Crystallographic Data for USO-3, USO-4, and USO-5.

compound	USO-3	USO-4	USO-5
formula	$[N_2C_4H_{12}][UO_2(H_2O)(SO_4)_2]$	$[N_2C_5H_{14}][UO_2(H_2O)(SO_4)_2]$	$[N_2C_6H_{14}][UO_2(H_2O)(SO_4)_2]$
fw	568.32	582.35	594.36
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	14.7676(3)	10.7537(2)	8.6480(1)
b (Å)	7.6585(2)	11.4297(2)	7.7135(1)
c (Å)	11.6807(2)	11.5797(2)	21.2554(3)
α (deg)	90	87.998(1)	90
β (deg)	104.8369(16)	79.660(1)	90.7254(9)
γ (deg)	90	80.6313(6)	90
V (Å^3)	1277.0	1381.5	1417.8
Z	2	4	4
D_c (g cm^{-1})	2.95	2.80	2.78
μ (mm^{-1})	13.098	12.111	11.804
reflections collected	2847	11531	6242
independent reflections	1450	6257	3423
R1[a]	0.0154	0.0238	0.0337
wR2[b]	0.0328	0.0560	0.0566

[a] R1 = $\Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] wR2 = $[\Sigma w(F_o^2 - F_c^2)^2/[\Sigma w(F_o^2)^2]^{1/2}$.

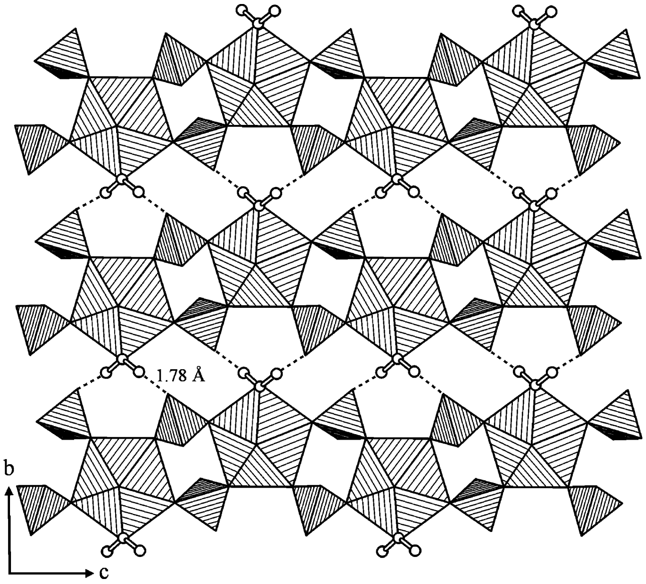

Figure 2. One-dimensional $[UO_2(H_2O)(SO_4)_2]^{2-}$ chains in USO-3. Pentagonal bipyramids and tetrahedra represent $[UO_7]$ and $[SO_4]$, respectively. Hydrogen bonds are shown as dashed line with lengths listed (Å).

of the four oxide ligands in the $[SO_4]^{2-}$ tetrahedron bridge to uranium, with S−O distances of 1.490(2) and 1.495(2) Å. The remaining oxides are terminal, with distances of 1.448(2) and 1.470(2) Å.

One-dimensional $[UO_2(H_2O)(SO_4)]^{2-}$ chains form along the c axis because each $[SO_4]^{2-}$ tetrahedron links adjacent $[UO_7]$ pentagonal bipyramids. See Figure 2. This chain topology is analogous to the mineral phases $Mn[(UO_2)(SO_4)_2(H_2O)]\cdot 4H_2O$[39] and $[(UO_2)(H_2PO_4)_2(H_2O)](H_2O)_2$.[40] Burns et al. have reviewed the crystal chemistry of inorganic U^{6+} compounds.[36,41] Hydrogen bonding between the bound water and terminal oxides on the $[SO_4]^{2-}$ tetrahedra links neighboring chains, forming layers in the bc plane. The O(4)−O(6) hydrogen bond distance is 2.741(3) Å. The positively charged piperazinium cation $\{[pipH_2]^{2+}\}$ templates lie parallel to the hydrogen-bonded layers. Each $[pipH_2]^{2+}$ ion donates four hydrogen bonds, two to the layer above and two to the layer below. Each nitrogen exhibits short distances to both the adjacent layers above and below. The N(1)−O distances are 2.797(3) and 2.785(3) Å to O(5) and O(6), respectively. The structure is stabilized through this extensive hydrogen bonding between the templates and the inorganic structure. See Figure 3.

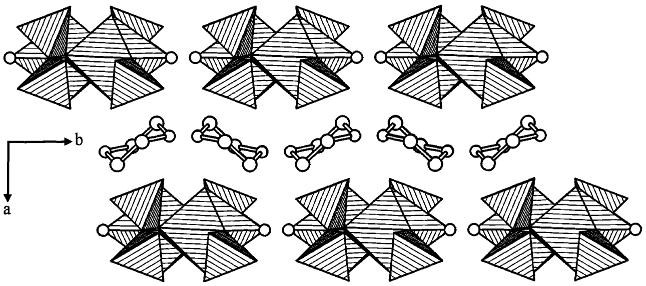

Figure 3. Three-dimensional packing of USO-3. Pentagonal bipyramids and tetrahedra represent $[UO_7]$ and $[SO_4]$, respectively. Hydrogen atoms have been removed for clarity.

Two N−H bands are observed in the infrared spectrum of USO-3 at 3100 and 1650 cm^{-1}. The asymmetric uranyl stretch is at 900 cm^{-1} and broad bands at 1000 and 1100 cm^{-1} correspond to S−O stretches.

The assignment of a bound water molecule in the USO-3 structure is confirmed using thermogravimetric analysis. A weight loss of 2.8% is observed between 200 and 250 °C, corresponding to the loss of the bound water molecule (3.2%). The material completely calcines to U_3O_8, as determined using powder X-ray diffraction, between 340 and 460 °C.

USO-4. Two unique uranium positions are observed in the crystal structure determination of USO-4. Both U^{6+} sites adopt a pentagonal bipyramidal coordination geometry. The two uranyl bonds to U(1) lengths, 1.771(4) and 1.775(3) Å, again are typical for uranium in this coordination environment.[36] The two uranyl bond angles are 179.25(15)° and 177.81(15)° for O(1)−U(1)−O(2) and O(8)−U(2)−O(9), respectively. One of the five equatorial oxide ligands is a bound water molecule, with a U−O distance of 2.423(4) Å, while the other four are part of $[SO_4]^{2-}$ tetrahedra. These four bond distances are

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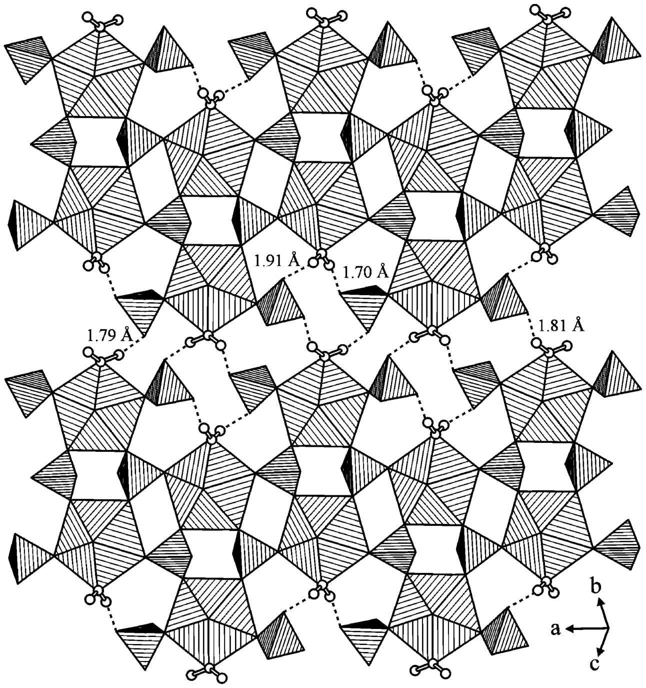

Figure 4. One-dimensional $[UO_2(H_2O)(SO_4)_2]^{2-}$ chains in USO-4. Pentagonal bipyramids and tetrahedra represent $[UO_7]$ and $[SO_4]$, respectively. Hydrogen bonds are shown as dashed lines with lengths listed (Å).

2.353(3), 2.368(3), 2.383(3), and 2.423(4) Å. The coordination around U(2) is similar to that around U(1). The uranyl bond lengths are 1.769(4) and 1.770(4) Å. The bond between U(2) and its coordinated water molecule is longer than the other four equatorial sites that are part of $[SO_4]^{2-}$ tetrahedra, 2.440(3) versus 2.374(3), 2.377(3), 2.382(3), and 2.386(3) Å. Bond valence calculations on U(1) and U(2) yielded values of 6.09 and 6.03, respectively.

Four unique sulfur environments are present in USO-4. S(1) and S(2) are part of tetrahedra bound to U(1). Only one oxide ligand on each of these two tetrahedra is bound to a uranium center. Two oxides bound to S(1) and two bound to S(2) participate in hydrogen bonding to adjacent water molecules. O(16) and O(17), bound to S(1), exhibit O−O hydrogen bond distances of 2.676(4) and 2.756(4) Å to O(7) and O(12), respectively. O−O hydrogen bond distances of 2.846(4) and 2.653(4) Å are observed with O(18) and O(19), both of which are bound to S(2). Three oxide ligands in the S(3) and S(4) tetrahedra bridge to uranium centers, while O(21) and O(22) are only bound to S(3) and S(4). The S(3)−O(21) and S(4)−O(22) bond distances are 1.446(4) and 1.454(4) Å, respectively.

The S(3) and S(4) tetrahedra link adjacent U(2) pentagonal bipyramids, forming one-dimensional chains that are analogous to those in USO-3. However, the S(3) and S(4) tetrahedra bridge between three uranium polyhedra in USO-4, whereas in USO-3 the sulfate tetrahedra bridge between only two uranium polyhedra. The extra bridge in USO-4 is to U(1). The result is a one-dimensional chain with attachment of an additional $[UO_2(H_2O)(SO_4)_2]$ moiety to each U(2) polyhedron perpendicular to the axis of the chain. This chain topology has not been observed previously in uranium chemistry. See Figure 4. Hydrogen bonding between the bound water and terminal oxides on the $[SO_4]^{2-}$ tetrahedra link neighboring chains, forming layers in the [0 1 1] plane. The methylpiperazinium cations $\{[mpipH_2]^{2+}\}$ reside between the layers. Both enantiomers are observed crystallographically. The $[mpipH_2]^{2+}$ cations are oriented between the layers such that the two hydrogens on each nitrogen donate hydrogen bonds to the same layer. The N−O distances of these interactions are 2.754(4) and 2.797(4) Å for N(1) to O(17) and O(19), 2.793(4) and 2.905(4) Å for N(2) to O(18) and O(22), 2.868(4) and 2.719(4) Å for N(3) to O(16) and O(20), and 2.725(4) and 2.911(4) Å for N(4) to O(15) and O(21). See Figure 5. Hydrogen bonding between adjacent chains and between the mpip and neighboring layers is responsible for the stabilization of the structure.

The asymmetric stretch of the uranyl group was observed at 920 cm^{-1} in the IR spectrum. S−O stretches were observed at 1020 and 1100 cm^{-1}. The presence of the organic template was confirmed through the observation of characteristic N−H (3100 and 1605 cm^{-1}) and C−H (2950 cm^{-1}) bands.

A weight loss of 3.2% is observed in USO-4 between 200 and 280 °C using thermogravimetric analysis, corresponding to the removal of the bound water molecules (3.1%). The $[mpipH_2]^{2+}$ cations decompose between 310 and 380 °C with a weight loss of 20% (18% calculated). The material is calcined to UO_2 by 800 °C, as determined using powder X-ray diffraction.

USO-5. One unique uranium position was observed in the crystal structure of USO-5. The seven-coordinate pentagonal bipyramidal U^{6+} center bonds to two uranyl oxide ligands through distances of 1.771(4) and 1.773(4) Å, which are typical of uranyl bond lengths.[36] The uranyl bond angle, O(1)−U(1)−O(2), is 178.55(13)°. One of the equatorial coordination sites is occupied by a bound water molecule; the U(1)−O(3) distance is 2.423(4) Å. The other four equatorial sites are occupied by oxide ligands that are part of $[SO_4]^{2-}$ tetrahedra. The average distance from the uranium center to these ligands is 2.359 Å.

Two unique sulfur sites are observed in USO-5. The $[SO_4]^{2-}$ tetrahedra containing both S(1) and S(2) bridge two uranium centers. The two-dimensional $[UO_2(H_2O)(SO_4)_2]^{2-}$ layers formed are analogous to the mineral phase $[NH_4][UO_2(H_2O)(SO_4)_2](H_2O)$.[42] See Figure 6. Bound water molecules donate hydrogen bonds to adjacent $[SO_4]^{2-}$ oxides; the O(3)−O(9) and O(3)−O(11) distances are 2.732(4) and 2.616(4) Å, respectively.

The three-dimensional structure of USO-5 consists of alternating layers of $[UO_2(H_2O)(SO_4)_2]^{2-}$ and $[dabcoH_2]^{2+}$, both of which lie in the [1 0 1] plane. Each cation donates two hydrogen bonds, one to each of the adjacent layers. See Figure 7. The distances are 2.685(4) and 2.570(4) Å for N(1)−O(8) and N(2)−O(10), respectively.

The presence of the organic template was confirmed using infrared spectroscopy through the observation of N−H bands at 3100 and 3300 cm^{-1} and C−H bands at 2900−3050, 1450, and 590 cm^{-1}. The uranyl asymmetric stretch and S−O bands were observed at 920 and 1000 cm^{-1}, respectively.

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(42) Niinisto, L.; Tolvonen, J.; Valkonen, J. *Acta Chem. Scand.* **1978**, *32*, 647.

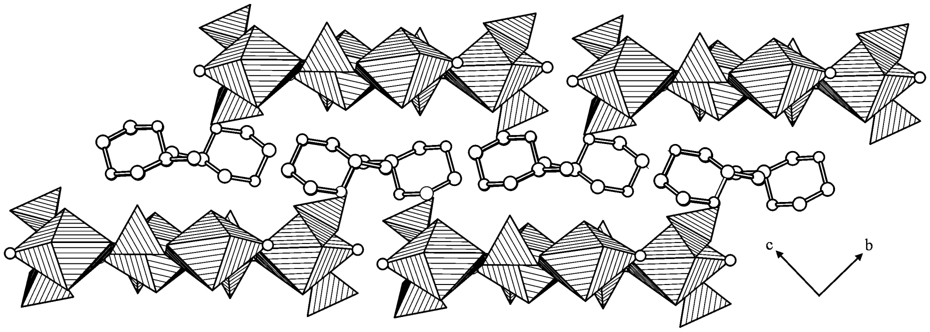

Figure 5. Three-dimensional packing of USO-4. Pentagonal bipyramids and tetrahedra represent [UO_7] and [SO_4], respectively. Hydrogen atoms have been removed for clarity.

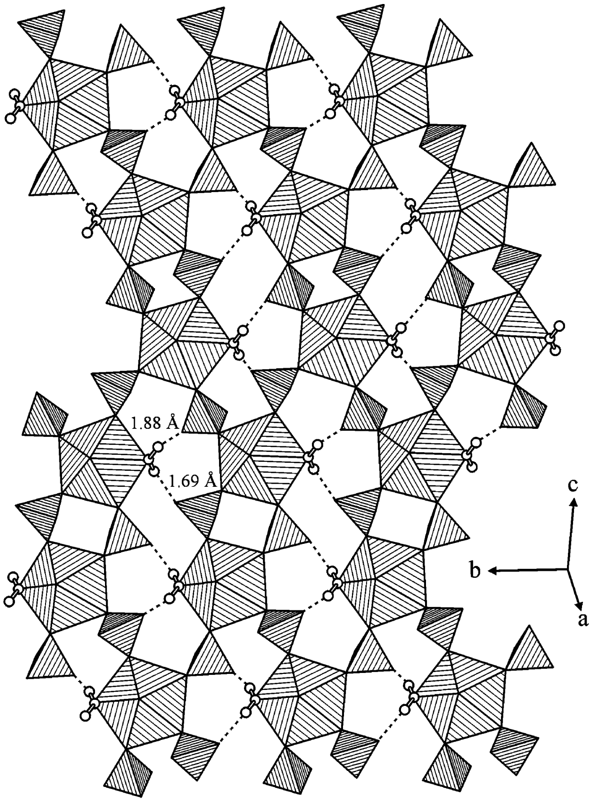

Figure 6. Two-dimensional $[UO_2(H_2O)(SO_4)_2]^{2-}$ layer in USO-5. Pentagonal bipyramids and tetrahedra represent [UO_7] and [SO_4], respectively. Hydrogen bonds are shown as dashed lines with lengths listed (Å).

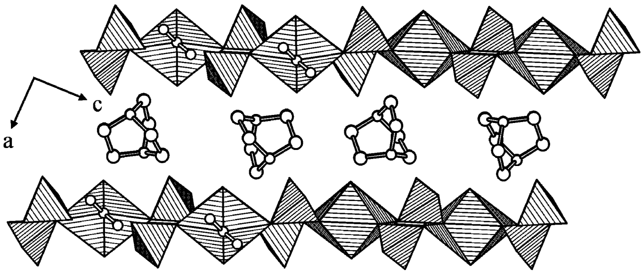

Figure 7. Three-dimensional packing of USO-5. Pentagonal bipyramids and tetrahedra represent [UO_7] and [SO_4], respectively. Selected hydrogen atoms have been removed for clarity.

A weight loss of 2.1% is observed in USO-5 between 200 and 280 °C using thermogravimetric analysis. This corresponds to the removal of the bound water molecules (3.0%). The organic template decomposes between 380 and 420 °C with a weight loss of 21% (22% calculated). The material is calcined to UO_2, as determined using powder X-ray diffraction, by 800 °C.

Discussion

Three new uranium-containing phases were synthesized using pip, mpip, and dabco as the organic templates. See Figure 1. The complexity of the template was increased from the basic pip unit in both mpip and dabco through the addition of a methyl group (and accompanying chiral center) and a two carbon bridge, respectively. All three exist as dications in USO-3, USO-4, and USO-5, and the formula of the inorganic structure remains the same, $[UO_2(H_2O)(SO_4)_2]^{2-}$. Despite their similarities the increase in template complexity has introduced marked differences in structure, both of the inorganic framework, and in the hydrogen bonding between template and framework.

USO-3 contains simple $[UO_2(H_2O)(SO_4)_2]^{2-}$ chains, as shown in Figure 2. The centroid of the piperazinium cation resides on a 4d site, an inversion center. This is possible because of the high symmetry of the cation. U(1) resides on a 4e site, a 2-fold axis perpendicular to the one-dimensional chains. When mpip is substituted for pip in the reaction mixture, several effects are observed. First, the additional methyl group prohibits the cation from occupying an inversion center. Each of the two crystallographically distinct mpip cations now reside on general positions. Second, mpip contains a chiral center. The mpip used in the synthesis contained both the R and S enantiomers, each of which is observed crystallographically. Third, the uranium centers, of which two are crystallographically distinct, reside on general positions as opposed to 2-fold axes of rotation. The lower symmetry of mpip is reflected in the lower symmetry of USO-4 with respect to USO-3; the crystal classes of the two compounds are triclinic and monoclinic, respectively. The result of this lower symmetry is a shift from simple one-dimensional chains in USO-3 to wider one-dimensional ribbons in USO-4 as shown in Figure 4, both the chains and ribbons form two-dimensional sheets through hydrogen bonding. The structural differences between USO-3 and USO-4 appear to be a direct result of the inability of mpip to reside on an inversion center.

The substitution of dabco for pip also results in dramatic changes in the structure of USO-5. The presence of the third two-carbon bridge between amines in dabco, as opposed to pip, drastically affects the way it acts as a template. The effects are 2-fold. First, dabco does not contain an inversion center and will not easily reside on one. Each of the atomic sites in the dabco cation in USO-5 are general positions. Just as in USO-4, a distinct change of structural symmetry is observed when dabco is incorporated into the structure. The uranium site in USO-5 no longer is on a special position as in USO-3, but instead resides on a general position. This change in symmetry is reflected in the change in space group from $C2/c$ in USO-3 to $P2_1/c$ in USO-5. The uranyl sulfate chains in USO-3 are not present in USO-5. Both structures contain dimers that consist of two uranyl centers connected by two sulfate bridges. The dimers in USO-3 are linked to one another through a 2-fold axis of rotation forming infinite chains. These building units are assembled into a different structure in USO-5, owing to the presence of a 2_1 screw axis. They no longer form one-dimensional chains. Instead, the screw axis introduces a rotation around ($^1/_4$, y, $^1/_4$) plus a translation of (0, $^1/_2$, 0). This staggers the dimers, and a two-dimensional layer is observed.

The second effect of amine substitution concerns hydrogen bonding. Each nitrogen in the $[\mathrm{pipH_2}]^{2+}$ cation is bound to two carbon atoms and two hydrogens that can donate hydrogen bonds. When a two-carbon bridge is added to the pip cation, each nitrogen is then bound to three carbon atoms and one hydrogen. The “chair” conformation of the six-membered pip ring is not present in dabco, where each ring exhibits the “boat” conformation. The orientation of the protonated amines in USO-3 and USO-5 are shown in Figures 3 and 7, respectively. The hydrogens on each nitrogen donate bonds to both the adjacent layers in USO-3. This is not possible for dabco because the direction of hydrogen bonding is greatly restricted. Both N−H bonds lie along the N−N direction in dabco, which results in the hydrogen-bonding nature of dabco being more like the linear diamine 4,4′-dipyridyl than pip. In order for one dabco to donate hydrogen bonds to two adjacent layers, it is constrained to lie perpendicular to those layers, a 90° shift from the pip in USO-3. The combination of these two factors greatly affects the structure of USO-5.

The inorganic components in USO-3, USO-4, and USO-5 are stable to approximately 340, 310, and 380 °C, respectively. These frameworks are not stable in the absence of the bound water molecules and organic templates and decompose to either UO_2 or U_3O_8.

Conclusions

Many different templates can be used in the hydrothermal synthesis of novel uranium sulfates. Piperazine, mpip, and dabco each contain the same basic six-membered ring but result in products of different structures when used under similar reaction conditions. The inorganic framework in USO-3, USO-4, and USO-5 is dependent on the point symmetry and hydrogen-bonding properties of the organic template present.

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Supporting Information Available: An X-ray crystallographic file (CIF) containing complete tables of atomic coordinates, thermal parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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