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The Role of Amine Sulfates in Hydrothermal Uranium Chemistry

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A series of novel uranium sulfates containing organic structure directing cations has been synthesized from amine sulfate precursors under hydrothermal conditions. The amine sulfates act as a soluble source of the protonated amines and sulfate ions at low temperature and provide a reaction pathway in which no amine decomposition is observed. The protonated amines act as both space fillers and hydrogen-bond donors in the three-dimensional structure. The factors governing the formation of the observed hydrogen-bonding networks were probed through the use of bond valence sums, which allow the quantification of residual negative charge and determination of the relative nucleophilicity of each oxide ligand. The hydrogen bonding in these new compounds is dependent upon two factors. First, the oxide ligands with the highest nucleophilicities are preferential acceptors with respect to their less nucleophilic counterparts. Second, geometric constraints that result from the formation of multiple hydrogen bonds from a single ammonium center can dictate the donation to oxides with smaller negative charges. Crystal data for $[N_4C_6H_{12}][SO_4]_2{\cdot}2H_2O$, $a = 7.2651(2)$ Å, $b = 7.3012(2)$ Å, $c = 8.3877(3)$ Å, $\alpha = 90.260(1)°$, $\beta = 100.323(1)°$, $\gamma = 113.0294(15)°$, triclinic, P-1 (No. 2), $Z = 1$; for $[N_4C_6H_{22}][UO_2(H_2O)(SO_4)_2]_2{\cdot}6H_2O$, $a = 6.7318(1)$ Å, $b = 9.2975(1)$ Å, $c = 13.1457(3)$ Å, $\alpha = 72.3395(6)°$, $\beta = 89.1401(7)°$, $\gamma = 70.0267(12)°$, triclinic, P-1 (No. 2), $Z = 1$; for $[N_4C_6H_{22}][UO_2(SO_4)_2]_2$, $a = 9.3771(2)$ Å, $b = 12.9523(3)$ Å, $c = 18.9065(6)$ Å, orthorhombic, *Pbca* (No. 61), $Z = 4$; for $[N_5C_8H_{28}]_2[(UO_2)_5(H_2O)_5(SO_4)_{10}]{\cdot}H_2O$, $a = 7.76380(5)$ Å, $b = 14.16890(5)$ Å, $c = 56.46930(5)$ Å, orthorhombic, *Pbnm* (No. 62), $Z = 4$.

Introduction

The synthesis of new materials under hydrothermal conditions using amine structure directing agents and aqueous acids has been employed to produce a host of new materials.[1] The ability of organic molecules to act as templates or structure directors is well-known;[2] however, the role of these molecules is poorly understood.[3] A series of reactions involving one of two amine sulfates, which contain structurally related amines, was conducted to help elucidate the factors governing the formation of organically templated materials.

Rao et al. have recently proposed a hypothesis concerning the role of amine phosphate salts in the formation of extended solids.[4] These compounds have been observed as both reaction byproducts[5] and transient intermediates[6] in the formation of open-framework materials. The use of amine phosphates as reaction starting materials has also been shown to provide a facile route to novel materials.[7] Despite the breadth of the amine phosphate work, the use of amine

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sulfates as reaction precursors is in its infancy, with the recent report of three amine sulfates[8] and their reactions with metal ions.[9]

The amine sulfates that have been used as starting materials in the formation of templated inorganic materials contain amines with vastly different structures. Ethylenediamine, piperazine, and 1,4-diazabicylo[2.2.2]octane (Dabco) contain either primary, secondary, or tertiary amines, respectively. To better probe the role of the amine is these reactions, two related amine sulfates were used in a series of reactions with uranium acetate hydrate, sulfuric acid, and water. The use of a series of structurally related amines to probe the affects of subtle structure variation on the reaction is well-known. For example, Davis et al. have studied the synthesis of zeolites using a series of 1,4-diazabicyclo[2.2.2]-octane derivatives,[10] alkylammonium polycations,[11] and sparteine cations,[12] and Férey and O'Hare have synthesized several gallium fluorophosphates[13] and uranium fluorides[14] and sulfates,[15] respectively.

The synthesis, structure, and characterization of an amine sulfate salt and the three new uranium sulfate materials are presented. These compounds are designated TETA-S (triethylenetetramine sulfate), USO-27, USO-28, and USO-29 (uranium sulfate from Oxford).

Experimental Section

Caution. Although all uranium materials used in these experiments were depleted, extra care and good laboratory practice should always be used when handling uranium containing materials.

Materials. Triethylenetetramine, (teta, tech. grade, Aldrich), tetraethylenepentamine, (tepa, tech. grade, Aldrich), and sulfuric acid (98%, Aldrich) were used as received. Deionized water was used in these syntheses. $UO_2(CH_2CO_2)_2 \cdot 2H_2O$ was prepared[16] from UO_3 (99.8%, Strem).

Synthesis. Single crystals of $[N_4C_6H_{12}][SO_4]_2 \cdot 2H_2O$ (TETA-S) were prepared by heating a mixture of 40 mL of 1 M H_2SO_4, 20 mL of deionized water, and 3.3567 g (2.299×10^{-2} mol) of teta to 80 °C in an uncovered beaker. Evaporation and concentration of reactants resulted in the formation of colorless rod-shaped crystals. Elemental microanalysis for TETA-S obsd (calcd): N, 14.79 (14.52); C, 19.02 (18.72); H, 6.87 (6.64); S, 16.94 (16.75). Syntheses of a tetraethylenepentamine derivative (TEPA-S) resulted in the formation of badly twinned crystals.

Bulk preparation of TETA-S and TEPA-S was accomplished through the dispersal of approximately 4 g of the amine in 40 mL of methanol, to which approximately 6.4 g of concentrated H_2SO_4 was added dropwise. The resulting thick white precipitates were filtered in air. The composition of TEPA-S, as synthesized using the bulk preparation, corresponded to a formula of $[N_5C_8H_{28}]_2[SO_4]_5 \cdot 5H_2O$. Elemental microanalysis for TEPA-S obsd (calcd): N, 14.21 (14.60); C, 19.72 (20.04); H, 6.39 (6.94); S, 16.36 (16.72).

All hydrothermal reactions were conducted in poly(fluoroethylene-propylene) lined 23-mL stainless steel autoclaves. Reactions 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}, and the autoclaves opened in air. Solid products were recovered using filtration and were washed with deionized water and acetone.

$[N_4C_6H_{22}][UO_2(H_2O)(SO_4)_2]_2 \cdot 6H_2O$ (USO-27) was synthesized through the reaction of 0.2608 g (6.15×10^{-4} mol) of $UO_2(CH_2CO_2)_2 \cdot 2H_2O$, 0.1071 g ($1.09 \times 10^{-3}$ mol) of H_2SO_4, 0.2777 g (7.34×10^{-4} mol) of TETA-S, and 1.0055 g (5.58×10^{-2} mol) of deionized water. Yellow blocks were isolated after reaction in a yield of 53%. Elemental microanalysis for USO-26 obsd (calcd): N, 4.61 (4.59); C, 5.93 (5.91); H, 3.12 (3.12); S, 10.05 (10.52); U, 38.64% (39.08%).

$[N_4C_6H_{22}][UO_2(SO_4)_2]_2$ (USO-28) was synthesized through the reaction of 0.2121 g (5.00×10^{-4} mol) of $UO_2(CH_2CO_2)_2 \cdot 2H_2O$, 0.3120 g ($3.18 \times 10^{-3}$ mol) of H_2SO_4, 0.5347 g (1.41×10^{-3} mol) of TETA-S, and 1.0319 g (5.73×10^{-2} mol) of deionized water. Yellow blocks were isolated after reaction in a yield of 67%. Elemental microanalysis for USO-26 obsd (calcd): N, 5.21 (5.23); C, 6.70 (6.75); H, 2.05 (2.22); S, 11.93 (12.52); U, 44.30% (43.59%).

$[N_5C_8H_{28}]_2[(UO_2)_5(H_2O)_5(SO_4)_{10}] \cdot H_2O$ (USO-29) was synthesized through the reaction of 0.4755 g (11.2×10^{-3} mol) of $UO_2(CH_2CO_2)_2 \cdot 2H_2O$, 0.2299 g ($2.346 \times 10^{-3}$ mol) of H_2SO_4, 0.1052 g (1.10×10^{-4} mol) of TEPA-S, and 1.0163 g (5.64×10^{-2} mol) of deionized water. Yellow plates were isolated after reaction in a yield of 42%. Elemental microanalysis for USO-26 obsd (calcd): N, 4.99 (5.02); C, 6.82 (6.99); H, 2.42 (2.41); S, 11.42 (10.17); U, 42.41% (42.05%).

Powder X-ray diffraction patterns of each bulk sample match the pattern generated from the respective single-crystal X-ray structure data.

X-ray Crystallographic Analysis. Single crystals of each compound were used for structure determination. Data were collected using an Enraf Nonius FR 590 Kappa CCD diffractometer with graphite monochromated Mo K 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.[17] The heavy atom positions were determined using SIR97.[18] All other non-hydrogen sites were located from Fourier difference maps. All non-hydrogen sites were refined using anisotropic thermal parameters using full matrix least squares

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Table 1. Crystallographic Data

compound	TETA-S	USO-27	USO-28	USO-29
formula	$[N_4C_6H_{12}][SO_4]_2 \cdot 2H_2O$	$[N_4C_6H_{22}][UO_2(H_2O)(SO_4)_2]_2 \cdot 6H_2O$	$[N_4C_6H_{22}][UO_2(SO_4)_2]_2$	$[N_5C_8H_{28}]_2[(UO_2)_5(H_2O)_5(SO_4)_{10}] \cdot H_2O$
fw	378.42	1218.70	1074.58	2807.66
space group	*P*-1 (No. 2)	*P*-1 (No. 2)	*Pbca* (No. 61)	*Pbnm* (No. 62)
a/Å	7.2651(2)	6.7318(1)	9.3771(2)	7.76380(5)
b/Å	7.3012(2)	9.2975(1)	12.9523(3)	14.16890(5)
c/Å	8.3877(3)	13.1457(3)	18.9065(6)	56.46930(5)
α/°	90.260(1)	72.3395(6)	90	90
β/°	100.323(1)	89.1401(7)	90	90
γ/°	113.0294(15)	70.0267(12)	90	90
V/Å^3	401.50(2)	733.20(2)	2296.3(1)	6211.9(1)
Z	1	1	4	4
D_c/g cm^{-1}	1.565	2.760	3.108	3.002
μ/mm^{-1}	0.387	11.430	14.552	13.462
reflections collected	3357	6176	5087	7617
independent reflections	1827	3321	2609	6914
R_1[a]	0.0307	0.0198	0.0243	0.0334
wR_2[b]	0.0746	0.0475	0.0600	0.0848

[a] $R_1 = \sum 1/2F_o1/2 - 1/2F_c1/2/\sum 1/2F_o1/2$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/[\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Lengths for TETA-S

bond	distance	bond	distance
S1−O1	1.4649(11)	N1−C1	1.4888(18)
S1−O2	1.480(1)	N2−C2	1.5020(18)
S1−O3	1.488(1)	N2−C3	1.4891(17)
S1−O4	1.4795(11)		

Table 3. Selected Bond Lengths (Å) for USO-27

bond	distance	bond	distance
U(1)−O(1)	1.766(3)	S(1)−O(3)	1.482(3)
U(1)−O(2)	1.770(3)	S(1)−O(4)	1.483(3)
U(1)−O(3)	2.418(3)	S(1)−O(7)	1.481(3)
U(1)−O(4)	2.374(3)	S(1)−O(8)	1.446(3)
U(1)−O(5)	2.343(3)	S(2)−O(5)	1.513(3)
U(1)−O(6)	2.440(3)	S(2)−O(9)	1.466(3)
U(1)−O(7)	2.391(3)	S(2)−O(10)	1.477(3)
		S(2)−O(11)	1.471(3)

Table 4. Selected Bond Lengths (Å) for USO-28

bond	distance	bond	distance
U(1)−O(1)	1.769(4)	S(1)−O(4)	1.499(4)
U(1)−O(2)	1.767(4)	S(1)−O(5)	1.515(4)
U(1)−O(3)	2.393(4)	S(1)−O(8)	1.447(5)
U(1)−O(4)	2.344(4)	S(1)−O(9)	1.453(5)
U(1)−O(5)	2.350(4)	S(2)−O(3)	1.486(4)
U(1)−O(6)	2.460(4)	S(2)−O(6)	1.487(4)
U(1)−O(7)	2.456(4)	S(2)−O(7)	1.483(4)
		S(2)−O(10)	1.436(4)

procedures on F_o^2 with $I > 3\sigma(I)$. Hydrogen atoms were placed in geometrically idealized positions. All calculations were performed using Crystals[19] and Cameron.[20] Relevant crystallographic data are listed in Table 1 and selected bond lengths are listed in Tables 2−5.

Powder X-ray Diffraction. Powder X-ray diffraction patterns were recorded on a Philips PW 1729 diffractometer. Samples were mounted on aluminum plates. Calculated powder patterns were generated from the single-crystal data using the computer program, ATOMS.[21]

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.

Table 5. Selected Bond Lengths (Å) for USO-29

bond	distance	bond	distance
U(1)−O(1)	1.779(5)	S(1)−O(4)	1.497(5)
U(1)−O(2)	1.777(5)	S(1)−O(5)	1.479(5)
U(1)−O(3)	2.443(5)	S(1)−O(20)	1.451(5)
U(1)−O(4)	2.365(5)	S(1)−O(21)	1.480(5)
U(1)−O(5)	2.415(5)	S(2)−O(6)	1.500(5)
U(1)−O(6)	2.346(5)	S(2)−O(11)	1.492(5)
U(1)−O(7)	2.393(5)	S(2)−O(22)	1.470(5)
U(2)−O(8)	1.792(5)	S(2)−O(23)	1.436(5)
U(2)−O(9)	1.800(5)	S(3)−O(7)	1.490(5)
U(2)−O(10)	2.416(5)	S(3)−O(12)	1.490(5)
U(2)−O(11)	2.391(5)	S(3)−O(24)	1.450(5)
U(2)−O(12)	2.342(4)	S(3)−O(25)	1.461(5)
U(2)−O(13)	2.392(5)	S(4)−O(13)	1.487(5)
U(2)−O(14)	2.372(5)	S(4)−O(18)	1.500(5)
U(3)−O(15)	1.789(7)	S(4)−O(26)	1.467(5)
U(3)−O(16)	1.782(7)	S(4)−O(27)	1.448(5)
U(3)−O(17)	2.459(7)	S(5)−O(14)	1.493(5)
U(3)−O(18)	2.432(5)	S(5)−O(19)	1.484(5)
U(3)−O(19)	2.351(5)	S(5)−O(28)	1.459(5)
		S(5)−O(29)	1.457(5)

Thermogravimetric Analysis. TGA measurements were performed on a Rheometric Scientific STA 1500H thermal analyzer. The samples were loaded into an alumina crucible and heated at 10 °C min^{-1} under flowing argon.

Results

The structure of TETA-S contains protonated $[N_4C_6H_{22}]^{4+}$ cations, $[SO_4]^{2-}$ anions, and occluded water molecules, all of which are held together through an extensive hydrogen-bonded network. Each $[N_4C_6H_{22}]^{4+}$ cation donates 10 hydrogen bonds: six through the two protonated primary amines (N1 × 2) and four through the two protonated secondary amines (N2). These hydrogen bonds are accepted by both occluded water molecules and sulfate oxides. Each occluded water molecule also donates two hydrogen bonds to neighboring sulfate oxides; see Figure 1.

The coordination of the U^{6+} centers in USO-27, USO-28, and USO-29 is similar. Each uranium center is bound to two axial oxides forming a uranyl unit, $[UO_2]^{2+}$. The $U-O_{uranyl}$ bond lengths range between 1.766(3) and 1.800(5) Å, in good agreement with the reported average uranyl bond length of 1.758(4) Å.[22] Each uranyl unit is coordinated to five equatorial oxides, forming a pentagonal bipyramid. These coor-

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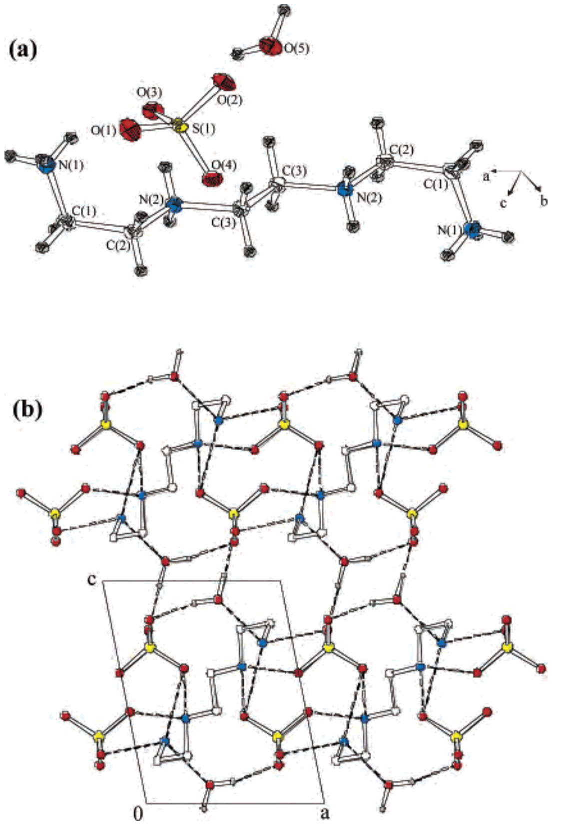

Figure 1. (**a**) Thermal ellipsoid plots (50% probability) of TETA-S and (**b**) three-dimensional packing of TETA-S. Red, yellow, and gray spheres represent oxygen, sulfur, and hydrogen atoms, respectively, while white and blue spheres represent carbon and nitrogen atoms. Hydrogen-bonding interactions are shown as dashed lines. $[\mathrm{tetaH_4}]^{4+}$ hydrogen atoms have been removed for clarity.

dination sites are occupied by bound water molecules and oxide ligands that bridge to sulfur centers. The $\mathrm{U-O_{bridging}}$ distances range between 2.342(4) and 2.460(4) Å, while the $\mathrm{U-O_{water}}$ distances range between 2.440(3) and 2.459(7) Å. Each sulfur site in USO-27, USO-28, and USO-29 is four coordinate in a tetrahedral geometry. S−O distances range between 1.436(4) and 1.515(4) Å.

USO-27. The inorganic structure and three-dimensional packing of USO-27 are shown in Figure 2. One unique uranium environment is observed in USO-27, in which four of the five equatorial coordination sites are occupied by oxide ligands that bridge to sulfur centers. The fifth equatorial coordination site is occupied by a bound water molecule. Two distinct sulfur centers are present: S1 is bound to three oxides that bridge to uranium centers and one terminal oxide and S2 is bound to one bridging and three terminal oxides. The sulfate tetrahedra containing S1 bridge between three adjacent uranium centers, each through a single shared oxide, forming extended chains. The formula of the chain backbone is $[\mathrm{UO_2(SO_4)_{3/3}}]$, a known structure type.[23] The two equatorial coordination sites on each uranium center that are not part of the chain backbone are occupied by a $[\mathrm{SO_4}]^{2-}$ tetrahedron and a bound water molecule, resulting in chains with the formula $[\mathrm{UO_2(H_2O)(SO_4)_{3/3}(SO_4)_{1/1}}]_n^{2n-}$.

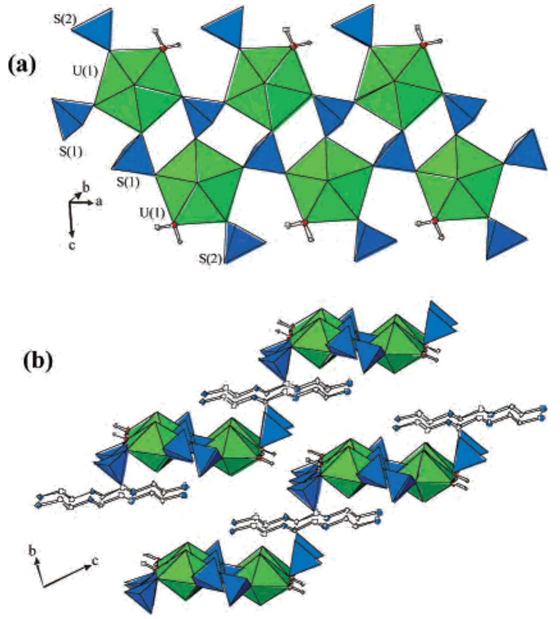

Figure 2. (**a**) One-dimensional $[\mathrm{UO_2(H_2O)(SO_4)_2}]_n^{2n-}$ chains and (**b**) three-dimensional packing of USO-27. Green and blue polyhedra represent $[\mathrm{UO_7}]$ and $[\mathrm{SO_4}]$, respectively. Selected uranium and sulfur sites are labeled, bound water molecules are shown, and templated hydrogen atoms have been removed for clarity.

The $[\mathrm{UO_2(H_2O)(SO_4)_2}]_n^{2n-}$ chains propagate along the [1 0 0] direction; see Figure 2b. Successive chains lie next to one another in the (0 1 1) plane, both donating and accepting hydrogen bonds through the bound water molecules and $[\mathrm{SO_{3/1}O_{1/2}}]$ tetrahedra, respectively. The result is the formation of pseudo-hydrogen-bonded layers. The $[\mathrm{tetaH_4}]^{4+}$ cations reside between chains, both balancing the negative charges associated with the inorganic structure and participating in an extensive hydrogen-bonding network.

The thermal stability of USO-27 was probed using thermogravimetric analysis. A weight loss of 10.6% was observed between 90 and 175 °C, corresponding to dehydration of the material (calcd 8.9%). Weight losses between 280 and 480 and between 480 to 800 °C correspond to loss of the organic templates and decomposition of the inorganic structure, respectively. This material calcines to $\mathrm{UO_2}$, as determined using powder X-ray diffraction, with an overall weight loss of 55.6% (calcd 55.7%).

USO-28. The inorganic structure and three-dimensional packing of USO-28 are shown in Figure 3. One unique uranium environment is observed in USO-28. Each of the five equatorial coordination sites is occupied by oxide ligands that bridge to sulfur centers. Two distinct sulfur sites are present in USO-28: S1 is bound to two bridging and two terminal oxides, while S2 is bound to one terminal and three bridging oxide ligands. The $[\mathrm{SO_{2/2}O_{2/1}}]$ tetrahedra containing S1 each bridge between two adjacent uranium centers through shared vertexes. In contrast, the tetrahedra containing

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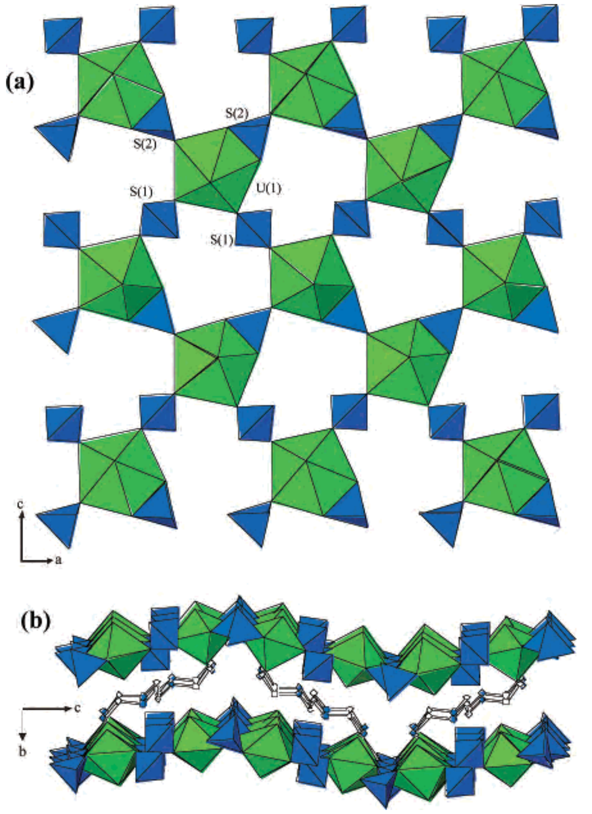

Figure 3. (a) Two-dimensional $[UO_2(SO_4)_2]_n^{2n-}$ layers and (b) three-dimensional packing of USO-28. Green and blue polyhedra represent $[UO_7]$ and $[SO_4]$, respectively. Selected uranium and sulfur sites are labeled, and hydrogen atoms have been removed for clarity.

S2 bridge between two uranium centers through one shared corner and one shared edge. O6 and O7 are both bound to U1 and S2. The result is a contraction of the O6−U1−O7 bond angle to 58.64(14)°, the other O_{eq}−U−O_{eq} bond angles range between 69.46(14) and 82.80(14)°. The layer formed through the connection of UO_7 pentagonal bipyramids with SO_4 tetrahedra is shown in Figure 3a. These layers are analogous to several known phases.[24]

The $[UO_2(SO_4)_{4/2}]_n^{2n-}$ layers lie in the (0 1 0) plane, with successive layers stacking along the [0 1 0] direction. Each layer is rotated 180° with respect to the layers above and below. The $[tetaH_4]^{4+}$ cations reside between layers, balancing charge and participating in hydrogen bonding with inorganic layers both above and below; see Figure 3b.

Upon heating, the organic component of USO-28 decomposes between 220 and 360 °C, with a collapse of the inorganic structure between 470 and 750 °C. USO-28 calcines to UO_2 by 800 °C, as demonstrated using powder X-ray diffraction, with a weight loss of 49.4% (calcd 49.7%).

USO-29. The inorganic structure and three-dimensional packing of USO-29 are shown in Figure 4 and Figure 5. Three unique uranium environments are observed in USO-29. Four of the five equatorial coordination sites are occupied by bridging oxides. In each instance, the fifth coordination site is occupied by a bound water molecule. Five distinct sulfur centers are observed, each of which exhibits the same connectivity: two terminal and two bridging oxide ligands. Each $[UO_6(H_2O)]$ pentagonal bipyramid is connected to four others through $[SO_4]$ bridges, the result of which is the formation of $[(UO_2)_5(H_2O)_5(SO_4)_{20/2}]_n^{10n-}$ layers. The $[UO_6(H_2O)]$ pentagonal bipyramids are similarly oriented, with the U−O_{water} bonds aligned along the [1 0 0] direction; see Figure 4. This layer topology was previously observed in $MgUO_2(SO_4)_2 \cdot 11H_2O$,[25] $UO_2SO_4(HSO_4) \cdot 5H_2O$,[26] and $K_2UO_2(H_2O)(SO_4)_2] \cdot H_2O$.[27]

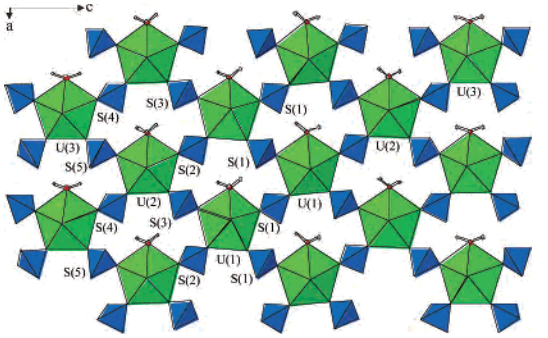

Figure 4. Two-dimensional $[(UO_2)_5(H_2O)_5(SO_4)_{10}]_n^{10n-}$ layers in USO-29. Selected uranium and sulfur sites are labeled, and bound water molecules are shown.

The $[(UO_2)_5(H_2O)_5(SO_4)_{10}]_n^{10n-}$ layers lie in the (0 1 0) plane, with successive layers stacking along the [0 1 0] direction; see Figure 5. The orientation of each layer is rotated 180 °C every *b*/2, resulting in a structural motif in which the orientation of the U−O_{water} bonds alternates. Each layer deviates from planarity, resulting in a "wavelike" structure with periodicity of approximately 56.5 Å. The interlayer space is occupied by $[tepaH_5]^{5+}$ cations and occluded water molecules, both of which participate in extensive hydrogen bonding involving adjacent inorganic layers and occluded water molecules.

USO-29 undergoes a weight loss of 3.8% between 150 and 210 °C, corresponding to dehydration of the material (calcd 3.9%). Weight losses between 290 and 490 and between 490 and 800 °C correspond to loss of the organic templates and decomposition of the inorganic structure. This material calcines to UO_2, as determined using powder X-ray diffraction, with an overall weight loss of 51.7% (calcd 51.9%).

Discussion

It has been reported previously that the use of amine phosphate starting materials can affect the reaction product in several ways. Lower reaction temperatures are accessible, different inorganic architectures are observed, template decomposition is less likely,[7b] and a correlation between the amine phosphate and reaction product can be observed.[4] Amine sulfates are believed to behave in a similar fashion.[9]

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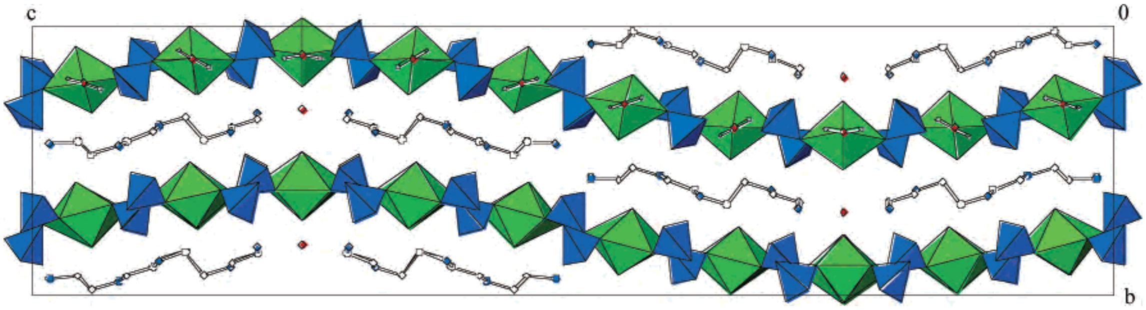

Figure 5. Unit cell contents of USO-29. Bound water molecules are shown, and template and occluded water hydrogen atoms have been removed for clarity.

USO-27, USO-28, and USO-29 were all synthesized using amine sulfate starting materials, which introduce two main differences from standard syntheses using amines. First, no template decomposition was observed when using amine sulfates. In contrast, a series of reactions were conducted in the $UO_2(CH_2CO_2)_2\cdot 2H_2O$ / H_2SO_4 / $H_3N[(CH_2)_2NH_2]_n(CH_2)_2NH_3$ ($n = 2, 3$) / H_2O systems to probe whether the amine sulfate was required. We were unable to grow single crystals of any organically templated uranium sulfates under a wide range of reaction concentrations, which suggests a dependence upon the amine sulfate. In fact, template decomposition was widely observed in these reactions. The prereaction of the amines with sulfuric acid in a large volume of methanol appears to provide a gentler route to the protonated forms, whereas reaction in a small, stoichiometric amount of water results in template decomposition in these systems.

Second, the use of amine sulfates resulted in the formation of a uranium sulfate layer that was previously unobserved in compounds containing organic amines. A host of organically templated uranium sulfates has been reported in recent years, none of which were synthesized using amine sulfate starting materials. Throughout all of these compounds, the layer structure present in USO-29 is only observed in this compound, although the layer topology is known.[25−27] As discussed by Rao et al., amine phosphates have been proposed to directly affect the nature of the secondary building unit−amine condensation,[3b] into complex architectures.[7b] The extension of this concept to include amine sulfates is supported by the formation of the uranium sulfate layer in USO-29.

No correlation between amine sulfate and uranium sulfate structure was observed. Amine sulfates are far more water soluble than amine phosphates, resulting in complete dissolution at room temperature under the conditions explored. The amine sulfate is exclusively in the form of protonated amines and sulfate ions (and occluded water), which can and do affect the crystallization but do not provide any correlation between amine sulfate and uranium sulfate structure.

Upon dissolution, the amine sulfates act as sources of protonated amines and sulfate ions. Amines adopt many different roles in such chemistry, including true templates, structure directors, and space fillers.[3] The amines in USO-27, USO-28, and USO-29 act exclusively as space fillers and hydrogen-bond donors.

Table 6. Bond Valence Sums[a] for USO-27

S_i	U1	S1	S2	H atoms[b]	ΣS_i	$V_i - \Sigma S_i$
O1	1.73				1.73	−0.27
O2	1.72				1.72	−0.28
O3	0.49	1.47			1.96	−0.04
O4	0.54	1.46			2.00	0.00
O5	0.57		1.35		1.92	−0.08
O6	0.47			0.8 × 2	2.1	0.1
O7	0.52	1.47			1.99	−0.07
O8		1.62			1.62	−0.38[c]
O9			1.53		1.53	−0.47[c]
O10			1.49		1.49	−0.51[c]
O11			1.51		1.51	−0.49[c]
O12				0.8 × 2	1.6	−0.4[c]
O13				0.8 × 2	1.6	−0.4[c]
O14				0.8 × 2	1.6	−0.4[c]
ΣS_i	6.04	6.02	5.88			

[a] Valence sums calculated with the formula $S_i = \exp[(R_0 - R_i)/B]$, where S_i is the bond valence of bond i, R_0 is a constant dependent upon the bonded elements, and R_i is the bond length of bond i. ΣS_i is the bond valence sum for each atom. V is the predicted valence for a site. U^{VI}−O: $R_0 = 2.051$, $B = 0.519$; S^{VI}−O: $R_0 = 1.624$, $B = 0.370$. [b] O−H bond valences on bound water molecules are approximated using $R_0 = 0.939$, $B = 0.370$. [c] Hydrogen-bond acceptor (determined experimentally by anion−anion distances).

Extended hydrogen-bonded networks are ubiquitous in the chemistry of organically templated inorganic materials. To systematize the study of these networks, the amines used are structurally analogous, with the general formula $H_3N[(CH_2)_2NH_2]_n(CH_2)_2NH_3$ ($n = 2, 3$). Each contains both RNH_3 and R_2NH_2 hydrogen-bonding sites, exclusively. This approach has enabled us to gain fundamental understanding into the formation of the extended hydrogen-bonding networks in USO-27, USO-28, and USO-29. Two main factors were observed to dictate hydrogen bonding: relative oxide ligand nucleophilicities and geometric constraints.

The primary influence dictating the hydrogen-bonding networks in USO-27, USO-28, and USO-29 can be understood when discussed in the context of bond valence sums,[28] a concept that is used to quantify both the relative strength and residual charges of each bond and respective ligand. All calculations were performed using parameters compiled by either Brese and O'Keeffe[29,30] or Burns et al.[19] The valence of each U−O, S−O, and O−H bond was calculated; see Tables 6−8. The overall charge on each U and S center can be calculated by adding the appropriate bond valences. In each case, the U and S valences are close to 6+, the expected value. The relative residual negative charge on each oxide ligand can be calculated by adding the valences of each

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Table 7. Bond Valence Sums for USO-28

S_i	U1	S1	S2	ΣS_i	$V_i - \Sigma S_i$
O1	1.72			1.72	−0.28
O2	1.73			1.73	−0.27
O3	0.52		1.45	1.97	−0.03
O4	0.57	1.40		1.97	−0.03
O5	0.56	1.34		1.91	−0.10[a]
O6	0.46		1.45	1.90	−0.10
O7	0.46		1.46	1.92	−0.08
O8		1.61		1.61	−0.39[a]
O9		1.59		1.59	−0.41[a]
O10			1.66	1.66	−0.34[a]
ΣS_i	6.01	5.95	6.03		

[a] Hydrogen-bond acceptor (determined experimentally by anion-anion distances).

Table 8. Bond Valence Sums for USO-29

S_i	U1	U2	U3	S1	S2	S3	S4	S5	H atoms	ΣS_i	$V_i - \Sigma S_i$
O1	1.69									1.69	−0.31
O2	1.70									1.70	−0.31
O3	0.47								0.8 × 2	2.1	0.1
O4	0.55			1.41						1.96	−0.04
O5	0.50			1.48						1.98	−0.02
O6	0.57				1.40					1.96	−0.04
O7	0.52					1.44				1.95	−0.05
O8		1.65								1.65	−0.35
O9		0.62								1.62	−0.38
O10		0.50							0.8 × 2	2.1	0.1
O11		0.52			1.43					1.95	−0.05
O12		0.57				1.44				2.01	0.01
O13		0.52					1.45			1.97	−0.03
O14		0.54						1.43		1.96	−0.04
O15			1.66							1.66	−0.34
O16			1.68							1.68	−0.32
O17			0.46						0.8 × 2	2.1	0.1
O18			0.48 × 2				1.40			1.88	−0.12
O19			0.56 × 2					1.46		2.02	0.02
O20				1.60						1.60	−0.40[a]
O21				1.48						1.48	−0.52[a]
O22					1.52					1.52	−0.48[a]
O23					1.66					1.66	−0.34[a]
O24						1.60				1.60	−0.40[a]
O25						1.55				1.55	−0.45[a]
O26							1.53			1.53	−0.47[a]
O27							1.61			1.61	−0.39[a]
O28								1.56		1.56	−0.44[a]
O29								1.57		1.57	−0.43[a]
O30									0.8 × 2	1.6	−0.4[a]
ΣS_i	5.98	5.91	5.87	5.96	6.01	6.03	5.98	6.02			

[a] Hydrogen-bond acceptor (determined experimentally by anion-anion distances).

U−O, S−O, and O−H bond in which a given ligand participates. The total bond valence (ΣS_i) is subtracted from the predicted valence of an oxide ligand, −2, to give the residual negative charge. The relative nucleophilicity of each ligand, which relates to the propensity to accept a hydrogen bond from either the organic cations or bound or occluded water molecules, is directly proportional to the residual negative charge. The residual negative charges on the oxide ligands vary considerably.

Calculation of the valences for O−H bonds in bound and occluded water molecules is difficult because hydrogen atoms were placed in idealized positions with fixed bond lengths; therefore, accurate hydrogen atomic positions are not known. Approximations are included because the water molecules are important participants in the hydrogen-bonding network, and neglecting the effects of the O−H valences on the oxide nucleophilicities leads to unreasonable values. The loss of nucleophilicty of bound water molecules after coordination in USO-27 and USO-29 is demonstrated through their calculated small positive values.

In each structure, the oxides that accept hydrogen bonds are dominated by terminal sulfate oxides and occluded water molecules, as suggested by their calculated nucleophilicities; see Tables 6−8. Each of these oxides is a hydrogen-bond acceptor in USO-27, USO-28, and USO-29. The uranyl oxides, those that are part of the central $[UO_2]^{2+}$ units, are less nucleophilic than sulfate oxides or occluded water molecules, therefore they do not participate in the hydrogen bonding. The least nucleophilic ligands are bound water molecules and oxides that bridge between uranium and sulfur centers. The observed hydrogen bonding in each structure is highly correlated with the ligand nucleophilicities.

An apparent exception is observed in the hydrogen bonding in USO-28. O5, a weakly nucleophilic oxide that acts as a μ^2 bridge between U1 and S1, is a hydrogen-bond acceptor, with the protonated secondary amine N2 and O5 only separated by 2.869(5) Å. The inclusion of O5 in the hydrogen-bonding motif is most likely a result of geometric constraints. Short anion−anion distances are observed between N2 and both O5 and O8, a highly nucleophilic terminal sulfate oxide. The formation of a hydrogen bond to O8, coupled with steric influences dictating an approximate H8−N2−H9 bond angle of 109.5°, limits the availability of hydrogen-bond acceptors. The position of O5, which is only moderately nucleophilic in the context of USO-28, allows the formation of two hydrogen bonds, separated by an appropriate angle. The experimental O5−N2−O8 bond angle is 139.9(3)°.

Conclusion

Amine sulfates can provide a facile route for the formation of organically templated inorganic materials. They reduce the incidence of amine decomposition and affect the product structures. The formation of the hydrogen-bonded networks in USO-27, USO-28, and USO-29 are dependent upon two factors. The primary influence is the relative oxide nucleophilicities; the oxides with the highest residual negative charge are the hydrogen-bond acceptors. A secondary influence arises from geometric constraints, which can result in less nucleophilic ligands accepting hydrogen bonds, as observed in USO-28. These two factors were shown to describe the hydrogen bonding in three new organically templated uranium sulfates.

Acknowledgment. The authors thank Dr. Andrew R. Cowley for crystallographic assistance and the EPSRC for funding.

Supporting Information Available: X-ray crystallographic files (CIF) containing complete tables of crystallographic details, atomic positions, 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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