Structural diversity in organically templated uranium sulfates †

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The potential of organic amine templates to direct the synthesis of metal sulfate frameworks has been investigated. Eight novel uranyl sulfates have been prepared using a templated uranyl sulfate precursor under hydrothermal conditions. The topologis of the isolated phases vary from the molecular (0-D), to chains (1-D) to layered (2-D) frameworks. $[N_4C_6H_{22}]_2[(UO_2)_2(SO_4)_6]$ (USO-10) is molecular or zero-dimensional. Two different types of one-dimensional uranyl-containing chains have been observed. $[N_2C_4H_{12}][UO_2(H_2O)(SO_4)_2]$ (USO-3), $[N_2C_5H_{14}]$-$[UO_2(H_2O)(SO_4)_2]$ (USO-4) and $[N_2C_3H_{12}][UO_2(H_2O)(SO_4)_2]$ (USO-9) contain chains based upon a $[UO_2(SO_4)_{4/2}]$ backbone. $[N_2C_{10}H_{10}][UO_2(SO_4)_2]\cdot H_2O$ (USO-6) and $[N_2C_6H_{18}][(UO_2)_2(H_2O)_3(SO_4)_3]$ (USO-7) contain chains based upon a $[UO_2(SO_4)_{3/3}]$ backbone. Two layered or two-dimensional compounds, $[N_2C_6H_{14}][UO_2(H_2O)(SO_4)_2]$ (USO-5) and $[N_2C_3H_5]_2[(UO_2)_2(SO_4)_3]$ (USO-8) have also been isolated. All the new phases have been characterised using a range of physical techniques including single crystal X-ray structure analysis.

Introduction

The chemistry of open framework metal phosphates is well known.[1] Considerable effort has been expended during the study of these compounds owing to the great structural diversity[2] and desirable physical properties.[3] Despite the rich chemistry of the phosphate tetrahedra in inorganic materials, the chemistry of organically templated metal sulfates is under explored. Few analogous sulfate containing materials have been reported.[4]

The number of organic structure directing agents that have been successfully employed in the synthesis of templated metal sulfates has been limited. Piperazine was used by Khan *et al.*,[4a] Rao *et al.*,[4b] and Louer *et al.*,[4f] cyclen was used by Wright *et al.*,[4c] and triethylenetetramine was used by Rao *et al.*,[4d] ethylenediamine was used by Rao *et al.*,[4e] and Louer *et al.*,[4f] and 1,3-diaminopropane and 1,6-diaminohexane were used by Rao *et al.*[4e] We recently reported six new uranium sulfates templated by either 1,3-diaminopropane,[5] a series of structurally related cyclical diamines[6] or tetramethylammonium.[7] Nonetheless this small set of structure directing amines is still insignificant when compared to the range that has been used in metal phosphate chemistry.

In order to expand upon the emergent chemistry of templated metal sulfates eight frameworks have been synthesised using eight different structure directing agents. The syntheses and structures of USO-3, USO-4 and USO-5 were reported previously.[5] See Fig. 1. Alternate syntheses of these compounds along with the synthesis of five new compounds and their corresponding structures are reported in this study. These compounds are designated USO-6 through USO-10 (Uranium Sulfate from Oxford).

Results

Synthesis and structure of $[N_2C_{10}H_{10}][UO_2(SO_4)_2]\cdot H_2O$, USO-6

Crystalline USO-6 can be prepared by heating USO-1 in the presence of 4,4′-bipyridyl (bpy) under hydrothermal conditions followed by slow cooling to room temperature. Yellow needles were isolated after reaction in 39% yield. One unique uranium environment is observed in USO-6. The U^{6+} cation is seven coordinate, in a pentagonal bipyramidal geometry. The uranyl bond lengths, 1.767(3) and 1.779(3) Å, are close to the average

reported value of 1.758(4) Å.[8] The O(1)–U(1)–O(2) bond angle is 179.39(14)°. Each of the five equatorial coordination sites are occupied by oxide ligands that are part of sulfate tetrahedra. The five $U(1)–O_{eq}$ bond lengths are 2.322(3), 2.336(3), 2.421(3), 2.442(3) and 2.336(3) Å. Bond valence calculations[9,10] on USO-1, using uranium parameters from Burns *et al.*,[8] resulted in a value of 6.12 for U(1).

Two sulfur environments exist in USO-6. Both S(1) and S(2) are four coordinate with bond lengths of 1.448(4), 1.516(3), 1.510(3) and 1.445(4) Å between S(1) and its oxide ligands and 1.489(3), 1.484(3), 1.444(3) and 1.484(3) Å between S(2) and its oxide ligands. The SO_4 tetrahedron containing S(1) contains two oxide ligands, O(3) and O(4), which bridge to the same uranium centre, resulting in a shared edge between the UO_7 and SO_4 polyhedra. O(8) and O(9) are terminal. The SO_4 tetrahedron containing S(2) contains three oxide ligands that bridge to adjacent uranium centres, while O(10) is terminal.

The uranium centres connect to form one-dimensional chains, which run along the *a* axis. This chain topology, excluding the edge shared tetrahedra, is found in several uranium mineral phases (Fig. 2, selected atomic coordinates are collected in Table 1).[11] Hydrogen bonding between the inorganic chains, occluded water and protonated 4,4′-bpy cations stabilises the structure. Each occluded water donates two hydrogen bonds with O–O distances of 2.719(5) and 2.713(5) Å to O(3) and O(4) respectively. Each $[H_2bpy]^{2+}$ donates a hydrogen bond to the occluded water, O(11), with a distance of 2.615(4) Å. The three-dimensional packing is shown in the ESI (Fig. S1).

Two N–H bands are observed in the infrared spectrum of USO-6 at 3100 and 1650 cm^{-1}. The asymmetric uranyl stretch is at 900 cm^{-1} and a broad band at 1100 cm^{-1} corresponds to S–O stretches. Thermogravimetric analysis indicates that USO-6 exhibits a weight loss of 2.8% between 100 and 180 °C, corresponding to the loss of occluded water (2.8%). The material completely calcines to UO_2 between 460 and 500 °C.

### Synthesis and structure of $[N_2C_6H_{18}][(UO_2)_2(H_2O)_3(SO_4)_3]$, USO-7

Crystalline USO-7 can be prepared by heating USO-1 in the presence of *N,N,N′,N′*-tetramethylethylenediamine (tmed) under hydrothermal conditions followed by slow cooling to room temperature. Yellow plates were isolated after reaction in 93% yield. The asymmetric unit in USO-7 was determined to contain two distinct U^{6+} centres using single crystal X-ray structure determination. Both metal centres are seven co-ordinate, and contain two uranyl bonds of typical length. The U(1)–O(1) and U(1)–O(2) bond distances are 1.764(6) and
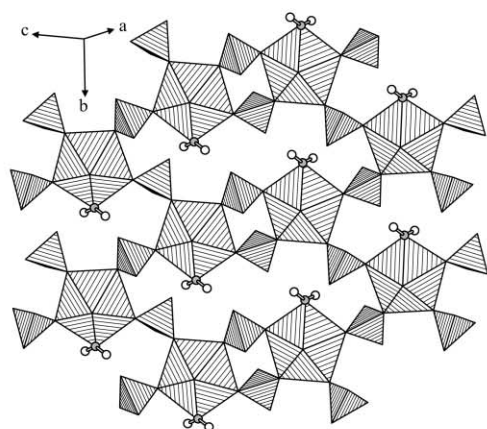
† Electronic supplementary information (ESI) available: three-dimensional packing diagrams for USO-6–USO-10. See http://www.rsc.org/suppdata/dt/b2/b209208e/
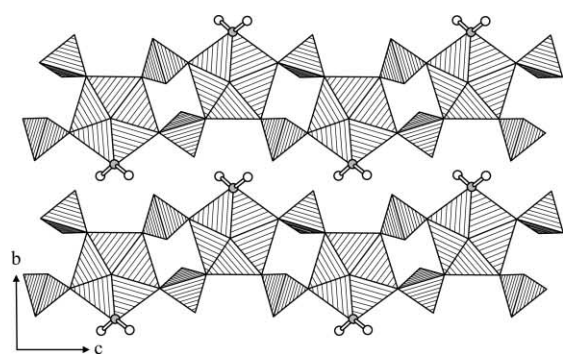
(a) [H₂pip][UO₂(H₂O)(SO₄)₂], USO-3
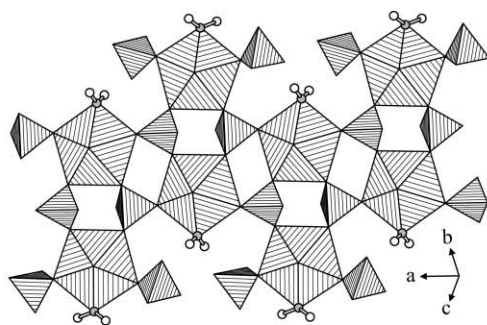
(a) [H₂mpip][UO₂(H₂O)(SO₄)₂], USO-4

(a) [H₂dabco][UO₂(H₂O)(SO₄)₂], USO-5

Fig. 1 (a) One-dimensional $[UO_2(H_2O)(SO_4)_2]^{2-}$ chains in USO-3. (b) One-dimensional $[UO_2(H_2O)(SO_4)_2]^{2-}$ chains in USO-4. (c) Two-dimensional $[UO_2(H_2O)(SO_4)_2]^{2-}$ layers in USO-5. Tetrahedra and pentagonal bipyramids represent $[SO_4]$ and $[UO_7]$ respectively. Shaded and unshaded circles represent oxygen and hydrogen atoms respectively.

Fig. 2 One-dimensional $[UO_2(SO_4)_2]^{2-}$ chains in USO-6. Tetrahedra and pentagonal bipyramids represent $[SO_4]$ and $[UO_7]$ respectively. Shaded and unshaded circles represent oxygen and hydrogen atoms respectively. Hydrogen bonds are shown as dashed lines with lengths given (Å).

Table 1 Selected atomic coordinates for USO-6

Atom	x	y	z	$U_{eq}{}^a$
U(1)	1.17371(2)	−0.38552(2)	0.634643(9)	0.0081
S(1)	1.08983(15)	−0.25959(14)	0.81264(7)	0.0154
S(2)	1.29331(14)	−0.61817(13)	0.44636(6)	0.0124
O(1)	1.1788(4)	−0.6066(4)	0.69049(19)	0.0169
O(2)	1.1667(4)	−0.1633(4)	0.57777(19)	0.0166
O(3)	0.9477(4)	−0.2684(4)	0.75213(19)	0.0176
O(4)	1.2844(4)	−0.3104(4)	0.7579(2)	0.0184
O(5)	1.5176(4)	−0.4189(5)	0.6085(2)	0.0215
O(6)	1.2318(5)	−0.4750(4)	0.5002(2)	0.0185
O(7)	0.8527(4)	−0.4012(4)	0.6138(2)	0.0194
O(8)	1.0798(5)	−0.0813(5)	0.8307(2)	0.0256
O(9)	1.0583(5)	−0.3893(5)	0.8906(2)	0.0267
O(10)	1.3074(6)	−0.7922(4)	0.4993(2)	0.0268
O(11)	0.6124(4)	−0.3994(4)	0.8357(2)	0.0199
N(1)	0.7135(6)	0.0581(5)	0.6059(2)	0.0205
N(2)	0.4681(6)	0.2815(5)	1.0169(2)	0.0226
C(1)	0.5389(7)	0.0218(6)	0.6517(3)	0.0195
C(2)	0.4856(7)	0.0636(6)	0.7338(3)	0.0198
C(3)	0.6147(6)	0.1428(6)	0.7673(3)	0.0173
C(4)	0.7934(6)	0.1810(6)	0.7180(3)	0.0183
C(5)	0.8402(7)	0.1372(6)	0.6359(3)	0.0204
C(6)	0.6567(7)	0.2162(7)	0.9905(3)	0.0266
C(7)	0.7069(7)	0.1683(7)	0.9096(3)	0.0252
C(8)	0.5629(7)	0.1876(6)	0.8557(3)	0.0183
C(9)	0.3689(7)	0.2528(6)	0.8861(3)	0.0204
C(10)	0.3256(7)	0.2995(6)	0.9680(3)	0.0231

^{a} $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

178.8(3) and 178.8(3)° respectively. The five equatorial coordination sites surrounding U(1) are occupied by three oxides that bridge to sulfur centres and two bound water molecules. The U(1)–O bond distances to bridging oxides are shorter than the U(1)–O$_{water}$ bond lengths, 2.367(6), 2.357(6) and 2.360(6) Å *versus* 2.404(6) and 2.419(6) Å. The five equatorial coordination sites around U(2) are occupied by four bridging oxides and one bound water molecule with distances of 2.354(6), 2.334(8), 2.357(6) and 2.390(6) Å for bridging oxides. The U(2)–O(14) distance is 2.482(6) Å.

Three unique sulfur environments exist in USO-7. S(1) is the central atom in the sulfate tetrahedra which bridge between adjacent U(1) centres. Three of the oxides bound to S(1) also bridge to U(1) with distances of 1.482(6), 1.476(6) and 1.472(6) Å. The fourth oxide is terminal, with a S(1)–O(8) bond distance of 1.432(7) Å. S(2) and S(3) are both part of SO₄ tetrahedra that bridge between U(2) centres. S(2) is bound to one bridging oxide, O(15), and three terminal oxides, O(16), O(17) and O(18), through distances of 1.515(5), 1.463(6), 1.460(6) and 1.468(7) Å. S(3) is bound to three bridging oxides, O(11), O(12) and O(13), and one terminal oxide, O(19), through distances of 1.492(6), 1.456(8), 1.495(6) and 1.432(7) Å.

Two distinct anionic one-dimensional chains are present in USO-7, each of which runs along the *a* axis. Each chain contains the same basic topology as observed in USO-6. The first chain (denoted USO-7 chain 1), which contains U(1) uranium centres, has the formula $[UO_2(H_2O)_2(SO_4)]$. The two bound water molecules are *cis* to one another, while each sulfate tetrahedron bridges between three UO₇ pentagonal bipyramids (Fig. 3a, selected atomic coordinates are collected in Table 2). The second chain (denoted USO-7 chain 2), which contains U(2) uranium centres exclusively, has the formula $[UO_2(H_2O)(SO_4)_2]^{2-}$. One sulfate bridges between three UO₇ polyhedra while the other is only bound to one uranium centre. The bound water molecule donates two hydrogen bonds to adjacent terminal sulfates through distances of 2.727(9) and 2.703(9) Å to O(15) and O(16) respectively (Fig. 3b).

These two distinct chains are connected through a series of hydrogen bonds donated from the two bound water molecules on U(1). Adjacent USO-7 chain 1s are connected through hydrogen bonds from both bound water molecules on U(1).

1.773(6) Å, while the U(2)–O(9) and U(2)–O(10) bond distances are 1.748(6) and 1.791(6) Å respectively. The two uranyl bond angles, O(1)–U(1)–O(2) and O(9)–U(2)–O(10), are

Table 2 Selected atomic coordinates for USO-7

Atom	x	y	z	$U_{eq}{}^a$
U(1)	0.22758(4)	0.23494(3)	0.436342(15)	0.0069
U(2)	0.29205(4)	−0.35153(3)	0.119713(15)	0.0089
S(1)	0.7499(3)	0.3343(2)	0.49252(11)	0.0112
S(2)	0.6284(3)	−0.0746(2)	0.24982(11)	0.0122
S(3)	−0.2344(3)	−0.3638(2)	0.05380(11)	0.0141
O(1)	0.268(1)	0.2207(7)	0.5274(3)	0.0181
O(2)	0.1823(9)	0.2464(7)	0.3445(3)	0.0165
O(3)	−0.0875(8)	0.3406(7)	0.4496(4)	0.0165
O(4)	0.2738(9)	0.5087(7)	0.4652(4)	0.0214
O(5)	0.5687(8)	0.2879(7)	0.4406(4)	0.0168
O(6)	0.3944(9)	−0.0071(7)	0.4091(4)	0.0206
O(7)	−0.0049(8)	0.0171(7)	0.4195(3)	0.0154
O(8)	0.7903(9)	0.2263(7)	0.5410(4)	0.0190
O(9)	0.279(1)	−0.1984(9)	0.0731(4)	0.0257
O(10)	0.3076(9)	−0.5043(7)	0.1700(3)	0.0161
O(11)	0.5957(8)	−0.4285(7)	0.0810(4)	0.0182
O(12)	0.2077(11)	−0.5376(12)	0.0144(5)	0.0451
O(13)	−0.0557(9)	−0.3788(8)	0.1065(3)	0.0187
O(14)	0.1616(9)	−0.1742(7)	0.2191(4)	0.0222
O(15)	0.5551(9)	−0.2367(6)	0.2108(3)	0.0145
O(16)	0.8089(9)	−0.0346(7)	0.2236(4)	0.0179
O(17)	0.4712(9)	0.0339(7)	0.2369(4)	0.0223
O(18)	0.6738(9)	−0.0800(7)	0.3262(4)	0.0173
O(19)	−0.2627(12)	−0.2049(9)	0.0467(5)	0.0414
N(1)	0.7041(12)	−0.4831(8)	0.2789(4)	0.0211
N(2)	0.8096(12)	−0.8260(9)	0.1358(5)	0.0220
C(1)	0.5543(15)	−0.4616(11)	0.3293(5)	0.0233
C(2)	0.9017(14)	−0.4192(11)	0.3179(6)	0.0279
C(3)	0.7094(13)	−0.6505(9)	0.2436(5)	0.0198
C(4)	0.8513(14)	−0.6716(11)	0.1884(5)	0.0237
C(5)	0.6171(16)	−0.8306(12)	0.0871(5)	0.0292
C(6)	0.9789(17)	−0.8615(13)	0.0945(6)	0.0345

^{a} $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

(a) USO-7 Chain 1

1.874(9) Å   1.981(9) Å
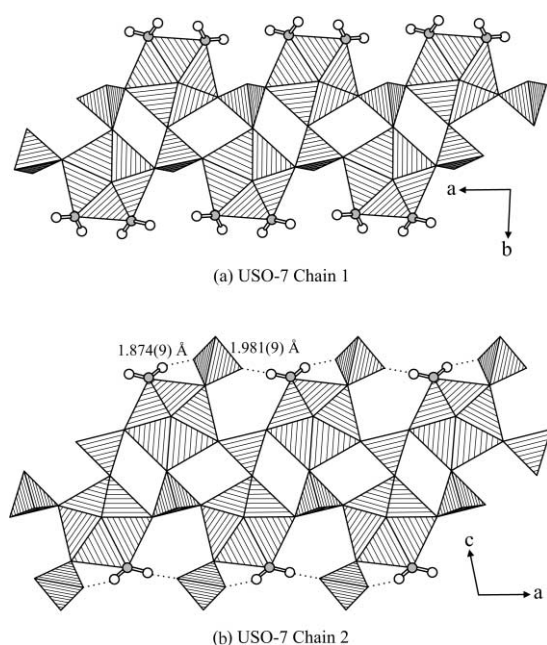
(b) USO-7 Chain 2

Fig. 3 (a) USO-7 chain 1. (b) USO-7 chain 2. Tetrahedra and pentagonal bipyramids represent [SO$_4$] and [UO$_7$] respectively. Shaded and unshaded circles represent oxygen and hydrogen atoms respectively. Hydrogen bonds are shown as dashed lines with lengths given (Å).

These distances are 2.692(9) and 2.754(9) Å for O(6)–O(19) and O(7)–O(19) respectively. USO-7 chain 1 and USO-7 chain 2 are connected through hydrogen bonds between both O(6) and O(7) and the neighbouring O(12), with distances of 2.653(9) and 2.649(9) Å respectively.

The organic cation, [H$_2$tmed]$^{2+}$, resides between flanking USO-7 chain 2s. The orientation of these cations is perpendicular to the direction of the chain. Each [H$_2$tmed]$^{2+}$ cation

donates two hydrogen bonds. The distances are 2.851(9) and 2.714(9) Å for N(1)–O(10) and N(2)–O(16) respectively. The packing of the organic template within the USO-7 structure is shown in the ESI (Fig. S2).

Bending and stretching modes emanating from N–H bonds are observed in the infrared spectrum of USO-7 at 3250 and 1650 cm^{-1}. The asymmetric uranyl stretch is observed at 925 cm^{-1}, while the S–O stretches are present as a broad band between 1000 and 1250 cm^{-1}. A C–H bending mode is visible at 1480 cm^{-1}.

The loss of bound water molecules between 150 and 200 °C was observed using thermogravimetric analysis. The experimental weight loss, 5.9%, is in agreement with the calculated value of 5.4%. On further heating the structure then collapses as the organic component is removed between 340 and 480 °C. This weight loss, 55.9%, is close to the calculated value of 56.1%. The material is calcined to U$_3$O$_8$ by 700 °C.

Synthesis and structure of [N$_2$C$_3$H$_5$]$_2$[(UO$_2$)$_2$(SO$_4$)$_3$], USO-8

Single crystals of USO-8 were grown by heating USO-1 in the presence of imidazole (imid) under hydrothermal conditions followed by slow cooling to room temperature. Yellow blocks were isolated after reaction in 87% yield. The asymmetric unit contains two uranium environments. Both U^{6+} centres contain uranyl bonds of typical length. The U(1)–O(1) and U(1)–O(2) bond lengths are 1.761(9) and 1.758(9) Å and the U(2)–O(8) and U(2)–O(9) bond lengths are 1.739(9) and 1.763(9) Å respectively. The two uranyl bond angles, O(1)–U(1)–O(2) and O(8)–U(2)–O(9), are 178.2(4) and 178.5(4)° respectively. Each uranium is seven coordinate, in a pentagonal bipyramidal geometry. The five equatorial coordination sites around U(1) are occupied by oxide ligands that are part of sulfate tetrahedra. These five U(1)–O$_{eq}$ bond lengths are 2.34(1), 2.445(8), 2.378(11), 2.362(8) and 2.412(9) Å. The bond valence of U(1) is 6.13. The five equatorial coordination sites around U(2) are also solely occupied by sulfate oxides. These U(2)–O$_{eq}$ bond lengths are 2.35(1), 2.350(9), 2.400(9), 2.351(9) and 2.472(9) Å. The bond valence of U(2) is 6.20.

Three sulfur sites are observed in USO-8. Each is the centre of an SO$_4$ tetrahedron. The tetrahedron that contains S(1) consists of three oxide ligands that bridge to uranium centres, O(3), O(6), and O(10), and one terminal oxide ligand, O(15). This is reflected in the S(1)–O bond lengths, where three long bonds are observed, with lengths of 1.488(9), 1.476(9) and 1.478(9) Å for S(1) to O(3), O(6) and O(9) respectively. The fourth bond to the terminal O(15) ligand is markedly shorter at 1.43(1) Å. The S(3) sulfate tetrahedron is analogous to that of S(1), with three longer bonds to bridging oxides of length 1.465(11), 1.489(9) and 1.476(9) Å to O(5), O(11) and O(13) respectively. The fourth bond to the terminal oxide O(6) is shorter at 1.453(9) Å. All four oxide ligands around S(2) bridge to adjacent uranium centres. The four S(2)–O bond lengths are 1.48(1), 1.458(9), 1.470(9) and 1.463(9) Å to O(4), O(7), O(12) and O(14) respectively.

The UO$_7$ and SO$_4$ polyhedra connect to form anionic two-dimensional layers in the *ab* plane with the formula [(UO$_2$)$_2$(SO$_4$)$_3$]$^{2-}$. This topology is unprecedented in uranium chemistry (Fig. 4, selected atomic coordinates are collected in Table 3). Two [Himid]$^+$ cations are present in the asymmetric unit. Both cations reside between inorganic layers and both balance charge and donate hydrogen bonds. However, the orientation of the cations differs. The first cation, which contains N(1) and N(2), is oriented such that the hydrogens attached to N(1) and N(2) donate hydrogen bonds to the same layer. These N–O distances are 2.72(1) and 2.70(1) Å for N(1)–O(15) and N(2)–O(16) respectively. The second cation donates hydrogen bonds to adjacent layers, through distances of 2.96(1) and 2.88(1) Å for N(3)–O(14) and N(4)–O(16) respectively.

Table 3 Selected atomic coordinates for USO-8

Atom	x	y	z	$U_{eq}{}^a$
U(1)	0.55074(5)	0.82471(4)	0.80466(2)	0.0088
U(2)	0.05218(5)	0.71810(3)	0.69656(2)	0.0085
S(1)	0.4073(3)	0.6746(3)	0.65390(15)	0.0105
S(2)	0.2501(3)	1.0225(3)	0.74564(14)	0.0103
S(3)	−0.0949(3)	0.8699(3)	0.84693(16)	0.0110
O(1)	0.631(1)	0.8958(9)	0.7340(5)	0.0200
O(2)	0.4753(9)	0.7548(9)	0.8767(4)	0.0148
O(3)	0.429(1)	0.695(1)	0.7271(5)	0.0176
O(4)	0.3352(9)	1.1080(9)	0.7018(5)	0.0212
O(5)	−0.2370(11)	0.836(1)	0.8629(5)	0.0242
O(6)	0.4302(11)	0.5319(8)	0.6396(4)	0.0206
O(7)	0.3357(9)	0.9382(9)	0.7881(5)	0.0188
O(8)	0.129(1)	0.6455(9)	0.7664(4)	0.0177
O(9)	−0.0231(9)	0.7885(9)	0.6243(4)	0.0135
O(10)	0.2627(9)	0.708(1)	0.6397(5)	0.0204
O(11)	0.0705(11)	0.5139(8)	0.6392(4)	0.0192
O(12)	−0.162(1)	0.6037(9)	0.7109(4)	0.0176
O(13)	−0.071(1)	0.8468(9)	0.7747(4)	0.0140
O(14)	0.1654(9)	0.9384(9)	0.7023(4)	0.0165
O(15)	0.495(1)	0.7551(11)	0.6131(5)	0.0267
O(16)	−0.004(1)	0.7931(9)	0.8897(5)	0.0215
N(1)	0.8121(12)	1.0658(13)	0.0725(6)	0.0213
N(2)	0.6592(13)	0.9147(11)	0.0785(6)	0.0201
N(3)	0.2737(15)	0.0183(15)	0.0583(7)	0.0322
N(4)	0.1703(15)	−0.0400(14)	−0.0293(7)	0.0323
C(1)	0.7477(18)	0.9867(15)	0.1142(7)	0.0260
C(2)	0.7712(17)	1.0474(17)	0.0103(8)	0.0288
C(3)	0.6676(16)	0.9478(16)	0.0126(7)	0.0258
C(4)	0.171(2)	−0.0502(18)	0.036(1)	0.0395
C(5)	0.3355(19)	0.0793(18)	0.0060(8)	0.0338
C(6)	0.2704(18)	0.0422(17)	−0.0494(8)	0.0330

$^a U_{eq} = (U_{11} + U_{22} + U_{33})/3.$
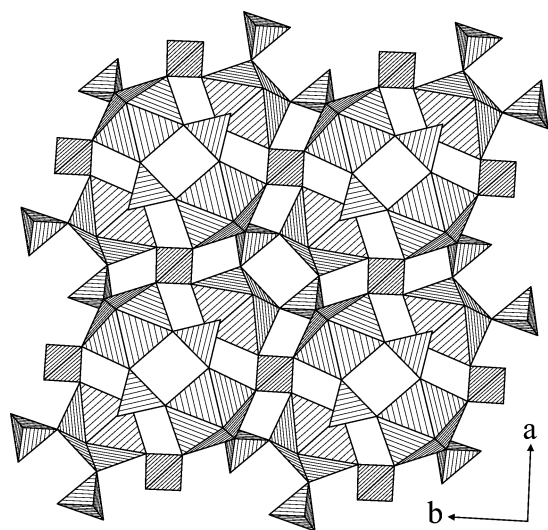
Fig. 4 Two-dimensional $[(UO_2)_2(SO_4)_3]^{2-}$ layers in USO-8. Tetrahedra and pentagonal bipyramids represent $[SO_4]$ and $[UO_7]$ respectively.

An asymmetric uranyl stretch was observed in the infrared spectrum at 906 cm^{-1}. S–O stretches were at 1100 cm^{-1} and two N–H bands were observed at 1590 and 3108 cm^{-1}.

Thermal analaysis shows that USO-8 is stable to 390 °C. On further heating a weight loss of 44.5% was observed between 390 and 490 °C, which corresponds to the loss of template and SO$_3$ (44.1% calc.). At 700 °C the material completely calcines to UO$_2$, as shown by powder X-ray diffraction.

Synthesis and structure of $[N_2C_3H_{12}][UO_2(H_2O)(SO_4)_2]$, USO-9

Crystals of USO-9 were grown by heating USO-1 in the presence of 1,2-diaminopropane (1,2-dap) under hydrothermal conditions followed by slow cooling to room temperature. Yellow rods were isolated after reaction in 83% yield. The

**Table 4** Selected atomic coordinates for USO-9

Atom	x	y	z	$U_{eq}{}^a$
U(1)	0.50464(3)	0.38012(2)	0.247086(16)	0.0065
S(1)	0.35188(17)	0.70356(16)	0.01742(11)	0.0102
S(2)	0.63401(17)	0.73169(16)	0.48248(11)	0.0097
O(1)	0.2539(5)	0.3511(5)	0.1908(3)	0.0146
O(2)	0.7563(5)	0.4036(5)	0.3027(3)	0.0148
O(3)	0.4855(6)	0.2841(5)	0.4347(4)	0.0156
O(4)	0.5112(6)	0.0520(5)	0.2542(3)	0.0180
O(5)	0.5323(6)	0.2455(5)	0.0648(3)	0.0144
O(6)	0.4854(5)	0.6301(5)	0.1228(3)	0.0145
O(7)	0.5102(5)	0.6546(5)	0.3643(3)	0.0137
O(8)	0.2795(6)	0.8708(5)	0.0578(4)	0.0153
O(9)	0.1946(6)	0.5718(5)	−0.0402(4)	0.0167
O(10)	0.8022(5)	0.6295(5)	0.5230(3)	0.0141
O(11)	0.6869(6)	0.9233(5)	0.4689(4)	0.0160
N(1)	1.1040(6)	0.7242(7)	0.4120(4)	0.0159
N(2)	0.8910(7)	0.7969(7)	0.0859(4)	0.0183
C(1)	1.0662(8)	0.7056(8)	0.2799(5)	0.0166
C(2)	0.9176(7)	0.8322(7)	0.2172(5)	0.0141
C(3)	0.9771(9)	1.0323(8)	0.2512(5)	0.0197

$^a U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

asymmetric unit contains one unique uranium site. This seven coordinate U^{6+} centre exhibits a pentagonal bipyramidal geometry. The uranyl bond lengths, 1.768(4) and 1.773(4) Å, are typical for a uranyl unit, and the O(1)–U(1)–O(2) bond angle is close to 180° at 178.61(18)°. Four oxides that bridge to adjacent sulfur centres and one bound water molecule occupy the five equatorial coordination sites. The bond lengths for the bridging oxides are 2.364(4), 2.382(4), 2.373(4) and 2.394(4) Å to O(3), O(5), O(6) and O(7). The U(1)–O(4)$_{water}$ bond length is 2.426(4) Å. The bond valence of U(1) is 6.05.

Two sulfur sites exist in USO-9. Both are part of SO$_4$ tetrahedra. S(1) and S(2) are each bound to two bridging oxides and two terminal oxides. The S(1)–O bond lengths are 1.489(4), 1.489(4), 1.484(4) and 1.451(4) Å to O(5), O(6), O(8) and O(9). The S(2)–O bond lengths are 1.477(4), 1.496(4), 1.460(4) and 1.466(4) Å to O(3), O(7), O(10) and O(11).

One-dimensional $[UO_2(H_2O)(SO_4)_2]^{2-}$ chains are formed because each SO$_4$ tetrahedron links neighbouring UO$_7$ pentagonal bipyramids. These chains are parallel to the c axis (Fig. 5, selected atomic coordinates are collected in Table 4). This chain topology is analogous to the mineral phases Mn[(UO$_2$)-(SO$_4$)$_2$(H$_2$O)]·4H$_2$O [12] and [(UO$_2$)(H$_2$PO$_4$)$_2$(H$_2$O)](H$_2$O)$_2$ [13] and the organically templated uranium phases USO-1 [15] and USO-3.[6] Hydrogen bonding between the bound water and terminal
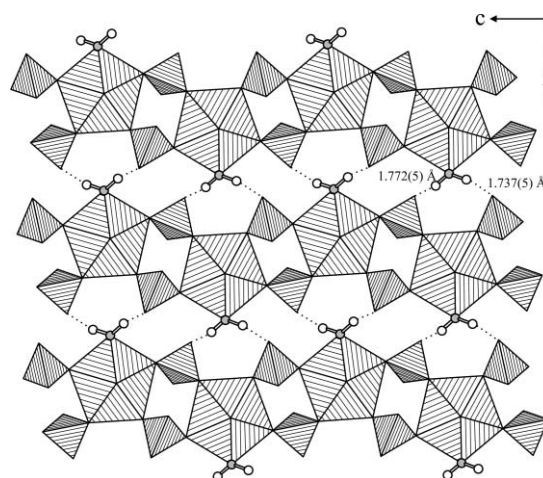
Fig. 5 One-dimensional $[UO_2(H_2O)(SO_4)_2]^{2-}$ chains in USO-9. Tetrahedra and pentagonal bipyramids represent $[SO_4]$ and $[UO_7]$ respectively. Shaded and unshaded circles represent oxygen and hydrogen atoms respectively. Hydrogen bonds are shown as dashed lines with lengths given (Å).

oxides on the SO_4 tetrahedra link adjacent chains, forming layers in the *bc*-plane. The O(4)–O(8) and O(4)–O(11) hydrogen bond distances are 2.696(5) and 2.718(5) Å. The positively charged $[H_2 1,2\text{-dap}]^{2+}$ templates reside between the layers balancing the charge of the anionic chains. The structure is stabilised through extensive hydrogen bonding between the templates and one-dimensional chains. The $[H_2 1,2\text{-dap}]^{2+}$ cations lie parallel to the hydrogen bonded chains. The hydrogens on each nitrogen donate hydrogen bonds both to the layer above and below. The N(1)–O distances are 2.815(5) and 2.718(5) Å to two different O(10) positions. The N(2)–O(8) and N(2)–O(9) distances are 2.971(7) and 2.748(5) Å respectively.

Bending and stretching modes emanating from N–H bonds are observed in the infrared spectrum of USO-9 at 3200 and 1600 cm^{-1}. The asymmetric uranyl stretch is observed at 936 cm^{-1}, while the S–O stretches are present as a broad band between 1028 and 1160 cm^{-1}.

A weight loss of 3.6% is observed using thermogravimetric methods between 140 and 260 °C, corresponding to the loss of bound water (3.3%). The material exhibits a 53.5% weight loss between 310 and 490 °C to give UO_2 (calc. loss 51.5%).

Synthesis and structure of $[N_4C_6H_{22}]_2[(UO_2)_2(SO_4)_6]\cdot H_2O$, USO-10

Crystals of USO-10 were grown by heating USO-1 in the presence of tris(2-aminoethyl)amine (tren) under hydrothermal conditions followed by slow cooling to room temperature. Yellow blocks were isolated after reaction in 63% yield. The asymmetric unit contains two uranium positions. The uranium atoms at both positions are seven coordinate in a pentagonal bipyramidal geometry. The U(1)–O(1), U(1)–O(2), U(2)–O(8) and U(2)–O(9) bond lengths are 1.776(3), 1.777(3), 1.767(3) and 1.778(3) Å. The O(1)–U(1)–O(2) and O(8)–U(2)–O(9) bond angles are 177.82(12) and 179.46(13)° respectively. The five equatorial coordination sites surrounding U(1) are all occupied by oxide ligands that are part of SO_4 tetrahedra. The U(1)–O_{eq} bond lengths are 2.451(3), 2.447(3), 2.333(3), 2.327(3) and 2.332(3) Å to O(3), O(4), O(5), O(6) and O(7). The coordination environment around U(2) is analogous to that of U(1). The U(2)–O_{eq} bond lengths are 2.501(3), 2.454(3), 2.330(3), 2.330(3) and 2.337(3) Å to O(10), O(11), O(12), O(13) and O(14).

Six unique sulfur environments are present in USO-10, although the coordination environments of S(4), S(5) and S(6) are analogous to S(1), S(2) and S(3). S(1) and S(4) are each bound to two bridging oxides and two terminal oxide ligands. The bond lengths to bridging oxides are longer than those to terminal oxides. S(1)–O(3) and O(4) are 1.500(3) and 1.508(3) Å *versus* 1.447(3) and 1.467(3) Å to O(15) and O(16). The S(4)–O(10) and O(11) bond lengths are 1.509(3) and 1.497(3) Å *versus* 1.453(3) and 1.458(3) Å to O(22) and O(23). S(2) and S(5) are each bound to three terminal oxides and one bridging oxide. The bridging bond lengths are 1.505(3) and 1.493(3) Å for S(2)–O(5) and S(5)–O(12) respectively. The six terminal bond lengths are 1.457(3), 1.476(3) and 1.471(3) Å for S(2) to O(17), O(18) and O(19) and 1.480(3), 1.461(3) and 1.446(3) Å for S(5) to O(24), O(25) and O(26). S(3) and S(6) are each bound to two bridging and two terminal oxides. These bond lengths are 1.496(3), 1.496(3), 1.458(3) and 1.457(3) Å for S(3) to O(6), O(7), O(20) and O(21). The S(6) to O(13), O(14), O(27) and O(28) bond lengths are 1.505(3), 1.493(3), 1.449(3) and 1.468(3) Å.

USO-10 contains molecular inorganic anions of the formula, $[(UO_2)_2(SO_4)_6]^{8-}$ (Fig. 6, selected atomic coordinates are collected in Table 5). These zero-dimensional anions contain two UO_2 centres connected by two bridging SO_4 tetrahedra. The remaining tetrahedra either share an edge or corner with the UO_7 pentagonal bipyramid. These dimers are aligned along the (1 1 −1) direction. These anions are similar in structure
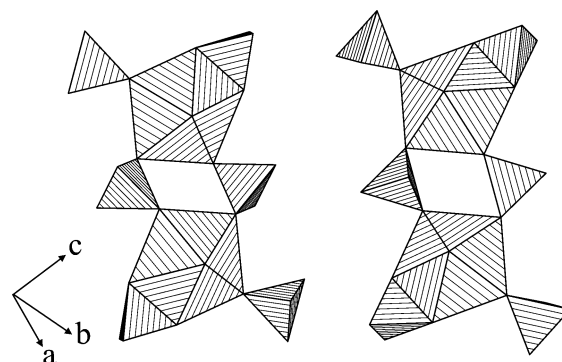

Fig. 6 $[(UO_2)_2(SO_4)_6]^{8-}$ molecular dimers from USO-10. Tetrahedra and pentagonal bipyramids represent $[SO_4]$ and $[UO_7]$ respectively.

to $K_4[(UO_2)(SO_4)_3]$.[14] The $[H_4tren]^{4+}$ cations reside between $[(UO_2)_2(SO_4)_6]^{8-}$ dimers. Numerous hydrogen bonds are donated from the eight unique nitrogen atoms. These hydrogen bonds stabilise the structure. The three-dimensional structure is shown in the ESI (Fig. S5).

Two N–H bands are observed in the infrared spectrum of USO-6 at 3100 and 1620 cm^{-1}. The asymmetric uranyl stretch is at 910 cm^{-1} and a broad band at 1150 cm^{-1} corresponds to S–O stretches.

Thermal analysis indicates that USO-10 exhibits a weight loss of 1.1% on heating to between 90 and 150 °C. This corresponds to the loss of the occluded water (calc. loss 1.3%). A further weight loss of 59.3% is observed between 280 and 490 °C, which corresponds to USO-10 completely calcining to U_3O_8 (calc. loss 59.4%). The identity of the U_3O_8 was confirmed using powder X-ray diffraction.

Discussion

$[N_2C_3H_{12}][UO_2(H_2O)(SO_4)_2]$ (USO-1, a uranium sulfate that contains protonated 1,3-diaminopropane cations),[5] H_2SO_4 and an organic structure directing agent were used in the synthesis of eight organically templated uranium sulfates. The solubility of USO-1 in the H_2SO_4/H_2O solution at room temperature is low. As the temperature increases the USO-1 starting material dissolves and all species become soluble, providing a source of U^{6+}, $[SO_4]^{2-}$ and $[N_2C_3H_{12}]^{2+}$. USO-1 functions in an analogous fashion to $UO_2(CH_3CO_2)_2\cdot 2H_2O$, which is the uranium source in the reported syntheses of USO-1, USO-3, USO-4 and USO-5. Both compounds constitute soluble sources of $[UO_2]^{2+}$ at high temperature. When the temperature is reduced, the decrease in solubility necessitates crystallisation. However, the relative concentration of the new amine is much higher than that of 1,3-diaminopropane, which originates in the USO-1 starting material. The increased concentration of the second amine results in its incorporation, and the formation of a new material.

The syntheses and structures of USO-1, USO-3, USO-4 and USO-5 have been previously reported.[5,6] The synthesis of USO-1 was shown to be sensitive to subtle changes in reactant concentrations.[5] USO-3, USO-4 and USO-5 each contain frameworks with the same $[UO_2(H_2O)(SO_4)_2]^{2-}$ formulae. However, the structures of these frameworks are dependent on the point symmetries of the templates present.[6]

Each compound contains UO_7 pentagonal bipyramids, SO_4 tetrahedra and a protonated amine. Despite using the same inorganic components, the structural diversity in these products is marked, ranging from a molecular, zero-dimensional material to layered two-dimensional compounds.

Zero-dimensional structures

USO-10 is the only zero-dimensional compound observed. Great diversity in the coordination around each SO_4 tetra-

Table 5 Selected atomic coordinates for USO-10

Atom	x	y	z	$U_{eq}{}^a$
U(1)	0.265138(13)	0.970507(11)	0.127264(9)	0.0075
U(2)	0.281284(13)	0.464452(11)	0.611949(9)	0.0089
S(1)	0.09801(9)	1.07433(8)	0.33537(6)	0.0135
S(2)	0.14780(9)	0.76265(7)	0.08140(6)	0.0128
S(3)	0.54702(9)	0.85966(7)	−0.08402(6)	0.0119
S(4)	0.09235(9)	0.55402(8)	0.82142(6)	0.0127
S(5)	0.2285(1)	0.22222(8)	0.54459(6)	0.0151
S(6)	0.58081(9)	0.32286(8)	0.41954(7)	0.0146
O(1)	0.1631(3)	1.0884(2)	0.0793(2)	0.0162
O(2)	0.3615(3)	0.8524(2)	0.1783(2)	0.0167
O(3)	0.2266(3)	1.0800(2)	0.27577(19)	0.0160
O(4)	0.0682(3)	1.0086(2)	0.26726(19)	0.0177
O(5)	0.1473(3)	0.8766(2)	0.0848(2)	0.0161
O(6)	0.4019(3)	0.8948(2)	−0.02812(19)	0.0148
O(7)	0.4339(3)	1.0361(2)	0.10884(19)	0.0149
O(8)	0.1498(3)	0.5310(2)	0.5570(2)	0.0187
O(9)	0.4128(3)	0.3967(2)	0.6678(2)	0.0190
O(10)	0.1879(3)	0.5990(2)	0.75886(19)	0.0166
O(11)	0.1067(3)	0.4612(2)	0.75590(19)	0.0161
O(12)	0.2588(3)	0.2976(2)	0.6011(2)	0.0209
O(13)	0.4308(3)	0.3873(2)	0.4600(2)	0.0190
O(14)	0.3517(3)	0.6061(3)	0.5608(2)	0.0221
O(15)	−0.0105(3)	1.1833(2)	0.3629(2)	0.0206
O(16)	0.1241(3)	1.0122(2)	0.41931(19)	0.0170
O(17)	0.0504(3)	0.7539(3)	0.1679(2)	0.0242
O(18)	0.2839(3)	0.6789(3)	0.0778(3)	0.0275
O(19)	0.1118(3)	0.7465(3)	−0.0067(2)	0.0234
O(20)	0.6337(3)	0.7983(3)	−0.0241(2)	0.0223
O(21)	0.5690(3)	0.7954(2)	−0.1726(2)	0.0209
O(22)	−0.0452(3)	0.6381(2)	0.8463(2)	0.0206
O(23)	0.1351(3)	0.5121(2)	0.9074(2)	0.0191
O(24)	0.1653(3)	0.1618(3)	0.6151(2)	0.0220
O(25)	0.3576(4)	0.1436(3)	0.4828(3)	0.0427
O(26)	0.1334(4)	0.2851(3)	0.4919(2)	0.0338
O(27)	0.6265(3)	0.2220(3)	0.4673(2)	0.0284
O(28)	0.6091(3)	0.3020(3)	0.3144(2)	0.0233
O(29)	0.5565(3)	0.6309(3)	0.0478(3)	0.0264
N(1)	0.2540(3)	0.5665(3)	0.2499(2)	0.0124
N(2)	0.1761(3)	0.3129(3)	0.3001(2)	0.0168
N(3)	0.0782(4)	0.8184(3)	0.4306(2)	0.0192
N(4)	0.6266(3)	0.4390(3)	0.1315(3)	0.0183
N(5)	0.7315(3)	0.9346(3)	0.2447(2)	0.0136
N(6)	0.8500(3)	1.1678(3)	0.1882(2)	0.0167
N(7)	0.8630(3)	0.7018(3)	0.0497(2)	0.0152
N(8)	0.4063(4)	0.9392(3)	0.4091(3)	0.0225
C(1)	0.2047(4)	0.4791(3)	0.2356(3)	0.0153
C(2)	0.1938(4)	0.4130(3)	0.3241(3)	0.0183
C(3)	0.1635(4)	0.6392(3)	0.3417(3)	0.0170
C(4)	0.1927(4)	0.7406(3)	0.3524(3)	0.0179
C(5)	0.4013(4)	0.5232(3)	0.2464(3)	0.0168
C(6)	0.4884(4)	0.4418(3)	0.1571(3)	0.0167
C(7)	0.8042(4)	1.0086(3)	0.2437(3)	0.0175
C(8)	0.7865(4)	1.0925(3)	0.1695(3)	0.0186
C(9)	0.7575(4)	0.8831(3)	0.1446(3)	0.0138
C(10)	0.7765(4)	0.7622(3)	0.1460(3)	0.0160
C(11)	0.5850(4)	0.9890(3)	0.3010(3)	0.0181
C(12)	0.5226(4)	0.9042(4)	0.3190(3)	0.0185

$^a U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

hedron exists in this structure. The tetrahedra around S(1) and S(4) share an edge with the UO_7 pentagonal bipyramid, S(2) and S(5) only share one oxide with a uranium centre and the S(3) and S(6) tetrahedra bridge between two U^{6+} cations. The resulting dimers, $[(UO_2)_2(SO_4)_6]^{8−}$, exhibit a high negative charge. This anion is shown in Fig. 6. The corresponding cations, $[H_4tren]^{4+}$, which are also highly charged when compared with the other protonated amines observed in this study, are able to balance the charge of the anions without charge reduction through increased dimensionality of the inorganic structure.

One-dimensional structures

Five compounds in this study contain one-dimensional chains; USO-3, USO-4, USO-6, USO-7 and USO-9. Two basic types of

one-dimensional chains are observed in these structures. The two types of chain differ in the manner in which consecutive UO_7 pentagonal bipyramids are connected. The best examples of the first type of chain exist in USO-3 and USO-9, as shown in Figs. 1a and 5. Each UO_7 polyhedra is connected to the next by two bridging SO_4 tetrahedra. Four of the five equatorial oxide ligands around each $[UO_2]^{2+}$ participate in this bonding. The remaining equatorial coordination site points away from the direction of the chain. The formula of the chain backbone in terms of connectivity can be written as $[UO_2(SO_4)_{4/2}]^{2−}$. The three compounds in this study that contain one-dimensional chains of this type are USO-3, USO-4 and USO-9. The chains in USO-3 and USO-9 are identical. A bound water molecule occupies the lone equatorial coordination site that does not participate in the chain backbone. The structure of the inorganic component of USO-4 is shown in Fig. 1b. A bound water molecule occupies the fifth coordination site, as in USO-3 and USO-9. However, the SO_4 tetrahedra within the chain backbone do not bridge between two uranium centres. Instead, an additional UO_7 polyhedron is bound to two adjacent backbone sulfates. Despite the increase in chain width from non-backbone $[UO_2(SO_4)_2]$ groups, the chain topology is retained.

The second chain type employs only three of the five equatorial oxides around the central U^{6+}; the best example is USO-6, as shown in Fig. 2. Bridging SO_4 tetrahedra again connect the UO_7 polyhedra, but only three neighbouring equatorial oxides are part of these bridging sulfates. The remaining two coordination sites face away from the chain in a perpendicular geometry. The formula in terms of connectivity can be written as $[UO_2(SO_4)_{3/3}]$. USO-6 and USO-7 are the two compounds in this study that contain this type of chain. The three one-dimensional chains in these two structures (two distinct chains exist in USO-7) are analogous, and differ only in the nature of the two equatorial coordination sites that do not participate in the chain backbone. In USO-6, these two sites both bridge to the same sulfur centre. This SO_4 tetrahedron shares an edge with the UO_7 pentagonal bipyramid. USO-7 chain 1 and USO-7 chain 2 are shown in Fig. 3. The two outward facing coordination sites in USO-7 chain 1 are occupied by bound water molecules, while in USO-7 chain 2 they are occupied by a bound water and a terminal SO_4 tetrahedron. Despite these differences the basic chain topology is the same for the three distinct one-dimensional chains.

Two-dimensional structures

Both USO-5 and USO-8 contain two-dimensional layered structures. However, two distinct differences exist in these two layers. First, the inorganic layer in USO-5 contains bound water molecules while none are present in USO-8. The result of this is to introduce the possibility of *intra* layer hydrogen bonding in USO-5, something that is not possible in USO-8. The introduction of a bound water molecule enables an equatorial coordination site to be occupied by a ligand that does not bridge to an adjacent sulfur or uranium centre. Instead, the bound water molecule is able to donate hydrogen bonds to neighbouring anions. Second, the number of terminal oxide ligands on each sulfate tetrahedron differs greatly. Every sulfur centre in USO-5 is bound to two bridging and two terminal oxides. Of the three unique sulfur centres in USO-8 two are bound to three bridging oxides and one is bound to four. USO-5 is shown in Fig. 1c and USO-8 is shown in Fig. 4. Every oxide ligand around each sulfur centre in USO-5 and USO-8 is either covalently bound to a uranium cation, accepts a hydrogen bond or both. The greater number of terminal oxides in USO-5 leads to an increase in available hydrogen bond acceptors. The effects of these two structural differences are manifested in the 'openness' of each layer. Both U(1) and U(2) in USO-8 have five adjacent uranium centres within 5.6 Å. In contrast, the

nearest U–U distance in USO-5 is 6.15 Å. Each uranium in USO-5 has only one neighbouring U^{6+} centre at this distance and only three within 6.9 Å.

Conclusion

Organically templated metal sulfates hold great promise for the discovery of new compounds with novel structures. Templated uranium sulfates form a new family of compounds with great structural diversity and variable dimensionality. The synthesis of organically templated uranium sulfates using $[N_2C_3H_{12}]$-$[UO_2(H_2O)(SO_4)_2]$ as a starting material resulted in the formation range of new compounds. The structures of these new compounds range from molecular dimers in USO-10 to two-dimensional layered materials in USO-5 and USO-8.

Experimental

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

Materials

1,3-Diaminopropane (1,3-dap, 99%, Aldrich), piperazine (pip, 99%, Aldrich), 2-methylpiperazine (mpip, 95%, Aldrich), 1,4-diazabicyclo[2.2.2]octane (dabco, 98%, Aldrich), 4,4′-dipyridyl (4,4′-bpy, 98%, Aldrich), $N,N,N′,N′$-tetramethylethylene-diamine (tmed, 99%, Aldrich), imidazole (imid, 99%, Aldrich), 1,2-diaminopropane (1,2-dap, 99%, Aldrich), tris(2-amino-ethyl)amine (tren, 96%, Aldrich), $UO_2(NO_3)_2·6H_2O$ (98%, BDH) and sulfuric acid (98%, Aldrich) were used as received. Deionized water was also used in these syntheses. UO_2-$(CH_3CO_2)_2·2H_2O$ was prepared [15] from UO_3 (99.8%, Strem).

Methods

All reactions were conducted in poly(fluoro-ethylene-pro-pylene) lined 23 mL autoclaves. The autoclaves were placed in an oven at 150 °C, 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 deionised water and acetone.

Synthesis

Bulk samples of $[N_2C_3H_{12}][UO_2(H_2O)(SO_4)_2]$ (USO-1) [5] were synthesised through the dissolution of 0.85 g $UO_2(NO_3)_2·6H_2O$ and 1 g of $[N_2C_3H_{12}][SO_4]$ [16] in 2 g of deionised water. USO-1 crystallised from solution over 2 days at room temperature. $[N_2C_3H_{12}][SO_4]$ was synthesised by adding 12 mL of 6 M H_2SO_4 to a solution of 4 g of diaminopropane in 40 mL of methanol in a dropwise fashion. A white precipitate formed immediately upon addition of the sulfuric acid solution. USO-3 was synthesised through the reaction of 0.2608 g (4.72×10^{-4} mol) of USO-1, 0.1014 g (1.18×10^{-3} mol) of piperazine, 0.3190 g (3.25×10^{-3} mol) of H_2SO_4 and 1.0324 g (5.73×10^{-2} mol) of deionised water. Yellow rods were isolated after reaction in 88% yield. USO-4 was synthesised through the reaction of 0.2835 g (5.13×10^{-4} mol) of USO-1, 0.1133 g (1.13×10^{-3} mol) of methylpiperazine, 0.3241 g (3.30×10^{-3} mol) of H_2SO_4 and 1.0407 g (5.78×10^{-2} mol) of deionised water. Yellow rods were isolated after reaction in 86% yield. USO-5 was synthesised through the reaction of 0.2513 g (4.55×10^{-4} mol) of USO-1, 0.1005 g (8.97×10^{-4} mol) of dabco, 0.3202 g (3.27×10^{-3} mol) of H_2SO_4 and 1.0387 g (5.77×10^{-2} mol) of deionised water. Yellow rods were isolated after reaction in 68% yield. Alternative syntheses of USO-3, USO-4 and USO-5 and their corresponding structures determined using single crystal X-ray

diffraction were reported earlier.[6] The structures of USO-3, USO-4 and USO-5 are shown in Fig. 1.

$[N_2C_{10}H_{10}][UO_2(SO_4)_2]·H_2O$, **USO-6.** USO-6 was synthesised through the reaction of 0.2446 g (4.43×10^{-4} mol) of USO-1, 0.1078 g (6.91×10^{-1} mol) of 4,4′-bpy, 0.2919 g (2.97×10^{-3} mol) of H_2SO_4 and 0.9922 g (5.51×10^{-2} mol) of deionised water. Obsd. (calc.): N, 2.89 (2.80); C, 7.33 (7.20); H, 2.89 (2.80); S, 10.42 (9.62); U, 48.10 (47.58)%.

$[N_2C_6H_{18}][(UO_2)_2(H_2O)_3(SO_4)_3]$, **USO-7.** USO-7 was synthesised through the reaction of 0.2584 g (4.67×10^{-4} mol) of USO-1, 0.1040 g (8.96×10^{-4} mol) of tmed, 0.2982 g (3.04×10^{-3} mol) of H_2SO_4 and 0.9998 g (5.55×10^{-2} mol) of deionised water. Obsd. (calc.): N, 4.43 (4.39); C, 18.93 (18.82); H, 1.84 (1.89); S, 10.51 (10.05); U, 36.84 (37.28)%.

$[N_2C_3H_5]_2[(UO_2)_2(SO_4)_3]$, **USO-8.** USO-8 was synthesised through the reaction of 0.2544 g (4.61×10^{-4} mol) of USO-1, 0.1179 g (1.73×10^{-3} mol) of imid, 0.3496 g (3.56×10^{-3} mol) of H_2SO_4 and 1.0433 g (5.79×10^{-2} mol) of deionised water. Obsd. (calc.); N, 5.79 (5.79); C, 7.65 (7.45); H, 1.16 (1.03); S, 10.66 (9.93); U, 49.10 (49.27)%.

$[N_2C_3H_{12}][UO_2(H_2O)(SO_4)_2]$, **USO-9.** USO-9 was synthesised through the reaction of 0.2705 g (4.89×10^{-4} mol) of USO-1, 0.1087 g (1.43×10^{-3} mol) of 1,2-dap, 0.3036 g (3.09×10^{-3} mol) of H_2SO_4 and 1.0031 g (5.57×10^{-2} mol) of deionised water. Obsd. (calc.): N, 5.07 (4.79); C, 6.58 (6.16); H, 2.72 (2.39); S, 11.91 (10.95); U, 41.27 (40.75)%.

$[N_4C_6H_{22}]_2[(UO_2)_2(SO_4)_6]·H_2O$, **USO-10.** USO-10 was synthesised through the reaction of 0.2567 g (4.64×10^{-4} mol) of USO-1, 0.1152 g (7.89×10^{-4} mol) of tren, 0.3120 g (3.18×10^{-3} mol) of H_2SO_4 and 1.0212 g (5.67×10^{-2} mol) of deionised water. Obsd. (calc.): N, 7.82 (7.81); C, 10.10 (10.04); H, 3.20 (3.21); S, 13.38 (13.77); U, 33.06 (33.19)%.

X-Ray powder diffraction patterns of all the bulk phases were consistent with the XRD patterns calculated using the atom positions determined by the single crystal X-ray structure determinations.

X-Ray crystallographic analysis

Single crystals of dimension $0.06 \times 0.06 \times 0.30$ mm for USO-6, $0.04 \times 0.12 \times 0.35$ mm for USO-7, $0.10 \times 0.10 \times 0.10$ mm for USO-8, $0.06 \times 0.06 \times 0.16$ mm for USO-9 and $0.20 \times 0.20 \times 0.20$ mm for USO-10 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 fibre 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] and other non-hydrogen atoms refined using CRYS-TALS.[19] All non-hydrogen sites 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 and CAMERON.[20] Relevant crystallographic data are listed in Table 6 and selected atomic coordinates are given in Tables 1–5.

CCDC reference numbers 194171–194175.

See http://www.rsc.org/suppdata/dt/b2/b209208e/ for crystallographic data in CIF or other electronic format.

Table 6 Crystallographic data for USO-6, USO-7 and USO-8, USO-9 and USO-10

Compound	USO-6	USO-7	USO-8	USO-9	USO-10
Formula	$[N_2C_{10}H_{10}][UO_2$-$(SO_4)_2]\cdot H_2O$	$[N_2C_6H_{18}][(UO_2)_2$-$(H_2O)_3(SO_4)_3]$	$[N_2C_3H_5]_2[(UO_2)_2$-$(SO_4)_3]$	$[N_2C_3H_{12}][UO_2$-$(H_2O)(SO_4)_2]$	$[N_4C_6H_{22}]_2[(UO_2)_2$-$(SO_4)_6]\cdot H_2O$
FW	638.37	1000.51	966.42	556.31	1434.99
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	6.9507(1)	6.8234(1)	9.7683(3)	7.3296(2)	11.2315(1)
b/Å	7.7097(1)	8.7384(1)	10.0252(3)	7.3702(2)	13.2136(1)
c/Å	15.9200(4)	19.2381(4)	19.9136(7)	11.6822(2)	14.3521(2)
a/°	79.1992(7)	101.3691(6)	90	92.0309(13)	88.4073(5)
β/°	80.1403(8)	98.1340(6)	90	106.0406(14)	74.5896(5)
γ/°	80.9717(14)	90.0480(11)	90	93.6783(9)	66.5370(6)
V/Å³	818.7	1112.8	1950.1	604.3	1876.27
Z	2	2	4	2	2
D_c/g cm^{-3}	2.59	2.986	3.291	3.057	2.540
μ/mm^{-1}	10.231	14.906	16.998	13.835	9.067
Reflections collected	6857	9209	4253	5014	15853
Independent reflections	3713	5016	4130	2734	8557
$R_1{}^a$	0.0208	0.0441	0.0315	0.0247	0.0224
$wR_2{}^b$	0.0495	0.1211	0.0708	0.0604	0.0498

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

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 analyser. Samples were loaded into an alumina crucible and heated from ambient temperature to 800 °C at 10 °C min^{-1} under flowing argon.

Elemental analysis

The analytical services department of the Inorganic Chemistry Laboratory, University of Oxford conducted carbon, hydrogen, nitrogen, sulfur and uranium analyses.

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