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$[NC_4H_{12}]_2[(UO_2)_6(H_2O)_2(SO_4)_7]$: the first organically templated actinide sulfate with a three-dimensional framework structure

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$[NC_4H_{12}][(UO_2)_6(H_2O)_2(SO_4)_7]$ is the first organically templated actinide sulfate with a three-dimensional framework structure; it has channels of dimensions 8.5 Å × 8.5 Å, running along the [001] direction, containing tetramethylammonium cations.

In recent years, hydrothermal techniques have been employed to synthesise a number of new materials with open frameworks containing organic amines as templates, the vast majority of which are metal phosphates.[1] Other examples of materials with extended structures include metal phosphites,[2] fluorides,[3] germanates,[4] arsenates,[5] oxalates[6] and selenites.[7] Despite the similarity between the phosphate and sulfate tetrahedra there are very few reports of metal sulfates with extended structures. Doedens *et al.* have synthesised a layered vanadyl sulfate.[8] Rao *et al.* recently reported two 1-D cadmium sulfates, which were synthesised using the 'amine-sulfate' method.[9] Rao *et al.* have also reported a layered iron sulfate.[10] The only organically templated 3-D metal sulfate was recently reported by Wright *et al.*,[11] which contains scandium and an azamacrocycle as the template.

We are interested in furthering the development of template directed hydrothermal synthesis of novel actinide containing materials, having previously reported several new organically templated uranium fluoride,[12] molybdate,[13] phosphate[14] and phosphite[2] phases, spanning the full range of dimensionality. Here, we report the synthesis† and structure‡ of $[NC_4H_{12}]_2[(UO_2)_6(H_2O)_2(SO_4)_7]$, MUS-1, which is the first organically templated actinide sulfate with a three-dimensional framework structure.

MUS-1 crystallised in the enantiomorphic, optically active space group $C222_1$ (Flack parameter = 0.025(9)). The structure contains three crystallographically distinct uranium sites. U(1), U(2) and U(3) are each seven coordinate, with two uranyl and five oxide ligands in a pentagonal bipyramidal geometry. The average uranyl bond length is 1.759, 1.757 and 1.752 Å for U(1), U(2) and U(3) respectively, with uranyl O–U–O angles of 179.6(4), 177.9(3) and 179.1(3)°. These values agree well with average reported values.[15] The five equatorial coordination sites around U(1) and U(3) are each occupied by oxide ligands that are part of sulfate tetrahedra. Average U(1)–O_{eq} and U(3)–O_{eq} bond lengths are 2.384 and 2.396 Å. Each of the five equatorial coordination sites around U(2) are also occupied by oxide ligands, however O(11) is part of a bound water molecule with the remaining four oxide ligands part of sulfate tetrahedra. The average U(2)–O_{eq} distance for the four sulfate oxide ligands is 2.376 Å. The U(2)–OH_2 distance is longer, at 2.540(8) Å. Bond valence calculations,[16,17] using parameters from Burns *et al.*,[15] give values of 6.151, 6.053 and 6.139 for U(1), U(2) and U(3).

Four crystallographically distinct sulfur sites are present in MUS-1. S(1), S(2), S(3) and S(4) are each four coordinate with four oxide ligands in a tetrahedral geometry. S–O bond lengths range between 1.442(9) and 1.478(8) Å. S(4) lies on an 2-fold axis.

A three-dimensional $[(UO_2)_6(H_2O)_2(SO_4)_7]^{2-}$ framework is formed because each of the four sulfate tetrahedra bridge to four adjacent uranium polyhedra (Fig. 1). Burns *et al.* have compiled the structures of uranium materials in a recent review.[18] MUS-1 is similar structurally to $Mg(UO_2)_6(MoO_4)_7(H_2O)_{15}$ and $Sr(UO_2)_6(MoO_4)_7(H_2O)_{19}$.[19] Channels run throughout the structure in the (001) direction. These channels are occupied by tetramethylammonium cations, which balance the charge on the anionic framework (Fig. 2). A view of the 1-D channels in

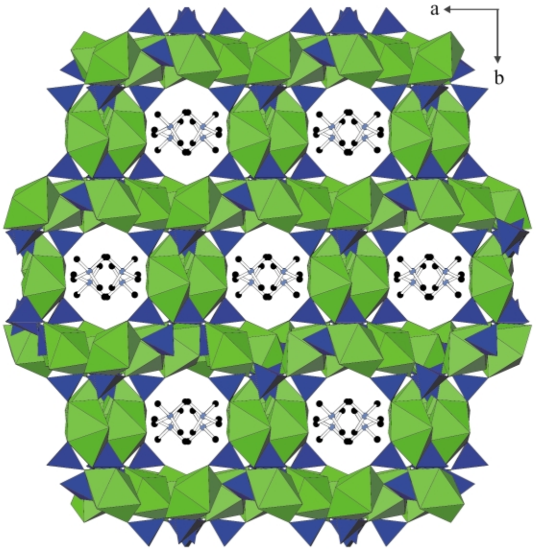

Fig. 1 MUS-1 as viewed along the [001] direction. UO_7 pentagonal bipyramids are green, SO_4 tetrahedra are blue. Hydrogen atoms have been removed for clarity.

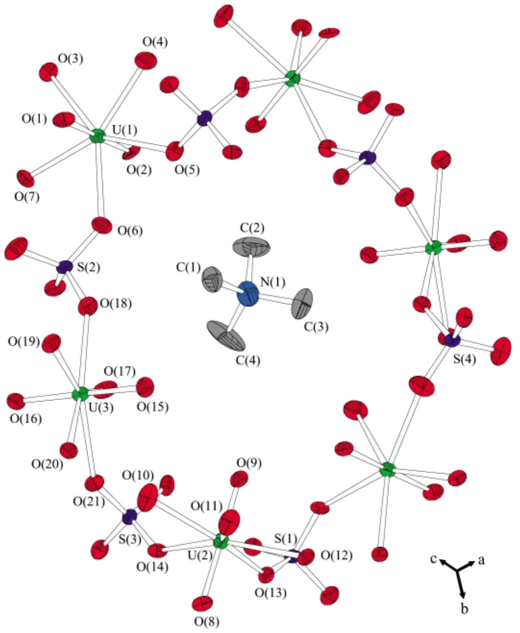

Fig. 2 Thermal ellipsoid view (50% probability) of the pore opening in MUS-1. Hydrogen atoms have been removed for clarity.

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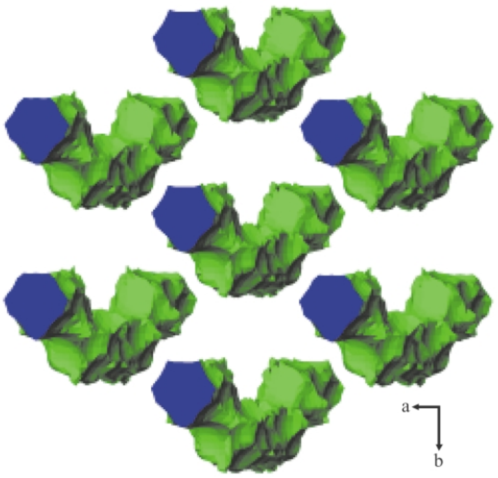

Fig. 3 The one-dimensional zigzag non-intersecting pores in MUS-1.

MUS-1, as calculated using ATOMS v.5.0.7,[20] is shown in Fig. 3. Note the channels are not straight, but undulate back and forth.

The powder X-ray diffraction pattern of a portion of the bulk sample is in agreement with the powder pattern predicted using the single crystal data. MUS-1 is thermally stable up to 375 °C. Above this temperature the framework collapses leaving a mixture of UO_2 and U_3O_8 which was confirmed using X-ray powder diffraction. Given that the MUS-1 is inherently chiral we plan to investigate whether the host exhibits enantioselective cation-exchange reactions.

The chemistry of organically templated metal sulfates is emerging as an important avenue of investigation in the development of new porous materials. Great structural diversity is observed despite the extremely small number of metal sulfates that incorporate organic structure directing agents. Further inquiry is required into this promising class of compounds.

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Notes and references

† MUS-1 (Microporous Uranium Sulfate), was synthesised by combining $UO_2Ac_2\cdot 2H_2O$ (0.6365 g), H_2SO_4 (98%) (0.3116 g), H_2O (1.0281 g), and $[NC_4H_{12}][OH]\cdot 5H_2O$ (0.0949 g) in a Teflon lined stainless steel autoclave, and heating at 180 °C for 24 h before cooling to room temperature at 6 °C h^{-1}. A monophasic yellow crystalline product was recovered, and allowed to dry in air. A yield of 25% (based upon uranium) was observed.

Elemental analyses: MUS-1: obsd (calcd): C 3.97 (3.89), H 1.00 (0.98), N 1.20 (1.13), S 10.16 (9.08); U 57.75 (57.41).

‡ *Crystallographic data*: A single crystal of dimensions 0.1 × 0.2 × 0.25 mm was used for structural determination. Data were collected using an Enraf Nonius FR 590 Kappa CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 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.[21] The heavy atom positions were determined using SIR97[22] and other non-hydrogen atoms refined using SHELXS.[23] All non-hydrogen atoms were located from Fourier difference maps and refined with anisotropic thermal parameters using full matrix least squares procedures on F_o^2 with $I > 2\sigma(I)$. All hydrogen atoms were placed in geometrically idealized positions. All calculations were performed using WINGX[24] and Cameron.[25]

For MUS-1: orthorhombic, space group $C222_1$ (No. 20), a = 10.3446(2), b = 18.5415(3), c = 22.7001(4) Å, V = 4354.82(13) Å^3, Z = 4, D_c = 3.772 g cm^{-3}, 4875 reflections collected of which 4863 were independent and 4519 were observed [$I > 2\sigma(I)$]. Refinement converged with R = 0.0377, wR = 0.0783. CCDC 195915. See http://www.rsc.org/suppdata/cc/b2/b210272b/ for crystallographic files in CIF or other electronic format.

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