[NC4H12]2 [(UO2)6(H2O)2(SO4)7]: the first organically templated actinide sulfate with a three-dimensional framework structure

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[NC₄H₁₂]₂[(UO₂)₆(H₂O)₂(SO₄)₇⁻]: the first organically templated actinide sulfate with a three-dimensional framework structure

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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 oxalates6 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 sulfite.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 phosphate14 and phosphite phases, spanning the full range of dimensionality. Here, we report the synthesis† and structure‡ of [NC₄H₁₂]₂[(UO₂)₆(H₂O)₂(SO₄)₇⁻], MUS-1, which is the first organically templated actinide sulfate with a three-dimensional framework structure.

MUS-1 crystallised in the enantiomorphically, optically active space group C222₁ (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)–Oeq and U(3)–Oeq 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)–Oeq distance for the four oxide sulfate ligands is 2.376 Å. The U(2)–OH₂ 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), respectively.

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 a 2-fold axis.

A three-dimensional [(UO₂)₆(H₂O)₂(SO₄)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 Mg₆(UO₂)₆(MoO₄)₂(H₂O)₁₅ and Sr₆(UO₂)₆(MoO₄)₂(H₂O)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
MUS-1, as calculated using ATOMS v.5.0.7,\(^\text{20}\) 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 single crystal data. MUS-1 is thermally stable up to 375°C.

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