

**catena-Poly[tetramethylammonium
[[nitrate- κ^2 O,O']dioxouranium]- μ_3 -sulfato]]****Michael B. Doran, Alexander J.
Norquist and Dermot O'Hare***Inorganic Chemistry Laboratory, University of
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EnglandCorrespondence e-mail:
dermot.ohare@chem.ox.ac.uk**Key indicators**

Single-crystal X-ray study

T = 150 K

Mean $\sigma(\text{N}-\text{C}) = 0.009 \text{ \AA}$

R factor = 0.024

wR factor = 0.048

Data-to-parameter ratio = 13.1

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\{(\text{C}_4\text{H}_{12}\text{N})[\text{UO}_2(\text{NO}_3)(\text{SO}_4)]\}_n$, contains one-dimensional anionic $[\text{UO}_2(\text{NO}_3)(\text{SO}_4)]^-$ chains, with the charge balanced by tetramethylammonium cations. Each U atom is seven-coordinate, in a pentagonal bipyramidal geometry. Each sulfate tetrahedron bridges three adjacent uranium centres and each nitrate anion shares an edge with a $[\text{UO}_7]$ polyhedron.

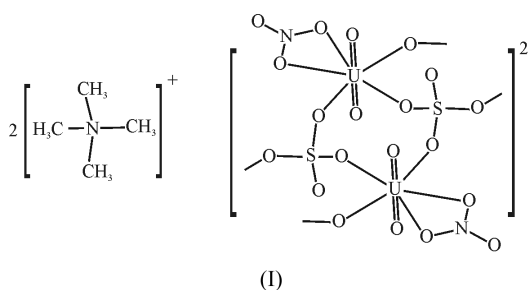
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Comment

The chemistry of open-framework metal phosphates is well known (Cheetham *et al.*, 1999). Despite the depth of this investigation, little effort has been expended upon the analogous sulfate systems. Reports of organically templated metal sulfates have appeared in the literature only in the last two years. Compounds incorporating Sc (Bull *et al.*, 2002), V (Paul, Choudhury, Nagarajan & Rao, 2003), Cd (Paul *et al.*, 2002*b*; Choudhury *et al.*, 2001), Fe (Paul *et al.*, 2002, 2002*a*; Paul, Choudhury & Rao, 2003), Ce (Wang *et al.*, 2002), La (Bataille & Louer, 2002; Xing *et al.*, 2003) and U (Doran *et al.*, 2002; Norquist *et al.*, 2002, 2003; Thomas *et al.*, 2003) are known. These compounds exhibit great structural diversity, with structures ranging from molecular anions to three-dimensional microporous materials. This report contains the synthesis and structure of an organically templated uranium(VI) nitrate sulfate, $(\text{C}_4\text{H}_{12}\text{N})[\text{UO}_2(\text{NO}_3)(\text{SO}_4)]$, denoted USO-21 (uranium sulfate from Oxford).



One unique uranium centre is present in USO-21. U1 is seven-coordinate in a pentagonal bipyramidal geometry. Two short 'uranyl' bonds to axial oxides are observed. The U1—O1 and U1—O2 bond lengths are both 1.763 (6) Å, close to the average reported value of 1.758 (4) Å (Burns *et al.*, 1997) and the O1—U1—O2 angle is close to 180°, with a value of 178.1 (3)°. Three of the five equatorial coordination sites around U1 are occupied by oxide ligands that are bound to sulfur centres through bonds with distances ranging between 2.317 (4) and 2.320 (6) Å. The fourth and fifth equatorial coordination sites are occupied by oxide ligands that are

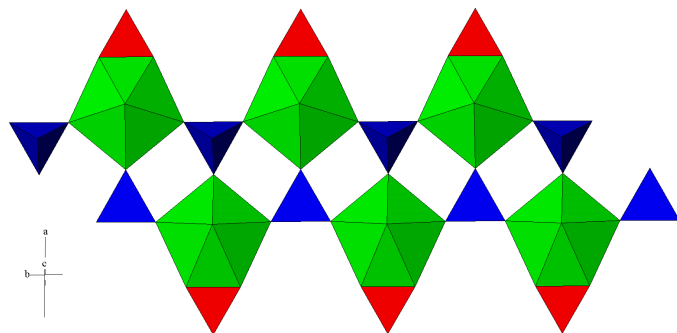


Figure 1
Chains in USO-21. Green pentagonal bipyramids, blue tetrahedra and red triangles represent $[\text{UO}_7]$, $[\text{SO}_4]$ and $[\text{NO}_3]$, respectively.

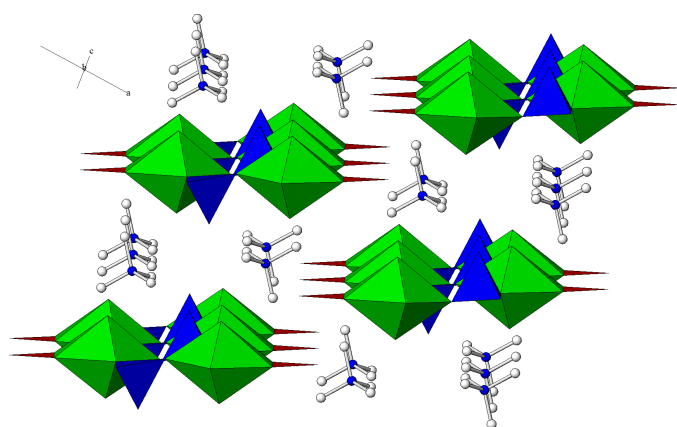


Figure 2
Three-dimensional packing of USO-21. Green pentagonal bipyramids, blue tetrahedra and red triangles represent $[\text{UO}_7]$, $[\text{SO}_4]$ and $[\text{NO}_3]$, respectively.

bound to a single nitrogen centre, with a U1—O3 distance of 2.498 (4) Å. There is one unique sulfur environment in USO-21. The sulfate tetrahedron, which contains S1, bridges three adjacent uranium centres. The bonds between S1 and the bridging oxides, O4 and O5, are longer than the bond from S1 to the lone terminal oxide, O7; these lengths are 1.486 (4) × 2 and 1.493 (6) Å *versus* 1.433 (7) Å. The nitrate anion, containing N1, shares an edge with the $[\text{UO}_7]$ pentagonal bipyramid through bridging O3 ligands. These distances are longer than the bond from N1 to O6, the terminal oxide. The distances are 1.282 (5) Å × 2 *versus* 1.213 (9) Å.

The $[\text{UO}_7]$ and $[\text{SO}_4]$ polyhedra share three corners with one another, creating one-dimensional chains (Fig. 1). The formula of the chain backbone is $[\text{UO}_2(\text{SO}_4)_{3/3}]$. This chain type is known in uranium chemistry (Norquist *et al.*, 2003; Brandeburg & Loopstra, 1973; van der Putten & Loopstra, 1974; Zalkin *et al.*, 1978; Serezhkin *et al.*, 1981). The two non-backbone equatorial coordination sites on each $[\text{UO}_7]$ polyhedron are occupied by an edge-shared nitrate anion. The tetramethylammonium cations, $[\text{C}_4\text{H}_{12}\text{N}]^+$, reside between chains, balancing the charge (Fig. 2). A displacement ellipsoid plot is shown in Fig. 3.

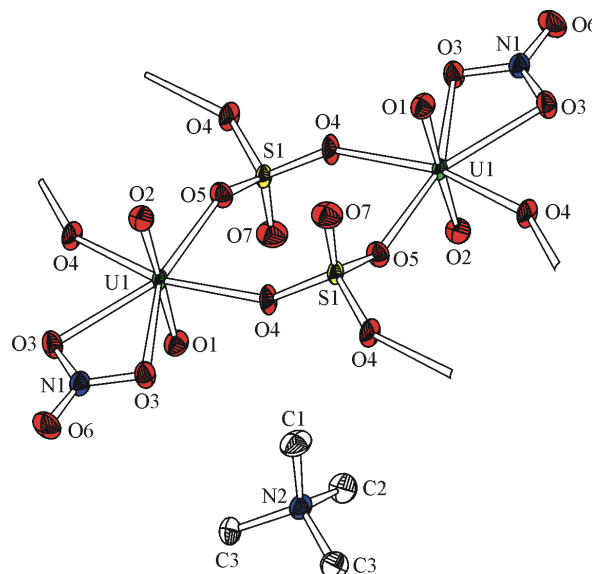


Figure 3
Displacement ellipsoid plot of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been removed for clarity.

Experimental

USO-21 was prepared by dissolving 0.2 g (8×10^{-5} mol) of $(\text{C}_4\text{H}_{12}\text{N})_2[(\text{UO}_2)_6(\text{H}_2\text{O})_2(\text{SO}_4)_7]$ (MUS-1; Doran *et al.*, 2002) in 5 ml of a 2 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution. The resulting solution was allowed to evaporate slowly. Yellow crystals were isolated after one month.

Crystal data

$(\text{C}_4\text{H}_{12}\text{N})[\text{UO}_2(\text{NO}_3)(\text{SO}_4)]$
 $M_r = 502.24$
 Monoclinic, $C2/m$
 $a = 21.106$ (1) Å
 $b = 6.9350$ (3) Å
 $c = 8.4284$ (5) Å
 $\beta = 97.5468$ (18)°
 $V = 1223.0$ (1) Å³
 $Z = 4$

$D_x = 2.728$ Mg m⁻³
 Mo K α radiation
 Cell parameters from 1226 reflections
 $\theta = 5\text{--}27^\circ$
 $\mu = 13.48$ mm⁻¹
 $T = 150$ K
 Block, yellow
 0.02 × 0.02 × 0.02 mm

Data collection

Enraf-Nonius KappaCCD diffractometer
 ω scans
 Absorption correction: multi-scan (Otwinowski & Minor, 1997)
 $T_{\min} = 0.76$, $T_{\max} = 0.76$
 2501 measured reflections

1483 independent reflections
 1240 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.03$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -27 \rightarrow 27$
 $k = -7 \rightarrow 8$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.048$
 $S = 0.86$
 1240 reflections
 95 parameters
 H-atom parameters constrained
 Weighting scheme: Chebyshev polynomial with 5 parameters

(Carruthers & Watkin, 1979),
 3.86, 4.01, 1.57, 0.107, 0.409
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.93$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.89$ e Å⁻³
 Extinction correction: Larson (1970) eq. 22
 Extinction coefficient: 6.3 (7)

Table 1

Selected geometric parameters (Å, °).

U1–O1	1.763 (6)	N1–O3	1.282 (5)
U1–O2	1.763 (6)	N1–O6	1.213 (9)
U1–O3	2.498 (4)	S1–O4	1.486 (4)
U1–O4	2.317 (4)	S1–O5 ⁱ	1.493 (6)
U1–O5	2.320 (6)	S1–O7	1.433 (7)
O1–U1–O2	178.1 (3)	O4–U1–O4 ⁱⁱ	161.05 (19)
O1–U1–O3	88.8 (2)	O4–U1–O5	80.6 (1)
O1–U1–O4	89.20 (12)	O4–S1–O4 ⁱⁱⁱ	105.4 (3)
O1–U1–O5	93.1 (3)	O4–S1–O5 ⁱ	106.9 (2)
O2–U1–O3	89.5 (2)	O4–S1–O7	112.6 (2)
O2–U1–O4	91.11 (12)	O5 ⁱ –S1–O7	112.0 (4)
O2–U1–O5	88.7 (2)	U1–O3–N1	97.0 (3)
O3–U1–O3 ⁱⁱ	51.23 (18)	U1–O4–S1	149.9 (3)
O3–U1–O4	73.81 (13)	U1–O5–S1 ⁱ	147.3 (4)
O3–U1–O4 ⁱⁱ	125.03 (13)	O3–N1–O3 ⁱⁱⁱ	114.7 (6)
O3–U1–O5	154.33 (9)	O3–N1–O6	122.6 (3)

Symmetry codes: (i) $\frac{3}{2} - x, -\frac{1}{2} - y, 1 - z$; (ii) $x, -1 - y, z$; (iii) $x, -y, z$.

H atoms placed geometrically after each cycle of refinement.

Data collection: *COLLECT* (Nonius, 1997–2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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