metal-organic papers

Poly[[1,4-bis-(3-aminopropyl)piperazinium] [[dioxouranium(VI)]-di-μ_2,μ_3-sulfato]]

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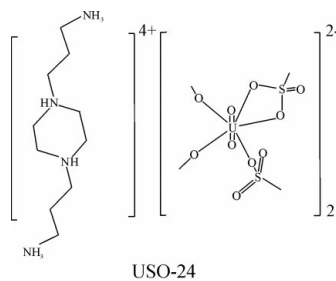
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The title compound, $\{(C_{10}H_{28}N_4)[(UO_2)_2(SO_4)_4]\}_n$, contains two-dimensional $[(UO_2)_2(SO_4)_4]^{4-}$ layers with 1,4-bis-(3-aminopropyl)piperazinium cations balancing the charge. Each U^{VI} cation is seven-coordinate in a pentagonal bipyramidal geometry, and each sulfate tetrahedron bridges beween two adjacent uranium centres to form layers.

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 only appeared in the literature in the last two years. Compounds incorporating Sc (Bull *et al.*, 2002), V (Paul, Choudhury, Nagarajan & Rao, 2003; Khan *et al.*, 1999), Cd (Paul *et al.*, 2002b; Choudhury *et al.*, 2001), Fe (Paul *et al.*, 2002, 2002a; Paul, Choudhury & Rao, 2003), Ce (Wang *et al.*, 2002), La (Bataille & Louer, 2002; Xing *et al.*, 2003) and U (Doran *et al.*, 2002, 2003a; Norquist *et al.*, 2002, 2003; Stuart *et al.*, 2003; Thomas *et al.*, 2003) are known. These compounds exhibit great structural diversity, with structures ranging from molecular anions to three-dimensional microporous materials. Here, we report the synthesis and structure of an organically templated uranium(VI) sulfate, $[C_{10}H_{28}N_4][(UO_2)_2(SO_4)_4]$, which is denoted USO-24 (uranium sulfate from Oxford). A displacement ellipsoid plot of USO-24 is shown in Fig. 1.

USO-24

One unique uranium centre is present in USO-24. Atom U1 is seven-coordinate in a pentagonal bipyramidal geometry. Two short 'uranyl' bonds to axial oxides are observed. The U1—O1 and U1—O2 bonds have lengths of 1.778 (4) and 1.764 (4) Å, respectively. These values are close to the average reported value of 1.758 (3) Å (Burns *et al.*, 1997) and the O1—U1—O2 angle is close to 180° with a value of 178.93 (18)°. All five equatorial coordination sites around U1 are occupied by oxide ligands that bridge to adjacent sulfur centres, with distances ranging between 2.332 (4) and 2.456 (4) Å. Two
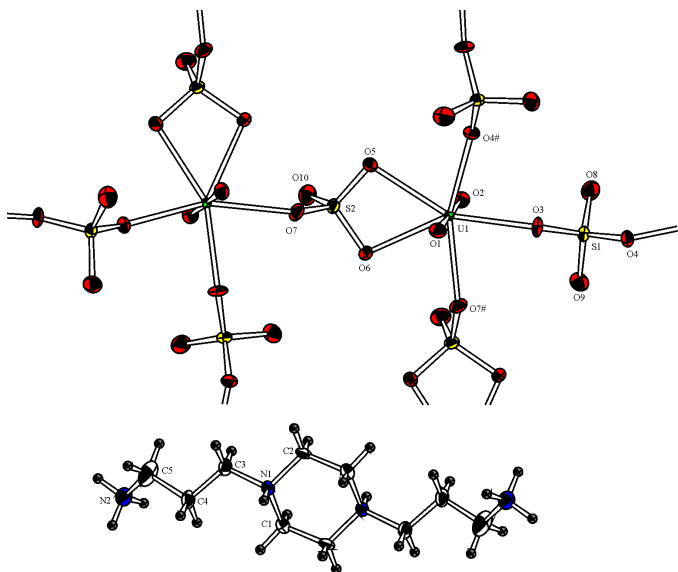
Figure 1
Displacement ellipsoid plot of the title compound, with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level. Atom O4# is at the symmetry position $(x - \frac{1}{2}, \frac{1}{2} - y, 1 - z)$ and O7# is at $(\frac{1}{2} + x, y, \frac{1}{2} - z)$.
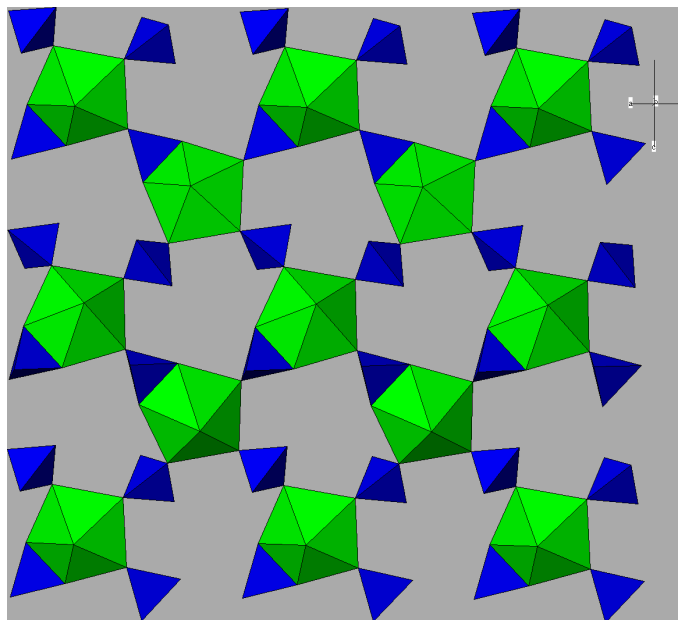

Figure 2
Layers in USO-24. Green pentagonal bipyramids and blue tetrahedra represent $[UO_7]$ and $[SO_4]$, respectively.

distinct sulfur sites are observed in USO-24. Both S1 and S2 are at the centre of $[SO_4]$ tetrahedra. Atom S1 is bound to two O atoms that bridge to adjacent uranium centres and two terminal O atoms. $S1—O_{bridging}$ distances are 1.492 (4) and 1.502 (4) Å, and $S1—O_{terminal}$ distances are 1.447 (5) and 1.465 (5) Å. Atom S2 is bound to three O atoms that bridge to uranium centres and one terminal O atom. Atoms O5 and O6 bridge the same $[UO_2]^{2+}$ cation, resulting in a shared edge between the U1 and S1 polyhedra. These S—O bridging
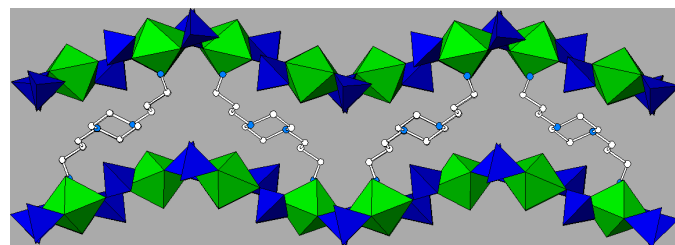

Figure 3
The three-dimensional packing of USO-24. Green pentagonal bipyramids and blue tetrahedra represent $[UO_7]$ and $[SO_4]$, respectively.

distances are 1.494 (4) and 1.497 (4) Å. The $S2—O_{terminal}$ distance is 1.437 (5) Å.

Layers are formed because each uranium centre is connected to four others through four bridging sulfate tetrahedra (see Fig. 2). This layer structure is known in uranium chemistry (Doran *et al.*, 2003*b*). These layers lie in the (101) plane and are separated by the template cations (See Fig. 3). The template cation is involved in hydrogen bonding with the layer (Table 2).

Experimental

0.2585 g (6.10×10^{-4} mol) of $UO_2(CH_3CO_2)_2 \cdot 2H_2O$, 0.4048 g ($4.13 \times 10^{-3}$ mol) of H_2SO_4, 0.1234 g (6.17×10^{-4} mol) of 1,4-bis(3-amino-propyl)piperazine and 1.0168 g (5.65×10^{-2} mol) of water were placed into a 23 ml Teflon-lined autoclave. The autoclave was heated to 453 K for 24 h, at which point it was cooled slowly to 297 K over an additional 24 h. The autoclave was opened in air and the products recovered by filtration.

Crystal data

$(C_{10}H_{28}N_4)[(UO_2)_2(SO_4)_4]$	Mo $K\alpha$ radiation
$M_r = 1128.66$	Cell parameters from 3482
Orthorhombic, *Pbca*	reflections
$a = 9.5831$ (2) Å	$\theta = 5–27°$
$b = 15.6060$ (3) Å	$\mu = 12.34$ mm^{-1}
$c = 18.1212$ (3) Å	$T = 150$ K
$V = 2710.10$ (9) Å^3	Block, yellow
$Z = 4$	$0.20 \times 0.16 \times 0.16$ mm
$D_x = 2.766$ Mg m^{-3}	

Data collection

Enraf–Nonius KappaCCD	3091 independent reflections
diffractometer	2219 reflections with $I > 3\sigma(I)$
ω scans	$R_{int} = 0.02$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(Otwinowski & Minor, 1997)	$h = -12 \rightarrow 12$
$T_{min} = 0.11$, $T_{max} = 0.14$	$k = -20 \rightarrow 20$
6194 measured reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	(Carruthers & Watkin, 1979):
$R[F^2 > 3\sigma(F^2)] = 0.023$	7.01, 10.1, 6.10, 2.43 and 1.09
$wR(F^2) = 0.053$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.89$	$\Delta\rho_{max} = 2.10$ e Å^{-3}
2219 reflections	$\Delta\rho_{min} = -0.93$ e Å^{-3}
182 parameters	Extinction correction: Larson
H-atom parameters not refined	(1970), Crystallographic
Weighting scheme: Chebychev	Computing eq 22
polynomial with 5 parameters	Extinction coefficient: 29.4 (27)

Table 1
Selected geometric parameters (Å, °).

U1—O1	1.778 (4)	S2—O5	1.497 (4)
U1—O2	1.764 (4)	S2—O6	1.494 (4)
U1—O3	2.348 (4)	S2—O7	1.489 (4)
U1—O4[i]	2.332 (4)	S2—O10	1.437 (5)
U1—O5	2.455 (4)	N1—C1	1.500 (7)
U1—O6	2.456 (4)	N1—C2	1.503 (8)
U1—O7[ii]	2.378 (4)	N1—C3	1.504 (8)
S1—O3	1.502 (4)	N2—C5	1.458 (9)
S1—O4	1.492 (4)	C1—C2[iii]	1.516 (9)
S1—O8	1.447 (5)	C4—C3	1.506 (9)
S1—O9	1.465 (5)	C4—C5	1.52 (1)
O1—U1—O2	178.93 (18)	O3—S1—O9	109.5 (3)
O1—U1—O3	89.54 (18)	O4—S1—O8	111.2 (3)
O1—U1—O4[i]	88.82 (17)	O4—S1—O9	108.3 (3)
O1—U1—O5	91.55 (17)	O8—S1—O9	111.4 (3)
O1—U1—O6	89.51 (18)	O5—S2—O6	103.7 (2)
O1—U1—O7[ii]	84.40 (17)	O5—S2—O7	107.5 (3)
O2—U1—O3	90.07 (18)	O5—S2—O10	112.3 (3)
O2—U1—O4[i]	90.13 (17)	O6—S2—O7	108.2 (3)
O2—U1—O5	88.36 (17)	O6—S2—O10	113.0 (3)
O2—U1—O6	91.34 (18)	O7—S2—O10	111.6 (3)
O2—U1—O7[ii]	96.49 (17)	U1—O3—S1	136.0 (3)
O3—U1—O4[i]	80.39 (15)	U1[iv]—O4—S1	141.7 (3)
O3—U1—O5	154.13 (15)	U1—O5—S2	99.5 (2)
O3—U1—O6	148.60 (14)	U1—O6—S2	99.5 (2)
O3—U1—O7[ii]	77.92 (15)	U1[v]—O7—S2	135.2 (3)
O4[i]—U1—O5	73.79 (14)	C1—N1—C2	109.4 (5)
O4[i]—U1—O6	130.96 (14)	C1—N1—C3	109.2 (5)
O4[i]—U1—O7[ii]	157.30 (15)	C2—N1—C3	113.5 (5)
O5—U1—O6	57.26 (13)	N1—C1—C2[iii]	112.0 (5)
O5—U1—O7[ii]	127.90 (14)	N1—C2—C1[iii]	110.8 (5)
O6—U1—O7[ii]	70.76 (14)	N1—C3—C4	114.7 (5)
O3—S1—O4	104.8 (3)	C3—C4—C5	108.2 (6)
O3—S1—O8	111.4 (3)	N2—C5—C4	112.7 (7)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O9[i]	1.00	1.80	2.763 (7)	161
N2—H12$\cdots$O9[ii]	1.00	2.05	3.033 (7)	168
N2—H13$\cdots$O8[iii]	1.00	1.94	2.894 (8)	158
N2—H14$\cdots$O7[iv]	1.00	2.21	3.200 (7)	171

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

H atoms were placed geometrically, with C—H and N—H distances fixed at 1.00 Å, and were unrefined. The highest peak in the difference map was located 1.89 Å from H11. Refinement treating this as a solvent water O atom resulted in a partial occupancy of 0.28 (1). Although the inclusion of this atom improves the various agreement analyses, it was not included in the final refinement as it is not chemically significant.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); 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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