metal-organic papers

catena-Poly[1-methylpiperazinium [[aqua-dioxouranium(VI)]-di-μ-sulfato-$\kappa^4 O$:O']]

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Key indicators

The title compound, $[C_5H_{14}N_2][UO_2(H_2O)(SO_4)_2]$, contains anionic $[UO_2(H_2O)(SO_4)_2]^{2-}$ chains with 1-methylpiperazinium cations balancing the charge. Each U^{VI} atom is seven-coordinate in a pentagonal bipyramidal geometry, and each sulfate tetrahedron bridges two adjacent uranium centres. Neighbouring chains hydrogen bond to one another though the bound water molecules.

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, Choudhury & Rao, 2002*b*; Choudhury *et al.*, 2001), Fe (Paul, Choudhury & Rao, 2002*a, b*, 2003; Paul, Choudhury, Sampathkumaran & Rao, 2002), Ce (Wang *et al.*, 2002), La (Bataille & Louer, 2002; Xing *et al.*, 2003) and U (Doran *et al.*, 2002; Norquist, Thomas *et al.*, 2002, Norquist, Doran *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. This report contains the synthesis and structure of an organically templated uranium(VI) sulfate: $[C_5H_{14}N_2][UO_2(H_2O)(SO_4)_2]$, (I), is denoted USO-22 (uranium sulfate from Oxford).

(I)
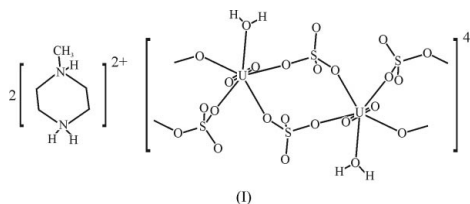
One unique uranium centre is present in USO-22. U1 is seven coordinate, in a pentagonal bipyramidal geometry. Two short 'uranyl' bonds to axial oxides are observed. The U1—O1 and U1—O2 bond lengths are 1.780 (3) and 1.776 (3) Å, respectively. These values are close to the average reported value of 1.758 (3) Å (Burns *et al.*, 1997), and the O1—U1—O2 angle is close to 180°, with a value of 178.31 (15)°. Four of the five equatorial coordination sites around U1 are occupied by oxide ligands that bridge U1 and a sulfur centre, through distances ranging between 2.332 (3) and 2.405 (3) Å. The fifth equatorial coordination site is occupied by a bound water molecule through a longer U—O bond; the length of U1—O3 is 2.479 (4) Å. Two distinct sulfur sites are observed in

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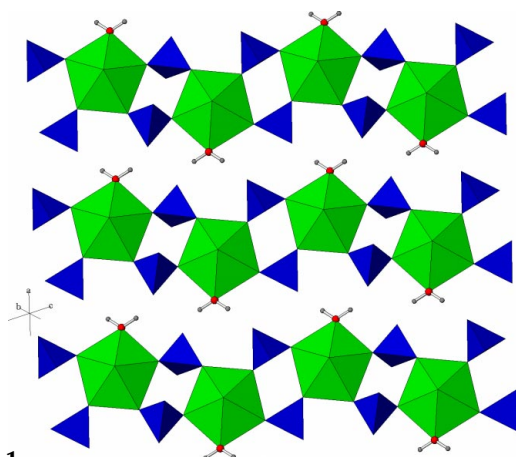
Figure 1
Chains in USO-22. Green pentagonal bipyramids and blue tetrahedra represent [UO$_7$] and [SO$_4$] respectively.

USO-22. Both S1 and S2 occupy the centre of [SO$_4$] tetrahedra. Each sulfur centre is bound to two O atoms that bridge adjacent uranium centres and to two terminal O atoms. The bonds to bridging O are longer than those to terminal O. The ranges of S—O$_{bridging}$ and S—O$_{terminal}$ bond lengths are 1.483 (3) to 1.506 (3) and 1.453 (4) to 1.467 (3) Å, respectively.

Chains are formed as each uranium centre is connected to two others through four bridging sulfate tetrahedra. This chain structure is known in uranium chemistry (Thomas *et al.*, 2003; Norquist *et al.*, 2002, 2003; Tabachenko *et al.*, 1984). Successive chains hydrogen bond to one another, forming pseudo layers (Fig. 1). These 'layers' lie in the (011) plane, and stack in an *aa* sequence(Fig. 2). A displacement ellipsoid plot is shown in Fig. 3.

Experimental

0.3150 g (7.43 × 10^{-4} mol) of UO$_2$(CH$_3$CO$_2$)$_2$·2H$_2$O, 0.4210 g (4.20 × 10^{-3} mol) of H$_2$SO$_4$, 0.0288 g (2.50 × 10^{-4} mol) of 1-amino-4-methylpiperazine and 0.9930 g (5.52 × 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 slowly cooled to 297 K over an additional 24 h. The autoclave was opened in air and the products recovered by filtration.

Crystal data

(C$_5$H$_{14}$N$_2$)[UO$_2$(H$_2$O)(SO$_4$)$_2$]
M_r = 582.35
Triclinic, $P\bar{1}$
a = 8.0031 (2) Å
b = 8.1873 (2) Å
c = 10.8911 (3) Å
α = 72.704 (1)°
β = 81.7766 (11)°
γ = 78.7917 (9)°
V = 665.60 (3) Å^3

Z = 2
D_x = 2.906 Mg m^{-3}
Mo Kα radiation
Cell parameters from 2832
  reflections
θ = 5–27°
μ = 12.57 mm^{-1}
T = 150 K
Block, yellow
0.10 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius KappaCCD
  diffractometer
ω scans
Absorption correction: multi-scan
  (Otwinowski & Minor, 1997)
  T_{min} = 0.28, T_{max} = 0.28
5594 measured reflections

3026 independent reflections
2640 reflections with $I > 3\sigma(I)$
R_{int} = 0.02
θ_{max} = 27.5°
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 14$
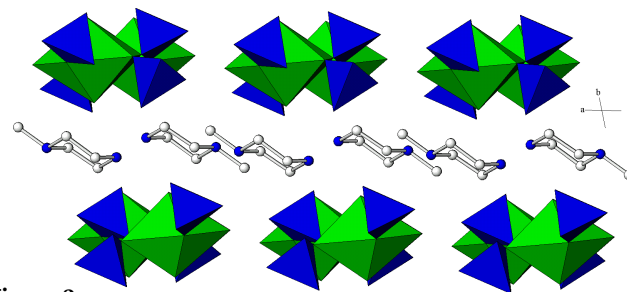
Figure 2
Three-dimensional packing of USO-22. Green pentagonal bipyramids and blue tetrahedra represent [UO$_7$] and [SO$_4$] respectively.
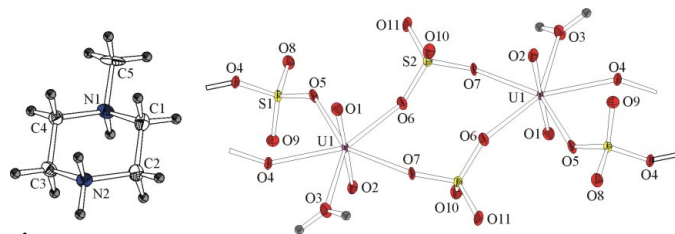
Figure 3
Displacement ellipsoid plot of the title compound, with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been removed for clarity.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.054$
$S = 1.01$
2640 reflections
191 parameters
H-atom parameters constrained

Weighting scheme: see text
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max}$ = 0.99 e Å^{-3}
$\Delta\rho_{min}$ = −0.92 e Å^{-3}
Extinction correction: Larson
  (1970), equation 22
Extinction coefficient: 16.5 (15)

Table 1
Selected geometric parameters (Å, °).

U1—O1	1.780 (3)	S2—O6	1.483 (3)
U1—O2	1.776 (3)	S2—O7	1.497 (3)
U1—O3	2.479 (4)	S2—O10	1.458 (4)
U1—O4	2.335 (4)	S2—O11	1.467 (3)
U1—O5	2.332 (3)	N1—C1	1.527 (7)
U1—O6	2.405 (3)	N1—C4	1.488 (6)
U1—O7^i	2.342 (3)	N1—C5	1.496 (7)
S1—O4	1.506 (3)	N2—C2	1.515 (7)
S1—O5^{ii}	1.496 (3)	N2—C3	1.485 (7)
S1—O8	1.453 (4)	C1—C2	1.516 (8)
S1—O9	1.458 (4)	C3—C4	1.508 (7)
O1—U1—O2	178.31 (15)	O5—U1—O7^i	144.81 (12)
O1—U1—O3	89.18 (15)	O6—U1—O7^i	74.35 (11)
O1—U1—O4	90.83 (14)	O4—S1—O5^{ii}	105.6 (2)
O1—U1—O5	91.77 (14)	O4—S1—O8	109.0 (2)
O1—U1—O6	91.66 (14)	O4—S1—O9	110.9 (2)
O1—U1—O7^i	90.42 (14)	O5^{ii}—S1—O8	109.4 (2)
O2—U1—O3	89.25 (14)	O5^{ii}—S1—O9	110.3 (2)
O2—U1—O4	89.29 (14)	O8—S1—O9	111.4 (2)
O2—U1—O5	89.88 (14)	O6—S2—O7	106.5 (2)
O2—U1—O6	89.21 (14)	O6—S2—O10	110.8 (2)
O2—U1—O7^i	88.42 (14)	O6—S2—O11	109.2 (2)
O3—U1—O4	72.07 (12)	O7—S2—O10	110.5 (2)
O3—U1—O5	146.50 (12)	O7—S2—O11	108.6 (2)
O3—U1—O6	142.97 (11)	O10—S2—O11	111.2 (2)
O3—U1—O7^i	68.63 (12)	U1—O4—S1	132.9 (2)
O4—U1—O5	74.44 (11)	U1—O5—S1^{ii}	141.6 (2)
O4—U1—O6	144.89 (11)	U1—O6—S2	137.6 (2)
O4—U1—O7^i	140.65 (12)	U1^i—O7—S2	139.7 (2)
O5—U1—O6	70.48 (11)		

Symmetry codes: (i) $-1-x, 1-y, 2-z$; (ii) $-1-x, -y, 3-z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H3$\cdots$S2	1.00	2.81	3.687 (5)	147
N1—H3$\cdots$O11	1.00	2.14	2.982 (6)	141
O3—H2$\cdots$S2^{iii}	1.00	2.92	3.786 (4)	145
O3—H2$\cdots$O11^{iv}	1.00	1.89	2.838 (5)	157
N2—H8$\cdots$O2^{v}	1.00	2.27	2.924 (5)	122
C4—H13$\cdots$O5^{v}	1.00	2.37	3.364 (7)	169
N2—H8$\cdots$O9^{v}	1.00	1.92	2.761 (6)	140
C2—H7$\cdots$O6^{vi}	1.00	2.41	3.184 (8)	134
N2—H9$\cdots$O10^{vii}	1.00	1.88	2.780 (7)	147

Symmetry codes: (iii) $x - 1, y, z$; (iv) x, y, z; (v) $-x, -y, 2 - z$; (vi) $-x, 1 - y, 2 - z$; (vii) $1 + x, y, z$.

A Chebychev polynomial was used for the weighting scheme, with five parameters (Carruthers & Watkin, 1979), 8.86, 4.95, 9.20, 0.0122, 2.37. H atoms were placed geometrically after each cycle.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.* 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001); molecular graphics: *CAMERON* (Watkin *et al.*, 2001); software used to prepare material for publication: *CRYSTALS*.

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