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catena-Poly[cyclohexane-1,4-diammonium [[dioxo(sulfato- κ^2 O, O')uranium(VI)]- μ -sulfato] dihydrate]

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Key indicators

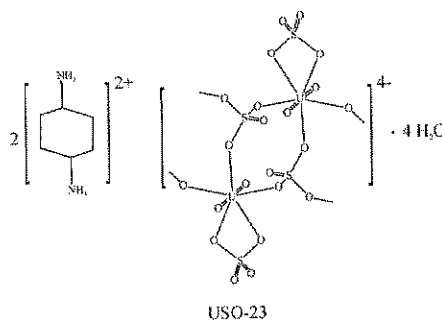
Single-crystal X-ray study
T = 150 K
Mean σ (C–C) = 0.006 Å
R factor = 0.020
wR factor = 0.047
Data-to-parameter ratio = 16.0

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

The title compound, (C₆H₁₆N₂)[UO₂(SO₄)₂]·2H₂O, contains anionic [UO₂(SO₄)₂]²⁻ chains with cyclohexane-1,4-diammonium cations balancing the charge. Each U^{VI} atom is seven-coordinate in a pentagonal bipyramidal geometry and the sulfate tetrahedra either bridge between two adjacent uranium centres or share an edge with a single [UO₇] polyhedron.

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.*, 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, 2003; 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) sulfate, [C₆H₁₆N₂][UO₂(SO₄)₂]·2H₂O, which is denoted USO-23 (uranium sulfate from Oxford).



One distinct uranium environment is observed in USO-23. U1 is seven-coordinate in a pentagonal bipyramidal geometry. It is bound to two oxide ligands through short 'uranyl' bonds. The U1=O1 and U1=O2 distances are 1.761 (3) and 1.771 (3) Å, respectively; these distances are close to the average reported value of 1.758 (4) Å (Burns *et al.*, 1997), and the O1–U1–O2 angle is close to linear, with a value of 178.73 (13)°. The five equatorial coordination sites are occu-

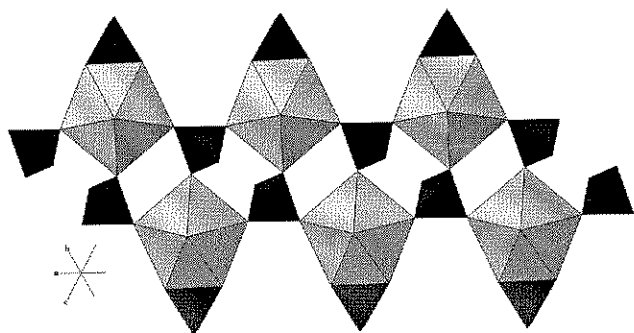


Figure 1
Chains in USO-23. Green pentagonal bipyramids and blue tetrahedra represent $[\text{UO}_7]$ and $[\text{SO}_4]$, respectively.

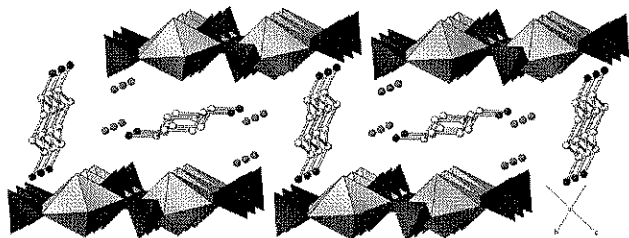


Figure 2
Three-dimensional packing of USO-23. Green pentagonal bipyramids and blue tetrahedra represent $[\text{UO}_7]$ and $[\text{SO}_4]$, respectively. H atoms have been omitted for clarity.

plied by O atoms that belong to the sulfates. Atoms O3, O4 and O5 bridge to different sulfur centres, through U—O distances ranging between 2.354 (3) and 2.381 (3) Å. The remaining two O atoms are bound to a single sulfur centre. These U—O bonds are longer, with distances of 2.450 (3) and 2.451 (3) Å to O6 and O7, respectively. Two different sulfur environments are present in USO-23. Both S1 and S2 are bound to four O atoms in a tetrahedral fashion. However, the tetrahedron containing S1 bridges between three adjacent uranium centres, each through a single shared corner, while the S2 tetrahedra share an edge with a single uranium centre. The bridging O atoms exhibit longer S—O bonds, with lengths ranging between 1.480 (3) and 1.510 (3) Å, than the terminal O atoms. These S—O_{term} bonds have lengths ranging between 1.445 (3) and 1.459 (3) 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; Doran *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 sulfate anion. The protonated 1,4-diaminocyclohexane cations, $(\text{C}_6\text{H}_{16}\text{N}_2)^{2+}$, reside between chains, balancing the charge (Fig. 2). A displacement ellipsoid plot is shown in Fig. 3.

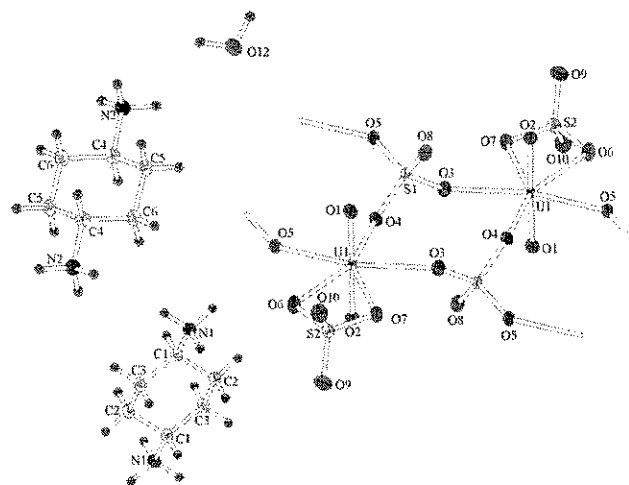


Figure 3
Displacement ellipsoid plot of the title compound, with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level.

Experimental

0.4419 g (1.04 mmol) of $\text{UO}_2(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, 0.3001 g (3.06 mmol) of H_2SO_4 , 0.024 g (0.211 mmol) of 1,4-diaminocyclohexane and 1.0002 g (55.5 mmol) of water were placed in 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

$(\text{C}_6\text{H}_{16}\text{N}_2)[\text{UO}_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$
 $M_r = 614.39$
 Triclinic, $P\bar{1}$
 $a = 6.7813$ (1) Å
 $b = 10.0636$ (2) Å
 $c = 12.9753$ (3) Å
 $\alpha = 76.7537$ (7)°
 $\beta = 75.6074$ (7)°
 $\gamma = 74.3971$ (13)°
 $V = 813.50$ (4) Å³

$Z = 2$
 $D_x = 2.508$ Mg m⁻³
 Mo K α radiation
 Cell parameters from 3432 reflections
 $\theta = 5\text{--}27^\circ$
 $\mu = 10.30$ mm⁻¹
 $T = 150$ K
 Rod, yellow
 $0.50 \times 0.06 \times 0.04$ mm

Data collection

Enraf-Nonius Kappa CCD diffractometer
 ω scans
 Absorption correction: multi-scan (Otwinowski & Minor, 1997)
 $T_{\text{min}} = 0.51$, $T_{\text{max}} = 0.66$
 6840 measured reflections

3700 independent reflections
 3353 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -8 \rightarrow 8$
 $k = -13 \rightarrow 13$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 3\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.047$
 $S = 0.87$
 3353 reflections
 209 parameters
 H-atom parameters not refined

Weighting scheme: Chebyshev polynomial (Carruthers & Watkin, 1979) with 5 parameters: 13.4, 18.9, 11.8, 4.59, 1.99
 $(\Delta\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.11$ e Å⁻³
 Extinction correction: Larson (1970), equation 22
 Extinction coefficient: 15.9 (15)

Table 1

Selected geometric parameters (Å, °).

U1—O1	1.761 (3)	S1—O4 ⁱⁱ	1.489 (3)
U1—O2	1.771 (3)	S1—O5	1.485 (3)
U1—O3	2.381 (3)	S1—O8	1.454 (3)
U1—O4	2.367 (3)	S2—O6	1.510 (3)
U1—O5	2.354 (3)	S2—O7	1.498 (3)
U1—O6	2.450 (3)	S2—O9	1.445 (3)
U1—O7	2.451 (3)	S2—O10	1.459 (3)
S1—O3 ⁱ	1.480 (3)		
O1—U1—O2	178.73 (13)	O4 ⁱⁱ —S1—O5	107.95 (15)
O1—U1—O3	92.29 (11)	O4 ⁱⁱ —S1—O8	111.40 (17)
O1—U1—O4	91.55 (11)	O5—S1—O8	110.47 (17)
O1—U1—O5	90.89 (12)	O6—S2—O7	101.85 (16)
O1—U1—O6	90.48 (12)	O6—S2—O9	111.16 (18)
O1—U1—O7	91.12 (12)	O6—S2—O10	109.02 (17)
O2—U1—O3	88.97 (11)	O7—S2—O9	110.66 (18)
O2—U1—O4	88.81 (11)	O7—S2—O10	111.43 (17)
O2—U1—O5	87.97 (11)	O9—S2—O10	112.26 (19)
O2—U1—O6	88.67 (11)	U1—O3—S1 ⁱⁱⁱ	135.88 (17)
O2—U1—O7	89.22 (11)	U1—O4—S1 ⁱⁱ	137.50 (17)
O3—U1—O4	76.52 (9)	U1—O5—S1	147.46 (17)
O3—U1—O5	157.2 (1)	U1—O6—S2	100.44 (14)
O3—U1—O6	128.23 (9)	U1—O7—S2	100.74 (14)
O3—U1—O7	71.36 (9)	N1—C1—C2	108.8 (3)
O4—U1—O5	80.81 (9)	N1—C1—C3	109.9 (3)
O4—U1—O6	155.06 (9)	C2—C1—C3	111.7 (3)
O4—U1—O7	147.84 (9)	C1—C2—C3 ^{iv}	110.5 (3)
O5—U1—O6	74.31 (9)	C1—C3—C2 ^{iv}	109.6 (3)
O5—U1—O7	131.18 (9)	N2—C4—C5	110.4 (3)
O6—U1—O7	56.91 (9)	N2—C4—C6	108.7 (3)
O3 ⁱ —S1—O4 ⁱⁱ	107.76 (16)	C5—C4—C6	111.6 (3)
O3 ⁱ —S1—O5	107.99 (17)	C4—C5—C6 ^v	108.4 (3)
O3 ⁱ —S1—O8	111.13 (16)	C4—C6—C5 ^v	110.4 (3)

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

H atoms were positioned geometrically, with bond lengths of 1.00 Å and U_{iso} set at $1.2U_{eq}$ of the carrier atom; the positions were recalculated after each refinement cycle. The highest peak is approximately 1.15 and 1.82 Å from O10 and S2, respectively. The deepest hole is approximately 1.05 Å from U1.

Data collection: COLLECT (Nonius, 1997); cell refinement: DENZO and SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO and 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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