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$(C_3H_{12}N_2)_2[UO_2(H_2O)_2(SO_4)_2]_2 \cdot 2H_2O$: an organically templated uranium sulfate with a novel dimer type

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The title compound, bis(propane-1,2-diaminium) tetraaquadi-μ_2-sulfato-disulfatotetraoxodiuranate(VI) dihydrate, $(C_3H_{12}N_2)_2[U_2O_4(SO_4)_4(H_2O)_4] \cdot 2H_2O$, contains discrete centrosymmetric anionic $\{[UO_2(H_2O)_2(SO_4)_2]_2\}^{4-}$ dimers with $C_3H_{12}N_2^{2+}$ cations balancing the charge. The dimers form hydrogen-bonded layers. The cations and occluded water molecules participate in an extensive hydrogen-bonding network. Each U^{VI} centre is seven-coordinate with a pentagonal–bipyramidal geometry. Both pendent and bridging sulfate tetrahedra are observed, as well as bound and occluded water molecules.

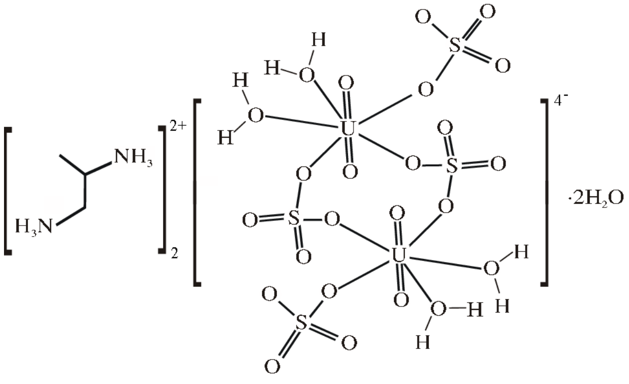
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.007 Å
R factor = 0.023
wR factor = 0.056
Data-to-parameter ratio = 14.8

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

Comment

Hydrothermal synthesis is a well established method for the formation of inorganic structures templated by organic ions. The majority of these compounds are metal phosphates (Cheetham *et al.*, 1999), with other examples including metal phosphites (Doran *et al.*, 2001; Fernandez *et al.*, 2002), fluorides (Walker *et al.*, 1999), germanates (Reisner *et al.*, 2001; Bu *et al.*, 1998; Conradsson *et al.*, 2000), arsenates (Ekambaram & Sevov, 2000; Bazan *et al.*, 2000), oxalates (Vaidhyanathan *et al.*, 2002) and selenites (Choudhury *et al.*, 2002; Harrison *et al.*, 2000).



(I)

A recently employed strategy for the design of new inorganic architectures involves the use of the sulfate tetrahedron as a primary substituent. Compounds incorporating U (Doran *et al.*, 2002, 2003*a*,*b*,*c*,*d*; Doran, Norquist *et al.*, 2004; Doran, Cockbain *et al.*, 2004; Norquist *et al.*, 2002, 2003*a*,*b*; Norquist *et al.*, 2003; Thomas *et al.*, 2003; Stuart *et al.*, 2003), Cd (Choudhury *et al.*, 2001; Paul *et al.*, 2002*b*), La (Bataille & Louer, 2002; Xing, Liu *et al.*, 2003; Xing Shi *et al.*, 2003), Ce (Wang *et al.*, 2002), Sc (Bull *et al.*, 2002), Fe (Paul, Choudhury

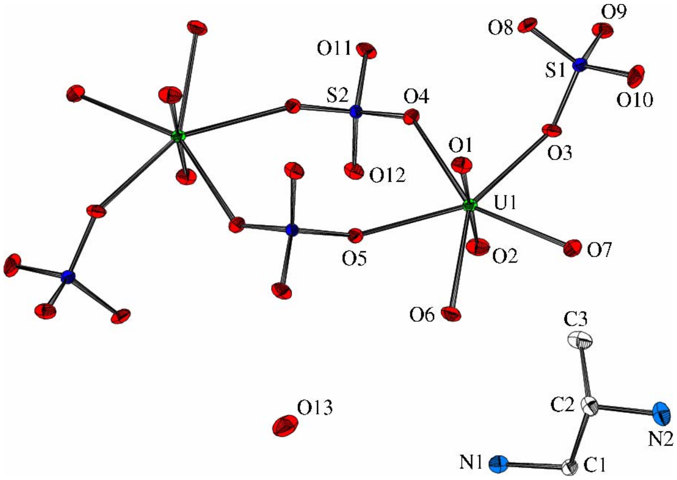


Figure 1
View of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted.

& Rao, 2002*a*, 2003; Paul *et al.*, 2002), V (Paul, Choudhury, Nagarajan & Rao, 2003; Khan *et al.*, 1999), Zn (Morimoto & Lingafelter, 1970) and Mo (Gutnick *et al.*, 2004) are known. These compounds exhibit great structural diversity, with structures ranging from molecular anions to three-dimensional frameworks. This report contains the synthesis and structure of an organically templated uranium sulfate, $[N_2C_3H_{12}]_2[UO_2(H_2O)_2(SO_4)_2]_2 \cdot 2H_2O$, (I), designated USO-31 (uranium sulfate from Oxford).

A single independent U atom is present in USO-31. U1 is seven-coordinate (Fig. 1 and Table 1) in a pentagonal–bipyramidal geometry. Two short 'uranyl' bonds to axial O atoms are observed, with U—O distances of 1.765 (3) Å and 1.772 (4) Å, close to the average reported value of 1.758 (3) Å (Burns *et al.*, 1997). The O1—U1—O2 angle is close to 180°, with a value of 178.91 (16)°. Three of the five equatorial coordination sites around U1 are occupied by O atoms of sulfate groups, with U—O distances of 2.335 (3), 2.380 (3) and 2.385 (3) Å. The remaining two equatorial coordination sites are occupied by bound water molecules, with U—O distances of 2.420 (3) and 2.437 (3) Å. The assignment of the bound water molecules was based on the longer U—O bond lengths and hydrogen-bonding interactions. Two distinct sulfur sites are observed in USO-31. S1 and S2 are both at the centre of $[SO_4]$ tetrahedra. S1 tetrahedra link to one U centre and have three terminal O atoms, in contrast with S2 tetrahedra, which bridge between two U centres and have two terminal O atoms. The $S—O_{bridging}$ distances range between 1.490 (3) and 1.500 (3) Å. The $S—O_{terminal}$ distances are shorter, ranging between 1.463 (4) and 1.475 (4) Å.

Centrosymmetric dimers are formed as a result of the connectivities between the $[UO_7]$ and $[SO_4]$ polyhedra. This dimer topology is, to the best of our knowledge, previously unknown in uranium chemistry. It is related to the $[(UO_2)_2(SO_4)_6]^{8-}$ dimers in USO-10 (Norquist *et al.*, 2003*a*) and USO-12 (Norquist *et al.*, 2003*b*), which contain edge-shared sulfate groups in place of the bound water molecules of USO-31. Hydrogen-bonded layers are formed (see Fig. 2), because the four bound water molecules of each dimer donate hydrogen bonds to the terminal sulfate O atoms of adjacent dimers. These pseudo-layers propagate in the (010) plane and are separated by template cations and occluded water molecules (see Fig. 3). The interlayer species are involved in hydrogen bonding with the layer (Table 2).

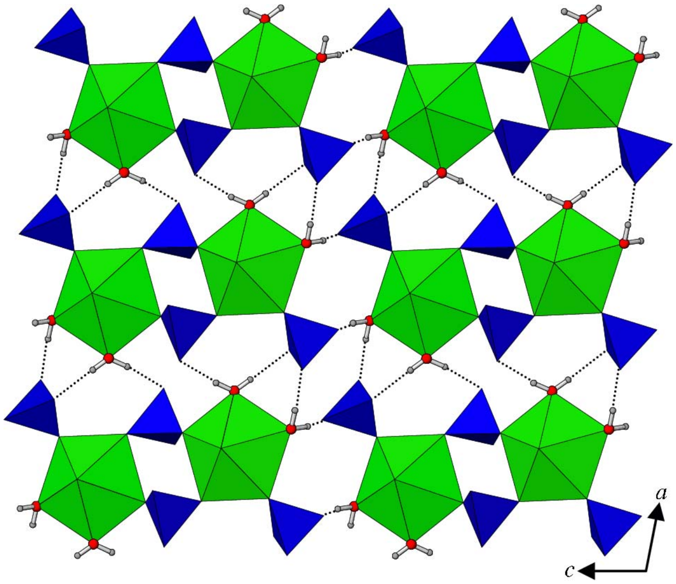


Figure 2
The formation of pseudo-layers by the dimers in USO-31. Green pentagonal bipyramids and blue tetrahedra represent $[UO_7]$ and $[SO_4]$, respectively.

Experimental

$UO_2(CH_3CO_2)_2 \cdot 2H_2O$ (0.1062 g, 0.249 × 10^{-3} mol), H_2SO_4 (0.2623 g, 2.61 × 10^{-3} mol), 1,2-diaminopropane (0.1544 g, 2.05 × 10^{-3} mol), HF (0.1302 g, 2.59 × 10^{-3} mol, 40% aq.) and water (0.7443 g, 41.3 × 10^{-3} mol) were placed in a 23 ml Teflon-lined autoclave. The autoclave was heated to 453 K for 24 h, and then slowly cooled to 297 K over an additional period of 24 h. The autoclave was opened in air and the products recovered by filtration. A yield of 31%, based on uranium, was observed. The yield can be increased with slow evaporation of the post-reaction supernatant solution. Template N—H bending and stretching modes were observed at 1600 and 3100 cm^{-1} in the IR spectrum of USO-31. The C—H bend was measured at 1472 cm^{-1}. A band centred at 1100 cm^{-1} corresponds to S—O stretches, with the asymmetric uranyl stretch at 936 cm^{-1}. Analysis found: N 4.90, C 6.26, H 3.15, S 11.19, U 38.21%; calculated: N 4.73, C 6.08, H 3.06, S 10.83, U 40.18%. The thermal stability of USO-31 was probed using thermogravimetric analysis. Weight losses between 373 and 403 K (2.7%), and 413 and 538 K (6.1%) result from the loss of occluded (calculated 3.0%) and bound water molecules (calculated 6.1%), respectively. A 16.5% weight loss was measured between 583 and 693 K, corresponding to template decomposition and the onset of breakdown of the inorganic moiety. The material calcines to UO_2, determined using powder X-ray diffraction, by 1173 K, with a total mass loss of 55.0% (calculated 54.4%). Structural analysis was conducted at 150 K.

Crystal data

$(C_3H_{12}N_2)_2[U_2O_4(SO_4)_4(H_2O)_4]\cdot 2H_2O$
$M_r = 1184.73$
Triclinic, $P\overline{1}$
$a = 7.3983$ (2) Å
$b = 7.6333$ (2) Å
$c = 12.5946$ (5) Å
$\alpha = 95.1761$ (12)°
$\beta = 94.6412$ (13)°
$\gamma = 96.578$ (2)°
$V = 700.70$ (4) Å^3
$Z = 1$
$D_x = 2.807$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2953 reflections
$\theta = 5$–27°
$\mu = 11.95$ mm^{-1}
$T = 150$ K
Plate, yellow
0.10 × 0.06 × 0.01 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (Otwinowski & Minor, 1997)
$T_{\min} = 0.46$, $T_{\max} = 0.89$
5870 measured reflections
3154 independent reflections
2820 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.02$
$\theta_{\max} = 27.4°$
$h = -8 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.056$
$S = 0.83$
2820 reflections
191 parameters
H-atom parameters constrained
Modified (Prince, 1982) Chebychev polynomial with four parameters (Watkin, 1994), 11.1, 14.6, 7.77, 2.08
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.22$ e Å^{-3}
$\Delta\rho_{\min} = -1.39$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 12.0 (11)

Table 1
Selected geometric parameters (Å, °).

U1—O1	1.765 (3)	S1—O10	1.463 (4)
U1—O2	1.772 (4)	S2—O4	1.493 (4)
U1—O3	2.335 (3)	S2$^{\rm i}$—O5	1.490 (3)
U1—O4	2.385 (3)	S2—O11	1.470 (3)
U1—O5	2.380 (3)	S2—O12	1.466 (4)
U1—O6	2.437 (3)	N1—C1	1.498 (6)
U1—O7	2.420 (3)	N2—C2	1.489 (7)
S1—O3	1.500 (3)	C1—C2	1.520 (7)
S1—O8	1.475 (3)	C2—C3	1.530 (7)
S1—O9	1.475 (4)		
O1—U1—O2	178.91 (16)	O6—U1—O7	69.66 (12)
O1—U1—O3	91.88 (14)	O3—S1—O8	109.3 (2)
O1—U1—O4	90.74 (14)	O3—S1—O9	106.8 (2)
O1—U1—O5	92.44 (14)	O3—S1—O10	108.9 (2)
O1—U1—O6	91.42 (14)	O8—S1—O9	109.9 (2)
O1—U1—O7	84.59 (15)	O8—S1—O10	111.2 (2)
O2—U1—O3	88.87 (15)	O9—S1—O10	110.7 (2)
O2—U1—O4	90.22 (15)	O4—S2—O5$^{\rm i}$	106.9 (2)
O2—U1—O5	87.36 (15)	O4—S2—O11	107.8 (2)
O2—U1—O6	87.51 (15)	O4—S2—O12	110.8 (2)
O2—U1—O7	94.84 (15)	O5$^{\rm i}$—S2—O11	109.6 (2)
O3—U1—O4	74.72 (12)	O5$^{\rm i}$—S2—O12	110.0 (2)
O3—U1—O5	147.53 (12)	O11—S2—O12	111.7 (2)
O3—U1—O6	143.92 (12)	U1—O3—S1	138.5 (2)
O3—U1—O7	74.91 (12)	U1—O4—S2	135.8 (2)
O4—U1—O5	73.06 (12)	U1—O5—S2$^{\rm i}$	142.6 (2)
O4—U1—O6	141.14 (12)	N1—C1—C2	112.2 (4)
O4—U1—O7	149.08 (12)	N2—C2—C1	106.6 (4)
O5—U1—O6	68.09 (12)	N2—C2—C3	109.1 (4)
O5—U1—O7	137.55 (12)	C1—C2—C3	114.6 (4)

Symmetry code: (i) $-x, -y+2, -z+2$.

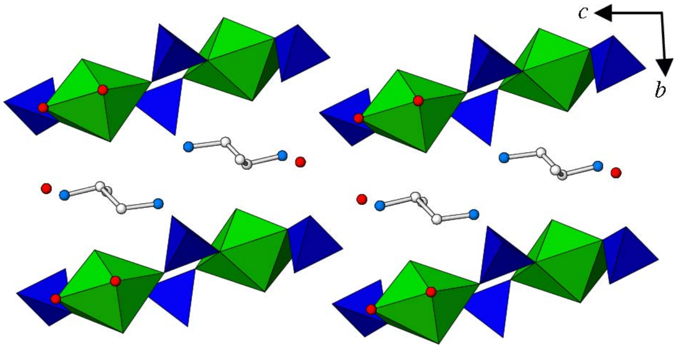


Figure 3
Three-dimensional packing of USO-31. Green pentagonal bipyramids and blue tetrahedra represent $[UO_7]$ and $[SO_4]$, respectively. H atoms have been omitted for clarity.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H1···O8$^{\rm ii}$	1.00	1.71	2.705 (5)	180
O6—H2···O11$^{\rm ii}$	1.00	1.76	2.756 (5)	180
O7—H3···O9$^{\rm ii}$	1.00	1.73	2.732 (5)	180
O7—H4···O10$^{\rm iii}$	1.00	1.67	2.665 (5)	180
N1—H5···O12$^{\rm iv}$	1.00	1.82	2.824 (6)	179
N1—H6···O11$^{\rm i}$	1.00	1.90	2.846 (5)	156
N1—H7···O12$^{\rm v}$	1.00	2.18	2.878 (6)	126
N2—H8···O13	1.00	1.82	2.812 (6)	170
N2—H9···O9$^{\rm iv}$	1.00	2.01	2.909 (6)	148
N2—H10···O8$^{\rm ii}$	1.00	1.97	2.911 (6)	156
O13—H18···O10$^{\rm vi}$	1.00	1.91	2.909 (5)	180

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

H atoms were placed geometrically after each cycle in idealized locations at 1.00 Å from the carrier atom, such that plausible hydrogen-bonding interactions are made, and refined as riding. The constraint $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$ (carrier atom) was applied in all cases. The highest peak is 0.96 Å from O1, and the deepest hole is 0.85 Å from U1.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *CRYSTALS* (Betteridge *et al.*, 2003).

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