Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

$(C_8H_{26}N_4)_{0.5}[(UO_2)_2(SO_4)_3(H_2O)]\cdot 2H_2O$, an organically templated uranyl sulfate with a novel layer type

Michael B. Doran,[a] Alexander J. Norquist,[b] Clair L. Stuart[a] and Dermot O'Hare[a]*

[a]Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, England, and [b]Department of Chemistry, Haverford College, 370 Lancaster Avenue, Haverford, PA 19041, USA

Correspondence e-mail:
dermot.ohare@chem.ox.ac.uk

Received 18 May 2004
Accepted 18 June 2004
Online 26 June 2004

Key indicators

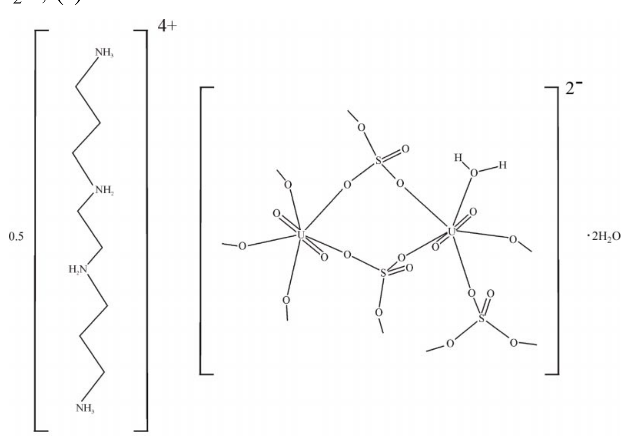
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.010 Å
R factor = 0.025
wR factor = 0.055
Data-to-parameter ratio = 13.0

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

The title compound, hemi[3,3′-(ethylenediiminio)dipropanaminium] aquatetraoxotri-μ-sulfato-diuranate(VI) dihydrate, $(C_8H_{26}N_4)_{0.5}[(UO_2)_2(SO_4)_3(H_2O)]\cdot 2H_2O$, contains infinite anionic $[(UO_2)_2(H_2O)(SO_4)_3]^{2-}$ layers with $[C_8H_{26}N_4]^{4+}$ cations balancing charge and participating in extensive hydrogen bonding, along with uncoordinated water molecules. Each U^{VI} centre is seven-coordinate with a pentagonal bipyramidal geometry, and each sulfate tetrahedron bridges three adjacent uranium centres.

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 recent 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*a*; Paul *et al.*, 2002; Paul, Choudhury & Rao, 2003), Zn (Morimoto & Lingafelter, 1970), Ce (Wang *et al.*, 2002), La (Bataille & Louer, 2002; Xing, Shi *et al.*, 2003; Xing, Liu *et al.*, 2003) and U (Doran *et al.*, 2002, 2003*a*,*b*,*c*,*d*; Norquist *et al.*, 2002, 2003*a*,*b*; Norquist, Doran & O'Hare, 2003; Thomas *et al.*, 2003; Stuart *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, USO-25 (uranium sulfate from Oxford), $(C_8H_{26}N_4)_{0.5}[(UO_2)_2(SO_4)_3(H_2O)]\cdot 2H_2O$, (I).



(I)

Two independent U atoms are present in (I). Both U1 and U2 are seven-coordinate, in pentagonal bipyramidal geometries. Two short 'uranyl' bonds to axial O atoms are observed

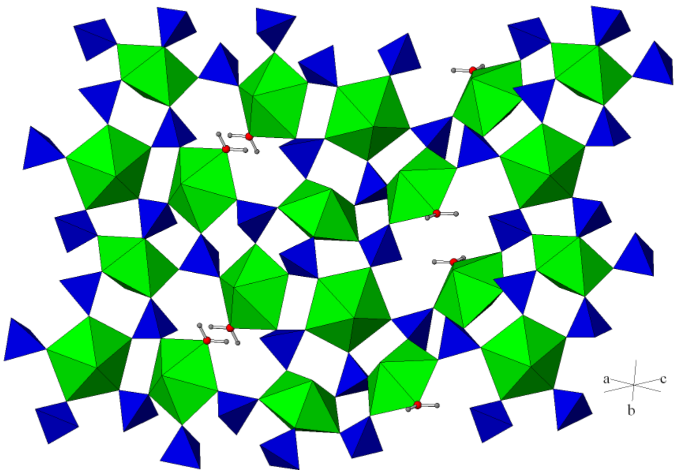


Figure 1
Inorganic layers in (I). Green pentagonal bipyramids and blue tetrahedra represent $[UO_7]$ and $[SO_4]$ groups, respectively, with the water molecules represented in ball-and-stick form.

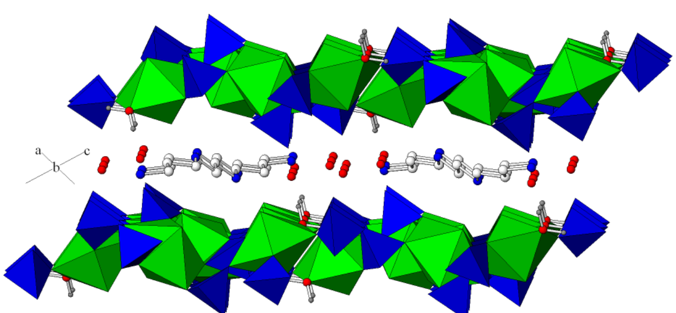


Figure 2
Three-dimensional packing of (I). Green pentagonal bipyramids and blue tetrahedra represent $[UO_7]$ and $[SO_4]$, respectively. Template and occluded water H atoms have been omitted for clarity.

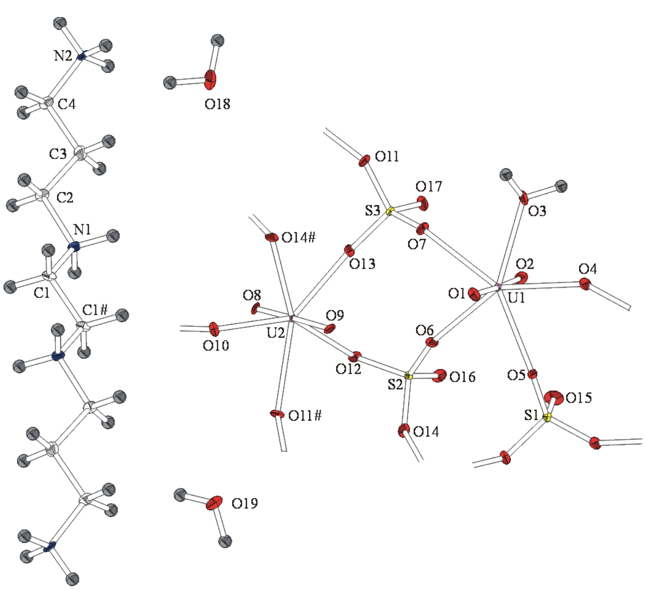


Figure 3
Displacement ellipsoid plot of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Atom O11# is at symmetry position $(2 - x, -1 - y, 2 - z)$ and O14# is at $(1 - x, -1 - y, 2 - z)$.

for each uranium environment, with distances that range from 1.751 (5) to 1.764 (5) Å, close to the average reported value of 1.758 (3) Å (Burns *et al.*, 1997). The O1—U1—O2 and O8—U2—O9 angles are close to 180°, with values of 177.8 (2) and 178.1 (2)°, respectively. Four of the five equatorial coordination sites around U1 are occupied by O atoms of sulfate groups, with U—O distances ranging between 2.359 (5) and 2.446 (5) Å. The last coordination site is occupied by a bound water molecule (O3); the U1—O3 distance is 2.421 (5) Å. The assignment of the bound water molecule was based upon hydrogen-bonding interactions. All five equatorial coordination sites around U2 are occupied by O atoms of sulfate groups, with U—O distances ranging from 2.332 (4) to 2.477 (5) Å. Three distinct sulfur sites are observed in (I): S1, S2 and S3 are all at the centre of $[SO_4]$ tetrahedra. Each sulfate group bridges three urananium centres and has one terminal O atom. The S—O_b (b = bridging) distances are 1.472 (5) and 1.504 (5) Å, while the S—O_t (t = terminal) distance are shorter, from 1.448 (5) to 1.456 (5) Å.

Layers are formed because each $[SO_4]$ tetrahedron bridges between three uranium centres (see Fig. 1). This layer topology was previously unknown in uranium chemistry, to the best of our knowledge. These layers propagate in the (101) plane and are separated by the template cations and water molecules (Fig. 2). The inter-layer species are involved in hydrogen bonding with the layer (Table 1).

Experimental

0.6356 g (1.50×10^{-3} mol) of $UO_2(CH_3CO_2)_2{\cdot}2H_2O$, 0.3403 g ($3.47 \times 10^{-3}$ mol) of H_2SO_4, 0.0863 g (4.95×10^{-4} mol) of *N*,*N*′-bis(3-aminopropyl)ethylenediamine and 1.009 g (5.60×10^{-2} mol) of water were placed into a 23 ml Teflon-lined autoclave. The autoclave was heated to 453 K for 24 h, after which 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

$(C_8H_{26}N_4)_{0.5}[U_2O_4(SO_4)_3(H_2O)]{\cdot}2H_2O$
M_r = 971.45
Monoclinic, $P2_1/n$
a = 11.8400 (2) Å
b = 10.3190 (2) Å
c = 16.5919 (4) Å
β = 107.7718 (9)°
V = 1930.41 (7) Å^3
Z = 4
D_x = 3.342 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3786 reflections
θ = 5–27°
μ = 17.18 mm^{-1}
T = 150 K
Block, yellow
0.16 × 0.10 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.14, T_{max} = 0.36
7982 measured reflections
4381 independent reflections
3523 reflections with $I > 3\sigma(I)$
R_{int} = 0.02
θ_{max} = 27.5°
$h = -15 \rightarrow 15$
$k = -11 \rightarrow 13$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.055
S = 0.98
3523 reflections
272 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + 4.55p]$ where $p = 0.333\max(F_o^2,0) + 0.667F_c^2$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 1.17 e Å^{-3}
$\Delta\rho_{min}$ = −1.42 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 36.0 (19)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1···O19	1.00	1.72	2.722 (7)	180
O3—H2···O17^{i}	1.00	1.78	2.766 (7)	168
O18—H17···O16^{ii}	1.00	1.98	2.977 (7)	173
O19—H18···O16^{iii}	1.00	1.93	2.826 (7)	148
O19—H19···O18^{iii}	1.00	1.77	2.757 (7)	171
N1—H12···O11	1.00	1.99	2.963 (7)	165
N1—H13···O19	1.00	1.85	2.827 (8)	167
N2—H3···O15^{iv}	1.00	1.86	2.795 (7)	154
N2—H4···O17^{v}	1.00	1.94	2.910 (8)	164
N2—H5···O16^{v}	1.00	1.90	2.894 (7)	175

Symmetry codes: (i) $2 - x, -1 - y, 2 - z$; (ii) $\frac{5}{2} - x, \frac{1}{2} + y, \frac{5}{2} - z$; (iii) $x - \frac{1}{2}, -\frac{1}{2} - y, z - \frac{1}{2}$; (iv) $x, y - 1, z$; (v) $x - \frac{1}{2}, -\frac{3}{2} - y, z - \frac{1}{2}$.

The CH and NH H atoms were positioned in idealized locations and refined by riding on their carrier atoms. The water H atoms were positioned geometrically to make plausible H···O hydrogen bonds, whilst maintaining the H—O—H bond angle of 109.5°. Atom H16, attached to O18, does not appear to form a hydrogen bond. Additionally, it makes close contacts (1.90 and 2.05 Å) with two CH H atoms, thus its location should be regarded as less certain. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier atom) was applied in all cases. The highest peak is at (0.7819, 0.7278, 0.0223) and the deepest hole is at (0.1111, 0.2500, 0.0000).

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2003); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *CRYSTALS*.

The authors thank the EPSRC for support.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Bataille, T. & Louer, D. (2002). *J. Mater. Chem.* **12**, 3487–3493.

Bull, I., Wheatley, P. S., Lightfoot, P., Morris, R. E., Sastre, E. & Wright, P. A. (2002). *Chem. Commun.* pp. 1180–1181.

Burns, P. C., Ewing, R. C. & Hawthorne, F. C. (1997). *Can. Mineral.* **35**, 1551–1570.

Cheetham, A. K., Ferey, G. & Loiseau, T. (1999). *Angew. Chem. Int. Ed.* **38**, 3269–3292.

Choudhury, A., Krishnamoorthy, J. & Rao, C. N. R. (2001). *Chem. Commun.* pp. 2610–2611.

Doran, M. B., Norquist, A. J. & O'Hare, D. (2002). *Chem. Commun.* pp. 2946–2947.

Doran, M. B., Norquist, A. J. & O'Hare, D. (2003*a*). *Inorg. Chem.* **42**, 6989–6995.

Doran, M. B., Norquist, A. J. & O'Hare, D. (2003*b*). *Acta Cryst.* E**59**, m373–m375.

Doran, M. B., Norquist, A. J. & O'Hare, D. (2003*c*). *Acta Cryst.* E**59**, m762–m764.

Doran, M. B., Norquist, A. J. & O'Hare, D. (2003*d*). *Acta Cryst.* E**59**, m765–m767.

Dowty, E. (2000). *ATOMS*. Version 6.0. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Khan, M. I., Cevik, S. & Doedens, R. J. (1999). *Inorg. Chim. Acta*, **292**, 112–116.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

Morimoto, C. N. & Lingafelter, E. C. (1970). *Acta Cryst.* B**26**, 335–341.

Nonius (1997). *COLLECT*. Nonius BV, Delft, The Netherlands.

Norquist, A. J., Doran, M. B. & O'Hare, D. (2003). *Solid State Sci.* **5**, 1149–1158.

Norquist, A. J., Doran, M. B., Thomas, P. M. & O'Hare, D. (2003*a*). *J. Chem. Soc. Dalton Trans.* pp. 1168–1175.

Norquist, A. J., Doran, M. B., Thomas, P. M. & O'Hare, D. (2003*b*). *Inorg. Chem.* **42**, 5949–5953.

Norquist, A. J., Thomas, P. M., Doran, M. B. & O'Hare, D. (2002). *Chem. Mater.* **14**, 5179–5184.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Paul, G., Choudhury, A., Nagarajan, R. & Rao, C. N. R. (2003). *Inorg. Chem.* **42**, 2004–2013.

Paul, G., Choudhury, A. & Rao, C. N. R. (2002*a*). *Chem. Commun.* pp. 1904–1905.

Paul, G., Choudhury, A. & Rao, C. N. R. (2002*b*). *J. Chem. Soc. Dalton Trans.* 3859–3867.

Paul, G., Choudhury, A. & Rao, C. N. R. (2003). *Chem. Mater.* **15**, 1174–1180.

Paul, G., Choudhury, A., Sampathkumaran, E. V. & Rao, C. N. R. (2002). *Angew. Chem. Int. Ed.* **41**, 4297–4300.

Stuart, C. L., Doran, M. B., Norquist, A. J. & O'Hare, D. (2003). *Acta Cryst.* E**59**, m446–m448.

Thomas, P. M., Norquist, A. J., Doran, M. B. & O'Hare, D. (2003). *J. Mater. Chem.* **13**, 88–92.

Wang, D., Yu, R., Xu, Y., Feng, S., Xu, R., Kumada, N., Kinomura, N., Matumura, Y. & Takano, M. (2002). *Chem. Lett.* pp. 1120–1121.

Watkin, D. J., Prout, C. K., Carruthers, J. R., Betteridge, P. W. & Cooper R. I. (2003). *CRYSTALS*. Issue 11. Chemical Crystallography Laboratory, Oxford, England.

Xing, Y., Liu, Y., Shi, Z., Meng, H. & Pang, W. (2003). *J. Solid State Chem.* **174**, 381–385.

Xing, Y., Shi, Z., Li, G., Pang, W. (2003). *Dalton Trans.* pp. 940–943.