Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

A novel uranium-containing coordination polymer: poly[[aqua(benzene-1,3,5-tricarboxylato)dioxouranium(VI)] monohydrate]

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The title compound, $\{[UO_2(C_9H_4O_6)(H_2O)]\cdot H_2O\}_n$, is a novel material consisting of a $[UO_2]^{2+}$ ion bonded to five O atoms, four of which are from three separate 1,3,5-tricarboxylic acid molecules, while the fifth is from a coordinated water molecule. This connectivity gives rise to chains running in the $[01\bar{1}]$ direction.

Received 19 December 2003
Accepted 12 January 2004
Online 17 January 2004

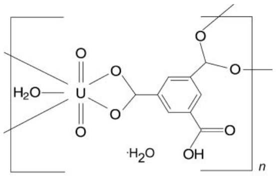
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
R factor = 0.039
wR factor = 0.071
Data-to-parameter ratio = 13.4

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

Comment

The title compound, (I), was synthesized during an ongoing effort to create novel metal–organic framework materials containing $[UO_2]^{2+}$ centers (Borkowksi & Cahill, 2003). The U atom in (I) is found in a pentagonal–bipyramidal coordination. Atoms O7 and O9 (also called the 'uranyl' O atoms) are found at an average distance of 1.746 (6) Å from the U atom. Four of the five equatorial O atoms attached to the U center belong to three distinct carboxylic acid molecules. Atoms O1 and O2 from one carboxylic acid group act as the bidentate end of the ligand, while atoms O3 and O4 from a second carboxylic acid group bridge adjacent uranyl polyhedra. There is a coordinated water molecule (O8) at a distance of 2.396 (5) Å from the U center. The remaining carboxylic acid group in the ligand, atoms O5 and O6, remains fully protontated and is not coordinated to the $[UO_2]^{2+}$ center.



(I)

Adjacent pentagonal bipyramids are bridged through O3—C8—O4 linkages to form 'pseudo-dimers'. These dimers are then connected to each other through a combination of bidentate and bridging bidentate linkages with the tricarboxylic acid molecules. The overall topology thus consists of chains of $[UO_2O_4(H_2O)]_2$ psuedo-dimers propagating along the $[01\bar{1}]$ direction. In between the chains is one water molucule for each of the U centers. Despite the diversity of uranyl–carboxylate structure types, (Leciejewicz *et al.*, 1995), compound (I) contains a novel U–carboxylate connectivity.

Experimental

Uranium oxynitrate hexahydrate and 1,3,5-benzenetricarboxylic acid are available commercially and were used without any further purification. Uranium oxynitrate hexahydrate (0.251 g) and 1,3,5-benzenetricarboxylic acid ($C_9H_6O_6$, 0.105 g) were dissolved in water (1.36 g). The solution (pH 6.03) was prepared in a 23 ml Teflon-lined

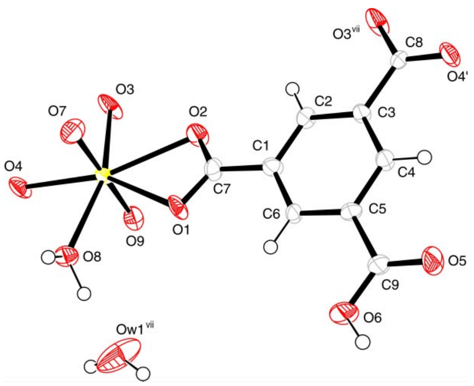


Figure 1

The asymmetric unit of (I), together with symmetry-equivalent atoms to complete the coordination sphere of the U atom. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (vii) $-x$, $-y$, $-z$.]

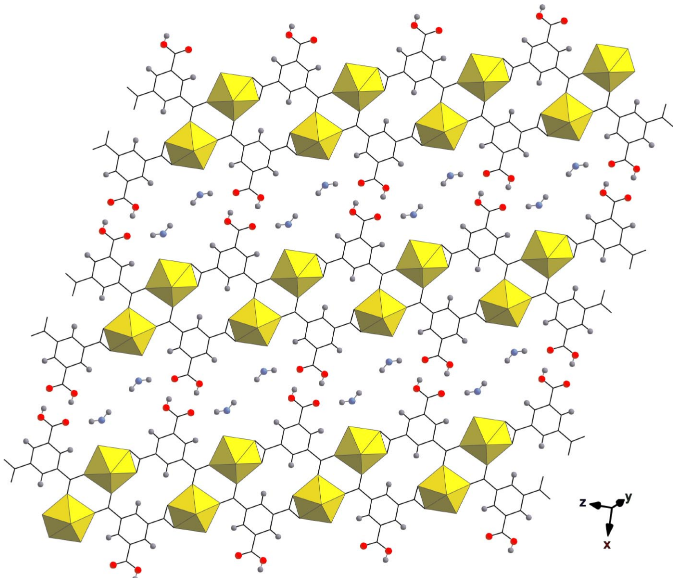


Figure 2

A single plane of (I), showing chains propagating in the $[01\overline{1}]$ direction. The H atoms on O8 have been omitted for clarity. Yellow polyhedra denote U atoms, red spheres O atoms, blue spheres water molecules, grey spheres H atoms; C atoms are black.

Parr bomb and then heated under hydrostatic pressure at 453 K for 3 d. Yellow crystals of (I) formed *in situ*, and they were insoluble in water, ethanol and acetone. Phase purity was confirmed by comparison of the observed and calculated powder X-ray diffraction patterns (*JADE*; Materials Data, 2003). Elemental analysis (Galbraith Laboratories, Knoxville, Tennessee, USA) of (I) confirmed the contents of the structure [observed (calculated): C 21.31 (21.18) and H 1.46% (1.57%)].

Crystal data

$[UO_2(C_9H_4O_6)(H_2O)]\cdot H_2O$
$M_r = 514.18$
Triclinic, $P\overline{1}$
$a = 7.8342$ (6) Å
$b = 8.3781$ (7) Å
$c = 10.6208$ (9) Å
$\alpha = 70.507$ (5)°
$\beta = 75.840$ (5)°
$\gamma = 87.002$ (5)°
$V = 636.85$ (9) Å^3
$Z = 2$
$D_x = 2.681$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1478 reflections
$\theta = 2.6$–24.5°
$\mu = 12.79$ mm^{-1}
$T = 293$ (2) K
Lath, yellow
0.19 × 0.05 × 0.02 mm

Data collection

Bruker APEX CCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{\min} = 0.469$, $T_{\max} = 0.774$
4649 measured reflections
2589 independent reflections
2237 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 26.4°$
$h = -8 \rightarrow 9$
$k = -10 \rightarrow 9$
$l = -13 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.071$
$S = 1.18$
2589 reflections
193 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0071P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.69$ e Å^{-3}
$\Delta\rho_{\min} = -2.01$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

U1—O9	1.741 (6)	U1—O8	2.396 (5)
U1—O7	1.750 (6)	U1—O1	2.463 (6)
U1—O3	2.315 (5)	U1—O2	2.465 (6)
U1—O4	2.323 (6)		
O9—U1—O7	178.9 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8A···O1^{i}	0.97 (7)	1.77 (7)	2.732 (8)	172 (9)
O8—H8B···OW1^{ii}	0.97 (5)	1.66 (5)	2.624 (10)	176 (9)
O6—H6···O5^{iii}	0.82	1.85	2.669 (8)	176
OW1—HW1···O7^{iv}	0.97 (11)	2.25 (8)	3.086 (10)	144 (11)
OW1—HW1···O7^{v}	0.97 (11)	2.36 (11)	2.987 (10)	122 (10)
OW1—HW2···O9	0.97 (9)	2.42 (11)	3.083 (10)	125 (10)
OW1—HW2···O5^{vi}	0.97 (9)	2.53 (10)	3.280 (12)	134 (10)
OW1—HW2···O3	0.97 (9)	2.64 (10)	3.363 (11)	131 (10)

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

H atoms on the ligand were placed in calculated positions, whereas those on atoms OW1 and O8 were located in a difference Fourier map. The bond distances to H were fixed at 0.93 Å for the C atoms, 0.83 Å for atom O6, and 0.97 Å for atoms O8 and OW1, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) and $1.5U_{\rm eq}$(O). Residual electron density (~1.7 e Å^{-3}) was found within 1.7 Å of the U center and is likely to be an artifact of the heavy atom site. The deepest hole can be found 1.50 Å from H6A. The crystal remained stable thoughout the data collection.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SIR*92 (Altomare et al., 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CrystalMaker* (CrystalMaker, 2003); software used to prepare material for publication: *WINGX* (Farrugia, 1999).

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