A second polymorph of catena-poly[[aquadioxidouranium(VI)]bis(μ-methanesulfonato-κ²O:O′)]

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The monoclinic (space group $P2_1/c$) title compound, $[UO_2(CH_3O_3S)_2(H_2O)]_n$, is a polymorphic modification of the known orthorhombic (space group $Pbcn$) variant of this stoichiometry [Wilson (1978). *Acta Cryst.* B**34**, 2302–2303]. The crystal structure consists of infinite $[UO_2(CH_3SO_3)_2(H_2O)]$ chains along the a axis. The coordination polyhedron of the U atom is a pentagonal bipyramid, whose equatorial plane consists of the O atoms of four methanesulfonate anions and one water molecule. The axial positions are occupied by O atoms of a nearly linear and symmetrical uranyl group. The methanesulfonate anions function as bidentate bridging ligands. The crystal structure involves intermolecular O—H···O hydrogen bonds.

Related literature

In contrast to the title compound, the corresponding structure of the known orthorhombic polymorph contains infinite $[(UO_2)(CH_3SO_3)_2(H_2O)]$ layers (Wilson, 1978).
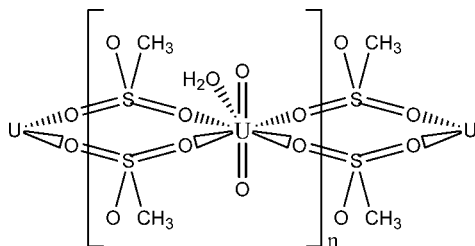
Experimental

Crystal data

$[U(CH_3O_3S)_2O_2(H_2O)]$	Monoclinic, $P2_1/c$
$M_r = 478.23$	$a = 11.2613$ (4) Å
$b = 7.9178$ (3) Å	Mo $K\alpha$ radiation
$c = 10.9061$ (4) Å	$\mu = 17.37$ mm^{-1}
$\beta = 99.261$ (1)°	$T = 100$ (2) K
$V = 959.76$ (6) Å^3	$0.20 \times 0.19 \times 0.16$ mm
$Z = 4$	

Data collection

Bruker Kappa APEXII area-detector diffractometer	10118 measured reflections
Absorption correction: numerical (*APEX2*; Bruker, 2006)	4958 independent reflections
$T_{min} = 0.039$, $T_{max} = 0.062$	4559 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.054$	
$S = 1.04$	$\Delta\rho_{max} = 3.27$ e Å^{-3}
4958 reflections	$\Delta\rho_{min} = -3.39$ e Å^{-3}
135 parameters	
2 restraints	

Table 1
Selected geometric parameters (Å, °).

U1—O1	1.7570 (19)	U1—O4^{ii}	2.3806 (19)
U1—O2	1.760 (2)	U1—O5	2.3857 (15)
U1—O6	2.3772 (17)	U1—O9	2.4670 (19)
U1—O8^i	2.3804 (17)		
O1—U1—O2	179.37 (9)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O9—H8···O3^{iii}	0.80 (4)	1.94 (2)	2.717 (3)	164 (5)
O9—H7···O7^{iv}	0.80 (5)	2.09 (4)	2.791 (3)	145 (7)

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *APEX2*; software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2245).

References

Bruker (2006). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Wilson, A. S. (1978). *Acta Cryst.* B**34**, 2302–2303.

supplementary materials

A second polymorph of *catena*-poly[[aquadioxidouranium(VI)]bis($^{\mu}$-methanesulfonato-κ^2O:*O*')]

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Comment

The structure of the title compound, (I), is shown in Fig. 1. The uranyl group is near linear and symmetrical. Coordination polyhedron of uranium atom is pentagonal bipyramide. Its equatorial plane is formed by oxygen atoms of one water molecule and four different methanesulfonate anions. The equatorial U—O distances are equal to 2.3772 (17)–2.3857 (15) and 2.4671 (18) Å for oxygen atoms of CH_3SO_3 anions and water molecule, respectively. Methanesulfonate anions function as bidentate bridging ligands linking adjacent uranium coordination polyhedra into infinite chains parallel to [100] (Figs. 2 and 3). In contrast to the compound (I), the corresponding structure of the known orthorhombic polymorph (II) contains infinite [(UO$_2$)(CH$_3$SO$_3$)$_2$(H$_2$O)] layers (Fig. 4; Wilson, 1978).

Experimental

The title compound (I) was obtained unintentionally as the product of an attempted synthesis of uranyl methanesulfonate with guanidinium cation in the outer sphere. 50 mg (0.175 mmol) of uranium oxide UO_3 was dissolved in 0.7 ml of 0.5 *M* methanesulfonic acid. Then 0.175 ml of 0.5 *M* solution of diguanidinium carbonte neutralized by 0.35 ml of 0.5 *M* methanesulfonic acid was added. The guanidinium:U molar ratio in the resulting mixture is 1:1. The single crystals were obtained after 2 days of isothermal (at ~22 °C) evaporation of the solution.

NIR/Vis and IR spectra were measured using Shimadzu UV3100 and Specord M80 spectrometers, respectively. The vibration frequencies of functional groups SO$_3$ and CS are slightly shifted to higher energies as compared to the free methanesulfonic acid. The stretching vibrations of UO_2^{2+} group are observed in typical for uranyl compounds region. The vibration frequencies (cm^{-1}) and their assignments: 3340, 3236m - ν(HOH); 1236 s, 1138 s - ν$_{as}$(SO$_3$); 3028w - ν$_{as}$(CH$_3$); 1098 s, 1052 s - ν$_s$(SO$_3$); 2944w - ν$_s$(CH$_3$), 980vw - ρ(CH$_3$); 1644$m-$ d(H$_2$O); 942m, 915s h - ν (UO$_2^{2+}$); 1422$m-$ d(CH$_3$); 790m - ν(CS); 1332w− d$_s$(CH$_3$); 560m, 528w− d(SO$_3$).

Refinement

H atoms of water molecule were located in a difference map and refined isotropically, with distance restraints of O–H = 0.82 (2) Å. Other H atoms were treated as riding atoms, with distances C–H = 0.98 (CH$_3$), and with U_{iso}(H) = $1.2U_{eq}$(C). The highest residual electron density peak and the deepest hole are located 0.67 and 0.45 Å, respectively, from atom U1.
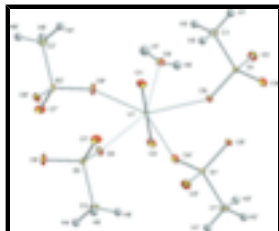
supplementary materials

Figures

Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms [symmetry codes: (i) $-x + 2$, $-y$, $-z$; (ii) $-x + 1$, $-y$, $-z$].

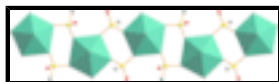

Fig. 2. Polyhedral representation of the infinite chains parallel to [100] in the structure of (I). H atoms have been omitted.
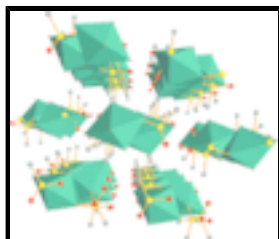

Fig. 3. The packing of infinite chain in the structure of (I), viewed down the *a* axis. H atoms have been omitted.
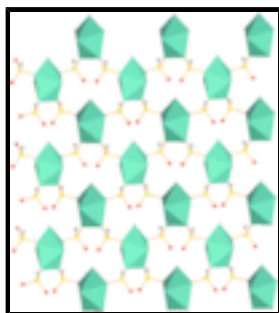
Fig. 4. Polyhedral representation of the infinite sheets in the structure of (II). H atoms have been omitted.

***catena*-poly[[aquadioxidouranium(VI)]bis(µ-methanesulfonato-$\kappa^2O:O'$)]**

Crystal data

$[U(CH_3O_3S_1)_2O_2(H_2O)]$	$F_{000} = 864$
$M_r = 478.23$	$D_x = 3.310$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 7994 reflections
$a = 11.2613 (4)$ Å	$\theta = 2.4–42.7°$
$b = 7.9178 (3)$ Å	$\mu = 17.37$ mm^{-1}
$c = 10.9061 (4)$ Å	$T = 100 (2)$ K
$\beta = 99.261 (1)°$	Prism, yellow
$V = 959.76 (6)$ Å^3	$0.20 \times 0.19 \times 0.16$ mm
$Z = 4$	

Data collection

Bruker Kappa APEXII area-detector diffractometer	4559 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.018$
$T = 100(2)$ K	$\theta_{max} = 37.5°$
φ and ω scans	$\theta_{min} = 3.2°$
Absorption correction: numerical (*APEX2*; Bruker, 2006)	$h = -19 \rightarrow 15$
$T_{min} = 0.039$, $T_{max} = 0.062$	$k = -8 \rightarrow 13$
10118 measured reflections	$l = -18 \rightarrow 18$
4958 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.022$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 1.1P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
4958 reflections	$\Delta\rho_{max} = 3.27$ e Å^{-3}
135 parameters	$\Delta\rho_{min} = -3.39$ e Å^{-3}
2 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
U1	0.752778 (6)	0.121075 (10)	0.011327 (7)	0.00498 (3)
S2	0.94159 (4)	−0.25209 (7)	0.04481 (5)	0.00625 (8)
S1	0.43671 (4)	0.23068 (7)	−0.10448 (5)	0.00632 (8)

O5	0.54270 (14)	0.1816 (2)	−0.01433 (17)	0.0090 (3)
O6	0.90791 (14)	−0.0786 (2)	0.07588 (19)	0.0093 (3)
O4	0.33894 (16)	0.1091 (3)	−0.1009 (2)	0.0164 (4)
O7	0.86707 (16)	−0.3194 (3)	−0.06341 (19)	0.0128 (3)
O2	0.77899 (15)	0.2103 (2)	0.16107 (19)	0.0118 (3)
O3	0.39990 (17)	0.4020 (2)	−0.0874 (2)	0.0133 (3)
O1	0.72636 (16)	0.0298 (2)	−0.13744 (18)	0.0109 (3)
O8	1.07021 (15)	−0.2558 (2)	0.0337 (2)	0.0146 (4)
C1	0.4747 (2)	0.2170 (3)	−0.2535 (2)	0.0118 (4)
H2	0.5419	0.2934	−0.2597	0.014*
H1	0.4052	0.2490	−0.3151	0.014*
H3	0.4983	0.1008	−0.2691	0.014*
C2	0.9270 (2)	−0.3769 (3)	0.1739 (3)	0.0116 (4)
H6	0.8598	−0.3353	0.2123	0.014*
H4	1.0015	−0.3712	0.2342	0.014*
H5	0.9117	−0.4942	0.1474	0.014*
O9	0.70849 (15)	0.4086 (2)	−0.0706 (2)	0.0099 (3)
H8	0.666 (3)	0.467 (5)	−0.036 (4)	0.024 (11)*
H7	0.759 (4)	0.465 (7)	−0.095 (6)	0.029 (12)*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.00484 (3)	0.00440 (4)	0.00563 (4)	−0.00024 (2)	0.00061 (2)	−0.00022 (2)
S2	0.00544 (16)	0.0047 (2)	0.0088 (2)	−0.00047 (15)	0.00190 (15)	0.00041 (16)
S1	0.00586 (17)	0.0063 (2)	0.0068 (2)	0.00020 (15)	0.00102 (15)	0.00188 (16)
O5	0.0060 (5)	0.0124 (8)	0.0081 (7)	0.0013 (5)	0.0001 (5)	0.0020 (6)
O6	0.0087 (6)	0.0060 (7)	0.0127 (8)	0.0014 (5)	0.0006 (5)	−0.0001 (6)
O4	0.0082 (6)	0.0165 (9)	0.0232 (11)	−0.0041 (6)	−0.0015 (6)	0.0119 (7)
O7	0.0174 (7)	0.0103 (8)	0.0100 (8)	−0.0035 (6)	0.0001 (6)	−0.0004 (6)
O2	0.0123 (7)	0.0127 (8)	0.0096 (8)	0.0020 (6)	−0.0005 (6)	−0.0022 (6)
O3	0.0174 (8)	0.0102 (8)	0.0125 (9)	0.0057 (6)	0.0034 (6)	−0.0011 (6)
O1	0.0149 (7)	0.0083 (7)	0.0089 (8)	0.0010 (5)	0.0000 (6)	−0.0010 (6)
O8	0.0072 (6)	0.0082 (8)	0.0301 (12)	0.0019 (5)	0.0083 (6)	0.0045 (7)
C1	0.0153 (9)	0.0131 (10)	0.0072 (9)	0.0020 (7)	0.0024 (7)	0.0001 (8)
C2	0.0142 (9)	0.0096 (10)	0.0110 (10)	0.0004 (7)	0.0023 (7)	0.0030 (8)
O9	0.0099 (6)	0.0059 (7)	0.0144 (9)	0.0000 (5)	0.0036 (6)	0.0006 (6)

Geometric parameters (Å, °)

U1—O1	1.7570 (19)	S1—O4	1.4677 (19)
U1—O2	1.760 (2)	S1—O5	1.4712 (18)
U1—O6	2.3772 (17)	S1—C1	1.749 (3)
U1—O8[i]	2.3804 (17)	C1—H2	0.9800
U1—O4[ii]	2.3806 (19)	C1—H1	0.9800
U1—O5	2.3857 (15)	C1—H3	0.9800
U1—O9	2.4670 (19)	C2—H6	0.9800
S2—O7	1.436 (2)	C2—H4	0.9800

S2—O8	1.4733 (16)	C2—H5	0.9800
S2—O6	1.4789 (19)	O9—H8	0.80 (4)
S2—C2	1.749 (3)	O9—H7	0.80 (5)
S1—O3	1.439 (2)		
O1—U1—O2	179.37 (9)	O6—S2—C2	106.25 (12)
O1—U1—O6	90.41 (8)	O3—S1—O4	112.44 (12)
O2—U1—O6	89.23 (8)	O3—S1—O5	112.45 (12)
O1—U1—O8^i	90.97 (8)	O4—S1—O5	109.90 (11)
O2—U1—O8^i	89.45 (8)	O3—S1—C1	107.32 (13)
O6—U1—O8^i	76.06 (6)	O4—S1—C1	106.30 (14)
O1—U1—O4^{ii}	92.52 (9)	O5—S1—C1	108.12 (11)
O2—U1—O4^{ii}	86.88 (9)	S1—O5—U1	144.49 (11)
O6—U1—O4^{ii}	73.50 (6)	S2—O6—U1	138.87 (11)
O8^i—U1—O4^{ii}	149.38 (6)	S1—O4—U1^{ii}	152.86 (13)
O1—U1—O5	87.53 (7)	S2—O8—U1^i	151.07 (12)
O2—U1—O5	92.48 (7)	S1—C1—H2	109.5
O6—U1—O5	146.71 (6)	S1—C1—H1	109.5
O8^i—U1—O5	137.16 (6)	H2—C1—H1	109.5
O4^{ii}—U1—O5	73.41 (6)	S1—C1—H3	109.5
O1—U1—O9	92.91 (8)	H2—C1—H3	109.5
O2—U1—O9	87.67 (8)	H1—C1—H3	109.5
O6—U1—O9	144.79 (6)	S2—C2—H6	109.5
O8^i—U1—O9	68.85 (6)	S2—C2—H4	109.5
O4^{ii}—U1—O9	141.19 (6)	H6—C2—H4	109.5
O5—U1—O9	68.49 (6)	S2—C2—H5	109.5
O7—S2—O8	112.15 (13)	H6—C2—H5	109.5
O7—S2—O6	113.29 (11)	H4—C2—H5	109.5
O8—S2—O6	109.22 (10)	U1—O9—H8	118 (3)
O7—S2—C2	109.49 (12)	U1—O9—H7	121 (5)
O8—S2—C2	106.03 (12)	H8—O9—H7	110 (6)

Symmetry codes: (i) −x+2, −y, −z; (ii) −x+1, −y, −z.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O9—H8···O3^{iii}	0.80 (4)	1.94 (2)	2.717 (3)	164 (5)
O9—H7···O7^{iv}	0.80 (5)	2.09 (4)	2.791 (3)	145 (7)

Symmetry codes: (iii) −x+1, −y+1, −z; (iv) x, y+1, z.

Fig. 1

Fig. 2

Fig. 3

Fig. 4