



Crystal structure of a trigonal polymorph of aqua-dioxidobis(pentane-2,4-dionato- κ^2O,O')-uranium(VI)

Alejandro Hernandez, Indranil Chakraborty, Gabriela Ortega and Christopher J. Dares*

Received 24 September 2021

Accepted 21 October 2021

Edited by J. Ellena, Universidade de São Paulo, Brazil

Keywords: crystal structure; uranium complex; dioxo species; X-ray structure; hydrogen bonding.

CCDC reference: 2117155

Supporting information: this article has supporting information at journals.iucr.org/e

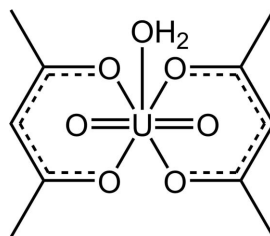
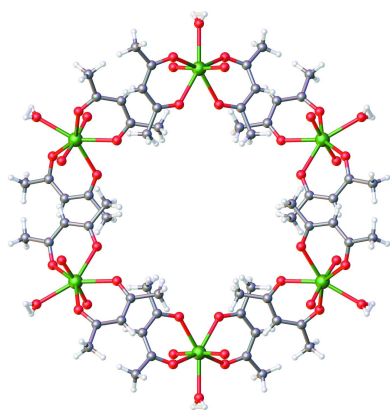
Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th St., Miami, FL 33199, USA.

*Correspondence e-mail: cdares@fiu.edu

The title compound, $[\text{UO}_2(\text{acac})_2(\text{H}_2\text{O})]$ consists of a uranyl(VI) unit ($[\text{O}=\text{U}=\text{O}]^{2+}$) coordinated to two monoanionic acetylacetonate (acac, $\text{C}_5\text{H}_7\text{O}_2$) ligands and one water molecule. The asymmetric unit includes a one-half of a uranium atom, one oxido ion, one-half of a water molecule and one acac ligand. The coordination about the uranium atom is distorted pentagonal-bipyramidal. The acac ligands and O_w atom comprise the equatorial plane, while the uranyl O atoms occupy the axial positions. Intermolecular hydrogen bonding between complexes results in the formation of two-dimensional hexagonal void channels along the *c*-axis direction with a diameter of 6.7 Å. The monoclinic ($P2_1/c$ space group) polymorph was reported by Alcock & Flanders [(1987). *Acta Cryst.* **C43**, 1480–1483].

1. Chemical context

Nuclear forensics applications often require the development of source materials for isotope-dilution mass-spectrometry measurements. One method for preparing actinide source materials includes the preparation of volatile compounds which can be deposited onto a conductive surface from the vapor phase. An alternative method involves electrochemical reduction to the zero-valent metal with concurrent deposition onto the electrode surface. This requires an organo-soluble actinide precursor. Hexavalent actinide complexes with β -diketonates are possibilities for either of these methods. They are neutrally charged, and with appropriate substituents on the β -diketonate may be volatile (Johnson *et al.*, 2017). β -Diketonates also provide a platform to prepare the organo-soluble precursors required for electrochemical reduction.



2. Structural commentary

The molecular structure of the title compound, $[\text{UO}_2(\text{acac})_2(\text{H}_2\text{O})]$ **1**, was determined by single crystal X-ray



Table 1
 Selected geometric parameters (Å, °).

U1–O4	2.392 (4)	U1–O2	2.361 (3)
U1–O1	2.381 (2)	U1–O3	1.769 (2)
O1–U1–O4	75.17 (6)	O3–U1–O1 ⁱ	86.27 (10)
O1 ⁱ –U1–O1	150.33 (12)	O3–U1–O1	92.50 (11)
O2–U1–O4	144.24 (7)	O3–U1–O2	86.10 (11)
O2 ⁱ –U1–O1	139.25 (9)	O3 ⁱ –U1–O2	97.81 (12)
O2–U1–O1	70.00 (9)	O3–U1–O3 ⁱ	175.21 (17)
O3–U1–O4	87.61 (9)		

 Symmetry code: (i) $x - y, -y, -z + \frac{3}{2}$.

diffraction. An *ORTEP* plot of the molecular structure is shown in Fig. 1 and selected geometric parameters are listed in Table 1. The complex crystallizes in the trigonal $P\bar{3}c1$ space group with one-half molecule per asymmetric unit, while the other half is generated by a twofold axis running through the U and O_w atoms. In the molecular structure, the U^{VI} center resides in a distorted pentagonal–bipyramidal coordination environment, with the equatorial positions occupied by the four O atoms of two chelating monoanionic acac ligands, and one water molecule, while the two oxido ions reside at the axial positions *trans* to each other. The equatorial plane composed of O1, O2 (and the two other symmetry-equivalent atoms) and O4 deviates noticeably from planarity [with a mean deviation of 0.172 (3) Å]. The two six-membered chelate rings composed of U1, O1, C1, C2, C3 and the symmetry-equivalent atoms deviate significantly from planarity [mean deviation, 0.211 (3) Å]. The dihedral angle between the two chelate best-fit planes is 26.02 (13)°.

3. Supramolecular features

Examination of the extended structure revealed a prominent intermolecular hydrogen bonding interaction (O4–H4···O1) involving one of the O atoms of the acac ligand and the O_w atom (Fig. 2, Table 2). This interaction results in pairing of two

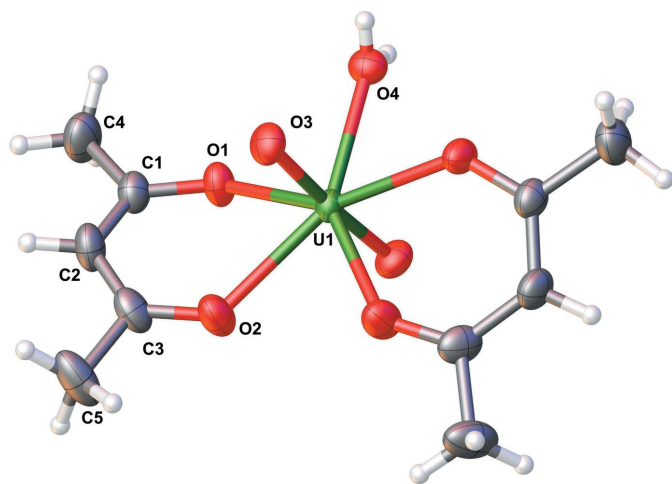

Figure 1
 Molecular structure of aquadioxidobis(pentane-2,4-dionato- κ^2O,O')uranium(VI). Displacement ellipsoids are drawn at the 50% probability level.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4–H4···O1 ⁱⁱ	0.72 (6)	2.01 (5)	2.704 (3)	164 (7)

 Symmetry code: (ii) $-x + 1, -y, -z + 1$.

mononuclear units, eventually consolidating the extended structure. The packing pattern along the *c*-axis direction reveals an extended pattern with considerably large hexagonal void channels, each one surrounded by six other smaller void channels. The void volume was determined using contact surface maps (which offer an estimate of the volume that could be filed by guest molecules) to be 325.41 Å³, representing 13.4% of the unit-cell volume (Barbour, 2006). This interesting packing pattern is shown in Figs. 3 and 4.

4. Database survey

A scrutiny of the CSD (*Conquest* version 2.0, 2021; Groom *et al.*, 2016) revealed two other crystal structures of [UO₂(acac)₂(H₂O)], **2** and **3**, available for comparison [there are few others for which coordinates are not available, see: Dornberger-Schiff & Titze (1969) and Comyns *et al.* (1958)]. Structure **2** is a polymorph of **1**, while structure **3** is a pyrazine solvate of [UO₂(acac)₂(H₂O)]. Selected metric parameters of **1–3** are listed in Table 3. Structures **1** and **2** differ in their crystal packing arrangement. Whereas **1** crystallizes in the trigonal $P\bar{3}c1$ space group with half a molecule per asymmetric

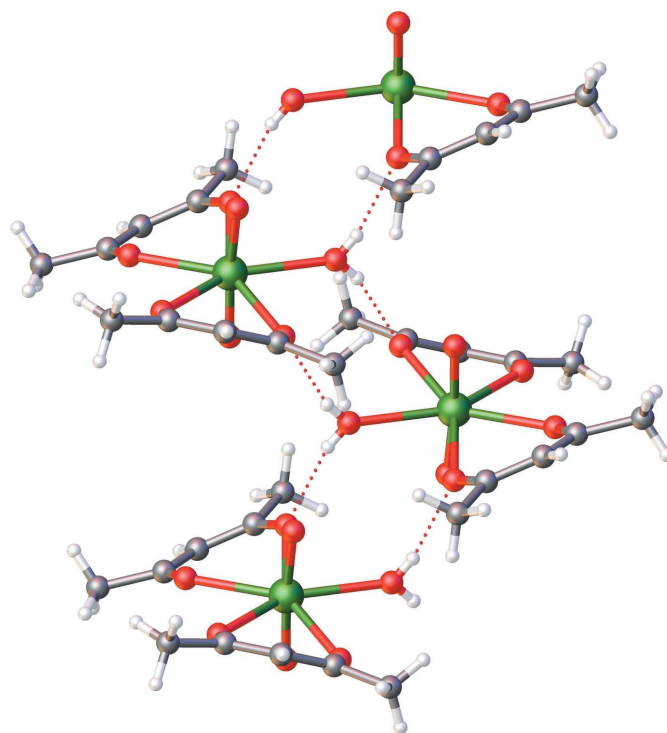

Figure 2
 Representation of the O–H···O intermolecular hydrogen-bonding interactions in aquadioxidobis(pentane-2,4-dionato- κ^2O,O')uranium(VI)

Table 3
Comparison of selected metric parameters (Å).

	1 ^a	2 ^b	3 ^c
U—O(H ₂ O)	2.392 (4)	2.489 (8)	2.409 (4)
U=O(oxo)	1.769 (2)	1.743 (6)	1.776 (3)
U—O(acac)	2.371 (3)	2.339 (6)	2.354 (4)

Notes: (a) this work; (b) Alcock & Flanders (1987); (c) Kawasaki & Kitazawa (2008).

unit, **2** crystallizes in the monoclinic $P2_1/c$ space group with the asymmetric unit consisting of the complete molecule (Alcock & Flanders, 1987). The differences in metric parameters between structures **1** and **2** are subtle (albeit with a slightly longer U—O_w distance in **2**), the differences being attributed to the different crystal packing. In case of **1**, classical hydrogen bonding dictates the packing pattern, while in **2**, the intermolecular interactions are chemically inconsequential. Structure **3** is also quite similar to **1** and **2**. However, **3** crystallizes in the triclinic $P\bar{1}$ space group with one interstitial pyrazine molecule (the asymmetric unit contains the full [UO₂(acac)₂(H₂O)] molecule and two half-molecules of pyrazine). The pyrazine molecules within the structure are engaged in hydrogen bonding with the coordinated water molecule [O_w—H—N(pyrazine), H···N = 1.95 (2) Å and O_w···N = 2.765 (5) Å; Kawasaki & Kitazawa 2008], thus preventing the supramolecular organization of the uranium complex (seen in **1**). Interestingly, the lower density of **1** compared to those of **2** and **3** (1.99, 2.27 and 2.03 g cm⁻³ for **1**, **2**, and **3** respectively) is attributed to the large voids within the hexagonal channels.

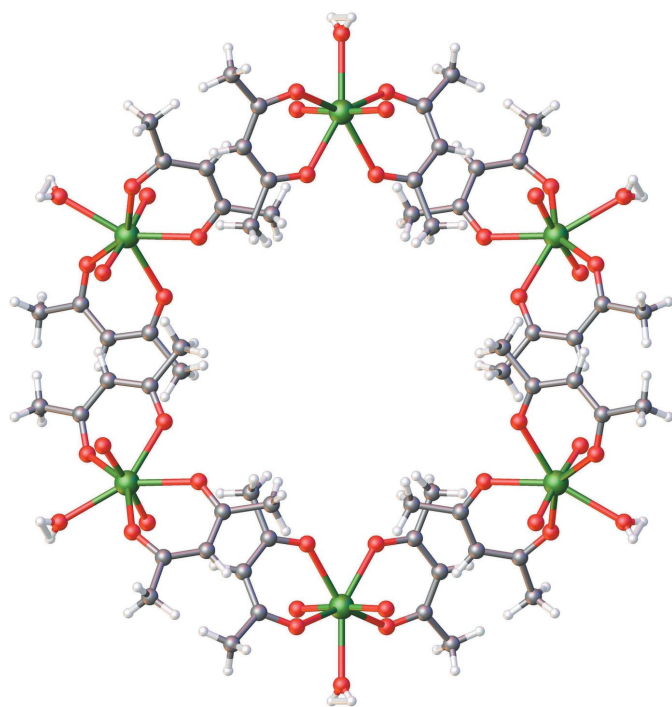


Figure 3
Formation of a ring structure extracted from the packing pattern of aquadioxidobis(pentane-2,4-dionato-κ²O,O')uranium(VI).

Table 4
Experimental details.

Crystal data	
Chemical formula	[UO ₂ (C ₅ H ₇ O ₂) ₂ (H ₂ O)]
<i>M_r</i>	486.26
Crystal system, space group	Trigonal, $P\bar{3}c1$
Temperature (K)	298
<i>a</i> , <i>c</i> (Å)	19.5774 (9), 7.3264 (5)
<i>V</i> (Å ³)	2431.8 (3)
<i>Z</i>	6
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	10.03
Crystal size (mm)	0.30 × 0.15 × 0.05
Data collection	
Diffractometer	Bruker D8 Quest PHOTON II
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.457, 0.745
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	26571, 1493, 1426
<i>R</i> _{int}	0.027
(sin θ/λ) _{max} (Å ⁻¹)	0.603
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.016, 0.042, 1.13
No. of reflections	1493
No. of parameters	89
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.51, -1.06

Computer programs: APEX3 and SAINT (Bruker, 2016), SHELXT2018/2 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), and OLEX2 (Dolomanov *et al.*, 2009).

5. Synthesis and crystallization

To a vial containing 377 mg (3.8 mmol) of 2,4-pentanedione (acac) in 7 mL of THF was added 20 mL of an aqueous

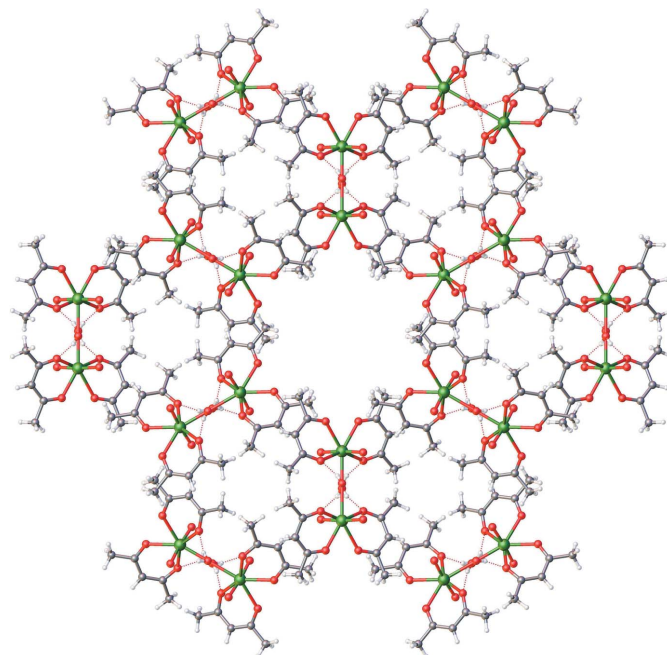


Figure 4
Packing pattern of aquadioxidobis(pentane-2,4-dionato-κ²O,O')uranium(VI) along the *c* axis.

solution containing 0.94 mmol of $\text{UO}_2(\text{OAc})_2(\text{H}_2\text{O})_2$. The reaction mixture rapidly changed color from colorless to yellow. A 10 M aqueous solution of KOH was added dropwise to the reaction mixture until the pH was approximately 9 (500 μL). The color of the solution intensified to a dark yellow concurrent with the formation of a suspension. The suspension was extracted with 50 mL of toluene, and the resultant yellow organic solution was dried over Na_2SO_4 . After reducing the volume by 50% at reduced pressure, the remaining solution was allowed to evaporate at room temperature. Over the course of 1 week, yellow crystals were formed (150 mg, 34% yield).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The water O atom was freely refined. C-bound H atoms were positioned geometrically ($\text{C}-\text{H} = 0.03-0.96$) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2-1.5U_{\text{eq}}(\text{C})$.

Funding information

Funding for this research was provided by: Idaho National Laboratory (contract No. 18A12-107); U.S. Nuclear Regulatory Commission (grant No. 31310018M0012).

References

- Alcock, N. W. & Flanders, D. J. (1987). *Acta Cryst.* **C43**, 1480–1483.
- Barbour, L. J. (2006). *Chem. Commun.* pp. 1163–1168.
- Bruker (2016). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Comyns, A. E., Gatehouse, B. M. & Wait, E. (1958). *J. Chem. Soc.* 4655–4665.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Dornberger-Schiff, K. & Titze, H. (1969). *Acta Chem. Scand.* **23**, 1685–1694.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Johnson, A. T., Parker, T. G., Dickens, S. M., Pfeiffer, J. K., Oliver, A. G., Wall, D., Wall, N. A., Finck, M. R. & Carney, K. P. (2017). *Inorg. Chem.* **56**, 13553–13561.
- Kawasaki, T. & Kitazawa, T. (2008). *Acta Cryst.* **E64**, m673–m674.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.

supporting information

Acta Cryst. (2022). E78, 40-43 [https://doi.org/10.1107/S2056989021011063]

Crystal structure of a trigonal polymorph of aquadioxidobis(pentane-2,4-dionato- κ^2O,O')uranium(VI)

Alejandro Hernandez, Indranil Chakraborty, Gabriela Ortega and Christopher J. Dares

Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Aquadioxidobis(pentane-2,4-dionato- κ^2O,O')uranium(VI)

Crystal data

[UO₂(C₅H₇O₂)₂(H₂O)]

$M_r = 486.26$

Trigonal, $P\bar{3}c1$

$a = 19.5774$ (9) Å

$c = 7.3264$ (5) Å

$V = 2431.8$ (3) Å³

$Z = 6$

$F(000) = 1344$

$D_x = 1.992$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9890 reflections

$\theta = 3.2\text{--}25.4^\circ$

$\mu = 10.03$ mm⁻¹

$T = 298$ K

Needle, yellow

$0.30 \times 0.15 \times 0.05$ mm

Data collection

Bruker D8 Quest PHOTON II
diffractometer

ω -scan

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.457$, $T_{\max} = 0.745$

26571 measured reflections

1493 independent reflections

1426 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 25.4^\circ$, $\theta_{\min} = 3.5^\circ$

$h = -23 \rightarrow 23$

$k = -23 \rightarrow 23$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.016$

$wR(F^2) = 0.042$

$S = 1.13$

1493 reflections

89 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 3.5627P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.51$ e Å⁻³

$\Delta\rho_{\min} = -1.06$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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. A suitable crystal of [UO₂(acac)₂(H₂O)] was selected and mounted on a Bruker D8 Quest diffractometer. The crystal was kept at 298.0?K during data collection. Using Olex2 (Dolomanov, 2009) the structure was solved with the SHELXT (Sheldrick 2015) structure solution program using Intrinsic Phasing and refined with the SHELXL (Sheldrick 2015) refinement package using Least Squares minimisation.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
U1	0.38611 (2)	0.000000	0.750000	0.03158 (8)
O4	0.5083 (2)	0.000000	0.750000	0.0415 (8)
O1	0.45776 (16)	0.08101 (15)	0.4979 (3)	0.0442 (6)
O2	0.31937 (16)	0.06227 (16)	0.6287 (4)	0.0525 (7)
O3	0.42991 (16)	0.08004 (14)	0.9047 (3)	0.0453 (6)
C1	0.4697 (2)	0.1489 (2)	0.4498 (5)	0.0437 (9)
C2	0.4199 (3)	0.1769 (2)	0.4902 (6)	0.0524 (10)
H2	0.436802	0.229520	0.464721	0.063*
C3	0.3450 (3)	0.1311 (3)	0.5675 (5)	0.0503 (9)
C4	0.5432 (3)	0.1979 (3)	0.3397 (7)	0.0674 (13)
H4A	0.588238	0.204246	0.406406	0.101*
H4B	0.548844	0.248675	0.316338	0.101*
H4C	0.539460	0.171870	0.225884	0.101*
C5	0.2896 (3)	0.1632 (4)	0.5750 (7)	0.0742 (15)
H5A	0.249096	0.134214	0.663397	0.111*
H5B	0.266109	0.158127	0.457143	0.111*
H5C	0.318349	0.217860	0.609141	0.111*
H4	0.525 (3)	-0.018 (3)	0.694 (7)	0.073 (17)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.03345 (9)	0.02596 (10)	0.03283 (11)	0.01298 (5)	0.00110 (3)	0.00219 (6)
O4	0.0423 (15)	0.044 (2)	0.0383 (19)	0.0222 (10)	-0.0026 (8)	-0.0052 (16)
O1	0.0552 (16)	0.0402 (14)	0.0435 (13)	0.0286 (12)	0.0131 (12)	0.0121 (11)
O2	0.0516 (16)	0.0580 (17)	0.0576 (18)	0.0345 (15)	0.0090 (13)	0.0207 (13)
O3	0.0560 (16)	0.0355 (13)	0.0447 (14)	0.0231 (12)	-0.0011 (12)	-0.0068 (11)
C1	0.054 (2)	0.0369 (19)	0.0394 (19)	0.0223 (18)	0.0035 (16)	0.0077 (15)
C2	0.068 (3)	0.041 (2)	0.054 (2)	0.032 (2)	0.011 (2)	0.0157 (18)
C3	0.071 (3)	0.061 (3)	0.0364 (19)	0.046 (2)	0.0031 (18)	0.0109 (18)
C4	0.062 (3)	0.054 (3)	0.082 (3)	0.025 (2)	0.022 (2)	0.027 (2)
C5	0.097 (4)	0.101 (4)	0.065 (3)	0.080 (3)	0.024 (3)	0.031 (3)

Geometric parameters (Å, °)

U1—O4	2.392 (4)	C1—C2	1.369 (6)
U1—O1	2.381 (2)	C1—C4	1.504 (5)
U1—O1 ⁱ	2.381 (2)	C2—H2	0.9300
U1—O2	2.361 (3)	C2—C3	1.400 (6)
U1—O2 ⁱ	2.361 (3)	C3—C5	1.502 (5)
U1—O3	1.769 (2)	C4—H4A	0.9600
U1—O3 ⁱ	1.769 (2)	C4—H4B	0.9600
O4—H4	0.71 (4)	C4—H4C	0.9600
O4—H4 ⁱ	0.71 (4)	C5—H5A	0.9600
O1—C1	1.279 (4)	C5—H5B	0.9600
O2—C3	1.261 (5)	C5—H5C	0.9600
O1 ⁱ —U1—O4	75.17 (6)	C1—O1—U1	130.3 (2)
O1—U1—O4	75.17 (6)	C3—O2—U1	131.1 (3)
O1 ⁱ —U1—O1	150.33 (12)	O1—C1—C2	124.0 (3)
O2—U1—O4	144.24 (7)	O1—C1—C4	115.4 (4)
O2 ⁱ —U1—O4	144.24 (6)	C2—C1—C4	120.5 (3)
O2 ⁱ —U1—O1	139.25 (9)	C1—C2—H2	118.0
O2—U1—O1 ⁱ	139.25 (9)	C1—C2—C3	124.0 (4)
O2 ⁱ —U1—O1 ⁱ	70.00 (9)	C3—C2—H2	118.0
O2—U1—O1	70.00 (9)	O2—C3—C2	124.0 (4)
O2 ⁱ —U1—O2	71.52 (13)	O2—C3—C5	116.7 (4)
O3—U1—O4	87.61 (9)	C2—C3—C5	119.3 (4)
O3 ⁱ —U1—O4	87.61 (9)	C1—C4—H4A	109.5
O3 ⁱ —U1—O1 ⁱ	92.50 (11)	C1—C4—H4B	109.5
O3—U1—O1 ⁱ	86.27 (10)	C1—C4—H4C	109.5
O3—U1—O1	92.50 (11)	H4A—C4—H4B	109.5
O3 ⁱ —U1—O1	86.27 (10)	H4A—C4—H4C	109.5
O3—U1—O2 ⁱ	97.81 (12)	H4B—C4—H4C	109.5
O3—U1—O2	86.10 (11)	C3—C5—H5A	109.5
O3 ⁱ —U1—O2	97.81 (12)	C3—C5—H5B	109.5
O3 ⁱ —U1—O2 ⁱ	86.10 (11)	C3—C5—H5C	109.5
O3—U1—O3 ⁱ	175.21 (17)	H5A—C5—H5B	109.5
U1—O4—H4 ⁱ	134 (4)	H5A—C5—H5C	109.5
U1—O4—H4	134 (4)	H5B—C5—H5C	109.5
H4—O4—H4 ⁱ	92 (8)		
U1—O1—C1—C2	-26.9 (6)	O1—C1—C2—C3	-8.8 (7)
U1—O1—C1—C4	154.2 (3)	C1—C2—C3—O2	9.1 (7)
U1—O2—C3—C2	27.1 (6)	C1—C2—C3—C5	-169.0 (4)
U1—O2—C3—C5	-154.8 (3)	C4—C1—C2—C3	170.0 (4)

Symmetry code: (i) $x-y, -y, -z+3/2$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O4—H4 \cdots O1 ⁱⁱ	0.72 (6)	2.01 (5)	2.704 (3)	164 (7)

Symmetry code: (ii) $-x+1, -y, -z+1$.