Crystal structure of a trigonal polymorph of aqua-dioxidobis(pentane-2,4-dionato-κ²O,O’)-uranium(VI)

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The title compound, [UO₂(acac)₂(H₂O)] consists of a uranyl(VI) unit ([O≡U≡O]²⁻) coordinated to two monoanionic acetylacetonate (acac, C₅H₇O₂) 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 Ow 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 (P2₁/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-diketone may be volatile (Johnson et al., 2017). β-Diketonates also provide a platform to prepare the organosoluble precursors required for electrochemical reduction.

2. Structural commentary

The molecular structure of the title compound, [UO₂(acac)₂(H₂O)] 1, was determined by single crystal X-ray
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 $P_3c_1$ space group with one-half molecule per asymmetric unit, while the other half is generated by a twofold axis running through the Un and Ow atoms. In the molecular structure, the UVI 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)$^\circ$.

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 Ow atom (Fig. 2, Table 2). This interaction results in pairing of two 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 Å$^3$, 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 $[\text{UO}_2(\text{acac})_2(\text{H}_2\text{O})]$, 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 $[\text{UO}_2(\text{acac})_2(\text{H}_2\text{O})]$. 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 $P_3c_1$ space group with half a molecule per asymmetric unit, 2 crystallizes in the trigonal $P_31$ space group with one molecule per asymmetric unit, and 3 crystallizes in the monoclinic $P2_1/c$ space group with one molecule per asymmetric unit.
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 \( U-O(H_2O) \) 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 \( P\overline{1} \) space group with one interstitial pyrazine molecule (the asymmetric unit contains the full \([UO_2(acac)(H_2O)]\) molecule and two half-molecules of pyrazine). The pyrazine molecules within the structure are engaged in hydrogen bonding with the coordinated water molecule \([O-H\cdots N(pyrazine), H\cdots N = 1.95 (2) \AA \) and \( O\cdots N = 2.765 (5) \AA \); 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.

| Table 3 | Comparison of selected metric parameters (\( \text{Å} \)). |
|---------|-------------------------------------------------------|
|         | 1\(^*\) | 2\(^*\) | 3\(^*\) |
| \( U-O(H_2O) \) | 2.392 (4) | 2.489 (8) | 2.409 (4) |
| \( U=O(\text{oxo}) \) | 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).

Table 4

| Crystal data | Chemical formula | \([UO_2(C_4H_7O_2)_2(H_2O)]\) |
|--------------|-----------------|-------------------------------|
| \( M_r \) | 486.26 | 486.26 |
| Crystal system, space group | Trigonal, \( P\overline{2}c1 \) | Trigonal, \( P\overline{2}c1 \) |
| Temperature (K) | 298 | 298 |
| \( a, c (\text{Å}) \) | 19.5774 (9), 7.3264 (5) | 2431.8 (3) |
| \( V (\text{Å}^3) \) | 6 | 6 |
| Radiation type | Mo K\( \alpha \) | Mo K\( \alpha \) |
| \( \mu (\text{mm}^{-1}) \) | 10.03 | 10.03 |
| Crystal size (mm) | 0.30 \( \times \) 0.15 \( \times \) 0.05 | 0.30 \( \times \) 0.15 \( \times \) 0.05 |

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 solution of \([UO_2(C_4H_7O_2)_2(H_2O)]\) (Hernandez et al., 2022). The solution was stirred for 24 h at room temperature, and the resulting dark brown solid was filtered, washed with diethyl ether, and dried under vacuum.

Figure 3

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

Figure 4

Packing pattern of aquadioxidobis(pentane-2,4-dionato-\( \kappa^2O,O' \))-uranium(VI) along the \( c \) axis.
solution containing 0.94 mmol of UO$_2$(OAc)$_2$(H$_2$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$_2$SO$_4$. 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 (C—H = 0.03–0.96) and refined as riding with $U_{	ext{iso}}$(H) = 1.2–1.5$U_{	ext{eq}}$(C).

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Crystal structure of a trigonal polymorph of aquadioxidobis(pentane-2,4-dionato-κ²O,O')uranium(VI)

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Computing details

Data collection: APEX3 (Bruker, 2016); cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (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-κ²O,O')uranium(VI)

Crystal data

[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2(\text{H}_2\text{O})]

M_r = 486.26

Trigonal, \( P\bar{3}c1 \)

\( a = 19.5774\) (9) Å

\( c = 7.3264\) (5) Å

\( V = 2431.8\) (3) Å³

\( Z = 6 \)

\( F(000) = 1344 \)

\( D_\lambda = 1.992\) Mg m⁻³

Mo Kα radiation, \( \lambda = 0.71073\) Å

Cell parameters from 9890 reflections

\( \theta = 3.2-25.4^\circ \)

\( \mu = 10.03\) mm⁻¹

\( T = 298\) K

Needle, yellow

0.30 × 0.15 × 0.05 mm

Data collection

Bruker D8 Quest PHOTON II diffractometer

\( \omega \)-scan

Absorption correction: multi-scan

(SADABS; Krause et al., 2015)

\( T_{\text{min}} = 0.457, T_{\text{max}} = 0.745 \)

26571 measured reflections

1493 independent reflections

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

\( R_{\text{int}} = 0.027 \)

\( \theta_{\text{max}} = 25.4^\circ, \theta_{\text{min}} = 3.5^\circ \)

\( h = -23\rightarrow23 \)

\( k = -23\rightarrow23 \)

\( l = -8\rightarrow8 \)

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

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

where \( P = (F_c^2 + 2F_s^2)/3 \)

\( \langle\Delta\sigma\rangle_{\text{max}} < 0.001 \)

\( \Delta\rho_{\text{max}} = 0.51\) e Å⁻³

\( \Delta\rho_{\text{min}} = -1.06\) 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 ($\AA^2$)**

|    | x       | y       | z       | $U_{iso}^*/U_{eq}$ |
|----|---------|---------|---------|-------------------|
| 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) |
| O1 | 0.4697 (2)  | 0.1489 (2) | 0.4498 (5) | 0.0437 (9)  |
| O3 | 0.2896 (3)  | 0.1632 (4) | 0.5750 (7) | 0.0742 (15) |
| H2 | 0.436802  | 0.229520 | 0.464721 | 0.063*  |
| C1 | 0.3450 (3)  | 0.1311 (3) | 0.5675 (5) | 0.0503 (9)  |
| H1 | 0.249096  | 0.134214 | 0.663397 | 0.111*  |
| C2 | 0.266109  | 0.158127 | 0.457143 | 0.111*  |
| C5 | 0.318349  | 0.217860 | 0.609141 | 0.111*  |
| H4 | 0.525 (3)  | −0.018 (3) | 0.694 (7) | 0.073 (17)* |

**Atomic displacement parameters ($\AA^2$)**

| U1    | U2    | U3    | U12   | U13   | U23   |
|-------|-------|-------|-------|-------|-------|
| 0.03345 (9) | 0.02596 (10) | 0.03283 (11) | 0.01298 (5) | 0.00110 (3) | 0.00219 (6) |
| 0.0423 (15) | 0.044 (2) | 0.0383 (19) | 0.0222 (10) | −0.0026 (8) | −0.0052 (16) |
| 0.0552 (16) | 0.0402 (14) | 0.0435 (13) | 0.0286 (12) | 0.0131 (12) | 0.0121 (11) |
| 0.0516 (16) | 0.0580 (17) | 0.0576 (18) | 0.0345 (15) | 0.0090 (13) | 0.0207 (13) |
| 0.0560 (16) | 0.0355 (13) | 0.0447 (14) | 0.0231 (12) | −0.0011 (12) | −0.0068 (11) |
| 0.054 (2) | 0.0369 (19) | 0.0394 (19) | 0.0223 (18) | 0.0035 (16) | 0.0077 (15) |
| 0.068 (3) | 0.041 (2) | 0.054 (2) | 0.032 (2) | 0.011 (2) | 0.0157 (18) |
| 0.071 (3) | 0.061 (3) | 0.0364 (19) | 0.046 (2) | 0.0031 (18) | 0.0109 (18) |
| 0.062 (3) | 0.054 (3) | 0.082 (3) | 0.025 (2) | 0.022 (2) | 0.027 (2) |
| 0.097 (4) | 0.101 (4) | 0.065 (3) | 0.080 (3) | 0.024 (3) | 0.031 (3) |

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### Geometric parameters (Å, °)

| Bond/Distance | Value (Å) | Bond/Distance | Value (Å) |
|---------------|-----------|---------------|-----------|
| U1—O4         | 2.392 (4) | C1—C2         | 1.369 (6) |
| U1—O1         | 2.381 (2) | C1—C4         | 1.504 (5) |
| U1—O1'        | 2.381 (2) | C2—H2         | 0.9300    |
| U1—O2         | 2.361 (3) | C2—C3         | 1.400 (6) |
| U1—O2'        | 2.361 (3) | C3—C5         | 1.502 (5) |
| U1—O3         | 1.769 (2) | C4—H4A        | 0.9600    |
| U1—O3'        | 1.769 (2) | C4—H4B        | 0.9600    |
| O4—H4         | 0.71 (4)  | C4—H4C        | 0.9600    |
| O4—H4'        | 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    |

| Angle          | Value (°) |
|---------------|-----------|
| O1i—U1—O4     | 75.17 (6) |
| O1—U1—O4      | 75.17 (6) |
| O1—U1—O1      | 150.33 (12) |
| O2—U1—O4      | 144.24 (7) |
| O2—U1—O4      | 144.24 (6) |
| O2—U1—O1      | 139.25 (9) |
| O2—U1—O1'     | 139.25 (9) |
| O2—U1—O1'     | 70.00 (9) |
| O2—U1—O2      | 71.52 (13) |
| O3—U1—O4      | 87.61 (9) |
| O3—U1—O4      | 87.61 (9) |
| O3—U1—O1      | 92.50 (11) |
| O3—U1—O1'     | 86.27 (10) |
| O3—U1—O1'     | 92.50 (11) |
| O3—U1—O1      | 86.27 (10) |
| O3—U1—O2      | 97.81 (12) |
| O3—U1—O2      | 86.10 (11) |
| O3—U1—O2      | 97.81 (12) |
| O3—U1—O2'     | 86.10 (11) |
| O3—U1—O2'     | 175.21 (17) |
| U1—O4—H4      | 134 (4)   |
| U1—O4—H4      | 134 (4)   |
| H4—O4—H4      | 92 (8)    |

| Symmetry code: (i) $x$, $-y$, $-z+3/2$. |
**Hydrogen-bond geometry (Å, °)**

| D—H···A     | D—H | H···A | D···A  | D—H···A |
|-------------|------|-------|--------|---------|
| O4···H4···O1^ii | 0.72 (6) | 2.01 (5) | 2.704 (3) | 164 (7) |

Symmetry code: (ii) −x+1, −y, −z+1.