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(Dimethylformamide)dioxobis(pentane-2,4-dionato)uranium(VI)

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Key indicators

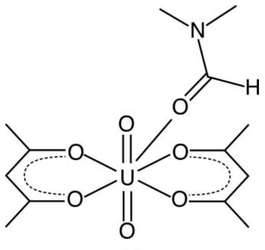
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.009 Å
R factor = 0.028
wR factor = 0.060
Data-to-parameter ratio = 20.7

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

The title complex, $[UO_2(C_5H_7O_2)_2(C_3H_7NO)]$, was obtained as an unexpected product from our attempts to prepare U^{IV} complexes with imine-type ligands. The title complex was also prepared directly from $[UO_2(OAc)_2]\cdot 2H_2O$, pentane-2,4-dione and DMF. The U^{VI} atom has a pentagonal-bipyramidal geometry and is surrounded by seven O atoms. The bond distances and angles are similar to those found previously in similar structures.

Comment

Uranyl β-diketonates with neutral donor ligands have been extensively studied due to interest in the processes of the solvent extraction of uranium from sea water (Shinkai *et al.*, 1987) and both organic and aqueous effluents (Beer *et al.*, 2002). Various uranyl complexes with pentane-2,4-dione have been reported; some of these complexes have solvent molecules such as tetrahydrofuran (Tahir *et al.*., 2006), H_2O (Alcock *et al.*, 1987) and pyridine (Alcock *et al.*, 1984) coordinated to the U atom. One uranyl β-diketonate complex in which *N*,*N*-dimethylformamide (DMF) is coordinated to the U atom has also been reported, but the ligand is 2,2,6,6-tetramethylheptane-3,5-dione (Charpin *et al.*, 1985) instead of pentane-2,4-dione.



(I)

The title complex, (I), crystallizes in a non-centrosymmetric space group. The coordination geometry around the U atom has a standard pentagonal-bipyramidal coordination (Fig. 1). The U—O bond lengths are in the range 1.769 (6)–1.777 (6) Å (mean 1.773 Å) for uranium–oxygen double bonds and 2.327 (5)–2.385 (6) Å (mean 2.354 Å) for U—O$_{acac}$. These are very similar to the values reported previously for (2-*N*-methylaminopentan-4-one)dioxobis(pentane-2,4-dionato)uranium(VI) (Haigh *et al.* 1976) and dioxobis(pentane-2,4-dionato)(tetrahydrofuran)uranium(VI) (Tahir *et al.*, 2006). The U—O$_{DMF}$ bond length [2.404 (4) Å] is longer than other U—O bond lengths found in this structure, but is similar to that in a similar structure (2.402 Å; Charpin *et al.*, 1985). The axial/equatorial O—U—O angles lie in the range 87.61 (17)–

92.1 (2)° and the axial/axial O—U—O angle is 178.37 (19)°, indicating an almost optimal pentagonal–bipyramidal coordination geometry around the U atom.

Experimental

$UO_2(NO_3)_2 \cdot 6H_2O$ (270 mg, 1.2 mmol) was dissolved in dimethylformamide (DMF, 2 ml). 4-[2-(3-Oxobutylideneamino)ethylimino]-butan-2-one (510 mg, 1.0 mmol) was dissolved in DMF (1 ml) and slowly added to the uranium solution. The colour of the solution turned slowly from yellow to light orange. The mixture was stirred at room temperature for 20 min and placed in the refrigerator for a few weeks. Orange crystals suitable for single-crystal X-ray analysis were formed. The complex was also prepared by mixing $[UO_2(OAc)_2] \cdot 2H_2O$ (750 mg, 1.76 mmol) and pentane-2,4-dione (355 mg, 3.55 mmol) in DMF (5 ml) at room temperature. The mixture was stirred for 1 h and then placed in a freezer over night. Orange crystals were filtered off, washed with a small amount of diethyl ether and dried in air (yield: 650 mg, 68%). These crystals gave a satisfactory elemental analysis.

Crystal data

$[UO_2(C_5H_7O_2)_2(C_3H_7NO)]$
$M_r = 541.34$
Orthorhombic, $P2_12_12_1$
$a = 8.5600$ (1) Å
$b = 12.8018$ (3) Å
$c = 15.5510$ (4) Å
$V = 1704.13$ (6) Å^3
$Z = 4$
$D_x = 2.110$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 9.56$ mm^{-1}
$T = 173$ K
Prism, orange
0.15 × 0.10 × 0.08 mm

Data collection

Bruker SMART APEXII diffractometer
φ & ω scans
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.33$, $T_{\max} = 0.47$
12643 measured reflections
4167 independent reflections
3943 reflections with $I > 2.0\sigma(I)$
$R_{\rm int} = 0.056$
$\theta_{\max} = 28.1°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.060$
$S = 0.98$
4154 reflections
201 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + 5.8P]$ where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.85$ e Å^{-3}
$\Delta\rho_{\min} = -1.08$ e Å^{-3}
Extinction correction: Larson (1970), Equation 22
Extinction coefficient: 53 (2)
Absolute structure: Flack (1983), 1788 Friedel pairs
Flack parameter: 0.02 (1)

The reflections were filtered with a limit of acceptance $[\sin(\theta)/\lambda)]^2 > 0.01$, to help eliminate reflections that may be poorly measured in the vicinity of the beam stop. H atoms were all located in a difference map, but those attached to C atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.97 Å) and with $U_{\rm iso}$(H) = 1.2 or 1.5 times $U_{\rm eq}$(parent atom), after which the positions were refined with riding constraints. The deepest residual density hole is located 0.83 Å from atom U1.

Data collection: *COLLECT* (Bruker, 2003); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *CRYSTALS*, CIFTAB (Sheldrick, 1993) and *PLATON*.

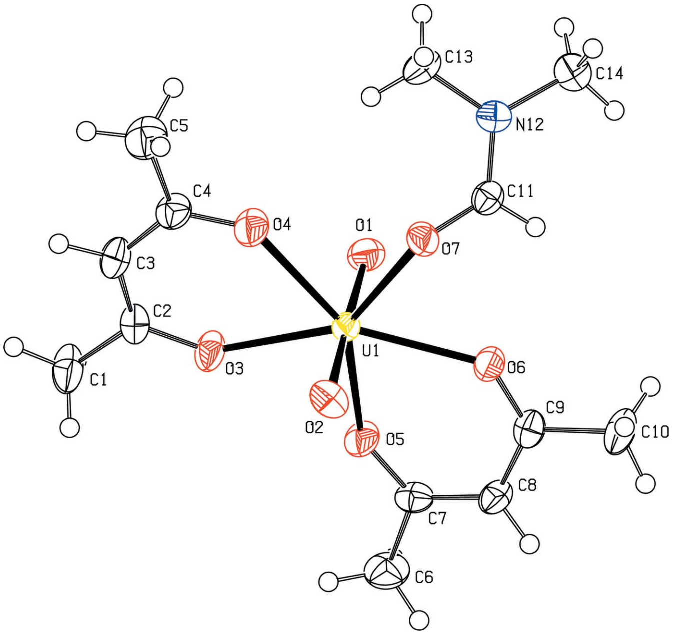


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

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References

Alcock, N. W. & Flanders, D. J. (1987). *Acta Cryst.* C**43**, 1480–1483.
Alcock, N. W., Flanders, D. J. & Brown, D. (1984). *J. Chem. Soc. Dalton Trans.* pp. 679–681.
Beer, P. D., Brindley, G. D., Fox, D. O., Grieve, A., Ogden, M. I., Szemes, F. & Drew, M. G. B. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3101–3111.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Bruker (2003). *COLLECT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Charpin, P., Lance, M., Nierlich, M. & Vigner, D. (1985). *Acta Cryst.* C**41**, 1615–1616.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Haigh, J. M., Nassimbeni, L. R., Pauptit, R. A., Rodgers, A. L. & Sheldrick, G. M. (1976). *Acta Cryst.* B**32**, 1398–1401.
Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
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.
Sheldrick, G. M. (1993). *CIFTAB*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97*. University of Göttingen, Germany.
Shinkai, S., Koreishi, H., Ueada, K., Arimura, T. & Manabe, O. (1987). *J. Am. Chem. Soc.* **109**, 6371–6376.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Tahir, A. A., Hamid, M., Mazhar, M., Zeller, M. & Hunter, A. D. (2006). *Acta Cryst.* E**62**, m1780–m1781.

m414 Huuskonen *et al.* • $[UO_2(C_5H_7O_2)_2(C_3H_7NO)]$ *Acta Cryst.* (2007). E**63**, m413–m414