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(Dibenzyl sulfoxide-κO)bis(1,3-diphenylpropane-1,3-dionato-$\kappa^2 O,O'$)-dioxouranium(VI)

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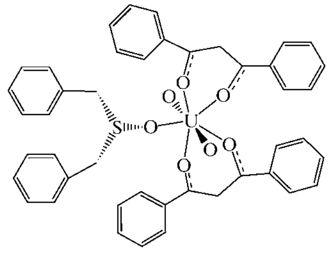
In the title compound, $[UO_2(C_{15}H_{11}O_2)_2(C_{14}H_{14}OS)]$, the U^{VI} atom is coordinated by seven O atoms in a distorted pentagonal–bipyramidal geometry. Both diphenylpropane-1,3-dionate systems are nearly planar. The sulfoxide moiety is in a distorted tetrahedral geometry, while its two aromatic rings are nearly orthogonal to one another. The crystal packing is stabilized by two bifurcated hydrogen-bonding interactions involving both uranyl O atoms.

Comment

The chemistry of adducts of uranyl bis(β-diketonates) with neutral donor ligands is important for understanding the nature of the species extracted during solvent-extraction separation of the uranyl ion using mixtures of β-diketones and neutral ligands (Ramakrishna & Patil, 1984).

We and several other research groups have isolated many of these compounds in the solid state, and these compounds have been characterized by spectroscopic and elemental analysis methods (Subramanian & Viswanatha, 1969; Lu *et al.*, 1977; Taylor & Waugh, 1977; Kramer *et al.*, 1980; Nagar *et al.*, 1989; Kannan & Venugopal, 1995; Kannan, Venugopal, Pillai, Droege & Barnes, 1996; Kannan, Venugopal, Pillai, Droege, Barnes & Schlember, 1996; Kannan *et al.*, 1997, 2000, 2001*a*,*b*; Kannan & Ferguson, 1997; Kannan, 2000). We have also carried out extensive studies on the structures of these compounds using single-crystal X-ray diffraction methods and related the spectroscopic results with the observed structures (Kannan, Venugopal, Pillai, Droege & Barnes, 1996; Kannan, Venugopal, Pillai, Droege, Barnes & Schlember, 1996; Kannan *et al.*, 1997, 2000, 2001*a*,*b*; Kannan & Ferguson, 1997).

Recently, we have prepared adducts of uranyl bis(β-diketonates) with sulfoxide ligands, and found a stronger shielding effect due to the CH_2 H atoms in dibenzyl sulfoxide compared with that in methyl benzyl sulfoxide. However, there are no structural studies to support this spectroscopic observation. As part of our systematic study, we have undertaken the X-ray structure determination of the title compound, (I), at 183 K, and the result is reported here.



(I)

The bond lengths and angles in (I) (Fig. 1) are within normal ranges (Allen *et al.*, 1987). The structure of the molecule shows that the U^{VI} ion is surrounded by seven O atoms in a pentagonal–bipyramidal geometry. Four O atoms (O3, O4, O5 and O6) of the diphenylpropane-1,3-dionate (DBM) moieties, together with atom O7 of the sulfoxide, form a pentagon, while the two uranyl O atoms occupy the apices.

The pentagonal O3/O4/O5/O6/O7 plane is distorted from planarity towards a twisted conformation, with a local twofold axis passing through atom O7 and O3···O6. Atom U1 is displaced by 0.0574 (3) Å from the O3/O4/O5/O6/O7 mean plane. The O—U—O bond angles for the pentagon are in the range 70.5 (2)–74.0 (2)°, while the $O_{pentagon}$—U—O_{apex} angle is 90.0 (3)°. The average U—O_{uranyl} distance is 1.792 Å, and the average U—$O_{diketonate}$ distance is 2.344 Å. These values

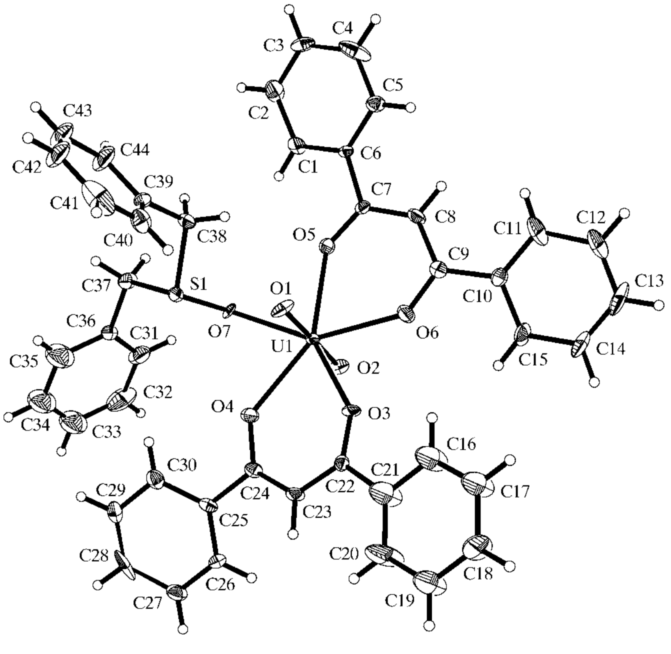


Figure 1
The structure of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

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are acceptable, and agree with previously reported values ($U-O_{uranyl}$ and $U-O_{diketonate}$ in the ranges 1.727–1.788 and 2.308–2.417 Å, respectively; Kannan, Venugopal, Pillai, Droege & Barnes, 1996; Kannan, Venugopal, Pillai, Droege, Barnes & Schlember, 1996; Kannan *et al.*, 1997, 2000, 2001*b*; Kannan & Ferguson, 1997). The $U-O_{sulfoxide}$ bond distance of 2.421 (6) Å is also comparable with values reported earlier for uranyl bis(β-diketonate) sulfoxide complexes [2.375 Å (Kannan, Venugopal, Pillai, Droege & Barnes, 1996) and 2.427 Å (Kannan *et al.*, 2000)].

Both DBM systems in (I) are nearly planar, with their two phenyl rings having slightly different configurations, corresponding to dihedral angles of 13.3 (5) and 30.9 (4)° between the rings in the two DBM systems. The planarity of the DBM system is due to C═O and C—C conjugation in the propane-1,3-dionate moiety joining the two phenyl rings.

The propane-1,3-dionate moieties, together with the U atom, also form six-membered rings, O5/O6/C7/C8/C9/U1 and O3/O4/C22/C23/C24/U1, in which atom U1 is displaced by 0.2082 (3) and 0.3121 (3) Å from the O5/O6/C7/C8/C9 and O3/O4/C22/C23/C24 planes, respectively.

The configuration of the two benzyl moieties is conditioned by the distorted tetrahedral geometry of the sulfoxide moiety. The angles subtended at atom S1 are 97.1 (4), 104.8 (4), and 104.9 (4)°, with S1—O7, S1—C37 and S1—C38 distances of 1.527 (6), 1.817 (9) and 1.831 (9) Å, respectively. The O7···C37, O7···C38 and C37···C38 distances are 2.66 (1), 2.67 (1) and 2.73 (1) Å, respectively. The aromatic rings of the two benzyl moieties are nearly orthogonal, with a dihedral angle of 83.2 (4)°.

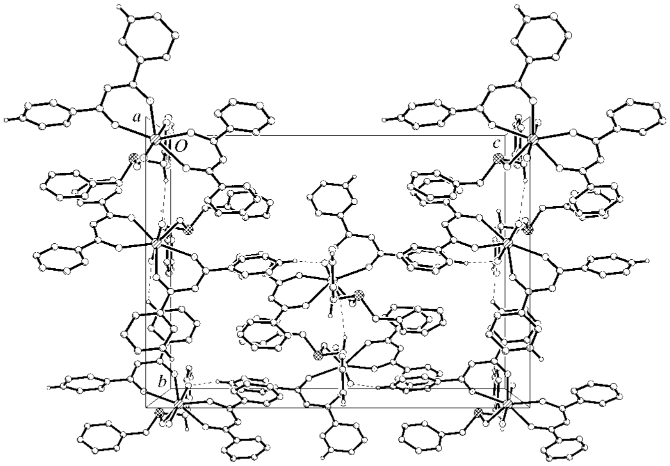

Figure 2
Packing diagram for (I) viewed along the *a* axis.

In the crystal structure of (I), there are hydrogen-bonding interactions involving the two uranyl O atoms (details are in Table 1). These interactions link the molecules into a three-dimensional network (Fig. 2) and, along with dipole–dipole and van der Waals interactions, stabilize the non-centrosymmetric crystal packing.

Experimental

The title compound was prepared and characterized using the method reported by Kannan, Venugopal, Pillai, Droege & Barnes (1996). Crystals of (I) suitable for X-ray diffraction analysis were obtained by slow evaporation of a chloroform–toluene solution.

Crystal data

$[UO_2(C_{15}H_{11}O_2)_2(C_{14}H_{14}OS)]$
M_r = 946.82
Orthorhombic, $P2_12_12_1$
a = 12.3178 (1) Å
b = 15.5281 (1) Å
c = 20.4617 (1) Å
V = 3913.75 (4) Å^3
Z = 4
D_x = 1.607 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
θ = 2.6–28.3°
μ = 4.25 mm^{-1}
T = 183 (2) K
Block, red
0.34 × 0.16 × 0.16 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.300, T_{max} = 0.507
23 363 measured reflections
9217 independent reflections
7611 reflections with $I > 2\sigma(I)$
R_{int} = 0.092
θ_{max} = 28.3°
$h = -16 \rightarrow 15$
$k = -20 \rightarrow 14$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.121
S = 0.98
9217 reflections
352 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.01 e Å^{-3}
$\Delta\rho_{min}$ = −3.10 e Å^{-3}
Absolute structure: Flack (1983), 3842 Friedel reflections
Flack parameter = 0.023 (10)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C19—H19···O1^{i}	0.93	2.48	3.15 (1)	130
C28—H28···O1^{ii}	0.93	2.50	3.25 (1)	138
C38—H38B···O2^{iii}	0.97	2.57	3.52 (1)	166
C43—H43···O2^{iv}	0.93	2.57	3.44 (1)	156

Symmetry codes: (i) $\frac{1}{2}+x, \frac{3}{2}-y, -z$; (ii) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (iv) $x-1, y, z$.

The Friedel opposites were not merged, and the choice of absolute structure was determined by the Flack parameter (Flack, 1983; Flack & Bernardinelli, 1999, 2000). All six phenyl groups were fitted as regular aromatic rings, with C—C distances of 1.39 Å, and were refined anisotropically. All H atoms were fixed geometrically and allowed to ride on their attached parent C atoms, with C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1108). Services for accessing these data are described at the back of the journal.

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