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Bis(1,3-diphenylpropane-1,3-dionato-*O*,*O*′)(diphenyl sulfoxide-*O*)dioxouranium(VI)

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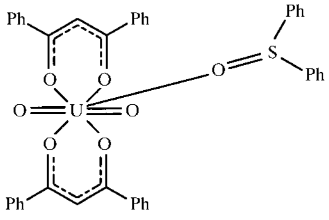
In the title complex, $[UO_2(dbm)_2(PhSOPh)]$ or $[UO_2(C_{15}H_{11}O_2)(C_{12}H_{10}OS)]$, where dbm is 1,3-diphenylpropane-1,3-dionate, the U atom is surrounded by seven O atoms to give a distorted pentagonal bipyramidal geometry. The $U—O_{uranyl}$ and $U—O_{dbm}$ distances (dbm is 1,3-diphenylpropane-1,3-dionate) are in the ranges 1.760 (6)–1.776 (5) and 2.308 (4)–2.417 (4) Å, respectively, while the $U—O_{sulfoxide}$ distance is 2.427 (4) Å.

Comment

An enhancement in solvent extraction separation of the uranium(VI) ion from nitric acid medium using a mixture of dibenzoylmethane (Hdbm) and diphenyl sulfoxide has been reported (Subramanian & Viswanatha, 1969). The species responsible for synergism has been isolated in the solid state and characterized by spectroscopy and elemental analyses (Subramanian & Viswanatha, 1969). However, there is no report on the structural characterization of the complex responsible for this extraction. As part of our systematic work on synergistic complexes (the species responsible for enhancement) of uranyl bis(β-diketonates) with neutral donor ligands (Kannan & Venugopal, 1995; Kannan, Venugopal, Pillai, Droege & Barnes, 1996; Kannan, Venugopal, Pillai, Droege, Barnes & Schlember, 1996; Kannan *et al.*, 1997; Kannan, 2000), we report here the structure of the title complex, (I).

The uranium(VI) ion is surrounded by seven O atoms (four dbm-O, two uranyl-O and one sulfoxide-O atom) to give pentagonal bipyramidal geometry. The four dbm O atoms and the sulfoxide O atom form a planar pentagon. Two uranyl O atoms occupy the apices. A psuedo-twofold axis passes through the U1, O1 and S1 atoms. The U—O bond distances [$U—O_{uranyl}$ 1.760 (6) and 1.776 (5) Å; $U—O_{diketonate}$ 2.308 (4), 2.329 (3), 2.345 (4) and 2.417 (4) Å] are within accepted ranges (Kannan, Venugopal, Pillai, Droege & Barnes, 1996; Kannan, Venugopal, Pillai, Droege, Barnes & Schlember, 1996; Kannan *et al.*, 1997). The $U—O_{sulfoxide}$ distance of 2.427 (4) Å is slightly longer than observed in $[UO_2(dbm)_2(PHCH_2SOCH_3)]$ [2.375 (6) Å; Kannan *et al.*, 1996]. This may be due to a steric effect caused by the bulkier phenyl group of PhSOPh in the title complex compared with the CH_2 or CH_3 group of $PhCH_2SOCH_3$ in $[UO_2(dbm)_2(PHCH_2SOCH_3)]$. The O—U—O angles are close to the regular pentagon value of 72°. The C—C—C angles of the β-diketonate group agree with the reported values of 124.4 (8) and 124.5 (8)° (Uchida *et al.*, 1977). The aromatic rings attached to S makes a dihedral angle of 79.3 (4)° with each other. Overall bond angles and distances show that the U atom has distorted pentagonal bipyramidal geometry.



(I)

This structural observation is in agreement with the IR spectral results that $\Delta\nu_{S=O}[\nu(\text{free ligand}) - \nu(\text{in complex})]$ of the title complex is lower (42 cm^{-1}) compared to that of $[UO_2(dbm)_2(PHCH_2SOCH_3)]$ (50 cm^{-1}). This further indicates that $PhCH_2SOCH_3$ forms stronger bond with $[UO_2(dbm)_2]$ than PhSOPh. The molecular packing is stabilized extensively by intermolecular $\pi\cdots\pi$ interactions [$Cg4\cdots Cg6(x+1, y, z)$ = 3.777 (4) Å] and C—H$\cdots\pi$ interactions involving the aromatic rings (Table 2; *Cg*1–*Cg*6 are the centroids of the aromatic rings C1–C6, C7–C12, C13–C18, C22–C27, C28–C33 and C37–C42, respectively). Because of these interactions the exterior O—C—C angles take low values, while their opposite C—C—C angles take higher values. In the solid state, the molecules are translated along the *ac* plane connected by C—H$\cdots\pi$ interactions.

Experimental

To a hot chloroform (10 ml) solution of $UO_2(dbm)_2\cdot 2H_2O$ (300 mg, 0.399 mmol) was added diphenyl sulfoxide (80.6 mg, 0.399 mmol) and the resulting solution was then refluxed for 15 min. The solution was layered with dodecane (2 ml) and allowed to evaporate slowly. The crystals obtained were washed with hexane and dried (yield 315 mg, 86%, m.p. 498 K). A crystal suitable for X-ray analysis was obtained from a chloroform/dodecane mixture on slow evaporation.

Crystal data

$[UO_2(C_{15}H_{11}O_2)(C_{12}H_{10}OS)]$
M_r = 918.77
Triclinic, $P\overline{1}$
a = 10.2673 (1) Å
b = 10.3671 (2) Å
c = 17.3596 (1) Å
α = 95.459 (1)°
β = 103.172 (1)°
γ = 96.048 (1)°
V = 1775.57 (4) Å^3

Z = 2
D_x = 1.718 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
θ = 1.21–29.51°
μ = 4.682 mm^{-1}
T = 293 (2) K
Rectangular block, orange
0.40 × 0.36 × 0.28 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.170$, $T_{\max} = 0.270$
12 473 measured reflections
8050 independent reflections
6366 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.058$
$\theta_{\max} = 27.5°$
$h = -11 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -22 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.107$
$S = 0.976$
8050 reflections
460 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0101P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 2.56$ e Å^{-3}
$\Delta\rho_{\min} = -2.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.496 (5)	O3—C21	1.269 (6)
S1—C7	1.773 (6)	O4—C36	1.268 (6)
S1—C1	1.804 (7)	O5—C34	1.280 (6)
O2—C19	1.277 (6)		
O5—U1—O3	72.0 (1)	O1—S1—C1	104.6 (3)
O3—U1—O2	70.4 (1)	C7—S1—C1	100.3 (3)
O5—U1—O4	70.6 (1)	S1—O1—U1	128.3 (3)
O2—U1—O1	73.9 (1)	C19—C20—C21	123.1 (5)
O4—U1—O1	73.4 (1)	C34—C35—C36	124.6 (5)
O1—S1—C7	105.8 (3)		

All the H atoms were fixed geometrically and were allowed to ride on their parent atoms.

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*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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

*Cg*1, *Cg*2, *Cg*3 and *Cg*5 are the centroids of the aromatic rings C1–C6, C7–C12, C13–C18 and C28–C33, respectively

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*A*···O1	0.93	2.59	2.939 (8)	103
C13—H13*A*···O2	0.93	2.38	2.710 (7)	101
C8—H8*A*···*Cg*5$^{\text{i}}$	0.93	2.81	3.597 (8)	144
C13—H13*A*···*Cg*1	0.93	3.17	3.891 (8)	136
C25—H25*A*···*Cg*1$^{\text{ii}}$	0.93	3.12	3.917 (8)	144
C26—H26*A*···*Cg*3$^{\text{iii}}$	0.93	2.93	3.493 (8)	121
C38—H38*A*···*Cg*2	0.93	2.93	3.700 (7)	141

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

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