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Bis[aquabis(1,3-diphenylpropane-1,3-dionato-$\kappa^2 O,O'$)dioxouranium(VI)] dicyclohexyl-18-crown-6-ether chloroform disolvate

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In the title compound, $[UO_2(DBM)_2(H_2O)]_2$.(dicyclohexyl-18-crown-6)·$2CHCl_3$ or $[UO_2(C_{30}H_{22}O_4)_2(H_2O)]_2\cdot C_{20}H_{36}O_6\cdot 2CHCl_3$, where DBM is 1,3-diphenylpropane-1,3-dionate, the U^{VI} atom is coordinated by seven O atoms to give a distorted pentagonal bipyramidal geometry. The structure is centrosymmetric. The 18-crown-6 molecule is hydrogen bonded (O—H···O) by the water molecule of $[UO_2(DBM)_2(H_2O)]$, and these binuclear units are interconnected by C—H···O interactions.

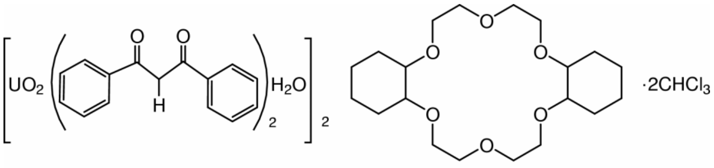
Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.010 Å
R factor = 0.046
wR factor = 0.116
Data-to-parameter ratio = 21.4

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

Comment

An enhancement in the solvent-extraction separation of the uranium(VI) ion from nitric acid medium using mixtures of β-diketones and crown ethers has been reported (Mathur & Choppin, 1993). The species responsible for this extraction have been isolated in the solid state and have been characterized by spectroscopy and X-ray diffraction methods (Kannan *et al.*, 2001). The structures of the compounds $[UO_2(TTA)_2(H_2O)]_2$·(benzo-15-crown-5), (1), and $[\{UO_2(TTA)_2(H_2O)_2\}$(benzo-18-crown-6)], (2) (TTA is the anion of 1-trifluoromethyl-3-thiophenyl-1,3-propanedione; Kannan *et al.*, 2001), showed that the nature of compound formed in the solid state is changed when the nature of the crown ether is changed for a given uranyl bis(β-diketonate). For example, in compound (1), the benzo-15-crown-5 molecule acts as a second-sphere ligand and bridges two $[UO_2(TTA)_2(H_2O)]$ moieties through hydrogen bonds. However, in compound (2), the benzo-18-crown-6 molecule acts as a third-sphere ligand and bridges two dinuclear $[UO_2(TTA)_2(\mu\text{-}H_2O)(H_2O)]_2$ moieties through hydrogen bonds. This observation prompted us to study the nature of compounds formed in the solid state when the nature of β-ketonate is changed. As part of our systematic work on synergistic compounds 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 & Ferguson, 1997; Kannan, 2000; Kannan *et al.*, 1997, 2000, 2001), we report the structure of the title compound, $[UO_2$(diphenylpropane-1,3-dionanto-$O,O')_2(H_2O)]_2$·(dicyclohexyl-18-crown-6)·$2CHCl_3$, (I).



(I)

The asymmetric unit of (I) contains one $[UO_2(DBM)_2(H_2O)]$ unit, half a dicyclohexyl-18-crown-6 molecule and one

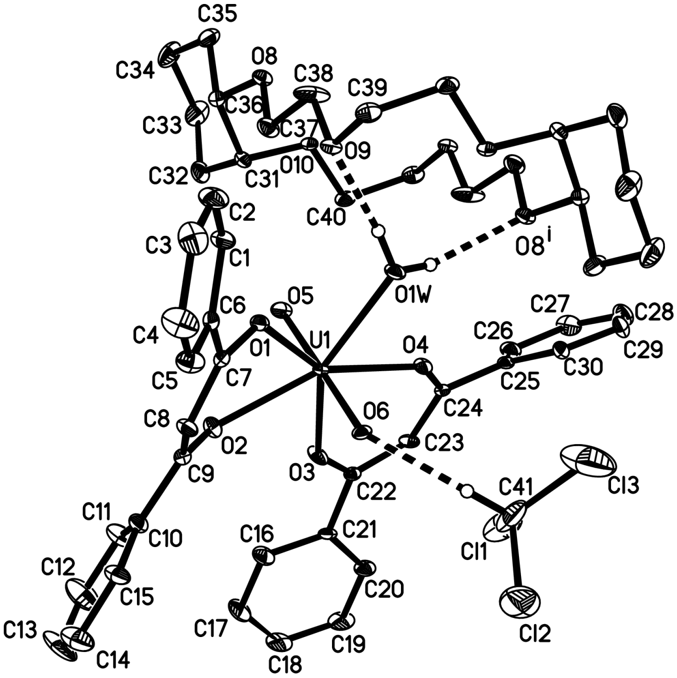


Figure 1

The asymmetric unit of compound (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. The symmetry code is as in Table 2.

$CHCl_3$ molecule. The remaining portion of the title compound are generated by an inversion center. The uranium(VI) ion is surrounded by seven O atoms, *viz.* four O atoms of the DBM ligand, two uranyl O atoms, and the O atom of a water molecule, to give a distorted pentagonal bipyramidal geometry. The four O atoms from the DBM ligand (O1, O2, O3 and O4) and atom O1*W* of the water molecule form a planar pentagon with a maximum deviation of 0.069 (4) Å for O1, while the two uranyl O atoms occupy the apices. The U atom is displaced by 0.0338 (2) Å from the pentagonal plane. The two $U-O_{uranyl}$ distances are 1.764 (4) and 1.771 (4) Å and $U-O_{diketonate}$ distances range from 2.312 (4) to 2.356 (4) Å; $U-O_{water}$ is 2.465 (4) Å. These values are within acceptable ranges, and agree with the values reported earlier (Kannan, Venugopal, Pillai, Droege & Barnes, 1996; Kannan *et al.*, 1997, 2001; Kannan & Ferguson, 1997).

The configuration of the two phenyl rings in the diphenylpropane-1,3-dionate (DBM) systems are different, corresponding to dihedral angles of 28.82 (4) and 60.2 (4)° between the phenyl rings in the two DBM systems. In the dicyclohexyl-18-crown-6 moiety, the cyclohexyl ring adopts a chair conformation, with puckering parameters (Cremer & Pople, 1975) Q_2 = 0.048 (7) Å, Q_3 = −0.552 (7) Å, Q_T = 0.555 (7) Å and θ = 174.9 (7)°.

The $O-H_{water}\cdots O_{crown}$ hydrogen bonds involving the crown atoms O8 and O9 link the crown ether with two $[UO_2(DBM)_2(H_2O)]$ units,; this is similar to that observed in the compound (1), while the two $[UO_2(DBM)_2(H_2O)]$ units are linked by $C-H\cdots O_{uranyl}$ hydrogen bonds. The chloroform molecules are $C-H\cdots O$ hydrogen bonded to the uranyl O atom (Table 2).

Experimental

Stoichiometric amounts of $[UO_2(DBM)_2(H_2O)_2]$ and dicyclohexyl-18-crown-6 were refluxed in chloroform (25 ml) for 15 min. The volume of the solution was reduced to 5 ml and was then layered with toluene (2 ml). The solution, on slow evaporation, yielded the title complex in 75% yield. The product was recrystallized from a chloroform–toluene mixture and was indentified by IR, ^{1}NMR and elemental analyses.

Crystal data

$[UO_2(C_{30}H_{22}O_4)_2(H_2O)]\cdot C_{20}H_{36}O_6\cdot 2CHCl_3$
M_r = 2080.27
Monoclinic, $P2_1/c$
a = 15.5427 (1) Å
b = 15.2483 (1) Å
c = 19.4582 (2) Å
β = 107.643 (1)°
V = 4394.67 (6) Å^3
Z = 2
D_x = 1.572 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
θ = 2.6–28.3°
μ = 3.93 mm^{-1}
T = 183 (2) K
Block, orange
0.12 × 0.10 × 0.08 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.650, T_{max} = 0.744
26358 measured reflections
10599 independent reflections
7581 reflections with $I > 2\sigma(I)$
R_{int} = 0.096
θ_{max} = 28.3°
$h = -20 \rightarrow 20$
$k = -20 \rightarrow 16$
$l = -25 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.116
S = 0.95
10599 reflections
496 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0272P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.57 e Å^{-3}
$\Delta\rho_{min}$ = −4.23 e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

U1—O5	1.764 (4)	U1—O4	2.348 (4)
U1—O6	1.771 (4)	U1—O3	2.356 (4)
U1—O2	2.312 (4)	U1—O1*W*	2.465 (4)
U1—O1	2.340 (4)		
O5—U1—O6	179.44 (19)	O6—U1—O3	89.34 (16)
O5—U1—O2	89.11 (16)	O2—U1—O3	73.28 (13)
O6—U1—O2	90.43 (16)	O1—U1—O3	144.03 (13)
O5—U1—O1	93.38 (16)	O4—U1—O3	70.28 (13)
O6—U1—O1	86.16 (15)	O5—U1—O1*W*	90.22 (16)
O2—U1—O1	71.09 (13)	O6—U1—O1*W*	89.95 (15)
O5—U1—O4	90.64 (16)	O2—U1—O1*W*	142.61 (13)
O6—U1—O4	89.93 (16)	O1—U1—O1*W*	71.64 (13)
O2—U1—O4	143.55 (13)	O4—U1—O1*W*	73.84 (13)
O1—U1—O4	145.24 (13)	O3—U1—O1*W*	144.11 (13)
O5—U1—O3	90.83 (17)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1*W*—H1*W*···O8^i	0.82	2.06	2.814 (6)	152
O1*W*—H2*W*···O9	0.84	1.96	2.775 (5)	166
C1—H1···O9	0.93	2.48	3.319 (8)	150
C5—H5···O6^{ii}	0.93	2.50	3.410 (8)	167
C15—H15···O6^{ii}	0.93	2.55	3.467 (8)	167
C41—H41···O6	0.98	2.30	3.153 (10)	145

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

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All H atoms were geometrically placed in ideal positions and allowed to ride on their attached parent atoms with C—H distances in the range 0.93—0.98 Å. The range of O—H distances is 0.82–0.84 Å. At this stage, the refinement converged to an *R* value of 0.054 (*wR* = 0.167). However, the difference map showed three peaks (4.11, 3.95 and 1.63 e Å^{-3}) around the inversion centre (1/2, 0, 1/2). A search for solvent-accessible voids in the crystal, using *PLATON* (Spek, 1990) showed a potential solvent volume of 197 e Å^{-3}. Since attempts to refine the structure with a rational solvent model failed, the SQUEEZE procedure in *PLATON* was used to obtain solvent-free reflection data. Further refinement of the structure with the solvent-free reflection data converged to an *R* value of 0.046 (*wR* = 0.111). The highest peak and the deepest hole were 0.64 and 0.92 Å from atom U1.

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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