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Aquabis(1,3-diphenylpropane-1,3-dionato-*O*,*O*′)-dioxouranium(VI) benzo-15-crown-5

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.033
wR factor = 0.072
Data-to-parameter ratio = 13.7

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

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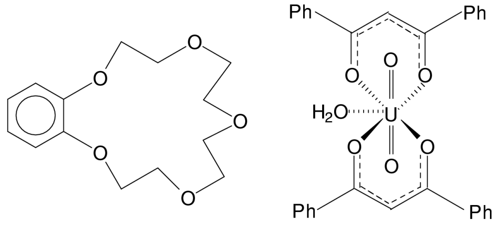
The U atom in the title compound, $[UO_2(PhCOCHCOPh)_2(H_2O)]\cdot C_{14}H_{20}O_5$, is surrounded by seven O atoms at the vertices of a distorted pentagonal bipyramid. The crown ether molecule is not coordinated directly to the U atom, but is linked to the aquabis(dibenzoylmethanato)dioxouranium complex *via* hydrogen bonds involving the water molecule. The U—O distances range from 1.751 (4) to 2.504 (3) Å.

Comment

An enhancement of the solvent-extraction separation of the uranium(VI) ion from a nitric acid medium using a mixture of β-diketones and crown ethers has been reported (Mathur & Choppin, 1993). The species responsible for this extraction have been isolated by us in the solid state, and characterized by spectroscopy and X-ray diffraction methods (Kannan *et al.*, 2001*b*). The structures of $[UO_2(TTA)_2(H_2O)]_2$(benzo-15-crown-5), (1), and $[UO_2(TTA)_2(\mu\text{-}H_2O)]_2(H_2O)_2$(dibenzo-18-crown-6), (2), where TTA is the thenoyl trifluoroacetonate anion, show that the nature of the compound formed in the solid state is altered when the nature of the crown ether is changed, for a given uranyl bis(β-diketonate). For example, in the crystal structure of (1), benzo-15-crown-5 acts as a second-sphere ligand and bridges two $[UO_2(TTA)_2(H_2O)]$ complexes *via* hydrogen bonds. However, in the structure of (2), dibenzo-18-crown-6 acts as a third-sphere ligand, *i.e.* it is hydrogen bonded to the water in the second sphere, and bridges two dinuclear $[UO_2(TTA)_2(\mu\text{-}H_2O)(H_2O)]_2$ complexes through hydrogen bonds. This observation prompted us to study the nature of the compound formed in the solid state when the nature of the uranyl bis(β-diketonate) is changed, for a given crown ether, in particular benzo-15-crown-5. 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 & Schlemper, 1996; Kannan & Ferguson, 1997; Kannan *et al.*, 1997; Kannan, 2000; Kannan *et al.*, 2001*a*, *b*), we report here the structure of $[UO_2(DBM)_2\cdot H_2O$(benzo-15-crown-5)], (I) (DBM is the dibenzoylmethanate anion).



(I)

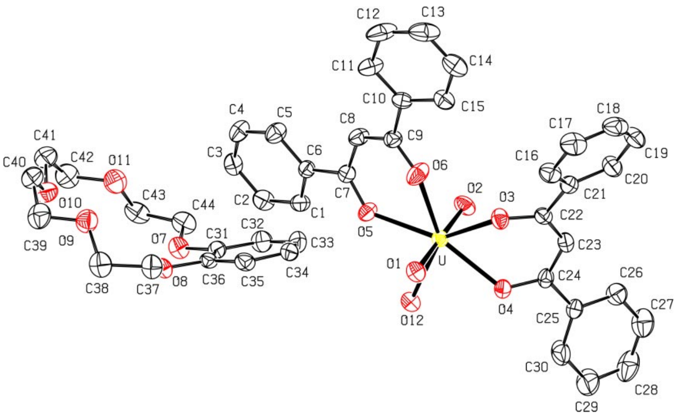


Figure 1
The molecular structure of (I), showing the atom-numbering scheme, with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Fig. 1 shows the title compound with the atomic numbering scheme adopted. The uranium(VI) ion is surrounded by seven O atoms (four from two DBM ligands, two uranyl O atoms and one water molecule) at the vertices of a distorted pentagonal bipyramid. The four O atoms from DBM together with the water O atom form a planar pentagon; the uranyl O atoms are in the apical positions. The bond lengths U—O(uranyl) [1.751 (4) and 1.777 (4) Å], U—O(DBM) [2.295 (4), 2.332 (4), 2.359 (4) and 2.380 (4) Å] and U—O(H_2O) [2.504 (3) Å] are within the accepted ranges for such distances.

It is interesting to note that benzo-15-crown-5 is hydrogen bonded to only one [$UO_2(DBM)_2(H_2O)$] molecule in the solid state; this is different from what is observed in compound (1), where the crown-ether molecule bridges two [$UO_2(TTA)_2(H_2O)$] complexes. This may be due to the steric conditions caused by the presence of the bulky DBM ligands (with four phenyl groups compared to much smaller CF_3 groups of TTA ligands), which would not allow two [$UO_2(DBM)_2(H_2O$] groups to come closer and thus form an arrangement similar to that observed in (1).

The crystal packing is stabilized by O—H···O hydrogen bonds involving the water O atoms and crown-ether O atoms (Table 1). It is noteworthy, however, that the O atoms belonging to the DBM moiety and participating in the uranium(VI) coordination sphere are not involved in the hydrogen-bonding network.

Experimental

Stoichiometric amounts of [$UO_2(DBM)_2$]·$2H_2O$ (300 mg, 0.404 mmol) and benzo-15-crown-5 (109 mg, 0.406 mmol) ether were refluxed in chloroform (25 ml) for 15 min. The solution was reduced in volume to 5 ml, and layered with toluene (2 ml). On slow evaporation, it gave the title compound in 75% yield. The product was recrystallized from a chloroform/toluene mixture and characterized by IR, ^{1}H NMR and elemental analysis.

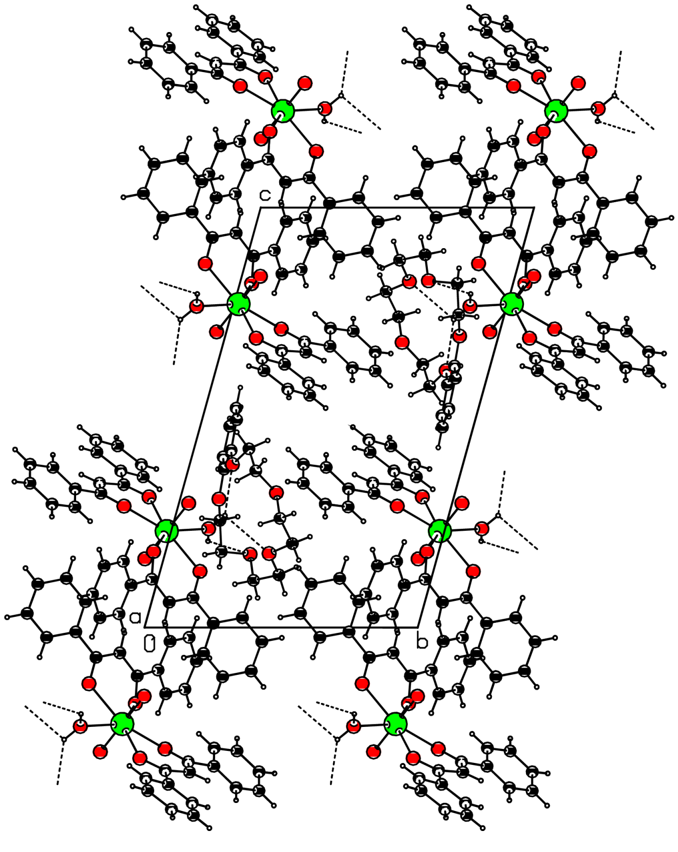


Figure 2
Packing of the molecules of (I), viewed down the *a* axis.

Crystal data

[$UO_2(C_{15}H_{11}O_2)_2(H_2O)$]·$C_{14}H_{20}O_5$
M_r = 1002.82
Triclinic, $P\overline{1}$
a = 9.210 (2) Å
b = 12.121 (2) Å
c = 19.374 (9) Å
α = 73.59 (2)°
β = 81.20 (2)°
γ = 81.89 (1)°
V = 2039.5 (11) Å^3

Z = 2
D_x = 1.633 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 7–14°
μ = 4.04 mm^{-1}
T = 293 (2) K
Block, orange
0.18 × 0.12 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.56, T_{max} = 0.69
7623 measured reflections
7136 independent reflections
5830 reflections with $I > 2\sigma(I)$

R_{int} = 0.032
θ_{max} = 25.0°
h = 0 → 10
k = −14 → 14
l = −22 → 23
2 standard reflections every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.072
S = 1.09
7136 reflections
522 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 3.7856P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.12 e Å^{-3}
$\Delta\rho_{min}$ = −1.33 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O12—H12A⋯O8^{i}	0.85	2.19	2.934 (5)	146
O12—H12A⋯O7^{i}	0.85	2.34	3.061 (5)	143
O12—H12B⋯O10^{i}	0.85	2.03	2.869 (6)	171

Symmetry code: (i) $1-x, -y, 1-z$.

All H atoms with the exception of those of the aqua ligand were generated geometrically and allowed to ride on their respective parent atoms with *SHELXL*97 (Sheldrick, 1997) defaults. The positions of water H atoms (H12*A* and H12*B*) were calculated using the *HYDROGEN* program (Nardelli, 1999), with O—H = 0.85 Å, H—O—H = 107° and $U_{\rm iso}$(H) = 0.05 Å^2, and were not refined. The residual density peaks in the final difference Fourier map (1.12 and −1.33 e Å^{-3}) indicate ripples around the U atom and have no structural significance.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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