metal-organic papers

Bis(1,3-diphenylpropane-1,3-dionato-κ^2O,O')-dioxo(triphenylphosphine oxide-κO)uranium(VI)

M. Alagar,[a] K. Rajagopal,[b] R. V. Krishnakumar,[c] M. Subha Nandhini,[d] S. Kannan[e] and S. Natarajan[d]*

[a]Department of Physics, Ayya Nadar Janaki Ammal College, Sivakasi 626 123, India, [b]Department of Physics, Sraswathi Narayanan College, Madurai 625 022, India, [c]Department of Physics, Thiagarajar College, Madurai 625 009, India, [d]Department of Physics, Madurai Kamaraj University, Madurai 625 021, India, and [e]Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

Correspondence e-mail:
s_natarajan50@yahoo.com

In the title compound, $[UO_2(C_{15}H_{11}O_2)_2(C_{18}H_{15}OP)]$ or $[UO_2(DBM)_2(Ph_3PO)]$, where DBM is dibenzoyl methanate, the U^{VI} atom is coordinated by seven O atoms in a distorted pentagonal–bipyramidal geometry. The diphenylpropane-1,3-dionate system acts as a chelating ligand and coordinates through both of its ketonate O atoms and the triphenyl phosphine oxide ligand coordinates through the O atom. The U—O distances range from 1.759 (4) to 2.385 (4) Å.

Comment

Compounds of uranyl bis(β-diketonates) with neutral donor ligands are of importance for understanding the nature of the species extracted during the solvent-extraction separation of the uranyl ion using mixtures of β-diketones and neutral ligands (Ramakrishna & Patil, 1984). An increase (or synergism) in solvent extraction separation of uranyl ion from nitric acid medium by using mixtures of β-diketones and phosphine oxides or phosphate has been reported (Irving & Edgington, 1960; Healy, 1961; Akiba, 1977). The species responsible for the extraction have been isolated in the solid state for some of the systems and characterized by IR (Ferraro & Healy, 1962), ^{1}H and ^{19}F NMR (Subramanian & Viswanatha, 1969) spectroscopic and elemental analysis methods. In a few cases the material has been characterized using single-crystal X-ray diffraction methods (Taylor & McLaren, 1979; Lu et al., 1977; Taylor & Waugh, 1977a,b; Kannan et al., 2001a). In continuation of our work on uranyl bis(β-diketones) with neutral donor ligands (Kannan & Venugopal, 1995; Kannan, Venugopal, Pillai, Droege & Barnes, 1996; Kannan, Venugopal, Pillai, Droege, Barnes & Schlmber, 1996; Kannan et al., 1997, 2001a,b; Kannan & Ferguson, 1997; Kannan, 2000; Fun et al., 2002; Rajagopal et al., 2002), we report here the structure of $[UO_2(DBM)_2(Ph_3PO)]$, (I), where DBM is dibenzoyl methanate.
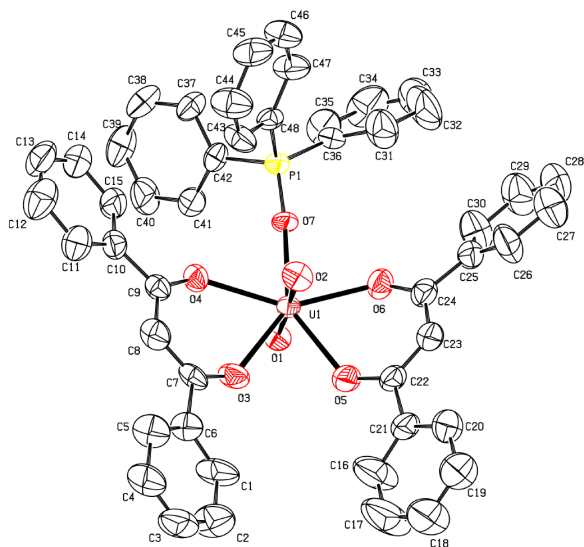

(I)
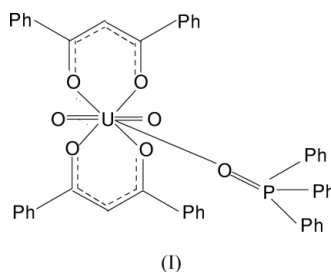
The structure of (I) is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. The structure of the molecule shows that the U atom is surrounded by seven O atoms in a pentagonal bipyramidal geometry. Four O atoms of
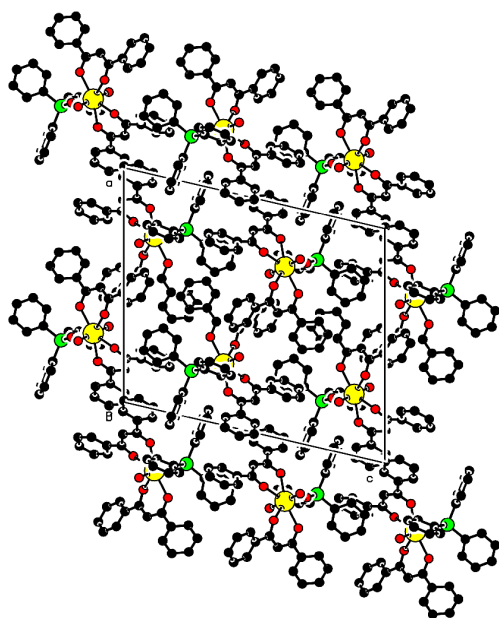
Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

Figure 2
The packing of the molecules of (I), viewed down the b axis.

DBM and one O atom of phosphine oxide form a planar pentagon and two uranyl O atoms occupy the apices. The average of U—O$_{uranyl}$ [1.767 (4) Å] and U—O$_{DBM}$ [2.365 (4) Å] distances are within the accepted ranges (Taylor & McLaren, 1979; Kannan, Venugopal, Pillai, Droege & Barnes, 1996; Kannan, Venugopal, Pillai, Droege, Barnes & Schlmber, 1996; Kannan et al., 1997, 2000, 2001b). The U—O(P) phosphine oxide distance [2.375 (4) Å] is comparable with those reported earlier for uranyl bis(β-diketone)–phosphine adducts (Taylor & McLaren, 1979; Lu et al., 1977; Kannan et al., 2001a). The overall bond lengths and angles show that the U atom has a distorted pentogonal bipyramidal geometry. In both the DBM ligands, the benzene rings are not

coplanar and they form dihedral angles of 11.9 (4) and 32.9 (5)°. Fig. 2 shows the crystal packing of the title compound viewed down the b axis. The structure is stabilized by van der Waals interactions.

Experimental

[UO2(DBM)2(Ph3PO)] was prepared by refuxing [UO2(DBM)2-(H2O)2] (300 mg) with Ph3PO (112 mg) in chloroform for 15 min. The solution was filtered and layered with dodecane. The solution, on slow evaporation, yielded the title compound in 90% yield. Crystals suitable for the X-ray diffraction analyses were obtained from a chloroform/toluene mixture.

Crystal data

[UO$_2$(C$_{15}$H$_{11}$O$_2$)$_2$(C$_{18}$H$_{15}$OP)]	$D_x = 1.604$ Mg m^{-3}
$M_r = 994.78$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
$a = 18.345$ (2) Å	reflections
$b = 11.022$ (4) Å	$\theta = 10–15°$
$c = 20.924$ (4) Å	$\mu = 4.03$ mm^{-1}
$\beta = 103.170$ (13)°	$T = 293$ (2) K
$V = 4119.5$ (18) Å^3	Rectangular block, orange
$Z = 4$	$0.30 \times 0.25 \times 0.13$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.023$
ω–2θ scans	$\theta_{max} = 25.0°$
Absorption correction: ψ scan (North et al., 1968)	$h = 0 \rightarrow 21$
$T_{min} = 0.325$, $T_{max} = 0.597$	$k = 0 \rightarrow 13$
7464 measured reflections	$l = -24 \rightarrow 24$
7221 independent reflections	2 standard reflections
5259 reflections with $I > 2\sigma(I)$	frequency: 60 min
	intensity decay: <1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0316P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$+ 1.9225P]$
$wR(F^2) = 0.084$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.29$	$(\Delta/\sigma)_{max} < 0.001$
7221 reflections	$\Delta\rho_{max} = 0.96$ e Å^{-3}
515 parameters	$\Delta\rho_{min} = -0.92$ e Å^{-3}
H-atom parameters constrained	Extinction correction: SHELXL97
	Extinction coefficient: 0.00049 (6)

Table 1
Selected geometric parameters (Å, °).

C7—O3	1.265 (7)	O2—U1	1.759 (4)
C9—O4	1.279 (7)	O3—U1	2.361 (4)
C22—O5	1.276 (7)	O4—U1	2.385 (4)
C24—O6	1.278 (8)	O5—U1	2.350 (4)
C36—P1	1.801 (7)	O6—U1	2.375 (4)
C42—P1	1.789 (6)	O7—P1	1.505 (4)
C48—P1	1.806 (6)	O7—U1	2.375 (4)
O1—U1	1.774 (4)		
C9—C8—C7	124.9 (6)	O2—U1—O6	88.20 (18)
C22—C23—C24	125.0 (7)	O1—U1—O6	93.28 (17)
O2—U1—O1	178.51 (19)	O5—U1—O6	69.91 (15)
O2—U1—O5	89.82 (18)	O3—U1—O6	142.29 (16)
O1—U1—O5	90.56 (18)	O7—U1—O6	74.26 (14)
O2—U1—O3	90.97 (18)	O2—U1—O4	86.51 (18)
O1—U1—O3	87.77 (17)	O1—U1—O4	92.30 (17)
O5—U1—O3	72.39 (16)	O5—U1—O4	141.31 (15)
O2—U1—O7	94.22 (17)	O3—U1—O4	69.19 (15)
O1—U1—O7	86.32 (16)	O7—U1—O4	74.90 (13)
O5—U1—O7	143.79 (15)	O6—U1—O4	148.20 (14)
O3—U1—O7	143.29 (15)		

metal-organic papers

All the H atoms were positioned geometrically and were allowed to ride on their respective parent atoms with *SHELXL*97 (Sheldrick, 1997) defaults (C—H = 0.96 Å and U_{iso} = 0.05 Å^2) for bond lengths and isotropic displacement parameters.

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.

References

Akiba, K. (1977). *J. Radioanal. Nucl. Chem.* **36**, 153–161.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Ferraro, J. R. & Healy, T. V. (1962). *J. Inorg. Nucl. Chem.* **24**, 1463–1474.
Fun, H.-K., Kannan, S., Usman, A. & Chantrapromma, S. (2002). *Acta Cryst.* C**58**, o368–o370.
Healy, T. V. (1961). *J. Inorg. Nucl. Chem.* **19**, 314–327.
Irving, H. & Edgington, D. N. (1960). *J. Inorg. Nucl. Chem.* **15**, 158–170.
Kannan, S. (2000). *J. Chem. Res.* pp. 344–345.
Kannan, S. & Ferguson, G. (1997). *Inorg. Chem.* **36**, 1724–1725.
Kannan, S., Pillai, M. R. A., Venugopal, V., Droege, P. A. & Barnes, C. L. (1997). *Inorg. Chim. Acta*, **254**, 113–117.
Kannan, S., Shunmugasundararaj, S. & Fun, H.-K. (2000). *Acta Cryst.* C**56**, e545–546.
Kannan, S., Shunmugasundararaj, S. & Fun, H.-K. (2001*a*). *J. Chem. Res.* pp. 50–51.
Kannan, S., Shunmugasundararaj, S. & Fun, H.-K. (2001*b*). *Polyhedron*, **20**, 2145–2150.
Kannan, S. & Venugopal, V. (1995). *Polyhedron*, **14**, 2349–2354.
Kannan, S., Venugopal, V., Pillai, M. R. A., Droege, P. A. & Barnes, C. L. (1996). *Polyhedron*, **15**, 97–101.
Kannan, S., Venugopal, V., Pillai, M. R. A., Droege, P. A., Barnes, C. L. & Schlemper, E. O. (1996). *Polyhedron*, **15**, 465–471.
Lu, T. H., Lee, T. J., Lee, T. Y. & Wong, C. (1977). *Inorg. Nucl. Chem. Lett.* **13**, 363–365.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Rajagopal, K., Krishnakumar, R. V., Subha Nandhini, M., Kannan, S. & Natarajan, S. (2002). *Acta Cryst.* E**58**, m316–m318.
Ramakrishna, V. V. & Patil, S. K. (1984). *Structure Bonding*, **56**, 35–90.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1999). *PLATON for Windows*. Utrecht University, The Netherlands.
Subramanian, M. S. & Viswanatha, A. (1969). *J. Inorg. Nucl. Chem.* **31**, 2575–2585.
Taylor, J. C. & McLaren, A. B. (1979). *J. Chem. Soc. Dalton Trans.* pp. 460–464.
Taylor, J. C. & Waugh, A. B. (1977*a*). *J. Chem. Soc. Dalton Trans.* pp. 1630–1636.
Taylor, J. C. & Waugh, A. B. (1977*b*). *J. Chem. Soc. Dalton Trans.* pp. 1636–1640.