Crystal and Molecular Structure of Dichlorodioxobis(triphenylphosphine oxide)uranium(VI)

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The crystal structure of $[UO_2Cl_2(PPh_3O)_2]$ has been determined from three-dimensional *X*-ray diffraction data. Crystals are triclinic, space group $P\bar{1}$, with $a = 10.0101(6)$, $b = 10.2589(9)$, $c = 9.2347(8)$ Å, $\alpha = 110.093(6)$, $\beta = 92.129(6)$, and $\gamma = 78.384(6)°$, and $Z = 1$. The structure has been solved by the heavy-atom method from counter data, and refined by least squares to a final *R* of 0.054. The co-ordination polyhedron around uranium is a distorted octahedron, with a linear uranyl group (U–O 1.764 Å) perpendicular to a plane in which the two chloride and two oxide ions *trans* to each other occupy the corners of a rectangle (U–O 2.300; U–Cl 2.645 Å).

THE uranium(VI) compounds $[UO_2X_2(PR_3O)_2]$ (X = Cl or Br; R = Me, Et, or Ph) were reported by Gans and Smith [1] and further studied by Day and Venanzi [2] who also prepared the iodo-compound (X = I). The compounds would be expected to contain a linear uranyl group (O–U–O) with the four other ligands approximately in the equatorial plane. From i.r. studies, and the general solubility of the compounds in low-polarity organic solvents, it was suggested [2] that the ligands adopt a *trans* configuration. However, since the (analytically isomeric) ionic uranium(VI) compounds, $[UO_2(PPh_3O)_4][UO_2X_4]$ were also prepared,[2] in which the cation presumably contains four triphenylphosphine oxide ligands co-ordinated in or near the equatorial plane, a *cis* configuration for $[UO_2Cl_2(PPh_3O)_2]$ could not be ruled out on steric grounds. Furthermore, the related uranium(IV) complex, $[UCl_4(PPh_3O)_2]$, has recently been shown [3] to contain *cis*-PPh$_3$O groups, in a pseudo-octahedral structure. It was of interest, therefore, to investigate the structure of $[UO_2Cl_2(PPh_3O)_2]$, which is reported in this paper.

EXPERIMENTAL

Dichlorodioxobis(triphenylphosphine oxide)uranium(VI) was prepared [2] by stoicheiometric addition of uranyl chloride (UCl_2O_2) and triphenylphosphine oxide in ethanol. Clear yellow crystals suitable for the single-crystal *X*-ray analysis were obtained by recrystallization from ethanol.

The crystal used was a prism with dimensions *ca.* 0.1 × 0.1 × 0.2 mm. All the *X*-ray experiments were performed using a single-crystal Philips PW-1100 diffractometer and graphite-monochromated Mo-K_α radiation (λ 0.710 7 Å). The triclinic unit cell was determined on the basis of 15 reflections found by mounting the crystal at random and varying the orientation angles ϕ and χ in ranges of 90 and 45°, respectively, with the detector position varying between $\theta = 6$ and 12°.

For the determination of precise lattice parameters, 47 reflections having $6 < \theta < 12°$ were considered, and the precise diffraction angles θ were evaluated as centres of gravity of their profiles $I = f(\theta)$, averaging over positive θ values.

Integrated intensities for *hkl* reflections with $l \geqslant 0$ and $3 < \theta < 25°$ were measured using the ω—2θ scan method, a scan speed of 2.4° min^{-1}, and a scan width of 1.50°, and two background counts of 10 s at each end of the scan of the 2 855 reflections thus considered. The 2 104 reflections having a net intensity greater than 3σ (σ = standard error based on counting statistics) were used in the structure determination and refinement. Every hour three standard reflections were counted to check the crystal's stability. Only statistical variations were observed, *i.e.* $\sigma(I) = [C_T + (t_c/t_b)^2(B_1 + B_2) + pI]^2$ where C_T is the total integrated peak count obtained in scan time t_c, B_1 and B_2 are background counts each obtained in time t_b, and $I = C_T - (t_c/t_b)(B_1 + B_2)$; a value of 0.04 was assigned to the factor p to allow for other error sources.

Structure Determination and Refinement.—Precise lattice parameters and their standard deviations were determined by means of least-squares calculations minimizing $(\sin\theta_{obs.} - \sin\theta_{calc.})^2$ for the 47 reflections cited above. They are: $a = 10.010\,1(6)$, $b = 10.258\,9(9)$, $c = 9.234\,7(8)$ Å, $\alpha = 110.093(6)$, $\beta = 92.129(6)$, $\gamma = 78.384(6)°$, $U = 871.85$ Å^3, $D_c = 1.71$ g cm^{-3} (M 897.5), $Z = 1$, $F(000) = 434$. Integrated intensities were corrected for Lorentz and polarization effects.

The Patterson function was in agreement with a centrosymmetric distribution of Cl, O, and C atoms, the uranium lying in the crystallographic inversion centre. The structure was then refined by the least-squares procedure using anisotropic thermal parameters for all the non-hydrogen atoms and minimizing $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$.

Computations were carried out on a CDC 7600 computer using the '*X*-Ray '72' program package.[4] In all the calculations of F_c, the atomic scattering factors for uranium were taken from Cromer and Waber,[5] and for Cl, P, O, and C from Cromer and Mann.[6] For uranium a correction was employed for the real and imaginary parts of the anomalous dispersion.[7] A final difference-Fourier map failed to reveal the positions of the hydrogen atoms. The final $R = \Sigma|\Delta F|/\Sigma|F_o|$, based on the 2 104 observed reflections, was 0.054.

DISCUSSION

The final positional parameters of the non-hydrogen atoms are given in Table 1, with their standard deviations

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[1] P. Gans and B. C. Smith, *J. Chem. Soc.*, 1964, 4172.

[2] J. P. Day and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 1363.

[3] G. Bombieri, D. Brown, and R. Graziani, *J.C.S. Dalton*, 1975, 1873.

[4] '*X*-Ray System,' version of June 1972, Technical Report TR-192, The Computer Science Center, University of Maryland, 1972.

[5] D. T. Cromer and J. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[7] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

estimated from the inverse matrix. The most significant bond lengths and valence angles are listed in Table 2. Contact distances and least-squares planes are shown in Tables 3 and 4 respectively. Observed and calculated structure factors and thermal parameters are in Supplementary Publication No. SUP 22242 (16 pp.).*

TABLE 1

Final atomic fractional (× 10^4) parameters with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
U	10 000	0 000	0 000
Cl	10 048(4)	1 880(4)	−1 358(5)
P	7 070(3)	2 500(4)	2 562(4)
O(1)	10 944(9)	921(10)	1 524(10)
O(2)	8 004(9)	1 333(9)	1 323(11)
C(1)	6 730(14)	1 915(15)	4 090(15)
C(2)	5 413(15)	2 276(16)	4 779(18)
C(3)	5 182(19)	1 838(20)	5 999(22)
C(4)	6 277(23)	1 062(21)	6 545(20)
C(5)	7 585(22)	664(20)	5 842(22)
C(6)	7 828(17)	1 096(18)	4 606(20)
C(7)	5 488(12)	3 010(15)	1 735(16)
C(8)	4 812(17)	1 908(19)	936(22)
C(9)	3 542(18)	2 291(25)	296(23)
C(10)	2 998(18)	3 638(26)	401(22)
C(11)	3 678(16)	4 743(21)	1 221(20)
C(12)	4 939(13)	4 392(16)	1 890(16)
C(13)	7 799(12)	4 047(13)	3 363(17)
C(14)	8 507(15)	4 451(17)	2 346(19)
C(15)	9 039(17)	5 704(19)	2 940(26)
C(16)	8 852(17)	6 507(16)	4 537(27)
C(17)	8 172(17)	6 095(18)	5 519(24)
C(18)	7 657(14)	4 829(15)	4 937(19)

TABLE 2

Bond distances (Å) and angles (°) with their estimated standard deviations in parentheses

U–Cl	2.645(5)	C(7)–C(8)	1.41(2)
U–O(1)	1.764(9)	C(8)–C(9)	1.42(2)
U–O(2)	2.300(8)	C(9)–C(10)	1.35(4)
O(2)–P	1.518(8)	C(10)–C(11)	1.42(3)
P–C(1)	1.78(2)	C(11)–C(12)	1.41(2)
P–C(7)	1.79(1)	C(12)–C(7)	1.37(2)
P–C(13)	1.79(1)	C(13)–C(14)	1.41(2)
C(1)–C(2)	1.41(2)	C(14)–C(15)	1.42(2)
C(2)–C(3)	1.39(3)	C(15)–C(16)	1.42(3)
C(3)–C(4)	1.40(3)	C(16)–C(17)	1.38(3)
C(4)–C(5)	1.40(3)	C(17)–C(18)	1.42(2)
C(5)–C(6)	1.40(3)	C(18)–C(13)	1.39(2)
C(6)–C(1)	1.42(2)		

Cl–U–O(2)	90.6(3)	P–C(7)–C(8)	116(1)
O(2)–U–Cl	89.4(3)	P–C(7)–C(12)	123(1)
U–O(2)–P	158.7(6)	C(8)–C(7)–C(12)	121(1)
O(2)–P–C(1)	110.9(6)	C(7)–C(8)–C(9)	117(2)
O(2)–P–C(7)	109.4(6)	C(8)–C(9)–C(10)	123(2)
O(2)–P–C(13)	111.7(6)	C(9)–C(10)–C(11)	120(2)
C(1)–P–C(7)	108.9(7)	C(10)–C(11)–C(12)	119(2)
C(1)–P–C(13)	108.2(7)	C(11)–C(12)–C(7)	121(1)
C(7)–P–C(13)	107.6(7)	P–C(13)–C(14)	118(1)
P–C(1)–C(2)	121(1)	P–C(13)–C(18)	121(1)
P–C(1)–C(6)	118(1)	C(14)–C(13)–C(18)	121(1)
C(2)–C(1)–C(6)	121(2)	C(13)–C(14)–C(15)	119(1)
C(1)–C(2)–C(3)	120(1)	C(14)–C(15)–C(16)	119(2)
C(2)–C(3)–C(4)	119(2)	C(15)–C(16)–C(17)	122(2)
C(3)–C(4)–C(5)	121(2)	C(16)–C(17)–C(18)	120(2)
C(4)–C(5)–C(6)	120(2)	C(17)–C(18)–C(13)	120(2)
C(5)–C(6)–C(1)	118(2)		

The crystal structure of $[UO_2Cl_2(PPh_3O)_2]$ is composed of discrete molecules. A perspective view of a single molecule, with the labelling of the atoms and the atomic thermal ellipsoids at 50% probability, is shown in Figure 1 which reproduces a plotter drawing obtained with the program ORTEP.[8] The uranium is six-co-ordinate with the ligands in *trans* positions as required by space-group conditions, the uranium lying in a crystallographic inversion centre. The co-ordination octahedron is distorted and the entire molecule has crystallographic $\bar{1}$ symmetry. The U–Cl bond [2.645(5) Å] is somewhat shorter than those of the $[UO_2Cl_4]^{2-}$ unit in

TABLE 3

Contact distances (Å) with estimated standard deviations in parentheses

(*a*) Selected intramolecular non-bonding

U · · · P	3.754(3)	O(2) · · · Cl^{I}	3.48(1)
O(2) · · · Cl	3.52(1)		

(*b*) Intermolecular carbon–carbon contacts

C(17) · · · C(16^{II})	3.57(2)	C(12) · · · C(2^{III})	3.69(2)
C(15) · · · C(17^{II})	3.56(3)	C(11) · · · C(11^{IV})	3.75(3)
C(18) · · · C(16^{II})	3.57(2)	C(12) · · · C(11^{IV})	3.67(3)
C(16) · · · C(16^{II})	3.79(3)	C(3) · · · C(3^{V})	3.67(3)
C(17) · · · C(2^{III})	3.68(2)	C(4) · · · C(3^{V})	3.63(3)
C(12) · · · C(3^{III})	3.63(2)	C(8) · · · C(8^{VI})	3.64(2)
C(18) · · · C(11^{III})	3.69(2)		

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I	$2 - x, -y, -z$	IV	$1 - x, 1 - y, -z$
II	$2 - x, 1 - y, 1 - z$	V	$1 - x, -y, 1 - z$
III	$1 - x, 1 - y, 1 - z$	VI	$1 - x, -y, -z$

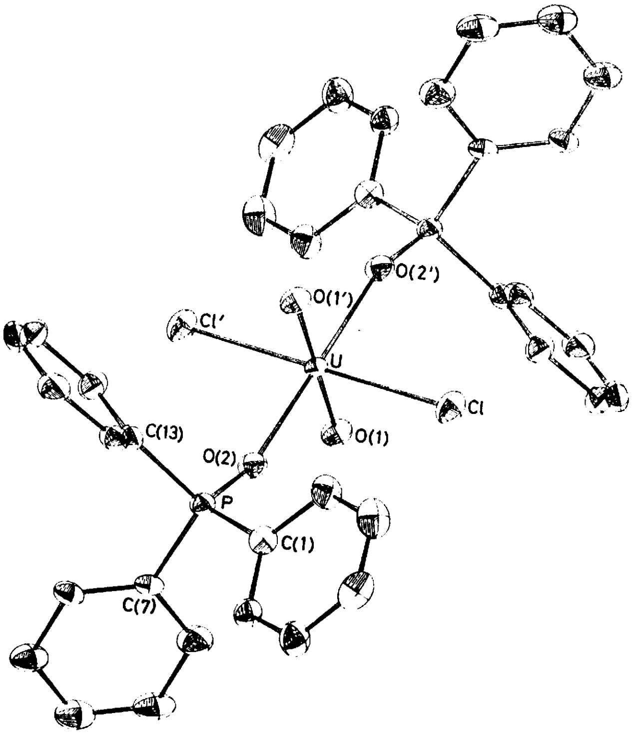

FIGURE 1 Perspective view of the molecule, showing 50% probability vibrational ellipsoids

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[8] C. K. Johnson, ORTEP, Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

tetrachlorodioxobis[protonated 2,6-diacetylpyridine bis-(phenylhydrazone)]uranate(VI)[9] [on average 2.702(6) Å], and longer than those observed[10] in $\mathrm{Cs_2[UO_2Cl_4]}$ (2.62 Å) and in the uranium(IV) compound[3] $\mathrm{[UCl_4(PPh_3O)_2]}$ [2.609(4) and 2.626(3) Å]. The values of the U–O(2) distance [2.300(8) Å] and of the U–O(2)–P angle [158.7(6)°] are quite similar to those encountered in the equatorially five- and six-co-ordinated uranyl compounds[11-13] with $\mathrm{PPh_3O}$ or $\mathrm{AsPh_3O}$ ligands, as is the U–O(1) distance [1.764(9) Å] of the linear uranyl group. The conformation of the $\mathrm{PPh_3O}$ ligand in the present case is slightly different from that in *cis*-$\mathrm{[UCl_4(PPh_3O)_2]}$; the angles between the phenyl rings are 76.5, 89.3, and 82.9° in the present case and 84.5, 85.9, and 77.9° in the *cis* compound.[3]

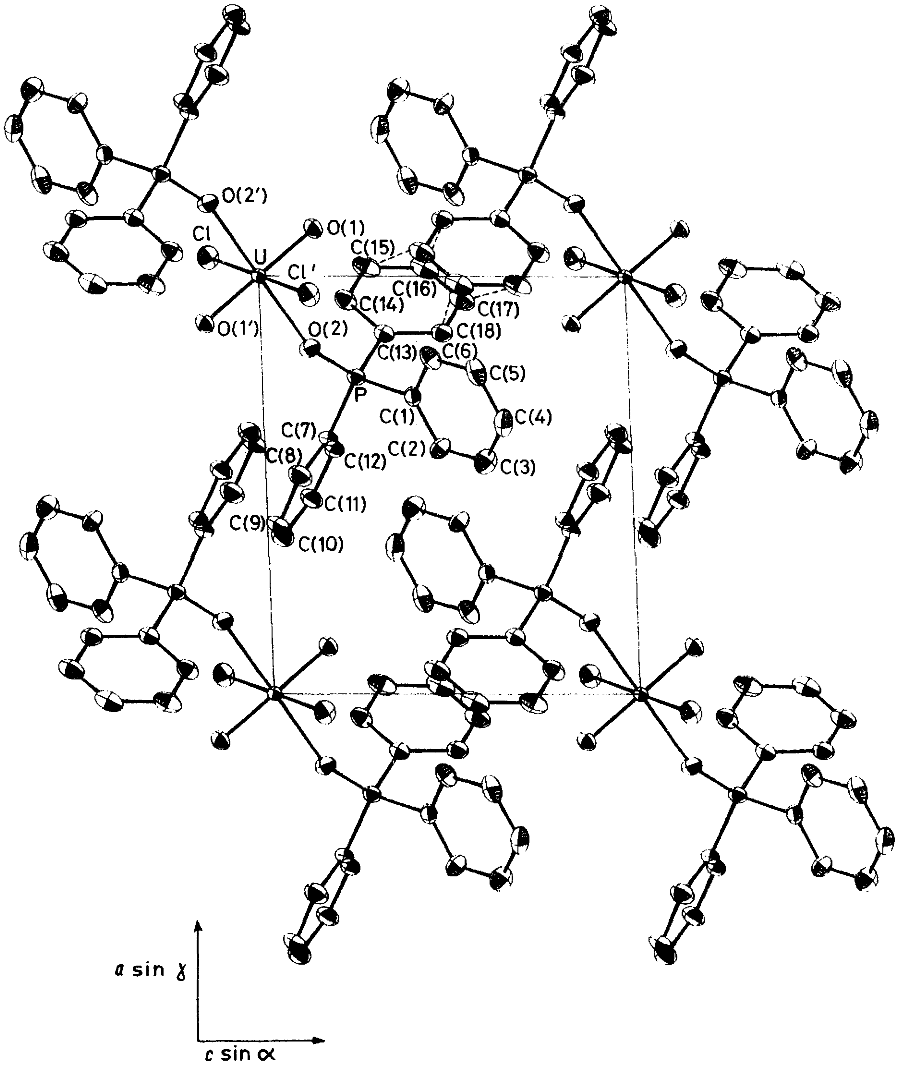

FIGURE 2 Projection of the unit-cell content down the *b*-axis

TABLE 4

Equations of best least-squares planes and, in square brackets, deviations (Å) of the atoms from these planes. The equations are in the form $Ax + By + Cz = D$, where x, y, and z are fractional co-ordinates referred to the crystallographic axes

	A	*B*	*C*	*D*
Plane (1): C(1)—C(6)	3.8695	7.4542	3.3315	5.3848
[C(1) 0.009, C(2) −0.002, C(3) −0.011, C(4) 0.016, C(5) −0.008, C(6) −0.004]				
Plane (2): C(7)—C(12)	−5.0193	−2.7954	8.0707	−2.1897
[C(7) −0.006, C(8) −0.004, C(9) 0.011, C(10) −0.008, C(11) −0.001, C(12) 0.008]				
Plane (3): C(13)—C(18)	7.5929	−4.7470	3.2280	5.1000
[C(13) −0.014, C(14) 0.004, C(15) 0.003, C(16) 0.003, C(17) 0.002, C(18) 0.002]				

Angles (°) between the planes:

(1)—(2) 76.5, (1)—(3) 89.3, (2)—(3) 82.9

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[9] R. Graziani, G. Bombieri, E. Forsellini, and G. Paolucci, *J. Cryst. Mol. Struct.*, 1975, **5**, 1.

[10] D. Hall, A. D. Rae, and T. N. Waters, *Acta Cryst.*, 1966, **20**, 160.

[11] R. Graziani, B. Zarli, A. Cassol, G. Bombieri, E. Forsellini, and E. Tondello, *Inorg. Chem.*, 1970, **9**, 2116.

[12] C. Panattoni, R. Graziani, G. Bandoli, E. Zarli, and G. Bombieri, *Inorg. Chem.*, 1969, **8**, 320.

[13] C. Panattoni, R. Graziani, U. Croatto, B. Zarli, and G. Bombieri, *Inorg. Chim. Acta*, 1968, **2**, 43.

As with $[UCl_4(PPh_3O)_2]$, in which a strong graphite-type interaction between the phenyl groups of different molecules appears to be present, in the present compound there are short intermolecular phenyl–phenyl distances which may stabilize the structure. Thus, in Figure 2, in which the unit-cell content is projected down the *b* axis, the broken lines indicate contacts between the C(13)–C(18) ring and the ring facing it and symmetrically related, by an inversion centre, at $2 - x$, $1 - y$, and $1 - z$. The entire structure appears to be stabilized by the interactions between the phenyl groups of different molecules. In this case, the *trans* configuration may achieve a more stable crystal packing, in contrast to the *cis* configuration adopted[3] by $[UCl_4(PPh_3O)_2]$. From these results it seems that the adoption of a *cis* or *trans* configuration in these compounds depends on the possibility for the phenyl rings to pack in the crystal in a position favourable to strong intermolecular π interactions, further stabilizing the entire crystal structure.

The structures of related uranium-(VI) and -(IV) compounds, $[UO_2X_2L_2]$ and $[UX_4L_2]$, are also of interest in relation to reactions in solution. These species appear to dissolve (*e.g.* in acetonitrile) unchanged.[2,14] The uranium(IV) complexes may be oxidized to their corresponding uranium(VI) compounds, and *vice versa*, and the kinetics of these reactions have recently been investigated.[15] The mechanisms of these reactions, which appear to involve a *cis–trans* configuration change, will be discussed elsewhere.

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[14] J. P. Day and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 197.

[15] J. P. Day and W. I. Azeez, unpublished work; W. I. Azeez, Ph.D. Thesis, Manchester University, 1973.