Crystal and Molecular Structure of Tetrachlorobis(triphenylphosphine oxide)uranium(IV)

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The crystal structure of the title compound has been determined from three-dimensional *X*-ray diffraction data collected on a diffractometer. The compound crystallises in space group *C*2/*c*, with *a* = 14.02, *b* = 13.21, *c* = 20.37 Å, β = 95.87°, and *Z* = 4. The structure was solved by Patterson and Fourier methods, and full-matrix least-squares refinement based on 2 381 reflections gave a final *R* of 0.047. The complex has a distorted octahedral configuration with the neutral ligands co-ordinated in *cis*-positions; U–O is 2.242, and U–Cl 2.609 and 2.626 Å. The results are discussed in relationship to the spectral data of related compounds.

ALTHOUGH a very large number of actinoid tetrahalide complexes of the type $M^{\mathrm{IV}}X_4L_2$(M^{IV} = Th—Pu inclusive, X = Cl or Br, L = oxygen-donor ligand) have been characterised [1-3] the only structural data [4] available are those for [$UCl_4(hmpa)_2$] (hmpa = hexamethylphosphoramide). Solid-state electronic spectral data have recently been recorded [5-7] for a range of protactinium(IV) and uranium(IV) complexes of the types $M^{\mathrm{I}}_2M^{\mathrm{IV}}X_6$ (M^{I} = univalent cation, M^{IV} = Pa and U, X = F—Br inclusive) and $M^{\mathrm{IV}}X_4L_2$ [M^{IV} = Pa or U, X = Cl or Br, L = triphenylphosphine oxide (tppo) or hmpa]. The spectra obtained for the protactinium complexes are very similar to those reported previously [8] for six-co-ordinate uranium(V) complexes in which the electronic configuration is also $5f^1$. In particular, the Γ_8' quartet level is split into two doublets. Selbin and Ortego [8] have suggested in the case of uranium(V) complexes that the magnitude of this splitting is an indication of the extent of the geometrical distortion from octahedral symmetry. However, as discussed previously [5] a close examination of the splitting for a range of compounds does not fully support this hypothesis although in the majority of instances structural data are not available. In an attempt to clarify this situation we are investigating the structures of a range of actinoid-(IV) and -(V) complexes and we report here structural results for [$UCl_4(tppo)_2$] which is isostructural with [$PaCl_4(tppo)_2$].[9]

EXPERIMENTAL

Clear green crystals were obtained by recrystallisation from anhydrous nitromethane. A single crystal, a parallelepiped of dimensions *ca.* 0.10 × 0.10 × 0.14 mm, elongated along the [110] direction, was selected and lodged in a glass capillary. Rotation and Weissenberg photographs indicated a monoclinic lattice. Approximate unit-cell dimensions were obtained from measurements on precession films. More precise cell parameters were determined by least-squares methods from the 2θ angles of *ca.* 30 reflections measured with a diffractometer using Mo-K_α radiation ($\lambda_{\alpha m}$ 0.7107 Å).

Crystal Data.—$C_{36}H_{30}Cl_4O_2P_2U$, $M = 936$, Monoclinic, $a = 14.02(1)$, $b = 13.21(1)$, $c = 20.37(2)$ Å, $\beta = 95.87(5)°$, $U = 3751$ Å³, $D_c = 1.66$ g cm^{-3}, $Z = 4$, $F(000) = 1\,808$. μ(Mo-K_α) = 58 cm^{-1}. Space group *Cc* or *C*2/*c* from systematically absent reflections: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$; *C*2/*c* was chosen and confirmed by the structure determination.

Diffraction intensities were collected on a computer-controlled Siemens automated diffractometer by the θ—2θ scan and the 5-points measuring procedure. 2 831 Unique reflections with $2\theta < 50°$ were examined with Mo-K_α radiation. A check reflection, monitored periodically, showed no detectable deterioration of the crystal during data collection. 511 Very weak reflections having $I < 2\,\sigma\,(I)$ were considered unobserved and were given zero weight in the subsequent refinement. Intensities were corrected for Lp and absorption effects following the Kopfmann–Huber procedure.[10,11]

Structure Determination.—Interpretation of a three-dimensional Patterson function showed the uranium atoms to lie on a two-fold axis (equipoints 4 *e* of space group *C*2/*c*) at *y ca.* 0.135. All other non-hydrogen atoms were located on difference-Fourier maps. Refinement was then carried out by a full-matrix least-squares method for positional parameters, and individual isotropic and anisotropic parameters. Atomic scattering factors for neutral atoms were taken from ref. 12, for uranium a correction was applied for the real and imaginary part of the anomalous dispersion.[13] At this point (*R* 0.075) a Fourier difference synthesis showed no unusual features except some peaks which could be attributed to hydrogen atoms. These were introduced in calculated positions, by use of scattering factors from ref. 14. Refinement of all non-hydrogen atoms was then continued allowing the atoms to vibrate

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TABLE 1

Fractional co-ordinates and anisotropic * temperature factors (× 10^4), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	0	1 364.3(4)	2 500	433(3)	407(3)	283(3)	0	39(2)	0
Cl(1)	511(3)	−26(3)	1 696(2)	738(24)	753(23)	744(22)	68(18)	112(18)	−361(19)
Cl(2)	1 786(2)	1 560(3)	3 015(1)	424(17)	831(25)	559(17)	35(15)	−74(13)	−114(16)
P	210(2)	3 343(2)	1 212(1)	421(17)	495(18)	330(14)	−24(12)	53(12)	38(12)
O	285(6)	2 576(6)	1 774(3)	602(52)	563(47)	343(37)	−74(38)	14(33)	109(33)
C(1)	1 376(8)	3 621(9)	990(5)	625(76)	437(58)	475(58)	−34(59)	91(52)	12(55)
C(2)	1 581(8)	3 730(11)	334(6)	428(68)	907(95)	580(68)	−56(68)	206(54)	116(70)
C(3)	2 478(12)	3 950(12)	194(7)	870(123)	929(118)	795(99)	−24(89)	362(91)	145(84)
C(4)	3 217(12)	4 042(13)	692(10)	662(112)	889(114)	1 236(142)	−65(85)	338(101)	61(103)
C(5)	3 044(11)	3 920(11)	1 345(8)	774(106)	687(102)	1 025(117)	−122(76)	8(86)	14(83)
C(6)	2 122(9)	3 715(11)	1 494(6)	564(82)	716(86)	688(76)	−273(73)	6(60)	9(70)
C(7)	−336(9)	4 483(9)	1 461(5)	603(78)	562(71)	350(55)	42(57)	100(51)	15(50)
C(8)	−1 231(10)	4 387(11)	1 707(6)	568(84)	807(96)	695(82)	85(69)	257(66)	−8(71)
C(9)	−1 698(12)	5 280(14)	1 876(8)	811(118)	1 014(132)	868(107)	317(98)	187(86)	−75(95)
C(10)	−1 271(15)	6 188(12)	1 830(9)	1 286(162)	622(106)	1 170(136)	169(100)	483(120)	−55(92)
C(11)	−425(14)	6 293(13)	1 586(9)	1 313(159)	672(102)	1 213(137)	90(110)	504(121)	128(103)
C(12)	69(11)	5 448(11)	1 395(7)	753(112)	700(94)	842(100)	−61(79)	273(83)	37(78)
C(13)	−527(9)	2 838(9)	496(5)	639(82)	657(77)	297(54)	−89(61)	79(51)	6(52)
C(14)	−1 141(9)	3 477(11)	102(5)	576(78)	912(102)	448(63)	−121(71)	36(54)	189(67)
C(15)	−1 641(11)	3 076(14)	−469(7)	628(99)	1 125(128)	537(80)	−139(85)	−51(66)	97(82)
C(16)	−1 511(12)	2 099(16)	−649(6)	749(112)	1 381(158)	407(73)	−343(104)	8(69)	24(89)
C(17)	−920(12)	1 456(13)	−252(7)	983(120)	1 023(119)	570(80)	−360(103)	238(78)	−284(88)
C(18)	−393(11)	1 834(11)	321(6)	945(117)	828(99)	419(67)	31(81)	80(67)	−159(66)

* In the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

anisotropically. When all parameter shifts were $<0.1\,\sigma$ the refinement was terminated with a final conventional R value of 0.047 for the observed reflections. Unit weight was assigned for all the reflections except those with zero intensity. Fourier, least-squares, bond lengths and angles, and best-plane calculations were carried out on a CDC 6600 computer by use of the '*X*-Ray '70' programme system.[15]

TABLE 2

Distances (A) and angles (°), with estimated standard deviations in parentheses

(*a*) Uranium environment			
U–Cl(1)	2.609(4)		
U–Cl(2)	2.626(3)	Cl(1)–U–Cl(2^{I})	97.5(1)
U–O	2.242(7)	Cl(1)–U–O^{I}	174.3(2)
Cl(1)–U–Cl(2)	90.4(1)	Cl(2)–U–O	88.1(2)
Cl(1)–U–O	90.5(2)	Cl(2)–U–Cl(2^{I})	168.7(1)
Cl(1)–U–Cl(1^{I})	90.6(1)	Cl(2)–U–O^{I}	83.9(2)
		O–U–O^{I}	88.9(3)
(*b*) Triphenylphosphine oxide			
P–O	1.524(7)	C(9)–C(10)	1.35(3)
P–C(1)	1.78(1)	C(10)–C(11)	1.34(3)
P–C(7)	1.79(1)	C(11)–C(12)	1.38(2)
P–C(13)	1.82(1)	C(12)–C(7)	1.40(2)
U–O–P	165.1(5)	C(7)–C(8)–C(9)	118(1)
O–P–C(1)	109.5(5)	C(8)–C(9)–C(10)	120(2)
O–P–C(7)	110.2(5)	C(9)–C(10)–C(11)	122(2)
O–P–C(13)	110.3(5)	C(10)–C(11)–C(12)	120(2)
C(1)–P–C(13)	109.4(5)	C(11)–C(12)–C(7)	120(1)
C(1)–P–C(7)	109.3(6)	C(12)–C(7)–C(8)	120(1)
C(7)–P–C(13)	108.1(5)	P–C(7)–C(8)	117(1)
C(1)–C(2)	1.40(2)	P–C(7)–C(12)	124(1)
C(2)–C(3)	1.35(2)		
C(3)–C(4)	1.38(2)	C(13)–C(14)	1.40(2)
C(4)–C(5)	1.39(3)	C(14)–C(15)	1.40(2)
C(5)–C(6)	1.38(2)	C(15)–C(16)	1.36(3)
C(6)–C(1)	1.39(2)	C(16)–C(17)	1.39(2)
C(1)–C(2)–C(3)	121(1)	C(17)–C(18)	1.41(2)
C(2)–C(3)–C(4)	121(1)	C(18)–C(13)	1.39(2)
C(3)–C(4)–C(5)	120(1)	C(13)–C(14)–C(15)	118(1)
C(4)–C(5)–C(6)	119(1)	C(14)–C(15)–C(16)	121(1)
C(5)–C(6)–C(1)	120(1)	C(15)–C(16)–C(17)	121(1)
C(6)–C(1)–C(2)	119(1)	C(16)–C(17)–C(18)	120(2)
P–C(1)–C(2)	123(1)	C(17)–C(18)–C(13)	119(1)
P–C(1)–C(6)	118(1)	C(18)–C(13)–C(14)	121(1)
C(7)–C(8)	1.40(2)	P–C(13)–C(14)	120(1)
C(8)–C(9)	1.41(2)	P–C(13)–C(18)	118(1)

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

I $-x, y, \frac{1}{2} - z$ II $-\frac{1}{2} - x, \frac{1}{2} - y, -z$.

RESULTS AND DISCUSSION

Final positional and temperature factors are given in Table 1 together with their standard deviations. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21383 (3 pp., 1 microfiche).* Bond lengths and bond angles are listed in Table 2 (see Figure 1 for atom labelling). Contact distances and least-squares planes are shown in Tables 3 and 4, respectively.

TABLE 3

Contact distances (Å), with estimated standard deviations in parentheses

(*a*) Selected intramolecular nonbonding contacts			
U · · · P	3.736(2)	C(1) · · · Cl(1^{I})	3.71(1)
O · · · Cl(1)	3.46(1)	Cl(1) · · · Cl(2^{I})	3.94(1)
O · · · Cl(2)	3.40(1)	C(9) · · · C(12^{I})	4.00(2)
O · · · Cl(2^{I})	3.27(1)	C(10) · · · C(11^{I})	3.81(3)
O · · · O^{I}	3.14(1)	C(10) · · · C(12^{I})	3.96(2)
Cl(1) · · · Cl(2)	3.72(1)	C(11) · · · C(11^{I})	3.79(3)
(*b*) Intermolecular carbon–carbon contacts			
C(14) · · · C(15^{II})	3.86(2)	C(15) · · · C(16^{II})	3.63(2)
C(14) · · · C(16^{II})	3.66(2)	C(15) · · · C(17^{II})	3.91(2)
C(15) · · · C(15^{II})	3.56(2)		

Superscripts are defined in footnote to Table 2.

As shown in Figure 1 in which the molecule is viewed along the [100] direction, the uranium atom is six-coordinated, with the neutral ligands in *cis*-positions. The

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

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

co-ordination octahedron is distorted, and the entire molecule has crystallographic C_2 symmetry. The two crystallographically equivalent U–O bonds [2.24(1) Å] are identical with those in tetrachlorobis(hexamethylphosphoramide)uranium(IV) [2.24(3) Å], in which the two hmpa molecules are mutually *trans* in the distorted octahedral array around the central atom. The U–O–P angles (165.1 and 163°) are also similar in the two compounds. The strong U–O interaction implied by the bond lengths, which are appreciably shorter than those in, *e.g.* eight-co-ordinate U^{IV} compounds,[4] is reflected by the large shift in the position of the P=O stretching vibration on co-ordination of the phosphine oxides. Thus the P–O band in tppo is observed at 1 192 cm^{-1} whilst in $[UCl_4(tppo)_2]$ it is at 1 068 cm^{-1}, a shift of 124 cm^{-1}. However this shift is larger in the UCl_4–hmpa system (167 cm^{-1}) and it is apparent that the magnitude of the shift is not solely related to the U–O bond length. In addition, the position of the P–O stretching vibration varies appreciably in complexes of this type with little change in P–O bond length, the respective values being 1 068 and 1.524(7) for $[UCl_4(tppo)_2]$ and 1 039 cm^{-1} and 1.51(1) Å for $[UCl_4(hmpa)_2]$. The P–O bond, 1.46(1) Å in free Ph_3PO,[16] is only slightly affected by the co-ordination to UCl_4 and obviously maintains strong double-bond character. The U–Cl distances in $[UCl_4(tppo)_2]$ are close to those in $[UCl_4(hmpa)_2]$ [2.58(1) and 2.60(1) Å], being significantly shorter than those in most uranyl complexes.[17-20]

TABLE 4

Equations of least-squares planes and, in square brackets, deviations (Å) of relevant atoms from the planes. The equations are in the form $AX + BY + CZ = D$, where X, Y, and Z represent fractional co-ordinates in the crystal system

Plane (1):

$$12.685X - 0.0Y + 6.736Z = 1.684$$

[O −0.128, Cl(1) 0.108, O^I 0.128, Cl(1^I) −0.108, U * 0.000]

Plane (2):

$$-4.007X - 9.262Y + 13.827Z = 2.094$$

[Cl(1) 0.070, Cl(2) −0.086, O^I 0.095, Cl(2^I) −0.079, U * 0.099]

Plane (3):

$$-2.727X + 12.934Y + 1.558Z = 4.456$$

[C(1) 0.006, C(2) −0.011, C(3) 0.007, C(4) 0.002, C(5) −0.007, C(6) 0.003, P * 0.000]

Plane (4):

$$5.078X - 1.056Y + 18.060Z = 1.987$$

[C(7) 0.007, C(8) 0.007, C(9) −0.020, C(10) 0.018, C(11) −0.004, C(12) −0.009, P * −0.045]

Plane (5):

$$-11.386X - 3.492Y + 12.228Z = 0.212$$

[C(13) 0.004, C(14) −0.002, C(15) 0.009, C(16) −0.018, C(17) 0.019, C(18) −0.012, P * −0.137]

Dihedral angles (°)

(1)–(2)	88.9	(3)–(5)	85.9
(2)–(2′)	89.1	(4)–(5)	77.9
(3)–(4)	84.5		

* Atoms excluded from the calculation of the least-squares plane.

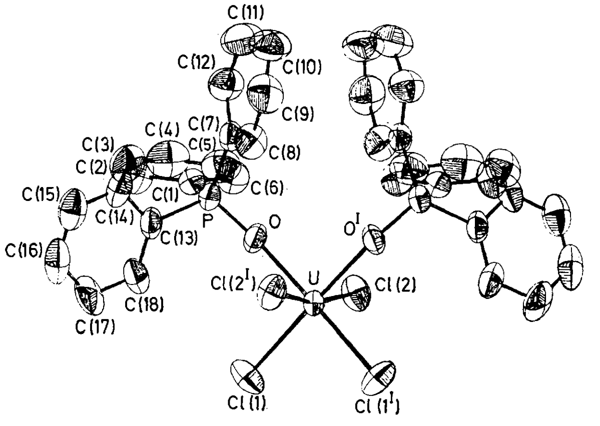

FIGURE 1 A drawing of the molecule showing the numbering scheme used

There are some significant intra- and inter-molecular contacts. In fact, as shown in Figure 2 in which the structure is projected down the *a* axis, there is a ring–ring type of interaction between the C(7)—(12) ring and the corresponding atoms at $x, y, \frac{1}{2} - z$: these two rings are related by the two-fold symmetry axis and are approximately parallel (the angle between the planes is 9.2°). Moreover the C(13)—(18) ring is faced with the corresponding one $-\frac{1}{2} - x, \frac{1}{2} - y, -z$ with an interplanar distance 3.52 Å. This strong graphite-type interaction between

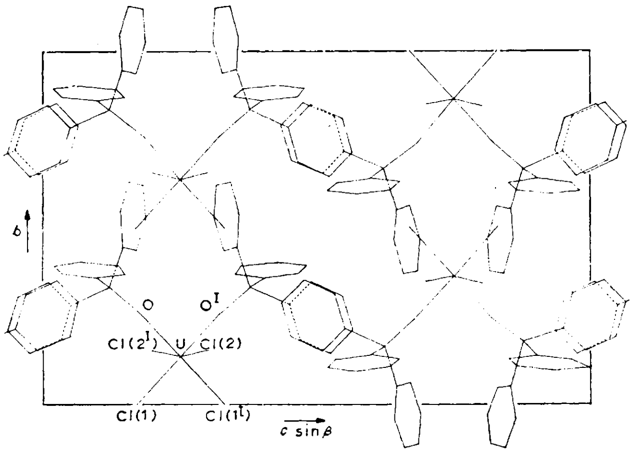

FIGURE 2 Projection of the structure down the *b* axis

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the phenyl groups of different molecules, which is consistent with some degree of π interaction between the aromatic systems, suggests that the *cis* is preferred to a *trans*-configuration in order to achieve more stable crystal packing.

The phosphorus atoms show tetrahedral co-ordination, being surrounded by the atoms C(1), C(7), C(12), and O. The tetrahedral angles vary from 108.1(5) to 110.3(5)°. The P–C(1) and P–C(7) bond lengths are similar [1.78(1) and 1.79(1) Å] but the P–C(13) bond is relatively longer [1.82(1) Å]. This lengthening may be caused by the intermolecular contacts in which the atoms of this ring are involved.

[$PaCl_4(tppo)_2$] Is isostructural with [$UCl_4(tppo)_2$] and the geometrical arrangement around the two actinide(IV) ions should be similar since there is little difference in their ionic radii (Pa^{4+} 0.994, U^{4+} 0.929 Å). It is interesting, therefore, to compare the splittings observed for the Γ_8' levels of [$PaCl_4(tppo)_2$] and Cs_2[$PaCl_6$], which is isostructural with Cs_2[$PuCl_6$], since the six chlorine atoms in the latter are at the vertices of an almost perfect octahedron.[21] The splitting * in [$PaCl_4(tppo)_2$] is 328 cm^{-1} whilst that in Cs_2[$PaCl_6$] is only very slightly smaller at 318 cm^{-1} (both spectra recorded at room temperature). In view of the extensive distortion from octahedral stereochemistry in [$PaCl_4(tppo)_2$], the suggestion [8] that the magnitude of this splitting is an indication of the extent of the geometrical distortion from pure octahedral symmetry appears to be incorrect. The splitting observed for [$PaCl_4(tppo)_2$] is, in addition, only slightly greater than that recorded for [NEt_4]$_2$-[$PaCl_6$] (265 cm^{-1}), particularly when one considers that the bands concerned [5,6] are relatively broad. Although full structural data are not available for this hexachloroprotactinate(IV), recent i.r. and Raman results [22] suggest little, if any, distortion from octahedral chemistry.

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* The band position reported in ref. 5 as 6 873 cm^{-1} is incorrect: the position is 7 163 cm^{-1}.

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