Crystal Structure of Pentachloro(triphenylphosphine oxide)uranium(V)

By **Gabriella Bombieri,*** Laboratorio di Chimica e Technologie dei Radioelementi C.N.R., Padova, Italy
David Brown,* Chemistry Division, AERE, Harwell, Oxfordshire OXH ORA
Carlo Mealli, University of Florence, Italy

The structure of the title compound has been determined by single-crystal *X*-ray diffraction methods from diffractometer data and refined to *R* 0.093. Crystals are monoclinic, space group $P2_1/n$ with a_0 = 15.404(5), b_0 = 13.552(5), c_0 = 10.868(5) Å, β = 93.64(5)°, Z = 4. The uranium atoms are surrounded by five chlorine atoms (U–Cl 2.47—2.50 Å) and one oxygen atom (U–O 2.11 Å) at the vertices of a distorted octahedron. Results are discussed in relation to spectral properties of UCl_5·tppo, for which optical absorption bands are assigned to transitions from the Γ_7 ground state, and hexachlorouranates(V).

DESPITE considerable interest [1–5] in the preparation and spectral properties of pentavalent protactinium and uranium complexes of the type MX_5·L and MX_5·2L (M = Pa or U, X = Cl or Br, L = donor ligand) no structural data have been reported for them. In the electronic spectra of octahedral or almost octahedral $5f^1$ uranium(V) complexes the Γ_8' quartet level is generally split into two doublets [1,6] and it has been suggested [1] that the magnitude of this splitting is an indication of the extent of geometrical distortion from octahedral symmetry. However, a close examination of the splitting

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for a range of compounds suggests [7] that this hypothesis may not be fully justified, although in the majority of instances structural data are not available. Spectra obtained [7-10] for six-co-ordinate protactinium(IV) complexes, also of $5f^1$ electronic configuration, are very similar to those of the ' octahedral ' uranium(V) complexes, and recent structural information [11] for $UCl_4 \cdot 2tppo$ (with which the Pa^{IV} analogue is isostructural) indicates that the degree of splitting may not be related solely to the geometrical distortion of the octahedron. In order to clarify the situation further we are investigating the structures of a range of actinoid-(IV) and -(V) compounds and we report here structural results for $UCl_5 \cdot tppo$ (tppo = triphenylphosphine oxide). Attempts to obtain suitable single crystals of a hexachlorouranate(V), M^IUCl_6, to permit a more satisfactory comparison of spectral and structural data, have been unsuccessful.

EXPERIMENTAL

$UCl_5 \cdot tppo$ was prepared as described previously [12] and recrystallised from dichloromethane–isopentane. It is very sensitive to atmospheric moisture and the yellow-orange crystals were therefore mounted in thin-walled Lindemann glass capillaries in an inert-atmosphere glove box. Solid-state spectra were recorded by the technique described earlier.[13]

Crystal Data.—$C_{18}H_{15}Cl_5OPU$, $M = 693.6$, Monoclinic, $a_0 = 15.404(5)$, $b_0 = 13.552(5)$, $c_0 = 10.868(5)$ Å, $\beta = 93{,}64(5)^\circ$, $U = 2\,264.18$ Å^3, $D_c = 2.034$ g cm^{-3}, $Z = 4$, $D_m = 1.99$ g cm^{-3}, $F(000) = 1\,724$. Mo-K_α radiation, $\lambda = 0.709\,3$ Å; μ(Mo-K_α) = 74.64 cm^{-1}. Space group $P2_1/n$ from systematic absences ($h0l$, $h + 1 \neq 2n$; $0k0$, $k \neq 2n$).

Data Collection.—A Philips PW 1 100 automatic diffractometer was used for data collection. The crystal was mounted at random on a goniometer head. By use of the ' peak-hunting ' procedure [14] the positions of twenty strong reflections were determined and used to calculate cell constants which were refined by a least-squares technique. The crystal employed for the structure determination had faces of the form (100), ($\bar{1}00$), (001), (011), ($02\bar{1}$), ($01\bar{1}$), ($0\bar{1}1$), ($0\bar{1}\bar{2}$), (010), and ($0\bar{1}0$). The maximum dimensions along the direct crystal axes a_0, b_0, and c_0 were 0.066, 0.55, and 0.50 mm, respectively. Intensity data were collected by use of graphite-monochromated Mo-K_α radiation. The θ—2θ scan technique, rate 0.05° s^{-1}, and width 0.94° was employed throughout data collection. Stationary-counter–stationary-crystal background counts of duration equal to half the peak scanning time were taken at each end of the scan. 4 295 Reflections were recorded in a unique data set with $6^\circ \leqslant 2\theta \leqslant 50^\circ$. The intensities of 3 standard reflections measured every 2 h showed only deviations from the mean attributable to counting statistics.

The standard deviations for the background-corrected intensities were calculated from: $\sigma(I) = [CT + (t_c/t_b)^2 (B_1 + B_2) + (pI)^2]^{\frac{1}{2}}$, where CT is the total integrated peak count obtained in scan time t_c, B_1 and B_2 are background counts each obtained in time $\frac{1}{2}t_b$, and $I = CT - (t_c/t_b^2)(B_1 + B_2)$. A value of 0.04 was assigned to the factor p to allow for other errors. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects and for absorption. For the crystal chosen the transmission coefficients evaluated by numerical integration range from 0.095 to 0.608. 1 997 Reflections with intensities $I > 3\sigma(I)$ were employed for the structure determination.

Structure Determination.—The structure was solved by use of a three-dimensional Patterson synthesis. Successive Fourier syntheses resulted in the location of all non-hydrogen atoms.

At the end of the Fourier refinement the value R [$= \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$] was 0.20. The least-squares method was then employed, the function minimized being $\Sigma w(|F_0| - |F_0|)^2$ where $w = 1/\sigma F_0$. In all calculations of F_c the atomic scattering factors were taken from ref. 15 except those for hydrogen which were taken from ref. 16. For uranium a correction was employed for the real and imaginary parts of the anomalous dispersion.[17] The phenyl rings were refined initially as rigid groups (symmetry D_{6h}, C–C 1.392 Å) by a modified version of the programme CRYLSQ.

After a first cycle in the isotropic mode, which gave R 0.16 and the weighted factor R' 0.18, where $R' = \{[\Sigma w(|F_o| - |F_c|)^2]/\Sigma w|F_o|^2\}^{\frac{1}{2}}$, the uranium, phosphorus, oxygen and chlorine atoms were treated anisotropically. Two cycles gave R 0.103 and R' 0.120. At this point hydrogen atoms were introduced at calculated positions (assuming C–H 0.95 Å, and C–C–H 120°) and assigned isotropic temperature factors equal to those of the carbon atoms to which they were attached.

Two final cycles of full-matrix least-squares refinement in which the non-group atoms were allowed anisotropic temperature factors while the phenyl group atoms had individual isotropic temperature factors lowered R and R' to 0.093 and 0.108, respectively. On the last cycle, the ratios of the parameter shift to standard deviations were $< 0.2\ \sigma$. The final difference-Fourier showed peaks as high as 2.2 eÅ^{-3} only in the region surrounding uranium. Programmes used were those of the ' X-Ray '72 ' package.[18]

RESULTS AND DISCUSSION

Final positional and thermal parameters of the non-group atoms are given in Table 1 with their standard deviations estimated from the inverse matrix. Similar results for the carbon and hydrogen atoms are listed in Table 2 with the rigid-body co-ordinates derived from the final group parameters. Observed and calculated structure factors are contained in Supplementary Publication No. SUP 21755 (3 pp., 1 microfiche).*

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

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TABLE 1

Fractional co-ordinates and anisotropic * temperature factors ($\times 10^4$), 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	2 076(1)	1 583(1)	611(1)	855(10)	360(6)	497(7)	−75(9)	148(6)	−72(7)
Cl(1)	1 146(6)	164(7)	−13(8)	768(73)	722(57)	743(57)	−232(56)	72(52)	−216(50)
Cl(2)	3 004(8)	488(9)	2 002(9)	1 024(92)	1 084(101)	846(67)	716(82)	−267(62)	−303(69)
Cl(3)	3 004(9)	3 002(9)	1 337(11)	1 906(130)	1 272(88)	1 437(95)	−1 118(93)	887(91)	−725(79)
Cl(4)	1 128(10)	2 694(8)	−716)9)	2 424(149)	1 130(82)	826(68)	1 056(96)	549(80)	463(63)
Cl(5)	3 010(7)	1 245(7)	−1 110(9)	1 151(91)	818(68)	844(62)	−225(64)	399(61)	−349(55)
O	1 223(13)	1 895(13)	2 008(17)	554(134)	426(112)	627(120)	304(103)	−179(106)	−89(97)
P	423(6)	2 171(5)	2 704(6)	646(66)	217(39)	391(41)	−3(40)	−8(42)	−53(32)

* In the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{12}a^*b^*hk + \ldots)]$.

TABLE 2

Group and derived parameters [a,b]

Group	x_c [a]	y_c	z_c	$\theta/°$ [b]	$\phi/°$	$\chi/°$
GP1	1 040(10)	3 150(9)	5 034(12)	64.2(9)	−72.4(8)	173.9(2.1)
GP2	−0 627(10)	3 572(12)	1 151(14)	61.9(9)	126.0(7)	−82.7(8)
GP3	−0 572(10)	0 362(11)	3 238(10)	16.8(7)	79.9(2.3)	42.7(2.4)

Derived phenyl-group carbon atoms						Derived phenyl-group hydrogen atoms			
Group	Atom	x/a	y/b	z/c	$B/\text{Å}^2$	Atom	x/a	y/b	z/c
Group (1)	C(1)	799(16)	2 759(14)	4 090(15)	4.2(7)				
	C(2)	200(15)	3 013(15)	4 942(16)	5.5(8)	H(2)	−388	2 835	4 784
	C(3)	482(14)	3 470(15)	6 044(15)	7.0(9)	H(3)	69	3 633	6 626
	C(4)	1 361(17)	3 673(14)	6 292(15)	6.4(9)	H(4)	1 541	4 022	7 032
	C(5)	1 960(14)	3 418(15)	5 439(16)	7.8(1.0)	H(5)	2 556	3 612	5 601
	C(6)	1 679(15)	2 960(14)	4 337(15)	7.4(1.0)	H(6)	2 099	2 814	3 759
Group (2)	C(7)	−198(16)	3 010(14)	1 778(15)	5.0(8)				
	C(8)	−128(14)	4 020(157)	1 989(14)	6.0(9)	H(8)	235	4 269	2 645
	C(9)	−627(15)	4 677(15)	1 257(14)	7.3(1.0)	H(9)	−601	5 367	1 399
	C(10)	−1 198(14)	4 322(13)	315(15)	9.0(1.3)	H(10)	−1 539	4 763	−208
	C(11)	−1 268(15)	3 311(14)	103(15)	10.9(1.4)	H(11)	−1 636	3 063	−575
	C(12)	−769(16)	2 655(14)	836(15)	10.8(1.5)	H(12)	−801	1 965	673
Group (3)	C(13)	−178(15)	1 088(14)	3 004(16)	5.2(8)				
	C(14)	−1 061(14)	1 148(13)	3 197(15)	5.7(9)	H(14)	−1 345	1 763	3 126
	C(15)	−1 521(15)	300(15)	3 469(16)	7.4(1.0)	H(15)	−2 121	339	3 593
	C(16)	−1 097(14)	−607(15)	3 549(16)	6.2(9)	H(16)	−1 408	−1 186	3 748
	C(17)	−214(16)	−667(14)	3 356(15)	6.8(1.0)	H(17)	78	−1 289	3 435
	C(18)	246(15)	181(13)	3 083(15)	5.0(8)	H(18)	854	134	2 695

[a] x_c, y_c, and z_c are the co-ordinates of the baricentre of the group. [b] The Goldstein definition is used for Euler angles (H. Goldstein, 'Classical Mechanics,' Addison–Wesley, Reading, Massachusetts, 1959).

The crystal structure is composed of discrete molecules. A perspective view of a single molecule, the asymmetric unit, is shown in Figure 1. Selected bond distances and angles are listed in Table 3, from which it is apparent that the distortion from octahedral stereochemistry in this compound is associated with the U–O bond length, rather than being angular. The U–Cl bond lengths (2.47—2.50 Å) are similar to the terminal U–Cl distances in U_2Cl_{10} (2.43 and 2.44 Å) in which the octahedral array of six chlorine atoms around each

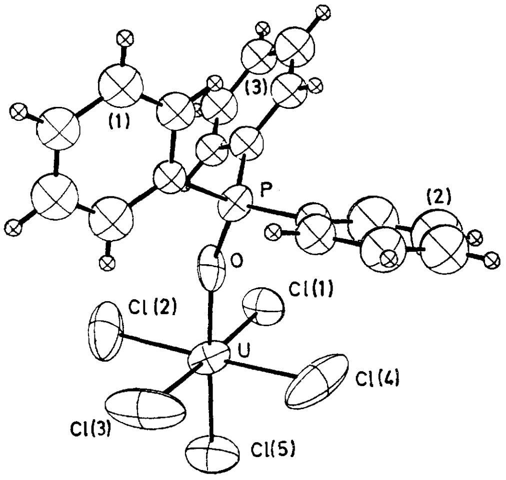

FIGURE 1 Perspective view of the asymmetric unit, showing 50% probability vibrational ellipsoids. Phenyl hydrogen atoms have an arbitrary size

TABLE 3

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

(a) Distances

U–O	2.11(2)	U–Cl(5)	2.47(1)
U–Cl(1)	2.47(1)	O–P	1.53(2)
U–Cl(2)	2.50(1)	P–C(1)	1.77(2)
U–Cl(3)	2.49(1)	P–C(7)	1.76(2)
U–Cl(4)	2.49(1)	P–C(13)	1.78(2)

(b) Angles

O–U–Cl(1)	88.7(5)	Cl(1)–U–Cl(2)	90.2(3)
O–U–Cl(2)	92.4(6)	Cl(1)–U–Cl(4)	90.2(4)
O–U–Cl(3)	89.3(6)	Cl(2)–U–Cl(3)	88.4(4)
O–U–Cl(4)	85.8(6)	Cl(3)–U–Cl(4)	91.1(4)
O–U–Cl(5)	176.8(8)	Cl(5)–U–Cl(1)	90.2(3)
U–O–P	163.7(1)	Cl(5)–U–Cl(2)	90.6(3)
Cl(1)–U–Cl(3)	177.5(4)	Cl(5)–U–Cl(3)	91.9(4)
Cl(2)–U–Cl(4)	178.1(7)	Cl(5)–U–Cl(4)	91.2(4)

uranium is also distorted.[19] They are, as would be expected, somewhat shorter than those [11] in the tetravalent complex UCl_4·2tppo (2.609 and 2.626 Å). Similarly, the U–O distance in UCl_5·tppo (2.11 Å) is 0.13 Å shorter than those reported for the tetravalent complex, reflecting the difference in the covalent radii of U^{IV} and U^{V}. The U–O–P angle (163.7°) is close to those for UCl_4·2tppo (165.1°).

The equation of the best plane in direct space through the atoms Cl(1) to Cl(4) is: $9.7751X - 2.3017Y - 8.6148Z = 1.0966$, where X, Y, and Z are the fractional co-ordinates of the atoms in the direct cell. The deviations (Å) from the plane are: Cl(1) −0.003, Cl(2) 0.003, Cl(3) −0.003, and Cl(4) 0.003. The uranium atom lies 0.04 Å out of the plane in the direction of Cl(5).

The high values of the thermal parameters for Cl(3) and Cl(4) (Table 1) are not fully understood. The higher components are perpendicular to the U–Cl(3) and U–Cl(3) and U–Cl(4) bond directions as illustrated by the thermal ellipsoids in Figure 2 which is a view of the structure perpendicular to the Cl(1)—(4) plane.

The strong U–O interaction implied by the bond length (2.11 Å) is reflected by the large shift in the position of the P=O stretching vibration on co-ordination of the ligand. Thus, the P–O band in tppo is observed at 1 192 cm^{-1} whilst in UCl_5·tppo it is at 973 cm^{-1}, a shift of 219 cm^{-1}. However, consideration of corresponding bond lengths and shifts for tetravalent complexes UCl_4·2L (L = tppo and hmpa = hexamethylphosphoramide) indicates [11] that the magnitude of the shift is not solely related to the U–O bond length. The P–O bond [1.46(1) Å] in free Ph_3PO [20] is only slightly affected by co-ordination to UCl_5 and obviously maintains strong double-bond character.

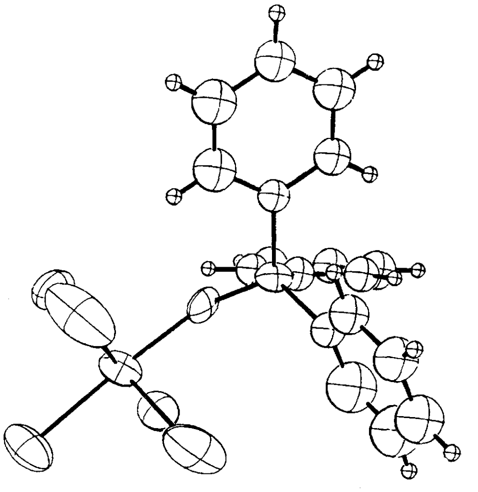

FIGURE 2 View of the molecule perpendicular to the plane of the chlorine atoms

Spectral Data.—The solid-state spectrum of UCl_5·tppo recorded at 85 K between 0.5 and 2.2 μm is shown in Figure 3. It is similar to those recorded previously [1,2,6,12,21] for six-co-ordinate hexachlorouranates(v), comprising three groups of bands; the fourth transition would be expected as a very weak band at longer wavelength. The spectrum is quite different from those reported recently [22,23] for pentahalogeno-oxouranates(v), $[NEt_4]_2[UOX_5]$ (X = F, Cl, or Br), which contain five groups of bands in this region as a consequence of the lower symmetry (D_{4h}). Thus the distortion from octahedral symmetry in UCl_5·tppo is insufficient to cause marked differences in the solid-state visible–near i.r. spectrum relative to the spectra of the hexachloro-complexes. Consequently the results have been interpreted on the basis of electronic transitions from the Γ_7 ground state to the Γ_7', Γ_8', and Γ_6 states by analogy with previous assignments for hexahalogeno-complexes.[1,6,8] Assignments are shown in Table 4. The mean frequencies

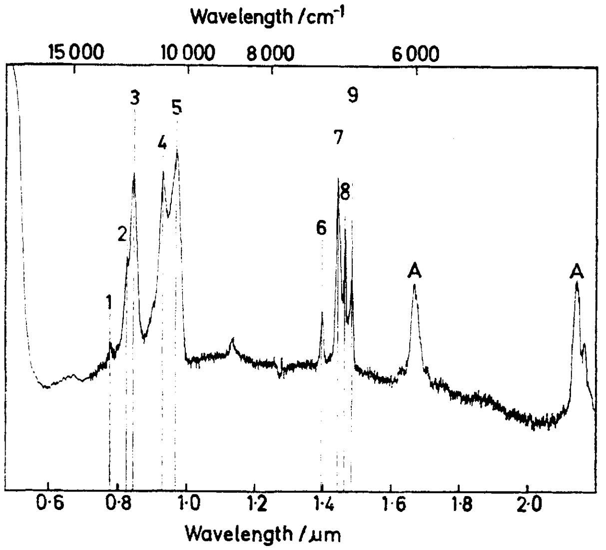

FIGURE 3 Solid state spectrum at 85 K; tppo bands are marked A

TABLE 4

Spectral assignments for solid UCl_5·tppo

	Room temperature		85 K		
Assignment	Band position [a] (cm^{-1})	Vib. freq. (cm^{-1})	Band position [a] (cm^{-1})	Vib. freq. (cm^{-1})	Band no. [b]
Γ_7–Γ_6			12 820sh, w		1
			12 165sh, w		2
	11 792s, b		11 848s		3
	10 708s, b		10 753s		4
Γ_7–Γ_8'	10 183s, b		10 352s		5
	7 148w	+313	7 170w	+321	6
	6 920s	+85	6 944s	+95	7
Γ_7–Γ_7'	6 835s	0	6 849m	0	8
	6 743s	−92	6 748m	−101	9
	6 515w	−320			

[a] s = strong, b = broad, sh = shoulder, w = weak, m = medium. [b] See Figure 3.

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deduced for certain of the vibrational modes which have coupled with the electronic transitions to produce the vibronic bands, 318 and 94 cm^{-1}, may be compared with bands observed in the i.r. spectrum of UCl_5·tppo, 310s, b and 110w cm^{-1}.

The splitting of the Γ_8' quartet level has repeatedly been observed [1,6,8] in the spectra of octahedral or near-octahedral uranium(V) complexes and it has been suggested [1] that the magnitude of this splitting is an indication of the extent of geometrical distortion from pure octahedral stereochemistry. Our results for solid UCl_5·tppo indicate (Table 4) a value of 525 cm^{-1} at room temperature compared with [1,2,6,12,21] the range 480—504 cm^{-1} for complexes of the type M^IUCl_6 (M^I = Cs, NEt_4, or $AsPh_4$). Although *X*-ray structural data are not available for these hexachlorouranates(V), and we have so far been unable to grow suitable single crystals, recent i.r. and Raman results indicate [24] little, if any, distortion from octahedral stereochemistry. Certainly it is unlikely that the arrangement in the $[UCl_6]^-$ ion in these complexes will be as distorted as that in UCl_5·tppo and since, in addition, the spectral bands are relatively broad, it appears that the magnitude of the splitting of the Γ_8' level should not be regarded as a reliable indication of the extent of geometrical distortion from octahedral stereochemistry.

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