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The Crystal Structures of Hexahalouranates. II. Triphenylbenzylphosphonium Hexachlorouranate(V)

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The crystal structure of triphenylbenzylphosphonium hexachlorouranate(V), $[P(C_6H_5)_3CH_2(C_6H_5)]UCl_6$, has been determined by the heavy-atom technique from 1646 independent reflexions collected on a Philips PW 1100 four-circle diffractometer and refined by blocked full-matrix least-squares methods to a final conventional R of 0.065. The crystals are monoclinic, space group $P2_1/c$ with $a = 11.72$ (1), $b = 18.78$ (1), $c = 13.61$ (1) Å, $\beta = 105.71$ (2)° and $Z = 4$. The mean of six crystallographically independent, but chemically identical, U^V-Cl distances is 2.496 (6) Å.

Introduction

This structural analysis was undertaken as part of a series of accurate $U-X$ ($X = \text{halogen}$) bond-length determinations [part I (Caira, de Wet, du Preez & Gellatly, 1978) dealt with the $U^{IV}-Cl$ and $U^{IV}-Br$ bonds]; the present analysis is therefore directed towards the U^V-Cl bond length in UCl_6^- , for which no reliable value is at present available.

The choice of aryl-substituted phosphonium cations of type $[P(C_6H_5)_3R]^+$ as counter ions for the hexahalouranates in these studies has already been motivated in part I of this series; in this particular instance the choice of $R = \text{benzyl}$, instead of ethyl, was dictated by the poor quality of crystals obtained with the ethyl derivative.

Experimental

$UO_2Cl_2 \cdot 3H_2O$ and $[(C_6H_5)_3PCH_2(C_6H_5)]Cl$ in a 1:1 molar ratio were refluxed in thionyl chloride for 12 h. After filtration and the addition of pentane, the resultant solid gave orange crystals of the title compound on recrystallization from pentane–thionyl chloride solvent. The compound discolours on exposure to the air and freshly prepared crystals were sealed in capillaries under dry conditions for X-ray analysis. Preliminary photographs (Cu $K\alpha$ radiation, $\lambda = 1.542$ Å) showed that the crystal was monoclinic, space group $P2_1/c$ (systematic absences: $h0l \ l \neq 2n$, $0k0 \ k \neq 2n$). The

density was determined by flotation in a mixture of CCl_4 and CH_3I . Crystal data are listed in Table 1.

Intensity data were collected on an automatic Philips PW 1100 four-circle diffractometer using the $\omega-2\theta$ scan technique (scan width $1.0^\circ\theta$, scan speed $0.04^\circ\theta \text{ s}^{-1}$) and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The crystal specimen was a ground sphere of radius 0.10 mm ($\pm 5\%$). Refined cell parameters were obtained from a least-squares analysis of the angular settings of 25 high-order reflexions. 2800 reflexions in the θ range 3 to 20° were measured; of these, 1038 with $F_o < 1.65\sigma(F_o)$ were omitted as unobserved, together with 116 systematically absent reflexions; 1646 independent structure amplitudes were thus used in the final refinement. Lorentz–polarization corrections were applied, but the low value of μ (~ 0.6) and crystal shape rendered absorption corrections unnecessary. The intensities of three reference reflexions, monitored throughout the data collection at regular intervals, gave evidence of slow decomposition of the crystal by X-rays; their mean intensity declined by about 8% overall.

Table 1. *Crystal data*

$C_{25}H_{22}PUCl_6$, $M_r = 803.7$	Monoclinic, $P2_1/c$ (2nd setting)
$a = 11.72$ (1) Å	$D_m = 1.85$ (1) g cm $^{-3}$
$b = 18.78$ (1)	$D_c = 1.851$
$c = 13.61$ (1)	$Z = 4$
$\beta = 105.71$ (2)°	$\mu(\text{Mo } K\alpha) = 59.58 \text{ cm}^{-1}$
$V = 2883.7$ Å 3	
$F(000) = 1524$	

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Structure determination and refinement

The structure was solved by conventional heavy-atom methods, the coordinates of the U atom being determined from a three-dimensional Patterson synthesis, and those of the six independent Cl atoms from a subsequent difference electron density synthesis; a further difference map, computed after refinement of the coordinates of the anion atoms for two cycles, yielded trial positions of all the remaining non-hydrogen atoms but one. The next stage of refinement was conducted with a model in which all atoms were thermally isotropic and the phenyl rings constrained to refine as rigid bodies with idealized benzene geometry ($C-C = 1.395 \text{ \AA}$), and the coordinates of the missing (phenyl C) atom were calculated on this basis. Two cycles of full-matrix refinement resulted in a value of 0.086 for the conventional R . Because of computer-memory limitations final refinement was conducted with a blocked-matrix approximation (see part I) and the following structural model was employed: the U and Cl atoms were thermally anisotropic, P and C atoms isotropic as before but with the ring constraints re-

leased, and H atoms were added artificially at positions recalculated after each cycle; these rode on their parent atoms at distances of 1.08 \AA , each type (methylene, phenyl) being assigned a common, refinable isotropic temperature factor. Altogether ten blocked refinement cycles followed; in the first, the anion and benzyl atoms and the P atom were allowed to interact, in the second, the C atoms of the remaining phenyl rings. In the final eight cycles the interacting parameter blocks were those of the anion, P and methylene C atoms, alternated in succession with those of the remaining (ring) C atoms. The function minimized was $\sum w\Delta^2$, with $\Delta = |F_o| - |F_c|$ and weights $w \propto 1/\sigma^2(F_o)$. Refinement was terminated at convergence of R to 0.065, when the mean and maximum shift/e.s.d. ratios were 0.01 and 0.06 respectively. The H temperature factors refined to final values of $U_{iso} = 0.09$ (5) \AA^2 (methylene H) and 0.11 (2) \AA^2 (phenyl H). The refined parameters* gave a difference synthesis which was generally 'clean', except for a few peaks with maximum densities of 0.55–1.28 $e \text{ \AA}^{-3}$ at distances of 1.5–2.5 \AA from the U atom; these are probably due to series-termination effects.

Constants for the analytical calculation of scattering factors for U were obtained from *International Tables for X-ray Crystallography* (1974), and those for the remaining atoms from Cromer & Mann (1968); anomalous dispersion corrections, based on data in the

Table 2. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^2 \text{ \AA}^2$) and their e.s.d.'s for the non-hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
U	3290 (1)	1556 (1)	515 (1)	—
Cl(1)	1879 (6)	2522 (3)	−291 (6)	—
Cl(2)	5049 (6)	2370 (4)	764 (6)	—
Cl(3)	1545 (6)	739 (4)	263 (5)	—
Cl(4)	4614 (5)	549 (4)	1310 (6)	—
Cl(5)	3154 (6)	1888 (4)	2234 (5)	—
Cl(6)	3504 (6)	1184 (4)	−1183 (5)	—
P	7819 (5)	1737 (3)	4024 (4)	4 (0)
C(1)	6408 (16)	1351 (10)	4013 (14)	5 (1)
C(11)	8879 (16)	1602 (14)	5241 (14)	5 (1)
C(12)	9221 (19)	2211 (13)	5879 (17)	6 (1)
C(13)	10081 (23)	2095 (16)	6793 (21)	10 (1)
C(14)	10627 (20)	1429 (14)	7056 (17)	7 (1)
C(15)	10266 (21)	884 (14)	6452 (18)	7 (1)
C(16)	9396 (18)	934 (12)	5508 (16)	5 (1)
C(21)	7601 (20)	2664 (12)	3768 (16)	5 (1)
C(22)	6492 (24)	2971 (16)	3538 (19)	9 (1)
C(23)	6343 (22)	3688 (13)	3303 (18)	7 (1)
C(24)	7310 (22)	4110 (14)	3234 (17)	7 (1)
C(25)	8392 (25)	3815 (15)	3465 (19)	8 (1)
C(26)	8547 (21)	3093 (13)	3705 (16)	6 (1)
C(31)	8383 (17)	1331 (10)	3049 (14)	4 (1)
C(32)	7600 (19)	1190 (11)	2120 (16)	5 (1)
C(33)	7999 (21)	893 (12)	1332 (19)	7 (1)
C(34)	9176 (21)	779 (12)	1496 (18)	7 (1)
C(35)	9932 (24)	932 (13)	2370 (19)	6 (1)
C(36)	9618 (19)	1203 (11)	3205 (16)	6 (1)
C(41)	6504 (18)	608 (11)	4484 (18)	5 (1)
C(42)	6631 (18)	6 (13)	3867 (18)	6 (1)
C(43)	6701 (17)	−688 (12)	4245 (15)	5 (1)
C(44)	6733 (20)	−796 (15)	5270 (19)	8 (1)
C(45)	6619 (19)	−234 (13)	5867 (18)	7 (1)
C(46)	6511 (17)	465 (12)	5477 (16)	5 (1)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33112 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Fractional atomic coordinates ($\times 10^3$) of the hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	588	132	323
H(2)	598	170	444
H(12)	884	273	567
H(13)	1034	253	732
H(14)	1134	137	775
H(15)	1065	37	669
H(16)	914	48	501
H(22)	573	265	354
H(23)	548	393	317
H(24)	718	466	300
H(25)	915	414	346
H(26)	942	286	385
H(32)	667	131	200
H(33)	738	76	61
H(34)	950	56	89
H(35)	1086	84	244
H(36)	1026	131	392
H(42)	667	9	309
H(43)	673	−114	375
H(44)	685	−133	559
H(45)	661	−32	665
H(46)	643	90	597

former reference, were applied in the case of U. The calculations for the solution and refinement of the structure were performed with the program system *SHELX* (Sheldrick, 1977), and those for the librational foreshortening of the U—Cl bond lengths with *XANADU* (Roberts & Sheldrick, 1977), using an ICL 1901T computer. Drawings were produced with the program *PLOT-2D*, written for the Hewlett-Packard HP 9862A desk plotter by one of us (JFdeW). Final atomic coordinates and isotropic temperature factors are listed in Tables 2 and 3.

Description of the structure and discussion

The asymmetric unit, illustrated in Fig. 1, consists of one formula unit (cation-anion pair); for clarity, H atoms other than those of the methylene group have

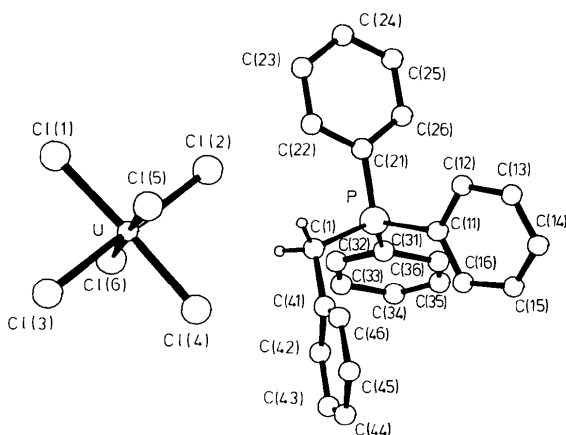


Fig. 1. Molecular configuration and atomic numbering scheme for the asymmetric unit.

Table 4. Bond lengths (Å) and *e.s.d.*'s in parentheses (U—Cl distances in the second column are corrected for rigid-body librational foreshortening)

U—Cl(1)	2.499 (6)	2.522	C(21)—C(22)	1.38 (4)
U—Cl(2)	2.513 (7)	2.534	C(22)—C(23)	1.38 (4)
U—Cl(3)	2.506 (7)	2.526	C(23)—C(24)	1.41 (4)
U—Cl(4)	2.500 (6)	2.524	C(24)—C(25)	1.34 (4)
U—Cl(5)	2.469 (7)	2.500	C(25)—C(26)	1.40 (4)
U—Cl(6)	2.491 (7)	2.523	C(26)—C(21)	1.39 (3)
P—C(1)	1.80 (2)		C(31)—C(32)	1.37 (3)
P—C(11)	1.80 (2)		C(32)—C(33)	1.40 (4)
P—C(21)	1.78 (2)		C(33)—C(34)	1.35 (4)
P—C(31)	1.80 (2)		C(34)—C(35)	1.31 (3)
C(1)—C(41)	1.53 (3)		C(35)—C(36)	1.38 (4)
C(11)—C(12)	1.43 (3)		C(36)—C(31)	1.43 (3)
C(12)—C(13)	1.39 (3)		C(41)—C(42)	1.44 (3)
C(13)—C(14)	1.41 (4)		C(42)—C(43)	1.40 (3)
C(14)—C(15)	1.31 (4)		C(43)—C(44)	1.40 (3)
C(15)—C(16)	1.41 (3)		C(44)—C(45)	1.36 (4)
C(16)—C(11)	1.40 (3)		C(45)—C(46)	1.41 (3)
			C(46)—C(41)	1.38 (3)

Table 5. Bond angles (°) and *e.s.d.*'s in parentheses

Cl(1)—U—Cl(4)	177.1 (2)	P—C(31)—C(36)	122 (1)
Cl(2)—U—Cl(3)	179.6 (2)	C(1)—C(41)—C(42)	119 (2)
Cl(5)—U—Cl(6)	177.4 (2)	C(1)—C(41)—C(46)	125 (2)
Cl(1)—U—Cl(2)	92.2 (2)	C(11)—C(12)—C(13)	116 (2)
Cl(2)—U—Cl(4)	90.7 (2)	C(12)—C(13)—C(14)	123 (3)
Cl(4)—U—Cl(3)	89.0 (2)	C(13)—C(14)—C(15)	119 (2)
Cl(3)—U—Cl(1)	88.0 (2)	C(14)—C(15)—C(16)	123 (2)
Cl(1)—U—Cl(5)	91.6 (3)	C(15)—C(16)—C(11)	117 (2)
Cl(2)—U—Cl(5)	88.9 (3)	C(16)—C(11)—C(12)	122 (2)
Cl(4)—U—Cl(5)	88.4 (2)	C(21)—C(22)—C(23)	121 (3)
Cl(3)—U—Cl(5)	91.4 (3)	C(22)—C(23)—C(24)	121 (2)
Cl(1)—U—Cl(6)	91.0 (3)	C(23)—C(24)—C(25)	119 (2)
Cl(2)—U—Cl(6)	90.6 (3)	C(24)—C(25)—C(26)	121 (3)
Cl(4)—U—Cl(6)	89.0 (3)	C(25)—C(26)—C(21)	122 (2)
Cl(3)—U—Cl(6)	89.1 (2)	C(26)—C(21)—C(22)	117 (2)
C(1)—P—C(11)	111 (1)	C(31)—C(32)—C(33)	120 (2)
C(1)—P—C(21)	108 (1)	C(32)—C(33)—C(34)	118 (2)
C(1)—P—C(31)	110 (1)	C(33)—C(34)—C(35)	122 (3)
C(21)—P—C(31)	109 (1)	C(34)—C(35)—C(36)	124 (3)
C(11)—P—C(21)	110 (1)	C(35)—C(36)—C(31)	115 (2)
C(11)—P—C(31)	109 (1)	C(36)—C(31)—C(32)	120 (2)
P—C(1)—C(41)	114 (1)	C(41)—C(42)—C(43)	122 (2)
P—C(11)—C(12)	117 (2)	C(42)—C(43)—C(44)	119 (2)
P—C(11)—C(16)	121 (2)	C(43)—C(44)—C(45)	120 (2)
P—C(21)—C(22)	122 (2)	C(44)—C(45)—C(46)	121 (2)
P—C(21)—C(26)	120 (2)	C(45)—C(46)—C(41)	122 (2)
P—C(31)—C(32)	118 (2)	C(46)—C(41)—C(42)	117 (2)

been omitted. Bond lengths and angles are listed in Tables 4 and 5. Of the six U—Cl bond lengths uncorrected for rigid-body motion, five average 2.502 Å, with a mean deviation of the order of the computed *e.s.d.*'s (0.007 Å), while the sixth bond, U—Cl(5), is about five standard deviations shorter.

Since the overall average of the six bonds (2.496 Å) shows a mean deviation of 0.011 Å, and the mean rigid-body-corrected length a mean deviation of 0.007 Å, the length of U—Cl(5) is probably not significantly different from the other bonds of this type. Furthermore, the remarks made previously (Caira *et al.*, 1978) with regard to the precision attainable for bonds such as these, particularly in view of the blocked-matrix approximation used for the refinement, apply here as well. A mean uncorrected bond length of 2.496 (10) Å is probably a realistic estimate. The mean foreshortening due to rigid-body librational motion was found to be 0.025 Å, with a mean deviation of 0.005 Å (Table 4). The mean corrected U—Cl bond length is 2.522 Å. As expected, bond lengths are shorter (by about 0.1 Å) than the corresponding value found for U^{IV}—Cl in a similar chemical environment (Caira *et al.*, 1978). The only other U^V—Cl bond length reported in the literature, 2.56 Å — which was derived from the relatively inaccurate structural determination of tri(azido)carbenium hexachlorouranate(V), [C(N₃)₃][UCl₆], (Kolitsch & Müller, 1974) — is in rough agreement. The 12 nonlinear Cl—U—Cl angles (Table 5) average 90.0° with a mean deviation of 1.3° and mean *e.s.d.* (probably underestimated) of 0.25°. We

conclude that the UCl_6^- anion possesses full octahedral (O_h) symmetry in this environment. It would be interesting to see if this is confirmed by laser Raman spectroscopy (a facility not available to us), since Stumpp & Piltz (1974) observed features in the Raman spectra of the MUCl_6 ($M = \text{alkali metal ion, Tl}^+$) salts

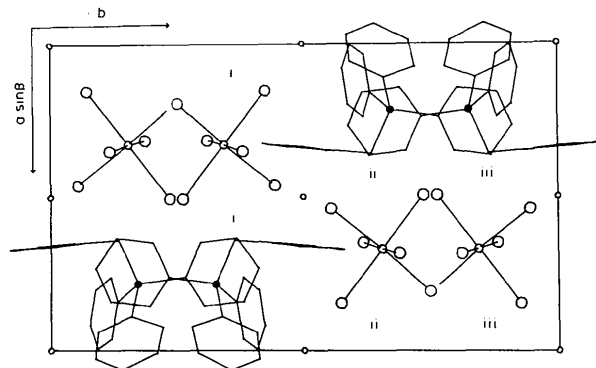


Fig. 2. Ionic packing viewed along c .

which indicate progressive distortion of the UCl_6^- symmetry from octahedral, through tetragonal, to orthorhombic as the cation radius increases.

Bond lengths and angles in the cation fall within the expected ranges. The packing of UCl_6^- octahedra, illustrated in the (001) projection of the structure (Fig. 2), permits relatively close mutual approaches of the anions. This is perhaps not unexpected for a cation: anion ratio of 1:1 where effective screening by cations is diminished in comparison with analogous 2:1 salts (Caira *et al.*, 1978). Selected $\text{Cl}\cdots\text{Cl}$ intermolecular distances and $\text{H}\cdots\text{Cl}$ contacts less than 3 Å are shown in Table 6. In addition to distances of 3.96 (1) and 4.42 (1) Å between centrosymmetrically related Cl atoms, two similar distances of 4.18 (1) and 4.19 (1) Å separate Cl atoms of c -glide-related UCl_6^- ions.

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Table 6. Selected $\text{Cl}\cdots\text{Cl}$ intermolecular distances (e.s.d.'s ~ 0.01 Å) and $\text{H}\cdots\text{Cl}$ contacts < 3 Å

$\text{Cl}(4)\cdots\text{Cl}(4^{\text{iv}})$	4.42	$\text{Cl}(1)\cdots\text{H}(26^{\text{vi}})$	2.89
$\text{Cl}(4)\cdots\text{Cl}(6^{\text{iv}})$	3.96	$\text{Cl}(1)\cdots\text{H}(36^{\text{vi}})$	2.91
$\text{Cl}(5)\cdots\text{Cl}(6^{\text{i}})$	4.18	$\text{Cl}(1)\cdots\text{H}(44^{\text{ii}})$	2.72
$\text{Cl}(5)\cdots\text{Cl}(1^{\text{i}})$	4.19	$\text{Cl}(2)\cdots\text{H}(2^{\text{vii}})$	2.93
$\text{Cl}(3)\cdots\text{Cl}(3^{\text{v}})$	4.46	$\text{Cl}(3)\cdots\text{H}(34^{\text{viii}})$	2.78
		$\text{Cl}(3)\cdots\text{H}(34^{\text{iv}})$	2.97
$\text{Cl}(2)\cdots\text{H}(32)$	2.95	$\text{Cl}(6)\cdots\text{H}(14^{\text{ix}})$	2.59
$\text{Cl}(4)\cdots\text{H}(32)$	2.74	$\text{Cl}(6)\cdots\text{H}(23^{\text{vii}})$	2.69

Symmetry code

(i)	$x, \frac{1}{2} - y, \frac{1}{2} + z$	(vi)	$x - 1, \frac{1}{2} - y, z - \frac{1}{2}$
(ii)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	(vii)	$x, \frac{1}{2} - y, z - \frac{1}{2}$
(iii)	$1 - x, 1 - y, 1 - z$	(viii)	$x - 1, y, z$
(iv)	$1 - x, -y, -z$	(ix)	$x - 1, y, z - 1$
(v)	$-x, -y, -z$		

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