Structure of Unsolvated Benzyltriphenylphosphonium Pentachloro(*p*-tolylimido)tungstate(VI)

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Abstract. $[P(C_6H_5)_3(C_7H_7)][W(C_7H_7N)Cl_5]$, $M_r =$ 819·7, monoclinic, $P2_1/n$, $a = 15·095$ (2), $b =$ 13·425 (2), $c = 16·550$ (2) Å, $\beta = 103·55$ (1)°, $V =$ 3260·5 Å^3, $Z = 4$, $D_x = 1·670$ g cm^{-3}, $\lambda(Mo\ K\alpha) =$ 0·71073 Å, $\mu = 0·410$ cm^{-1}, $F(000) = 1608$, $T =$ 295 K, $R = 0·048$ for 5196 unique observed reflections. The W atom is octahedrally coordinated, and lies 0·147 (1) Å out of the plane of four equatorial Cl atoms [r.m.s. $\Delta = 0·008$ (3) Å], towards the imido N atom. The axial W—Cl bond length, 2·451 (2) Å, is significantly lengthened by the *trans*-influence of the imido group; equatorial W—Cl bonds average 2·347 (2) Å. The imido group is almost linearly coordinated to W: W—N—C = 170·8 (5)°.

Experimental. The compound was prepared from $[P(C_6H_5)_3(CH_2C_6H_5)][W_2O_2Cl_7]$ and *p*-tolyl azide in dichloromethane, and recrystallized from dichloromethane/hexane to give brown block crystals.

Crystal size 0·23 × 0·38 × 0·80 mm, mounted in Lindemann capillary, Siemens AED2 diffractometer, cell parameters refined from 2θ values of 32 reflections $(20 < 2\theta < 25°)$ measured at $\pm\omega$. ω/θ scan mode, on-line profile fitting (Clegg, 1981), $2\theta_{max}$ 50°, whole sphere of data with $|h|_{max}$ 17, $|k|_{max}$ 15, $|l|_{max}$ 19, no significant variation observed for three standard reflections, semi-empirical absorption corrections, transmission 0·07–0·15. 22974 reflections measured, 5748 unique, 5196 with $F > 4\sigma_c(F)$ for structure determination (σ_c from counting statistics only), $R_{int} = 0·021$.

Structure solved by Patterson and difference syntheses, blocked-cascade least-squares refinement on F, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 55 - 157G + 696G^2 - 110S + 64S^2 - 17GS$ $(G = F_o/F_{max}, S = \sin\theta/\sin\theta_{max}$; Hong & Robertson, 1985), anisotropic thermal parameters, cation phenyl rings constrained as rigid ideal hexagons with C—C = 1·395 Å, H atoms constrained to give C—H = 0·96 Å, H—C—H = 109·5°, aromatic H on ring-angle external bisectors, $U(H) = 1·2U_{eq}(C)$, insignificant extinction effects, scattering factors from *International Tables for X-ray Crystallography* (1974), *SHELXTL* (Sheldrick, 1985) and local computer programs.

$R = 0·048$, $wR = 0·034$ for 316 parameters, goodness of fit = 1·26, $(\Delta/\sigma)_{max} = 0·059$, $(\Delta/\sigma)_{mean} = 0·004$,

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$)

$U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
W	3170·4 (1)	3151·0 (2)	4738·1 (1)	62·8 (1)
Cl(1)	1659·7 (8)	3626·9 (11)	3914·9 (10)	76·7 (4)
Cl(2)	2424·7 (8)	1806·3 (11)	5201·7 (8)	73·2 (4)
Cl(3)	2865 (1)	4146 (1)	5807 (1)	92·4 (6)
Cl(4)	3740 (1)	4572 (2)	4209 (1)	112·6 (8)
Cl(5)	3296 (1)	2242 (2)	3560 (1)	104·2 (7)
N	4224 (3)	2705 (4)	5284 (3)	75 (2)
C(1)	4989 (3)	2207 (6)	5685 (3)	80 (2)
C(2)	5007 (5)	1174 (7)	5735 (8)	111 (3)
C(3)	5744 (7)	661 (9)	6140 (8)	118 (4)
C(4)	6542 (5)	1181 (8)	6499 (4)	96 (3)
C(5)	6544 (6)	2192 (10)	6424 (6)	125 (4)
C(6)	5787 (6)	2724 (7)	6017 (6)	107 (3)
C(7)	7367 (8)	631 (12)	6932 (5)	132 (5)
P	5992·6 (7)	3414·7 (8)	.2515·3 (7)	55·2 (3)
C(12)	4705 (2)	1917 (3)	2082 (2)	71 (2)
C(13)	4240	1180	1555	82 (2)
C(14)	4509	937	828	83 (2)
C(15)	5243	1429	629	100 (3)
C(16)	5709	2166	1156	72 (2)
C(11)	5440	2409	1883	61 (1)
C(22)	4831 (3)	5038 (3)	2468 (2)	84 (2)
C(23)	4368	5879	2094	103 (3)
C(24)	4513	6227	1341	100 (3)
C(25)	5121	5732	962	101 (3)
C(26)	5584	4890	1336	83 (2)
C(21)	5439	4543	2089	63 (1)
C(32)	7654 (2)	2600 (2)	2465 (3)	79 (2)
C(33)	8593	2644	2536	91 (2)
C(34)	9040	3561	2639	94 (3)
C(35)	8548	4434	2670	97 (3)
C(36)	7610	4390	2598	73 (2)
C(31)	7163	3473	2496	56 (1)
C(41)	5911 (3)	3272 (4)	3590 (3)	65 (2)
C(43)	6311 (2)	1494 (2)	3966 (3)	85 (2)
C(44)	6926	771	4360	99 (3)
C(45)	7783	1052	4827	89 (2)
C(46)	8025	2057	4900	100 (3)
C(47)	7410	2780	4506	87 (2)
C(42)	6553	2498	4039	63 (2)

$(\Delta\rho)_{max} = 1·57$, $(\Delta\rho)_{min} = -1·00$ e Å^{-3}. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* The structure of the anion is shown in Fig. 1.

Related literature. The structure of the same compound, probably as a dichloromethane solvate, has been

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51341 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Unconstrained bond lengths (Å) and angles (°)*

W—Cl(1)	2·451 (2)	W—Cl(2)	2·349 (2)
W—Cl(3)	2·347 (2)	W—Cl(4)	2·345 (3)
W—Cl(5)	2·345 (2)	W—N	1·741 (4)
N—C(1)	1·365 (8)	C(1)—C(2)	1·390 (13)
C(1)—C(6)	1·387 (10)	C(2)—C(3)	1·346 (13)
C(3)—C(4)	1·399 (13)	C(4)—C(5)	1·363 (17)
C(4)—C(7)	1·481 (14)	C(5)—C(6)	1·380 (13)
P—C(11)	1·790 (4)	P—C(21)	1·793 (4)
P—C(31)	1·776 (4)	P—C(41)	1·822 (5)
C(41)—C(42)	1·494 (6)		

Cl(1)—W—Cl(2)	85·8 (1)	Cl(1)—W—Cl(3)	87·1 (1)
Cl(2)—W—Cl(3)	89·8 (1)	Cl(1)—W—Cl(4)	87·4 (1)
Cl(2)—W—Cl(4)	173·1 (1)	Cl(3)—W—Cl(4)	88·4 (1)
Cl(1)—W—Cl(5)	85·4 (1)	Cl(2)—W—Cl(5)	90·6 (1)
Cl(3)—W—Cl(5)	172·4 (1)	Cl(4)—W—Cl(5)	90·3 (1)
Cl(1)—W—N	174·8 (2)	Cl(2)—W—N	90·9 (2)
Cl(3)—W—N	97·0 (2)	Cl(4)—W—N	95·9 (2)
Cl(5)—W—N	90·6 (2)	W—N—C(1)	170·8 (5)
N—C(1)—C(2)	121·3 (6)	N—C(1)—C(6)	120·4 (8)
C(2)—C(1)—C(6)	118·2 (7)	C(1)—C(2)—C(3)	122·8 (8)
C(2)—C(3)—C(4)	119·0 (10)	C(3)—C(4)—C(5)	118·6 (8)
C(3)—C(4)—C(7)	120·0 (10)	C(5)—C(4)—C(7)	121·4 (9)
C(4)—C(5)—C(6)	122·7 (9)	C(1)—C(6)—C(5)	118·5 (9)
C(11)—P—C(21)	107·3 (2)	C(11)—P—C(31)	110·6 (2)
C(21)—P—C(31)	109·2 (2)	C(11)—P—C(41)	111·3 (2)
C(21)—P—C(41)	109·9 (2)	C(31)—P—C(41)	108·5 (2)
P—C(11)—C(12)	120·5 (1)	P—C(11)—C(16)	119·4 (1)
P—C(21)—C(22)	121·4 (1)	P—C(21)—C(26)	118·5 (1)
P—C(31)—C(32)	120·2 (1)	P—C(31)—C(36)	119·4 (1)
P—C(41)—C(42)	112·0 (4)	C(41)—C(42)—C(43)	120·2 (2)
C(41)—C(42)—C(47)	119·8 (2)		

Fig. 1. Structure of the anion, with the atom-numbering scheme. Thermal motion is shown by ellipsoids at the 40% probability level.

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reported by Bradley, Errington, Hursthouse, Short, Ashcroft, Clark, Nielson & Rickard (1987); it suffered from disorder in both the solvent molecules and the *p*-tolyl substituent, giving results consistent with, but less precise than, those presented here.

Reinvestigation of the Structure of Dibenzo-12-crown-4 Ether*

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Abstract. $C_{16}H_{16}O_4$, $M_r = 272 \cdot 30$, orthorhombic, *Pbca*, $a = 6 \cdot 9774$ (2), $b = 13 \cdot 0730$ (3), $c = 14 \cdot 6363$ (3) Å, $V = 1335 \cdot 06$ Å³, $Z = 4$, $D_x = 1 \cdot 355$ g cm⁻³, $\lambda(\text{Cu } K\bar{\alpha}) = 1 \cdot 54178$ Å, $\mu = 0 \cdot 076$ cm⁻¹, $F(000) = 576$, room temperature, $R = 0 \cdot 038$ for all 1400 unique reflections. The structure of 6,7,14,15-tetrahydrodibenzo[*b,h*]-[1,4,7,10]tetraoxacyclododecin (dibenzo-12-crown-4 ether) was redetermined in order to provide more
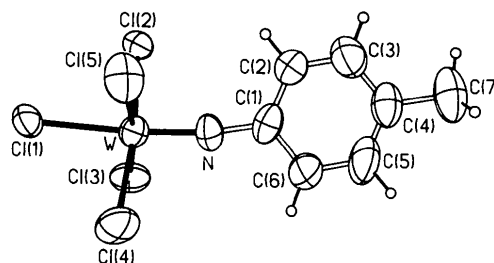
complete and reliable data for structural comparison purposes. In addition to better residuals, this reinvestigation has yielded more precise structural parameters (C—C and C—O bond-length and -angle e.s.d.'s 0·0017 Å, 0·1°, and C—H bond-length and -angle e.s.d.'s of 0·02 Å, 1°) than the previous results of Hughes & Nowell [*J. Chem. Res.* (*M*) (1978), pp. 1534–1556] ($R = 0 \cdot 086$, C—C and C—O bond-length and -angle e.s.d.'s of 0·004 Å, 0·3° and C—H bond-length and -angle e.s.d.'s of 0·03 Å, 2°). The molecule