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Structure of Iodo(methylene)tetrakis(trimethylphosphine)tungsten Trifluoromethanesulfonate, $[WI(CH_2)\{P(CH_3)_3\}_4][CF_3SO_3]$

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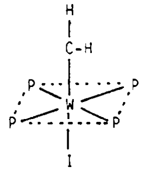
Abstract. $M_r = 778\cdot163$, rhombohedral (hexagonal), $R\bar{3}c$, $a = 16\cdot730\,(4)$, $c = 50\cdot380\,(5)$ Å, $V = 12211\,(4)$ Å^3, $Z = 18$, $D_x = 1\cdot90$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0\cdot71069$ Å, $\mu = 6\cdot00$ mm^{-1}, $F(000) = 6768$, $T = 295$ K. Final $R = 0\cdot064$ for 2041 observed reflections. The coordination geometry about the tungsten is pseudooctahedral with the methylene and iodo ligands in a *trans* configuration. The W—C(1) distance of 1·83 (2) Å indicates a W—C bond order of between 2 and 3. Other bond distances are W—I = 2·881 (2) Å and W—P = 2·519 (4) and 2·507 (4) Å.

Introduction. In the neutron diffraction structures of the electron-deficient molecules $[Ta(=CHCMe_3)(PMe_3)Cl_3]_2$ and $[Ta(=CHCMe_3)(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_2H_4)(PMe_3)]$, the angles about the neopentylidene α-carbon atoms are highly distorted from normal sp^2 hybrid angles of 120° [*i.e.* Ta—C$_\alpha$—C$_\beta$ = 161·2 (1) and 171·8 (6)° respectively, and Ta—C$_\alpha$—H$_\alpha$ = 84·8 (2) and 78·1 (3)° respectively] (Schultz, Brown, Williams & Schrock, 1981). For the unsubstituted methylene ligand in the 18-electron complex $[Ta(=CH_2)(\eta^5\text{-}C_5H_5)_2(CH_3)]$, an X-ray diffraction study indicates that C$_\alpha$ is apparently normal (Guggenberger & Schrock, 1975). However, a highly distorted T-shaped structure is postulated for the 16-electron cationic methylene complex $[W(CH_2)(PMe_3)_4Cl]^+$, based on variable-temperature proton NMR data (Holmes & Schrock, 1981; Holmes, Clark, Turner & Schrock, 1982).

In order to characterize the coordination of the methylene ligand in this and related molecules, large crystals of the analogous iodo complex (I) were obtained for a neutron diffraction study. Although we have often been able to solve structures directly using neutron diffraction data (Broach *et al.*, 1979; Schultz *et al.*, 1981), in this case we decided to collect also an X-ray data set. This paper presents the results of the X-ray diffraction study. The neutron diffraction data that were measured at the University of Missouri Research Reactor Facility were apparently affected by crystal decomposition and, therefore, could not be successfully refined using the X-ray structural model.



(I)

Experimental. Crystal 0·10 × 0·10 × 0·35 mm. Lattice parameters from 25 reflections. A total of 4212 data (range of *hkl*: 0–13, 0–13, −48–48) were measured out to $(\sin\theta)/\lambda = 0\cdot48$ Å^{-1} on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator. Integrated intensities of three check reflections (664, $13,7,\overline{10}$, $19\bar{5}$) measured periodically during data collection decreased by an average of 32% (26, 33 and 39%, respectively) during an exposure time of 120 h. Data corrected for Lorentz and polarization factors and for crystal decay. A ψ-scan for the 12,0,0 reflection at $2\theta = 25\cdot87°$ exhibited an intensity variation of $I_{\max}/I_{\min} = 2\cdot2$ and was used for an empirical absorption correction. Except for Friedel pairs which appeared to differ due to anomalous scattering, symmetry-equivalent data were averaged to yield 2622 data with averaging R factors $R(F) = 0\cdot025$, $R(F^2) = 0\cdot055$. Structure solved by direct methods using *MULTAN* (Declercq, Germain, Main & Woolfson, 1973) followed by full-matrix least-squares refinements and Fourier syntheses. Neutral-atom scattering factors and corrections for anomalous scattering for all atoms from *International Tables for X-ray Crystallography* (1974). There are two crystallographically independent $CF_3SO_3^-$ anions, one of which has $\bar{3}$ site symmetry which imposes C/S and O/F disorder. Scattering factors for disordered atoms are derived by averaging the values of the two elements occupying the respective disorder sites. Function

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minimized in least-squares refinements $\sum w(|F_o^2 - F_c^2|)$, where $w = 1/\sigma(F_o^2)$ and $\sigma(F_o^2) = [\sigma_0^2(F_o^2) + (0{\cdot}02F_o^2)^2]^{1/2}$, where $\sigma_0(F_o^2)$ is based on counting statistics. In final cycles of least-squares refinement based on 2041 data with $F_o^2 \geq 3\sigma(F_o^2)$, all atoms were refined with anisotropic temperature factors. Final agreement indices $R(F_o) = 0{\cdot}064$, $R(F_o^2) = 0{\cdot}119$, $wR(F_o^2) = 0{\cdot}146$, $S = 3{\cdot}30$. $(\Delta/\sigma)_{\max} = 0{\cdot}08$. The four largest peaks in final difference Fourier synthesis, with heights ranging from 4·5 to 1·3 e Å^{-3}, were close to the W or I atoms.

Although the radiation damage has apparently resulted in large residuals and standard deviations, the final model, including bonding distances and angles, is entirely consistent with predictions based on chemical data and with previous structural results on related compounds.

Discussion. Final atomic coordinates are presented in Table 1.* The structure of the cation is shown in Fig. 1 and a stereoscopic view of the unit-cell packing is shown in Fig. 2. Table 2 contains selected interatomic distances and angles.

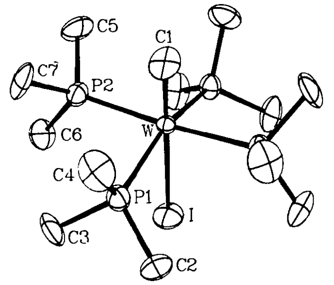

Fig. 1. A perspective view of the $[W(CH_2)(PMe_3)I]^+$ cation. The thermal ellipsoids are drawn at the 50% probability level.

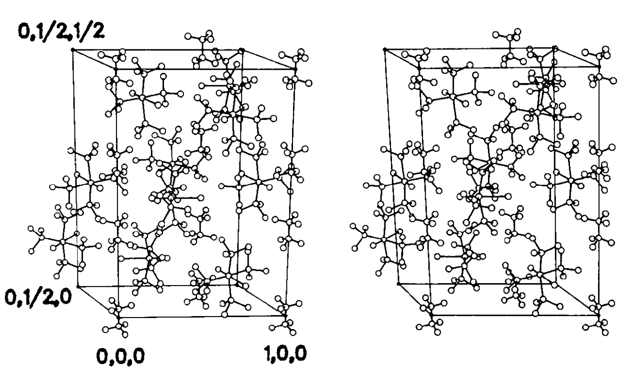

Fig. 2. A stereoscopic view of the crystal packing in a portion of the unit cell.

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*(Å^2)
W	0·30817 (5)	0·0	0·25	0·0230 (4)
I	0·4804 (1)	0·0	0·25	0·0542 (8)
S	0·0	0·0	0·1993 (2)	0·079 (3)
S/C	0·0	0·0	0·0187 (2)	0·040 (3)
P(1)	0·3369 (3)	0·0038 (3)	0·29918 (8)	0·037 (2)
P(2)	0·2144 (3)	−0·1728 (3)	0·25138 (8)	0·037 (2)
F	0·0008 (8)	0·0744 (7)	0·1530 (2)	0·078 (7)
F/O	0·0778 (8)	−0·0010 (7)	0·0261 (2)	0·056 (6)
O	−0·083 (1)	0·001 (1)	0·2052 (3)	0·11 (1)
C(1)	0·199 (1)	0·0	0·25	0·08 (1)
C(2)	0·445 (1)	0·098 (1)	0·3125 (3)	0·06 (1)
C(3)	0·343 (1)	−0·092 (1)	0·3148 (3)	0·06 (1)
C(4)	0·248 (1)	0·010 (1)	0·3190 (3)	0·06 (1)
C(5)	0·134 (1)	−0·228 (1)	0·2234 (4)	0·07 (1)
C(6)	0·269 (1)	−0·246 (1)	0·2544 (3)	0·06 (1)
C(7)	0·128 (1)	−0·218 (1)	0·2787 (4)	0·07 (1)
C(8)	0·0	0·0	0·1634 (6)	0·06 (1)

$$* \; U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

W–C(1)	1·83 (2)	P(2)–C(5)	1·85 (2)
W–P(1)	2·519 (4)	P(2)–C(6)	1·87 (2)
W–P(2)	2·507 (4)	P(2)–C(7)	1·86 (2)
W–I	2·881 (2)	S–C(8)	1·81 (3)
P(1)–C(2)	1·84 (2)	S–O	1·43 (2)
P(1)–C(3)	1·84 (2)	C(8)–F	1·34 (2)
P(1)–C(4)	1·84 (2)	S/C–S/C′	1·88 (2)
		S/C–F/O	1·36 (1)
C(1)–W–P(1)	100·3 (1)	W–P(2)–C(5)	115·6 (6)
C(1)–W–P(2)	87·2 (1)	W–P(2)–C(6)	121·9 (6)
C(1)–W–I	180·0	W–P(2)–C(7)	113·8 (6)
P(1) W P(1)′	159·5 (2)	O–S–O′	115·8 (5)
P(1)–W–P(2)	90·2 (1)	O–S–C(8)	102·0 (8)
P(1)–W–P(2)′	90·8 (1)	F–C(8)–F′	106 (2)
P(2)–W–P(2)′	174·3 (2)	F–C(8)–S	113 (1)
W–P(1)–C(2)	118·4 (6)	F/O–S/C–F/O′	112·9 (5)
W–P(1)–C(3)	119·4 (6)	F/O–S/C–S/C′	105·8 (6)
W–P(1)–C(4)	112·7 (6)		

The W, I and C(1) atoms of the cation lie on a crystallographic twofold axis and the W atom possesses a distorted octahedral coordination geometry very similar to that in *trans*-$[W(CH)(Cl)(PMe_3)_4]$ (II) (Churchill, Rheingold & Wasserman, 1981). However, in (II), the methylidyne and chloro ligands are site-disordered by a crystallographic twofold axis through the W atom and perpendicular to the Cl—W—C vector, and the eight L—W—P angles (L = CH or Cl) are all within 1° of 90 ±9°. In (I), C(1)—W—P(1) = 100·3 (1) and C(1)—W—P(2) = 87·2 (1)°, indicating that the more closely bound methylene ligand exerts a stronger steric influence than the iodo ligand.

The W—C(1) distance of 1·83 (2) Å appears to be intermediate between that of W—C double and triple bonds. Examples of triple-bond distances are 1·785 (8) Å in $[W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)\{Me_2P(CH_2)_2PMe_2\}]$ (III) (Churchill

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39022 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

& Youngs, 1979), 1·807 (6) Å in $[\mathrm{W}(\equiv\mathrm{CH{\cdot}AlMe_{1{\cdot}82}Cl_{1{\cdot}18}})(\mathrm{Cl})(\mathrm{PMe_3})_3]$ (Churchill, Rheingold & Wasserman, 1981), 1·82 (2) Å in $[\mathrm{W}\{\equiv\mathrm{C}(p\text{-tolyl})\}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]$ (Huttner, Frank & Fischer, 1976) and 1·89 (3) Å in $[\mathrm{W}(\equiv\mathrm{CMe})(\mathrm{Me})(\mathrm{PMe_3})_4]$ (IV) (Chiu, Jones, Wilkinson, Galas, Hursthouse & Malik, 1981). Reported values for W—C double bonds are 1·88 (1) Å in $[\mathrm{W(O)}(=\mathrm{CHCMe_3})(\mathrm{PEt_3})\mathrm{Cl_2}]$ (Churchill, Missert & Youngs, 1981) and 1·942 (9) Å in (III).

The W—I distance of 2·881 (2) Å is slightly longer than the value of 2·845 (5) Å in $[\mathrm{W}(=\mathrm{CC_6H_5})(\mathrm{CO})_4\mathrm{I}]$ (Huttner, Lorenz & Gartzke, 1974). Also, the W—P distances of 2·519 (4) and 2·507 (4) Å are slightly longer than the average W—P distances of 2·450 (2) Å in (IV) and 2·467 (2) Å in (II). Other distances and angles in the cation and anion appear to be normal.

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References

BROACH, R. W., SCHULTZ, A. J., WILLIAMS, J. M., BROWN, G. M., MANRIQUEZ, J. M., FAGAN, P. J. & MARKS, T. J. (1979). *Science*, **203**, 172–174.

CHIU, K. W., JONES, R. A., WILKINSON, G., GALAS, A. M. R., HURSTHOUSE, M. B. & MALIK, K. M. A. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1204–1211.

CHURCHILL, M. R., MISSERT, J. R. & YOUNGS, W. J. (1981). *Inorg. Chem.* **20**, 3388–3391.

CHURCHILL, M. R., RHEINGOLD, A. L. & WASSERMAN, H. J. (1981). *Inorg. Chem.* **20**, 3392–3399.

CHURCHILL, M. R. & YOUNGS, W. J. (1979). *Inorg. Chem.* **18**, 2454–2458.

DECLERCQ, J.-P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* A**29**, 231–234.

GUGGENBERGER, L. J. & SCHROCK, R. R. (1975). *J. Am. Chem. Soc.* **97**, 6578–6579.

HOLMES, S. J., CLARK, D. N., TURNER, H. W. & SCHROCK, R. R. (1982). *J. Am. Chem. Soc.* **104**, 6322–6329.

HOLMES, S. J. & SCHROCK, R. R. (1981). *J. Am. Chem. Soc.* **103**, 4599–4600.

HUTTNER, G., FRANK, A. & FISCHER, E. O. (1976). *Isr. J. Chem.* **15**, 133–142.

HUTTNER, G., LORENZ, H. & GARTZKE, W. (1974). *Angew. Chem. Int. Ed. Engl.* **13**, 609–611.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

SCHULTZ, A. J., BROWN, R. K., WILLIAMS, J. M. & SCHROCK, R. R. (1981). *J. Am. Chem. Soc.* **103**, 169–176.

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The Structures of 1,4,7,14,23-Pentaoxa[7]orthobenzeno[2](2,6)pyridino[2]orthobenzenophane* ('Dibenzopyridino-18-crown-6') in its Hydrated Ethanol Inclusion Compound (1), $\mathbf{C_{23}H_{23}NO_5.CH_3CH_2OH.0{\cdot}12H_2O}$, and its Sodium Isothiocyanate Complex (2), $\mathbf{C_{23}H_{23}NO_5.NaNCS}$

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Abstract. (1): $M_r = 441{\cdot}67$, tetragonal, $I4/m$, $a = 15{\cdot}342\ (5)$, $c = 19{\cdot}397\ (6)$ Å, $U = 4565{\cdot}6$ Å^3, $Z = 8$, $D_x = 1{\cdot}285$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}08$ mm^{-1}, $F(000) = 1882$ (calculated for one water molecule per unit cell), $T = 291$ K, $R = 0{\cdot}058$ for 1403 diffractometer data. (2): $M_r = 474{\cdot}51$, triclinic, $P\bar{1}$, $a = 11{\cdot}529\ (4)$, $b = 14{\cdot}667\ (6)$, $c = 14{\cdot}724\ (6)$ Å, $\alpha = 87{\cdot}12\ (5)$, $\beta = 81{\cdot}11\ (6)$, $\gamma = 68{\cdot}58\ (6)^\circ$, $U = 2289{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}376$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}19$ mm^{-1}, $F(000) = 988$, $T = 291$ K, $R = 0{\cdot}054$ for 4900 reflections. In its ethanol inclusion compound, the title crown ether possesses nearly the same molecular geometry and conformation as its xylylene analogue, but a different packing; on sodium uptake, the slight conformational changes imply weak cation–dipole interactions involving the six heteroatoms.

Introduction. The current macrocycle L was reported to coordinate alkali, alkaline-earth and transition-metal ions (Weber & Vögtle, 1976) and also to form a variety of stoicheiometric and non-stoicheiometric crystalline compounds with small neutral molecules (Vögtle & Müller, 1980; Vögtle, Müller & Weber, 1980). In

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[*] Nomenclature from Weber & Vögtle (1976).

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