# Structure of Di-$\mu$-chloro-bis[trichloro($p$-tolylimino)tungsten(VI)], [{WCl$_3$($p$-CH$_3$C$_6$H$_4$N)}$_2$($\mu$-Cl)$_2$]

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**Abstract.** [W$_2$(C$_7$H$_7$N)$_2$Cl$_8$], $M_r$ = 861·6, triclinic, $P\bar{1}$, $a$ = 6·129 (8), $b$ = 9·257 (11), $c$ = 10·028 (13) Å, $\alpha$ = 88·88 (9), $\beta$ = 83·33 (10), $\gamma$ = 85·18 (11)°, $V$ = 563·1 Å$^3$, $Z$ = 1, $D_x$ = 2·541 Mg m$^{-3}$, $\lambda$(Mo K$\alpha$) = 0·71073 Å, $\mu$ = 11·4 mm$^{-1}$, $F$(000) = 396, $T$ = 293 K, $R$ = 0·068 for 1196 unique reflections with $F > 4\sigma(F)$. In the centrosymmetric dimeric molecules, octahedrally coordinated W atoms are bridged asymmetrically by Cl ligands [W—Cl = 2·415 (6) and 2·717(6) Å, W—Cl—W = 101·6 (2)°]. The imino ligands, with W—N = 1·712 (18) Å, are situated *trans* to the longer W—Cl bridge bonds, and the remaining coordination sites are occupied by terminal Cl [W—Cl = 2·286 (7)–2·298 (7) Å]. The central W$_2$Cl$_2$ ring is strictly planar. The essentially planar imino ligands [r.m.s. $\Delta$ = 0·01 (1) Å for C and N atoms] are inclined at only 7 (1)° to the central ring and the bonding is linear at N [W—N—C = 177 (2)°]. The octahedral coordination of W is considerably distorted, major deviations from regular octahedral angles being Cl(1)—W—Cl(1′) = 78·4 (2)° involving the bridging Cl, and Cl(2)—W—Cl(3) = 166·9 (2)° involving the terminal Cl atoms above and below the main molecular plane, which are displaced towards the bridging region.

**Experimental.** Compound prepared from WOCl$_4$ and $p$-CH$_3$C$_6$H$_4$NCO in refluxing toluene, large brown prisms obtained by cooling to room temperature. Cleaved fragment size 0·50 × 0·54 × 0·58 mm, mounted in Lindemann capillary. Siemens AED2 diffractometer, graphite-monochromated Mo K$\alpha$ radiation, cell parameters from 2$\theta$ values of 32 reflections (20 < 2$\theta$ < 25°) measured at $\pm\omega$. Intensity measurements in $\omega/\theta$ scan mode, scan range 0·85° below $\alpha_1$ to 0·85° above $\alpha_2$, scan time 17·5 s, 2$\theta_{max}$ = 45°, $h$ −6→5, $k$ −9→9, $l$ −10→10, no significant variation in intensity for three standard reflections. Reflection profiles were generally broad and of poor shape. Semi-empirical absorption correction (transmission 0·002–0·015). 2735 reflections, 1255 unique ($R_{int}$ = 0·16), 1196 with $F > 4\sigma(F)$ for structure determination (by Patterson and difference syntheses) and refinement (blocked-cascade least squares on $F$), $w^{-1} = \sigma^2(F) + 0·005F^2$. Anisotropic thermal parameters for all non-H atoms, aromatic H atoms constrained [C—H = 0·96 Å on

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 | 5103 (1) | 3547 (1) | 3550 (1) | 47 (1) |
| Cl(1) | 7407 (7) | 5319 (6) | 4245 (7) | 53 (2) |
| Cl(2) | 6606 (8) | 1981 (6) | 5069 (6) | 60 (2) |
| Cl(3) | 3285 (9) | 5417 (7) | 2460 (7) | 64 (2) |
| Cl(4) | 2255 (9) | 2119 (7) | 3473 (7) | 70 (2) |
| N | 6678 (26) | 2952 (17) | 2114 (20) | 59 (7) |
| C(1) | 7944 (28) | 2522 (24) | 899 (22) | 51 (7) |
| C(2) | 9910 (33) | 3106 (25) | 493 (30) | 73 (10) |
| C(3) | 11051 (31) | 2565 (25) | −787 (32) | 85 (11) |
| C(4) | 10235 (29) | 1643 (19) | −1441 (17) | 44 (6) |
| C(5) | 8214 (35) | 1098 (25) | −1076 (24) | 61 (8) |
| C(6) | 7063 (27) | 1518 (23) | 139 (21) | 50 (7) |
| C(7) | 11374 (44) | 1106 (29) | −2839 (26) | 79 (9) |

Table 2. *Bond lengths* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| W—Cl(1) | 2·415 (6) | W—Cl(1′) | 2·717 (6) |
| W—Cl(2) | 2·298 (7) | W—Cl(3) | 2·307 (7) |
| W—Cl(4) | 2·286 (7) | W—N | 1·712 (18) |
| N—C(1) | 1·411 (27) | C(1)—C(2) | 1·377 (28) |
| C(1)—C(6) | 1·395 (31) | C(2)—C(3) | 1·464 (39) |
| C(3)—C(4) | 1·257 (33) | C(4)—C(5) | 1·384 (28) |
| C(4)—C(7) | 1·562 (30) | C(5)—C(6) | 1·381 (30) |

| | | | |
|---|---|---|---|
| Cl(1)—W—Cl(2) | 87·0 (2) | Cl(1)—W—Cl(3) | 87·2 (2) |
| Cl(2)—W—Cl(3) | 166·9 (2) | Cl(1)—W—Cl(4) | 162·3 (2) |
| Cl(2)—W—Cl(4) | 90·6 (2) | Cl(3)—W—Cl(4) | 91·4 (2) |
| Cl(1)—W—N | 99·6 (6) | Cl(2)—W—N | 99·2 (6) |
| Cl(3)—W—N | 93·4 (6) | Cl(4)—W—N | 98·1 (6) |
| Cl(1)—W—Cl(1′) | 78·4 (2) | Cl(2)—W—Cl(1′) | 84·2 (2) |
| Cl(3)—W—Cl(1′) | 83·1 (2) | Cl(4)—W—Cl(1′) | 84·0 (2) |
| N—W—Cl(1′) | 176·0 (6) | W—Cl(1)—W′ | 101·6 (2) |
| W—N—C(1) | 177·3 (15) | N—C(1)—C(2) | 120·8 (21) |
| N—C(1)—C(6) | 116·3 (16) | C(2)—C(1)—C(6) | 122·9 (20) |
| C(1)—C(2)—C(3) | 115·1 (22) | C(2)—C(3)—C(4) | 120·7 (19) |
| C(3)—C(4)—C(5) | 124·8 (19) | C(3)—C(4)—C(7) | 121·4 (20) |
| C(5)—C(4)—C(7) | 113·6 (19) | C(4)—C(5)—C(6) | 118·1 (21) |
| C(1)—C(6)—C(5) | 118·3 (18) | | |

Symmetry operator (inversion) for primed atoms: 1−$x$, 1−$y$, 1−$z$.

ring-angle external bisectors, $U$(H) = 1·2$U_{eq}$(C)], no methyl H atoms, negligible extinction. 118 parameters, max. $\Delta/\sigma$ = 0·009, mean = 0·002, $R$ = 0·068, $wR$ = 0·105, slope of normal probability plot = 0·87, max. $\Delta\rho$ = 2·68, min. = −1·87 e Å$^{-3}$ (largest features close to W atom). Scattering factors from *International Tables for X-ray Crystallography* (1974); *SHELXTL* programs (Sheldrick, 1985).
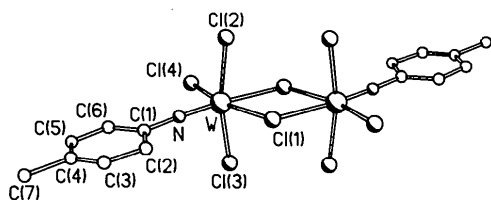
Fig. 1. Structure of the dimeric molecule, without H atoms, showing the atom-labelling scheme.

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,* bond lengths and angles in Table 2. The molecular structure is shown in Fig. 1.

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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 44157 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Related literature.** A similar structure has been observed for the alkylimido complexes $[\{WCl_3(NR)\}_2(\mu\text{-}Cl)_2]$ with $R = C_2H_5$ (Bradley, Errington, Hursthouse & Short, 1987), $R = C_2Cl_5$ (Drew, Fowles, Rice & Rolfe, 1971), and $R = CH(CH_3)_2$ (Ashcroft, Clark, Nielson & Rickard, 1986).

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# A *trans*-Chelating Oxybisphosphine Complex of PtBr$_2$

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**Abstract.** Dibromo$\{[3,3'\text{-oxybis(phenylene-methylene)}]$bis(diphenylphosphine)$\}$platinum(II)–acetonitrile (2/1), $[PtBr_2(C_{38}H_{32}OP_2)].\frac{1}{2}C_2H_3N$, $M_r = 942\cdot1$, monoclinic, $P2_1/n$, $a = 9\cdot923$ (8), $b = 16\cdot389$ (2), $c = 21\cdot527$ (2) Å, $\beta = 97\cdot26$ (4)°, $V = 3472\cdot8$ Å$^3$, $Z = 4$, $D_x = 1\cdot802$ g cm$^{-3}$, $F(000) = 1828$, $\lambda$(Mo $K\alpha$) = $0\cdot71073$ Å, $\mu = 62\cdot4$ cm$^{-1}$, room temperature, final $R = 0\cdot035$ for 5561 unique reflections with $F_o > 5\sigma(F_o)$. The coordination about the Pt atom is square planar. The Pt atom is displaced by $0\cdot04$ (1) Å towards the O atom from the best plane through atoms $P_2Br_2$. The phenyl rings in the *trans*-spanning $3,3'$-oxydibenzyl ligand are inclined at an angle of 60 (1)°, and angle C(Ph)—O—C(Ph) is $121\cdot6$ (5)°. Angles C(Ph)—P—Pt in the equatorial plane are opened to an average value of $120\cdot1$ (1)° owing to steric hindrance involving the Br atoms.

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**Experimental.** Yellow bipyramidal crystals grown from a CH$_3$CN/toluene solution. Stoe–Siemens AED2 four-circle diffractometer, monochromated Mo $K\alpha$ radiation, $\omega/\theta$ scan mode, $2\theta_{max}$ 55°, 8506 reflections $\pm h+k+l$. Four check reflections, 3% intensity variation. Crystal cut to $0\cdot27 \times 0\cdot27 \times 0\cdot42$ mm, empirical absorption correction [programs *REDU*4 and *EMPIR* (Stoe & Co., 1985)], 8 $\psi$ scans in $2\theta$ range 11–39°, max., min. transmission $0\cdot253$, $0\cdot170$ respectively. 7700 unique reflections ($R_{int} = 0\cdot033$), 5566 with $F_o > 5\sigma(F_o)$, 5561 used for all calculations, five (probably suffering from extinction) removed. Index range $h -12\rightarrow12$, $k\ 0\rightarrow21\ l\ 0\rightarrow27$. Cell constants from $\pm\omega$ values of 12 reflections and their equivalents in the $2\theta$ range 15–28°. Structure solved by Patterson and Fourier methods. H atoms from difference syntheses, refined isotropically. A disordered CH$_3$CN molecule with the central C atom located on a center of symmetry was assumed to occupy two alternative orientations inclined at an angle of 5(2)°, hence C(H$_3$) and N atoms given occupancy of $0\cdot5$. Despite large correlation coefficients between the