Structure of Bis-μ-[bis(diphenylphosphino)methane]-bis(chloroplatinum) (*Pt—Pt*)

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Abstract. $C_{50}H_{44}Cl_2P_4Pt_2$, $[Pt_2(C_{25}H_{22}P_2)_2Cl_2]$, $M_r = 1229.9$, monoclinic, $P2_1/c$, $a = 13.592$ (3), $b = 16.577$ (10), $c = 21.439$ (4) Å, $\beta = 105.63$ (2)°, $U = 4652$ Å^3, $Z = 4$, $D_c = 1.756$ Mg m^{-3}, μ(Mo $K\alpha$) = 6.4 mm^{-1}; $R = 0.086$ for 4307 independent reflections. The crystal structure is built from binuclear molecules, which contain two Pt—Cl fragments linked to one another by a Pt—Pt bond and by two bridging bis(diphenylphosphino)methane ligands. The Pt atoms are in square-planar environments and the angle between the two coordination planes is 38.6°. Selected bond lengths are: Pt—Pt 2.651 (1), Pt—Cl 2.401 (5) and 2.408 (5), and Pt—P 2.250 (7)–2.294 (7) Å.

Introduction. The Pt^I complex [{PtCl(μ-dppm)}$_2$], where dppm = bis(diphenylphosphino)methane, was first obtained and characterized spectroscopically by

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Glockling & Pollock (1972, 1974), who assigned it a Cl-bridged structure, and later by Brown, Puddephatt & Rashidi (1976) and Brown, Puddephatt, Rashidi & Seddon (1977), who proposed a dppm-bridged structure. The work reported here establishes that the latter structure is correct, as briefly noted elsewhere (Brown, Puddephatt, Rashidi, Manojlović-Muir, Muir, Solomun & Seddon, 1977).

Measurements were made on a Hilger & Watts Y290 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The analysis was based on 4307 unique reflections with $2 \leq \theta \leq 30°$ and $I \geq 3\sigma(I)$, where $\sigma(I)$ is derived from counting statistics. Corrections were applied for Lorentz–polarization effects and for variations in intensities of two periodically remeasured standard reflections.

The structure was solved by the heavy-atom method and refined by block-diagonal least squares. Scattering

Table 1. *Fractional atomic coordinates* ($\times 10^3$)

	x	y	z		x	y	z
Pt(1)	289.76 (6)	63.08 (6)	236.40 (4)	C(22)	382 (2)	−110 (2)	435 (2)
Pt(2)	95.31 (6)	75.84 (5)	170.05 (4)	C(23)	383 (3)	−87 (3)	501 (2)
Cl(1)	467.4 (4)	54.6 (6)	295.3 (3)	C(24)	332 (3)	−22 (3)	510 (2)
Cl(2)	−77.3 (4)	83.3 (5)	103.1 (3)	C(25)	296 (3)	31 (2)	459 (2)
P(1)	329.4 (4)	25.6 (4)	143.1 (3)	C(26)	395 (3)	199 (3)	395 (2)
P(2)	249.8 (4)	89.9 (4)	330.2 (3)	C(27)	421 (3)	280 (3)	426 (2)
P(3)	51.3 (4)	21.9 (4)	255.5 (3)	C(28)	358 (2)	333 (2)	430 (2)
P(4)	156.8 (4)	135.2 (4)	93.9 (3)	C(29)	253 (2)	323 (2)	406 (1)
C(1)	237 (2)	63 (2)	66 (1)	C(30)	216 (2)	247 (2)	373 (1)
C(2)	113 (2)	90 (2)	324 (1)	C(31)	−120 (3)	82 (2)	296 (2)
C(3)	342 (2)	−83 (2)	135 (1)	C(32)	−227 (3)	70 (3)	295 (2)
C(4)	446 (2)	65 (2)	131 (1)	C(33)	−289 (2)	34 (2)	252 (2)
C(5)	305 (2)	14 (2)	397 (1)	C(34)	−254 (2)	−19 (2)	216 (2)
C(6)	285 (2)	190 (2)	369 (1)	C(35)	−149 (2)	−22 (2)	214 (1)
C(7)	−85 (2)	25 (2)	256 (1)	C(36)	39 (3)	−123 (2)	320 (2)
C(8)	88 (2)	−85 (2)	279 (1)	C(37)	67 (3)	−206 (2)	337 (2)
C(9)	240 (2)	226 (2)	118 (1)	C(38)	138 (2)	−240 (2)	314 (2)
C(10)	66 (2)	171 (2)	17 (1)	C(39)	184 (4)	−205 (2)	273 (1)
C(11)	296 (2)	−127 (2)	79 (1)	C(40)	158 (2)	−121 (2)	254 (1)
C(12)	304 (2)	−206 (2)	77 (1)	C(41)	254 (2)	258 (2)	181 (1)
C(13)	358 (3)	−251 (2)	128 (2)	C(42)	325 (3)	323 (2)	199 (2)
C(14)	404 (2)	−205 (2)	187 (2)	C(43)	372 (2)	354 (2)	156 (2)
C(15)	398 (2)	−127 (2)	191 (1)	C(44)	360 (2)	324 (2)	96 (1)
C(16)	498 (2)	27 (2)	90 (1)	C(45)	291 (2)	256 (2)	75 (1)
C(17)	582 (2)	63 (2)	77 (2)	C(46)	39 (2)	249 (2)	11 (1)
C(18)	617 (2)	141 (2)	102 (1)	C(47)	−29 (2)	278 (2)	−52 (2)
C(19)	569 (2)	178 (2)	142 (1)	C(48)	−59 (2)	219 (2)	−101 (1)
C(20)	485 (2)	143 (2)	157 (1)	C(49)	−28 (2)	139 (2)	−92 (1)
C(21)	346 (2)	−48 (2)	385 (1)	C(50)	35 (2)	111 (2)	−30 (1)

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

Pt(1)—Cl(1)	2·408 (5)		Pt(2)—Cl(2)	2·401 (5)
Pt(1)—P(1)	2·294 (7)		Pt(2)—P(3)	2·259 (7)
Pt(1)—P(2)	2·264 (7)		Pt(2)—P(4)	2·250 (7)
Pt(1)—Pt(2)	2·651 (1)			

P(1)—Pt(1)—P(2)	175·6 (2)	P(3)—Pt(2)—P(4)	172·9 (2)
Cl(1)—Pt(1)—Pt(2)	178·5 (2)	Cl(2)—Pt(2)—Pt(1)	175·7 (2)
Cl(1)—Pt(1)—P(1)	90·2 (2)	Cl(2)—Pt(2)—P(3)	94·3 (2)
Cl(1)—Pt(1)—P(2)	89·6 (2)	Cl(2)—Pt(2)—P(4)	92·2 (2)
Pt(2)—Pt(1)—P(1)	89·3 (2)	Pt(1)—Pt(2)—P(3)	88·7 (2)
Pt(2)—Pt(1)—P(2)	91·0 (2)	Pt(1)—Pt(2)—P(4)	85·0 (2)
Pt(1)—P(1)—C(1)	114·4 (8)	Pt(2)—P(3)—C(2)	103·8 (8)
Pt(1)—P(2)—C(2)	114·4 (8)	Pt(2)—P(4)—C(1)	108·7 (8)
P(1)—C(1)—P(4)	104·5 (12)	P(2)—C(2)—P(3)	107·2 (13)

Pt(2)—Pt(1)—P(1)—C(1)	25·4 (9)
Pt(1)—P(1)—C(1)—P(4)	11 (1)
P(1)—C(1)—P(4)—Pt(2)	−52 (1)
C(1)—P(4)—Pt(2)—Pt(1)	61·6 (9)
P(4)—Pt(2)—Pt(1)—P(1)	−42·4 (2)
Pt(2)—Pt(1)—P(2)—C(2)	10·2 (9)
Pt(1)—P(2)—C(2)—P(3)	27 (1)
P(2)—C(2)—P(3)—Pt(2)	−58 (1)
C(2)—P(3)—Pt(2)—Pt(1)	56·2 (8)
P(3)—Pt(2)—Pt(1)—P(2)	−34·7 (2)

Fig. 1. A view of the molecular structure of [{PtCl(μ-dppm)}₂]. The vibrational ellipsoids of the Pt, Cl and P atoms display 50% probability. For clarity, all C atoms are represented by circles of arbitrary size; they are labelled by numbers only, corresponding to those listed in Table 1.

factors, and anomalous-dispersion corrections for Pt, Cl and P, were taken from *International Tables for X-ray Crystallography* (1974). The refinement, with anisotropic thermal vibrations for Pt, Cl and P atoms only, converged at $R = 0·086$ and $R' = 0·108$. No allowance was made for the H atoms.

The final atomic coordinates and selected bond lengths and angles are presented in Tables 1 and 2.* The computer programs were those listed by Caldwell, Manojlović-Muir & Muir (1977).

Discussion. The crystal structure is built from discrete binuclear molecules separated by van der Waals contacts.

The molecular structure, shown in Fig. 1, comprises two Pt—Cl fragments linked directly through a metal—metal bond and bridged by two dppm ligands. The conformations of the ligands are similar and the molecule therefore approximates to C_2 symmetry, the diad axis coinciding with an essentially linear Cl—Pt—Pt—Cl unit.

The geometry of the dppm ligands reflects their ability to rotate internally about each of the two methylene C—P bonds (Cotton & Troup, 1974). Thus the conformations about C(1)—P(4) and C(2)—P(3) are practically staggered, the P—C—P—Pt(2) torsion angles

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* Lists of structure factors, thermal parameters and all bond lengths, bond angles and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34294 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
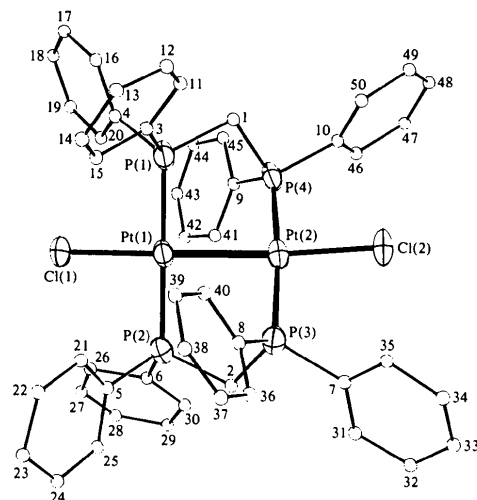
being −52 (1) and −58 (1)°, while those about C(1)—P(1) and C(2)—P(2) are closer to eclipsed, the P—C—P—Pt(1) torsion angles being 11 (1) and 27 (1)°. P(1)—C(1) and P(2)—C(2) are nearer to eclipsing the Pt(1)—Pt(2) vector than are P(3)—C(2) and P(4)—C(1), as is apparent from the Pt—Pt—P—C torsion angles of 25·4 (9), 10·2 (9), 56·2 (8) and 61·6 (9)° respectively (Table 2). Such conformational differences lead to variations in the Pt—P—CH₂ angles, which are larger at P(1) and P(2) than at P(3) and P(4) (Table 2). The bond lengths and angles within the dppm ligands are unexceptional. The mean P—C and C—C distances are 1·85 (1) and 1·39 (1) Å.

The coordination geometry around the Pt atoms is square-planar with small tetrahedral distortions, which are evident from the bond angles subtended at the Pt atoms (Table 2), and also from the displacements of atoms from the two Pt₂P₂Cl coordination planes. These displacements do not exceed 0·13 Å.

Pt(1)—Pt(2) [2·651 (1) Å] is somewhat shorter than the Pd—Pd bond [2·699 (5) Å] in the isomorphous and isostructural [{PdBr(μ-dppm)}₂] analogue (Holloway, Penfold, Colton & McCormick, 1976). In the few other Ptᴵ complexes examined so far the Pt—Pt distances are 2·581 (4)—2·647 (2) Å (Brown, Puddephatt, Rashidi, Manojlović-Muir, Muir, Solomun & Seddon, 1977).

The Pt—Cl lengths [2·401 (5) and 2·408 (5) Å] are similar to those in [{Pt(CO)Cl₂}₂]²⁻ [2·382 (10) and 2·426 (9) Å] (Modinos & Woodward, 1975). They are close to the upper end of the range of Pt—Cl distances in square-planar Ptᴵᴵ complexes (Manojlović-Muir & Muir, 1974), and may suggest a relatively high *trans* influence of the Pt—Pt bond. The Pt—P distances

[2·250 (7)–2·294 (7) Å] are comparable with those [2·291 (5)–2·308 (5) Å] in [Pt₂(CO)Cl(μ-dppm)₂] (Manojlović-Muir, Muir & Solomun, 1979).

Perhaps the most interesting structural feature is the twisted configuration of the molecule as a whole. The two Pt_2P_2Cl coordination planes are mutually rotated about Pt(1)–Pt(2) to afford a dihedral angle of 38·6°. This, however, leads to only slight angular distortions in the Pt_2P_2C rings (see above). Thus the flexibility of the dppm ligands allows the molecule almost to minimize any antibonding interactions between filled interaxial *d* orbitals of the metal atoms. In the Pt^I anion $[\{Pt(CO)Cl_2\}_2]^{2-}$, where the constraint of the bridging groups is not present, the corresponding dihedral angle is *ca* 60°; this has been interpreted as a compromise between the tendency of the filled interaxial metal *d* orbitals to be positioned as far from one another as possible (dihedral angle 45°) and the tendency of the ligands attached to the adjacent metal atoms to minimize their steric repulsions (dihedral angle 90°) (Modinos & Woodward, 1975).

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Structure of (Chloromercurio)acetaldehyde

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Abstract. C_2H_3ClHgO, $Hg(C_2H_3O)Cl$, triclinic, $P\bar{1}$, $a = 8·147\,(8)$, $b = 6·377\,(6)$, $c = 4·511\,(4)$ Å, $\alpha = 92·0\,(1)$, $\beta = 81·3\,(1)$, $\gamma = 101·6\,(1)°$, $D_c = 4·09$ Mg m⁻³, $Z = 2$; final $R = 0·030$ for 484 diffractometer-measured intensities (Mo $K\alpha$, $\lambda = 0·7107$ Å). Hg is coordinated to Cl [Hg–Cl = 2·326 (6) Å] and to C [Hg–C = 2·11 (2) Å] with the angle Cl–Hg–C = 172·2 (5)°, and also to O of *c*-related and centrosymmetrically related molecules [Hg–O = 2·87 (1) and 2·84 (2) Å respectively]. There is also an intermolecular Hg···Cl contact at 3·370 (6) Å.

Introduction. The title compound was supplied by Dr F. G. Thorpe, and had been prepared by the method of Makarova & Nesmayanov (1967). The crystals, used without further recrystallization, were thin laths twinned about *b*; with care the twins could be separated. The cell dimensions were obtained from Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1·5418$ Å); the crystal density was not measured as it was too high for the flotation method and the compound was not available in sufficient quantity for an alternative method. Intensities were collected on a Stoe STADI-2 automatic two-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Although decomposition of the crystals occurred continuously under irradiation, it was sufficiently slow to permit all measurements to be made with one crystal with dimensions 0·31 × 0·03 × 1·13 mm. Of 537 intensities measured within the range $2\theta = 4–40°$, 484 had $I > 3\sigma(I)$ and were used for the structure determination. Absorption corrections ($\mu = 33·095$ mm⁻¹) were applied with *SHELX* (Sheldrick, 1976), which was also

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