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Structure of *cis*-[1,2-Bis(dicyclohexylphosphino)ethane-*P*,*P'*]dichloroplatinum(II) Chloroform Solvate

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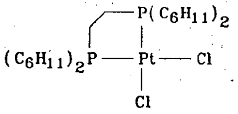
Abstract

The structure of *cis*-$PtCl_2$(dcpe) [dcpe = 1,2-bis(dicyclohexylphosphino)ethane] consists of an approximately square planar Pt^{II} ion coordinated by a chelating dcpe ligand and two Cl ions. The coordination sphere of the Pt shows a slight tetrahedral distortion, while the five-membered chelate ring is puckered about the mean coordination plane.

Comment

The title compound, *cis*-$PtCl_2$(dcpe) (1), is a convenient precursor to sterically protected polysilyl–platinum complexes (Chang, Johnson & Fink, 1989). In an attempt to grow crystals of *cis*-PtH_2(dcpe) from purified chloroform, a chloroform solvate of (1), formed from the reaction of the hydride complex with the solvent, was obtained instead. To the best of our knowledge, the structure of (1), originally prepared over eight years ago (Clark, Kapoor & McMahon, 1984), has not been determined. We report it now together with a comparison with the structures of two closely related complexes.


$$(C_6H_{11})_2P—Pt(Cl)_2—P(C_6H_{11})_2$$

(1)

The coordination sphere of the Pt atom is essentially square planar with a slight tetrahedral distortion which can be seen from the displacements of the ligating atoms from the weighted least-squares plane through Pt, P(1), P(2), Cl(1), Cl(2): P(1) −0.084 (2); P(2) 0.064 (2); Cl(1) −0.099 (2); Cl(2) 0.078 (3) Å. Alternatively, the dihedral angle between planes defined by Pt, P(1) and P(2) and by Pt, Cl(1) and Cl(2) is 5.86 (52)°. The five-membered chelate ring is puckered with C(25) and C(26) lying, respectively, 0.099 (9) and −0.263 (8) Å from the weighted coordination plane. All the cyclohexyl groups adopt the standard chair conformation.

Selected structural features of (1) are compared with those of the related complexes *cis*-dichloro[1,2-bis(diphenylphosphino)ethane]platinum(II), $PtCl_2$(dppe) (2), and *cis*-dichloro[1,2-bis(di-*tert*-butylphosphino)ethane]platinum(II), $PtCl_2$(dtpe) (3) (Table 3). As the bulk of the diphosphine ligand increases (dppe < dcpe < dtpe) the most notable effect is on the P—Pt—P and Cl—Pt—Cl angles with the former increasing and the latter decreasing significantly, features which can be attributed to the increased steric interaction between the substituents on the P atom and both the ligand backbone and the Cl ligands. The same interactions also appear to affect the Pt—P distances which increase in the order (2) < (1) < (3), although the comparatively low accuracy of the structure of (2) makes the significance of the apparent increase in the Pt—P distance in going from (2) to (1) less certain than that between (1) and (3). A marginal increase in the average Pt—Cl distance is also seen.

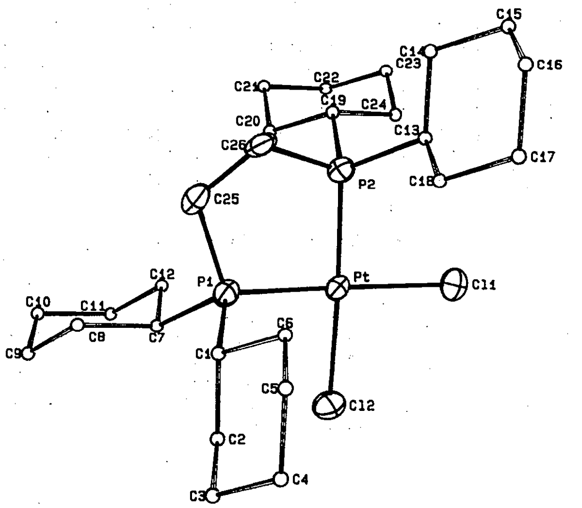


Fig. 1. A perspective view of *cis*-$PtCl_2$(dcpe). Thermal ellipsoids are drawn at the 35% probability level. C atoms of the cyclohexyl groups are drawn arbitrarily small and H atoms are omitted for clarity.

Experimental

Crystal data

$[PtCl_2(C_{26}H_{48}P_2)].\frac{3}{4}CHCl_3$
M_r = 778.20
Monoclinic
$P2_1/n$
a = 11.771 (1) Å
b = 20.353 (3) Å
c = 14.704 (2) Å
β = 109.719 (8)°
V = 3316 (1) $Å^3$

λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11.36–15.83°
μ = 4.79 mm^{-1}
T = 296 K
Prism
0.45 × 0.31 × 0.22 mm
Colorless

$Z = 4$
$D_x = 1.56$ Mg m^{-3}
Mo $K\alpha$ radiation

Crystal source: slow evaporation of chloroform solution

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans, width $(0.8 + 0.2\tan\theta)^\circ$, speed 16.4-1.3° min^{-1}
Absorption correction: empirical (ψ scans)
$T_{\min} = 0.7687$, $T_{\max} = 0.9990$
5659 measured reflections
5197 independent reflections

3263 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.023$
$\theta_{\max} = 24^\circ$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 23$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity variation: −14.5% over 4200 min

Refinement

Refinement on F
Final $R = 0.035$
$wR = 0.045$
$S = 1.394$
3263 reflections
308 parameters
H-atom parameters not refined

$w = 4F/[\sigma_I^2 + (0.04F^2)^2]$
$(\Delta/\sigma)_{\max} = 0.10$
$\Delta\rho_{\max} = 1.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2) *for* (1)

$B_{\rm eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Chloroform atoms were refined isotropically with occupancy factors: Cl(1*S*) 0.5; Cl(2*S*) 0.5; Cl(3*S*) 0.5; C(1*S*) 0.75; Cl(4*S*) 0.25; Cl(5*S*) 0.25; Cl(6*S*) 0.25.

	x	y	z	$B_{\rm eq}/B_{\rm iso}$
Pt	0.23832 (2)	0.25402 (1)	0.44143 (2)	2.628 (5)
Cl(1)	0.4328 (2)	0.2076 (1)	0.4768 (2)	4.47 (5)
Cl(2)	0.2374 (2)	0.2193 (1)	0.5947 (2)	4.56 (5)
P(1)	0.0630 (2)	0.3053 (1)	0.4122 (2)	2.84 (5)
P(2)	0.2301 (2)	0.2819 (1)	0.2930 (1)	2.87 (4)
C(1)	0.0765 (7)	0.3802 (4)	0.4855 (6)	3.5 (2)
C(2)	0.0840 (8)	0.3666 (5)	0.5891 (7)	4.3 (2)
C(3)	0.0987 (9)	0.4289 (5)	0.6478 (7)	4.7 (2)
C(4)	0.2047 (9)	0.4684 (5)	0.6443 (7)	5.4 (3)
C(5)	0.2021 (9)	0.4835 (5)	0.5433 (7)	5.0 (2)
C(6)	0.1838 (8)	0.4200 (4)	0.4840 (7)	4.1 (2)
C(7)	−0.0603 (7)	0.2576 (4)	0.4295 (6)	3.5 (2)
C(8)	−0.1808 (7)	0.2954 (4)	0.4024 (7)	4.0 (2)
C(9)	−0.2770 (7)	0.2543 (5)	0.4214 (7)	4.8 (2)
C(10)	−0.2949 (9)	0.1892 (5)	0.3677 (7)	5.1 (3)
C(11)	−0.1794 (9)	0.1522 (5)	0.3926 (8)	5.3 (3)
C(12)	−0.0781 (8)	0.1923 (5)	0.3745 (6)	3.9 (2)
C(13)	0.3655 (8)	0.3229 (4)	0.2866 (6)	3.7 (2)
C(14)	0.3631 (9)	0.3376 (5)	0.1839 (7)	5.7 (3)
C(15)	0.4818 (9)	0.3686 (7)	0.1860 (7)	7.5 (3)
C(16)	0.509 (1)	0.4305 (6)	0.2461 (9)	7.2 (3)
C(17)	0.5109 (9)	0.4163 (5)	0.3479 (8)	4.9 (3)
C(18)	0.3956 (8)	0.3837 (4)	0.3487 (7)	4.3 (2)
C(19)	0.1986 (7)	0.2134 (4)	0.2061 (5)	3.3 (2)
C(20)	0.0855 (8)	0.1761 (5)	0.2024 (6)	4.0 (2)
C(21)	0.0567 (9)	0.1217 (5)	0.1283 (7)	5.0 (2)
C(22)	0.164 (1)	0.0748 (5)	0.1466 (7)	5.5 (3)
C(23)	0.2766 (9)	0.1119 (5)	0.1513 (7)	5.8 (3)
C(24)	0.3043 (8)	0.1663 (5)	0.2248 (7)	4.7 (2)
C(25)	0.0070 (7)	0.3329 (4)	0.2862 (6)	3.5 (2)
C(26)	0.1060 (7)	0.3393 (4)	0.2425 (6)	3.2 (2)
Cl(1*S*)	0.3602 (7)	0.0204 (4)	0.6289 (6)	9.0 (2)
Cl(2*S*)	0.3256 (8)	0.0175 (4)	0.4299 (6)	9.5 (2)
Cl(3*S*)	0.1306 (8)	0.0405 (4)	0.4889 (6)	10.4 (2)
C(1*S*)	0.292 (1)	0.0572 (8)	0.530 (1)	6.5 (4)
Cl(4*S*)	0.422 (1)	0.0117 (6)	0.62238 (9)	6.4 (3)
Cl(5*S*)	0.185 (2)	0.0394 (8)	0.582 (1)	9.8 (4)
Cl(6*S*)	0.243 (2)	0.038 (1)	0.424 (2)	13.2 (7)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

Pt—Cl(1)	2.366 (2)	Pt—P(1)	2.222 (2)
Pt—Cl(2)	2.365 (2)	Pt—P(2)	2.225 (2)
Cl(1)—Pt—Cl(2)	89.23 (9)	Cl(2)—Pt—P(1)	91.24 (8)
Cl(1)—Pt—P(1)	175.39 (9)	Cl(2)—Pt—P(2)	176.31 (9)
Cl(1)—Pt—P(2)	92.06 (9)	P(1)—Pt—P(2)	87.75 (8)

Table 3. *Comparison of selected structural parameters* (Å, °) *for complexes* (1), (2) *and* (3)

	(2)*	(1)†	(3)‡
Pt—P	2.208(6), 2.208(6)	2.222(2), 2.225(2)	2.262(3), 2.265(3)
Pt—Cl	2.341(6), 2.355(6)	2.365(2), 2.366(2)	2.365(4), 2.374(4)
Cl—Pt—Cl	90.2(2)	89.23(9)	86.29(13)
P—Pt—P	86.3(2)	87.75(8)	89.42(12)

* Farrar & Ferguson (1992).
† This work.
‡ Harada, Kai, Yasouka & Kasai (1976).

Crystal orientation, unit-cell determination and refinement, and data collection: CAD-4 Version 5.0 (Schagen, Staver, van Meurs & Williams, 1989). Data reduction, structure solution and refinement: *MolEN* (Enraf-Nonius, 1990). Graphics: *ORTEP*II (Johnson, 1976). All calculations were performed on a VAXstation 3100. The structure was solved by Patterson and difference Fourier syntheses and refined by full-matrix least squares. H atoms were included in calculated positions (C—H = 0.95 Å) with isotropic thermal parameters 20% larger than those of the attached C atoms and updated every two cycles of refinement. H atoms are numbered to correspond to their attached C atoms. Two alternate locations for the molecule of solvent chloroform having the C atom in common were observed. Trial refinement of occupancy factors indicated an overall occupancy of 0.75 distributed 2:1 over the two sites. Because of the disorder the solvent molecule was refined isotropically. The largest peaks in the final difference map were in the regions of the Cl atoms of the solvent molecule and are attributable to anistropic thermal motion and/or additional disorder.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances and angles, least-squares-planes data and r.m.s. amplitudes of anisotropic vibration have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55803 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1017]

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Interactions of Thiamine with Anions. Structure of Thiamine Dithiocyanate†

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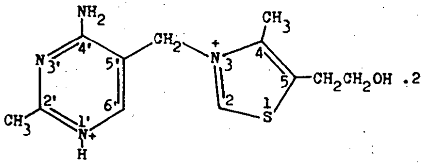
Abstract

The crystal structure analysis of {3-[(4-amino-2-methyl-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-4-methylthiazol}ium dithiocyanate reveals that there are two types of anion bridges between the two aromatic rings of the same thiamine which adopts the usual *F* conformation, one of which involves a contact between H(C2) on the thiazolium ring and the hydroxy O atom from a neighbouring molecule. The crystal packing shows a novel triple helical structure formed by strongly hydrogen-bonded thiamine–SCN$^-$ molecular chains.

Comment

Thiamine, as its pyrophosphate ester, is a coenzyme in a number of important metabolic processes such as the decarboxylation of α-keto acids. The reactions proceed through C(2)-substituted thiamines, which are intermediates in the reaction pathway (Breslow, 1958). It has been suggested that thiamine–anion salts can serve as model compounds for thiamine–substrate interactions based on the fact that the thiamine molecule fixes an anionic group near the active C(2)-position through both hydrogen bonding and electrostatic interactions (Aoki, Yamazaki, Waragai & Itokawa, 1988). In order to further examine such interactions we have determined the structure of thiamine dithiocyanate (I).



(I)

The crystal cleaves easily along {001} planes. In the structure, the thiamine cation adopts the usual *F* conformation in terms of the torsion angles (Pletcher, Sax, Blank & Wood, 1977): φ_T = C(5′)—C(35′)—N(3)—C(2) = 0.4 (6)° and φ_P = N(3)—C(35′)—C(5′)—C(4′) = 81.2 (5)°; the dihedral angle between the pyrimidine and thiazolium rings is 78.1 (2)°. The C(5) hydroxyethyl side chain folds back towards the thiazolium moiety to make a close contact of 2.868 (4) Å between O(53) and S(1). These structural features are similar to those found in thiamine.SCN and its monohydrate (Aoki, Hu, Yamazaki & Adeyemo, 1990), in which the thiamines are in free-base form. The molecular dimensions of the thiamine are in good agreement with those of thiamine containing a protonated pyrimidine ring (Shin & Lah, 1987; Aoki *et al.*, 1988). Compared with the free-base form, the protonation of N(1′) in this structure causes the C(6′)—N(1′)—C(2′) bond angle and the N(1′)—C(2′) bond length to increase and the C(2′)—N(3′) and C(4′)—N(41′) bond lengths to decrease.

Two types of anion bridges between the two aromatic rings of the same thiamine have been suggested to be factors affecting the *F* conformation of thiamine and provide a model for thiamine–substrate interactions (Aoki, Yamazaki & Adeyemo, 1991). In the present structure the thiocyanate anion, S(12)—C(12)—N(12), bridges the two aromatic rings through an N(41′)—H···N(12) hydrogen bond and an SCN$^-$···thiazolium-ring electrostatic interaction (Fig. 1) [closest contact N(12)···N(3) = 3.066 (6) Å]. An O(53) atom from a neighbouring thiamine ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $-z$) seems to act as another bridge. The O(53) atom is involved in a stacking interaction with the pyrimidine ring by locating over the ring plane [closest contact O(53)···N(1′) = 3.079 (6) Å and perpendicular distance O(53)···pyrimidine ring = 2.955 (3) Å] and an O···H—C interaction with the acidic H atom at C(2) [O(53)···C(2) = 3.676 (6), O(53)···H(C2) = 2.66 Å; sum of van der Waals radii

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† 4-Amino-5-[(5-hydroxyethyl-4-methylthiazol-3-ylio)methyl]-2-methyl-1-pyrimidinium dithiocyanate.

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