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Crystal and Molecular Structure of *Trans*-dichlorobis(tricyclohexylphosphine)-platinum(II)

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The crystal and molecular structure of the title compound have been determined. Crystals are triclinic, space group $P\bar{1}$, a = 10.008(4), b = 10.260(4), c = 10.653(4) Å, α = 112.87(9), β = 109.62(9), γ = 91.43(9)°, Z = 1. 4352 observed reflections were measured with a diffractometer; the structure was solved by Patterson-Fourier methods and refined by full-matrix least-squares to a final conventional R value of 0.039 (R_w = 0.041). The crystal contains discrete neutral trans-$Pt[P(C_6H_{11})_3]_2Cl_2$ *molecules, separated by normal van der Waals contacts. The complex is a typical square-planar Pt(II) species. Structural parameters: Pt–Cl, 2.317(2), Pt–P, 2.337(2) Å and Cl–Pt–P, 91.2(1)°.*

Introduction

We are studying a number of Pt(II) complexes in an attempt to find correlations between molecular structure and chemical behaviour [1–4]. In the course of these researches we had the opportunity of obtaining good crystals of *trans*-dichlorobis(tricyclohexylphosphine)platinum(II), *A*, suitable for crystal structure studies. Alcock and Leviston performed a single-crystal X-ray structure determination on the corresponding diiodide, *trans*-$Pt[P(C_6H_{11})_3]_2I_2$, *B*, and determined the cell constants and the space group of *A*. Unfortunately, they were not able to obtain suitably sized crystals of *A* for an X-ray structure determination. The structure analysis of *B* revealed that the complex is very highly crowded, resulting in great interligand repulsions and unusual increase in the phosphorus–platinum distance [5]. Mainly to compare bonding parameters and ligand–ligand steric interactions of *A* with those of *B*, we have undertaken an X-ray structure analysis of the title compound.

Experimental

Precession photographs and single-crystal diffractometry confirmed the crystal data obtained by Alcock and Leviston [5]. The crystals are triclinic space group $P\bar{1}$ (after structure analysis) with *a* = 10.008(4), *b* = 10.260(4), *c* = 10.653(4) Å, α = 112.87(9), β = 109.62(9), γ = 91.43(9)°, D_c = 1.470 g cm^{-3} for *Z* = 1, MoK$\bar{\alpha}$ radiation λ = 0.71069 Å, μ(MoK$\bar{\alpha}$) = 42.0 cm^{-1}.

Intensity data were collected from a crystal of approximate dimensions 0.15 × 0.20 × 0.22 mm on a Philips PW 1100 four-circle diffractometer in the range $6 \leqslant 2\theta \leqslant 56°$, using MoK$\bar{\alpha}$ radiation (graphite monochromator; $\theta/2\theta$ scan mode; scan width 1.3° scan speed 0.03° s^{-1}). During data collection, two standard reflections were measured every 180 min to check the stability of the crystals and electronics. Using the criterion $I \geqslant 2.5\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation derived from counting statistics, 4352 of the 4385 intensities recorded were deemed independent and observable and only these were used in the solution and refinement of the structure. Corrections were made for Lorentz, polarisation and X-ray absorption effects [6].

Structure Solution and Refinement

The chlorine and phosphorus atoms were readily located on a Patterson synthesis and the carbon atoms found by Fourier methods. A full-matrix least-squares refinement on F was computed. The function $\Sigma_w(|F_o|-|F_c|)^2$ was minimized in which $w = [\sigma^2(F_o) + 0.001\ F_o^2]^{-1}$. Throughout the analysis the scattering factors from International Tables for X-ray Crystallography were used [7]; both the real and imaginary components of anomalous dispersion were included for platinum, chlorine and phosphorus [7]. The Pt, Cl and P atoms were allowed to vibrate anisotropically, while the C atoms of the cyclohexane rings were assigned isotropic thermal parameters. Hydrogens were located in calculated idealized positions (C–H = 1.08 Å), but not varied. The final conventional R value for the 4352 observed reflections with $I \geqslant 2.5\sigma(I)$ was 0.039 (R_w = 0.041).

The calculations were carried out on the CYBER 76 computer of the C.I.N.E.C.A., with the SHELX-76 system of crystallographic programs [8].

TABLE I. Atomic Coordinates ($\times 10^4$) and Temperature Factors[a] ($\times 10^4$) with e.s.d.s in Parentheses.

	X/*a*	Y/*b*	Z/*c*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt	0	0	0	255(1)	398(2)	237(1)	169(1)	81(1)	69(1)
P	2019(1)	320(1)	2069(1)	279(5)	353(5)	259(5)	156(4)	68(4(	62(4)
Cl	1439(1)	624(2)	−1060(2)	368(6)	947(10)	426(7)	391(7)	133(5)	28(6)
C(1)	3684(5)	1316(5)	2229(6)	374(10)					
C(2)	5126(7)	1129(7)	3197(7)	506(13)					
C(3)	6367(8)	1827(8)	2990(8)	595(15)					
C(4)	6339(10)	3415(9)	3344(10)	725(20)					
C(5)	4893(9)	3589(8)	2423(9)	667(18)					
C(6)	3638(7)	2923(6)	2643(7)	492(12)					
C(7)	1673(5)	1107(5)	3789(6)	368(9)					
C(8)	2933(7)	1298(6)	5193(7)	481(12)					
C(9)	2411(7)	1670(7)	6473(8)	564(14)					
C(10)	1750(8)	3037(8)	6706(8)	580(15)					
C(11)	524(8)	2902(8)	5302(8)	617(16)					
C(12)	1042(7)	2494(7)	4016(7)	506(13)					
C(13)	2537(5)	−1429(5)	1982(5)	357(9)					
C(14)	2801(6)	−2230(6)	549(6)	458(12)					
C(15)	3295(7)	−3652(7)	486(7)	524(13)					
C(16)	2204(7)	−4586(7)	620(8)	551(14)					
C(17)	1953(7)	−3798(7)	2059(7)	519(13)					
C(18)	1425(7)	−2389(6)	2108(7)	467(12)					

[a] Anisotropic temperature factors are in the form $\exp\{-2\pi^2(\Sigma_{ij}h_ih_ja_i^*a_j^*U_{ij})\}$; isotropic temperature factors are listed as U_{11}.

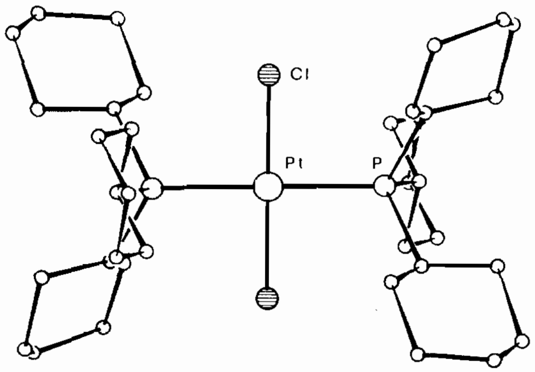

Fig. 1. The molecular structure of *trans*-$Pt[P(C_6H_{11})_3]_2Cl_2$.

Results and Discussion

The stereochemical arrangement of the complex is shown in Fig. 1. The final positional and thermal parameters of atoms are listed in Table I. In Table II bond lengths and valence angles, uncorrected for changes due to thermal vibrations are given. Shorter intramolecular non-bonded chlorine–carbon distances are in Table III.

The structure described by the cell constants, the symmetry operation of the space group and the atomic parameters consists of the packing of discrete neutral molecules of *trans*-$PtCl_2[P(C_6H_{11})_3]_2$ separated by van der Waals contacts. None of these distances are shorter than the sum of relevant van der Waals radii.

The complex was confirmed to have a *trans*-square-planar geometry about platinum. Platinum, chlorine and phosphorus atoms lie strictly on the same plane owing to crystallographic symmetry requirements. Therefore the only departure from the exact square-planar configuration is represented by the different values of the two Cl–Pt–P angles (88.8(1) and 91.2(1)°). The phosphine substituents are staggered about the P–Pt–P axis. The cyclohexane rings are all in the 'chair' conformation. Bond lengths and valence angles within the rings have values very similar to those found for this kind of aliphatic rings [9]. As was expected from the cell constants and the space group, the complex is isostructural with *trans*-$Pt[P(C_6H_{11})_3]_2I_2$ [5] and with *trans*-$NiCl_2\{P(C_6H_{11})_3\}_2$ [10]. However the structural determination of the latter compound, in two dimensions, is not sufficiently accurate for comparison to be made. Some comparative data between the title compound and the iodine analogue are given in Table IV.

The Pt–P bond length of 2.371(2) Å in *trans*-$Pt[P(C_6H_{11})_3]_2I_2$ is 0.034 Å longer than that reported here. It is significant that even in *trans*-$Pt[P(C_6H_{11})_3]_2I_2$ the bond length does not reach 2.41 Å, the sum of the single bond covalent radii of Pt and P [11]; this shortening has been used as evidence of Pt–P double bond, *i.e.*, d_π–d_π bonding from the nonbonding *d* orbitals on platinum to the empty

TABLE II. Distances (A) and Angles (°), with e.s.d.s in Parentheses. The e.s.d.s for C–C bonds and C–C–C angles are ~0.005 A and 0.3° respectively.

Distances					
Pt–Cl	2.317(2)	C(1)–C(2)	1.533	C(7)–C(8)	1.536
Pt–P	2.337(2)	C(2)–C(3)	1.538	C(8)–C(9)	1.537
P–C(1)	1.855(4)	C(3)–C(4)	1.527	C(9)–C(10)	1.533
P–C(7)	1.849(4)	C(4)–C(5)	1.511	C(10)–C(11)	1.536
P–C(13)	1.856(4)	C(5)–C(6)	1.542	C(11)–C(12)	1.537
Mean P–C	1.853	C(6)–C(1)	1.539	C(12)–C(7)	1.537
		Mean	1.532	Mean	1.536
C(13)–C(14)	1.543				
C(14)–C(15)	1.537				
C(15)–C(16)	1.514				
C(16)–C(17)	1.541				
C(17)–C(18)	1.539				
C(18)–C(13)	1.542				
Mean	1.536				
Overall Mean	1.535				
Angles					
Cl–Pt–P	88.8(1)	P–C(1)–C(6)	112.4(3)		
Pt–P–C(1)	114.0(2)	P–C(7)–C(8)	115.6(3)		
Pt–P–C(7)	112.5(2)	P–C(7)–C(12)	114.2(3)		
Pt–P–C(13)	111.2(2)	P–C(13)–C(14)	109.5(3)		
P–C(1)–C(2)	117.2(3)	P–C(13)–C(18)	113.5(3)		
C(1)–P–C(7)	111.4(2)				
C(1)–P–C(13)	102.5(2)				
C(7)–P–C(13)	104.3(2)				
C(6)–C(1)–C(2)	110.2	C(12)–C(7)–C(8)	110.6		
C(1)–C(2)–C(3)	109.4	C(7)–C(8)–C(9)	109.9		
C(2)–C(3)–C(4)	111.8	C(8)–C(9)–C(10)	110.2		
C(3)–C(4)–C(5)	110.0	C(9)–C(10)–C(11)	112.1		
C(4)–C(5)–C(6)	111.9	C(10)–C(11)–C(12)	110.9		
C(5)–C(6)–C(1)	108.6	C(11)–C(12)–C(7)	110.1		
Mean	110.3	Mean	110.6		
C(18)–C(13)–C(14)	110.4				
C(13)–C(14)–C(15)	110.3				
C(14)–C(15)–C(16)	110.9				
C(15)–C(16)–C(17)	111.0				
C(16)–C(17)–C(18)	109.7				
C(17)–C(18)–C(13)	110.0				
Mean	110.4				
Overall Mean	110.4				

TABLE III. Shorter Intramolecular Non-bonded Chlorine–Carbon Distances (A). Primed atoms are related to unprimed ones by the centre of symmetry at the origin.

Cl....C(1)	3.245(4)
Cl....C(6)	3.556(4)
Cl....C(18)	3.525(4)
Cl....C(9)	3.586(4)
Cl....C(7′)	3.307(4)

phosphorus *d* orbitals [11]. The present results lend weight to this hypothesis. In addition the Pt–P bond length found here is 0.035 Å longer than the weighted average 2.302(1) Å for Pt(II)–P bond lengths in 22 complexes containing mutually *trans* tertiary phosphines of the type PR_nPh_{3-n} (R = alkyl, n = 0–3) [12].

The Pt–Cl distance of 2.317(2) Å in the present complex is slightly greater than that predicted from available covalent radii (2.30 Å), but falls within the

TABLE IV. Comparison of Geometry of *trans*-Pt[P(C_6H_{11})$_3$]$_2$Cl$_2$ and *trans*-Pt[P(C_6H_{11})$_3$]$_2$I$_2$.

	trans-Pt[P(C_6H_{11})$_3$]$_2$Cl$_2$	*trans*-Pt[P(C_6H_{11})$_3$]$_2$I$_2$
Pt–P	2.337(2) Å	2.371(2) Å
Pt–P–X	91.2(1)°	90.63(5)°
Pt–P–C(1)	114.0(2)°	113.80(27)°
Pt–P–C(7)	112.5(2)°	111.03(27)°
Pt–P–C(13)	111.2(2)°	115.48(28)°
Mean Pt–P–C	112.6	113.43

TABLE V. Pt–P Distances (Å) in Complexes of the Type *trans*-PtX$_2$L$_2$, X = Cl, Br, I; L = tertiary phosphine.

Compound	Pt–P (Å)	Reference
trans-PtCl$_2$[P(C_6H_{11})$_3$]$_2$	2.337(2)	Present Work
trans-PtBr$_2$(PEt$_3$)$_2$	2.314(8)	11
trans-PtI$_2$(PMe$_3$)$_2$	2.315(4)	15
trans-PtI$_2$[P(C_6H_{11})$_3$]$_2$	2.371(2)	5

range of Pt–Cl distances (*trans* to Cl) for structures having approximately linear arrangements Cl–Pt–Cl with terminal chlorine ligands and with differing *cis* groups [13]. A close inspection of these values indicates, in addition, that any influence of *cis* ligands on Pt–Cl bond lengths is smaller than the uncertainties in the X-ray determinations [13].

We tried to detect differences in the *cis*-influence of the halide ligands on the basis of the changes in the lengths of *cis* Pt–P bonds in complexes of the type *trans*-PtX$_2$L$_2$ where X = Cl, Br, I and L = tertiary phosphine. The available numbers, listed in Table V, suggest that it is very difficult to predict differences in the *cis*-influence of the halide ligands on the basis of measurements of the Pt–P bond lengths only. It is now recognized [14] that in severely overcrowded platinum(II) complexes the steric repulsion between ligands can lead the considerable lengthening of Pt–P bonds. Thus, in *trans*-PtI$_2$[P(C_6H_{11})$_3$]$_2$ the Pt–P bonds are 0.057 Å longer than in *trans*-PtBr$_2$(PEt$_3$)$_2$, 0.056 Å longer than in *trans*-PtI$_2$(PMe$_3$)$_2$, and 0.034 Å longer than in *trans*-Pt[P(C_6H_{11})$_3$]$_2$Cl$_2$. This should be attributed, mainly, to changes in steric demands in the four complexes.

The Pt–P–C(n) (n = 1, 7, 13) angles are all significantly greater than the value for a tetrahedral angle and are close to the values found in the iodine analogous complex, possibly indicating that neither ligand can fold back to relieve the carbon–halogen interactions of intraligand repulsions.

Both in *trans*-Pt[P(C_6H_{11})$_3$]$_2$Cl$_2$ and in *trans*-Pt[P(C_6H_{11})$_3$]$_2$I$_2$ there are short intramolecular nonbonded distances between carbon and halogen. In the former the P–Pt–X angle is increased by 1.2(1)° reflecting the inequivalence of the nonbonding steric interactions between the tertiary phosphine and chlorine. In the iodine analogue, the extra opening is only 0.063(5)°, and a model shows that the interactions are spread over both phosphine ligands; it is suggested, therefore, that the P–Pt–I angle more closely approaches 90° because the two sets of interactions are more nearly balanced [5].

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