

The Molecular Structure of Dinuclear Complexes of Platinum(II). I. *trans*-Dichlorobistripropylphosphine- $\mu\mu'$ -dichlorodiplatinum

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Crystals of *trans*-dichlorobistripropylphosphine- $\mu\mu'$ -dichlorodiplatinum are triclinic: $a = 10.91 \pm 0.02$, $b = 8.54 \pm 0.01$, $c = 7.75 \pm 0.02$ Å, $\alpha = 93.8 \pm 0.2^\circ$, $\beta = 80.8 \pm 0.2^\circ$, $\gamma = 97.4 \pm 0.2^\circ$. The space group is $P\bar{1}$ and the unit cell contains one centrosymmetric molecule. 1804 independent values of $|F(hkl)|$ were obtained from intensity measurements estimated visually from Weissenberg equi-inclination photographs. The structure was refined by a least-squares method, and a final R value of 0.10 was obtained. The central bridge in the molecule is planar, and the bond lengths indicate a strong Pt-P bond [2.230(9) Å] with a weak *trans* Pt-Cl bond [2.425(8) Å]. The two Pt-Cl distances *cis* to the phosphine are approximately normal, that in the bridge being 2.315(8) and that to the terminal chlorine 2.279(9) Å. The two weak Pt-Cl bonds in the bridge preclude the possibility of the transmission of strong bonding effects across the bridge. The α -carbon atoms attached to phosphorus are symmetrically arranged about the coordination plane, a conformation apparently dictated by steric repulsion.

Although $\mu\mu'$ -dichloro-bridged complexes have been known and studied for many years, little detailed structural information is available for them. They usually have a *trans*-configuration, which can be explained most easily as the result of simple electrostatic effects. It is however possible that there is some property of $\mu\mu'$ bridges, other than the simple electrostatic repulsion of charged ligands, that governs the stereochemistry of dinuclear complexes, since stable *cis* complexes are known (Chatt & Hart, 1953, 1960, 1961) in a few cases, where, for example, the bridging groups contain sulphur atoms. We are therefore studying a series of dinuclear complexes of platinum(II), and in this paper we describe the structure of *trans*-[Pt₂Cl₄(PPR₃)₂].

Molecular structure and discussion

The structure is illustrated in Fig. 1, and the bond lengths and angles are shown in Table 1 and Fig. 2. The molecule has the expected *trans*-planar configuration, and has the approximate symmetry $2/m$ (C_2^h), the coordination plane being approximately a plane of symmetry.

Table 1. Bond lengths (Å) and angles ($^\circ$)
with estimated standard deviations*

Pt-Cl(1)	2.425 (8)
Pt-Cl(1')	2.315 (8)
Pt-Cl(2)	2.279 (9)
Pt-P	2.230 (9)
P-C(1)	1.81 (3)
P-C(4)	1.82 (3)
P-C(7)	1.78 (3)
C(1)-C(2)	1.47 (7)
C(2)-C(3)	1.43 (8)
C(4)-C(5)	1.47 (5)

Table 1. (cont.)

C(5)-C(6)	1.61 (6)
C(7)-C(8)	1.55 (5)
C(8)-C(9)	1.51 (7)
Pt(1)-Cl(1)-Pt(1')	96.4 (3)
Cl(1)-Pt(1)-Cl(1')	83.6 (2)
Cl(1)-Pt(1)-Cl(2)	91.5 (3)
Cl(1)-Pt(1)-P(1)	173.4 (3)
Cl(1')-Pt(1)-P(1)	96.5 (3)
Cl(2)-Pt(1)-P(1)	88.4 (4)
Pt(1)-P(1)-C(1)	109.6 (13)
Pt(1)-P(1)-C(4)	113.2 (12)
Pt(1)-P(1)-C(7)	113.2 (11)
C(1)-P-C(4)	105.7 (17)
C(7)-P-C(4)	107.4 (15)
C(7)-P-C(1)	107.3 (17)
P(1)-C(1)-C(2)	115 (3)
P(1)-C(4)-C(5)	113 (3)
P(1)-C(7)-C(8)	120 (3)
C(1)-C(2)-C(3)	115 (6)
C(4)-C(5)-C(6)	112 (4)
C(7)-C(8)-C(9)	112 (4)

* The figures in parenthesis represent the e.s.d. of the last significant digit.

If the normal atomic radii are taken to be Pt^{II}, 1.32; P, 1.10; and Cl, 0.99 Å, the Pt-P bond [2.23(1) Å] is seen to be much shorter than the sum of atomic radii. The Pt-Cl bond *trans* to it [2.43(1) Å] is much longer than the radius sum, 2.31 Å, and longer than in 'normal' Pt-Cl bonds [*cf.* 2.33(1) and 2.32(1) Å in *cis* and *trans*-[PtCl₂(NH₃)₂] (Milburn & Truter, 1966), and 2.308(1) Å in K₂PtCl₄ (Mais, Owston & Wood, 1969)]. Similar bond lengths are found in *cis*-[PtCl₂(PMe₃)₂] (Messmer, Amma & Ibers, 1967) where Pt-P = 2.25(1) Å and Pt-Cl = 2.37(1) Å.

The unusual shortness of the Pt-P bond could be attributed to strong π -bonding. The π -bonding theory of the *trans*-effect (Chatt, Duncanson & Venanzi,

1955) then predicts that, if Pt-Cl normally has any double-bond character, this character will be reduced, and the Pt-Cl bond *trans* to phosphorus will be correspondingly longer than usual. If the Pt-Cl bond normally has double-bond character, the Pt-Cl bond lengths in *trans* [PtCl₂(NH₃)₂], in which the Cl atoms are *trans* to each other, should be longer than in the *cis*-isomer, where Cl is *trans* to N which cannot π -bond to platinum. The bonds in these two complexes are equal however, indicating that the Pt-Cl bond has little or no π -character. Some other explanation is

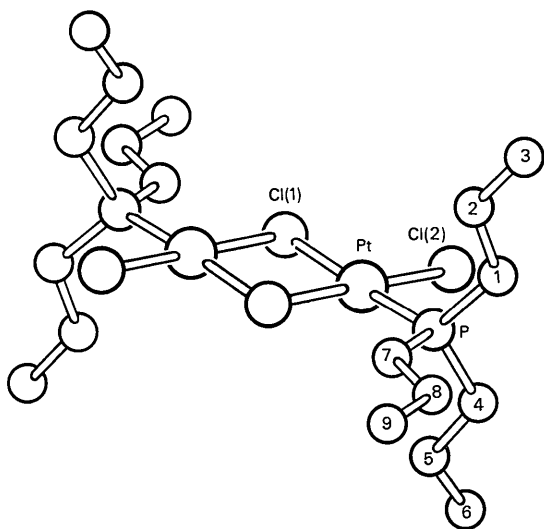


Fig. 1. The molecular structure of *trans*-[Pt₂Cl₄(PPR₃)₂].

therefore needed for the unusual length of Pt-Cl bonds *trans* to phosphines.

Venanzi (1968) has recently discussed evidence indicating that it is unnecessary to invoke π -bonding and that variations in the σ -character of the bonds, involving a rehybridization of the metal atom, provide a better explanation. If this is so, the effective σ -bonding radius of Pt^{II} will vary, according to the ligands present; our results suggest that the radius would then lie between 1.4 Å *trans* to phosphines and similar ligands, and 1.15 Å *cis* towards these ligands, with the 'normal' value of 1.3 Å when ligands of this type are absent. There is at present insufficient accurate structural information to show whether bond lengths in platinum complexes vary consistently in this way.

The coordination round the phosphorus atom is approximately tetrahedral, the Pt-P-C angles being slightly larger than 109½°, and the C-P-C angles slightly smaller, as is usual in metal-phosphine complexes. The P-C(7) bond lies in the platinum coordination plane with P-C(1) and P-C(4) symmetrically above and below the plane. This orientation involves considerable steric strain since the Cl-Pt-P angle is enlarged to 96.5° and the Cl(1')-C(7) contact distance is short (3.26 Å, see Fig. 2); it is evidently adopted because it minimizes steric interaction between Cl(1') and the hydrogen atoms on C(7). Since both C(7) and C(8) lie in the coordination plane, the two hydrogen atoms on C(7) must lie symmetrically above and below it (see Fig. 3), and are close to Cl(1'). Any displacement away from this position (*e.g.* by rotation about the Pt-P bond or about the P-C(7) bond) will bring one of the hydrogen atoms even closer to Cl(1') and decrease the stability

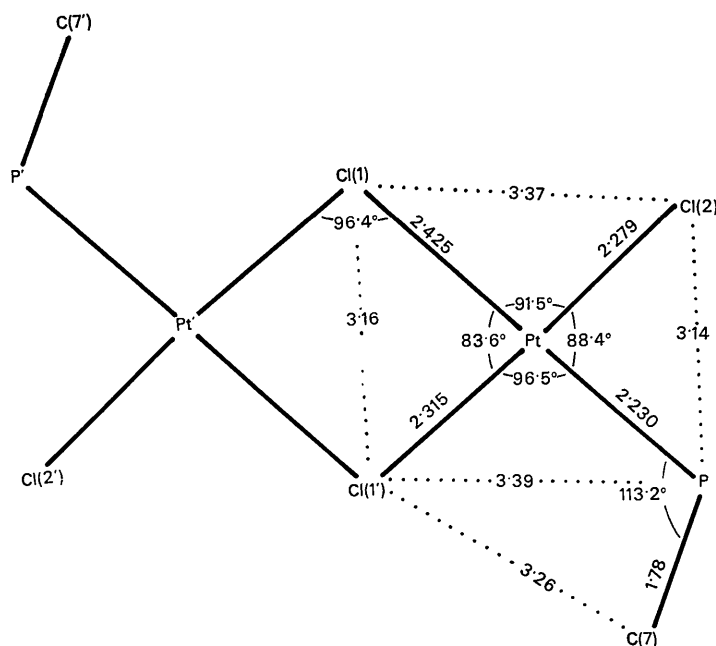


Fig. 2. Bond lengths (Å) and angles in the *trans*-[Pt₂Cl₄(PPR₃)₂] molecule.

of the complex. [The approximate H...Cl distances, assuming C-H = 1.0 Å and P-C-H = 109½°, are 3.25 Å in this structure, and would be reduced to 3.1 Å by rotating 30° about the P-C(7) bond (Fig. 3)].

There is a similar conformation, and a similar balance of steric forces, in [Ni(PEt₃)₂(C≡CPh)₂] (Davies, Mais & Owston, 1967; Amma, Carfagna & Spofford, 1967, 1968), where there is also an unusually short metal-phosphorus bond, and both carbon atoms of one ethyl group in each phosphine ligand lie in the coordination plane.

In the dichloro-bridge the bond lengths are similar to those in related mononuclear complexes, and the molecule apparently consists of two relatively strongly bound units of composition {PtCl₂(PPr₃)}, bound only by two weak Pt-Cl bonds. There is no pathway for the transmission of strong directing effects across the bridge.

The other two Pt-Cl bonds, which are *trans* to each other, have lengths within the normal range. The rather short terminal Pt-Cl(2) bond may indicate that the phosphine group has a *cis*-strengthening effect, but the ease with which changes of 0.02-0.03 Å are produced in Pt-Cl bonds by electrostatic forces (Black, Mais & Owston, 1969) makes this interpretation rather uncertain.

Experimental

Crystal data

Orange-yellow needles, (C₉H₂₁PPtCl₂)₂, *M* = 852.8; triclinic *a* = 10.91 ± 0.02, *b* = 8.54 ± 0.01, *c* = 7.75 ± 0.02 Å, α = 93.8 ± 0.2°, β = 80.8 ± 0.2°, γ = 97.4 ± 0.2°.

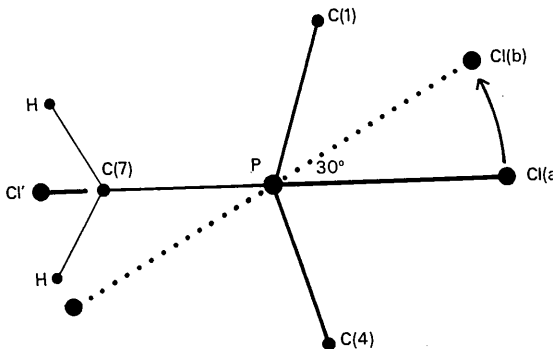


Fig. 3. The coordination around the phosphorus atom. The symmetrical positions of the C(7) hydrogen atoms above and below the coordination plane are shown. The effect of rotating the coordination plane about the P-Pt bond [for example by 30°, as shown, from position (a) to position (b)] is to decrease the hydrogen-chlorine separation and thus increase the steric strain.

Table 2(a). Atomic positional parameters and their standard deviations

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Pt(1)	0.15023 (10)	-0.02320 (13)	0.04476 (14)
Cl(1)	0.0549 (8)	0.0893 (12)	-0.1728 (11)
Cl(2)	0.3453 (8)	0.0423 (12)	-0.1054 (14)
P(1)	0.2386 (9)	-0.1199 (9)	0.2486 (11)
C(1)	0.328 (4)	-0.277 (4)	0.152 (5)
C(2)	0.252 (7)	-0.418 (7)	0.089 (9)
C(3)	0.320 (10)	-0.521 (8)	-0.033 (10)
C(4)	0.349 (3)	0.025 (4)	0.343 (5)
C(5)	0.297 (4)	0.174 (4)	0.402 (5)
C(6)	0.402 (8)	0.307 (6)	0.465 (6)
C(7)	0.128 (3)	-0.200 (4)	0.424 (4)
C(8)	0.173 (6)	-0.285 (6)	0.569 (6)
C(9)	0.065 (4)	-0.370 (6)	0.688 (7)

Table 2 (b). Mean square atomic vibrations and standard deviations (Å²)

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	2 <i>U</i> ₁₂	2 <i>U</i> ₁₃	2 <i>U</i> ₂₃
Pt(1)	0.0315 (6)	0.0544 (5)	0.0422 (5)	0.0128 (9)	-0.0009 (10)	-0.0027 (8)
Cl(1)	0.032 (4)	0.101 (6)	0.053 (4)	-0.006 (8)	-0.009 (8)	0.059 (8)
Cl(2)	0.030 (4)	0.091 (6)	0.087 (6)	0.035 (8)	-0.018 (10)	0.020 (10)
P(1)	0.058 (6)	0.046 (4)	0.055 (4)	0.023 (7)	-0.029 (9)	-0.012 (6)
C(1)	0.06 (2)	0.06 (2)	0.09 (2)	0.05 (3)	-0.05 (4)	-0.02 (3)
C(2)	0.11 (5)	0.13 (4)	0.16 (5)	0.13 (8)	-0.12 (9)	-0.13 (8)
C(3)	0.35 (13)	0.11 (5)	0.15 (6)	0.17 (13)	-0.19 (2)	0.13 (3)
C(4)	0.06 (2)	0.05 (2)	0.07 (2)	0.01 (3)	-0.03 (4)	-0.03 (3)
C(5)	0.07 (3)	0.05 (2)	0.09 (3)	-0.01 (3)	-0.09 (5)	-0.03 (3)
C(6)	0.25 (8)	0.09 (3)	0.08 (3)	-0.03 (3)	-0.10 (8)	-0.06 (5)
C(7)	0.03 (2)	0.07 (2)	0.06 (2)	0.01 (3)	-0.05 (3)	0.01 (3)
C(8)	0.15 (5)	0.10 (3)	0.08 (3)	0.05 (6)	-0.18 (7)	0.01 (4)
C(9)	0.06 (3)	0.12 (4)	0.11 (4)	0.01 (5)	-0.01 (5)	0.11 (6)

Table 3(a). Observed and calculated structure factors

Table with columns for L fo fc, L fo fc, L fo fc, L fo fc, L fo fc, L fo fc, L fo fc, and L fo fc. Each column contains a list of values for different hkl indices (e.g., hmo kmo, hmo km3, hmo km4, hmo km5, hmo km6, hmo km7, hmo km8, hmo km10). The values include both observed and calculated structure factors, often separated by a plus sign (+).

$V=691 \text{ \AA}^3$; D_m (by flotation) $=1.96 \pm 0.10 \text{ g.cm}^{-3}$, $Z=1$, $D_c=2.050 \text{ g.cm}^{-3}$; $F(000)=404$; space group $P\bar{1}$ or $P\bar{1}$, the structure refining satisfactorily in $P\bar{1}$; Cu $K\alpha$ radiation, single-crystal Weissenberg photographs; $\mu=120 \text{ cm}^{-1}$. The crystals were soft and imperfect, which accounts for the low density measurement.

Data were collected from two crystals, each approximately $0.1 \times 0.05 \times 0.05 \text{ mm}$, mounted on glass fibres using shellac adhesive. 1804 independent values of $|F(hkl)|$ were obtained from intensity measurements estimated visually from Weissenberg equi-inclination photographs of the layers $0kl-5kl$, $7kl$, and $h0l-h2l$, by the multiple film technique, and were correlated by the method of Rollett & Sparks (1960). There were 460 reflexions too weak to be observed. The crystal was damaged before the layer $6kl$ could be checked and all $6kl$ reflexions have therefore been omitted. Corrections were made for the Lorentz and polarization factors, but not for absorption or extinction.

Structure determination

Assuming the centrosymmetric space group $P\bar{1}$, the positions of the platinum, phosphorus and chlorine atoms were found from a three-dimensional Patterson synthesis, and a trial structure containing only these atoms gave an R value of 0.17. A difference synthesis showed the positions of all the carbon atoms. After six cycles of least-squares refinement of positional and isotropic thermal parameters, the positional and anisotropic thermal parameters were refined for a further 12 cycles, which reduced the R value to 0.10. The independent positional parameters were refined in a single matrix-block and the thermal parameters were

refined using the block-diagonal approximation with a six-by-six block for each atom. The refinement was carried out using weights

$$w=1/[1+(f_o-b)^2/a^2],$$

with $a=30$, $b=30$. The constant term in Cromer & Waber's (1965) exponential form factors for Pt was corrected for the real part of anomalous dispersion. The standard deviations of bond lengths and angles were calculated by the method of Busing, Martin & Levy (1964). None of the calculated intensities for the 460 unobserved reflexions was more than twice the minimum observable intensity.

The final atomic parameters are listed in Table 2, and observed and calculated structure factors in Table 3(a), with an analysis of their agreement in Table 3(b).

All calculations were carried out on the English Electric KDF9 computer at I.C.I. Wilton Works, using programs written by R. H. B. Mais. We are indebted to Dr S. O'Brien for preparing the crystals.

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Table 3(b). Agreement analysis of observed and calculated structure factors

Range (F_{obs})	Number	$\Sigma F_{\text{obs}} $	$\Sigma F_{\text{calc}} $	$\Sigma \Delta F $	Average $w \Delta F ^2$	R
0-6	2	11	13	2	0.12	0.210
6-12	42	417	454	90	0.38	0.217
12-17	202	3037	3204	532	0.36	0.175
17-23	289	5836	5835	816	0.36	0.140
23-29	239	6189	6067	696	0.50	0.113
29-35	180	5693	5537	507	0.25	0.089
35-41	153	5741	5572	454	0.24	0.079
41-46	120	5192	5024	443	0.33	0.085
46-52	112	5516	5421	495	0.51	0.090
52-58	96	5308	5111	443	0.35	0.083
58-70	139	8802	8687	769	0.49	0.087
70-81	88	6635	6640	556	0.59	0.084
81-104	82	7520	7678	738	0.66	0.098
104-174	60	7612	7753	774	0.64	0.102
Sin θ/λ						
0.00-0.10	8	644	818	174	2.64	0.271
0.10-0.20	77	6050	6286	653	0.83	0.108
0.20-0.30	220	15106	14895	1494	0.52	0.099
0.30-0.40	357	18067	17896	1551	0.47	0.086
0.40-0.50	486	18606	17804	1675	0.34	0.090
0.50-0.60	490	12316	12228	1297	0.27	0.105
0.60-0.70	166	2722	3071	472	0.41	0.173

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The Crystal Structure of Iodinin

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A crystal-structure analysis of iodinin, $C_{12}H_8N_2O_4$, has been carried out at -160°C and at room temperature. The crystals are monoclinic, space group $P2_1/a$, with (at -160°C) $a=15.634$, $b=5.028$, $c=6.037$ Å, $\beta=91.00^\circ$, $Z=2$. The structure was determined entirely by symbolic-addition methods and refined by block-diagonal least-squares to a final R index of 0.060. The structure consists of endless ribbons of nearly coplanar molecules, extended in the directions $\langle 011 \rangle$. Adjacent molecules in a ribbon are linked by the intermolecular branches of bifurcated hydrogen bonds. The binding force is sufficient to cause a non-bonded oxygen-oxygen contact of 2.591 Å.

Introduction

The X-ray crystal structure analysis of myxin (I) has revealed an unexpectedly short intermolecular distance, a phenomenon tentatively attributed to the formation of bifurcated hydrogen bonds (Hanson, 1968). The intermolecular branches of these bonds join adjacent molecules together as weak dimers (II) in which the innermost oxygen atoms, although not bonded to each other, are constrained to lie only 2.577 Å apart. (The dimerization must be described as 'weak' in recognition of the fact that it occurs for only one of the two independent pairs of molecules in the structure; for the other pair the reduction in energy offered by dimerization is presumably less than that realized by more efficient packing.)

It was considered that the crystal structure of iodinin (III) might present a further example of intermolecular attraction by bifurcated hydrogen bonds. However, iodinin has the opportunity to form such bonds on both sides, and thus polymerization, rather than dimerization, is to be expected. The expectation is strengthened by the high density and sparing solubility of the material. The crystal structure analysis was undertaken in order to investigate this point and to provide data for the further study of the bifurcated hydrogen bond.

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