The Crystal Structure of Dipentene Platinum(II) Chloride

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The crystal structure of dipentene platinum (II) chloride was determined by single-crystal methods. The orthorhombic unit cell, $a = 10.188$, $b = 7.992$, $c = 14.401$ Å, space group $P2_1cn$, contains four monomeric molecules. The coordination about Pt is planar square with the two Cl atoms occupying *cis* positions. The two double bonds of the olefin occupy the remaining two coordination positions. The two planes defined by the two double bonds and their attached atoms are oriented perpendicularly to the Pt–Cl plane and to the Pt dsp^2 orbitals. The axis of one of the double bonds is perpendicular to the Pt–Cl plane, but the other one is tilted to make a 62° angle with the plane.

Introduction

The crystal structure of dipentene platinum (II) chloride was determined as a part of a general study dealing with metal–olefin compounds. The principal goal of the investigation was to define the general configuration of a diolefin relative to the metal atom. Since light atoms (carbon) cannot be easily located accurately in the presence of an extremely heavy atom, a precise structure of the dipentene molecule was not expected. A summary of previous work has been provided by Baenziger, Doyle, Richards & Carpenter (1961).

Experimental procedure and crystal data

The crystals were prepared by the method of Chatt & Wilkins (1952) in which dipentene (DL-limonene) is added to ethylene platinum(II) chloride in alcohol solution to form the β isomer. Recrystallization is difficult, but once obtained, the crystals are stable in air and in the X-ray beam.

Crystal data: Dipentene platinum(II) chloride, $PtCl_2C_{10}H_{16}$, orthorhombic, $a = 10.188 \pm 0.005$, $b = 7.992 \pm 0.002$, $c = 14.401 \pm 0.009$ Å; unit-cell volume = 1173 Å³; formula weight = 402.24; $D_m = 2.21$ g.cm⁻³ (pycnometric method); $Z = 4$; $D_x = 2.28$ g.cm⁻³; absorption coefficient for X-rays, $\mu = 267$ cm⁻¹ for Cu $K\alpha$ ($\lambda = 1.5418$ Å), $\mu = 130$ cm⁻¹ for Mo $K\alpha$ ($\lambda = 0.7107$ Å); systematic absences: $hk0$, $h+k = 2n+1$; $h0l$, $l = 2n+1$; space group, $P2_1cn$ (standard setting, $Pna2_1$). From the systematic absences alone, the space group could also be $Pmcn$, but then each molecule must lie on a mirror plane. Since this compound is a racemic mixture of optical isomers, such a requirement cannot be met. The most probable space group has only a fourfold general set, which means that the asymmetric unit is one molecule.

The a cell dimension was determined from an $hk0$ precession photograph, the others from a $0kl$ back-

reflection Weissenberg photograph. A least-squares extrapolation method was used to determine b and c.

Three-dimensional data were taken at room temperature from an approximately cylindrical crystal, 0.103 mm in maximum cross-section (equivalent cylinder for absorption correction = 0.094 mm diameter). Layers $0kl$–$8kl$ were taken by an equi-inclination Weissenberg camera with Ni-filtered Cu $K\alpha$ radiation and multiple-film technique. The upper layer intensities were corrected for the oblique angle of incidence of the X-ray beam (Bullen, 1953). Layers $h0l$–$h4l$ were obtained on a precession camera with Zr-filtered Mo $K\alpha$ radiation and timed exposures. All intensities were estimated visually with a standard scale. Lorentz, polarization and absorption corrections were applied with programs written for the Royal McBee LGP-30 computer.

The data were brought to a common scale by equating sums of $|F_o|^2$ for common reciprocal lattice rows. Absolute scaling was done later by comparison with the calculated structure amplitudes. Just over ninety-six per cent of the independent reflections within the Cu sphere were obtained (1311 of 1356, 932 of these were observable).

The atomic scattering factors used for Pt, Cl, and C are the exponential approximations of Forsyth & Wells (1959). The real part of the anomalous dispersion correction was applied to the Pt atom (Dauben & Templeton, 1955). The least-squares program written

Table 1. *Progress of the refinement*

Least-squares cycle	R	$\sqrt{[\Sigma w(\Delta F)^2/(m-n)]}$	Reflections
1	0.129	7.72	present only
10	0.109	6.68	present only
11	0.102	5.88	present only
15	0.095	5.32	present only
18a	0.093	5.20	present only
18b	0.098	4.36	all
19	0.092	5.16	present only
A	0.096	4.07	present only
B	0.071	3.27	present only

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Table 2. *Observed and calculated structure factors*

Values are 2·5 times absolute scale

h	k	l	Fo	Fc

The table consists of seven side-by-side blocks, each with column headings h, k, l, Fo, |Fc|, listing observed and calculated structure factor values.

for this analysis uses an individual isotropic temperature factor for each atom and the diagonal approximation to the least-squares matrix.

Structure determination

The x parameter of platinum was fixed at 0·25, and a (100) Patterson projection disclosed y and z. A (100)

electron density difference map gave y and z coordinates for the chlorine atoms; their x parameters were estimated by use of the sums of single-bond covalent radii of Pauling (1960). Attempts to locate carbon atoms in projection were unsuccessful.

Structure factors were calculated for the above mentioned three atoms, and a three-dimensional electron density difference map was calculated from which six carbon atoms were located. The remaining four atoms were located by alternate application of the electron density difference map technique and least-squares refinement.

Refinement and results

All present reflections were used in the final least-squares refinement. Reflections duplicated on the
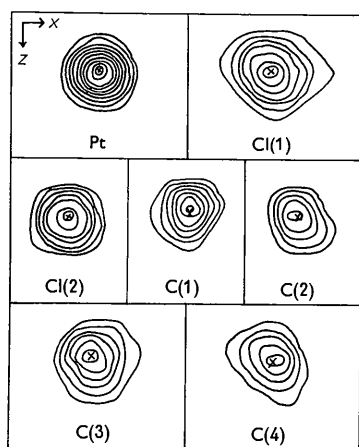
(a)
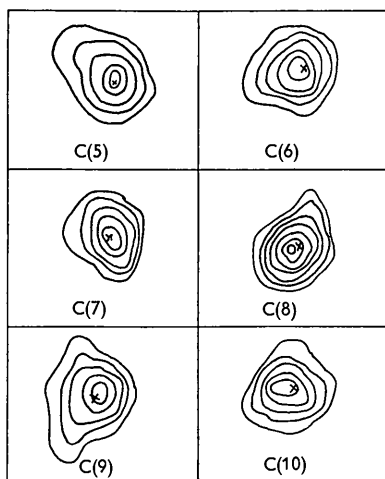
(b)

Fig. 1. Electron density sections along the b axis through each atom center (the y coordinates are listed in Table 3). The cross indicates the position of the x and z coordinates after the final least-squares cycle. The contour levels are at 14 e.Å^{-3} for Pt, 2 e.Å^{-3} for Cl and 0·7 e.Å^{-3} for C.

Weissenberg and precession sets of data were assigned unit weight, while reflections appearing on only one set were given weight one-half. Absent reflections were included on least-squares cycle 18 only and were given weight one-half if $|F_o| < |F_c|$ and zero weight if $|F_o| > |F_c|$. The R value was also calculated in this manner. To guard against oscillation of the parameter shifts, a shift factor of one-half was always used.

The five lowest-angle reflections (011, 110, 002, 200, and 020) were given weight zero after least-squares cycle 10 because they were considered to be affected by extinction. Their strong influence can be seen by comparing the results of cycles 10 and 11 in Table 1. Significant shifts in some carbon parameters were noted after this change.

The refinement was continued until the calculated parameter shifts were roughly two-tenths of one estimated standard deviation (e.s.d.). Table 2 shows the values of the observed and calculated structure factors after cycle 18 for all present reflections excluding those assumed to be affected by extinction.

A difference synthesis calculated after least-squares cycle 15 showed one spurious peak of height slightly less than that of a carbon atom. A three-dimensional electron density map was calculated as well as electron density sections through the center of each atom (shown in Fig. 1).

Several full-matrix least-squares refinements were carried out with the Busing–Levy program. Refinement A: full matrix, individual isotropic temperature factors, atom positions, scaling factors were varied, and the real part of the dispersion corrections made to the scattering factors. Refinement B: the same as A
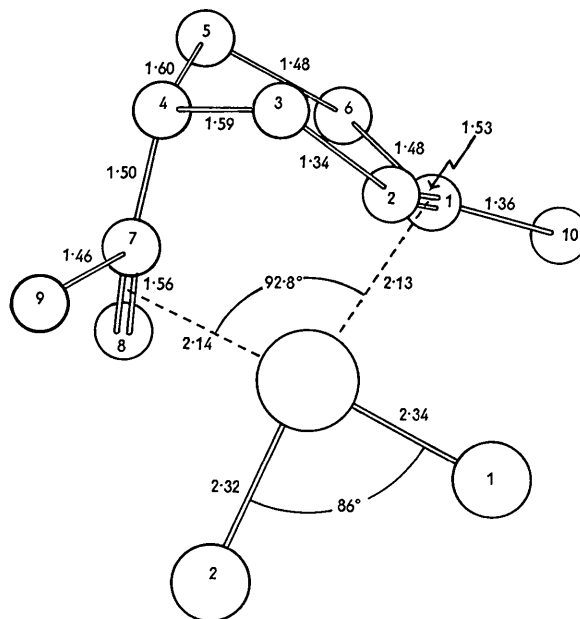
Fig. 2. Projection of one molecule on (100).

Table 3. *Atomic and thermal parameters and their estimated standard deviations*

	x $s(x)$ $s(X)*$	y $s(y)$ $s(Y)$	z $s(z)$ $s(Z)$	B_{11} $s(B_{11})$	B_{22} $s(B_{22})$	B_{33} $s(B_{33})$	B_{12} $s(B_{12})$	B_{13} $s(B_{13})$	B_{23} $s(B_{23})$
Pt	0·25000 — —	0·09693 0·00016 0·0013	0·01738 0·00009 0·0009	3·432 0·195	5·772 0·062	4·003 0·039	1·111 0·091	−0·425 0·119	−0·518 0·045
Cl(1)	0·3360 0·0012 0·012	0·3415 0·0017 0·014	−0·0485 0·0008 0·12	8·46 0·28					
Cl(2)	0·2486 0·0024 0·024	−0·0098 0·0012 0·010	−0·1321 0·0005 0·007	7·46 0·19					
C(1)	0·1864 0·0031 0·032	0·2362 0·0044 0·035	0·1449 0·0021 0·030	3·83 0·60					
C(2)	0·3291 0·0038 0·039	0·1800 0·0049 0·039	0·1559 0·0025 0·036	4·57 0·74					
C(3)	0·3850 0·0031 0·032	0·0536 0·0041 0·033	0·2031 0·0020 0·029	3·51 0·53					
C(4)	0·2837 0·0041 0·042	−0·0970 0·0057 0·046	0·1998 0·0024 0·035	7·76 1·10					
C(5)	0·1532 0·0044 0·045	−0·0387 0·0061 0·049	0·2530 0·0028 0·040	7·63 1·00					
C(6)	0·1217 0·0049 0·050	0·1278 0·0069 0·055	0·2147 0·0033 0·048	7·46 1·21					
C(7)	0·2771 0·0036 0·037	−0·1320 0·0042 0·034	0·0973 0·0018 0·026	5·49 0·74					
C(8)	0·1458 0·0033 0·034	−0·1269 0·0048 0·038	0·0414 0·0020 0·029	5·05 0·67					
C(9)	0·3827 0·0041 0·042	−0·2395 0·0059 0·047	0·0631 0·0027 0·039	6·99 0·89					
C(10)	0·1388 0·0044 0·045	0·3910 0·0064 0·051	0·1238 0·0026 0·037	7·68 0·99					

* In Å.

except that anisotropic temperature factors were varied for Pt. A three-dimensional electron density difference map following refinement B showed much reduced spurious detail. No significant changes in bond distances occurred in any of these refinements.

A prediction of the possible precision of the parameter determination was made with the formula given by Cruickshank (1960). When the average values of the thermal parameters for each kind of atom are used, the predicted e.s.d.'s for Pt, Cl and C are 0·0014, 0·017, and 0·054 Å, respectively. These figures compare well with those values calculated by the least-squares refinement which are shown in Table 3. Table 4 shows the bond lengths with e.s.d.'s, and Table 5 shows the bond angles with e.s.d.'s. Fig. 2

Table 4. *Bond lengths with estimated standard deviations*

	Bond length	s (B.l.)
Pt–Cl(1)	2·343 Å	0·013 Å
Pt–Cl(2)	2·316	0·008
Pt–C(1)	2·24	0·03
Pt–C(2)	2·25	0·04
Pt–C(7)	2·18	0·02
Pt–C(8)	2·11	0·04
C(1)–C(2)	1·53	0·05
C(7)–C(8)	1·56	0·05
C(1)–C(6)	1·48	0·06
C(2)–C(3)	1·34	0·05
C(3)–C(4)	1·59	0·06
C(4)–C(5)	1·60	0·06
C(5)–C(6)	1·48	0·07
C(4)–C(7)	1·50	0·04
C(7)–C(9)	1·46	0·06
C(1)–C(10)	1·36	0·06

Table 5. *Bond angles with estimated standard deviations*

	Bond angle	s (B.a.)
Cl(1)–Pt–Cl(2)	86·2°	0·8°
Cl(1)–Pt–(C(1)–C(2))$_c$	90·1	1·1
(C(1)–C(2))$_c$–Pt–(C(7)–C(8))$_c$	92·8	2·1
(C(7)–C(8))$_c$–Pt–Cl(2)	90·8	2·0
C(6)–C(1)–C(2)	100·4	3·4
C(10)–C(1)–C(2)	128·9	4·0
C(1)–C(2)–C(3)	132·5	5·0
C(2)–C(3)–C(4)	106·2	3·2
C(3)–C(4)–C(5)	107·7	3·4
C(4)–C(5)–C(6)	105·3	4·5
C(5)–C(6)–C(1)	133·2	5·0
C(10)–C(1)–C(6)	121·6	3·3
C(3)–C(4)–C(7)	101·5	3·6
C(5)–C(4)–C(7)	119·1	3·8
C(4)–C(7)–C(8)	122·6	2·8
C(4)–C(7)–C(9)	114·0	2·8
C(8)–C(7)–C(9)	118·2	2·9

Subscript c = center.

shows one molecule in projection along (100) with the bond lengths and angles.

The closest intermolecular contacts are between C(3) and Cl(2) of molecules related by the twofold screw axis, 3·84 Å; and between Cl(1) and C(8), 3·57 Å. All others are greater than 4 Å. Fig. 3 shows the relationship between molecules.

Discussion

In similar fashion to that of Hazell & Truter (1960), the following criteria have been used to determine
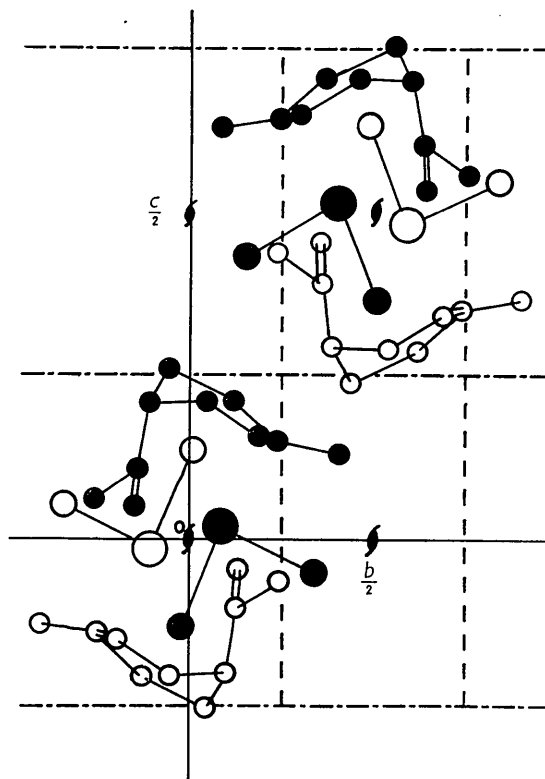

Fig. 3. Projection of unit-cell contents on (100), showing the molecular packing arrangement. The Pt atoms of the black molecules are at $x = \frac{1}{4}$; those of the white molecules are at $x = \frac{3}{4}$.

Table 6. *Interatomic and plane-normal vector summary*

Vector $= u_1\mathbf{i} + u_2\mathbf{j} + u_3\mathbf{k}$; plane: $Xu_1 + Yu_2 + Zu_3 = d$

Unit vector or plane	u_1	u_2	u_3	d
Cl(1) → Pt	−0·3741 Å	−0·8344 Å	+0·4048 Å	
Cl(2) → Pt	0·0060	0·3685	0·9296	
C(1) → C(2)	0·9504	−0·2935	0·1033	
C(7) → C(8)	−0·8566	0·0262	−0·5154	
Pt → (C(1)–C(2))$_c$	0·0374	0·4206	0·9065	
Pt → (C(7)–C(8))$_c$	−0·1968	−0·9060	0·3746	
(Pt, Cl(1), Cl(2)) intersection with				
(C(1), C(2), C(10), C(6), C(3))	−0·3600	−0·7358	0·5661	
(Pt, Cl(1), Cl(2)) intersection with				
(C(4), C(7), C(8), C(9))	0·0107	−0·3295	−0·9438	
(Pt, Cl(1), Cl(2)) plane	−0·9269	0·3510	−0·1331	−2·122
(C(1), C(2), C(10), C(6), C(3)) plane	−0·1801	−0·5401	−0·8206	3·286
(deviations from plane in Å: −0·20, −0·04, +0·08, +0·13, +0·04)				
(C(4), C(7), C(8), C(9)) plane	0·3525	0·8847	−0·3049	−0·515
(deviations from plane in Å: −0·03, 0·15, −0·04, −0·08)				

Inter-vector or inter-planar angles	Angle
(Pt, Cl(1), Cl(2)) and (C(1), C(2), C(10), C(6), C(3))	84·7°
C(1) → C(2) and (Pt, Cl(1), Cl(2))–(C(1), C(2), C(10), C(6), C(3)) intersection	93·9
(C(1), C(2), C(10), C(6), C(3)) and Cl(2) → Pt	164·4
(Pt, Cl(1), Cl(2)) and (C(4), C(7), C(8), C(9))	88·6
C(7) → C(8) and (Pt, Cl(1), Cl(2))–(C(4), C(7), C(8), C(9)) intersection	62·1
(C(4), C(7), C(8), C(9)) and Cl(1) → Pt	186·5
Pt → (C(1)–C(2))$_c$ and Cl(2) → Pt	3·7
Pt → (C(7)–C(8))$_c$ and Cl(1) → Pt	11·1

Subscript c = center.

whether or not the carbon atoms have been correctly located: (1) The thermal parameters refined to finite values; calculated thermal parameter changes were only a fraction of the standard deviation on the least-squares cycle. The thermal parameters have reasonable values for a structure of this type. (When comparing thermal parameters with other work, it must be kept in mind that the neglect of an absorption correction produces a systematic error in the thermal parameters toward lower values.) Owing to vibrational and torsional motion of the molecular unit, the thermal parameters of atoms furthest from the center of mass might be expected to be larger than those near platinum. The observed temperature factors are not inconsistent with this idea. (2) A three-dimensional electron density map evaluated with the final set of phase angles showed only thirteen peaks (in a quarter cell) and no significant spurious detail. (3) The final difference electron density map showed only one spurious peak which was smaller than the smallest carbon peak. (4) The least-squares refinement produced a low R value and a model having reasonable bond distances, considering the magnitude of the standard deviations in the bond distances.

All bond lengths and bond angles except angle $C(5)-C(6)-C(1)$ are not significantly different from the ideal values. Since work on norbornadiene palladium(II) chloride (Baenziger, Doyle, Richards & Carpenter, 1961) has shown that more accurate intensity data tend to make bond lengths more reasonable, no speculation on the existing deviations seems worthwhile.

The unit cell contains two right-handed and two left-handed molecules. The pairs related by the screw axes at $(0, 0)$ and $(\frac{1}{2}, \frac{1}{2})$ in Fig. 3 are of the same kind.

The metal–carbon bonding can be explained following the theory of Dewar (1951). (Fig. 2 and Table 6 will be useful in the interpretation of this description.) The $C(1)-C(2)$ double bond is in the same position relative to the metal atom that has been found in ethylene palladium(II) chloride (Dempsey & Baenziger, 1955), styrene palladium(II) chloride (Holden & Baenziger, 1955), trans-ethylene dimethylamine platinum(II) chloride (Alderman, Owston & Rowe, 1960), and norbornadiene palladium(II) chloride (Baenziger, Doyle & Carpenter, 1961; Baenziger, Doyle, Richards & Carpenter, 1961); that is, occupying one of the coordination positions and lying perpendicular to the plane formed by the metal and the two chlorine atoms. The center of this double bond lies approximately on a line passing through the metal atom and Cl(2), which means that it is directly in line to interact with the dsp^2 bonding orbital of the platinum. This line is also nearly normal to the plane formed by the atoms involved in the trigonal sp^2 bonding of the double bond — the $(C(1), C(2), C(10), C(6), C(3))$ plane. The $C(7)-C(8)$ double bond center

also lies approximately on a line through Cl(1) and the metal atom, and the line is also nearly normal to the sp^2 plane of this double bond (plane $(C(4), C(7), C(8), C(9))$). The double bond itself, however, is not perpendicular to the dsp^2 bonding plane as is the $C(1)-C(2)$ bond, but the double-bond axis makes an angle of 62·1° with the intersection of the planes $(Pt, Cl(1), Cl(2))$ and $(C(4), C(7), C(8), C(9))$.

Although this inclination does not affect the σ bond, it reduces considerably the amount of overlap between the filled d orbital of platinum and the π antibonding orbital of the double bond which have maximum overlap when the double bond is perpendicular to or lies in the bonding plane. Thus, the 'back bonding' modification of Dewar's ideas by Chatt (1953) could apply to the $C(1)-C(2)$ bond but not to the $C(7)-C(8)$ bond. The weakening of the metal bond to the $C(7)-C(8)$ bond may be the reason for the greater ease of olefin displacement relative to that of similar complexes in which both double bonds are presumably perpendicular to the bonding plane (Chatt & Wilkins, 1952).

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