

ABSOLUTE CONFIGURATION AND CRYSTAL STRUCTURE OF (+)-*cis*-DICHLORO[(*S*)-1-BUTENE][(*S*)- α -METHYL- BENZYLAMINE]PLATINUM(II)

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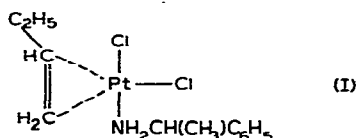
SUMMARY

The absolute configuration and the crystal structure of (+)-*cis*-dichloro-[(*S*)-1-butene][(*S*)- α -methylbenzylamine]platinum(II) has been elucidated by single-crystal X-ray analysis. The crystals belong to the orthorhombic system, space group $P2_12_12_1$, with $a=17.28 \text{ \AA}$, $b=13.08 \text{ \AA}$, $c=6.52 \text{ \AA}$ and four molecules per unit cell. Intensity measurements were carried out by automated counter techniques (Mo- K_{α}). The structure was solved by Patterson and Fourier syntheses.

The final conventional R value for 1108 independent non-zero reflections was 0.042 (0.058 if 250 reflections below the limit of detectability are taken into account). The ligands lie in the square-planar arrangement around the platinum atom. The olefin double bond deviates by 11° from the ideal arrangement having the C=C bond perpendicular to the square of coordination. The absolute configurations of the two asymmetric centers in the molecule have been determined and are compared with the chemical and physical data available for the complex.

INTRODUCTION

The determination of the absolute configuration and the crystal structure of (+)-*cis*-dichloro[(*S*)-1-butene][(*S*)-methylbenzylamine]platinum(II) is part of a



program^{1,2} on the study of asymmetric transition metal complexes in which a prochiral olefin³ is coordinated to the metal. The absolute configuration of the asymmetric centers in the present case is particularly interesting because its determination is important for the elucidation of the reaction mechanism between a nucleophile and an olefin-transition metal complex⁴.

As previously described¹, the knowledge of the absolute configuration of one

of the two asymmetric groupings provides a straightforward method for the assignment of the absolute configuration of the diastereoisomeric complex. In the present case, the configuration of the coordinated α -methylbenzylamine was known to be (S)⁵.

EXPERIMENTAL SECTION

A. X-ray data collection

Needle-like, single crystals of (I), prepared by Panunzi *et al.*⁴ were obtained by slow evaporation of a methanol solution ($[\alpha]_D^{20} = +2.7$, $c=0.1$, acetone).

From preliminary Weissenberg photographs the crystals were found to belong to the orthorhombic $P2_12_12_1$ space group (systematic $h00$, $0k0$, and $00l$ absences with h , k , and l odd respectively). A crystal of approximately cylindrical shape ($r=0.015$ cm, $l=0.05$ cm) was centered on a Picker four circles automated diffractometer equipped with a PDP-8 digital computer.

The determination of the lattice constants was carried out by a least-squares treatment of the 2θ , χ , and φ setting angles of twelve reflections with $2\theta > 40^\circ$ (Mo- K_α , $\lambda=0.71069$ Å), using a program prepared by Busing and Levy⁶. The resulting parameters are: $a=17.284 \pm 0.009$ Å, $b=13.086 \pm 0.009$ Å, $c=6.522 \pm 0.004$ Å. The experimental density ($D_{\text{exp}}=1.99$ g/cm³ by flotation) agreed with the calculated density assuming four molecules of (I) per unit cell ($D_{\text{X-Ray}}=1.99$ g/cm³). A total of 1358 integrated intensities were collected using a θ - 2θ scan mode (1.67°) with Zr-filtered Mo- K_α radiation ($\lambda=0.71069$ Å) in the range of 0 - 50° of 2θ . Two stationary crystal stationary counter background counts of 20 seconds were taken at each end of each scan. The intensities of the reflection were corrected for the absorption in the cylindrical approximation ($\mu R=2.03$).

B. Structure determination and refinement

The structure of (I) has been solved by straightforward application of the heavy-atom method. The atomic coordinates of the platinum and the two chlorines obtained from the Patterson synthesis were refined through three cycles of full-matrix least-squares.

The positions of the light atoms (C and N) were obtained from the successive three-dimensional difference Fourier. The refinement of the atomic parameters was carried out by means of seven cycles of 9×9 block diagonal least-squares procedures (the last three cycles were performed with anisotropic thermal parameters for all the atoms). The imaginary part of the atomic scattering factor of the platinum⁷ was introduced (correction made on the F_c values) and refinement was continued until the maximum shifts in the atomic coordinates and the anisotropic thermal shifts on the average were less than $\frac{1}{3}$ of the corresponding standard deviations.

The weighting scheme adopted throughout the refinement corresponds to that suggested by Cruickshank and Philling⁸:

$$w(hkl) = \frac{1}{a + bF_0(hkl) + cF_0^2(hkl)}$$

where $a=0.11111$, $b=0.05555 F_0(\text{min})$, and $c=2b/F_0(\text{max})$.

At the end of the refinement the R value ($R = \sum ||F_0| - |F_c|| / \sum F_0$) was 0.042 for 1108 independent non-zero reflections ($R=0.058$ if 250 reflections below the limit of the counter detectability were included).

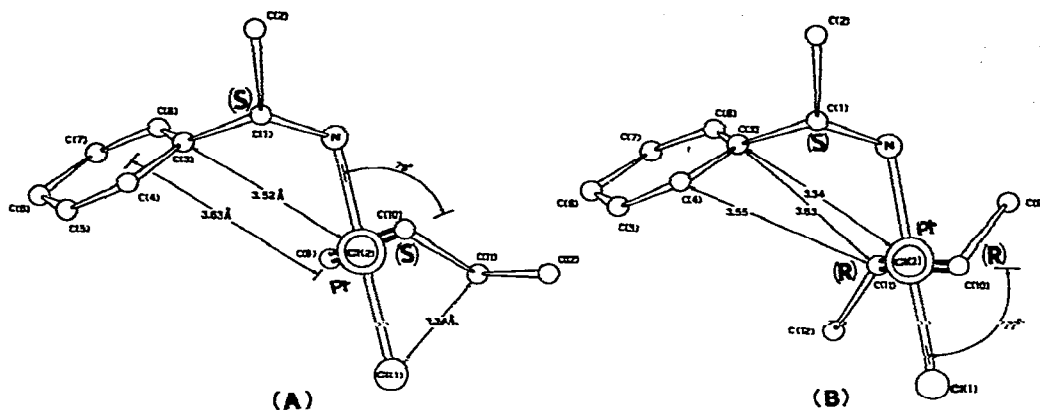


Fig. 1. Molecular models of *cis*-dichloro[(*S*)-1-butene][(*S*)- α -methylbenzylamine]platinum(II) (A) and *cis*-dichloro[*trans*-(*RR*)-2-butene][(*S*)- α -methylbenzylamine]platinum(II) (B). The absolute configurations of the asymmetric centers are given. The deviation from perpendicularity of the double bond is indicated for the two models and some relevant short intramolecular contacts are reported.

In the refined model both the asymmetric carbon atom C(1) and C(10) have the *S* configuration (Fig. 1a). The incorrect solution with the amine having the *R* configuration (according to the preparation of the compound the chiral amine has the *S* configuration) gave a value for the *R* factor of 0.052 (0.077 on the total number of reflections). According to the Hamilton test⁹ we may reject at a significance level less than 0.005 the hypothesis that the absolute configuration is the one having the *R* configuration of both the asymmetric carbon atoms. This result may be thus taken as a further proof of the absolute configuration of the (–)- α -methylbenzylamine. Because of the noise level of the difference Fourier no attempts were made to localize

TABLE I

FINAL ATOMIC PARAMETERS

E.s.d. in unit of the last significant digit.

A. ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS

Atom	x	y	z
Pt	-0.1775(1)	-0.1780(1)	-0.1169(1)
Cl(1)	-0.0764(4)	-0.2158(5)	0.0966(10)
Cl(2)	-0.2493(3)	-0.1126(4)	0.1618(7)
N	-0.2707(9)	-0.1413(11)	-0.3039(21)
C(1)	-0.3461(11)	-0.1848(17)	-0.2570(37)
C(2)	-0.4105(12)	-0.1389(18)	-0.3880(43)
C(3)	-0.3461(14)	-0.3028(16)	-0.2902(40)
C(4)	-0.3681(14)	-0.3650(19)	-0.1301(60)
C(5)	-0.3633(19)	-0.4650(23)	-0.1584(57)
C(6)	-0.3485(23)	-0.5173(21)	-0.3083(66)
C(7)	-0.3244(19)	-0.4552(28)	-0.4994(63)
C(8)	-0.3217(13)	-0.3425(16)	-0.4798(33)
C(9)	-0.1246(13)	-0.2726(18)	-0.3499(40)
C(10)	-0.1078(14)	-0.1743(17)	-0.3941(35)
C(11)	-0.0274(14)	-0.1337(19)	-0.3703(47)
C(12)	-0.0369(15)	-0.0151(21)	-0.3309(50)

B. FINAL THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS

Temperature factors are given in the form:

$$\exp -\frac{1}{2}(h^2 \cdot a^{*2} \cdot B_{11} + k^2 \cdot b^{*2} \cdot B_{22} + l^2 \cdot c^{*2} \cdot B_{33} + 2h \cdot k \cdot a^* \cdot b^* \cdot B_{12} + 2h \cdot l \cdot a^* \cdot c^* \cdot B_{13} + 2k \cdot l \cdot b^* \cdot c^* \cdot B_{23})$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	5.1(0)	3.4(0)	2.3(0)	-0.3(0)	-0.3(0)	-0.1(0)
Cl(1)	6.4(3)	8.5(4)	4.2(2)	0.2(3)	-1.6(3)	1.1(3)
Cl(2)	6.2(3)	5.1(2)	2.4(2)	-0.4(2)	0.2(2)	-0.4(2)
N	5.9(7)	3.7(6)	2.0(5)	0.9(6)	-1.0(5)	0.5(5)
C(1)	3.7(8)	5.4(10)	6.8(12)	-1.6(8)	-1.7(8)	3.3(11)
C(2)	4.5(9)	7.2(12)	6.3(12)	-1.0(9)	0.6(11)	2.6(12)
C(3)	6.4(12)	4.6(10)	6.7(13)	-0.9(9)	-2.0(10)	2.3(10)
C(4)	5.2(11)	5.7(11)	11.1(20)	0.2(9)	-0.4(15)	3.4(16)
C(5)	12.0(21)	6.6(13)	12.2(23)	0.8(15)	-8.6(20)	-3.7(17)
C(6)	16.3(32)	4.7(12)	15.2(32)	-1.1(16)	-8.8(27)	2.9(17)
C(7)	9.5(19)	10.9(21)	16.9(31)	3.2(17)	-9.1(21)	-10.5(23)
C(8)	5.7(10)	5.3(11)	5.2(10)	-1.1(10)	3.0(10)	2.2(9)
C(9)	5.7(11)	6.6(12)	5.6(12)	2.6(10)	-0.4(10)	-1.7(11)
C(10)	7.8(12)	5.8(10)	5.2(11)	-3.0(10)	4.3(11)	-4.1(11)
C(11)	6.1(11)	6.9(12)	6.0(12)	-1.1(10)	0.9(12)	0.4(13)
C(12)	7.0(12)	7.5(14)	9.1(19)	-2.5(12)	4.5(14)	-0.7(15)

the hydrogen atoms. The final atomic coordinates and thermal factors are reported in Table 1. A list of the observed and calculated structure factors for the 1358 independent measured reflections has been deposited as document NAPS, with the American Society for Information Science*.

RESULT AND DISCUSSION

In Table 2 (*cf.* Fig. 1a) the most significant bond distances, bond angles and internal rotation angles of the molecule are given together with their standard deviations. The carbon-carbon distances and bond angles in the benzene ring, not given in Table 2, have a mean value of $1.40 \pm 0.08 \text{ \AA}$ and $120 \pm 6^\circ$, respectively.

While the large errors on the light atoms parameters are disappointing, the overall geometry appears to be reliable; as an example, the benzene ring is planar and the mean square distance of the six benzene atoms and C(1) from the best plane passing through them is 0.02 \AA . The complex shows the usual almost undistorted square-planar arrangement of the ligands around the platinum atom with the two chlorines in *cis* position, the nitrogen and the center of the coordinated double bond occupying the other two sites of coordination. The significantly increased length of the Pt-Cl(2) bond distance (2.36 \AA) with respect to Pt-Cl(1) (2.29 \AA) may be ascribed to the *trans*-effect of the coordinated double bond in agreement to what found in similar compounds^{1,10}. The Pt-C(9) and Pt-C(10) bond distances are equal within the experimental error and comparable with analogous data earlier reported^{1,10}. However, the direction of the double bond is tilted and it makes an angle of 79° with the plane of coordination (Fig. 1a). This behavior of the olefin can be ascribed to

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TABLE 2

MOST SIGNIFICANT MOLECULAR PARAMETERS
E.s.d. in unit of the last significant digit.

A. Bond distances (\AA)		B. Bond angles ($^\circ$)	
Pt-Cl(1)	2.289(7)	Cl(1)-Pt-Cl(2)	90.6(1)
Pt-Cl(2)	2.361(5)	Cl(1)-Pt-N	178.3(3)
Pt-N	2.076(15)	Cl(2)-Pt-N	87.8(2)
Pt-C(9)	2.163(25)	Cl(1)-Pt-Center ^a	91.5(3)
Pt-C(10)	2.173(23)	Cl(2)-Pt-Center	88.6(3)
N-C(1)	1.455(25)	N-Pt-Center	89.7(3)
C(1)-C(2)	1.526(32)	Pt-N-C(1)	118.8(8)
C(9)-C(10)	1.350(3)	N-C(1)-C(2)	112.5(8)
C(10)-C(11)	1.496(34)	N-C(1)-C(3)	111.0(8)
C(11)-C(12)	1.582(38)	C(2)-C(1)-C(3)	108.2(8)
		C(1)-C(3)-C(4)	118.7(12)
		C(1)-C(3)-C(8)	119.2(10)
		C(9)-C(10)-C(11)	121.1(10)
		C(10)-C(11)-C(12)	105.6(9)
C. Internal rotation angles ^b ($^\circ$)			
Cl(1)-Pt-N-C(1)	-68		
Cl(2)-Pt-N-C(1)	-57		
Center-Pt-N-C(1)	127		
Pt-N-C(1)-C(2)	172		
Pt-N-C(1)-C(3)	-67		
N-C(1)-C(3)-C(4)	125		
N-C(1)-C(3)-C(8)	-54		
C(9)-C(10)-C(11)-C(12)	206		

^a With "Center" we indicate the center of the CH=CH double bond in the 1-Butene. ^b *trans* Conformation = 180°.

the necessity of relaxing short intramolecular contacts such as C(11)-Cl(1) (3.34 \AA).

The value obtained in the present study of the internal rotation angle about the single bond adjacent to the double bond C(9)-C(10)-C(11)-C(12) seems particularly interesting. Its value (206°) is well removed from that of minimum energy usually assigned to such angle in the free olefin. From other types of measurement on small unsaturated molecules this rotation angle has been found¹¹ to assume preferentially values near 0° or $\pm 120^\circ$. It is obvious that the coordination of the olefin to the platinum atom is responsible for a large perturbation in the geometry of the olefin. This has been predicted¹² and experimentally verified previously^{1,13}. In the present case a detailed rationalization of the entire effect could be obtained from knowledge of the hydrogen positions which, unfortunately, cannot be located with certainty. However, the expected repulsion from the platinum atom of the hydrogen bonded to C(10)¹², and the repulsion between the platinum and the C(11) carbon atom¹ would both give rise to a marked staggering of the bonds in the conformation observed.

In Fig. 2 is presented the Newman projection along the C(10)-C(11) bond. The approximate possible direction of the hydrogens bonded to C(10) and C(11) are indicated. The conformation experimentally found for the (*S*)- α -methylbenzylamine with respect to the square of coordination is similar to that previously observed in

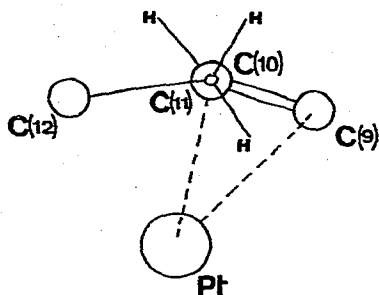


Fig. 2. Newman projection along the C(11)-C(10) bond. The approximate expected positions of the hydrogen atoms (see text) bonded to C(10) and C(11) are reported.

the case of the *cis*-dichloro[*trans*-(*RR*)-2-butene][(*S*)- α -methylbenzylamine]platinum(II)¹ (II) and the *trans*-dichloro[*cis*-2-butene][(*S*)- α -methylbenzylamine]platinum(II)¹³ (I). A comparison between the molecular models of (II) and (I) is given in Fig. 1. In the same Figure the shortest intramolecular distances are reported together with the absolute configurations of the asymmetric carbon atoms for both models. In Fig. 3 a view of the molecular packing along (001) for complex (I) is presented; the shortest non-bonded contacts ($< 4.0 \text{ \AA}$) are indicated.

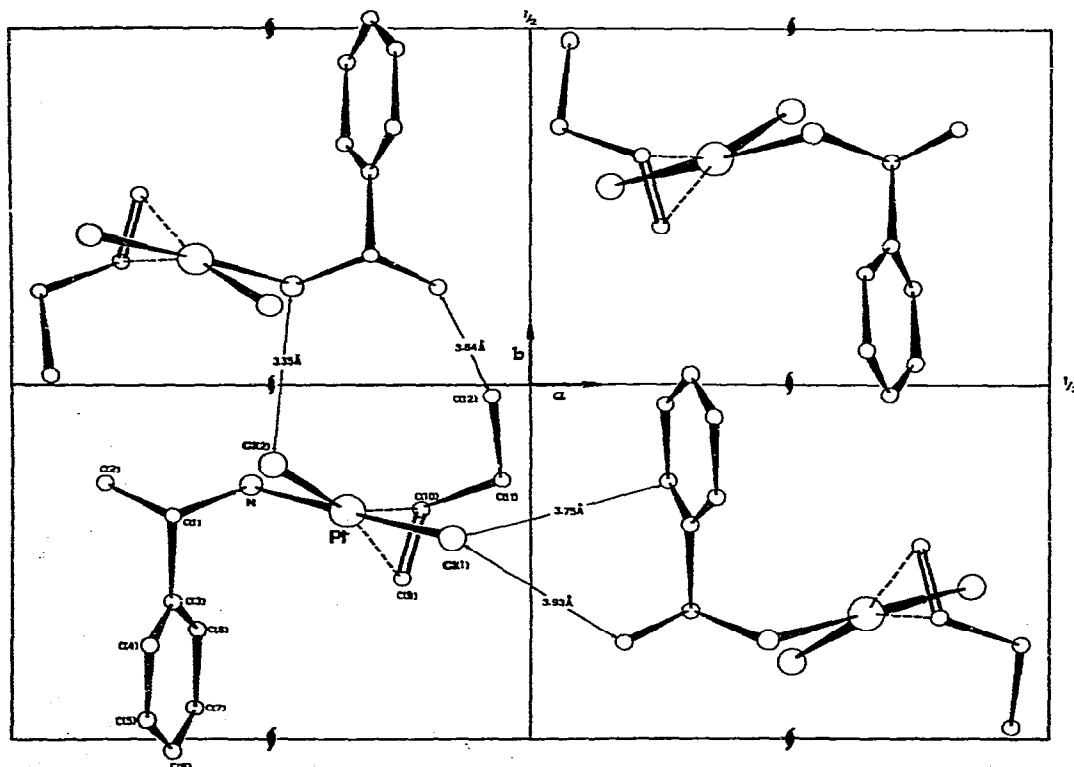


Fig. 3. Molecular packing as view along the *c* axis. Some of the shortest intermolecular contacts are indicated.

A knowledge of the absolute configuration of the asymmetric carbon of the olefin in complex (I) is essential to consideration of possible mechanisms of the reaction between a nucleophile and an olefin transition metal complex⁴. The authors of ref. 4 used the resolved diastereoisomeric complex (I) as a substrate for the reaction with nucleophilic agents, and proposed a *trans* addition as a possible steric pathway for the nucleophilic attack. In fact, from the reactions between the resolved diastereoisomeric complex (I) and diethylamine and successive acid hydrolysis of the alkyl derivative, they obtained the dextrorotatory enantiomer of the diethyl-*sec*-butylamine which has the (*S*) configuration¹⁵. A *cis* addition of the nucleophile would yield the opposite enantiomeric amine.

The absolute configuration of the coordinated olefin in complex (I) is to be related to the positive circular dichroism band at 375 nm. This is in agreement with what has been previously found¹ for the *cis*-dichloro[*trans*-(*RR*)-2-butene][(*S*)- α -methylbenzylamine]platinum(II), which has a circular dichroism band of opposite sign at this wavelength.

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