Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ABSOLUTE CONFIGURATION AND CRYSTAL STRUCTURE OF (−)-*cis*-DICHLORO(*trans*-2-BUTENE)[(*S*)-α-PHENETHYLAMINE]-PLATINUM(II)

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(Received January 23rd, 1969)

SUMMARY

The crystal structure of (−)-*cis*-dichloro(*trans*-2-butene)[(*S*)-α-phenethylamine]platinum(II) has been determined by single-crystal three-dimensional X-ray analysis. The crystals belong to the monoclinic system, space group $P2_1$, with the following unit cell constants $a=12.87$, $b=6.58$, $c=8.86$ Å, $\beta=102°38'$ and with two molecules per unit cell. Intensities measurements were carried out by an automated counter method. The structure has been solved by three-dimensional Patterson and Fourier syntheses. The final conventional R value for 713 non-zero independent reflections was 0.053. The ligands around the platinum are arranged in a square-planar configuration. The olefin double bond deviates slightly from the idealized arrangement in which the C=C is perpendicular to the plane defined by the Pt, N and Cl atoms. The relevant features of the structure are reported and discussed in terms of non-bonded interactions and molecular orbitals.

INTRODUCTION

To date few crystal structures of platinum–olefin complexes have been determined. The study of platinum complexes is in fact complicated by the large atomic number of the metal atom, which yields generally a good agreement between calculated and observed structure factors, but poor values of bond lengths and bond angles.

We have become recently interested in the study of the asymmetric platinum complexes[1] in which a prochiral olefin (that is, having "prochiral[2]" or "enantiotopic[3]" faces) is coordinated to the metal. We wish to report in this paper the results of an X-ray investigation on the (−)-*cis*-dichloro(*trans*-2-butene)[(*S*)-α-phenethylamine]-platinum(II)[4]. The purpose of this research was to establish the absolute configuration of the "face" of the olefin coordinated to the platinum atom[5]; in fact, the X-ray analysis of a molecule which contains two asymmetric groupings, provides a direct physical method for the determination of the absolute configuration, once the absolute configuration of one of those groupings is known[6]. In our case, the absolute configuration of the coordinated α-phenethylamine was known to be *S*. Preliminary structural data on the compound were reported at a meeting in Naples (Italy)[7].

EXPERIMENTAL

Crystals of the sample were obtained by slow evaporation of an acetone solution. A small crystal of approximately cylindrical shape was carefully centered on a Picker four-circle automatic diffractometer equipped with a PDP-8 digital computer. The unit cell constants were calculated by a least-square fit of the setting angles of twelve high angle reflections and they are reported in Table 1*. The intensity data were collected using θ–2θ scan mode (1.5°) with Zr-filtered Mo-K_α radiation. Two stationary-crystal-stationary-counter background counts of 10 seconds were taken at each end of the scan. Because of the smallness of the intensities beyond 0.92 Å, the maximum value of 2θ explored was chosen to be 50° and the intensities of 713 non-zero independent reflections were collected. The cylindrically shaped crystal was in fact very small, the radius and the length of the cylinder being respectively less than 0.01 mm, and about 0.5 mm. Under these conditions, since $\mu = 104\ \text{cm}^{-1}$, we felt it unnecessary to perform any absorption correction.

TABLE. 1

UNIT CELL DIMENSIONS OF (–)-*cis*-DICHLORO[(*R*,*R*)-*trans*-2-BUTENE] [(*S*)-α-PHENETHYLAMINE] PLATINUM(II), [$PtCl_2NC_{12}H_{17}$] (MOL. WT. 443.27)

Monoclinic, space group $P2_1$	$Z = 2$	$F(000) = 416$
$a = 12.87$ Å ± 0.02		
$b = 6.58$ Å ± 0.01	$\beta = 102°38' \pm 15'$	
$c = 8.86$ Å ± 0.01		
$D_{X\text{-ray}} = 2.01$ g/cm^3	$D_{exp} = 1.99$ g/cm^3	
$\mu = 104\ \text{cm}^{-1}$ for $\lambda = 0.70926$ Å		

STRUCTURE DETERMINATION AND REFINEMENT

The positions of the heavy atoms were established with a Patterson synthesis and refined to $R = 0.15$ without taking into consideration the lighter atoms. At this point, approximate positions of the lighter atoms were obtained by means of a three-dimensional Fourier synthesis. The scattering factor tables reported by Hanson *et al.*[8] were used throughout the present investigation and a unity weight was assigned to each reflection. The structure was finally refined by standard least-square procedures, using 713 non-zero independent reflections to a value:

$$R = \frac{\sum ||F_c| - |F_o||}{\sum |F_o|} = 5.4\%$$

At this stage, two enantiomorphous solutions of the structure are still possible (ignoring the chemical knowledge of the absolute configuration of the amine), while the relative configuration of amine and olefin is established with certainty [(*R*,*R*)-olefin, (*S*)-amine or (*S*,*S*)-olefin, (*R*)-amine[9]]. The imaginary part of the atomic scattering factor of the platinum[10] was then introduced (correction made to the F_c

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* The preliminary cell dimensions of several platinum complexes were reported earlier [*Acta Crystallogr.*, 20 (1966) 458]. For our compound the $\vec{a}$ axis value was erroneously reported as $\vec{a} \cdot \sin \beta$ (= 12.55 Å).

values) and resulted in a decrease of the *R* value to 5.3% for one, (I), of the enantiomorphous solutions (the one in which, according to the preparation of the compound[1], the chiral amine had the *S* configuration) and 5.5% for the other, (II), where, incorrectly, the amine had an absolute *R* configuration. The incorrect (refined) solution (II) can be essentially related to the correct one (I) by a change in sign of all the coordinates of the atoms, together with a shift of 0.020 along *y* of the platinum atom ($y^{\mathrm{I}}_{\mathrm{Pt}}=0$ $y^{\mathrm{II}}_{\mathrm{Pt}}=-0.020$). A final electron density map, calculated with the positional parameters of the correct solution (I) and from which the 16 input atoms had been subtracted, yielded no residual peaks of height greater than 1.8 $e \cdot Å^{-3}$. Several peaks may have corresponded to hydrogen atoms, but these were not sufficiently above the noise level to warrant refinement. The final standard deviation of an observation of unit weight is 0.95, indicating a slight overestimation in the standard deviation of the intensity data. According to the Hamilton test, we may reject, at a significance level less than 0.005, the hypothesis that the absolute configuration is the second of the two tried. A list of the observed and calculated structure factor for the 713 non-zero independent reflections has been deposited as Document No. NAPS-00351 with the American Society for Information Science★.

TABLE 2

FINAL ATOMIC PARAMETERS

A. POSITIONAL AND ISOTROPIC THERMAL PARAMETERS

Atom	x	y	z	B
Pt	−0.2086	0.0000	−0.0717	2.8
Cl(1)	−0.322	0.025	0.006	5.5
Cl(2)	−0.108	0.076	−0.131	4.3
N	−0.108	−0.404	−0.162	1.5
C(1)	−0.091	−0.373	−0.311	4.1
C(2)	−0.013	−0.515	−0.353	6.1
C(3)	−0.208	−0.388	−0.422	4.4
C(4)	−0.256	−0.591	−0.438	4.2
C(5)	−0.355	−0.589	−0.537	7.4
C(6)	−0.405	−0.423	−0.608	7.5
C(7)	−0.353	−0.230	−0.591	5.7
C(8)	−0.260	−0.180	−0.492	5.5
C(9)	−0.173	−0.533	0.171	4.6
C(10)	−0.262	−0.420	0.076	1.8
C(11)	−0.310	−0.464	−0.073	2.5
C(12)	−0.432	−0.413	−0.138	6.3

B. ANISOTROPIC THERMAL FACTORS ($\times 10^4$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	41	134	119	−23	11	−40
Cl(1)	69	302	394	1	85	−37
Cl(2)	92	174	100	−57	−2	−77

[a] $T=\exp\left[-(\beta_{11}\cdot h^2+\beta_{22}\cdot k^2+\beta_{33}\cdot l^2+2\beta_{12}\cdot h\cdot k+2\beta_{13}\cdot h\cdot l+2\beta_{23}\cdot k\cdot l)\right]$

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RESULTS AND DISCUSSION

In Table 2 the coordinates of the atoms together with their temperature factors (anisotropic only for platinum and chlorine atoms) are reported as obtained from the least-square refinement. In Table 3 the most significant bond distances, bond angles and internal rotation angles of the molecule are given, together with their standard errors calculated from inversion of the least-square variance-covariance matrices. The bond distances concerning the platinum atom agree with similar data available in the literature[12]. The carbon–carbon distances in the benzene ring, which are not reported, have a mean value of 1.43±0.06 Å. The carbon–carbon distances in the coordinated olefin are: mean value of the $CH-CH_3$ distance: 1.53±0.06 Å, CH–CH: 1.36±0.06 Å. The distance between the platinum atom and the center of the CH–CH double bond is 2.05±0.02 Å. The various angles ligand–Pt–ligand are typical of an almost undistorted square-planar configuration of the platinum atom. All the other angles are acceptable, within the limits of the large standard deviations in the positional parameters of the lighter atoms. As it may be seen from the internal rotation angle (Table 3), the atoms of the *trans*-2-butene ligand are definitely not coplanar, the two methyl groups being displaced away from the platinum atom. Moreover, the CH=CH double bond is not perpendicular to the plane of the square of coordination but displaced of 13±4° from perpendicularity. Similar observations were performed by us[13] in the case of another *trans*-olefin (fumaric acid) coordinated to a transition metal (iron), and ascribed substantially to a better relaxation of non-bonded interactions. In our case, the deviation from perpendicularity of the CH–CH bond, with respect to the plane of square-planar coordination, seems to be associated with the conformation of the amine which is quite similar to that observed by Ganis and Pedone[14] in the case of (−)-*trans*-dichloro(*cis*-2-butene)[(*S*)-α-phenethylamine]-platinum(II). The internal rotation angle Pt–N–C(1)–C(2) is very near to a *trans*

TABLE 3

STRUCTURAL PARAMETERS

	Bond lengths (Å)	Bond angles (°)		Internal rotation angles (°)	
Pt–Cl(1)	2.29±0.02[a]	Cl(1)–Pt–Cl(2)	89±1	Cl(1)–Pt–N–C(1)	25±18
Pt–Cl(2)	2.35±0.02	Cl(2)–Pt–N	90±1	Cl(2)–Pt–N–C(1)	52± 3
Pt–C(10)	2.16±0.05	Cl(1)–Pt–Center	91±1	Pt–N–C(1)–C(2)	175± 3
Pt–C(11)	2.17±0.05	N–Pt–Center	90±1	Pt–N–C(1)–C(3)	61± 4
Pt–Center[b]	2.05±0.02	Cl(2)–Pt–Center	174±1	Center–Pt–N–C(1)	133± 3
Pt–N	2.14±0.03	Cl(1)–Pt–N	176±1	C(9)–C(10)–C(11)–C(12)	150± 5
C(1)–N	1.40±0.06	Pt–N–C(1)	119±3		
C(1)–C(2)	1.49±0.08	C(9)–C(10)–C(11)	125±5		
		C(10)–C(11)–C(12)	120±4		
		C(2)–C(1)–C(3)	113±4		

[a] This distance after correction for "riding" became 2.31±0.02 Å. The function used in this correction is $\bar{R}=\bar{R}_0+(\bar{r}_2^2-\bar{\xi}_2^2-\bar{r}_i^2+\bar{\xi}_i^2)/2R_0$ where R_0 is the uncorrected interatomic distance, $\bar{r}_i^2$ is the mean square radial thermal displacement of atom *i*, and $\bar{\xi}_i^2$ is the mean square component of displacement of atom *i* in the direction defined by the interatomic vector. [b] With "Center" we indicate the center of the CH=CH double bond in the *trans*-2-butene.

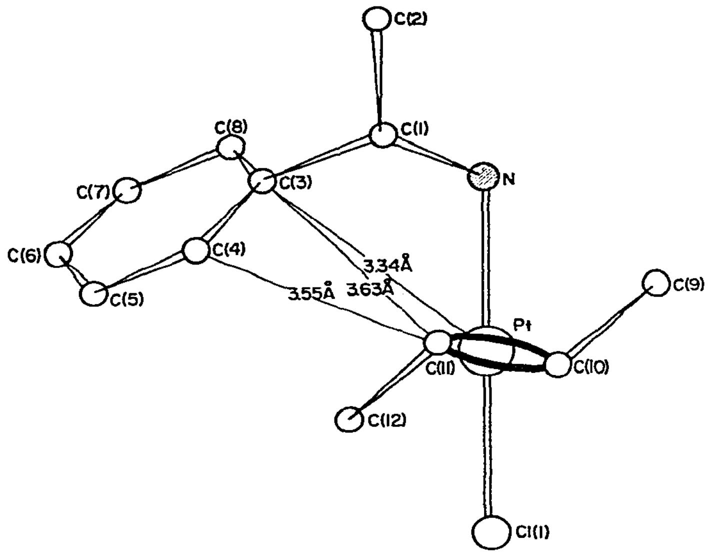

Fig. 1. Molecular model of (−)-*cis*-dichloro(*trans*-2 butene)[(*S*)-α-phenethylamine]platinum(II). The shortest intramolecular distances are indicated. In this projection the Cl(2) atom lies under the Pt atom.

conformation, so that the benzene ring is bent toward the platinum atom, with carbon–platinum distances as low as 3.34 Å. The stability of this conformation may arise from a slight interaction between a filled π-orbital of the benzene ring and the vacant p_z orbital of the platinum atom. The need of relaxing non-bonded interactions (the shorter

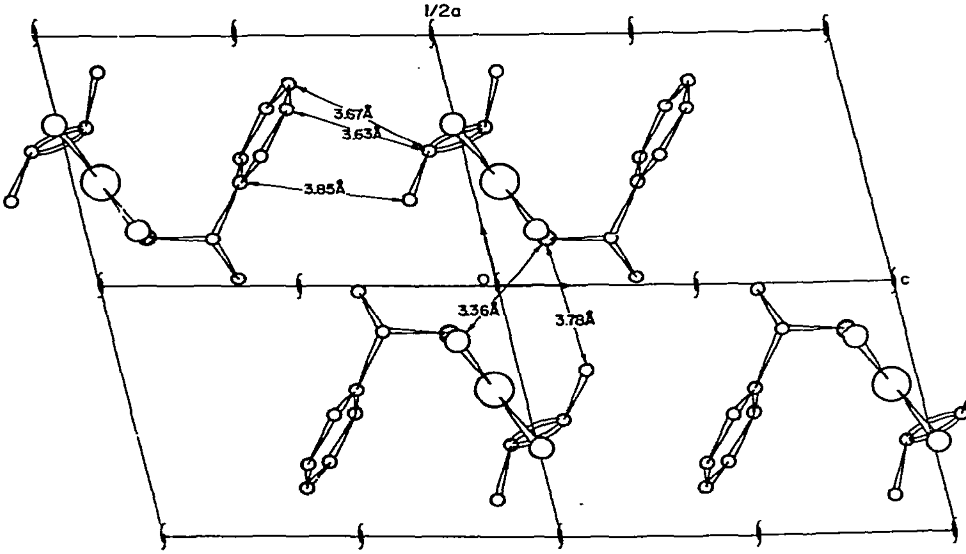

Fig. 2. A packing drawing of the molecules of (−)-*cis*-dichloro(*trans*-2-butene)[(*S*)-α-phenethylamine]-platinum(II) viewed in the (010) projection.

distances between carbon atoms of the olefin and carbon atoms of the benzene ring observed in this molecule are in the range of 3.55–3.65 Å) forces the CH–CH bond to deviate from perpendicularity, as discussed above (Fig. 1). Since appropriate orbitals of the transition metal are always available for the overlapping with the δ-antibonding orbitals of the olefin, for whatever rotation of the double bond, it seems reasonable that this rotation be such as to give rise to the more favorable non-bonded interactions within the molecule. The mode of packing of the molecules is illustrated in Fig. 2. The shortest Van der Waals distances between atoms of different molecules are reported.

The absolute configuration of the reported platinum (II) complex, which gives a negative circular dichroism bond at 375 mμ[4] is thus established to be (*R*,*R*)-olefin, (*S*)-amine: that is (−)-*cis*-dichloro[(*R*,*R*)-*trans*-2-butene][(*S*)-α-phenethylamine] platinum(II).

ACKNOWLEDGEMENT

We wish to thank Prof. M. Goodman for useful discussions and Professors G. Paiaro and A. Panunzi, who kindly supplied the compound. We also gratefully acknowledge the support of research grants from the National Science Foundation (GB 7558) and the National Institutes of Health (GM 08974).

REFERENCES

1 G. Paiaro, P. Corradini, R. Palumbo and A. Panunzi, *Makromol. Chem.*, 71 (1964) 184; P. Corradini, G. Paiaro and A. Panunzi, *J. Polym. Sci., Part C*, 16 (1967) 2905; G. Paiaro and A. Panunzi, *J. Amer. Chem. Soc.*, 86 (1964) 5148.
2 K. R. Hanson, *J. Amer. Chem. Soc.*, 88 (1966) 2731.
3 K. Mislow and M. Raban, in N. L. Allinger and E. L. Eliel (Eds.), *Topics in Stereochemistry*, Interscience, New York, 1967, p. 7.
4 G. Paiaro, R. Palumbo, A. Musco and A. Panunzi, *Tetrahedron Lett.*, (1965) 1067; P. Corradini, G. Paiaro, A. Panunzi, S. F. Mason and G. H. Searle, *J. Amer. Chem. Soc.*, 88 (1966) 2731; A. Panunzi and G. Paiaro, *J. Amer. Chem. Soc.*, 88 (1966) 4843.
5 G. Natta, M. Peraldo, M. Farina and G. Bressan, *Makromol. Chem.*, 55 (1962) 139.
6 E. L. Eliel, *Stereochemistry of Carbon Compound*, McGraw-Hill, New York, 1962, p. 93.
7 P. Corradini and C. Pedone, *Chim. Ind. (Milan)*, 47 (1965) 664.
8 H. P. Hanson, F. Herman, J. D. Lea and S. Skillman, *Acta Crystallogr.*, 17 (1964) 1040.
9 R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, 12 (1956) 81; *Angew. Chem. Int. Ed. Engl.*, 5 (1966) 385.
10 J. A. Ibers, *International Tables for X-Ray Crystallography*, Vol. III, The Kynoch Press, Birmingham, England, 1962, Table 3.3.2.C.
11 W. C. Hamilton, *Acta Crystallogr.*, 18 (1965) 502.
12 P. R. H. Alderman, P. G. Owston and J. M. Rowe, *Acta Crystallogr.*, 13 (1960) 149.
13 P. Corradini, C. Pedone and A. Sirigu, *Chem. Commun.*, 5 (1968) 275.
14 P. Ganis and C. Pedone, *Ric. Sci.*, 35 (1965) 1462.