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ABSOLUTE CONFIGURATIONS AND CRYSTAL STRUCTURES OF THE DIASTEREOISOMERIC COMPLEXES OF *cis*-DICHLORO(1,5-HEXADIENE)-PLATINUM(II) WITH (*S*)-α-METHYLBENZYLAMINE

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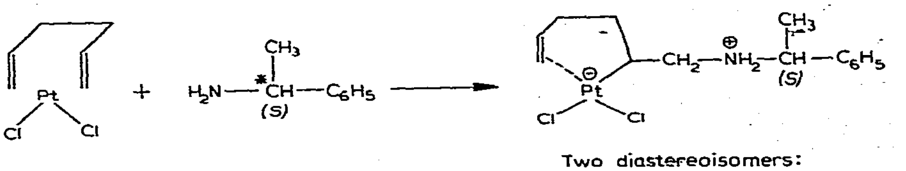
SUMMARY

The crystal structures of the two diastereoisomeric complexes of *cis*-dichloro-(1,5-hexadiene)platinum(II) with (*S*)-α-methylbenzylamine and the absolute configurations of the three asymmetric centers present in each molecule have been determined. Both complexes crystallize in the orthorombic system, space group $P2_12_12_1$ with $a = 16.21$ Å, $b = 12.23$ Å, $c = 8.01$ Å [complex (I)] and $a = 23.53$ Å, $b = 7.49$ Å, $c = 8.69$ Å [complex (II)]. The structures have been solved by Patterson and Fourier methods and refined to R factors of 0.062 and 0.074 for complexes (I) and (II), using 1454 and 1132 independent reflections measured with counter techniques (Mo-K_α), respectively.

The two complexes present the usual square-planar arrangement of the ligands around the platinum atom, showing different conformations. The diastereoisomers undergo an antiracemization process in dichloromethane, but it is difficult to rationalize the differing stabilities of the two forms in terms of the conformations available to the isolated molecule.

INTRODUCTION

Additions of nucleophilic agents to coordinated olefinic ligands in transition metal complexes have been the subject of recent investigations[1]. These reactions are generally stereospecific, and to a certain degree they become stereoselective when optically active ligands or reagents are involved[2]. In the case recently reported by De Renzi *et al.*[3], the reaction of (*S*)-α-methylbenzylamine with *cis*-dichloro(1,5-hexadiene)platinum(II) gives two diastereoisomeric species [eqn. (1)]. On the basis of the chemical evidence, a possible pathway for the reaction is the insertion of the amine, which takes place through a *trans*-opening of one of the two double bonds coordinated to the platinum atom. The two diastereoisomeric species have opposite



Two diastereoisomers:
complex (I) and complex (II)

configurations R and S or S and R of the π-coordinated double bond and the carbon atom σ-bonded to the platinum, respectively. Two crystalline compounds were isolated: (I) which has optical activity $[\alpha]^{20°}_{578\,m\mu} = -23°$ ($c = 0.28$, methanol), and (II), which has $[\alpha]^{20°}_{578\,m\mu} = +24°$ ($c = 0.35$, methanol). It has been found that in methylene chloride solutions complex (I) transforms to complex (II). If, on the other hand, the precipitation of the diastereoisomer (I) is prevented by dilution of the reaction mixture, only complex (II) is obtained.

Determination by X-ray analysis of the structure of the two diastereoisomeric compounds seemed of interest for the following reasons:

(*i*). It would permit assignment of the absolute configurations of the three asymmetric centers in the molecule; that is the enantiotopic face[4] of the coordinated olefin, the carbon atom σ-bonded to the platinum, and the α-carbon atom of the optically active amine. Since in our case the absolute configuration of the amine is known to be (S), the X-ray analysis provides a direct method for the assignment of the absolute configuration of the other two asymmetric groupings;

(*ii*). It would establish the conformations of the two diastereoisomers in the solid state, from which it might be possible to account for the different stabilities of the complexes in solution.

These investigations are part of a program which is being carried on in our laboratories on the study of asymmetric transition metal complexes in which a prochiral olefin is coordinated to the metal[5-9].

EXPERIMENTAL

A. X-ray data collection

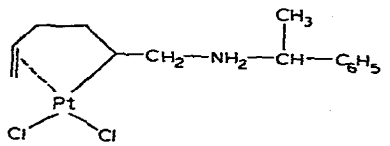
Single crystals for the two complexes were obtained by slow evaporation of methanol solutions. Several attempts to growth single crystals of complex (II) from methylene chloride solutions were unsuccessful. From methanol solutions it was possible to obtain only very poor single crystals of (II), although complex (I) gave good single crystals. For both compounds the same experimental techniques were used. Small crystals of approximately cylindrical shapes were chosen for the data collections [$R = 0.025$ mm for complex (I), $R = 0.023$ mm for complex (II)]. From preliminary Weissenberg photographs taken with Cu-K_α radiation both crystals were found to belong to the orthorombic system. The systematic extinctions of the $h00$, $0k0$, and $00l$ for h, k, and l odd respectively indicate the acentric space group $P2_12_12_1$ for both complexes.

The determination of the lattice constants for the two compounds was carried out by a least-squares treatment of the 2θ, χ and φ setting angles (automatically refined on a Picker four circle automated diffractometer) of twelve reflections with $2\theta > 40°$ (Mo-K_α, $\lambda = 0.71069$ Å) using a program prepared by Busing and Levy[10]. The parameters obtained are reported in Table 1.

The X-ray data collection was carried out on the Picker–FACS I diffractometer equipped with a PDP-8 digital computer according to a procedure described before[11], using a $\theta - 2\theta$ scan mode with Zr-filtered Mo-K_α radiation. In the range of 2θ examined a total of 1419 and 1454 independent reflections were measured by counter techniques for complex (I) and complex (II), respectively. The intensities of the reflections have been corrected for absorption in the cylindrical approximation [$\mu \cdot R = 2.39$ for complex (I), $\mu \cdot R = 2.30$ for complex (II)].

TABLE 1

CRYSTAL DATA OF $C_{14}H_{21}NPtCl_2$



Orthorombic, space group $P2_12_12_1$.

Complex	*a* (Å)	*b* (Å)	*c* (Å)	*Z*	$d_{X\text{-ray}}$ ($g \cdot cm^{-3}$)
(I)	16.21 ± 0.02	12.23 ± 0.02	8.01 ± 0.01	4	1.96
(II)	23.53 ± 0.02	7.49 ± 0.01	8.69 ± 0.01	4	2.03

B. Structure determination and refinement

The structures of both complexes have been solved by the Patterson method. From the three dimensional maps of the interatomic vectors it was possible to obtain the coordinates of the heaviest atoms (Pt and Cl). The structures were then solved by successive Fourier maps calculated after stepwise introduction of all the atoms. The refinement of the atomic parameters was carried out by means of eight cycles of 9 × 9 block-diagonal least squares procedures. The last three cycles in the case of complex (I) were performed with anisotropic thermal parameters for all the atoms. In the case of complex (II), only the heavy atoms have been refined anisotropically because of the smaller number of reflections above the limit of detectability and because the data in the case of complex (II) were less accurate since the crystal available for the X-ray data collection was rather poor. The imaginary part of the atomic scattering factor of the platinum[12] was introduced (correction made on the F_c values) and refinement was continued until the maximum shifts in the atomic coordinates on the average were less than $\frac{1}{3}$rd of the corresponding standard deviations.

The weighting scheme adopted in the refinement processes correspond to that suggested by Cruickshank and Philling[13].

At the end of the refinement process the *R* value

$$R = \frac{\Sigma||F_o|-|F_c||}{\Sigma F_o}$$

was 0.062 for 1454 independent reflections for complex (I) and 0.074 for 1132 independent reflections for complex (II) [For complex (II) during the refinement 322 reflections under the limit of detectability were discharged].

In the refined models the asymmetric centers C(2), C(5), C(7) have respectively the configurations *R*, *S*, *S* for complex (I) and *S*, *R*, *S* for complex (II).

The incorrect solutions with the C(7) carbon atom of the amine having the *R* configuration (according to the preparation of the compounds the amine has the *S* configuration) gave for the *R* factor the values of 0.073 and 0.080 for complex (I) and complex (II), respectively.

According to the Hamilton test[14] we may reject at a significance level less than 0.005 the hypothesis that the absolute configuration is that having the *R* configuration of the C(7) carbon atom. No attempt was made to localize the hydrogen atoms. The

TABLE 2a

FINAL ATOMIC PARAMETER OF COMPLEX (I)

A. Positional parameters
E.s.d. in unit of the last significant figure.

Atom	x	y	z
Pt	0.1633(1)	0.0370(1)	0.1938(1)
Cl(1)	0.1496(6)	0.2247(6)	0.0973(9)
Cl(2)	0.3022(5)	0.0706(6)	0.2541(9)
N	0.312(2)	−0.176(3)	0.216(4)
C(1)	0.053(2)	0.002(3)	0.065(4)
C(2)	0.034(2)	0.019(2)	0.234(4)
C(3)	0.024(2)	−0.082(3)	0.353(4)
C(4)	0.083(2)	−0.168(2)	0.302(5)
C(5)	0.176(2)	−0.120(2)	0.279(3)
C(6)	0.219(1)	−0.198(2)	0.181(2)
C(7)	0.371(2)	−0.233(3)	0.091(4)
C(8)	0.461(2)	−0.198(2)	0.137(3)
C(9)	0.358(2)	−0.361(3)	0.107(4)
C(10)	0.377(3)	−0.413(2)	0.251(4)
C(11)	0.367(1)	−0.531(2)	0.271(5)
C(12)	0.334(2)	−0.586(2)	0.130(4)
C(13)	0.314(2)	−0.530(3)	−0.017(4)
C(14)	0.329(2)	−0.415(2)	−0.035(4)

B. Thermal parameters
$T=\exp-\frac{1}{4}(B_{11}\cdot h^2\cdot a^{*2}+B_{22}\cdot k^2\cdot b^{*2}+B_{33}\cdot l^2\cdot c^{*2}+2B_{12}\cdot h\cdot k\cdot a^*\cdot b^*+2B_{13}\cdot h\cdot l\cdot a^*\cdot c^*+2B_{23}\cdot k\cdot l\cdot b^*\cdot c^*)$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	4.96(4)	3.86(4)	2.36(3)	0.12(5)	0.03(4)	0.12(4)
Cl(1)	7.36(47)	4.34(32)	3.77(29)	1.12(35)	0.26(35)	0.44(27)
Cl(2)	5.73(37)	4.68(36)	4.62(34)	0.66(29)	0.75(28)	0.08(26)
N	6.9(18)	4.8(13)	1.8(10)	1.5(11)	2.4(13)	0.1(10)
C(1)	4.3(13)	9.1(26)	4.1(13)	−0.4(14)	1.4(11)	0.5(15)
C(2)	3.6(11)	4.7(15)	6.6(18)	0.5(11)	0.5(11)	−1.8(14)
C(3)	7.5(20)	7.4(21)	4.9(16)	−0.4(18)	1.5(15)	3.0(15)
C(4)	5.9(16)	5.3(16)	6.5(18)	−1.5(14)	−0.5(17)	3.4(17)
C(5)	7.6(18)	3.4(10)	3.5(11)	−1.2(12)	−5.0(13)	0.6(10)
C(6)	3.8(10)	8.2(16)	0.2(6)	1.0(11)	0.2(8)	0.6(10)
C(7)	8.3(21)	5.7(15)	3.8(12)	0.7(10)	1.5(12)	−1.2(14)
C(8)	8.2(19)	3.9(11)	11.0(25)	−1.2(12)	2.7(17)	−2.0(12)
C(9)	8.3(23)	3.6(10)	4.9(15)	0.7(13)	1.2(11)	−0.3(10)
C(10)	9.4(25)	3.5(13)	4.9(14)	0.8(10)	−0.2(10)	1.1(10)
C(11)	6.5(15)	4.3(12)	9.1(18)	0.9(10)	2.6(15)	2.1(13)
C(12)	8.8(18)	3.4(11)	10.4(22)	1.7(13)	−1.0(12)	0.5(11)
C(13)	9.5(21)	6.0(18)	7.2(19)	0.8(10)	−1.0(10)	−1.8(12)
C(14)	13.0(31)	4.6(16)	7.2(20)	1.6(14)	2.3(17)	−2.2(14)

final atomic coordinates and anisotropic thermal factor of complex (I) are reported in Table 2a, and in Table 2b are listed the coordinates and the thermal factors for complex (II).

A list of the observed and calculated structure factors for both complexes can be obtained from the authors.

TABLE 2b

FINAL ATOMIC PARAMETERS FOR COMPLEX (II)

A. Positional parameters

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

Atom	*x*	*y*	*z*
Pt	0.3044(1)	0.943(1)	0.5455(1)
Cl(1)	0.3628(4)	0.6949(11)	0.6309(11)
Cl(2)	0.2298(4)	0.7494(10)	0.4877(14
N	0.172(1)	1.339(4)	0.482(3)
C(1)	0.357(1)	1.121(4)	0.669(4)
C(2)	0.371(1)	1.131(5)	0.522(4)
C(3)	0.357(1)	1.262(4)	0.400(4)
C(4)	0.295(1)	1.321(3)	0.429(3)
C(5)	0.257(1)	1.141(4)	0.443(4)
C(6)	0.205(1)	1.194(4)	0.558(4)
C(7)	0.118(1)	1.387(4)	0.565(4)
C(8)	0.092(1)	1.557(5)	0.506(4)
C(9)	0.075(1)	1.230(4)	0.567(3)
C(10)	0.072(1)	1.114(5)	0.696(4)
C(11)	0.029(1)	0.986(5)	0.686(4)
C(12)	−0.002(1)	0.955(4)	0.572(4)
C(13)	0.002(1)	1.066(6)	0.447(6)
C(14)	0.042(1)	1.199(4)	0.434(4)

B. Thermal parameters

Atom	*B*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt		3.45(3)	2.25(3)	3.28(4)	0.07(4)	0.04(5)	−0.25(5)
Cl(1)		5.4(3)	3.4(3)	4.4(4)	0.7(3)	0.2(4)	0.2(3)
Cl(2)		4.6(4)	2.2(2)	8.2(7)	−0.7(2)	−0.8(4)	0.0(3)
N	4.1(5)						
C(1)	3.9(6)						
C(2)	4.7(7)						
C(3)	3.9(6)						
C(4)	2.4(4)						
C(5)	3.2(5)						
C(6)	4.0(6)						
C(7)	3.6(6)						
C(8)	4.5(6)						
C(9)	2.7(5)						
C(10)	4.1(7)						
C(11)	5.0(8)						
C(12)	3.5(5)						
C(13)	6.3(8)						
C(14)	4.2(6)						

RESULTS AND DISCUSSION

In Table 3 is given a list of the most significant dihedral angles for the two diastereoisomeric complexes. In Figs. 1 and 2, molecular models for the two complexes are shown; the absolute configurations of the asymmetric centers are indi-

TABLE 3

SOME RELEVANT DIHEDRAL ANGLES

Trans conformation = 180°.

	Complex (I)	Complex (II)
Cl(1)–Pt–C(5)–C(4)	123	261
Cl(1)–Pt–C(5)–C(6)	242	147
Cl(2)–Pt–C(5)–C(4)	166	188
Cl(2)–Pt–C(5)–C(6)	−74	74
C(1)–C(2)–C(3)–C(4)	37	−39
C(2)–C(3)–C(4)–C(5)	49	−49
C(3)–C(4)–C(5)–Pt	−33	34
Pt–C(5)–C(6)–N	81	179
C(3)–C(4)–C(5)–C(6)	199	150
C(4)–C(5)–C(6)–N	201	62
C(5)–C(6)–N–C(7)	194	173
C(6)–N–C(7)–C(8)	177	168
C(6)–N–C(7)–C(9)	−61	−64
N–C(7)–C(9)–C(10)	117	96
N–C(7)–C(9)–C(14)	−65	−79

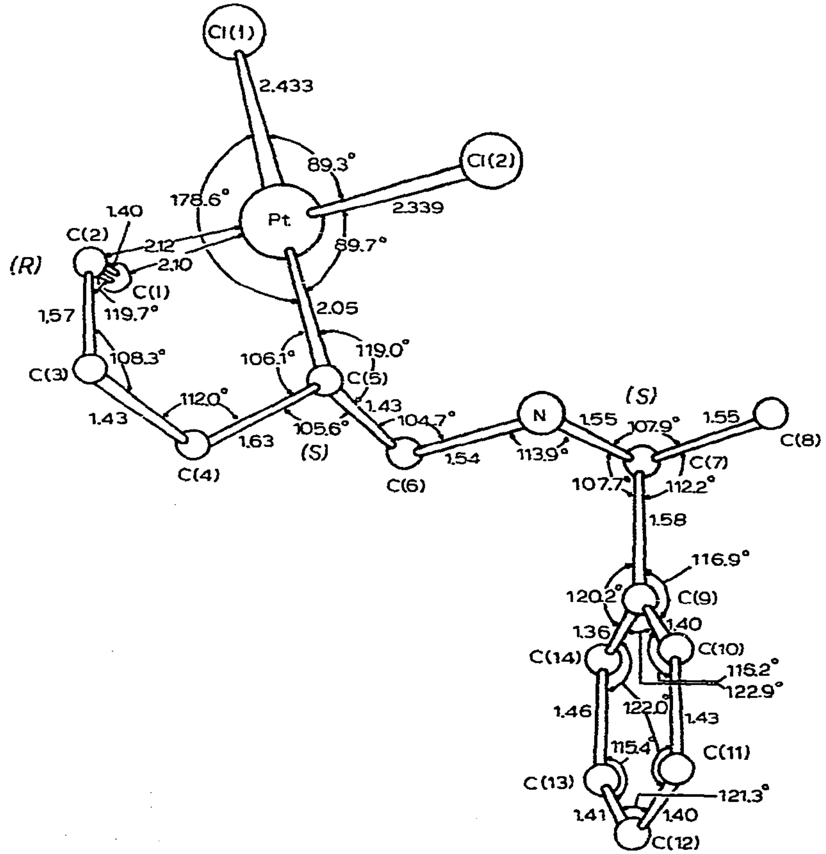


Fig. 1. Molecular model for complex (I). Bond lengths and bond angles are indicated; their estimated standard deviations are 0.02 Å and 1°, respectively. The absolute configurations of the asymmetric centers are also reported.

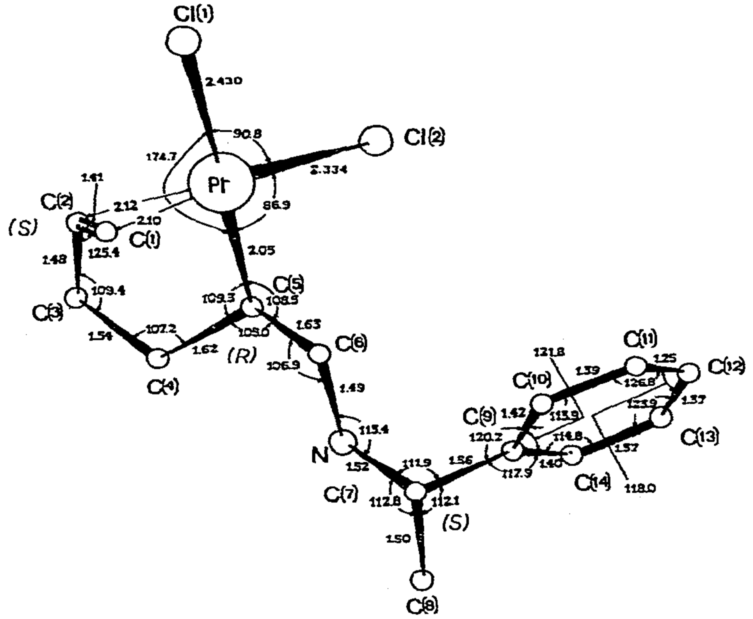


Fig. 2. Molecular model for complex (II). Bond lengths and bond angles are indicated; their estimated standard deviations (e.s.d.) are 0.02 Å and 1°, respectively. The absolute configurations of the asymmetric centers are also indicated.

cated, together with bond lengths and bond angles. Because of the large errors in the atomic parameters of the light atoms, many differences in bond lengths and bond angles are not significant. However, the overall geometry involving the light atoms is correct: in both compounds the benzene rings are planar, as expected, and the mean square distance for C(7) and the six atoms of the benzene ring from the best plane passing through them is 0.01 Å and 0.03 Å for complex (I) and (II), respectively.

The most significant features of the molecular geometries are the following: (*cf.* Table 3 and Figs. 1 and 2):

(1). In both compounds the ligands around the platinum atom are found in the usual square-planar arrangement, with the two chlorine atoms in *cis* positions, the C(5) carbon atom σ-bonded to the Pt atom [average Pt–C(5) = 2.050 ± 0.004 Å*] and the center of the double bond (average Pt–"Center"** = 1.990 ± 0.003 Å) occupy the other sites of coordination.

(2). The large *trans*-effect of the σ-bonded carbon atom, C(5), is reflected in the significant increase of the Pt–Cl(1) bond length (average 2.431 ± 0.002 Å) with respect to the Pt–Cl(2) bond length (average 2.336 ± 0.003 Å). On the other hand this latter value is also significantly larger than that usually quoted for Pt–Cl distances[8,9,15], because of the *trans*-effect of the coordinated double bond.

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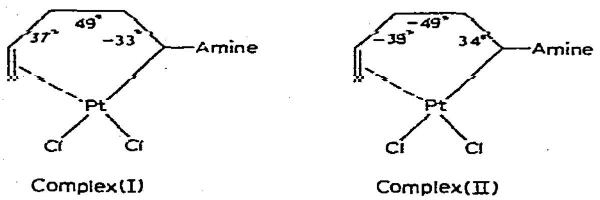
* In the present study the deviation associated to any average value indicate the range of the individual values.

** With "Center" we indicate the center of the CH_2=CH–double bond.

(3). The conformation of the ring obtained by the coordination of the 1,5-hexadiene to the Pt atom is characterized by a sequence of internal rotation angles which are reported in the following scheme:



The conformations of these rings for the two diastereoisomers are equivalent within the experimental errors but mirror images. This is in agreement with the circular dichroism spectra of the two complexes which correspond in the absorption region of the olefin chromophore to enantiomeric configurations^3.

(4). The stereochemistry of the two molecules is illustrated by the projections of a portion of the molecule along the Pt–C(5) and C(5)–C(6) bonds (Fig. 3). The major difference between the two complexes is indeed in the conformation. More precisely, while the conformations in the views along the Pt–C(5) bonds correspond to mirror images, the internal rotation angle around the C(5)–C(6) bond is nearly *trans* for complex (II), whereas for complex (I) its value is near that of a *gauche* conformation: Pt–C(5)–C(6)–N is 179° and 81° and C(4)–C(5)–C(6)–N is 62° and

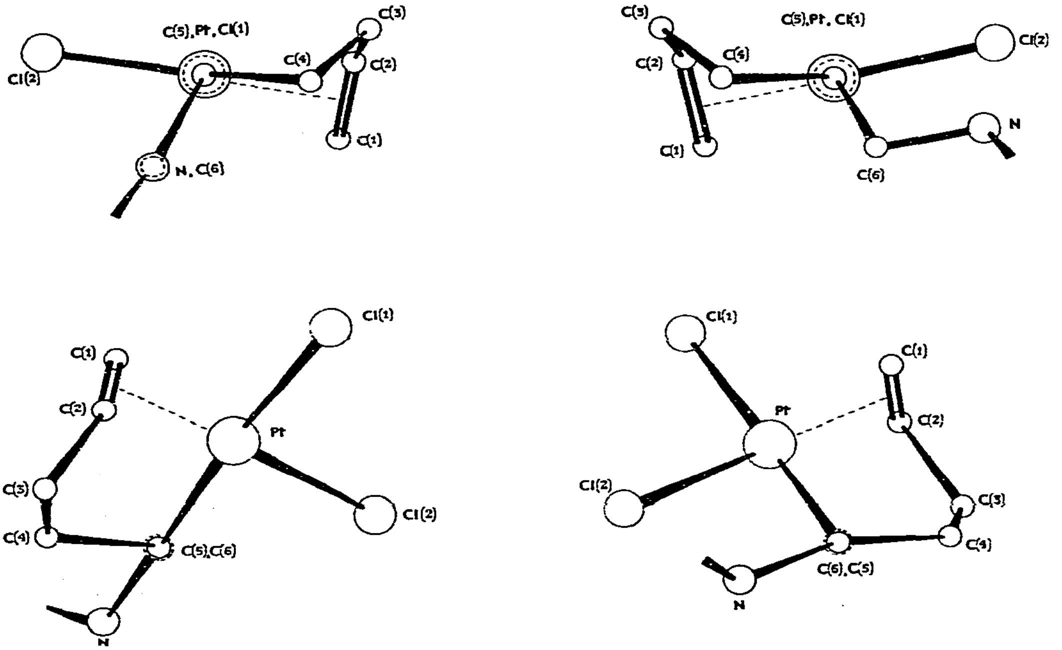


Fig. 3. Projections of the molecular models for complex (I) (left side) and for complex (II) (right side). The projections along the Pt–Cl(1) bond are reported on the top of the figure, while on the bottom are represented the projections along the C(5)–C(6) bond.

201° for complex (II) and complex (I), respectively. This latter conformation is responsible of short intramolecular contacts between atoms separated by three or more bonds. The intramolecular N---Cl(2) and N---Pt distances are 3.04 Å and 3.55 Å in complex (I) and they became greater than 4.0 Å in complex (II); on the other hand the C(4)---N intramolecular distance is 2.93 Å in complex (II) and it increases to 3.77 Å in complex (I). In complex (I) the hydrogens bonded to the nitrogen atom, which unfortunately can not be localized, must also experience short intramolecular contacts. The internal rotation angles around the N–C(7) bond are essentially equivalent for the two complexes with the methyl group in *trans*-conformation C(6)–N–C(7)–C(8) = 177° and 168° for complex (I) and complex (II), respectively. The same conformation has already been observed in other platinum complexes containing the (*S*)-α-methylbenzylamine[5,8,11].

(5). The mode of packing of the molecules in the two crystal structures is shown in Fig. 4 for complex (I) and in Figs. 5 and 6 for complex (II). The shortest

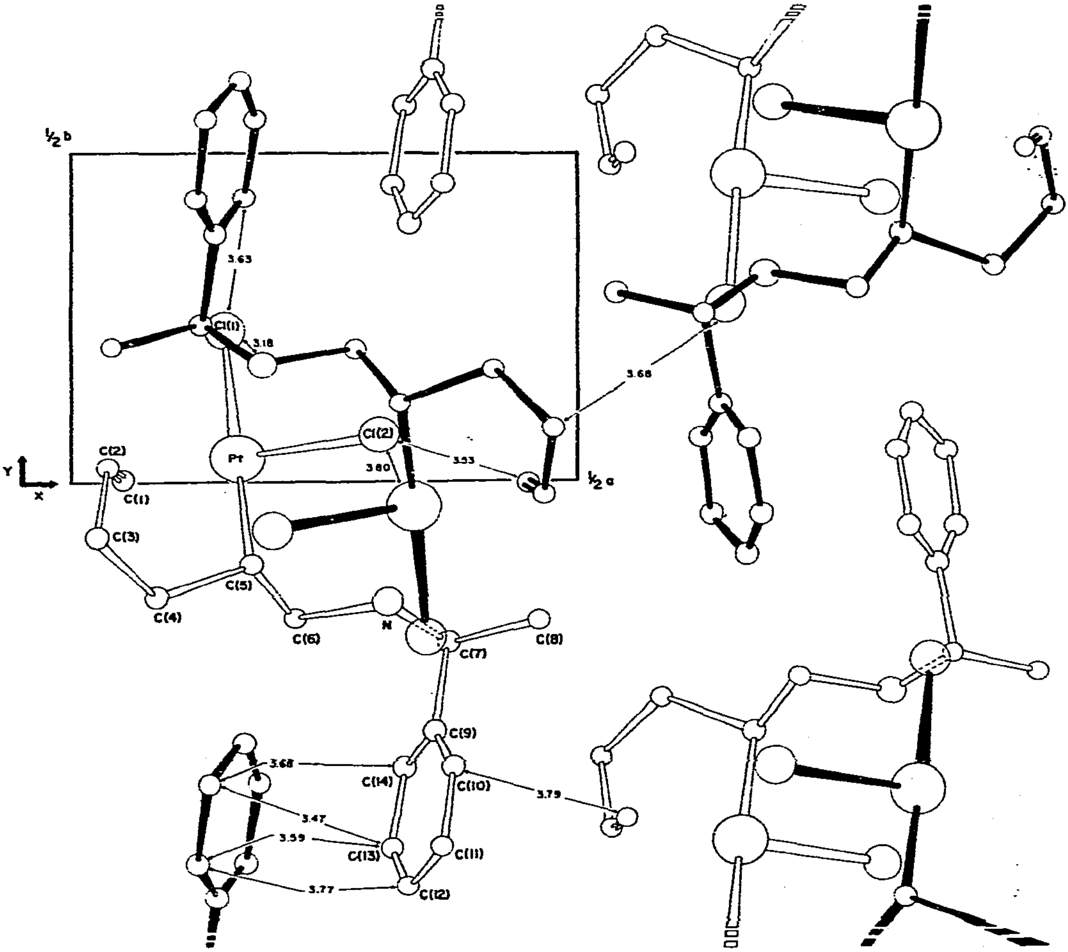


Fig. 4. Molecular packing of complex (I) as view along the *c* axis. The shortest intermolecular constants are reported.

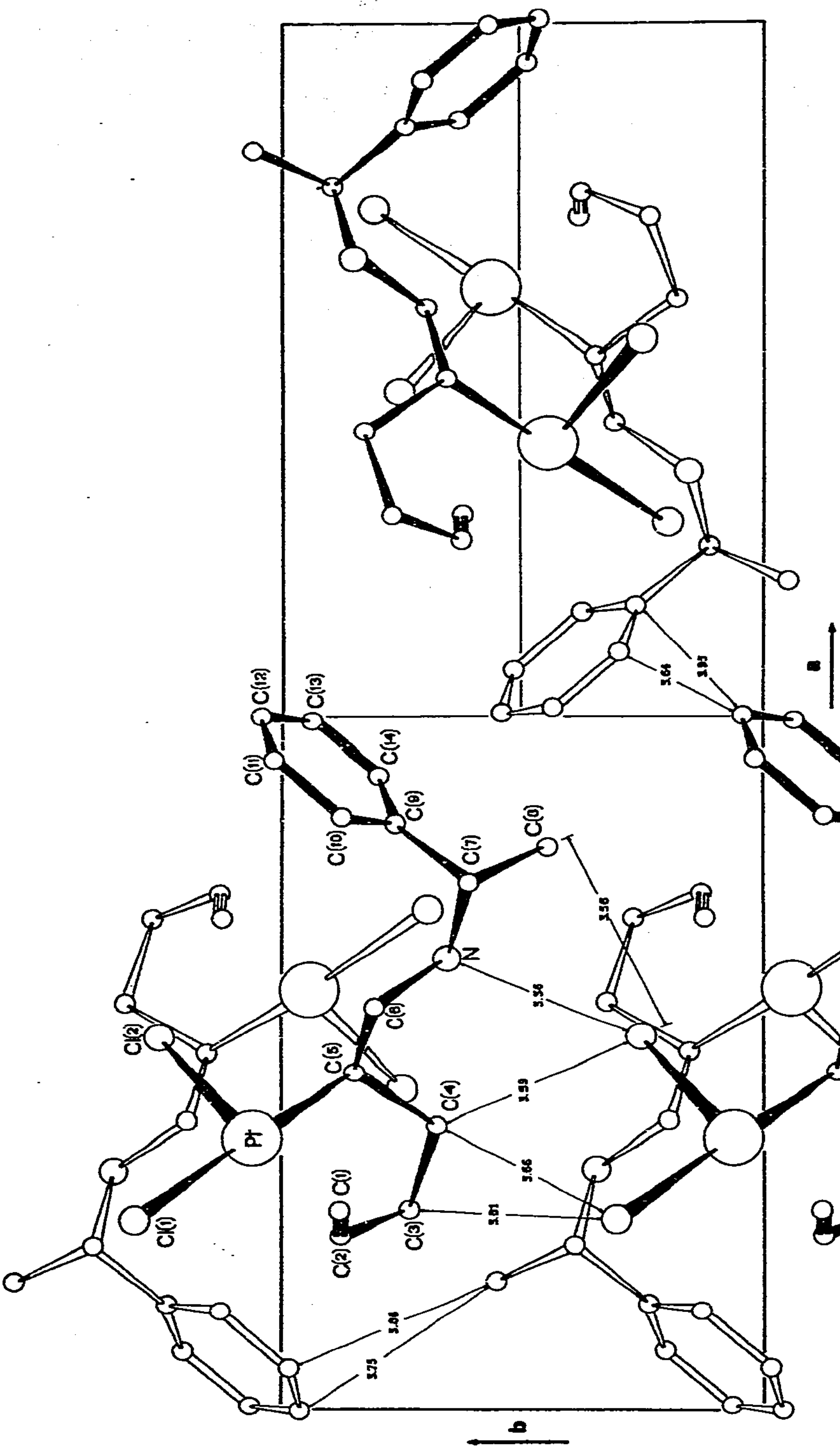


Fig. 5. Molecular packing of complex (II) as view along the c axis. The shortest intermolecular contacts are reported.

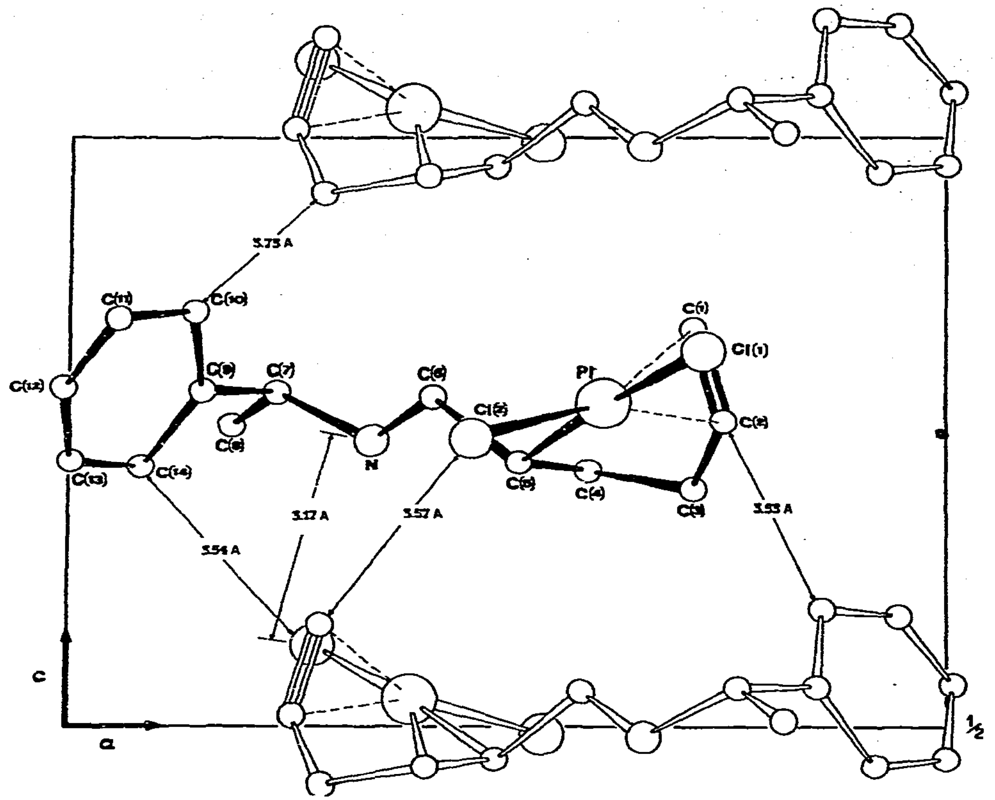


Fig. 6. Molecular packing of complex (II) as view along the *b* axis. The shortest intermolecular contacts are reported.

intermolecular distances less than 4.0 Å are indicated. It is worth noting that a short intermolecular distance between the nitrogen and only one chlorine atom in present in complex (II) N---Cl(1)=3.17 Å, while the nitrogen atom experiences two short contacts, one intramolecular N---Cl(2)=3.04 Å and one intermolecular N---Cl(1)=3.18 Å, in complex (I). If we suppose that the negative charge is localized on the chlorine atoms and the positive charge on the nitrogen atom, a more uniform distribution of the charges is achieved in complex (I) in which then electrostatic interactions should play an essential role in stabilizing the whole structure.

As reported above, complex (I) and complex (II) are obtained in almost 1/1 ratio from the reaction of dichloro(1,5-hexadiene)platinum(II) with (*S*)-α-methylbenzylamine and standing in CH_2Cl_2 solution, complex (I) is transformed in complex (II). As suggested by Bosnich[16], this asymmetric transformation can be called antiracemization.

The mechanism of transformation proposed by the authors of ref. 3 is based on the existence of an equilibrium between complex (I) and complex (II) via a dissociation and subsequent attack of the amine group.

On the basis of the solved crystal structure we believe that for the isolated molecule there should be no appreciable differences in the relative stability of the two complexes. This is based on the following consideration: The asymmetric centers in complex (I) have the absolute configuration in the sequence *RSS* (*cf.* Fig. 1). We expect no conformational change for the enantiomeric sequence *SRR*. This latter sequence corresponds to that present in complex (II) with the only exception of an opposite configuration of the amine (*cf.* Fig. 2). A change in this sense for complex (II) on the basis of space filling molecular models does not show any short intramolecular contacts between non-bonded atoms. Thus, for the isolated molecule, in which free rotation around single bonds is allowed, it is difficult to visualize preferred conformations for complex (II) in view of the possibility of the concerted coupling of rotations around the C(5)–C(6), C(6)–N and N–C(7) single bonds. A tentative explanation of the antiracemization process could be the occurrence of selective interactions with solvent molecules*. Further investigations would be required in order to confirm the existence of this type of solute solvent interactions.

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* Solvent interactions are clearly indicated by the fact that the rate of the antiracemization process depends on the solvent used, being fast for example in methylene chloride and very slow in methanol solutions[17].