The Crystal and Molecular Structure of cis-Dichloro[(R)-α-methylbenzylamine]-[(S)-1,2,2-trimethylpropyl (R)-vinyl ether]platinum(II)

By Franco Sartori and Leonardo Leoni

Istituto di Mineralogia dell'Università di Pisa, Italy

The crystal and molecular structure of the title compound has been determined by single-crystal three-dimensional X-ray analysis. The crystals belong to the orthorhombic system, space group $P2_12_12_1$, with $a=25.56(3)$, $b=11.37(1)$, $c=6.84(1)$ Å, $Z=4$. The structure, solved by standard methods, has been refined by full-matrix least-squares methods to a final conventional R index of 0.069, by use of 1764 independent reflexions collected by the Weissenberg method with Cu $K\alpha$ radiation. Chemical knowledge of the absolute configuration of the amine and vinyl ether indicated the absolute configuration of the whole molecule. The platinum atom has a square-planar configuration, but its principal coordination plane does not bisect the olefinic double bond, the midpoint of such a bond lying 0.38 Å above this plane. Furthermore the double bond is slightly displaced from the perpendicular to the coordination plane. While the molecules are held together only by van der Waals interactions, a hydrogen bond, which could play an important role in determining the conformation of the coordinated vinyl ether, links the nitrogen of the amine group and the oxygen atom.

Introduction

The current interest in olefin–platinum complexes with optically active ligands stems largely from their utility in the study of stereospecific coordination phenomena.

After the solution, in our laboratory, of the structure of the *trans*-dichloro(benzylamine)[(2R,3S)3-methyl-1-pentene]platinum(II) complex (Merlino, Lazzaroni & Montagnoli, 1971), we undertook the investigation of the crystal and molecular structure of *cis*-dichloro-[(R)-α-methylbenzylamine] [(S)-1,2,2-trimethylpropyl-vinyl ether]platinum(II), for which also two diastereo-isomers are possible. The n.m.r. spectra however gave evidence of the formation in the crystallization of only one of them, which probably represents the more stable one at least in the solid state. The purpose of this research was to establish its absolute configuration; the chemical knowledge of the configuration of two asymmetric groupings present in the molecule, besides the olefin asymmetric centre, made this determination possible (Mathieson, 1956).

Information about the conformation of the molecule in the solid state was briefly reported in a preliminary communication (Sartori, Leoni, Lazzaroni & Salvadori, 1974); the results of the full crystal structure investigation and refinement of the compound are reported here.

Experimental

As previously reported (Sartori *et al.*, 1974), the compound was prepared by displacement of ethylene with (S)-1,2,2-trimethylpropyl vinyl ether from the corresponding ethylene–Pt(II) complex. Beautiful air-stable yellow crystals were grown from solution in a mixture of acetone, diethyl ether and pentane (1:1:2). Most of them were blade-shaped, platy normal to **a**. From Weissenberg and precession photographs the space group was determined as $P2_12_12_1$. The lattice constants were derived from least-squares refinement of powder diffraction data: $a=25.56\pm0.03$, $b=11.37\pm0.01$, $c=6.84\pm0.01$ Å; $V=1988$ Å^3. The formula weight is 515.4 ($C_{16}H_{27}NOCl_2Pt$); the density, measured at 20°C by flotation in a concentrated aqueous solution of ferric sulphate, is $D_m=1.70$ g cm^{-3}; the calculated density is $D_c=1.72$ g cm^{-3} for $Z=4$. The linear absorption coefficient for Cu $K\alpha$ radiation ($\lambda=1.5418$ Å) is $\mu=159.4$ cm^{-1}. The intensity data were recorded with nickel-filtered Cu $K\alpha$ radiation by means of Weissenberg photographs, with the multiple-film technique and integration process. Seven layers with c as rotation axis ($l=0$ to 6) were recorded and 2294 independent reflexions (1764 observed) were collected. The intensities, measured with a Nonius microdensitometer, have been corrected for Lorentz and polarization factors and for incipient but incomplete $\alpha_1-\alpha_2$ spot doubling. The absorption correction was performed by computing the transmission factors by means of a program (Alberti, 1968) based on the Monte Carlo method proposed by Alberti & Gottardi (1966) for crystals of any shape and absorption; for this purpose the dimensions of the crystal used for intensity data collection (a small parallelepiped $0.09\times0.16\times0.44$ mm in size, cleaved from a larger plate) were carefully measured under a microscope with a micrometer eyepiece and its faces were identified. For this crystal and for the linear absorption coefficient of the compound the transmission coefficients were found to range from 0.11 to 0.35.

Determination and refinement of the structure

The position of the platinum atom was readily located from a three-dimensional Patterson synthesis. After a cycle of least-squares refinement of the Pt coordinates

Table 1. *Observed and calculated structure factors*

Columns within each group contain the values h, $10\,F_o$, $10|F_c|$ and α (expressed in millicycles). Six reflexions, which are probably strongly affected by secondary extinction, are marked with an asterisk.

by means of the full-matrix least-squares program of Busing, Martin & Levy, adapted for the X-RAY 70 System (Stewart, 1970), a difference Fourier synthesis revealed all the nonhydrogen atoms.

The knowledge of the absolute configuration of the amine and the vinyl ether used (R and S respectively), allowed us to choose, between the two possible enantiomorphous arrangements of the atoms, the solution corresponding to the correct absolute configuration of the whole molecule.

Three subsequent least-squares refinement cycles of positional coordinates and isotropic thermal parameters of all the non-hydrogen atoms yielded an agreement index $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.091$. Two more refinement cycles, in which anisotropic temperature factors in the form $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$ were introduced for platinum and chlorine atoms, reduced the R_1 value to 0.074.

During the later stages of refinements six reflexions (marked with an asterisk in Table 1) were excluded from further refinement because they are probably affected by secondary extinction.
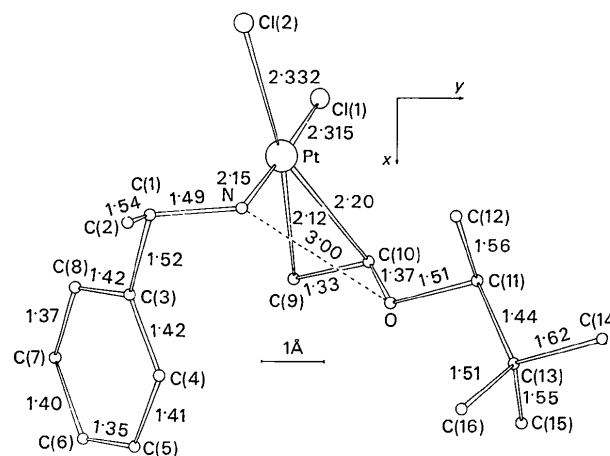

Fig. 1. The molecular structure of cis-dichloro[(R)-α-methyl-benzylamine] [(S)-1,2,2-trimethylpropyl (R)-vinyl ether]-platinum(II).

Moreover, while initially unit weights were assigned to all observed reflexions, at this point the following weighting scheme was introduced: $\sqrt{w} = 1.0/(A + F_o + BF_o^2)$; following the suggestions of Cruickshank (Stewart, 1970) that the coefficients A and B can be conveniently chosen as $A = 2F_{min}$ and $B = 2/F_{max}$, we found most suitable for them the values $A = 32.0$, $B = 0.005$. A final analysis of the average $w|\Delta F|^2$ as a function of $|F_o|$ and $\sin\theta$ showed in fact a smooth distribution indicating the validity of the weighting scheme.

The final R values obtained were $R_1 = 0.069$ and $R_2 = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2} = 0.089$. The shifts of the parameters in the last cycle were less than one tenth of the corresponding standard deviations.

The whole least-squares refinement process was performed without introduction of the hydrogen atoms. In a three-dimensional Fourier difference synthesis calculated at the end of the refinement only a few hydrogen atoms were in fact unequivocally located (among them the proton involved in an intra-molecular hydrogen bond and some of those bonded to the carbons of the benzene ring), but for most of them the most reasonable positions were occupied by very smeared peaks or obscured by residual electron density from the heavier atoms.

The atomic scattering factors used in the structure-factor calculations were taken from *International Tables for X-ray Crystallography* (1962).

The observed and calculated structure factors are compared in Table 1. The final positional and thermal parameters are given in Table 2.

Description and discussion of the structure

The molecular structure of the examined diastereo-isomer is illustrated in Fig. 1, which shows a projection of the molecule onto the ab plane. The chiral centre of the coordinated vinyl group appears to have an absolute configuration R, and then the diastereoisomer is defined as RRS.

Table 2. *Positional and thermal parameters for the nonhydrogen atoms*

Standard deviations are given in parentheses. Values of the anisotropic thermal parameters for platinum and chlorine atoms are respectively multiplied by 10^5 and by 10^4.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.03647 (4)	0.83667 (8)	0.28517 (14)	166 (1)	627 (5)	1823 (19)	23 (3)	16 (5)	11 (11)
Cl(1)	0.0007 (3)	0.8888 (6)	−0.0134 (10)	22 (1)	88 (5)	162 (15)	18 (2)	−4 (3)	12 (8)
Cl(2)	−0.0455 (3)	0.7832 (7)	0.4061 (11)	17 (1)	104 (6)	214 (18)	−5 (2)	3 (3)	15 (8)

	x	y	z	B (Å^2)		x	y	z	B (Å^2)
C(1)	0.0729 (9)	0.6509 (24)	0.5770 (38)	3.82 (45)	C(10)	0.1009 (10)	0.9614 (23)	0.2399 (44)	4.37 (49)
C(2)	0.0772 (12)	0.6180 (29)	0.7955 (58)	5.68 (62)	C(11)	0.1147 (11)	1.1112 (25)	0.4995 (44)	4.42 (52)
C(3)	0.1225 (10)	0.6212 (21)	0.4665 (40)	3.47 (43)	C(12)	0.0747 (17)	1.0847 (40)	0.6665 (73)	7.79 (95)
C(4)	0.1722 (12)	0.6645 (31)	0.5230 (47)	5.31 (56)	C(13)	0.1631 (13)	1.1638 (35)	0.5637 (53)	6.08 (67)
C(5)	0.2166 (14)	0.6300 (29)	0.4158 (55)	5.78 (72)	C(14)	0.1488 (14)	1.2889 (33)	0.6631 (58)	6.51 (80)
C(6)	0.2115 (14)	0.5586 (30)	0.2589 (57)	6.32 (72)	C(15)	0.1990 (22)	1.1727 (55)	0.3822 (95)	11.61 (1.58)
C(7)	0.1624 (13)	0.5148 (31)	0.2035 (59)	6.19 (67)	C(16)	0.1937 (22)	1.0898 (51)	0.7073 (100)	11.36 (1.53)
C(8)	0.1178 (11)	0.5466 (24)	0.3010 (51)	4.79 (51)	N	0.0679 (9)	0.7809 (20)	0.5615 (36)	4.20 (43)
C(9)	0.1122 (11)	0.8563 (23)	0.1644 (40)	4.40 (52)	O	0.1258 (7)	0.9921 (16)	0.4099 (28)	3.98 (33)

A C 32B – 10*

Table 3. *Bond distances (Å) with their standard deviations*

Pt—Cl(1)	2·315 (7)	C(6)—C(7)	1·40 (5)
Pt—Cl(2)	2·332 (7)	C(7)—C(8)	1·37 (5)
Pt—C(9)	2·12 (3)	C(8)—C(3)	1·42 (4)
Pt—C(10)	2·20 (3)	C(9)—C(10)	1·33 (4)
Pt—X*	2·05 (3)	C(10)-O	1·37 (3)
Pt—N	2·15 (2)	O——C(11)	1·51 (3)
N——C(1)	1·49 (4)	C(11)-C(12)	1·56 (5)
C(1)-C(2)	1·54 (5)	C(11)-C(13)	1·44 (5)
C(1)-C(3)	1·52 (4)	C(13)-C(14)	1·62 (6)
C(3)-C(4)	1·42 (4)	C(13)-C(15)	1·55 (7)
C(4)-C(5)	1·41 (5)	C(13)-C(16)	1·51 (7)
C(5)-C(6)	1·35 (5)		

* X defines the midpoint of the olefinic double bond.

Table 4. *Bond angles with their standard deviations*

Cl(1)–Pt——Cl(2)	91°25 (16)'
Cl(1)–Pt——C(9)	89 26 (46)
Cl(1)–Pt——C(10)	90 23 (47)
Cl(1)–Pt——X*	89 55 (49)
Cl(1)–Pt——N	177 26 (32)
Cl(2)–Pt——N	86 58 (38)
Cl(2)–Pt——C(9)	170 49 (44)
Cl(2)–Pt——C(10)	153 6 (43)
Cl(2)–Pt——X*	170 44 (48)
C(9)—Pt——C(10)	35 59 (60)
C(9)—Pt——N	91 50 (58)
C(10)-Pt——N	91 58 (58)
N——Pt——X*	92 0 (59)
Pt——C(9)—C(10)	75 (1·6)°
Pt——C(10)-C(9)	69 (1·6)
C(9)—C(10)-O	117 (2·4)
C(10)-O——C(11)	119 (2)
O——C(11)-C(12)	104 (2)
O——C(11)-C(13)	109 (2)
C(12)-C(11)-C(13)	115 (3)
C(11)-C(13)-C(14)	107 (3)
C(11)-C(13)-C(15)	107 (3)
C(11)-C(13)-C(16)	114 (3)
C(14)-C(13)-C(15)	114 (4)
C(15)-C(13)-C(16)	105 (4)
C(14)-C(13)-C(16)	109 (4)
N——C(1)—C(2)	108 (2)
N——C(1)—C(3)	105 (2)
C(2)—C(1)—C(3)	112 (2)
C(1)—C(3)—C(4)	122 (2)
C(1)—C(3)—C(8)	117 (2)
C(3)—C(4)—C(5)	119 (3)
C(4)—C(5)—C(6)	120 (3)
C(5)—C(6)—C(7)	121 (3)
C(6)—C(7)—C(8)	121 (3)
C(7)—C(8)—C(3)	118 (3)
C(8)—C(3)—C(4)	120 (2)

* X defines the midpoint of the olefinic double bond.

The bond distances are reported both in Fig. 1 and in Table 3, while the bond angles are listed in Table 4; finally some selected least-squares planes and the angles between pairs of them are given in Table 5. These structural parameters were calculated respectively by means of the programs *BONDLA* and *LSQPL*; both of them are incorporated in the 'Crystal Structure Calculations System X-RAY 70' (Stewart, 1970).

The bond distances concerning the platinum atom agree well with similar data available in the literature (Alderman, Owston & Rowe; 1960, Benedetti, Corradini & Pedone, 1969; Spagna & Zambonelli, 1971; Merlino *et al.*, 1971; Cotton, Francis, Frenz & Tsutsui, 1973); among such distances it is interesting to observe that our platinum–chlorine bond lengths are, within the error limits, nearly equal, unlike other Pt–olefin complexes in which the bonds *trans* to the olefin appear significantly longer than the *cis* ones. Such equality is well explained by observing that in our compound one Pt–Cl bond is *trans* to the olefin while the other is *trans* to a N-bonded amine; in fact, the influence of modest σ-donor ligands such as N-bonded amines is comparable with that of modest σ-donors which are also π-acceptors such as olefins, both of them giving rise to *trans* Pt–Cl bond lengths up to 2·33 Å (Hartley, 1973).

The various ligand–Pt–ligand angles are typical of an almost undistorted square-planar configuration of the platinum atom; the second least-squares plane listed in Table 5 confirms that the atoms Pt, Cl(1), Cl(2) and N really lie in the same plane, since their
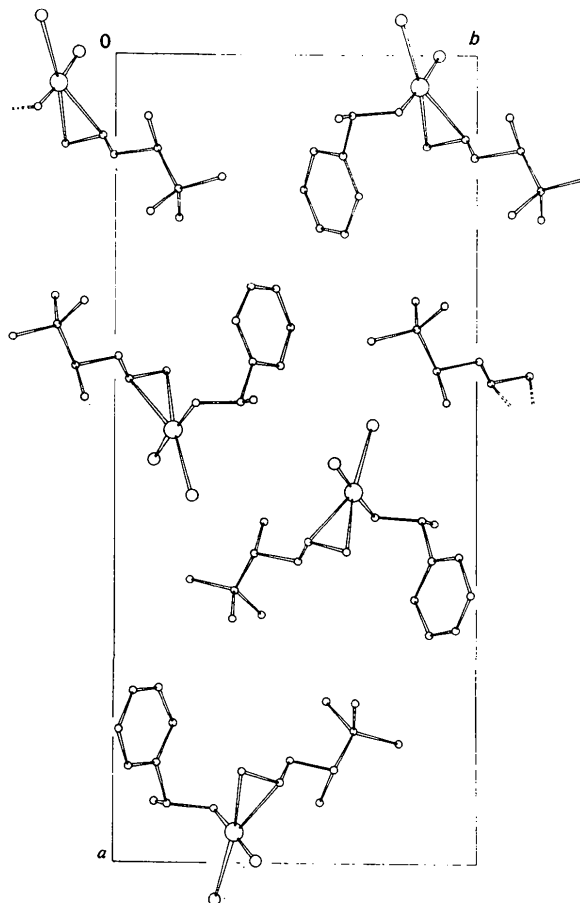

Fig. 2. Projection of the crystal structure of *cis*-dichloro[(R)-α-methylbenzylamine] [(S)-1,2,2-trimethylpropyl (R)-vinyl ether]platinum(II) along [001].

Table 5. *Parameters of some selected least-squares planes*

The equation of the plane is in the form $Ax + By + Cz = D$, where x, y and z are fractional coordinates, calculated after Schomaker, Waser, Marsh & Bergman (1959).

Plane		A	B	C	D
1	Atoms defining the plane				
	C(3), C(4), C(5), C(6), C(7), C(8)	−3·0185	9·0180	−4·0868	3·3323
	Deviations: C(3), −0·007; C(4) 0·003; C(5) −0·004; C(6) 0·008; C(7) −0·012; C(8) 0·011; C(1) −0·041 Å				
2	Atoms defining the plane				
	Pt, Cl(1), Cl(2), N	−3·1270	10·5863	2·3510	9·3876
	Deviations: Pt 0·026; Cl(1) −0·013; Cl(2) 0·000; N −0·014; X* 0·376; C(9) −0·287; C(10) 1·039 Å				
	The acute angle between plane 2 and plane 1 is 56·80°.				
3	Atoms defining the plane				
	Pt, N, C(1)	23·6463	0·5964	−2·5719	0·6279
	The acute angles between plane 3 and planes 1 and 2 are 80·97 and 78·84° respectively.				
4	Atoms defining the plane				
	Pt, C(9), C(10)	10·3232	−3·1652	5·9605	−0·5720
	The acute angle between plane 4 and plane 2 is 89·48°.				

* X defines the midpoint of the olefinic double bond.

mean deviation from the plane is only 0·013 Å. On the other hand the mid-point of the olefin C(9)–C(10) double bond deviates by as much as 0·38 Å from the plane. Such a value, apart from the dramatically greater deviation of 0·59 Å reported for PtCl(acac) (H_2C=CHOH) (where acac⁻ is the acetylacetonate anion), is the highest of a series of deviations reported by Cotton *et al.* (1973) for platinum(II) π-complexes. The plane defined by the C(9)–C(10) double bond and by the Pt atom lies practically perpendicular to the plane of the square of coordination (dihedral angle 89°29′); however, within the Pt, C(9), C(10) plane, the double bond appears slightly displaced (6°20′) from the perpendicular to the coordination plane. Furthermore, Table 5 shows that the Pt,N,C(1) plane deviates from perpendicularity to the Pt,Cl(1),Cl(2),N plane (dihedral angle 78°50′).

All the other distances and angles, not involving the Pt atom, are acceptable within the limits of the large standard deviations in the positional parameters of the lighter atoms. The atoms of the benzene ring lie in a plane (mean deviation from the best plane 0·017 Å), which appears to be inclined toward the Pt atom [C(3)···Pt distance = 3·52 Å] and contains also the C(1)–H bond. Finally the methyl group C(2) is in a quasi-*anti* position with respect to Pt.

Noteworthy is the presence of an intramolecular hydrogen bond between the nitrogen of the amine group and the oxygen atom, which can be inferred from the N···O distance as low as 3·00 Å. Such a bond is confirmed also by inspection of the ΔF map in which the proton involved in this bond is one of the few hydrogen atoms clearly visible; from its coordinates ($x = 0.0961$, $y = 0.8321$, $z = 0.5476$) we calculated distances N–H = 0·93 Å and H···O = 2·18 Å and an angle N–H–O = 146°29′, which are in a good agreement with the values reported for the N–H···O bond by Hamilton & Ibers (1968).

There are no hydrogen bonds between different molecules. Since all the intermolecular contacts cor-

respond to distances greater than 3·50 Å (the shortest intermolecular distance, 3·55 Å, being that of the contact between C(1) and the symmetry-equivalent $[-x, y-\frac{1}{2}, \frac{1}{2}-z]$ of Cl(1)), we can conclude that the molecules of *cis*-dichloro[(R)-α-methylbenzylamine]-[(S)-1,2,2-trimethylpropyl (R)-vinyl ether]platinum(II) are held together only by van der Waals interactions.

A drawing of the molecular packing, as viewed along c, is given in Fig. 2.

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