

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

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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)[(2*R*,3*S*)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*)- $\alpha$ -methylbenzylamine] [(*S*)-1,2,2-trimethylpropyl-vinyl ether]platinum(II), for which also two diastereoisomers 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:  $a=25.56 \pm 0.03$ ,  $b=11.37 \pm 0.01$ ,  $c=6.84 \pm 0.01$  Å;  $V=1988$  Å<sup>3</sup>. The formula weight is 515.4 (C<sub>16</sub>H<sub>27</sub>NOCl<sub>2</sub>Pt); the density, measured at 20°C by flotation in a concentrated aqueous solution of ferric sulphate, is  $D_m=1.70$  g cm<sup>-3</sup>; the calculated density is  $D_c=1.72$  g cm<sup>-3</sup> for  $Z=4$ . The linear absorption coefficient for Cu  $K\alpha$  radiation ( $\lambda=1.5418$  Å) is  $\mu=159.4$  cm<sup>-1</sup>. 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 × 0.16 × 0.44 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<sub>o</sub>*, 10|*F<sub>c</sub>*| and  $\alpha$  (expressed in millicycles). Six reflexions, which are probably strongly affected by secondary extinction, are marked with an asterisk.

h	10 F <sub>o</sub>	10  F <sub>c</sub>	α	h	10 F <sub>o</sub>	10  F <sub>c</sub>	α	h	10 F <sub>o</sub>	10  F <sub>c</sub>	α
0 10 0	16 127	16 127	0	10 0 10	16 127	16 127	0	20 0 0	32 254	32 254	0
0 20 0	32 254	32 254	0	10 0 20	16 127	16 127	0	20 0 10	32 254	32 254	0
0 30 0	48 381	48 381	0	10 0 30	16 127	16 127	0	20 0 20	32 254	32 254	0
0 40 0	64 508	64 508	0	10 0 40	16 127	16 127	0	20 0 30	32 254	32 254	0
0 50 0	80 635	80 635	0	10 0 50	16 127	16 127	0	20 0 40	32 254	32 254	0
0 60 0	96 762	96 762	0	10 0 60	16 127	16 127	0	20 0 50	32 254	32 254	0
0 70 0	112 889	112 889	0	10 0 70	16 127	16 127	0	20 0 60	32 254	32 254	0
0 80 0	128 1016	128 1016	0	10 0 80	16 127	16 127	0	20 0 70	32 254	32 254	0
0 90 0	144 1143	144 1143	0	10 0 90	16 127	16 127	0	20 0 80	32 254	32 254	0
0 100 0	160 1270	160 1270	0	10 0 100	16 127	16 127	0	20 0 90	32 254	32 254	0
0 110 0	176 1397	176 1397	0	10 0 110	16 127	16 127	0	20 0 100	32 254	32 254	0
0 120 0	192 1524	192 1524	0	10 0 120	16 127	16 127	0	20 0 110	32 254	32 254	0
0 130 0	208 1651	208 1651	0	10 0 130	16 127	16 127	0	20 0 120	32 254	32 254	0
0 140 0	224 1778	224 1778	0	10 0 140	16 127	16 127	0	20 0 130	32 254	32 254	0
0 150 0	240 1905	240 1905	0	10 0 150	16 127	16 127	0	20 0 140	32 254	32 254	0
0 160 0	256 2032	256 2032	0	10 0 160	16 127	16 127	0	20 0 150	32 254	32 254	0
0 170 0	272 2159	272 2159	0	10 0 170	16 127	16 127	0	20 0 160	32 254	32 254	0
0 180 0	288 2286	288 2286	0	10 0 180	16 127	16 127	0	20 0 170	32 254	32 254	0
0 190 0	304 2413	304 2413	0	10 0 190	16 127	16 127	0	20 0 180	32 254	32 254	0
0 200 0	320 2540	320 2540	0	10 0 200	16 127	16 127	0	20 0 190	32 254	32 254	0
0 210 0	336 2667	336 2667	0	10 0 210	16 127	16 127	0	20 0 200	32 254	32 254	0
0 220 0	352 2794	352 2794	0	10 0 220	16 127	16 127	0	20 0 210	32 254	32 254	0
0 230 0	368 2921	368 2921	0	10 0 230	16 127	16 127	0	20 0 220	32 254	32 254	0
0 240 0	384 3048	384 3048	0	10 0 240	16 127	16 127	0	20 0 230	32 254	32 254	0
0 250 0	400 3175	400 3175	0	10 0 250	16 127	16 127	0	20 0 240	32 254	32 254	0
0 260 0	416 3302	416 3302	0	10 0 260	16 127	16 127	0	20 0 250	32 254	32 254	0
0 270 0	432 3429	432 3429	0	10 0 270	16 127	16 127	0	20 0 260	32 254	32 254	0
0 280 0	448 3556	448 3556	0	10 0 280	16 127	16 127	0	20 0 270	32 254	32 254	0
0 290 0	464 3683	464 3683	0	10 0 290	16 127	16 127	0	20 0 280	32 254	32 254	0
0 300 0	480 3810	480 3810	0	10 0 300	16 127	16 127	0	20 0 290	32 254	32 254	0
0 310 0	496 3937	496 3937	0	10 0 310	16 127	16 127	0	20 0 300	32 254	32 254	0
0 320 0	512 4064	512 4064	0	10 0 320	16 127	16 127	0	20 0 310	32 254	32 254	0
0 330 0	528 4191	528 4191	0	10 0 330	16 127	16 127	0	20 0 320	32 254	32 254	0
0 340 0	544 4318	544 4318	0	10 0 340	16 127	16 127	0	20 0 330	32 254	32 254	0
0 350 0	560 4445	560 4445	0	10 0 350	16 127	16 127	0	20 0 340	32 254	32 254	0
0 360 0	576 4572	576 4572	0	10 0 360	16 127	16 127	0	20 0 350	32 254	32 254	0
0 370 0	592 4699	592 4699	0	10 0 370	16 127	16 127	0	20 0 360	32 254	32 254	0
0 380 0	608 4826	608 4826	0	10 0 380	16 127	16 127	0	20 0 370	32 254	32 254	0
0 390 0	624 4953	624 4953	0	10 0 390	16 127	16 127	0	20 0 380	32 254	32 254	0
0 400 0	640 5080	640 5080	0	10 0 400	16 127	16 127	0	20 0 390	32 254	32 254	0
0 410 0	656 5207	656 5207	0	10 0 410	16 127	16 127	0	20 0 400	32 254	32 254	0
0 420 0	672 5334	672 5334	0	10 0 420	16 127	16 127	0	20 0 410	32 254	32 254	0
0 430 0	688 5461	688 5461	0	10 0 430	16 127	16 127	0	20 0 420	32 254	32 254	0
0 440 0	704 5588	704 5588	0	10 0 440	16 127	16 127	0	20 0 430	32 254	32 254	0
0 450 0	720 5715	720 5715	0	10 0 450	16 127	16 127	0	20 0 440	32 254	32 254	0
0 460 0	736 5842	736 5842	0	10 0 460	16 127	16 127	0	20 0 450	32 254	32 254	0
0 470 0	752 5969	752 5969	0	10 0 470	16 127	16 127	0	20 0 460	32 254	32 254	0
0 480 0	768 6096	768 6096	0	10 0 480	16 127	16 127	0	20 0 470	32 254	32 254	0
0 490 0	784 6223	784 6223	0	10 0 490	16 127	16 127	0	20 0 480	32 254	32 254	0
0 500 0	800 6350	800 6350	0	10 0 500	16 127	16 127	0	20 0 490	32 254	32 254	0
0 510 0	816 6477	816 6477	0	10 0 510	16 127	16 127	0	20 0 500	32 254	32 254	0
0 520 0	832 6604	832 6604	0	10 0 520	16 127	16 127	0	20 0 510	32 254	32 254	0
0 530 0	848 6731	848 6731	0	10 0 530	16 127	16 127	0	20 0 520	32 254	32 254	0
0 540 0	864 6858	864 6858	0	10 0 540	16 127	16 127	0	20 0 530	32 254	32 254	0
0 550 0	880 6985	880 6985	0	10 0 550	16 127	16 127	0	20 0 540	32 254	32 254	0
0 560 0	896 7112	896 7112	0	10 0 560	16 127	16 127	0	20 0 550	32 254	32 254	0
0 570 0	912 7239	912 7239	0	10 0 570	16 127	16 127	0	20 0 560	32 254	32 254	0
0 580 0	928 7366	928 7366	0	10 0 580	16 127	16 127	0	20 0 570	32 254	32 254	0
0 590 0	944 7493	944 7493	0	10 0 590	16 127	16 127	0	20 0 580	32 254	32 254	0
0 600 0	960 7620	960 7620	0	10 0 600	16 127	16 127	0	20 0 590	32 254	32 254	0
0 610 0	976 7747	976 7747	0	10 0 610	16 127	16 127	0	20 0 600	32 254	32 254	0
0 620 0	992 7874	992 7874	0	10 0 620	16 127	16 127	0	20 0 610	32 254	32 254	0
0 630 0	1008 8001	1008 8001	0	10 0 630	16 127	16 127	0	20 0 620	32 254	32 254	0
0 640 0	1024 8128	1024 8128	0	10 0 640	16 127	16 127	0	20 0 630	32 254	32 254	0
0 650 0	1040 8255	1040 8255	0	10 0 650	16 127	16 127	0	20 0 640	32 254	32 254	0
0 660 0	1056 8382	1056 8382	0	10 0 660	16 127	16 127	0	20 0 650	32 254	32 254	0
0 670 0	1072 8509	1072 8509	0	10 0 670	16 127	16 127	0	20 0 660	32 254	32 254	0
0 680 0	1088 8636	1088 8636	0	10 0 680	16 127	16 127	0	20 0 670	32 254	32 254	0
0 690 0	1104 8763	1104 8763	0	10 0 690	16 127	16 127	0	20 0 680	32 254	32 254	0
0 700 0	1120 8890	1120 8890	0	10 0 700	16 127	16 127	0	20 0 690	32 254	32 254	0
0 710 0	1136 9017	1136 9017	0	10 0 710	16 127	16 127	0	20 0 700	32 254	32 254	0
0 720 0	1152 9144	1152 9144	0	10 0 720	16 127	16 127	0	20 0 710	32 254	32 254	0
0 730 0	1168 9271	1168 9271	0	10 0 730	16 127	16 127	0	20 0 720	32 254	32 254	0
0 740 0	1184 9398	1184 9398	0	10 0 740	16 127	16 127	0	20 0 730	32 254	32 254	0
0 750 0	1200 9525	1200 9525	0	10 0 750	16 127	16 127	0	20 0 740	32 254	32 254	0
0 760 0	1216 9652	1216 9652	0	10 0 760	16 127	16 127	0	20 0 750	32 254	32 254	0
0 770 0	1232 9779	1232 9779	0	10 0 770	16 127	16 127	0	20 0 760	32 254	32 254	0
0 780 0	1248 9906	1248 9906	0	10 0 780	16 127	16 127	0	20 0 770	32 254	32 254	0
0 790 0	1264 10033	1264 10033	0	10 0 790	16 127	16 127	0	20 0 780	32 254	32 254	0
0 800 0	1280 10160	1280 10160	0	10 0 800	16 127	16 127	0	20 0 790	32 254	32 254	0
0 810 0	1296 10287	1296 10287	0	10 0 810	16 127	16 127	0	20 0 800	32 254	32 254	0
0 820 0	1312 10414	1312 10414	0	10 0 820	16 127	16 127	0	20 0 810	32 254	32 254	0
0 830 0	1328 10541	1328 10541	0</								

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.

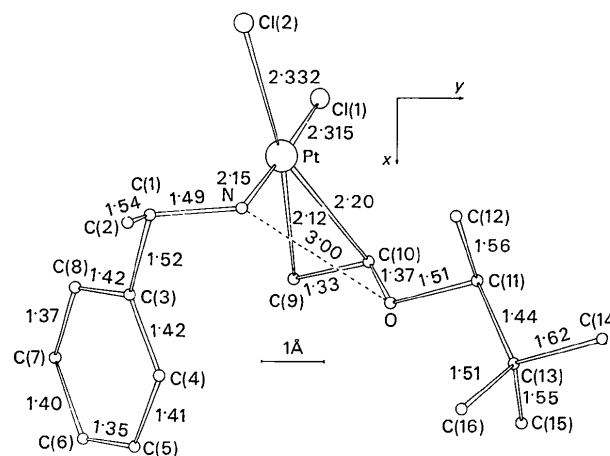


Fig. 1. The molecular structure of *cis*-dichloro[(*R*)- $\alpha$ -methylbenzylamine][(*S*)-1,2,2-trimethylpropyl (*R*)-vinyl ether]platinum(II).

Moreover, while initially unit weights were assigned to all observed reflexions, at this point the following weighting scheme was introduced:  $w = 1.0 / (A + F_o + BF_o^2)$ ; 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 intramolecular 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 diastereoisomer 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  $10^4$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
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)
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2$ )					
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)

Table 3. Bond distances ( $\text{\AA}$ ) 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  $\sigma$ -donor ligands such as N-bonded amines is comparable with that of modest  $\sigma$ -donors which are also  $\pi$ -acceptors such as olefins, both of them giving rise to *trans* Pt–Cl bond lengths up to 2.33  $\text{\AA}$  (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

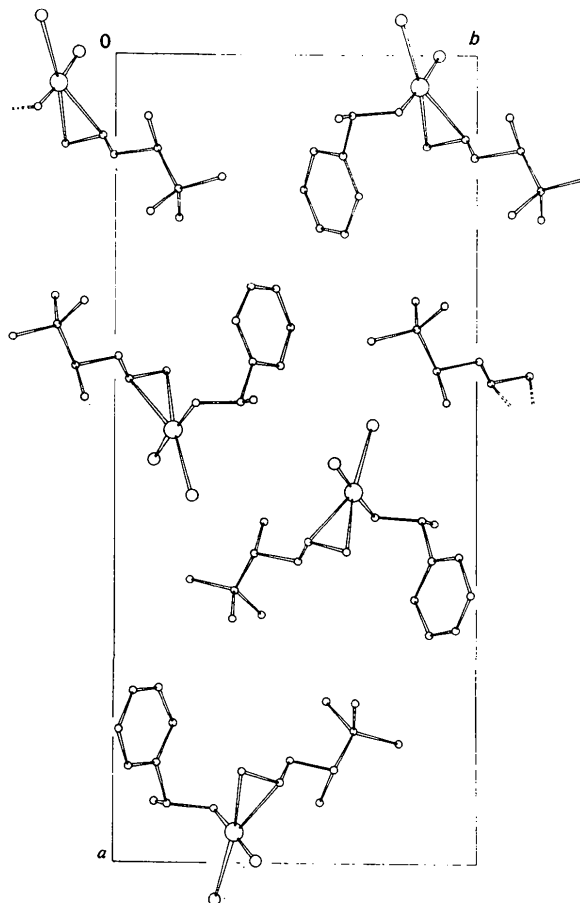


Fig. 2. Projection of the crystal structure of *cis*-dichloro[(*R*)- $\alpha$ -methylbenzylamine] [(*S*)-1,2,2-trimethylpropyl (*R*)-vinyl ether]platinum(II) along [001].

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	Atoms defining the plane	A	B	C	D
1	C(3), C(4), C(5), C(6), C(7), C(8) 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	-3.0185	9.0180	-4.0868	3.3323
2	Pt, Cl(1), Cl(2), N 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°.	-3.1270	10.5863	2.3510	9.3876
3	Pt, N, C(1) The acute angles between plane 3 and planes 1 and 2 are 80.97 and 78.84° respectively.	23.6463	0.5964	-2.5719	0.6279
4	Pt, C(9), C(10) The acute angle between plane 4 and plane 2 is 89.48°.	10.3232	-3.1652	5.9605	-0.5720

\* 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<sub>2</sub>C=CHOH) (where acac<sup>-</sup> is the acetylacetonate anion), is the highest of a series of deviations reported by Cotton *et al.* (1973) for platinum(II)  $\pi$ -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  $\Delta F$  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*)- $\alpha$ -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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