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## The Structures of *trans*-Dichloro(pyrrolidine)(triethylphosphine)platinum(II) and *trans*-Dichloro(*trans*-2,5-dimethylpyrrolidine)(triethylphosphine)platinum(II)

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### Abstract

The structures of *trans*-[PtCl<sub>2</sub>(Et<sub>3</sub>P)(C<sub>4</sub>H<sub>9</sub>N)] (I) [C<sub>10</sub>H<sub>24</sub>Cl<sub>2</sub>NPt, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 11·110 (4), *b* = 11·370 (3), *c* = 13·167 (6) Å, β = 110·76 (4)°], and *trans*-[PtCl<sub>2</sub>(Et<sub>3</sub>P)(C<sub>6</sub>H<sub>13</sub>N)] (II) [C<sub>12</sub>H<sub>28</sub>Cl<sub>2</sub>NPt, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 7·608 (3), *b* = 21·749 (8), *c* = 11·075 (3) Å, β = 100·56 (2)°] have been determined. (I) and (II) are square-planar complexes of Pt<sup>II</sup>; their geometries are similar, the main differences being the arrangements of the pyrrolidine ligand with respect to the PtCl<sub>2</sub>(Et<sub>3</sub>P) moiety, and the conformations assumed by the puckered five-membered rings. The

structures have been refined to *R* = 0·045 (I) and 0·040 (II).

### Introduction

Recently, the structures of *trans*-[PtCl<sub>2</sub>(Et<sub>3</sub>P)(*cis*-2,3-dimethylpyrrolidine)] (III) and *trans*-[PtCl<sub>2</sub>(Et<sub>3</sub>P)(*cis*-2,4-dimethylpyrrolidine)] (IV) were determined by X-ray analysis to assign *cis* or *trans* configurations to the products of the Pt-promoted cyclization of the unsaturated amines CH<sub>2</sub>=CH-CH(CH<sub>3</sub>)-CH<sub>2</sub>CH<sub>2</sub>-NH<sub>2</sub> and CH<sub>2</sub>=CH-CH<sub>2</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>-NH<sub>2</sub>

respectively (Ambuehl, Pregosin, Venanzi, Consiglio, Bachechi & Zambonelli, 1979). The two structures reveal the different conformations assumed by the puckered five-membered rings of the coordinated pyrrolidines.

It seemed interesting to continue the structural study on other derivatives of the cyclic amine to acquire more details on the possible conformations assumed by the five-membered ring.

In particular, the study of complexes of the type *trans*-[PtCl<sub>2</sub>(Et<sub>3</sub>P)L] was planned in which L is either one of the eight possible isomers of C,C'-dimethylpyrrolidine [two of which have already been studied in (III) and (IV)], or unsubstituted pyrrolidine.

In the present paper, the structures of *trans*-[PtCl<sub>2</sub>(Et<sub>3</sub>P)(pyrrolidine)] (I) and *trans*-[PtCl<sub>2</sub>(Et<sub>3</sub>P)(*trans*-2,5-dimethylpyrrolidine)] (II) are reported.

### Experimental

(I) and (II) were prepared by reaction of the appropriate amine with *sym-trans*-[Pt<sub>2</sub>Cl<sub>4</sub>(Et<sub>3</sub>P)<sub>2</sub>] (Chatt & Venanzi, 1955). Purified commercial pyrrolidine was used, while *trans*-2,5-dimethylpyrrolidine was recovered from a commercial *cis-trans* mixture through rectification on an auto annular still.\* Crystals of the complexes were grown from acetone-petroleum ether (313–343 K) solutions.

Diffraction data were gathered by an automatic four-circle diffractometer (Syntex P2<sub>1</sub>) with graphite-monochromated Mo K $\alpha$  radiation.

The cell parameters were refined by least squares from the angular positions of 15 strong reflections. The crystal data for both compounds are listed in Table 1. Relevant details for the data collection are given in Table 2.

The data were processed to yield values of  $I$  and  $\sigma(I)$  (Bachechi, Zambonelli & Marcotrigiano, 1977). In the

\* The authors are indebted to Dr G. Consiglio (ETH, Zürich) who supplied the rectified isomers.

Table 1. Summary of crystal data

	(I)	(II)
Formula	C <sub>10</sub> H <sub>24</sub> Cl <sub>2</sub> NPt	C <sub>12</sub> H <sub>28</sub> Cl <sub>2</sub> NPt
Formula weight	455.28	483.33
<i>a</i> (Å)	11.110 (4)	7.608 (3)
<i>b</i> (Å)	11.370 (3)	21.749 (8)
<i>c</i> (Å)	13.167 (6)	11.075 (3)
$\beta$ (°)	110.76 (4)	100.56 (2)
<i>V</i> (Å <sup>3</sup> )	1555 (1)	1802 (1)
<i>D<sub>c</sub></i> (Mg m <sup>-3</sup> )	1.944	1.782
<i>D<sub>m</sub></i> (Mg m <sup>-3</sup> )*	1.95 (1)	1.75 (1)
<i>Z</i>	4	4
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	9.54	8.24

\* Measured by flotation in ZnI<sub>2</sub> solutions.

Table 2. Data-collection details

	(I)	(II)
Radiation	Graphite-monochromated Mo K $\alpha$ ( $\lambda = 0.71069$ Å)	
Crystal dimensions (mm)	0.13 × 0.20 × 0.35	0.15 × 0.18 × 0.30
Scan mode	$\omega$	$\omega$
Scan speed (° min <sup>-1</sup> )	1–29.3	1–29.3
Scan range (°)	0.8	0.8
Background counts	for $\frac{1}{4}$ the scan time at $\pm 0.6^\circ$	for the scan time at $\pm 0.7^\circ$
Check reflections	3 every 100 reflections: no decay	
Data collection limits	3–56° in 2 $\theta$	3–56° in 2 $\theta$
Number of data	4419	4944

estimation of  $\sigma(I)$  the uncertainty factor  $p$  was set equal to 0.005 (I) and 0.006 (II), as calculated from the variance of the standard reflections (McCandlish, Stout & Andrews, 1975). The values of  $I$  and  $\sigma(I)$  were corrected for Lorentz, polarization and shape-anisotropy effects (North, Phillips & Mathews, 1968; Spagna & Zambonelli, 1971).

1366 and 2188 independent reflections for (I) and (II), respectively, having  $F_o^2 > 3\sigma(F_o^2)$ , were used in all subsequent calculations.

### Structure analysis and refinement

The two structures were solved by Patterson and Fourier methods, and refined by full-matrix least squares. The isotropic refinement converged at  $R = 0.092$  (I) and  $R = 0.100$  (II); the anisotropic refinement led to  $R = 0.057$  and 0.044 respectively. At this stage the fixed contribution of the H atoms was included. The positions of the H atoms were idealized and readjusted after each cycle; each H atom was assigned the  $B$  value of the nearest C atom at the end of the isotropic refinement. The final  $R$  was 0.045 ( $R_w = 0.031$ ) for (I) and 0.040 ( $R_w = 0.028$ ) for (II). In both cases the final difference syntheses did not reveal any region exceeding  $\pm 3\sigma(\rho)$  [ $\sigma(\rho) = 0.30$  and 0.22 e Å<sup>-3</sup> for (I) and (II) respectively].

The function minimized was  $\sum w(|F_o| - |F_c|)^2$  with  $w = 4F_o^2/\sigma(F_o^2)$ ; this function was not appreciably dependent on either  $\theta$  or  $F_o$ .

Scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974).

The calculations were performed with local programs on the Univac 1110 computer of the University of Rome (Carruthers & Spagna, 1975) and on the HP 21MX minicomputer of the CNR Research Area (Cerrini & Spagna, 1977).

The final positional parameters of the non-hydrogen atoms are given in Table 3.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35425 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Positional parameters ( $\times 10^4$ ) of (I) and (II) with *e.s.d.*'s in parentheses

	(I)			(II)		
	x	y	z	x	y	z
Pt	2143 (1)	1320 (1)	2719 (1)	340 (1)	1180 (0)	3248 (0)
Cl(1)	2592 (5)	3289 (3)	2674 (4)	542 (4)	1388 (1)	1244 (2)
Cl(2)	1638 (5)	-621 (4)	2880 (4)	2 (4)	933 (1)	5208 (2)
N	670 (15)	1858 (12)	3321 (11)	-1029 (10)	335 (3)	2730 (6)
P	3742 (5)	722 (4)	2180 (4)	1835 (4)	2027 (1)	3948 (2)
C(1)	-631 (17)	1371 (19)	2841 (13)	-583 (15)	-42 (4)	1698 (8)
C(2)	-1239 (20)	1514 (20)	3687 (19)	-1977 (17)	-556 (4)	1538 (8)
C(3)	-209 (25)	1903 (18)	4714 (19)	-3577 (16)	-292 (6)	1961 (12)
C(4)	981 (19)	1692 (16)	4484 (14)	-3064 (14)	339 (5)	2552 (9)
C(5)	3324 (19)	-447 (14)	1198 (16)	3679 (18)	1874 (6)	5183 (11)
C(6)	2237 (24)	-185 (18)	128 (18)	4962 (20)	1387 (8)	4929 (17)
C(7)	4455 (17)	1876 (13)	1604 (13)	2715 (23)	2470 (6)	2802 (11)
C(8)	5529 (18)	1446 (18)	1210 (15)	3642 (28)	3034 (7)	3136 (14)
C(9)	5069 (17)	171 (15)	3309 (14)	524 (24)	2534 (6)	4768 (16)
C(10)	5630 (17)	1040 (17)	4251 (13)	-1046 (27)	2774 (8)	4032 (21)
Me(1)	-	-	-	1350 (15)	-251 (5)	1963 (9)
Me(2)	-	-	-	-3845 (15)	868 (5)	1708 (10)

### Discussion

Perspective views of the molecules are shown in Fig. 1, bond lengths and angles in Table 4.

In both molecules the Pt atom has square-planar coordination, the donor atoms being the two Cl atoms in *trans* positions, the P atom and the N atom. In both compounds the donor atoms are almost exactly coplanar with the Pt atom.

Corresponding bond lengths and angles in (I) and (II) agree well. Their values compare with those already observed in the analogous complexes (III) and (IV), and appear to be normal.

Table 5 reports the torsion angles defining the arrangements of the ligands. The triethylphosphine ligand assumes a similar arrangement in (I) and (II), comparable with that observed in (III) and (IV). However, the pyrrolidine ligand assumes different arrangements with respect to the  $PtCl_2(Et_3P)$  moiety in (I) and (II), differing also from those in (III) and (IV).

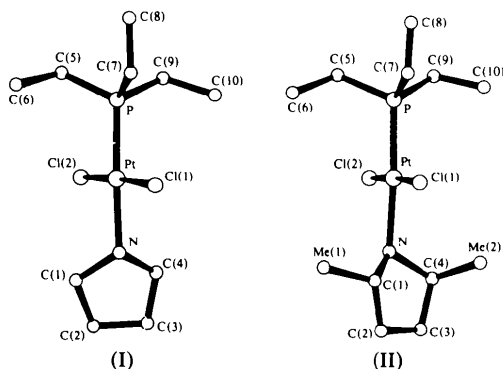


Fig. 1. Computer-generated drawings of the molecules of *trans*- $[PtCl_2(Et_3P)(pyrrolidine)]$  (I) and *trans*- $[PtCl_2(Et_3P)(trans-2,5-dimethylpyrrolidine)]$  (II).

As in (III) and (IV) also, in (I) and (II) the  $PtCl_2(Et_3P)$  moiety is in an equatorial position with respect to the pyrrolidine ligand. In (II), Me(1)(equatorial) is in a *trans*, and Me(2)(axial) is in a *cis* position with respect to the  $PtCl_2(Et_3P)$  moiety.

(II), which has chiral atoms [N,\* C(1) and C(4)], is present in the crystal in the racemic form. Coordinates, torsion-angle signs (Klyne & Prelog, 1960) and the drawing of the molecule in Fig. 1 refer to the N(*R*):C(1)(*S*):C(4)(*S*) configuration (Cahn, Ingold & Prelog, 1956).

The torsion angles concerning the pyrrolidine ligand are reported in Table 6.

As in (IV) also, in (I) and (II) the puckered pyrrolidine ring has a conformation which could be regarded as intermediate between an envelope form ( $C_s$  symmetry) and a half-chair form ( $C_2$  symmetry) (Eliel, Allinger, Angyal & Morrison, 1965; Adams, Geise & Bartell, 1970). However, in the three cases the conformation of the ring is quite different. In fact, the maximum puckering occurs at C(4)-N in (I), N-C(1) in (II) and C(1)-C(2) in (IV).

Schematic representations of the pyrrolidine rings in the four complexes studied are drawn in Fig. 2. In the figure the configurations are reported which maintain the same arrangement of the  $PtCl_2(Et_3P)$  moiety with respect to the rings for the chosen numbering of the atoms. It can be seen that the conformation of the ring in (I) can be considered an intermediate between the configuration of the ring in (III) and that in (II), perhaps closer to the conformation in (III) which has an envelope-like form with C(4) at the flap. Therefore,

\* The asymmetry of N depends on the stereochemical differences between two of the groups bonded to it: its configuration is defined by subrule 2 of Cahn, Ingold & Prelog (1956).

Table 4. Bond lengths (Å) and angles (°) for (I) and (II) (e.s.d.'s in parentheses)

	(I)	(II)
Pt—Cl(1)	2.299 (4)	2.298 (3)
Pt—Cl(2)	2.305 (4)	2.296 (2)
Pt—P	2.240 (6)	2.228 (3)
Pt—N	2.144 (18)	2.138 (7)
N—C(1)	1.466 (23)	1.495 (12)
C(1)—C(2)	1.502 (35)	1.528 (15)
C(2)—C(3)	1.496 (29)	1.497 (18)
C(3)—C(4)	1.476 (38)	1.539 (16)
C(4)—N	1.459 (23)	1.524 (14)
C(1)—Me(1)	—	1.516 (16)
C(4)—Me(2)	—	1.533 (15)
P—C(5)	1.797 (18)	1.802 (12)
P—C(7)	1.830 (19)	1.815 (15)
P—C(9)	1.795 (16)	1.836 (18)
C(5)—C(6)	1.525 (26)	1.503 (22)
C(7)—C(8)	1.540 (31)	1.429 (21)
C(9)—C(10)	1.535 (24)	1.417 (25)
Cl(1)—Pt—Cl(2)	175.4 (2)	176.6 (1)
Cl(1)—Pt—P	94.7 (2)	93.0 (1)
Cl(1)—Pt—N	86.1 (4)	91.5 (2)
Cl(2)—Pt—P	89.2 (2)	90.2 (1)
Cl(2)—Pt—N	89.8 (4)	85.3 (2)
P—Pt—N	176.9 (3)	175.1 (2)
Pt—N—C(1)	119.9 (11)	120.6 (6)
Pt—N—C(4)	115.1 (11)	117.6 (6)
Pt—P—C(5)	114.9 (8)	112.8 (4)
Pt—P—C(7)	115.0 (6)	115.2 (4)
Pt—P—C(9)	110.7 (7)	112.3 (5)
C(5)—P—C(7)	105.8 (9)	107.1 (7)
C(5)—P—C(9)	105.3 (8)	98.8 (7)
C(7)—P—C(9)	104.2 (8)	109.3 (7)
P—C(5)—C(6)	116.0 (13)	115.5 (10)
P—C(7)—C(8)	114.4 (12)	120.2 (10)
P—C(9)—C(10)	115.1 (12)	114.5 (14)
N—C(1)—C(2)	105.9 (14)	103.9 (9)
C(1)—C(2)—C(3)	107.5 (19)	105.6 (9)
C(2)—C(3)—C(4)	102.8 (20)	108.5 (10)
C(3)—C(4)—N	107.4 (15)	102.9 (8)
C(4)—N—C(1)	103.5 (15)	105.7 (7)
N—C(1)—Me(1)	—	111.4 (7)
C(2)—C(1)—Me(1)	—	115.5 (8)
N—C(4)—Me(2)	—	110.8 (9)
C(3)—C(4)—Me(2)	—	111.7 (8)

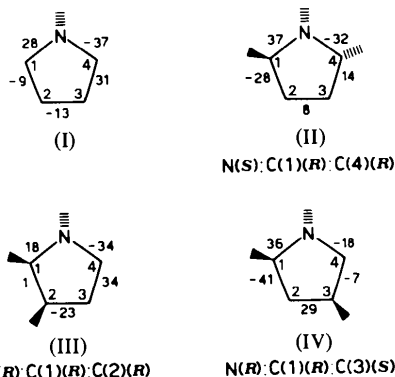

 Fig. 2. Torsion angles (°) internal to the pyrrolidine ring observed in the four complexes (I), (II), (III) and (IV). The signs refer to the configurations which maintain the same arrangement of the PtCl<sub>2</sub>(Et<sub>3</sub>P) moiety for the given numbering of the atoms.

Table 5. Torsion angles (°) defining the arrangements of the ligands in (I) and (II) (e.s.d.'s in parentheses)

	(I)	(II)	(III), (IV)*
Cl(1)—Pt—P—C(5)	-138 (1)	-128 (1)	-153
Cl(1)—Pt—P—C(7)	-15 (1)	-5 (1)	-32
Cl(1)—Pt—P—C(9)	103 (1)	121 (1)	90
Cl(2)—Pt—P—C(5)	45 (1)	53 (1)	31
Cl(2)—Pt—P—C(7)	168 (1)	176 (1)	153
Cl(2)—Pt—P—C(9)	-75 (1)	-58 (1)	-85
Pt—P—C(5)—C(6)	60 (2)	52 (1)	61
Pt—P—C(7)—C(8)	-179 (1)	178 (1)	179
Pt—P—C(9)—C(10)	-57 (2)	-64 (1)	-60
Cl(1)—Pt—N—C(1)	132 (1)	35 (1)	-66
Cl(1)—Pt—N—C(4)	-103 (1)	-97 (1)	61
Cl(2)—Pt—N—C(1)	-50 (1)	-147 (1)	110
Cl(2)—Pt—N—C(4)	74 (1)	82 (1)	-124

\* Averaged values of the torsion angles in (III) and (IV) consistent with those in (I) and (II) are reported for comparison.

Table 6. Torsion angles (°) concerning the pyrrolidine ligands in (I) and (II) (e.s.d.'s in parentheses)

	(I)	(II)
N—C(1)—C(2)—C(3)	-9 (2)	28 (1)
C(1)—C(2)—C(3)—C(4)	-13 (2)	-8 (1)
C(2)—C(3)—C(4)—N	31 (2)	-14 (1)
C(3)—C(4)—N—C(1)	-37 (2)	32 (1)
C(4)—N—C(1)—C(2)	28 (2)	-37 (1)
Pt—N—C(1)—C(2)	158 (1)	-174 (1)
Pt—N—C(1)—Me(1)	—	61 (1)
C(4)—N—C(1)—Me(1)	—	-162 (1)
Me(1)—C(1)—C(2)—C(3)	—	150 (1)
C(2)—C(3)—C(4)—Me(2)	—	105 (1)
C(3)—C(4)—N—Pt	-170 (1)	170 (1)
Me(2)—C(4)—N—C(1)	—	-88 (1)
Me(2)—C(4)—N—Pt	—	50 (1)

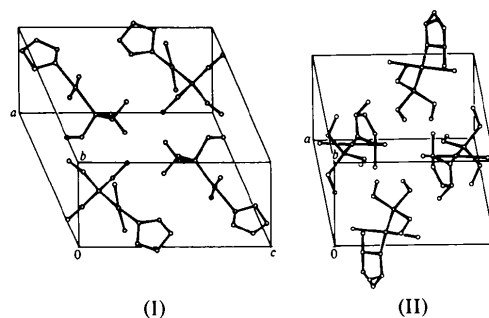


Fig. 3. Packing arrangements of the molecules in the structures of (I) and (II).

these four structures seem to represent four phases of the pseudorotation of the pyrrolidine ring in the sequence (III) → (I) → (II) → (IV) or, to stress the influence of the methyl substituents, (III) ← (I) → (II) → (IV).

All the intermolecular contacts in the crystals of (I) and (II) are longer than the van der Waals sum of the

radii. The shortest  $N \cdots Cl$  intermolecular contacts are  $Cl(2) \cdots N(-x, y - \frac{1}{2}, \frac{1}{2} - z)$ , 3.80 (2) Å in (I), and  $Cl(2) \cdots N(-x, -y, 1 - z)$ , 3.57 (1) Å in (II). They can be hardly attributed to weak hydrogen bonds. The packing arrangements for (I) and (II) are shown in Fig. 3.

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## Structure de Bis[ $\mu$ -(*N,N*-diméthyl-acétamide)]-bis[aquatris(*N,N*-diméthyl-acétamide)diperchloratobaryum] à 143 K

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#### Abstract

Crystals of  $[Ba_2(C_4H_9NO)_8(ClO_4)_4(H_2O)_2]$  are triclinic, space group  $P\bar{1}$ , with  $a = 14.183$  (5),  $b = 11.150$  (5),  $c = 10.249$  (5) Å,  $\alpha = 92.88$  (5),  $\beta = 104.81$  (5),  $\gamma = 111.24$  (5)° and  $Z = 1$ . Intensity data were collected with a four-circle diffractometer using  $Mo\ K\alpha$  radiation. The structure was solved by direct methods and refined by full-matrix least-squares calculations to  $R = 0.048$  for 4702 observed reflections. The two Ba atoms are each octacoordinated and constitute a binuclear complex. The structure is compared to that of  $[Cu\{CH_3CON(CH_3)_2\}_4(ClO_4)_2]$ .

#### Introduction

Ce travail s'insère dans un programme de recherche sur les complexes perchlorate de la *N,N*-diméthyl-acétamide [dma:  $CH_3CON(CH_3)_2$ ]. La détermination structurale du composé  $Cu(ClO_4)_2 \cdot 4dma$  (Lemoine & Herpin, 1980) a permis de décrire en particulier le mode d'environnement du cuivre et la conformation de la *N,N*-diméthyl-acétamide à l'état cristallin et complexée.

L'étude du composé  $Ba(ClO_4)_2 \cdot 4dma \cdot H_2O$  précise l'influence de la nature du cation central sur la géométrie moléculaire du complexe et sur la structure de la molécule de dma.

#### Détermination de la structure

La détermination structurale à 293 K ( $R = 0,066$  et  $R_w = 0,080$ ) ayant montré une agitation thermique élevée notamment pour les atomes d'oxygène des groupements perchlorate et n'ayant pas permis de positionner les atomes d'hydrogène des molécules de *N,N*-diméthyl-acétamide, une étude de ce complexe a été effectuée à 143 K. Les résultats rapportés ici sont ceux obtenus à basse température.

L'enregistrement des intensités diffractées a été réalisé au moyen d'un diffractomètre automatique quatre cercles, Philips PW 1100, équipé d'un système de refroidissement par jet d'azote gazeux. Aucune anomalie, ni transformation n'est apparue entre 293 et 143 K. La maille cristalline de symétrie triclinique, groupe spatial  $P\bar{1}$ , subit une contraction de réseau en volume de 3,3% entre les deux températures en-