

## The Crystal and Molecular Structure of *cis*-Dichlorobis(cyclohexylamine)platinum(II)

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The structure of *cis*-dichlorobis(cyclohexylamine)platinum(II) has been determined by the heavy-atom method and refined by full-matrix least squares to  $R = 0.054$  for 650 absorption corrected data. The crystals are orthorhombic with  $a = 26.12$  (2),  $b = 6.660$  (6),  $c = 8.981$  (8) Å,  $Z = 4$ , space group *Pbcn*. The Pt atom is surrounded by two N and two Cl atoms in an approximately *cis* square-planar arrangement. The cyclohexyl ring adopts a chair conformation with the N atom equatorial. The shortest intermolecular Pt...Pt distance is 4.49 Å.

### Introduction

Rosenberg, van Camp & Krigas (1965) showed that certain complexes of Pt exhibited interesting biological effects. Some of these complexes are broad-spectrum anti-tumour agents and the effects of *cis*-dichlorodiamineplatinum(II) on experimental tumours (Rosenberg, van Camp, Trosko & Mansaur, 1969) and in man (Talley, O'Bryan, Brownlee & Gastesi, 1972) have led to the search for related compounds with anti-tumour activity. One series of Pt complexes that are significantly better anti-tumour agents than the parent *cis*-dichlorodiamineplatinum(II) are *cis*-dichloro derivatives of Pt coordinated to an aromatic or alicyclic diamine or two alicyclic amines (Connors, Jones, Ross, Braddock, Khokhar & Tobe, 1972). The structures of *cis*-dichloroethylenediamineplatinum(II) (Iball, Macdougall & Scrimgeour, 1975) and *cis*- and *trans*-dichlorobis(ethyleneimine)platinum(II) (Barnes, Iball & Weakley, 1975) of this series have been reported. We now report the structure of the bis(cyclohexylamine) derivative, which is 30 times more selective than *cis*-dichlorodiamineplatinum(II) against certain tumours.

### Experimental

The crystals are colourless rectangular plates. Cell dimensions and space group were determined from Weissenberg photographs (Cu  $K\alpha$ ) and confirmed by measurements on a Wooster four-circle diffractometer. The crystals deteriorated after a few days on exposure to X-rays, and so intensities were collected on film by the equi-inclination Weissenberg technique with relatively short exposure times.

Two crystals were used for data collection: a *b* axis crystal,  $0.279 \times 0.155 \times 0.031$  mm, from which layers  $h0l \rightarrow h4l$  were collected and a *c* axis crystal,  $0.186 \times 0.155 \times 0.093$  mm, from which layers  $hk0 \rightarrow hk6$

were collected. Intensities were measured on a scanning densitometer at the Atlas Computing Laboratory. Absorption corrections were applied to the data from each crystal, and the data placed on a common scale and converted to structure factors (738 reflexions above background of which 650 were used in the final stages of refinement). The *c* axis Weissenberg photographs of odd layers were very weak and, throughout,  $hkl$  were weak when  $h + k = 2n + 1$ .

### Crystal data

*cis*-Dichlorobis(cyclohexylamine)platinum(II),  $\text{PtCl}_2 \cdot \text{C}_{12}\text{N}_2\text{H}_{26}$ ,  $M_r = 1857.3$ , orthorhombic, *Pbcn*,  $a = 26.12$  (2),  $b = 6.660$  (6),  $c = 8.981$  (8) Å,  $Z = 4$ ,  $D_x = 1.973$  g cm<sup>-3</sup>,  $F(000) = 896$ ,  $\mu(\text{Cu } K\alpha) = 202$  cm<sup>-1</sup>.

### Structure determination

The intensities of  $hkl$  reflexions with  $h + k = 2n + 1$  were very weak which suggested that the Pt atom was at  $0, y, \frac{1}{4}$  and examination of a Patterson map indicated  $0, 0, \frac{1}{4}$  as the Pt position. Successive Fourier syntheses gave the positions of the Cl, N and C atoms ( $R = 0.174$ ). Refinement was by full-matrix least squares with the *SHELX* 76 system (Sheldrick, 1976) on the IBM 370/165 at Cambridge. Scattering factors were from *International Tables for X-ray Crystallography* (1974). The Pt and Cl atoms were refined anisotropically and C and N isotropically. H atom positions with  $U_{\text{iso}} = 0.08$  Å<sup>2</sup> were included in the final stages but were not refined. The final  $R$  was 0.054\* for 650 observed reflexions.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32215 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional and thermal parameters*

(a) Final positional parameters ( $\times 10^4$ ) and for C and N atoms isotropic temperature factors ( $\times 10^3$ ). Estimated standard deviations are in parentheses.

	x	y	z	$U_{\text{iso}}$ ( $\text{\AA}^2$ )
C(1)	2038 (10)	-3335 (42)	3446 (30)	19 (6)
C(2)	1988 (13)	-2759 (60)	1841 (41)	42 (9)
C(3)	1451 (10)	-3105 (43)	1271 (31)	25 (6)
C(4)	1706 (11)	-2002 (46)	4314 (33)	30 (7)
C(5)	1124 (12)	-2142 (53)	3819 (36)	37 (8)
C(6)	1106 (9)	-1749 (39)	2206 (28)	22 (6)
N(1)	549 (9)	-2051 (37)	1626 (25)	25 (6)
Pt	0	-7 (5)	2500	
Cl	547 (3)	2685 (11)	2800 (7)	
H(11)	2430	-3161	3807	
H(12)	1923	-4881	3584	
H(21)	2067	-1172	1742	
H(22)	2260	-3593	1179	
H(31)	1418	-2739	104	
H(32)	1350	-4661	1439	
H(41)	1730	-2438	5470	
H(42)	1842	-479	4189	
H(51)	913	-972	4382	
H(52)	960	-3585	4093	
H(61)	1245	-231	2083	
H(71)	553	-1924	427	
H(72)	431	-3547	1938	

(b) Anisotropic temperature parameters ( $\times 10^4$ ) for Pt and Cl. Estimated standard deviations are in parentheses.

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Pt	109 (5)	156 (5)	165 (5)	0	-8 (11)	0
Cl	238 (26)	302 (34)	297 (42)	-24 (35)	-22 (28)	-107 (28)

Table 2. *Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )*

Estimated standard deviations are in parentheses.

C(2)—C(1)	1.50 (4)	C(6)—C(5)	1.47 (4)
C(4)—C(1)	1.47 (4)	N(1)—C(6)	1.56 (3)
C(3)—C(2)	1.51 (4)	Pt—N(1)	2.13 (2)
C(6)—C(3)	1.53 (4)	Pt—Cl	2.308 (7)
C(5)—C(4)	1.59 (4)		
C(4)—C(1)—C(2)	107 (2)	N(1)—C(6)—C(3)	107 (2)
C(3)—C(2)—C(1)	112 (3)	N(1)—C(6)—C(5)	110 (2)
C(6)—C(3)—C(2)	106 (3)	Pt—N(1)—C(6)	115 (2)
C(5)—C(4)—C(1)	113 (3)	Cl—Pt—N(1)	97 (1)
C(6)—C(5)—C(4)	107 (3)	Cl—Pt—Cl'	151 (1)
C(5)—C(6)—C(3)	114 (2)	N(1)—Pt—N(1)'	151 (1)

## Results

Atomic parameters are given in Table 1(a) and (b) and bond lengths and angles in Table 2. The two Cl and two N atoms are arranged about the Pt atom in an approxi-

mately *cis* square-planar arrangement. The mean plane of the Pt, two Cl and two N atoms is given by

$$0.2035X + 0.9791Z = 2.1982$$

and the deviations of Cl and N from this plane are 0.55 and  $-0.48 \text{ \AA}$  respectively. These deviations are significant and the geometry about the Pt atom differs from that found in for example *cis*-dichloroethylenediamineplatinum(II) and many other complexes of Pt where the arrangement is truly square planar. The Pt—Cl [2.308 (7)  $\text{\AA}$ ] and Pt—N [2.13 (2)  $\text{\AA}$ ] distances are similar to those reported for *cis*-dichlorodiamineplatinum(II) (Milburn & Truter, 1966) and for *cis*-dichloroethylenediamineplatinum(II). The shortest intermolecular Pt...Pt distance is 4.49  $\text{\AA}$ . The molecule, projected onto the mean plane of the Pt, Cl and N atoms, is shown in Fig. 1.

The cyclohexyl ring adopts a chair conformation with the N atom equatorial. The mean C—C distance in the ring is 1.51  $\text{\AA}$  though individual distances range from 1.47 to 1.58  $\text{\AA}$ . This range probably reflects the lack of accuracy in determining light-atom positions in the presence of an atom as heavy as Pt. The mean plane through C(2), C(3), C(4) and C(5) is given by

$$-0.0228X + 0.9668Y - 0.2544Z = -2.3468$$

with deviations of each atom from the mean plane of  $\pm 0.03 \text{ \AA}$ . C(1) and C(6) are  $-0.71$  and  $0.65 \text{ \AA}$  respectively from this plane. The angles between this plane and those of C(1), C(2), C(4) and C(6), C(3), C(5) are 127 and  $125^\circ$  respectively. The deviation of the N atom from the mean plane of C(2), C(3), C(4) and C(5) is 0.62  $\text{\AA}$  while that of Pt is 1.77 and of Cl 3.40  $\text{\AA}$ . Torsion angles for the cyclohexyl ring are given in Table 3.

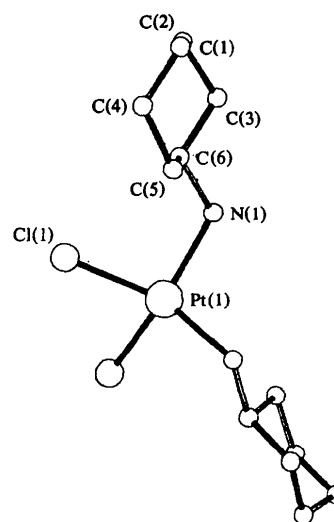


Fig. 1. *cis*-Dichlorobis(cyclohexylamine)platinum(II): atomic numbering.

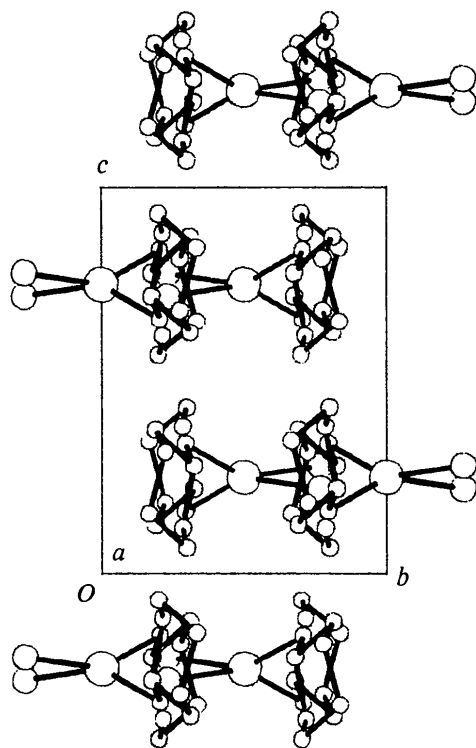


Fig. 2. The contents of the unit cell viewed down *a*.

The contents of the unit cell viewed along *a* are shown in Fig. 2. The only intermolecular contact less than 3.5 Å is N...Cl, 3.46 Å (N at *x*, 1 + *y*, *z* and Cl at -*x*, 1 - *y*, 1 - *z*).

Table 3. Torsion angles (°) for the cyclohexyl ring

C(4)—C(1)C(2)—C(3)	-63.94
C(2)—C(1)C(4)—C(5)	58.87
C(1)—C(2)C(3)—C(6)	61.56
C(2)—C(3)C(6)—C(5)	-59.13
C(1)—C(4)C(5)—C(6)	-54.73
C(4)—C(5)C(6)—C(3)	54.86

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