

## Cyclohexylammonium Trichloro(cyclohexylamine)platinate(II)

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**Abstract.**  $[\text{C}_6\text{H}_{11}\text{NH}_3][\text{PtCl}_3(\text{C}_6\text{H}_{11}\text{NH}_2)]$ ,  $\text{C}_6\text{H}_{14}\text{N}^+ \cdot \text{C}_6\text{H}_{13}\text{Cl}_3\text{N}^-\text{Pt}^-$ , monoclinic,  $P2_1/c$ ,  $a = 12.154$  (2),  $b = 7.940$  (2),  $c = 20.324$  (4) Å,  $\beta = 115.28$  (1)°,  $V = 1773.7$  (6) Å<sup>3</sup>,  $D_c = 1.88$ ,  $D_o = 1.89$  (2) Mg m<sup>-3</sup>. The structure was determined by Patterson and electron density difference methods and refined by full-matrix least squares to  $R = 0.049$ ,  $R_w = 0.055$  for all 3721 reflections. The structure comprises discrete cations and anions, hydrogen bonded together in double layers. Bond distances and angles around platinum are normal.

**Introduction.** We have made a number of unsuccessful attempts to synthesize suitable crystals of *cis*-dichlorobis(cyclohexylamine)platinum(II) for an X-ray structure determination, particularly since we have shown that the reported structure of this compound (Iball & Scrimgeour, 1977) is an incorrect solution of the structure of the corresponding *trans* isomer (Zanotti, Del Pra, Bombieri & Tamburro, 1978; Lock, Speranzini & Zvagulis, 1980). So far we have had no success, although we have examined the structure of the compound solvated with hexamethylphosphoramide (Lock *et al.*, 1980). One of the compounds we isolated during these attempts was the salt cyclohexylammonium trichloro(cyclohexylamine)platinate(II) and we describe the structure of this compound herein. The compound was prepared by reacting cyclohexylamine (0.44 g, 4.4 mmol) dropwise with an aqueous solution (20 ml) of potassium tetrachloroplatinate(II) (0.909 g, 2.2 mmol). After a week a light-brown precipitate had formed and was removed by filtration. The residual yellow solution after slow evaporation for one month yielded yellow crystals of cyclohexylammonium trichloro(cyclohexylamine)platinate(II): yield ~3.5 mg; calculated: C, 28.8; H, 5.4; N, 5.6%; found: C, 28.5; H, 5.5; N, 5.6%.

A pale-yellow crystal, homogeneous under the polarizing microscope, was ground to a cylinder, radius 0.1 mm, length 0.6 mm. The crystal symmetry was obtained from precession photographs and the unit cell was determined by a least-squares fit of 15 well centred reflections ( $19^\circ < 2\theta < 26^\circ$ ) at 295 K on a Syntex  $P2_1$  diffractometer. The density of the crystal was deter-

mined by flotation in a bromoform–chloroform mixture yielding  $Z = 4$ . The intensities of 4082 independent reflections up to  $2\theta = 55^\circ$  were measured with Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) using a crystal monochromator. The intensities were measured in the  $2\theta$  (counter)– $\theta$ (crystal) scan mode. After removal of reflections with  $I < 0$  (361), 2703 reflections were considered observed [ $I > 3\sigma(I)$ ] and were used for the structure determination; 1018 were considered unobserved [ $3\sigma(I) > I > 0$ ] and were given no weight in the structure determination unless  $|F_c| > |F_o|$  (442). The method of data treatment has been described previously (Hughes, Krishnamachari, Lock, Powell & Turner, 1977; Lippert, Lock, Rosenberg & Zvagulis, 1977). Corrections were made for absorption ( $\mu = 8.75$  mm<sup>-1</sup>, range of  $A^*$ , 4.01–4.31), Lorentz–polarization and extinction (Larson, 1967,  $g = 6.670 \times 10^{-8}$ ). The stability of the experimental system was monitored by measuring two standard reflections after every 48 reflections (015,  $\bar{1}30$ ). They showed e.s.d.'s of 2.30, 2.11% respectively with no time variation.

The Pt atom was found from a three-dimensional Patterson synthesis. Subsequent refinement and a

Table 1. Final atomic positional parameters and temperature factors ( $U_{eq}$ , Å<sup>2</sup>) ( $\times 10^3$ )

	$x$	$y$	$z$	$U_{eq}$
Pt	87.44 (2)	292.88 (4)	179.70 (2)	40.5 (2)
Cl(1)	-12.4 (2)	46.6 (3)	128.8 (1)	58 (2)
Cl(2)	97.4 (3)	361.0 (4)	71.9 (1)	69 (2)
Cl(3)	177.4 (2)	542.9 (3)	232.1 (1)	53 (1)
N(1)	80.5 (7)	234.9 (9)	276.5 (4)	44 (4)
C(1)	197.2 (9)	159 (1)	334.6 (5)	51 (6)
C(2)	178 (1)	132 (2)	403.3 (5)	66 (8)
C(3)	297 (1)	58 (2)	464.2 (6)	93 (12)
C(4)	329 (1)	-103 (2)	437.2 (8)	95 (11)
C(5)	348 (1)	-72 (2)	369.1 (7)	94 (12)
C(6)	231 (1)	1 (2)	308.5 (6)	82 (9)
N(1a)	867.0 (9)	231 (1)	923.9 (6)	74 (8)
C(1a)	733 (1)	180 (2)	904.4 (8)	87 (11)
C(2a)	733 (1)	25 (2)	944 (1)	136 (17)
C(3a)	601 (2)	-20 (4)	926 (1)	232 (34)
C(4a)	518 (2)	-12 (3)	856 (1)	154 (22)
C(5a)	524 (1)	137 (4)	817 (1)	166 (25)
C(6a)	657 (2)	188 (3)	835 (1)	204 (34)

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difference map revealed all the non-hydrogen atoms. Anisotropic full-matrix least-squares refinement, minimizing  $\sum w(|F_o| - |F_c|)^2$ , was terminated at  $R = 0.042$  (0.049),  $R_w = 0.052$  (0.055) for the observed (all) reflections with a final maximum shift/error of 0.007. The weighting scheme applied was  $w = [\sigma_F^2 + (0.03F_o)^2]^{-1}$ ;\* the error in an observation of unit weight was 1.189. Scattering factors were taken from Cromer & Waber (1974) and corrections for anomalous dispersion were applied to Pt and Cl (Cromer, 1974). The final positional parameters are given in Table 1.† All calculations were carried out on CDC 6400 or CYBER 170/730 computers.‡

**Discussion.** The product obtained was not the expected *cis*-PtCl<sub>2</sub>(C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>)<sub>2</sub> but [C<sub>6</sub>H<sub>11</sub>NH<sub>3</sub>][PtCl<sub>3</sub>(C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>)] suggesting that the reaction conditions which have been used for the preparation of *cis*-diamine complexes of Pt<sup>II</sup> (Kauffman & Cowan, 1963) are too acid. Kong & Rochon (1975, 1978) have produced salts containing similar [PtCl<sub>3</sub>(amine)]<sup>-</sup> anions in dimethylformamide but as the potassium salts; the protonated amine was not formed.

Selected interatomic distances and angles are given in Table 2, and the anion is illustrated in Fig. 1. The anion has the expected square-planar configuration about Pt with minor deviations from the plane (Table 3). On the basis of the *trans* influence (Appleton, Clark & Manzer, 1973) Pt—Cl(2) should be shorter than Pt—Cl(1) and Pt—Cl(3), although the differences should be small. The *trans* influence does not seem to hold, however, since Pt—Cl(2) is significantly longer than Pt—Cl(3) [although not than Pt—Cl(1)]. There is a correspondence, however, between the number of strong hydrogen bonds to the Cl atoms, and the Pt—Cl distances. They are within the range normally observed (Lock *et al.*, 1980, and references therein). Similarly the Pt—N distance agrees with values we have found previously (Lock *et al.*, 1980).

The torsional angles (Table 3) in the rings are very similar to those observed previously (Zanotti *et al.*, 1978; Lock *et al.*, 1980) but the torsional angle involving Pt and distances of C(1), C(2), C(6) from the

Table 2. Interatomic distances (Å) and angles (°) with *e.s.d.*'s in parentheses

Pt—Cl(1)	2.301 (3)	Pt—N(1)	2.058 (9)
Pt—Cl(2)	2.310 (3)	N(1)—C(1)	1.53 (1)
Pt—Cl(3)	2.297 (2)	N(1a)—C(1a)	1.56 (2)
C(1)—C(2)	1.52 (2)	C(1a)—C(2a)	1.47 (3)
C(2)—C(3)	1.56 (2)	C(2a)—C(3a)	1.53 (3)
C(3)—C(4)	1.51 (2)	C(3a)—C(4a)	1.35 (3)
C(4)—C(5)	1.52 (2)	C(4a)—C(5a)	1.45 (4)
C(5)—C(6)	1.54 (2)	C(5a)—C(6a)	1.55 (3)
C(6)—C(1)	1.48 (2)	C(6a)—C(1a)	1.31 (2)
Possible hydrogen bonds			
Cl(1)⋯N(1) <sup>b</sup>	3.447 (9)	Cl(2)⋯N(1a) <sup>d</sup>	3.26 (1)
Cl(1)⋯N(1a) <sup>c</sup>	3.28 (1)	Cl(2)⋯N(1a) <sup>e</sup>	3.280 (9)
		Cl(3)⋯N(1) <sup>f</sup>	3.422 (9)
Cl(1)—Pt—Cl(2)	90.2 (1)	Cl(2)—Pt—N(1)	179.1 (2)
Cl(1)—Pt—Cl(3)	176.6 (1)	Cl(3)—Pt—N(1)	87.4 (2)
Cl(1)—Pt—N(1)	90.6 (2)	Pt—N(1)—C(1)	115.1 (7)
Cl(2)—Pt—Cl(3)	91.7 (1)		
N(1)—C(1)—C(2)	108 (1)	N(1a)—C(1a)—C(2a)	109 (1)
N(1)—C(1)—C(6)	111.3 (7)	N(1a)—C(1a)—C(6a)	116 (2)
C(6)—C(1)—C(2)	113 (1)	C(6a)—C(1a)—C(2a)	117 (2)
C(1)—C(2)—C(3)	109 (1)	C(1a)—C(2a)—C(3a)	108 (2)
C(2)—C(3)—C(4)	109 (1)	C(2a)—C(3a)—C(4a)	118 (3)
C(3)—C(4)—C(5)	111 (1)	C(3a)—C(4a)—C(5a)	115 (2)
C(4)—C(5)—C(6)	110 (1)	C(4a)—C(5a)—C(6a)	112 (2)
C(5)—C(6)—C(1)	109.4 (9)	C(5a)—C(6a)—C(1a)	116 (2)

Atoms with superscripts *b–f* are related to those in Table 1 by (b)  $-x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (c)  $1 - x, -y, 1 - z$ ; (d)  $1 - x, 1 - y, 1 - z$ ; (e)  $x - 1, y, z - 1$ ; (f)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ .

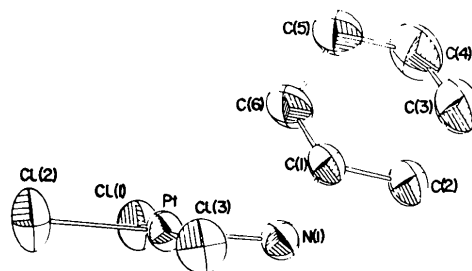


Fig. 1. The molecular anion trichloro(cyclohexylamine)platinate(II).

square plane show that the arrangement of the ring is closer to that in *cis*-PtCl<sub>2</sub>(C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>)<sub>2</sub>·2[(CH<sub>3</sub>)<sub>2</sub>N]<sub>3</sub>PO. In this arrangement C(6) is above the square plane only 3.38 (2) Å from the Pt atom and 3.61 (2) Å from Cl(1). Thus the C atom and the attached H atoms will be covering the axial position above Pt from attack. In this case, with three Cl atoms attached to Pt, there are no other attached bulky groups which can force this conformation by intramolecular interaction. Rosenberg (1976) suggested that the low toxicity of *cis*-PtCl<sub>2</sub>(C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>)<sub>2</sub> may arise from this protection preventing coordination to S atoms in the kidney tubules. It is dangerous, for these molecules with a certain amount of flexibility, to extrapolate from the

\* The value of 0.03 was chosen to make  $\langle w(|F_o| - |F_c|)^2 \rangle$  locally independent of  $|F_o|$  and  $\sin \theta/\lambda$ .

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35903 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

‡ Most programs for initial data treatment were from the XRAY package (Stewart, 1976). The structure was solved using SHELX (Sheldrick, 1976). Final refinements and difference syntheses used the internally written Fourier and full-matrix least-squares programs SYMFOU and CUDLS written by J. S. Rutherford and J. S. Stephens respectively. The planes and torsional angles were calculated using NRC-22 (Pippy & Ahmed, 1978). The diagrams were prepared using ORTEP II (Johnson, 1976).

Table 3. *Least-squares planes and torsional angles*

Plane	Distance from plane in Å		
Cl(1)Cl(2)Cl(3)N(1)	Cl(1), 0.030 (3); Cl(2), -0.028 (4); Cl(3), 0.031 (3); Pt, -0.026 (1); C(1), -1.41 (1); C(2), -1.22 (1); C(6), -2.35 (1); N(1), -0.033 (9)		
Torsion angles (°)			
Cl(1)PtN(1)C(1)	99.1 (2)	Cl(3)PtN(1)C(1)	-83.7 (2)
PtN(1)C(1)C(2)	177 (1)	PtN(1)C(1)C(6)	-59 (1)
N(1)C(1)C(2)C(3)	-179 (1)	N(1a)C(1a)C(2a)C(3a)	178 (1)
C(1)C(2)C(3)C(4)	-57 (1)	C(1a)C(2a)C(3a)C(4a)	46 (2)
C(2)C(3)C(4)C(5)	60 (1)	C(2a)C(3a)C(4a)C(5a)	-45 (2)
C(3)C(4)C(5)C(6)	-60 (1)	C(3a)C(4a)C(5a)C(6a)	41 (2)
C(4)C(5)C(6)C(1)	58 (1)	C(4a)C(5a)C(6a)C(1a)	-43 (2)
C(5)C(6)C(1)C(2)	-58 (1)	C(5a)C(6a)C(1a)C(2a)	49 (2)
C(6)C(1)C(2)C(3)	58 (1)	C(6a)C(1a)C(2a)C(3a)	-47 (2)
N(1)C(1)C(6)C(5)	-179 (1)	N(1a)C(1a)C(6a)C(5a)	-180 (1)

solid state to solution conditions, but we think it is interesting that in the three Pt-C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub> compounds for which structures have been determined (Zanotti *et al.*, 1978; Lock *et al.*, 1980; this work) the same effect is found.

The cation shows very high anisotropic temperature factors but there is no evidence of conformational disorder. A careful examination of the difference map shows the highest residual peak near the cation is 0.7 e Å<sup>-3</sup> between N(1A) and C(1A). The thermal ellipsoids are all oriented roughly in the same direction and probably correspond to the motion of the ring like a leaf flapping in the wind. Consideration of the packing (see below) shows that the intermolecular forces between cations are very weak.

The packing of the ions in the unit cell is shown in Fig. 2. The anions are arranged such that they form a double layer with the ligand square planes close to the *bc* plane and the cyclohexyl rings on the outside of the double layer. Double layers related by the *a* translation are separated by a zigzag layer of cations centred at  $x = \frac{1}{2}$ . Within the double layer along the *b* direction there are spiral chains of molecules related by the 2<sub>1</sub> axis, and bound to adjacent molecules by rather weak N(1)···Cl(1) and N(1)···Cl(3) hydrogen bonds

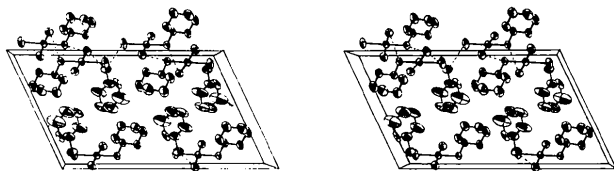


Fig. 2. The packing of the cations and anions in the unit cell. *c* and *a*\* are parallel to the bottom and side of the page respectively and the view is down *b*. Hydrogen bonds are represented by dotted lines.

[3.44 (1), 3.42 (2) Å]. There are no direct hydrogen bonds between these chains along the *c* direction, but hydrogen bonding to the NH<sub>3</sub> group of the cation holds adjacent chains together with strong hydrogen bonds N(1a)<sup>e</sup>···Cl(1), N(1a)<sup>d</sup>···Cl(2), N(1a)<sup>e</sup>···Cl(2) [3.28 (1), 3.26 (1), 3.28 (1) Å]. This hydrogen bonding of the cation to the double layer means the cyclohexyl ring of the cation is also pointing out of the double layer. Thus any contacts near  $x = \frac{1}{2}$  are H···H contacts and the forces are van der Waals.

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