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trans-Dibromobis(cyclohexylamine)platinum(II)

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Abstract. $[PtBr_2(C_6H_{11}NH_2)_2]$, monoclinic, $P2_1/c$, $Z = 2$, $a = 6{\cdot}154\,(2)$, $b = 8{\cdot}823\,(3)$, $c = 15{\cdot}111\,(3)$ Å, $\beta = 96{\cdot}79\,(2)°$, $V = 814{\cdot}7\,(3)$ Å^3, $D_c = 2{\cdot}26$, $D_o = 2{\cdot}25\,(2)$ Mg m^{-3}. The structure was solved by heavy-atom methods and refined to $R = 0{\cdot}052$, $R_w = 0{\cdot}083$ based on 1885 independent reflections. The molecular structure is very like that of the corresponding chloro complex with normal bond parameters [Pt—Br 2·388 (2); Pt—N 2·06 (1) Å], but the packing of the molecules within the cell is different.

Introduction. The title compound was prepared by a modification of Dhara's (1970) method involving the reaction of $K_2[PtCl_4]$ (0·97 g) with KI (1·6 g) in water (10 ml). Cyclohexylamine (0·49 g) was added dropwise to the resulting solution and the yellow precipitate of $[Pt(C_6H_{11}NH_2)_2I_2]$ was filtered off and dried. The yellow powder (0·66 g) was stirred with aqueous silver nitrate (0·34 g, 50 ml) for a week. AgI was removed by filtration and KBr solution (0·14 g, 25 ml) was added dropwise to the filtrate. A pale-yellow powder precipitated and was separated by filtration. This powder was dissolved in acetone and crystals of the title compound were obtained by slow evaporation of this solution. Composition: calculated, C, 26·1; H, 4·7; N, 5·1%; found, C, 26·3; H, 4·7; N, 5·0%. The crystals were long needles, the needle axis being *a*. A crystal, which was homogeneous under the polarizing microscope, was cut and ground into a cylinder of dimensions $r = 0{\cdot}07$, $l = 0{\cdot}25$ mm. Photographs showed the systematic absences of $P2_1/c$. The cell was determined by the least-squares fit of 15 well centred reflections ($17° < 2\theta < 25°$) on a Syntex $P2_1$ diffractometer at 296 K and the density was determined by flotation in aqueous zinc bromide solutions, yielding $Z = 2$. The intensities of 1885 independent reflections up to $2\theta = 55°$ ($hk \pm l$) were measured with Mo $K\alpha$ radiation at 296 K. The computer-controlled Syntex $P2_1$ diffractometer was operated in a 2θ(counter)–θ(crystal) scan mode with a crystal monochromator. After removal of systematically absent reflections and of those for which $I < \sigma(I)$, 1306 were considered observed $[I > 3{\cdot}0\sigma(I)]$ and were used for the structure determination; 191 were considered unobserved and were given no weight in the structure determination unless $|F_c| > |F_o|$. The method of data treatment has been described previously (Hughes, Krishnamachari, Lock, Powell & Turner, 1977; Lippert, Lock, Rosenberg & Zvagulis, 1977). Correction was made for absorption ($\mu = 14{\cdot}15$ mm^{-1}, absorption coefficient, A^*, limits, 4·996, 5·563) and secondary extinction (Larson, 1967; $g = 5{\cdot}548 \times 10^{-8}$). The stability of the experimental system was monitored by measuring two standard reflections after every 48 reflections (106, 142). They showed an e.s.d. of 1·7% with no time variation.

The structure was solved by placing the Pt atom at the inversion centre (*a*). A three-dimensional difference map revealed the Br and N atoms. Subsequent full-matrix least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, followed by an electron density difference synthesis revealed all the remaining non-hydrogen atoms. At this stage the temperature factors for all atoms were made sequentially anisotropic. Statistical tests (Hamilton, 1965) were applied to show that each increase in the number of variables was justified. Convergence was obtained with 80 variables at $R = 0{\cdot}0505$ (0·0516), and $R_w = 0{\cdot}0822$ (0·0828) for the observed (all) reflections, with a final maximum shift/error of 0·00125. The weighting scheme was $1/w = \sigma_F^2 + (0{\cdot}03F_o)^2$.† Scattering factors were taken from Cromer & Waber (1974) and correction for anomalous scattering was applied to Pt and Br (Cromer, 1974). The final difference map showed a peak of 1·7 e Å^{-3} between N and C(1) and a valley of −2·4 e Å^{-3} near Br. No attempt was made to find the H atoms. All calculations were carried out on a CDC 6400 computer.‡ The final positional parameters and U_{eq} of the non-hydrogen atoms are given in Table 1.§

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† The value 0·03 was chosen to make $\langle w(|F_o| - |F_c|)^2\rangle$ locally independent of $|F_o|$ and $\sin\theta/\lambda$.

‡ Most programs used were from the XRAY package (Stewart, 1976). The full-matrix least-squares program *CUDLS* was written internally (J. S. Stephens). The diagrams were prepared using *ORTEP* II (Johnson, 1976).

§ Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35283 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final positional parameters and equivalent isotropic thermal parameters (with e.s.d.'s in parentheses) for the non-hydrogen atoms*

	x	y	z	U_{eq}(Å^2)*
Pt	0	0·5	0·5	0·0344 (4)
Br	0·2926 (4)	0·3474 (2)	0·5692 (2)	0·0695 (12)
N	0·1923 (19)	0·6910 (14)	0·5110 (8)	0·039 (7)
C(1)	0·255 (2)	0·752 (2)	0·602 (1)	0·038 (8)
C(2)	0·058 (2)	0·794 (2)	0·648 (1)	0·052 (11)
C(3)	0·125 (3)	0·856 (2)	0·740 (1)	0·058 (12)
C(4)	0·273 (3)	0·993 (2)	0·738 (1)	0·058 (11)
C(5)	0·471 (3)	0·958 (3)	0·689 (2)	0·079 (18)
C(6)	0·404 (3)	0·891 (2)	0·598 (1)	0·051 (10)

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$.

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

Pt—Br	2·388 (2)	Br—Pt—N	91·7 (3)
Pt—N	2·06 (1)	Pt—N—C(1)	117·3 (9)
N—C(1)	1·49 (2)	N—C(1)—C(2)	112 (1)
C(1)—C(2)	1·51 (2)	N—C(1)—C(6)	110 (1)
C(2)—C(3)	1·51 (2)	C(1)—C(2)—C(3)	111 (1)
C(3)—C(4)	1·52 (3)	C(2)—C(3)—C(4)	112 (1)
C(4)—C(5)	1·53 (3)	C(3)—C(4)—C(5)	111 (2)
C(5)—C(6)	1·51 (3)	C(4)—C(5)—C(6)	112 (2)
C(6)—C(1)	1·53 (2)	C(5)—C(6)—C(1)	112 (2)
Br···N	3·20 (1)	C(6)—C(1)—C(2)	110 (1)
Br···N^a	3·10 (1)		
Possible hydrogen-bond distance			
Br···N^b	3·54 (1)		

Symmetry code: the atoms N^a, N^b are related to those in Table 1 by (a) $-x$, $1-y$, $1-z$ and (b) $1-x$, $1-y$, $1-z$.

Discussion. The method of preparation described should give the *cis* form of the title compound, and certainly we have demonstrated that with the corresponding chloride and other amines, *cis* complexes are obtained. Crystallization was, however, generally from other solvents. It appears that the formation of the *trans* complex in this case is because of the crystallization from acetone. We have shown that *trans*-dichlorobis(cyclobutylamine)platinum(II) is also obtained from Dhara's method if recrystallization is from acetone. Thus the choice of solvent used for recrystallization and purification of these compounds is important in light of the current interest in the *cis* forms of these complexes as anticancer agents (Connors, Jones, Ross, Braddock, Khokhar & Tobe, 1972; Braddock, Connors, Jones, Khokhar, Melzack & Tobe, 1975). The *trans* forms are inactive.

The molecule is shown in Fig. 1 and selected interatomic distances and angles are given in Table 2. The molecular structure is very similar to that observed for the corresponding chloro complex (Zanotti, Del Pra, Bombieri & Tamburro, 1978). Thus the bonded ligand atoms form a strict square plane, and there is no twisting of the two halves of the square plane as was claimed for *cis*-dichlorobis(cyclohexylamine)platinum(II) (Iball & Scrimgeour, 1977). The Pt—Br distance [2·388 (2) Å] is 0·086 Å longer than the corresponding Pt—Cl distance whereas both the covalent radii and ionic radii of Br and Cl differ by about 0·16 Å (Cotton & Wilkinson, 1972). This implies that the Pt—Br bond is stronger than the Pt—Cl bond, which is consistent with the B-metal behaviour of Pt. The Pt—N distance [2·06 (1) Å] does not differ significantly from that found in the chloro complex [2·078 (5) Å]. Distances and angles within the hydrocarbon rings do not differ for the two complexes.

Despite the broad similarities in the two compounds there are distinct differences in certain of the intramolecular non-bonding distances and in torsional angles (see Table 3). This leads to different packing within the cell and even to a different space group. Thus in the chloro complex (Zanotti *et al.*, 1978) the torsional angle Cl—Pt—N—C(1) is only 10·0° so that the C(1) atom is only slightly out of the ligand square plane and close to the Cl atom and the torsional angle Pt—N—C(1)—C(2) is 66·5° and C(2) lies roughly above C(1) (referred to the ligand square plane as base) and still close to the same Cl atom. In the bromo complex the Br—Pt—N—C(1) angle is −69° and thus C(1) is much farther above the ligand plane and the C(1)—Br distance is longer (3·63 *vs* 3·30 Å). The Pt—N—C(1)—C(2) angle of −59° means that C(2) is now rotated away from the Br atom, giving a long C(2)—Br distance (4·43 *vs* 3·71 Å). Indeed, the

Table 3. *Torsion and dihedral angles* (°) (*maximum e.s.d.* 2°)

Br—Pt—N—C(1)	−69	C(1)—C(2)—C(3)—C(4)	57
Pt—N—C(1)—C(2)	−59	C(2)—C(3)—C(4)—C(5)	−54
Pt—N—C(1)—C(6)	178	C(3)—C(4)—C(5)—C(6)	52
N—C(1)—C(2)—C(3)	−180	C(4)—C(5)—C(6)—C(1)	−54
N—C(1)—C(6)—C(5)	180	C(5)—C(6)—C(1)—C(2)	56
		C(6)—C(1)—C(2)—C(3)	−57

Dihedral angles between planes

C(1)C(2)C(3)—C(4)C(5)C(6)	4
C(2)C(3)C(4)—C(5)C(6)C(1)	1
C(2)C(1)C(6)—C(3)C(4)C(5)	3
PtNC(1)—C(2)C(1)C(6)	57

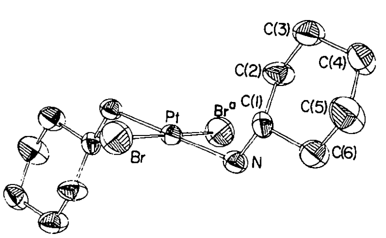

Fig. 1. A molecule of *trans*-dibromobis(cyclohexylamine)platinum(II) showing the atom numbering.

rotation brings C(2) much closer to Br^a (3·91 Å). The two close contacts of C(1) and C(2) with the same Cl atom were used to explain the inequality of the Cl—Pt—N angles (85·4, 94·6°). The explanation is clearly reasonable since the Br—Pt—N angles (88·3, 91·7°) are more nearly equal. The torsional angles in the ring (72·3–53·5°; average 61·5°) are generally larger than in the chloro complex (58·0–54·4°), giving a more compact ring.

The crystal packing for the two compounds is clearly different, as can be seen by comparing shortest Pt—Pt distances. For the bromo complex these are 8·823 Å (**b** translation), 6·154 Å (**a** translation) and 8·75 Å (**c** glide), and for the chloro complex, 4·95 Å ($\frac{1}{2}$**b** translation), 6·673 Å (**c** translation) and 13·50 Å ($\frac{1}{2}$**a** + $\frac{1}{2}$**b** translation). The principal difference can be seen by considering the Pt atoms in the *bc* plane for the bromo complex and in the (101) plane for the chloro complex, illustrated in Fig. 2. The eclipsed arrangement along **b** for the chloro complex gives a somewhat longer *b* axis than the staggered arrangement in the bromo complex, whereas the *n*-glide distance is shorter than the *c* axis. The packing efficiency in the two space groups is very similar. The difference in molecular volume of 14·4 Å^3 is comparable to the differences in volume of two Cl^- and two Br^- ions, ranging from 7·3 to 19·1 Å^3 calculated from such diverse structures as KX, NaX, $[Pt(NH_3)_4X_2]$, $K_2[PtX_4]$ and $K_2[PtX_6]$ (X = Cl, Br).

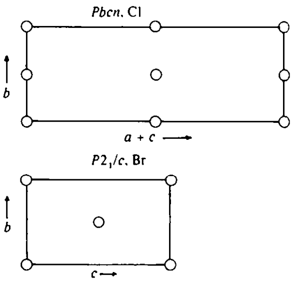

Fig. 2. Comparison of the Pt arrangement in the *bc* plane for the bromo complex and the (101) plane for the chloro complex.

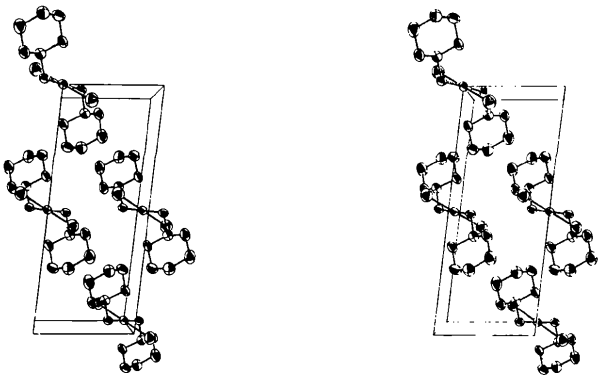

Fig. 3. The packing of the molecules within the unit cell.

The packing is illustrated in Fig. 3. The molecules form chains along the **a** direction at $y = 0$, $z = 0$ and $y = \frac{1}{2}$, $z = \frac{1}{2}$ with weak hydrogen bonds between N and Br of adjacent molecules (N···Br, 3·54 Å; *cf.* 3·47–3·51 Å in NH_4Br, Levy & Peterson, 1953). Contact between these chains in the **c** direction is primarily between the hydrocarbon ring on one molecule and Br atoms in molecules in the chain related by the **c** glide. In the **b** direction the hydrocarbon rings are interleaved, therefore. The other important contact in the **b** direction is between a Br atom on one molecule and the H atoms attached to C(6) of the next.

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References

Braddock, P. D., Connors, T. A., Jones, M., Khokhar, A. R., Melzack, D. H. & Tobe, M. L. (1975). *Chem. Biol. Interact.* **11**, 145–161.

Connors, T. A., Jones, M., Ross, W. C. J., Braddock, P. D., Khokhar, A. R. & Tobe, M. L. (1972). *Chem. Biol. Interact.* **5**, 415–424.

Cotton, F. A. & Wilkinson, G. (1972). *Advanced Inorganic Chemistry*, 3rd ed., pp. 52, 117. New York: Interscience.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1, p. 149. Birmingham: Kynoch Press.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 72ff. Birmingham: Kynoch Press.

Dhara, S. C. (1970). *Indian J. Chem.* **8**, 193–194.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

Hughes, R. P., Krishnamachari, N., Lock, C. J. L., Powell, J. & Turner, G. (1977). *Inorg. Chem.* **16**, 314–319.

Iball, J. & Scrimgeour, S. N. (1977). *Acta Cryst.* **B33**, 1194–1196.

Johnson, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.

Levy, H. A. & Peterson, S. W. (1953). *J. Am. Chem. Soc.* **75**, 1536–1542.

Lippert, B., Lock, C. J. L., Rosenberg, B. & Zvagulis, M. (1977). *Inorg. Chem.* **16**, 1525–1529.

Stewart, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Zanotti, G., Del Pra, A., Bombieri, G. & Tamburro, A. M. (1978). *Acta Cryst.* **B34**, 2138–2141.