Tris[*cis*-dichloro(1,2-diaminocyclohexane)platinum(II)] Hydrate and *cis*-Dibromo(1,2-diaminocyclohexane)platinum(II)

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Abstract

$[Pt(C_6H_{14}N_2)Cl_2]_3 \cdot H_2O$ (*A*) is monoclinic, $C2/c$, $Z = 8$, $a = 24\cdot31$ (2), $b = 12\cdot439$ (5), $c = 20\cdot981$ (9) Å, $\beta = 110\cdot59$ (5)°. $[Pt(C_6H_{14}N_2)Br_2]$ (*B*) is monoclinic, $C2/c$, $Z = 8$, $a = 15\cdot212$ (4), $b = 11\cdot612$ (5), $c = 13\cdot268$ (5) Å, $\beta = 121\cdot17$ (2)°. The structure of (*A*) was determined by direct methods and that of (*B*) by heavy-atom methods. Both were refined by full-matrix least-squares procedures to $R = 0\cdot059$, $R_w = 0\cdot072$ for (*A*) and $R = 0\cdot041$, $R_w = 0\cdot056$ for (*B*). The basic structures of the molecular units are similar for the chloro and bromo complexes. Bond lengths [Pt—Cl $2\cdot284$ (7)–$2\cdot310$ (6) Å; Pt—Br $2\cdot429$ (1), $2\cdot439$ (2) Å; Pt—N $2\cdot01$ (2)–$2\cdot06$ (2) Å] are normal. Both structures contain pairs of molecules packed square plane to square plane and hydrogen bonded together through N—H···X (X = Cl, Br) to give relatively short Pt···Pt distances [$3\cdot479$ (1), $3\cdot368$ (1) Å, (*A*); $3\cdot511$ (1) Å, (*B*)], but in addition the chloro complex contains a third molecule which is not packed in this way. Hydrogen bonds are important in determining the packing in the chloro complex, but surprisingly the water molecule is not involved in strong hydrogen bonding.

Introduction

Since Rosenberg, Van Camp, Trosko & Mansour (1969) discovered that *cis*-diamminedichloroplatinum-(II) was an effective anti-cancer agent, there have been extensive studies to see if other Pt compounds would act in the same way. One series of complexes, which shows promise, is based on the [(1,2-diaminocyclo-hexane)platinum(II)]$^{2+}$ moiety and a number of complexes have been tested (Gale, Walker, Atkins, Smith & Meischen, 1974; Gale, Atkins, Meischen, Smith & Walker, 1976, 1977; Gale, Atkins, Meischen & Schwartz, 1978; Gale, Smith & Schwartz, 1979; Ogawa, Gale, Meischen & Cooke, 1976; Ward, Young, Fauvie, Wolpert, Davis & Guarino, 1976; Ridgway, Speer, Hall, Stewart, Newman & Hill, 1977; Schwartz, Meischen, Gale, Atkins, Smith & Walker, 1977; Speer,

Ridgway, Stewart, Hall, Zapata & Hill, 1977; Loeb, Hill, Pardue, Hill, Khan & King, 1977; Hill *et al.*, 1977; Burchenal, Kalaher, O'Toole & Chisholm, 1977; Burchenal, Kalaher, O'Toole & Chisholm, 1977; Burchenal, Kalaher, Dew, Lokys & Gale, 1978). In the early work it was not realized apparently that 1,2-diaminocyclohexane (dac) can exist as *cis*, *RR*, and *SS* isomers. The first work to show that complexes of the three different isomers behaved differently physiologically was by Kidani, Inagaki, Saito & Tsukagochi (1977). Since that time studies have been concentrated on the action of complexes of the separated isomers (Kidani, Inagaki, Iigo, Hoshi & Kuretani, 1978; Ridgway *et al.*, 1978; Speer *et al.*, 1978). This is the first structural work on two Pt complexes of the *cis* isomer of 1,2-diaminocyclohexane. In this isomer, the amino donor groups are considered to occupy axial and equatorial positions of the chain conformation of the cyclohexane ring, while in the *trans* isomer the amino groups are either both axial (*SS*) or both equatorial (*RR*).

Experiments

Separation of 1,2-diaminocyclohexane (dac) into its cis and racemic RR, SS components

Commercial 1,2-diaminocyclohexane from ICN Pharmaceuticals was used as the starting compound. The procedure of Saito & Kidani (1976) was followed exactly to give [Ni(*cis*-dac)$_2$Cl$_2$] (yield 13·49 g) and (*cis*-dac).H$_2$SO$_4$ (yield 10·32 g, 67%).

Preparation of [Pt(cis-dac)Cl₂]₃·H₂O

This was prepared by a modification of the procedure of Ito, Fujita & Saito (1967) in which (*cis*-dac).H$_2$SO$_4$ (0·56 g) was used instead of *cis*-dac and the reaction time was 36 h. The solid was recrystallized by solution in dimethylformamide followed by the addition of 0·1 *M* HCl, dropwise, until the solution just turned cloudy. The mixture was cooled in a refrigerator (273 K) for 3 d. Yellow crystals formed as thin plates. They were separated by filtration and air

dried (calc. for $C_{18}H_{44}Cl_6N_6OPt_3$: C, 18·7; H, 3·8; N, 7·3%; found: C, 19·4; H, 3·9; N, 7·2%).

Preparation of [Pt(cis-dac)Br₂]

$[Pt(cis\text{-}dac)Cl_2]_3.H_2O$ (0·107 g) was reacted, as a suspension in water, with two molar equivalents (0·090 g) of silver nitrate. The bulk of the silver chloride precipitate was removed by centrifugation; residual traces were removed by filtration. The filtrate was reacted with potassium bromide (0·04 g). A yellow precipitate of $[Pt(cis\text{-}dac)Br_2]$ was separated by filtration and recrystallized by precipitation from an acetone solution by vapour diffusion of water. Yellow crystals were obtained after two weeks (calc. for $C_6H_{14}Br_2N_2Pt$: C, 15·4; H, 3·0; N, 6·0%; found: C, 15·1; H, 2·8; N, 5·7%).

Collection of the X-ray data

Crystals of the two compounds were selected after examination under a polarizing microscope for homogeneity. Precession photographs of both crystals showed they were monoclinic with the systematic absences of Cc or $C2/c$. The E statistics showed the crystals to be centrosymmetric so the latter space group

was chosen for both crystals and justified by the satisfactory solution of the crystal structure. Unit-cell parameters were obtained from a least-squares fit of χ, φ and 2θ for 15 reflections for each crystal in the range $16° < 2\theta < 33°$ recorded on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å at 295 K). Crystal and experimental data are summarized in Table 1. Densities were obtained by flotation in chloroform–bromoform (chloride) and bromoform–diiodoethane (bromide) mixtures. Intensity data were also recorded on the Syntex $P2_1$ diffractometer using a coupled θ(crystal)–2θ(counter) scan. The methods of selection of scan rates and initial data treatment have been described (Lippert, Lock, Rosenberg & Zvagulis, 1977; Hughes, Krishnamachari, Lock, Powell & Turner, 1977). Corrections were made for Lorentz–polarization effects. No correction was made for absorption; this introduces a maximum error in $|F_o|$ of 2% (Cl) and 3% (Br).

Solution of the structure

For the bromide the coordinates of the Pt atom were found from a three-dimensional Patterson synthesis. For the chloride the phase problem was solved by direct methods using 50 reflections with $|E| > 1·68$ and 14 sets of starting phases. A subsequent E map with the most reliable phases yielded one Pt atom [Pt(1)]. A series of full-matrix least-squares refinements followed by three-dimensional difference syntheses revealed all the non-hydrogen atoms for both crystals. After refinement, the temperature factors of the Pt and halogen atoms, which were previously isotropic, were made anisotropic. Tests were carried out to determine whether the use of increased parameters was significant (Hamilton, 1965). Further refinement using

Table 1. Crystal and refinement data

Compound	$[Pt(C_6H_{14}N_2)Cl_2]_3.H_2O$	$[Pt(C_6H_{14}N_2)Br_2]$
M_r	1158·3	469·0
Crystal shape, size (mm)	Cylinder, $r = 0·06$, $l = 0·4$	Cylinder, $r = 0·05$, $l = 0·4$
Space group	$C2/c$	$C2/c$
Unit-cell parameters		
a (Å)	24·31 (2)	15·212 (4)
b (Å)	12·439 (5)	11·612 (5)
c (Å)	20·981 (9)	13·268 (5)
β (°)	110·59 (5)	121·17 (2)
Volume (Å³)	5938 (6)	2006 (1)
Z	8	8
ρ_{calc} (Mg m⁻³)	2·59	3·11
ρ_{obs} (Mg m⁻³)	2·56	3·12
Linear absorption coefficient (mm⁻¹)	15·39	23·10
Absorption correction factor, A^*, limits	4·17, 4·50	5·65, 6·43
Maximum 2θ quadrant or octant	55°	55°
Standard reflections	062, 208	225, 22̄1
Temperature (K)	295	295
Number of independent reflections	6048	2515
Number with		
$I > 3\sigma(I)$	3022	1677
$3\sigma(I) > I > \sigma(I)$ where $F_c > F_o$	863†	368
$3\sigma(I) > I > \sigma(I)$ where $F_c < F_o$	1289†	278
$I < \sigma(I)$, rejected	874†	192
Final R, observed (all)	0·059 (0·077)	0·041 (0·055)
Final R_w observed (all)	0·072 (0·076)	0·056 (0·058)
Final shift in e.s.d.		
Maximum	0·01	0·03
Average	0·0007	0·004
g (secondary extinction)	$1·11 \times 10^{-8}$	$2·93 \times 10^{-8}$
Final difference map		
Highest peak (e Å⁻³)	1·52	1·02
Lowest trough (e Å⁻³)	−1·68	−0·57
Weighting scheme	$1/w = \sigma_F^2 + (0·03F_o)^2$	$1/w = \sigma_F^2 + (0·03F_o)^2$
Error in an observation of unit weight	1·200	1·249

$$R = \sum (|F_o| - |F_c|)/\sum |F_o|, \quad R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$$

† Most of the unobserved and weak reflections were above $2\theta = 35°$.

Table 2. *Positional parameters and isotropic temperature factors* $(\times 10^4)$ *for cis-dibromo(cis-1,2-diaminocyclohexane)platinum(II)*

	x	y	z	U_{eq}^* or U_{iso} (Å²)
Pt	1820·8 (3)	1307·4 (4)	62·7 (4)	212 (2)*
Br(2)	3351 (1)	175 (1)	1311 (1)	377 (8)*
Br(1)	1707 (1)	795 (1)	−1784 (1)	328 (7)*
N(1)	555 (7)	2364 (9)	−791 (9)	320 (20)
N(2)	1815 (7)	1821 (9)	1540 (8)	310 (20)
C(1)	490 (9)	3078 (10)	100 (10)	310 (20)
C(2)	817 (9)	2378 (10)	1210 (10)	280 (20)
C(3)	30 (10)	1492 (10)	1044 (10)	320 (30)
C(4)	−1028 (10)	2054 (11)	631 (11)	380 (30)
C(5)	−1395 (10)	2677 (11)	−543 (11)	390 (30)
C(6)	−597 (10)	3596 (11)	−404 (11)	370 (30)

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

Table 3. *Positional parameters and isotropic temperature factors* ($\times 10^3$) *for tris[cis-dichloro(cis-1,2-diaminocyclohexane)platinum(II)] hydrate*

	x	y	z	U^*_{eq} or U_{iso} (Å²)
Pt(1)	442·30 (4)	339·59 (7)	280·87 (5)	23·5 (6)*
Pt(1A)	266·74 (4)	202·18 (7)	292·25 (5)	22·9 (5)*
Pt(1B)	69·81 (4)	339·04 (7)	251·75 (5)	22·0 (5)*
Cl(2)	488·9 (3)	469·2 (6)	358·7 (4)	41 (5)*
Cl(1)	480·0 (3)	201·5 (5)	355·4 (3)	34 (4)*
Cl(2A)	183·4 (3)	139·2 (5)	209·7 (3)	40 (4)*
Cl(1A)	321·1 (3)	63·6 (5)	274·2 (3)	37 (4)*
Cl(2B)	96·4 (3)	468·7 (5)	335·9 (3)	33 (4)*
Cl(1B)	100·4 (3)	204·0 (5)	331·1 (3)	34 (4)*
N(1)	400·7 (9)	237 (2)	204 (1)	38 (5)
N(2)	403 (1)	454 (2)	208 (1)	40 (5)
N(1A)	338·5 (8)	266 (2)	366 (1)	28 (5)
N(2A)	224 (1)	331 (2)	310 (1)	42 (5)
N(1B)	46·8 (7)	235 (2)	173 (1)	24 (4)
N(2B)	43·6 (8)	448 (2)	176 (1)	31 (5)
C(1)	377 (1)	294 (2)	141 (1)	35 (6)
C(2)	356 (1)	402 (2)	154 (1)	25 (5)
C(3)	300 (1)	398 (2)	169 (1)	38 (6)
C(4)	250 (2)	341 (3)	111 (2)	67 (9)
C(5)	273 (1)	227 (3)	102 (2)	57 (8)
C(6)	327 (1)	230 (2)	85 (1)	43 (7)
C(1A)	324 (1)	385 (2)	369 (1)	27 (5)
C(2A)	262 (1)	391 (2)	370 (1)	34 (6)
C(3A)	256 (1)	347 (2)	435 (1)	39 (6)
C(4A)	296 (1)	412 (2)	496 (1)	52 (7)
C(5A)	363 (1)	397 (2)	501 (1)	49 (7)
C(6A)	367 (1)	436 (2)	433 (1)	42 (7)
C(1B)	10 (1)	290 (2)	109 (1)	34 (6)
C(2B)	34 (1)	402 (2)	108 (1)	30 (6)
C(3B)	93 (1)	403 (2)	95 (1)	37 (6)
C(4B)	84 (1)	344 (3)	28 (1)	49 (7)
C(5B)	64 (1)	226 (3)	31 (2)	62 (9)
C(6B)	7 (1)	226 (2)	43 (1)	44 (7)
O	136 (1)	391 (2)	504 (1)	94 (8)

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

full-matrix least squares and minimizing $\sum w(|F_o| - |F_c|)^2$ was terminated when the maximum shift/error was 0·03. Secondary-extinction correction was applied using the method of Larson (1967). Scattering factors were from Cromer & Waber (1974) and corrections for anomalous dispersion (Cromer, 1974) were applied to the curves for Pt, Cl and Br. The final positional parameters and U_{eq} or U_{iso} are given in Tables 2 and 3.* All calculations were carried out on a CDC 6400 computer.†

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35469 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Initial data treatment used the programs *DATCO5, DATRDN* from the XRAY 76 package (Stewart, 1976). Most data treatment used programs from the *SHELX* package (Sheldrick, 1976). Final data treatment used the full-matrix least-squares program *CUDLS*, Fourier program *SYMFOU* and least-squares-planes program *PALS*, written internally by J. S. Stephens, J. S. Rutherford, and P. G. Ashmore, respectively. Diagrams were prepared using *ORTEP* II (Johnson, 1976).

Results and discussion

The molecular structures of the chloro and the bromo complexes are very similar. Coordination of the ligand introduces an asymmetry such that the NCCN system can exist in the δ or λ form. Fig. 1 shows the δ form of the bromo complex and the atom numbering, which is the same in the chloro complex. The chloro complex has three molecules in the asymmetric unit compared to one for the bromide, the difference being caused by the extra water molecule in the chloro complex. Interatomic distances and angles for the bromide and three chloride molecules are given in Table 4 and dihedral angles between various planes in the molecules are given in Table 5. The Pt—Br distances are significantly different. There are no obvious reasons for the difference. The Pt—Cl distances [2·284 (7)–2·310 (6) Å] are not significantly different in each molecule of the chloride, and the average value (2·293 Å) is shorter than the average Pt—Br distance (2·434 Å) by about the difference in the Cl and Br covalent and ionic radii of 0·16 Å. The Pt—N distances [2·01 (2)–2·06 (2) Å] are not significantly different in the four molecules. Equivalent C—N and C—C distances within the rings do not differ significantly within the sets and the minor differences in interplanar angles (Table 5) are probably caused by exigencies of crystal packing.

The packing of the bromo complex is illustrated in Fig. 2. The structure consists of layers parallel to the *ab* plane at $z = 0$ and $\frac{1}{2}$. Within each layer the molecules are arranged as centrosymmetrically related $\delta\lambda$ pairs, with the square planes of the ligand atoms hydrogen bonded through N(1)^a···Br(2) and N(2)^a···Br(1) interactions,* giving a Pt···Pt' distance of 3·511 (1) Å. In the *a* direction the dimer unit is in contact with its translationally equivalent dimer unit through the cyclohexane rings. These dimer units are staggered with respect to their *C*-centred analogues so that in the *b* direction at $a = 0$ and $\frac{1}{2}$ in each layer the dimer units

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* Atoms with superscripts are related to those in Tables 2 and 3 by (a) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (b) $1 - x, y, \frac{1}{2} - z$; (c) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (d) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (e) $-x, y, \frac{1}{2} - z$; (f) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

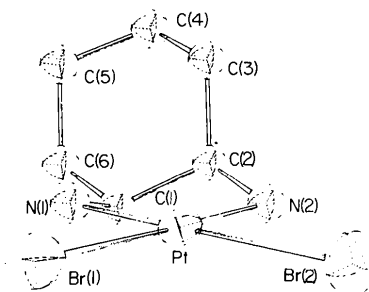Fig. 1. The molecule [Pt(*cis*-dac)Br₂] showing the atom numbering. The three molecules of the chloro complex are almost identical.

Table 4. *Selected interatomic distances (Å) and angles (°)*

$X =$	Br	Cl	Cl(A)	Cl(B)
Pt–X(1)	2·439 (2)	2·286 (6)	2·284 (7)	2·296 (6)
Pt–X(2)	2·429 (1)	2·291 (6)	2·291 (6)	2·310 (6)
Pt–N(1)	2·06 (1)	2·03 (2)	2·05 (2)	2·02 (2)
Pt–N(2)	2·05 (1)	2·06 (2)	2·02 (2)	2·01 (2)
N(1)–C(1)	1·49 (2)	1·43 (3)	1·53 (3)	1·48 (3)
N(2)–C(2)	1·49 (2)	1·45 (3)	1·47 (3)	1·48 (3)
C(1)–C(2)	1·52 (2)	1·51 (4)	1·52 (4)	1·52 (4)
C(2)–C(3)	1·51 (2)	1·49 (4)	1·52 (4)	1·56 (4)
C(3)–C(4)	1·55 (2)	1·55 (4)	1·54 (4)	1·52 (4)
C(4)–C(5)	1·54 (2)	1·57 (5)	1·60 (4)	1·55 (5)
C(5)–C(6)	1·55 (2)	1·47 (5)	1·55 (4)	1·49 (5)
C(6)–C(1)	1·55 (2)	1·58 (3)	1·53 (3)	1·58 (4)
Pt–Pt′	3·511 (1)	3·479 (1)	–	3·368 (1)
X(1)–Pt–X(2)	95·61 (6)	93·6 (2)	91·5 (2)	91·4 (2)
X(1)–Pt–N(2)	175·4 (3)	174·8 (6)	175·9 (6)	174·9 (6)
X(1)–Pt–N(1)	91·9 (3)	92·1 (6)	91·8 (6)	93·1 (5)
X(2)–Pt–N(2)	89·0 (3)	91·5 (6)	92·2 (5)	93·3 (6)
X(2)–Pt–N(1)	172·4 (3)	173·8 (7)	176·7 (6)	175·2 (6)
N(1)–Pt–N(2)	83·5 (4)	82·9 (8)	84·6 (8)	82·1 (7)
Pt–N(1)–C(1)	108·9 (6)	110 (2)	105 (1)	110 (1)
Pt–N(2)–C(2)	110·6 (7)	108 (1)	111 (1)	113 (1)
N(1)–C(1)–C(2)	110 (1)	109 (2)	107 (2)	108 (2)
N(2)–C(2)–C(1)	107 (1)	108 (2)	107 (2)	106 (2)
C(1)–C(2)–C(3)	112·7 (8)	114 (2)	114 (2)	114 (2)
C(2)–C(3)–C(4)	111 (1)	112 (2)	109 (2)	109 (2)
C(3)–C(4)–C(5)	109 (1)	107 (2)	110 (3)	111 (3)
C(4)–C(5)–C(6)	110·6 (9)	113 (3)	107 (2)	109 (3)
C(5)–C(6)–C(1)	112 (1)	111 (2)	115 (2)	113 (2)
C(6)–C(1)–C(2)	112 (1)	111 (2)	111 (2)	110 (2)
N(1)–C(1)–C(6)	111·6 (9)	113 (2)	110 (2)	112 (2)
N(2)–C(2)–C(3)	111·0 (9)	113 (2)	111 (2)	109 (2)

Table 5. *Interplanar angles and deviations from the best least-squares plane*

$X =$	Br	Cl	Cl(A)	Cl(B)
Dihedral angles (°)*				
N(1)C(1)C(2)N(2)	49 (1)	52 (3)	55 (3)	48 (3)
N(1)C(1)C(2)C(3)	73 (1)	74 (3)	68 (3)	72 (3)
N(2)C(1)C(2)C(3)	58 (1)	54 (3)	58 (3)	60 (3)
C(1)C(2)C(3)C(4)	57 (1)	56 (3)	59 (3)	56 (3)
C(2)C(3)C(4)C(5)	60 (1)	56 (3)	63 (4)	59 (4)
C(3)C(4)C(5)C(6)	58 (1)	59 (4)	59 (4)	61 (4)
C(4)C(5)C(6)C(1)	55 (1)	57 (4)	54 (3)	56 (3)
C(5)C(6)C(1)C(2)	51 (1)	52 (3)	51 (3)	52 (3)
C(6)C(1)C(2)C(3)	52 (1)	52 (3)	52 (3)	51 (3)
C(6)C(1)C(2)N(1)	55 (1)	54 (3)	60 (3)	57 (3)
C(6)C(1)C(2)N(2)	6 (1)	2 (3)	6 (3)	9 (3)
PtN(1)C(1)C(2)	37 (1)	36 (3)	46 (2)	40 (2)
PtN(2)C(2)C(1)	38 (1)	41 (2)	36 (2)	35 (2)
PtN(1)N(2)–PtX(1)X(2)	1·5 (4)	2·9 (8)	2·1 (8)	2·3 (7)
Deviation from plane (Å)				
Pt†	−0·015 (1)	−0·011 (1)	−0·024 (1)	0·030 (1)
X(1)	−0·011 (1)	−0·032 (8)	0·013 (6)	0·000 (8)
X(2)	0·011 (1)	0·032 (8)	−0·013 (6)	0·000 (8)
N(1)	0·02 (1)	0·04 (2)	−0·02 (2)	0·00 (2)
N(2)	−0·02 (1)	−0·04 (2)	0·02 (2)	0·00 (2)
C(1)†	0·32 (1)	0·27 (3)	0·55 (2)	0·36 (3)
C(2)†	−0·35 (1)	−0·43 (2)	−0·17 (2)	−0·30 (3)

* For the four atom labels the dihedral angle is between the planes defined by the first three atoms and the last three atoms. Thus for *ABCD*, the dihedral angle is between the planes *ABC* and *BCD*.

† Atoms given no weight in the refinement, other atoms given unit weights.

are arranged in the layers like bricks in a wall. There is a stack of cyclohexane rings. The forces between the dimer units within the layer are van der Waals as are the forces between layers in the *c* direction.
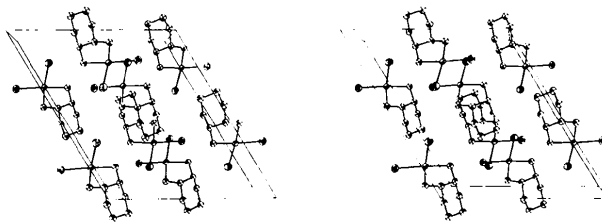

Fig. 2. The contents of the unit cell of $[Pt(cis\text{-dac})Br_2]$. a^* and c are parallel to the side and bottom of the page respectively and the view is down *b*.

The structure of the chloro complex is shown in Fig. 3. It may be considered as comprising very complex chains along the *a* direction centred at $x = \frac{1}{4}$, $y = \frac{1}{4}$ and symmetry-equivalent positions. These chains consist of two sets of pairs of molecules held square plane to square plane within the pair by hydrogen bonds through Cl(1)···N(1)^b, Cl(2)···N(2)^b and Cl(1B)··· N(1B)^e, Cl(2B)···N(2B)^e giving Pt···Pt distances of 3·479 (1) and 3·368 (1) Å. The conformation of the molecules is such that each pair exists in either the $\delta\delta$ or $\lambda\lambda$ form. The pairs are interspersed by the third molecule, which is not arranged in pairs, so that one has an arrangement pair(1)–monomer–pair(2)– monomer– *etc.* The monomer is bound to pair(2) by the hydrogen bond Cl(2A)···N(1B). Within a given complex chain the monomer molecule has only one conformation while one pair has a conformation that is the opposite of the other. Thus, in the left-hand upper (looking down c^*) chain the arrangement is $\delta\delta[Pt-(1B)]-\delta-\lambda\lambda[Pt(1)]-\delta-$ and the right-hand upper chain is $\lambda\lambda[Pt(1B)]-\delta-\delta\delta[Pt(1)]-\delta-$. The λ conformation of the monomer is observed in the lower chains.

Contact between the chains in the *c* direction at roughly $z = 0$, $\frac{1}{2}$ is only between hydrocarbon units and Cl atoms and the interaction is van der Waals. The water molecule lies close to the $z = 0$, $\frac{1}{2}$ plane but does not provide a major cross-link between the chains. It is
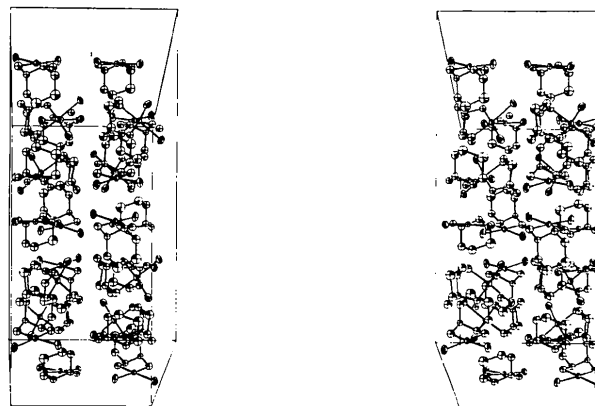

Fig. 3. The contents of the unit cell of $[Pt(cis\text{-dac})Cl_2]_3 \cdot H_2O$. *a* and *b* are parallel to the side and bottom of the page respectively and the view is down c^*.

only relatively weakly hydrogen bonded to Cl(2B), 3·44 (3), and N(1A), 3·25 (3) Å, and probably is only present in a space-filling function. This is confirmed by the infrared spectrum which shows very sharp bands at 3660, 3526 and 1670 cm^{-1}, close to those observed in free and liquid water and higher in energy than those observed for water molecules involved in normal hydrogen bonding (Nakamoto, 1978).

Along b there is a fairly extensive network of hydrogen bonds between adjacent chains through Cl(1)···N(2B)^c 3·23 (2), Cl(2)···N(1B)^d 3·43 (2), Cl(1A)···N(2B)^d 3·40 (2), Cl(1A)···N(2A)^c 3·37 (2), Cl(1B)···N(2)^c 3·21 (2), Cl(2B)···N(1)^d 3·44 (2) Å. Generally, in structures of cis-diamminedihaloplatinum(II) compounds the molecules are arranged in square-plane–square-plane pairs, with a Pt···Pt distance of about 3·4–3·5 Å (Lock, Speranzini & Zvagulis, 1980), and this is observed in both the title compounds. The existence of the third molecule as a monomeric unit is unusual and we assume this is to maximize hydrogen-bonding interactions. These separate molecules are also arranged along b so as to give a dipole–dipole interaction.

References

BURCHENAL, J. H., KALAHER, K., DEW, K., LOKYS, L. & GALE, G. (1978). Biochimie, 60, 961–965.

BURCHENAL, J. H., KALAHER, K., O'TOOLE, T. & CHISHOLM, J. (1977). Cancer Res. 37, 3455–3457.

CROMER, D. T. (1974). International Tables for X-ray Crystallography, Vol. IV, Table 2.3.1, pp. 149–150. Birmingham: Kynoch Press.

CROMER, D. T. & WABER, J. T. (1974). International Tables for X-ray Crystallography, Vol. IV, Table 2.2A, p. 72 ff. Birmingham: Kynoch Press.

GALE, G. R., ATKINS, L. M., MEISCHEN, S. J. & SCHWARTZ, P. (1978). Cancer (Philadelphia), 41, 1230–1234.

GALE, G. R., ATKINS, L. M., MEISCHEN, S. J., SMITH, A. B. & WALKER, E. M. JR (1976). J. Natl Cancer Inst. 57, 1363–1365.

GALE, G. R., ATKINS, L. M., MEISCHEN, S. J., SMITH, A. B. & WALKER, E. M. JR (1977). Cancer Treat. Rep. 61, 445–450.

GALE, G. R., SMITH, A. B. & SCHWARTZ, P. (1979). J. Clin. Hematol. Oncol. 9, 217–234.

GALE, G. R., WALKER, E. M. JR, ATKINS, L. M., SMITH, A. B. & MEISCHEN, S. J. (1974). Res. Commun. Chem. Pathol. Pharmacol. 7, 529–538.

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

HILL, J. M., LOEB, E., PARDUE, A. S., KHAN, A., HILL, N. O., KING, J. J. & HILL, R. W. (1977). J. Clin. Hematol. Oncol. 7, 681–700.

HUGHES, R. P., KRISHNAMACHARI, N., LOCK, C. J. L., POWELL, J. & TURNER, G. (1977). Inorg. Chem. 16, 314–319.

ITO, H., FUJITA, J. & SAITO, K. (1967). Bull. Chem. Soc. Jpn, 40, 2584–2591.

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

KIDANI, Y., INAGAKI, K., IIGO, M., HOSHI, A. & KURETANI, K. (1978). J. Med. Chem. 21, 1315–1318.

KIDANI, Y., INAGAKI, K., SAITO, R. & TSUKAGOCHI, S. (1977). J. Clin. Hematol. Oncol. 7, 197–209.

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

LIPPERT, B., LOCK, C. J. L., ROSENBERG, B. & ZVAGULIS, M. (1977). Inorg. Chem. 16, 1525–1529.

LOCK, C. J. L., SPERANZINI, R. A. & ZVAGULIS, M. (1980). Acta Cryst. B36, 1789–1793.

LOEB, E., HILL, J. M., PARDUE, A. S., HILL, N. O., KHAN, A. & KING, J. J. (1977). J. Clin. Hematol. Oncol. 7, 701–710.

NAKAMOTO, K. (1978). Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed., pp. 119, 227–229. New York: John Wiley.

OGAWA, M., GALE, G. R., MEISCHEN, S. J. & COOKE, V. A. (1976). Cancer Res. 36, 3185–3188.

RIDGWAY, H., SPEER, R. J., HALL, L. M., STEWART, D. P., NEWMAN, A. D., GENNINGS, A., ZAPATA, A., BROOM, V. & HILL, J. M. (1978). J. Clin. Hematol. Oncol. 8, 1–10.

RIDGWAY, H. J., SPEER, R. J., HALL, L. M., STEWART, D. P., NEWMAN, A. D. & HILL, J. M. (1977). J. Clin. Hematol. Oncol. 7, 220–230.

ROSENBERG, B., VAN CAMP, L., TROSKO, J. E. & MANSOUR, V. H. (1969). Nature (London), 222, 385–386.

SAITO, R. & KIDANI, Y. (1976). Chem. Lett. pp. 123–126.

SCHWARTZ, P., MEISCHEN, S. J., GALE, G. R., ATKINS, L. M., SMITH, A. B. & WALKER, E. M. JR (1977). Cancer Treat. Rep. 61, 1519–1525.

SHELDRICK, G. M. (1976). SHELX. Program for crystal structure determination. Univ. of Cambridge, England.

SPEER, R. J., HALL, L. M., STEWART, D. P., RIDGWAY, H. J., HILL, J. M., KIDANI, Y., INAGAKI, K., NOJI, M. & TSUKAGOCHI, S. (1978). J. Clin. Hematol. Oncol. 8, 44–50.

SPEER, R. J., RIDGWAY, H., STEWART, D. P., HALL, L. M., ZAPATA, A. & HILL, J. M. (1977). J. Clin. Hematol. Oncol. 7, 210–219.

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

WARD, J. M., YOUNG, D. M., FAUVIE, K. A., WOLPERT, M. K., DAVIS, R. & GUARINO, A. M. (1976). Cancer Treat. Rep. 60, 1675–1678.