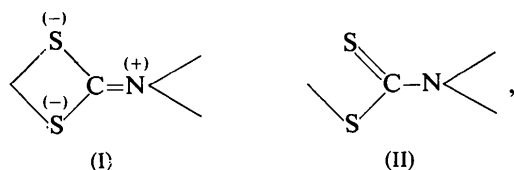


The contributions of the resonance structures usually assumed for the dithiocarbamate ligands,



calculated according to the valence-bond theory (Pauling, 1960), are 65% for structure (I) and 35% for structure (II). Once more it is confirmed that the form $\cdots\overset{(-)}{S}_2\overset{(+)}{C}=\overset{(+)}{N}R_2$, makes a major contribution to the structure of dithiocarbamates (cf. Chatt, Duncanson & Venanzi, 1956; Bonamico, Dessy, Mariani, Vaciano & Zambonelli, 1965; Bonamico, Dessy, Mugnoli, Vaciano & Zambonelli, 1965; Peyronel & Pignedoli, 1967).

The three pyrrolidine rings of the molecule are puckered. As in the case of other compounds (cf. Pitzer & Donath, 1959; Eliel, Allinger, Angyal & Morrison, 1965) the maximum puckering occurs at the carbon atoms C(3), C(4); C(8), C(9); C(13), C(14) respectively, away from the N heteroatom.* Thus, the conformation of the rings is closer to the half-chair than to the envelope form. The temperature factors of the above C atoms are, naturally enough, relatively large (Table 1).

In Fig. 3 is given a projection of the structure showing the molecular packing of TPCA in the unit cell. The roughly coplanar systems formed by ligands L2 and L3 are approximately parallel to (104).

Thanks are due to the University of Thessaloniki for the use of its computing facilities.

* See first footnote.

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fac-Trichloro(diethylenetriamine- N^1, N^2, N^3)platinum(IV) Chloride Monohydrate

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Abstract

$[Pt(C_4H_{13}N_3)Cl_3]Cl \cdot H_2O$, $C_4H_{13}Cl_3N_3Pt^+ \cdot Cl^- \cdot H_2O$, $M_r = 458.08$, orthorhombic, *Pbca*, $a = 16.606$ (8), $b = 12.490$ (4), $c = 11.293$ (2) Å, $V = 2342$ (1) Å³, $Z = 8$,

0567-7408/80/122958-06\$01.00

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$D_{\text{calc}} = 2.60$, $D_{\text{obs}} = 2.60$ (2) Mg m⁻³. The structure was determined by Patterson and electron density difference methods and refined by full-matrix least squares to $R = 0.058$, $R_w = 0.059$ based on 2207 independent reflections. The structure comprises dis-

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crete *fac*-trichloro(diethylenetriamine)platinum(IV) and chloride ions and water molecules. Bond distances [Pt—Cl 2.315 (3) to 2.332 (4), Pt—N 2.05 (1) to 2.08 (1) Å] are normal. The crystal is held together by an extensive hydrogen-bonding network.

Introduction

The title compound was prepared by a modification of the method (Watt & Cude, 1968) used to prepare $C_8H_{30}Cl_8N_6OPt_3$. To a suspension of K_2PtCl_6 in water (2.306 g, 20 ml) was added oven-dried (363 K) $N_2H_4 \cdot 2HCl$ (0.249 g) and the mixture was stirred for 20 h giving the expected deep-red solution. The solution was cooled to 278 K and filtered and the pH adjusted to 7.0 with 20% aqueous KOH solution. At this point, however, a black precipitate formed, which was not found in the original procedure. The solution was refiltered and an excess of dien.3HCl (2.0167 g) (as called for by Watt & Cude) was added to the supernatant to test for Pt^{II} or Pt^{IV} . The title compound was obtained as large yellow crystals. The crystals were used directly for the crystallographic study. (Analysis: calculated C 10.5; H 3.3; Cl 31.0; N 9.2%; found C 10.8; H 3.6; Cl 31.2; N 9.4%.)

A crystal, homogeneous under the polarizing microscope, was bounded by sets of faces (100), (010), (001), (021), (210) and the partial set (111, $11\bar{1}$, $1\bar{1}1$, $1\bar{1}\bar{1}$), which was approximated, for absorption purposes, by a sphere of radius 0.101 mm. Precession photographs showed the crystal was orthorhombic and had the unique systematic absences of *Pbca*. The cell parameters were determined by a least-squares fit of 15 well-centred reflections ($22.5 < 2\theta < 34.4^\circ$) on a Syntex $P2_1$ diffractometer and the density was determined by flotation in a diiodomethane-carbon tetrachloride mixture yielding $Z = 8$ for the title formula. Intensities were measured up to $2\theta = 55^\circ$ using the computer-controlled $P2_1$ diffractometer operated in a

$2\theta(\text{counter})-\theta(\text{crystal})$ scan mode with a crystal monochromator and Mo $K\alpha$ radiation.

After averaging and removal of systematically absent reflections, 2207 reflections were obtained of which 1514 were considered significant [$I > 3\sigma(I)$] and were used for the structure determination: 504 were considered unobserved [$3\sigma(I) > I > 0$] and were given no weight in the structure determination unless $F_c > F_o$ (208). Reflections with $I \leq 0$ (189) were rejected. 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 ($\mu = 13.5 \text{ mm}^{-1}$, A^* , the absorption factor, varied from 4.67 to 6.90) and secondary extinction (Larson, 1967; $g = 6.97 \times 10^{-7}$). The stability of the experimental system was monitored by measuring two standard reflections (106; 214); these showed e.s.d.'s of 1.7 and 1.4% with no time variation.

The platinum atom was located from a three-dimensional Patterson map and all other non-hydrogen atoms were found from electron density difference syntheses. In subsequent full-matrix least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, the temperature factors of the Pt and Cl atoms were anisotropic. Convergence was obtained with 79 variables at $R = 0.043$ (0.058) and $R_w = 0.056$ (0.059) for the observed (all) reflections.† The weighting scheme applied was $1/w = \sigma_F^2 + (0.035F_o)^2$; the standard deviation of an observation of unit weight was 1.128. Scattering factors were taken from Cromer & Waber (1974) and correction for anomalous scattering was applied to Pt and Cl (Cromer, 1974). H atoms were not detected. In the last cycle of refinement, no parameter shifted by more than 0.033 of its error; the average was 0.007. A final difference map was essentially featureless, the maximum being $2.1 \text{ e } \text{Å}^{-3}$ and the minimum $-3.8 \text{ e } \text{Å}^{-3}$, both close to platinum. Positional parameters and U_{iso} or U_{eq} are given in Table 1.‡ All calculations were carried out on CDC 6400 or CYBER 170/730 computers.§

Table 1. Atomic positional parameters ($\times 10^3$) and isotropic temperature factors ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{iso} or U_{eq}^*
Pt	151.05 (3)	135.10 (3)	230.23 (4)	20.4 (4)*
Cl(1)	154.8 (2)	121.2 (2)	25.9 (3)	34 (2)*
Cl(2)	152.7 (2)	321.2 (2)	223.5 (3)	30 (2)*
Cl(3)	291.2 (3)	125.8 (3)	236.2 (3)	37 (2)*
N(1)	27.9 (7)	137.9 (8)	220.2 (8)	25 (2)
C(1)	-2 (1)	31 (1)	182 (2)	59 (5)
C(2)	46 (1)	-55 (1)	238 (1)	42 (3)
N(2)	137.0 (7)	-28.7 (9)	248.3 (9)	28 (2)
C(3)	171.9 (8)	-60 (1)	363 (1)	28 (3)
C(4)	142.3 (8)	20 (1)	456 (1)	28 (3)
N(3)	153.7 (6)	133.0 (8)	414 (1)	26 (2)
Cl(4)	474.6 (2)	215.5 (3)	16.3 (3)	34 (2)*
O	307.2 (6)	167.0 (7)	552.3 (8)	36 (2)

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

† The temperature factor of C(1) is large and we considered the possibility of disorder, particularly since in the structural packing of the crystal C(1) in one molecule is close to C(1) of another. Attempts to refine C(1) in two different positions using partial occupancies led to the occupancy at the present position tending to 1.0.

‡ Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35524 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

§ Most programs used for initial data treatment were from the XRAY package (Stewart, 1976). The structure was solved using programs from SHELX (Sheldrick, 1976). Final data treatment used the internal Fourier and full-matrix least-squares programs SYMFOU and CUDLS written by J. S. Rutherford and J. S. Stephens, respectively. The least-squares planes were calculated using PALS (P. G. Ashmore) and diagrams were prepared using ORTEP II (Johnson, 1976).

Discussion

The title compound was produced as the result of our second unsuccessful attempt (Britten & Lock, 1979) to prepare C₈H₃₀Cl₈N₆OPt₃ by the method of Watt & Cude (1968). That the compound obtained was different is perhaps not surprising since the black precipitate formed in our experiments was not observed by Watt & Cude (1968). Clearly, aerial oxidation has given a Pt^{IV} complex. Our investigations of the infrared spectrum of the title compound and of the conformation of the rings led us to the work of Schmidtke & Garthoff (1968). This paper made some predictions about unstable ring conformations in *fac*-diethylenetriamine complexes which were at variance with results found in our literature search. In addition the conformation of *fac*-MoO₃(dien) was incorrectly assigned. We have therefore made a detailed study of the ring conformations in *fac*-dien complexes.

The infrared spectrum of the title compound is shown in Fig. 1. It differs significantly from those of the complexes prepared by Watt & Cude (1968) but is very similar to those reported for [*fac*-M(dien)L₃] complexes by Schmidtke & Garthoff (1968). There are minor variations; in particular the band at 1250 cm⁻¹ is stronger than we would have expected for a pure *fac*-dien complex and we have considered the possibility that the undue strength might have arisen from a *mer*-dien contaminant which normally has a strong band at 1250 cm⁻¹ (Schmidtke & Garthoff, 1968). The spectrum is repeatable, however, even when using selected single crystals to prepare the sample for vibrational spectroscopy. In addition, the X-ray powder diffraction pattern of the same sample matched that of one generated from the single-crystal parameters. We feel, therefore, that the observed spectrum is that of a pure compound.

The molecular cation is illustrated in Fig. 2. Bond distances and angles are given in Table 2. The Pt-N distances [range 2.05 (1)–2.08 (1) Å] do not differ significantly and agree well with normal values for Pt-N(amine) bonds (Lock, Speranzini & Zvagulis, 1980 and references therein).

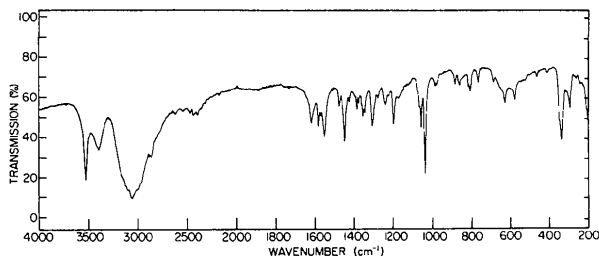


Fig. 1. The infrared spectrum of *fac*-trichloro(diethylenetriamine)-platinum(IV) chloride monohydrate. (KBr disc, Perkin Elmer 283.)

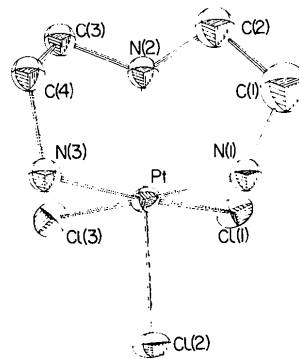


Fig. 2. The molecular cation [*fac*-trichloro(diethylenetriamine)-platinum(IV)]⁺.

Table 2. Selected interatomic distances (Å) and angles (°)

Pt—Cl(1)	2.315 (3)	Pt—N(1)	2.05 (1)
Pt—Cl(2)	2.326 (3)	Pt—N(2)	2.07 (1)
Pt—Cl(3)	2.332 (4)	Pt—N(3)	2.08 (1)
N(1)—C(1)	1.50 (2)	C(1)—C(2)	1.48 (2)
N(3)—C(4)	1.50 (2)	C(4)—C(3)	1.53 (2)
C(2)—N(2)	1.54 (2)	C(3)—N(2)	1.48 (2)
Possible hydrogen bonds			
N(3)—Cl(1) ^e	3.32 (1)	Cl(2)—O ^a	3.22 (1)
Cl(3)—O ^a	3.33 (1)	N(1)—Cl(4) ^b	3.36 (1)
N(1)—Cl(4) ^c	3.25 (1)	N(2)—O ^d	2.96 (1)
N(3)—Cl(4) ^c	3.24 (1)	N(3)—O	3.02 (1)
Cl(4)—O ^a	3.17 (1)		
Cl(1)—Pt—Cl(2)	92.4 (1)	Cl(1)—Pt—Cl(3)	89.9 (1)
Cl(1)—Pt—N(1)	88.5 (3)	Cl(1)—Pt—N(2)	91.6 (3)
Cl(1)—Pt—N(3)	174.3 (3)	Cl(2)—Pt—Cl(3)	92.2 (1)
Cl(2)—Pt—N(1)	89.6 (3)	Cl(2)—Pt—N(2)	173.1 (3)
Cl(2)—Pt—N(3)	92.6 (3)	Cl(3)—Pt—N(1)	177.6 (3)
Cl(3)—Pt—N(2)	93.5 (3)	Cl(3)—Pt—N(3)	87.1 (3)
N(1)—Pt—N(2)	84.8 (4)	N(1)—Pt—N(3)	94.4 (4)
N(2)—Pt—N(3)	83.8 (4)	Pt—N(1)—C(1)	109.5 (9)
N(1)—C(1)—C(2)	110 (1)	C(1)—C(2)—N(2)	114 (1)
C(2)—N(2)—C(3)	113 (1)	N(2)—C(3)—C(4)	108 (1)
C(3)—C(4)—N(3)	111 (1)	C(4)—N(3)—Pt	108.8 (7)
Pt—N(2)—C(2)	108.2 (8)	Pt—N(2)—C(3)	107.7 (8)

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

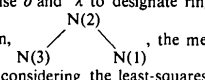
The Pt—Cl(1) distance is significantly shorter than the Pt—Cl(3) distance [2.315 (3) vs 2.332 (4) Å] although we can see no chemical or structural reason why this should be so. All Pt—Cl distances are within the range previously observed (Lock *et al.*, 1980 and references therein), as are Cl—Pt—Cl, N—Pt—N and N—Pt—Cl angles. Bond distances and bond angles within the diethylenetriamine group agree well with those found previously (see the references given in Table 3).

There are various possible combinations of conformations for the two rings of diethylenetriamine and

Table 3. Bond distances and angles in the diethylenetriamine group for various compounds

Compound	Distance of C atoms from MNN plane (Å)		Distance of C and M atoms from $MN\langle C \rangle$ plane (Å)*				Torsional angles NCCN (°)†		Conformation I II	Reference
	N(1)M	N(2)M	N(1)N(2)- C(1)C(2)	N(2)N(3)- C(3)C(4)	N(1)C(1)- C(2)N(2)	N(2)C(3)- C(4)N(3)				
<i>fac</i> -Mo(dien)O ₃	C(1) 0.04 C(2) -0.54	C(3) 0.54 C(4) -0.04	Mo -0.36 C(1) 0.30 C(2) -0.30	Mo 0.36 C(3) 0.30 C(4) -0.30	45.1°	-45.1°	$\delta\lambda$	kk'	A	
<i>fac</i> -Mo(dien)(CO) ₃	C(1) -0.11 C(2) 0.30	C(3) -0.09 C(4) -0.65	Mo -0.58 C(1) 0.30 C(2) -0.30	Mo 0.55 C(3) -0.30 C(4) 0.30	48.6	46.7	$\delta\delta$	$k'k'$	B	
<i>fac</i> -Cr(dien)(CO) ₃	C(1) -0.08 C(2) -0.67	C(3) 0.17 C(4) 0.65	Cr -0.49 C(1) 0.31 C(2) -0.31	Cr 0.54 C(3) -0.25 C(4) 0.25	45.9	40.3	$\delta\delta$	$k'k'$	C	
<i>fac</i> -Cr(dien)Cl ₃	C(1) 0.28 C(2) -0.30	C(3) 0.53 C(4) -0.07	Cr -0.01 C(1) 0.29 C(2) -0.29	Cr 0.28 C(3) 0.31 C(4) -0.31	44.6	-47.8	$\delta\lambda$	kk'	D	
$[\pi$ -Co(en)(dien)Cl] ²⁺	C(1) 0.04 C(2) -0.58	C(3) 0.23 C(4) -0.38	Co -0.28 C(1) 0.32 C(2) -0.32	Co -0.08 C(3) 0.30 C(4) -0.30	50.3	-41.8	$\delta\lambda$	kk'	E	
[<i>s</i> - <i>fac</i> -Co(dien) ₂] ³⁺	C(1) 0.11 C(2) -0.48	C(3) 0.41 C(4) -0.18	Co -0.21 C(1) 0.30 C(2) -0.30	Co 0.12 C(3) 0.30 C(4) -0.30	47.1	-34.3	$\delta\lambda$	kk'	F	
[<i>u</i> - <i>fac</i> -Co(dien) ₂] ³⁺ (A)	C(1) 0.35 C(2) -0.24	C(3) 0.55 C(4) -0.05	Co 0.06 C(1) 0.29 C(2) -0.29	Co 0.28 C(3) 0.31 C(4) -0.31	43.5	-44.8	$\delta\lambda$	kk'	G	
[<i>u</i> - <i>fac</i> -Co(dien) ₂] ³⁺ (B)	C(1) -0.53 C(2) 0.04	C(3) 0.68 C(4) 0.14	Co -0.27 C(1) -0.29 C(2) 0.29	Co 0.45 C(3) 0.28 C(4) -0.28	-42.7	-41.4	$\lambda\lambda$	kk	G	
$[\omega$ -Co(en)(dien)Cl] ²⁺	C(1) 0.21 C(2) -0.42	C(3) 0.41 C(4) -0.10	Co -0.12 C(1) 0.32 C(2) -0.32	Co 0.16 C(3) 0.26 C(4) -0.26	48.7	-43.1	$\delta\lambda$	kk'	H	
[<i>fac</i> -Co(dien)(NO ₂ - (NH ₃)(H ₂ O))] ²⁺	C(1) 0.16 C(2) 0.66	C(3) 0.08 C(4) 0.54	Co -0.46 C(1) 0.26 C(2) -0.26	Co 0.33 C(3) -0.25 C(4) 0.25	36.6	37.9	$\delta\delta$	$k'k'$	I	
[<i>fac</i> -Pt(dien)Cl ₃] ⁺	C(1) -0.54 C(2) -0.07	C(3) 0.59 C(4) -0.03	Pt -0.35 C(1) -0.25 C(2) 0.25	Pt 0.34 C(3) 0.32 C(4) -0.32	-38.1	-48.8	$\lambda\lambda$	kk	J	

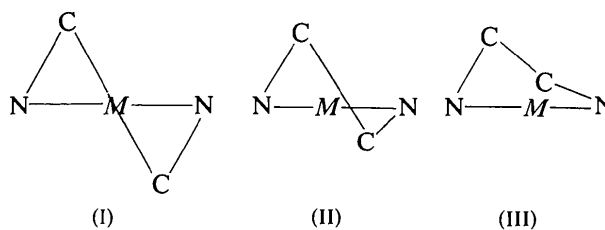
References: (A) Cotton & Elder (1964); (B) Cotton & Wing (1965); (C) Cotton & Richardson (1966); (D) Fowle, House, Robinson & Rumball (1970); (E) Gainsford, House & Robinson (1971); (F) Kobayashi, Marumo & Saito (1972); (G) Konno, Marumo & Saito (1973); (H) Johnston & Freeman (1975); (I) Popa, Ablov, Mazus, Bilyushkin & Malinovskii (1977); (J) This work.

All atoms in the original papers were relabelled to correspond to the geometry shown in Fig. 2. The labelling convention has been deposited. The convention for conformation we have adopted here (I) is based on the IUPAC (1970) rules which use δ and λ to designate ring conformations. We have numbered the diethylenetriamine ligand so that if the three nitrogen atoms are placed in the plane of the paper as shown, , the metal atom is behind the plane of the paper and the numbering is as shown. This is the same convention as that used by Konno *et al.* (1973). In considering the least-squares planes, we have in each case placed the NH₂ group on the left, as in NH₂CH₂CH₂NH-, and placed the metal behind the four N and C atoms. (This means that for both rings, a positive dihedral angle corresponds to a δ configuration and a negative angle to a λ configuration.) The convention used by Schmidtke & Garthoff (1968) is based on the kk' convention of Corey & Bailar (1959) for ethylenediamine rings. The correspondence is $k \equiv \lambda$, $k' \equiv \delta$. Note, however, that Schmidtke & Garthoff number their rings in the opposite sense to us and therefore the ring conformation symbols have to be reversed before conversion. Thus, $\delta\lambda$ in our convention must be reversed to $\lambda\delta$ to give kk' in Schmidtke & Garthoff's convention rather than the direct conversion $k'k$. The kk' column (II) for the conformation is as Schmidtke & Garthoff (1968) would have labelled the rings.

* $\langle C \rangle$ or $\langle C(A)C(B) \rangle$ represents the midpoint of the line joining the atoms C(A) and C(B).

† The torsional angle represented by N(A)C(A)C(B)N(B) is the dihedral angle between the planes N(A)C(A)C(B) and C(A)C(B)N(B).

these have been extensively studied and discussed (see references in Table 3). Two methods of discussing the conformation are (1) in terms of the torsional angles about the C—C bonds, in other words the dihedral angle between the N(A)C(A)C(B) and C(A)C(B)N(B) planes, and (2) in terms of the distances of the carbon atoms from the $MN(A)N(B)$ plane. Here three types of distortion can be seen. The carbon atoms can be symmetrically distributed about the plane (I), asymmetrically distributed about the plane (II) or both asymmetrically distributed on the same side of the plane (III).



These distortions have generally been explained in terms of non-bonding hydrogen interactions on adjacent CH₂ or NH₂ groups, following the discussions of Corey & Bailar (1959) concerning ethylenediamine

complexes. There is an alternative, and we feel better, way of looking at these structures which shows more clearly that they represent a continuum. We work in terms of a plane $N(A)N(B)\langle C \rangle$, where $\langle C \rangle$ is the midpoint between $C(A)$ and $C(B)$. This has the advantage that $C(A)$ and $C(B)$ are symmetrically displaced about the plane and the distance of $C(A)$ and $C(B)$ out of the plane correlates well with the torsion angle (see Table 3). The most important feature is that one now measures the distance of M out of the $N(A)N(B)\langle C \rangle$ plane, and I, II, III represent points on a continuum as the metal moves increasingly out of the plane. Considering the problem in this way raises the question of why the metal atom moves out of the plane. We suggest that an important reason is that it is caused by the rotation of the NH_2 and NH groups in order to maximize hydrogen-bonding interactions.

The same effect is probably important in determining the ring conformations. Keene & Searle (1972, 1974) have shown that this is an important factor in determining the geometry of the bis(diethylenetriamine)cobalt(III) cation. The other factor determining ring conformation is intramolecular non-bonded hydrogen interactions on the CH_2 and NH_2 groups. Based on the arguments of Corey & Bailar (1959), it has been suggested (Schmidtke & Garthoff, 1968) that $\lambda\delta$ should be the stable conformation for *mer* complexes, while $\lambda\lambda$ or $\delta\delta$ should be the stable conformation for *fac* complexes. In particular, it is argued that the $\delta\lambda$ conformation will be 'ruled out because of the steric hindrance due to hydrogen atoms which approach each other appreciably in this ring structure'. As can be seen from Table 3, the $\delta\lambda$ conformation is found for *fac* complexes.

Since the $\delta\lambda$ ring conformation is observed for *fac* metal complexes of diethylenetriamine, despite the prediction, based on calculations of intramolecular CH_2 and NH_2 repulsions, that it should not occur, we conclude that this interaction is not the most important factor in determining ring conformation. We conclude that the more important factor is the directionality requirements of intramolecular hydrogen bonds. Possible hydrogen-bond angles around the N atoms agree well with Brown's (1976) distance-angle relationship.

The packing within the crystal is shown in Fig. 3. The molecular ion is arranged such that $N(1)\cdots Cl(3)$, $N(2)\cdots Cl(2)$ and $N(3)\cdots Cl(1)$ are almost parallel to **a**, **b** and **c** respectively. As a consequence the $PtN(1)C(2)N(2)$ and $PtN(2)N(3)$ planes are almost parallel to the *ab* and *bc* planes respectively. Thus there are weak dipole-dipole interactions in the **a**, **b** and **c** directions between molecules related by the *a*, *b* and *c* glides respectively. These are not the most important forces holding the crystal together, however. The most important are the hydrogen bonds. The molecular cations can be considered as packing in double layers about planes centred at $x = \frac{1}{4}, \frac{3}{4}$ with molecules in the

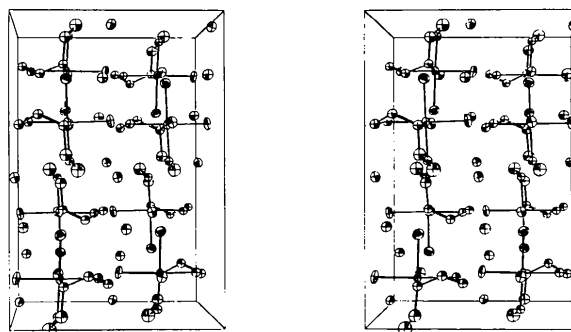


Fig. 3. The packing of *fac*-trichloro(diethylenetriamine)platinum(IV) chloride monohydrate within the unit cell. **a** and **b** are parallel to the side and bottom of the page respectively. The view is down **b**.

double layer being related by the *a*- and *c*-glide operations. Thus the hydrocarbon fragments are parallel to the double layer or point out of it, providing hydrocarbon-hydrocarbon contacts between double layers at $x = 0, \frac{1}{2}$. Within the layer, important hydrogen bonding is between $Cl(1)$ and $N(3)$ of adjacent molecules related by the *c* glide and between the water molecule and $Cl(2)$ and $Cl(3)$ of one molecule, $N(3)$ of a cation related to the first by the *c* glide and $N(2)$ of a cation related to the first by the *b* glide. In addition the water molecule provides cross linking between double layers since it is hydrogen bonded to $Cl(4)$ which is in turn hydrogen bonded to $N(1)$ and $N(3)$ of a molecule in the next double layer and to $N(1)$ of its *c*-glide-related neighbour.

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The Structure of Phthalocyaninatomanganese(II) at 5·8 K Determined by Neutron Diffraction

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Abstract

The molecular structure of the β -polymorphic form of phthalocyaninatomanganese(II), [Mn(pc)], ($C_{32}H_{16}MnN_8$) has been determined at 5·8 K by single-crystal neutron diffraction methods. The crystals are monoclinic, space group $P2_1/c$, $a = 14\cdot601$ (5), $b = 4\cdot69$ (1), $c = 19\cdot327$ (5) Å, $\beta = 121\cdot10$ (1)°, $U = 1133\cdot3$ Å³, $Z = 2$. Intensities for 1133 independent $h0l$ and $h1l$ Bragg reflections were measured using an automatic diffractometer. In addition, a number of reflections forbidden by the space group were examined. The structure has been refined by full-matrix

least-squares methods to R_F 0·027, R_{F^2} 0·038 and χ 3·24. Bond lengths at 5·8 K show systematic deviations from those determined previously at 295 and 116 K by X-ray diffraction data of moderate resolution. As in the case of phthalocyaninatomanganese(II), these deviations are ascribed largely to the effects of asphericity of the valence electron density. The intermolecular axial Mn···N contact, of importance in the ferromagnetic exchange path in [Mn(pc)] ($T_c = 8\cdot6$ K), is 3·115 (4) Å at 5·8 K, compared with 3·148 (2) and 3·169 (6) Å at 116 and 295 K respectively. The neutron scattering length of manganese was found by least-squares refinement to be $-3\cdot59$ (8) fm. The data have been examined for any contribution to the Bragg intensities by magnetic scattering from the ferromagnetic crystal. The possibility that the

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