

diniques étudiés jusqu'à présent (Wetherington *et al.*, 1974; Chion & Lajzerowicz, 1973; Chion & Thomas, 1975).

2. Structures

Les Figs. 6 et 7 sont des projections des structures sur les plans *ac*. Dans les deux cas les molécules sont reliées entre elles par des réseaux de liaisons hydrogène, très faibles dans le cas de l'amide *O* (voir Figs. 6, 7).

En fait le moins grand nombre de liaisons hydrogène de l'amide *O* s'accompagne d'une compacité d'empilement plus grande comme le montre la comparaison des densités. Ces deux effets doivent se compléter, donnant des énergies libres voisines pour les deux structures.

Les comparaisons entre structures de racémates et d'isomères optiques qui ont déjà été menées (Benedetti, Pedone & Sirigu, 1973; Pérucaud-Brianso, 1973; Césario-Guilhem, 1973) montrent qu'en général ces structures présentent des chaînes ou des plans analogues. Dans le composé ici étudié, l'analogie de mailles signalées au paragraphe I met en évidence dans les deux structures de plans de molécules analogues (translations \mathbf{b}_0 et \mathbf{c}_0 pour l'amide *O* et \mathbf{b}_R , \mathbf{c}_R pour l'amide *R*) mais l'orientation des molécules par rapport au plan dans chacun des cas n'est pas tout à fait la même. De plus, comme nous l'avons signalé précédemment, les réseaux de liaisons hydrogène sont très différents dans les deux cas.

IV. Conclusion

La cristallisation simultanée d'un mélange racémique sous forme d'un conglomérat et d'un racémate (comme c'est le cas pour l'amide) est extrêmement rare. Nous envisageons d'étudier les conditions de cristallisation et de stabilité de ces deux types de cristaux. Toujours

dans le but d'obtenir des informations sur les conditions de formation des conglomérats, c'est-à-dire sur la séparation spontanée d'énantiomères au moment de la cristallisation, nous travaillons également sur d'autres systèmes de molécules chirales à cycles pyrrolidiniques (tétraméthyl-2,2,5,5 hydroxy-3 pyrrolidine oxyle-1 et tétraméthyl-2,2,5,5 hydroxyméthyl-3 pyrrolidine oxyle-1).

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The Crystal and Molecular Structure of *cis*- and *trans*-Dichlorobis(ethyleneimine)platinum(II)

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The structures of *cis*- and *trans*-dichlorobis(ethyleneimine)platinum(II) have been solved by Patterson methods and refined by block-diagonal least-squares calculations to $R=0.083$ (*cis*) and $R=0.065$ (*trans*) with data collected on a linear diffractometer. In both isomers there are no short intermolecular distances and the bond lengths and angles are normal. Cell parameters are: (*cis*) $a=16.16$, $b=9.54$, $c=10.74$ Å, $Z=8$, space group *Pbca*; (*trans*) $a=6.652$, $b=5.117$, $c=6.410$ Å, $\alpha=105.4$, $\beta=81.75$, $\gamma=97.16^\circ$, $Z=1$, space group *P1*.

As part of a study of platinum halide complexes the structures of the *cis* (I) and *trans* (II) isomers of dichlorobis(ethyleneimine)platinum(II), $\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{NH})_2$, have been determined. The *cis*

isomer was originally reported by Jackson & Edwards (1962); the *trans* compound has been described by Connors, Jones, Ross, Braddock, Khokhar & Tobe (1972).

Experimental

Crystals of (I) were pale yellow and lath-shaped. They were elongated parallel to *b*, and were readily cleaved parallel to (010), the main face being (100). (II) was supplied as a yellow powder and was recrystallized from methanol as needles.

Cell dimensions were obtained from Weissenberg photographs and refined on a Hilger linear diffractometer.

Crystal data

(I): *cis*-Dichlorobis(ethyleneimine)platinum(II), $C_4H_{10}Cl_2N_2Pt$. $M = 352.5$, orthorhombic, $a = 16.16$ (2), $b = 9.54$ (1), $c = 10.74$ (1) Å, $U = 1656$ Å³, $D_m = 2.84$ (floatation), $D_x = 2.83$ g cm⁻³, $Z = 8$, $F(000) = 1280$. Space group $Pbca$ from systematic absences.

(II): *trans*-Dichlorobis(ethyleneimine)platinum(II), $C_4H_{10}Cl_2N_2Pt$. $M = 352.5$, triclinic, $a = 6.652$ (5), $b = 5.117$ (5), $c = 6.410$ (5) Å, $\alpha = 105.4$ (1), $\beta = 81.75$ (5), $\gamma = 97.16$ (5)°, $U = 207$ Å³, $D_x = 2.8$ g cm⁻³, $Z = 1$, $F(000) = 160$. Space group $P\bar{1}$.

Intensities for both compounds were collected on a Hilger linear diffractometer with Mo $K\alpha$ radiation and balanced filters. Lorentz and polarization corrections were applied but absorption was not allowed for. For (I) two crystals were used and the following reciprocal lattice layers were measured: *a* axis, $0kl$ to $9kl$; *b* axis, $h0l$ to $h2l$. 1592 independent reflexions were examined and 928 gave intensities above background.

For (II) three crystals were used and the following data measured: *a* axis, $0kl$; *b* axis, $h0l$ to $h3l$; *c* axis, $hk0$ to $hk4$. Of 1630 possible reflexions, 1022 were observed.

Structure determination

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

(I) The asymmetric unit contains one molecule with all atoms in general positions (Fig. 1). After location

Table 1. Atomic coordinates and thermal parameters for *cis*-dichlorobis(ethyleneimine)platinum(II)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
Pt	0.1931 (2)	0.1368 (3)	0.1855 (2)	
Cl(1)	0.0693 (17)	0.0244 (2)	0.2173 (20)	
Cl(2)	0.2491 (15)	0.0256 (24)	0.3556 (19)	
N(1)	0.1510 (34)	0.2386 (62)	0.0327 (52)	2.6 (1.1)
N(2)	0.2888 (39)	0.2392 (65)	0.1610 (53)	3.1 (1.2)
C(1)	0.0688 (54)	0.3007 (91)	0.0263 (73)	3.8 (1.6)
C(2)	0.0032 (54)	0.1808 (80)	0.0542 (72)	3.3 (1.4)
C(3)	0.3508 (67)	0.2335 (107)	0.0478 (93)	5.0 (2.1)
C(4)	0.3920 (53)	0.1728 (86)	0.1662 (74)	4.4 (1.7)

of the Pt atoms from a Patterson map, successive Fourier syntheses gave the positions of the Cl and N atoms ($R = 0.173$). A difference map showed three of the C atoms and when these were included R was reduced to 0.137. Subsequent F_o and $(F_o - F_c)$ syntheses revealed the remaining non-hydrogen atoms. The introduction of anisotropic thermal parameters for Pt and Cl with isotropic parameters for C and N atoms followed by block-diagonal least-squares refinement reduced R to 0.100. Two large low-angle structure factors which were affected by extinction were removed from the refinement as were some 117 very weak re-

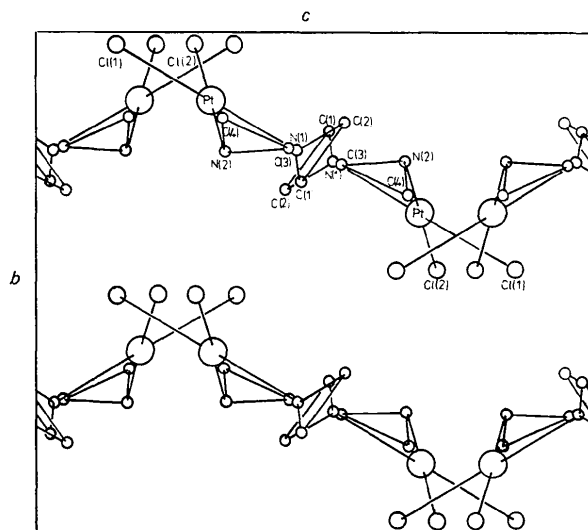


Fig. 1. *cis*-Bis(ethyleneimine)dichloroplatinum, *bc* projection.

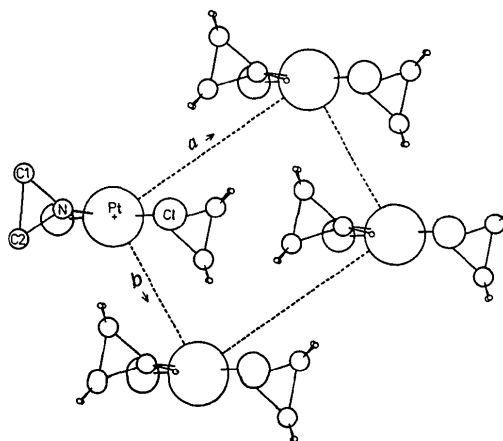


Fig. 2. *trans*-Bis(ethyleneimine)dichloroplatinum, *ab* projection.

Table 1 (cont.)

	Anisotropic thermal parameters $\times 10^5$					
	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Pt	273 (10)	-3 (51)	6 (36)	662 (21)	-164 (52)	586 (17)
Cl(1)	364 (92)	244 (374)	-21 (255)	929 (225)	165 (347)	768 (178)
Cl(2)	342 (101)	-287 (367)	95 (242)	1138 (264)	-67 (356)	702 (205)

Table 2. Atomic coordinates and thermal parameters for *trans*-dichlorobis(ethyleneimine)platinum(II)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
Pt	0	0	0	
Cl	0.2111 (14)	0.1696 (21)	-0.2592 (13)	
N	0.1747 (44)	0.2029 (60)	0.2410 (49)	2.9 (5)
C(1)	0.2438 (64)	0.4969 (86)	0.2862 (70)	3.8 (7)
C(2)	0.3949 (60)	0.2890 (80)	0.2196 (66)	3.5 (7)

other along the normal to the molecular plane as in dichloroethylenediamineplatinum(II) (Iball, MacDougall & Scrimgeour, 1975) and many other Pt^{II} complexes. Both (I) and (II) have shortest Pt-Pt distances of 5.11 Å, far longer than the values of about 3.4 Å found in compounds where parallel stacking occurs. The packing of (I) and (II) is shown in Figs. 1 and 2.

Table 2 (cont.)

Anisotropic thermal parameters × 10⁵

$$T = \exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hl\beta_{13} + kh\beta_{23} + lk\beta_{12})].$$

	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Pt	1529 (30)	-716 (73)	-1310 (49)	2314 (57)	431 (70)	808 (29)
Cl	2234 (190)	-2250 (490)	-1320 (290)	5257 (422)	1964 (425)	1193 (157)

Table 3. Bond lengths (Å) and angles (°) in dichlorobis(ethyleneimine)platinum(II)

	<i>cis</i> (I)	<i>trans</i> (II)		<i>cis</i> (I)	<i>trans</i> (II)
Pt—Cl(1)	2.30 (2)	2.20 (1)	N(1)—Pt—Cl(1)	93.0 (1.5)	92.53
Pt—Cl(2)	2.30 (2)		N(2)—Pt—Cl(2)	91.6 (1.7)	
Pt—N(1)	2.03 (6)	2.04 (3)	N(1)—Pt—N(2)	84.9 (2.5)	(180)
Pt—N(2)	1.85 (6)		Cl(1)—Pt—Cl(2)	90.5 (0.75)	(180)
N(1)—C(1)	1.46 (11)	1.48 (5)	C(1)—N(1)—C(2)	57.9 (4.9)	60.8 (2.5)
N(2)—C(3)	1.58 (12)		C(3)—N(2)—C(4)	54.4 (4.9)	
N(1)—C(2)	1.54 (10)	1.47 (5)	C(1)—C(2)—N(1)	58.1 (4.9)	59.8 (2.5)
N(2)—C(4)	1.78 (11)		C(3)—C(4)—N(2)	55.9 (4.8)	
C(1)—C(2)	1.45 (11)	1.49 (6)	C(2)—C(1)—N(1)	64.0 (5.2)	59.3 (2.5)
C(3)—C(4)	1.55 (13)		C(4)—C(3)—N(2)	69.6 (5.6)	

flexions. The five H atoms of one ethyleneimine ligand, on N(1), C(1) and C(2), were located in a difference map; these were included in the F_c calculation, but not refined. The final R was 0.083. In the later stages of refinement the weighting scheme was $\sqrt{w}=1$ for $|F_o| < 140$, $\sqrt{w}=140/|F_o|$ for $|F_o| \geq 140$.

(II) Space-group symmetry placed the Pt atom at the origin. A Fourier map phased on this requirement showed the positions of all the remaining non-hydrogen atoms (Fig. 2). Block-diagonal least-squares refinement with isotropic C and N and anisotropic Pt and Cl reduced R to 0.070. At this stage 12 reflexions which appeared to show extinction were removed. After three more cycles $R=0.065$. The introduction of H atoms at calculated positions did not alter R . The weighting scheme was: $\sqrt{w}=1/\{1+[(|F_o|-F^*)/G^*]^2\}$ with $F^*=35$, $G^*=30$.†

Discussion

The coordinates and thermal parameters for (I) and (II) are given in Tables 1 and 2. Bond lengths and angles are compared in Table 3. All the values are close to those expected with no significant differences between the two isomers. In neither (I) nor (II) are the PtCl₂N₂ molecular planes stacked parallel to each

In the orthorhombic *cis* isomer neighbouring molecules are related by glide and screw operations. Each molecule is tilted with respect to all the cell edges. The shortest distances between non-hydrogen atoms are 3.34 Å (N—Cl) and 3.42 Å (C—Cl). In the *trans* isomer the closest intermolecular distances involve H—H contacts between an H atom of C(1) and the H atom of N of an adjacent molecule (2.51 Å) and between an H atom of C(2) with the corresponding H atom of C(2) of another adjacent molecule (2.55 Å). The angle between the mean plane of the NC₂ ring and that of the PtN₂Cl₂ group is 95.2° in the *trans* compound. In the *cis* compound the mean plane of the ring involving N(1) makes an angle of 94.0° to the PtN₂Cl₂ mean plane but the second NC₂ ring is in a different orientation with an interplanar angle of 45.2°. The mean planes of the two NC₂ rings make an angle of 60.7°.

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† A list of structure factors is available from the authors and has also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30888 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.