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## Dichloro(*N,N*-dimethylethylenediamine)platinum(II)

BY R. MELANSON, C. DE LA CHEVROTIÈRE AND F. D. ROCHON

*Département de Chimie, Université du Québec à Montréal, CP 8888, succ. A, Montréal, Canada H3C 3P8*

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**Abstract.** [PtCl<sub>2</sub>(C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>)], *M<sub>r</sub>* = 354.15, monoclinic, *P*2<sub>1</sub>, *a* = 5.639 (2), *b* = 10.661 (4), *c* = 7.244 (3) Å, β = 95.88 (3)°, *V* = 433.2 (3) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 2.714, *D<sub>m</sub>* = 2.71 (2) g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 169.1 cm<sup>-1</sup>, *F*(000) = 324, *T* = 295 K, *R* = 0.032 for 905 unique observed reflections. Pt has square-planar coordination with a slight distortion caused by the bidentate ligand [N–Pt–N angle = 84.0 (5)°]. The bond distances are Pt–Cl 2.303 (4), 2.317 (4) and Pt–N 2.039 (14), 2.067 (12) Å. The crystal is stabilized by hydrogen bonds between the –NH<sub>2</sub> group and one chloride ligand.

**Introduction.** Recently, we have started a study on the reactions of platinum(II) compounds with ethylenediamine derivatives. We have synthesized as starting materials the dihalo complexes. In order to characterize well all the compounds involved in these reactions, we have decided to determine the crystal structure of some of these dihalo compounds. Up to now, only the dichloro Pt complex of *N,N*-dimethylethylenediamine [PtCl<sub>2</sub>{N(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>}] has given suitable crystals for X-ray diffraction. Its structure is reported below.

**Experimental. Synthesis.** [PtCl<sub>2</sub>{N(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>}] was synthesized from the aqueous reaction of K<sub>2</sub>PtCl<sub>4</sub> with *N,N*-dimethylethylenediamine in a 1:1 ratio. The

yellow compound was recrystallized from water at 333 K. Yield 70%. Dec. at 488–503 K. Elemental analysis: calc. 13.56% C and 3.41% H, exp. 13.49% C and 3.31% H.

The crystals used for the structure determination were obtained by slow evaporation of an aqueous solution.

Platelet, dimensions (mm): 0.084 (100– $\bar{1}00$ ) × 0.038 (001–00 $\bar{1}$ ) × ~0.29 (010–110 and  $\bar{1}10$ ); density by flotation in bromoform–dibromomethane mixture; precession photographs showed space group *P*2<sub>1</sub>; Syntax *P* $\bar{1}$  diffractometer, graphite-monochromatized Mo *K*α radiation; cell parameters from refined angles of 15 centered reflections (2θ range: 10–21°); 1056 independent reflections measured up to 2θ < 55° by θ–2θ scan technique; range of *hkl*: *h*: 0→7, *k*: 0→13, *l*: –9→9; standard reflections 060, 200 and 011, variations < 2.5%; reflections with *I*<sub>net</sub> < 2.5σ(*I*) unobserved, σ(*I*) calculated as in Melanson & Rochon (1975); absorption correction based on equations of crystal faces, transmission factors from 0.278 to 0.536; data corrected for Lorentz and polarization effects; 905 unique observed reflections; atomic scattering factors of Cromer & Waber (1965) for Pt, Cl, N, C and of Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion terms of Pt and Cl from Cromer (1965).

The Patterson map showed the position of Pt; other atoms (except H) were located by structure-factor and Fourier-map calculations; isotropic secondary-extinction correction (Coppens & Hamilton, 1970);  $w$

Table 1. Positional parameters ( $\times 10^4$ ) with their e.s.d.'s and equivalent isotropic temperature factors ( $\times 10^4$ )

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}(\text{\AA}^2)$
Pt	2210.0 (8)	3000	3965.7 (7)	279
Cl(1)	4906 (7)	3310 (5)	6535 (6)	506
Cl(2)	2672 (7)	5062 (4)	3058 (7)	420
N(1)	1792 (20)	1161 (13)	4634 (18)	351
N(2)	-220 (20)	2580 (11)	1718 (16)	319
C(1)	650 (32)	514 (18)	2990 (26)	501
C(2)	-1226 (26)	1334 (17)	2116 (23)	431
C(3)	987 (27)	2606 (16)	-100 (22)	418
C(4)	-2264 (27)	3505 (18)	1439 (24)	511

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Pt—Cl(1)	2.303 (4)	N(2)—C(2)	1.48 (2)
Pt—Cl(2)	2.317 (4)	N(2)—C(3)	1.54 (2)
Pt—N(1)	2.039 (14)	N(2)—C(4)	1.51 (2)
Pt—N(2)	2.067 (12)	C(1)—C(2)	1.47 (2)
N(1)—C(1)	1.47 (2)		
Cl(1)—Pt—Cl(2)	90.5 (1)	Pt—N(2)—C(2)	106 (1)
Cl(1)—Pt—N(1)	91.7 (4)	Pt—N(2)—C(3)	111 (1)
Cl(1)—Pt—N(2)	175.7 (4)	Pt—N(2)—C(4)	113 (1)
Cl(2)—Pt—N(1)	177.3 (4)	N(1)—C(1)—C(2)	108 (1)
Cl(2)—Pt—N(2)	93.8 (3)	N(2)—C(2)—C(1)	110 (1)
N(1)—Pt—N(2)	84.0 (5)	C(2)—N(2)—C(3)	113 (1)
Pt—N(1)—C(1)	108 (1)	C(2)—N(2)—C(4)	108 (1)

Distances and angles of atoms possibly involved in hydrogen bonds

N(1)⋯Cl(2 <sup>i</sup> )	3.37 (1) $\text{\AA}$	N(1)⋯Cl(2 <sup>ii</sup> )	3.58 (1) $\text{\AA}$
H(2)⋯Cl(2)	2.61	H(1)⋯Cl(2 <sup>ii</sup> )	2.76
C(1)—N(1)⋯Cl(2)	87 (1) $^\circ$	C(1)—N(1)⋯Cl(2)	121 (1) $^\circ$
N(1)—H(2)⋯Cl(2)	150	N(1)—H(1)⋯Cl(2)	149

Symmetry code: (i)  $-x, y - \frac{1}{2}, 1 - x$ ; (ii)  $1 - x, y - \frac{1}{2}, 1 - z$ .

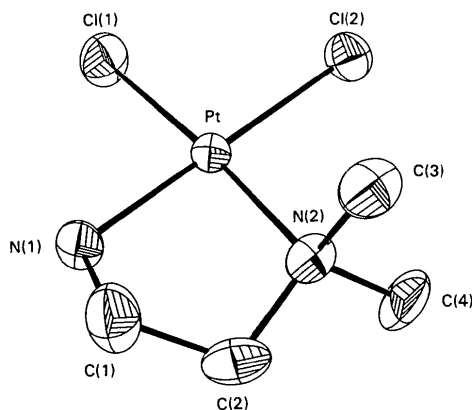


Fig. 1. Labeled diagram of the molecule  $[\text{PtCl}_2\{\text{N}(\text{CH}_3)_2\text{C}_2\text{H}_4\text{NH}_2\}]$ . The ellipsoids correspond to 50% probability.

$= 1/\sigma^2(F)$ ; H atoms fixed at calculated positions ( $\text{C}-\text{H} = 0.95$  and  $\text{N}-\text{H} = 0.85 \text{\AA}$ ) with isotropic  $B = 6.0 \text{\AA}^2$ . Ratio of maximum least-squares shift to e.s.d. in final refinement cycle (on  $F$ )  $< 0.13$ ;  $\rho_{\text{max}} = 1.1 \text{e \AA}^{-3}$  (close to Pt) in final Fourier synthesis.  $R = 0.032$ ,  $wR = 0.031$ ; calculations on a Cyber 830 with programs of Melanson & Rochon (1975).\*

**Discussion.** The refined atomic parameters are listed in Table 1. A labeled diagram of the molecule is shown in Fig. 1. The coordination around the Pt atom is square planar. The deviations from the weighted best plane are Pt  $-0.0001$  (5), Cl(1)  $0.001$  (4), Cl(2)  $0.005$  (4), N(1)  $0.054$  (12) and N(2)  $0.009$  (12)  $\text{\AA}$ . The bond lengths and angles are given in Table 2. The angles around the Pt atom are close to the expected values of  $90$  and  $180^\circ$ , but there are some distortions due to a slight strain caused by the bidentate ligand. The chelate angle N(1)—Pt—N(2) is smaller [ $84.0$  (5) $^\circ$ ] than the other angles as observed in other Pt—ethylenediamine structures (Faggiani, Lippert & Lock, 1980; Bau, Gellert, Lehovc & Louie, 1977). In  $[\text{PtCl}_2(\text{en})]$  (Iball, MacDougall & Scrimgeour, 1975) the angle N—Pt—N is only  $73$  (2) $^\circ$ , but we do not believe that this value is reliable. The standard deviations must be much higher than estimated by the authors.

The Pt—Cl bonds [ $2.303$  (4) and  $2.317$  (4)  $\text{\AA}$ ] are of normal lengths. The IR spectrum of the compound showed two stretching  $\nu(\text{Pt}-\text{Cl})$  vibrations at  $320$  and  $340 \text{cm}^{-1}$ , which are typical of *cis* isomers.

The two Pt—N bond distances [ $2.039$  (14) and  $2.067$  (12)  $\text{\AA}$ ] are not significantly different even though there are two methyl groups on one of the N atoms. These distances are normal and agree with the values found in other Pt—(en) compounds (Faggiani *et*

\* Lists of structure factors, anisotropic thermal parameters, H coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43317 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

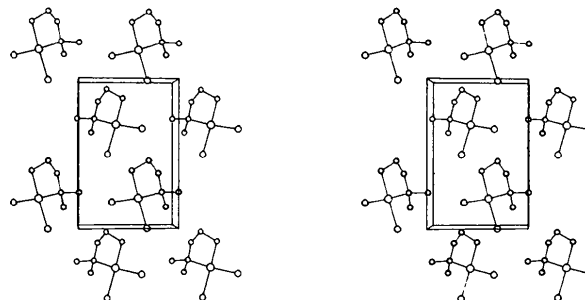


Fig. 2. Stereoscopic diagram of the packing in the  $[\text{PtCl}_2\{\text{N}(\text{CH}_3)_2\text{C}_2\text{H}_4\text{NH}_2\}]$  crystal (*b* axis vertical and *c* axis horizontal).

*al.*, 1980; Bau *et al.*, 1977; Iball *et al.*, 1975). The bond distances and angles within the *N,N*-dimethylethylenediamine ligand are normal (Table 2). The torsion angles have been calculated and deposited.

In the structure of [PtCl<sub>2</sub>(en)] the Pt(en) chelate rings are puckered and the distance between adjacent Pt atoms is 3.38 Å (Iball *et al.*, 1975). In the present structure, the Pt atoms cannot be so close because of the presence of two methyl groups, one on each side of the Pt coordination plane. The shortest distance is 5.639 Å. The packing of the molecules in the crystal is shown in Fig. 2. It consists of layers of molecules parallel to the *ac* plane and centered at *y* = 0.3 and 0.8. The crystal is probably stabilized by intermolecular hydrogen bonding between the -NH<sub>2</sub> group and Cl(2). The N(1)···Cl(2) distances are 3.37 (1) and 3.58 (1) Å and the angles are acceptable (Table 2).

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## Structure of the Phosphorin Derivative [Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>{(CH<sub>3</sub>)PC<sub>5</sub>H<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}]

BY BERNHARD NUBER AND MANFRED L. ZIEGLER\*

*Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg, Federal Republic of Germany*

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**Abstract.** Dicarboxyl( $\eta$ -cyclopentadienyl)(1-methyl-2,4,6-triphenylphosphorin)iron, C<sub>31</sub>H<sub>25</sub>FeO<sub>2</sub>P, *M<sub>r</sub>* = 516.36, monoclinic, *P*2<sub>1</sub>/*a*, *a* = 9.482 (3), *b* = 14.051 (4), *c* = 18.941 (4) Å,  $\beta$  = 94.80 (2)°, *V* = 2514.7 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.364, *D<sub>m</sub>* (by flotation) = 1.39 Mg m<sup>-3</sup>,  $\lambda$ (Mo *K*α) = 0.71069 Å,  $\mu$  = 6.35 mm<sup>-1</sup>, *F*(000) = 1072, *T* = 298 K. Final *wR* = 0.050 (*R* = 0.071) for 994 observed independent reflections. The structure consists of discrete molecules; the phosphorin ligand is bound to the iron *via* the P atom. The five C atoms of the phosphorin ring do not deviate noticeably from planarity; the C–C distances are equal within 1σ [mean 1.40 (2) Å]. The 'chair angle' between the carbon plane C(1)–C(5) and the plane C(1), P, C(5) is 23.2°. There exists an obvious relationship with the 'open ferrocenes'.

**Introduction.** The complex chemistry of phosphorin ligands has only recently been studied in detail (Dave, Berger, Bilger, Kaletsch, Pebler, Knecht & Dimroth, 1985; Lehmkuhl, Elsässer, Benn, Gabor, Rufinska,

Goddard & Krüger, 1985). Interest in this chemistry stems from the close relationship with the ferrocenes (I) and the so-called 'open ferrocenes' (II) with an open five-membered pentadienyl ligand (Ernst, 1985). Phosphorin ligands can coordinate in several ways, as shown in the scheme. The phosphorin sandwich (III) has a *gauche*-eclipsed conformation with both ligands  $\eta^5$ -bonded (Baum & Massa, 1985) and the same type of bonding was found in chloro(diethyl ether)(1-isopropyl-2,4,6-triphenylphosphorin)magnesium, [MgCl(CH<sub>3</sub>)<sub>2</sub>CHPC<sub>5</sub>H<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>{O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}]<sub>2</sub>, (Krüger, 1985, unpublished). The  $\eta^3$ -allyl-type bonding in (V) has been deduced from NMR experiments (Lehmkuhl, Elsässer, Benn, Gabor, Rufinska, Goddard & Krüger, 1985) and an X-ray structure determination established bonding of the P atom to the central Ni atom in (IV) (Lehmkuhl, Elsässer, Benn, Gabor, Rufinska, Goddard & Krüger, 1985). To elucidate more of the complex chemistry of phosphorin ligands a single X-ray structure determination has been performed of the title compound (VI). (VI) can be synthesized by reacting cpFe(CO)<sub>2</sub>I with (1-methyl-2,4,6-triphenylphosphorin)lithium (Dave, Berger, Bilger, Kaletsch, Pebler, Knecht & Dimroth, 1985).

\* To whom correspondence should be addressed.