

Structure of Dichloro[1,2-ethanedione bis(dimethylhydrazone)](η -ethylene)platinum(II), [PtCl₂(C₂H₄)(C₆H₁₄N₄)]

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Abstract. $M_r = 436.26$, monoclinic, $P2_1$, $a = 8.998$ (3), $b = 8.133$ (4), $c = 9.872$ (2) Å, $\beta = 106.72$ (3)°, $V = 691.9$ (5) Å³, $Z = 2$, $D_m = 2.09$, $D_x = 2.094$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 106.15$ cm⁻¹, $F(000) = 412$, $T = 298$ K, $R = 0.050$, $R_w = 0.057$ for 1404 reflections. The compound has a trigonal-bipyramidal structure with the Cl atoms in apical positions and the bidentate ligand (which coordinates through its α -diimine units) and ethylene in the equatorial plane. The bidentate ligand is in a *cis* conformation with some distortion from planarity. The Pt–Cl and Pt–olefin bond distances are usual for five-coordinate complexes of Pt^{II}.

Introduction. Recently, the preparation of a series of Pt^{II} complexes of formula PtCl₂(olefin)(L₂), with L₂ a potentially bidentate N-donor ligand, has been reported (Cattalini, Gasparrini, Maresca & Natile, 1973; De Renzi, Panunzi, Saporito & Vitagliano, 1977). Among these compounds two different coordination geometries are known. The first is trigonal-bipyramidal and is obtained when L₂ really acts as a bidentate ligand; the second corresponds to the usual square-planar arrangement of the ligands with L₂, acting as monodentate, *trans* to the olefin. Different arrangements can easily be discriminated by ¹H NMR spectroscopy, since the chemical shift of the olefinic protons is markedly dependent on the Pt coordination number (Albano, De Renzi & Morelli, 1984). In some complexes, however, these signals appear at an intermediate frequency. Thus, it is not possible to establish the coordination geometry. In these complexes it has been observed that the ¹H NMR spectra are temperature-dependent. At low temperature the ¹H NMR signals move towards the chemical-shift range typical of the five-coordinate species. The above reported observations prompted us to carry out a structural investigation concerning one of these compounds, namely [PtCl₂(C₂H₄)(L₂)] with L₂ = 1,2-ethanedione bis(dimethylhydrazone). Only a few structures of five-coordinate Pt^{II} complexes are presently known (Cattalini, Maresca & Natile, 1975; De Renzi, Di Blasio, Saporito, Scalone & Vitagliano, 1980; Van der Poel, Van Koten, Kokkes & Stam, 1981).

Experimental. Yellow–orange crystals, synthesized by Albano *et al.* (1984), obtained by evaporation of a concentrated methanol solution. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation. Unit-cell parameters by least-squares refinement of the setting angles of 25 reflections in the θ range 8°–11°. 1683 reflections collected in the range 0° < 2 θ < 54°, $\bar{1} < h < 11$, 0 < k < 10, 0 < l < 12, ω -2 θ scan mode, scan width (0.9 + 0.35 tan θ)°. No significant variation (<4%) in the intensity of reflection 232. No absorption correction for the approximately spherical crystal ($\mu R = 1.1$). Scattering factors f' and f'' calculated according to Cromer & Waber (1974). Pt and Cl atoms located by a Patterson map; a subsequent Fourier map revealed all the non-hydrogen atoms; H atoms not located. Refinement (non-H atoms anisotropic) by full-matrix least squares terminated when $(\Delta/\sigma)_{\text{max}} < 0.3$. Final $R = 0.050$, $R_w = 0.057$ and $S = 2.48$ for 1404 reflections with $I > 3.0\sigma(I)$. Max. and min. heights in final difference Fourier map 3.2 and -1.6 e Å⁻³. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/\sigma^2(F_o)$. No correction for secondary extinction. All calculations carried out on a PDP-11/34 digital computer of the Centro di Metodologie Chimico-Fisiche, University of Naples, using the Enraf–Nonius *SDP* package of crystallographic programs.

Discussion. Table 1 contains the atomic coordinates and thermal parameters.† Bond lengths and angles for the organic moiety are reported in Table 2 with their estimated standard deviations; they are in agreement with the literature data. In Fig. 1 the packing of the molecules in the unit cell is shown. The crystal consists of discrete molecules of Pt(C₂H₄)Cl₂{Me₂N–N=C(H)–C(H)=N–NMe₂} with no particularly short distances involved in the molecular packing. In Fig. 2 a perspective view of the molecule is shown (along the [121] direction) and the coordination distances are also reported. A comparison of these geometrical parameters with those of similar five-coordinate complex structures is reported in Table 3.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39649 (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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The geometry of the inner coordination sphere of the Pt is trigonal bipyramidal, if the ethylene molecule is assumed to be monodentate. The Cl atoms occupy the axial positions, whereas ethylene and the bidentate bis(hydrazone) molecule occupy the equatorial positions. The bidentate ligand coordinates through its α -diimine units.

The molecule does not contain any symmetry element as indicated by the analysis of the coordination geometry:

(i) the Pt—Cl, Pt—N and Pt—C distances are slightly different;

(ii) the N(3) atom is 0.36 Å outside the equatorial least-squares plane, the N(1)—C(5)—C(6)—N(3) torsion angle being 19.4 (3)°;

(iii) the two external N atoms [N(2) and N(4)] have different geometries, the former corresponding to an sp^2 and the latter to an sp^3 hybridization. The distance of N from the plane through the atoms to which it is attached is -0.18 (4) for N(2) and +0.41 (2) Å for N(4).

This analysis seems to suggest that a stronger coordination occurs between N(1) and Pt than between N(2) and Pt.

Table 1. Final atomic parameters ($\times 10^4$) and their standard deviations (in parentheses)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)*
Pt	7580 (1)	1250	1696 (1)	3.3 (1)
Cl(1)	7636 (8)	4122 (9)	1799 (8)	5.4 (2)
Cl(2)	7526 (6)	-1515 (11)	1631 (8)	5.3 (2)
C(1)	5177 (13)	1067 (32)	1492 (15)	3.6 (4)
C(2)	6145 (19)	1067 (33)	3005 (19)	3.5 (4)
C(3)	6012 (22)	1361 (95)	-1779 (26)	5.9 (6)
C(4)	8326 (26)	1681 (52)	-2612 (22)	7.3 (7)
N(1)	8454 (14)	1518 (35)	-210 (14)	4.2 (3)
N(2)	7576 (18)	1733 (50)	-1503 (19)	6.2 (7)
C(5)	9993 (20)	1577 (30)	144 (19)	3.5 (5)
C(6)	10880 (18)	1574 (29)	1489 (21)	3.8 (5)
N(3)	10261 (12)	1019 (20)	2532 (15)	2.9 (4)
N(4)	11006 (15)	901 (21)	3893 (17)	3.8 (5)
C(7)	12648 (26)	1623 (58)	4235 (32)	7.6 (9)
C(8)	10222 (37)	1608 (26)	4825 (28)	5.7 (6)

$$* B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} g_{ij} \quad (g = \text{metric tensor}).$$

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

C(1)—C(2)	1.50 (2)	C(5)—C(6)	1.34 (2)
C(3)—N(2)	1.39 (3)	C(6)—N(3)	1.38 (3)
C(4)—N(2)	1.44 (2)	N(3)—N(4)	1.32 (2)
N(1)—N(2)	1.31 (2)	N(4)—C(7)	1.53 (3)
N(1)—C(5)	1.33 (2)	N(4)—C(8)	1.43 (3)
N(2)—N(1)—C(5)	123 (4)	C(5)—C(6)—N(3)	119 (3)
C(3)—N(2)—C(4)	121 (5)	C(6)—N(3)—N(4)	126 (2)
C(3)—N(2)—N(1)	117 (5)	N(3)—N(4)—C(7)	112 (3)
C(4)—N(2)—N(1)	117 (5)	N(3)—N(4)—C(8)	115 (3)
N(1)—C(5)—C(6)	123 (3)	C(7)—N(4)—C(8)	109 (3)

Table 3. Geometrical parameters of five-coordinate Pt^{II} complexes

	Pt—Cl	Bond distances (Å)			Torsion angle (°) N=C—C=N
		Pt—N	Pt—C=	C=C	
[Pt(C ₂ H ₄)Cl ₂ {Me ₂ N—N=C(H)—C(H)=N—NMe ₂ }] ^(a)	$\begin{cases} 2.338 (7) \\ 2.250 (9) \end{cases}$	$\begin{cases} 2.249 (11) \\ 2.321 (11) \end{cases}$	$\begin{cases} 2.119 (12) \\ 2.079 (15) \end{cases}$	1.497 (19)	19.4 (3)
[Pt(C ₂ H ₄)Cl ₂ {Me(H)N—N=C(Me)—C(Me)=N—N(H)Me}] ^(b)	2.304 (3)	2.221 (10)	2.073 (12)	1.46 (2)	0
[Pt(C ₂ H ₄)Cl ₂ {C ₆ H ₅ CH(CH ₃)N(CH ₃)CH ₂ —CH ₂ N(CH ₃)—CH(CH ₃)C ₆ H ₅ }] ^(c)	2.319 (5)	2.372 (12)	2.087 (24)	1.57 (4)	180
[Pt(CH ₂ CH=CH ₂)Cl ₂ {C ₆ H ₅ CH(CH ₃)N(CH ₃)CH ₂ —CH ₂ —N(CH ₃)CH(CH ₃)C ₆ H ₅ }] ^(c)	2.300 (5)	2.354 (9)	2.148 (29)	—	180
[PtCl ₂ (η^2 -styrene){ <i>t</i> -Bu—N=CH—CH=N— <i>t</i> -Bu}] ^(d)	$\begin{cases} 2.299 (9) \\ 2.323 (8) \end{cases}$	$\begin{cases} 2.20 (3) \\ 2.31 (3) \end{cases}$	$\begin{cases} 2.16 (4) \\ 2.20 (4) \end{cases}$	1.53 (2)	3.2
[PtCl ₂ (<i>E</i> -2-butene){Me ₂ N—N=C(CH ₃)—C(CH ₃)=N—N(Me ₂)}] ^(e)	2.307 (5)	2.259 (18)	2.044 (24)	—	0

References: (a) this work; (b) Calligaris, Delise, Maresca, Natile & Randaccio (1976); (c) De Renzi, Di Blasio, Saporito, Scalone & Vitagliano (1980); (d) Van der Poel, Van Koten, Kokkes & Stam (1981); (e) B. Di Blasio, A. De Renzi & G. Morelli (unpublished results).

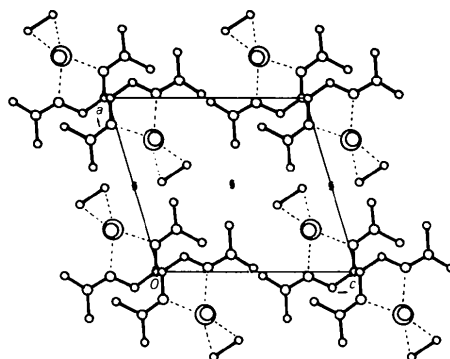


Fig. 1. Packing of the molecules projected down the *b* axis.

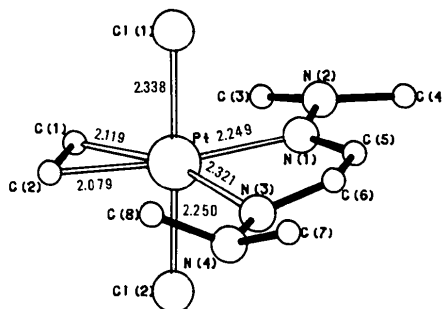


Fig. 2. Perspective view of the molecule down the [121] direction with the coordination distances (Å).

These data and the ^1H NMR studies (Albano *et al.*, 1984) indicate that an equilibrium exists in solution between the five-coordinate and a square-planar complex while in the solid state only the former complex is isolated. Breaking of either of the N–Pt bonds in the five-coordinate complex should lead to the formation of the other species, as reported for a similar Pt^{II} -ethylene complex containing N,N,N',N' -tetramethyl-1,3-propanediamine (Cattalini, Maresca & Natile, 1979). The Pt–olefin, C=C, and both the Pt–N bond lengths are in the range reported for five-coordinate Pt complexes (see Table 3). The Pt–N bond lengths are significantly longer than the Pt–N(sp^2) values reported for square-planar Pt complexes, which range from 1.73 to 2.05 Å.

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Structure of Bis(*meso*-1,2-diphenyl-1,2-ethanediamine)nickel(II) Dichloride Dihydrate, $[\text{Ni}(\text{C}_{14}\text{H}_{16}\text{N}_2)_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

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Abstract. $M_r = 590$, orthorhombic, *Pccn*, $a = 26.831$ (5), $b = 15.366$ (4), $c = 7.1773$ (6) Å, $V = 2959.1$ (6) Å³, $Z = 4$, $D_x = 1.32$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.87$ mm⁻¹, $T = 298$ K, $F(000) = 1240$, final $R = 0.046$ for 1075 observed reflections. The Ni coordination is square planar, with Ni–N distances 1.922 (4) and 1.921 (4) Å and N–Ni–N angle 86.4 (2)°. Bond lengths and angles are normal.

Introduction. The structure of the title compound was determined in order to provide further structural information on complexes of Ni with ethylenediamine and C-substituted ethylenediamines. In this case we have studied the complex with *meso*-1,2-diphenyl-1,2-ethanediamine (*meso*-stien). In previous work we determined the structures of two very similar Ni complexes, those formed by tetramethylethylenediamine (Alcalá-Aranda, Fernández, Gómez-Beltrán & Larena, 1977) and 1,2-cyclohexanediamine (Valero-Capilla, Alcalá-Aranda & Gómez-Beltrán, 1980), in which the environments of Ni are respectively square planar and octahedral. The molecular structures of two different

bis(*meso*-stien)nickel(II) bis(dichloroacetates) have previously been determined by X-ray diffraction (Nyburg & Wood, 1964).

Experimental. Yellow crystal 0.27 × 0.15 × 0.27 mm. D_m not determined. Unit-cell parameters and intensity data obtained on an Enraf–Nonius CAD-4F diffractometer with graphite-monochromated Mo $K\alpha$ radiation in $\omega/2\theta$ scan mode ($0 < \theta < 28^\circ$). Cell dimensions refined by least-squares fitting of the θ values of 25 reflections. No appreciable drop in intensity of three standard reflections checked every hour. 3555 reflections collected in the hkl range 0,0,0 to 35,20,9; 1075 with $I > 2\sigma(I)$ used in subsequent calculations. Intensities corrected for Lorentz and polarization effects, but not for absorption ($\mu R = 0.23$). Scattering factors for neutral atoms and anomalous-dispersion corrections for Ni and Cl from *International Tables for X-ray Crystallography* (1974). A statistical test showed a centrosymmetric intensity distribution. Structure solved with *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) and standard Fourier