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Two Forms of *cis*-Dimethylbis-(methyl isocyanide)platinum(II)

N. H. DRYDEN, R. J. PUDDEPHATT, S. ROY AND J. J. VITTAL

Chemistry Department, The University of Western Ontario, London, Ontario, Canada N6A 5B7

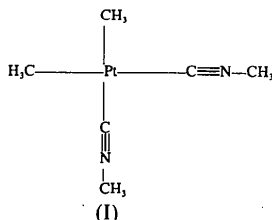
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Abstract

The compound $[\text{Pt}(\text{CH}_3)_2(\text{C}_2\text{H}_3\text{N})_2]$ crystallized in two different space groups [orthorhombic, (1), and monoclinic, (2)] depending on the solvent used. The structures were solved by single-crystal X-ray diffraction analyses. In both structures, the stereochemistry at Pt^{II} is *cis* square planar. The Pt—C(methyl) distances are 2.066 (7) and 2.078 (8) Å in (1) and 2.07 (3) and 2.06 (2) Å in (2), and the Pt—C(isocyanide) distances are 1.979 (8) and 1.953 (7) Å in (1) and 1.96 (2) and 2.02 (3) Å in (2). The difference in the quality of these two structure determinations appears to have stemmed from a poor absorption correction resulting from the cut faces and platy nature of the crystal of (2).

Comment

The complex $[\text{Pt}(\text{CH}_3)_2(\text{C}_2\text{H}_3\text{N})_2]$ can be sublimed under vacuum and acts as a useful precursor for the chemical-vapour deposition (CVD) of Pt films (Kumar, Roy, Rashidi & Puddephatt, 1989). When prepared in the presence of H_2 , these films are free of impurities, but, under other conditions of CVD, carbon impurities are significant (Dryden *et al.*, 1991). The CVD process is catalyzed by Pt and so the absorption of the complex onto Pt is a key step (Nixon *et al.*, 1991). In order to model this absorption, it was necessary to know the molecular dimensions of the complex (I). Two crystalline forms were obtained and their structures are reported here.



A perspective view of molecule (1) (Johnson, 1971) including the atom-numbering scheme is presented in Fig. 1. Unit-cell packing diagrams for (1) and (2) are

shown in Figs. 2 and 3, respectively. The crystals consist of discrete molecules. The shortest intermolecular contact is $\text{Pt}\cdots\text{H}(62)(1-x, y, \frac{1}{2}-z) = 2.971$ Å in (1) and $\text{Pt}\cdots\text{H}(53)(-x, y, \frac{1}{2}-z) = 2.945$ Å in (2). The closest Pt \cdots Pt distance is 5.747 Å in (1) and 5.728 Å in (2).

The molecular structures of the compound $[\text{PtMe}_2(\text{CNMe})_2]$ in the orthorhombic form (1) and the monoclinic form (2) have some common features. In the neutral molecule Pt^{II} is bonded to two Me and two MeNC ligands in a *cis* geometry. Furthermore, the stereochemistry at Pt^{II} is essentially square-planar with a slight tetrahedral distortion, as indicated by the weighted least-squares planes and C—Pt—C angles (Table 2). The bond distances and angles are, in general, comparable between (1) and (2). The two Pt—CH₃ distances in each crystalline form are equal. A number of complexes containing the Pt—CH₃ group have been characterized structurally (Wisner, Bartczak & Ibers, 1986, and references therein) with bond distances ranging from 2.0 to 2.2 Å, depending on the group *trans* to it. For the Me group *trans* to a weaker 'trans-influence' ligand the Pt—CH₃ distance is expected to be equal to the sum of the covalent radii of C (sp^3 , 0.772 Å) and Pt (1.31 Å) (2.08 Å; Hartley, 1982). Thus, the Pt—CH₃ distances in these compounds are typical of *cis*-dimethylplatinum complexes. The coordination of the MeNC ligands to the metal is essentially linear. The geometry of the $\text{Pt}(\text{CNMe})_2$ group is comparable to that observed for a similar *cis*-bis(methyl isocyanide)-platinum(II) complex reported by Butler, Enemark, Parks & Balch (1973). The

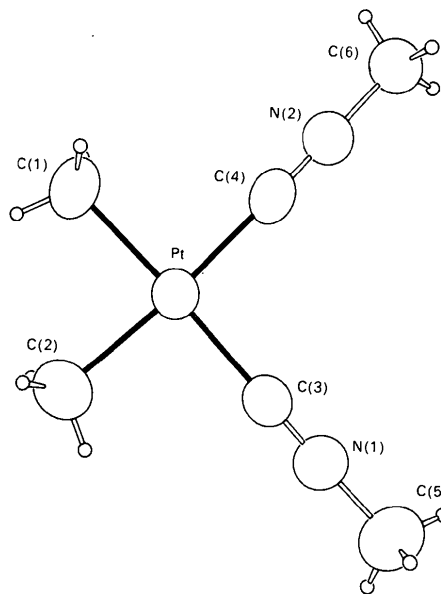


Fig. 1. A perspective view of molecule (1) showing 50% probability displacement ellipsoids. The H atoms are given as small spheres of arbitrary radii.

Pt—CH₃ distances are found to be slightly longer than the Pt—CNMe distances in both forms (1) and (2).

Since the molecules are flat and the ligands small, it was expected that the molecules might form stacks in the crystal lattice, but the above observations and packing shown in Figs. 2 and 3 clearly show that this is not the case. The absence of strong intermolecular forces is consistent with the high volatility of the complex, which is required for its use in chemical-vapour deposition.

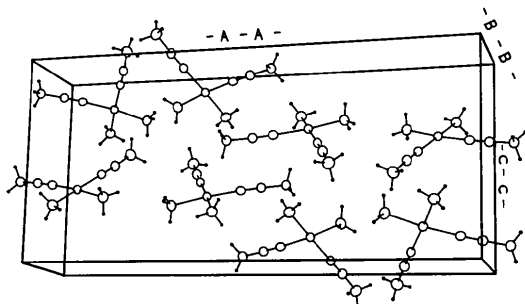


Fig. 2. Unit-cell packing diagram for molecule (1).

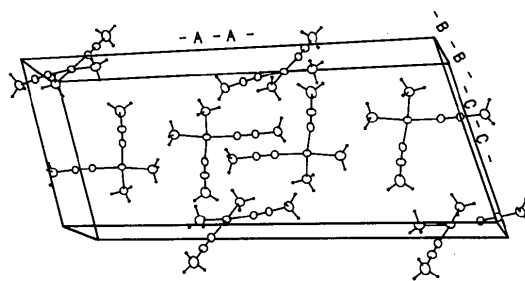


Fig. 3. Unit-cell packing diagram for molecule (2).

Experimental

The title compound was synthesized by a procedure described by Roy, Puddephatt & Scott (1989). Crystals of (1) and (2) were obtained by the recrystallization of $[\text{Pt}(\text{CH}_3)_2(\text{C}_2\text{H}_3\text{N})_2]$ from diethyl ether and toluene, respectively. On prolonged exposure to light they decompose, as indicated by a color change from clear yellow-white to opaque brown.

Compound (1)

Crystal data

$[\text{Pt}(\text{CH}_3)_2(\text{C}_2\text{H}_3\text{N})_2]$

$M_r = 307.266$

Orthorhombic

Pbcn

$a = 25.3136$ (15) Å

$b = 6.0161$ (7) Å

$c = 11.3754$ (12) Å

$V = 1732.4$ (3) Å³

$Z = 8$

$D_x = 2.355$ Mg m⁻³

$D_m = 2.39$ (5) Mg m⁻³

Cu $K\alpha$ radiation

$\lambda = 1.54184$ Å

Cell parameters from 20 reflections

$\theta = 30.85$ – 37.81°

$\mu = 28.14$ mm⁻¹

$T = 298$ K

Hexagonal shape with ten faces

$0.23 \times 0.13 \times 0.12$ mm

Colorless, transparent

Data collection

Enraf-Nonius CAD-4F diffractometer

ω - 2θ scans

Absorption correction: analytical (AGNOST; Cahen & Ibers, 1972)

$T_{\min} = 0.019$, $T_{\max} = 0.154$

4142 measured reflections

1290 independent reflections

Refinement

Refinement on F

$R = 0.0239$

$wR = 0.0250$

937 reflections

84 parameters

$w = 1/[\sigma^2(F) + 0.001234F^2]$

$(\Delta/\sigma)_{\max} = -0.0017$

$\Delta\rho_{\max} = 0.56$ e Å⁻³

$\Delta\rho_{\min} = -0.87$ e Å⁻³

937 observed reflections

$[I > 3.0\sigma(I)]$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 60^\circ$

$h = -28 \rightarrow 28$

$k = -2 \rightarrow 6$

$l = -2 \rightarrow 12$

3 standard reflections

frequency: 180 min

intensity variation: 22.5%

Extinction correction:

$F^* = F(1 - 0.001\chi F^2/\sin\theta)$

(SHELX76; Sheldrick, 1976)

Extinction coefficient:

$\chi = 0.002417$ (82)

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) (non-H); Stewart, Davidson & Simpson (1965) (H)

Compound (2)

Crystal data

$[\text{Pt}(\text{CH}_3)_2(\text{C}_2\text{H}_3\text{N})_2]$

$M_r = 307.266$

Monoclinic

C2/c

$a = 26.584$ (2) Å

$b = 6.062$ (1) Å

$c = 11.318$ (1) Å

$\beta = 108.038$ (7)°

$V = 1734$ (2) Å³

$Z = 8$

$D_x = 2.353$ Mg m⁻³

$D_m = 2.39$ (5) Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 20 reflections

$\theta = 13.0$ – 17.8°

$\mu = 15.50$ mm⁻¹

$T = 298$ K

Platy crystal

$0.45 \times 0.41 \times 0.12$ mm

Colorless, transparent

Data collection

Enraf-Nonius CAD-4F diffractometer

ω - 2θ scans

Absorption correction: analytical (AGNOST; Cahen & Ibers, 1972)

$T_{\min} = 0.038$, $T_{\max} = 0.171$

2838 measured reflections

1203 independent reflections

Refinement

Refinement on F

$R = 0.0703$

$wR = 0.0715$

1010 reflections

84 parameters

$w = 1/[\sigma^2(F) + 0.008409F^2]$

1010 observed reflections

$[I > 3.0\sigma(I)]$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 23^\circ$

$h = -29 \rightarrow 29$

$k = -6 \rightarrow 0$

$l = 0 \rightarrow 12$

3 standard reflections

frequency: 180 min

intensity variation: 17.4%

Extinction correction:

$F^* = F(1 - 0.001\chi F^2/\sin\theta)$

(SHELX76; Sheldrick, 1976)

Extinction coefficient:

$\chi = 0.00043$ (83)

$$(\Delta/\sigma)_{\max} < 0.0001$$

$$\Delta\rho_{\max} = 3.73 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -1.53 \text{ e } \text{Å}^{-3}$$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) (non-H); Stewart, Davidson & Simpson (1965) (H)

running on a DEC PDP11/23+ computer. The structures were solved by *SHELXS86* (Sheldrick, 1985) and were refined by full-matrix least-squares techniques using *SHELX76* (Sheldrick, 1976) software, both running on a SUN3/50 workstation. The real component of anomalous scattering was included for all non-H atoms (Cromer & Liberman, 1970). All the non-H atoms were assigned anisotropic displacement parameters and refined in the least-squares cycles. All H atoms were located in a subsequent Fourier synthesis and were placed in calculated positions (C—H = 0.90 Å). They were included only for the structure-factor calculations. A common temperature factor was assigned for all the H atoms and was refined in the least-squares cycles.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1) and (2)

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

	x	y	z	<i>U</i> _{eq}
(1)				
Pt	0.38143 (1)	0.43166 (4)	0.35107 (2)	0.0496 (1)
N(1)	0.3282 (3)	0.0610 (10)	0.5009 (6)	0.062 (2)
N(2)	0.4957 (3)	0.2706 (9)	0.4040 (5)	0.058 (2)
C(1)	0.4130 (3)	0.6909 (12)	0.2549 (8)	0.069 (2)
C(2)	0.3080 (3)	0.5518 (15)	0.2997 (8)	0.075 (3)
C(3)	0.3475 (3)	0.1961 (12)	0.4460 (6)	0.053 (2)
C(4)	0.4530 (3)	0.3303 (12)	0.3862 (6)	0.055 (2)
C(5)	0.3061 (4)	-0.1079 (15)	0.5737 (8)	0.086 (3)
C(6)	0.5484 (3)	0.1922 (13)	0.4210 (7)	0.063 (2)
(2)				
Pt	0.11865 (3)	0.07315 (10)	0.43563 (6)	0.0465 (4)
N(1)	0.0044 (6)	0.2321 (26)	0.4080 (14)	0.054 (5)
N(2)	0.1726 (7)	0.4439 (25)	0.6252 (15)	0.052 (6)
C(1)	0.1914 (11)	-0.0334 (49)	0.4281 (24)	0.081 (10)
C(2)	0.0887 (9)	-0.1828 (31)	0.3140 (19)	0.061 (7)
C(3)	0.0466 (7)	0.1653 (37)	0.4228 (17)	0.051 (6)
C(4)	0.1547 (7)	0.3136 (37)	0.5556 (20)	0.053 (6)
C(5)	-0.0493 (8)	0.3092 (36)	0.3878 (21)	0.068 (7)
C(6)	0.1931 (12)	0.6168 (60)	0.7129 (35)	0.111 (14)

Table 2. Selected geometric parameters (Å, °) for (1) and (2)

	(1)	(2)
Pt—C(1)	2.066 (7)	2.07 (3)
Pt—C(2)	2.078 (8)	2.06 (2)
Pt—C(3)	1.979 (8)	1.96 (2)
Pt—C(4)	1.953 (7)	2.02 (3)
N(1)—C(3)	1.135 (9)	1.16 (2)
N(1)—C(5)	1.426 (10)	1.45 (2)
N(2)—C(4)	1.157 (9)	1.11 (3)
N(2)—C(6)	1.429 (9)	1.43 (4)
C(1)—Pt—C(2)	86.2 (3)	84.9 (10)
C(1)—Pt—C(3)	176.3 (3)	173.5 (9)
C(2)—Pt—C(3)	90.8 (3)	89.9 (9)
C(1)—Pt—C(4)	89.2 (3)	89.9 (9)
C(2)—Pt—C(4)	174.8 (3)	174.8 (7)
C(3)—Pt—C(4)	93.9 (3)	95.3 (8)
C(3)—N(1)—C(5)	177.2 (9)	178 (2)
C(4)—N(2)—C(6)	177.4 (7)	177 (2)
N(1)—C(3)—Pt	179.6 (4)	174 (2)
N(2)—C(4)—Pt	178.3 (6)	176 (2)

Only approximate crystal densities could be measured by the neutral buoyancy method using a mixture of dibromoethane and bromomethane, as the crystals dissolved slowly in these liquids. Both crystals were examined employing similar procedures.

Corrections were made for Lorentz, polarization and background radiation but not for decay as the variations in intensity of the standards were random. The faces of the data crystal were indexed and the distances between them were measured under a Filar microscope for a Gaussian absorption correction. Observation of the Niggli matrix and symmetry-equivalent reflections revealed the Laue symmetry for (1) and (2). The space groups were deduced from the systematic absences (*International Tables for Crystallography*, 1983, Vol. A). Data were processed using the *Structure Determination Package* (Enraf-Nonius, 1985)

Of the top eight peaks in the final difference Fourier synthesis for (2), six peaks were around the Pt atom at distances 0.90–1.14 Å and two peaks were at distances 1.68 and 1.70 Å (with electron densities 1.67 and 1.53 e Å⁻³, respectively) from Pt. Poor agreement factors and high residual electron densities around the Pt atom may be attributed to the platy nature of the crystal and poor absorption correction caused by the cut faces.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71670 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1043]

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Absolute Configuration of Di(perchlorato-*O*)tetra(pyridine-*N*)copper(II), $[\text{Cu}(\text{ClO}_4)_2(\text{py})_4]$

YVETTE AGNUS

URA 405 du CNRS, Université Louis Pasteur,
1 rue Blaise Pascal, 67008 Strasbourg CEDEX, France

MARC LABARELLE, RÉMY LOUIS AND BERNARD METZ

UPR de Biologie Structurale 9004, IBMC CNRS,
15 rue René Descartes, 67084 Strasbourg CEDEX,
France

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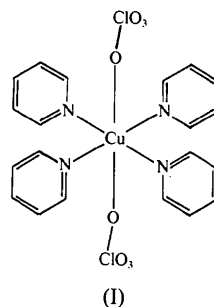
Abstract

The crystal of the title complex consists of neutral $[\text{Cu}(\text{ClO}_4)_2(\text{C}_5\text{H}_5\text{N})_4]$ units. The two perchlorate ligands occupy the axial positions of a distorted octahedral environment around the metal ion; the axial Cu—O bonds are relatively weak. The absolute configuration has been established; the four pyridine molecules display a right-handed screw arrangement around the Cu^{2+} ion.

Comment

The preparation of the title compound was first reported by Ripan (1924). Papers dealing with magnetic, infrared, electronic absorption and ESR studies, and X-ray data of $[\text{Cu}(\text{ClO}_4)_2(\text{py})_4]$ and related $[\text{Cu}X_2(\text{py})_4]$ ($\text{py} = \text{C}_5\text{H}_5\text{N}$; $X = \text{BF}_4^-$, NO_3^- , $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$, CF_3CO_2^-) began to appear about 30 years later (Ibers, 1953; Brown, Nuttall, McAvoy & Sharp, 1966; Jones & Bull, 1968; Alleyne & Thompson, 1974; Pradilla, Chen, Koknat & Fackler, 1979; Barker & Stobart, 1980; Gowda, Naikar & Reddy, 1984). The only complete structural study was made on tetra(pyridine)bis(trifluoroacetato)copper(II) (Pradilla, Chen, Koknat & Fackler, 1979). It crystallizes in the triclinic centrosymmetric space group $P\bar{1}$ and the Cu^{II} ion possesses the classic elongated octahedral environment.

The crystal of $[\text{Cu}(\text{ClO}_4)_2(\text{py})_4]$ (I) used in our study is optically active, consistent with the orthorhombic $P2_12_12_1$ space group. A comparison with



$[\text{Cu}(\text{BF}_4)_2(\text{py})_4]$ (Ibers, 1953) shows that both crystallize in the same space group with similar cell parameters. These preliminary results and the surprising conclusions of the study of Barker & Stobart (1980) about the Cu stereochemistry, prompted us to perform the determination of the molecular structure of $[\text{Cu}(\text{ClO}_4)_2(\text{py})_4]$.

The atom-numbering scheme and absolute configuration of $[\text{Cu}(\text{ClO}_4)_2(\text{py})_4]$ are depicted in Fig. 1. The molecule adopts an elongated octahedral geometry about the Cu atom involving four pyridine N atoms in the equatorial plane and two perchlorate O atoms in axial positions. The Cu—N distances of 2.006 (5)–2.042 (5) Å and the two long Cu—O (perchlorate) distances of 2.476 (7) and 2.559 (6) Å are common for hexacoordinate Cu compounds (Gowda, Naikar & Reddy, 1984). The contacts between neighbouring molecules are normal, the shortest being an $\text{O}_3\text{ClO}\cdots\text{CH}$ distance of 3.04 Å.

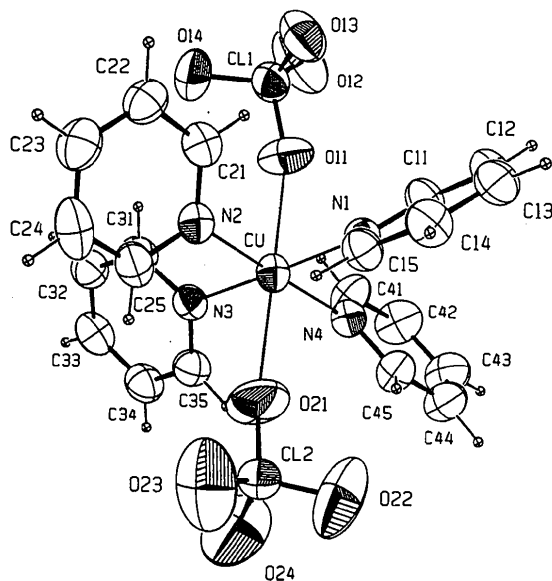


Fig. 1. Molecular geometry and atomic numbering scheme with non-H atoms as principal ellipsoids at the 40% probability level and H atoms as small spheres of arbitrary size.