cis-Dichlorobis(4-methylpyridine-κN)platinum(II)

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Sakai et al. • [PtCl2(C6H7N)2]
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Key indicators

Single-crystal X-ray study

T = 113 K

Mean |C–C| = 0.008 Å

R factor = 0.031

wR factor = 0.087

Data-to-parameter ratio = 20.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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Abstract

In the title molecule, cis-[PtCl₂(C₅H₇N)₂], the Pt

II coordination plane has a distorted structure in which the cis-PtCl₂ unit is tilted by 4.3 (2)° with respect to the cis-PtN₂ unit. The two pyridyl planes are inclined at angles of 64.8 (1)° and 77.5 (2)° with respect to the cis-PtN₂ unit, which is partly interpreted in terms of the intermolecular C--H(methyl)--π(pyridine) interactions in the crystal structure.

Comment

Since we found that amidate-bridged dinuclear platinum(II) complexes are active as hydrogen-evolving catalysts in the photoreduction of water to molecular hydrogen (Sakai & Matsumoto, 1990; Sakai et al., 1993), a large variety of platinum(II) complexes, including mononuclear Pt

II complexes, have been synthesized and tested in our research group. As a result of our ongoing research, we recently reported the first success in the development of a ‘photo-hydrogen-evolving molecular device’ which consists of a tris(2,2'-bipyridine)-ruthenium(II) derivative and a cis-PtCl₂ unit (Ozawa et al., 2006). The former serves as a photosensitizing center, generating a reductant site upon the visible-light illumination, while the latter serves as an active site for the hydrogenic activation, leading to hydrogen production from water. Thus, one of our research interests has recently been focused on the structure–activity relationship for a series of compounds having a cis-PtCl₂ unit. As part of this project, we report here the crystal structure of the title compound, (I).

The molecular structure of (I) is shown in Fig. 1. The mean-plane calculation carried out for the cis-PtCl₂N₂ unit (Pt1/Cl1/Cl2/N1/N2) reveals that the coordination does not have a perfectly planar geometry, the five-atom r.m.s. deviation being 0.05 (4) Å. As shown in Fig. 2, the plane defined by atoms Pt1, Cl1, and Cl2 is tilted by 4.3 (2)° with respect to that defined by atoms Pt1, N1, and N2. In other words, these two planes are twisted about the vector from the mid-point of N1--N2 to the mid-point of Cl1--Cl2. The two pyridyl planes are tilted with
respect to the plane defined by atoms Pt1, N1, and N2: the dihedral angle of the pyridyl unit with respect to the Pt1/N1/N2 plane is 64.8° for the N1/C1–C5 plane and 77.5° for the N2/C7–C11 plane. These values compare with values of 55.8° and 62.0° reported for cis-PtIICl2(pyridine)2 (Colamarino & Orioli, 1975; s.u.'s are not reported), the value of 54° reported for cis-PtIICl2(4-vinylpyridine)2 (Kubiak & Kuduk-Jaworska, 1986), the values of 58.2° and 48.8° reported for cis-PtIICl2(3-ferrocenylpyridine)2 (Carugo et al., 1992; s.u. values are not reported), and the values of 70.5° and 85.9° reported for cis-PtIICl2(2-pmpe)2 (2-pmpe = 2-pyridylmethylphosphonate) (Che˛cin´ ska et al., 2003).

A view of the crystal packing is shown in Fig. 3. The shortest intermolecular Pt···Pt, Pt···Cl, and Pt···H distances (see Table 1) reveal that there are no unusual intermolecular interactions. It seems probable that the conformational features of the pyridyl ligands are partly related to the intermolecular C—H(methyl)–···π(pyridyl) interactions in the crystal structure (see the C···C contacts in Table 1; see also Fig. 4).

Experimental

Compound (I) was prepared according to a literature method (Najajrech et al., 2003). The colorless crystals used in the structure determination were grown by slow evaporation of a solution of (I) in acetonitrile in air at ca 290 K. Analysis calculated for C12H14Cl2N2Pt2: C 31.87, H 3.12, N 6.19%; found: C 31.67, H 3.08, N 6.22%.

Crystal data

[PtCl2(C6H7N)2]

Mr = 452.24
Monoclinic, C2/c
a = 14.105 (4) Å
b = 12.530 (3) Å
c = 16.644 (4) Å
\( \beta = 107.429 (2) \)°
V = 2806.5 (12) Å³

Z = 8
\( D_x = 2.141 \) Mg m⁻³
Mo Kα radiation
\( \mu = 10.36 \) mm⁻¹
\( T = 113 (2) \) K
Prism, colorless
0.38 \times 0.23 \times 0.13 mm

Data collection

Rigaku Mercury CCD-detector diffractometer
w scans
Absorption correction: numerical (NUMABS: Higashi, 1999)
\( T_{min} = 0.090, T_{max} = 0.271 \)

10554 measured reflections
3135 independent reflections
2822 reflections with \( I > 2 \sigma(I) \)
\( R_{int} = 0.063 \)
\( \theta_{max} = 27.5° \)

Refinement

Refinement on \( F^2 \)
\( R(F^2) > 2 \sigma(F^2) = 0.031 \)
\( wR(F^2) = 0.087 \)
\( S = 1.16 \)
3135 reflections
157 parameters
H-atom parameters constrained

\( w = 1/[\sigma^2(Fo^2) + (0.0319PF)^2] \)
where \( P = (Fo^2 + 2Fe^2)/3 \)
\( (\Delta \sigma)_{max} = 0.001 \)
\( \Delta P_{max} = 3.49 \) e Å⁻³
\( \Delta P_{min} = -3.82 \) e Å⁻³
Extinction correction: SHELXL97
Extinction coefficient: 0.00037 (7)
Table 1
Selected geometric parameters (Å, °).

Pt1—N2 2.005 (4)
Pt1—N1 2.017 (5)
Pt1—Cl1 2.2993 (13)
Pt1—Cl2 2.3023 (16)

Pt1···Cl1‘ 4.1394 (15)
Pt1···Pt1‘ 4.6508 (9)
Pt1···H11ii 2.8554

Symmetry codes: (i) x+1/2, y, z; (ii) x+1/2, y+1/2, z;
(iii) x+1, y, z; (iv) x, y+1/2, z.

All H atoms were placed in idealized positions (methyl C—H = 0.98 Å and aromatic C—H = 0.95 Å), and included in the refinement in a riding-model approximation, with \(U_{iso}(H) = 1.5U_{eq}(methyl~C)\) and \(U_{iso}(H) = 1.2U_{eq}(aromatic~C)\). In the final difference Fourier map, the highest peak was located 0.02 Å from atom Pt1. Two relatively large residual peaks (2.69 and 2.14 e Å\(^{-3}\)) were located near atoms C6 and C8. Moreover, five residual peaks (1.1–1.62 e Å\(^{-3}\)) were observed near atom Pt1. The deepest hole was located 0.95 Å from atom Pt1.

Data collection: CrystalClear (Rigaku/MSC, 2002); cell refinement: CrystalClear; data reduction: CrystalStructure (Rigaku/MSC, 2003); program(s) used to solve structure: SIR92 (Altomare et al., 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: KENX (Sakai, 2004) and ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97, TEXSAN (Molecular Structure Corporation, 2001) and KENX.

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References


