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

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Key indicators

Single-crystal X-ray study
T = 113 K
Mean σ(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.

In the title molecule, cis-[PtCl$_2$(C$_6$H$_7$N)$_2$], the Pt^{II} coordination plane has a distorted structure in which the cis-PtCl$_2$ unit is tilted by 4.3 (2)° with respect to the cis-PtN$_2$ unit. The two pyridyl planes are inclined at angles of 64.8 (1) and 77.5 (2)° with respect to the cis-PtN$_2$ 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-Pt^{II}Cl$_2$ 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 compounds having a cis-Pt^{II}Cl$_2$ unit. As part of this project, we report here the crystal structure of the title compound, (I).

(I)
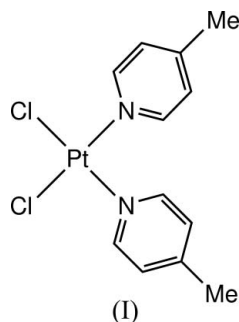
The molecular structure of (I) is shown in Fig. 1. The mean-plane calculation carried out for the cis-PtCl$_2$N$_2$ unit (Pt1/Cl1/Cl2/N1/N2) reveals that the coordination does not have a perfectly planar geometry, the five-atom r.m.s. deviation being 0.05 (4) Å. As shown in Fig. 2, the plane defined 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
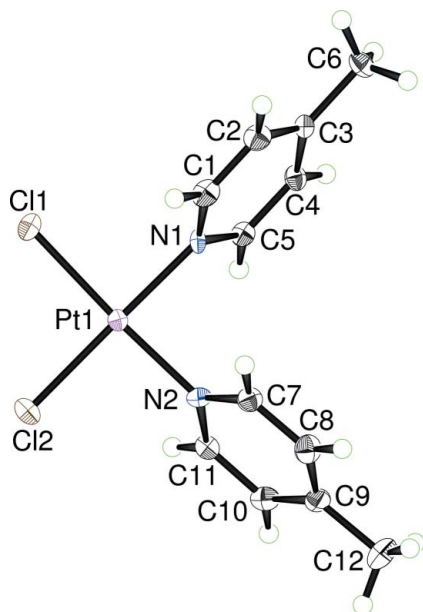
Figure 1
The molecular structure of (I) showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.
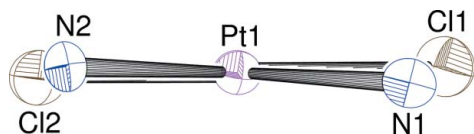

Figure 2
A view of the coodination of Pt1, showing the manner in which the *cis*-PtCl$_2$ and the *cis*-PtN$_2$ units are twisted with respect to each other.
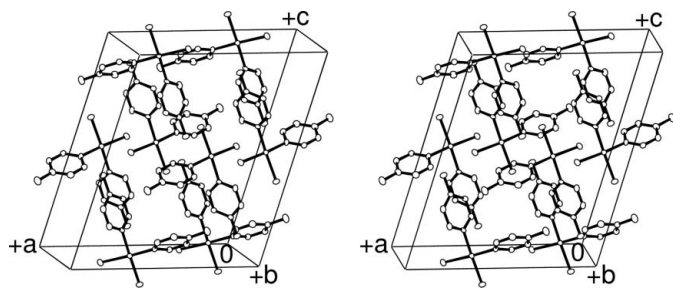

Figure 3
A stereoscopic view of part of the crystal structure of (I). Atoms have been drawn as spheres and H atoms have been omitted for clarity.

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 (1)° for the N1/C1–C5 plane and 77.5 (2)° for the N2/C7–C11 plane. These values compare with values of 55.8° and 62.0° reported for *cis*-Pt^{II}Cl$_2$(pyridine)$_2$ (Colamarino & Orioli, 1975; s.u.'s are not reported), the value of 54 (3)° reported for *cis*-Pt^{II}Cl$_2$(4-vinylpyridine)$_2$ (Kubiak & Kuduk-Jaworska, 1986), the values of 58.2 and 48.8° reported for *cis*-Pt^{II}Cl$_2$(3-ferrocenylpyridine)$_2$ (Carugo *et al.*, 1992; s.u. values are not reported), and the values of 70.5 (2) and 85.9 (2)° reported for *cis*-Pt^{II}Cl$_2$(2-pmpe)$_2$ (2-pmpe = 2-pyridylmethylphosphonate) (Checińska *et al.*, 2003).
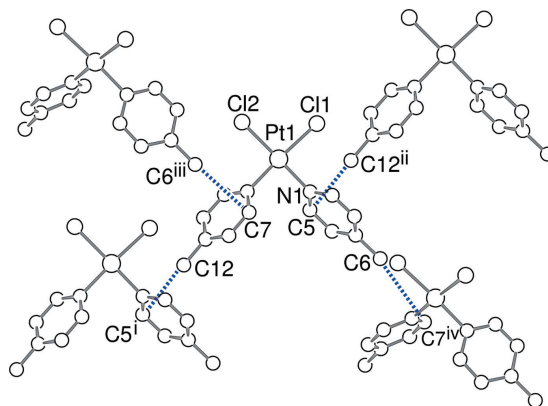

Figure 4
A view showing the intermolecular C—H···π interactions between the 4-methylpyridine ligands (dashed lines), indicating the closest non-bonded C···C distances. Atoms have been drawn as spheres and H atoms have been omitted for clarity. [Symmetry codes: (i) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (ii) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.]

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 C$_{12}$H$_{14}$Cl$_2$N$_2$Pt$_2$: C 31.87, H 3.12, N 6.19%; found: C 31.67, H 3.08, N 6.22%.

Crystal data

[PtCl$_2$(C$_6$H$_7$N)$_2$]	$Z = 8$
$M_r = 452.24$	$D_x = 2.141$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 14.105$ (4) Å	$\mu = 10.36$ mm^{-1}
$b = 12.530$ (3) Å	$T = 113$ (2) K
$c = 16.644$ (4) Å	Prism, colorless
$\beta = 107.429$ (2)°	$0.38 \times 0.23 \times 0.13$ mm
$V = 2806.5$ (12) Å^3	

Data collection

Rigaku Mercury CCD-detector diffractometer	10554 measured reflections
ω scans	3135 independent reflections
	2822 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (*NUMABS*; Higashi, 1999)	$R_{int} = 0.063$
$T_{min} = 0.090$, $T_{max} = 0.271$	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.087$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.16$	$\Delta\rho_{max} = 3.49$ e Å^{-3}
3135 reflections	$\Delta\rho_{min} = -1.82$ e Å^{-3}
157 parameters	Extinction correction: *SHELXL97*
H-atom parameters constrained	Extinction coefficient: 0.00037 (7)

Table 1
Selected geometric parameters (Å, °).

Pt1—N2	2.005 (4)	Pt1—Cl1	2.2993 (13)
Pt1—N1	2.017 (5)	Pt1—Cl2	2.3023 (16)
Pt1···Cl1^i	4.1394 (15)	C5···C12^{iii}	3.405 (7)
Pt1···Pt1^i	4.6508 (9)	C7···C6^{iv}	3.474 (8)
Pt1···H11^{ii}	2.8554		
N2—Pt1—N1	88.24 (18)	N2—Pt1—Cl2	91.01 (13)
N2—Pt1—Cl1	175.95 (12)	N1—Pt1—Cl2	176.43 (12)
N1—Pt1—Cl1	88.73 (14)	Cl1—Pt1—Cl2	92.18 (5)

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

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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