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Two-Dimensional Stacking of Dichloro(dipyridophenazine)platinum(II)

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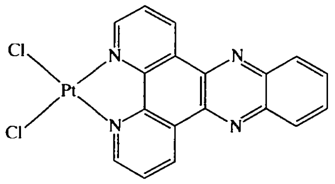
Abstract

A novel platinum(II) complex, dichloro(dipyrido[3,2-*a*:2′,3′-*c*]phenazine-N^4,N^5)platinum(II), [$PtCl_2(C_{18}H_{10}N_4)$], forms a two-dimensional stacking structure which is constructed with both platinum–platinum and ligand π–π interactions in the crystal.

Comment

Platinum complexes with α-diimines display characteristic emission properties which arise from various intermolecular interactions such as metal–metal and ligand π–π interactions (Houlding & Miskowski, 1991; Kato *et al.*, 1996). They are also of interest as building blocks for new network systems with a view to charge transport or electrical conductivity. We report here a novel platinum(II) complex containing dipyridophenazine (dppz), namely, [$PtCl_2$(dppz)], (I), which forms a unique two-dimensional stacking structure constructed with platinum–platinum and ligand π–π interactions in the crystal.



(I)

The dppz ligand has been one of the most attractive ligands since [$Ru(bpy)_2(dppz)]^{2+}$ (bpy is 2,2′-bipyridine) was found to be a good luminescence probe for DNA (Friedman *et al.*, 1990). The emission properties of the ruthenium complex are very sensitive to the environment because of the π–π and hydrogen-bonding interactions of dppz (Amouyal *et al.*, 1990; Chambron & Sauvage, 1991; Sabatani *et al.*, 1996). Thus, similar interesting intermolecular interactions are expected for the platinum complexes with square-planar geometry.

The [$PtCl_2$(dppz)] complex has planar geometry although it does not have any crystallographic symmetry (Fig. 1). Deviations of all atoms in the complex from the mean plane defined by platinum and its four coordination atoms are within 0.1 Å. In the crystal, the platinum complexes are stacked in an antiparallel arrangement, but slipped laterally to make a two-dimensional (2D) layer (Fig. 2). This layer consists of zigzag chains of Pt atoms with alternating Pt···Pt distances [3.4765 (7) and 4.2854 (7) Å] and infinite π-stacks of phenazine moieties [interplanar spacings of 3.44 (1) and 3.45 (1) Å]. The 2D layer seems to be formed as a result of the two competing intermolecular interactions. It was initially obtained using dppz with a π-system extended toward the opposite side of the coordinating N atoms. Furthermore, it is noteworthy that weak C—H···N hydrogen bonds exist between the phenazine sites of the adjacent 2D layers, forming channels between the layers [N4···C16^i 3.48 (1), N4···H9^i 2.90 Å and N4···H9^i—

$C16^i$ 119°; symmetry code: (i) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$]. The orientation of the complexes in the 2D layer is tilted by about 30° with respect to that in the adjacent layers. The $[PtCl_2(dppz)]$ crystal exhibits no observable emission, although a structured $^3\pi\pi^*$ emission spectrum was obtained in a glassy solution (EtOH:MeOH 4:1 *v*/*v*) at 77 K (λ_{max} = 546 nm). No emission from the crystal, contrary to what is observed in other platinum–diimine complexes with Pt···Pt interactions, could be attributed to fast non-radiative decay of the excited states based on intermolecular interactions among the dppz ligands.

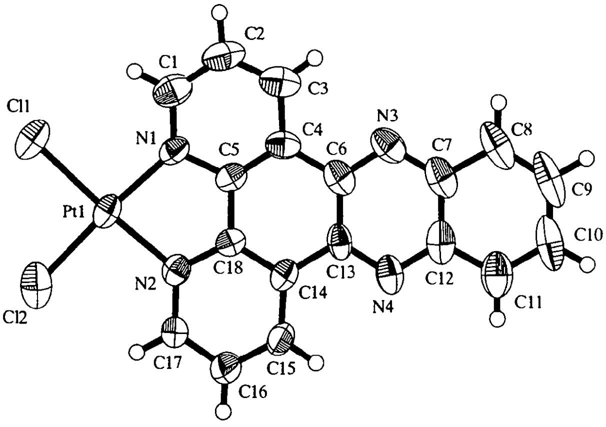


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

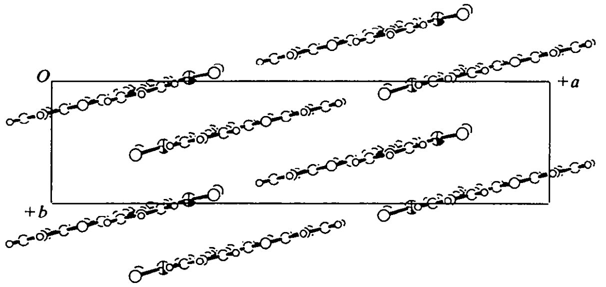


Fig. 2. The two-dimensional stacking of $[PtCl_2(dppz)]$. The shaded octants denote Pt atoms.

Experimental

The yellow crystalline deposit of $[PtCl_2(dppz)]$ was obtained by the reaction of $K_2[PtCl_4]$ in acidic water with dppz in methanol (molar ratio 1:1). Recrystallization from *N*,*N*-dimethylformamide gave dark-orange needle crystals.

Crystal data

$[PtCl_2(C_{18}H_{10}N_4)]$
$M_r = 548.30$
Monoclinic
$C2/c$
$a = 29.357\,(4)$ Å
$b = 7.096\,(6)$ Å
$c = 20.201\,(4)$ Å
$\beta = 128.472\,(8)°$
$V = 3294\,(2)$ Å^3
$Z = 8$
$D_x = 2.211$ Mg m^{-3}
$D_m = 2.205$ Mg m^{-3}
D_m measured by flotation in dibromomethane–benzene

Mo *Kα* radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 13.8–14.7°$
$\mu = 8.850$ mm^{-1}
$T = 293.2$ K
Prismatic
0.38 × 0.23 × 0.14 mm
Dark orange

Data collection

Rigaku AFC-7*R* diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.27$, $T_{max} = 0.29$
4170 measured reflections
4088 independent reflections

3782 reflections with $I > 0$
$R_{int} = 0.021$
$\theta_{max} = 27.51°$
$h = -38 \rightarrow 0$
$k = 0 \rightarrow 9$
$l = -20 \rightarrow 26$
3 standard reflections every 150 reflections intensity decay: 2.5%

Refinement

Refinement on F^2
$R(F) = 0.076$
$wR(F^2) = 0.103$
$S = 1.176$
3782 reflections
227 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.0009|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.0008$

$\Delta\rho_{max} = 2.92$ e Å^{-3}
$\Delta\rho_{min} = -2.48$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: 0.00026 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pt1—Cl1	2.291 (2)	Pt1—N1	2.011 (7)
Pt1—Cl2	2.267 (3)	Pt1—N2	2.013 (7)
Cl1—Pt1—Cl2	89.5 (1)	Cl2—Pt1—N1	175.8 (2)
Cl1—Pt1—N1	94.7 (2)	Cl2—Pt1—N2	94.3 (2)
Cl1—Pt1—N2	176.1 (2)	N1—Pt1—N2	81.5 (3)

H atoms were placed at calculated positions with a C—H distance of 0.95 Å and $U(H) = 1.2U_{eq}(C)$. In the final difference Fourier map, small peaks of 2.92 and 2.00 e Å^{-3} were found to remain close to the Pt1 atom (0.85 and 0.80 Å, respectively).

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku Corporation, 1995). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *MITHRIL90* (Gilmore, 1990). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1194). Services for accessing these data are described at the back of the journal.

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{2-[(2-Hydroxy-5-methylphenyl)iminomethyl]-4,6-dinitrophenolato(2–)-*O*,*N*,*O*′}-tris(3-methylpyridine-*N*)nickel(II)

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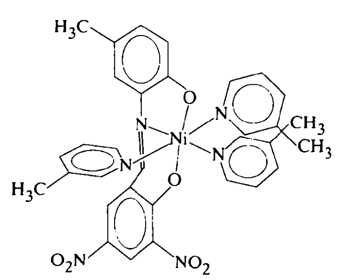
Abstract

In the title compound, $[Ni(C_{14}H_9N_3O_6)(C_6H_7N)_3]$, the coordination polyhedron around the Ni^{II} atom is a slightly distorted octahedron, with one N atom of the tridentate ligand and three N atoms of three monodentate ligands forming the equatorial plane. The apical positions are occupied by the two phenolic O atoms of the tridentate ligand. The Ni—O distances are 2.013 (2) and 2.008 (2) Å, and the Ni—N distances range from 2.043 (2) to 2.168 (3) Å. The *cis* bond angles at Ni^{II} range from 82.75 (9) to 96.2 (1)°. There are intramolecular, as well as intermolecular, hydrogen bonds in the structure.

Comment

The behaviour of tridentate ONO or ONS Schiff base ligands in the presence of monodentate ligands has been studied previously with four-coordinate nickel(II). In such complexes, the coordination of nickel is square planar or distorted square planar (Atakol *et al.*, 1996; Ülkü *et al.*, 1996; Tahir *et al.*, 1996; Ercan *et al.*, 1996). The title complex, (I), was studied to determine the effect on coordination when the tridentate ligand has nitro substituents.



(I)

As can be seen from Fig. 1, if a nitro-substituted tridentate Schiff base ligand is present in the reaction, the coordination around Ni^{II} becomes sixfold. We attribute this to the inductive effects of the nitro groups, whereby the ability of the tridentate ligands to donate electron density through their O and N atoms is reduced; the increase in the coordination number of the Ni^{II} centre offsets this potential electron deficit. The equatorial plane of the slightly distorted octahedral environment around Ni^{II} involves the coordination of one N atom of the tridentate 2-[(2-hydroxy-5-methylphenyl)iminomethyl]-4,6-dinitrophenolate ligand and three N atoms of three monodentate 3-methylpyridine ligands. The two phenolic O atoms of the tridentate ligand occupy the apical positions. The equatorial plane is defined by atoms N3, N4, N5 and N6 [maximum deviation 0.045 (2) Å], and Ni^{II} is located only 0.0022 (4) Å from this plane. The Ni—O bond lengths are practically equal [2.008 (2) and 2.013 (2) Å]. The Ni—N distances in the equatorial plane range from 2.043 (2) to 2.168 (3) Å. Among the *cis* bond angles, O6—Ni—N3 [82.75 (9)°] has the greatest deviation from 90°.

A comparison of the Ni—N and Ni—O bond lengths of the title complex with those of a nickel complex of 3,5-dinitrosalicylaldehyde [Ni—N 2.059 (2)–2.084 (3) and Ni—O 2.072 (2) Å; Tahir *et al.*, 1997] shows that they have similar values.

The dihedral angle between the planes of the two chelating moieties (O1, C1, C6, C7, N3 and N3, C8,

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