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Dichloro[6,7-dimethyl-2,3-bis(2-pyridyl-*N*)-quinoxaline]palladium(II) Monohydrate

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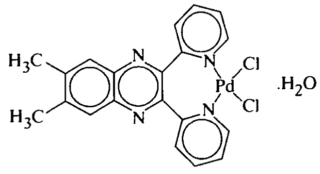
Abstract

The title compound, $[PdCl_2(C_{20}H_{16}N_4)].H_2O$, contains the first example of 6,7-dimethyl-2,3-bis(2-pyridyl)-quinoxaline chelating a square-planar-coordinated metal *via* its pyridine N atoms. In the solid state, pairs of centrosymmetrically-related molecules form a 'head-to-tail' arrangement, with a significant graphitic interaction between the parallel aromatic rings. The layers formed by these pairs are interconnected by Cl···H—C bonds. Molecules of water of crystallization are interposed between these layers.

Comment

We are interested in the synthesis of square-planar complexes having aromatic ligands containing N-donor atoms for study as potential DNA intercalators (Cusumano *et al.*, 1996; Cusumano & Giannetto, 1997). In this context, we have begun the synthesis of a series of platinum(II) and palladium(II) complexes of 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline (DMeDPQ); this ligand is known to bind metal ions either through one pyrazine N and one pyridine N atom, forming a five-membered ring, or through both pyridine N atoms, disposed in a *cis* conformation to form a seven-membered ring. Several structures showing this type of coordination with DMeDPQ or related ligands have been described (Rillema *et al.*, 1987; Escuer *et al.*, 1989, 1991; Bandoli *et al.*, 1994; Goodwin *et al.*, 1990; Gordon *et al.*, 1996), however, as far as we know, no square-planar complexes of this ligand have been reported. We now describe the crystal structure of $[Pd(DMeDPQ)Cl_2].H_2O$, (I).



(I)

The crystal packing is characterized mainly by the presence of discrete pairs of complex molecules related by inversion centres. These two centrosymmetric molecules show a 'head-to-tail' arrangement with a parallel-ligand-plane disposition that allows overlap of the aromatic rings at a distance of 3.56 (1) Å, which indicates a significant graphitic interaction. The ring separation is slightly longer than the usual π–π (ligand–ligand) distance, probably as a result of hindrance between the two methyl substituents of one quinoxaline and the fused pyrazine ring of the paired molecule. Each pair of complex molecules is connected to neighbouring pairs by intermolecular hydrogen-bonding interactions between the coordinated Cl^- anions and pyridine H atoms: Cl1···HC1($1-x$, $1-y$, z) 2.802 (3) and Cl2···HC17($x-1$, y, z) 2.763 (3) Å. The hydrogen-bonded pairs form layers orthogonal to the crystallographic *b* axis; the co-crystallized water molecules (1:1 ratio with the complex) are located in cavities so as to constitute an intermediate aqueous layer between adjacent layers of the bimolecular units. The crystal packing is thus formed by alternate parallel layers of complex and water molecules.

Conjugation between the aromatic quinoxaline fragment, and the N1 and N4 pyridine rings seems slight in view of the N1—C5—C6—C13 and C6—C13—C14—N4 torsion angles [−57.1 (3) and 57.8 (3)°, respectively]. This typical butterfly arrangement, with a dihedral angle of 85.0 (1)° between the pyridine rings, allows the nitrogen lone pairs to be oriented out of the ligand plane towards the metal atom. This distortion might appear to be caused by coordination-geometry requirements, but it is also observed in the uncoordinated ligand (Wozniak, 1991). The steric requirements of the ligand bite may also be responsible for the significant deformations from planarity of the quinoxaline (Rasmussen *et al.*, 1990) and the enlargement of the pyridine substituent angles up to 130° (protonated free ligand; Wozniak *et al.*, 1994).

The pyridyl orientation causes the palladium coordination plane to be normal to the ligand mean plane, with a dihedral angle between them of 86.39 (3)°. The angles between the pyridine rings and the palladium coordination plane [63.26 (7) and 67.72 (5)°] may indicate possible interaction of the π orbitals of both rings with the

d_{xz}, d_{yz} and d_{xy} orbitals of the metal atom, as suggested by Albinati *et al.* (1987). The two Pd—Cl bond lengths are equivalent within experimental error and agree with comparable distances, as do the Pd—N bond lengths (*cf.* Horike *et al.*, 1975; Viossat *et al.*, 1993).

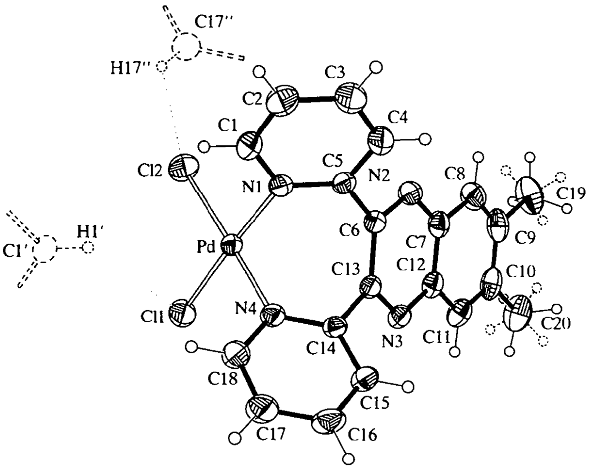


Fig. 1. A view of a molecule of the title compound showing the atomic numbering scheme with displacement ellipsoids drawn at the 50% probability level for non-H atoms. The disorder in the methyl groups is shown and intermolecular hydrogen-bond interactions with neighbouring fragments are indicated [symmetry operations: (') $1-x, 1-y, z$; ('') $x-1, y, z$].

Experimental

The title compound was obtained by reacting $K[Pd(dmso)Cl_3]$ (dmso is dimethylsulfoxide) with DMeDPQ in methanol (ratio 1:1). The reaction occurs as

$$[Pd(dmso)Cl_3]^- + \text{DMeDPQ} \longrightarrow [Pd(\text{DMeDPQ})Cl_2] + Cl^- + \text{DMSO}$$

and leads to the rapid formation of a white precipitate. Crystals suitable for X-ray analysis were obtained by slow evaporation from a water–methanol mixture. The complex $[Pt(bipy)(DMeDPQ)](PF_6)_2$ (bipy is bipyridyl) was obtained by an analogous synthesis using $[Pt(bipy)Cl_2]$. The crystal structure of this substance, which interacts non-covalently with DNA, will be described elsewhere (Bruno & Cusumano, 1998).

Crystal data

$[PdCl_2(C_{20}H_{16}N_4)].H_2O$
$M_r = 507.68$
Monoclinic
$P2_1/n$
$a = 9.7495 (9)$ Å
$b = 13.0024 (14)$ Å
$c = 16.358 (2)$ Å
$\beta = 94.096 (8)°$
$V = 2068.4 (4)$ Å^3
$Z = 4$
$D_x = 1.630$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 27 reflections
$\theta = 7.27–17.61°$
$\mu = 1.174$ mm^{-1}
$T = 293 (2)$ K
Irregular
0.25 × 0.23 × 0.10 mm
Orange

Data collection

Siemens $R3m/V$ diffractometer
ω scans
Absorption correction: ψ scan (Kopfmann & Huber, 1968)
$T_{min} = 0.535$, $T_{max} = 0.889$
5072 measured reflections
4781 independent reflections

3817 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 27.56°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 16$
$l = -21 \rightarrow 21$
3 standard reflections every 197 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.088$
$S = 1.050$
4781 reflections
254 parameters
H atoms: riding model with $U_{iso} = 0.050$ Å^2; water H atoms were not located
$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -1.00$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0028 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Pd—N4	2.010 (2)	C8—C9	1.370 (4)
Pd—N1	2.028 (2)	C9—C10	1.423 (5)
Pd—Cl1	2.2871 (7)	C9—C19	1.511 (4)
Pd—Cl2	2.2874 (8)	C10—C11	1.367 (4)
N1—C5	1.346 (3)	C10—C20	1.513 (4)
C5—C6	1.493 (3)	C11—C12	1.412 (4)
C6—N2	1.318 (3)	C12—N3	1.364 (3)
C6—C13	1.434 (3)	N3—C13	1.310 (3)
N2—C7	1.355 (3)	C13—C14	1.496 (3)
C7—C12	1.407 (4)	C14—N4	1.344 (3)
C7—C8	1.412 (4)		
N4—Pd—N1	86.99 (8)	N2—C6—C13	121.0 (2)
N4—Pd—Cl1	89.15 (6)	C13—C6—C5	124.0 (2)
N1—Pd—Cl1	176.13 (6)	C6—N2—C7	117.8 (2)
N4—Pd—Cl2	175.71 (6)	C13—N3—C12	117.5 (2)
N1—Pd—Cl2	91.29 (6)	N3—C13—C6	121.8 (2)
Cl1—Pd—Cl2	92.57 (3)	C6—C13—C14	123.5 (2)
C5—N1—Pd	121.4 (2)	N4—C14—C13	119.1 (2)
N1—C5—C6	119.6 (2)		
N1—C5—C6—C13	−57.1 (3)	C5—C6—C13—C14	−1.1 (4)
C5—C6—C13—N3	−176.7 (2)	C6—C13—C14—N4	57.8 (3)
N2—C6—C13—C14	173.2 (2)		

Reflection intensities were evaluated by profile fitting of a 96-step peak scan in shells of 2θ (Diamond, 1969). $\sigma(I)$ values were estimated from counting statistics. A semi-empirical absorption correction was applied using azimuthal-scan data for 22 reflections with $60 < \chi < 90°$ (Kopfmann & Huber, 1968). The correction, although characterized by a rather large T_{min}:T_{max} ratio of *ca* 0.6, gave a significant reduction of $R_{int}(F^2)$ from 0.064 to 0.027. H atoms were placed in idealized positions. Both the methyl groups showed rotational disorder which was treated by splitting the H-atom sites into two symmetrically-related groups, each with an occupancy of 0.5. All calculations were performed on a μ-VAX 3400 and on an AXP DecStation 3000/400.

Data collection: *P*3/*V* (Siemens, 1989). Cell refinement: *P*3/*V*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990*a*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*b*).

Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: locally-modified *PARST*95 (Nardelli, 1995) and *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1352). Services for accessing these data are described at the back of the journal.

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