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(Di-2-pyridylamine-κ^2N,N')(naphthalene-2,3-diolato-κ^2O,O')palladium(II) monohydrate and (di-2-pyridylamine-κ^2N,N')(3-oxidonaphthalene-2-carboxylato-κ^2O,O')palladium(II)

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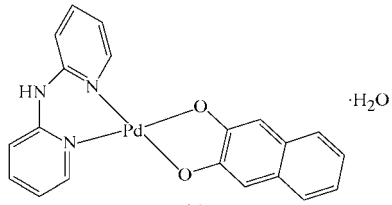
In the title complexes, $[Pd(C_{10}H_6O_2)(C_{10}H_9N_3)]\cdot H_2O$, (I), and $[Pd(C_{11}H_6O_3)(C_{10}H_9N_3)]$, (II), the Pd^{II} centers have a distorted *cis*-square-planar geometry. In (I), the Pd^{II} atom is coordinated to two N atoms of the di-2-pyridylamine (DPA) ligand and two O atoms of the naphthalene-2,3-diolate (ND) dianion. In (II), the Pd^{II} atom is coordinated to two N atoms of the DPA ligand, one carboxylate O atom and one oxide O atom from the 3-oxidonaphthalene-2-carboxylate (NC) ligand. The dihedral angle between the planes of the two pyridine rings of DPA in (I) is 16.20 (12)° and that in (II) is 29.45 (10)°. In (I), the molecules are linked by N—H···O and O—H···O hydrogen bonds to generate centrosymmetric dimers. In (II), molecules are linked by N—H···O and C—H···O hydrogen bonds to generate spirals.

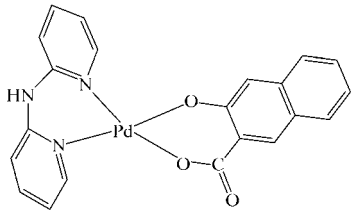
Comment

Di-2-pyridylamine (DPA) is an aromatic amine similar to bipyridine. DPA has three possible conformations when coordinating to metal centers, *viz*. *trans–trans*, *cis–trans* and *cis–cis*, in which the orientations of the pyridyl N atoms, respectively, are opposite, the reverse of one another and on the same side relative to the orientation of the N—H bond at the central linking N atom (Du *et al.*, 2003). The two pyridine rings of the DPA molecule are bridged by the NH group; the molecule is flexible and the two rings can adopt either coplanar or non-planar conformations in the coordination to the metal centers (Bolm *et al.*, 2004; Youngme *et al.*, 2003; Du *et al.*, 2003; Romeo *et al.*, 1998).

Many Pt^{II} and Pd^{II} complexes with various kinds of ligands have been widely studied in relation to their cytotoxic activity, because they are usually isostructural (Barnham *et al.*, 1995). Pt^{II} and Pd^{II} complexes of DPA bind to DNA and also have cytotoxic activity. The mode of binding between the complexes and DNA appears to be non-covalent groove binding or intercalation, and the NH group of DPA appears to play an important role for the interactions (Tu *et al.*, 2003; Paul *et al.*, 1993). DNA intercalation has been considered as an important mode of non-covalent interaction of heterocyclic compounds with DNA (Lerman, 1961), and the intercalation of homologous square-planar Pd^{II} and Pt^{II} complexes with bipyridine or biquinoline has been suggested (Cusumano & Giannetto, 1997). Although the molecular structures of a few Pt^{II} complexes of DPA have been reported (Romeo *et al.*, 1998; Paul *et al.*, 1993; Tu *et al.*, 2004), little is known about the Pd^{II} complex of DPA.



(I)



(II)

In this study, we have prepared two *cis*-coordinated ternary Pd^{II} complexes with DPA and other planar ligands, naphthalene-2,3-diolate (ND), $[Pd(DPA)(ND)]\cdot H_2O$, (I), and 3-oxidonaphthalene-2-carboxylate (NC), [Pd(DPA)(NC)], (II), and determined their structures. The present study is the first determination of the crystal structures of Pd^{II} complexes with DPA.

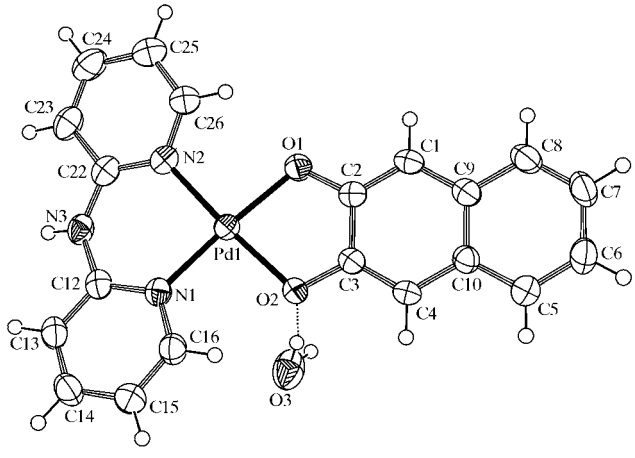


Figure 1
An *ORTEP-3* (Farrugia, 1997) drawing of (I), showing the atomic numbering scheme. Displacement ellipsoids for non-H atoms are shown at the 50% probability level.

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The structure of complex (I) is shown in Fig. 1 and selected geometric parameters are listed in Table 1. DPA adopts a *trans–trans* conformation. The coordination around the Pd^{II} ion is distorted *cis*-square-planar, and the Pd^{II} ion is coordinated by two N atoms from the bidentate DPA ligand and two O atoms from the bidentate ND ligand. In the square-planar coordination, atoms Pd1, O1, O2, N1 and N2 deviate by 0.0001 (2), 0.0242 (15), −0.0306 (16), 0.0332 (18) and −0.0407 (18) Å, respectively, from the mean plane through these five atoms. The Pd—O distances are slightly longer than the analogous ternary Pd^{II} complexes with the heterocyclic 2,2′-bipyridine (BPY) and NC ligands, *viz*. [Pd(BPY)(NC)] [1.981 (3)–1.984 (2) Å], or with biquinoline (BQ) and NC, *viz*. [Pd(BQ)(NC)] [1.982 (4)–1.992 (4) Å; Okabe *et al.*, 2004].

In the coordination environment of the Pd atom, the largest angular deviation is that for O1—Pd1—O2; the other angles around the Pd atom are similar. The dihedral angle between the two pyridyl rings of DPA is 16.20 (12)°, indicating that the two DPA pyridine rings are nearly coplanar. A six-membered chelate ring, Pd1/N1/C12/N3/C22/N2, and a five-membered ring, Pd1/O1/C2/C3/O2, are formed between the Pd^{II} ion and the DPA ligand, and between the Pd^{II} ion and the ND ligand, respectively. The six-membered chelate ring adopts a boat conformation in which atoms Pd1 and N3 are displaced by 0.304 (3) and 0.138 (3) Å, respectively, from the mean plane through atoms N1, N2, C12 and C22. The angles between the mean ND plane and the two pyridine rings containing atoms N1 and N2 are 11.57 (11) and 4.63 (12)°, respectively, indicating that the ND ligand is nearly coplanar with the DPA ligand.

The structure of complex (II) is shown in Fig. 2 and selected geometric parameters are listed in Table 3. The DPA molecule adopts a distorted *trans–trans* conformation. The Pd^{II} atom has distorted *cis*-square-planar coordination, and it is bonded to two N atoms of the DPA molecule, one naphthol O atom and one carboxylate O atom of the NC ligand. In the coordination environment around atom Pd1, the largest angular deviation is for N2—Pd1—O1. In the square-planar coordination, atoms Pd1, O1, O2, N1 and N2 deviate by −0.0257 (6), 0.0392 (8), −0.0245 (8), 0.0379 (8) and −0.0269 (9) Å, respectively, from the mean plane through these five atoms. The Pd ^{II}

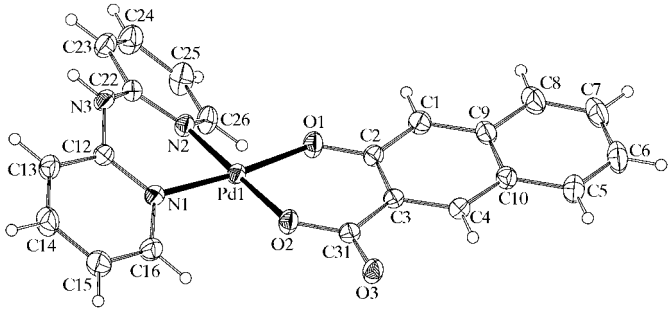

Figure 2
An *ORTEP-3* (Farrugia, 1997) drawing of (II), showing the atomic numbering scheme. Displacement ellipsoids for non-H atoms are shown at the 50% probability level.

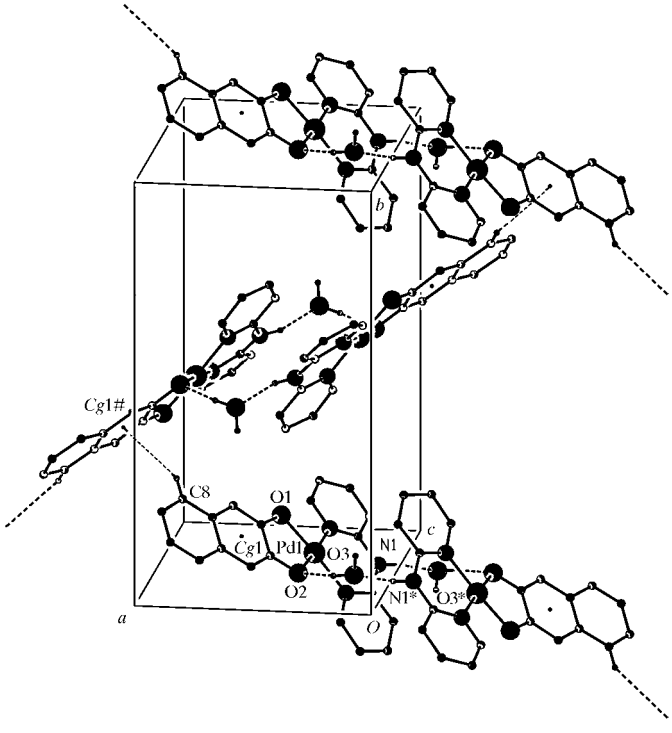

Figure 3
The packing of (I), showing centrosymmetric dimers and the weak C—H···π interactions (dashed lines). [Symmetry codes: (*) −*x*, −*y*, 1 − *z*; (#) $\frac{1}{2}+x, \frac{1}{2}-y, z$.]

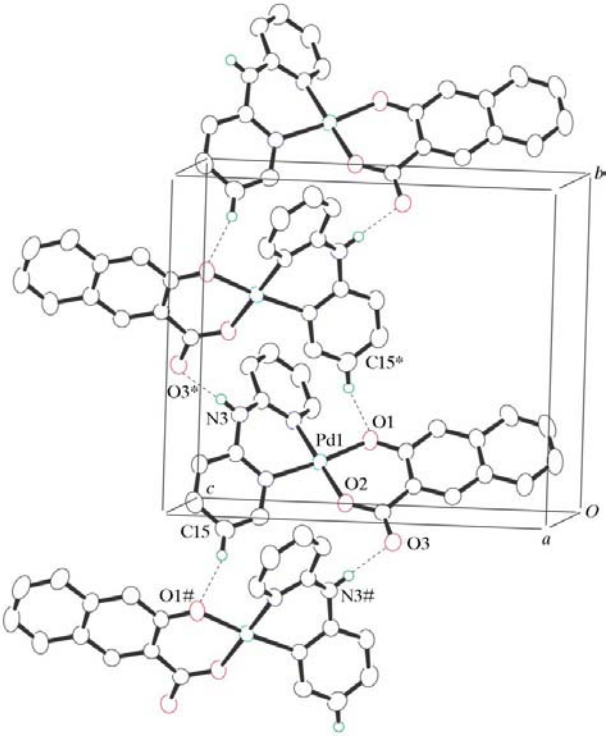

Figure 4
The packing of (II), with hydrogen bonds indicated by broken lines. [Symmetry codes: (*) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (#) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$.]

ion and DPA molecule form a six-membered chelate ring with a boat conformation, in which atoms Pd1 and N3 are displaced by 0.688 (3) and 0.268 (3) Å, respectively, from the mean plane through atoms N1, N2, C12 and C22. This boat deformation is larger than that in (I).

The two pyridine rings of the DPA ligand adopt a non-planar conformation, with a dihedral angle between the pyridine rings of 29.45 (10)°, significantly larger than that in (I). A similarly large distortion of the DPA group was also observed in $[Cu(DPA)_2(N_3)_2]$ [dihedral angle = 40.9 (2)°; Du *et al.*, 2003] and $[PtMe(DPA)(Me_2SO)]CF_3SO_3$ [dihedral angle = 46.4 (1)°].

The distorted conformation of the DPA ligand in (II) may be explained by intramolecular steric hindrance between the N2-containing pyridine ring of the DPA ligand and the NC ligand, because the NC ligand with different substituents at the 2- and 3-positions is near the N2-containing pyridine ring by coordinating to the Pd^{II} atom. The O1···H26 and O2···H16 separations in (II) are 2.40 and 2.46 Å, respectively. These values are significantly longer than the corresponding values in (I) (O1—H26 = 2.23 Å and O2—H16 = 2.27 Å). These differences arise from the slightly different conformations of the DPA ligands in (I) and (II), which are presumably a direct result of the different modes of N—H···O hydrogen bonding and packing in (I) and (II).

In the crystal structure of (I), centrosymmetric dimers are formed by N—H···O and O—H···O intermolecular hydrogen bonds (Table 2 and Fig. 3). Between the dimers there is a further weak C—H···π interaction involving the C8—H8 group and the centroid, *viz*. *Cg*1#, of the C1–C4/C9/C10 ring [at $(\frac{1}{2}+x, \frac{1}{2}-y, z)$] with a H8···*Cg*1# distance of 2.86 Å and a C8—H8···*Cg*1# angle of 136°. This interaction leads to the formation of sheets in the [100] plane. The crystal structure of (II) is also stabilized by an N—H···O hydrogen bond, which with an associated C—H···O hydrogen bond generates spirals by the operation of a 2_1 screw axis along the *b* direction (Fig. 4 and Table 4).

Experimental

Red prismatic crystals of (I) were obtained by slow evaporation of a dimethylformamide solution of a mixture of 2,3-naphthalenediol, di-2-pyridylamine and $Pd(CH_3COO)_2$ (molar ratio 1:1:1) at room temperature. Yellow needle-shaped crystals of (II) were obtained by slow evaporation of a dimethylformamide solution of a mixture of 3-hydroxynaphthalene-2-carboxylic acid, di-2-pyridylamine and $Pd(CH_3COO)_2$ (molar ratio 1:1:1) at room temperature.

Compound (I)

Crystal data

$[Pd(C_{10}H_6O_2)(C_{10}H_9N_3)]\cdot H_2O$
M_r = 453.77
Monoclinic, $P2_1/a$
a = 9.202 (9) Å
b = 17.136 (16) Å
c = 11.087 (9) Å
β = 92.53 (3)°
V = 1747 (3) Å^3
Z = 4
D_x = 1.726 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15 210 reflections
θ = 3.0–27.5°
μ = 1.09 mm^{-1}
T = 296.1 K
Prism, red
0.20 × 0.10 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.792, T_{max} = 0.947
16 994 measured reflections
3988 independent reflections
3516 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 27.5°
$h = -11 \rightarrow 11$
$k = -22 \rightarrow 22$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.054
S = 1.05
3988 reflections
245 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 0.2332P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

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

Pd1—O1	1.9885 (18)	Pd1—N1	2.010 (2)
Pd1—O2	2.0030 (19)	Pd1—N2	2.019 (2)
O1—Pd1—O2	83.66 (5)	O1—Pd1—N2	92.21 (6)
O1—Pd1—N1	175.67 (5)	O2—Pd1—N2	175.38 (5)
O2—Pd1—N1	92.35 (6)	N1—Pd1—N2	91.83 (7)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O3^{i}	0.86	2.01	2.845 (4)	163
O3—H31···O2	0.91	1.83	2.726 (3)	165

Symmetry code: (i) $-x, -y, 1-z$.

Compound (II)

Crystal data

$[Pd(C_{11}H_6O_3)(C_{10}H_9N_3)]$
M_r = 463.76
Monoclinic, $P2_1/n$
a = 12.168 (9) Å
b = 11.500 (10) Å
c = 13.195 (8) Å
β = 94.94 (3)°
V = 1840 (2) Å^3
Z = 4
D_x = 1.675 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13 283 reflections
θ = 3.1–27.5°
μ = 1.04 mm^{-1}
T = 296.1 K
Needle, yellow
0.20 × 0.20 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.808, T_{max} = 0.901
18 070 measured reflections
4149 independent reflections
3016 reflections with $I > 2\sigma(I)$
θ_{max} = 27.5°
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.049
S = 0.90
4149 reflections
253 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Pd1—O1	1.9600 (16)	Pd1—N2	2.0084 (19)
Pd1—O2	1.9938 (17)	Pd1—N1	2.0165 (19)
O1—Pd1—O2	92.95 (7)	O1—Pd1—N1	174.61 (6)
O1—Pd1—N2	86.80 (8)	O2—Pd1—N1	90.96 (7)
O2—Pd1—N2	179.75 (6)	N2—Pd1—N1	89.29 (8)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O3^{i}	0.86	2.01	2.783 (2)	149
C15—H15···O1^{ii}	0.93	2.50	3.371 (4)	157

Symmetry codes: (i) $\frac{1}{2}-x,\frac{1}{2}+y,\frac{3}{2}-z$; (ii) $\frac{1}{2}-x,y-\frac{1}{2},\frac{3}{2}-z$.

All H atoms, including water H atoms, were located from difference Fourier maps and were then treated as riding, with C—H distances of 0.93 Å, N—H distances of 0.86 Å and O—H distances of 0.90 and 0.91 Å, and with U_{iso}(H) values of $1.2U_{eq}$(C,N,O). The weighting scheme was optimized.

For both compounds, data collection: *RAPID-AUTO* (Rigaku, 2003); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004) and *CRYSTALS* (Watkin *et al.*, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999) and *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1798). Services for accessing these data are described at the back of the journal.

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