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(2,2′-Bipyridine-κ^2N,N')(2,3-naphthalenediolato-κ^2O,O')palladium(II) and (2,2′-biquinoline-κ^2N,N')(2,3-naphthalenediolato-κ^2O,O')palladium(II)

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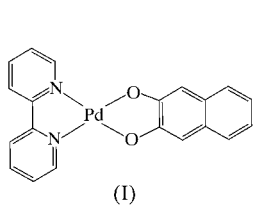
In the title compounds, $[Pd(C_{10}H_6O_2)(C_{10}H_8N_2)]$, (I), and $[Pd(C_{10}H_6O_2)(C_{18}H_{12}N_2)]$, (II), each Pd^{II} atom has a similar distorted *cis*-planar four-coordination geometry involving two O atoms of the 2,3-naphthalenediolate dianion and two N atoms of the 2,2′-bipyridine or 2,2′-biquinoline ligand. The overall structure of (I) is essentially planar, but that of (II) is not, as a result of intramolecular overcrowding leading to bowing of the biquinoline ligand.

Comment

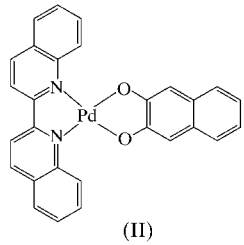
Recently, the palladium complex [Pd(bpy)(cbdca)] (bpy is 2,2′-bipyridine and cbdca is the 1,1-cyclobutanedicarboxylate ligand), with a *cis*-square-planar coordination geometry, has been shown to have better cytotoxic activity than cisplatin [*cis*-diamminedichloroplatinum(II)] against P_{388} lymphocytic leukemia cells (Mansuri-Torshizi *et al.*, 2001). The planar aromatic ligands interact with DNA, which is the principal target in the chemotherapy of tumors (Neidle *et al.*, 1987; Cusumano & Giannetto, 1997; Shehata, 2001).

In the present study, we have prepared two *cis*-coordinated ternary complexes of Pd^{II}, namely the title complexes [Pd(bpy)(nad)], (I), and [Pd(biq)(nad)], (II), with the aromatic ligands bpy, 2,2′-biquinoline (biq) and 2,3-naphthalenediol (nad), and determined their structures. The same complexes were synthesized previously by a different method for electrochemical studies into their use as photosensitizers in inorganic photochemistry (Kamath *et al.*, 1989). Structures have been determined for complexes of nad with Si (Holmes *et al.*, 1985; Strohmann *et al.*, 1991; Tacke *et al.*, 1991, 1993; Sperlich *et al.*, 1993), Fe (Jüstel *et al.*, 1999), Ge (Tacke *et al.*, 1994), Rb (Yang *et al.*, 1997), Mo (Mondal *et al.*, 1988; El-Hendawy *et al.*, 1989; Kang *et al.*, 1989) and Sb (Holmes *et al.*, 1987). The present study is the first determination of the crystal structures of Pd complexes with nad.

The central Pd atoms of (I) and (II) have the same distorted *cis*-square-planar coordination geometry, involving the two heterocyclic N atoms and the two O atoms of the nad dianion (Figs. 1 and 2). The overall structure of (I) is essentially planar, with atom C14 of the bpy ligand showing the maximum deviation from the mean molecular plane [0.085 (3) Å].



(I)



(II)

In contrast, the overall structure of (II) is not planar; the dihedral angle between the biq and Pd(nad) planes is 148.73 (7)°. In the square-planar coordination, atoms Pd1, N1, N2, O1 and O2 deviate by 0.0055 (1), −0.135 (3), −0.073 (3), −0.093 (3) and −0.167 (3) Å, respectively, from the plane through these five atoms. The Pd(nad) moiety, including the square-planar coordination plane, is mostly planar, the maximum deviation from the plane being that of atom C26 [0.139 (7) Å]. The biq molecule is bowed in order to relieve intramolecular overcrowding between biq moieties (C9—H9 and C19—H19) and nad atoms (O1 and O2). The H9···O1 and H19···O2 separations are 2.23 and 2.28 Å, respectively. As a result, the angle between the two quinoline ring planes is 19.9 (1)°.

The Pd—O bond lengths in (I) and (II) are similar, but the Pd—N distances in (I) are slightly shorter than those in (II). The values can be compared with those reported for [Pd(NH$_3$)$_2$(cbdca)], (III) (Barnham *et al.*, 1994), [Pd(en)(cbdca)], (IV) (en is ethylenediamine; Tercero *et al.*, 2003), and [Pd(cat)(phen)], (V) (cat is cathecholate and phen is 1,10-phenanthroline; Okabe *et al.*, 2003), since the central Pd atoms

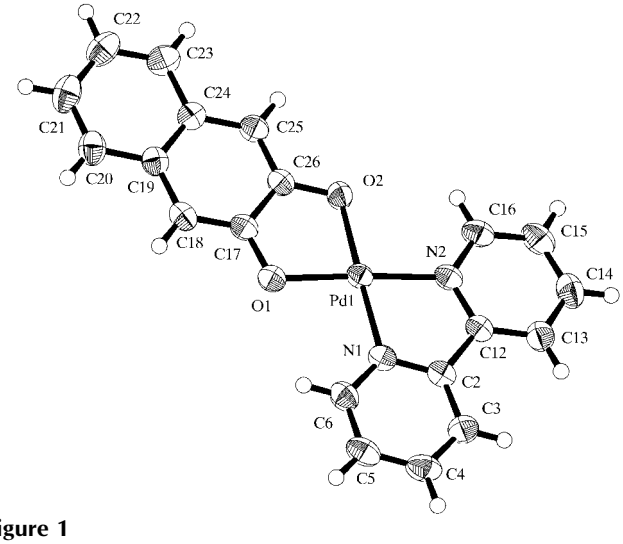


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are shown at the 50% probability level.

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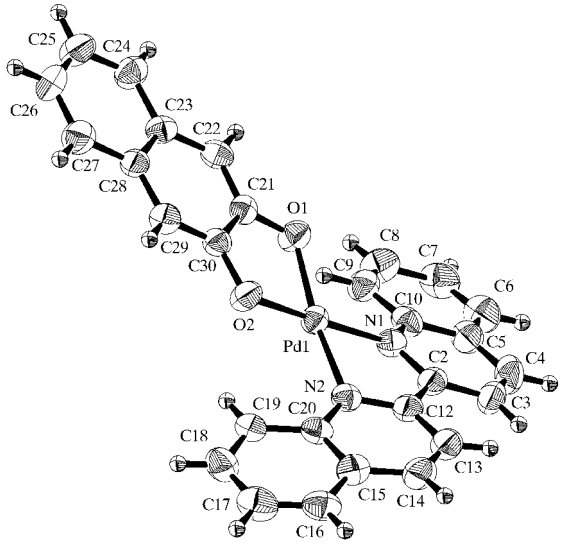

Figure 2
The molecular structure of (II), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are shown at the 50% probability level.

of all of these compounds have the same distorted *cis*-square-planar coordination geometry, with the formula [Pd(NN)-(OO)]. The Pd—N bonds in (I) are slightly shorter than those in (III) and (IV) [2.020 (7)–2.030 (2) Å], and are nearly the same as those in (V) [2.003 (2)–2.019 (2) Å]. The Pd—N distances in (II) are slightly longer than those in (III)–(V). The Pd—O bond lengths in (I) and (II) are also slightly shorter than those in (III) and (IV) [2.005 (2)–2.017 (6) Å], and nearly the same as those in (V) [1.981 (2)–1.989 (2) Å]. It thus appears that the coordination bonds in (I) are stronger than those in (III) and (IV), and nearly identical to those in (V). The Pd—N bonds in (II) are the weakest of all, possibly as a result of intramolecular steric hindrance between the O atoms of the nad molecule and the H atoms attached to atoms C9 and C19 of the biq molecule, as noted above.

The O—Pd—O angles in the five-membered rings in (I) and (II) are small compared with those in the six-membered rings of (III) and (IV) [90.9–92.69 (7)°], and are slightly smaller than that reported for the five-membered ring in (V) [85.09 (7)°]. The N—Pd—N angles in (I) and (II) are also smaller than those in (IV) [84.15 (8)° for en] and (III) (95.0° for NH_3PdNH_3), and slightly smaller than that in (V) [81.69 (8)° for cat].

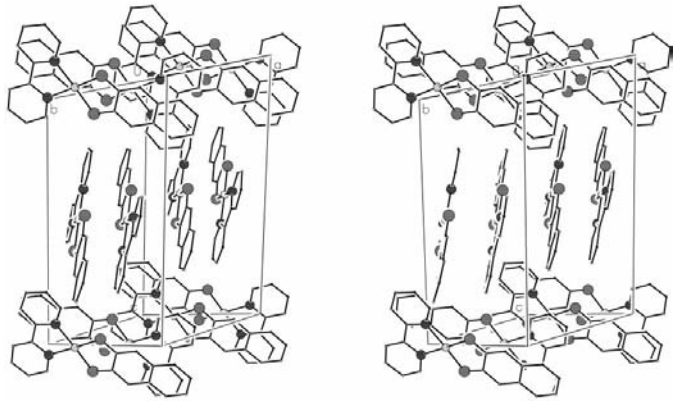

Figure 3
A stereoview of the packing in (I), showing the ring interactions.

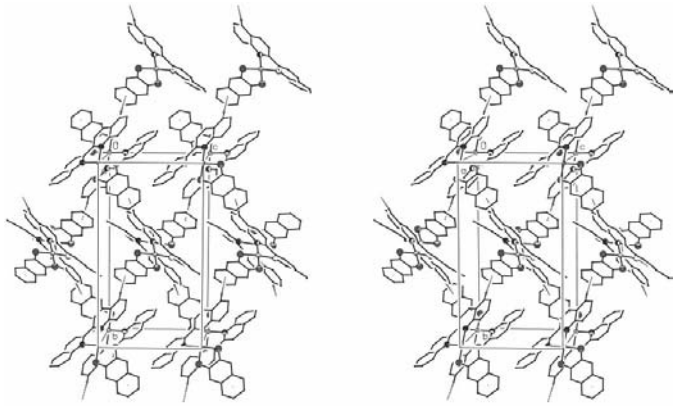

Figure 4
A stereoview of the packing of (II), showing the ring and C—H$\cdots\pi$ interactions

The crystal structure of (I) is stabilized by centrosymmetric stacking interactions between molecules at $(1-x, -y, 1-z)$, (x, y, z), $(1-x, 1-y, 1-z)$, $(x, 1+y, z)$ *etc.*, as shown in Fig. 3, the shortest separations being Pd1$\cdots$C26$(1-x, 1-y, 1-z)$ of 3.391 (2) Å and Pd1$\cdots$C12$(1-x, -y, 1-z)$ of 3.414 (2) Å. The crystal structure of (II) exhibits interactions between inversion-related molecules, as shown in Fig. 4, the shortest separations being Pd1$\cdots$C3$(1-x, -y, 1-z)$ of 3.219 (6) Å and Pd1$\cdots$C30$(2-x, -y, 1-z)$ of 3.449 (5) Å. These stacks are then connected by C—H$\cdots\pi$(arene) interactions [H6$\cdots$*Cg*1 = 2.50 Å, C6$\cdots$*Cg*1 = 3.43 Å and C6—H6$\cdots$*Cg*1 = 176°; *Cg*1 is the centroid of the C23–C28 ring at $(\frac{3}{2}-x, -\frac{1}{2}+y, \frac{5}{2}-z)$].

Experimental

For the preparation of (I), bpy was reacted with palladium acetate, $[Pd(CH_3COOH)_2]$, for 30 min at room temperature (molar ratio 2:3) in dimethylformamide (DMF), and then nad (equivalent to bpy) dissolved in DMF was added. This mixture was left to stand at room temperature, and red plate-shaped crystals appeared after a few days. Complex (II) was synthesized by a similar method, except that biq was used instead of bpy. Colorless prismatic crystals appeared after a few days.

Compound (I)

Crystal data

$[Pd(C_{10}H_6O_2)(C_{10}H_8N_2)]$
M_r = 420.75
Monoclinic, $P2_1/c$
a = 12.117 (2) Å
b = 8.239 (2) Å
c = 16.857 (1) Å
β = 108.804 (8)°
V = 1593.1 (5) Å^3
Z = 4
D_x = 1.754 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 14.8–15.0°
μ = 1.18 mm^{-1}
T = 296.2 K
Plate, red
0.50 × 0.20 × 0.20 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.936, T_{max} = 1.000
4095 measured reflections
3658 independent reflections
3090 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 27.5°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = -21 \rightarrow 20$
3 standard reflections
every 150 reflections
intensity decay: 1.1%

Refinement

Refinement on F^2
$R(F)$ = 0.027
$wR(F^2)$ = 0.078
S = 1.14
3658 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 0.8904P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.88 e Å^{-3}

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

Pd1—O1	1.981 (3)	Pd1—N1	2.003 (2)
Pd1—O2	1.984 (2)	Pd1—N2	2.001 (3)
O1—Pd1—O2	84.84 (9)	O2—Pd1—N1	177.58 (10)
O1—Pd1—N1	97.06 (9)	O2—Pd1—N2	97.29 (9)
O1—Pd1—N2	177.54 (9)	N1—Pd1—N2	80.78 (9)

Compound (II)

Crystal data

$[Pd(C_{10}H_6O_2)(C_{18}H_{12}N_2)]$
M_r = 520.86
Monoclinic, $P2_1/n$
a = 9.859 (5) Å
b = 19.67 (1) Å
c = 10.922 (5) Å
β = 94.33 (4)°
V = 2112.0 (18) Å^3
Z = 4
D_x = 1.638 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 18 reflections
θ = 10.6–13.2°
μ = 0.91 mm^{-1}
T = 296.2 K
Prism, colorless
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.917, T_{max} = 0.998
5278 measured reflections
4849 independent reflections
2647 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 27.5°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 25$
$l = -14 \rightarrow 14$
3 standard reflections
every 150 reflections
intensity decay: 0.2%

Refinement

Refinement on F^2
$R(F)$ = 0.044
$wR(F^2)$ = 0.135
S = 0.98
4849 reflections
298 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 e Å^{-3}

For (I) and (II), all H atoms were located from difference Fourier maps and then placed at idealized positions and treated as riding, with C—H distances of 0.93 Å and U_{iso}(H) values equal to 1.2U_{eq}(C).

For both compounds, data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999) for (I) and *SHELXS*97 (Sheldrick, 1997) for (II); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

Table 2
Selected geometric parameters (Å, °) for (II).

Pd1—O1	1.992 (4)	Pd1—N1	2.039 (4)
Pd1—O2	1.982 (4)	Pd1—N2	2.037 (4)
O1—Pd1—O2	83.6 (2)	O2—Pd1—N1	174.4 (2)
O1—Pd1—N1	98.4 (2)	O2—Pd1—N2	97.0 (2)
O1—Pd1—N2	171.1 (2)	N1—Pd1—N2	80.3 (2)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1730). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Barnham, K. J., Djuran, M. I., Frey, U., Mazid, M. A. & Sadler, P. J. (1994). *J. Chem. Soc. Chem. Commun.* pp. 65–66.

Cusumano, M. & Giannetto, A. (1997). *J. Inorg. Biochem.* **65**, 137–144.

El-Hendawy, A. M., Griffith, W. P., O'Mahoney, C. A. & Williams, D. J. (1989). *Polyhedron*, **8**, 519–525.

Holmes, R. R., Day, R. O., Chandrasekhar, V. & Holmes, J. M. (1985). *Inorg. Chem.* **24**, 2009–2015.

Holmes, R. R., Day, R. O., Chandrasekhar, V. & Holmes, J. M. (1987). *Inorg. Chem.* **26**, 157–163.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Jüstel, T., Müller, M., Weyhermüller, T., Kressl, C., Bill, E., Hildebrandt, P., Lengen, M., Grodzicki, M., Trautwein, A. X., Nuber, B. & Wieghardt, K. (1999). *Chem. Eur. J.* **5**, 793–810.

Kamath, S. S., Uma, V. & Srivastava, T. S. (1989). *Inorg. Chim. Acta*, **166**, 91–98.

Kang, H., Liu, S., Shaikh, S. N., Nicholson, T. & Zubieta, J. (1989). *Inorg. Chem.* **28**, 920–933.

Mansuri-Torshizi, H., Ghadimy, S. & Akbarzadeh, N. (2001). *Chem. Pharm. Bull.* **49**, 1517–1520.

Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (2000). *TEXSAN.* Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.

Mondal, J. U., Schultz, F. A., Brennan, T. D. & Scheidt, W. R. (1988). *Inorg. Chem.* **27**, 3950–3956.

Neidle, S., Pearl, L. & Skelly, J. V. (1987). *Biochem. J.* **243**, 1–13.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Okabe, N., Muranishi, Y. & Ajiyama, T. (2003). *Acta Cryst.* E**59**, m936–m938.

Shehata, M. (2001). *Transition Met. Chem.* **26**, 198–204.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Sperlich, J., Becht, J., Mühleisen, M., Wagner, S. A., Mattern, G. & Tacke, R. (1993). *Z. Naturforsch. Teil B*, **48**, 1693–1706.

Strohmann, C., Tacke, R., Mattern, G. & Kuhs, W. F. (1991). *J. Organomet. Chem.* **403**, 63–71.

Tacke, R., Lopez-Mras, A., Sheldrick, W. S. & Sebald, A. (1993). *Z. Anorg. Allg. Chem.* **619**, 347–358.

Tacke, R., Sperlich, J. & Becker, B. (1994). *Chem. Ber.* **127**, 643–646.

Tacke, R., Sperlich, J., Strohmann, C. & Mattern, G. (1991). *Chem. Ber.* **124**, 1491–1496.

Tercero, J. M., Matilla, A., Sanjuan, M. A., Moreno, C. F., Martin, J. D. & Walmsley, J. A. (2003). *Inorg. Chem. Acta*, **342**, 77–87.

Yang, K., Martin, J. A., Bott, S. G. & Richmond, M. G. (1997). *Inorg. Chim. Acta*, **254**, 19–27.