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(2,2′-Biquinoline-κ^2N,N')dichloropalladium(II), -copper(II) and -zinc(II)

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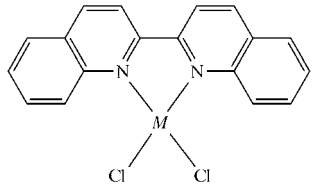
In the three title complexes, namely (2,2′-biquinoline-κ^2N,N')dichloropalladium(II), $[PdCl_2(C_{18}H_{12}N_2)]$, (I), and the corresponding copper(II), $[CuCl_2(C_{18}H_{12}N_2)]$, (II), and zinc(II) complexes, $[ZnCl_2(C_{18}H_{12}N_2)]$, (III), each metal atom is four-coordinate and bonded by two N atoms of a 2,2′-biquinoline molecule and two Cl atoms. The Pd^{II} atom has a distorted *cis*-square-planar coordination geometry, whereas the Cu^{II} and Zn^{II} atoms both have a distorted tetrahedral geometry. The dihedral angles between the N—*M*—N and Cl—*M*—Cl planes are 14.53 (13), 65.42 (15) and 85.19 (9)° for (I), (II) and (III), respectively. The structure of (II) has twofold imposed symmetry.

Comment

Pt^{II} complexes, such as *cis*-diamminedichloroplatinum(II) (cisplatin), *cis*-$[PtCl_2(NH_3)_2]$ (Rosenberg *et al.*, 1969), *cis*-diammine(1,1-cyclobutanedicarboxylato)platinum(II) (carboplatin), *cis*-$[Pt(C_6H_3O_4)(NH_3)_2]$, and (*trans*-*R*,*R*-cyclohexane-1,2-diamineoxalato)platinum(II) (oxaliplatin), $[Pt(C_2O_4)(C_6H_{12}N_2)]$ (Wong & Giadomenico, 1999), are well known as therapeutic anticancer drugs (Jakupec *et al.*, 2003). As a consequence of the similar coordination behaviour of Pd^{II} and Pt^{II}, Pd^{II} complexes have been treated as ideal models for studies of square-planar complexes (Rau & van Eldik, 1996), such as $[PdCl_2(en)]$ (en is ethylenediamine) and *cis*-$[PdCl_2(NH_3)_2]$, and much interest has been focused on the creation of new antitumour Pd^{II} complexes, such as $[Pd(asme)_2]$ (asme is an anionic form of the acetone Schiff base of *S*-methyl dithiocarbazate; Ali *et al.*, 2002) or [Pd(cbdca)(bpy)] (bpy is 2,2′-bipyridine and cbdca is 1,1-cyclobutanedicarboxylate; Mansuri-Torshizi *et al.*, 2001).

We have previously synthesized mixed-ligand Pd^{II} complexes of a *cis*-square-planar coordination geometry with N and O ligand atoms and have determined their structures, *e.g.* [Pd(bd)(phen)] (bd is 1,2-benzenediolate and phen is 1,10-phenanthroline; Okabe *et al.*, 2003), [Pd(nad)(bpy)] (nad is 2,3-naphthalenediolate and bpy is 2,2′-bipyridine), [Pd(nad)(biq)] (biq is 2,2′-biquinoline; Okabe *et al.*, 2004), or [Pd(cbdca)(bpy)] and [Pd(cbdca)(phen)] (Muranishi & Okabe, 2004). The complex of Pd^{II} with the heterocyclic *N*,*N*′-bidentate ligand biq, namely $[Pd(biq)(en)](ClO_4)_2$, shows antitumour activity (Cusumano & Giannetto, 1997).



(I) *M* = Pd
(II) *M* = Cu
(III) *M* = Zn

It is important to clarify whether the transition metals Cu^{II} and Zn^{II} have a *cis*-square-planar coordination geometry with the same ligands as the Pd^{II} or Pt^{II} complexes, since Cu^{II} and Zn^{II} are also able to have a square-planar [see, for example, Koman *et al.* (1998), Fun *et al.* (2002) and Liu *et al.* (2002) for Cu^{II}, and Wu (2004) and Dastidar & Goldberg (1996) for Zn^{II}] or tetrahedral coordination geometry [see, for example, Malkov *et al.* (2001), Małecka *et al.* (1998) and Dessy & Fares (1985) for Cu^{II}, and Zhu *et al.* (2002) and Halvorsen *et al.* (1995) for Zn^{II}]. Furthermore, Cu^{II} and Zn^{II} have both many important biological functions as cofactors in enzymes and antimicrobial activity as complexes (Okide *et al.*, 2000; Patel *et al.*, 1999).

In this study, the structures of Pd^{II}, Cu^{II} and Zn^{II} complexes with biq and Cl^- ligands have been characterized, *viz.* $[PdCl_2(biq)]$, (I), $[CuCl_2(biq)]$, (II), and $[ZnCl_2(biq)]$, (III), and these are shown in Figs. 1, 2 and 3, respectively. Selected coordination bond distances and angles are compared in Table 1. A search of the February 2005 release of the Cambridge Structural Database (Allen, 2002) for relevant MN_2Cl_2 complexes (error-free, non-disordered, $R < 0.05$) gave 94, 100 and 37 hits for *M* = Pd, Cu and Zn, respectively. Analysis with *VISTA* (Allen 2002) gave the following distance ranges and mean values (Å), respectively: Pd—N 2.000–2.114, 2.034; Pd—Cl 2.262–2.331, 2.994; Cu—N 1.948–2.106, 2.105;

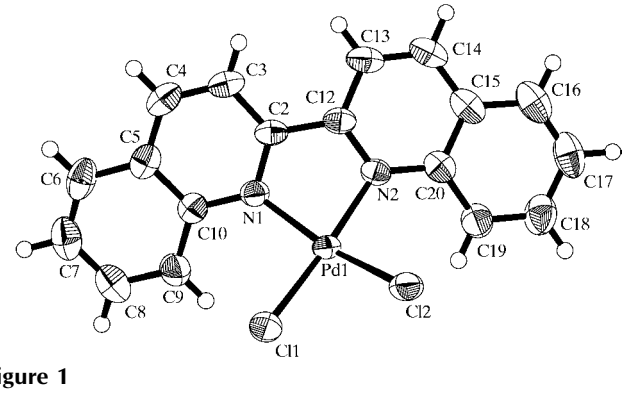


Figure 1
A view of the molecule of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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Cu—Cl 2.186–2.498, 2.286; Zn—N 2.009–2.138, 2.056; Zn—Cl 2.171–2.290, 2.217. The dimensions in Table 1 are entirely in accord with these known dimensions.

The coordination geometry around the central metal Pd^{II} atom of (I) is remarkably different from those in (II) and (III). In (I), the Pd^{II} atom has a distorted *cis*-square-planar coordination geometry, whereas in (II) and (III), the Cu^{II} and Zn^{II} atoms have a distorted tetrahedral geometry. The dihedral angles between the N—*M*—N and Cl—*M*—Cl planes are 14.53 (13), 65.42 (15) and 85.19 (9)° for (I), (II) and (III), respectively.

In (I), the overall structure is not planar. The Pd^{II} and two Cl atoms deviate from the mean plane formed through atoms N1/C2/C12/N2 in the same direction, by 0.810 (4) Å for Pd1, 1.739 (8) Å for Cl1 and 2.128 (7) Å for Cl2. As a result of this distortion, the five-membered ring (Pd/N1/C2/C12/N2) forms a half-chair with the Pd^{II} atom as the flap. This deviation seems to be caused by intramolecular steric hindrance between biq moieties (C9—H9 and C19—H19) and Cl atoms (Cl1 and Cl2), as reflected by the relatively short Cl1···H9 and Cl2···H19 separations of 2.70 and 2.68 Å, respectively. The two quinoline rings of the biq ligand of (I) are bowed in the same direction, like two wings, with a dihedral angle of 17.81 (8) Å.

In (II) and (III), the deviations of the central metal atoms from the mean plane (N1/C2/C12/N2) are zero for Cu^{II} and 0.267 (7) Å for Zn^{II}, as the five-membered rings (*M*/N1/C2/C12/N2) form a planar and a slight half-chair form for *M* = Cu^{II} and *M* = Zn^{II}, respectively. The Cl···H separations are Cl1···H9($1-x$, y, $\frac{3}{2}-z$) [= Cl1($1-x$, y, $\frac{3}{2}-z$)···H9] = 2.77 Å in (II), and Cl1···H19 = 3.15 Å and Cl2···H9 = 3.63 Å in (III). The dihedral angles between the quinoline rings in the biq ligand are 1.4 (2) and 10.3 (2) Å for (II) and (III), respectively. These indicate that the conformation of the biq ligand of (II) is almost planar, while that of (III) is slightly bowed.

Figs. 4, 5 and 6 show the crystal packing of complexes (I), (II) and (III), respectively. The crystal structures of the three complexes are stabilized by π–π interactions between inversion-related biq ligands. In (I) and (III), C—H···Cl hydrogen bonds are present (Table 2). In (I), the N1 ring (N1/C2–C10) stacks with the inversion-related N1 ring, with a centroid–centroid separation of 3.770 (3) Å [between the centroids of rings N1/C2–C5/C10 and C5–C10($-x$, $-y$, $-z$)]. The N2 ring (N2/C12–C20) also stacks with neighbouring N2 rings, with centroid–centroid separations of 3.653 (3) and 3.689 (3) Å

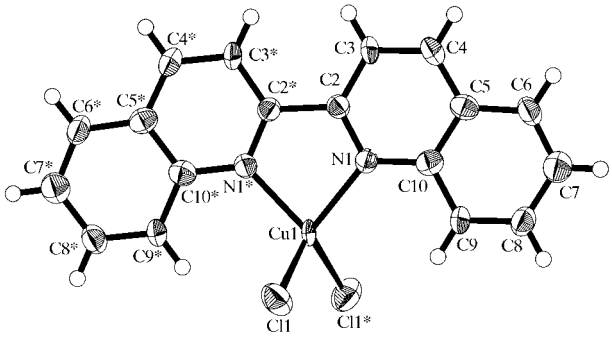

Figure 2
A view of the molecule of (II), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms labelled with an asterisk (*) are at the symmetry position ($1-x$, y, $\frac{3}{2}-z$).

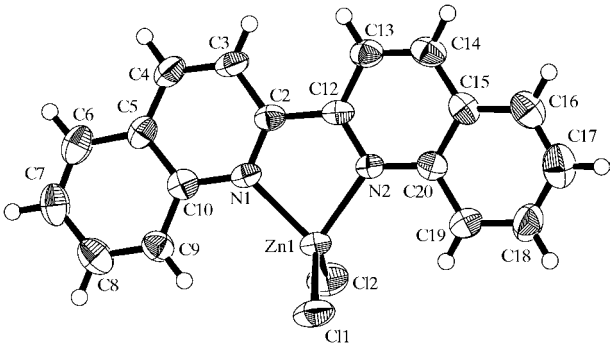

Figure 3
A view of the molecule of (III), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

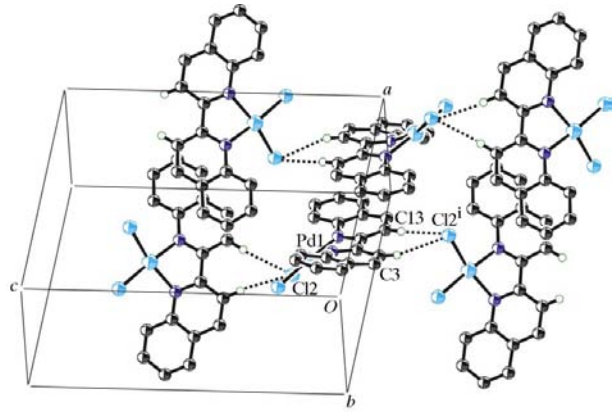

Figure 4
The packing of (I), showing the π–π interactions between inversion-related ligand molecules and the C—H···Cl hydrogen bonds (dashed lines). [Symmetry code: (i) x, $\frac{1}{2}-y$, $-\frac{1}{2}-z$.]

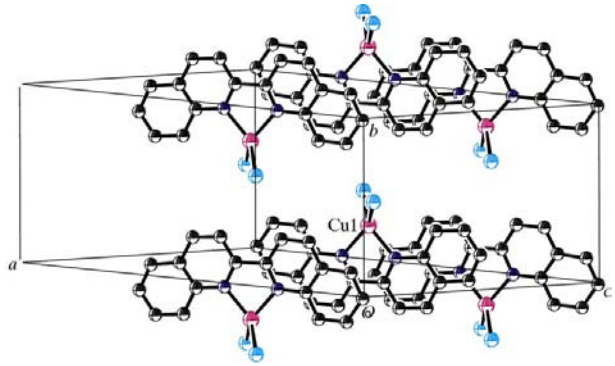

Figure 5
The packing of (II), showing the π–π interactions between inversion-related ligand molecules.

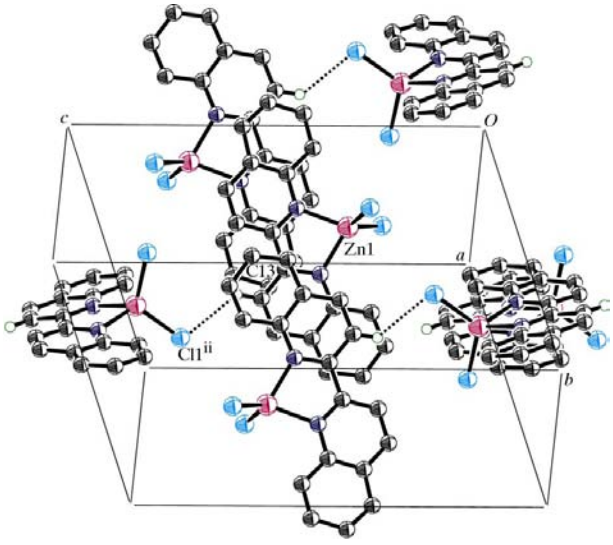

Figure 6
The packing of (III), showing the π–π interactions between inversion-related ligand molecules and the C—H···Cl hydrogen bonds (dashed lines). [Symmetry code: (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.]

[between the centroids of rings N2/C12–C15/C20 and C15–C20($1-x, 1-y, -z$), and between the centroids of rings N2/C12–C15/C20 and N2/C12–C15/C20($1-x, -y, -z$), respectively]. In (II), the N1 ring (N1/C2–C5/C10) stacks with the inversion-related N1 ring at ($1-x, -y, 1-z$), with a centroid–centroid separation of 3.769 (3) Å. In (III), the N1 ring (N1/C2–C10) stacks with the inversion-related neighbouring N1 ring at ($-x, -y, 1-z$), with a centroid–centroid separation of 3.519 (3) Å between the C5–C10 rings. The N2 ring (N2/C12–C20) stacks with the inversion-related neighbouring N2 ring at ($1-x, 1-y, 1-z$), with a centroid–centroid separation of 3.539 (3) Å between inversion-related N2/C12–C15/C20 rings.

Experimental

Orange plate-shaped crystals of (I) were obtained by slow evaporation of a dimethylformamide (DMF) solution of a mixture of biq and $PdCl_2$ (molar ratio 1:1) at room temperature. Red plate-shaped crystals of (II) were obtained by slow evaporation of a DMF solution of a mixture of biq and $CuCl_2{\cdot}2H_2O$ (molar ratio 1:1) at room temperature. Colourless plate-shaped crystals of (III) were obtained by slow evaporation of a DMF solution of a mixture of biq and $ZnCl_2$ (molar ratio 1:1) at room temperature.

Compound (I)

Crystal data

$[PdCl_2(C_{18}H_{12}N_2)]$
M_r = 433.62
Monoclinic, $P2_1/c$
a = 13.017 (4) Å
b = 7.726 (4) Å
c = 15.972 (3) Å
β = 95.675 (19)°
V = 1598.4 (10) Å^3
Z = 4
D_x = 1.802 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 14.5–15.0°
μ = 1.49 mm^{-1}
T = 296.2 K
Plate, orange
0.30 × 0.20 × 0.05 mm

Data collection

Rigaku AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.606, T_{max} = 0.928
3825 measured reflections
3669 independent reflections
2724 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 27.5°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 10$
$l = -20 \rightarrow 20$
3 standard reflections
every 150 reflections
intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.076
S = 1.03
3669 reflections
208 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.034P)^2 + 0.2227P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Compound (II)

Crystal data

$[CuCl_2(C_{18}H_{12}N_2)]$
M_r = 390.75
Monoclinic, $C2/c$
a = 19.430 (3) Å
b = 8.528 (2) Å
c = 11.884 (3) Å
β = 125.991 (10)°
V = 1593.2 (6) Å^3
Z = 4
D_x = 1.629 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 11.0–14.5°
μ = 1.71 mm^{-1}
T = 296.2 K
Plate, red
0.30 × 0.10 × 0.10 mm

Data collection

Rigaku AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.715, T_{max} = 0.843
1877 measured reflections
1825 independent reflections
1032 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
θ_{max} = 27.5°
$h = 0 \rightarrow 25$
$k = 0 \rightarrow 11$
$l = -15 \rightarrow 12$
3 standard reflections
every 150 reflections
intensity decay: none

Table 1
Selected bond distances (Å) and angles (°) for compounds (I), (II) and (III).

M = Pd in (I), Cu in (II) and Zn in (III).

	(I)	(II)	(III)
M—N1	2.067 (3)	1.997 (3)	2.070 (3)
M—N2	2.032 (2)		2.058 (3)
M—Cl1	2.2819 (10)	2.2175 (13)	2.2044 (14)
M—Cl2	2.2878 (13)		2.2143 (15)
N—M—N	79.24 (10)	82.24 (18)	80.49 (14)
Cl—M—Cl	86.74 (3)	102.09 (8)	118.53 (5)

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

	D—H···A	D—H	H···A	D···A	D—H···A
(I)	C3—H3···Cl2^{i}	0.93	2.82	3.705 (3)	161
	C13—H13···Cl2^{i}	0.93	2.78	3.705 (4)	176
(III)	C13—H13···Cl1^{ii}	0.93	2.80	3.466 (5)	130

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.131$
$S = 0.99$
1825 reflections
105 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -0.71$ e Å^{-3}

Compound (III)

Crystal data

$[ZnCl_2(C_{18}H_{12}N_2)]$
$M_r = 392.59$
Monoclinic, $P2_1/n$
$a = 7.986$ (2) Å
$b = 12.257$ (6) Å
$c = 16.8390$ (16) Å
$\beta = 102.464$ (13)°
$V = 1609.4$ (9) Å^3
$Z = 4$
$D_x = 1.620$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 11.6$–$14.7°$
$\mu = 1.86$ mm^{-1}
$T = 296.2$ K
Plate, colourless
0.50 × 0.20 × 0.05 mm

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.547$, $T_{max} = 0.911$
3943 measured reflections
3686 independent reflections
1835 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = -21 \rightarrow 21$
3 standard reflections
every 150 reflections
intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.122$
$S = 0.96$
3686 reflections
208 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

All H atoms were located in the difference Fourier maps and were then treated as riding, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); structure solution: *SIR97* (Altomare *et al.*, 1999); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); publication software: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1828). Services for accessing these data are described at the back of the journal.

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