metal-organic papers

(1,1-Cyclobutanedicarboxylato-$\kappa^2 O,O'$)-(2,2'-biquinoline-$\kappa^2 N,N'$)palladium(II) monohydrate

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In the title compound, [Pd(C₆H₆O₄)(C₁₈H₁₂N₂)]·H₂O, the Pd^{II} atom has a distorted *cis*-planar four-coordination geometry defined by two O atoms of a bidentate 1,1-cyclobutane-dicarboxylate anion and two N atoms of the 2,2'-biquinoline ligand. In the crystal structure, centrosymmetric clusters of the complex molecules and water molecules are formed through O—H···O hydrogen bonds.

Comment

cis-Square-planar coordinated Pt^{II} complexes such as cisplatin [*cis*-diamminedichloroplatinum(II)], carboplatin [*cis*-diam-mine(1,1-cyclobutanedicarboxylato)platinum(II)] and oxali-platin [*trans*-l-1,2-diaminocyclohexane platinum(II) oxalate], are well known anticancer drugs. Carboplatin with a bidentate 1,1-cyclobutanedicarboxylato (cbdca) ligand has fewer side effects than cisplatin (Jakupec *et al.*, 2003). Pd^{II} analogues of Pt^{II} complexes have been used as good models for studies of the chemistry of square planar complexes (Rau & van Eldik, 1996). For example, *cis*-diammine(1,1-cyclobutanedicarboxyl-ate)palladium(II) (Barnham *et al.*, 1994) is isostructural with carboplatin (Beagley *et al.*, 1985; Neidle *et al.*, 1980). Recently, the palladium complex with the aromatic heterocyclic ligand [Pd(bpy)(cbdca)] (bpy = 2,2'-bipyridine) has been shown to have better cytotoxic activity than cisplatin against P₃₈₈ lymphocytic leukemia cells (Mansuri-Torshizi *et al.*, 2001). Aromatic heterocycles can stack with nucleobases and enhance complex formation with DNA, which is the principal target in the chemotherapy of tumors (Shehata, 2001).

(I)
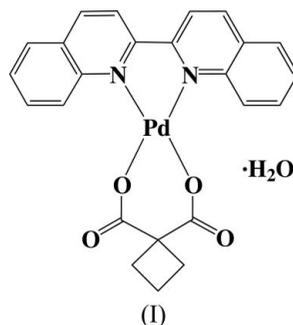
In a previous study (Muranishi & Okabe, 2004), we deter-mined the structures of the carboplatin analogs of Pd^{II} complexes with *N,N'*-bidentate aromatic heterocycle ligands bipyridine(bpy), [Pd(bpy)(cbdca)], and 1,10-phenanthroline (phen), [Pd(phen)(cbdca)]·H₂O and [Pd(phen)(cbdca)]·2H₂O. Because biq (biq = 2,2'-biquinoline) is an aromatic hetero-cyclic compound with interesting characteristics, such as
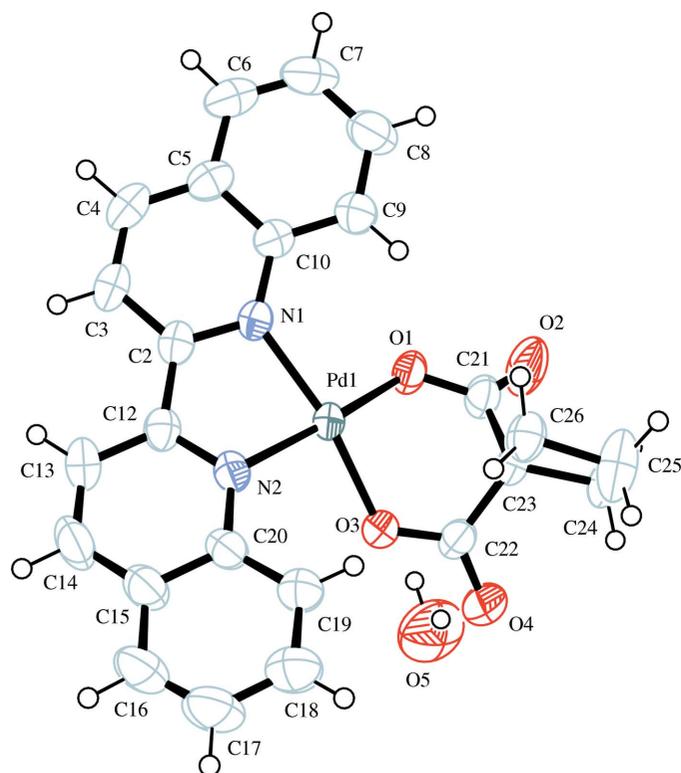
Figure 1
Molecular structure of (I), with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

inhibition activity against the formation of an abnormal prion protein (Murakami-Kubo *et al.*, 2004) and mutagenic activity as the rhodamin(III) complex (Sadiq & Zaghal, 1996), we present in this study the structure of [Pd(biq)(cbdca)]·H₂O, (I).

The central Pd atom of (I) has a distorted *cis*-square planar coordination geometry, from two N atoms of biq and two O atoms of the cbdca ligand (Fig. 1). The overall structure of (I) resembles those of [Pd(bpy)(cbdca)], (II), [Pd(phen)(cbdca)]·H₂O, (III*a*), and [Pd(phen)(cbdca)]·2H₂O, (III*b*) (Muranishi & Okabe, 2004). The bond lengths and bond angles in (I) are similar to those in (II), (III*a*) and (III*b*) and selected values are compared in Table 2. The Pd atom makes a six-membered chelate ring with cbdca in a boat conformation, and a five-membered chelate ring with biq in an envelope conformation, in which the deviation of atom Pd1 from the N1/C2/C12/N12 plane is 0.671 (4) Å. The biq group is non-planar, with a dihedral angle of 20.5 (1)° between the two quinoline ring systems. The cyclobutane least-squares plane is almost perpendicular to the N1—C2—C12—N12 plane in biq, with a dihedral angle of 86.8 (2)°.

The N—Pd—N chelate angle in (I), as well as in (II), (III*a*) and (III*b*), is smaller than those in the ethylenediamine (en) ligand in [Pd(en)(cbdca)] [84.15 (8)°; Tercero *et al.*, 2003] or the NH₃ ligand in [Pd(NH₃)₂(cbdca)] [95.0°; Barnham *et al.*, 1994]. In the crystal structure, centrosymmetric clusters of the title complex and water molecules are formed through O—H···O hydrogen bonds (Table 1).

Experimental

Biq (5.0 mg) dissolved in dimethylformamide (DMF, 2 ml) was reacted with palladium acetate, [Pd(CH₃COOH)₂] (4.4 mg), dissolved in DMF (2 ml) for 15 min at room temperature (molar ratio of 1:1), and then an equimolar amount of 1,1-cyclobutanedicarboxylic acid dissolved in DMF (1 ml) was added with stirring. This mixture was left to stand at room temperature, and yellow block-like crystals appeared in a few days.

Crystal data

[Pd(C₆H₆O₄)(C₁₈H₁₂N₂)]·H₂O	$Z = 2$
$M_r = 522.84$	$D_x = 1.661$ Mg m⁻³
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.363$ (2) Å	Cell parameters from 25
$b = 10.438$ (2) Å	reflections
$c = 11.450$ (2) Å	$\theta = 14.9–15.0°$
$\alpha = 64.66$ (1)°	$\mu = 0.93$ mm⁻¹
$\beta = 80.87$ (2)°	$T = 296.2$ K
$\gamma = 69.07$ (1)°	Block, yellow
$V = 1045.5$ (4) Å³	$0.35 \times 0.15 \times 0.10$ mm

Data collection

Rigaku AFC-5R diffractometer	$R_{int} = 0.025$
$\omega–2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = -13 \rightarrow 12$
(North *et al.*, 1968)	$k = -13 \rightarrow 0$
$T_{min} = 0.846$, $T_{max} = 0.911$	$l = -14 \rightarrow 13$
5074 measured reflections	3 standard reflections
4809 independent reflections	every 150 reflections
4179 reflections with $I > 2\sigma(I)$	intensity decay: 0.9%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.1P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.075$	$(\Delta/\sigma)_{max} = -0.001$
$S = 1.22$	$\Delta\rho_{max} = 0.32$ e Å⁻³
4809 reflections	$\Delta\rho_{min} = -0.44$ e Å⁻³
289 parameters	Extinction correction: *SHELXL97*
H-atom parameters constrained	Extinction coefficient: 0.0000

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O4	0.90	2.07	2.958 (4)	169
O5—H5B···O2ⁱ	0.96	1.85	2.794 (6)	166

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

Table 2
Comparative selected geometric parameters (Å, °).

	(I)	(II)ⁱ	(III*a*)ⁱ	(III*b*)ⁱ
Pd1—O1	1.995 (2)	2.002 (2)	2.003 (4)	2.001 (3)
Pd1—O3	1.988 (3)	2.004 (2)	2.005 (4)	1.982 (3)
Pd1—N1	2.037 (3)	1.999 (2)	1.991 (5)	2.002 (4)
Pd1—N2	2.020 (2)	1.998 (2)	1.994 (5)	2.010 (4)
O1—Pd1—O3	88.20 (8)	91.68 (7)	91.3 (2)	92.8 (1)
O1—Pd1—N1	96.49 (9)	93.94 (8)	93.0 (2)	93.3 (1)
O1—Pd1—N2	171.53 (9)	174.40 (6)	173.2 (2)	174.7 (1)
O3—Pd1—N1	168.17 (8)	174.37 (9)	174.7 (2)	172.7 (1)
O3—Pd1—N2	93.51 (9)	93.57 (8)	93.2 (2)	91.6 (1)
N1—Pd1—N2	80.31 (9)	80.80 (8)	82.2 (2)	82.1 (1)

Note: (i) From Muranishi & Okabe (2004).

All H atoms were located in difference Fourier maps, and were then treated as riding with C—H = 0.93 and 0.97 Å, and $U_{iso}(H)$ = $1.2U_{eq}(C)$. The H atoms of the water molecule were located in a difference Fourier map but their parameters were not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN* (Molecular Structure Corporation, 2000).

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.

Beagley, B., Cruickshank, D. W. J., McAuliffe, C. A., Pritchard, R. G., Zaki, A. M., Beddoes, R. L., Cernik, R. J. & Mills, O. S. (1985). *J. Mol. Struct.* **130**, 97–102.

Jakupec, M. A., Galanski, M. & Keooler, B. K. (2003). *Rev. Physiol. Biochem. Pharmacol.* **146**, 1–53.

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

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.

Murakami-Kubo, I., Doh-ura, K., Ishikawa, K., Kawatake, S., Sasaki, K., Kira, J., Ohta, S. & Iwaki, T. (2004). *J. Virol.* **78**, 1281–1288.

Muranishi, Y. & Okabe, N. (2004). *Acta Cryst.* C**60**, m47–m50.

Neidle, S., Ismail, I. M. & Sadler, P. J. (1980). *J. Inorg. Biochem.* **13**, 205–212.

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

Rau, T. & van Eldik, R. (1996). *Metal Ions in Biological Systems*, Vol. 32, edited by A. Sigel & M. Sigel, pp. 339–378. New York: Marcel Dekker.

Sadiq, M. F. & Zaghal, M. H. (1996). *Polyhedron*, **16**, 1483–1486.

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

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

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