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(1,2-Benzenediolato-κ^2O,O')(1,10-phenanthroline-κ^2N,N')palladium(II) dihydrate

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
R factor = 0.026
wR factor = 0.071
Data-to-parameter ratio = 16.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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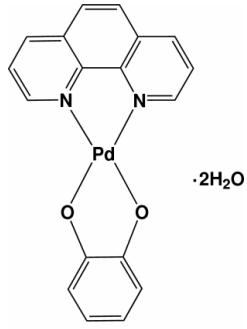
In the mononuclear catecholate complex, $[Pd(C_6H_4O_2)(C_{12}H_8N_2)]\cdot 2H_2O$, the Pd^{II} has a distorted *cis* square-planar four-coordinate geometry. It is bonded to two O atoms of a bidentate catecholate dianion and two N atoms of the bidentate phenanthroline. The overall conformation of the complex including catechol and phenanthroline rings is almost planar.

Comment

Numerous transition metal catecholates have been studied extensively in the solid state and in solution because of their unique redox characteristics (Pierpont, 2001; Sheriff *et al.*, 2003; Hamilton *et al.*, 1966). Platinum(II) catecholates have been reported to have anticancer activity and are used for metalloantigens (Pal *et al.*, 2001; Rauth *et al.*, 2001; Lesley *et al.*, 1999). Pd^{II} complexes of bis(2-acetylpyridine-3-hexamethyleneiminyl-thiosemicarbazonate) (Kovala-Demertzi *et al.*, 2002), dithiocarbamates and amines (Faraglia *et al.*, 2001) and 5,7-dihydro-7-oxo-5-methyl[1,2,4]triazolopyrimidine (Akdi *et al.*, 2002) exhibit antitumor activity. In the present study, we report the preparation and crystal structure of the title compound, (I), a catecholate complex of Pd^{II} with 1,10-phenanthroline. To the best of our knowledge, this is the first structural report of a palladium(II) catecholate complex.



(I)

In the crystal structure of (I), the Pd^{II} has a distorted *cis* square-planar four-coordination geometry (Fig. 1), and is bonded to two O atoms of a bidentate catecholate dianion and two N atoms of the bidentate 1,10-phenanthroline. The overall conformation of the complex (I) is almost planar with a dihedral angle of 11.46 (8)° between the catecholate and 1,10-phenanthroline ligands. The central Pd^{II} forms five-membered chelate rings with the ligand atoms. The bond lengths and angles of (I) may be compared to those reported for the complexes of Pd^{II} with ethylenediamine (en) and dicarboxylate ligands of the type [Pd(en)*M*], where *M* = methylmalonato,

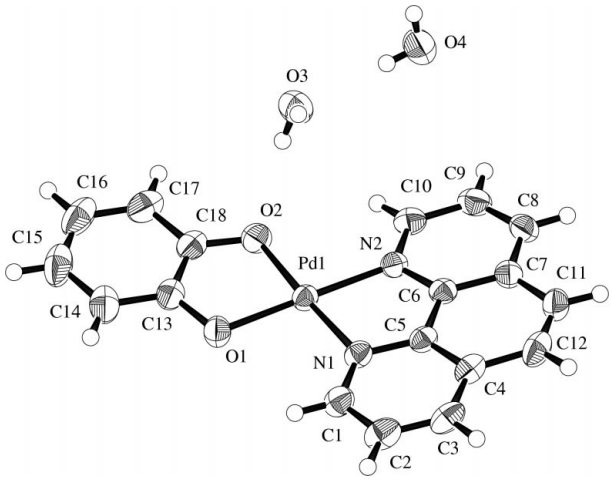


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I), with the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

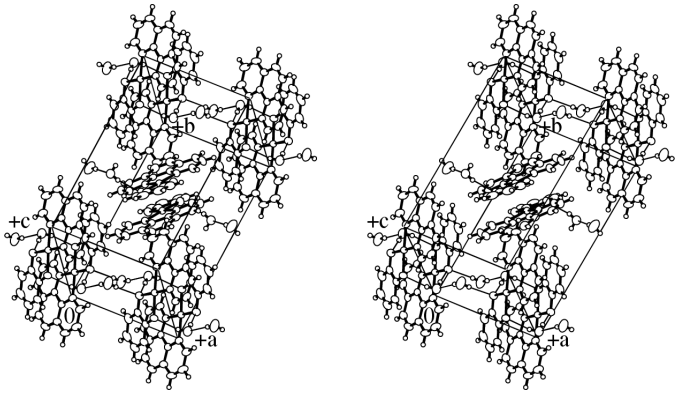


Figure 2
A stereoview of the molecular packing of (I). Hydrogen bonds are indicated by thin lines.

and [Pd(en)*C*], where *C* = 1,1-cyclobutanedicarboxylato (Tercero *et al.*, 2003). In these complexes, Pd^{II} has a *cis* square-planar coordination geometry with two O atoms of the dicarboxylate ligand and two N atoms of ethylenediamine, as in (I). The Pd—O and Pd—N bond lengths of (I) (Table 1) are slightly shorter than those of [Pd(en)*M*] and [Pd(en)*C*], in which the bond lengths range from 1.995 (10) to 2.027 (10) Å for Pd—O and 2.009 (11) to 2.030 (2) Å for Pd—N. This means that the coordinate bonds of (I) are somewhat stronger than those of [Pd(en)*M*] and [Pd(en)*C*]. Furthermore, the O—Pd—O and N—Pd—N angles of (I) are smaller than those of [Pd(en)*M*] and [Pd(en)*C*], in which the O—Pd—O angles lie in the range 89.51 (17) to 92.69 (7)° and N—Pd—N angles lie in the range 84.09 (18) to 84.15 (8)°. This may be attributed to the different intramolecular mobility of the O and N atoms in the ligand molecules. The mobility of the O atoms of catecholate and N atoms of 1,10-phenanthroline ligands are smaller than that of the O atoms of methylmalonate, O atoms of 1,1-cyclobutanedicarboxylate and N atoms of ethylenediamine ligands.

The crystal packing of (I) is shown in Fig. 2. The 1,10-phenanthroline ligand is stacked along the *c* axis with the symmetry-related catecholate ring at $(-x, 2-y, 1-z)$, and with another 1,10-phenanthroline ligand related by the symmetry operation $(-x, 2-y, 2-z)$; their centroids are separated by 3.710 (2) and 4.083 (2) Å, respectively. O—H···O hydrogen bonds involving the water molecules and catecholate O atoms (Table 2) link the complexes to form chains along the *a* axis.

Experimental

Dark red plate crystals of (I) were obtained by slow evaporation of a dimethylformamide solution of a mixture of catechol, 1,10-phenanthroline and $Pd(CH_3COO)_2$ (molar ratio 1:1:1) at room temperature.

Crystal data

$[Pd(C_6H_4O_2)(C_{12}H_8N_2)]\cdot 2H_2O$	$D_x = 1.746$ Mg m^{-3}
$M_r = 430.75$	Mo Kα radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 9.248$ (2) Å	$\theta = 14.7$–$15.0°$
$b = 16.462$ (2) Å	$\mu = 1.16$ mm^{-1}
$c = 10.802$ (1) Å	$T = 296.2$ K
$\beta = 94.70$ (1)°	Block, dark red
$V = 1639.0$ (4) Å^3	0.50 × 0.20 × 0.20 mm
$Z = 4$	

Data collection

Rigaku AFC-5*R* diffractometer	$R_{int} = 0.042$
ω–2θ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 12$
$T_{min} = 0.757$, $T_{max} = 0.793$	$k = 0 \rightarrow 21$
4127 measured reflections	$l = -14 \rightarrow 13$
3760 independent reflections	3 standard reflections every 150 reflections
3021 reflections with $I > 2\sigma(I)$	intensity decay: 0.7%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.034P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.071$	$(\Delta/\sigma)_{max} = 0.003$
$S = 1.13$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
3760 reflections	$\Delta\rho_{min} = -0.66$ e Å^{-3}
226 parameters	

Table 1
Selected geometric parameters (Å, °).

Pd1—O1	1.989 (2)	Pd1—N2	2.003 (2)
Pd1—O2	1.981 (2)	O1—C13	1.365 (3)
Pd1—N1	2.019 (2)	O2—C18	1.344 (3)
O1—Pd1—O2	85.09 (7)	O2—Pd1—N1	176.80 (8)
O1—Pd1—N1	97.51 (7)	O2—Pd1—N2	95.72 (8)
O1—Pd1—N2	179.19 (8)	N1—Pd1—N2	81.69 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O2	0.77	2.07	2.826 (3)	166
O3—H3*B*···O1^{i}	0.76	2.04	2.772 (3)	163
O4—H4*B*···O1^{ii}	0.76	2.15	2.907 (3)	174
O4—H4*A*···O3	0.76	2.07	2.823 (3)	176

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

The H atoms of the water molecules were located in a difference Fourier map but their parameters were not refined. The C-bound H atoms were placed at ideal positions (C—H = 0.93 Å) and allowed to ride on the attached atom. For all H atoms, the isotropic displacement parameter was set equal to $1.2U_{eq}$(parent atom).

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 Corporation, 2000); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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