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

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Key indicators

Single-crystal X-ray study
$T = 296$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.026
wR factor = 0.072
Data-to-parameter ratio = 14.7

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

In the title complex, [Pd($C_3H_2O_4$)($C_{12}H_8N_2$)], the Pd^{II} center has a distorted *cis*-square-planar geometry defined by an O,O'-bidentate malonate ligand and a chelating 1,10-phenanthroline ligand. The crystal structure is stabilized by intermolecular π–π stacking interactions between pairs of 1,10-phenanthroline rings, as well as C—H···O hydrogen bonding.

Comment

Cisplatin, *cis*-diamminedichloroplatinum(II), and carboplatin, *cis*-diammine(cbdca)platinum(II), where cbdca is 1,1-cyclo-butanedicarboxylate, are well known as therapeutic Pt^{II} anticancer drugs. The Pd^{II} analogs of Pt^{II} complexes have also been used as models for Pt^{II} complexes (Rau & van Eldik, 1996). For example, *cis*-diammine(cbdca)palladium(II) (Barnham *et al.*, 1994) is isostructural with carboplatin (Beagley *et al.*, 1985; Neidle *et al.*, 1980). Furthermore, [Pd(byp)(cbdca)], where bpy is 2,2′-bipyridine, has greater cytotoxicity than the Pt^{II} complex against lymphocytic leukemia cells (Mansuri-Torshizi *et al.*, 2001). Thus, many Pd^{II} complexes with aromatic heterocyclic ligands, such as 1,10-phenanthroline (phen) and bpy, have been synthesized and examined for their anticancer potential (Liu *et al.*, 1999; Jin & Ranford, 2000; Mansuri-Torshizi *et al.*, 2001; Gao & Liu, 2002; Shehata, 2001). For these reasons, we have synthesized novel Pd^{II} complexes with heterocyclic ligands and analyzed their crystal structures to clarify their coordination modes (Okabe *et al.*, 2003; Muranishi & Okabe, 2004; Odoko *et al.*, 2004; Wang, Mizubayashi *et al.*, 2005; Wang, Okabe *et al.*, 2005). In the present study, the title complex, (I), has been synthesized and its crystal structure determined.

(I)
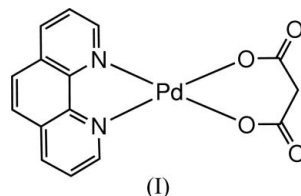
The central Pd^{II} atom in (I) (Fig. 1 and Table 1) displays a distorted *cis*-square-planar geometry, defined by two N atoms of the phen ligand and two O atoms of the malonate ligand. The six-membered chelate ring formed by the malonate has a somewhat flattened boat conformation, which resembles that in the Pd^{II} complex with cbdca (Barnham *et al.*, 1994); the five-membered chelate ring formed by phen is planar.

The bond lengths in (I) are similar to those of [Pd(cbdca)(phen)]H$_2$O and [Pd(cbdca)(phen)](H$_2$O)$_2$ [Pd—O = 1.982 (3)–2.005 (4) Å; Pd—N = 1.991 (5)–2.010 (4) Å;
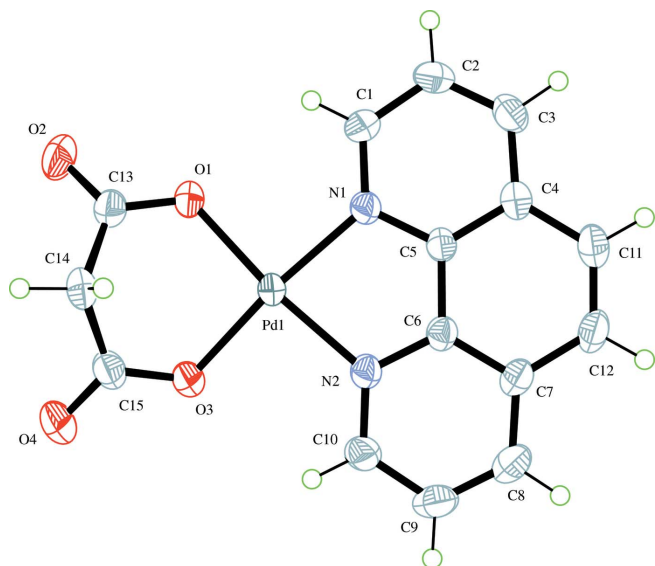
Figure 1
The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Figure 2
The molecular packing in (I). Hydrogen bonds are indicated by dashed lines. H atoms not involved in the interactions shown have been omitted.

Muranishi & Okabe, 2004] and [Pd(oxalato)(phen)]H$_2$O [Pd—O = 1.986 (3)–2.009 (2) Å; Pd—N = 2.006 (2)–2.007 (2) Å; Odoko *et al.*, 2004]. Likewise, the O—Pd—O bond angles are similar to those for [Pd(NH$_3$)$_2$(cbdca)] (90.9°; Barnham *et al.*, 1994; standard uncertainty unavailable), [Pd(ethylenediamine)(cbdca)] [92.69 (7)°; Tercero *et al.*, 2003], [Pd(cbdca)(phen)]H$_2$O [91.3 (2)°] and [Pd(cbdca)(phen)]-(H$_2$O)$_2$ [92.6 (1)–92.8 (1)°; Muranishi & Okabe, 2004]], but slightly wider than found in [Pd(oxal)(phen)]H$_2$O [83.80 (9)–83.3 (7)°; Odoko *et al.*, 2004]. The N—Pd—N bond angle is similar to those in all of the above Pd^{II} complexes with phen, but slightly narrower than found in [Pd(en)(cbdca)] [84.15 (8)°] and [Pd(NH$_3$)$_2$(cbdca)] (95.0°; Barnham *et al.*, 1994; standard uncertainty unavailable).

The crystal structure is stabilized by C—H⋯O hydrogen bonds (Table 2 and Fig. 2) and π–π stacking interactions between phen rings; the distance between the ring centroids of N1/C1–C5 and (N2/C6–C10)^{iii} [symmetry code (iii) −1 + x, y, z] is 3.727 (5) Å.
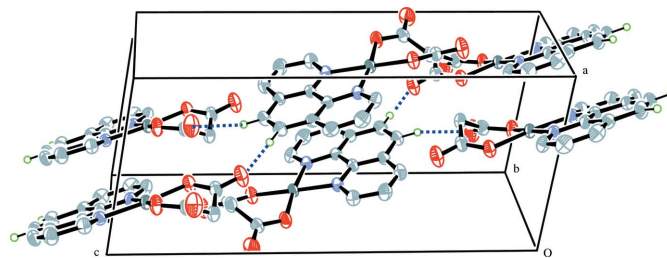
Experimental

Complex (I) was prepared by reacting phen with [Pd(CH$_3$COOH)$_2$] for 15 min at room temperature (molar ratio of 1:1) in dimethylformamide (DMF) solution, followed by the addition of an equimolar amount of malonic acid. This mixture was left to stand at room temperature and pale-yellow prismatic crystals of (I) appeared after a few days.

Crystal data

[Pd(C$_3$H$_2$O$_4$)(C$_{12}$H$_8$N$_2$)]	$Z = 4$
$M_r = 388.67$	$D_x = 2.011$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 7.825$ (2) Å	$\mu = 1.47$ mm^{-1}
$b = 9.180$ (3) Å	$T = 296$ K
$c = 18.087$ (2) Å	Prism, yellow
$\beta = 98.86$ (2)°	$0.20 \times 0.15 \times 0.15$ mm
$V = 1283.8$ (6) Å^3	

Data collection

Rigaku AFC-5R diffractometer	2947 independent reflections
ω–2θ scans	2419 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan	$R_{int} = 0.025$
(North *et al.*, 1968)	$\theta_{max} = 27.5°$
$T_{min} = 0.964$, $T_{max} = 1$	3 standard reflections
(expected range = 0.774–0.802)	every 150 reflections
3355 measured reflections	intensity decay: 1.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$+ 0.8246P]$
$wR(F^2) = 0.072$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
2947 reflections	$\Delta\rho_{max} = 0.45$ e Å^{-3}
200 parameters	$\Delta\rho_{min} = -0.70$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Pd1—O1	1.987 (2)	Pd1—N1	2.004 (2)
Pd1—O3	1.990 (2)	Pd1—N2	2.012 (3)
O1—Pd1—O3	94.08 (9)	O3—Pd1—N1	173.48 (9)
O1—Pd1—N1	91.60 (9)	O3—Pd1—N2	92.15 (9)
O1—Pd1—N2	173.04 (9)	N1—Pd1—N2	82.01 (10)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C11—H11⋯O2^i	0.93	2.66	3.514 (4)	154
C12—H12⋯O4^{ii}	0.93	2.50	3.426 (4)	177

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

H atoms were included in the riding model approximation with C—H = 0.93-0.97 Å, and with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005) and *CRYSTALS* (Betteridge *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CrystalStructure*.

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