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(Malonato-κ^2O,O')(propane-1,3-diamine-κ^2N,N')-palladium(II)

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.003 Å
R factor = 0.016
wR factor = 0.043
Data-to-parameter ratio = 16.5

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

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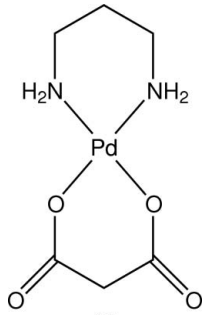
In the title compound, [$Pd^{II}(C_3H_2O_4)(C_3H_{10}N_2)$], the Pd^{II} atom adopts a distorted *cis*-square-planar geometry. The ligands form two six-membered chelate rings, with propane-1,3-diamine adopting a chair conformation and the malonato ligand a boat conformation. The crystal packing is stabilized by a network of N—H···O and C—H···O hydrogen bonds.

Comment

The anticancer activity of Pt^{II} and Pd^{II} complexes with *N*,*N*-diamino *cis*-chelating ligands or with propane-1,3-diamine (tn) have been extensively studied (Mohamed & Shoukry, 2001; González *et al.*, 1997; Matilla *et al.*, 1994; Navarro-Ranninger *et al.*, 1992; Akdi *et al.*, 2005; Alvarez-Valdes *et al.*, 2002; Marzilli *et al.*, 1980). We have recently reported the structures of [$M^{II}Cl_2$(tn)] (M = Pt or Pd) and [$Pt_2^{II}Cl_4$(spn)] (spn = spermine) (Odoko & Okabe, 2006) and report here the structure of [Pd^{II}(mal)(tn)] (mal = malonate), (I) (Fig. 1).



(I)

The Pd^{II} atom is coordinated by two N atoms from tn and two O atoms from the mal ligand, in a slightly distorted *cis*-square-planar coordination geometry [r.m.s. deviation = 0.0252Å]. The Pd^{II}—N distances and N—Pd^{II}—N angles are similar to those in [$M^{II}Cl_2$(tn)] (M = Pd or Pt; Odoko & Okabe, 2006). Compound (I) contains two six-membered chelate rings. The tn ring adopts a chair conformation while the mal ring is in a boat conformation, as in the structures of other M^{II} complexes with mal (Baker *et al.*, 1993; Brown & Lock, 1989; Rochon *et al.*, 1985; Cutbush *et al.*, 1983; van Kralingen *et al.*, 1980). In the tn ring, the dihedral angles of the planes Pd1/N1/N2 and C1/C2/C3 with respect to the plane N1/C1/C3/N2 are 32.2 (1) and 60.5 (2)°, respectively, which shows a less flattened conformation than those in [$M^{II}Cl_2$(tn)] {24.3 (2) and 62.1 (5)° in [$Pt^{II}Cl_2$(tn)], 22.2 (1) and 62.1 (3)° in [$Pd^{II}Cl_2$(tn)]}. In the mal ring, the dihedral angles of the Pd1/O1/O3 and C4/C5/C6 planes with respect to the O1/C4/C6/O3 plane are 24.4 (1) and 52.7 (1)°, respectively. In the previously

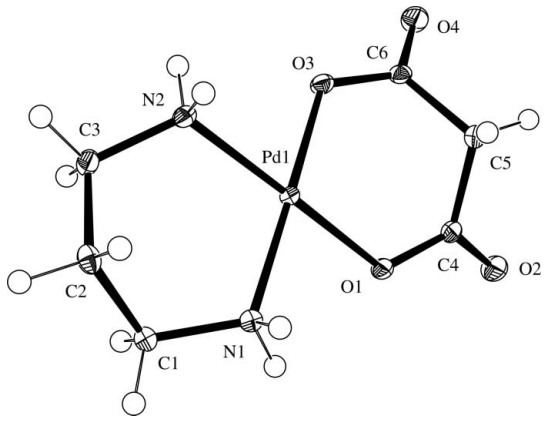


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radius.

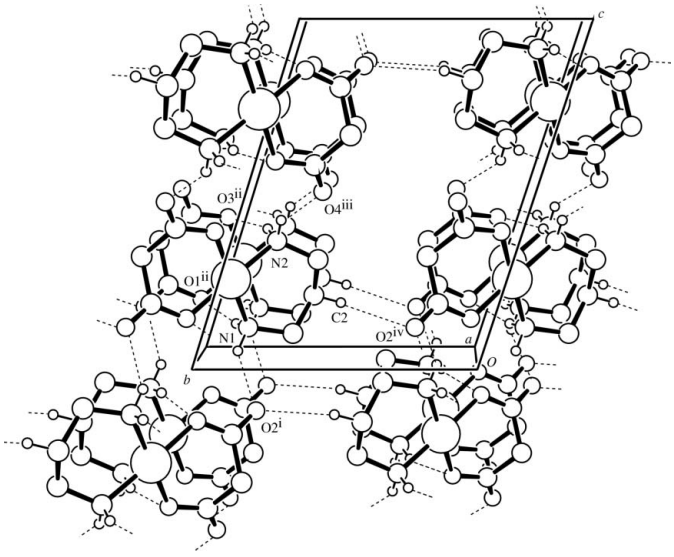


Figure 2
The crystal packing of (I), showing the N—H···O and C—H···O hydrogen-bond network. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $-x$, $-y+2$, $-z$; (ii) $x+1$, y, z; (iii) $-x$, $-y+2$, $-z+1$; (iv) $x+1$, $y-1$, z.]

reported M^{II} mal complexes, the corresponding values for the *M*/O/O plane range from 21.98 to 37.68°, and the values for the C/C/C plane range from 36.05 to 51.48°. These values point to the considerable flexibility of the mal ligand.

The crystal packing is stabilized by N—H···O and C—H···O hydrogen bonds (Fig. 2 and Table 1). N—H···O hydrogen bonds link the complexes, forming an infinite ribbon; these are connected by additional N—H···O interactions along the *a* axis. C—H···O hydrogen bonds also connect neighboring complexes into a sheet.

Experimental

$[Pd^{II}Cl_2(tn)]$ (5 mg, 0.02 mol), prepared as described previously (Odoko & Okabe, 2006), was dissolved in dimethyl sulfoxide (DMSO, 0.25 ml), and a disodium malonate aqueous solution (2.9 mg, 0.02 mol per 5 ml) added at room temperature. After slow evaporation over two months, colorless needle-like crystals appeared.

Crystal data

$[Pd(C_3H_2O_4)(C_3H_{10}N_2)]$
$M_r = 282.60$
Triclinic, $P\overline{1}$
$a = 4.430$ (5) Å
$b = 8.94$ (1) Å
$c = 11.40$ (1) Å
$\alpha = 106.93$ (3)°
$\beta = 90.83$ (4)°
$\gamma = 95.03$ (4)°
$V = 429.9$ (8) Å^3
$Z = 2$
$D_x = 2.183$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.14$ mm^{-1}
$T = 123$ K
Needle, colorless
0.50 × 0.05 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.574$, $T_{max} = 0.898$
4252 measured reflections
1958 independent reflections
1889 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.018$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.043$
$S = 1.09$
1958 reflections
119 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0242P)^2 + 0.1199P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.89$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O2^{i}	0.90	2.19	2.956 (3)	143
N1—H1B···O1^{ii}	0.90	2.16	3.027 (4)	163
N2—H2A···O3^{ii}	0.90	2.18	3.030 (4)	158
N2—H2B···O4^{iii}	0.90	2.10	2.894 (3)	147
C2—H2C···O2^{iv}	0.97	2.51	3.445 (4)	163

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

All H atoms were located in difference Fourier maps, and were then placed in idealized positions and treated as riding, with C—H = 0.97, N—H = 0.90 Å and U_{iso}(H) = 1.2U_{eq}(carrier atom).

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: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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