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

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The title compound, $[Pd^{II}(C_2O_4)(C_3H_{10}N_2)]$, crystallizes with two unique molecules in the asymmetric unit. The Pd^{II} atom adopts distorted *cis*-square-planar geometry. The oxalate ligand lies in the coordination plane and the six-membered chelate ring formed by the Pd^{II} atom and the propane-1,3-diamine ligand adopts a chair conformation. The crystal packing is stabilized by a complex three-dimensional N—H···O hydrogen-bond network.

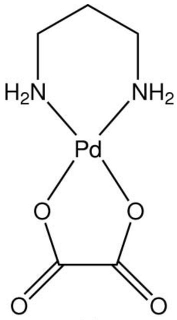
Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.004 Å
R factor = 0.018
wR factor = 0.038
Data-to-parameter ratio = 17.2

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

Comment

The *cis*-square-planar Pt^{II} complex cisplatin, $Cl_2Pt(NH_3)_2$, is known as an anticancer agent (Momekov & Momekova, 2006) but some toxic side effects and natural resistance still remain. It is important, therefore, to prepare new Pt^{II} compounds with improved pharmacological properties and with wide-ranging anticancer activities. Pd^{II} compounds have been used as model anticancer drugs because of the coordination analogy with Pt^{II} compounds (Akdi *et al.*, 2005). Previous studies have examined Pd^{II} complexes with *N*,*N*′-diamino *cis*-chelating ligands as anticancer drugs (Mohamed & Shoukry, 2001; González *et al.*, 1997; Matilla *et al.*, 1994; Navarro-Ranninger *et al.*, 1992), also Pt^{II} and Pd^{II} complexes with propane-1,3-diamine (tn) for their action on DNA (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 $[Pd^{II}(oxa)(tn)]$ (ox = oxalate), (I) (Fig. 1).



(I)

The title compound crystallizes with two independent molecules in the asymmetric unit. Each complex comprises a Pd^{II} centre coordinated by two N atoms from the tn ligand and two O atoms from ox in a slightly distorted *cis*-square-planar environment. The Pd^{II} atoms and ox form five-membered chelate rings, which lie in the coordination planes (r.m.s. deviations are 0.114 Å for Pd1 and 0.040 Å for Pd2). The Pd^{II} atoms and tn form six-membered chelate rings which adopt

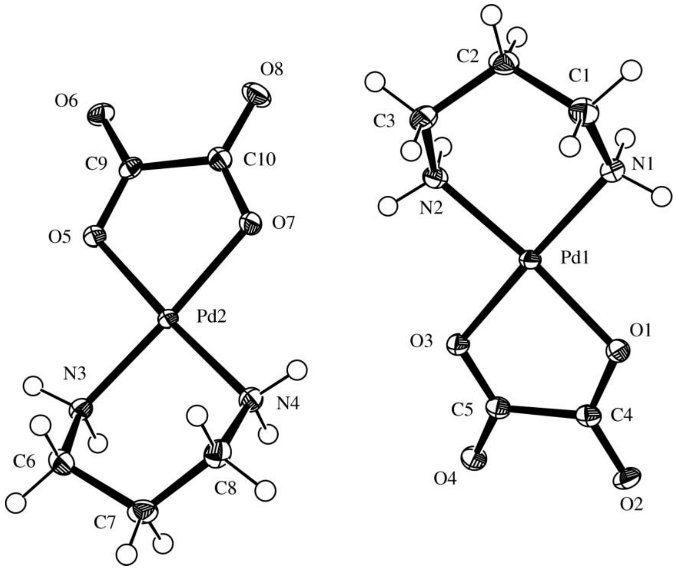


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radius.

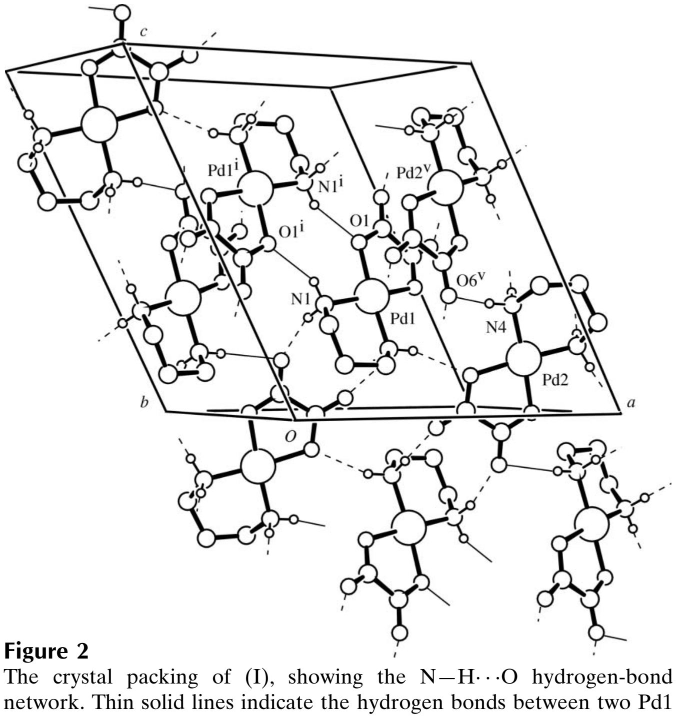


Figure 2
The crystal packing of (I), showing the N—H⋯O hydrogen-bond network. Thin solid lines indicate the hydrogen bonds between two Pd1 complexes related by the inversion centre, and those between Pd2 complexes forming infinite twisted sheet along the *c* axis. Dashed lines indicate the other hydrogen bonds. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (v) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.]

chair conformations. In the Pd1 complex, the dihedral angles of the Pd1/N1/N2 and C1/C2/C3 planes with respect to the N1/C1/C3/N2 plane are 38.5 (2) and 61.0 (2)°, respectively. The corresponding values for the Pd2 complex are 43.4 (1) and 58.9 (2)°. These rings are therefore less flattened than those in [$M^{II}Cl_2$(tn)], where the corresponding values are 24.3 (2) and 62.1 (5)° in [$Pt^{II}Cl_2$(tn)], and 22.2 (1) and 62.1 (3)° in [$Pd^{II}Cl_2$(tn)] (Odoko & Okabe, 2006).

The crystal structure is stabilized by N—H⋯O hydrogen bonds (Fig. 2 and Table 1). Two Pd1 complexes related by an inversion centre are connected between N1 and O1^{i} [symmetry code (i) $-x + 1, -y + 1, -z + 1$]. Pd2 complexes are linked between N4 and O6^{v} [symmetry code: (v) $x, -y + \frac{1}{2}, z + \frac{1}{2}$], forming an infinite twisted sheet along the *c* axis. Additional intermolecular N—H⋯O hydrogen bonds between the Pd1 and Pd2 complexes further stabilize the crystal packing.

Experimental

[$Pd^{II}Cl_2$(tn)] (10 mg, 0.04 mol), prepared as described previously (Odoko & Okabe, 2006), was dissolved in dimethyl sulfoxide (DMSO) (0.1 ml) at room temperature and MeOH–water (40% *v*/*v*, 5 ml) was added. To this was added potassium oxalate monohydrate (7.5 mg, 0.04 mol) dissolved in water (0.1 ml) and, after slow evaporation for one month, brown prismatic crystals appeared.

Crystal data

[$Pd(C_2O_4)(C_3H_{10}N_2)$]
$M_r = 268.57$
Monoclinic, $P2_1/c$
$a = 12.88$ (1) Å
$b = 10.49$ (1) Å
$c = 13.59$ (1) Å
$\beta = 116.91$ (3)°
$V = 1637$ (2) Å^3

$Z = 8$
$D_x = 2.180$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.25$ mm^{-1}
$T = 123$ K
Prism, brown
0.10 × 0.10 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.685$, $T_{max} = 0.799$

15689 measured reflections
3755 independent reflections
2832 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.033$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.038$
$S = 0.91$
3755 reflections
218 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0178P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1*A*⋯O1^{i}	0.90	2.21	3.040 (3)	154
N1—H1*B*⋯O6^{ii}	0.90	2.16	3.030 (3)	164
N2—H2*A*⋯O8^{ii}	0.90	2.00	2.899 (4)	176
N2—H2*B*⋯O7	0.90	2.24	3.061 (3)	152
N3—H3*A*⋯O4^{iii}	0.90	2.10	2.997 (3)	172
N3—H3*B*⋯O2^{iv}	0.90	2.22	3.071 (4)	158
N4—H4*A*⋯O4^{iv}	0.90	2.13	2.968 (3)	155
N4—H4*B*⋯O6^{v}	0.90	2.19	3.030 (3)	155

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

All H atoms were located in difference Fourier maps, and placed at 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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