Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

Mamiko Odoko,[a]* Yue Wang[b] and Nobuo Okabe[a]

[a]Faculty of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, Higashiosaka, Osaka 577-8502, Japan, and [b]Laboratory of Inorganic Chemistry, China Pharmaceutical University, Nanjing 210009, People's Republic of China

Correspondence e-mail: odoko@phar.kindai.ac.jp

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.025
wR factor = 0.073
Data-to-parameter ratio = 14.4

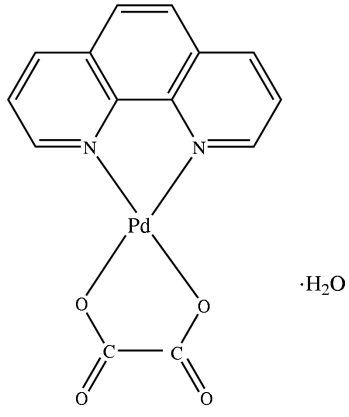
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 9 September 2004
Accepted 27 October 2004
Online 13 November 2004

In the title compound, $[Pd(C_2O_4)(C_{12}H_8N_2)]\cdot H_2O$, the Pd^{II} atom is coordinated by two N atoms of 1,10-phenanthroline and two O atoms of an oxalate ligand, with *cis*-square-planar geometry. The oxalate C—C bonds are elongated compared with oxalic acid. The asymmetric unit contains two complex molecules and two molecules of water.

Comment

The square-planar Pt^{2+} complex cisplatin is a potent anti-cancer drug. However, the side effects of this agent, especially nephrotoxicity (Ozols & Young, 1985), limit its widespread use in high doses. It is necessary to develop new complexes which have fewer side effects than cisplatin. Pd^{2+} analogues have been used as good models for studies of the chemistry of square-planar complexes (Rau & van Eldik, 1996). Pd^{2+} complexes containing 1,10-phenanthroline (phen) have been synthesized and examined for their anticancer abilities (Gao & Liu, 2002; Jin & Ranford, 2000; Liu *et al.*, 1999). For these reasons, we have synthesized new Pd^{2+}–phen complexes and analyzed their crystal structures (Okabe *et al.*, 2003; Muranishi & Okabe, 2004). In the present study, the title compound, (I), has been synthesized and its crystal structure determined.



(I)

The central Pd^{2+} atom of (I) lies in a *cis*-square-planar coordination geometry, formed by two phen N atoms and two oxalate O atoms. The Pd^{2+} atom forms a five-membered ring with each chelating ligand. There are two complex molecules and two molecules of water in the asymmetric unit.

With respect to the structure of the oxalate ligands of (I), the C—C bonds are longer than in uncomplexed oxalic acid molecules [ranging from 1.538 (2) to 1.544 (1) Å; Dam *et al.*, 1983; Stevens & Coppens, 1980; Delaplane & Ibers, 1969; Zobel *et al.*, 1992]. The average length of the single C—O

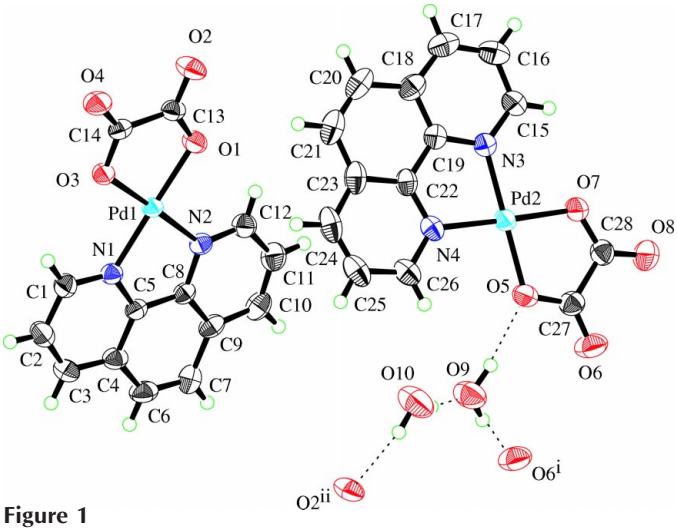


Figure 1
A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines represent O—H···O hydrogen-bonding interactions [symmetry codes: (i) $1-x, -y, 1-z$; (ii) $x, y-1, z$].

bonds which coordinate to Pd^{2+} (1.295 Å) is greater than the lengths of the single bonds of oxalic acid molecules [1.2882 (4)–1.289 (1) Å], and the average C═O bond length in (I) (1.207 Å) is less than the corresponding lengths in free molecules [1.212 (1)–1.2239 (4) Å].

In the packing of (I), π–π interactions exist between symmetry-related phen ligands [C6···C7^{iii} 3.388 (4) and C7···C6^{iii} 3.388 (4) Å; symmetry code: (iii) $1-x, 1-y, -z$] and stabilize the crystal structure. Hydrogen-bonding interactions between water molecules, and between water and phen ligands, also stabilize the crystal structure (Fig. 1 and Table 2).

Experimental

Brown crystals of the title compound were obtained at room temperature by the slow evaporation of a dimethylformamide solution of 1,10-phenanthroline, palladium(II) acetate and oxalic acid dihydrate (molar ratio 1:1:1).

Crystal data

$[Pd(C_2O_4)(C_{12}H_8N_2)]\cdot H_2O$
$M_r = 392.66$
Triclinic, $P\overline{1}$
$a = 7.028$ (7) Å
$b = 11.527$ (15) Å
$c = 17.85$ (2) Å
$\alpha = 72.36$ (4)°
$\beta = 88.96$ (3)°
$\gamma = 75.55$ (4)°
$V = 1332$ (2) Å^3
$Z = 4$
$D_x = 1.958$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11 758 reflections
$\theta = 3.0$–27.5°
$\mu = 1.42$ mm^{-1}
$T = 296.1$ K
Needle, brown
0.50 × 0.10 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.601$, $T_{max} = 0.867$
12 903 measured reflections
5903 independent reflections
5030 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -22 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.073$
$S = 1.13$
5903 reflections
410 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.4089P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.85$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—O1	2.009 (2)	O2—C13	1.217 (4)
Pd1—O3	1.986 (3)	O3—C14	1.295 (3)
Pd1—N1	2.007 (2)	O4—C14	1.208 (3)
Pd1—N2	2.006 (2)	O5—C27	1.304 (3)
Pd2—O5	1.999 (2)	O6—C27	1.200 (4)
Pd2—O7	1.985 (2)	O7—C28	1.295 (4)
Pd2—N3	1.997 (3)	O8—C28	1.201 (3)
Pd2—N4	2.007 (2)	C13—C14	1.569 (4)
O1—C13	1.287 (3)	C27—C28	1.566 (5)
O1—Pd1—O3	83.93 (7)	O5—Pd2—O7	83.80 (9)
O1—Pd1—N1	178.60 (9)	O5—Pd2—N3	179.80 (9)
O1—Pd1—N2	98.12 (8)	O5—Pd2—N4	98.2 (1)
O3—Pd1—N1	95.97 (7)	O7—Pd2—N3	96.23 (9)
O3—Pd1—N2	177.87 (9)	O7—Pd2—N4	177.9 (1)
N1—Pd1—N2	81.96 (8)	N3—Pd2—N4	81.8 (1)

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

D—H···A	D—H	H···A	D···A	D—H···A
O9—H17···O5	0.92	2.00	2.915 (4)	169
O9—H18···O6^{i}	0.91	2.03	2.921 (3)	165
O10—H19···O9	0.92	1.99	2.887 (3)	163
O10—H20···O2^{ii}	0.92	1.97	2.879 (4)	168

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

Water H atoms were located in a difference map and refined as riding in their as-found relative positions, with $U_{iso}(H) = 1.5U_{eq}(O)$. All other H atoms were placed in calculated positions (C—H = 0.93 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *CrystalStructure*.

References

Dam, J., Harkema, S. & Feil, D. (1983). *Acta Cryst.* B**39**, 760–768.
Delaplane, R. G. & Ibers, J. A. (1969). *Acta Cryst.* B**25**, 2423–2437.
Gao, E. J. & Liu, Q. T. (2002). *Huaxue Xuebao*, **60**, 674–680.
Higashi, T. (1995). *ABSCOR.* Rigaku Corporation, Tokyo, Japan.
Jin, V. X. & Ranford, J. D. (2000). *Inorg. Chim. Acta*, **304**, 38–44.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Liu, X., Gao, E. J., Yang, C. Y & Luo, D. F. (1999). *Shenyang Huagong Xueyuan Xuebao*, **13**, 168–171.
Muranishi, Y. & Okabe, N. (2004). *Acta Cryst.* C**60**, m47–m50.
Okabe, N., Muranishi, Y. & Aziyama, T. (2003). *Acta Cryst.* E**59**, m936–m938.

Ozols, R. F. & Young, R. C. (1985). *Semin. Oncol.* **12**, 21–30.
Rau, T. & van Eldik, R. (1996). *Met. Ions Biol. Syst.* **32**, 339–378.
Rigaku/MSC (2004). *PROCESS-AUTO* and *CrystalStructure* (Version 3.6.0). Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Stevens, E. D. & Coppens, P. (1980). *Acta Cryst.* B**36**, 1864–1876.
Zobel, D., Luger, W., Dreissig, W. & Koritsanszky, T. (1992). *Acta Cryst.* B**48**, 837–848.