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[*N*,*N*′-Bis(2-pyridylmethyl)oxamidato]-palladium(II) monohydrate chloroform hemisolvate

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Key indicators

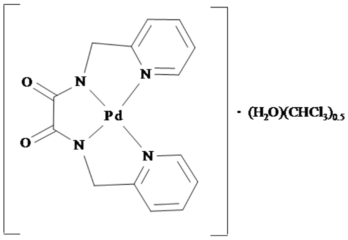
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.024
wR factor = 0.062
Data-to-parameter ratio = 14.4

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

The title compound, $[Pd(C_{14}H_{12}N_4O_2)]\cdot H_2O\cdot 0.5CHCl_3$, features a Pd^{2+} metal center chelated by the four N atoms of the organic ligand *N*,*N*′-bis(2-pyridylmethyl)oxamide. The asymmetric unit is composed of two similar independent $Pd(C_{14}H_{12}N_4O_2)$ molecules, two water molecules and one molecule of $CHCl_3$. Hydrogen bonds between the carbonyl O atoms of the chelating ligand and the water molecules link the molecules into two-dimensional layers parallel to the crystallographic *ac* plane.

Comment

As part of our synthetic study of new mixed organic–inorganic supramolecular compounds, we report here the structure of [*N*,*N*′-bis(2-pyridylmethyl)oxamidato]palladium(II) monohydrate chloroform hemisolvate, (I), the product of the reaction of the versatile organic ligand *N*,*N*′-bis(2-pyridylmethyl)oxamide with Pd^{2+}. We have employed this ligand owing to its capacity to form multiple hydrogen bonds and hence to contribute to the construction of novel supramolecular networks (Schauer *et al.*, 1998; Nguyen *et al.*, 2001; Coe *et al.*, 1997; Lloret *et al.*, 1989; Zhang *et al.*, 2001; Fraser *et al.*, 2002). A previous study of the same metal–ligand system assigned various structural features on the basis of spectroscopic data alone; no structure determination was performed (Laussac & Laurent, 1979). The present study confirms these earlier authors' contention that the ligand coordinates Pd^{2+} in a tetradentate fashion and elucidates further structural details of the properties of this ligand as well as the crystal packing.



(I)

The asymmetric unit (Fig. 1) of (I) consists of two independent molecules of $Pd(C_{14}H_{12}N_4O_2)$, two molecules of water and a molecule of $CHCl_3$. The ligand is a dianion due to the deprotonation of both amide H atoms by acetate during the reaction. The tetracoordinate environment of Pd can be described as a slightly distorted square-planar arrangement. The chelation of the metal center occurs through the N atoms exclusively: two *cis* pyridine N atoms and two *cis* amide N atoms. The Pd—N_{amide} bonds are *ca* 0.13 Å shorter than the Pd—$N_{pyridyl}$ bonds (Table 1), but all of them are consistent with the values found in the literature.

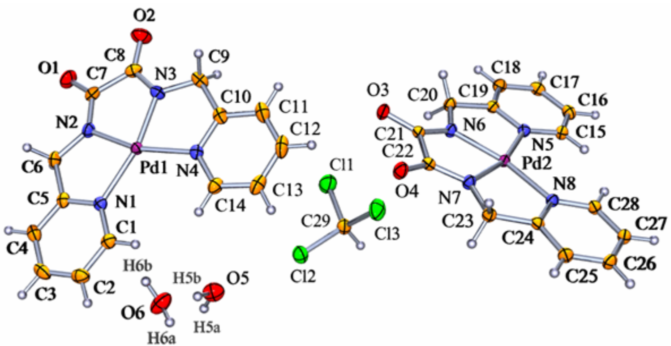


Figure 1
View of the asymmetric unit, with 50% probability displacement ellipsoids.

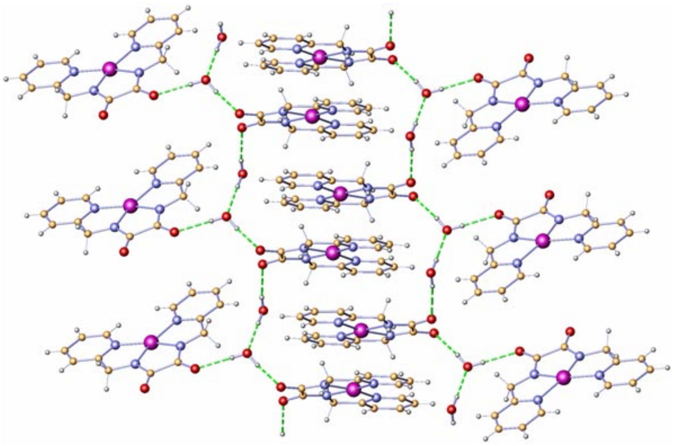


Figure 2
Two interdigitated hydrogen-bonded chains. View perpendicular to the *ac* plane (the chloroform molecules have been omitted for clarity).

Both Pd($C_{14}H_{12}N_4O_2$) molecules are almost perfectly planar. The mean deviation from the least-squares plane for the Pd1-containing molecule is 0.070 Å, while in the case of the Pd2-containing molecule, the mean deviation is 0.068 Å. Small values for the dihedral angles between the pyridyl rings [5.06 (10) and 4.79 (09)°, respectively] also confirm the planarity of the molecules. The two independent Pd-containing molecules in the asymmetric unit are not coplanar but form a dihedral angle of 47.94 (1)°.

Two independent uncoordinated water molecules (O5 and O6) present in the structure are involved in multiple intermolecular O—H$\cdots$O hydrogen bonds (Table 2). The water molecules are located between rows of Pd1 and Pd2 complexes and connect them into one-dimensional interdigitated chains, running along the crystallographic *a* axis (Fig. 2). Every O6 water molecule bridges a pair of (Pd1 and Pd2) complexes belonging to two adjacent rows, through the water H atoms and carbonyl atoms O2 (Pd1) and O3 (Pd2). Atom O6 also acts as acceptor for an O5 H atom, forming a bridging H_4O_2 unit. The remaining H atom on O5 is connected to O1 of a Pd1 complex that is located two molecules above the first Pd1 complex. Hence the linkage between Pd1 complexes is accomplished through a bridge of two hydrogen-bonded water molecules which connect the O1 and O2 carbonyl O atoms of alternate complexes in one row. The chloroform intercalated in the structure does not participate in the hydrogen-bonding network.

Experimental

The ligand *N*,*N*′-bis(2-pyridylmethyl)oxamide was prepared according to the literature method of Schauer *et al.* (1998). A methylene chloride solution (4 ml) of Pd(Ac)$_2$ (22.4 mg, 0.10 mmol) was slowly layered on top of a chloroform (6 ml) solution of *N*,*N*′-bis(2-pyridylmethyl)oxamide (27.0 mg, 0.10 mmol). Yellow crystals grew at the interface of the two solutions after 5 d.

Crystal data

[Pd($C_{14}H_{12}N_4O_2$)]·H_2O·0.5$CHCl_3$
M_r = 452.38
Triclinic, $P\overline{1}$
a = 7.3145 (5) Å
b = 10.2252 (6) Å
c = 21.7212 (14) Å
α = 80.233 (2)°
β = 89.126 (2)°
γ = 82.418 (2)°
V = 1586.99 (18) Å^3
Z = 4
D_x = 1.893 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6121 reflections
θ = 2.4–26.4°
μ = 1.44 mm^{-1}
T = 150 (2) K
Irregular, yellow
0.32 × 0.22 × 0.16 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min}$ = 0.649, $T_{\max}$ = 0.794
14485 measured reflections
6448 independent reflections
6116 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.020
$\theta_{\max}$ = 26.4°
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.062
S = 1.06
6448 reflections
449 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 1.3475P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.54 e Å^{-3}
$\Delta\rho_{\min}$ = −0.59 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—N3	1.9402 (19)	Pd2—N6	1.9352 (18)
Pd1—N2	1.9420 (19)	Pd2—N7	1.9420 (18)
Pd1—N4	2.0640 (19)	Pd2—N8	2.0648 (18)
Pd1—N1	2.0734 (19)	Pd2—N5	2.0741 (18)
N3—Pd1—N2	82.09 (8)	N6—Pd2—N7	82.19 (8)
N3—Pd1—N4	81.72 (8)	N6—Pd2—N8	164.04 (8)
N2—Pd1—N4	163.65 (8)	N7—Pd2—N8	81.85 (7)
N3—Pd1—N1	163.68 (8)	N6—Pd2—N5	81.49 (7)
N2—Pd1—N1	81.70 (8)	N7—Pd2—N5	163.67 (8)
N4—Pd1—N1	114.40 (8)	N8—Pd2—N5	114.46 (7)

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
O5—H5$A$$\cdots$O1$^{\rm i}$	0.841 (18)	2.046 (19)	2.883 (3)	173 (4)
O5—H5$B$$\cdots$O6	0.844 (18)	1.941 (18)	2.784 (3)	177 (4)
O6—H6$A$$\cdots$O3$^{\rm ii}$	0.824 (14)	2.022 (15)	2.845 (3)	176 (3)
O6—H6$B$$\cdots$O2$^{\rm iii}$	0.835 (14)	2.25 (2)	2.999 (3)	150 (4)

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

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H atoms attached to C atoms were treated as riding atoms, with C—H = 0.95, 0.99 or 1.00 Å for alkene, methylene and chloroform H atoms, respectively, and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. Water H atoms were located by difference synthesis and refined isotropically subject to distance restraints [O—H = 0.84 (2) Å and H—H = 1.50 (2) Å].

Data collection: *SMART-NT* (Bruker, 1999); cell refinement: *SAINT-Plus-NT* (Bruker, 1999); data reduction: SAINT-*Plus-NT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *ATOMS* (Dowty, 2001); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997*b*).

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