Crystal structure of dichloro(2-pyridinealdoxime-κ^2N,N')palladium(II), $PdCl_2(C_6H_6N_2O)$

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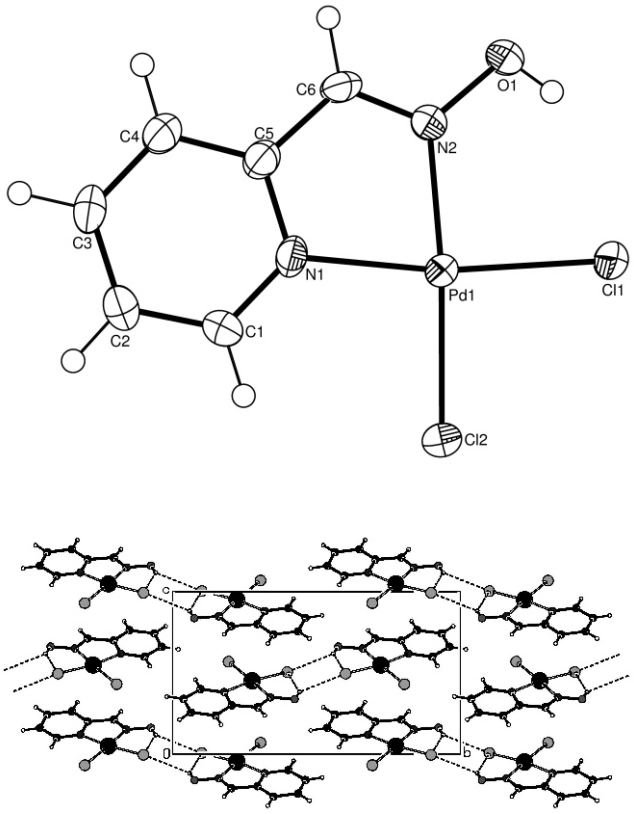

Abstract

$C_6H_6Cl_2N_2OPd$, monoclinic, $P12_1/c1$ (no. 14), a = 6.1726(7) Å, b = 15.948(2) Å, c = 9.115(1) Å, β = 100.506(2)°, V = 882.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.099, T = 200 K.

Source of material

To a solution of Na_2PdCl_4 (0.2942 g, 1.000 mmol) in H_2O (20 ml) was added *syn*-2-pyridinealdoxime (0.2444 g, 2.001 mmol) and stirred for 3 h at room temperature. The formed precipitate was separated by filtration, washed with H_2O and acetone, and dried at 50 °C to give a yellow powder (0.2302 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from an acetone solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å and U_{iso}(H) = 1.2 U_{eq}(C). The hydroxy H atom was located from Fourier difference maps and refined isotropically: d(O—H) = 0.79(6) Å. The highest peak (1.54 e Å^{-3}) and the deepest hole (–1.37 e Å^{-3}) in the difference Fourier map are located 1.25 Å and 0.80 Å from the atoms N1 and Pd1, respectively.

Discussion

In the title crystal structure, the central Pd(II) ion has a distorted square-planar coordination defined by two N atoms of the chelating 2-pyridinealdoxime ligand and two Cl^- anions (figure, top). The compound crystallized in the monoclinic space group $P2_1/c$, whereas the previously reported analogous Hg(II) complex $[HgCl_2(C_6H_6N_2O)]$ crystallized in the triclinic space group $P\bar{1}$ [1]. The tight N1–Pd1–N2 chelate angle of 79.7(2)° and the weak Cl–Cl repelling with ∠Cl1–Pd1–Cl2 = 93.27(5)° contribute to the distortion of the square-planar structure. The *trans* bond angles are ∠Cl1–Pd1–N1 = 170.9(1)° and ∠Cl2–Pd1–N2 = 175.0(1)°. The bond lengths d(Pd—N) and d(Pd—Cl) are almost equivalent, respectively (d(Pd1—$N1_{pyridine}$) = 2.034(4) Å and d(Pd1—$N2_{oxime}$) = 2.002(4) Å; d(Pd—Cl) = 2.292(1) Å and 2.288(1) Å).

In the crystal structure, the complexes are stacked in columns along [100]. When viewed down the b axis, the successive complexes are stacked in an opposite manner. In the columns, weak intermolecular π–π interactions between adjacent pyridine rings are present. For Cg1 (the centroid of ring N1-C5) and Cg1^1 (symmetry code i: 1–x,–y,1–z), the centroid-centroid distance is 5.470(3) Å, the planes are parallel and shifted by 3.975 Å. In addition, the complex reveals intramolecular O–H···Cl hydrogen bonding with d(O···Cl) = 3.091(4) Å, thus forming a nearly planar five-membered ring, and pairs of complex molecules are assembled by intermolecular O–H···Cl hydrogen bonds with d(O···Cl) = 3.202(5) Å (figure, bottom).

Table 1. Data collection and handling.

Crystal:	yellow stick, size 0.07 × 0.08 × 0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	26.57 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6412, 2169
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1465
$N(param)_{refined}$:	113
Programs:	SHELXS-97, SHELXL-97 [2], ORTEP-3 [3], PLATON [4]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1O)	4*e*	0.12(1)	0.441(4)	0.382(8)	0.05(2)
H(1)	4*e*	0.0297	0.0793	0.4573	0.045
H(2)	4*e*	0.2333	–0.0199	0.3546	0.052
H(3)	4*e*	0.4915	0.0242	0.2124	0.047
H(4)	4*e*	0.5444	0.1687	0.1810	0.041
H(6)	4*e*	0.4417	0.3204	0.2380	0.036

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	4*e*	–0.00742(7)	0.27638(3)	0.45139(5)	0.0254(2)	0.0221(2)	0.0308(3)	0.0002(2)	0.0122(2)	–0.0005(2)
Cl(1)	4*e*	–0.1734(2)	0.39831(9)	0.5049(2)	0.0388(8)	0.0247(8)	0.056(1)	0.0025(6)	0.0264(7)	–0.0023(7)
Cl(2)	4*e*	–0.2273(2)	0.19458(9)	0.5695(2)	0.0329(8)	0.0295(8)	0.0402(8)	–0.0009(6)	0.0181(7)	0.0037(6)
O(1)	4*e*	0.2148(7)	0.4243(3)	0.3381(6)	0.046(3)	0.020(2)	0.072(3)	–0.006(2)	0.034(3)	–0.001(2)
N(1)	4*e*	0.1622(7)	0.1794(3)	0.3813(5)	0.025(2)	0.026(3)	0.033(3)	0.005(2)	0.008(2)	–0.006(2)
N(2)	4*e*	0.2030(7)	0.3394(3)	0.3492(5)	0.030(3)	0.022(3)	0.040(3)	–0.002(2)	0.013(2)	–0.002(2)
C(1)	4*e*	0.1352(9)	0.0975(4)	0.4002(7)	0.037(3)	0.024(3)	0.056(4)	–0.004(2)	0.020(3)	0.002(3)
C(2)	4*e*	0.256(1)	0.0382(4)	0.3393(7)	0.058(4)	0.023(3)	0.056(4)	0.004(3)	0.026(4)	–0.001(3)
C(3)	4*e*	0.4082(9)	0.0641(4)	0.2561(7)	0.040(4)	0.031(4)	0.051(4)	0.008(3)	0.018(3)	–0.008(3)
C(4)	4*e*	0.4388(9)	0.1494(4)	0.2371(7)	0.029(3)	0.034(3)	0.042(4)	0.000(2)	0.015(3)	–0.004(3)
C(5)	4*e*	0.3144(9)	0.2053(3)	0.3003(6)	0.026(3)	0.031(3)	0.032(3)	0.000(2)	0.009(3)	–0.004(2)
C(6)	4*e*	0.3358(9)	0.2955(3)	0.2881(6)	0.028(3)	0.031(3)	0.036(3)	–0.007(2)	0.016(3)	–0.001(3)

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