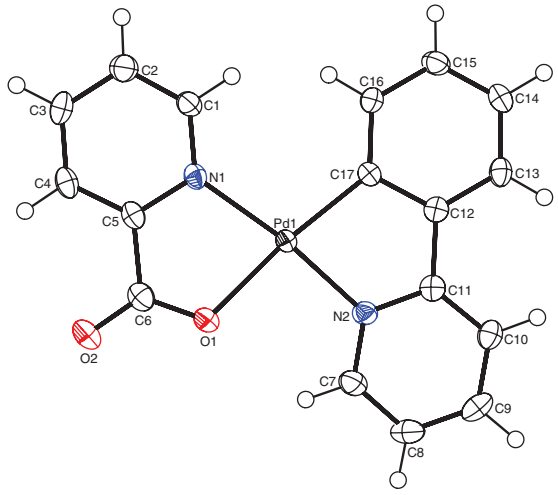
Kwang Ha*

Crystal structure of (pyridine-2-carboxylato-κ²*N*,*O*)-[2-(2-pyridyl)phenyl-κ²*N*,*C*¹]palladium(II), $C_{17}H_{12}N_2O_2Pd$



https://doi.org/10.1515/ncrs-2019-0423
Received June 18, 2019; accepted July 12, 2019; available online July 25, 2019

Abstract

$C_{17}H_{12}N_2O_2Pd$, orthorhombic, $Pna2_1$ (no. 33), $a = 20.6775(12)$ Å, $b = 11.7539(7)$ Å, $c = 5.4868(3)$ Å, $V = 1333.52(13)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0154$, $wR_{ref}(F^2) = 0.0373$, $T = 223(2)$ K.

CCDC no.: 1939858

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

To a solution of bis(μ₂-acetato)bis[2-(2-pyridyl)phenyl] dipalladium(II) [5] (0.1984 g, 0.310 mmol) in acetone (30 mL) was added pyridine-2-carboxylic acid (0.0768 g, 0.624 mmol) and stirred for 3 h at room temperature. The formed precipitate was separated by filtration, washed with acetone and MeOH, and dried at 50 °C, to give a pale yellow powder (0.2326 g). Crystals were obtained by slow evaporation from a dimethyl sulfoxide (DMSO) solution at 90 °C.

***Corresponding author: Kwang Ha,** Chonnam National University, School of Chemical Engineering, Research Institute of Catalysis, Gwangju 61186, Republic of Korea, e-mail: hakwang@chonnam.ac.kr

Table 1: Data collection and handling.

Crystal:	Yellow stick
Size:	0.24 × 0.16 × 0.08 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.40 mm^{-1}
Diffractometer, scan mode:	PHOTON 100 CMOS, φ and ω
θ_{max}, completeness:	26.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	35546, 2632, 0.039
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2504
$N(param)_{refined}$:	199
Programs:	Bruker [1], SHELX [2], ORTEP-III [3], PLATON [4]

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.94 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ with the help of the SHELXL program (AFIX 43 option) [2]. The highest peak (0.31 e Å^{-3}) and the deepest hole (−0.19 e Å^{-3}) in the difference Fourier map are located 1.07 Å and 1.21 Å from the atoms O1 and H8, respectively.

Comment

This contribution is part of my continuing interest in the structural chemistry of palladium 2-phenylpyridine (ppy-H) complexes [6–8].

In the title crystal structure, Pd^{2+} ion has a slightly distorted square-planar coordination defined by one N atom and one O atom from the pyridine-2-carboxylate (pic) ligand and one N atom and one C atom from the ortho-metalated anionic 2-(2-pyridyl)phenyl ligand, similar to a related Pt complex [9]. The N atoms are disposed in the *trans* position. The main contributions to the distortion are the tight N—Pd—O/C chelate angles (<N1—Pd1—O1 = 79.73(10)° and <N2—Pd1—C17 = 80.99(12)°). The Pd—C, Pd—N and Pd—O bond lengths are almost equal (Pd—C: 2.002(3) Å; Pd—N 2.008(3) and 2.075(3) Å; Pd—O: 2.089(2) Å). The complex is nearly

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.12211(2)	0.21429(2)	0.57143(9)	0.01919(7)
O1	0.11682(11)	0.3681(2)	0.3816(5)	0.0298(6)
O2	0.15704(11)	0.45801(18)	0.0592(7)	0.0372(5)
N1	0.19748(13)	0.1927(2)	0.3261(5)	0.0207(6)
N2	0.04798(12)	0.2547(2)	0.7914(5)	0.0220(6)
C1	0.24097(15)	0.1085(3)	0.3061(7)	0.0250(7)
H1	0.2421	0.0524	0.4280	0.030*
C2	0.28395(16)	0.1004(3)	0.1159(7)	0.0285(9)
H2	0.3136	0.0399	0.1085	0.034*
C3	0.28310(17)	0.1822(3)	−0.0637(7)	0.0275(8)
H3	0.3108	0.1770	−0.1992	0.033*
C4	0.24051(18)	0.2721(3)	−0.0397(7)	0.0245(7)
H4	0.2400	0.3306	−0.1566	0.029*
C5	0.19899(17)	0.2761(3)	0.1547(6)	0.0206(7)
C6	0.15395(15)	0.3763(3)	0.1957(6)	0.0252(7)
C7	0.01218(17)	0.3487(3)	0.7632(7)	0.0296(8)
H7	0.0201	0.3960	0.6283	0.036*
C8	−0.03583(17)	0.3783(3)	0.9252(7)	0.0317(8)
H8	−0.0611	0.4437	0.9001	0.038*
C9	−0.04577(16)	0.3093(3)	1.1258(6)	0.0314(10)
H9	−0.0769	0.3292	1.2431	0.038*
C10	−0.00992(17)	0.2112(3)	1.1533(6)	0.0260(8)
H10	−0.0173	0.1627	1.2866	0.031*
C11	0.03708(16)	0.1848(3)	0.9821(6)	0.0207(7)
C12	0.07794(15)	0.0825(3)	0.9784(5)	0.0201(7)
C13	0.07357(15)	−0.0025(3)	1.1536(6)	0.0240(7)
H13	0.0448	0.0058	1.2851	0.029*
C14	0.11138(16)	−0.0992(3)	1.1352(6)	0.0255(8)
H14	0.1094	−0.1561	1.2553	0.031*
C15	0.15196(18)	−0.1106(3)	0.9379(7)	0.0271(8)
H15	0.1770	−0.1768	0.9216	0.033*
C16	0.15641(16)	−0.0259(3)	0.7628(6)	0.0251(7)
H16	0.1842	−0.0365	0.6292	0.030*
C17	0.12098(14)	0.0742(3)	0.7791(6)	0.0187(6)

planar and the two anionic ligands are almost parallel: the dihedral angle between the nearly planar pic and ppy chelating ligands (maximum deviations = 0.094(2) and 0.079(3) Å, respectively) is 0.9(1)°. The pyridine and phenyl rings of the ppy ligand are slightly bent: the dihedral angle between the ring planes is 5.6(2)°. The title complex displays weak intra- and intermolecular C—H···O hydrogen bonding with d(C···O) = 3.083(4)–3.428(4) Å, forming a three-dimensional network. In the crystal, the complexes are stacked in columns along [001]. In the columns, several intermolecular π-π stacking interactions between adjacent six-membered rings are present. For Cg1 (the centroid of ring N1—C5) and Cg2^i (the centroid of ring C12—C17; symmetry code i: x, y, z − 1), the centroid-centroid distance is 3.6479(2) Å [4].

Acknowledgements: This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (grant number: 2018R1D1A1B07050550). The author thanks the KBSI, Seoul Center, for the X-ray data collection.

References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2009).
2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
3. Farrugia, L. J.: ORTEP-3 for Windows-a version of ORTEP-III with a graphical user interface (GUI). J. Appl. Crystallogr. **30** (1997) 565.
4. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7–13.
5. Aiello, I.; Crispini, A.; Ghedini, M.; La Deda, M.; Barigelletti, F.: Synthesis and characterization of a homologous series of mononuclear palladium complexes containing different cyclometalated ligands. Inorg. Chim. Acta **308** (2000) 121–128.
6. Ha, K.: Crystal structure of dichlorobis(2-phenylpyridine-κ*N*)palladium(II), $PdCl_2(C_{11}H_9N)_2$. Z. Kristallogr. NCS **226** (2011) 501–502.
7. Ha, K.: *trans*-Diiodidobis(2-phenylpyridine-κ*N*)palladium(II). Acta Crystallogr. **E68** (2012) m102.
8. Ha, K.: Crystal structure of di(μ_2-chlorido)bis[2-(2-pyridyl) phenyl-$\kappa^2 N,C^1$]dipalladium(II), $C_{22}H_{16}Cl_2N_2Pd_2$. Z. Kristallogr. NCS **231** (2016) 331–332.
9. Ebina, M.; Kobayashi, A.; Ogawa, T.; Yoshida, M.; Kato, M.: Impact of a carboxyl group on a cyclometalated ligand: hydrogen-bond- and coordination-driven self-assembly of a luminescent platinum(II) complex. Inorg. Chem. **54** (2015) 8878–8880.