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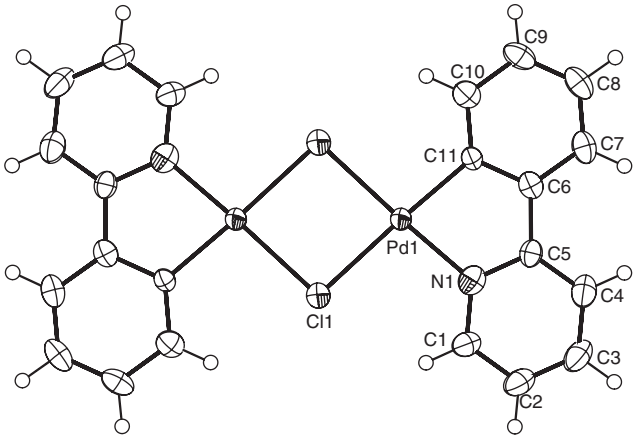
Kwang Ha*

Crystal structure of di(μ$_2$-chlorido)bis[2-(2-pyridyl)phenyl-κ^2*N*,*C*^{1}]dipalladium(II), $C_{22}H_{16}Cl_2N_2Pd_2$



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Abstract

$C_{22}H_{16}Cl_2N_2Pd_2$, monoclinic, $P2_1/c$ (no. 14), $a = 7.2249(6)$ Å, $b = 17.0538(14)$ Å, $c = 8.4291(7)$ Å, $\beta = 112.211(2)°$, $V = 961.50(14)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0217$, $wR_{ref}(F^2) = 0.0496$, $T = 200(2)$ K.

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The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow, block, size 0.09×0.20×0.36 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	21.59 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ and ω scans
$2\theta_{max}$:	52.07°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5610, 1847
$N(param)_{refined}$:	127
Programs:	SHELX [6], WinGX [7], PLATON [8]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	0.2297	0.3293	0.2095	0.042
H(2)	4*e*	0.0660	0.2521	−0.0314	0.049
H(3)	4*e*	−0.0317	0.3064	−0.3046	0.055
H(4)	4*e*	0.0400	0.4378	−0.3365	0.048
H(7)	4*e*	0.1418	0.5646	−0.3391	0.045
H(8)	4*e*	0.2587	0.6930	−0.3158	0.048
H(9)	4*e*	0.4285	0.7474	−0.0436	0.045
H(10)	4*e*	0.4847	0.6718	0.2008	0.041

Source of material

To a solution of 2-phenylpyridine (ppyH; 0.3658 g, 2.357 mmol) and 2,6-pyridinedicarboxylic acid (0.1745 g, 1.044 mmol) in EtOH (30 mL)/H_2O (20 mL) was added Na_2PdCl_4 (0.3047 g, 1.036 mmol) and refluxed for 3 h. The formed precipitate was separated by filtration, washed with H_2O and acetone, and dried at 50 °C, to give a yellow powder (0.2545 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from an *N*,*N*-dimethylformamide solution at 60 °C.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The structure shows a 1:1 disorder in the sites N1 and C11, (not shown in the figure).

Discussion

This contribution is part of my continuing interest in the structural chemistry of palladium 2-phenylpyridine (ppyH) complexes [1, 2]. The title complex $[Pd_2(\mu\text{-}Cl)_2(ppy)_2]$ was

***Corresponding author: Kwang Ha,** Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500–757, Republic of Korea, e-mail: hakwang@chonnam.ac.kr

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

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	4*e*	0.38634(3)	0.50092(2)	0.27423(2)	0.0333(1)	0.0223(1)	0.0210(1)	0.00044(9)	0.00955(9)	−0.00016(8)
Cl(1)	4*e*	0.4173(1)	0.41079(5)	0.50327(9)	0.0725(6)	0.0331(4)	0.0264(4)	−0.0101(4)	0.0113(4)	0.0002(3)
N(1)[a]	4*e*	0.2342(4)	0.4287(2)	0.0812(3)	0.026(1)	0.030(2)	0.029(1)	0.002(1)	0.011(1)	−0.004(1)
C(11A)[a]	4*e*	0.2342(4)	0.4287(2)	0.0812(3)	0.026(1)	0.030(2)	0.029(1)	0.002(1)	0.011(1)	−0.004(1)
C(1)	4*e*	0.1917(4)	0.3515(2)	0.0984(4)	0.036(2)	0.033(2)	0.039(2)	−0.003(1)	0.017(1)	−0.005(1)
C(2)	4*e*	0.0938(5)	0.3056(2)	−0.0448(4)	0.043(2)	0.037(2)	0.048(2)	−0.012(1)	0.023(2)	−0.013(2)
C(3)	4*e*	0.0369(5)	0.3376(2)	−0.2065(4)	0.043(2)	0.055(2)	0.040(2)	−0.019(2)	0.018(2)	−0.019(2)
C(4)	4*e*	0.0799(4)	0.4154(2)	−0.2253(4)	0.037(2)	0.055(2)	0.027(2)	−0.006(2)	0.012(1)	−0.006(2)
C(5)	4*e*	0.1818(4)	0.4606(2)	−0.0813(3)	0.023(1)	0.036(2)	0.028(2)	0.002(1)	0.010(1)	−0.004(1)
C(6)	4*e*	0.2428(4)	0.5422(2)	−0.0827(3)	0.027(1)	0.033(2)	0.026(2)	0.007(1)	0.012(1)	0.003(1)
C(7)	4*e*	0.2114(4)	0.5868(2)	−0.2292(4)	0.034(2)	0.049(2)	0.028(2)	0.006(2)	0.010(1)	0.007(1)
C(8)	4*e*	0.2804(4)	0.6628(2)	−0.2157(4)	0.039(2)	0.046(2)	0.037(2)	0.012(2)	0.017(1)	0.019(2)
C(9)	4*e*	0.3818(5)	0.6948(2)	−0.0544(4)	0.042(2)	0.030(2)	0.048(2)	0.010(1)	0.025(2)	0.013(1)
C(10)	4*e*	0.4147(4)	0.6498(2)	0.0907(4)	0.038(2)	0.029(2)	0.038(2)	0.005(1)	0.019(1)	0.001(1)
C(11)[a]	4*e*	0.3473(4)	0.5738(2)	0.0774(3)	0.031(1)	0.028(1)	0.029(1)	0.006(1)	0.013(1)	0.002(1)
N(1A)[a]	4*e*	0.3473(4)	0.5738(2)	0.0774(3)	0.031(1)	0.028(1)	0.029(1)	0.006(1)	0.013(1)	0.002(1)

[a]Disordered, occupancy factor: 0.5.

unexpectedly obtained from the reaction of Na_2PdCl_4, 2,6-pyridinedicarboxylic acid and ppyH, and has a *trans* chlorido-bridged dimeric structure, whereas the *cis* analogue was prepared by the reaction of 2-phenylpyridine with Na_2PdCl_4 or Li_2PdCl_4, and its crystal structure was reported previously [3–5]. Both *cis*- and *trans*-complexes crystallize in the monoclinic space group $P2_1/c$, but the latter has an inversion center in the middle of the molecule, and therefore the asymmetric unit contains one half of the complex. In the title crystal structure, each Pd(II) ion has a slightly distorted square-planar coordination defined by one N atom and one C atom from the ortho-metalated anionic 2-(2-pyridyl)phenyl ligand and two bridging chlorido ligands. The main contribution to the distortion is the tight N1—Pd1—C11 chelate angle of 81.27(12)°. The complex is nearly planar: the Pd_2Cl_2 moiety is exactly plane, and the dihedral angle between the moiety and the nearly planar chelating ligand (maximum deviation = 0.053(3) Å) is 4.30(5)°. The pyridine and phenyl rings are almost parallel: the dihedral angle between the ring planes is 3.4(1)°. In the complex, the Pd···Pd distance is 3.5298(4) Å, and Pd—C and Pd—N bond lengths are almost equal (2.001(3) Å and 2.006(3) Å). In the crystal, the molecules are stacked in columns along [100]. 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 C6—C11; symmetry code i: 1−*x*, 1−*y*, −*z*), the centroid-centroid distance is 3.704(2) Å.

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References

1. 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.
2. Ha, K.: *trans*-Diiodidobis(2-phenylpyridine-κ*N*)palladium(II). Acta Crystallogr. **E68** (2012) m102.
3. Constable, E. C.; Thompson, A. M. W. C.; Leese, T. A.; Reese, D. G. J.; Tocher, D. A.: Cyclometallation reactions of 2-phenylpyridine; crystal and molecular structure of (2-{2-pyridyl} phenyl)palladium(II) tetramer and (2-{2-pyridyl} phenyl)mercury(II) tetramer. Inorg. Chim. Acta **182** (1991) 93–100.
4. Klement, U.: Crystal structure of di-μ-chloro-bis(2-phenylpyridinao-C2,N′-palladium(II)), $((C_{11}H_8N)PdCl)_2$. Z. Kristallogr. **208** (1993) 299–301.
5. Bercaw, J. E.; Durrell, A. C.; Gray, H. B.; Green, J. C.; Hazari, N.; Labinger, J. A.; Winkler, J. R.: Electronic structures of Pd^{II} dimers. Inorg. Chem. **49** (2010) 1801–1810.
6. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
7. Farrugia, L. J.: ORTEP-3 for Windows – a version of ORTEP-III with a Graphical User Interface. J. Appl. Crystallogr. **30** (1997) 565.
8. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7–13.