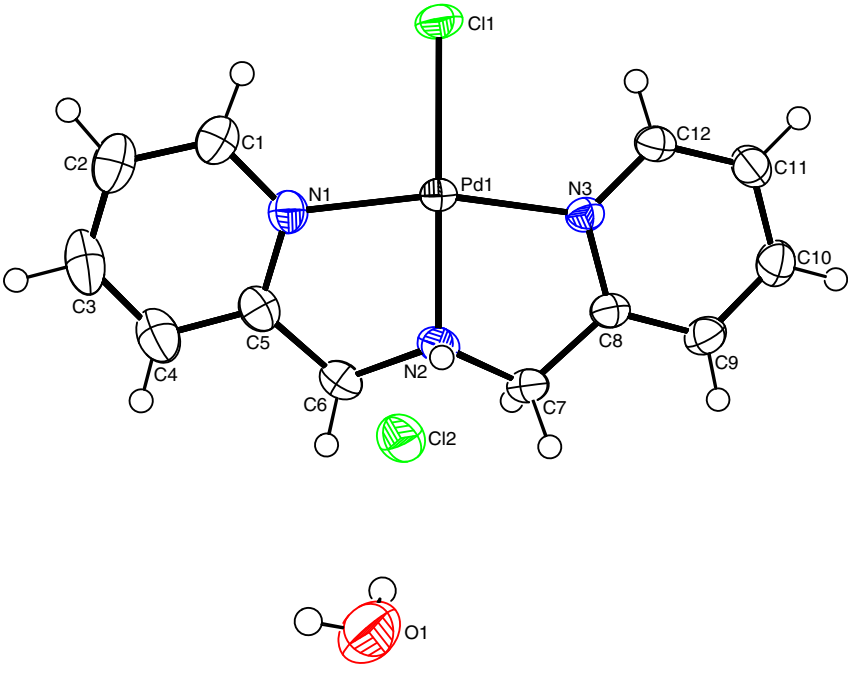
Kwang Ha*

Redetermination of crystal structure of [bis(pyridin-2-ylmethyl)amine-κ^3N,N',N''] chloridopalladium(II) chloride monohydrate



https://doi.org/10.1515/ncrs-2023-0037
Received January 25, 2023; accepted February 6, 2023;
published online February 20, 2023

Abstract

$C_{12}H_{13}Cl_2N_3Pd{\cdot}H_2O$, triclinic, $P\bar{1}$ (no. 2), a = 7.0698(4) Å, b = 8.5546(6) Å, c = 12.8539(9) Å, α = 106.541(2)°, β = 102.510(2)°, γ = 91.572(2)°, V = 724.23(8) Å^3, Z = 2, $R_{gt}(F)$ = 0.0199, $wR_{ref}(F^2)$ = 0.0438, T = 223 K.

CCDC no.: 2240090

The title crystal 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.

Table 1: Data collection and handling.

Crystal:	Yellow rod
Size:	0.60 × 0.60 × 0.06 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.64 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	24317, 3612, 0.036
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3354
$N(param)_{refined}$:	232
Programs:	Bruker [1], SHELX [2], ORTEP-III [3], PLATON [4]

1 Source of materials

To a solution of bis(pyridin-2-ylmethyl)amine (0.1274 g, 0.639 mmol) in acetone (10 mL) was added Na_2PdCl_4 (0.1921 g, 0.653 mmol) in H_2O (5 mL) and stirred for 2 h at room temperature. The formed precipitate was separated by filtration, washed with acetone, and dried at 60 °C, to give a yellow powder (0.1448 g). Crystals were obtained by slow evaporation from MeOH at room temperature.

***Corresponding author: Kwang Ha**, School of Chemical Engineering, Research Institute of Catalysis, Chonnam National University, Gwangju 61186, Republic of Korea, E-mail: hakwang@chonnam.ac.kr.
https://orcid.org/0000-0003-4628-2296

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.18329 (2)	0.47625 (2)	0.41472 (2)	0.02368 (5)
Cl1	0.22208 (7)	0.26532 (6)	0.49396 (4)	0.03540 (11)
Cl2	0.45300 (8)	0.62868 (6)	0.18328 (4)	0.03726 (11)
O1	0.6865 (3)	0.7159 (3)	0.0123 (2)	0.0569 (5)
H1A	0.628 (4)	0.710 (4)	0.056 (3)	0.063 (10)*
H1B	0.660 (5)	0.642 (4)	−0.037 (3)	0.065 (10)*
N1	0.0347 (2)	0.3392 (2)	0.26184 (13)	0.0300 (3)
N2	0.1702 (3)	0.6540 (2)	0.34080 (14)	0.0310 (3)
H2N	0.285 (4)	0.640 (3)	0.309 (2)	0.060 (8)*
N3	0.3083 (2)	0.65980 (18)	0.55242 (12)	0.0249 (3)
C1	0.0056 (3)	0.1748 (3)	0.22164 (19)	0.0372 (5)
H1	0.057 (3)	0.118 (3)	0.2725 (19)	0.039 (6)*
C2	−0.0999 (3)	0.0969 (3)	0.1144 (2)	0.0460 (6)
H2	−0.120 (4)	−0.015 (3)	0.093 (2)	0.061 (8)*
C3	−0.1731 (4)	0.1899 (3)	0.0468 (2)	0.0525 (6)
H3	−0.243 (4)	0.141 (3)	−0.026 (2)	0.061 (8)*
C4	−0.1417 (3)	0.3587 (3)	0.08649 (19)	0.0453 (5)
H4	−0.184 (4)	0.423 (3)	0.043 (2)	0.054 (8)*
C5	−0.0383 (3)	0.4317 (3)	0.19513 (16)	0.0325 (4)
C6	−0.0078 (3)	0.6137 (3)	0.24837 (18)	0.0346 (4)
H6A	0.002 (3)	0.668 (3)	0.196 (2)	0.043 (6)*
H6B	−0.116 (4)	0.649 (3)	0.280 (2)	0.048 (7)*
C7	0.1923 (3)	0.8166 (2)	0.42369 (17)	0.0310 (4)
H7A	0.064 (3)	0.853 (3)	0.4302 (17)	0.032 (6)*
H7B	0.252 (3)	0.898 (3)	0.4028 (18)	0.034 (6)*
C8	0.2972 (3)	0.8102 (2)	0.53739 (16)	0.0261 (4)
C9	0.3725 (3)	0.9496 (2)	0.62468 (18)	0.0341 (4)
H9	0.362 (3)	1.047 (3)	0.6107 (18)	0.034 (6)*
C10	0.4606 (3)	0.9356 (3)	0.72816 (18)	0.0386 (5)
H10	0.504 (3)	1.027 (3)	0.786 (2)	0.047 (7)*
C11	0.4739 (3)	0.7821 (3)	0.74253 (17)	0.0346 (4)
H11	0.530 (3)	0.774 (3)	0.813 (2)	0.042 (6)*
C12	0.3971 (3)	0.6467 (2)	0.65318 (16)	0.0285 (4)
H12	0.402 (3)	0.546 (3)	0.6594 (18)	0.034 (6)*

2 Experimental details

All H atoms were located from Fourier difference maps and refined isotropically: C–H = 0.89(2)–0.98(2) Å, N–H = 0.98(3) Å and O–H = 0.74(3), 0.78(3) Å.

3 Comment

The crystal structures of the related bis(pyridin-2-ylmethyl) amine (bpa) metal complexes [Cu(bpa) (NCS) (ClO_4)] [5], [Re(bpa)($CO)_3$]Br·0.5H_2O [6] and [Fe(bpa)Cl_3] [7] have been determined previously. The X-ray structure analysis of the title compound was previously carried out by Bugarčić et al. [8], but they did not give a complete description of the hydrogen atoms. The structure presented herein is essentially the same as the published structure, however, the geometric properties and parameters here presented are slightly different and more accurate, respectively.

The title compound consists of a cationic Pd(II) complex [Pd(bpa)Cl]$^+$, a Cl^- anion and one water molecule. In the complex, the central Pd^{2+} cation is four-coordinated in a distorted square-planar coordination geometry defined by three N atoms of the tridentate bpa ligand and one anionic Cl ligand. The tight N–Pd–N chelating angles of <N1–Pd1–N2 = 82.88(7)° and <N2–Pd1–N3 = 83.35(6)° contribute the distortion of the square-plane. The three Pd-N bond lengths are almost equal with d(Pd–N) = 2.0037(16)–2.0163(16) Å. In the crystal, the complex is nearly planar: the dihedral angles between the pyridine ring and the least-squares plane of the $PdClN_3$ unit [maximum deviation = 0.0955(9) Å] are 10.85(6)° (ring N1–C5) and 7.23(5)° (ring N3–C12). The dihedral angle between the pyridine ring planes is 4.54(7)°. The Pd-complex, the anion and the solvent molecule are connected by O/N–H···Cl and C–H···Cl/O hydrogen bonds with distances of 3.110(2)–3.635(2) Å between the donor and acceptor atoms [4]. The cationic complexes are stacked in columns along [100]. In the columns, several π–π interactions between adjacent pyridine rings are present. The shortest distance between Cg1 (the centroid of ring N1–C5) and Cg2^i (ring N3–C12; symmetry code i: $-x, 1-y, 1-z$) is 3.948(1) Å, and the dihedral angle between the ring planes is 4.5(1)° [4].

Acknowledgements: The author thanks the KBSI, Seoul Center, for the X-ray data collection.
Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: Chonnam National University (Grant number: 2022–0170).
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. *APEX2*, *SAINT* and *SADABS*; Bruker AXS Inc.: Madison, WI, USA, 2016.
2. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
3. Farrugia L. J. ORTEP-3 for Windows-a version of ORTEP–III with a graphical user interface (GUI). *J. Appl. Crystallogr.* 1997, *30*, 565.

4. Spek A. L. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* 2003, *36*, 7–13.
5. Mautner F. A., Albering J. H., Harrelson E. V., Gallo A. A., Massoud S. S. N-bonding *vs.* S-bonding in thiocyanato-copper(II) complexes. *J. Mol. Struct.* 2011, *1006*, 570–575.
6. Schutte M., Muller T. J., Visser H. G., Roodt A. [Bis(pyridin-2-ylmethyl) amine-κ^3N,N',N'']tricarbonylrhenium(I) bromide hemihydrate. *Acta Crystallogr.* 2012, *E68*, m741–m742.
7. Viswanathan R., Palaniandavar M., Balasubramanian T., Muthiah P. T. Synthesis, structure, spectra and redox chemistry of iron(III) complexes of tridentate pyridyl and benzimidazolyl ligands. *J. Chem. Soc., Dalton Trans.* 1996, 2519–2525.
8. Bugarčić Ž. D., Liehr G., van Eldik R. Kinetics and mechanism of the reaction of chelated Pd(II) complexes with thiols in acidic aqueous solution. Synthesis and crystal structure of $[Pd(bpma)Cl]Cl.H_2O$ (bpma = bis(2-pyridylmethyl)amine). *J. Chem. Soc., Dalton Trans.* 2002, 951–956.