Kwang Ha*

Crystal structure of (1,4,8,11-tetraazacyclotetradecane)palladium(II) tetracyanoplatinate(II), $C_{14}H_{24}N_8PdPt$

<https://doi.org/10.1515/ncrs-2019-0421>

Received June 18, 2019; accepted July 12, 2019; available online August 1, 2019

Abstract

$C_{14}H_{24}N_8PdPt$, monoclinic, $P2_1/c$ (no. 14), $a = 9.0747(3)$ Å, $b = 8.3376(3)$ Å, $c = 14.4578(6)$ Å, $\beta = 123.8260(10)^\circ$, $V = 908.73(6)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0115$, $wR_{ref}(F^2) = 0.0235$, $T = 223$ K.

CCDC no.: 1940058

The asymmetric unit of 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.

Source of material

To a solution of (1,4,8,11-tetraazacyclotetradecane) palladium(II) dichloride (0.228 g, 0.604 mmol) in H_2O (20 mL) was added $K_2Pt(CN)_4$ (0.228 g; 0.604 mmol) and stirred for 1 h at room temperature. The formed precipitate was separated by filtration, washed with H_2O and MeOH, and dried at 50 °C, to give a white powder (0.2117 g). Crystals suitable for X-ray diffraction analysis 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:	Colorless block
Size:	0.14 × 0.10 × 0.07 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	8.69 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} :	27411, 1802, 0.037
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1402
$N(param)_{refined}$:	121
Programs:	Bruker [1], SHELX [2], ORTEP-III [3], PLATON [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Pd1	0.5000	0.5000	0.5000	0.01966(5)
N1	0.6713(3)	0.3347(2)	0.61287(16)	0.0255(4)
H1	0.613(3)	0.286(3)	0.635(2)	0.033(7)*
N2	0.4614(3)	0.3363(2)	0.38349(16)	0.0274(4)
H2	0.521(3)	0.369(3)	0.3619(19)	0.027(7)*
C1	0.7069(3)	0.2148(3)	0.5517(2)	0.0332(6)
H1A	0.7535	0.1158	0.5952	0.040*
H1B	0.7952	0.2567	0.5390	0.040*
C2	0.5351(3)	0.1811(3)	0.4418(2)	0.0334(6)
H2A	0.5565	0.1099	0.3965	0.040*
H2B	0.4511	0.1286	0.4543	0.040*
C3	0.2788(3)	0.3213(3)	0.28359(19)	0.0364(6)
H3A	0.2023	0.2769	0.3053	0.044*
H3B	0.2785	0.2460	0.2314	0.044*
C4	0.2036(3)	0.4807(3)	0.22556(19)	0.0370(6)
H4A	0.0935	0.4604	0.1530	0.044*
H4B	0.2879	0.5300	0.2120	0.044*
C5	0.1646(3)	0.5991(3)	0.2888(2)	0.0339(6)
H5A	0.0927	0.6872	0.2391	0.041*
H5B	0.0955	0.5455	0.3131	0.041*
Pt1	0.0000	0.0000	0.0000	0.02245(5)
N3	0.3336(3)	-0.1092(2)	0.22936(17)	0.0350(5)
N4	0.2139(3)	0.2958(3)	-0.00079(19)	0.0480(6)
C6	0.2092(3)	-0.0686(3)	0.14660(19)	0.0259(5)
C7	0.1366(3)	0.1879(3)	0.00002(19)	0.0301(5)

Experimental details

Hydrogen atoms on C atoms were positioned geometrically and allowed to ride on their parent atoms with

$d(\text{C}-\text{H}) = 0.98 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ with the help of the SHELXL program (AFIX 23 option) [2]. Hydrogen atoms bonded to N atoms were located from Fourier difference maps and refined isotropically; $d(\text{N}-\text{H}) = 0.81(2)$ and $0.86(2) \text{ \AA}$. The highest peak ($0.26 \text{ e \AA}^{-3}$) and the deepest hole ($-0.39 \text{ e \AA}^{-3}$) in the difference Fourier map are located $0.97 \text{ \AA}$ and $0.96 \text{ \AA}$ from the atoms Pt1 and Pd1, respectively.

Comment

The crystal structures of the related heterometallic complexes $[\text{Ag}(\text{cyclam})\text{M1}(\text{CN})_4]_n$ (cyclam = 1,4,8,11-tetraazacyclotetradecane; M1 = Pd, Pt) [5] and $[\text{Cu}(\text{cyclam})\text{M2}(\text{CN})_4]_n$ (M2 = Ni, Pd, Pt) [6] have been determined previously. The structures are formed by one-dimensional cyanido-bridged chains.

The title compound consists of a cationic Pd(II) complex $[\text{Pd}(\text{cyclam})]^{2+}$ and an anionic Pt(II) complex $[\text{Pt}(\text{CN})_4]^{2-}$, and is isostructural with the previously reported analogous cyanido-Pd complex $[\text{Pd}(\text{cyclam})][\text{Pd}(\text{CN})_4]$ [7]. Pd(II) and Pt(II) ions are four-coordinated in a slightly distorted square-planar environment and are located on an inversion center, respectively, and thus the asymmetric unit contains one half of the compound. In the cationic complex, the Pd(II) ion is coordinated by four N atoms from the tetradentate cyclam ligand, whereas in the anionic complex, the Pt(II) ion is coordinated by four C atoms from four CN^- ligands. The Pd–N and Pt–C bond lengths are almost equal with $d(\text{Pd}-\text{N}) = 2.0381(18) - 2.0408(19) \text{ \AA}$ and $d(\text{Pt}-\text{C}) = 1.986(2) - 1.998(2) \text{ \AA}$, respectively. In the crystal structure, the cationic and anionic complexes are linked by intermolecular $\text{N}-\text{H} \cdots \text{N3}(\text{cyanido})$ hydrogen bonds with $d(\text{N} \cdots \text{N}) = 2.975(3) - 3.116(4) \text{ \AA}$, forming a three-dimensional network [4].

In the reported heterometallic complexes, the metal ions (Ag, Cu) are coordinated by different bridging cyanido ligands

in axial positions with $d(\text{Ag}-\text{N}) = 2.567(9) \text{ \AA}$ in Pd complex and $2.529(9) \text{ \AA}$ in Pt complex [5], and $d(\text{Cu}-\text{N}) = 2.518(2) \text{ \AA}$ in Pd complex and $2.549(3) \text{ \AA}$ in Pt complex [6], respectively. In the title compound, on the contrary, such a cyanido-bridging is not observed: the distance between the Pd1 and N4(cyanido) atoms is relatively long with $3.576(3) \text{ \AA}$ [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. Munakata, M.; Zhong, J. C.; Ino, I.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Oiji, N.: 1-D cyano-bridged heterometallic complexes consisting of 1,4,8,11-tetraazacyclotetradecanesilver(II) and tetracyanopalladium(II) or tetracyanoplatinum(II). *Inorg. Chim. Acta* **317** (2001) 268–275.
6. Černák, J.; Kuchár, J.; Stolárová, M.; Kajňáková, M.; Vavra, M.; Potočník, I.; Falvello, L. R.; Tomás, M.: Preparation, spectroscopic and magnetic characterization of $\text{Cu}(\text{cyclam})\text{M}(\text{CN})_4$ complexes exhibiting one-dimensional crystal structures (cyclam = 1,4,8,11-tetraazacyclotetradecane, M = Ni, Pd, Pt). *Transition Met. Chem.* **35** (2010) 737–744.
7. Ha, K.: Crystal structure of (1,4,8,11-tetraazacyclotetradecane)palladium(II) tetracyanopalladate(II), $\text{C}_{14}\text{H}_{24}\text{N}_8\text{Pd}_2$. *Z. Kristallogr. NCS* **232** (2017) 139–140.