Tatsuto Kiwada*, Aika Hirasaki and Akira Odani*

Crystal structure of dichlorido-(4,4'-dichloro-2,2'-bipyridine- $\kappa^2 N, N'$)platinum(II) – acetone (1/1), $C_{13}H_{12}Cl_4N_2PtO$

Abstract

$C_{13}H_{12}Cl_4N_2PtO$, monoclinic, $C2/m$ (no. 12), $a = 17.497(4)$ Å, $b = 6.8214(15)$ Å, $c = 14.183(3)$ Å, $\beta = 93.441(7)^\circ$, $Z = 4$, $V = 1689.7(6)$ Å³, $R_{gt}(F) = 0.0309$, $wR_{ref}(F^2) = 0.0696$, $T = 93$ K.

CCDC no.: 1961125

The asymmetric unit of the title 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:	Red needle
Size:	$0.45 \times 0.25 \times 0.15$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	8.93 mm^{-1}
Diffractometer, scan mode:	Rigaku R-Axis RAPID, φ and ω
$\theta_{\max}$, completeness:	27.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8112, 2089, 0.056
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1962
$N(\text{param})_{\text{refined}}$:	127
Programs:	WinGX/ORTEP [1], SHELX [2], Mercury [3]

<https://doi.org/10.1515/ncrs-2019-0728>

Received September 28, 2019; accepted October 24, 2019; available online November 9, 2019

*Corresponding authors: Tatsuto Kiwada and Akira Odani, Faculty of Pharmacy, Institute of Medical, Pharmaceutical and Health Sciences, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan, e-mail: kiwada@p.kanazawa-u.ac.jp (T. Kiwada), odani@p.kanazawa-u.ac.jp (A. Odani). <https://orcid.org/0000-0002-4928-5620> (T. Kiwada)

Aika Hirasaki: Division of Pharmaceutical Sciences, Graduate School of Medical Sciences, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

Source of material

The 4,4'-dichloro-2,2'-bipyridine was synthesized according to the literature [4, 5]. To a suspension of 4,4'-dichloro-2,2'-bipyridine (100 mg, 0.44 mmol) in water (20 mL), K_2PtCl_4 (182 mg, 0.44 mmol) was added. The mixture was stirred at 373 K for 24 h. The orange precipitate was obtained by filtration. The precipitate was washed with H_2O , CH_2Cl_2 , EtOH, ether, and dried under a vacuum. Yield: 150 mg.

Experimental details

Hydrogen atoms were placed in calculated positions and included in the refinement in the riding model approximation, with $U_{\text{iso}}(H)$ set to $1.2U_{\text{eq}}(C)$.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.1021(4)	0.000000	1.0676(5)	0.0515(16)
H1	0.0804(3)	0.000000	1.0045(5)	0.062*
C2	0.0544(4)	0.000000	1.1417(6)	0.0542(17)
H2	0.0003(7)	0.000000	1.1299(8)	0.065*
C3	0.0852(4)	0.000000	1.2295(5)	0.0481(15)
C4	0.1648(3)	0.000000	1.2480(5)	0.0410(13)
H4	0.1866(19)	0.000000	1.3110(30)	0.049*
C5	0.2104(3)	0.000000	1.1728(4)	0.0335(11)
C6	0.2947(3)	0.000000	1.1814(5)	0.0375(12)
C7	0.3358(3)	0.000000	1.2675(5)	0.0451(14)
H7	0.3108(4)	0.000000	1.3251(9)	0.054*
C8	0.4148(4)	0.000000	1.2665(6)	0.0527(17)
C9	0.4500(4)	0.000000	1.1829(7)	0.0590(19)
H9	0.5043(16)	0.000000	1.1823(9)	0.071*
C10	0.4057(4)	0.000000	1.1002(6)	0.0496(16)
H10	0.4302(9)	0.000000	1.0422(5)	0.059*
C11	0.2395(5)	0.000000	1.5454(6)	0.062(2)
C12	0.1614(7)	0.000000	1.5823(9)	0.105(4)
H12A	0.2900(7)	0.000000	1.6785(9)	0.156*
H12B ^a	0.3381(7)	−0.1173(2)	1.6044(3)	0.156*
H12C ^a	0.3381(7)	0.1173(2)	1.6044(3)	0.156*
C13	0.3073(7)	0.000000	1.6141(9)	0.104(4)
H13A	0.1657(9)	0.000000	1.6515(3)	0.157*
H13B ^a	0.1335(8)	0.1173(2)	1.5598(4)	0.157*
H13C ^a	0.1335(8)	−0.1173(2)	1.5598(4)	0.157*
Cl1	0.1647(4)	0.000000	0.8561(2)	0.0521(4)
Cl2	0.3499(3)	0.000000	0.8753(4)	0.0574(4)
Cl3	0.0274(7)	0.000000	1.3246(4)	0.0785(7)
Cl4	0.4683(13)	0.000000	1.3739(2)	0.0826(7)
N1	0.1793(3)	0.000000	1.0832(4)	0.0381(10)
N2	0.3283(3)	0.000000	1.0976(4)	0.0404(11)
O1	0.2472(4)	0.000000	1.4622(5)	0.087(2)
Pt1	0.2556(2)	0.000000	0.9813(2)	0.0368(9)

^aOccupancy: 0.5.

Comment

Pt(II) complex with a 2,2'-bipyridine derivative have been synthesized for use as anti-cancer drugs [6], intermediate material of platinum complexes [7] and luminescent complexes [8].

In the crystal structure of the title complex, the asymmetric unit consists of one half of (4,4'-dichloro-2,2'-bipyridine platinum(II) complex and one half of acetone molecule, both located on a mirror plane (see the figure). The Pt atom is four-coordinated by two nitrogen atoms of 4,4'-dichloro-2,2'-bipyridine and two Cl atoms. The bond lengths of Pt1–N1, Pt1–N2, Pt1–Cl1, Pt1–Cl2 are 2.024(5) Å, 2.021(6) Å, 2.3119(19) Å, 2.2988(17) Å, respectively. The bond lengths of

C3–Cl3, C8–Cl4 are 1.733(7) Å, 1.740(8) Å. These lengths are comparable with those previously reported compounds [8, 9] and similar to Pt(IV) complexes [10]. The distances of O1–H4, O1–H7 are 2.334(7) Å and 2.297(7) Å, respectively suggest non-classical hydrogen bonds between dichlorobipyridine and acetone. The Cl ligands of the Pt complex also form C–H···Cl hydrogen bonds with acetone [11].

Acknowledgements: We gratefully acknowledge support by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) (award No. 25288027).

References

- Ferrugia, L. G.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.
- Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
- Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A.: Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* **41** (2008) 466–470.
- McCusker, C. E.; McCusker, J. K.: Synthesis and spectroscopic characterization of CN-substituted bipyridyl complexes of Ru(II). *Inorg. Chem.* **50** (2011) 1656–1669.
- Brink, G.-J. T.; Arends, I. W. C. E.; Hoogenraad, M.; Verspui, G.; Sheldon, R. A.: Catalytic conversions in water. part 22: electronic effects in the (diimine)palladium(II)-catalysed aerobic oxidation of alcohols. *Adv. Synth. Catal.* **345** (2003) 497–505.
- Pages, B. J.; Zhang, Y.; Li, F.; Sakoff, J.; Gilbert, J.; Aldrich-Wright, J. R.: Cytotoxicity and structural analyses of 2,2'-bipyridine-, 4,4'-dimethyl-2,2'-bipyridine- and 2-(2'-pyridyl)-quinoxalineplatinum(II) complexes. *Eur. J. Inorg. Chem.* **2015** (2015) 4167–4175.
- McFadyen, W. D.; Wakelin, L. P. G.; Roos, I. A. G.; Leopold, V. A.: Activity of platinum(II) intercalating agents against murine leukemia L1210. *J. Med. Chem.* **28** (1985) 1113–1116.
- Connick, W. B.; Henling, L. M.; Marsh, R. E.; Gray, H. B.: Emission spectroscopic properties of the red form of dichloro (2,2'-bipyridine) platinum(II). role of intermolecular stacking interactions. *Inorg. Chem.* **35** (1996) 6261–6265.
- Kato, M.; Okada, Y.; Shishido, Y.; Kishi, S.: Dichloro(4,4'-dialkyl-2,2'-bipyridine-κ²N,N')platinum(II), where alkyl is pentyl and heptyl. *Acta Crystallogr.* **C62** (2006) m171–m173.
- Ghosh, B. N.: Synthesis and structure of new trimethylplatinum(IV) iodide complexes of 2,2'-bipyridine ligands. *Z. Anorg. Allg. Chem.* **645** (2019) 1085–1091.
- Lu, N.; Wei, R.-J.; Lin, K.-Y.; Alagesan, M.; Wen, Y.-S.; Liu, L.-K.: Weak hydrogen bonding and fluorine interactions in the chloride and bromide salts of 4-[(2,2,3,3-tetrafluoropropoxy)methyl]pyridinium. *Acta Crystallogr.* **C73** (2017) 343–349.