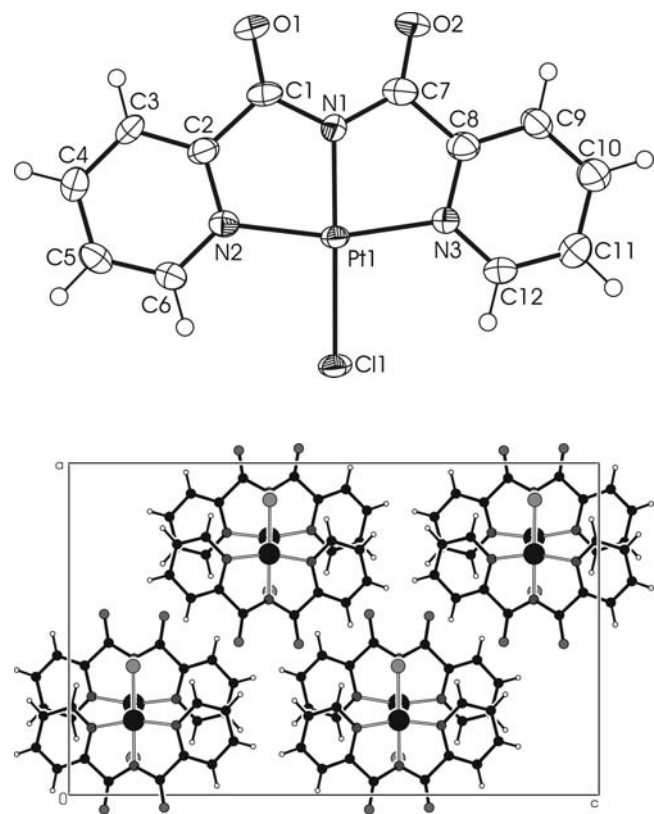


Crystal structure of (bis(2-pyridyl)imido)chloroplatinum(II), $\text{PtCl}(\text{C}_{12}\text{H}_8\text{N}_3\text{O}_2)$

Kwang Ha*

Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea

Received October 9, 2010, accepted and available on-line December 6, 2010; CCDC no. 1267/3235



Abstract

$\text{C}_{12}\text{H}_8\text{ClN}_3\text{O}_2\text{Pt}$, orthorhombic, *Pbca* (no. 61), $a = 14.1952(7)$ Å, $b = 7.4719(4)$ Å, $c = 22.630(1)$ Å, $V = 2400.3$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.034$, $wR_{\text{ref}}(F^2) = 0.079$, $T = 200$ K.

Source of material

To a solution of K_2PtCl_6 (0.5832 g, 1.200 mmol) in H_2O (50 ml) was added 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz, 0.1249 g, 0.400 mmol; $\text{C}_{18}\text{H}_{12}\text{N}_6$), and the mixture was stirred at room temperature for 24 h. During the reaction, the yellow precipitate formed. The precipitate was separated by filtration, washed with water and acetone, and dried at 50 °C, to give a yellow powder (0.2566 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from an *N,N*-dimethylformamide solution at 50 °C.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with $d(\text{C}—\text{H}) = 0.95$ Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The highest peak ($2.52 \text{ e} \cdot \text{Å}^{-3}$) and the deepest hole ($-2.48 \text{ e} \cdot \text{Å}^{-3}$) in the difference Fourier map are located 1.00 and 0.90 Å, from the atoms Cl1 and Pt1, respectively.

Discussion

The title complex $[\text{PtCl}(\text{C}_{12}\text{H}_8\text{N}_3\text{O}_2)]$ was unexpectedly prepared by the reaction of K_2PtCl_6 with tptz. When the tptz ligand was added to an aqueous solution of K_2PtCl_6 , a white precipitate formed immediately that turned slowly yellow during the reaction at room temperature. Lerner and Lippard reported that Cu(II) ion promotes the hydrolysis of the tptz molecule to form the bis(2-pyridyl)carboximidatocopper(II) chelate complex and free picolinamide, and other metal ions, Co(II), Pd(II) and Pt(II), assist also the hydrolytic reaction of the triazine ring [1,2]. Later, the Cu(II) complex $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_3\text{O}_2)(\text{tptz})](\text{CF}_3\text{SO}_3)$, in which the Cu(II) ion is coordinated by the tptz and the fragment resulting from the hydrolysis of tptz, was obtained from an aqueous solution of tptz and $\text{Cu}(\text{CF}_3\text{SO}_3)_2$, and characterized by the X-ray structure analysis [3]. In the reaction of K_2PtCl_6 with tptz in water, it seems that the tptz ligand bound to the Pt(IV) ion first and the Pt(IV) ion assisted the nucleophilic hydrolysis of the coordinated tptz to form the anionic ligand $\text{C}_{12}\text{H}_8\text{N}_3\text{O}_2$ and the picolinamide as in the reaction of Cu(II) ion. In parallel, the reduction of the Pt(IV) ion to the Pt(II) ion probably occurred by the formed picolinamide.

In the title complex, the Pt(II) ion is four-coordinated in a distorted square-planar arrangement by three N atoms from the imide anionic ligand and a chloride ion (figure, top). The main contribution to the distortion is the tight N–Pt–N chelate angles ($82.6(2)^\circ$ and $82.1(2)^\circ$), which results in non-linear *trans* arrangement of the N2–Pt1–N3 bond ($\angle\text{N2–Pt1–N3} = 164.6(2)^\circ$), whereas the N1–Pt1–Cl1 bond is almost linear ($\angle\text{N1–Pt1–Cl1} = 178.2(2)^\circ$). The Pt1–N1_{imide} bond length ($1.956(6)$ Å) is slightly shorter than the Pt1–N2/3_{pyridine} bond lengths ($2.007(6)$ Å and $2.011(6)$ Å).

In the crystal structure, the nearly planar complexes are arranged in a V-shaped packing pattern and stacked in columns along [010] (figure, bottom). When viewed down the *b* axis, the successive complexes are stacked in the opposite direction with the Pt...Pt distance of $3.8001(5)$ Å. In the columns, numerous intermolecular π – π interactions between adjacent pyridine rings are present. The shortest distance between Cg1 (the centroid of ring N2–C6) and Cg1ⁱ (symmetry code $i: \frac{1}{2}-x, -\frac{1}{2}+y, z$) is $4.156(4)$ Å, and the dihedral angle between the ring planes is 7° . In addition, the intermolecular C–H...O hydrogen bonds with $d(\text{C} \cdots \text{O}) = 3.102(9) - 3.11(1)$ Å, and intra- and intermolecular C–H...Cl hydrogen bonds with $d(\text{C} \cdots \text{Cl}) = 3.369(8) - 3.593(8)$ Å are present.

* e-mail: hakwang@chonnam.ac.kr

Table 1. Data collection and handling.

Crystal:	yellow rod, size 0.09 × 0.13 × 0.30 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71073 Å)
μ :	119.14 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{\max}$:	56.52°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	16386, 2954
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1842
$N(\text{param})_{\text{refined}}$:	172
Programs:	SHELXS-97, SHELXL-97 [4], ORTEP-III [5], PLATON [6]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(3)	8c	0.4722	0.6373	0.2791	0.038
H(4)	8c	0.3538	0.7165	0.3474	0.044
H(5)	8c	0.1963	0.6617	0.3232	0.040
H(6)	8c	0.1590	0.5377	0.2323	0.035
H(9)	8c	0.4864	0.1998	-0.0308	0.043
H(10)	8c	0.3771	0.0866	-0.0984	0.048
H(11)	8c	0.2153	0.1025	-0.0746	0.041
H(12)	8c	0.1696	0.2342	0.0141	0.035

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Pt(1)	8c	0.27449(2)	0.40612(4)	0.12223(1)	0.0161(2)	0.0285(2)	0.0243(2)	-0.0000(1)	-0.0010(1)	0.0031(1)
Cl(1)	8c	0.1110(1)	0.4047(3)	0.12105(8)	0.0167(8)	0.042(1)	0.036(1)	-0.0003(8)	-0.0029(8)	0.001(1)
O(1)	8c	0.5381(4)	0.5217(8)	0.1796(3)	0.020(3)	0.058(4)	0.044(4)	0.001(3)	-0.008(3)	-0.007(3)
O(2)	8c	0.5441(4)	0.3413(9)	0.0665(3)	0.019(3)	0.083(5)	0.044(4)	0.001(3)	0.004(3)	-0.013(3)
N(1)	8c	0.4122(4)	0.4153(8)	0.1229(3)	0.025(3)	0.030(3)	0.022(3)	-0.002(3)	-0.001(3)	-0.002(3)
N(2)	8c	0.2897(4)	0.5169(8)	0.2025(3)	0.023(4)	0.025(3)	0.028(4)	0.001(3)	0.000(3)	0.004(3)
N(3)	8c	0.2971(4)	0.2928(8)	0.0429(2)	0.022(4)	0.023(3)	0.023(3)	0.000(3)	0.000(3)	0.002(3)
C(1)	8c	0.4543(5)	0.495(1)	0.1716(4)	0.020(4)	0.031(5)	0.038(5)	0.003(4)	-0.006(4)	0.009(4)
C(2)	8c	0.3815(5)	0.546(1)	0.2168(3)	0.023(4)	0.036(5)	0.032(5)	-0.002(4)	-0.004(4)	0.001(4)
C(3)	8c	0.4076(6)	0.619(1)	0.2700(3)	0.028(4)	0.040(5)	0.028(5)	-0.002(4)	-0.010(3)	-0.005(4)
C(4)	8c	0.3378(6)	0.664(1)	0.3105(4)	0.039(5)	0.042(5)	0.029(5)	0.000(4)	-0.004(4)	-0.007(4)
C(5)	8c	0.2450(5)	0.633(1)	0.2960(4)	0.032(5)	0.030(5)	0.038(5)	-0.002(4)	0.012(4)	0.000(3)
C(6)	8c	0.2232(5)	0.559(1)	0.2419(3)	0.025(4)	0.031(5)	0.031(4)	0.001(3)	0.003(4)	0.004(3)
C(7)	8c	0.4591(5)	0.351(1)	0.0749(4)	0.024(4)	0.040(5)	0.034(5)	0.001(4)	0.001(4)	0.010(4)
C(8)	8c	0.3909(6)	0.283(1)	0.0297(3)	0.027(5)	0.041(5)	0.031(5)	0.004(4)	-0.002(4)	0.005(4)
C(9)	8c	0.4210(6)	0.206(1)	-0.0224(3)	0.030(5)	0.049(5)	0.029(5)	0.006(4)	0.004(4)	-0.001(4)
C(10)	8c	0.3568(6)	0.139(1)	-0.0622(4)	0.036(5)	0.051(6)	0.035(5)	0.002(4)	0.001(4)	-0.002(4)
C(11)	8c	0.2614(6)	0.149(1)	-0.0483(3)	0.040(5)	0.034(5)	0.028(4)	-0.003(4)	-0.006(4)	0.007(4)
C(12)	8c	0.2347(5)	0.227(1)	0.0047(3)	0.023(4)	0.031(4)	0.034(5)	-0.002(4)	0.000(4)	0.006(4)

Acknowledgment. This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant no. 2009-0094056).

References

- Lerner, E. I.; Lippard, S. J.: 2,4,6-Tris(2-pyrimidyl)- and 2,4,6-tris(2-pyridyl)-1,3,5-triazines hydrolyze in the presence of copper(II) to form a novel bis(aryl)carboximidato chelate complex. *J. Am. Chem. Soc.* **98** (1976) 5397-5398.
- Lerner, E. I.; Lippard, S. J.: Hydrolysis reactions of 2,4,6-tris(2-pyrimidyl)- and 2,4,6-tris(2-pyridyl)-1,3,5-triazines with divalent copper. Structure of a bis(2-pyrimidylcarbonyl)aminatocopper(II) complex. *Inorg. Chem.* **16** (1977) 1546-1551.
- Faus, J.; Julve, M.; Amigó, J. M.; Debaerdemaeker, T.: Copper(II)-assisted hydrolysis of 2,4,6-tris(2-pyridyl)-1,3,5-triazine. Part 2. Crystal structures of [bis(2-pyridylcarbonyl)amido](pyridine-2-carboxamide)-copper(II) trifluoromethanesulphonate and [bis(2-pyridylcarbonyl)-amido][2,4,6-tris(2-pyridyl)-1,3,5-triazine]copper(II) trifluoromethanesulphonate. *J. Chem. Soc., Dalton Trans.* (1989) 1681-1687.
- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112-122.
- Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) *J. Appl. Crystallogr.* **30** (1997) 565.
- Spek, A. L.: Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **36** (2003) 7-13.