Crystal structure of (bis(2-pyridyl)imido)chloropalladium(II), PdCl(C$_{12}$H$_8$N$_3$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 October 23, 2010; CCDC no. 1267/3234

Abstract

C$_{12}$H$_8$ClN$_3$O$_2$Pd, orthorhombic, Pbcn (no. 60),

$\alpha = 11.962(1)$ Å, $b = 14.179(1)$ Å, $c = 6.9203(7)$ Å,

$V = 1173.8$ Å$^3$, $Z = 4$, $R_p(F) = 0.024$, $wR_{	ext{ref}}(F^2) = 0.070$,

$T = 200$ K.

Source of material

To a solution of Na$_2$PdCl$_4$ (0.4414 g, 1.5 mmol) in H$_2$O (40 ml) was added 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz, 0.1561 g, 0.5 mmol; C$_{18}$H$_{12}$N$_6$), and the mixture was stirred at room temperature for 4 h. The precipitate was then separated by filtration, washed with water and acetone, and dried at 50 °C to give an orange powder (0.3199 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a dimethyl sulfoxide solution at 80 °C.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with $d$(C—H) = 0.95 Å and $U_{	ext{iso}}$(H) = 1.2 $U_{	ext{ref}}$(C). The highest peak (0.45 e·Å$^{-3}$) and the deepest hole (-0.77 e·Å$^{-3}$) in the difference Fourier map are located 1.30 and 0.67 Å apart the atoms C2 and Pd1, respectively.

Discussion

The title complex [PdCl(C$_{12}$H$_8$N$_3$O$_2$)] was unexpectedly prepared by the reaction of K$_2$PdCl$_4$ with tptz. It seems that either the tptz ligand decomposed into the bis(2-pyridyl)imide (C$_{12}$H$_8$N$_3$O$_2$, N-picolinoylpicolinamide) molecule or the anion arisen from the imide by the Pd(II)-assisted hydrolysis. The hydrolysis phenomenon of the tptz molecule by Cu(II) ion was previously reported and the formed Cu(II)-imido complex [Cu(C$_{12}$H$_8$N$_3$O$_2$)(tptz)](CF$_3$SO$_3$) was characterized by the X-ray structure analysis [1].

In the title complex, the Pd(II) ion is four-coordinated in a distorted square-planar manner by three Na toms from the imide anionic ligand and the chloride ion (figure, top). The complex is located on a two-fold rotation axis running in the [010] direction and passing through the Pd1, Cl1 and N1 atoms. Thus the asymmetric unit contains one half of the formula unit. The tight ionic ligand and the chloride ion (figure, bottom). When viewed down the Pd—Pd distance of 3.5875(4) Å. In the crystal structure, the nearly planar complexes are arranged in a V-shaped packing pattern and stacked in columns along [001] (figure, bottom). When viewed down the c axis, the successive complexes are stacked in the opposite direction with the Pd—Pd distance of 3.5875(4) Å. In the columns, several intermolecular π–π interactions between adjacent pyridine rings are present. The shortest distance between Cg1 (the centroid of ring N2-C6) and Cg1$^{	ext{II}}$ (symmetry code ii: $-x,y,-1/2-z$) is 4.167(2) Å, and the dihedral angle between the ring planes is 9°. Moreover, there are intermolecular C–H···O hydrogen bonds with $d$(C···O) = 3.092(3) Å.

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