Crystal structure of bis(nitrito-κ*N*)bis(3-phenylpyridine-κ*N*) palladium(II), $C_{22}H_{18}N_4O_4Pd$

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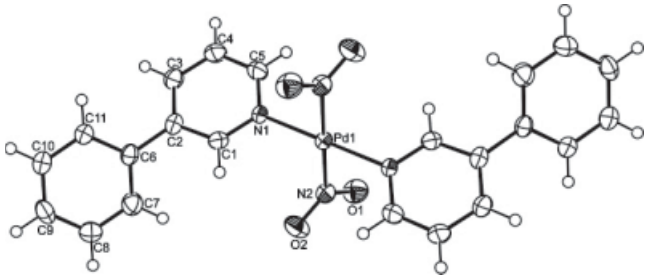

Abstract

$C_{22}H_{18}N_4O_4Pd$, monoclinic, $P2_1/c$ (no. 14), a = 7.474(1) Å, b = 13.496(2) Å, c = 10.587(2) Å, β = 108.549(4)°, V = 1012.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.0403, $wR_{ref}(F^2)$ = 0.0794, T = 200 K.

Table 1. Data collection and handling.

Crystal:	yellow blocks, size 0.08×0.11×0.12 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.55 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ and ω
$2\theta_{max}$:	56.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7374, 2478
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1384
$N(param)_{refined}$:	142
Programs:	SHELX [3], ORTEP-3[4], PLATON [5]

Source of material

To a solution of $Pd(NO_3)_2{\cdot}2H_2O$ (0.132 g, 0.495 mmol) in acetone (30 ml) was added 3-phenylpyridine (*ppy*; 0.157 g, 1.011 mmol) and stirred for 24 h at room temperature. The formed brown precipitate was extracted by the solid-phase extraction column (25 ml) with silica (5 g), and the solvent of the eluate was evaporated. The residue was washed with ether, and dried under vacuum, to give a dark yellow powder (0.123 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a CH_3CN solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C–H) = 0.95 Å and U_{iso}(H) = 1.2 U_{eq}(C). The highest peak (1.02 e·Å^{-3}) and the deepest hole (–1.34 e·Å^{-3}) in the difference Fourier map are located 1.17 Å and 0.80 Å from the atom Pd1, respectively.

Discussion

The title complex $[Pd(NO_2)_2(ppy)_2]$ was unexpectedly prepared by the reaction of $Pd(NO_3)_2{\cdot}2H_2O$ with *ppy*. It seems that the NO_3^- ion reduced to the NO_2^- ion during the reaction or the filtration over silica. Crystal structure of the related chlorido-Pd(II) complex $[PdCl_2(ppy)_2]$ has been investigated previously [1]. In the title crystal structure, the central Pd(II) ion is four-coordinated by two N atoms from two *ppy* ligands and two N atoms of two NO_2^- ligands in a slightly distorted square-planar manner. The Pd atom is located on an inversion center, and thus the asymmetric unit contains one half of the complex and the PdN_4 moiety is exactly planar. The dihedral angle between the PdN_4 unit plane and the nearly planar pyridine ring is 67.4(1)°. In the crystal, the *ppy* ligand is not planar, the dihedral angle between the pyridine and phenyl ring is 41.6(1)°. The nitrito ligand has nearly equivalent N–O bond lengths (1.226(4) Å and 1.227(4) Å). The O–N–O bond angle of the nitrito group is 119.9(4)°. The complexes are stacked in columns along [010]. In the columns, several intermolecular π-π interactions between the aromatic rings are present. The shortest distance between Cg1 (the centroid of ring N1-C5) and $Cg2^i$ (the centroid of ring C6-C11, symmetry code i: x, $\frac{1}{2}$-y, $\frac{1}{2}$+z) is 3.772(2) Å, and the dihedral angle between the ring planes is 13.0(2)°.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.9672	0.0516	0.7214	0.033
H(3)	4*e*	0.4662	0.1822	0.5448	0.043
H(4)	4*e*	0.4045	0.1729	0.7463	0.046
H(5)	4*e*	0.6212	0.0997	0.9285	0.041
H(7)	4*e*	1.0508	0.1613	0.5727	0.047
H(8)	4*e*	1.1235	0.1784	0.3771	0.049
H(9)	4*e*	0.8954	0.1466	0.1722	0.046
H(10)	4*e*	0.5940	0.0972	0.1658	0.053
H(11)	4*e*	0.5169	0.0860	0.3610	0.046

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	2*a*	1	0	1	0.0208(2)	0.0304(3)	0.0227(2)	0.0003(2)	0.0049(2)	0.0024(3)
O(1)	4*e*	1.2278(4)	0.1645(2)	1.1164(3)	0.043(2)	0.044(2)	0.049(2)	–0.007(2)	0.013(2)	–0.009(2)
O(2)	4*e*	1.2723(4)	0.1184(2)	0.9370(3)	0.048(2)	0.069(3)	0.048(2)	–0.011(2)	0.027(2)	0.001(2)
N(1)	4*e*	0.8142(4)	0.0697(2)	0.8417(3)	0.021(2)	0.030(2)	0.023(2)	0.001(2)	0.005(2)	0.004(2)
N(2)	4*e*	1.1908(5)	0.1086(3)	1.0203(4)	0.029(2)	0.036(2)	0.029(2)	0.003(2)	0.006(2)	0.002(2)
C(1)	4*e*	0.8504(5)	0.0766(3)	0.7256(4)	0.024(2)	0.030(3)	0.030(3)	0.000(2)	0.010(2)	0.000(2)
C(2)	4*e*	0.7266(5)	0.1180(3)	0.6120(4)	0.028(2)	0.024(2)	0.024(2)	–0.001(2)	0.002(2)	0.001(2)
C(3)	4*e*	0.5564(6)	0.1537(3)	0.6206(4)	0.031(2)	0.041(3)	0.033(3)	0.007(2)	0.006(2)	0.012(2)
C(4)	4*e*	0.5195(6)	0.1475(3)	0.7391(4)	0.027(2)	0.049(3)	0.041(3)	0.010(2)	0.013(2)	0.007(2)
C(5)	4*e*	0.6492(5)	0.1047(3)	0.8473(4)	0.032(2)	0.041(3)	0.030(3)	0.003(2)	0.013(2)	0.003(2)
C(6)	4*e*	0.7755(5)	0.1241(3)	0.4873(4)	0.032(2)	0.024(2)	0.025(2)	0.005(2)	0.007(2)	0.003(2)
C(7)	4*e*	0.9560(6)	0.1498(3)	0.4897(5)	0.041(3)	0.044(3)	0.031(3)	–0.009(2)	0.009(2)	–0.003(2)
C(8)	4*e*	0.9999(6)	0.1590(3)	0.3738(5)	0.031(3)	0.051(3)	0.043(3)	–0.008(2)	0.014(2)	0.000(3)
C(9)	4*e*	0.8651(6)	0.1401(3)	0.2525(4)	0.049(3)	0.043(3)	0.030(3)	0.010(2)	0.021(2)	0.005(2)
C(10)	4*e*	0.6865(6)	0.1118(4)	0.2488(5)	0.037(3)	0.064(4)	0.027(3)	0.000(2)	0.004(2)	0.001(2)
C(11)	4*e*	0.6411(6)	0.1045(3)	0.3648(4)	0.029(2)	0.057(3)	0.026(3)	0.003(2)	0.006(2)	0.003(2)

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