Crystal structure of (2,2'-bipyrimidine-κ^2N,N')dibromidopalladium(II), $C_8H_6Br_2N_4Pd$

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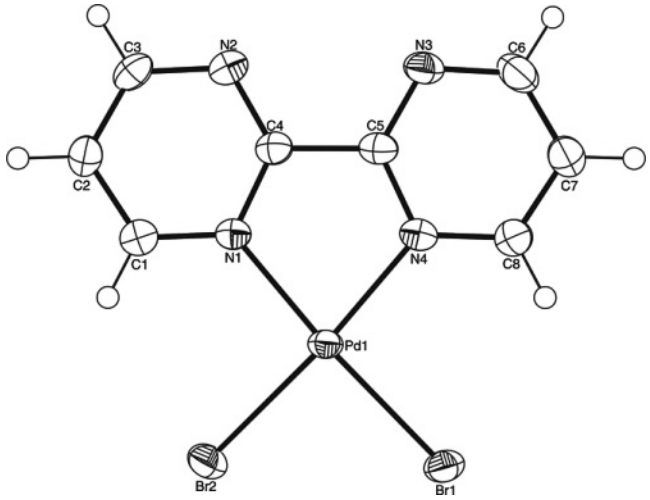

Abstract

$C_8H_6Br_2N_4Pd$, monoclinic, $P2_1/c$ (no. 14), a = 5.1117(6) Å, b = 14.786(2) Å, c = 14.208(2) Å, β = 92.829(2)°, V = 1072.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.0263, $wR_{ref}(F^2)$ = 0.0652, T = 200 K.

Table 1. Data collection and handling.

Crystal:	orange needles, size 0.01×0.05×0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	91.50 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ and ω
$2\theta_{max}$:	52.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6439, 2070
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1783
$N(param)_{refined}$:	136
Programs:	SHELX [4], ORTEP-3 [5], PLATON [6]

Source of material

To a solution of K_2PdBr_4 (0.505 g, 1.00 mmol) in H_2O (30 ml) and MeOH (30 ml) was added 2,2'-bipyrimidine (*bpym*, 0.162 g, 1.03 mmol), and the mixture was stirred for 3 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 dark yellow powder (0.357 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from an *N*,*N*-dimethylformamide solution at 60 °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_{iso}(H) = 1.2U_{eq}(C).

Discussion

This contribution is part of my continuing interest in the structural chemistry of palladium-*bpym* complexes [1-3]. The title complex is isomorphous with the previously reported dichlorido-Pd(II) complex [$PdCl_2$(*bpym*)] [1], whereas the analogous diiodido complex [PdI_2(*bpym*)] crystallizes in the monoclinic space group *C*2/*c* [2]. The central Pd(II) ion is four-coordinated in a slightly distorted square-planar environment defined by two pyrimidine N atoms derived from a chelating *bpym* ligand and two mutually *cis* bromido ligands. The main contribution to the distortion is the tight N1–Pd1–N4 chelate angle of 80.3(1)°, which results in non-linear trans axes (<N1–Pd1–Br1 = 175.2(1)° and <N4–Pd1–Br2 = 174.3(1)°). The Pd–N and Pd–Br bond lengths are pairwise almost equal, respectively (d(Pd1–N1/N4) = 2.036(3) Å and 2.043(3) Å; d(Pd1–Br1/Br2 = 2.4062(6) Å and 2.4124(6) Å). The nearly planar *bpym* ligand [maximum deviation = 0.083(3) Å] is slightly inclined to the least-squares plane of the $PdCl_2N_2$ unit [maximum deviation = 0.055(2) Å], making a dihedral angle of 7.9(1)°. The molecules are stacked in columns along [100] and display numerous intermolecular π-π interactions between the adjacent pyrimidine rings. For Cg1 (the centroid of ring N1-C4) and Cg1^i (symmetry code i: 1–x,–y,–z), the centroid-centroid distance is 3.873(2) Å, the planes are parallel and shifted by 2.069 Å. In the crystal, the complex molecules are connected by intermolecular C–H···Br hydrogen bonds with d(C···Br) = 3.556(4) Å, forming chains along [010].

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.3472	–0.0765	0.2408	0.037
H(2)	4*e*	0.6515	–0.1633	0.1623	0.035
H(3)	4*e*	0.9186	–0.0906	0.0579	0.035
H(6)	4*e*	0.7161	0.3345	–0.0287	0.046
H(7)	4*e*	0.3678	0.4064	0.0394	0.046
H(8)	4*e*	0.1255	0.3243	0.1456	0.037

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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)	4*e*	0.16924(6)	0.12746(2)	0.23423(2)	0.0202(2)	0.0250(2)	0.0232(2)	–0.0021(1)	0.0056(1)	–0.0013(1)
Br(1)	4*e*	–0.13132(9)	0.23868(3)	0.28907(3)	0.0285(3)	0.0321(3)	0.0349(3)	0.0012(2)	0.0112(2)	–0.0045(2)
Br(2)	4*e*	0.0320(1)	0.02440(3)	0.35383(3)	0.0436(3)	0.0325(3)	0.0342(3)	–0.0047(2)	0.0158(2)	0.0025(2)
N(1)	4*e*	0.4248(7)	0.0394(2)	0.1778(2)	0.021(2)	0.026(2)	0.022(2)	–0.001(2)	0.002(2)	–0.001(1)
N(2)	4*e*	0.7603(7)	0.0322(3)	0.0685(2)	0.026(2)	0.032(2)	0.030(2)	0.003(2)	0.004(2)	–0.003(2)
N(3)	4*e*	0.6715(8)	0.2147(3)	0.0300(2)	0.039(2)	0.033(2)	0.027(2)	–0.002(2)	0.012(2)	–0.001(2)
N(4)	4*e*	0.3218(7)	0.2093(2)	0.1349(2)	0.022(2)	0.029(2)	0.022(2)	–0.003(2)	0.002(2)	–0.000(1)
C(1)	4*e*	0.4533(9)	–0.0488(3)	0.1959(3)	0.031(3)	0.031(2)	0.031(2)	0.002(2)	0.005(2)	–0.000(2)
C(2)	4*e*	0.6343(9)	–0.1003(3)	0.1507(3)	0.029(2)	0.024(2)	0.035(2)	0.002(2)	–0.001(2)	–0.001(2)
C(3)	4*e*	0.7884(9)	–0.0570(3)	0.0882(3)	0.022(2)	0.032(2)	0.034(2)	0.005(2)	0.000(2)	–0.007(2)
C(4)	4*e*	0.5777(8)	0.0760(3)	0.1127(3)	0.024(2)	0.026(2)	0.023(2)	–0.003(2)	0.002(2)	–0.005(2)
C(5)	4*e*	0.5256(8)	0.1726(3)	0.0907(3)	0.024(2)	0.030(2)	0.023(2)	–0.005(2)	0.004(2)	–0.004(2)
C(6)	4*e*	0.613(1)	0.3015(3)	0.0131(3)	0.050(3)	0.033(3)	0.032(3)	–0.009(2)	0.011(2)	0.004(2)
C(7)	4*e*	0.409(1)	0.3451(3)	0.0537(3)	0.049(3)	0.030(3)	0.035(3)	0.002(2)	0.009(2)	0.005(2)
C(8)	4*e*	0.2661(9)	0.2960(3)	0.1158(3)	0.031(2)	0.032(3)	0.031(2)	0.003(2)	0.004(2)	0.002(2)

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