

Dibromo(*N,N'*-di-2-pyridylamine- κ^2N,N')palladium(II)

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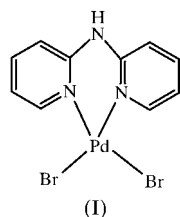
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The palladium center of the title compound, $[\text{PdBr}_2(\text{C}_{10}\text{H}_9\text{N}_3)]$, has a slightly distorted square-planar conformation, with the Pd atom bonded to the two pyridine N atoms of the di-2-pyridylamine moiety and to two Br atoms. The Pd—Br and Pd—N bond lengths are 2.4168 (6)/2.4201 (5) and 2.036 (3)/2.042 (3) Å, respectively.

Comment

Palladium-mediated reactions, such as polymerization, C—C coupling reactions and aminations, have attracted significant interest during recent years, as these reactions are versatile tools in synthetic chemistry and industrial catalysis (Miyaura & Suzuki, 1995). Recently, di-2-pyridylamines have been obtained by sequential palladium-catalyzed aryl amination reactions starting from a primary amine (Buchmeiser & Wurst, 1999). Such compounds have three sites where coordination to a transition metal may occur, *viz.* the two pyridine moieties and the amine function. In contrast to the structure of the classical 2,2'-bipyridine-type ligand, six-membered rings are formed. The coordination chemistry of the simplest member of the dipyridylamine group, *viz.* di-2-pyridylamine or $(2\text{-py})_2\text{NH}$, has been described in detail for Cu complexes (Thompson & Whitney, 1984). However, complexes of palladium are much rarer (Schareina *et al.*, 2001). We report here the crystal structure of a neutral mononuclear palladium(II) complex of di-2-pyridylamine, namely $[\text{PdBr}_2\{(2\text{-py})_2\text{NH}\}]$, (I), with selective catalytic activity.



In compound (I) (Fig. 1), the coordination of the palladium center is slightly distorted square planar, with the N—Pd—N and Br—Pd—Br bond angles deviating slightly from the

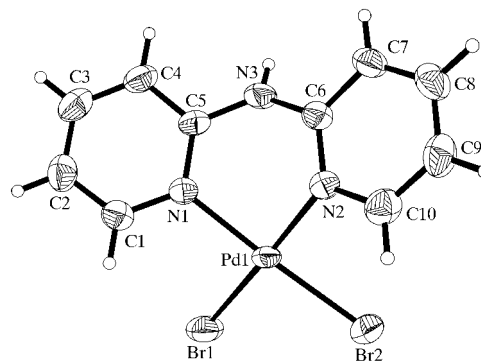


Figure 1

The molecular structure of (I), showing displacement ellipsoids at the 50% probability level.

standard planar angle of 90° (Table 1). However, in contrast to the geometry of $(2,2'\text{-bipyridyl})\text{dichloropalladium(II)}$, $[\text{PdCl}_2\text{-}(\text{bipy})]$, in which the N—Pd—N bond angle is $80.1(7)^\circ$ (Canty *et al.*, 1992), the geometry of the Pd atom in (I) is best described as square planar. The average Pd—N bond length of 2.039 (3) Å in (I) agrees reasonably well with the corresponding distances in $[\text{PdCl}_2\{(2\text{-py})_2\text{N}(\text{COCH}_3)\}]$ [mean = 2.040 (3) Å; Buchmeiser & Wurst, 1999] and $[\text{PdCl}_2\{(4\text{-Me-}2\text{-py})_2\text{N}(\text{CH}_2\text{Ph})\}]$ [mean = 2.022 (3) Å; Schareina *et al.*, 2001]. The mean Pd—Br bond length of 2.4184 (6) Å in (I) is also comparable to those of related compounds (Smeets *et al.*, 1997).

The configuration around the sp^2 -hybridized amide atom N3 is virtually distorted triangular and, consequently, the C5—N3—C6 bond angle deviates from the standard value of 120° . The C5—N1—C1 and C6—N2—C10 angles are very close to the value for a standard six-membered planar ring. The deviations of the six-membered ring from an eclipsed conformation at atoms Pd1 and N3 are 0.45 and 0.39 Å, respectively, in the same direction. This distortion can be explained by the Gillespie—Nyholm rules (Gillespie, 1992). The high selectivity of (I) results from its geometry, as indi-

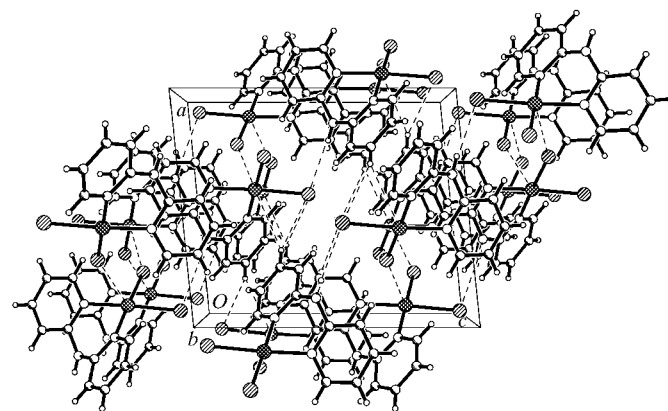


Figure 2

The three-dimensional packing framework of (I), viewed down the *b* axis, showing intermolecular contacts.

cated by the molecular packing shown in Fig. 2. There are weak C1AA—H1AA···Br1A [3.216 (3) Å] and N3AA—H3AA···Br1A($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$) [3.411 (3) Å] intermolecular interactions, and atom Pd1 is also involved in weaker interactions with the amine N atom. The separation between Pd1A and N3AA is 3.102 (3) Å, which indicates the presence of *d*– π -stacking interactions.

Experimental

Di-2-pyridylamine (171 mg, 1.0 mmol) was dissolved in dichloromethane (5 ml) and added to [PdBr₂(SMe₂)₂] (395 mg, 1.0 mmol) in acetonitrile (5 ml) in a Schlenk vessel. After 3 d at room temperature, orange crystals separated from the solution and these were used for X-ray analysis without further purification.

Crystal data

[PdBr ₂ (C ₁₀ H ₉ N ₃)]	$D_x = 2.369 \text{ Mg m}^{-3}$
$M_r = 437.42$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 3136 reflections
$a = 10.3274$ (8) Å	$\theta = 2.5\text{--}28.3^\circ$
$b = 9.6764$ (7) Å	$\mu = 8.00 \text{ mm}^{-1}$
$c = 12.3385$ (10) Å	$T = 294$ (2) K
$\beta = 95.880$ (2)°	Block, orange
$V = 1226.52$ (16) Å ³	$0.32 \times 0.30 \times 0.26 \text{ mm}$
$Z = 4$	

Data collection

Bruker APEX CCD area-detector diffractometer	3047 independent reflections
φ and ω scans	2561 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.030$
$T_{\text{min}} = 0.840$, $T_{\text{max}} = 1.000$	$\theta_{\text{max}} = 28.3^\circ$
9229 measured reflections	$h = -13 \rightarrow 8$
	$k = -12 \rightarrow 12$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 1.2599P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.093$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 1.21 \text{ e \AA}^{-3}$
3047 reflections	$\Delta\rho_{\text{min}} = -0.83 \text{ e \AA}^{-3}$
145 parameters	
H-atom parameters constrained	

50 of the initial frames were repeated at the end of data collection and an analysis of the duplicate reflections found that crystal decay was negligible. H atoms were treated as riding atoms, with C—H distances of 0.93 Å and N—H distances of 0.86 Å.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine

Table 1

Selected geometric parameters (Å, °).

Pd1—Br1	2.4168 (6)	N1—C5	1.335 (5)
Pd1—Br2	2.4201 (5)	N2—C6	1.332 (5)
Pd1—N1	2.042 (3)	N2—C10	1.362 (5)
Pd1—N2	2.036 (3)	N3—C5	1.380 (5)
N1—C1	1.345 (5)	N3—C6	1.389 (5)
Br1—Pd1—Br2	89.07 (2)	C5—N1—Pd1	119.2 (3)
N1—Pd1—N2	87.79 (13)	C1—N1—C5	119.0 (3)
N1—Pd1—Br1	91.01 (9)	C6—N2—Pd1	119.8 (3)
N2—Pd1—Br1	176.17 (9)	C10—N2—Pd1	120.8 (3)
N1—Pd1—Br2	175.38 (9)	C6—N2—C10	118.4 (4)
N2—Pd1—Br2	91.83 (9)	C5—N3—C6	127.2 (3)
C1—N1—Pd1	121.2 (3)		
Br1—Pd1—N1—C1	35.0 (3)	Pd1—N1—C5—N3	−12.5 (5)
Br2—Pd1—N2—C10	−35.7 (3)	Pd1—N2—C6—N3	15.2 (5)

structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998) and PLATON (Spek, 2003); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1159). Services for accessing these data are described at the back of the journal.

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