Data collection: Syntex $P2_1$ software (Syntex, 1976). Cell refinement: Syntex $P2_1$ software. Data reduction: Syntex $P2_1$ software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) implemented on an IBM-PC/AT.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1310). Services for accessing these data are described at the back of the journal.

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(2,2′-Bipyridyl-*N*,*N*′)dibromopalladium(II)

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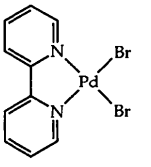
Abstract

The title complex, $[PdBr_2(C_{10}H_8N_2)]$, has square-planar geometry for palladium with Pd—N 2.047 (5) and Pd—Br 2.4102 (9) Å. The mean planes of the coordinated pyridine groups form a dihedral angle of 1.7 (3)° with the coordination square plane; the parallel complexes stack with an interplanar spacing of 3.41 (1) Å and a Pd···Pd separation of 5.246 (1) Å to form a chain structure as reported for isomorphous PtI_2(bipy) (where bipy is 2,2′-bipyridyl, $C_{10}H_8N_2$). The structure differs from those found for related chain structures in the 'red' form of $PtCl_2$(bipy) and in $PdCl_2$(bipy) which is isomorphous with the 'yellow' form of $PtCl_2$(bipy).

Comment

Molecules of stoichiometry MX_2(bipy) (X = halide and bipy = 2,2′-bipyridyl) have been central to the development of the chemistry of Pd and Pt, *e.g.* $PdCl_2$(bipy) was first reported in 1952 (Livingstone, 1952) and $Pd(CH_3)_2$(bipy) (Calvin & Coates, 1960) is the precursor to the first reported alkylpalladium(IV) complex (Byers, Canty, Skelton & White, 1986). In addition, the complexes exhibit interesting structural chemistry in which molecules are stacked in columnar arrays with different relationships between neighbouring molecules, *e.g.* $PdCl_2$(bipy) is isomorphous with the 'yellow' form of $PtCl_2$(bipy) and has a Pd···Pd distance of 4.587 (2) Å (Canty, Skelton, Traill & White, 1992), longer than observed in the closely related 'red' form of $PtCl_2$(bipy), Pt···Pt 3.45 Å (Osborn & Rogers, 1974; Textor & Oswald, 1974), but shorter than a third structural type, PtI_2(bipy) with Pt···Pt 5.291 (1) Å (Connick & Gray, 1994).

The title complex, (I), crystallized during the slow decomposition of an organopalladium(IV) complex; in view of current interest in the structural chemistry of MX_2(bipy) complexes, it was examined by X-ray crystallography and found to be isomorphous with PtI_2(bipy) (Connick & Gray, 1994), crystallizing in space group $C2/c$ with similar cell dimensions. The complex PtI_2(bipy) has a = 17.400 (4), b = 9.809 (2), c = 7.693 (2) Å and β = 111.97 (2)°.



(I)

The molecule lies on a twofold axis passing through the Pd atom and the centre of the bond between the two pyridyl moieties (Fig. 1), and Pd has regular square-planar geometry with Pd—N 2.047 (5) and Pd—Br 2.4102 (9) Å, and angles of 80.1 (2) (chelate) and 89.50 (3)° ($PdBr_2$) at the Pd atom. The pyridine rings are planar [χ^2 9.7, maximum deviation from mean plane 0.014 (7) Å for C5]. The coordinated rings form a dihedral angle of 1.7 (3)° with the coordination mean

plane. The Pd···Pd separation of 5.246 (1) Å is greater than the interplanar spacing of 3.41 (1) Å due to the displacement of consecutive molecules (Fig. 2), as noted for PtI_2(bipy) [5.291 (1) and 3.510 (11) Å, respectively; Connick & Gray, 1994]. The $M\cdots M$ separation in these structures is greater than that found for $PdCl_2$(bipy) [4.587 (2) Å; Canty, Skelton, Traill & White, 1992] and in both of these structures, the Br and I atoms are further removed from the neighbouring bipy groups than observed for $PdCl_2$(bipy), presumably as a result of the presence of larger halogen atoms. The stacking direction down the c axis makes an angle of 65.98 (6)° with the molecular plane (Fig. 2).

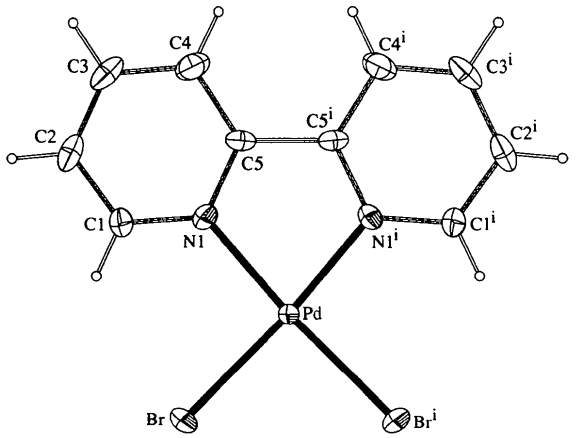


Fig. 1. An *ORTEP* (Johnson, 1965) drawing of the molecule showing the atom-numbering system; displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as circles of arbitrary size.

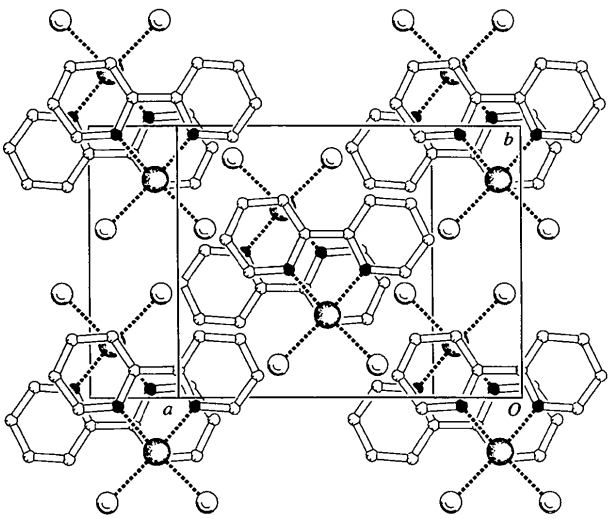


Fig. 2. Projection of the unit cell illustrating the parallel stacking of molecules in columns and the rotation of 180° between neighbouring molecules.

Experimental

The title complex was obtained as orange crystals on the slow decomposition of [$PdBr(CH_3)\{C_6H_4(OCH_2Ph)_4\}(CH_2Ph)$(bipy)] in chloroform over two weeks. The preparation of the reagent complex is to be reported separately (Hoare *et al.*, 1997).

Crystal data

[$PdBr_2(C_{10}H_8N_2)$]
M_r = 422.41
Monoclinic
$C2/c$
a = 16.8637 (14) Å
b = 9.3561 (6) Å
c = 7.4402 (13) Å
β = 111.934 (11)°
V = 1088.9 (2) Å^3
Z = 4
D_x = 2.577 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–14°
μ = 9.01 mm^{-1}
T = 150 K
Needle
0.62 × 0.16 × 0.12 mm
Orange

Data collection

Enraf–Nonius CAD-4T diffractometer on rotating anode
ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.215, T_{max} = 0.380
1663 measured reflections
1247 independent reflections

1073 reflections with $I > 2\sigma(I)$
R_{int} = 0.067
θ_{max} = 27.44°
h = −20 → 21
k = −12 → 0
l = −9 → 6
3 standard reflections
frequency: 60 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R(F)$ = 0.051
$wR(F^2)$ = 0.135
S = 1.044
1247 reflections
69 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0949P)^2 + 0.0887P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.000
$\Delta\rho_{max}$ = 1.147 e Å^{-3}
$\Delta\rho_{min}$ = −3.261 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Pd	0	−0.19766 (6)	1/4	0.0161 (2)
Br	0.09931 (4)	−0.38060 (7)	0.42583 (9)	0.0289 (2)
N1	0.0773 (3)	−0.0302 (6)	0.3859 (7)	0.0195 (14)
C1	0.1560 (4)	−0.0391 (7)	0.5239 (9)	0.0228 (17)
C2	0.2028 (4)	0.0795 (8)	0.6088 (10)	0.0297 (19)
C3	0.1664 (5)	0.2121 (8)	0.5521 (10)	0.0296 (17)
C4	0.0859 (4)	0.2230 (8)	0.4113 (10)	0.0284 (19)
C5	0.0433 (4)	0.1003 (6)	0.3281 (9)	0.0207 (17)

Table 2. *Selected geometric parameters (Å, °)*

Pd—Br	2.4102 (9)	N1—C1	1.343 (8)
Pd—N1	2.047 (5)	N1—C5	1.349 (8)
Br—Pd—N1	95.18 (15)	Pd—N1—C5	114.8 (4)
Br—Pd—Br^i	89.50 (3)	C1—N1—C5	118.7 (6)

Br—Pd—N1^{i}	175.31 (15)	N1—C1—C2	122.4 (6)
N1—Pd—N1^{i}	80.1 (2)	N1—C5—C4	121.6 (6)
Pd—N1—C1	126.5 (5)	N1—C5—C5^{i}	115.2 (5)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

In order to check the C-centering of the monoclinic lattice, a small sphere of reflections was collected for general reflections *hkl* with $h + k = 2n + 1$. None of those reflections was above the noise level, indicating that the lattice is not monoclinic *P*. H atoms were taken into account at calculated positions riding on their carrier atoms. Final residual features in the difference map are within 0.8 Å of Pd, indicating that the analytical correction for absorption (de Meulenaer & Tompa, 1965) was not completely satisfactory in this case. Test calculations based on additional refinement of an empirical isotropic extinction correction parameter [converging to 0.002 (1)] as implemented in *SHELXL*96 (Sheldrick, 1996) showed marginal improvements [$R(F) = 0.049$, $wR(F^2) = 0.134$ ($\Delta\rho$ range 1.362 to -2.950 e Å^{-3})]. Test calculations based on *DIFABS* as implemented in *PLATON* (Spek, 1990*a*) (correcting for absorption, extinction and other global effects with the same mathematical structure such as overall anisotropic thermal motion) showed that the residual density features near Pd can be largely removed (range $\Delta\rho = 1.04$ to -1.73 e Å^{-3}), resulting in good overall agreement [$R(F) = 0.04$ and $wR(F^2) = 0.107$].

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1990*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*96. Molecular graphics: *PLATON* (Spek, 1990*a*) and *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1200). Services for accessing these data are described at the back of the journal.

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trans-Diaquabis(2,2′-bipyridine-*N*,*N*′)-ruthenium(II) Bis(hexafluorophosphate)

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Abstract

The Ru atom of the title complex, $[Ru(C_{10}H_8N_2)_2(H_2O)_2](PF_6)_2$, is located on a crystallographic inversion center; the bipyridine ligands are bowed [dihedral angle between C_5N planes is 162.68 (12)°] due to the inter-ligand steric interactions of the *trans* bipyridyl units. The Ru—O distance is 2.116 (2) Å and the mean Ru—N distance is 2.074 (2) Å.

Comment

Octahedral complexes of Ru^{II} and Ru^{III} with *trans* bipyridyl ligands involve non-planar (bowed or twisted) bipyridine units because of inter-ligand steric interactions (Cordes *et al.*, 1982). For the title complex, (I), the pyramidalization angles ($T_{N1C5C6N2} - T_{C4C5C6N2} + 180$ and $T_{C4C5C6C7} - T_{C4C5C6N2} + 180$) are 7.0 (5) and 5.6 (5)° and the twist angle [$(T_{N1C5C6N2} + T_{C4C5C6C7})/2$] is −3.2 (3)°, where *T* is torsion angle and the calculation is parallel to that used by Dunitz (1979) for analysis of non-planar amide groups. These pyramidalization and twist values are comparable to conformations found for $[Ru(bpy)_2(PPh_3)_2]^{2+}$ and $[Ru(Me_2bpy)_2py_2]^{2+}$, where bpy is bipyridine and py is pyridine (Cordes *et al.*, 1982) and indicate that the distortion is primarily a bowing of the bipyridine ligands. The Ru^{III} complex, $[Ru(bpy)_2(H_2O)(OH)]^{2+}$, which is most comparable to the Ru^{II} title complex, has the twisted conformation (Durham, Wilson, Hodgson & Meyer, 1980). As expected, the Ru^{III} complex has shorter Ru—O distances [2.007 (3) *versus* 2.116 (2) Å]. Consistent with the spe-