

# metal-organic compounds

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## Tetrakis(pyridine- $\kappa N$ )palladium(II) bis(tetrafluoroborate)

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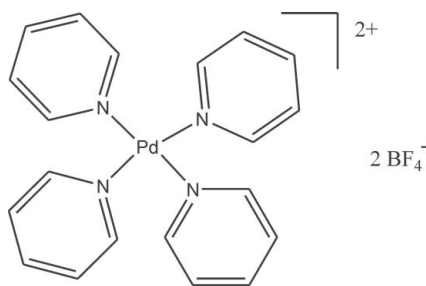
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Key indicators: single-crystal X-ray study;  $T = 295$  K; mean  $\sigma(\text{C}-\text{C}) = 0.011$  Å; disorder in solvent or counterion;  $R$  factor = 0.046;  $wR$  factor = 0.154; data-to-parameter ratio = 16.2.

The title complex,  $[\text{Pd}(\text{C}_5\text{H}_5\text{N})_4](\text{BF}_4)_2$ , contains tetrapyridinepalladium(II) cations residing on crystallographic inversion centres. These are linked by weak  $\text{C}-\text{H}\cdots\text{F}$  interactions (involving disordered  $\text{BF}_4^-$  anions) [range 2.988 (12)–3.431 (10) Å], together with  $\text{C}-\text{H}\cdots\pi$ (pyridine) interactions. The F atoms are disordered equally over two positions.

### Related literature

For related literature, see: Braga *et al.* (1998); Holzbock *et al.* (2000); Lehn (1995); Lutz *et al.* (2000); Ma *et al.* (2005); Tebbe *et al.* (1996).



### Experimental

#### Crystal data

$[\text{Pd}(\text{C}_5\text{H}_5\text{N})_4](\text{BF}_4)_2$   
 $M_r = 596.42$   
 Monoclinic,  $C2/c$

$a = 15.640$  (7) Å  
 $b = 10.886$  (7) Å  
 $c = 15.711$  (7) Å

$\beta = 115.63$  (3)°  
 $V = 2412$  (2) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation

$\mu = 0.85$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 $0.18 \times 0.15 \times 0.11$  mm

#### Data collection

Enraf–Nonius CAD-4 diffractometer  
 Absorption correction: none  
 6864 measured reflections  
 3521 independent reflections

1872 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.064$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: none

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.154$   
 $S = 0.97$   
 3521 reflections  
 217 parameters  
 20 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.96$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.52$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C4}-\text{H4}\cdots\text{Cg1}^i$	0.93	2.97	3.800 (10)	150

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

Data collection: *CAD-4-PC* (Kretschmar, 1996); cell refinement: *CAD-4-PC*; data reduction: *WinGX-PC* (Farrugia, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Brueggemann & Schmid, 1990); software used to prepare material for publication: *PLATON* (Spek, 2003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GG2027).

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**supplementary materials**

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## Tetrakis(pyridine-*N*)palladium(II) bis(tetrafluoroborate)

A. De León, J. Pons, X. Solans and M. Font-Bardia

### Comment

The design of supramolecular coordination compounds by self-assembly is a developing research area (Lehn, 1995, Braga *et al.*, 1998). Four-coordinate Pd<sup>II</sup> complexes with square-planar geometry and four pyridine ligands, in particular, is a potentially useful building block for producing an array of interesting molecular architectures by means of C—H $\cdots$  $\pi$ -ring interactions, thanks to the mobility of pyridine planes. It is for that reason that we have tried to prepare the title compound (I) to be able to compare the results with the structure of the same compound with acetone solvate (Lutz *et al.*, 2000).

Normally, the tetrakis(pyridine-*N*)palladium(II) ion has a square-planar coordination, with the anion occupying the apical positions of an octahedron. Pd $\cdots$ X lengths are 4.299 (5) Å in (I) (*X* = B); 4.028 (7) Å (*X* = B, Lutz *et al.*, 2000); 4.4759 (11) Å in the orthorhombic phase and 4.100 (2) Å in the triclinic phase (*X* = I, Tebbe *et al.*, 1996); 3.112 (2) Å (*X* = O, Liqing *et al.* 2005) and 3.079 (4) or 3.031 (3) Å (*X* = F, Holzbock *et al.*, 2000). The packing will come defined by the solvate presence and the size of the anion which will alter, in addition, the dihedral angle between the pyridine planes. This angle is equal to 89.53 (19)° in (I), 89.62° in the Liqing structure, a range of 85.73 to 81.13° in the Holzbock structure, 85.33° in orthorhombic phase and 83.37° in triclinic phase of the Tebbe structure and 78.25 to 58.13° in the Lutz structure. The C—H $\cdots$  $\pi$ -(ring) interaction only takes place in (I) and the triclinic phase of the Tebbe structure producing a one-dimensional-structure. The data for C4—H4 $\cdots$ N2 (pyridine ring) (symmetry = 1/2 + *x*, 1/2 - *y*, 1/2 + *z*) are H-centroid distance 2.97 Å,  $\gamma$  = 20.28°. This fact suggests that the solvate absence and a dihedral angle between the pyridine planes next to 90° facilitate this interaction.

### Experimental

A solution of 0.070 g (0.308 mmol) [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] was dissolved in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (10 ml) and methanol (10 ml). About 0.1230 g, (0.625 mmol) of pyridine was added to a solution. Then, a solution of 0.070 g, (0.625 mmol) of NaBF<sub>4</sub> in methanol (2 ml) was added dropwise with vigorous stirring. After 2 h, stirring was stopped, and the product precipitated as yellow solid, was filtered, washed with diethylether, and dried under vacuum. Crystals were obtained by evaporation of acetonitrile solution. Yield: 0.15 g, (81%) - C<sub>20</sub>H<sub>20</sub>B<sub>2</sub>F<sub>8</sub>N<sub>4</sub>Pd (596.42). (%): C, 40.27; H, 3.38; N, 9.39; found: C, 40.26; H, 3.37; N, 9.39. Conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, 1.03  $\times$  10<sup>-3</sup> M in acetonitrile): 279. IR(KBr, cm<sup>-1</sup>):  $\nu$ (C=C)<sub>py</sub>;  $\nu$ (C=N)<sub>py</sub> 1603,  $\delta$ (C=C)<sub>py</sub>;  $\delta$ (C=N)<sub>py</sub> 1448,  $\nu$ (B—F) 1068,  $\delta$ (C—H)<sub>oop</sub> 769, 695. IR (polyethylene, cm<sup>-1</sup>):  $\nu$ (Pd—N)<sub>as(py)</sub> 472. <sup>1</sup>H NMR (250 MHz, [D<sub>3</sub>]-acetonitrile solution)  $\delta$  = 7.58–7.43 (m, 8H, py), 8.85–8.72 (m, 8H, py), 8.04–7.90 (m, 4H, py). <sup>13</sup>C NMR (63 MHz, [D<sub>3</sub>]-acetonitrile solution)  $\delta$  = 128–126(py), 142–140(py), 154–152(py).

## Figures

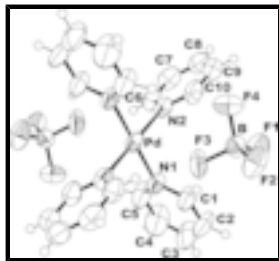


Fig. 1. The asymmetric unit of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. A position of the disorder of the  $\text{BF}_4$  has only been drawn for greater clarity of the figure.

## Tetrakis(pyridine- $\kappa$ N)palladium(II) bis(tetrafluoridoborate)

### Crystal data

$[\text{Pd}(\text{C}_5\text{H}_5\text{N})_4](\text{BF}_4)_2$

$M_r = 596.42$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 15.640\ (7)\ \text{\AA}$

$b = 10.886\ (7)\ \text{\AA}$

$c = 15.711\ (7)\ \text{\AA}$

$\beta = 115.63\ (3)^\circ$

$V = 2412\ (2)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1184$

$D_x = 1.643\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 9\text{--}18^\circ$

$\mu = 0.85\ \text{mm}^{-1}$

$T = 295\ (2)\ \text{K}$

Prism, yellow

$0.18 \times 0.15 \times 0.11\ \text{mm}$

### Data collection

Enraf–Nonius CAD-4  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 295\ (2)\ \text{K}$

$\omega/2\theta'$  scans

Absorption correction: none

6864 measured reflections

3521 independent reflections

1872 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.064$

$\theta_{\text{max}} = 30.0^\circ$

$\theta_{\text{min}} = 2.4^\circ$

$h = -21 \rightarrow 21$

$k = -14 \rightarrow 15$

$l = -22 \rightarrow 12$

3 standard reflections

every 120 min

intensity decay: none

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.154$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0885P)^2]$

$S = 0.97$   
 3521 reflections  
 217 parameters  
 20 restraints  
 Primary atom site location: structure-invariant direct methods

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.96 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: none

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Pd	0.2500	0.2500	0.5000	0.04425 (17)	
N1	0.3643 (3)	0.3627 (3)	0.5562 (3)	0.0524 (10)	
N2	0.2482 (3)	0.2718 (3)	0.3707 (3)	0.0515 (10)	
C1	0.3518 (4)	0.4830 (5)	0.5591 (5)	0.0706 (16)	
H1	0.281 (4)	0.507 (6)	0.540 (4)	0.085*	
C2	0.4256 (5)	0.5640 (5)	0.5942 (5)	0.090 (2)	
H2	0.4145	0.6479	0.5939	0.107*	
C3	0.5147 (5)	0.5201 (7)	0.6291 (6)	0.107 (3)	
H3	0.5662	0.5730	0.6560	0.128*	
C4	0.5284 (5)	0.3985 (8)	0.6246 (7)	0.119 (3)	
H4	0.5897	0.3678	0.6460	0.142*	
C5	0.4529 (4)	0.3202 (5)	0.5888 (5)	0.081 (2)	
H5	0.466 (6)	0.234 (5)	0.602 (5)	0.097*	
C6	0.3069 (5)	0.2063 (5)	0.3457 (4)	0.0618 (14)	
H6	0.339 (4)	0.159 (5)	0.392 (4)	0.074*	
C7	0.3078 (5)	0.2172 (6)	0.2601 (5)	0.0747 (19)	
H7	0.359 (4)	0.175 (6)	0.251 (4)	0.090*	
C8	0.2451 (5)	0.2970 (7)	0.1942 (5)	0.0736 (17)	
H8	0.246 (5)	0.302 (6)	0.139 (5)	0.088*	
C9	0.1841 (5)	0.3641 (5)	0.2183 (4)	0.0753 (17)	
H9	0.130 (4)	0.420 (6)	0.181 (4)	0.090*	
C10	0.1872 (5)	0.3496 (5)	0.3071 (5)	0.0682 (15)	
H10	0.139 (4)	0.375 (5)	0.328 (4)	0.082*	
B	0.4188 (3)	0.0789 (4)	0.0683 (3)	0.0520 (13)	
F1	0.3608 (6)	0.1363 (7)	0.1009 (6)	0.087 (4)	0.50
F1'	0.3416 (6)	0.1358 (9)	0.0789 (9)	0.126 (6)	0.50
F2	0.4665 (5)	0.1591 (5)	0.0370 (5)	0.074 (2)	0.50
F2'	0.4267 (10)	0.1392 (11)	-0.0085 (7)	0.209 (9)	0.50
F3	0.3647 (5)	-0.0047 (5)	-0.0055 (5)	0.078 (2)	0.50
F3'	0.3989 (8)	-0.0435 (5)	0.0473 (11)	0.171 (8)	0.50
F4	0.4867 (5)	0.0047 (7)	0.1429 (4)	0.095 (3)	0.50
F4'	0.5011 (6)	0.0967 (14)	0.1496 (6)	0.206 (8)	0.50

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Pd	0.0444 (3)	0.0326 (2)	0.0633 (3)	-0.0010 (3)	0.0304 (2)	-0.0053 (3)

## supplementary materials

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N1	0.047 (2)	0.0369 (19)	0.075 (3)	0.0015 (16)	0.028 (2)	0.0004 (18)
N2	0.056 (2)	0.037 (2)	0.069 (2)	-0.0016 (15)	0.034 (2)	-0.0049 (16)
C1	0.064 (3)	0.037 (2)	0.107 (5)	0.000 (2)	0.033 (3)	0.002 (3)
C2	0.089 (5)	0.036 (3)	0.135 (6)	-0.014 (3)	0.041 (5)	-0.014 (4)
C3	0.070 (4)	0.070 (4)	0.149 (7)	-0.031 (4)	0.018 (4)	0.019 (5)
C4	0.046 (3)	0.093 (6)	0.184 (9)	0.002 (4)	0.020 (4)	0.028 (6)
C5	0.053 (3)	0.049 (3)	0.131 (6)	0.001 (2)	0.032 (4)	0.011 (3)
C6	0.073 (4)	0.048 (2)	0.082 (4)	0.001 (2)	0.050 (3)	-0.002 (3)
C7	0.087 (4)	0.068 (4)	0.094 (5)	-0.013 (3)	0.063 (4)	-0.018 (3)
C8	0.091 (5)	0.069 (3)	0.071 (4)	-0.018 (3)	0.044 (4)	-0.011 (3)
C9	0.094 (4)	0.055 (3)	0.069 (4)	-0.002 (3)	0.027 (3)	0.001 (3)
C10	0.084 (4)	0.045 (3)	0.084 (4)	0.005 (3)	0.044 (3)	0.001 (3)
B	0.057 (3)	0.050 (3)	0.053 (3)	-0.009 (3)	0.027 (3)	0.000 (2)
F1	0.106 (7)	0.068 (7)	0.130 (8)	0.010 (6)	0.092 (7)	-0.010 (6)
F1'	0.087 (7)	0.124 (12)	0.189 (13)	-0.034 (7)	0.079 (8)	-0.083 (10)
F2	0.083 (5)	0.050 (4)	0.123 (7)	-0.013 (3)	0.076 (5)	0.007 (4)
F2'	0.31 (2)	0.232 (19)	0.121 (11)	0.107 (17)	0.131 (13)	0.071 (11)
F3	0.075 (5)	0.051 (4)	0.096 (5)	-0.010 (4)	0.026 (4)	-0.032 (4)
F3'	0.166 (12)	0.038 (4)	0.39 (2)	-0.003 (6)	0.201 (15)	-0.006 (9)
F4	0.097 (6)	0.101 (7)	0.062 (5)	0.015 (5)	0.013 (4)	0.020 (5)
F4'	0.139 (11)	0.25 (2)	0.138 (11)	0.006 (13)	-0.023 (8)	-0.043 (12)

### *Geometric parameters (Å, °)*

Pd—N1 <sup>i</sup>	2.028 (4)	C6—C7	1.357 (9)
Pd—N1	2.028 (4)	C6—H6	0.85 (6)
Pd—N2 <sup>i</sup>	2.033 (5)	C7—C8	1.382 (11)
Pd—N2	2.033 (5)	C7—H7	0.99 (6)
N1—C1	1.328 (6)	C8—C9	1.379 (9)
N1—C5	1.335 (7)	C8—H8	0.88 (7)
N2—C10	1.342 (7)	C9—C10	1.384 (9)
N2—C6	1.348 (7)	C9—H9	1.00 (6)
C1—C2	1.365 (8)	C10—H10	0.99 (6)
C1—H1	1.05 (6)	B—F1	1.370 (6)
C2—C3	1.344 (10)	B—F2	1.371 (5)
C2—H2	0.9300	B—F3'	1.375 (6)
C3—C4	1.348 (11)	B—F4'	1.380 (7)
C3—H3	0.9300	B—F2'	1.425 (7)
C4—C5	1.365 (9)	B—F3	1.428 (6)
C4—H4	0.9300	B—F1'	1.430 (7)
C5—H5	0.96 (6)	B—F4	1.441 (6)
N1 <sup>i</sup> —Pd—N1	180.00 (17)	N2—C6—C7	122.9 (6)
N1 <sup>i</sup> —Pd—N2 <sup>i</sup>	89.63 (17)	N2—C6—H6	108 (4)
N1—Pd—N2 <sup>i</sup>	90.37 (17)	C7—C6—H6	129 (4)
N1 <sup>i</sup> —Pd—N2	90.37 (17)	C6—C7—C8	119.3 (6)
N1—Pd—N2	89.63 (17)	C6—C7—H7	117 (4)
N2 <sup>i</sup> —Pd—N2	180.0	C8—C7—H7	123 (4)

C1—N1—C5	118.2 (5)	C9—C8—C7	118.6 (6)
C1—N1—Pd	119.8 (4)	C9—C8—H8	123 (5)
C5—N1—Pd	122.0 (4)	C7—C8—H8	118 (5)
C10—N2—C6	118.1 (5)	C8—C9—C10	119.3 (6)
C10—N2—Pd	121.1 (4)	C8—C9—H9	132 (4)
C6—N2—Pd	120.8 (4)	C10—C9—H9	108 (4)
N1—C1—C2	122.7 (6)	N2—C10—C9	121.8 (6)
N1—C1—H1	113 (4)	N2—C10—H10	109 (3)
C2—C1—H1	124 (4)	C9—C10—H10	128 (3)
C3—C2—C1	118.8 (6)	F1—B—F2	113.2 (4)
C3—C2—H2	120.6	F1—B—F3	109.8 (4)
C1—C2—H2	120.6	F2—B—F3	109.7 (4)
C2—C3—C4	119.2 (6)	F1—B—F4	109.0 (4)
C2—C3—H3	120.4	F2—B—F4	109.0 (4)
C4—C3—H3	120.4	F3—B—F4	105.8 (4)
C3—C4—C5	120.4 (7)	F3'—B—F4'	112.4 (4)
C3—C4—H4	119.8	F3'—B—F2'	109.7 (4)
C5—C4—H4	119.8	F3'—B—F1'	109.4 (4)
N1—C5—C4	120.7 (6)	F4'—B—F2'	109.4 (4)
N1—C5—H5	121 (5)	F4'—B—F1'	109.1 (4)
C4—C5—H5	117 (5)	F2'—B—F1'	106.6 (4)

Symmetry codes: (i)  $-x+1/2, -y+1/2, -z+1$ .

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H4 $\cdots$ Cg1 <sup>ii</sup>	0.93	2.97	3.800 (10)	150

Symmetry codes: (ii)  $x+1/2, -y+1/2, z-1/2$ .

Fig. 1

