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Tetrakis(pyridine-κN)palladium(II) bis(tetrafluoridoborate)

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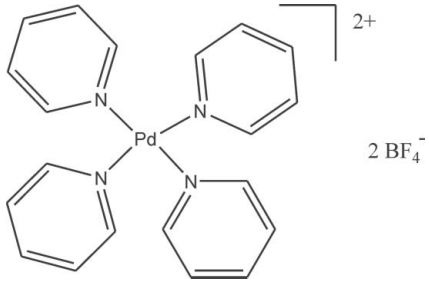
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.011 Å; disorder in solvent or counterion; R factor = 0.046; wR factor = 0.154; data-to-parameter ratio = 16.2.

The title complex, $[Pd(C_5H_5N)_4](BF_4)_2$, contains tetrapyridinepalladium(II) cations residing on crystallographic inversion centres. These are linked by weak C—H···F interactions (involving disordered BF_4^- anions) [range 2.988 (12)–3.431 (10) Å], together with C—H···π(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

$[Pd(C_5H_5N)_4](BF_4)_2$
M_r = 596.42
Monoclinic, $C2/c$
a = 15.640 (7) Å
b = 10.886 (7) Å
c = 15.711 (7) Å
β = 115.63 (3)°
V = 2412 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.85 mm^{-1}
T = 295 (2) K
0.18 × 0.15 × 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_{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
$\Delta\rho_{max}$ = 0.96 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···$Cg1^{i}$	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-*κN*)palladium(II) bis(tetrafluoridoborate)

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Comment

The design of supramolecular coordination compounds by self-assembly is a developing research area (Lehn, 1995, Braga *et al.*, 1998). Four-coordinate Pd^{II} 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···π-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···*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···π-(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···N2 (pyridine ring) (symmetry = 1/2 + *x*, 1/2 − *y*, 1/2 + *z*) are H-centroid distance 2.97 Å, γ = 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) $[PdCl_2(CH_3CN)_2]$ was dissolved in a mixture of CH_2Cl_2 (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 $NaBF_4$ 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%) - $C_{20}H_{20}B_2F_8N_4Pd$ (596.42). (%): C, 40.27; H, 3.38; N, 9.39; found: C, 40.26; H, 3.37; N, 9.39. Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.03 *x* 10^{-3} *M* in acetonitrile): 279. IR(KBr, cm^{-1}): ν(C=C)$_{py}$; ν(C=N)$_{py}$ 1603, δ(C=C)$_{py}$; δ(C=N)$_{py}$ 1448, ν(B—F) 1068, δ(C—H)$_{oop}$ 769, 695. IR (polyethylene, cm^{-1}): ν(Pd—N)as(py) 472. ^{1}H NMR (250 MHz, [D_3]-acetonitrile solution) δ = 7.58–7.43 (m, 8H, py), 8.85–8.72 (m, 8H, py), 8.04–7.90 (m, 4H, py). ^{13}C NMR (63 MHz, [D_3]-acetonitrile solution) δ = 128–126(py), 142–140(py), 154–152(py).

Figures

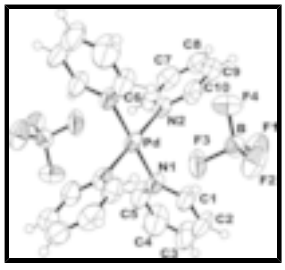

Fig. 1. The asymmetric unit of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. A position of the disorder of the BF_4 has only been drawn for greater clarity of the figure.

Tetrakis(pyridine-κ*N*)palladium(II) bis(tetrafluoridoborate)

Crystal data

$[Pd(C_5H_5N)_4](BF_4)_2$	F_{000} = 1184
M_r = 596.42	D_x = 1.643 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 25 reflections
a = 15.640 (7) Å	θ = 9–18º
b = 10.886 (7) Å	μ = 0.85 mm^{-1}
c = 15.711 (7) Å	*T* = 295 (2) K
β = 115.63 (3)º	Prism, yellow
V = 2412 (2) Å^3	0.18 × 0.15 × 0.11 mm
Z = 4	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.064
Radiation source: fine-focus sealed tube	θ_{max} = 30.0º
Monochromator: graphite	θ_{min} = 2.4º
T = 295(2) K	*h* = −21→21
ω/2θ' scans	*k* = −14→15
Absorption correction: none	*l* = −22→12
6864 measured reflections	3 standard reflections
3521 independent reflections	every 120 min
1872 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.046	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.154	$w = 1/[\sigma^2(F_o^2) + (0.0885P)^2]$

	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{max} = 0.001$
3521 reflections	$\Delta\rho_{max} = 0.96$ e Å^{-3}
217 parameters	$\Delta\rho_{min} = -0.52$ e Å^{-3}
20 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{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 (Å^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)

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^{i}	2.028 (4)	C6—C7	1.357 (9)
Pd—N1	2.028 (4)	C6—H6	0.85 (6)
Pd—N2^{i}	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^{i}—Pd—N1	180.00 (17)	N2—C6—C7	122.9 (6)
N1^{i}—Pd—N2^{i}	89.63 (17)	N2—C6—H6	108 (4)
N1—Pd—N2^{i}	90.37 (17)	C7—C6—H6	129 (4)
N1^{i}—Pd—N2	90.37 (17)	C6—C7—C8	119.3 (6)
N1—Pd—N2	89.63 (17)	C6—C7—H7	117 (4)
N2^{i}—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 (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···Cg1^{ii}	0.93	2.97	3.800 (10)	150

Symmetry codes: (ii) *x*+1/2, −*y*+1/2, *z*−1/2.

Fig. 1