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Pseudopolymorphism of [2,5-bis(2-pyridyl)pyrazine]ferrocenyl(methyl)boron hexafluorophosphate

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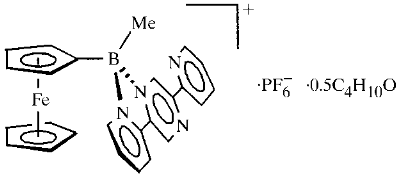
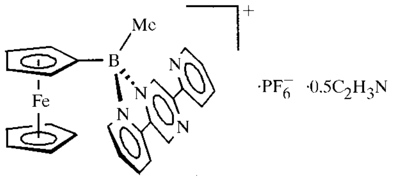
Two pseudopolymorphs of [2,5-bis(2-pyridyl)pyrazine]-ferrocenyl(methyl)boron hexafluorophosphate have been determined at 173 K, namely the diethyl ether hemisolvate, $[Fe(C_5H_5)(C_{20}H_{17}BN_4)]PF_6{\cdot}0.5C_4H_{10}O$, (I), which forms red crystals with $Z' = 1$, and the acetonitrile hemisolvate, $[Fe(C_5H_5)(C_{20}H_{17}BN_4)]PF_6{\cdot}0.5CH_3CN$, (II), which yields green–brown crystals with $Z' = 2$. Despite the different crystal packing, the cations in (I) and (II) are similar. The 2,5-bis(2-pyridyl)pyrazine moiety is almost planar and displays bending along its long axis compared with free 2,5-bis(2-pyridyl)-pyrazine. It is remarkable that both crystals were obtained from the same acetonitrile/diethyl ether solution.

Comment

Metal-containing polymers are of special interest in the development of new materials with important applications in the fields of molecular-based ferromagnets, synthetic metal conductors and non-linear optics (Nguyen *et al.*, 1999; Bruce & O'Hare, 1992; Long, 1995; Oriol & Serrano, 1995). One particularly successful approach was found to be coordination polymer synthesis employing multidentate ligands, which contain a delocalized π-system and are able to serve as bridges between transition metals. In this context, 2,5-bis(2-pyridyl)-pyrazine (bppz) has already been used for the generation of various interesting supra- or nanomolecular species (Neels *et al.*, 1995, and references therein). Despite the high potential of this ligand, only a few X-ray crystal structure analyses of its complexes have been reported to date (Neels & Stoeckli-Evans, 1993; Neels *et al.*, 1995; Neels, Stoeckli-Evans *et al.*, 1997). In the course of our work on metal-containing macromolecular aggregates, we developed a variant method of coordination polymer synthesis by coordinatively linking saturated building blocks (*e.g.* ferrocene) to nitrogen ligands *via* Lewis acidic boryl anchor groups (Jäkle *et al.*, 1995). In previous studies, we have prepared a charge-transfer polymer (Fontani *et al.*, 1998), as well as electron storage systems (de Biani, Gmeinwieser *et al.*, 1997), by combining borylated ferrocenes with pyrazine and 2,2′-bipyridine, respectively. This paper reports on the X-ray crystal structure determination of [2,5-bis(2-pyridyl)pyrazine]ferrocenyl(methyl)boron, consisting of monoborylated ferrocene and the Lewis base bppz, which contains 2,2′-bipyridine and pyrazine functionalities. The air- and moisture-stable title compound can conveniently be prepared by treating monoborylated ferrocene with an equimolar amount of bppz (see *Experimental*). [2,5-Bis(2-pyridyl)pyrazine]ferrocenyl(methyl)boron, which still supplies two Lewis basic nitrogen centres, is a promising redox-active chelating ligand to transition metals, similar to ferrocene-based tris(1-pyrazolyl)borates reported earlier by our group (Jäkle *et al.*, 1996; de Biani, Jäkle *et al.*, 1997). Gas-phase diffusion of diethyl ether into an acetonitrile solution of the title compound afforded single crystals of two different compositions and colours (red and green–brown). The red crystals, (I), were found to be ether clathrates containing only one complex in the asymmetric unit. The green–brown crystals, (II), on the other hand, feature two crystallographically independent molecules, (II*a*) and (II*b*), together with one equivalent of acetonitrile in the asymmetric unit.



(I)



(II)

A comparison of (I) and (II) reveals that despite the different crystal structures, the geometry of the cation does not change markedly. A least-squares fit of all non-H atoms of (I) with (II*a*) and (II*b*) (r.m.s. deviation = 0.28 and 0.17 Å, respectively) shows that the different environment does not induce a significant change in the molecular framework. Thus, only (I) is explicitly discussed and the corresponding values of (II) can be found in Table 2. Plots of the cation of (I), (II*a*) and (II*b*) are presented in Figs. 1(*a*), 1(*b*) and 1(*c*). It contains a tetra-coordinated B atom possessing a distorted tetrahedral geometry with an N21—B1—N31 bite angle of 94.3 (4)°. The bond lengths between boron and the two N atoms are almost equal within experimental error. The five-membered ring consisting of B1, N21, C22, N31 and C32 is almost planar [r.m.s. deviation = 0.015, 0.001 and 0.008 Å in (I), (II*a*) and (II*b*), respectively] and forms a dihedral angle of 74.6 (2)°

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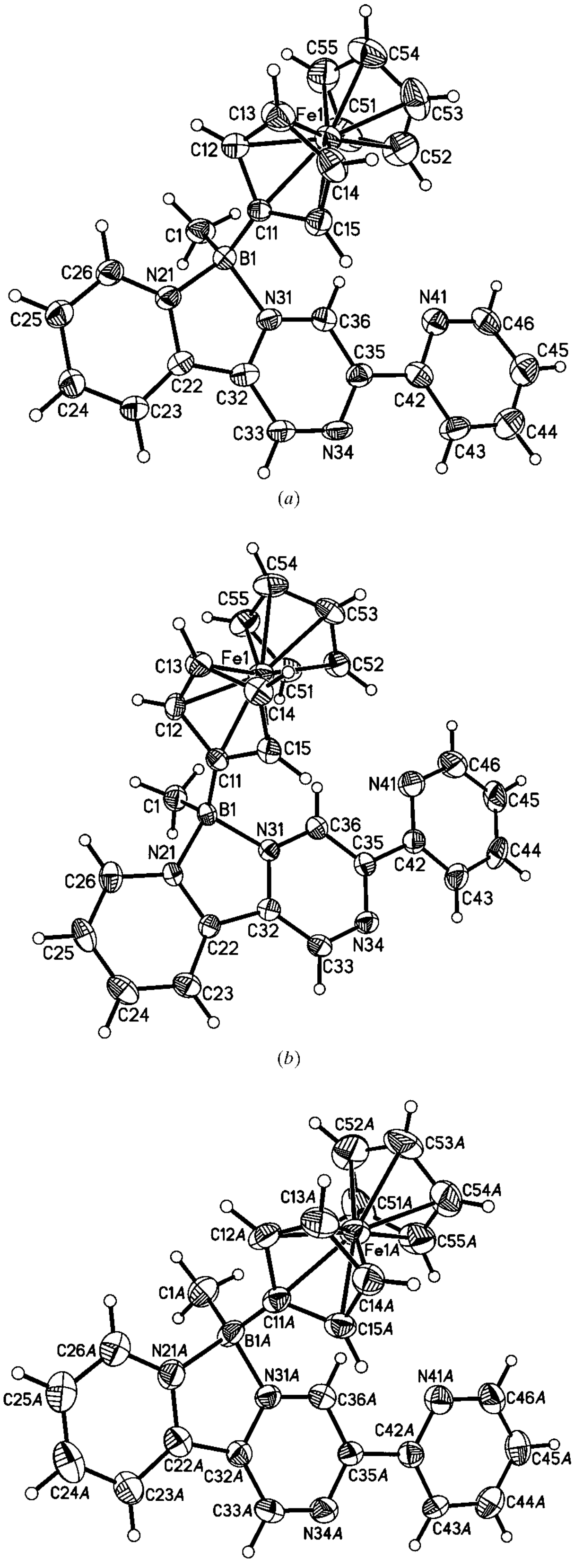
† Contact author on chemical matters.



(*a*)

(*b*)

(*c*)

Figure 1
Perspective views of the cations of (*a*) (I), (*b*) (II*a*) and (*c*) (II*b*) with the atom-numbering schemes. Displacement ellipsoids are at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

[(II*a*) 74.0 (2)° and (II*b*) 71.6 (2)°] with the plane of the substituted cyclopentadienyl ring (C11–C15). The complexation of B1 by N21 and N31 leads to decreased bond angles at C22 and C32 in the newly formed five-membered ring and to a severe distortion of the chelating bppz ligand shown by the angle between the vectors C22—C25 and C32—C35 which is 20.3 (5)° in (I) and (II*a*), 20.5 (5)° in (II*b*), but 0° in free bppz. The bppz ligand is almost planar in (I), with the two pyridine rings tilted by only 5.2 (2)° [(II*a*) 3.9 (1)° and (II*b*) 3.5 (1)°] (N21–C26) and 4.9 (2)° [(II*a*) 8.1 (1)° and (II*b*) 10.6 (1)°] (N41–C46) with respect to the pyrazine moiety and similar to the binuclear Ni^{II}–bppz complex (5.4 and 3.8°, respectively; Neels, Neels *et al.*, 1997). In the free bppz ligand (Neels & Stoeckli-Evans, 1993), which is centrosymmetric, the angle between the central pyrazine and the pyridine rings is 7.9°.

In the centrosymmetric Mn^{II}, Fe^{II} and Cu^{II} binuclear complexes of bppz, the corresponding dihedral angles were found to be 2.9, 4.0 and 9.2°, respectively (Neels & Stoeckli-Evans, 1993).

Experimental

A toluene (10 ml) solution of FcBMeBr [Fc = (η^5-C_5H_5)Fe(η^5-C_5H_4)] (0.29 g, 1.00 mmol) was added dropwise with stirring at room temperature to a solution of bppz (0.23 g, 1.00 mmol) in toluene (60 ml). The mixture instantaneously turned a green–blue colour, and a blue precipitate formed immediately. The slurry was stirred for 3 h, filtered, triturated with hexane (3 × 20 ml), and dried *in vacuo*. The resulting material was dissolved in water (50 ml) and the clear green solution was added dropwise at room temperature to an aqueous solution of NH_4PF_6 (0.33 g, 2.00 mmol), whereupon the title compound precipitated quantitatively. Deep-red X-ray-quality crystals of (I) were grown by layering its acetonitrile solution with diethyl ether [yield 0.51 g (86%)]. A second crop consisting of green–brown crystals of (II) precipitated from the same solution.

Compound (I)

Crystal data

[Fe(C_5H_5)($C_{20}H_{17}BN_4$)]PF_6·0.5$C_4H_{10}O$
M_r = 627.16
Triclinic, $P\overline{1}$
a = 9.435 (1) Å
b = 10.562 (1) Å
c = 14.698 (1) Å
α = 97.76 (1)°
β = 102.39 (1)°
γ = 105.37 (1)°
V = 1350.5 (2) Å^3
Z = 2
D_x = 1.542 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3943 reflections
θ = 1–20°
μ = 0.687 mm^{-1}
T = 173 (2) K
Plate, red
0.60 × 0.36 × 0.02 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.683, $T_{\max}$ = 0.986
12 251 measured reflections
4771 independent reflections
3227 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.010
$\theta_{\max}$ = 25.03°
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -17 \rightarrow 17$
101 standard reflections
frequency: 1200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.080$
$wR(F^2) = 0.203$
$S = 1.08$
4771 reflections
379 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0744P)^2 + 3.7568P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.017$
$\Delta\rho_{\max} = 0.83$ e Å^{-3}
$\Delta\rho_{\min} = -0.68$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

B1—C1	1.567 (8)	B1—N21	1.580 (8)
B1—C11	1.567 (9)	B1—N31	1.603 (8)
C1—B1—C11	119.1 (5)	N21—B1—N31	94.3 (4)
C1—B1—N21	110.7 (5)	N21—C22—C32	108.6 (5)
C11—B1—N21	109.7 (5)	N31—C32—C22	110.5 (5)
C1—B1—N31	111.5 (5)	B1—C11—Fe1	132.3 (4)
C11—B1—N31	108.7 (5)		
N21—B1—C11—C15	92.0 (7)	C1—B1—C11—Fe1	−43.9 (8)

Compound (II)

Crystal data

$[Fe(C_5H_5)(C_{20}H_{17}BN_4)]PF_6\cdot0.5C_2H_3N$
$M_r = 610.62$
Triclinic, $P\overline{1}$
$a = 8.011$ (1) Å
$b = 16.630$ (1) Å
$c = 20.384$ (1) Å
$\alpha = 98.55$ (1)°
$\beta = 99.47$ (1)°
$\gamma = 92.03$ (1)°
$V = 2643.8$ (4) Å^3

$Z = 4$
$D_x = 1.534$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7688 reflections
$\theta = 1$–20°
$\mu = 0.699$ mm^{-1}
$T = 173$ (2) K
Needle, green–brown
0.30 × 0.05 × 0.05 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.818$, $T_{\max} = 0.966$
27291 measured reflections
9300 independent reflections
5307 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.098$
$\theta_{\max} = 25.02°$
$h = -9 \rightarrow 9$
$k = -19 \rightarrow 19$
$l = -24 \rightarrow 24$
123 standard reflections
frequency: 2400 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.076$
$wR(F^2) = 0.138$
$S = 1.08$
9300 reflections
767 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2 + 2.1697P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.010$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

B1—C1	1.590 (8)	B1*A*—C1*A*	1.588 (8)
B1—C11	1.592 (8)	B1*A*—C11*A*	1.572 (8)
B1—N21	1.622 (7)	B1*A*—N21*A*	1.604 (8)
B1—N31	1.598 (7)	B1*A*—N31*A*	1.606 (7)
C1—B1—N21	109.5 (4)	C1*A*—B1*A*—N31*A*	113.5 (5)
C1—B1—N31	112.0 (4)	C1*A*—B1*A*—C11*A*	119.6 (5)
C1—B1—C11	118.5 (5)	N21*A*—B1*A*—N31*A*	94.1 (4)
N21—B1—N31	93.4 (4)	C11*A*—B1*A*—N21*A*	110.2 (5)
C11—B1—N31	109.8 (4)	C11*A*—B1*A*—N31*A*	106.8 (5)
C11—B1—N21	110.9 (4)	N21*A*—C22*A*—C32*A*	108.7 (5)
N21—C22—C32	108.4 (4)	N31*A*—C32*A*—C22*A*	110.0 (5)
N31—C32—C22	110.1 (4)	B1—C11—Fe1	128.4 (4)
C1*A*—B1*A*—N21*A*	109.5 (5)	B1*A*—C11*A*—Fe1*A*	130.9 (4)
N21—B1—C11—C15	84.5 (6)	N21*A*—B1*A*—C11*A*—C15*A*	95.1 (6)
C1—B1—C11—Fe1	−54.7 (6)	C1*A*—B1*A*—C11*A*—Fe1*A*	−44.2 (8)

All H atoms, except those of the disordered solvent, were located by difference Fourier synthesis and treated as riding, with U(H) = $1.5U_{\rm eq}$(C$_{\rm methyl}$) or U(H) = $1.2U_{\rm eq}$(C) and with C—H$_{\rm aromatic}$ = 0.95 Å and C—H$_{\rm methyl}$ = 0.98 Å. One of the hexafluorophosphate anions of (II) is disordered. The ratio of the site-occupation factors of the F atoms refined to 0.57 (1)/0.43 (1). Bond lengths and angles of the disordered F atoms were restrained to have the same values as those in the ordered PF_6^- anion.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1027). Services for accessing these data are described at the back of the journal.

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