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Bis[dihydrobis(pyrazol-1-yl-κN^2)borato]bis(methanol-κO)iron(II)

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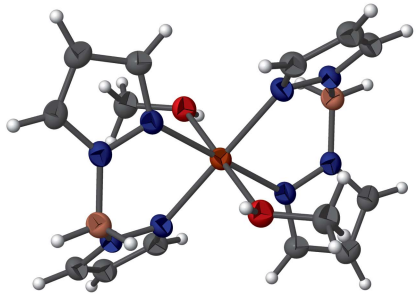
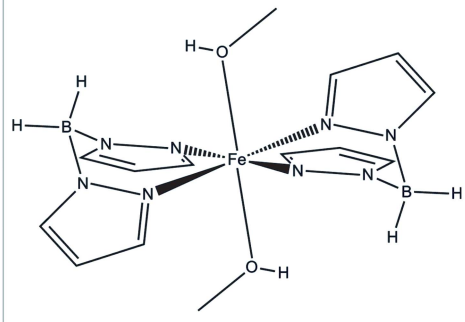
Structural data: full structural data are available from iucrdata.iucr.org

The structure determination was undertaken as part of a project on the synthesis of new spin-crossover compounds based on octahedral Fe^{II} bis(pyrazolyl)borate complexes. The asymmetric unit of the title compound, $[Fe(H_2B(pz)_2)_2(CH_3OH)_2]$ [$H_2B(pz)_2$ = dihydrobis(pyrazol-1-yl)borate, $C_6H_8BN_4$], consists of one Fe^{II} cation that is located on a centre of inversion, as well as one methanol molecule and one $H_2B(pz)_2$ dianion that occupy general positions. In the crystal, the Fe^{II} cations are coordinated by two methanol molecules and four N atoms of two $H_2B(pz)_2$ anions within a slightly distorted octahedron. Bond lengths and angles between the Fe^{II} atom and the $H_2B(pz)_2$ anion are comparable to those in related Fe^{II} complexes.

3D view



Chemical scheme



Structure description

Concerning the background of this project, see Naggert *et al.* (2015). For related crystal structures of discrete octahedral Fe^{II} bis(pyrazolyl)borate complexes with N-donor ligands, see: Real *et al.* (1997); Thompson *et al.* (2004); Milek *et al.* (2013); Nihei *et al.* (2013); Kulmaczewski *et al.* (2014); Naggert *et al.* (2015). The title compound is illustrated in Fig. 1. Despite the presence of a hydroxy group, classical hydrogen-bonding interactions are not evident in the crystal structure.

Synthesis and crystallization

Iron(II) perchlorate hydrate and solvents were purchased by Sigma–Aldrich. All reactions were carried out using dry solvents and under an inert atmosphere. Potassium dihydrobis(pyrazolyl)borate $K[H_2B(pz)_2]$ and $[Fe(H_2B(pz)_2)_2(CH_3OH)_2]$ were prepared according to literature methods (Trofimenko, 1967; Real *et al.*, 1997).

A solution of $K[H_2B(pz)_2]$ (283 mg, 1.52 mmol) in methanol (3 ml) was added dropwise to a solution of $Fe(ClO_4)_2{\cdot}6H_2O$ (276 mg, 0.76 mmol) in methanol (1 ml). The yellow

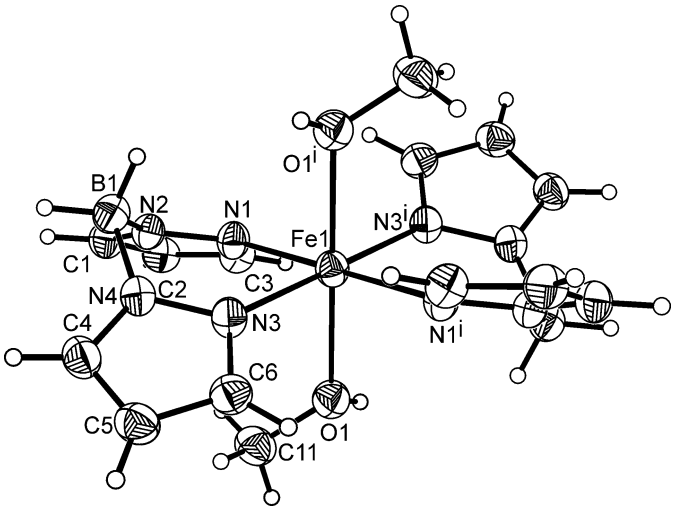


Figure 1
Perspective view of the title compound with the atom labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry code for the generation of equivalent atoms: (i) $-x, -y+1, -z+1$.]

$Fe[H_2B(pz)_2]_2$ solution was stirred for 10 min at room temperature. The resulting $KClO_4$ precipitate was removed by filtration and washed with methanol (6 ml). After further stirring for one h the solution was stored at 245 K. After four days colorless crystals of $[Fe(H_2B(pz)_2)_2(CH_3OH)_2]$ were collected by suction filtration. They decompose in air within a few days.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Fe(C_6H_8BN_4)_2(CH_4O)_2]$
M_r	413.88
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	170
a, b, c (Å)	9.7430 (5), 8.6535 (3), 12.3173 (6)
β (°)	111.670 (4)
V (Å^3)	965.09 (8)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.81
Crystal size (mm)	0.20 × 0.12 × 0.06
Data collection	
Diffractometer	Stoe IPDS2
Absorption correction	Numerical (*X-RED* and *X-SHAPE*; Stoe & Cie, 2008)
T_{min}, T_{max}	0.781, 0.898
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11312, 2103, 1898
R_{int}	0.026
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.089, 1.07
No. of reflections	2103
No. of parameters	125
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.45

Computer programs: *X-AREA* (Stoe & Cie, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *XP* in *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

Acknowledgements

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full crystallographic data

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Bis[dihydrobis(pyrazol-1-yl-κN^2)borato]bis(methanol-κO)iron(II)

Crystal data

$[Fe(C_6H_8B_2N_4)_2(CH_4O)_2]$
M_r = 413.88
Monoclinic, $P2_1/n$
a = 9.7430 (5) Å
b = 8.6535 (3) Å
c = 12.3173 (6) Å
β = 111.670 (4)°
V = 965.09 (8) Å^3
Z = 2
$F(000)$ = 432
D_x = 1.424 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 11751 reflections
θ = 2.3–27.0°
μ = 0.81 mm^{-1}
T = 170 K
Block, colorless
0.20 × 0.12 × 0.06 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: numerical (X-RED and X-SHAPE; Stoe & Cie, 2008)
T_{min} = 0.781, T_{max} = 0.898
11312 measured reflections
2103 independent reflections
1898 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 27.0°, θ_{min} = 2.3°
h = −12→12
k = −11→11
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.089
S = 1.07
2103 reflections
125 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.3892P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}
Fe1	0.0000	0.5000	0.5000	0.02887 (12)

N1	0.20696 (15)	0.55724 (18)	0.64018 (12)	0.0315 (3)
N2	0.31387 (15)	0.64416 (17)	0.62205 (13)	0.0306 (3)
N3	0.09829 (15)	0.55320 (19)	0.37541 (13)	0.0314 (3)
N4	0.22449 (15)	0.63870 (17)	0.40243 (13)	0.0310 (3)
B1	0.2792 (2)	0.7456 (2)	0.51128 (18)	0.0339 (4)
H1A	0.3691	0.8017	0.5143	0.041*
H1B	0.2021	0.8225	0.5069	0.041*
C1	0.44303 (18)	0.6245 (2)	0.71101 (16)	0.0344 (4)
H1	0.5336	0.6730	0.7186	0.041*
C2	0.4231 (2)	0.5218 (2)	0.79007 (16)	0.0365 (4)
H2	0.4947	0.4860	0.8614	0.044*
C3	0.2736 (2)	0.4828 (2)	0.74114 (16)	0.0350 (4)
H3	0.2258	0.4128	0.7750	0.042*
C4	0.2818 (2)	0.6172 (2)	0.32000 (17)	0.0361 (4)
H4	0.3698	0.6636	0.3193	0.043*
C5	0.1932 (2)	0.5174 (2)	0.23664 (17)	0.0383 (4)
H5	0.2059	0.4823	0.1679	0.046*
C6	0.0806 (2)	0.4795 (2)	0.27593 (16)	0.0353 (4)
H6	0.0019	0.4105	0.2372	0.042*
O1	0.09492 (14)	0.26492 (15)	0.51071 (11)	0.0370 (3)
H1O1	0.0844	0.2074	0.5620	0.056*
C11	0.2429 (2)	0.2333 (2)	0.51817 (19)	0.0433 (4)
H11A	0.2564	0.2732	0.4483	0.065*
H11B	0.2599	0.1214	0.5236	0.065*
H11C	0.3133	0.2836	0.5877	0.065*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.02591 (19)	0.0335 (2)	0.02633 (19)	−0.00137 (13)	0.00856 (13)	−0.00076 (13)
N1	0.0277 (7)	0.0358 (8)	0.0289 (7)	−0.0039 (6)	0.0082 (6)	−0.0006 (6)
N2	0.0269 (7)	0.0315 (7)	0.0317 (7)	−0.0026 (5)	0.0090 (6)	−0.0022 (6)
N3	0.0286 (7)	0.0362 (7)	0.0296 (7)	−0.0034 (6)	0.0111 (6)	−0.0008 (6)
N4	0.0287 (7)	0.0330 (7)	0.0320 (7)	−0.0015 (6)	0.0121 (6)	0.0018 (6)
B1	0.0330 (9)	0.0320 (10)	0.0357 (10)	−0.0018 (8)	0.0115 (8)	0.0011 (8)
C1	0.0267 (8)	0.0381 (9)	0.0350 (9)	−0.0009 (7)	0.0072 (7)	−0.0035 (7)
C2	0.0331 (9)	0.0401 (10)	0.0310 (8)	0.0034 (7)	0.0055 (7)	−0.0008 (7)
C3	0.0366 (9)	0.0369 (9)	0.0299 (8)	−0.0016 (7)	0.0105 (7)	0.0010 (7)
C4	0.0350 (9)	0.0369 (9)	0.0406 (9)	0.0015 (7)	0.0190 (7)	0.0038 (7)
C5	0.0440 (10)	0.0388 (10)	0.0367 (9)	0.0022 (8)	0.0203 (8)	−0.0005 (7)
C6	0.0365 (9)	0.0363 (9)	0.0325 (9)	−0.0010 (7)	0.0122 (7)	−0.0033 (7)
O1	0.0362 (6)	0.0355 (7)	0.0398 (7)	−0.0003 (5)	0.0144 (5)	0.0009 (5)
C11	0.0380 (10)	0.0438 (11)	0.0480 (11)	0.0066 (8)	0.0157 (9)	−0.0003 (9)

Geometric parameters (Å, º)

Fe1—N3^{i}	2.1376 (14)	C1—C2	1.384 (3)
Fe1—N3	2.1376 (14)	C1—H1	0.9500

Fe1—N1^{i}	2.1728 (14)	C2—C3	1.396 (3)
Fe1—N1	2.1729 (14)	C2—H2	0.9500
Fe1—O1	2.2183 (13)	C3—H3	0.9500
Fe1—O1^{i}	2.2183 (13)	C4—C5	1.375 (3)
N1—C3	1.337 (2)	C4—H4	0.9500
N1—N2	1.368 (2)	C5—C6	1.392 (3)
N2—C1	1.340 (2)	C5—H5	0.9500
N2—B1	1.551 (2)	C6—H6	0.9500
N3—C6	1.335 (2)	O1—C11	1.437 (2)
N3—N4	1.367 (2)	O1—H1O1	0.8400
N4—C4	1.340 (2)	C11—H11A	0.9800
N4—B1	1.552 (2)	C11—H11B	0.9800
B1—H1A	0.9900	C11—H11C	0.9800
B1—H1B	0.9900		

N3^{i}—Fe1—N3	180.0	N2—B1—H1B	110.0
N3^{i}—Fe1—N1^{i}	89.49 (5)	N4—B1—H1B	110.0
N3—Fe1—N1^{i}	90.51 (5)	H1A—B1—H1B	108.4
N3^{i}—Fe1—N1	90.51 (5)	N2—C1—C2	108.88 (16)
N3—Fe1—N1	89.49 (5)	N2—C1—H1	125.6
N1^{i}—Fe1—N1	180.0	C2—C1—H1	125.6
N3^{i}—Fe1—O1	92.71 (5)	C1—C2—C3	104.27 (16)
N3—Fe1—O1	87.29 (5)	C1—C2—H2	127.9
N1^{i}—Fe1—O1	94.73 (5)	C3—C2—H2	127.9
N1—Fe1—O1	85.27 (5)	N1—C3—C2	110.88 (16)
N3^{i}—Fe1—O1^{i}	87.29 (5)	N1—C3—H3	124.6
N3—Fe1—O1^{i}	92.71 (5)	C2—C3—H3	124.6
N1^{i}—Fe1—O1^{i}	85.27 (5)	N4—C4—C5	109.31 (16)
N1—Fe1—O1^{i}	94.73 (5)	N4—C4—H4	125.3
O1—Fe1—O1^{i}	180.0	C5—C4—H4	125.3
C3—N1—N2	106.20 (14)	C4—C5—C6	104.27 (17)
C3—N1—Fe1	128.24 (12)	C4—C5—H5	127.9
N2—N1—Fe1	122.32 (11)	C6—C5—H5	127.9
C1—N2—N1	109.77 (14)	N3—C6—C5	110.81 (17)
C1—N2—B1	128.69 (15)	N3—C6—H6	124.6
N1—N2—B1	121.54 (13)	C5—C6—H6	124.6
C6—N3—N4	106.37 (14)	C11—O1—Fe1	124.41 (12)
C6—N3—Fe1	128.01 (13)	C11—O1—H1O1	103.7
N4—N3—Fe1	122.89 (11)	Fe1—O1—H1O1	115.1
C4—N4—N3	109.23 (15)	O1—C11—H11A	109.5
C4—N4—B1	129.11 (15)	O1—C11—H11B	109.5
N3—N4—B1	121.61 (13)	H11A—C11—H11B	109.5
N2—B1—N4	108.45 (15)	O1—C11—H11C	109.5
N2—B1—H1A	110.0	H11A—C11—H11C	109.5
N4—B1—H1A	110.0	H11B—C11—H11C	109.5

Symmetry code: (i) $-x$, $-y+1$, $-z+1$.