

Hemi{tris(picolinic acid- κ^2N,O)iron(II)/tris(picolinato- κ^2N,O)iron(II)} hemi(tetrafluoroborate)Djulia Onggo,^a Fatimah Martak,^a
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Key indicators

Single-crystal X-ray study

T = 295 K

Mean $\sigma(C-C) = 0.008 \text{ \AA}$

Disorder in solvent or counterion

R factor = 0.065

wR factor = 0.154

Data-to-parameter ratio = 11.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

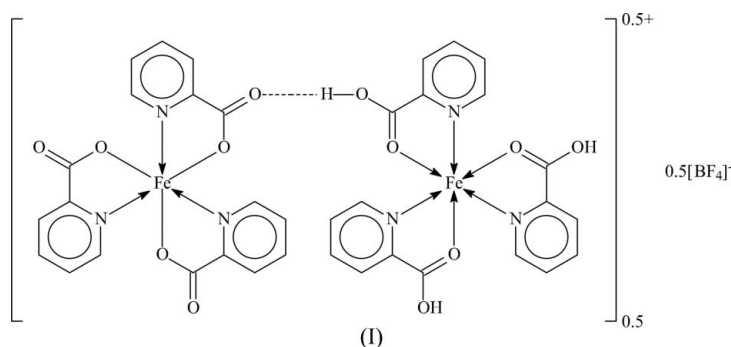
The crystal structure of the title compound, $[\text{Fe}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_6\text{H}_4.5\text{NO}_2)(\text{C}_6\text{H}_5\text{NO}_2)](\text{BF}_4)_{0.5}$, is regarded as consisting of disordered mononuclear $[\text{Fe}^{\text{II}}(\text{C}_6\text{H}_4.5\text{NO}_2)_3]^{+0.5+}$ cations and tetrafluoroborate anions. The *N,O*-chelated Fe lies on a special position of site symmetry $\bar{3}$ and the acid H atom on a special position of site symmetry $\bar{1}$. The B atom is located on a special position of site symmetry $\bar{3}$. The disordered mononuclear units are linked through the acid H atom into a layer motif.

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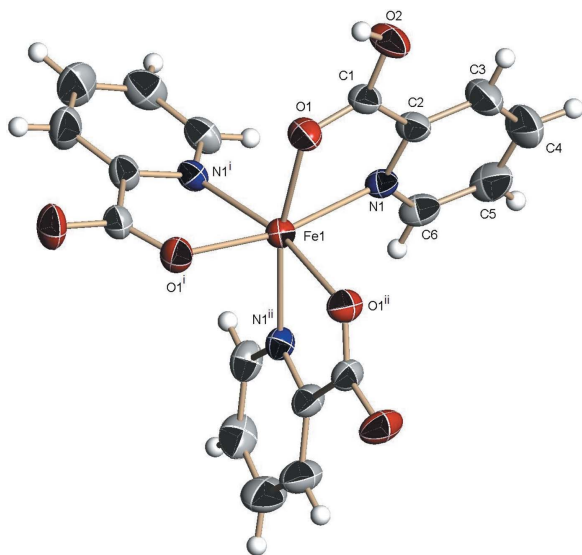
Comment

The picolinate ion chelates to a large number of metal atoms, as shown by a search through the Cambridge Structural Database (Version 5.27; Allen, 2002). Among the complexes are iron(II) derivatives; the iron derivative exists in two forms, as an octahedral diaqua dihydrate (Shova *et al.*, 1996) and as a square-planar dihydrate (Kiani *et al.*, 2000). Yet another iron(II) derivative is known. This light-green compound has a $[(\text{C}_6\text{H}_4\text{NO}_2)_3\text{Fe}^{\text{II}}]\cdot\text{H}_2\text{O}$ formulation (Shova *et al.*, 1996); however, the location of the missing hydrogen that would ensure electroneutrality cannot be ascertained. In the title compound, (I), the half negative charge of the anion is balanced by a disordered hemication. The mononuclear unit lies on a special position of site symmetry $\bar{3}$. The metal center lies in an octahedron as it is *N,O*-chelated by three pairs of atoms (Fig. 1). Hydrogen bonds link the metal-bearing groups into a layer motif, and the anions occupy the spaces between the layers.



Experimental

Iron(II) tetrafluoroborate hexahydrate (0.07 g, 0.2 mmol) was dissolved in methanol (10 ml). To the solution was added 2,2'-pyridil (0.02 g, 0.1 mmol) dissolved in methanol (5 ml). The solvent was allowed to evaporate for more than a week to afford small orange crystals.

**Figure 1**

Plot of the disordered cation, with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, -y, -z$.] The anion is not shown.

Crystal data

$[\text{Fe}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_6\text{H}_4.5\text{NO}_2)\text{-(C}_6\text{H}_5\text{NO}_2)](\text{BF}_4)_{0.5}$
 $M_r = 467.07$
 Trigonal, $P\bar{3}$
 $a = 13.564(2) \text{ \AA}$
 $c = 6.0108(9) \text{ \AA}$
 $V = 957.7(2) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.620 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.85 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Block, orange
 $0.17 \times 0.15 \times 0.10 \text{ mm}$

Data collection

Bruker APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.437, T_{\max} = 0.920$

4988 measured reflections
 1128 independent reflections
 1055 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.062$
 $\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.154$
 $S = 1.21$
 1128 reflections
 97 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0655P)^2 + 1.2441P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Fe1—O1	2.130 (3)	Fe1—N1	2.165 (3)
O1—Fe1—O1 ⁱⁱⁱ	91.9 (1)	O1 ^{iv} —Fe1—N1	94.3 (1)
O1—Fe1—O1 ^{iv}	91.9 (1)	O1—Fe1—N1 ^{iv}	166.5 (1)
O1—Fe1—N1	76.0 (1)	N1—Fe1—N1 ⁱⁱⁱ	98.8 (1)

Symmetry codes: (iii) $-y + 1, x - y, z$; (iv) $-x + y + 1, -x + 1, z$.

The BF_4^- ion was initially allowed to refine about the threefold axis, with the four B—F distances restrained to $1.37(1) \text{ \AA}$ and the F...F distances to $2.24(1) \text{ \AA}$. Other restraints were imposed to prevent the atomic displacement parameters from becoming too large. A somewhat more satisfactory refinement was obtained by constraining the B and F atoms to special positions, and only the B atom was restrained to nearly isotropic behavior. The occupancy of the lone F atom is 0.1667. C-bound H atoms were positioned geometrically ($\text{C—H} = 0.93 \text{ \AA}$) and were included in the refinement in the riding-model approximation, with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$. The acid H atom is probably disordered over a special position of site symmetry $\bar{1}$; it was instead allowed to ride, with $\text{O—H} = 0.82 \text{ \AA}$ [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$]. The occupancy is 0.5.

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998); software used to prepare material for publication: SHELXL97.

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