

Bis[bis(2-pyridylcarbonyl)aminato]-iron(III) perchlorate acetonitrile disolvate

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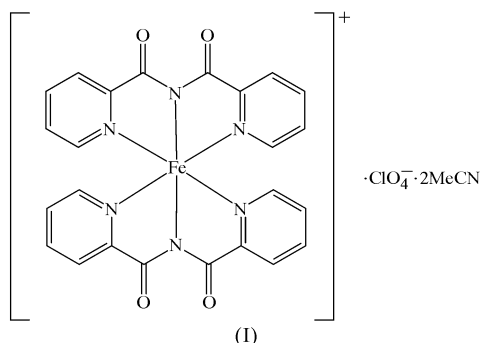
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The title compound, $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_3\text{O}_2)_2]\text{ClO}_4 \cdot 2\text{C}_2\text{H}_3\text{N}$, contains Fe^{III} in a distorted octahedral coordination environment, with the $\text{Fe}-\text{N}(\text{pyridine})$ bonds significantly longer than the $\text{Fe}-\text{N}(\text{amine})$ bonds. The crystal packing involves a bifurcated $\text{C}-\text{H}\cdots(\text{O},\text{O})$ contact that is also found in all other $[\text{M}(\text{C}_{12}\text{H}_8\text{N}_3\text{O}_2)_2]$ complexes reported previously.

Comment

During our investigations of iron complexes with bis(2-picolyl)amine, we have noticed an unusual reactivity of the $-\text{CH}_2-$ group attached to the picolyl unit. In the presence of air, this group can be oxidized into a carbonyl group. The storage of a reaction mixture containing $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, bis(2-picolyl)amine and Et_3N in the presence of air therefore unintentionally resulted in the formation of the title compound, $[\text{Fe}^{\text{III}}(\text{bpca})_2]\text{ClO}_4 \cdot 2\text{MeCN}$, (I), where bpca is bis(2-pyridylcarbonyl)aminato. We report here the crystal structure of this complex.



The bpca ligand is present in 68 crystal structures included in the Cambridge Structural Database (CSD; Version 5.27 of November 2005, with updates in January, May and August 2006; Allen, 2002), ten of which contain complexes of type $[\text{M}(\text{bpca})_2]$. Among these are several 'pseudopolymorphic',

crystal structures containing the same coordination complexes but different counter-ions or solvent molecules. Two main types can be discerned, viz. neutral complexes with M^{II} and cationic complexes with M^{III} as the central ion. Neutral complexes have been reported where M^{II} is Cu with water as cocrystallized solvent (Marcos, Martinez-Mañez *et al.*, 1989), Fe with water (Wocadlo *et al.*, 1993), Fe without solvent (Kamiyama *et al.*, 2002), Mn with water (Marcos, Folgado *et al.*, 1990), Rh with water (Paul, Tyagi, Bilakhiya *et al.*, 1999) and Ni without solvent (Kamiyama *et al.*, 2002). In the reported cationic complexes, M^{III} is Rh with PF_6^- counter-ions (Paul, Tyagi, Bhadbhade *et al.*, 1997), Fe with NO_3^- and water (Wocadlo *et al.*, 1993), Co with ClO_4^- and MeOH (Rowland *et al.*, 2002), and Co with ClO_4^- and water (Kajiwarra *et al.*, 2002). The structure reported here is a pseudopolymorph of the Fe^{III} cationic complex reported by Wocadlo and co-workers, which crystallizes in the space group $P\bar{1}$.

The iron(III) ion in the structure of (I) has a distorted octahedral coordination, similar to that found in the nitrate/water pseudopolymorph. The two bpca ligands coordinate the Fe ion in a meridional configuration. The average $\text{N}-\text{Fe}-\text{N}$ bite angle in the four five-membered chelate rings is $81.9(3)^\circ$. As a consequence of this small bite angle, the $\text{N}(\text{pyridine})-\text{Fe}-\text{N}(\text{pyridine})$ angles in one ligand [average value $163.8(6)^\circ$] have the largest deviation from the ideal octahedral value of 180° . The $\text{Fe}-\text{N}(\text{pyridine})$ bonds are, with an average value of $1.969(8) \text{ \AA}$, significantly longer than the $\text{Fe}-\text{N}(\text{amine})$ bonds, with an average value of $1.920(8) \text{ \AA}$ (Table 1 and Fig. 1). This difference in bond lengths is found in all structures containing bpca ligands coordinating metal ions. The average difference between the $\text{M}-\text{N}(\text{pyridine})$ and $\text{M}-\text{N}(\text{amine})$ bonds is 0.07 \AA .

The structure of (I) contains a number of short $\text{C}-\text{H}\cdots\text{O}$ contacts (Table 2), with $\text{C}\cdots\text{O}$ distances as small as $2.981(3) \text{ \AA}$, i.e. 0.24 \AA shorter than the sum of their van der Waals radii (Bondi, 1964). Neighbouring molecules are linked by a bifurcated $\text{C}-\text{H}\cdots(\text{O},\text{O})$ contact linking a pyridine H

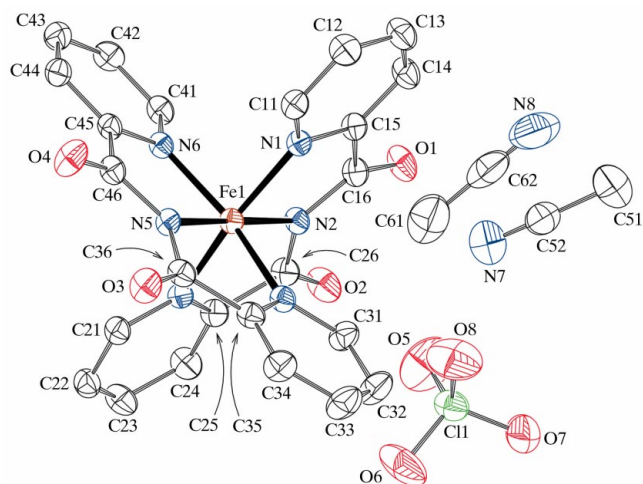
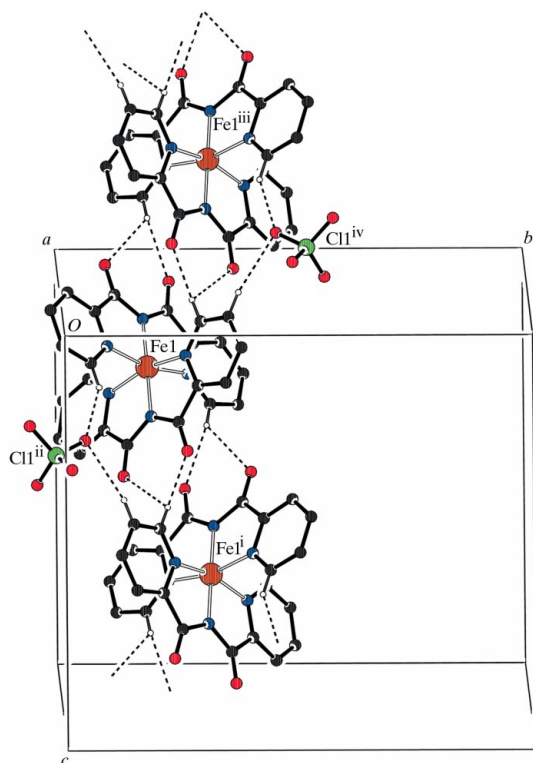


Figure 1

A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms have been omitted.

**Figure 2**

The one-dimensional chain of C—H...O-linked [Fe(bpca)₂] complexes and perchlorate ions, viewed approximately perpendicular to the *bc* plane. Dashed lines indicate the C—H...O contacts; H atoms not involved in these interactions have been omitted. Symmetry codes are as given in Table 2.

atom at an *ortho* position to the two O atoms of the ligand. Since these contacts occur for both independent ligands, the molecules are linked into an infinite one-dimensional chain, running in the *c* direction (Fig. 2). Inversion centres are located between C—H...O(O,O)-linked molecules. The ClO₄[−] counter-ion is also involved in this chain through C—H...O contacts and provides an extra link between two neighbouring molecules. In the nitrate/water pseudopolymorph, the same packing motif is found; bifurcated C—H...O(O,O) contacts link the molecules into infinite one-dimensional chains with inversion centres located between the neighbouring molecules. Here also the counter-ion provides an extra link between neighbouring molecules through C—H...O contacts. The other *M*(bpca)₂ structures for which coordinates are included in the CSD display a great variety in packing, from one-dimensional chains to three-dimensional networks. However, all these structures contain the bifurcated pyridine-*ortho*-H...O(O,O)-urea motif for at least one bpca ligand, even in the presence of classical hydrogen-bond donors, such as methanol and water.

Experimental

Compound (I) was obtained as orange crystals by slow evaporation of an acetonitrile solution containing Fe(ClO₄)₂·6H₂O (0.1 mmol), bis(2-picoly)amine (0.2 mmol) and Et₃N (0.2 mmol). The resulting crystals were collected by filtration, washed with diethyl ether and

dried in a vacuum (yield 23%). Elemental analysis calculated for C₂₈H₂₂ClFeN₈O₈: C 48.75, H 3.21, N 16.24%; found: C 49.17, H 3.93, N 16.53%. Spectroscopic details are given in the CIF.

Crystal data

[Fe(C₁₂H₈N₃O₂)₂](ClO₄)·2C₂H₃N
M_r = 689.84
 Monoclinic, *P*2₁/*c*
a = 12.800 (2) Å
b = 16.565 (3) Å
c = 14.895 (2) Å
 β = 113.356 (16)°
V = 2899.4 (9) Å³

Z = 4
D_x = 1.580 Mg m^{−3}
 Mo *K*α radiation
 μ = 0.68 mm^{−1}
T = 150 K
 Plate, orange
 0.40 × 0.18 × 0.02 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans, and ω scans with κ offset
 Absorption correction: multi-scan (MULABS in PLATON; Spek, 2003)
T_{min} = 0.875, *T_{max}* = 0.989

70020 measured reflections
 6607 independent reflections
 4867 reflections with *I* > 2σ(*I*)
R_{int} = 0.080
 θ_{\max} = 27.4°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.039
wR (*F*²) = 0.095
S = 1.03
 6607 reflections
 417 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 1.4P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.38 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å).

Fe1—N1	1.9722 (18)	Fe1—N4	1.9798 (18)
Fe1—N2	1.9145 (18)	Fe1—N5	1.9257 (17)
Fe1—N3	1.9627 (17)	Fe1—N6	1.9617 (18)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C11—H11...O1 ⁱ	0.95	2.41	3.152 (3)	134
C11—H11...O2 ⁱ	0.95	2.54	3.269 (3)	134
C21—H21...O6 ⁱⁱ	0.95	2.29	3.119 (3)	146
C41—H41...O3 ⁱⁱⁱ	0.95	2.47	3.074 (3)	121
C41—H41...O4 ⁱⁱⁱ	0.95	2.12	2.981 (3)	150
C42—H42...O6 ^{iv}	0.95	2.55	3.434 (3)	156
C61—H61A...O5	0.98	2.43	3.370 (5)	161
C61—H61C...O1 ⁱ	0.98	2.45	3.413 (5)	168

Symmetry codes: (i) *x*, −*y* + $\frac{1}{2}$, *z* + $\frac{1}{2}$; (ii) −*x* + 1, −*y*, −*z* + 1; (iii) *x*, −*y* + $\frac{1}{2}$, *z* − $\frac{1}{2}$; (iv) −*x* + 1, *y* + $\frac{1}{2}$, −*z* + $\frac{1}{2}$.

H atoms were introduced in calculated positions and treated as riding on their carrier atoms, with C—H distances of 0.95 Å for the aromatic H atoms and 0.98 Å for the acetonitrile methyl H atoms. The methyl groups were allowed to rotate around the C—C bonds during refinement. *U*_{iso}(H) values were set at 1.5*U*_{eq}(methyl C) or 1.2*U*_{eq}(aromatic C).

Data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: DENZO; program(s) used to solve structure: SHELXS86 (Sheldrick, 1985); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3019). Services for accessing these data are described at the back of the journal.

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