

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

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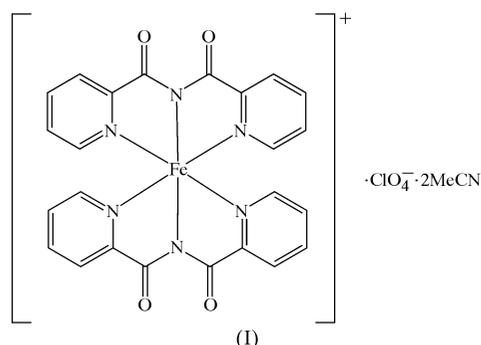
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The title compound,  $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_3\text{O}_2)_2]\text{ClO}_4 \cdot 2\text{C}_2\text{H}_3\text{N}$ , contains  $\text{Fe}^{\text{III}}$  in a distorted octahedral coordination environment, with the  $\text{Fe}-\text{N}(\text{pyridine})$  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  $\text{Et}_3\text{N}$  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.

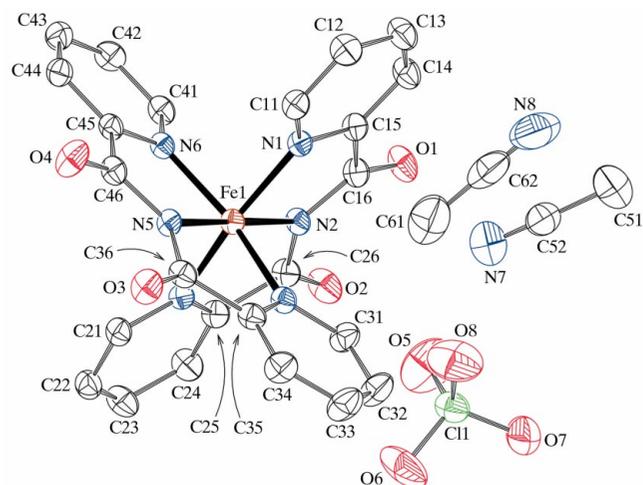


The bpca ligand is present in 68 crystal structures included in the Cambridge Structural Database (CSD; Version 5.27 of November 2005, with updates in January, May and August 2006; Allen, 2002), ten of which contain complexes of type  $[\text{M}(\text{bpca})_2]$ . Among these are several 'pseudopolymorphic',

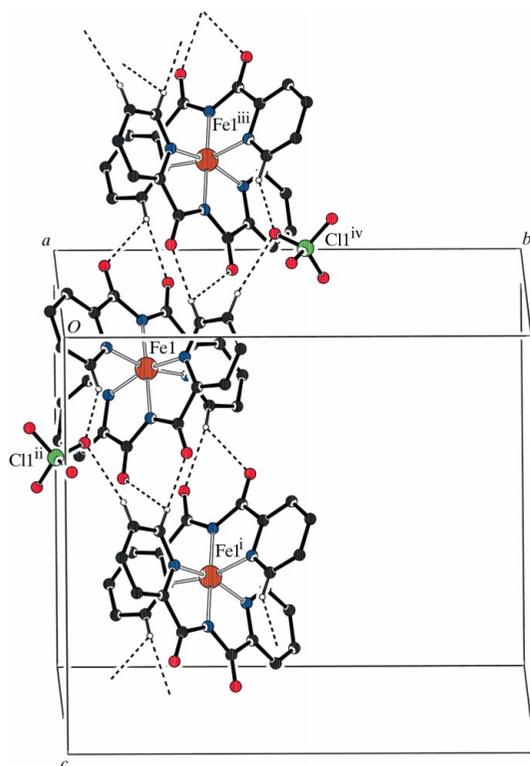
crystal structures containing the same coordination complexes but different counter-ions or solvent molecules. Two main types can be discerned, *viz.* neutral complexes with  $M^{\text{II}}$  and cationic complexes with  $M^{\text{III}}$  as the central ion. Neutral complexes have been reported where  $M^{\text{II}}$  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,  $M^{\text{III}}$  is Rh with  $\text{PF}_6^-$  counter-ions (Paul, Tyagi, Bhadbhade *et al.*, 1997), Fe with  $\text{NO}_3^-$  and water (Wocadlo *et al.*, 1993), Co with  $\text{ClO}_4^-$  and MeOH (Rowland *et al.*, 2002), and Co with  $\text{ClO}_4^-$  and water (Kajiwarra *et al.*, 2002). The structure reported here is a pseudopolymorph of the  $\text{Fe}^{\text{III}}$  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  $180^\circ$ . 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  $M-\text{N}(\text{pyridine})$  and  $M-\text{N}(\text{amine})$  bonds is  $0.07 \text{ \AA}$ .

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.*  $0.24 \text{ \AA}$  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)<sub>2</sub>] 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 ClO<sub>4</sub><sup>−</sup> 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)<sub>2</sub> 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(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1 mmol), bis(2-picolyl)amine (0.2 mmol) and Et<sub>3</sub>N (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 C<sub>28</sub>H<sub>22</sub>ClFeN<sub>8</sub>O<sub>8</sub>: 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(C<sub>12</sub>H<sub>8</sub>N<sub>3</sub>O<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>·2C<sub>2</sub>H<sub>3</sub>N  
*M<sub>r</sub>* = 689.84  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 12.800 (2) Å  
*b* = 16.565 (3) Å  
*c* = 14.895 (2) Å  
 β = 113.356 (16)°  
*V* = 2899.4 (9) Å<sup>3</sup>

*Z* = 4  
*D<sub>x</sub>* = 1.580 Mg m<sup>−3</sup>  
 Mo Kα radiation  
 μ = 0.68 mm<sup>−1</sup>  
*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<sub>min</sub>* = 0.875, *T<sub>max</sub>* = 0.989

70020 measured reflections  
 6607 independent reflections  
 4867 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.080  
 θ<sub>max</sub> = 27.4°

### Refinement

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

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0423*P*)<sup>2</sup> + 1.4*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.38 e Å<sup>−3</sup>  
 Δρ<sub>min</sub> = −0.36 e Å<sup>−3</sup>

**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 <sup>i</sup>	0.95	2.41	3.152 (3)	134
C11—H11...O2 <sup>i</sup>	0.95	2.54	3.269 (3)	134
C21—H21...O6 <sup>ii</sup>	0.95	2.29	3.119 (3)	146
C41—H41...O3 <sup>iii</sup>	0.95	2.47	3.074 (3)	121
C41—H41...O4 <sup>iii</sup>	0.95	2.12	2.981 (3)	150
C42—H42...O6 <sup>iv</sup>	0.95	2.55	3.434 (3)	156
C61—H61A...O5	0.98	2.43	3.370 (5)	161
C61—H61C...O1 <sup>i</sup>	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*<sub>iso</sub>(H) values were set at 1.5*U*<sub>eq</sub>(methyl C) or 1.2*U*<sub>eq</sub>(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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