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

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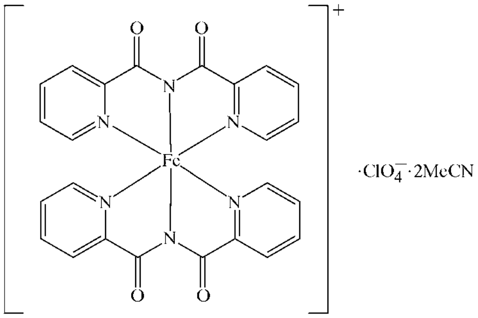
The title compound, $[Fe(C_{12}H_8N_3O_2)_2]ClO_4\cdot 2C_2H_3N$, contains Fe^{III} in a distorted octahedral coordination environment, with the Fe—N(pyridine) bonds significantly longer than the Fe—N(amine) bonds. The crystal packing involves a bifurcated C—H···(O,O) contact that is also found in all other $[M(C_{12}H_8N_3O_2)_2]$ complexes reported previously.

Comment

During our investigations of iron complexes with bis(2-picolyl)amine, we have noticed an unusual reactivity of the –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 $Fe(ClO_4)_2\cdot 6H_2O$, bis(2-picolyl)amine and Et_3N in the presence of air therefore unintentionally resulted in the formation of the title compound, $[Fe^{III}(bpca)_2]ClO_4\cdot 2MeCN$, (I), where bpca is bis(2-pyridylcarbonyl)aminate. We report here the crystal structure of this complex.



(I)

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 $[M(bpca)_2]$. 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 (Kajiwara *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 $P\overline{1}$.

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 N—Fe—N bite angle in the four five-membered chelate rings is 81.9 (3)°. As a consequence of this small bite angle, the N(pyridine)—Fe—N(pyridine) angles in one ligand [average value 163.8 (6)°] have the largest deviation from the ideal octahedral value of 180°. The Fe—N(pyridine) bonds are, with an average value of 1.969 (8) Å, significantly longer than the Fe—N(amine) bonds, with an average value of 1.920 (8) Å (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*—N(pyridine) and *M*—N(amine) bonds is 0.07 Å.

The structure of (I) contains a number of short C—H···O contacts (Table 2), with C···O distances as small as 2.981 (3) Å, *i.e.* 0.24 Å shorter then the sum of their van der Waals radii (Bondi, 1964). Neighbouring molecules are linked by a bifurcated C—H···(O,O) contact linking a pyridine H

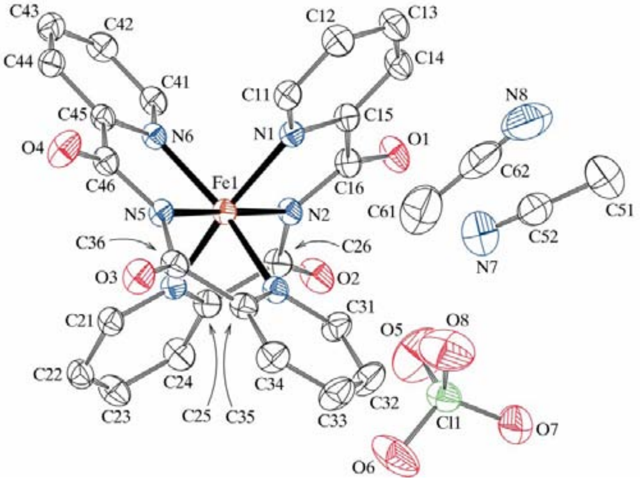


Figure 1
A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms have been omitted.

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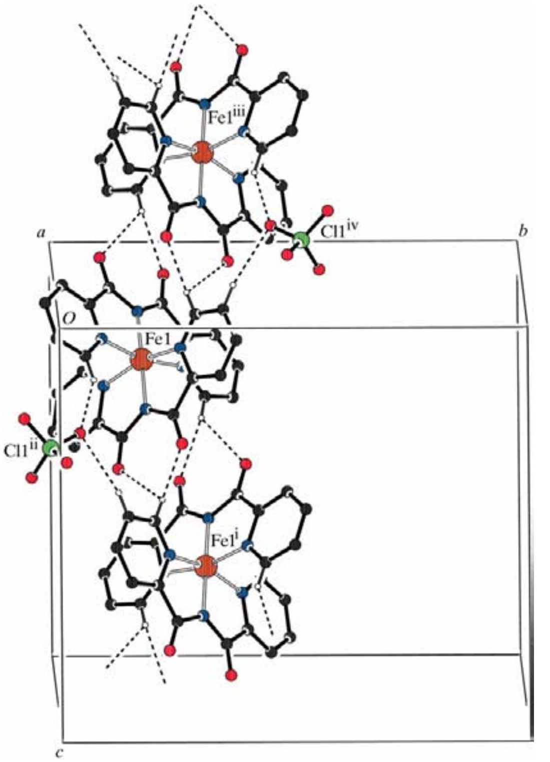

Figure 2
The one-dimensional chain of C—H···O-linked [Fe(bpca)$_2$] complexes and perchlorate ions, viewed approximately perpendicular to the *bc* plane. Dashed lines indicate the C—H···O contacts; H atoms not involved in these interactions have been omitted. Symmetry codes are as given in Table 2.

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)-linked molecules. The ClO_4^- 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) 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)-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 $Fe(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol), bis(2-picolyl)amine (0.2 mmol) and Et_3N (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 $C_{28}H_{22}ClFeN_8O_8$: 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

$[Fe(C_{12}H_8N_3O_2)_2]ClO_4 \cdot 2C_2H_3N$
$M_r = 689.84$
Monoclinic, $P2_1/c$
$a = 12.800$ (2) Å
$b = 16.565$ (3) Å
$c = 14.895$ (2) Å
$\beta = 113.356$ (16)°
$V = 2899.4$ (9) Å^3
$Z = 4$
$D_x = 1.580$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.68$ 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 $I > 2\sigma(I)$
$R_{int} = 0.080$
$\theta_{max} = 27.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.095$
$S = 1.03$
6607 reflections
417 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 1.4P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-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, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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—H61*A*···O5	0.98	2.43	3.370 (5)	161
C61—H61*C*···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 $1.5U_{eq}$(methyl C) or $1.2U_{eq}$(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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