

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

Huib Kooijman,^{a*} Stefania Tanase,^b Elisabeth Bouwman,^b
Jan Reedijk^b and Anthony L. Spek^a

^aCrystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and

^bLeiden Institute of Chemistry, Gorlaeus Laboratories, PO Box 9502, 2300 RA Leiden, The Netherlands

Correspondence e-mail: h.kooijman@chem.uu.nl

Received 24 August 2006

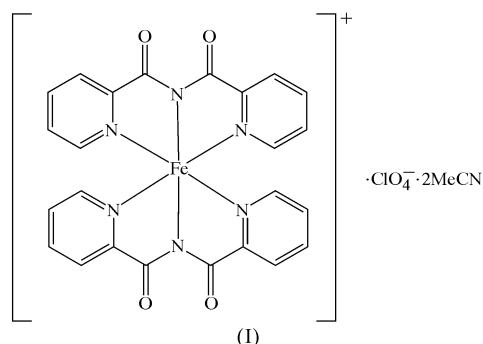
Accepted 13 September 2006

Online 14 October 2006

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 $M-\text{N}(\text{pyridine})$ and $M-\text{N}(\text{amine})$ 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

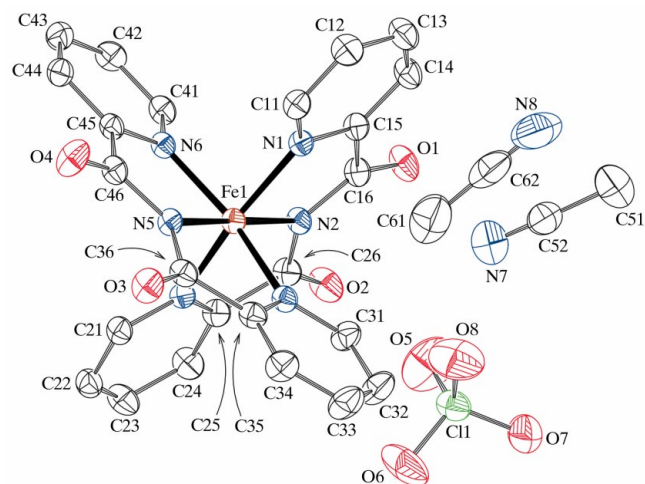
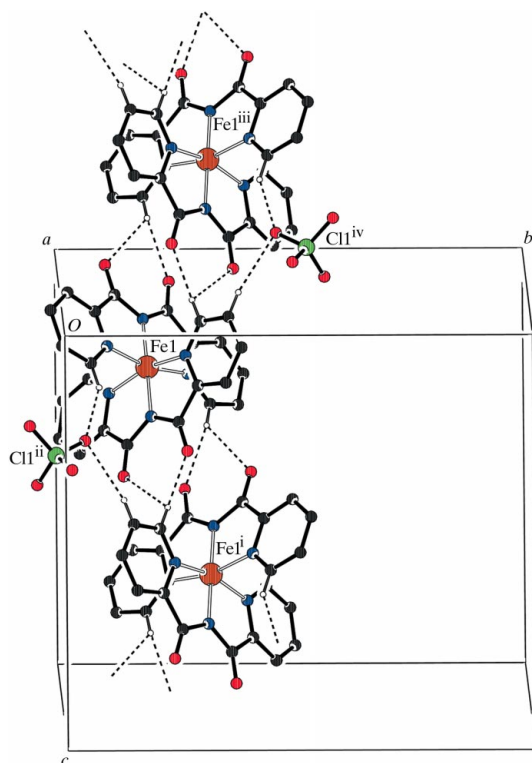


Figure 1

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-picolyl)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 Kα 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/[σ²(*F_o*²) + (0.0423*P*)² + 1.4*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.38 e Å^{−3}
 Δρ_{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, °).

| <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.

This work was supported in part (ALS) by the Council for the Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO). The results from this project have been obtained with financial support of the Dutch Economy, Ecology, Technology (EET) programme, a joint programme of the Ministry of Economic Affairs, the Ministry of Education, Culture and Science, and the Ministry of Housing, Spatial Planning and the Environment.

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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