

Triethylammonium dichloro[1,2-bis(2-pyridine-carboxamido)-4,5-dimethylbenzene]ferrate(III)

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Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.040

wR factor = 0.120

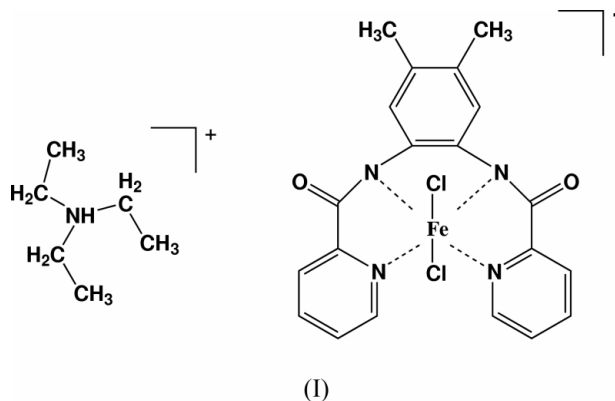
Data-to-parameter ratio = 16.0

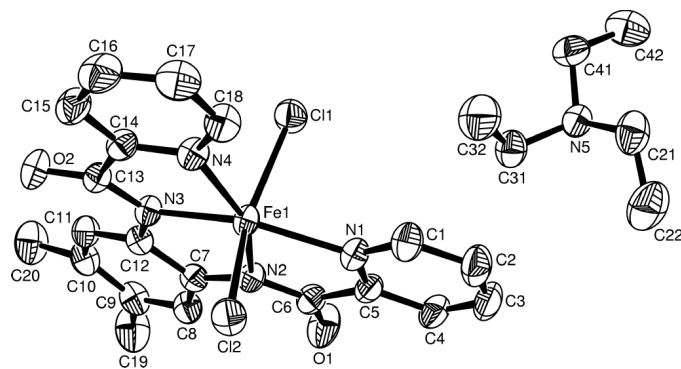
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the title compound, $[\text{Et}_3\text{NH}][(\text{Me}_2\text{bpb})\text{FeCl}_2]$ or $(\text{C}_6\text{H}_{16}\text{N})[\text{FeCl}_2(\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_2)]$, has been determined. Four N atoms of the Me_2bpb [1,2-bis(2-pyridine-carboxamido)-4,5-dimethylbenzene] ligand and two chloro ligands are coordinated to the iron(III) ion. The geometry of the complex anion is distorted octahedral, with a $\text{Cl}-\text{Fe}-\text{Cl}$ angle of $156.59(3)^\circ$. The 4,5-dimethylbenzene ring of the Me_2bpb ligand is tilted from the N_4 plane by $9.5(1)^\circ$.

Comment

The discovery that mononuclear nonheme iron proteins, such as lipoxygenase, isopenicillin N synthase and phenylalanine hydroxylase, can oxidize inert substrates selectively has stimulated chemists to investigate the biomimetic reactions of nonheme iron complexes with various oxidants such as H_2O_2 , iodosylbenzene (PhIO), *m*-chloroperbenzoic acid (MCPBA), *etc.* (Que & Ho, 1996). However, few examples have shown biomimetic reactivity in a nonheme ligand environment (Chen & Que, 2001; Kim *et al.*, 1997; Leung *et al.*, 1991; Mekmouche *et al.*, 2001). Yang *et al.* (1991) have first reported the crystal structure of the complex $[(\text{Et}_3\text{NH})\text{Fe}(\text{bpb})\text{X}_2]$ [H_2bpb is 1,2-bis(2-pyridinecarboxamido)benzene; $\text{X} = \text{Cl}^-$ and CH_3SO_3^-], with a tetradentate pyridine/amide ligand, and have found that it can catalyse the epoxidation of olefins by iodosylbenzene. In order to further develop functional models for mononuclear nonheme iron oxygenases, therefore, we have studied a family of the nonheme iron catalyst, represented by $[(\text{bpb})\text{FeCl}_2]$. First of all, to examine the electronic effect of the ligand on the reactivity of the complex $[(\text{bpb})\text{FeCl}_2]$, we have synthesized the title complex, with two methyl groups on the phenyl ring of the bpb ligand, $\text{H}_2\text{Me}_2\text{bpb}$ [1,2-bis(2-pyridinecarboxamido)-4,5-dimethylbenzene] and obtained crystals of its iron(III) complex. We now report the structure of this electron-rich iron complex, $[\text{Et}_3\text{NH}][(\text{Me}_2\text{bpb})\text{FeCl}_2]$, (I).




Figure 1

View of compound (I) showing the atom-labeling scheme. Ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

The asymmetric unit contains a $[(\text{Me}_2\text{bpb})\text{FeCl}_2]^-$ anion and a triethylammonium cation $[\text{Et}_3\text{NH}]^+$ in $P2_1/n$ with $Z = 4$. Four N atoms of the $\text{Me}_2\text{bpb}^{2-}$ ligand are coordinated to the iron(III) ion. The Fe–N distances range from 2.041 (2) to 2.153 (2) Å. Two chloro ligands are also coordinated to the iron(III) ion, with Fe–Cl distances of 2.3457 (7) and 2.3546 (7) Å. The geometry of the complex anion is distorted octahedral, with a Cl–Fe–Cl angle of $156.59(3)^\circ$. The N1–Fe1–N3 and N2–Fe1–N4 angles are $155.59(7)$ and $155.53(8)^\circ$, respectively. The 4,5-dimethylbenzene ring of the $\text{Me}_2\text{bpb}^{2-}$ ligand is tilted from the N1/N2/N3/N4 plane, with torsion angles of $9.4(4)$ and $12.1(4)^\circ$ for C6–N2–C7–C8 and C13–N3–C12–C11, respectively. The C–O bond distances of the $\text{Me}_2\text{bpb}^{2-}$ ligand are 1.243 (3) and 1.234 (3) Å. There is a hydrogen bond between the N atom of a triethylammonium cation and the carbonyl O atom of a neighbouring complex anion, with an $\text{N5}\cdots\text{O1}$ distance of 2.73 (1) Å.

Experimental

For the preparation of the ligand 1,2-bis(pyridine-2-carboxamido)-4,5-dimethylbenzene ($\text{H}_2\text{Me}_2\text{bpb}$), a modification of the method of Patra *et al.* (2000) was used. To a stirred solution of picolinic acid (0.246 g, 2 mmol) in pyridine (1 ml), a solution of 4,5-dimethyl-1,2-diaminobenzene (0.136 g, 1 mmol) in pyridine (1.5 ml) was added dropwise. The solution was stirred for 15 min and triphenyl phosphite (520 μl , 2 mmol) was added dropwise. The temperature of the reaction mixture was increased to 393 K, and the mixture was stirred for 4 h. The volume was then reduced to 2 ml and kept in air. After 24 h, a white precipitate that resulted was collected by filtration. Recrystallization from CHCl_3 and diethyl ether afforded white needles. For the preparation of (I), a modification of the method of Yang *et al.* (1991) was used. $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$ (0.162 g, 1 mmol) was added to a solution of $\text{H}_2\text{Me}_2\text{bpb}$ (0.346 g, 1 mmol) and 300 μl of Et_3N in 30 ml of dry acetonitrile under a nitrogen atmosphere. The solution turned dark green immediately. The solution was stirred overnight. A small amount of brown precipitate was removed by filtration. A mixture of dark-green crystals of $[(\text{Et}_3\text{NH})][(\text{Me}_2\text{bpb})\text{FeCl}_2]$ and a white powder of Et_3NHCl was formed and isolated by filtration. Dark-green single crystals of $[(\text{Et}_3\text{NH})][(\text{Me}_2\text{bpb})\text{FeCl}_2]$ were grown from acetonitrile with an over-layer of ether at room temperature.

Crystal data

$(\text{C}_6\text{H}_{16}\text{N})[\text{FeCl}_2(\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_2)]$
 $M_r = 573.32$
 Monoclinic, $P2_1/n$
 $a = 11.0038(10)$ Å
 $b = 16.273(2)$ Å
 $c = 15.578(2)$ Å
 $\beta = 100.789(10)^\circ$
 $V = 2740.2(5)$ Å³
 $Z = 4$

$D_x = 1.390$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 9.6\text{--}12.3^\circ$
 $\mu = 0.78$ mm⁻¹
 $T = 298(2)$ K
 Block cut from plate, dark green
 $0.35 \times 0.35 \times 0.25$ mm

Data collection

Enraf–Nonius CAD-4 MACH3 diffractometer
 2θ – ω scans
 Absorption correction: none
 5637 measured reflections
 5352 independent reflections
 4515 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

$\theta_{\text{max}} = 26.0^\circ$
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 20$
 $l = -19 \rightarrow 18$
 3 standard reflections
 frequency: 60 min
 intensity decay: negligible

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.120$
 $S = 1.04$
 5352 reflections
 334 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0774P)^2 + 1.2196P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.70$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.64$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Fe1–N3	2.0408 (19)	Fe1–Cl2	2.3546 (7)
Fe1–N2	2.0535 (18)	O1–C6	1.243 (3)
Fe1–N4	2.1438 (19)	O1–N5 ⁱ	2.742 (3)
Fe1–N1	2.1531 (19)	O2–C13	1.234 (3)
Fe1–Cl1	2.3457 (7)		
N3–Fe1–N2	78.10 (7)	N4–Fe1–Cl1	85.17 (6)
N3–Fe1–N4	77.47 (7)	N1–Fe1–Cl1	84.42 (6)
N2–Fe1–N4	155.53 (8)	N3–Fe1–Cl2	100.74 (6)
N3–Fe1–N1	155.59 (7)	N2–Fe1–Cl2	98.57 (6)
N2–Fe1–N1	77.58 (7)	N4–Fe1–Cl2	84.73 (6)
N4–Fe1–N1	126.89 (7)	N1–Fe1–Cl2	84.87 (5)
N3–Fe1–Cl1	97.59 (6)	Cl1–Fe1–Cl2	156.59 (3)
N2–Fe1–Cl1	99.36 (6)		
C6–N2–C7–C8	9.4 (4)	C13–N3–C12–C11	12.1 (4)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

The H atoms attached to C atoms were placed at calculated positions and treated as riding with isotropic displacement parameters.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD-4-PC Software*; data reduction: *XCAD4* (Harms, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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