

Tetraethylammonium dichloro[4,5-dichloro-1,2-bis-(2-pyridine-2-carboxamido)benzene]ferrate(III), [Et₄N][*(bpc)*FeCl₂]

Sung Jea Lee,^a Jun Yong Lee,^a Hyun Woong Yang,^a Cheal Kim,^{a†} Wonwoo Nam^b and Youngmee Kim^{c*}

^aDepartment of Fine Chemistry, Seoul National University of Technology, Seoul 139-743, South Korea, ^bDepartment of Chemistry and Division of Molecular Life Sciences (BK 21), Ewha Womans University, Seoul 120-750, South Korea, and ^cDepartment of Chemistry, Ewha Womans University, Seoul 120-750, South Korea

† Additional correspondence author.

Correspondence e-mail: ymeekim@ewha.ac.kr

Key indicators

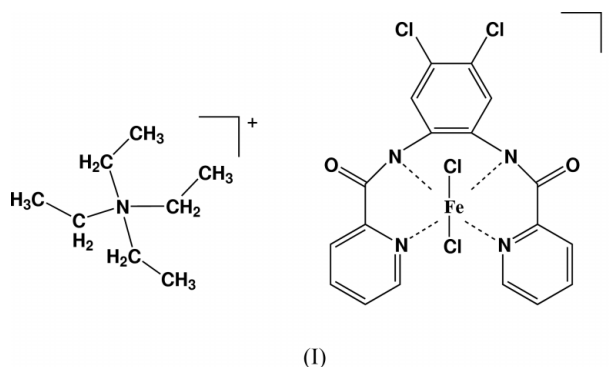
Single-crystal X-ray study
T = 298 K
 Mean $\sigma(\text{C}-\text{C}) = 0.012 \text{ \AA}$
R factor = 0.044
wR factor = 0.102
 Data-to-parameter ratio = 8.3

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

In the title compound, [Et₄N][*(bpc)*FeCl₂] or (C₈H₂₀N)[FeCl₂(C₁₈H₁₀N₄O₂)], the metal ion is located in the *bpc* mean plane and two chloro ligands complete the coordination. The Cl—Fe—Cl angle is 144.26 (8)°. The 4,5-dichlorobenzene ring of the *bpc* ligand is slightly tilted from the N1/N2/N3/N4 plane by 1.97 (3)°.

Comment

The discovery that mononuclear non-heme iron proteins, such as lipoxygenase, isopenicillin *N* synthase, and phenylalanine hydroxylase, can selectively oxidize inert substrates (Que & Ho, 1996) has attracted much attention from the chemical and biochemical communities and several mononuclear iron model complexes have been developed (Chen & Que, 2001; Kim *et al.*, 1997; Lee *et al.*, 2002; Leung *et al.*, 1991; Mekmouche *et al.*, 2001; Yang *et al.*, 1991). In this field, we studied a family of the non-heme iron catalysts, represented by [*(bpb)*FeCl₂], and recently reported the structure of the electron-rich iron complex [Et₃NH][*(Me*₂*bpb)*FeCl₂], with methyl groups on the phenyl ring of the *bpb* ligand, H₂Me₂*bpb* [H₂Me₂*bpb* is 1,2-bis(2-pyridinecarboxamido)-4,5-dimethylbenzene] (Lee *et al.*, 2002). In the course of a systematic study to discover the factors that control the catalytic reactivity of the non-heme iron center in this family of complexes, we have undertaken the synthesis and characterization of [*(bpc)*FeCl₂], a derivative of [*(bpb)*FeCl₂], with two Cl atoms as electron-deficient substituents on the phenyl ring of the *bpb* ligand, where *bpc* is the dianion form of 4,5-dichloro-1,2-bis(2-pyridine-2-carboxamido)benzene (H₂*bpc*). We synthesized the title complex according to the literature procedure of Ray *et al.* (1993) and report here the structure of this electron-deficient iron complex, [Et₄N][*(bpc)*FeCl₂], (I).

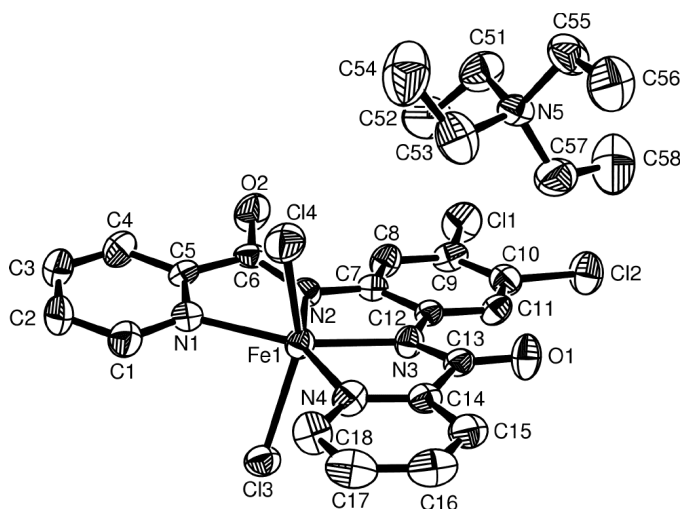


The asymmetric unit of (I) contains a [*(bpc)*FeCl₂][−] anion and a tetraethylammonium cation. Four N atoms of the *bpc*^{2−} ligand and two chloro ligands are coordinated to the iron(III) ion. The coordination of these four N atoms results in the

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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.

formation of three fused five-membered rings. The two inner Fe–N distances, 2.041 (6) and 2.042 (5) Å, are somewhat shorter than the outer Fe–N distances of 2.202 (6) and 2.202 (5) Å. The Fe–Cl distances are 2.324 (3) and 2.334 (3) Å. The Cl–Fe–Cl angle is 144.22 (9)°, which is more bent than the corresponding angle of 156.59 (3)° in [(Me₂bpb)FeCl₂][−] (Lee *et al.*, 2002). The N1–Fe1–N3 and N2–Fe1–N4 angles are 152.5 (2) and 153.1 (2)°, respectively. The 4,5-dichlorobenzene ring of the bpc^{2−} ligand is slightly tilted from the N1/N2/N3/N4 plane by only 1.97 (3)°, while the 4,5-dimethylbenzene ring of the Me₂bpb ligand is tilted by 9.5 (1)° from the N₄ plane. The C–O bond distances of the bpc^{2−} ligand are 1.220 (8) and 1.232 (8) Å.

Experimental

The ligand 4,5-dichloro-1,2-bis(pyridine-2-carboxamide)benzene (H₂bpc) (Leung *et al.*, 1991) and the complex [Et₄N][FeCl₄] (Ginsberg & Robin, 1963) were prepared according to literature methods. For the preparation of the title complex (I), a slightly modified version of the published procedure (Ray *et al.*, 1993) was used. A solution of the complex [Et₄N][FeCl₄] (0.328 g, 1.0 mmol) in DMF (5 ml) was stirred for 5 min and then H₂bpc (0.387 g, 1.0 mmol) was added while stirring. After the resulting suspension was stirred for 10 min, triethylamine (0.27 ml, 2.0 mmol) in DMF (2.7 ml) was added dropwise. The reaction solution immediately turned deep green. It was warmed in a water bath at 343 K for 5 min, stirred for 2 h, and then filtered. The resulting solution was evaporated to dryness and cooled to room temperature. On the addition of CH₃CN to the solution, the product separated as dark-green crystals, which were filtered off for isolation. Single crystals of [Et₄N][(bpc)FeCl₂] with a dark-green color were grown from acetonitrile under a layer of ether at room temperature.

Crystal data

(C₈H₂₀N)[FeCl₂(C₁₈H₁₀N₄O₂)]
 $M_r = 642.20$
 Monoclinic, $P2_1$
 $a = 8.752$ (2) Å
 $b = 10.473$ (2) Å
 $c = 15.685$ (3) Å
 $\beta = 101.94$ (2)°
 $V = 1406.6$ (5) Å³
 $Z = 2$

$D_x = 1.516$ Mg m^{−3}
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 7.7$ – 13.9 °
 $\mu = 0.95$ mm^{−1}
 $T = 298$ (2) K
 Block, dark green
 0.20 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius MACH-3 diffractometer
 ω – 2θ scans
 Absorption correction: none
 3094 measured reflections
 2905 independent reflections
 1907 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.034$

$\theta_{max} = 26.0$ °
 $h = 0 \rightarrow 10$
 $k = 0 \rightarrow 12$
 $l = -19 \rightarrow 18$
 3 standard reflections
 frequency: 60 min
 intensity decay: negligible

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.102$
 $S = 1.03$
 2905 reflections
 348 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.35$ e Å^{−3}
 $\Delta\rho_{min} = -0.48$ e Å^{−3}
 Absolute structure: Flack (1983);
 189 Friedel reflections
 Flack parameter = 0.09 (8)

Table 1

Selected geometric parameters (Å, °).

Fe1–N2	2.041 (6)	Fe1–Cl3	2.324 (3)
Fe1–N3	2.042 (5)	Fe1–Cl4	2.334 (3)
Fe1–N4	2.202 (6)	O1–C13	1.219 (8)
Fe1–N1	2.202 (5)	O2–C6	1.232 (8)
N2–Fe1–N3	77.6 (2)	N4–Fe1–Cl3	82.89 (19)
N2–Fe1–N4	153.1 (2)	N1–Fe1–Cl3	83.2 (2)
N3–Fe1–N4	75.5 (2)	N2–Fe1–Cl4	101.6 (2)
N2–Fe1–N1	74.9 (2)	N3–Fe1–Cl4	102.33 (19)
N3–Fe1–N1	152.5 (2)	N4–Fe1–Cl4	82.86 (17)
N4–Fe1–N1	132.0 (2)	N1–Fe1–Cl4	82.35 (18)
N2–Fe1–Cl3	105.86 (19)	Cl3–Fe1–Cl4	144.22 (9)
N3–Fe1–Cl3	105.56 (19)		

All H atoms were placed at calculated positions and refined as riding with C–H distances in the range 0.96–0.98 Å.

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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