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Chloro[*N,N'*-ethylenebis(5-carboxysalicylideneiminato)]iron(III)

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Key indicators

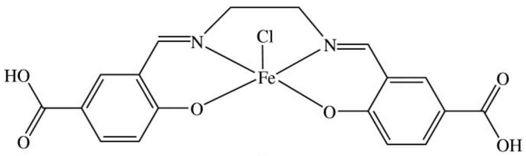
Single-crystal X-ray study
T = 102 K
Mean σ(C–C) = 0.010 Å
R factor = 0.074
wR factor = 0.167
Data-to-parameter ratio = 13.9

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

In the title compound, [FeCl($C_{18}H_{14}N_2O_6$)], the iron(III) is coordinated by N and O atoms at the basal sites and Cl at the apical site to form a distorted square pyramid. Hydrogen bonding in carboxylic acid dimers and π–π stacking interactions through benzene rings of the ligand lead to paired chains, which are alternately crosslinked with each other to form a non-porous solid. The title compound is potentially a good building block for the construction of highly porous mixed-metal-organic frameworks (M'MOFs). The O···O distances in the carboxylic acid dimers are 2.555 (6) and 2.664 (6) Å.

Comment

Porous metal-organic frameworks (MOFs) self-assembled by the coordination of suitable metal ions/clusters with organic building blocks are of extensive interest for their potential applications in gas storage, separation, molecular recognition, magnetism and catalysis (Eddaoudi *et al.*, 2001; Kitagawa & Kondo, 1998; Yaghi *et al.*, 2003; Janiak, 2003). Recently, the pre-constructed building block approach, in which metal-containing molecular complexes pre-constructed from simple organic linkers are further assembled with metal ions/clusters to construct their mixed metal-organic frameworks (M'MOFs), has been paid much attention (Abrahams *et al.*, 1994; Dong *et al.*, 2000; Carlucci *et al.*, 2002; Noro *et al.*, 2002; Vreshch *et al.*, 2003; Chen *et al.*, 2003). Such a straightforward strategy has provided a rational design principle to incorporate unsaturated, catalytically active and heterometallic metal centers into the porous M'MOFs for their functional properties. Given the fact that metal–salen [salen = *N,N'*-(ethylene)bis(salicylideneaminate)] complexes are good homogeneous catalysts in a variety of organic syntheses (Jacobsen, 2000), we have initiated an approach to incorporate metal–salen moieties into the porous M'MOFs for their potential applications in gas storage, sensors and heterogeneous catalysis. It has been well established that carboxylic acids are very good organic linkers for the construction of highly porous and robust MOFs (Chen *et al.*, 2001; Eddaoudi *et al.*, 2001; Yaghi *et al.*, 2003); thus metal complexes of salen carboxylic acid derivatives will presumably be good building blocks for highly porous M'MOFs. The title compound, (I), is one such pre-constructed building block, and its structure is reported here.



(I)

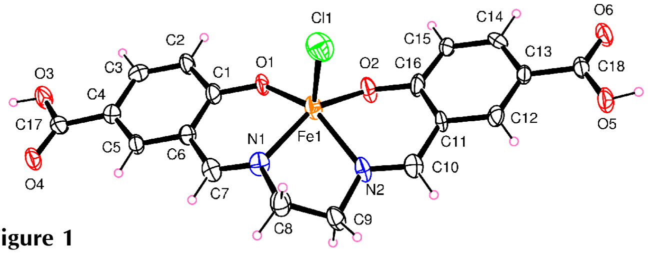


Figure 1
The structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

The structure of (I) is shown in Fig. 1. The Fe atom is in a distorted square-pyramidal geometry in which the basal sites are occupied by atoms N1, N2, O1 and O2 of the ligand, and the apical site is occupied by Cl1. The molecular compound is self-assembled into one-dimensional polymeric chains through pairwise, intermolecular hydrogen bonding between carboxylic acid groups of the type $R_2^2(8)$ (Bernstein *et al.*, 1995). Further π–π stacking interactions between benzene rings of the ligand, with the centroid distance between neighboring benzene rings of 3.614 Å, lead to the formation of paired chains (Fig. 2*a*). The packing indicates that (I) is a nonporous solid in which the paired chains are alternately crosslinked by van der Waals interactions (Fig. 2*b*).

The title compound, with two carboxylic functional groups, is a good extended 1,4-benzenedicarboxylic acid analog. The potential bridging length of 15.2 Å makes (I) a suitable building block for the construction of isoreticular mixed-metal-organic frameworks for their potential applications in gas storage and heterogeneous catalysis (Eddaoudi *et al.*, 2002; Smithenry *et al.*, 2003).

Experimental

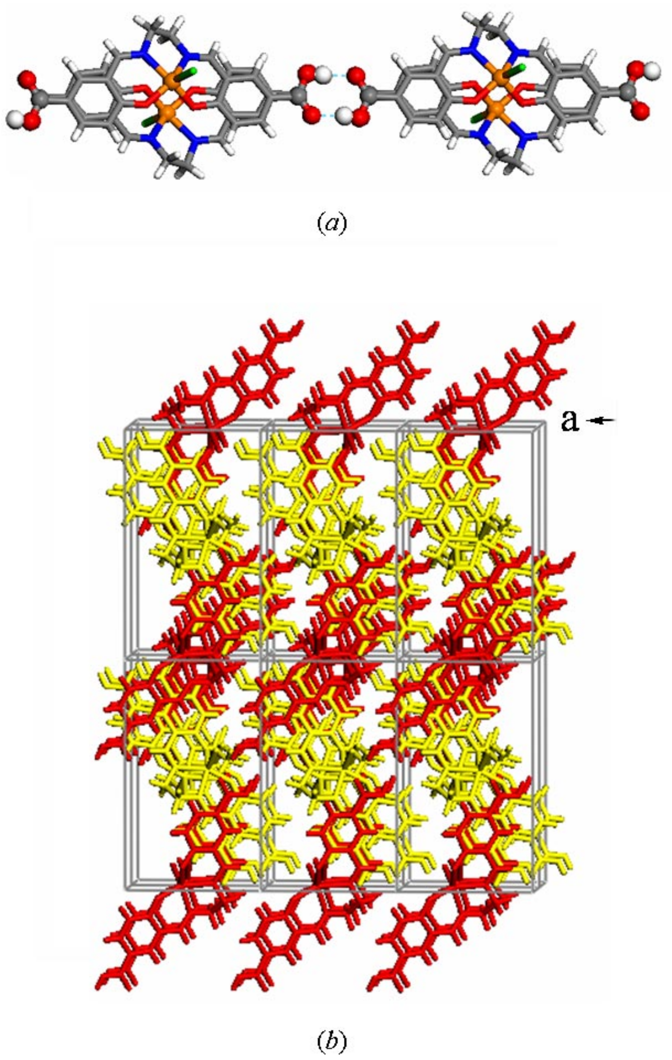
The ligand *N*,*N'*-ethylenebis(5-carboxysalicylideneiminate) was synthesized according to the procedure of Cheng & Lu (1998). The ligand (0.018 g, 0.05 mmol), $FeCl_3\cdot6H_2O$ (0.010 g, 0.04 mmol), DMF (1 ml) and ethanol (4 ml) were added to a vessel that was sealed and heated to 358 K at the rate of 2 K min^{-1} for 2 h and then cooled to room temperature at a rate of 0.2 K min^{-1}. Small red lath-shaped crystals of the title compound were formed and collected in 75% yield.

Crystal data

$[FeCl(C_{18}H_{14}N_2O_6)]$
$M_r = 445.61$
Monoclinic, $P2_1/c$
$a = 9.177$ (5) Å
$b = 15.124$ (10) Å
$c = 13.334$ (7) Å
$\beta = 101.73$ (2)°
$V = 1812.0$ (18) Å^3
$Z = 4$
$D_x = 1.633$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6177 reflections
$\theta = 2.5$–26.0°
$\mu = 1.02$ mm^{-1}
$T = 102$ K
Lath, red
0.13 × 0.05 × 0.01 mm

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler
ω scans with κ offsets
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.933$, $T_{max} = 0.990$
19 196 measured reflections
3554 independent reflections
1615 reflections with $I > 2\sigma(I)$
$R_{int} = 0.214$
$\theta_{max} = 26.2°$
$h = -10 \rightarrow 11$
$k = -18 \rightarrow 18$
$l = -16 \rightarrow 16$



(*a*)

(*b*)

Figure 2
The crystal packing in the structure of (I), indicating (*a*) the pairwise hydrogen bonding and π-stacking interactions between a pair of one-dimensional chains and (*b*) and alternate crosslinking between paired one-dimensional chains (red and yellow, respectively) to form a non-porous solid, viewed slightly oblique to the *c* axis.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.074$
$wR(F^2) = 0.167$
$S = 1.01$
3554 reflections
255 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.9967P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—O1	1.881 (4)	Fe1—N2	2.116 (6)
Fe1—O2	1.907 (5)	Fe1—Cl1	2.225 (3)
Fe1—N1	2.086 (6)		
O1—Fe1—O2	95.1 (2)	N1—Fe1—N2	77.4 (2)
O1—Fe1—N1	87.3 (2)	O1—Fe1—Cl1	107.07 (16)
O2—Fe1—N1	149.3 (2)	O2—Fe1—Cl1	102.90 (16)
O1—Fe1—N2	149.2 (2)	N1—Fe1—Cl1	105.63 (18)
O2—Fe1—N2	85.4 (2)	N2—Fe1—Cl1	102.78 (17)

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Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H3O⋯O6^{i}	0.84	1.72	2.555 (6)	172
O5—H5O⋯O4^{ii}	0.84	1.83	2.664 (6)	171

Symmetry codes: (i) $1 + x, y - 1, z$; (ii) $x - 1, 1 + y, z$.

The precision of the structure determination was limited by the very small size of the crystals. C—H H atoms were placed in idealized positions, with bond distances in the range 0.95–0.99 Å. COOH H atoms were located, utilizing difference maps, in the expected toruses (O—H = 0.84 Å) and a torsional parameter was refined for each. Displacement parameters for H were assigned as $U_{\rm iso} = 1.2U_{\rm eq}$ of the attached atom ($1.5U_{\rm eq}$ for O—H).

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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