

## Poly[iron(II)-di- $\mu$ -imidazole-4,5-dicarboxylato- $\kappa^3 N^3, O^4: O^5$ ]

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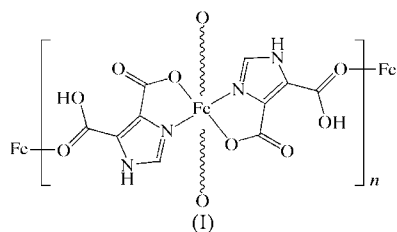
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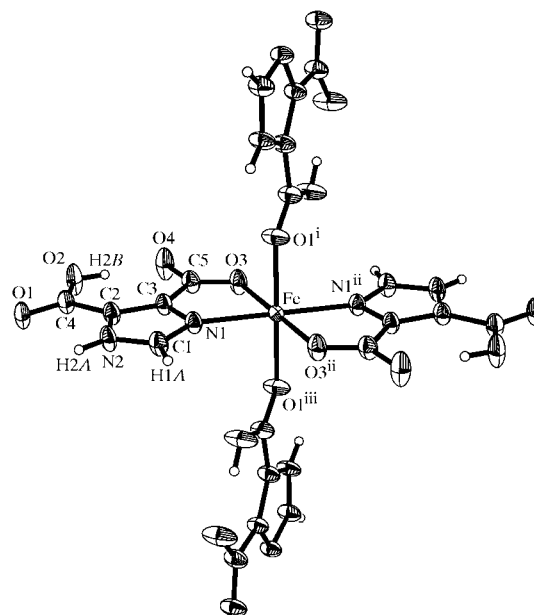
In the title compound,  $[\text{Fe}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2]_n$ , each Fe atom lies on a centre of symmetry, in an octahedral coordination environment consisting of two chelate rings [ $\text{Fe}-\text{N} = 2.154(3) \text{ \AA}$  and  $\text{Fe}-\text{O} = 2.180(3) \text{ \AA}$ ] and two carboxylate O atoms [ $\text{Fe}-\text{O} = 2.111(2) \text{ \AA}$ ] from imidazole-4,5-dicarboxylate ligands. Extensive hydrogen-bonding interactions exist between layers constructed of  $\text{Fe}_4$  squares, forming tunnels along the  $a$  axis with large voids.

### Comment

The structures and properties of metal complexes with biologically relevant ligands are currently attracting much interest on account of their promising contribution to understanding the active mechanism of metalloproteins by means of modelling their metal binding site (Chauvin *et al.*, 2003; Mukherjee, 2000). However, as a derivative of imidazole which is ubiquitous at the active site of many metalloproteins, imidazole-4,5-dicarboxylic acid ( $\text{H}_3\text{IMDC}$ ) has been less well studied (Wang *et al.*, 2004; Rajendiran *et al.*, 2003; Huang *et al.*, 2001; Sengupta *et al.*, 2001; Caudle *et al.*, 1997). We report here the synthesis and crystal structure of the title compound,  $[\text{Fe}(\text{H}_2\text{IMDC})_2]_n$ , (I).



In compound (I), the Fe atom lies on centre of symmetry and the coordination environment is octahedral (Fig. 1 and Table 1). Each Fe atom is hexacoordinated by  $\text{N}_2\text{O}_4$ , with two chelating rings from  $\text{H}_2\text{IMDC}^-$  ligands [ $\text{Fe}-\text{N}1 = 2.154(3) \text{ \AA}$  and  $\text{Fe}-\text{O}3 = 2.180(3) \text{ \AA}$ ] arranged symmetrically in the equatorial plane and two O atoms from  $\text{H}_2\text{IMDC}^-$  ligands

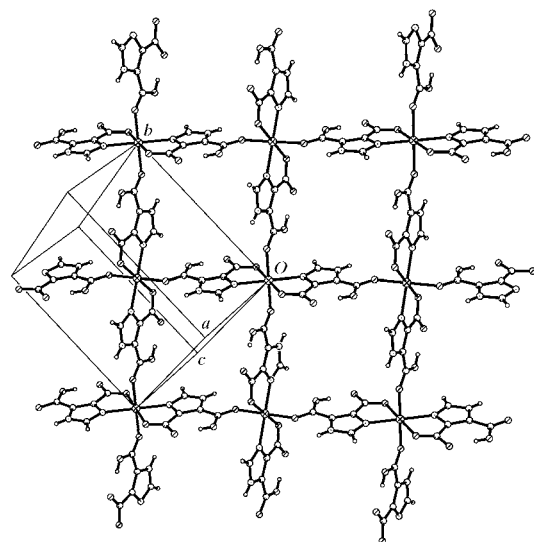


**Figure 1**

The coordination environment of the Fe atom in (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (ii)  $-x, -y, -z$ ; (iii)  $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$ ]

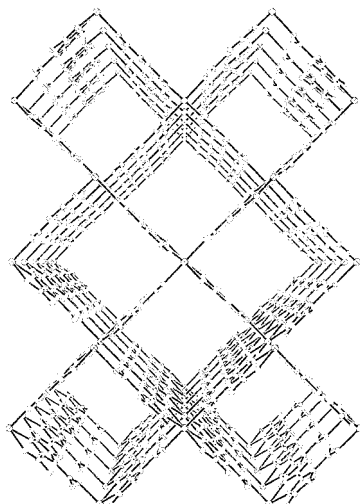
[ $\text{Fe}-\text{O}1(\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z) = 2.111(2) \text{ \AA}$ ] occupying the apical sites.

Complex (I) displays an extended two-dimensional layer structure constructed of quasi-squares, with four Fe atoms at the corners and  $\text{H}_2\text{IMDC}^-$  anions as linkers (Fig. 2). Each  $\text{H}_2\text{IMDC}^-$  anion is nearly planar and connects two  $\text{Fe}^{\text{II}}$  ions in an individual mono- and bidentate mode. The lateral  $\text{Fe} \cdots \text{Fe}$  lengths of the  $\text{Fe}_4$  square are all  $8.572(1) \text{ \AA}$ , the diagonal  $\text{Fe} \cdots \text{Fe}$  distances are  $11.719(2)$  and  $12.512(2) \text{ \AA}$ , and the vertex angles are  $86.25(1)$  and  $93.75(1)^\circ$ , indicating only slight deviations from the ideal square geometry.



**Figure 2**

The extended lamellar structure of (I).



**Figure 3**  
A packing diagram for (I), viewed along the *a* axis.

Recently, a cobalt complex containing  $\text{Co}_4$  molecular squares with imidazole-4,5-dicarboxylate bridges has been reported (Wang *et al.*, 2004), in which  $\text{IMDC}^{3-}$  links two cobalt ions in a bis-bidentate mode and the two chelating rings of two  $\text{IMDC}^{3-}$  ligands coordinated to one metal atom are almost perpendicular to each other. Furthermore, 2,2'-bipyridine exists as a terminal ligand, chelating the central atom to prevent the structure expanding in two dimensions. However, in (I), the  $\text{Fe}_4$  squares are extended by the  $\text{H}_2\text{IMDC}^-$  ligand and form an infinite layer structure without terminal ligands. It is noted that the  $\text{H}_2\text{IMDC}^-$  ligand in (I) is less geometrically symmetrical than the  $\text{IMDC}^{3-}$  ligand in the reported molecular squares, but it provides much smaller deviations from the ideal square geometry.

The layers of complex (I) are connected by  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds, leading to the formation of a three-dimensional network structure with tunnels along the *a* axis (Fig. 3). The packing diagram of (I) along the *b* axis is shown in Fig. 4. It is very interesting that this crystal structure of hydrogen-bonded networks survives with solvent-accessible voids of  $180 \text{ \AA}^3$ . The total void space per unit cell is  $360 \text{ \AA}^3$ , centred at  $(0, \frac{1}{2}, 0)$  and  $(0, 0, \frac{1}{2})$  and at their symmetry-related positions. It is the combination of these voids which generates the channels along  $(x, \frac{1}{2}, 0)$  and  $(x, 0, \frac{1}{2})$ . The maximum peak in the final difference Fourier map is  $0.83 \text{ e \AA}^{-3}$  at the Fe atom, and the minimum peak is  $-0.37 \text{ e \AA}^{-3}$  at a distance of  $0.69 \text{ \AA}$  from atom H2A.

According to charge-balance requirements, the oxidation state of Fe in (I) is tentatively assigned as +2, since the reaction of aromatic N-containing ligands, such as imidazole or pyridine derivatives, with transition metal salts can result in spontaneous metal ion reduction (Stupka *et al.*, 2004; Wang *et al.*, 2004; Lu & Babb, 2002; Sugiyama *et al.*, 2002). In addition, we have also recently obtained a type of  $\text{Fe}^{\text{II}}$  coordination complex from the reaction of  $\text{FeCl}_3$  and pyridine-2,5-dicarboxylic acid *via* the solvothermal method in *N,N*-dimethylformamide. The mechanisms of the redox reactions

involving the usual aromatic ligands with N or  $\text{N}_2$  donors under solvo(hydro)thermal conditions are still under study.

## Experimental

The title compound, (I), was prepared by the solvothermal reaction of iron(III) chloride (0.008 g, 0.05 mmol) and imidazole-4,5-dicarboxylic acid (0.016 g, 0.1 mmol) in 99.5% ethanol (10 ml). The reaction was performed in a 23 ml Teflon-lined stainless-steel Parr bomb under autogenous pressure. After heating at a rate of 433 K for 2 d and cooling to room temperature at a rate of  $13 \text{ K h}^{-1}$ , light-yellow crystals of (I) were obtained. The title compound was the only product (yield: 0.4 mg, 2%).

### Crystal data

$[\text{Fe}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2]$	$D_x = 1.328 \text{ Mg m}^{-3}$
$M_r = 366.04$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2242 reflections
$a = 6.9909 (14) \text{ \AA}$	$\theta = 3.3\text{--}25.0^\circ$
$b = 11.719 (2) \text{ \AA}$	$\mu = 0.86 \text{ mm}^{-1}$
$c = 11.2519 (16) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 96.909 (9)^\circ$	Dipyramid, light yellow
$V = 915.2 (3) \text{ \AA}^3$	$0.30 \times 0.18 \times 0.10 \text{ mm}$
$Z = 2$	

### Data collection

Rigaku Mercury CCD area-detector diffractometer	1614 independent reflections
$\omega$ scans	1455 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ( <i>CrystalClear</i> ; Rigaku, 2000)	$R_{\text{int}} = 0.031$
$T_{\text{min}} = 0.599, T_{\text{max}} = 0.917$	$\theta_{\text{max}} = 25.0^\circ$
5462 measured reflections	$h = -5 \rightarrow 8$
	$k = -13 \rightarrow 13$
	$l = -12 \rightarrow 13$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.113P)^2 + 0.6498P]$
$R(F) = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.178$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.18$	$\Delta\rho_{\text{max}} = 0.83 \text{ e \AA}^{-3}$
1614 reflections	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$
106 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

Fe—O1 <sup>i</sup>	2.111 (2)	N1—C1	1.318 (5)
Fe—N1	2.154 (3)	N1—C3	1.372 (5)
Fe—O3	2.180 (3)	N2—C1	1.337 (5)
O1—C4	1.231 (5)	N2—C2	1.362 (5)
O2—C4	1.285 (5)	C2—C3	1.374 (5)
O3—C5	1.250 (5)	C2—C4	1.476 (5)
O4—C5	1.273 (5)	C3—C5	1.474 (5)
O1 <sup>i</sup> —Fe—N1	90.50 (11)	N1—Fe—O3	77.32 (10)
O1 <sup>i</sup> —Fe—O3	90.30 (11)		

Symmetry code: (i)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ .

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}, ^\circ$ ).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O2—H2B $\cdots$ O4	0.82	1.66	2.477 (4)	179
N2—H2A $\cdots$ O4 <sup>iv</sup>	0.86	2.07	2.897 (4)	162

Symmetry code: (iv)  $1 + x, y, z$ .

The H atoms were positioned geometrically, with O—H = 0.82 Å, N—H = 0.86 Å and C—H = 0.93 Å, and were constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$  or  $1.2U_{\text{eq}}(\text{C,N})$ .

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997b).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1176). Services for accessing these data are described at the back of the journal.

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