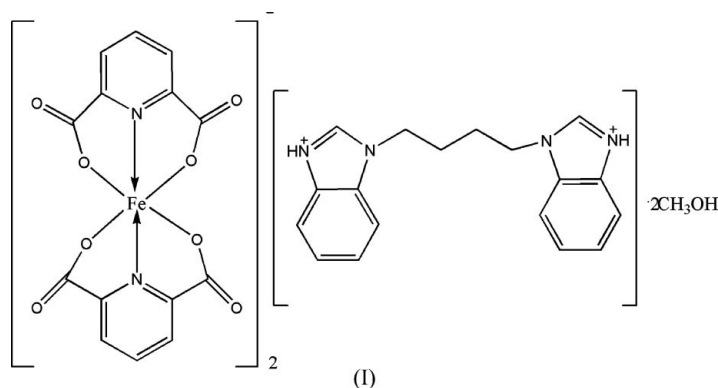


1,1'-(Butane-1,4-diyl)bis(1*H*-benzimidazol-3-ium)bis[bis(pyridine-2,6-dicarboxylato- κ^3 O,*N*,O')-ferrate(III)] methanol disolvate**Zhen-Yu Hou^{a*} and Dong-Mei Zhu^b**^aDepartment of Chemical Engineering, Henan Institute of Science and Technology, Xinxiang 453003, People's Republic of China, and^bSchool of Materials and Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou 450002, People's Republic of ChinaCorrespondence e-mail:
zhenyuhou1996@yahoo.com**Key indicators**Single-crystal X-ray study
T = 291 K
Mean σ (C–C) = 0.005 Å
R factor = 0.056
wR factor = 0.131
Data-to-parameter ratio = 13.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title complex, (C₁₈H₂₀N₄)[Fe(C₇O₄H₃N)₂]₂·2CH₃O, the Fe atom exists in an approximately octahedral geometry, chelated by two pyridine-2,6-dicarboxylate ligands. Extensive hydrogen bonding among the carboxylate groups, the 1,1'-(butane-1,4-diyl)bis-1*H*-benzimidazol-3-ium ion and solvent methanol molecules as well as π – π stacking are present in the structure.

Comment

Proton transfer is one of the most important elementary processes in physics, chemistry and biochemistry, as it is the key process in important reactions such as auto-ionization in water, acid–base neutralization reactions and enzyme catalysis (MacDonald *et al.*, 2000). Extensive studies on the reaction of pyridine-2,6-dicarboxylic acid (H₂pdc) with lanthanides and transition metals in the presence of Lewis bases such as pyridine-2,6-diamine (pda), 1,10-phenanthroline (phen) and creatinine (creat) have led to the isolation of proton transfer ionic complexes [pdaH]₂[La₂(pdc)₄(H₂O)₄]₂·2H₂O, [pdaH]₂[Co(pdc)₂]₂·H₂O (Moghimi *et al.*, 2002), (creatH)[Zn(pdc)(pdcH)]·4H₂O (Moghimi, Sharif *et al.*, 2005) and [Zn(pdc)₂][Zn(phen)₂(H₂O)₂]₂·7H₂O (Moghimi, Sheshmani *et al.*, 2005). On the other hand, the 1,1'-(butane-1,4-diyl)bis-1*H*-benzimidazole (bbbm) *N*-heterocycle as a flexible bidentate ligand affords adducts with some transition metal salts (Meng *et al.*, 2003; Xiao *et al.*, 2004). In this work, we selected H₂pdc as the proton donor and bbbm as the proton acceptor, and successfully prepared a new proton transfer Fe^{III} complex, (I).



Complex (I) consists of two mononuclear [Fe(pdc)₂]²⁻ anions, one (H₂bbbm)²⁺ dication and two solvent methanol molecules (Fig. 1). The central Fe atom is hexacoordinated by two pyridine N and four carboxylate O atoms from two deprotonated pdc²⁻ ligands in an approximately octahedral geometry; the carboxylate group coordinates in a mono-

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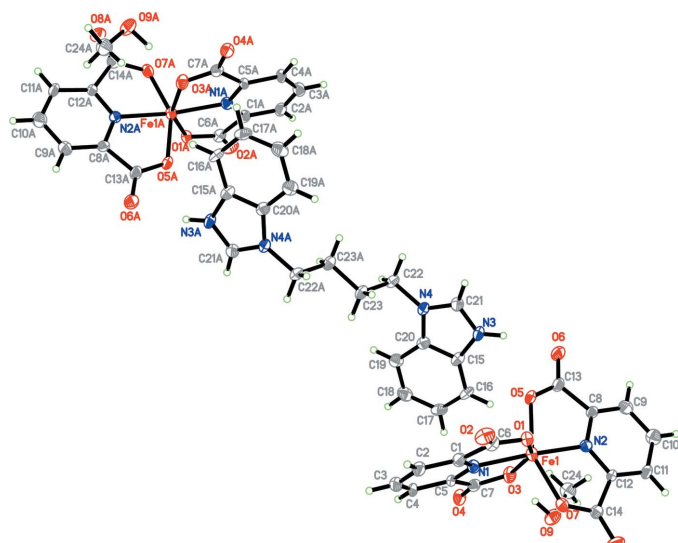


Figure 1
The molecular structure of the anion of (I), with 30% probability displacement ellipsoids [symmetry code: (A) $-x, 1-y, 2-z$].

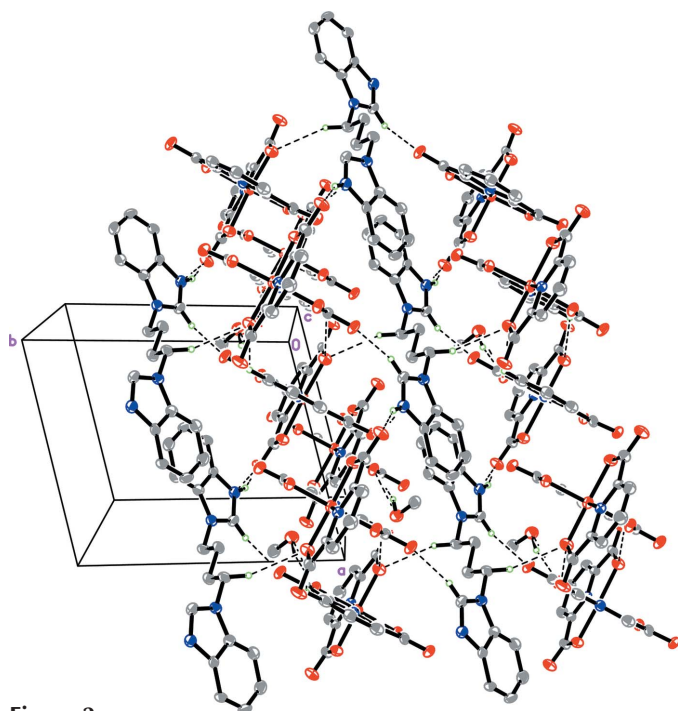


Figure 2
A perspective view of the hydrogen-bonding interactions (dashed lines) in (I). For clarity, H atoms not involved in hydrogen bonding have been omitted.

dentate fashion. The two ligands are almost perpendicular to each other.

Anions interact with the $(\text{H}_2\text{bbbm})^{2+}$ dication and solvent methanol molecules to produce a hydrogen-bonded layered structure by three types of hydrogen bond ($\text{N}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$) (Table 2 and Fig. 2). The $[\text{Fe}(\text{pdc})_2]^-$ units are linked into layers, and the space between these layers is occupied by the $(\text{H}_2\text{bbbm})^{2+}$ cations. A face-to-face separation of 3.642 (2) Å between the N2-containing pyridine rings from two neighboring anions suggests the existence of $\pi-\pi$ aromatic stacking interactions.

Experimental

1,1'-(Butane-1,4-diyl)bis-1*H*-benzimidazole (bbbm) was prepared according to a literature method (Xie *et al.*, 2000). A methanol solution (5 ml) of H_2pdc (16.7 mg, 0.1 mmol) was added dropwise to a methanol solution (5 ml) of $\text{Fe}(\text{ClO}_4)_3\cdot 7\text{H}_2\text{O}$ (23.2 mg, 0.05 mmol) and bbbm (29.0 mg, 0.1 mmol) to give a clear solution. Light-green block-like crystals (55% yield) of (I) were obtained one week later. IR (KBr, cm^{-1}): 3081 (*w*), 1675 (*s*), 1452 (*w*), 1322 (*s*), 1167 (*s*), 1072 (*s*), 914 (*m*), 742 (*s*), 681 (*m*), 439 (*w*). Analysis calculated for $\text{C}_{48}\text{H}_{40}\text{Fe}_2\text{N}_8\text{O}_{18}$: C 51.08, H 3.57, N 9.93%; found: C 51.23, H 3.47, N 9.85%.

Crystal data

$(\text{C}_{18}\text{H}_{20}\text{N}_4)[\text{Fe}(\text{C}_7\text{H}_3\text{NO}_4)_2]_2\cdot 2\text{CH}_4\text{O}$
 $M_r = 1128.58$
 Triclinic, $P\bar{1}$
 $a = 9.2751$ (19) Å
 $b = 11.035$ (2) Å
 $c = 13.167$ (3) Å
 $\alpha = 106.50$ (3)°
 $\beta = 101.19$ (3)°
 $\gamma = 103.07$ (3)°
 $V = 1209.6$ (6) Å³

$Z = 1$
 $D_x = 1.549$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 779 reflections
 $\theta = 2.1-18.0^\circ$
 $\mu = 0.69$ mm⁻¹
 $T = 291$ (2) K
 Block, light green
 $0.20 \times 0.18 \times 0.17$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.875$, $T_{\max} = 0.892$
 8712 measured reflections

4764 independent reflections
 3875 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$
 $\theta_{\max} = 26.0^\circ$
 $h = -11 \rightarrow 11$
 $k = -13 \rightarrow 13$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.131$
 $S = 1.02$
 4764 reflections
 344 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.88P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.43$ e Å⁻³
 $\Delta\rho_{\min} = -0.74$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C1—N1	1.335 (4)	C15—N3	1.395 (4)
C5—N1	1.330 (4)	C20—N4	1.391 (4)
C6—O2	1.210 (4)	C21—N3	1.313 (4)
C6—O1	1.303 (4)	C21—N4	1.327 (4)
C7—O4	1.229 (4)	C22—N4	1.482 (4)
C7—O3	1.303 (4)	C24—O9	1.407 (5)
C8—N2	1.336 (4)	Fe1—O1	1.992 (2)
C12—N2	1.328 (4)	Fe1—O7	1.996 (3)
C13—O6	1.233 (4)	Fe1—O5	2.039 (3)
C13—O5	1.282 (4)	Fe1—N1	2.061 (3)
C14—O8	1.205 (4)	Fe1—O3	2.066 (2)
C14—O7	1.310 (4)	Fe1—N2	2.073 (3)
O1—Fe1—O7	93.60 (10)	N1—Fe1—O3	75.03 (10)
O1—Fe1—O5	93.73 (10)	O1—Fe1—N2	117.19 (10)
O7—Fe1—O5	150.61 (9)	O7—Fe1—N2	75.91 (10)
O1—Fe1—N1	76.79 (10)	O5—Fe1—N2	75.43 (10)
O7—Fe1—N1	105.10 (10)	N1—Fe1—N2	166.01 (10)
O5—Fe1—N1	104.28 (10)	O3—Fe1—N2	91.00 (10)
O1—Fe1—O3	151.81 (9)	C5—N1—C1	122.2 (3)
O7—Fe1—O3	93.24 (10)	C5—N1—Fe1	120.2 (2)
O5—Fe1—O3	93.59 (10)	C1—N1—Fe1	117.6 (2)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3E \cdots O6	0.88	2.03	2.879 (4)	161
O9—H9E \cdots O3	0.96	1.91	2.843 (4)	161
C22—H22A \cdots O7 ⁱ	0.97	2.55	3.460 (4)	157

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

All H atoms were placed in calculated positions and were refined isotropically, with $U_{\text{iso}}(\text{H})$ values constrained to $1.2U_{\text{eq}}(\text{C}, \text{N}, \text{O})$ or $1.5U_{\text{eq}}(\text{C})$, using a riding model with $\text{C}-\text{H} = 0.93\text{--}0.97$ Å; $\text{N}-\text{H} = 0.88$ Å and $\text{O}-\text{H} = 0.96$ Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine

structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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