

2-(2-Pyridyl)pyridinium bis(pyridine-2,6-dicarboxylato- $\kappa^2O^2,O^6$ )iron(III) trihydrateQi-Hua Zhao,\* Mei-Su Zhang  
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The title compound,  $(C_{10}H_9N_2)[Fe(C_7H_3NO_4)_2] \cdot 3H_2O$ , was prepared from the ligand pyridine-2,6-dicarboxylic acid with  $FeCl_3 \cdot 6H_2O$  in the presence of 2,2-bipyridine. The  $Fe^{III}$  atom is six-coordinate in a distorted octahedral geometry. The compound contains protonated 2,2'-bipyridine and doubly deprotonated pyridine-2,6-dicarboxylate (pydc) units; the protonated 2,2'-bipyridine bridges adjacent  $[Fe(pydc)_2]^-$  complex units through hydrogen bonding.

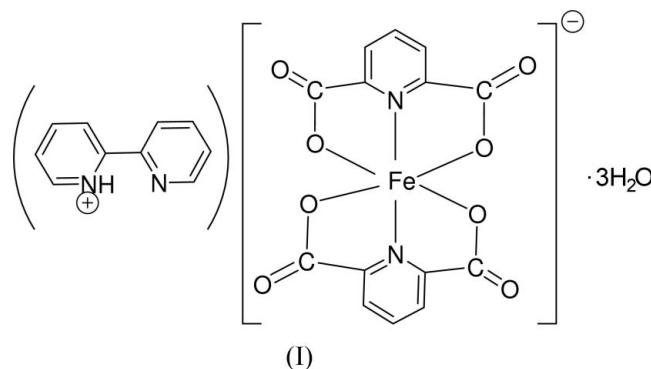
## Key indicators

Single-crystal X-ray study  
 $T = 289\text{ K}$   
 Mean  $\sigma(C-C) = 0.002\text{ \AA}$   
 $R$  factor = 0.029  
 $wR$  factor = 0.089  
 Data-to-parameter ratio = 13.7

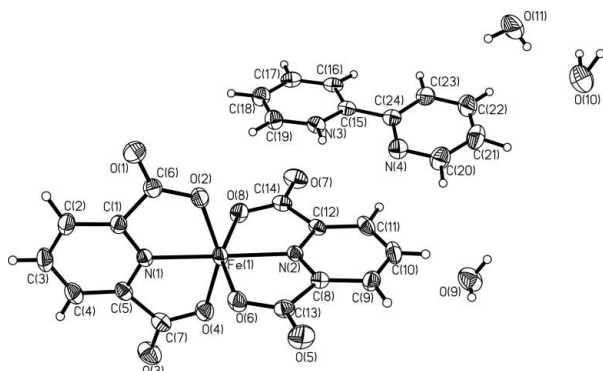
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Comment

In the past decade, much attention has been paid to the design and synthesis of self-assembling systems (Seto *et al.*, 1990; Conn & Reber, 1997; Zafar *et al.*, 2000). The molecular self-assembly organized by non-covalent interactions is an attractive approach in crystal engineering for the synthesis and design of new compounds with potentially useful properties for relevant scientific and technological applications (Lehn, 1995; Ko *et al.*, 2002; Hagrman *et al.*, 1999). The ligand pydc is widely used in coordination chemistry, forming stable complexes with most metal ions by adopting the tridentate coordination mode (Perrin *et al.*, 1979). In the literature, there are also reports on the reaction of pyridine-2,6-dicarboxylate (pydc) with lanthanides and transition metals in the presence of Lewis acids, such as pyridine-2,6-diamine (pyda), 1,10-phenanthroline (phen) and creatinine (creat), which led to the ionic complexes  $[pydaH]_2[La_2(pydc)_4(H_2O)_4] \cdot 2H_2O$  (Moghimi *et al.*, 2002),  $[pydaH]_2[Co(pydc)_2] \cdot H_2O$  (Moghimi *et al.*, 2002),  $[Zn(pydc)_2][Zn(phen)_2(H_2O)_2] \cdot 7H_2O$  (Moghimi, Sheshmani *et al.*, 2005) and  $(creatH)[Zn(pydc)(pydcH)] \cdot 4H_2O$  (Moghimi, Sharif *et al.*, 2005). We selected  $pydcH_2$  as the proton donor and bipy as the proton acceptor, and successfully prepared a new proton transfer  $Fe^{III}$  complex, (I).



Compound (I) consists of an anionic complex,  $[Fe(pydc)_2]^-$ , a cationic counter-ion,  $(bipyH)^+$ , and uncoordinated water (Fig. 1). In each anionic  $[Fe(pydc)_2]^-$  unit, the  $(pydc)^{2-}$  acts as



**Figure 1**  
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

a tridentate ligand. The protonated N atom in the cationic bipy counter-ion is N3. The angle C19–N3–C15 is 124.01 (13)°, which is larger than the value of C20–N4–C24 [117.21 (1)°]. The Fe<sup>III</sup> atom is coordinated by two N and four O atoms of two (pydc)<sup>2-</sup> units. The O4–Fe1–O2 and O6–Fe1–O8 angles are 151.77 (5) and 151.63 (4)°, respectively, which shows that the four carboxylate groups of two (pydc)<sup>2-</sup> ligands are arranged in an equatorial plane around the Fe<sup>III</sup> atom. The N1–Fe1–N2 angle is 177.63 (4)°, a small deviation (*i.e.* 2.37°) from linearity being observed. The dihedral angle between the two pyridine rings of pydc units is 89.68 (5)°, which shows that they are almost perpendicular to each other. Selected bond lengths and angles are listed in Table 1. There is an extensive network of hydrogen bonds (Fig. 2) involving bipyH counter-ions and pydc O atoms, uncoordinated water and pydc H atoms and pydc O atoms. The bipy co-ligand bridges adjacent [Fe(pydc)<sub>2</sub>]<sup>-</sup> complex units through extensive hydrogen bonding, resulting in a layered structure for this complex. Hydrogen-bond lengths and angles are listed in Table 2.

## Experimental

An MeOH–H<sub>2</sub>O (1:1 *v/v*) solution (5 ml) of bipy (32.95 mg, 0.210 mmol) was added to an MeOH–H<sub>2</sub>O solution (15 ml) containing FeCl<sub>3</sub>·6H<sub>2</sub>O (60.4 mg, 0.223 mmol) and pydcH<sub>2</sub> (39.6 mg, 0.237 mmol) with continuous stirring for 15 min. The mixed solution was filtered and X-ray quality light-green block-shaped crystals of (I) were grown from the resulting solution by slow evaporation at room temperature (yield 42.3%. m.p. > 563 K). IR (KBr) (cm<sup>-1</sup>): 3500 (*w*), 3140 (*s*), 1670 (*s*), 1600 (*w*), 1580 (*s*), 1520 (*s*), 1446 (*s*), 1420 (*m*), 1330 (*vs*), 1210 (*m*), 1180 (*vs*), 1070 (*vs*), 910 (*vs*), 750 (*s*), 720 (*vs*), 680 (*vs*), 450 (*s*).

### Crystal data

(C<sub>10</sub>H<sub>9</sub>N<sub>2</sub>)[Fe(C<sub>7</sub>H<sub>3</sub>NO<sub>4</sub>)<sub>2</sub>]·3H<sub>2</sub>O  
*M<sub>r</sub>* = 597.30  
 Triclinic, *P* $\bar{1}$   
*a* = 9.4528 (19) Å  
*b* = 10.840 (2) Å  
*c* = 13.178 (3) Å  
 $\alpha$  = 104.62 (3)°  
 $\beta$  = 99.57 (3)°  
 $\gamma$  = 97.02 (3)°  
*V* = 1269.3 (4) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.563 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 1694 reflections  
 $\theta$  = 2.2–28.2°  
 $\mu$  = 0.66 mm<sup>-1</sup>  
*T* = 289 (2) K  
 Block, green  
 0.19 × 0.16 × 0.14 mm

### Data collection

Bruker SMART CCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 1998)  
*T<sub>min</sub>* = 0.884, *T<sub>max</sub>* = 0.913  
 15248 measured reflections

6109 independent reflections  
 5427 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.018  
 $\theta_{\max}$  = 28.2°  
*h* = -12 → 12  
*k* = -14 → 14  
*l* = -17 → 17

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.029  
*wR* (*F*<sup>2</sup>) = 0.089  
*S* = 1.05  
 6109 reflections  
 446 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.1599P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.003$   
 $\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.042 (2)

**Table 1**

Selected geometric parameters (Å, °).

Fe1–O4	2.0139 (12)	Fe1–N1	2.0612 (12)
Fe1–O6	2.0185 (11)	C15–N3	1.3499 (18)
Fe1–O2	2.0209 (13)	C19–N3	1.331 (2)
Fe1–O8	2.0243 (12)	C20–N4	1.334 (2)
Fe1–N2	2.0553 (11)	C24–N4	1.340 (2)
O4–Fe1–O6	94.09 (5)	O8–Fe1–N2	75.93 (5)
O4–Fe1–O2	151.76 (4)	O4–Fe1–N1	75.92 (6)
O6–Fe1–O2	93.87 (5)	O6–Fe1–N1	103.12 (5)
O4–Fe1–O8	93.80 (5)	O2–Fe1–N1	75.89 (5)
O6–Fe1–O8	151.63 (4)	O8–Fe1–N1	105.23 (5)
O2–Fe1–O8	91.94 (5)	N2–Fe1–N1	177.64 (4)
O4–Fe1–N2	106.14 (5)	C19–N3–H10	114.9 (15)
O6–Fe1–N2	75.70 (5)	C15–N3–H10	121.0 (15)
O2–Fe1–N2	102.08 (5)	C20–N4–C24	117.24 (17)

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C4–H15...O11 <sup>i</sup>	0.94 (2)	2.56 (2)	3.457 (3)	159 (2)
O10–H6...O3 <sup>ii</sup>	0.99 (3)	1.91 (3)	2.880 (2)	167 (3)
C17–H12...O5 <sup>iii</sup>	0.92 (2)	2.32 (2)	3.115 (2)	144 (2)
N3–H10...O7	0.80 (2)	2.04 (2)	2.7246 (17)	143 (2)
O9–H5...O11 <sup>iv</sup>	0.75 (2)	2.11 (2)	2.823 (3)	161 (4)

Symmetry codes: (i) *x* + 1, *y*, *z* – 1; (ii) *x* – 1, *y*, *z* + 1; (iii) *x* – 1, *y* + 1, *z*; (iv) *x* + 1, *y*, *z*.

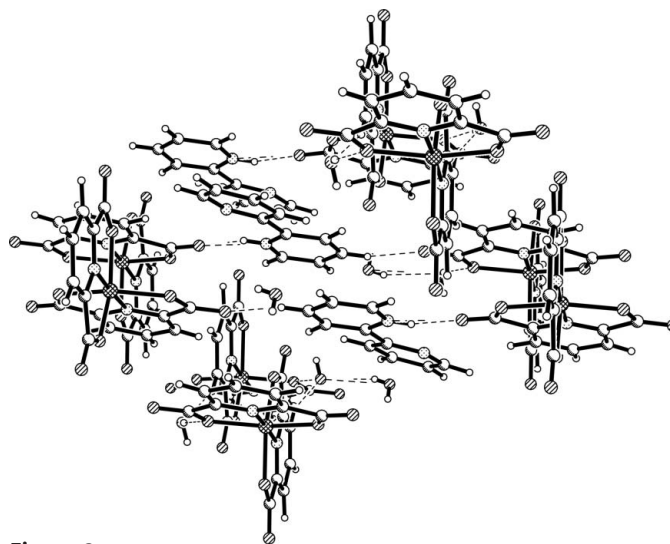
All H atoms were located in a difference Fourier map and refined freely.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998); software used to prepare material for publication: SHELXTL.

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## References

- Bruker (1998). *SMART, SAINT, SADABS and SHELXTL*. Bruker AXS, Inc., Madison, Wisconsin, USA.
- Conn, M. M. & Reber, J. Jr (1997). *Chem. Rev.* **97**, 1647–1668.
- Hagrman, P. J., Hagrman, D. & Zubieta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 2638–2684.
- Ko, J. W., Min, K. S. & Suh, M. P. (2002). *Inorg. Chem.* **41**, 2151–2157.
- Lehn, J. M. (1995). *Supramolecular Chemistry*. Weinheim: VCH.
- Moghimi, A., Ranjbar, M., Aghabozorg, H., Jalali, F., Shamsipur, M. & Chadah, R. K. (2002). *Can. J. Chem.* **80**, 1687–1696.
- Moghimi, A., Sharif, M. A. Shokrollahi, A., Shamsipur, M. & Aghabozorg, H. (2005). *Z. Anorg. Allg. Chem.* **631**, 902–908.
- Moghimi, A., Sheshmani, S., Shokrollahi, A., Shamsipur, M., Kickelbick, G. & Aghabozorg, H. (2005). *Z. Anorg. Allg. Chem.* **631**, 160–169.
- Perrin, D. D. (1979). *Stability Constants of Metal Ion Complex, Part B, Organic Ligands*. Oxford: Pergamon Press.
- Seto, C. T. & Whitesides, G. M. (1990). *J. Am. Chem. Soc.* **112**, 6409–6411.
- Sheldrick, G. M. (1997). *SHELXS97 and SHELXL97*. University of Göttingen, Germany.
- Zafar, A., Geib, S. J., Hamuro, Y., Carr, A. J. & Hamilton, A. D. (2000). *Tetrahedron*, **56**, 8419–8427.



**Figure 2**  
The crystal packing of (I), showing the hydrogen bonds as dashed lines.