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Tetraaqua(2,2′-bipyridine-5,5′-dicarboxylato)-iron(II) dihydrate

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.085
Data-to-parameter ratio = 13.2

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

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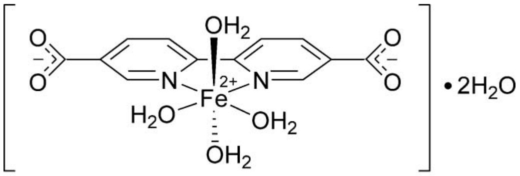
In the title compound, $[Fe(C_{12}H_6N_2O_4)(H_2O)_4]\cdot 2H_2O$, the Fe^{II} ion (site symmetry 2) is bonded to one *N*,*N*′-bidentate 2,2′-bipyridine-5,5′-dicarboxylate ligand and four water molecules, resulting in a distorted *cis*-FeN_2O_4 coordination geometry. A network of π–π interactions and O—H···O hydrogen bonds gives rise to a robust supramolecular network in the crystal structure.

Comment

The 2,2′-bipyridine-5,5′-dicarboxylate (5,5′-BPDC^{2-}) dianion has been widely used as an organic building block in supramolecular chemistry because this ligand can coordinate to a metal ion through the bipyridine unit and additionally bond to further metal ions *via* its two carboxylate groups, leading to novel polymeric topologies (Matthews *et al.*, 2004; Tynan *et al.*, 2003; Lee & Suh, 2004). Here, we report the synthesis and structure of the molecular title compound, (I).



(I)

As shown in Fig. 1, the iron(II) ion (site symmetry 2) in (I) is coordinated by two N atoms of the 5,5′-BPDC^{2-} ligand and four water molecules, resulting in a distorted *cis*-FeN_2O_4 octahedral coordination geometry (Table 1). The axial Fe—O bond length is longer than the equatorial one, which can be attributed to the Jahn–Teller distortion of the Fe^{II} ion. The Fe—(O,N) bond lengths in (I) are slightly longer than the equivalent Co—(O,N) distances in $[Co(4,4'\text{-BPDC})(H_2O)_4]\cdot 4H_2O$ (4,4′-BPDC = 2,2′-bipyridine-4,4′-dicarboxylate) (Tynan *et al.*, 2003) as a result of the larger ionic radius of iron(II) [$r_{Fe(II)}$ = 0.920 Å and $r_{Co(II)}$ = 0.885 Å; Shannon & Prewitt, 1970]. The 5,5′-BPDC^{2-} ligand in (I) is twisted about both the C2—C6 and the C5—C5^{i} (see Table 1 for symmetry code) bonds, as reflected in the dihedral angles between the C1–C5/N1 mean plane and the C6/O1/O2 plane and C1^{i}–C5^{i}/N1^{i} mean plane of 9.2 (3) and 12.66 (9)°, respectively. The near identical C—O bond lengths indicate that the carboxylate group in (I) is delocalized, as also seen in $[Co(4,4'\text{-BPDC})(H_2O)_4]\cdot 4H_2O$ (Tynan *et al.*, 2003).

The pyridine rings of the 5,5′-BPDC^{2-} ligand (Fig. 2) in (I) are involved in offset face-to-face π–π interactions [centroid–centroid separation = 3.664 (3) Å], which leads to a supra-

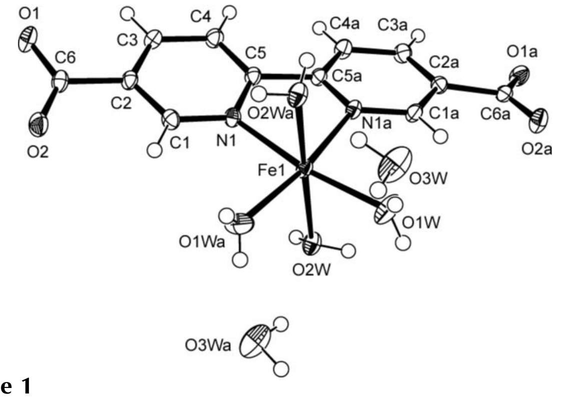


Figure 1
View of the molecular structure of (I), showing 50% displacement ellipsoids for the non-H atoms. Atoms labeled with the suffix a are at the symmetry position $(-x, y, \frac{1}{2} - z)$.

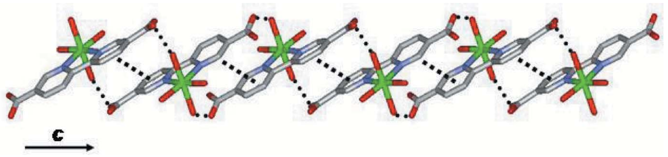


Figure 2
Perspective view of (I), showing a one-dimensional chain along the *c* axis by hydrogen-bonding interactions (black circles) and offset face-to-face π–π interactions (black squares).

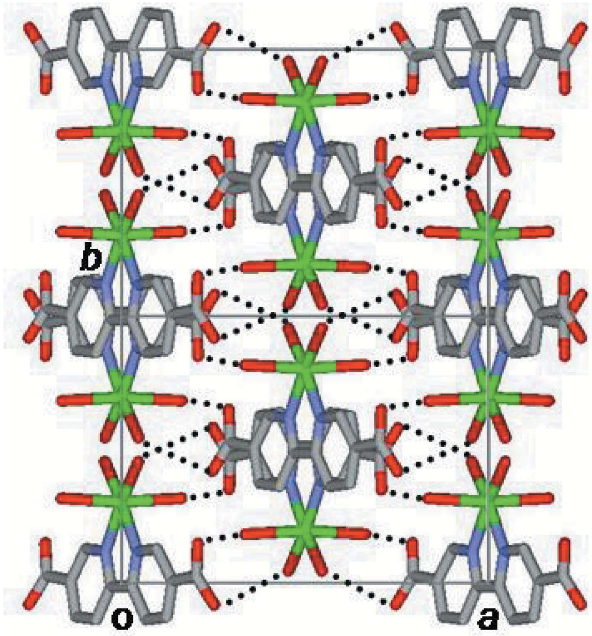


Figure 3
View of the packing of (I), displaying a three-dimensional network by extensive hydrogen-bonding interactions (dotted lines).

molecular chain propagating along the *c* axis. The interplanar separation between the ring planes of adjacent 5,5′-BPDC^{2-} anions, which are parallel by symmetry, is 3.332 (3) Å. Within a chain, intermolecular O—H⋯O hydrogen-bonding interactions exist between the H atom of an aqua ligand and the uncoordinated carboxylate O atom of a 5,5′-BPDC^{2-} ligand belonging to the adjacent complex (Fig. 2; Table 2). The shortest Fe⋯Fe distance within a chain is 8.692 (1) Å and that between the chains is 7.535 (1) Å.

The polymeric chains are crosslinked in the [110] and [$1\overline{1}0$] directions by further O—H⋯O links involving both the coordinated and the uncoordinated water molecules (Fig. 3). A C—H⋯O hydrogen-bonding interaction is also present (Table 2).

Experimental

2,2′-Bipyridine-5,5′-dicarboxylic acid (H_2BPDC) was prepared by the literature procedure (Elliott & Hershenhart, 1982). An aqueous solution (10 ml) of H_2BPDC (50 mg, 0.20 mmol) was added dropwise to an aqueous solution (10 ml) of $FeCl_2 \cdot 6H_2O$ (26 mg, 0.20 mmol). The pH of the solution was adjusted to *ca* 8 by the addition of 0.1 *M* NaOH solution under a nitrogen atmosphere. The mixture was then stirred for 2 h at room temperature. The red solution was allowed to stand under a nitrogen blanketing atmosphere until red microcrystals formed, which were collected by filtration and dried *in vacuo*. Single crystals of (I) suitable for X-ray crystallography were obtained by recrystallization from a 1:1 water/ethanol mixture. Yield 58 mg (72%).

Crystal data

$[Fe(C_{12}H_6N_2O_4)(H_2O)_4]\cdot 2H_2O$
$M_r = 406.13$
Monoclinic, $C2/c$
$a = 12.7597$ (11) Å
$b = 9.2615$ (8) Å
$c = 13.2195$ (11) Å
$\beta = 93.620$ (2)°
$V = 1559.1$ (2) Å^3
$Z = 4$
$D_x = 1.730$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.03$ mm^{-1}
$T = 173$ (2) K
Prism, red
0.30 × 0.15 × 0.12 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.777$, $T_{max} = 0.884$
4812 measured reflections
1827 independent reflections
1666 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.085$
$S = 1.19$
1827 reflections
138 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 2.755P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—N1	2.1709 (19)	C6—O1	1.256 (3)
Fe1—O1*W*	2.0671 (18)	C6—O2	1.255 (3)
Fe1—O2*W*	2.2026 (16)		
N1—Fe1—N1^{i}	75.17 (9)	O1—C6—C2	117.5 (2)
O1—C6—O2	124.69 (19)	O2—C6—C2	117.80 (19)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1A···O1$^{\rm ii}$	0.79 (3)	2.03 (4)	2.815 (3)	173 (3)
O1W—H1B···O3W	0.74 (3)	1.93 (4)	2.629 (3)	158 (3)
O2W—H2A···O2$^{\rm ii}$	0.84 (3)	1.85 (4)	2.691 (2)	177 (3)
O2W—H2B···O1$^{\rm iii}$	0.76 (4)	2.00 (4)	2.755 (3)	172 (4)
O3W—H3A···O2$^{\rm iv}$	0.88 (5)	1.89 (5)	2.737 (3)	159 (4)
O3W—H3B···O2$W^{\rm i}$	0.82 (4)	2.12 (4)	2.848 (3)	148 (4)
C1—H1···O3$W^{\rm v}$	0.95	2.54	3.458 (3)	163

Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $-x, -y + 2, -z + 1$; (iv) $x, -y + 1, z - \frac{1}{2}$; (v) $x, -y + 1, z + \frac{1}{2}$.

All C-bound H atoms were refined using a riding model, with C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The H atoms of the water molecules were found in difference maps and their positions and $U_{\rm iso}$ values were allowed to refine freely.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SHELXTL* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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