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Hydrogen bonding and π–π stacking in the three-dimensional supramolecular complex bis(4,4′-bipyridinium) diaquadioxalatoferrate(II) bis(hydrogen oxalate)

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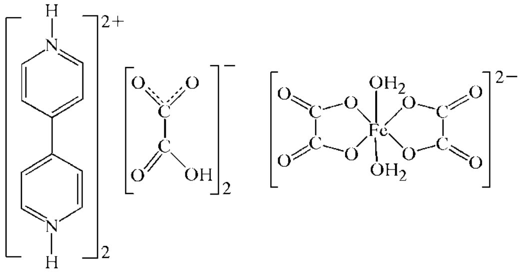
The title compound, $(C_{10}H_{10}N_2)_2[Fe(C_2O_4)_2(H_2O)_2]$-$(C_2HO_4)_2$, appears to be a modular associate consisting of a complex anion containing bivalent Fe as the central atom, a bridging hydrogen oxalate anion and a diprotonated 4,4-bipyridine acting as the counter-cation. The Fe^{II} ion in the complex anion occupies a position on a centre of inversion. Its coordination environment is formed by six O atoms from two bidentate oxalate ligands, forming a basal plane, and two water molecules approximately perpendicular to the plane, representing a distorted octahedral geometry. These three kinds of ions are connected by strong hydrogen bonds, with donor–acceptor distances (N$\cdots$O and O$\cdots$O) lying in the range 2.54–2.98 Å, and π–π stacking interactions between the 4,4′-bipyridinium cations, thus forming a three-dimensional supramolecular structure.

Comment

Crystal engineering has provided powerful tools for building a great variety of novel supramolecular structures and to date the construction of metal–organic supramolecular framework can be achieved *via* many kinds of interactions, such as coordinate covalent bonds, hydrogen bonds and π–π stacking interactions. 4,4′-Bipyridine (4,4′-bipy) and oxalic acid and its anions are attractive ligands for the construction of metal–organic frameworks due to their ambidentate coordinating ability (Hernández-Molina *et al.*, 2001). 4,4′-Bipy is commonly used as a rigid rod-like organic building block for pillared–layer structures, while oxalic acid (H_2ox) and its anions are also donors and acceptors for hydrogen bonds. Several transition metal complexes containing these two ligands have been reported for molecular-based magnetic materials. Layered structures are predominant among these crystals, as represented by the compounds [M(ox)(bipy)] (M = Fe^{II}, Co^{II}, Ni^{II}, Zn^{II}) (Lu *et al.*, 1999), $[Zn_3(ox)_3(4,4'\text{-bipy})_4]_7$ (Nordell *et al.*, 2003; Hao *et al.*, 2004), $[Fe_3(ox)_3(4,4'\text{-bipy})_4]$ and [Co(ox)-(4,4′-bipy)] (Zheng *et al.*, 1999), and $[Cu_3(\mu\text{-ox})_3(\mu\text{-}4,4'\text{-bipy})_2(4,4'\text{-bipy})_2]_n$ (Castillo *et al.*, 2003). Although the above-mentioned complex chemistry of oxalate and 4,4′-bipy is well documented, chemical information on supramolecular structures containing these two ligands acting as a combination of coordinating ligand and hydrogen-bond donors/acceptors is rare. We report here the supramolecular crystal structure of the title compound, (I), containing coordinating π–π stacking and hydrogen-bond interactions.



(I)

Compound (I) consists of a diprotonated bipyridine ion, acting as the counter-cation, and two different anions, $[Fe(ox)_2(H_2O)_2]^{2-}$ and Hox^-, both containing an oxalate unit. These three supramolecular building blocks are held together by an extensive hydrogen-bonding network and intermolecular π–π stacking interactions. A view of the supramolecular building blocks with the atom numbering is given in Fig. 1. Selected geometric parameters are listed in Table 1.

The Fe^{II} atom, lying on an inversion centre, is six-coordinated by four O atoms from the two bidentate oxalate anions,

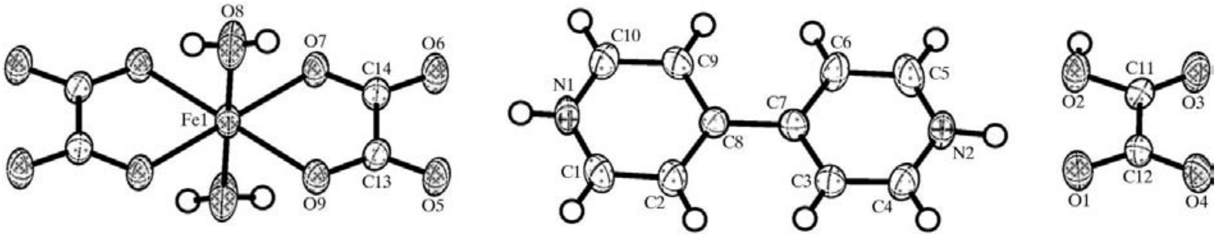


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by the symmetry operator ($-x$, $-y$, $-z$).

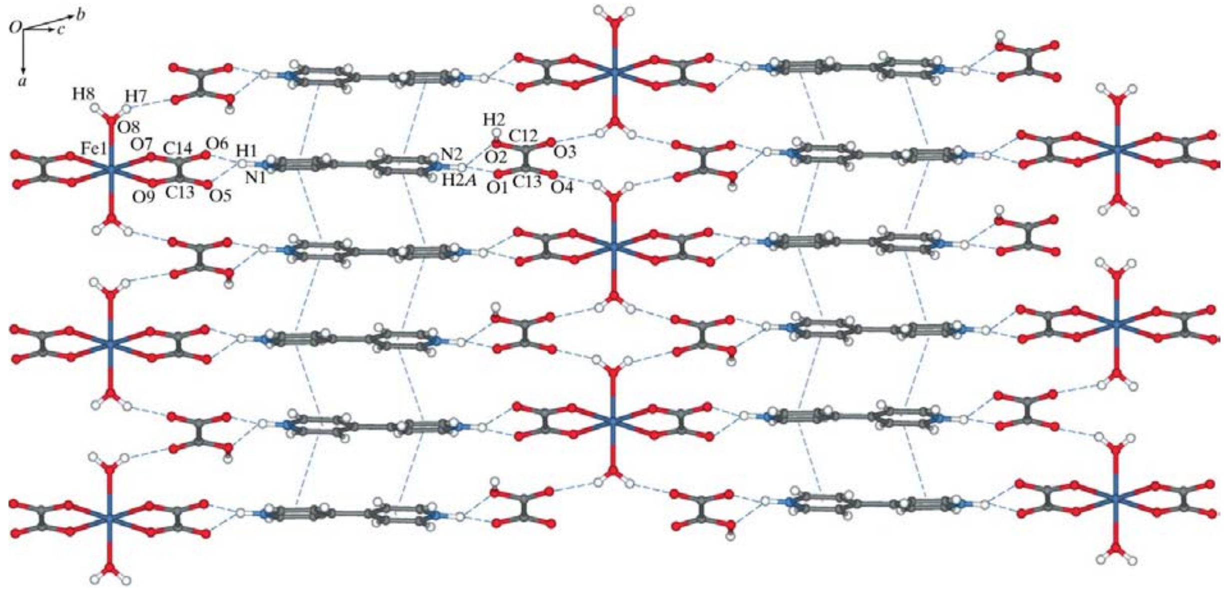


Figure 2
Part of the packing of the crystal structure of (I), viewed approximately along the *c* axis, showing the formation of two-dimensional planes. Thin dashed lines indicate hydrogen bonds and π–π stacking interactions.

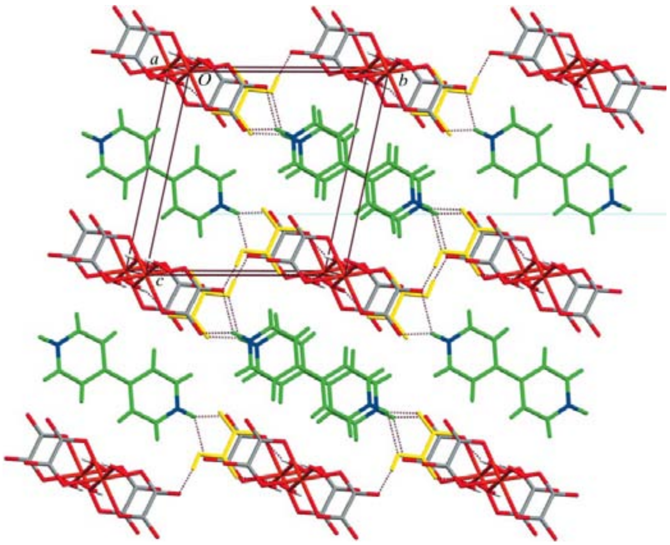


Figure 3
A partial packing diagram of the supramolecular structure of (I). Dotted lines indicate hydrogen bonds.

which form a basal plane, and two O atoms from the water molecules, approximately perpendicular to the plane, thus forming a slightly distorted octahedral coordination geometry. The Fe—O distances [2.097 (2)–2.134 (2) Å] in the Fe–oxalate plane are comparable with those in [$Fe_3(ox)_3(4,4'\text{-bipy})_4$] [2.102 (2) and 2.126 (2) Å; Zheng *et al.*, 1999] and [Fe(ox)(bipy)] [2.116 (4) Å; Lu *et al.*, 1999]. The C—O bond lengths in the coordinated oxalate (Fig. 1 and Table 1) are in the range 1.24–1.26 Å, between the values for a C═O double bond and a C—O single bond, and are typical of a delocalized carboxylate C···O bond (Allen *et al.*, 1987). They are a little shorter than those in the bimetallic bridged oxalate ligand in [$Fe_3(ox)_3(4,4'\text{-bipy})_4$] (1.25–1.27 Å; Zheng *et al.*, 1999).

The [$Fe(ox)_2(H_2O)_2$]$^{2-}$ anions are connected by the isolated hydrogen oxalate anions through hydrogen bonding between O atoms of the water molecules and O atoms of the hydrogen oxalate anions, forming an anionic chain. The diprotonated bipyridine cations link the anionic chains through two different bifurcated hydrogen bonds from N—H to O in the chelating oxalate anion or O in the isolated hydrogen oxalate anion. This results in a two-dimensional layer structure (Fig. 2). Neighbouring layers are linked together by hydrogen bonding from the isolated hydrogen oxalate anion in one layer to the chelating oxalate anion in an adjacent layer, building a three-dimensional supramolecular crystal structure (Fig. 3).

In the crystal structure of (I), the distance between the aromatic rings of the 4,4′-bipyridinium cations is 3.547 Å, which indicates that stronger π–π stacking interactions exist between these aromatic rings (Janiak, 2000), making the supramolecular crystal structure more stable.

Experimental

The title compound was prepared by the hydrothermal reaction of $FeSO_4\cdot 2H_2O$ (139 mg, 0.376 mmol), 4,4′-bipyridine (78 mg, 0.5 mmol), oxalic acid (90 mg, 1 mmol) and methanol (1 ml) at 383 K for 3 d in a sealed thick-walled Pyrex tube. Brown prism-shaped crystals of (I) were obtained in 40–50% yield.

Crystal data

$(C_{10}H_{10}N_2)_2[Fe(C_2O_4)_2(H_2O)_2]$-$(C_2HO_4)_2$
$M_r = 762.38$
Triclinic, $P\overline{1}$
$a = 7.0927\ (14)$ Å
$b = 10.092\ (2)$ Å
$c = 10.633\ (2)$ Å
$\alpha = 101.76\ (3)^\circ$
$\beta = 96.29\ (3)^\circ$
$\gamma = 98.09\ (3)^\circ$
$V = 730.2\ (3)$ Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.62$ mm^{-1}
$T = 293\ (2)$ K
0.16 × 0.08 × 0.08 mm

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Data collection

Bruker *P*4 diffractometer
3600 measured reflections
2474 independent reflections
1934 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.123$
$S = 1.08$
2474 reflections
244 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.37$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—O7	2.097 (2)	O5—C13	1.251 (4)
Fe1—O9	2.134 (2)	O6—C14	1.242 (4)
Fe1—O8	2.143 (3)	O7—C14	1.261 (4)
O1—C12	1.257 (4)	O9—C13	1.255 (4)
O2—C11	1.303 (4)	C11—C12	1.542 (5)
O3—C11	1.211 (4)	C13—C14	1.546 (5)
O4—C12	1.239 (4)		
O7—Fe1—O9	78.53 (9)	O4—C12—C11	116.6 (3)
O7—Fe1—O8	90.03 (12)	O1—C12—C11	117.3 (3)
O9—Fe1—O8	91.08 (12)	O5—C13—O9	126.2 (3)
C14—O7—Fe1	114.4 (2)	O5—C13—C14	117.1 (3)
C13—O9—Fe1	113.5 (2)	O9—C13—C14	116.7 (3)
O3—C11—O2	124.6 (4)	O6—C14—O7	125.0 (3)
O3—C11—C12	122.1 (3)	O6—C14—C13	118.2 (3)
O2—C11—C12	113.3 (3)	O7—C14—C13	116.8 (3)
O4—C12—O1	126.1 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O5$^{\rm i}$	0.83 (4)	1.72 (2)	2.548 (4)	175 (5)
O8—H7···O3$^{\rm ii}$	0.83 (4)	2.09 (3)	2.818 (4)	148 (5)
O8—H8···O4$^{\rm iii}$	0.83 (4)	1.95 (3)	2.705 (4)	149 (5)
N1—H1···O6	0.86	1.85	2.625 (4)	150
N1—H1···O5	0.86	2.32	2.952 (4)	130
N2—H2*A*···O1	0.86	1.80	2.601 (4)	153
N2—H2*A*···O2	0.86	2.36	2.979 (4)	129

Symmetry codes: (i) $x, 1+y, z$; (ii) $x, y-2, z-1$; (iii) $1-x, 2-y, 1-z$.

Hydroxyl and water H atoms were located in a difference Fourier map and their positions were refined with geometric restraints of O—H = 0.82 (2) Å and H···H = 1.30 (2) Å for the water H atoms. All other H atoms were placed in calculated positions and treated as riding, with C—H = 0.93 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$, and N—H = 0.86 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm N})$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3025). Services for accessing these data are described at the back of the journal.

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