

## Poly[*diaqua*( $\mu$ -4,4'-bipyridine)tetrakis-( $\mu$ -ferrocenecarboxylato)bis(ferrocenecarboxylato)trimanganese(II)]

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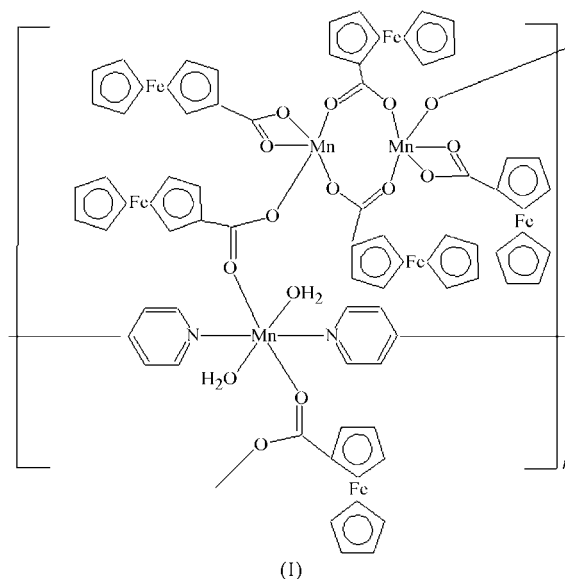
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The title compound,  $[\text{Mn}_3\text{Fe}_6(\text{C}_5\text{H}_5)_6(\text{C}_6\text{H}_4\text{O}_2)_6(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]_n$ , consists of two crystallographically unique  $\text{Mn}^{\text{II}}$  centers. One is situated on an inversion center and is octahedrally coordinated by two N atoms from two bridging 4,4'-bipyridine (4,4'-bipy) ligands and four O atoms, two from different bridging ferrocenecarboxylate ( $\mu_2$ -FcCOO<sup>-</sup>; Fc is ferrocene) units and two from aqua ligands. The two halves of each 4,4'-bipy ligand are related by a center of symmetry. The second  $\text{Mn}^{\text{II}}$  center is in a strongly distorted tetragonal-pyramidal geometry, coordinated by five O atoms, three from three  $\mu_2$ -FcCOO<sup>-</sup> units and two from a fourth, chelating,  $\eta^2$ -FcCOO<sup>-</sup> unit. The FcCOO<sup>-</sup> units function as bridging ligands to adjacent  $\text{Mn}^{\text{II}}$  centers, leading to the formation of linear  $\cdots\text{Mn1Mn2Mn2Mn1}\cdots$  chains. Adjacent chains are further bridged by 4,4'-bipy ligands, resulting in a two-dimensional layered polymer.

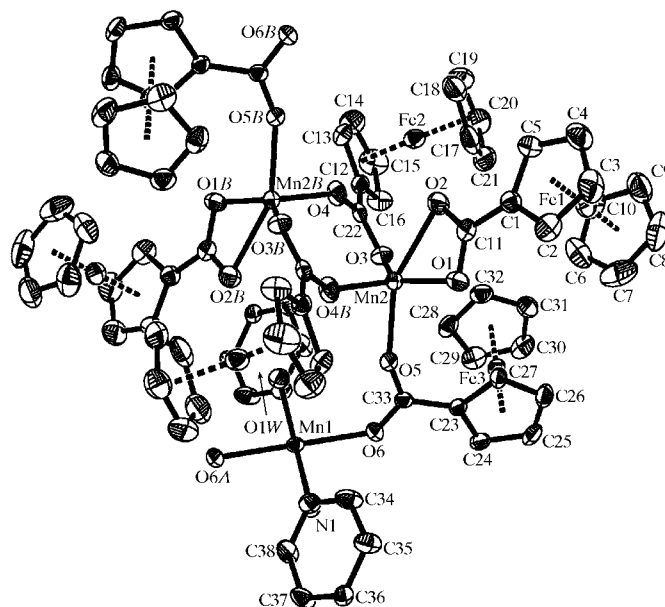
### Comment

The supramolecular assembly and crystal engineering of metal-organic coordination frameworks have recently attracted great interest, owing to their intriguing structural topologies and potential applications as functional materials (Batten & Robson, 1998; Eddaoudi *et al.*, 2001). The construction of metal-organic coordination frameworks of mixed ligands with different metals continues to be an area of special interest in crystal engineering. The ferrocenecarboxylate (FcCOO<sup>-</sup>) ligand, like most carboxylate units, has been found to be versatile when generating complexes with various labile metal units. It can act not only as a bridging ligand, giving rise to one-dimensional polymers, but also as a simple ligand when combined with other bridging bipyridyl ligands (Hou *et al.*, 2003; Li *et al.*, 2003). As such, the coordination modes can be tailored by introducing different neutral ligands into the complexes. Recent examples have afforded a two-dimensional coordination polymer containing a mixture of carboxylate and bipyridyl (bipy) ligands,  $\{[\text{Mn}(\text{maleate})(\mu\text{-}4,4'\text{-bipy})]\cdot 0.5\text{H}_2\text{O}\}_n$  (Zhan *et al.*, 2000), and

one with a mixture of phosphate and bipyridine ligands,  $\{[\text{Mn}[\text{O}_2\text{PH}(\text{C}_6\text{H}_5)]_2(\mu\text{-}4,4'\text{-bipy})]_n$  (Liao *et al.*, 2001). We report here the crystal structure of the title two-dimensional polymeric compound,  $[\text{Mn}_3(\text{FcCOO})_6(4,4'\text{-bipy})(\text{H}_2\text{O})_2]_n$ , (I).



The structural unit of (I) is shown in Fig. 1. There are two types of  $\text{Mn}^{\text{II}}$  center. Atom Mn1 is situated on an inversion center with six-coordinated geometry, in which two O atoms from two  $\mu_2$ -FcCOO<sup>-</sup> units and two coordinated water molecules complete the equatorial plane, and two N atoms from two bridging 4,4'-bipy ligands occupy the axial positions (Table 1). Atoms Mn1, O6, O6A, O1W and O1WA [symmetry code: (A)  $-x + 2, -y + 1, -z + 2$ ] are coplanar and the bond

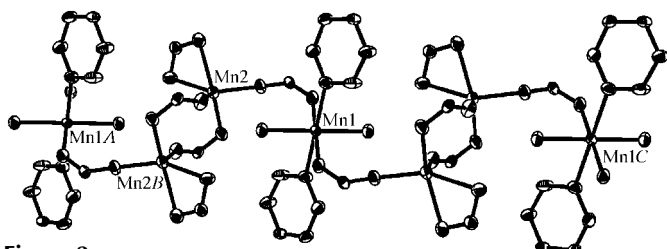

**Figure 1**

The structure unit of (I), showing the atom-numbering scheme and displacement ellipsoids at the 35% probability level. H atoms have been omitted for clarity. [Symmetry codes: (A)  $-x + 2, -y + 1, -z + 2$ ; (B)  $-x + 1, -y + 1, -z + 2$ ]. Only half of the 4,4'-bipy ligand is shown; the other half is generated by the action of symmetry operation  $(-x + 2, -y + 2, -z + 2)$ .

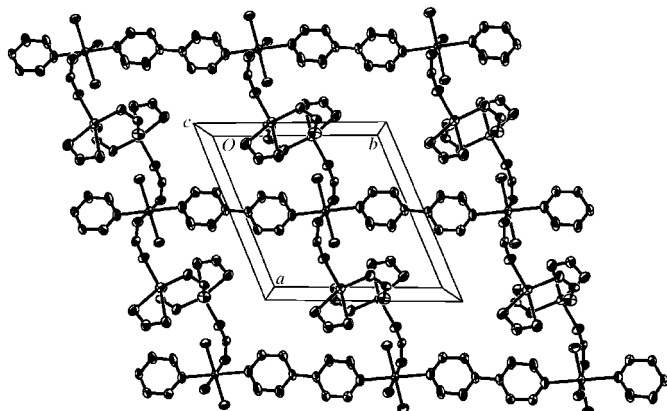
angles around each Mn1 center are in the range 83.84 (12)–96.16 (12)° (Table 1), giving rise to a slightly distorted octahedral coordination environment. Each Mn2 center coordinates to five O atoms, two from one  $\eta^2$ -FcCOO<sup>−</sup> unit and three from three  $\mu_2$ -FcCOO<sup>−</sup> units (Table 1). Atoms Mn2, O1, O2, O3 and O5 are nearly coplanar (the mean deviation from the plane is 0.2215 Å). The five coordinating O atoms around the Mn2 center exhibit strongly distorted tetragonal–pyramidal geometry, mainly because of the presence of a chelating unit.

The FcCOO<sup>−</sup> ligands function as bridging linkers to adjacent Mn<sup>II</sup> centers, leading to the formation of linear  $\cdots$ Mn1Mn2Mn2Mn1 $\cdots$  chains (Fig. 2). The Mn1 $\cdots$ Mn1*B* [symmetry code: (*B*)  $-x + 1, -y + 1, -z + 2$ ] and Mn2 $\cdots$ Mn2*C* [symmetry code: (*C*)  $-x + 1, -y + 1, -z + 2$ ] distances are 10.9891 (11) and 3.7731 (12) Å, respectively. The Mn1 centers of adjacent chains are further connected by centrosymmetric 4,4′-bipy ligands, leading to a layered structure (Fig. 3); the nearest Mn1 $\cdots$ Mn1( $-x + 2, -y + 2, -z + 2$ ) inter-chain separation is 11.4986 (11) Å. It is noteworthy that there are three types of FcCOO<sup>−</sup> unit; one is a chelating bidentate ligand ( $\eta^2$ -FcCOO<sup>−</sup>), and the other two are bridging bidentate  $\mu_2$ -FcCOO<sup>−</sup> ligands, of which one connects two Mn2 centers and the other bridges Mn1 and Mn2 centers (Fig. 1).

Analysis of the crystal packing of (I) reveals that there are two classical intramolecular O–H $\cdots$ O hydrogen-bonding interactions involving the aqua ligands and carboxylate groups (Table 2).



**Figure 2**  
The one-dimensional polymeric chain running parallel to the *a* axis. Fc units and H atoms have been omitted for clarity. [Symmetry codes: (*A,B*)  $-x + 1, -y + 1, -z + 2$ ; (*C*)  $x + 1, y, z$ .]



**Figure 3**  
The crystal structure of the title compound, viewed along the *c* axis. Ferrocene groups and H atoms have been omitted for clarity.

## Experimental

A mixture of sodium ferrocenecarboxylate (0.1 mmol), 4,4′-bipyridine (0.1 mmol), MnSO<sub>4</sub>·H<sub>2</sub>O (0.1 mmol), ethane-1,2-diol (1.40 ml) and water (0.70 ml) were placed in a thick Pyrex tube. The tube was sealed and heated at 353 K for 18 h to give red block-shaped crystals. Analysis found: C 52.78, H 3.92, N 1.96%; calculated for C<sub>76</sub>H<sub>66</sub>Fe<sub>6</sub>Mn<sub>3</sub>N<sub>2</sub>O<sub>14</sub>: C 52.73, H 3.84, N 1.62%.

### Crystal data

[Mn <sub>3</sub> Fe <sub>6</sub> (C <sub>5</sub> H <sub>5</sub> ) <sub>6</sub> (C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> ) <sub>6</sub> · (C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> ]	$\gamma = 66.000$ (2)°
$M_r = 1731.23$	$V = 1699.9$ (3) Å <sup>3</sup>
Triclinic, $P\bar{1}$	$Z = 1$
$a = 10.9891$ (11) Å	$D_x = 1.691$ Mg m <sup>−3</sup>
$b = 11.4986$ (11) Å	Mo $K\alpha$ radiation
$c = 14.8928$ (15) Å	$\mu = 1.85$ mm <sup>−1</sup>
$\alpha = 82.308$ (2)°	$T = 293$ (2) K
$\beta = 83.418$ (2)°	Block, red
	$0.40 \times 0.30 \times 0.21$ mm

### Data collection

Bruker SMART CCD 1K area- detector diffractometer	9365 measured reflections
$\varphi$ and $\omega$ scans	5972 independent reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 1996)	4258 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.525, T_{\max} = 0.698$	$R_{\text{int}} = 0.027$
	$\theta_{\max} = 25.0^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.8034P]$
$wR(F^2) = 0.102$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{\max} = 0.001$
5972 reflections	$\Delta\rho_{\max} = 0.71$ e Å <sup>−3</sup>
465 parameters	$\Delta\rho_{\min} = -0.44$ e Å <sup>−3</sup>
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Selected geometric parameters (Å, °).

Mn1–O6	2.167 (3)	Mn2–O5	2.073 (3)
Mn1–O1 <i>W</i>	2.192 (3)	Mn2–O3	2.123 (3)
Mn1–N1	2.252 (3)	Mn2–O1	2.174 (3)
Mn2–O4 <sup>i</sup>	2.055 (3)	Mn2–O2	2.273 (3)
O6–Mn1–O1 <i>W</i>	96.16 (12)	O5–Mn2–O3	96.43 (11)
O6 <sup>ii</sup> –Mn1–O1 <i>W</i>	83.84 (12)	O4 <sup>i</sup> –Mn2–O1	101.24 (12)
O6–Mn1–N1	88.43 (12)	O5–Mn2–O1	100.32 (11)
O6 <sup>ii</sup> –Mn1–N1	91.57 (12)	O3–Mn2–O1	139.01 (12)
O1 <i>W</i> –Mn1–N1	92.86 (13)	O4 <sup>i</sup> –Mn2–O2	110.57 (12)
O1 <i>W</i> <sup>ii</sup> –Mn1–N1	87.14 (13)	O5–Mn2–O2	153.78 (11)
O4 <sup>i</sup> –Mn2–O5	87.53 (11)	O3–Mn2–O2	92.14 (11)
O4 <sup>i</sup> –Mn2–O3	116.69 (12)	O1–Mn2–O2	58.64 (10)

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

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> –H $\cdots$ <i>A</i>	<i>D</i> –H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> –H $\cdots$ <i>A</i>
O1 <i>W</i> –H1 <i>WA</i> $\cdots$ O2 <sup>i</sup>	0.76 (3)	2.14 (3)	2.884 (5)	164 (6)
O1 <i>W</i> –H1 <i>WB</i> $\cdots$ O4 <sup>i</sup>	0.76 (3)	2.26 (4)	2.878 (4)	139 (6)

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

The H atoms of CH groups were positioned geometrically and allowed to ride on their parent atoms [ $C$ –H = 0.98 (Fc) and 0.93 Å (4,4′-bipy), with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ]. The H atoms of water mol-

ecules were located in a difference Fourier map and refined with restraints on the O–H bond lengths [O–H = 0.82 (5) Å].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; 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*.

X-ray data were collected at the Chinese University of Hong Kong.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3022). Services for accessing these data are described at the back of the journal.

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