

# Poly[[[aquamanganese(II)]- $\mu_2$ -4,4'-bipyridine- $\mu_3$ -succinato] 4,4'-bipyridine hemisolvate]

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Received 14 April 2004

Accepted 23 April 2004

Online 31 May 2004

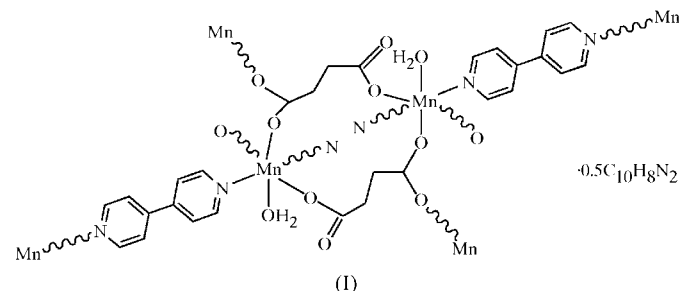
The polymeric title complex,  $\{[\text{Mn}(\text{C}_4\text{H}_4\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})] \cdot 0.5\text{C}_{10}\text{H}_8\text{N}_2\}_n$ , possesses a three-dimensional open-framework structure, with the solvate 4,4'-bipyridine (bipy) molecules, which lie around centers of inversion, clathrated in the channels of the framework. The  $\text{Mn}^{\text{II}}$  center is surrounded by three succinate (succ) ligands, one water molecule and two bipy ligands, and displays a slightly distorted octahedral coordination environment, with *cis* angles ranging from 84.14 (12) to 96.56 (11)°. Each succ dianion coordinates to three  $\text{Mn}^{\text{II}}$  atoms, thus acting as a bridging tridentate ligand; in turn, the  $\text{Mn}^{\text{II}}$  atoms are bridged by three succ ligands, thus forming a two-dimensional Mn–succ sheet pillared by the bridging bipy ligands. Two hydrogen-bonding interactions, involving the water molecules and the carboxy O atoms of the succ ligands, are present in the crystal structure.

## Comment

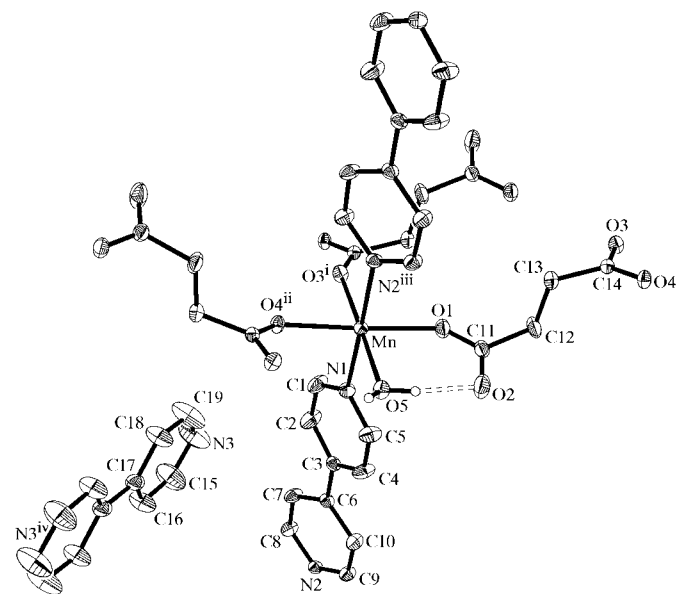
The crystal engineering of extended coordination polymers based on a metal node and an organic spacer has been investigated actively owing to the great variety of intriguing structural topologies that these compounds exhibit (Zaworotko, 1994) and their potential as functional materials in such fields as separation technology (Biradha & Fujita, 2002), catalysis (Fujita *et al.*, 1994) and molecular magnetism (Miller and Epstein, 1994). One strategy that is commonly used to construct such extended frameworks is to select appropriate organic bridging ligands with versatile bonding modes capable of binding more than one metal ion. In this respect, rigid aromatic dicarboxylates, such as phthalate isomers, often in combination with other auxiliary ligands, such as 4,4'-bipyridine (bipy), have been used extensively in the design of such species because of the rigidity and versatile bonding modes of this type of ligand (Lo *et al.*, 2000; Bourne *et al.*, 2001; Suresh *et al.*, 2001; Ma, Chen, Liu, Liao *et al.*, 2003).

We and other workers have explored the ability of structurally unsaturated aliphatic  $\alpha,\omega$ -dicarboxylates, such as

maleate and fumarate, to build extended structural frameworks (Shi *et al.*, 2000; Ma, Chen, Liu, Chen *et al.*, 2003). For comparison, we have also investigated the reaction of the structurally saturated counterpart, *i.e.* succinate (succ), with  $\text{Mn}^{2+}$  salts under hydrothermal conditions, and we obtained the title compound, (I). Complex (I) represents a rare example of a three-dimensional metal–organic open framework with large channels encapsulating organic molecules, based on the combination of a rigid linear ligand and a structurally flexible saturated aliphatic  $\alpha,\omega$ -dicarboxylate ligand. In this paper, we report the single-crystal structure of (I).



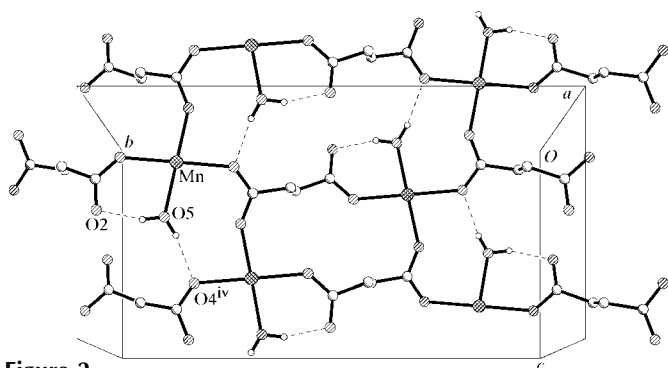
The title compound contains neutral  $[\text{Mn}(\text{succ})(\text{bipy})(\text{H}_2\text{O})]_n$  polymers and bipy solvent molecules in a molar ratio of 2:1. As shown in Fig. 1, the  $\text{Mn}^{\text{II}}$  center is six-coordinated by three carboxylate O atoms of three succ ligands, one water O atom and two pyridyl N atoms of bipy ligands, and displays slightly distorted  $\text{MnO}_4\text{N}_2$  octahedral coordination geometry (Table 1), with the three *trans* angles [176.79 (12), 177.14 (12) and 178.14 (13)°] deviating slightly from the ideal value of 180°. The  $\text{Mn}-\text{O}_{\text{carboxy}}$  distances [2.145 (3)–2.195 (3) Å] are comparable to those found in other Mn–succ complexes (McCann *et al.*, 1997; Fleck *et al.*, 2000; Zheng *et al.*, 2002; Xiang *et al.*, 1998; Kim *et al.*, 2001; Liu *et al.*, 2001), and the



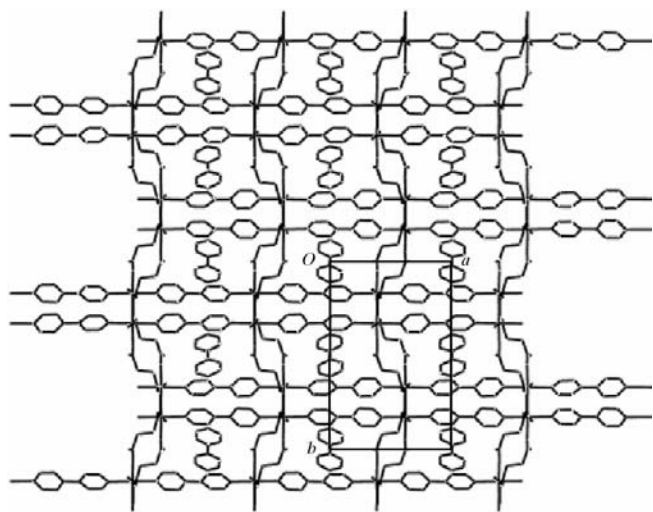
**Figure 1**  
A view of (I), showing the atom-labeling scheme and the completed  $\text{Mn}^{2+}$  coordination sphere. Displacement ellipsoids are drawn at the 30% probability level. The symmetry codes are as in Table 1, with the addition of (iv)  $2 - x, 1 - y, 1 - z$ .

slightly longer Mn–N distances [2.305 (3) and 2.295 (3) Å] and Mn–O<sub>water</sub> distance [2.173 (3) Å] are similar to those found for a reported fumarate–manganese(II) complex (Shi *et al.*, 2000).

As shown in Fig. 2, each succ dianion acts as a tridentate bridging ligand, joining three Mn atoms through one bidentate bridging carboxylate group and one monodentate carboxylate group. Every two Mn atoms, at a distance of 5.274 (2) Å, are bridged by the bidentate carboxylate group of one succ ligand to form an [Mn( $\mu$ -OCO)(H<sub>2</sub>O)]<sub>n</sub> zigzag chain, and the neighboring chains are crosslinked *via* the other, monodentate, end of the same succ ligand, forming [Mn(succ)-(H<sub>2</sub>O)]<sub>n</sub> corrugated sheets, the *syn* Mn···Mn and *anti* Mn···Mn separations *via* the same succ ligand being 7.392 (2) and 9.435 (2) Å, respectively. Two intra-sheet hydrogen bonds are observed in the crystal structure, as listed in Table 2. The coordinated water molecule donates one of its H atoms to uncoordinated carboxyl atom O2 to form an O5–H5C···O2 hydrogen bond; the second water H atom is donated to form another hydrogen bond with coordinated carboxyl atom O4 [O5–H5B···O4(–x + 1, –y + 2, –z + 1)].



**Figure 2**  
Part of the two-dimensional succinate–Mn<sup>II</sup> layered network, showing the two hydrogen-bond interactions. Non-water H atoms have been omitted for clarity. The symmetry code is as in Table 2.



**Figure 3**  
A partial packing diagram of (I), showing the open framework exhibiting two kind of channels, with the uncoordinated 4,4'-bipyridine (bipy) molecules clathrated within.

Finally, the bipy ligands link neighboring [Mn(succ)(H<sub>2</sub>O)]<sub>n</sub> sheets into an infinite three-dimensional framework, exhibiting two kinds of channels parallel to the *c* direction, with the uncoordinated bipy molecules encapsulated in these channels, as shown in Fig. 3. The Mn···Mn distance through the bipy bridging ligand is 11.707 (2) Å. The two pyridine rings of the uncoordinated bipy molecule are coplanar and strictly parallel as a result of the middle of the C17–C17(*x* – 1, 1 – *y*, 1 – *z*) single bond lying on the inversion center, whereas the pyridine rings of the coordinated bipy ligand are slightly twisted, as indicated by the small dihedral angle [9.1 (9)°] between them.

## Experimental

The pH value of an aqueous mixture (10 ml) of Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.29 g, 1 mmol), succinic acid (0.12 g, 1 mmol) and 4,4'-bipyridine (0.24 g, 1.5 mmol) was pre-adjusted to about 7 with a 0.1 M NaOH aqueous solution, and the mixture was transferred into a sealed Teflon-lined stainless-steel vessel (20 ml). The vessel was heated at 323 K for 4 d and then cooled to room temperature, yielding pale-yellow crystals of (I). Analysis calculated for C<sub>19</sub>H<sub>18</sub>MnN<sub>3</sub>O<sub>5</sub>: C 53.91, H 4.29, N 9.93%; found C 53.87, H 4.32, N 9.89%. FT-IR (KBr, cm<sup>-1</sup>): 3317 (*br, s*), 1603 (*s*), 1535 (*vs*), 1487 (*m*), 1452 (*m*), 1410 (*vs*), 1387 (*vs*), 1319 (*m*), 1237 (*w*), 1215 (*m*), 1153 (*m*), 1086 (*w*), 1061 (*m*), 1043 (*w*), 1005 (*w*), 989 (*w*), 872 (*w*), 814(*s*), 802 (*s*), 731 (*m*), 652 (*s*), 627 (*s*), 607 (*m*), 498 (*w*), 472 (*w*).

### Crystal data

[Mn(C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)]·0.5C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>  
*M<sub>r</sub>* = 423.30  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 11.7070 (11) Å  
*b* = 17.8824 (16) Å  
*c* = 8.8647 (8) Å  
 $\beta$  = 99.713 (2)°  
*V* = 1829.2 (3) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.537 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 2349 reflections  
 $\theta$  = 1.8–25.1°  
 $\mu$  = 0.76 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism, pale yellow  
 0.30 × 0.24 × 0.10 mm

### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.804, *T<sub>max</sub>* = 0.927  
 5491 measured reflections

3178 independent reflections  
 2302 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.033  
 $\theta_{\max}$  = 25.1°  
*h* = –8 → 13  
*k* = –19 → 21  
*l* = –10 → 6

**Table 1**

Selected geometric parameters (Å, °).

Mn–O3 <sup>i</sup>	2.145 (3)	Mn–N2 <sup>iii</sup>	2.295 (3)
Mn–O1	2.165 (3)	Mn–N1	2.305 (3)
Mn–O5	2.173 (3)	C12–C13	1.512 (6)
Mn–O4 <sup>ii</sup>	2.195 (3)		
O3 <sup>i</sup> –Mn–O1	96.56 (11)	O5–Mn–N2 <sup>iii</sup>	92.89 (12)
O3 <sup>i</sup> –Mn–O5	177.14 (12)	O4 <sup>ii</sup> –Mn–N2 <sup>iii</sup>	87.61 (12)
O1–Mn–O5	84.14 (12)	O3 <sup>i</sup> –Mn–N1	88.28 (12)
O3 <sup>i</sup> –Mn–O4 <sup>ii</sup>	82.93 (11)	O1–Mn–N1	91.36 (13)
O1–Mn–O4 <sup>ii</sup>	176.79 (12)	O5–Mn–N1	88.93 (13)
O5–Mn–O4 <sup>ii</sup>	96.53 (11)	O4 <sup>ii</sup> –Mn–N1	91.79 (12)
O3 <sup>i</sup> –Mn–N2 <sup>iii</sup>	89.90 (12)	N2 <sup>iii</sup> –Mn–N1	178.14 (13)
O1–Mn–N2 <sup>iii</sup>	89.22 (13)		

Symmetry codes: (i) 1 – *x*, 2 – *y*, –*z*; (ii) 1 – *x*, *y* –  $\frac{1}{2}$ ,  $\frac{1}{2}$  – *z*; (iii) *x* – 1, *y*, *z*.

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.138$   
 $S = 1.09$   
 3178 reflections  
 261 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 3.436P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O5-H5B \cdots O4^{iv}$	0.84 (4)	1.98 (2)	2.807 (4)	169 (4)
$O5-H5C \cdots O2$	0.85 (2)	1.78 (3)	2.602 (5)	161 (7)

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

The water H atoms were located from difference maps and refined with a DFIX restraint of 0.85 (2)  $\text{\AA}$  applied to the two O—H distances. Other H atoms were placed in calculated positions and treated as riding atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1994); data reduction: *SHELXTL* (Siemens, 1994) and *SAINTE*; program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by the NNSFC (grant Nos. 30170229 and 29973047), the State Key Basic Research and Development Plan of China (grant No. G1998010100), and the Expert Project of Key Basic Research of the Ministry of Science and Technology, People's Republic of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1183). Services for accessing these data are described at the back of the journal.

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