

Poly[[[aqua(2,2'-bipyridine- κ^2N,N')-manganese(II)]- μ_3 -acetylenedicarboxylato- $\kappa^3O:O':O''$] monohydrate]

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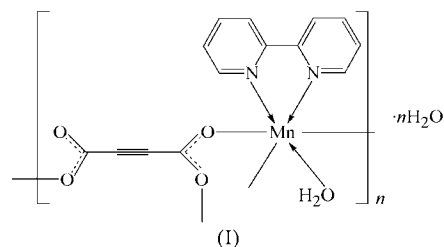
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In the title complex, $\{[\text{Mn}(\text{C}_4\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$, each Mn^{II} ion has a distorted octahedral coordination formed by two N atoms of a 2,2'-bipyridine ligand, three carboxyl O atoms of three different acetylenedicarboxylate ligands and one coordinated water molecule. The acetylenedicarboxylate ligands act in a tridentate mode connecting adjacent Mn^{II} ions and constructing a two-dimensional structure which can be regarded as an unusual plywood-like stacked network.

Comment

As one of the great challenges encountered in crystal engineering of functional materials, the structural diversity of coordination polymers formed by similar metal-organic building blocks is of intense interest, both as a result of its scientific significance and its intrinsic aesthetic appeal (Carlucci *et al.*, 2003). The deliberate design and control of self-assembly by the selection of ligands and transition metals has become extremely important to chemists (Bu *et al.*, 2001; Reger *et al.*, 2001). A number of metal-organic polymers with one-, two- and three-dimensional infinite frameworks have been generated, in which aliphatic carboxylic acids, such as maleic acid (Zheng & Xie, 2005), malonic acid (Zhang & Lu, 2004) or related species, have often been chosen to fabricate the complexes. Recently, our group has been interested in the solid-state coordination chemistry of acetylenedicarboxylic acid. As an aliphatic carboxylic acid, it can also be considered as a good candidate with specific properties for the construction of coordination polymers. However, the reaction of acetylenedicarboxylic acid with transition metal ions remains relatively unexplored (Sieroń & Bukowska-Strzyżewska, 1998; Stein & Ruschewitz, 2005). In these complexes, the acetylenedicarboxylic acid ligand (H_2ace) displays diverse coordination modes, such as bis-monodentate (Billetter *et al.*, 2003; Wang *et al.*, 2006), chelating bis-bidentate (Ruschewitz & Pantenburg, 2002) and bridging bis-bidentate (Pantenburg &

Ruschewitz, 2002; Hohn *et al.*, 2002). In order to explore the behaviour of this ligand further, the novel title manganese complex, $\{[\text{Mn}(\text{ace})(2,2'\text{-bipy})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (2,2'-bipy is 2,2'-bipyridine), (I), has been synthesized and we present its structure here.



Complex (I) crystallizes in the non-centrosymmetric space group $Fdd2$. The asymmetric unit consists of one Mn^{II} ion, one 2,2'-bipy ligand, one ace ligand, one coordinated water molecule and one free water molecule (Fig. 1). Each Mn^{II} ion displays a slightly distorted octahedral geometry, defined by three carboxylate O atoms of three different ace ligands [$\text{Mn1}-\text{O1} = 2.2581(12)$ Å, $\text{Mn}-\text{O2}^{\text{i}} = 2.1454(11)$ Å and $\text{Mn}-\text{O3}^{\text{ii}} = 2.1648(11)$ Å; symmetry codes: (i) $-x-1, -y-\frac{1}{2}, z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, y, z+\frac{1}{2}$], the two N atoms of the 2,2'-bipy ligand and one water molecule. The C—O bond distances are similar [$\text{C11}-\text{O1} = 1.2360(18)$ Å, $\text{C11}-\text{O2} = 1.2615(18)$ Å, $\text{C14}-\text{O3} = 1.260(2)$ Å and $\text{C14}-\text{O4} = 1.229(2)$ Å], suggesting delocalization of electrons throughout. The equatorial plane is defined by atoms $\text{O1W}/\text{O2}^{\text{i}}/\text{N2}/\text{N1}$ [r.m.s. deviation = $0.02(2)$ Å; deviation of atom $\text{Mn}^{\text{II}} = 0.19(1)$ Å]. Atoms O1 and O3^{ii} occupy the apical sites, with an angle of $165.12(5)^\circ$. There are two long Csp^2-Csp bonds ($\text{C11}-\text{C12}$ and $\text{C13}-\text{C14}$), a result of the $\text{C12}\equiv\text{C13}$ triple bond and the double bonds of the carboxylate groups.

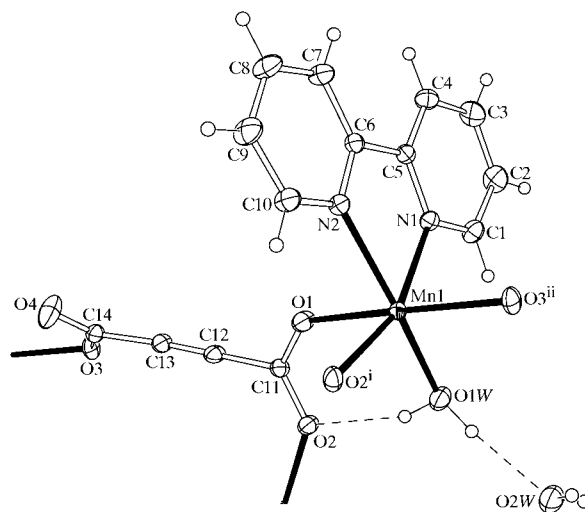


Figure 1

The asymmetric unit of (I), showing 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $-x-1, -y-\frac{1}{2}, z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, y, z+\frac{1}{2}$]

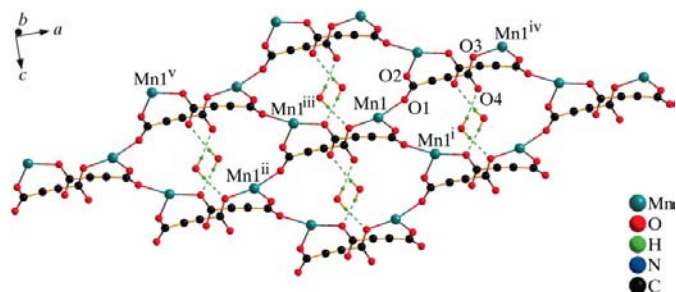


Figure 2

The two-dimensional structure of the title complex. Coordinated water and 2,2'-bipy molecules have been omitted. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $-x - 1, -y - \frac{1}{2}, z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, y, z + \frac{1}{2}$; (iii) $-x - \frac{3}{2}, -y - \frac{1}{2}, z$; (iv) $x + \frac{1}{2}, y, z - \frac{1}{2}$; (v) $-x - 2, -y - \frac{1}{2}, z - \frac{1}{2}$]

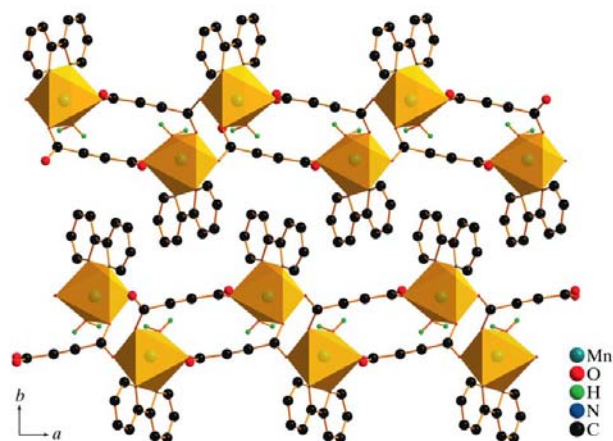


Figure 3

The packing of (I), projected along the *c* axis, showing the π - π stacking interactions.

The unusual feature of (I) is that the ace groups act as tridentate bridging ligands to connect the Mn^{II} ions into a two-dimensional layer structure. The two carboxyl units of the ace ligand adopt two different coordination modes, one monodentate and another bidentate. Firstly, the ace ligands connect the Mn^{II} ions into one-dimensional chains, which span two directions to give rise to a plywood-like stacking mode. The angle between adjacent chains in the two different directions is 42° . Secondly, the non-coplanar chains are bridged by the bidentate carboxylate groups into a two-dimensional structure along (010). Free water molecules occupy the hollow regions and form hydrogen bonds with carboxylate O atoms [$O2W-H2W1 \cdots O4^{iii} = 3.145(2) \text{ \AA}$ and $O2W-H2W2 \cdots O3^i = 2.9054(19) \text{ \AA}$; symmetry code: (iii) $-x - 1, -y - \frac{1}{2}, z - \frac{1}{2}$] (Fig. 2). Adjacent layers are stacked in an offset manner through π - π stacking interactions between one of the rings of the 2,2'-bipy ligand (C6-C10/N2) and a symmetry-related ring at $(\frac{1}{4} + x, -\frac{3}{4} - y, \frac{1}{4} + z)$, with a centroid-to-centroid distance of 3.692 \AA , thus forming a three-dimensional supramolecular network (Fig. 3).

Experimental

The title complex was prepared by the addition of stoichiometric amounts of $MnCl_2 \cdot 6H_2O$ (0.234 g, 1 mmol) and 2,2'-bipy (0.156 g, 1 mmol) to an ethanol-water (1:1 v/v) solution of acetylenedicarboxylic acid (0.144 g, 1 mmol). The pH of the mixture was adjusted to 7 with 1.0 M NaOH solution. After stirring for 30 min, the mixture was filtered. The filtrate was allowed to stand for several days to give yellow crystals of (I). Analysis calculated for $C_{14}H_{12}MnN_2O_6$: C 46.81, H 3.37, N 7.80%; found: C 46.75, H 3.34, N 7.76%.

Crystal data

$[Mn(C_4O_4)(C_{10}H_8N_2)(H_2O)] \cdot H_2O$
 $M_r = 359.20$
 Orthorhombic, *Fdd2*
 $a = 18.769(4) \text{ \AA}$
 $b = 42.406(9) \text{ \AA}$
 $c = 7.2170(14) \text{ \AA}$
 $V = 5744(2) \text{ \AA}^3$

$Z = 16$
 $D_x = 1.661 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.95 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Block, yellow
 $0.30 \times 0.20 \times 0.15 \text{ mm}$

Data collection

Rigaku R-Axis RAPID area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{min} = 0.763, T_{max} = 0.870$

13905 measured reflections
 3284 independent reflections
 3135 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.023$
 $\theta_{max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.019$
 $wR(F^2) = 0.049$
 $S = 1.05$
 3284 reflections
 220 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 1.958P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.003$
 $\Delta\rho_{max} = 0.18 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.20 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983), with 1512 Friedel pairs
 Flack parameter: 0.007 (10)

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Mn1—O2 ⁱ	2.1454 (11)	Mn1—N2	2.2772 (12)
Mn1—O3 ⁱⁱ	2.1648 (11)	C11—C12	1.469 (2)
Mn1—O1W	2.1796 (12)	C12—C13	1.192 (2)
Mn1—N1	2.2452 (12)	C13—C14	1.478 (2)
Mn1—O1	2.2581 (12)		
O2 ⁱ —Mn1—O3 ⁱⁱ	106.22 (4)	O1W—Mn1—O1	83.46 (4)
O2 ⁱ —Mn1—O1W	97.81 (5)	N1—Mn1—O1	85.08 (4)
O3 ⁱⁱ —Mn1—O1W	86.60 (4)	O2 ⁱ —Mn1—N2	90.02 (5)
O2 ⁱ —Mn1—N1	160.68 (4)	O3 ⁱⁱ —Mn1—N2	102.80 (4)
O3 ⁱⁱ —Mn1—N1	85.41 (4)	O1W—Mn1—N2	165.64 (5)
O1W—Mn1—N1	98.23 (5)	N1—Mn1—N2	72.12 (5)
O2 ⁱ —Mn1—O1	86.14 (5)	O1—Mn1—N2	85.09 (4)
O3 ⁱⁱ —Mn1—O1	165.12 (5)		

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

Table 2

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

<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>
O1W—H1W1 \cdots O2	0.85 (2)	2.01 (2)	2.8139 (16)	159 (2)
O1W—H1W2 \cdots O2W	0.85 (2)	1.92 (2)	2.7629 (17)	174 (2)
O2W—H2W1 \cdots O4 ⁱⁱⁱ	0.85 (2)	2.32 (2)	3.145 (2)	165 (2)
O2W—H2W2 \cdots O3 ⁱ	0.85 (2)	2.06 (2)	2.9054 (19)	176 (2)

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

Water H atoms were located in a difference Fourier map and refined with O—H and H···H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. All other H atoms were placed in calculated positions, with C—H = 0.93 Å, and were refined in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3056). Services for accessing these data are described at the back of the journal.

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