

A three-dimensional framework in 2,2'-biimidazolium bis(2,2'-biimidazole- κ^2N,N')bis(biphenyl-2,4'-dicarboxylato- κO)manganese(II) hexahydrate

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Received 11 October 2010

Accepted 11 November 2010

Online 23 November 2010

In the title salt, $(C_6H_8N_4)[Mn(C_{14}H_8O_4)_2(C_6H_6N_4)_2] \cdot 6H_2O$, the Mn^{II} atom lies on an inversion centre and is coordinated by four N atoms from two 2,2'-biimidazole (biim) ligands and two O atoms from two biphenyl-2,4'-dicarboxylate (bpdc) anions to give a slightly distorted octahedral coordination, while the cation lies about another inversion centre. Adjacent $[Mn(bpdc)_2(biim)_2]^{2-}$ anions are linked *via* two pairs of N—H...O hydrogen bonds, leading to an infinite chain along the

[100] direction. The protonated $[H_2biim]^{2+}$ moiety acts as a charge-compensating cation and space-filling structural subunit. It bridges two $[Mn(bpdc)_2(biim)_2]^{2-}$ anions through two pairs of N—H...O hydrogen bonds, constructing two $R_2^2(9)$ rings, leading to a zigzag chain in the $[2\bar{1}\bar{1}]$ direction, which gives rise to a ruffled set of $[H_2biim]^{2+}[Mn(bpdc)_2(biim)_2]^{2-}$ moieties in the $[01\bar{1}]$ plane. The water molecules give rise to a chain structure in which O—H...O hydrogen bonds generate a chain of alternating four- and six-membered water–oxygen $R_4^2(8)$ and $R_6^6(12)$ rings, each lying about independent inversion centres giving rise to a chain along the [100] direction. Within the water chain, the $(H_2O)_6$ water rings are hydrogen bonded to two O atoms from two $[Mn(bpdc)_2(biim)_2]^{2-}$ anions, giving rise to a three-dimensional framework.

Comment

The design and synthesis of coordination polymers is an attractive area of research owing to the fascinating structures and potential applications in the catalysis and gas storage fields (Desiraju, 1995; Yaghi *et al.*, 1998; Belof *et al.*, 2007). In the case of coordination complexes, the resulting structures will be affected by factors such as metal-to-ligand ratios, metal coordination modes, and the type and flexibility of the organic ligand and guest molecules. With respect to these factors, not only can the organic components be introduced as ligands bonded directly to a secondary metal site, but they can also serve as a charge-compensating ion or space-filling structural subunit. During the past decade, there have been many reports of the successful synthesis of coordination compounds in which polycarboxylic acids combining with N-containing

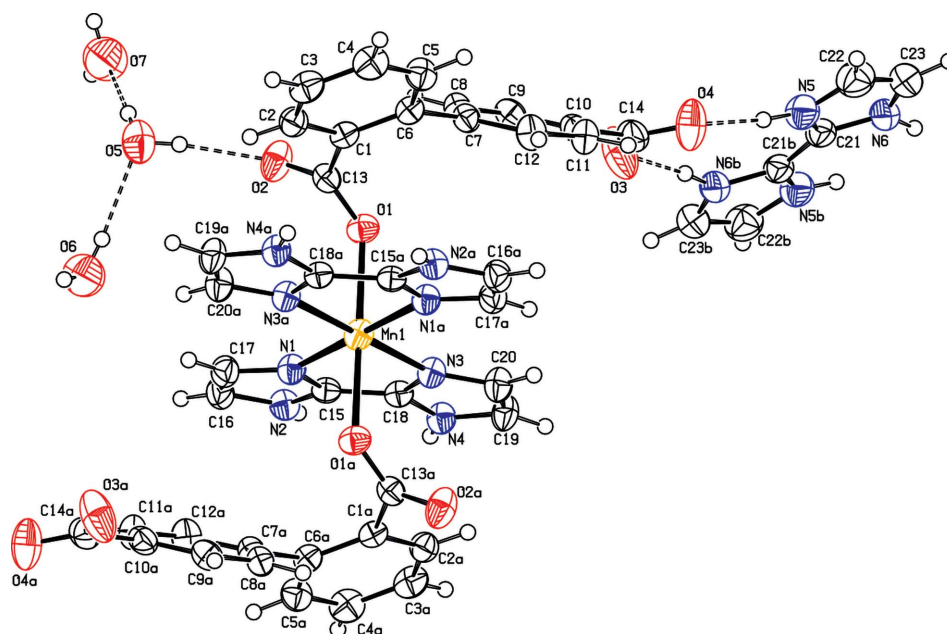


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate hydrogen bonds. [Symmetry codes: (a) $-x + 1, -y + 1, -z + 1$; (b) $-x - 1, -y + 2, -z + 2$.]

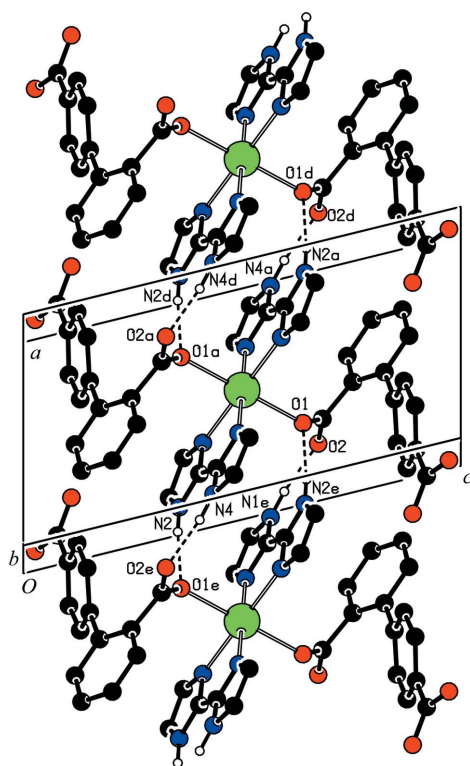


Figure 2
View of the chain of $[\text{Mn}(\text{bpdc})_2(\text{biim})_2]^{2-}$ anions in the $[100]$ direction. [Symmetry codes: (a) $-x + 1, -y + 1, -z + 1$; (d) $x + 1, y, z$; (e) $-x, -y + 1, -z + 1$.]

ligands have been used to assemble coordination polymers because of their multiple coordination sites and versatile coordination modes (Wang *et al.*, 2004, 2010; Duan *et al.*, 2007, 2010; Liu *et al.*, 2008; Ghosh *et al.*, 2009). Coordination polymers associated with the biphenyl-2,4'-dicarboxylic acid (Liu *et al.*, 2010) and the 2,2'-biimidazole ligand have not often been reported (Larsson & Öhrström, 2003; Ye *et al.*, 2004; Fang *et al.*, 2009). We report here the structure of the title compound, $[\text{H}_2\text{biim}]^{2+}[\text{Mn}(\text{bpdc})_2(\text{biim})_2]^{2-} \cdot 6\text{H}_2\text{O}$, (I), where $[\text{H}_2\text{biim}]^{2+}$ is 2,2'-biimidazolium and H_2bpdc is biphenyl-2,4'-dicarboxylic acid.

As shown in Fig. 1, the structural unit consists of a $[\text{Mn}(\text{bpdc})_2(\text{biim})_2]^{2-}$ anion with the Mn atom chosen to lie on the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and one doubly protonated $[\text{H}_2\text{biim}]^{2+}$ cation lying about an inversion centre at $(\frac{1}{2}, 1, 1)$; the asymmetric unit also has three water molecules. In the $[\text{Mn}(\text{bpdc})_2(\text{biim})_2]^{2-}$ anion, the Mn^{2+} ion is coordinated by four N atoms from two biim ligands and two O atoms from two bpdc anions in a slightly distorted octahedral configuration. The unique Mn—O distance is 2.2879 (14) Å, while Mn—N lengths are 2.1966 (17) and 2.2334 (18) Å. The bpdc²⁻ dianion is monodentate with a dihedral angle of 42.01 (10)° between its two benzene rings.

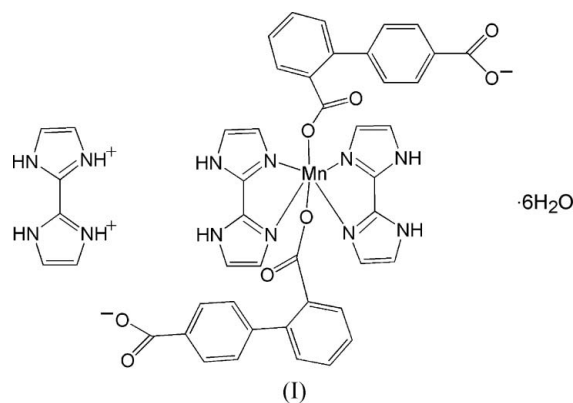


Figure 3
View of the chain along the $[2\bar{1}\bar{1}]$ direction. [Symmetry codes: (a) $-x + 1, -y + 1, -z + 1$; (b) $-x - 1, -y + 2, -z + 2$; (c) $x + 2, y - 1, z - 1$.]

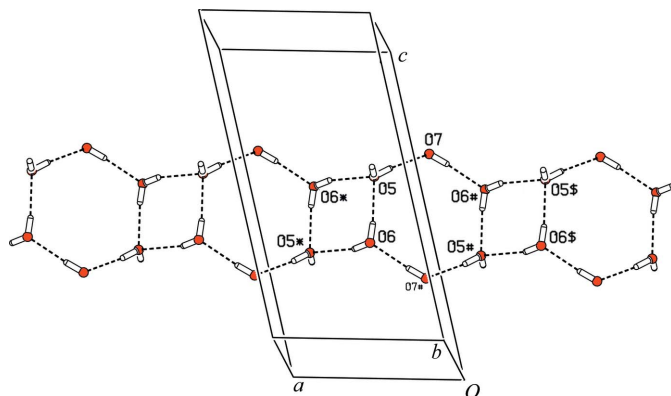


Figure 4
View of the water chain along the [100] direction. [Symmetry codes: (*) $-x + 1, -y, -z + 1$; (#) $-x, -y, -z + 1$; (\$) $x - 1, y, z$.]

this chain with that of the $[\text{Mn}(\text{bpdc})_2(\text{biim})_2]^{2-}$ anions gives rise to a ruffled layer in the $[01\bar{1}]$ plane.

The three water molecules give rise to a water chain (Fig. 4) which extends in the [100] direction (geometric details are given in Table 1). The chain is composed of six- and four-membered rings constructed from water O atoms lying about inversion centres at $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$, etc., with graph-set notations $R_6^6(12)$ and $R_4^2(8)$ for the six- and four-membered rings, respectively. The four O atoms of the $R_4^2(8)$ ring are exactly coplanar because of the inversion symmetry, while the six O atoms within the hexamer are almost coplanar, with a mean deviation of $0.1383(2)$ Å, and construct an essentially equilateral hexagon. The O5 water molecules in each water chain are hydrogen bonded to O2 atoms from $[\text{Mn}(\text{bpdc})_2(\text{biim})_2]^{2-}$ anions so that the two-dimensional zigzag layers are arranged into a three-dimensional framework.

Experimental

A mixture of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (0.5 mmol, 0.085 g), H_2bpdc (0.5 mmol, 0.17 g), biim (0.2 mmol, 0.04 g) and H_2O (15 ml) was placed in a Parr Teflon-lined stainless steel vessel (23 ml), which was sealed and heated at 403 K for 5 d. After the mixture had been cooled slowly to room temperature, colourless block-shaped crystals of (I) were obtained.

Crystal data

$(\text{C}_6\text{H}_8\text{N}_4)[\text{Mn}(\text{C}_{14}\text{H}_8\text{O}_4)_2 \cdot (\text{C}_6\text{H}_6\text{N}_4)_2] \cdot 6\text{H}_2\text{O}$	$\beta = 76.269(1)^\circ$
$M_r = 1047.90$	$\gamma = 85.793(1)^\circ$
Triclinic, $P\bar{1}$	$V = 1193.4(3) \text{ \AA}^3$
$a = 7.278(1) \text{ \AA}$	$Z = 1$
$b = 11.977(2) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 14.268(1) \text{ \AA}$	$\mu = 0.36 \text{ mm}^{-1}$
$\alpha = 81.310(2)^\circ$	$T = 296 \text{ K}$
	$0.30 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer	8661 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	4629 independent reflections
$T_{\min} = 0.900, T_{\max} = 0.932$	3821 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.1117$
 $S = 1.05$
 4629 reflections
 361 parameters
 13 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N2}-\text{H2A} \cdots \text{O1}^i$	0.86 (2)	1.92 (2)	2.771 (2)	172 (2)
$\text{N4}-\text{H4A} \cdots \text{O2}^i$	0.90 (2)	1.88 (2)	2.772 (2)	172 (2)
$\text{O5}-\text{H5WA} \cdots \text{O7}$	0.85 (2)	1.96 (2)	2.810 (3)	173 (4)
$\text{O5}-\text{H5WB} \cdots \text{O2}$	0.83 (2)	1.94 (2)	2.760 (3)	171 (4)
$\text{O6}-\text{H6WA} \cdots \text{O5}^{ii}$	0.79 (2)	2.08 (3)	2.851 (3)	165 (4)
$\text{O6}-\text{H6WB} \cdots \text{O5}$	0.81 (2)	2.06 (2)	2.861 (3)	171 (4)
$\text{O7}-\text{H7WB} \cdots \text{O6}^{iii}$	0.84 (2)	1.98 (2)	2.818 (3)	175 (4)
$\text{N5}-\text{H5A} \cdots \text{O4}$	0.89 (2)	1.79 (2)	2.676 (3)	172 (3)
$\text{N6}-\text{H6A} \cdots \text{O3}^{iv}$	0.87 (2)	1.82 (2)	2.678 (3)	169 (3)

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

Water and nitrogen-bound H atoms were located in difference Fourier maps and refined with restraints $[\text{O}-\text{H} = 0.85(3) \text{ \AA}, \text{H} \cdots \text{H} = 1.34(3) \text{ \AA}$ and $\text{N}-\text{H} = 0.89(3) \text{ \AA}]$ and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{O})$. The remaining H atoms were positioned geometrically and allowed for using a riding model, with $\text{C}-\text{H} = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms.

Data collection: SMART (Bruker, 2001); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 2001); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON.

This work was supported by the Natural Science Foundation of Henan Province (grant Nos. 092300410119 and 102300410093).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3201). Services for accessing these data are described at the back of the journal.

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