

Poly[diaqua[μ -1,4-bis(imidazol-1-ylmethyl)benzene- $\kappa^2 N^3:N^{3'}$](μ -*trans*-cyclohexane-1,4-carboxylato- $\kappa^2 O^1:O^4$)-manganese(II)]: a three-dimensional hydrogen-bonding α -polonium net

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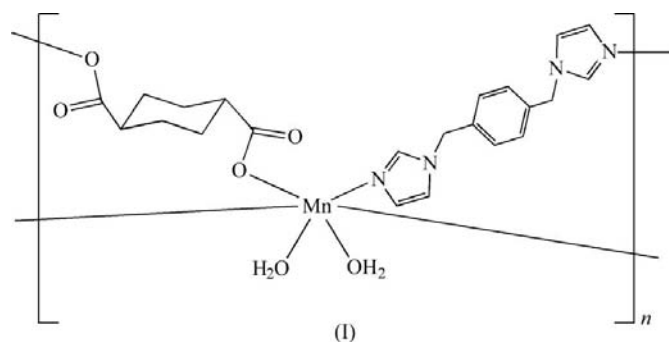
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In the title coordination compound, $[\text{Mn}(\text{C}_8\text{H}_{10}\text{O}_4)(\text{C}_{14}\text{H}_{14}\text{N}_4)(\text{H}_2\text{O})_2]_n$, each Mn^{II} centre occupies an inversion centre. The 1,4-bis(imidazol-1-ylmethyl)benzene (1,4-bix) ligand and the *trans*-cyclohexane-1,4-dicarboxylate dianion (chdc) both function in bridging modes, linking adjacent Mn^{II} centres into a two-dimensional four-connected (4,4) network. These two-dimensional layers are stacked in a parallel mode. Hydrogen bonds between water molecules and carboxylate O atoms link neighbouring (4,4) networks, yielding a three-dimensional α -polonium net.

Comment

The design and synthesis of metal-organic coordination polymers are of great interest, not only because of their wide range of potential applications in nonlinear optics, catalysis, gas absorption, luminescence, magnetism and medicine, but also because of their intriguing variety of architectures and topologies (Eddaoudi *et al.*, 2001; Noveron *et al.*, 2002; Batten & Robson, 1998). Generally, the topology of a coordination polymer can be controlled and modified by selecting the coordination geometry preferred by the metal ion and the chemical structure of the organic ligand (Carlucci *et al.*, 2003). The use of aromatic carboxylic acids in the synthesis of coordination polymers has aroused enormous interest due to the versatility of their coordination modes and the variety of their conformations (Wang *et al.*, 2005). Aromatic multicarboxylate ligands, such as 1,2-, 1,3- and 1,4-benzenedicarboxylic acid, are widely used to construct coordination polymers with interesting properties (Tao *et al.*, 2002). However, flexible dicarboxylate ligands are rarely used in the construction of coordination polymers. The cyclohexane-1,4-dicarboxylate dianion (chdc) is an example of a flexible

dianion because of the presence of *cis* and *trans* configurations. [The H_2chdc ligand has three possible conformations, *viz.* a,a-*trans*-, e,e-*trans*- and e,a-*cis*- H_2chdc ; usually, the e,e-*trans* form is thermodynamically more stable than the e,a-*cis* form because of the presence of two equatorial substituents in the latter, and the a,a-*trans* form is the least stable due to 1,3-diaxial hindrance (Bi *et al.*, 2004).] On the other hand, 4,4'-bipyridine is a rigid rod-like spacer, well known in the construction of metal-organic polymers, and it has adopted numerous interesting supramolecular architectures (Batten, 2001). However, flexible N-donor ligands such as 1,4-bis(imidazol-1-ylmethyl)benzene (1,4-bix) have not been so well explored to date (Wang *et al.*, 2006). In this work, 1,4-bix assembles with manganese cyclohexane-1,4-dicarboxylate to furnish the title complex, $[\text{Mn}(\text{chdc})(1,4\text{-bix})(\text{H}_2\text{O})_2]$, (I), which exists as an unusual six-connected α -polonium network.



Selected bond lengths and angles for (I) are given in Table 1. As shown in Fig. 1, the repeat unit of (I) contains one Mn^{II} atom, one 1,4-bix ligand, one chdc anion and two coordinated water molecules. Each Mn^{II} centre lies on a centre of symmetry and is six-coordinated in an octahedral environment by two carboxylate O atoms from two different chdc anions, two water O atoms and two N atoms from two distinct 1,4-bix ligands. Atoms O1, O1ⁱⁱⁱ, N1 and N1ⁱⁱⁱ comprise the basal

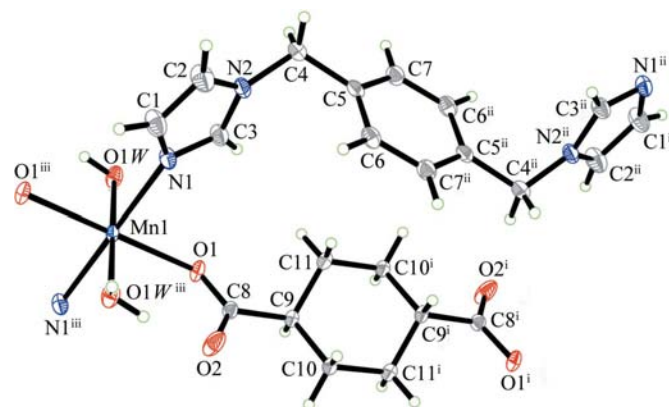


Figure 1
A view of the local coordination of the Mn^{II} centre in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. O1W wholly obscures one of the attached H atoms. [Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $-x, -y, -z$.]

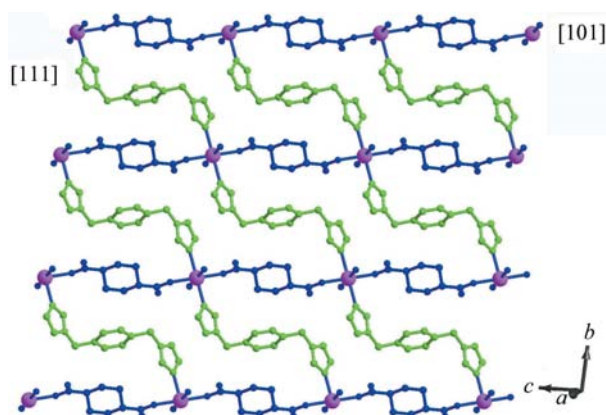


Figure 2
A view of the (4,4) network of (I) in the $(10\bar{1})$ plane.

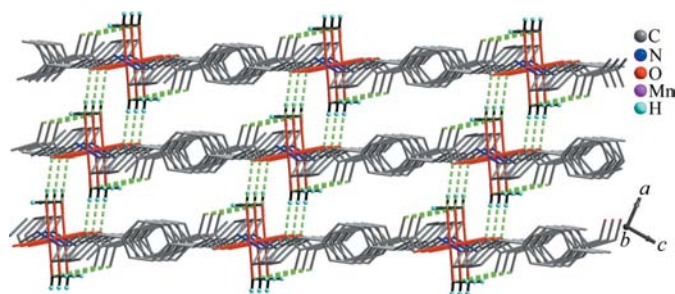


Figure 3
A view of the three-dimensional hydrogen-bonding framework structure of (I) along the $[010]$ direction.

plane, and atoms O1W and O1Wⁱⁱⁱ occupy the axial positions of the octahedron [symmetry code: (iii) $-x, -y, -z$]. The average Mn—O(carboxylate) and Mn—N distances in (I) (Table 1) are comparable with those observed for $[\text{Mn}(\text{bza})_2(\text{ppz})_2]$ [bza is benzoate and ppz is 3-(2-pyridyl)-pyrazole; Zou *et al.*, 2005]. As depicted in Fig. 2, Mn^{II} centres are bridged by the chdc dianions and 1,4-bix ligands to give a two-dimensional four-connected (4,4) network. Along the $[101]$ direction, adjacent Mn^{II} centres are linked *via* the two monodentate carboxylate groups of the chdc ligands to form one-dimensional chains. The 1,4-bix ligands further extend these chains along the $[111]$ direction, resulting in the final two-dimensional (4,4) network, with dimensions of $13.96(2) \times 11.65(2) \text{ \AA}$ for the repeat unit [the Mn \cdots Mn distances bridged by *L* and chdc are $13.9607(9)$ and $11.6506(7) \text{ \AA}$, respectively]. Analysis of the crystal packing of (I) reveals that these two-dimensional layers adopt a parallel stacking mode in the $(10\bar{1})$ plane.

The driving force for the formation of this unusual topology becomes apparent when the structure of (I) is examined in detail. Along the $[100]$ direction, there are hydrogen-bonding interactions between the water molecules and carboxylate O atoms (Table 2) of neighbouring (4,4) networks. The hydrogen bonds link neighbouring (4,4) networks, yielding a three-dimensional supramolecular architecture (Fig. 3). If each double hydrogen-bonded bridge is considered as one linker, each Mn^{II} centre can be regarded as a six-connected node, and

the overall network topology is that of α -polonium (Batten & Robson, 1998). Recently, several six-connected nets, such as $4^4.6^{11}$, LB-1 ($4^4.6^{10}.8$), pcu ($4^{12}.6^3$), roa ($4^4.6^{10}.8$) and rob ($4^8.6^6.8$), have been observed in coordination polymers (Zhang *et al.*, 2007). It is noteworthy that the α -polonium net presented here is clearly different from the six-connected three-dimensional nets mentioned above. Although α -polonium nets have been widely reported in coordination polymers, only in a few cases does their construction involve hydrogen-bonding interactions (*e.g.* Burke *et al.*, 2008; Roesky & Andruh, 2003).

Experimental

Manganese chloride hexahydrate (0.119 g, 0.5 mmol), H₂chdc (0.135 g, 0.5 mmol) and 1,4-bix (0.093 g, 0.5 mmol) were dissolved in water (13 ml), and triethylamine was added until a pH of 5.5 was achieved. The solution was heated in a 23 ml Teflon-lined stainless steel autoclave at 445 K for 3 d. The autoclave was allowed to cool to room temperature over a period of several hours. Block-like crystals of (I) were isolated in about 47% yield.

Crystal data

| | |
|--|---|
| $[\text{Mn}(\text{C}_8\text{H}_{10}\text{O}_4)(\text{C}_{14}\text{H}_{14}\text{N}_4)(\text{H}_2\text{O})_2]$ | $\gamma = 102.426(4)^\circ$ |
| $M_r = 499.42$ | $V = 556.84(5) \text{ \AA}^3$ |
| Triclinic, $P\bar{1}$ | $Z = 1$ |
| $a = 5.6645(2) \text{ \AA}$ | Mo $K\alpha$ radiation |
| $b = 9.4282(6) \text{ \AA}$ | $\mu = 0.64 \text{ mm}^{-1}$ |
| $c = 10.7437(5) \text{ \AA}$ | $T = 293 \text{ K}$ |
| $\alpha = 91.907(4)^\circ$ | $0.23 \times 0.19 \times 0.16 \text{ mm}$ |
| $\beta = 95.553(3)^\circ$ | |

Data collection

| | |
|---|--|
| Bruker APEX diffractometer | 5312 measured reflections |
| Absorption correction: multi-scan | 2255 independent reflections |
| (SADABS; Sheldrick, 1996) | 1887 reflections with $I > 2\sigma(I)$ |
| $T_{\min} = 0.861$, $T_{\max} = 0.906$ | $R_{\text{int}} = 0.025$ |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.076$ | $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$ |
| $S = 1.05$ | $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$ |
| 2255 reflections | |
| 159 parameters | |

Table 1

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

| | | | |
|------------|-------------|------------|-------------|
| Mn1—N1 | 2.2515 (15) | Mn1—O1W | 2.2203 (12) |
| Mn1—O1 | 2.1819 (10) | | |
| O1—Mn1—O1W | 87.96 (5) | O1W—Mn1—N1 | 88.10 (5) |
| O1—Mn1—N1 | 88.47 (5) | | |

Table 2

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

| $D\cdots H\cdots A$ | $D\cdots H$ | $H\cdots A$ | $D\cdots A$ | $D\cdots H\cdots A$ |
|------------------------------------|-------------|-------------|-------------|---------------------|
| O1W—Hw11 \cdots O1 ⁱⁱ | 0.83 (2) | 2.00 (2) | 2.8103 (18) | 165 (2) |
| O1W—Hw12 \cdots O2 ⁱ | 0.83 (3) | 1.81 (3) | 2.6150 (18) | 163 (2) |

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

Carbon-bound H atoms were positioned geometrically, with C—H = 0.93 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The water H atoms were located in a difference Fourier map and were refined freely.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); 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: SK3329). Services for accessing these data are described at the back of the journal.

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