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Hexaimidazolemanganese(II) terephthalate tetrahydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.100
Data-to-parameter ratio = 12.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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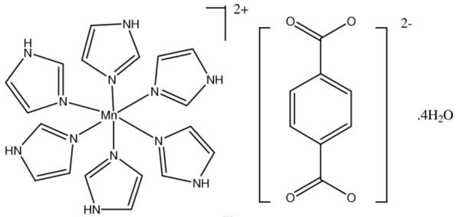
In the title compound, $[Mn(C_3H_4N_2)_6](C_8H_4O_4)\cdot 4H_2O$, the Mn atom is in an octahedral geometry formed by the tertiary N atoms of the imidazole moieties. The Mn atom lies on an inversion centre, as does the centroid of the terephthalate ring.The molecules are connected into a three-dimensional network by intermolecular interactions. The packing is further stabilized by C—H$\cdots\pi$ interactions.

Comment

Imidazole is of considerable interest as a ligand in that its presence in many biological systems (for example, in the histidine residue of proteins) provides a potential binding site for metal ions. Imidazole as a unidentate ligand can form complexes with metal ions through its tertiary N atom. Some complexes of imidazole and its derivatives with transition-metal ions have been reported (*e.g.* Brooks & Davidson, 1960). Manganese is one of several first-row transition-metal elements that have been found to play an important role in biological systems. Perhaps the best known is in the process of photosynthesis, during which water is oxidized to yield dioxygen, and it is generally believed that the process involves a tetranuclear manganese cluster (Wieghardt, 1989). In the present paper, we describe the synthesis of $[Mn(Im)_6]$-(teph)$\cdot 4H_2O$ (Im is imidazole and teph is terephthalate), (I). An X-ray crystallographic analysis was undertaken to establish its stereochemical configuration.



(I)

The asymmetric unit of the title complex consists of one-half each of a monomeric $[Mn(Im)_6]^{2+}$ cation and a terephthalate anion, linked by electrostatic forces and hydrogen bonds, and two water molecules. The other halves of the cation and anion are generated by crystallographic inversion centres; the Mn atom lies on a crystallographic inversion centre. The coordination mode of the Mn^{II} atom can be described as an MnN_6 chromophore, with octahedral geometry. Six imidazole molecules are coordinated through their tertiary N atoms to each Mn^{II} ion and one terephthalate group is outside the coordination sphere, balancing the charge. The Mn1—N5, Mn1—N1 and Mn1—N3 bond distances for $[Mn(Im)_6]$-(teph)$\cdot 4H_2O$ are 2.251 (2), 2.276 (2) and 2.289 (2) Å, respectively. All these bonds are longer than the Mn—N distance

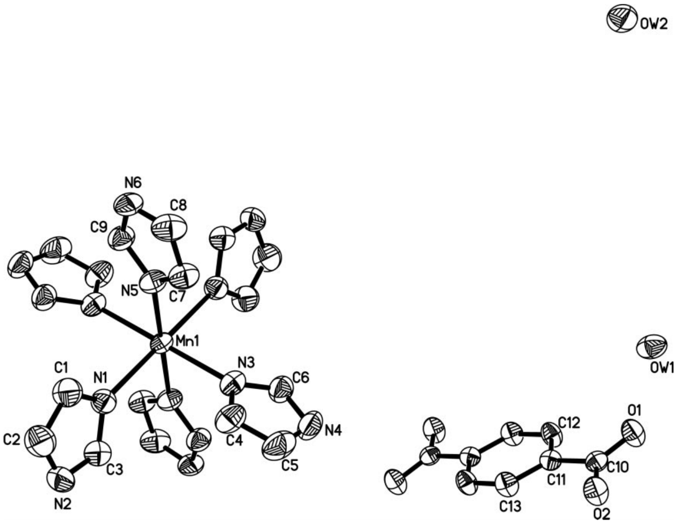


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme for the asymmetric unit. Hydrogen atoms have been omitted, as have the two water oxygen atoms centrosymmetrically related to OW1 and OW2.

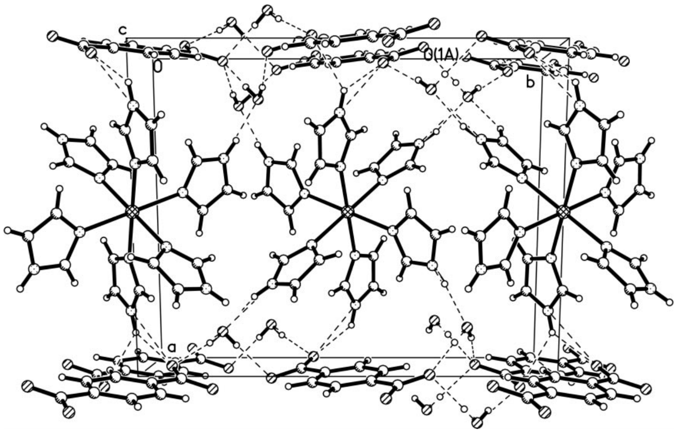


Figure 2
A view of the molecular packing down the c axis, showing the formation of the three-dimensional network. Hydrogen bonds are shown as dashed lines.

[2.201 (4) Å] observed in *trans*-diaquabis(1H-imidazole-4,5-dicarboxylato-$^2N^3$,O^4)manganese(II) (Ma *et al.*, 2003). All the imidazole rings are individually planar. In the terephthalate moiety, the $-COO^-$ group is slightly twisted away from the aromatic ring, with the O2—C10—C11—C13 and O1—C10—C11—C12 torsion angles of 8.3 (3) and 9.3 (3)°, respectively.

In the crystal structure, the molecules are connected by intermolecular interactions into a three-dimensional network (Table 2 and Fig. 2) in which the two water molecules act as both acceptors and donors. The packing is further stabilized by C—H···π interactions involving the imidazole rings (see Table 2 for details).

Experimental

Manganese(II) terephthalate dihydrate was prepared according to the literature method (Wan *et al.*, 2003). To a warm solution of imidazole (2.0 g, 30 mmol) in H_2O (50 ml) was added the manganese salt (1.0 g, 3.8 mmol) with stirring, and the mixture was refluxed for 30 min. The colourless solution was filtered and the filtrate was left to stand undisturbed. Colourless single crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation at room temperature.

Crystal data

$[Mn(C_3H_4N_2)_6](C_8H_4O_4)\cdot 4H_2O$	$D_x = 1.416$ Mg m^{-3}
$M_r = 699.61$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2286 reflections
$a = 13.050$ (3) Å	$\theta = 1.6$–$25.0°$
$b = 16.068$ (3) Å	$\mu = 0.47$ mm^{-1}
$c = 8.0948$ (16) Å	$T = 293$ (2) K
$\beta = 104.75$ (3)°	Block, colourless
$V = 1641.4$ (6) Å^3	0.24 × 0.22 × 0.18 mm
$Z = 2$	

Data collection

Bruker SMART 1000 CCD diffractometer	2882 independent reflections
ω scans	2286 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.037$
$T_{min} = 0.896$, $T_{max} = 0.921$	$\theta_{max} = 25.0°$
3102 measured reflections	$h = -14 \rightarrow 15$
	$k = -19 \rightarrow 19$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 0.8199P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.100$	$\Delta\rho_{max} = 0.19$ e Å^{-3}
$S = 1.11$	$\Delta\rho_{min} = -0.50$ e Å^{-3}
2882 reflections	
230 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Mn1—N5	2.251 (2)	Mn1—N3	2.289 (2)
Mn1—N1	2.276 (2)		
N5—Mn1—N1	91.21 (7)	N1—Mn1—N3	89.28 (8)
N5—Mn1—N3	91.41 (7)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O1W^{i}	0.86	1.91	2.766 (3)	171
N4—H4A···O2W^{ii}	0.86	1.93	2.766 (3)	164
O1W—H1W1···O1^{iii}	0.70 (4)	2.30 (4)	2.995 (3)	169 (4)
O2W—H1W2···O1^{iv}	0.82 (4)	2.04 (4)	2.851 (3)	178 (4)
O1W—H2W1···O1	0.91 (4)	1.83 (4)	2.735 (3)	178 (4)
O2W—H2W2···O2^{v}	0.81 (4)	1.97 (4)	2.772 (3)	171 (3)
C5—H5A···O2W^{vi}	0.93	2.52	3.376 (4)	153
C2—H2B···$Cg1^{vii}$	0.93	2.95	3.816 (3)	156
C9—H9A···$Cg2^{viii}$	0.93	2.91	3.668 (3)	140

Symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (iv) $x-1, y, z$; (v) $x-1, \frac{3}{2}-y, z-\frac{1}{2}$; (vi) $1-x, 1-y, 1-z$; (vii) $x, -\frac{1}{2}-y, \frac{1}{2}+z$; (viii) $1-x, -y, -z$. Cg1 and Cg2 denote the centroids of the N1/N2/C1–C3 and N3/N4/C4–C6 rin>gs, respectively.

H atoms of the water molecules were located in a difference Fourier map and were refined isotropically [O—H = 0.71 (4)–0.91 (4) Å]. The remaining H atoms were placed in calculated positions [N—H = 0.86 Å and C—H = 0.93 Å] and refined as riding atoms, with U_{iso}(H) equal to $1.2U_{eq}$(carrier atom).

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Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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