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Poly[aquamanganese(II)-μ_3-1*H*-imidazole-4,5-dicarboxylato]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.022
wR factor = 0.049
Data-to-parameter ratio = 12.4

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

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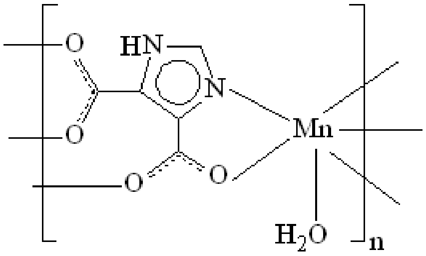
In the title coordination polymer, $[Mn(HIDC)(H_2O)]_n$ ($HIDC^{2-}$ is the 1*H*-imidazole-4,5-dicarboxylate dianion, $C_5H_2N_2O_4$), each Mn^{II} atom is in an octahedral coordination by one N atom and four carboxylate O atoms from three $HIDC^{2-}$ anions, and one water molecule. The Mn^{II} atoms are linked by $HIDC^{2-}$ anions into a layer structure. A three-dimensional coordination network is formed by O—H···N and O—H···O hydrogen bonding.

Comment

The rapidly growing area of coordination polymers, based on the interactions of metal cations with organic ligands, has given rise to a wide variety of fascinating one-, two- and three-dimensional structures (Sun *et al.*, 2004; Ma *et al.*, 2004). The structures and properties of such systems depend on the coordination properties and geometric preferences of both metal ions and bridging ligands, as well as on the influence of weak non-covalent interactions, such as hydrogen bonds (Choi & Jeon, 2003). 1*H*-Imidazole-4,5-dicarboxylic acid (H_3IDC) is well known as an efficient N/O donor with versatile binding and hydrogen-bonding abilities. It can be successively deprotonated to generate H_2IDC^-, $HIDC^{2-}$ and IDC^{3-} anions, and hence may result in a variety of structural topologies (Liu *et al.*, 2004; Xiao *et al.*, 2004). Some Mn^{II} complexes with mononuclear (Ma *et al.*, 2003; Huang *et al.*, 2001), binuclear (Rajendiran *et al.*, 2003) and chain structures (Zhang *et al.*, 2004) have been reported. Recently, we have reported the structures of two one-dimensional Cd^{II} coordination polymers, $[Cd(HIDC)(1,10\text{-phen})]_n$, (II) (1,10-phen is 1,10-phenanthroline; Gao, Gu *et al.*, 2004), and $[Cd(HIDC)(2,2'\text{-bipy})]_n$, (III) (2,2′-bipy is 2,2′-bipyridine; Gao, Liu *et al.*, 2004). Here, we report the crystal structure of the first layered Mn^{II} coordination polymer, the title compound, $[Mn(HIDC)(H_2O)]_n$, (I), obtained by the hydrothermal reaction of $MnCl_2.6H_2O$ with 1*H*-imidazole-4,5-dicarboxylic acid and pyridine.



(I)

In compound (I), both carboxyl groups of the H_3IDC ligand are deprotonated, whereas in the Cd compounds, (II) and

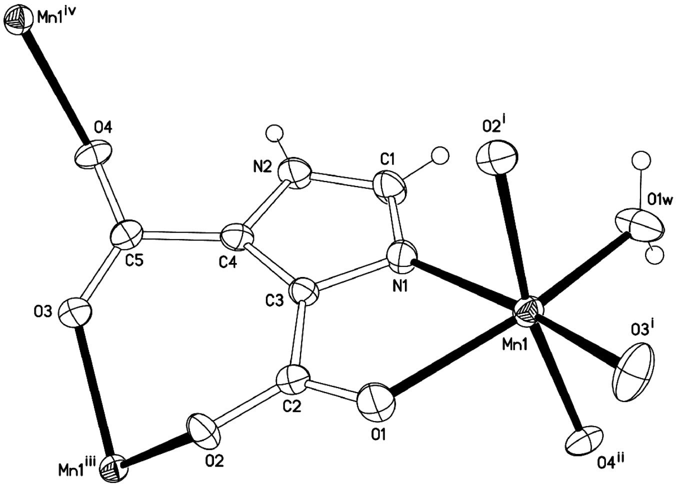


Figure 1
A view of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $1 - x, y + \frac{1}{2}, 1 - z$; (ii) $-x - 1, -y - 1, 2 - z$; (iii) $1 - x, y - \frac{1}{2}, -z$; (vi) $x, y, z + 1$.]

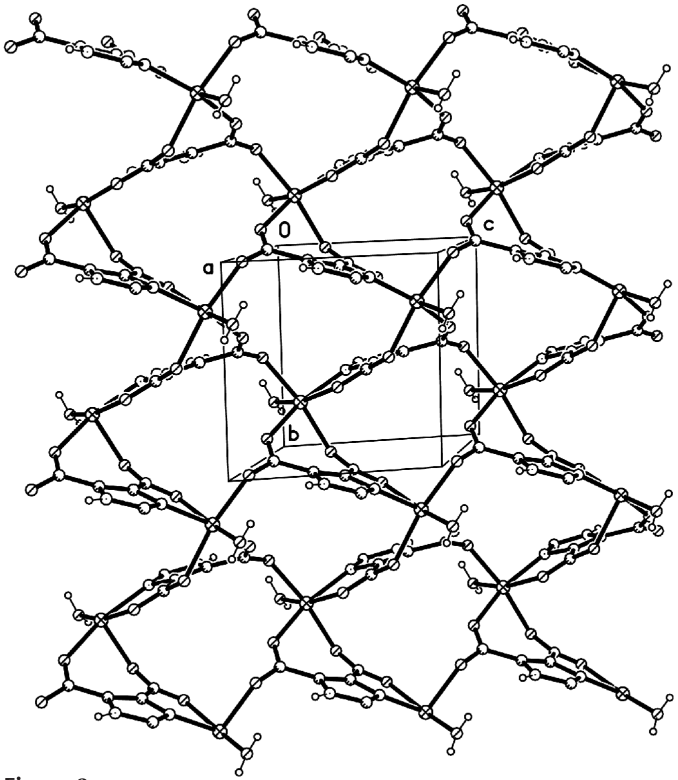


Figure 2
A packing diagram for (I), viewed approximately along the *a* axis.

(III), one NH H atom and only one carboxyl group are deprotonated. The asymmetric unit of (I) is composed of one Mn^{II} atom, one HIDC^{2-} dianion and one coordinated water molecule, all located in general positions. The coordination of the Mn^{II} ion can be described as having a slightly distorted octahedral geometry, defined by one N atom and four carboxyl O atoms from three different HIDC^{2-} groups, and one water molecule. All the Mn—O distances are somewhat shorter than than those in [Mn(HIDC)(1,10-phen)]$_n$, (IV) (Zhang *et al.*, 2004) (Table 1). Atoms O1, N1, O3^{i} and O1*W* form the equatorial plane of the octahedron, with an average atomic displacement of 0.12 (4) Å, while the Mn^{II} ion is located out of this plane by 0.02 (4) Å [symmetry code: (i) $1 - x, y + \frac{1}{2}, 1 - z$]. The two carboxyl atoms, O2^{i} and O4^{ii}, are located in the axial positions, with an O—Mn—O angle of 170.11 (6)° [symmetry code: (ii) $-x - 1, -y - 1, 2 - z$].

The dihedral angles between the carboxyl groups and the imidazole ring are 13.6 (5)° [O1—C2—O2] and 26.9 (5)° [O4—C5—O5], whereas in compounds (II), (III) and (IV), the HIDC^{2-} ligands are nearly planar, with overall r.m.s. deviations of 0.06 (3), 0.05 (4) and 0.048 Å, respectively.

The HIDC^{2-} anion in (I) shows three different coordination modes. Firstly, it acts in a monodentate coordination mode through carboxyl atom O4. Secondly, it binds to the Mn^{II} atom in an *N*,*O*-bidentate coordination mode through imidazole atom N1 and carboxyl atom O1, forming a five-membered chelate ring. Thirdly, it coordinates to the Mn^{II} atom in an *O*,*O*-bidentate coordination mode through two carboxyl atoms, O2 and O3, generating a seven-membered chelate ring with an envelope-like conformation. In contrast, in compounds (II), (III) and (IV), the HIDC^{2-} groups coordinate to the metal centres in only an *N*,*O*-bidentate coordination mode, forming two five-membered chelate rings.

Based on these different coordination modes, a ring structure is formed by three Mn^{II} atoms and three different HIDC^{2-} anions, which are linked by additional HIDC^{2-} anions into layers parallel to the crystallographic *bc* plane (Fig. 2). These layers are connected *via* intermolecular O—H···N and O—H···O hydrogen bonds into a three-dimensional network (Table 2).

Experimental

MnCl$_2$·6H$_2$O (4.68 g, 20 mmol), 1*H*-imidazole-4,5-dicarboxylic acid (4.60 g, 20 mmol) and pyridine (3 ml) were dissolved in water (35 ml). The mixture was sealed in a 50 ml Teflon-lined stainless steel bomb and held at 403 K for 5 d. The bomb was then cooled to room temperature, and colourless prismatic crystals of (I) were obtained after several days. CHN analysis, calculated for C$_5$H$_4$N$_2$O$_5$Mn: C 26.45, H 1.78, N 12.34%; found: C 26.60, H 1.71, N 12.38%.

Crystal data

[Mn(C$_5$H$_2$N$_2$O$_4$)(H$_2$O)]
$M_r = 227.04$
Monoclinic, $P2_1$
$a = 7.0561$ (14) Å
$b = 7.5531$ (15) Å
$c = 7.6261$ (15) Å
$\beta = 117.36$ (3)°
$V = 360.97$ (16) Å^3
$Z = 2$
$D_x = 2.089$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 3428 reflections
$\theta = 3.0$–$27.5°$
$\mu = 1.82$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.32 × 0.24 × 0.11 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.594$, $T_{\max} = 0.825$
3525 measured reflections
1534 independent reflections
1456 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -9 \rightarrow 9$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.049$
$S = 1.04$
1534 reflections
124 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Absolute structure: Flack (1983); 649 Friedel pairs
Flack parameter: 0.013 (17)

Table 1
Selected geometric parameters (Å, °).

Mn1—N1	2.228 (2)	Mn1—O1*W*	2.1399 (18)
Mn1—O1	2.2125 (18)	O1—C2	1.242 (3)
Mn1—O2^{i}	2.2197 (16)	O2—C2	1.273 (3)
Mn1—O3^{i}	2.1246 (18)	O3—C5	1.248 (3)
Mn1—O4^{ii}	2.1700 (16)	O4—C5	1.256 (3)
O1—Mn1—N1	73.76 (7)	O4^{ii}—Mn1—N1	98.91 (7)
O1—Mn1—O2^{i}	95.83 (7)	O4^{ii}—Mn1—O1	92.88 (7)
O2^{i}—Mn1—N1	88.03 (7)	O4^{ii}—Mn1—O2^{i}	170.11 (6)
O3^{i}—Mn1—N1	165.64 (7)	O1*W*—Mn1—N1	90.29 (8)
O3^{i}—Mn1—O1	94.61 (7)	O1*W*—Mn1—O1	162.79 (7)
O3^{i}—Mn1—O2^{i}	84.76 (7)	O1*W*—Mn1—O2^{i}	89.92 (6)
O3^{i}—Mn1—O4^{ii}	89.90 (7)	O1*W*—Mn1—O4^{ii}	83.05 (7)
O3^{i}—Mn1—O1*W*	102.08 (8)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1^{iii}	0.86	2.59	3.101 (3)	119
N2—H2···O2^{iii}	0.86	2.10	2.958 (3)	173
O1*W*—H4···O2^{iv}	0.85 (3)	1.96 (3)	2.808 (2)	171 (3)
O1*W*—H3···O4^{v}	0.85 (3)	1.87 (3)	2.692 (2)	162 (3)

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

H atoms on C and N atoms were placed in ideal positions, with C—H = 0.93 Å and N—H = 0.86 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$, and were refined in the riding-model approximation. Water H atoms were located in difference Fourier maps and refined with O—H and H···H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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