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Diaquabis(1*H*-imidazole-4-carboxylato- κ^2N^3,O^4)manganese(II)Zhi-Yong Xiong,^{a,b,c} Lin Li,^{a*} Xiang-Jie Zhao^a and Hai-Ming Chen^a

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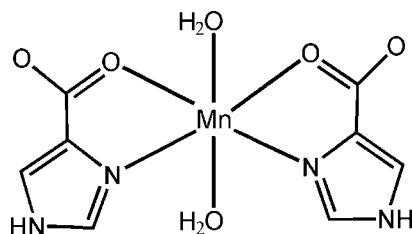
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.039; wR factor = 0.109; data-to-parameter ratio = 13.2.

In the title compound, $[Mn(C_4H_3N_2O_2)_2(H_2O)_2]$, the Mn^{II} ion is located on a twofold rotation axis and displays a distorted octahedral coordination environment, defined by two N,O -bidentate 1*H*-imidazole-4-carboxylate ligands in the equatorial plane and two water molecules in axial positions. In the crystal, $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds link the molecules into a three-dimensional supramolecular network. $\pi-\pi$ stacking interactions between the imidazole rings [centroid-centroid distances = 3.5188 (15) and 3.6687 (15) Å] further stabilize the structure.

Related literature

For related structures, see: Cai *et al.* (2012); Chen (2012); Gryz *et al.* (2007); Haggag (2005); Shuai *et al.* (2011); Starosta & Leciejewicz (2006); Yin *et al.* (2009); Zheng *et al.* (2011).



Experimental

Crystal data

 $[Mn(C_4H_3N_2O_2)_2(H_2O)_2]$ $M_r = 313.14$ Orthorhombic, *Pccn* $a = 7.3052$ (10) Å $b = 11.7997$ (17) Å $c = 13.5156$ (19) Å $V = 1165.0$ (3) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 1.16$ mm⁻¹ $T = 298$ K $0.36 \times 0.32 \times 0.30$ mm

Data collection

Bruker APEXII CCD

diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2001)

 $T_{\min} = 0.679$, $T_{\max} = 0.721$

5775 measured reflections

1145 independent reflections

972 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.067$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.039$ $wR(F^2) = 0.109$ $S = 1.07$

1145 reflections

87 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.57$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2\cdots O2^i$	0.86	1.95	2.811 (3)	173
$O1W-H1WA\cdots O2^{ii}$	0.87	1.96	2.818 (2)	167
$O1W-H1WB\cdots O2^{iii}$	0.73	2.02	2.751 (2)	176

Symmetry codes: (i) $-x + \frac{1}{2}, y, z - \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{3}{2}, z$.

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEPIII (Burnett & Johnson, 1996) and PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2616).

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supporting information

Acta Cryst. (2013). E69, m172 [doi:10.1107/S1600536813004091]

Diaquabis(1*H*-imidazole-4-carboxylato- κ^2N^3,O^4)manganese(II)**Zhi-Yong Xiong, Lin Li, Xiang-Jie Zhao and Hai-Ming Chen****S1. Comment**

In the past few years, structures containing metals and *N*-heterocyclic carboxylic acids have attracted much attention due to their fascinating structures and potential applications in many fields. 1*H*-Imidazole-4-carboxylic acid (H₂imc), which contains two N atoms of an imidazole group and one carboxylate group, has been widely used to prepare a variety of coordination polymers with different structures and exceptional properties (Cai *et al.*, 2012; Gryz *et al.*, 2007; Haggag, 2005; Starosta & Leciejewicz, 2006; Zheng *et al.*, 2011). For instance, three mononuclear complexes, [Cd(Himc)₂(H₂O)₂] (Yin *et al.*, 2009), [Zn(Himc)₂(H₂O)₂] (Shuai *et al.*, 2011) and [Co(Himc)₂(H₂O)₂] (Chen, 2012), have been reported. In this paper, we report the synthesis and structure of a new Mn(II) coordination polymer, [Mn(Himc)₂(H₂O)₂], which is isomorphous with the Cd(II), Zn(II) and Co(II) analogs.

The asymmetric unit of the title compound contains a half of [Mn(Himc)₂(H₂O)₂] formula unit. The Mn^{II} ion, lying on a twofold rotation axis, is six-coordinated by two N and two O atoms from two *cis*-oriented *N,O*-bidentate Himc ligands in the equatorial plane, and two water molecules in the axial positions, forming a slightly distorted octahedral geometry (Fig. 1). The bond lengths and angles around the Mn atom are normal. In the crystal structure, intermolecular O—H \cdots O and N—H \cdots O hydrogen bonds (Table 1) involving the coordinated water O atoms, carboxylate O atoms and imidazole N atoms link the molecules into a three-dimensional supramolecular network, as presented in Fig. 2. π – π stacking interactions between the imidazole rings [centroid–centroid distances = 3.5188 (15) and 3.6687 (15) Å] further stabilize the crystal structure.

S2. Experimental

A mixture of H₂imc (0.30 mmol), MnCl₂·6H₂O (0.30 mmol) and 6 ml EtOH/H₂O (v/v 1:1) was sealed into a 10 ml sample bottle reactor and heated at 373 K for 72 h under autogenous pressure, and then slowly cooled to room temperature at a rate of 5 K/h. Colorless block crystals of the title compound were obtained, washed with distilled water and dried in air (yield: 30%).

S3. Refinement

C- and N-bound H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 and N—H = 0.86 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. H atoms of the water molecule were located from a difference Fourier map and refined as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

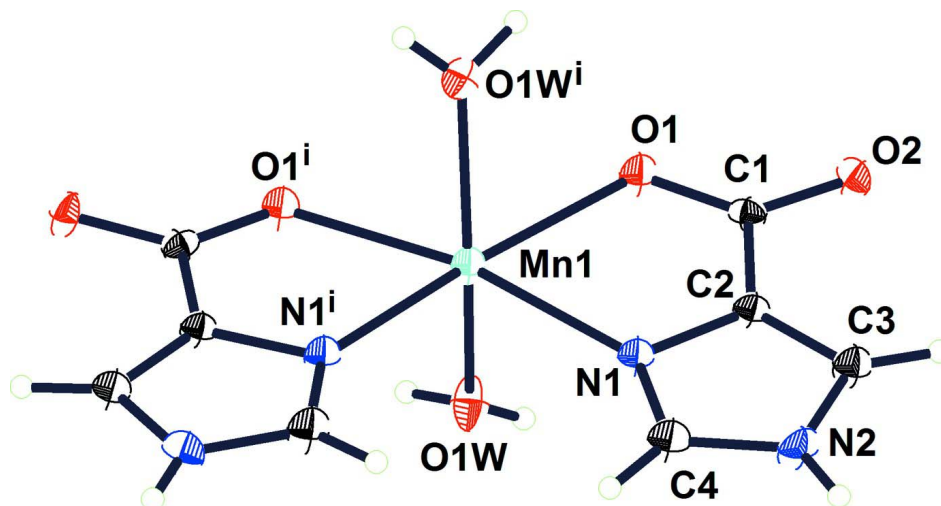


Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x+3/2, -y+3/2, z$.]

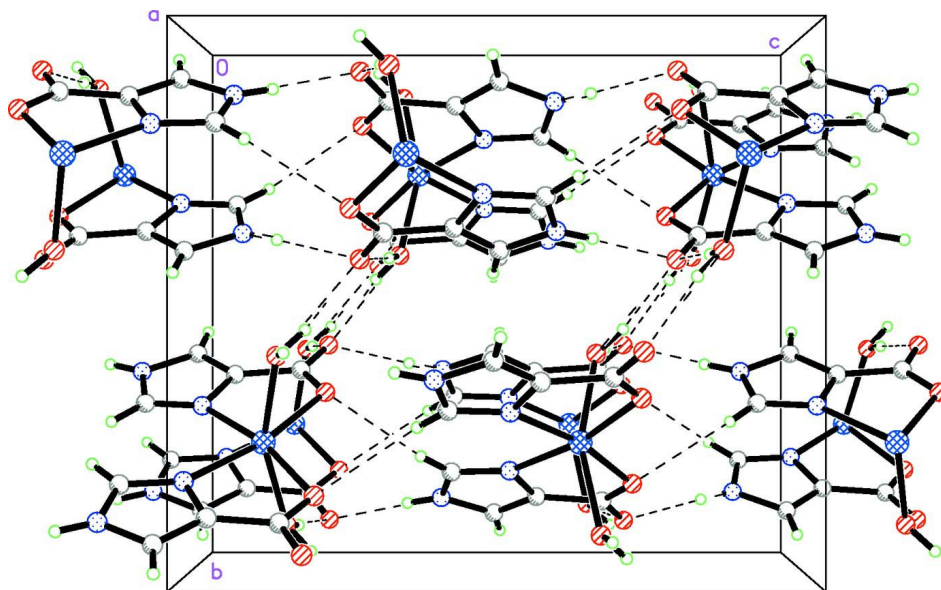


Figure 2

The crystal packing of the title compound, showing the three-dimensional supramolecular network. Hydrogen bonds are shown as dashed lines.

Diaquabis(1*H*-imidazole-4-carboxylato- κ^2N^3,O^4)manganese(II)

Crystal data

[Mn(C₄H₃N₂O₂)₂(H₂O)₂]
 $M_r = 313.14$
 Orthorhombic, *Pccn*
 Hall symbol: -P 2ab 2ac
 $a = 7.3052(10) \text{ \AA}$
 $b = 11.7997(17) \text{ \AA}$

$c = 13.5156(19) \text{ \AA}$
 $V = 1165.0(3) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 636$
 $D_x = 1.785 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1516 reflections
 $\theta = 3.3\text{--}24.9^\circ$
 $\mu = 1.16 \text{ mm}^{-1}$

$T = 298 \text{ K}$
 Block, colourless
 $0.36 \times 0.32 \times 0.30 \text{ mm}$

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2001)
 $T_{\min} = 0.679$, $T_{\max} = 0.721$

5775 measured reflections
 1145 independent reflections
 972 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.067$
 $\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 3.0^\circ$
 $h = -8 \rightarrow 9$
 $k = -14 \rightarrow 10$
 $l = -16 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.109$
 $S = 1.07$
 1145 reflections
 87 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 0.3284P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.57 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.7500	0.7500	0.63202 (3)	0.0256 (2)
N1	0.5501 (2)	0.81048 (17)	0.52125 (14)	0.0282 (5)
N2	0.3599 (3)	0.87066 (19)	0.40742 (14)	0.0342 (5)
H2	0.3136	0.8835	0.3500	0.041*
C1	0.4022 (3)	0.87462 (18)	0.67505 (16)	0.0238 (5)
C2	0.4063 (3)	0.86601 (18)	0.56583 (16)	0.0241 (5)
C4	0.5155 (3)	0.8144 (2)	0.42597 (17)	0.0350 (6)
H4	0.5895	0.7822	0.3775	0.042*
C3	0.2882 (4)	0.9039 (2)	0.49557 (18)	0.0312 (5)
H3	0.1804	0.9442	0.5057	0.037*
O1	0.5374 (2)	0.83532 (14)	0.72111 (11)	0.0310 (4)
O2	0.2642 (2)	0.91985 (15)	0.71532 (12)	0.0302 (4)
O1W	0.5981 (2)	0.59207 (14)	0.66084 (14)	0.0392 (5)

H1WA	0.6528	0.5466	0.7024	0.059*
H1WB	0.5022	0.5856	0.6758	0.059*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0235 (4)	0.0344 (4)	0.0189 (3)	0.00646 (18)	0.000	0.000
N1	0.0272 (11)	0.0389 (12)	0.0184 (10)	0.0068 (8)	-0.0009 (8)	-0.0021 (8)
N2	0.0348 (13)	0.0490 (13)	0.0186 (10)	0.0037 (9)	-0.0074 (8)	0.0014 (8)
C1	0.0247 (12)	0.0233 (11)	0.0233 (12)	-0.0029 (9)	0.0020 (9)	-0.0011 (8)
C2	0.0243 (12)	0.0288 (12)	0.0192 (12)	0.0008 (9)	0.0002 (9)	-0.0007 (8)
C4	0.0359 (15)	0.0506 (16)	0.0186 (12)	0.0067 (11)	0.0000 (10)	-0.0031 (10)
C3	0.0289 (12)	0.0391 (13)	0.0256 (13)	0.0037 (10)	-0.0008 (10)	0.0009 (10)
O1	0.0287 (10)	0.0457 (10)	0.0186 (8)	0.0087 (7)	-0.0010 (7)	-0.0002 (7)
O2	0.0243 (10)	0.0432 (11)	0.0232 (10)	0.0047 (6)	0.0048 (6)	-0.0051 (7)
O1W	0.0279 (10)	0.0429 (11)	0.0467 (12)	0.0036 (7)	0.0039 (8)	0.0133 (8)

Geometric parameters (Å, °)

Mn1—O1W	2.2037 (17)	N2—H2	0.8600
Mn1—O1W ⁱ	2.2038 (17)	C1—O1	1.257 (3)
Mn1—O1 ⁱ	2.2079 (16)	C1—O2	1.264 (3)
Mn1—O1	2.2079 (16)	C1—C2	1.480 (3)
Mn1—N1	2.2097 (19)	C2—C3	1.359 (3)
Mn1—N1 ⁱ	2.2097 (19)	C4—H4	0.9300
N1—C4	1.313 (3)	C3—H3	0.9300
N1—C2	1.377 (3)	O1W—H1WA	0.87
N2—C4	1.340 (3)	O1W—H1WB	0.73
N2—C3	1.359 (3)		
O1W—Mn1—O1W ⁱ	159.64 (10)	C4—N2—H2	126.1
O1W—Mn1—O1 ⁱ	82.66 (6)	C3—N2—H2	126.1
O1W ⁱ —Mn1—O1 ⁱ	86.27 (6)	O1—C1—O2	124.7 (2)
O1W—Mn1—O1	86.27 (6)	O1—C1—C2	116.93 (18)
O1W ⁱ —Mn1—O1	82.66 (6)	O2—C1—C2	118.34 (19)
O1 ⁱ —Mn1—O1	113.90 (8)	C3—C2—N1	109.6 (2)
O1W—Mn1—N1	93.44 (7)	C3—C2—C1	131.4 (2)
O1W ⁱ —Mn1—N1	100.34 (7)	N1—C2—C1	118.98 (18)
O1 ⁱ —Mn1—N1	168.96 (6)	N1—C4—N2	111.4 (2)
O1—Mn1—N1	75.97 (7)	N1—C4—H4	124.3
O1W—Mn1—N1 ⁱ	100.34 (7)	N2—C4—H4	124.3
O1W ⁱ —Mn1—N1 ⁱ	93.44 (7)	C2—C3—N2	105.9 (2)
O1 ⁱ —Mn1—N1 ⁱ	75.96 (7)	C2—C3—H3	127.1
O1—Mn1—N1 ⁱ	168.97 (6)	N2—C3—H3	127.1
N1—Mn1—N1 ⁱ	94.70 (10)	C1—O1—Mn1	116.82 (14)
C4—N1—C2	105.38 (19)	Mn1—O1W—H1WA	113.7
C4—N1—Mn1	143.43 (17)	Mn1—O1W—H1WB	128.2
C2—N1—Mn1	111.19 (14)	H1WA—O1W—H1WB	101.3

C4—N2—C3	107.8 (2)		
O1W—Mn1—N1—C4	-95.6 (3)	O1—C1—C2—N1	3.7 (3)
O1W ⁱ —Mn1—N1—C4	99.5 (3)	O2—C1—C2—N1	-175.9 (2)
O1 ⁱ —Mn1—N1—C4	-26.7 (5)	C2—N1—C4—N2	1.0 (3)
O1—Mn1—N1—C4	179.1 (3)	Mn1—N1—C4—N2	-178.4 (2)
N1 ⁱ —Mn1—N1—C4	5.1 (3)	C3—N2—C4—N1	-0.8 (3)
O1W—Mn1—N1—C2	85.01 (16)	N1—C2—C3—N2	0.3 (3)
O1W ⁱ —Mn1—N1—C2	-79.94 (16)	C1—C2—C3—N2	-179.3 (2)
O1 ⁱ —Mn1—N1—C2	153.9 (3)	C4—N2—C3—C2	0.3 (3)
O1—Mn1—N1—C2	-0.28 (15)	O2—C1—O1—Mn1	175.69 (16)
N1 ⁱ —Mn1—N1—C2	-174.31 (19)	C2—C1—O1—Mn1	-3.9 (2)
C4—N1—C2—C3	-0.8 (3)	O1W—Mn1—O1—C1	-92.12 (16)
Mn1—N1—C2—C3	178.83 (16)	O1W ⁱ —Mn1—O1—C1	105.01 (16)
C4—N1—C2—C1	178.8 (2)	O1 ⁱ —Mn1—O1—C1	-172.39 (18)
Mn1—N1—C2—C1	-1.5 (2)	N1—Mn1—O1—C1	2.38 (16)
O1—C1—C2—C3	-176.7 (2)	N1 ⁱ —Mn1—O1—C1	35.2 (4)
O2—C1—C2—C3	3.7 (3)		

Symmetry code: (i) $-x+3/2, -y+3/2, z$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...O2 ⁱⁱ	0.86	1.95	2.811 (3)	173
O1W—H1WA...O2 ⁱⁱⁱ	0.87	1.96	2.818 (2)	167
O1W—H1WB...O2 ^{iv}	0.73	2.02	2.751 (2)	176

Symmetry codes: (ii) $-x+1/2, y, z-1/2$; (iii) $-x+1, y-1/2, -z+3/2$; (iv) $-x+1/2, -y+3/2, z$.