

trans-Diaquabis(1*H*-imidazole-4,5-dicarboxylate- κ^2N^3,O^4)manganese(II)

Chengbing Ma, Feng Chen, Changneng Chen and Qiutian Liu*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou, Fujian, 350002, People's Republic of China
Correspondence e-mail: lqt@ms.fjirsm.ac.cn

Received 14 October 2003

Accepted 22 October 2003

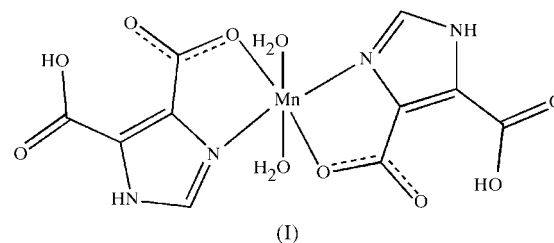
Online 8 November 2003

In the title compound, $[\text{Mn}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$, the Mn^{II} atom lies on an inversion centre, is *trans*-coordinated by two *N,O*-bidentate 1*H*-imidazole-4,5-dicarboxylate monoanionic ligands [$\text{Mn}-\text{O} = 2.202$ (3) Å and $\text{Mn}-\text{N} = 2.201$ (4) Å] and two water molecules [$\text{Mn}-\text{O} = 2.197$ (4) Å], and exhibits a distorted octahedral geometry, with adjacent *cis* angles of 76.45 (13), 86.09 (13) and 89.20 (13)°. The complete solid-state structure can be described as a three-dimensional supramolecular framework, stabilized by extensive hydrogen-bonding interactions involving the coordinated water molecules, the carboxy O atoms and the protonated imidazole N atoms of the imidazole-4,5-dicarboxylate ligands.

Comment

It is well established that manganese is one of the trace elements in biosystems and it plays an important role in the active sites of various redox-based enzymes (Weighardt, 1989). In addition to the well known oxygen-evolving complex, which is generally believed to contain a tetranuclear manganese cluster catalyzing the oxidation of water to yield O_2 during photosynthesis (Debus, 1992), there are three known enzymes containing a mononuclear manganese site, *viz.* superoxide dismutase, peroxidase and dioxygenase, which participate in the redox changes of biological systems (Law *et al.*, 1999). In order to better understand the exact nature and mechanism of action of these active sites, *N,O*-containing ligands are often employed to prepare model compounds, based on the knowledge that the coordination sphere of the Mn centres in these enzymes are dominated by *N,O*-donors from available amino acid residues (Pecoraro & Butler, 1986). In the course of our studies of manganese biochemistry, we have investigated manganese complexation by imidazole-4,5-dicarboxylic acid (H_3ida), considering that it possesses the biologically important imidazole ring, which is known as a functional group of histidine, and potentially versatile bonding modes with the metal ion. We report here the single-crystal structure of a new compound, (I), in which the H_2ida monoanion

coordinates to the Mn atom, acting as a bidentate ligand. The coordination mode of the ligand exhibited in (I) is unique and has not been reported previously in other manganese-imidazole-4,5-dicarboxylate complexes.



As shown in Fig. 1, the molecule of (I) is a discrete neutral monomer, in which the Mn atom resides on a crystallographic inversion centre and the asymmetric unit contains one-half of the $[\text{Mn}(\text{H}_2\text{ida})_2(\text{H}_2\text{O})_2]$ formula unit. The octahedral sphere on the manganese(II) centre is highly distorted because of the *N,O*-chelation of the rigid H_2ida ligand (Table 1), with the *cis* angles [76.45 (13)–103.55 (13)°] deviating significantly from the ideal value of 90°.

The Mn atom, atoms O1 and N2, and the inversion-related *O/N*-atom pair are strictly coplanar as a result of the Mn atom lying on the inversion centre. The two O atoms of the symmetry-related water molecules complete the octahedral coordination. The Mn–O5 distance (Table 1) is comparable to those in Mn^{II} -water complexes (Okabe & Koizumi, 1997; Hao *et al.*, 2000; Ma *et al.*, 2002; Schlueter & Geiser, 2003).

The H_2ida ligand adopts a bidentate coordination mode to the Mn atom through one imidazole N atom and one O atom from one deprotonated carboxy group; the other carboxy group is protonated, as indicated by the significant difference between the O3–C5 [1.321 (6) Å] and O4–C5 [1.204 (6) Å] bond lengths. This type of binding mode is different from those found in the previously reported Mn complexes $[\text{Mn}(\text{salen})(\text{H}_2\text{ida})(\text{H}_2\text{O})]$ (Huang *et al.*, 2001) and $[\text{Mn}_2(\text{salpn})_2(\text{ida})]^+$ (Caudle *et al.*, 1997). The N2–Mn–O1 angle is 76.45 (13)°, and the Mn–N2 and Mn–O1 (H_2ida) bond lengths [2.201 (4) and 2.202 (3) Å, respectively] are comparable to those reported in Mn complexes similar to the title compound, with the formula $[\text{MnL}_2(\text{H}_2\text{O})_2]$ [*L* is an *N*-hetero aromatic acid, *e.g.* pyridine-2,5-dicarboxylate (Goher & Mak, 1994) or pyridine-2-carboxylate (Okabe & Koizumi, 1998)]. All non-H atoms in the H_2ida ligand are nearly coplanar [the mean deviation is 0.090 (9) Å], with the maximum deviation

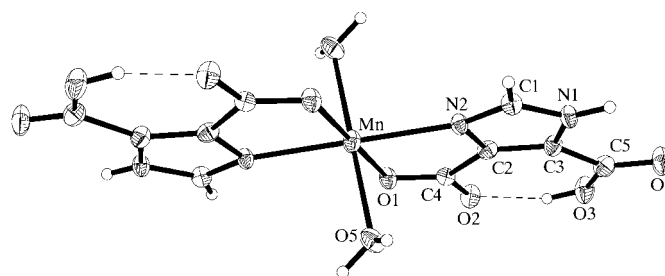


Figure 1

A view of the molecule of (I), showing the atom-labelling scheme and displacement ellipsoids at the 30% probability level.

of 0.196 (3) Å for atom O1 being the result of a hydrogen-bonding interaction involving atoms O1 and O5.

As listed in Table 2, N1—H1 \cdots O3($x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$) hydrogen bonds link the molecules, thus generating a two-dimensional hydrogen-bonded sheet (Fig. 2). These sheets are

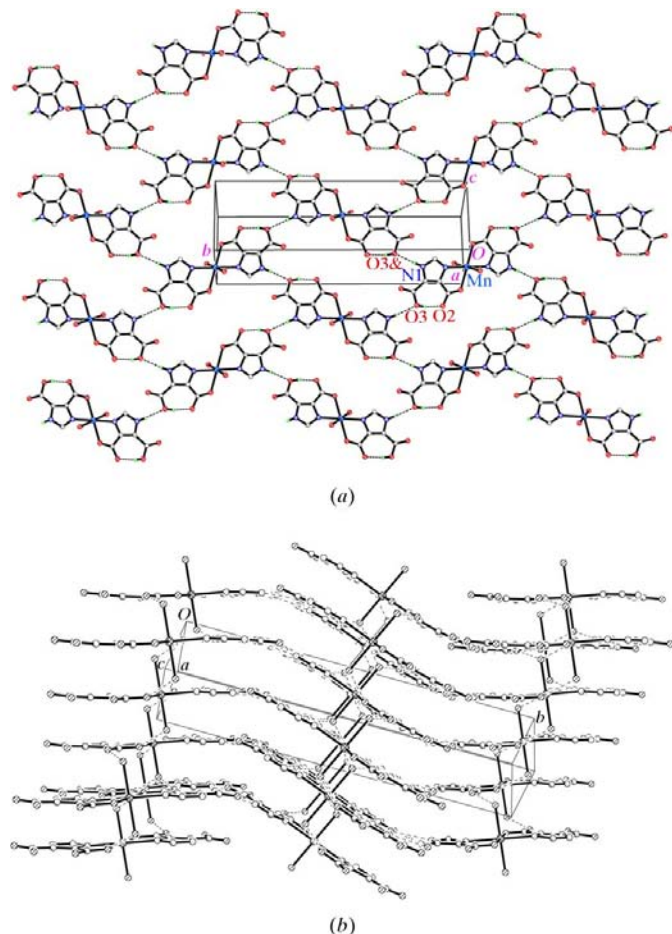


Figure 2
The crystal packing of (I), showing (a) part of the two-dimensional hydrogen-bonding network [atoms labelled with an ampersand (&) are at the symmetry position ($x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$)] and (b) the hydrogen-bonded three-dimensional stacked-layer network.

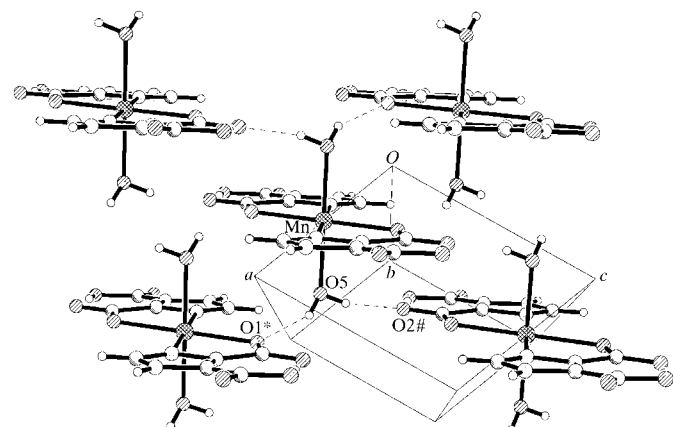


Figure 3
The centrosymmetric pentamers produced by the coordinated water molecules of (I). Atoms labelled with an asterisk (*) or a hash (#) are at the symmetry positions ($-x + 2, -y, -z$) and ($x, y, z + 1$), respectively.

further linked *via* pairs of hydrogen bonds involving the coordinated water O atoms and two carboxy O atoms (O1 and O2) of symmetry-related monomers. Each of the monomers in one sheet is further connected to four monomers belonging to the two symmetry-related sheets above and below, thus generating centrosymmetric pentamers (Fig. 3) and giving rise to an overall three-dimensional hydrogen-bonded network.

Experimental

To a refluxing suspension of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.40 g, 2 mmol) and H_3id a (0.31 g, 2 mmol) in water (50 ml), NaOH (0.1 M) was added dropwise, *via* a dropping funnel, under continuous stirring until the mixture became clear. The mixture was refluxed and stirred for a further 8 h. The resulting hot solution was filtered and the filtrate was left undisturbed for 4 h at room temperature, resulting in the deposition of pale-yellow crystals of (I).

Crystal data

$[\text{Mn}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$
 $M_r = 401.16$
 Monoclinic, $P2_1/n$
 $a = 5.0550$ (3) Å
 $b = 22.9305$ (7) Å
 $c = 6.5918$ (4) Å
 $\beta = 111.596$ (2)°
 $V = 710.44$ (6) Å³
 $Z = 2$

$D_x = 1.875$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1282 reflections
 $\theta = 1.8$ – 25.0 °
 $\mu = 1.00$ mm⁻¹
 $T = 293$ (2) K
 Needle, pale yellow
 $0.49 \times 0.15 \times 0.14$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.836, T_{\max} = 0.870$
 2152 measured reflections

1216 independent reflections
 852 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
 $\theta_{\text{max}} = 25.0$ °
 $h = -6 \rightarrow 5$
 $k = -14 \rightarrow 27$
 $l = -7 \rightarrow 7$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.156$
 $S = 1.01$
 1216 reflections
 126 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.08P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.74$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.13$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Mn—O5	2.197 (4)	O2—C4	1.255 (5)
Mn—N2	2.201 (4)	O3—C5	1.321 (6)
Mn—O1	2.202 (3)	O4—C5	1.204 (6)
O1—C4	1.261 (6)		
O5—Mn—N2	86.09 (14)	N2—Mn—O1	76.45 (13)
O5—Mn—O1	89.20 (13)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5B \cdots O1 ⁱ	0.86 (4)	1.95 (4)	2.733 (5)	151 (5)
O5—H5A \cdots O2 ⁱⁱ	0.84 (5)	1.94 (5)	2.770 (5)	165 (5)
N1—H1 \cdots O3 ⁱⁱⁱ	0.86	2.05	2.895 (5)	169
O3—H3 \cdots O2	0.85 (5)	1.69 (3)	2.515 (5)	163 (8)

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

Water H atoms and the carboxylic acid H atom were located from difference maps and refined with a DFIX restraint of 0.85 (2) Å applied to the three O—H distances. Aromatic H atoms were placed in calculated positions and treated as riding atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1994); data reduction: *XPREF* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

This work was supported by the NNSFC (grant Nos. 30170229 and 29973047), the State Key Basic Research and Development Plan of China (grant No. G1998010100) and the Expert Project of Key Basic Research from the Ministry of Science and Technology, People's Republic of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1711). Services for accessing these data are described at the back of the journal.

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