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Aqua(dipicolinato-κ^3O^2,N,O^6)-(1,10-phenanthroline-κ^2N,N')-manganese(II) monohydrate

Chengbing Ma, Cheng Fan, 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

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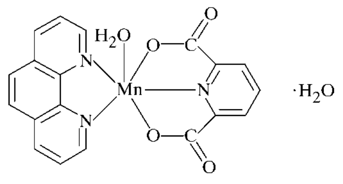
In the title compound [systematic name: aqua(1,10-phenanthroline-κ^2N,N')(pyridine-2,6-dicarboxylato-κ^3O^2,N,O^6)-manganese(II) monohydrate, $[Mn(C_7H_3NO_4)(C_{12}H_8N_2)(H_2O)]\cdot H_2O$, the manganese(II) centre is surrounded by one bidentate phenanthroline ligand [Mn—N = 2.248 (3) and 2.278 (3) Å], one tridentate dipicolinate ligand [Mn—N = 2.179 (3) Å, and Mn—O = 2.237 (2) and 2.266 (2) Å] and one water molecule [Mn—O = 2.117 (3) Å], and it exhibits a strongly distorted octahedral geometry, with *trans* angles ranging from 144.12 (9) to 158.88 (11)°. Extensive intermolecular hydrogen-bonding interactions involving coordinated and uncoordinated water molecules and the carboxyl O atoms of the dipicolinate ligand, as well as a stacking interaction involving the phenanthroline rings, are observed in the crystal structure.

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 best known oxygen-evolving complex, which is believed to contain a tetranuclear manganese cluster catalyzing the oxidation of water to yield O_2 during photosynthesis (Debus, 1992), there are three enzymes containing a mononuclear Mn site, *viz*. superoxide dismutase, peroxidase and dioxygenase, which participate in the redox changes of biological systems (Law *et al.*, 1999). Based on the knowledge that the coordination sphere of the Mn centres in these enzymes is dominated by N,O-donors from available amino acid residues (Pecoraro & Butler, 1986), N,O-containing ligands are often employed to prepare model compounds for the better understanding of their exact nature and mechanism of action. As part of our systematic study of manganese chemistry, we have selected dipicolinic acid as the primary ligand to react with Mn^{2+} salts containing diimine ligands. Dipicolinic acid possesses versatile yet unpredictable coordination modes (Herring *et al.*, 1991; Quaglieri *et al.*, 1972; Starynowicz, 1992; Lawrence & Tuyetha, 2000) and diverse biological activities (Church & Halvorson, 1959; Chung *et al.*, 1971; Scapin *et al.*, 1997), and we obtained the title compound, (I), which represents a new example of a mononuclear manganese complex with mixed ligands.



(I)

Compound (I) (Fig. 1) consists of a neutral [Mn(dpc)-(phen)(H_2O)] unit (dpc is dipicolinate and phen is phenanthroline) and one solvate water molecule. The octahedral sphere on the Mn centre is severely distorted because of the chelation of the two rigid planar ligands, *i.e.* phen and dpc (Table 1). The mean Mn—N(phen) bond length [2.263 (15) Å] is in agreement with that reported in other Mn–phen complexes, *e.g.* in $[Mn(phen)(H_2O)_4]^{2+}$ [2.263 (9) Å; Ma *et al.*, 2002], and the N1—Mn—N2 phen chelate angle of 73.50 (1)° is as expected for Mn complexes (Drew *et al.*, 1989; McCann *et al.*, 1997; Ramalakshmi *et al.*, 1999; Wang *et al.*, 2000; Deng *et al.*, 2000).

The Mn—N3 distance of 2.179 (3) Å, significantly shorter than the two Mn—N(phen) distances, indicates that N3 is a stronger donor, since the two carboxylate groups in *ortho* positions enhance the electron density on N3. The average Mn—O(dpc) distance [2.252 (15) Å] and the dpc chelate angles are comparable with those found in other Mn complexes (Limburg *et al.*, 1997; Chandra *et al.*, 1992; Okabe & Oya, 2000). The phen ligand is reasonably planar, with a mean deviation of 0.044 (1) Å, and bond distances and angles are consistent with those in the free base (Nishigaki *et al.*, 1978). All atoms in the dpc ligand are also nearly coplanar, with a maximum deviation of 0.075 (1) Å for O2. The dihedral angle between the phen and dpc planes is 81.5 (1)°.

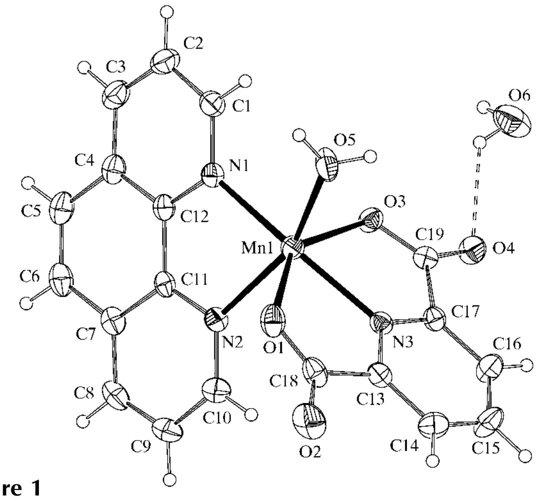


Figure 1
A view of the molecule of (I), showing the atomic labelling scheme and 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

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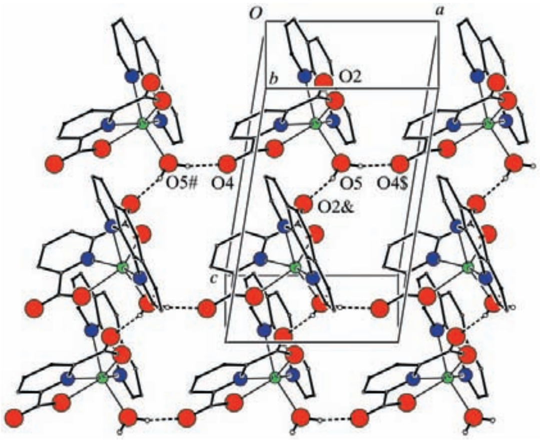

Figure 2
A packing diagram for (I), showing part of the two-dimensional hydrogen-bonded network. Atoms labelled with a hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(x-1, y, z)$, $(1+x, y, z)$ and $(x, \frac{3}{2}-y, \frac{1}{2}+z)$, respectively.

As listed in Table 2, two normal hydrogen bonds link the coordinated water molecule (O5) and two carboxyl O atoms (O2 and O4) of symmetry-related molecules to generate a two-dimensional network sheet (Fig. 2). Two weaker hydrogen bonds link the uncoordinated water molecule to carboxyl atom O4 and to a symmetry-related carboxyl atom O3 to generate centrosymmetric dimers (Fig. 3), and give rise to an overall three-dimensional hydrogen-bonded network. In addition, there are π–π-stacking interactions between inversion-related phen ligands along the *a* direction (Fig. 4), with perpendicular ring separations of 3.455 (2) and 3.405 (6) Å, which are comparable with the sum of the van der Waals contact radii for two C atoms (3.4 Å; Bondi, 1964).

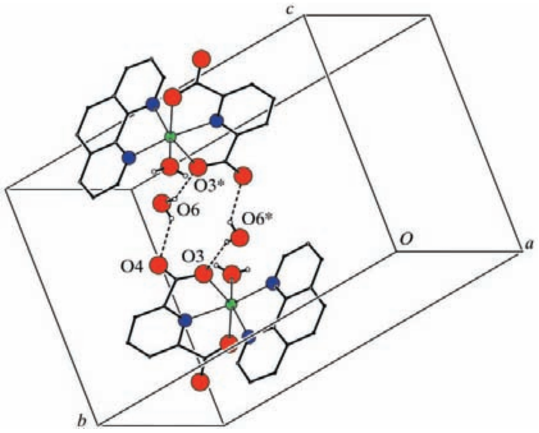

Figure 3
A view of the centrosymmetric dimer produced by the lattice water molecules of (I). Atoms labelled with an asterisk (*) are at the symmetry position $(-x, 1-y, 1-z)$.

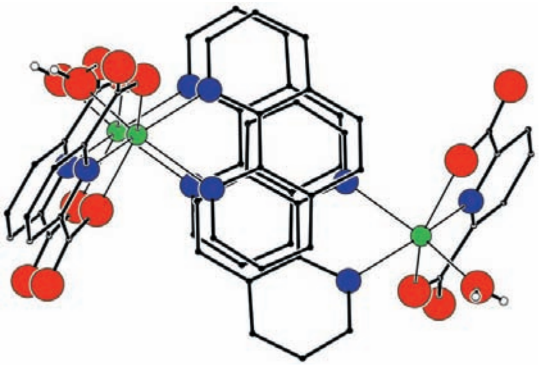

Figure 4
A view of some of the π–π-stacking interactions in (I).

Experimental

To an EtOH–H_2O solution (30 ml, *ca* 1:1 *v*/*v*) containing $MnCl_2\cdot4H_2O$ (1 mmol) and disodium dipicolinate (2 mmol), 1,10-phenanthroline (1 mmol) was added slowly with continuous stirring. The resulting solution was refluxed for 1 h and then filtered. The yellow filtrate was allowed to stand for 21 d at room temperature, after which time yellow crystals of (I) suitable for X-ray diffraction analysis were obtained.

Crystal data

$[Mn(C_7H_3NO_4)(C_{12}H_8N_2)(H_2O)]\cdot H_2O$
$M_r = 436.28$
Monoclinic, $P2_1/c$
$a = 7.6006$ (6) Å
$b = 21.1600$ (16) Å
$c = 11.4733$ (9) Å
$\beta = 98.916$ (1)°
$V = 1822.9$ (2) Å^3
$Z = 4$
$D_x = 1.590$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2918 reflections
$\theta = 1.9$–25.1°
$\mu = 0.77$ mm^{-1}
$T = 293$ (2) K
Needle, yellow
0.59 × 0.20 × 0.16 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.630$, $T_{max} = 0.880$
6177 measured reflections
3198 independent reflections
2264 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 25.1$°
$h = -8 \rightarrow 9$
$k = -21 \rightarrow 25$
$l = -13 \rightarrow 9$

Table 1
Selected geometric parameters (Å, °).

Mn—N1	2.248 (3)	Mn—O1	2.237 (2)
Mn—N2	2.278 (3)	Mn—O3	2.266 (2)
Mn—N3	2.179 (3)	Mn—O5	2.117 (3)
O5—Mn—N3	103.07 (11)	O1—Mn—O3	144.12 (9)
O5—Mn—O1	91.54 (12)	N1—Mn—O3	88.09 (9)
N3—Mn—O1	72.79 (10)	O5—Mn—N2	158.88 (11)
O5—Mn—N1	91.65 (12)	N3—Mn—N2	96.20 (10)
N3—Mn—N1	155.45 (10)	O1—Mn—N2	85.93 (10)
O1—Mn—N1	127.03 (10)	N1—Mn—N2	73.50 (10)
O5—Mn—O3	94.88 (10)	O3—Mn—N2	99.43 (9)
N3—Mn—O3	71.36 (9)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*B*···O2^{i}	0.83 (4)	1.81 (2)	2.605 (4)	160 (4)
O5—H5*C*···O4^{ii}	0.88 (4)	1.83 (4)	2.699 (4)	168 (4)
O6—H6*B*···O4	0.85 (5)	2.20 (4)	2.845 (4)	133 (5)
O6—H6*C*···O3^{iii}	0.84 (2)	2.20 (4)	2.962 (4)	152 (6)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.125$
$S = 1.03$
3198 reflections
278 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}

H atoms bonded to C atoms were placed in calculated positions, with C—H distances of 0.93 Å, and treated as riding atoms. Water H-atom coordinates were located from difference maps and refined isotropically; the four O—H distances involving the water molecules were refined with a *DFIX* restraint of 0.85 (2) Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1665). Services for accessing these data are described at the back of the journal.

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