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catena-Poly[[[aqua(1,10-phenanthroline)-manganese(II)]-μ-*endo*-norbornene-*cis*-5,6-dicarboxylato] monohydrate]

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.040
wR factor = 0.099
Data-to-parameter ratio = 12.9

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

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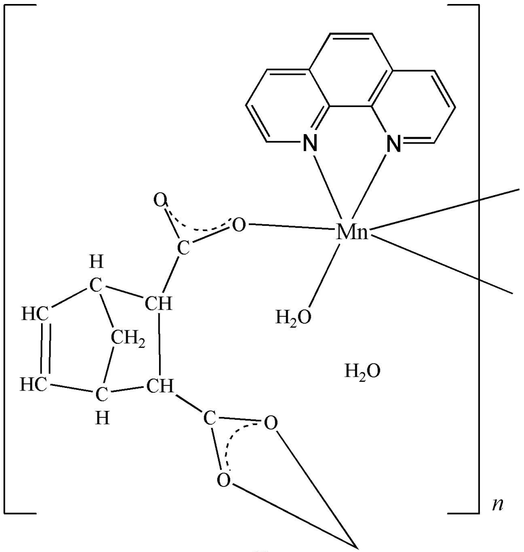
In the title compound, $\{[Mn(endc)(phen)(H_2O)]\cdot H_2O\}_n$ [phen is 1,10-phenanthroline ($C_{12}H_8N_2$) and endc is the *endo*-norbornene-*cis*-5,6-dicarboxylate anion ($C_9H_8O_4$)], each Mn^{II} ion is surrounded by two N atoms from a phen ligand, four O atoms from water molecules and two carboxylate groups of two endc anions, with one endc carboxylate group coordinating in a monodentate fashion and the other in a chelating fashion, forming a distorted MnO_4N_2 octahedron. The endc anions act as bridges between Mn^{II} ions, resulting in a zigzag chain structure along the [010] axis.

Comment

Carboxylate anions can coordinate to metal ions in versatile binding modes, such as monodentate, chelating bidentate, bridging bidentate and bridging tridentate, generating varied and sometimes surprising molecular architectures (Zhang *et al.*, 1990). Numerous complexes with carboxylate anions have been extensively studied (Hu *et al.*, 2003, 2004; Wang *et al.*, 2003), but only three Mn complexes including *endo*-norbornene-*cis*-5,6-dicarboxylate anions (endc) have been characterized to date (Hartung *et al.*, 1993; Devereux *et al.*, 1995; Baumeister & Hartung, 1997). Thus, we have selected the Mn–endc–phen system (phen is 1,10-phenanthroline) in order to extend this research and we present here the crystal structure of the title compound, namely $[Mn(endc)(phen)(H_2O)]\cdot H_2O$, (I).



(I)

In the polymeric structure of (I), the Mn centre possesses a distorted octahedral geometry (Fig. 1 and Table 1). The equatorial plane consists of one phen N atom, one carboxylate

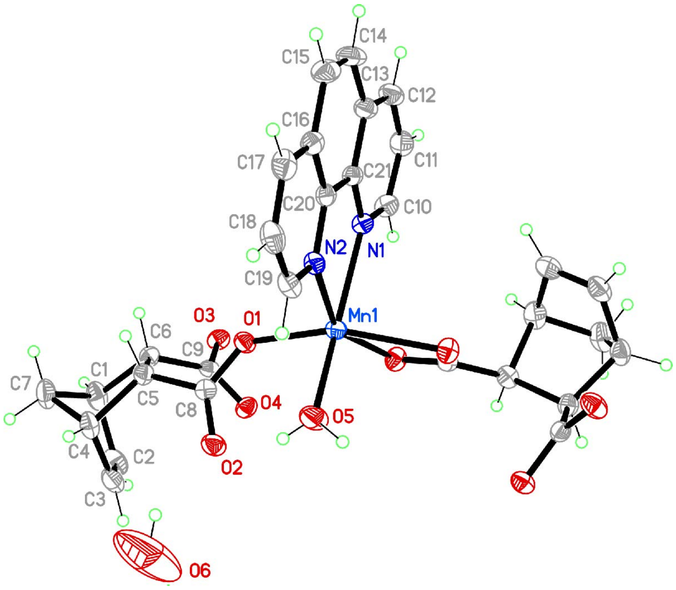


Figure 1
The coordination environment of the Mn^{II} ion in (I), with the atom numbering for the asymmetric unit, showing displacement ellipsoids at the 30% probability level. Unlabelled atoms are related by the symmetry operator ($1 - x, y - \frac{1}{2}, \frac{1}{2} - z$).

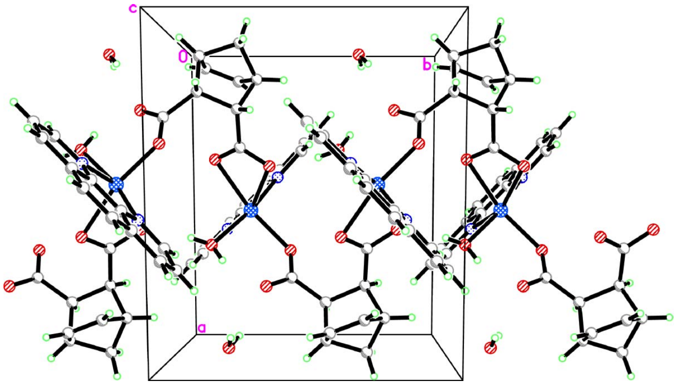


Figure 2
The zigzag chain structure of (I), viewed along the c axis.

O atom from an endc anion and two carboxylate O atoms from another symmetry-related endc anion, while the two axial sites are occupied by an aqua O atom and the other phen N atom. The equatorial plane N2/O1/O3^{i}/O4^{i} [symmetry code: (i) $1 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$] is seriously distorted, with an r.m.s. deviation of 0.233 Å. The interaxial O5—Mn1—N1 angle [160.44 (7)°] is also distorted.

The two carboxylate functionalities of each endc anion show different coordination modes: one is chelating bidentate, the other is monodentate. Moreover, each endc anion acts as a bridge to link two adjacent Mn^{II} ions, with an Mn$\cdots$Mn^{i} separation of 5.6983 (10) Å [symmetry code: (i) $1 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$], forming a zigzag chain structure along the [010] axis (Fig. 2).

In the crystal structure, O—H$\cdots$O hydrogen-bond interactions strengthen the above-mentioned zigzag chains (Table 2).

Experimental

The title compound was synthesized by the hydrothermal method using a mixture of 1,10-phenanthroline (2 mmol, 0.36 g), $MnCl_2 \cdot 2H_2O$ (1 mmol, 0.16 g), *endo*-norbornene-*cis*-5,6-dicarboxylic acid (1 mmol, 0.18 g) and water (20 ml) in a 30 ml Teflon-lined stainless steel reactor. The solution was heated to 432 K for 4 d. After slow cooling of the reaction system to room temperature, pink block crystals of (I) were collected and washed with distilled water.

Crystal data

$[Mn(C_9H_8O_4)(C_{12}H_8N_2)(H_2O)] \cdot H_2O$
$M_r = 451.33$
Monoclinic, $P2_1/c$
$a = 10.941$ (3) Å
$b = 9.135$ (2) Å
$c = 20.013$ (4) Å
$\beta = 103.605$ (4)°
$V = 1944.1$ (8) Å^3
$Z = 4$
$D_x = 1.542$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4067 reflections
$\theta = 2.5$–24.9°
$\mu = 0.72$ mm^{-1}
$T = 298$ (2) K
Block, pink
0.27 × 0.23 × 0.21 mm

Data collection

Bruker APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.829$, $T_{max} = 0.863$
9928 measured reflections
3501 independent reflections
3002 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 25.3$°
$h = -13 \rightarrow 9$
$k = -9 \rightarrow 10$
$l = -24 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.099$
$S = 1.07$
3501 reflections
271 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.9627P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	2.0992 (16)	Mn1—O4^{i}	2.3015 (16)
Mn1—O5	2.1384 (18)	Mn1—N1	2.3045 (19)
Mn1—O3^{i}	2.2165 (17)	Mn1—Mn1^{i}	5.6983 (10)
Mn1—N2	2.2633 (19)		
O1—Mn1—O5	86.91 (7)	O3^{i}—Mn1—O4^{i}	57.73 (6)
O1—Mn1—O3^{i}	98.63 (6)	N2—Mn1—O4^{i}	101.98 (6)
O5—Mn1—O3^{i}	108.27 (7)	O1—Mn1—N1	103.44 (6)
O1—Mn1—N2	104.11 (7)	O5—Mn1—N1	160.44 (7)
O5—Mn1—N2	88.88 (8)	O3^{i}—Mn1—N1	86.83 (7)
O3^{i}—Mn1—N2	152.23 (7)	N2—Mn1—N1	72.62 (7)
O1—Mn1—O4^{i}	153.64 (6)	O4^{i}—Mn1—N1	87.83 (6)
O5—Mn1—O4^{i}	89.91 (7)		

Symmetry code: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
O5—H5$A\cdots$O2	0.82	1.91	2.666 (2)	152
O5—H5$B\cdots$O3^{ii}	0.82	1.87	2.677 (2)	169
O6—H6$A\cdots$O2	0.82	2.06	2.773 (4)	145

Symmetry code: (ii) $x, y - 1, z$.

Water H atoms were found in difference maps and regularized using the restraints O—H = 0.820 (1) Å and H···H = 1.39 (1) Å. In the final cycles of refinement, these H atoms were constrained to ride on their parent O atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom). H atoms bonded to C atoms were positioned geometrically and allowed to ride on their parent atoms at distances of C*sp*^{2}—H = 0.93 Å with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom), C*sp*^{3}—H = 0.97 Å with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(parent atom) for methylene H, and C*sp*^{3}—H = 0.98 Å with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(parent atom) for methine H.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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