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Aqua(4-hydroxybenzoato-κO)bis(1,10-phenanthroline-$\kappa^2 N,N'$)manganese(II) 4-hydroxybenzoate monohydrate

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The title compound, $[Mn(C_7H_5O_3)(C_{12}H_8N_2)_2(H_2O)](C_7H_5O_3)\cdot H_2O$, consists of Mn^{II} complex cations, 4-hydroxybenzoate anions and uncoordinated water molecules. The Mn^{II} complex cation assumes a distorted octahedral coordination geometry formed by two 1,10-phenanthroline (phen) ligands, one 4-hydroxybenzoate anion and a water molecule. The face-to-face distances of 3.39 (2) and 3.364 (12) Å between partially overlapped parallel phen ligands suggest the existence of π–π stacking between neighboring complex cations.

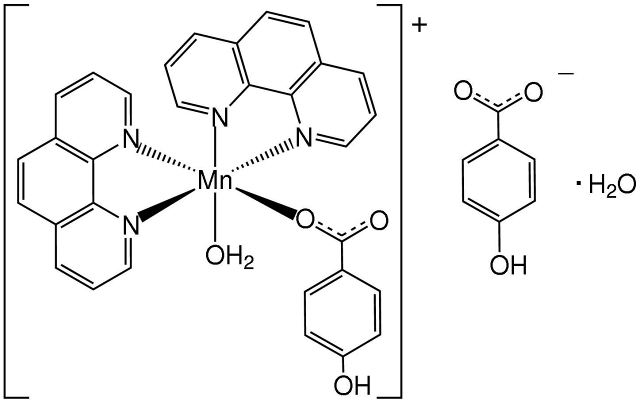
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.046
wR factor = 0.088
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.

Comment

The π–π stacking interaction has attracted much scientific attention because it is correlated with electron transfer in some biological systems (Deisenhofer & Michel, 1989). In order to study further the nature of π–π stacking, a series of metal complexes incorporating aromatic ligands have been synthesized, and their crystal structures have been determined in our laboratory (Su *et al.*, 2005; Li *et al.*, 2005). As part of this ongoing work, the title compound, (I) (Fig. 1), has been prepared and structurally characterized.



(I)

The crystal structure of (I) contains Mn^{II} complex cations, 4-hydroxybenzoate anions and uncoordinated water molecules. The Mn^{II} ion displays a distorted octahedral MnN_4O_2 coordination geometry (Table 1), involving two bidentate phen ligands, one monodentate 4-hydroxybenzoate anion and a coordinated water molecule. The uncoordinated carboxy atom O32 is intramolecularly hydrogen bonded to the coordinated water molecule (Fig. 1 and Table 2). The coordinated carboxyl O31 and water O1 atoms are in *cis* positions, while the two phen ligands are nearly perpendicular to each other, with a dihedral angle of 75.59 (3)°.

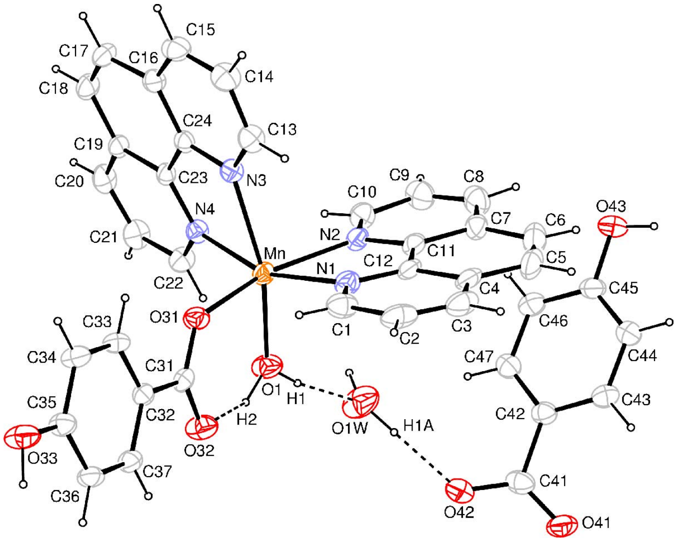


Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids (arbitrary spheres for the H atoms) and with dashed lines showing the hydrogen bonding.

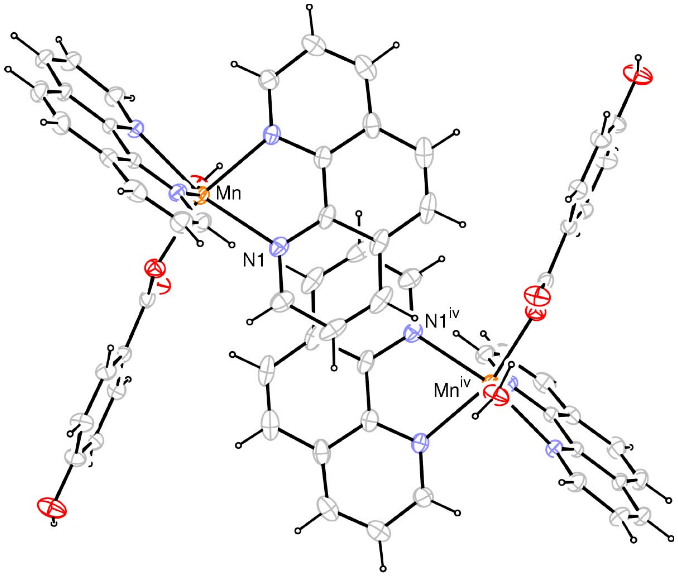


Figure 2
π–π stacking between parallel N1-phen and N1^{iv}-phen groups of neighboring Mn^{II} complex cations. [Symmetry code: (iv) $1 - x, 1 - y, -z$.]

The π–π stacking interactions occur between parallel 1,10-phenanthroline (phen) ligands of neighboring Mn^{II} complex cations. The parallel N1-phen and N1^{iv}-phen [symmetry code: (iv) $1 - x, 1 - y, -z$] species overlap one another, as shown in Fig. 2. The face-to-face distance between py rings is 3.39 (2) Å. Another parallel N4-phen–N4^{v}-phen [symmetry code: (v) $1 - x, 1 - y, 1 - z$] overlap is shown in Fig. 3; the face-to-face distance between these ligands is 3.364 (12) Å.

The uncoordinated (O1*W*) water molecules link neighboring Mn^{II} complex cations and uncoordinated 4-hydroxybenzoate anions *via* O1—H1···O1*W*, O1*W*—H1*A*···O42 (Fig. 1) and O1*W*—H1*B*···O33^{i} (see Table 2 for symmetry code) hydrogen bonds, to form an extended structure. Intermolecular hydrogen bonding also occurs between uncoordinated 4-hydroxybenzoate anions and between Mn^{II} complex cations and uncoordinated 4-hydroxybenzoate anions (Table 2).

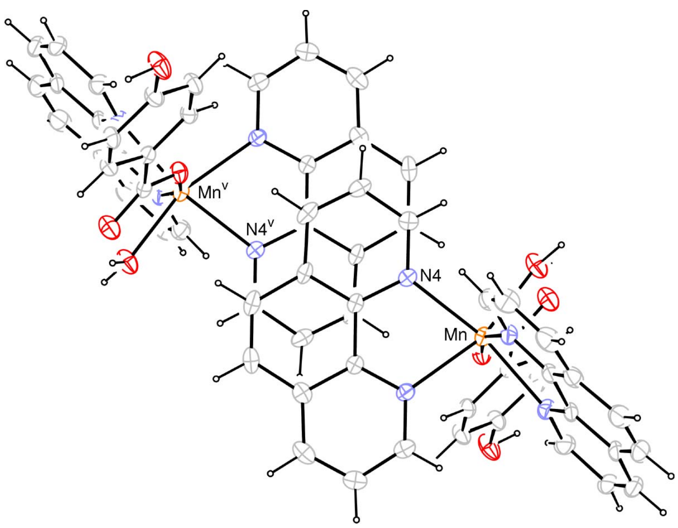


Figure 3
π–π stacking between parallel N4-phen and N4^{v}-phen groups of neighboring Mn^{II} complex cations. [Symmetry code: (v) $1 - x, 1 - y, 1 - z$.]

Experimental

All reagents were commercially available and of analytical grade. $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.25 g, 1 mmol), 4-hydroxybenzoic acid (0.14 g, 1 mmol), phen (0.20 g, 1 mmol) and Na_2CO_3 (0.05 g, 1 mmol) were dissolved in a water/ethanol solution (20 ml, 1:1). The solution was refluxed for 3 h, then cooled to room temperature and filtered. Yellow single crystals of (I) were obtained from the filtrate after 4 d.

Crystal data

$[Mn(C_7H_5O_3)(C_{12}H_8N_2)_2(H_2O)]$-$(C_7H_5O_3) \cdot H_2O$
$M_r = 725.60$
Monoclinic, $P2_1/n$
$a = 8.4429$ (2) Å
$b = 24.1805$ (6) Å
$c = 17.0825$ (4) Å
$\beta = 103.495$ (7)°
$V = 3391.17$ (17) Å^3
$Z = 4$

$D_x = 1.421$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 10 848 reflections
$\theta = 2.6$–24.6°
$\mu = 0.45$ mm^{-1}
$T = 295$ (3) K
Platelet, yellow
0.20 × 0.20 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.916$, $T_{max} = 0.979$
22 265 measured reflections

5716 independent reflections
3936 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 25.0°$
$h = -9 \rightarrow 10$
$k = -27 \rightarrow 28$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.088$
$S = 1.03$
5716 reflections
460 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 2.0463P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

m940 Su et al. • $[Mn(C_7H_5O_3)(C_{12}H_8N_2)_2(H_2O)](C_7H_5O_3) \cdot H_2O$ Acta Cryst. (2005). E61, m939–m941

Table 1
Selected geometric parameters (Å, °).

Mn—O1	2.1471 (19)	Mn—N4	2.276 (2)
Mn—O31	2.1054 (17)	C31—O31	1.276 (3)
Mn—N1	2.284 (2)	C31—O32	1.249 (3)
Mn—N2	2.265 (2)	C41—O41	1.243 (4)
Mn—N3	2.263 (2)	C41—O42	1.260 (4)
O1—Mn—O31	87.31 (7)	O31—Mn—N4	103.87 (7)
O1—Mn—N1	103.17 (8)	N1—Mn—N2	73.54 (8)
O1—Mn—N2	91.81 (8)	N1—Mn—N3	94.34 (8)
O1—Mn—N3	162.37 (8)	N1—Mn—N4	161.26 (8)
O1—Mn—N4	90.58 (8)	N2—Mn—N3	95.22 (7)
O31—Mn—N1	89.62 (8)	N2—Mn—N4	93.62 (8)
O31—Mn—N2	162.49 (8)	N3—Mn—N4	72.87 (8)
O31—Mn—N3	90.73 (7)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O1*W*	0.92	1.75	2.661 (3)	171
O1*W*—H1*A*···O42	0.93	1.88	2.808 (3)	174
O1*W*—H1*B*···O33^{i}	0.98	2.09	3.069 (3)	174
O33—H33···O41^{ii}	0.91	1.68	2.565 (3)	163
O43—H43···O42^{iii}	0.96	1.83	2.636 (3)	139

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

H atoms on the aromatic rings were placed in calculated positions, with C—H = 0.93 Å, and refined as riding, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier). H atoms of the water and hydroxy groups were located in a difference Fourier map and refined as riding in their as-found relative positions (O—H = 0.92–0.98 Å), with a fixed isotropic displacement parameter of 0.08 Å.

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku Corporation, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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