

Gui-Quan Guo,^a Fu-Ping Chen,^b
Xian-Wen Wang,^{b*} Bo Hu^b and
Jing-Zhong Chen^b^aDepartment of Chemistry, Anyang Normal University, Anyang, Henan 455000, People's Republic of China, and ^bFaculty of Material Science and Chemical Engineering, China University of Geoscience, Wuhan, Hubei 430074, People's Republic of ChinaCorrespondence e-mail:
wangxw10108092@163.com

Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.049
wR factor = 0.142
Data-to-parameter ratio = 17.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

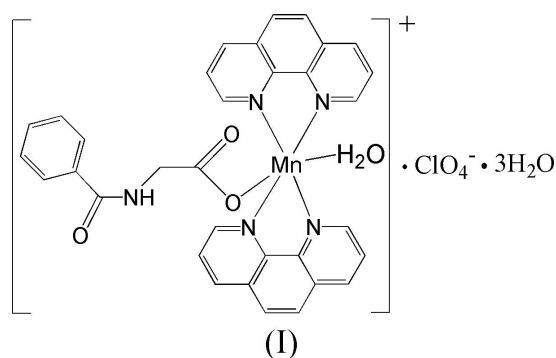
Aqua(hippurato)bis(1,10-phenanthroline)-manganese(II) perchlorate trihydrate

In the cation of the title compound, $[\text{Mn}(\text{C}_9\text{H}_7\text{NO}_3)(\text{C}_{12}\text{H}_{10}\text{N}_2)_2(\text{H}_2\text{O})]\text{ClO}_4 \cdot 3\text{H}_2\text{O}$, the Mn^{II} atom is coordinated by two O atoms, one from a hippurate ligand and the other from a coordinated water molecule, and four N atoms from two 1,10-phenanthroline ligands. In the crystal structure, the cations and water molecules are linked by intra- and intermolecular hydrogen bonds, forming $R_6^4(12)$ rings; these rings are further connected by intermolecular hydrogen bonds and $\text{C}-\text{H} \cdots \pi$ interactions into a three-dimensional supramolecular framework.

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Comment

Manganese complexes with carboxylate ligands have received extensive attention as carboxylates are good candidates for the investigation of exchange coupling interactions between adjacent metal ions (Soler *et al.*, 2004). Hippuratic acid, an *N*-protected amino acid, was previously found to act as an oxygen-donor anionic ligand in the construction of coordination compounds (Morelock *et al.*, 1979, 1982; Grewe *et al.*, 1982; Brown & Trefonas, 1973; Huber *et al.* 1988; Jones & Schelbach, 1988; Darenbourg *et al.*, 1994; Battistuzzi *et al.*, 1996; Severin *et al.*, 1996). However, there are only a few reported crystal structures of mixed-ligand complexes of hippuratic acid and heteroaromatic ligands such as 1,10-phenanthroline, 2,2-bipyridine and 4,4-bipyridine (*e.g.* Antolini *et al.*, 1982; Capllonch *et al.*, 2001). We recently reported the structure of one such complex (Guo *et al.*, 2006) and present here the crystal structure of another compound, (I).



In (I), the Mn^{II} atom is six-coordinated by two O atoms, one from a hippurate ligand and the other from a coordinated water molecule, and four N atoms from two 1,10-phenanthroline ligands, forming a distorted octahedral geometry (Fig. 1). The $\text{Mn1}-\text{N1}$ bond distance is longer than the other $\text{Mn}-\text{N}$ and $\text{Mn}-\text{O}$ bond lengths and the three *trans* angles at Mn1 deviate considerably from the linear values of a perfect octahedron (Table 1).

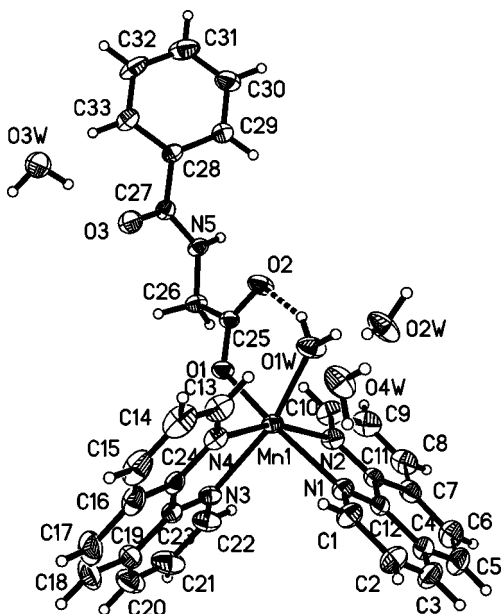


Figure 1
The cation and water molecules of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level. The perchlorate anion is omitted for clarity and the dashed line indicates a hydrogen bond.

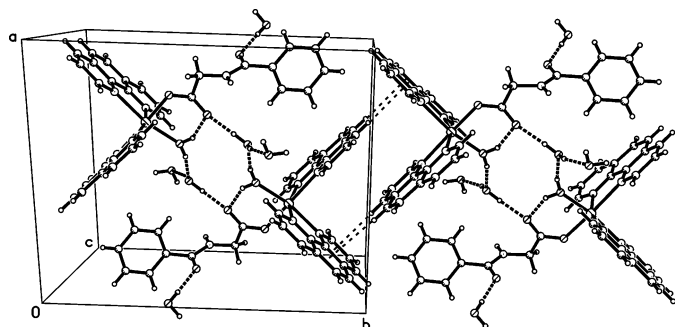


Figure 2
Part of the crystal structure of (I), showing the formation of a one-dimensional chain of rings parallel to the [010] direction. Dashed lines indicate hydrogen bonds and weak C—H... π interactions.

In the crystal structure, the uncoordinated atom O2 acts as an acceptor, forming intra- and intermolecular hydrogen bonds with O1W and O2W respectively, while O1W also acts as an intermolecular hydrogen-bond donor, *via* H1A, to atom O2W (Table 2), generating centrosymmetric $R_6^2(12)$ rings (Bernstein *et al.*, 1995) (Fig. 2). These rings are further connected by C—H... π interactions into one-dimensional chains along [010], with $R_6^2(12)$ rings centred at $(\frac{1}{2}, \frac{1}{2} + n, \frac{1}{2})$ ($n =$ zero or integer). These chains are, in turn, interlinked by intermolecular O—H...O hydrogen bonds, forming a three-dimensional supramolecular framework in which O3W and O4W act both as hydrogen-bond donors and acceptors.

Experimental

An aqueous solution (10 ml) of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.345 g, 1.0 mmol) was slowly added to a stirred solution of 1,10-phenanthroline monohydrate (0.396 g, 2.0 mmol) and hippuric acid (0.179 g,

1.0 mmol) in 20 ml ethanol. The mixture was further stirred for *ca* 30 min at room temperature, and the pH of the mixture solution was adjusted to the range 6–7 with a 1 M NaOH solution. The mixture was stirred for a further 2 h and then filtered; the filtrate was allowed to evaporate slowly at room temperature. Yellow crystals were obtained after one week in a yield of 65% based on the initial $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Analysis calculated for $\text{C}_{33}\text{H}_{28}\text{ClMnN}_5\text{O}_9$: C 51.76, H 3.66, N 9.15%; found: C 51.70, H 3.74, N 9.18%.

Crystal data

$[\text{Mn}(\text{C}_9\text{H}_7\text{NO}_3)(\text{C}_{12}\text{H}_{10}\text{N}_2)(\text{H}_2\text{O})\text{ClO}_4 \cdot 3\text{H}_2\text{O}]$	$V = 3537.8 (5) \text{ \AA}^3$
$M_r = 765.03$	$Z = 4$
Monoclinic, $P2_1/n$	$D_x = 1.436 \text{ Mg m}^{-3}$
$a = 14.1328 (12) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 16.0110 (14) \text{ \AA}$	$\mu = 0.52 \text{ mm}^{-1}$
$c = 16.8357 (14) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\beta = 111.774 (1)^\circ$	Block, yellow
	$0.45 \times 0.24 \times 0.22 \text{ mm}$

Data collection

Bruker SMART CCD APEXII diffractometer	25123 measured reflections
ω scans	8777 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4663 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.856$, $T_{\max} = 0.885$	$R_{\text{int}} = 0.037$
	$\theta_{\max} = 28.6^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.3436P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.142$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.03$	$\Delta\rho_{\max} = 0.36 \text{ e \AA}^{-3}$
8777 reflections	$\Delta\rho_{\min} = -0.39 \text{ e \AA}^{-3}$
497 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Mn1—O1W	2.123 (2)	Mn1—N2	2.288 (2)
Mn1—O1	2.1249 (17)	Mn1—N4	2.289 (2)
Mn1—N3	2.264 (2)	Mn1—N1	2.300 (2)
O1W—Mn1—O1	88.04 (7)	N3—Mn1—N4	72.82 (8)
O1W—Mn1—N3	162.17 (9)	N2—Mn1—N4	161.82 (9)
O1—Mn1—N3	88.40 (7)	O1W—Mn1—N1	96.74 (8)
O1W—Mn1—N2	99.55 (9)	O1—Mn1—N1	162.53 (8)
O1—Mn1—N2	90.30 (8)	N3—Mn1—N1	91.85 (8)
N3—Mn1—N2	97.93 (8)	N2—Mn1—N1	72.36 (8)
O1W—Mn1—N4	91.24 (9)	N4—Mn1—N1	91.98 (8)
O1—Mn1—N4	104.75 (7)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O1W—H1B...O2	0.90	1.83	2.645 (3)	152
O2W—H2B...O2 ⁱ	0.90	1.84	2.701 (3)	160
O3W—H3B...O3	0.90	1.85	2.745 (3)	178
O1W—H1A...O2W	0.90	1.71	2.595 (4)	166
O2W—H2A...O4W	0.90	1.90	2.760 (4)	158
O4W—H4B...O3W ⁱⁱ	0.88	1.98	2.816 (4)	157
C3—H3...Cg1 ⁱⁱⁱ	0.93	2.75	3.680 (4)	174
C5—H5...Cg2 ⁱⁱⁱ	0.93	3.04	3.961 (5)	172

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y + 2, -z + 1$. Cg1 and Cg2 are the centroids of the N3,C19–C23 and C16–C24 rings, respectively.

All H atoms attached to C atoms and N atom were positioned geometrically and refined as riding, with C–H = 0.93–0.97 Å, N–H = 0.86 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. The H atoms of the water molecules were located in a difference map and were included in their as-found positions, with O–H = 0.88–0.93 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The O atoms of the perchlorate anion are disordered over two sites with refined occupancies of 0.731 (9) and 0.269 (9) for the major and minor components, respectively.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXS97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

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