

Aqua(bromomaleato- κ O)bis(phenanthroline- κ^2 N,N')manganese(II) monohydrateDai-Xi Li, Duan-Jun Xu* and
Yuan-Zhi XuDepartment of Chemistry, Zhejiang University,
People's Republic of China

Correspondence e-mail: xudj@mail.hz.zj.cn

Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in main residue
 R factor = 0.032
 wR factor = 0.081
Data-to-parameter ratio = 11.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title complex, $[\text{Mn}(\text{C}_4\text{HBrO}_4)(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, the Mn^{II} atom has a distorted octahedral coordination geometry formed by two bidentate phenanthroline (phen) molecules, one bromomaleate dianion and one water molecule. The large $\text{Mn}-\text{O}-\text{C}$ bond angle of 143.31 (17) $^\circ$ implies poor overlap between the atomic orbitals of manganese and those of the carboxyl O atom, but despite this the $\text{Mn}-\text{O}$ bond distance of 2.0574 (16) Å is short, suggesting a substantial electrostatic interaction in this bond. The overlapped arrangement and short face-to-face distances of 3.368 (5) and 3.501 (11) Å between neighboring parallel phen planes show $\pi-\pi$ stacking in the crystal structure.

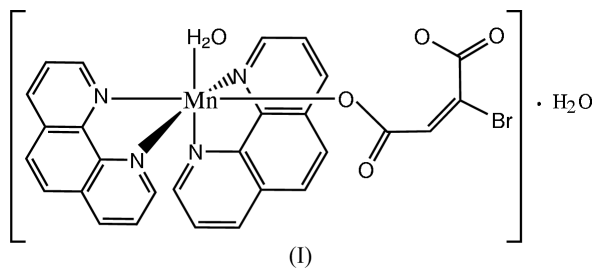
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Comment

As $\pi-\pi$ stacking between aromatic rings is correlated with the electron transfer process in some biological systems (Deisenhofer & Michel, 1989), metal complexes incorporating aromatic ligands have attracted our attention. As part of our ongoing investigations into $\pi-\pi$ stacking (Li *et al.*, 2005; Wu *et al.*, 2003), the crystal structure of the title manganese(II) complex, (I) (Fig. 1), is presented here.



The Mn^{II} atom in (I) assumes a distorted octahedral coordination geometry formed by two bidentate phenanthroline (phen) molecules, one water molecule and one bromomaleate dianion. One of the carboxylate groups of the bromomaleate dianion coordinates to the Mn^{II} atom in a monodentate mode, while the other carboxylate group is free from coordination but links with a neighboring coordinated water molecule *via* hydrogen bonding. The $\text{Mn}-\text{O}1-\text{C}31$ angle of 143.31 (17) $^\circ$ is much larger than the value of 120° expected for a normal sp^2 -hybridized O atom and implies a poor overlap between atomic orbitals of the Mn and O1 atoms. Despite this, the $\text{Mn}-\text{O}1$ bond is much shorter than the $\text{Mn}-\text{O}5$ bond (Table 1). This clearly shows a significant electrostatic component to the $\text{Mn}-\text{O}1$ bond (Liu & Xu, 2003). The two phen ligands are nearly perpendicular to each other with a dihedral angle of 87.32 (4) $^\circ$.

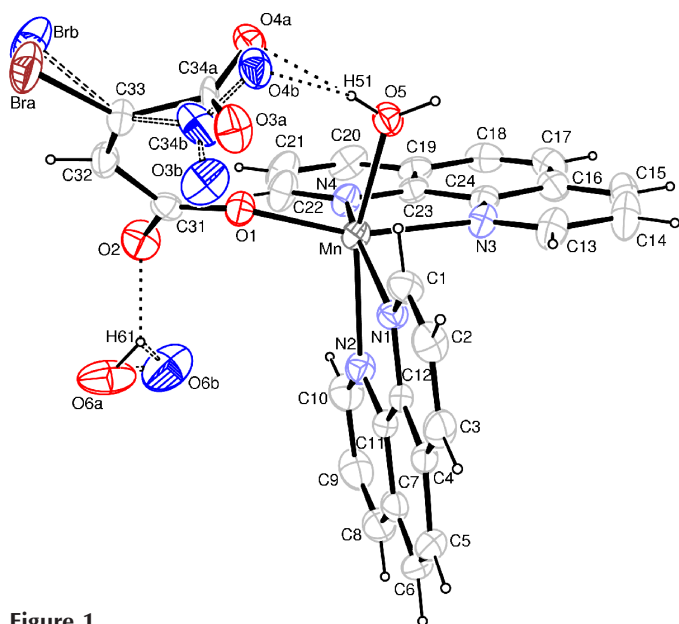


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids (arbitrary spheres for the H atoms). Dashed lines indicate the second disorder components and dotted lines indicate the hydrogen bonding.

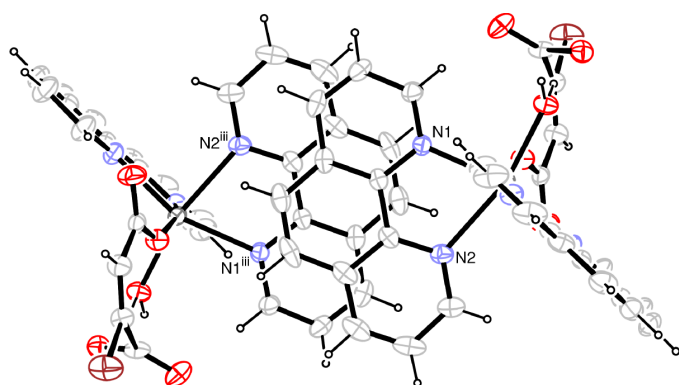


Figure 2
Detail of (I), showing the π - π stacking between neighboring symmetry-generated N1-phen rings [symmetry code: (iii) $1 - x, 1 - y, 1 - z$].

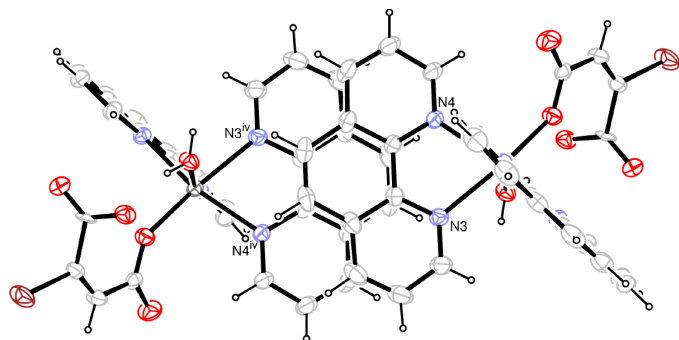


Figure 3
Detail of (I), showing the π - π stacking between neighboring symmetry-generated N3-phen rings [symmetry code: (iv) $2 - x, -y, 1 - z$].

In the crystal packing of (I), an overlapped arrangement of parallel phen rings of neighboring complex molecules is

observed (Figs. 2 and 3). The face-to-face distance of 3.368 (5) Å between N1-phen and N1ⁱⁱⁱ-phen, and 3.501 (11) Å between N3-phen and N3^{iv}-phen [symmetry codes: (iii) $1 - x, 1 - y, 1 - z$; (iv) $2 - x, -y, 1 - z$] imply the existence of π - π stacking in the crystal.

The bromomaleate dianion and uncoordinated water molecule are disordered in (I). The disordered components have similar hydrogen-bond linkages (Table 2 and Fig. 1); atoms O4a and O4b link with the coordinated water molecule, while atoms O6a and O6b link with carboxylate atom O2.

Experimental

An aqueous solution (10 ml) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (2 mmol) and phen (4 mmol) was mixed with an aqueous solution (10 ml) containing dibromosuccinic acid (2 mmol) and Na_2CO_3 (2 mmol). The mixture was refluxed for 1 h and then filtered. Yellow single crystals of (I) were obtained from the filtrate after 3 d.

Crystal data

$[\text{Mn}(\text{C}_4\text{HBrO}_4)(\text{C}_{12}\text{H}_8\text{N}_2)_2 \cdot (\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$
 $M_r = 644.34$
 Monoclinic, $P2_1/n$
 $a = 12.2038$ (4) Å
 $b = 12.6561$ (4) Å
 $c = 16.9518$ (6) Å
 $\beta = 95.714$ (1)°
 $V = 2605.24$ (15) Å³
 $Z = 4$

$D_x = 1.643$ Mg m⁻³
 Mo K α radiation
 Cell parameters from 8266 reflections
 $\theta = 2.5$ – 24.5 °
 $\mu = 2.09$ mm⁻¹
 $T = 295$ (2) K
 Prism, yellow
 $0.45 \times 0.41 \times 0.32$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\text{min}} = 0.412$, $T_{\text{max}} = 0.516$
 8880 measured reflections

4585 independent reflections
 3384 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\text{max}} = 25.0$ °
 $h = -14 \rightarrow 14$
 $k = -15 \rightarrow 15$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.081$
 $S = 1.03$
 4585 reflections
 408 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.0618P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.20$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Mn—O1	2.0574 (16)	Mn—N2	2.357 (2)
Mn—O5	2.1991 (17)	Mn—N3	2.285 (2)
Mn—N1	2.2487 (19)	Mn—N4	2.263 (2)
O1—Mn—O5	83.11 (6)	N1—Mn—N3	95.25 (7)
O1—Mn—N1	95.12 (7)	N4—Mn—N3	73.02 (7)
O5—Mn—N1	92.98 (7)	O1—Mn—N2	109.18 (7)
O1—Mn—N4	101.55 (7)	O5—Mn—N2	161.13 (7)
O5—Mn—N4	104.21 (7)	N1—Mn—N2	72.15 (7)
N1—Mn—N4	157.26 (7)	N4—Mn—N2	87.69 (8)
O1—Mn—N3	162.18 (8)	N3—Mn—N2	87.82 (7)
O5—Mn—N3	81.91 (7)		

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O5—H51···O4 <i>a</i>	0.84	1.93	2.747 (5)	166
O5—H51···O4 <i>b</i>	0.84	2.03	2.849 (9)	165
O5—H52···O3 <i>a</i> ⁱ	0.89	1.92	2.796 (5)	167
O5—H52···O4 <i>b</i> ⁱ	0.89	2.05	2.854 (8)	149
O6 <i>a</i> —H61···O2	0.93	1.92	2.706 (5)	141
O6 <i>a</i> —H62···O4 <i>a</i> ⁱⁱ	0.91	2.09	2.909 (6)	148
O6 <i>b</i> —H61···O2	0.99	1.92	2.736 (10)	138
O6 <i>b</i> —H62···O4 <i>a</i> ⁱⁱ	0.95	2.09	2.851 (10)	136

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

The disordered non-coordinated water O atom and the disordered atoms of the bromomaleate anion were found in a difference Fourier map. The occupancies of the disorder components were initially refined and then fixed at 0.61 (for component *a*) and 0.39 (for component *b*) in the final cycles of refinement. H atoms on C atoms were placed in calculated positions, with C—H = 0.93 Å, and included in the final cycles of refinement in the riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$. The H atoms of the water molecules were located in a difference Fourier map and included in the refinement with fixed positional and displacement parameters of $U_{\text{iso}} = 0.08 \text{ \AA}^2$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 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 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Deisenhofer, J. & Michel, H. (1989). *EMBO. J.* **8**, 2149–2170.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Li, H., Yin, K.-L. & Xu, D.-J. (2005). *Acta Cryst.* **C61**, m19–m21.
- Liu, Y. & Xu, D.-J. (2003). *J. Coord. Chem.* **56**, 59–64.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MS (2002). *CrystalStructure*. Version 3.00. Rigaku/MS, 9009 New Trails Drive, The Woodlands, TX, USA 77381-5209, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Wu, Z.-Y., Xue, Y.-H. & Xu, D.-J. (2003). *Acta Cryst.* **E59**, m809–m811.