

Aqua[bis(5-bromosalicylidene)ethylenediaminato]chloromanganese(III)

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.014 \text{ \AA}$

R factor = 0.073

wR factor = 0.164

Data-to-parameter ratio = 13.5

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

The title compound (systematic name: aqua{4,4'-dibromo-2,2'-[1,2-ethanediylbis(nitrilomethylidene)]diphenolato}chloromanganese(III)), $[\text{Mn}(\text{C}_{16}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_2)\text{Cl}(\text{H}_2\text{O})]$ or $[\text{Mn}(\text{Br}_2\text{salen})\text{Cl}(\text{H}_2\text{O})]$, was prepared from a methanol solution. The Mn^{3+} ion displays an elongated octahedral geometry, coordinated by two N and two O atoms from salen, one O atom from the water ligand and one Cl^- anion, and is slightly displaced out of the Schiff base N_2O_2 plane toward the axial Cl^- ion. Hydrogen bonds between the coordinated water O and Cl atoms link pairs of molecules into a three-dimensional network.

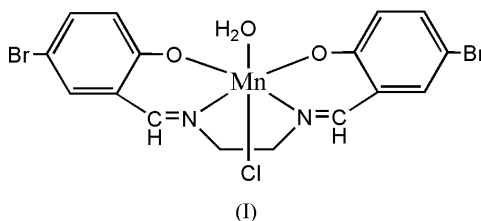
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Comment

There has been considerable attention focused on the study of manganese complexes in recent decades, because of their novel structures and applications in organic synthesis (Ruttinger & Dismukes, 1997; Manchanda *et al.*, 1995). At the same time, manganese complexes have great significance in the oxygen-evolving complex (OEC) of photosystem II (PSII) (Pecoraro *et al.*, 1994; Wieghardt, 1989). The Schiff base complexes of manganese are considered to be the simplest models for the reactivity of active sites of manganese catalases. A large number of manganese complexes with Schiff base ligands have been reported (Oki & Hodgson, 1990; Bermejo *et al.*, 1996; Hulme *et al.*, 1997; Watkinson *et al.*, 1999; Asada *et al.*, 2000; Li *et al.*, 2000; Panja *et al.*, 2003). We present here a new manganese– Br_2salen complex [Br_2salen is bis(5-bromosalicylidene)ethylenediaminate], (I), and describe its crystal structure.



In (I), the Mn^{3+} ion is six-coordinate with four donor atoms of the Br_2salen ligand (two N and two O atoms) located in the equatorial plane of a slightly distorted octahedron. In addition, a Cl^- ion and a water molecule are bonded axially and occupy the fifth and sixth coordination positions (Fig. 1 and Table 1). The Mn atom is displaced out of the N_2O_2 Schiff base plane toward the axial Cl^- ion by 0.055 (13) Å . The Mn–O1W and Mn–Cl distances are consistent with the presence of a Jahn–Teller elongation of the coordination octahedron for a high-spin $d^4 \text{Mn}^{3+}$ ion in which the e_g electron occupies the d_{z^2} orbital.

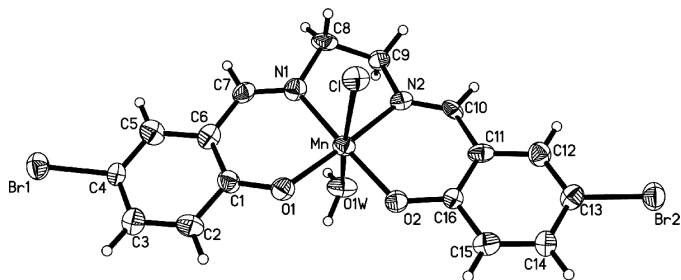


Figure 1

A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Two molecules related by a crystallographic center of symmetry are linked together by two O1W...O2 hydrogen bonds as well as two Br...Br interactions of length 3.844 (9) Å. Hydrogen bonds between O1W and Cl link pairs of molecules into a three-dimensional network (Fig. 2).

Experimental

5-Bromosalicylidene and ethylenediamine (2:1 ratio) were mixed in anhydrous ethanol. This solution was distilled and filtered, yielding bis(5-bromosalicylidene)ethylenediamine. MnCl₂ was obtained commercially from Across and was used without further purification. Crystals of (I) were grown from a methanol solution of the ligand and metal chloride *via* the following steps: a solution of the metal chloride (*M*) was dropped into a solution of the ligand (*L*) (ratio 1:1 *M*:*L*) with stirring. The brown solution was filtered and the filtrate was left to stand at room temperature. Brown crystals formed at the bottom of the flask after a few days. Elemental analysis results are completely in agreement with the structural composition of (I).

Crystal data

[Mn(C ₁₆ H ₁₂ Br ₂ N ₂ O ₂)Cl(H ₂ O)]	$D_x = 1.978 \text{ Mg m}^{-3}$
$M_r = 532.50$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 8335 reflections
$a = 12.2994 (18) \text{ \AA}$	$\theta = 3.1\text{--}27.5^\circ$
$b = 11.6445 (17) \text{ \AA}$	$\mu = 5.37 \text{ mm}^{-1}$
$c = 13.660 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 113.909 (2)^\circ$	Block, brown
$V = 1788.5 (5) \text{ \AA}^3$	$0.3 \times 0.2 \times 0.1 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	3134 independent reflections
φ and ω scans	2766 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.055$
$T_{\text{min}} = 0.280$, $T_{\text{max}} = 0.584$	$\theta_{\text{max}} = 25.0^\circ$
7093 measured reflections	$h = -12 \rightarrow 14$
	$k = -13 \rightarrow 13$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 25.603P]$
$R[F^2 > 2\sigma(F^2)] = 0.073$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.164$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.19$	$\Delta\rho_{\text{max}} = 1.16 \text{ e \AA}^{-3}$
3134 reflections	$\Delta\rho_{\text{min}} = -1.32 \text{ e \AA}^{-3}$
232 parameters	
H atoms treated by a mixture of independent and constrained refinement	

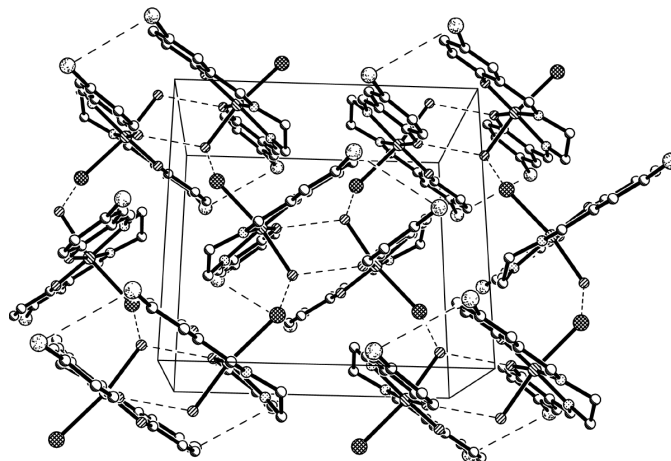


Figure 2

A view of the packing of the title compound. Dashed lines indicate hydrogen bonds and Br...Br interactions.

Table 1

Selected geometric parameters (Å, °).

Mn1—O1	1.875 (6)	Mn1—N2	1.985 (7)
Mn1—O2	1.875 (6)	Mn1—O1W	2.274 (7)
Mn1—N1	1.978 (7)	Mn1—Cl1	2.587 (3)
O1—Mn1—O2	91.4 (3)	N1—Mn1—O1W	87.9 (3)
O1—Mn1—N1	92.7 (3)	N2—Mn1—O1W	83.6 (3)
O2—Mn1—N1	174.2 (3)	O1—Mn1—Cl1	96.2 (2)
O1—Mn1—N2	174.5 (3)	O2—Mn1—Cl1	95.33 (19)
O2—Mn1—N2	92.6 (3)	N1—Mn1—Cl1	88.3 (2)
N1—Mn1—N2	83.0 (3)	N2—Mn1—Cl1	87.1 (2)
O1—Mn1—O1W	92.9 (3)	O1W—Mn1—Cl1	170.3 (2)
O2—Mn1—O1W	87.8 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O1W—H1W1...O2 ⁱ	0.85 (12)	2.02 (12)	2.847 (9)	164 (11)
O1W—H1W2...Cl1 ⁱⁱ	0.78 (12)	2.32 (12)	3.102 (7)	171 (11)

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

H atoms on carbon were treated as riding, with C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. H atoms on N or O were refined with $U_{\text{iso}}(\text{H}) = 0.03 \text{ \AA}^2$ (0.08 Å² for O) and N—H distances in the range 0.81–0.89 Å (0.78–0.84 Å for O—H). The deepest hole is located 0.61 Å from atom C11 and the highest peak is located 0.96 Å from atom C12.

Data collection: SMART (Bruker, 1994); cell refinement: SAINT (Bruker, 1994); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: please provide; software used to prepare material for publication: SHELXL97.

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References

- Asada, H., Fujiwara, M. & Matsushita, T. (2000). *Chem. Lett.* pp. 772–773.
- Bermejo, M. R., Castineiras, A., Garcia-Monteagudo, J. C. & Rey, M. J. (1996). *J. Chem. Soc. Dalton Trans.* pp. 2935–2944.
- Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Hulme, C. E., Watkinson, M., Haynes, M., Pritchard, R. G. & McAuliffe, C. A. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1805–1814.
- Li, J., Yang, S. M., Zhang, F. X., Tang, Z. X., Shi, Q. Z., Wu, Q. J. & Huang, Z. X. (2000). *Chin. J. Inorg. Chem.* **16**, 84–88.
- Manchanda, R., Brudvig, G. W. & Crabtree, R. H. (1995). *Coord. Chem. Rev.* **144**, 1–38.
- Oki, A. R. & Hodgson, D. J. (1990). *Inorg. Chim. Acta*, **170**, 65–73.
- Panja, A., Shaikh, N., Ali, M., Vojtisek, P. & Banerjee, P. (2003) *Polyhedron*, **22**, 1191–1198.
- Pecoraro, V. L., Baldwin, M. J. & Gelasco, A. (1994). *Chem. Rev.* **94**, 807–826.
- Ruttiger, W. & Dismukes, C. C. (1997). *Chem. Rev.* **97**, 1–24.
- Sheldrick. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Watkinson, M., Fondo, M., Bermejo, M. R. & Sousa, A. (1999). *J. Chem. Soc. Dalton Trans.* pp. 31–41.
- Wieghardt, K. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1153–1172.