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[2-(3,5-Dibromo-2-oxidobenzylamino)-3-phenylpropionato-κ^3O,N,O'](1,10-phenanthroline-κ^2N,N')manganese(II) dihydrate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.016 Å
R factor = 0.062
wR factor = 0.212
Data-to-parameter ratio = 14.3

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

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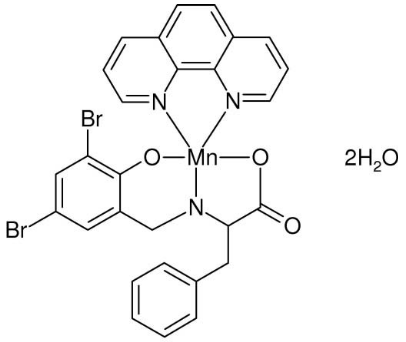
In the title compound, $[Mn(C_{16}H_{13}Br_2NO_3)(C_{12}H_8N_2)]\cdot 2H_2O$, the Mn^{II} atom is coordinated in a slightly distorted square-pyramidal geometry by one N and two O atoms from the tridentate 2-(3,5-dibromo-2-oxidobenzylamino)-3-phenylpropionate ligand and two N atoms from the bidentate 1,10-phenanthroline ligand. The benzyl group is oriented so that an additional axial interaction with the aromatic ring imparts pseudo-octahedral coordination geometry to the Mn^{II} atom.

Comment

Schiff base complexes containing amino acids have been studied for many years (Wang *et al.*, 1994; Casella & Gullotti, 1986; Jiang *et al.*, 2003; Zhang *et al.*, 2003; Sreenivasulu *et al.*, 2005), and have recently aroused increasing interest because of their antiviral, anticancer and antibacterial activities. X-ray crystallographic studies of metal complexes of Schiff-base ligands containing salicylaldehyde and amino acids (Nakajima, *et al.*, 1989; Kettmann *et al.*, 1993) demonstrate that Schiff bases act as tridentate ligands, coordinating through the phenolato O, imine N, and carboxylate O atoms. We are interested in tridentate reduced Schiff bases, which are more flexible as a consequence of reduction of the C=N bond (Sreenivasulu *et al.*, 2005; Zhang, 2006).



(I)

The title compound, (I) (Fig. 1), includes [Mn(*L*)(phen)] (where LH_2 = 2-(3,5-dibromo-2-hydroxybenzylamino)-3-phenylpropionic acid) and two uncoordinated water molecules per complex. The Mn^{II} atom is coordinated by one N atom and two O atoms from L^{2-}, and two N atoms from phen, forming a slightly distorted square-pyramidal geometry. The apical Mn1—O3 bond (Table 1) is significantly longer than the Mn1—(O/N) bonds in the square plane. The distance between Mn1 and the centroid of the ring (C4–C9) of the benzyl substituent is 3.50 Å, which is in good agreement with values reported for similar complexes (Okabe & Hokaze, 1993). This axial interaction imparts a pseudo-octahedral coordination

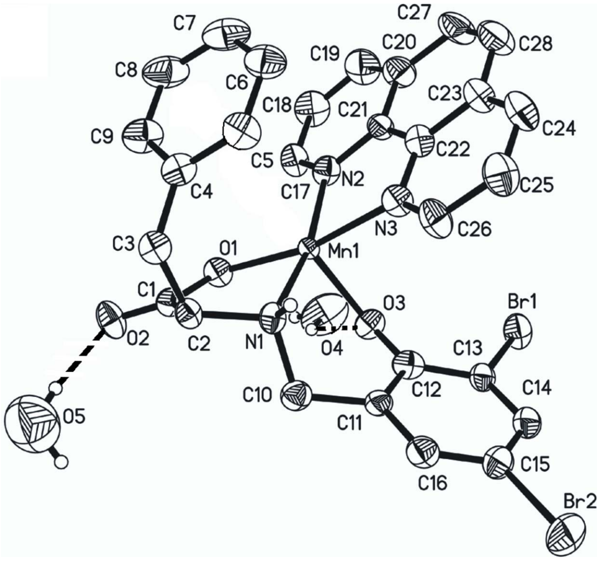


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level for non-H atoms. Dashed lines indicate hydrogen bonds. H atoms of the complex have been omitted.

geometry to Mn^{II} (Fig. 1). Complexes are linked into chains running along the *a* axis by N—H···O hydrogen bonds and O—H···O hydrogen bonds involving the uncoordinated water molecules (Table 2).

Experimental

A solution of 2-amino-3-phenyl-propionic acid (2 mmol, 0.340 g) and caustic potash (2 mmol, 0.112 g) in distilled water (15 ml) was added slowly to a solution of 3,5-dibromo-2-hydroxybenzaldehyde (2 mmol, 0.560 g) in ethanol (20 ml). The mixture was stirred for 30 min at 333 K, then sodium borohydride (2 mmol, 0.076 g) was added. After stirring for 2 h (during which time the yellow solution became colourless), a solution of $MnCl_2$ (2 mmol, 0.396 g) in distilled water (10 ml) was added slowly, and the mixture was stirred and refluxed again at 348 K for 2 h. Finally, phenanthroline (2 mmol, 0.36 g) was added and refluxing was continued for a further 4 h, after which time the reaction mixture was filtered and concentrated. The filtrate was left to stand at room temperature, yielding colourless prismatic crystals (yield 62%, based on $MnCl_2$).

Crystal data

$[Mn(C_{16}H_{13}Br_2NO_3)(C_{12}H_8N_2)]\cdot 2H_2O$
$M_r = 698.27$
Orthorhombic, *Pbca*
$a = 11.199\ (3)$ Å
$b = 18.962\ (2)$ Å
$c = 26.932\ (3)$ Å
$V = 5719.4\ (17)$ Å^3

$Z = 8$
$D_x = 1.622$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 3.30$ mm^{-1}
$T = 298\ (2)$ K
Prism, colourless
0.48 × 0.40 × 0.33 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.247$, $T_{max} = 0.337$

28160 measured reflections
5044 independent reflections
2646 reflections with $I > 2\sigma(I)$
$R_{int} = 0.118$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.212$
$S = 1.06$
5044 reflections
352 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 33.98P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.48$ e Å^{-3}
$\Delta\rho_{min} = -0.93$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	1.972 (6)	Mn1—N3	2.064 (8)
Mn1—N1	2.004 (7)	Mn1—O3	2.128 (6)
Mn1—N2	2.003 (8)		
O1—Mn1—N2	93.0 (3)	N1—Mn1—N3	99.5 (3)
O1—Mn1—N1	83.0 (3)	O1—Mn1—O3	97.1 (3)
N2—Mn1—N1	167.8 (3)	N2—Mn1—O3	96.3 (3)
O1—Mn1—N3	167.5 (3)	N1—Mn1—O3	95.6 (3)
N2—Mn1—N3	82.0 (3)	N3—Mn1—O3	94.8 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.91	2.07	2.948 (9)	163
O4—H30···O3	0.85	2.19	2.764 (11)	125
O4—H29···O5^{ii}	0.85	2.41	2.868 (17)	114
O5—H31···O2	0.85	2.03	2.876 (15)	171
O5—H32···O4^{i}	0.85	2.30	2.868 (17)	125

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

H atoms were positioned geometrically with C—H = 0.93 (aromatic) or 0.97Å (CH_2) and N—H = 0.91Å, and allowed to ride during subsequent refinement with $U_{iso}(H) = 1.2U_{eq}(C,N)$. H atoms of the water molecules were located in a difference Fourier map. The O—H distances were normalized to 0.85 Å and the H atoms were allowed to ride during subsequent refinement, with $U_{iso}(H) = 1.2U_{eq}(O)$. The displacement parameters of atoms Br2, O4 and O5 were restrained to approximately isotropic behaviour. The highest peak in the difference density map is located 0.54Å from Mn1.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); 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, 1997); software used to prepare material for publication: *SHELXTL*.

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