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μ-Oxido-bis({4,4′-dibromo-2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}manganese(III))

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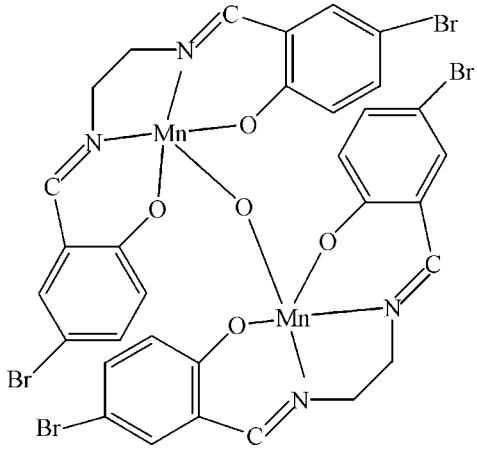
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.008 Å; R factor = 0.059; wR factor = 0.150; data-to-parameter ratio = 14.9.

The title compound, $[Mn_2(C_{16}H_{12}Br_2N_2O_2)_2O]$, is an unusual dinuclear manganese(III) complex. Each Mn^{III} ion has a distorted square-pyramidal coordination geometry. In the basal plane, the Mn atom is coordinated by two N atoms and two O atoms of the Schiff base ligand. The apical position is occupied by a bridging O^{2-} ion, which links to the other Mn^{III} ion in the complex; this bridging O atom lies on a twofold rotation axis.

Related literature

For related literature, see: Garnovskii *et al.* (1993); Huang *et al.* (2002); Chen *et al.* (2006); Karacan & Somer (2004).



Experimental

Crystal data

$[Mn_2(C_{16}H_{12}Br_2N_2O_2)_2O]$
M_r = 974.07
Orthorhombic, *Pcca*
a = 20.720 (4) Å
b = 14.066 (3) Å
c = 11.750 (2) Å
V = 3424.5 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 5.45 mm^{-1}
T = 293 (2) K
0.43 × 0.28 × 0.22 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.203, T_{max} = 0.380
(expected range = 0.161–0.301)
11498 measured reflections
3164 independent reflections
2262 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.150
S = 1.00
3164 reflections
213 parameters
H-atom parameters not refined
$\Delta\rho_{max}$ = 1.00 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 e Å^{-3}

Table 1
Selected bond lengths (Å).

Mn1—O1	1.791 (2)	Mn1—N1	2.114 (4)
Mn1—O2	1.918 (4)	Mn1—N2	2.121 (4)
Mn1—O3	1.934 (4)		

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2108).

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supplementary materials

Acta Cryst. (2007). E**63**, m2771 [**doi:10.1107/S1600536807051008**]

μ-Oxido-bis({4,4'-dibromo-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}manganese(III))

Y. Liu, J. Dou, M. Niu and X. Zhang

Comment

The design of Schiff base complexes has attracted long-lasting research interest due to their important role in the development of coordination chemistry as well as inorganic biochemistry, catalysis, optical materials and so on (Garnovskii *et al.*, 1993; Huang *et al.*, 2002). Recently, the Schiff base ligands, especially the relative flexible symmetrical or unsymmetrical Schiff base ligands and their hydrogenerated derivatives have been widely employed to assembly alkoxo- or phenoxo-bridged manganese clusters and polymers with novel topological structures and interesting magnetic, catalysis and photochemical properties. (Chen *et al.*, 2006; Karacan & Somer, 2004). We report here the structure of the title compound, (I).

As shown in Fig. 1, Mn^{III} is chelated by Schiff base ligand of *N*,*N*'-bis(2-hydroxy-5-bromobenzyl)ethylenediamine with two N and two O atoms. The coordination geometry for Mn^{III} ion can be described as square-pyramidal, whose square plane is determined by O(1), O(3), N(1), and N(2) from Schiff base ligand with an average Mn—O bond length of 1.926 (3) Å, Mn—N, 2.137 (4) Å. While Mn—O(1) (a cap atom) distance is much shorter (1.791 (2) Å), Table 1. Along the axial site, two Mn^{III} is linked into dimer by oxygen atom. The Mn···Mn distance is 3.346 (3) Å.

Experimental

A mixture of manganese(III) acetate hydrate (1 mmol, 0.23 g) and *N*,*N*'-bis(2-hydroxy-5-bromobenzyl)ethylenediamine purchased from Shanghai Chemical Co. Ltd (1 mmol, 0.45 g) in 20 ml me thanol was refluxed for two h. The above cooled solution was filterated and the filtrate was evaporated at room temperature. Two day later, yellow blocks of (I) were obtained with a yield of 16%. Anal. Calc. for $C_{32}H_{24}Br_4Mn_2N_4O_5$: C 39.43, H 2.46, N 5.75%; Found: C 39.40, H 2.49, N 5.71%.

Refinement

All H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms, with C—H = 0.93 Å (aromatic and CHN), and 0.97 Å (CH2) and U_{iso}(H) = 1.2–1.5 U_{eq}(C).

Figures

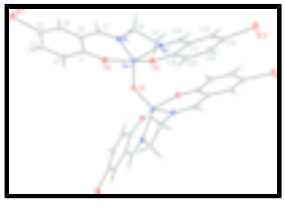


Fig. 1. The molecular structure of (I), drawn with 30% probability displacement ellipsoids for the non-hydrogen atoms.

μ-Oxido-bis({4,4'-dibromo-2,2'-[ethane-1,2- diylbis(nitrilomethylidyne)]diphenolato}manganese(III))

Crystal data

$[Mn_2(C_{16}H_{12}Br_2N_2O_2)_2O]$	F_{000} = 1896
M_r = 974.07	D_x = 1.889 Mg m^{-3}
Orthorhombic, *Pcca*	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2a 2ac	Cell parameters from 3164 reflections
a = 20.720 (4) Å	θ = 3.0–25.5º
b = 14.066 (3) Å	μ = 5.45 mm^{-1}
c = 11.750 (2) Å	*T* = 293 (2) K
V = 3424.5 (11) Å^3	Block, yellow
Z = 4	0.43 × 0.28 × 0.22 mm

Data collection

Bruker APEXII CCD area-detector diffractometer	3164 independent reflections
Radiation source: fine-focus sealed tube	2262 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.049
T = 293(2) K	θ_{max} = 25.5º
φ and ω scans	θ_{min} = 3.0º
Absorption correction: multi-scan (SADABS; Bruker, 2001)	*h* = −25→25
T_{min} = 0.203, T_{max} = 0.380	*k* = −17→17
11498 measured reflections	*l* = 0→14

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.059	H-atom parameters not refined
$wR(F^2)$ = 0.150	$w = 1/[\sigma^2(F_o^2) + (0.08P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.00	$(\Delta/\sigma)_{max} < 0.001$
3164 reflections	$\Delta\rho_{max}$ = 1.01 e Å^{-3}
213 parameters	$\Delta\rho_{min}$ = −0.82 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.07194 (4)	0.12985 (5)	0.31467 (6)	0.0309 (2)
Br1	0.28253 (3)	−0.28114 (5)	0.48699 (6)	0.0669 (3)
Br2	0.10796 (4)	0.66035 (5)	0.24479 (7)	0.0771 (3)
C1	0.1643 (3)	−0.0342 (3)	0.3170 (4)	0.0363 (11)
C2	0.2039 (3)	−0.0951 (4)	0.2518 (5)	0.0414 (13)
H2	0.2072	−0.0854	0.1737	0.050*
C3	0.2371 (3)	−0.1672 (4)	0.3003 (5)	0.0478 (14)
H3	0.2643	−0.2048	0.2561	0.057*
C4	0.2308 (3)	−0.1853 (4)	0.4172 (5)	0.0469 (14)
C5	0.1904 (3)	−0.1313 (4)	0.4829 (5)	0.0440 (14)
H5	0.1857	−0.1446	0.5600	0.053*
C6	0.1559 (3)	−0.0556 (4)	0.4331 (4)	0.0377 (12)
C7	0.1147 (3)	−0.0005 (4)	0.5088 (4)	0.0386 (13)
H7	0.1138	−0.0182	0.5851	0.046*
C8	0.0460 (3)	0.1214 (4)	0.5719 (4)	0.0438 (13)
H8A	0.0772	0.1523	0.6210	0.053*
H8B	0.0213	0.0768	0.6174	0.053*
C9	0.0008 (3)	0.1956 (4)	0.5199 (5)	0.0445 (14)
H9A	−0.0390	0.1660	0.4952	0.053*
H9B	−0.0094	0.2443	0.5754	0.053*
C10	0.0404 (3)	0.3281 (4)	0.4136 (5)	0.0414 (13)
H10	0.0222	0.3659	0.4701	0.050*
C11	0.0737 (3)	0.3751 (4)	0.3200 (5)	0.0399 (13)
C12	0.0745 (3)	0.4749 (4)	0.3233 (5)	0.0478 (14)
H12	0.0551	0.5069	0.3836	0.057*
C13	0.1039 (3)	0.5256 (4)	0.2369 (5)	0.0523 (16)
C14	0.1315 (3)	0.4779 (4)	0.1448 (6)	0.0565 (16)
H14	0.1505	0.5121	0.0860	0.068*
C15	0.1302 (3)	0.3797 (4)	0.1413 (5)	0.0522 (15)
H15	0.1479	0.3485	0.0789	0.063*
C16	0.1030 (3)	0.3260 (4)	0.2296 (5)	0.0417 (13)
N1	0.0797 (2)	0.0703 (3)	0.4793 (4)	0.0377 (10)
N2	0.0345 (2)	0.2371 (3)	0.4229 (4)	0.0364 (10)
O1	0.0000	0.0843 (4)	0.2500	0.0387 (12)
O2	0.13711 (19)	0.0410 (3)	0.2687 (3)	0.0419 (9)
O3	0.10571 (18)	0.2322 (3)	0.2223 (3)	0.0438 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0386 (4)	0.0261 (4)	0.0280 (4)	0.0004 (3)	0.0005 (3)	−0.0001 (3)
Br1	0.0648 (5)	0.0631 (5)	0.0728 (5)	0.0227 (3)	0.0084 (4)	0.0254 (4)
Br2	0.1059 (7)	0.0323 (4)	0.0931 (6)	−0.0025 (3)	0.0271 (5)	0.0093 (4)
C1	0.043 (3)	0.029 (2)	0.038 (3)	−0.001 (2)	0.002 (2)	0.000 (2)
C2	0.049 (3)	0.036 (3)	0.039 (3)	0.003 (2)	0.002 (2)	0.001 (2)
C3	0.047 (3)	0.041 (3)	0.055 (4)	0.004 (3)	0.007 (3)	0.003 (3)
C4	0.042 (3)	0.045 (3)	0.053 (3)	0.006 (3)	0.005 (3)	0.016 (3)
C5	0.048 (3)	0.042 (3)	0.042 (3)	−0.001 (3)	0.002 (3)	0.009 (3)
C6	0.042 (3)	0.033 (3)	0.039 (3)	−0.002 (2)	−0.002 (2)	0.003 (2)
C7	0.050 (3)	0.032 (3)	0.034 (3)	−0.003 (2)	−0.002 (2)	0.002 (2)
C8	0.054 (3)	0.041 (3)	0.037 (3)	0.000 (3)	0.010 (3)	−0.002 (3)
C9	0.047 (3)	0.044 (3)	0.043 (3)	−0.001 (3)	0.010 (3)	0.004 (3)
C10	0.044 (3)	0.042 (3)	0.039 (3)	0.002 (2)	0.000 (3)	−0.007 (3)
C11	0.042 (3)	0.034 (3)	0.044 (3)	0.000 (2)	0.000 (3)	0.003 (3)
C12	0.050 (4)	0.036 (3)	0.057 (4)	0.000 (3)	0.004 (3)	0.003 (3)
C13	0.062 (4)	0.031 (3)	0.064 (4)	−0.002 (3)	0.005 (3)	0.014 (3)
C14	0.065 (4)	0.042 (3)	0.063 (4)	−0.004 (3)	0.011 (3)	0.007 (3)
C15	0.062 (4)	0.045 (3)	0.050 (3)	0.002 (3)	0.009 (3)	0.010 (3)
C16	0.039 (3)	0.040 (3)	0.046 (3)	−0.003 (2)	0.002 (3)	0.002 (3)
N1	0.045 (3)	0.034 (2)	0.034 (2)	0.000 (2)	0.0032 (19)	−0.002 (2)
N2	0.042 (3)	0.029 (2)	0.038 (2)	−0.0043 (19)	0.006 (2)	0.0018 (19)
O1	0.043 (3)	0.030 (3)	0.042 (3)	0.000	−0.008 (2)	0.000
O2	0.054 (2)	0.038 (2)	0.0332 (18)	0.0108 (17)	−0.0016 (17)	0.0028 (16)
O3	0.054 (3)	0.035 (2)	0.043 (2)	−0.0017 (17)	0.0100 (19)	0.0020 (17)

Geometric parameters (Å, °)

Mn1—O1	1.791 (2)	C8—C9	1.530 (8)
Mn1—O2	1.918 (4)	C8—H8A	0.9700
Mn1—O3	1.934 (4)	C8—H8B	0.9700
Mn1—N1	2.114 (4)	C9—N2	1.458 (7)
Mn1—N2	2.121 (4)	C9—H9A	0.9700
Br1—C4	1.907 (6)	C9—H9B	0.9700
Br2—C13	1.900 (6)	C10—N2	1.289 (7)
C1—O2	1.327 (6)	C10—C11	1.457 (7)
C1—C6	1.408 (7)	C10—H10	0.9300
C1—C2	1.411 (7)	C11—C12	1.405 (8)
C2—C3	1.352 (8)	C11—C16	1.406 (8)
C2—H2	0.9300	C12—C13	1.382 (8)
C3—C4	1.404 (8)	C12—H12	0.9300
C3—H3	0.9300	C13—C14	1.395 (9)
C4—C5	1.368 (8)	C14—C15	1.382 (8)
C5—C6	1.410 (7)	C14—H14	0.9300
C5—H5	0.9300	C15—C16	1.402 (8)
C6—C7	1.457 (7)	C15—H15	0.9300

C7—N1	1.279 (7)	C16—O3	1.323 (7)
C7—H7	0.9300	O1—Mn1^{i}	1.791 (2)
C8—N1	1.480 (7)		
O1—Mn1—O2	103.49 (17)	N2—C9—C8	107.1 (4)
O1—Mn1—O3	109.23 (17)	N2—C9—H9A	110.3
O2—Mn1—O3	94.14 (16)	C8—C9—H9A	110.3
O1—Mn1—N1	108.05 (16)	N2—C9—H9B	110.3
O2—Mn1—N1	86.89 (16)	C8—C9—H9B	110.3
O3—Mn1—N1	141.33 (18)	H9A—C9—H9B	108.6
O1—Mn1—N2	101.80 (16)	N2—C10—C11	124.0 (5)
O2—Mn1—N2	152.92 (17)	N2—C10—H10	118.0
O3—Mn1—N2	86.50 (16)	C11—C10—H10	118.0
N1—Mn1—N2	76.19 (17)	C12—C11—C16	120.4 (5)
O2—C1—C6	122.2 (5)	C12—C11—C10	116.0 (5)
O2—C1—C2	119.9 (5)	C16—C11—C10	123.5 (5)
C6—C1—C2	117.9 (5)	C13—C12—C11	120.0 (6)
C3—C2—C1	121.5 (5)	C13—C12—H12	120.0
C3—C2—H2	119.2	C11—C12—H12	120.0
C1—C2—H2	119.2	C12—C13—C14	120.2 (6)
C2—C3—C4	120.0 (6)	C12—C13—Br2	119.9 (5)
C2—C3—H3	120.0	C14—C13—Br2	120.0 (4)
C4—C3—H3	120.0	C15—C14—C13	119.7 (6)
C5—C4—C3	120.6 (5)	C15—C14—H14	120.1
C5—C4—Br1	119.6 (4)	C13—C14—H14	120.1
C3—C4—Br1	119.7 (4)	C14—C15—C16	121.6 (6)
C4—C5—C6	119.7 (5)	C14—C15—H15	119.2
C4—C5—H5	120.1	C16—C15—H15	119.2
C6—C5—H5	120.1	O3—C16—C15	118.2 (5)
C1—C6—C5	120.0 (5)	O3—C16—C11	123.8 (5)
C1—C6—C7	123.4 (5)	C15—C16—C11	118.0 (5)
C5—C6—C7	116.5 (5)	C7—N1—C8	116.5 (4)
N1—C7—C6	125.5 (5)	C7—N1—Mn1	126.9 (4)
N1—C7—H7	117.3	C8—N1—Mn1	116.4 (3)
C6—C7—H7	117.3	C10—N2—C9	120.6 (5)
N1—C8—C9	109.0 (4)	C10—N2—Mn1	128.4 (4)
N1—C8—H8A	109.9	C9—N2—Mn1	111.0 (3)
C9—C8—H8A	109.9	Mn1^{i}—O1—Mn1	138.1 (3)
N1—C8—H8B	109.9	C1—O2—Mn1	134.3 (3)
C9—C8—H8B	109.9	C16—O3—Mn1	133.7 (3)
H8A—C8—H8B	108.3		

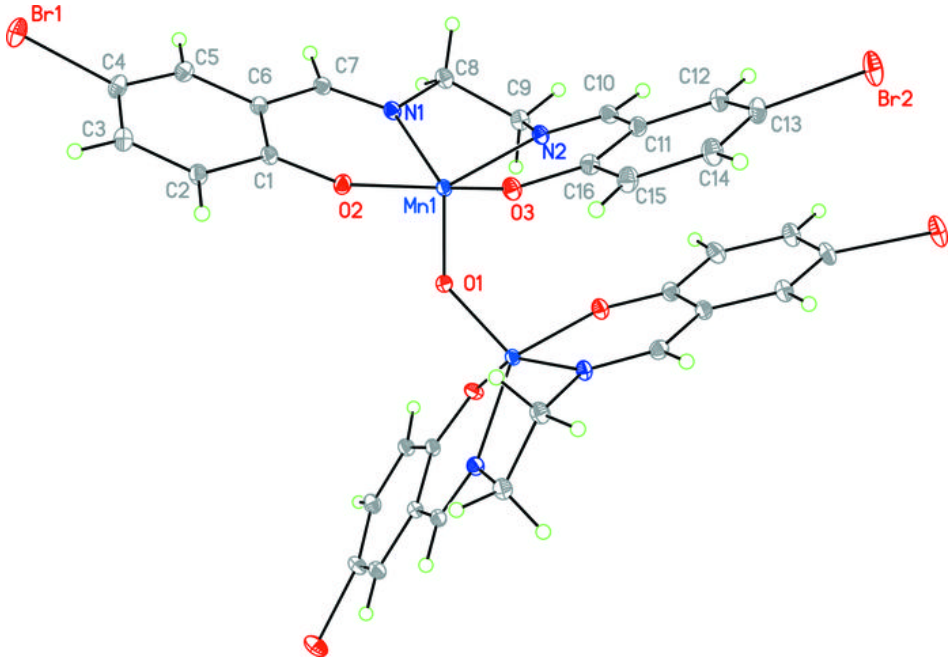
Symmetry codes: (i) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···O2^{ii}	0.93	2.23	3.141 (6)	165

Symmetry codes: (ii) *x*, −*y*, *z*−1/2.

Fig. 1


Br1
C4
C5
C6
C7
C8
C9
C10
C12
Br2
C3
N1
N2
C11
C13
C2
C1
O2
Mn1
O3
C16
C15
C14
O1