Bis{μ-2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}bis[(thiocyanato)manganese(III)]

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The reported structure is a monoclinic polymorph of the title compound, $[Mn_2(C_{16}H_{14}N_2O_2)_2(NCS)_2]$, which has been characterized previously in an orthorhombic form. Each Mn^{III} atom is chelated by a tetradentate 2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolate ligand and by the N atom of a thiocyanate anion, in a square-pyramidal arrangement. The complexes form centrosymmetric dimers, with an Mn—O contact of 2.557 (3) Å *trans* to each thiocyanate anion, completing a distorted octahedral coordination geometry.

Related literature

For the orthorhombic polymorph, see: Mikuriya *et al.* (1992); Li *et al.* (1997).
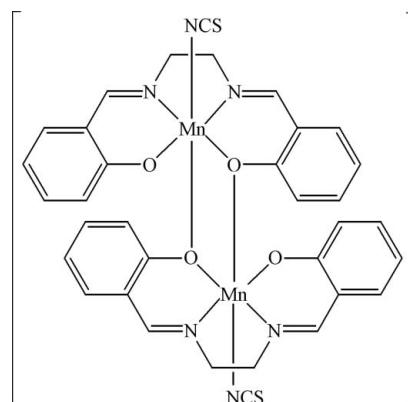
Experimental

Crystal data

$[Mn_2(C_{16}H_{14}N_2O_2)_2(NCS)_2]$	$V = 1816.1$ (4) Å³
$M_r = 758.62$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.0026$ (10) Å	$\mu = 0.85$ mm⁻¹
$b = 14.0629$ (16) Å	$T = 293$ (2) K
$c = 14.9884$ (17) Å	$0.43 \times 0.28 \times 0.22$ mm
$\beta = 106.848$ (1)°	

Data collection

Bruker APEXII CCD diffractometer	13254 measured reflections
	3296 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	2627 reflections with $I > 2\sigma(I)$
$T_{min} = 0.710$, $T_{max} = 0.834$	$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.066$	193 parameters
$wR(F^2) = 0.231$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{max} = 1.47$ e Å⁻³
3296 reflections	$\Delta\rho_{min} = -0.33$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	1.874 (3)	Mn1—N2	1.990 (5)
Mn1—O2	1.902 (3)	Mn1—N3	2.181 (5)
Mn1—N1	1.979 (4)	Mn1—O2ⁱ	2.557 (3)
O1—Mn1—O2	94.95 (14)	O2—Mn1—O2ⁱ	80.14 (14)
O1—Mn1—N1	92.1 (2)	N1—Mn1—N2	81.9 (2)
O1—Mn1—N2	170.90 (17)	N1—Mn1—N3	95.4 (2)
O1—Mn1—N3	93.94 (18)	N1—Mn1—O2ⁱ	87.29 (16)
O1—Mn1—O2ⁱ	88.62 (15)	N2—Mn1—N3	93.4 (2)
O2—Mn1—N1	165.40 (19)	N2—Mn1—O2ⁱ	84.35 (17)
O2—Mn1—N2	89.51 (17)	N3—Mn1—O2ⁱ	176.24 (17)
O2—Mn1—N3	96.85 (17)		

Symmetry code: (i) $-x + 1, -y, -z$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

References

Bruker (2001). *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2004). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Li, H., Zhong, Z. J., Duan, C.-Y., You, X.-Z., Mak, T. C. W. & Wu, B. (1997). *J. Coord. Chem.* **41**, 183–189.
Mikuriya, M., Yamato, Y. & Tokii, T. (1992). *Bull. Chem. Soc. Jpn*, **65**, 1466–1468.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Bis{*μ*-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}bis[(thiocyanato)manganese(III)]

S.-B. Wang, K. Tang, B.-H. Yang and S. Li

Comment

As shown in Fig. 1, the Mn atom is chelated by two N and two O atoms of the *N*,*N*'-ethylenebis(salicylideneamine) ligand and by the N atom of the thiocyanate anion in the apical site. The Mn—N and Mn—O bond lengths are in the range of 1.979 (4)–2.181 (5) and 1.874 (3)–1.902 (3) %A, respectively (Table 1).

Experimental

A mixture of manganese(III) acetate (1 mmol) and *N*,*N*'-bis(2-hydroxybenzyl)ethylenediamine (1 mmol) in 20 ml me thanol was refluxed for several hours. The solution was then cooled and filtered, and the filtrate was left to evaporate at room temperature. Pink blocks of the title compound were obtained after 2 days with a yield of 12%. Elemental analysis calculated: C 53.72, H 3.67, N 5.49%; found: C 53.78, H 3.69, N 5.54%.

Refinement

H atoms were placed in calculated positions and refined as riding with $U_{iso}(H) = 1.2\ U_{eq}(C)$. The phenyl rings were constrained to have regular hexagonal geometry.

Figures
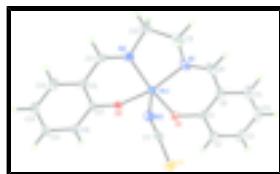
Fig. 1. Asymmetric unit drawn with 30% probability displacement ellipsoids for the non-H atoms.

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Crystal data

[Mn$_2$(C$_{16}$H$_{14}$N$_2$O$_2$)$_2$(NCS)$_2$]	$F_{000} = 776$
$M_r = 758.62$	$D_x = 1.387$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 4497 reflections
$a = 9.0026$ (10) Å	$\theta = 2.4$–24.4º
$b = 14.0629$ (16) Å	$\mu = 0.86$ mm^{-1}
$c = 14.9884$ (17) Å	$T = 293$ (2) K
$\beta = 106.848$ (1)º	Block, pink

$V = 1816.1\ (4)\ \text{Å}^3$

$Z = 2$

$0.43 \times 0.28 \times 0.22$ mm

Data collection

Bruker APEXII CCD diffractometer	3296 independent reflections
Radiation source: fine-focus sealed tube	2627 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.023$
$T = 295(2)$ K	$\theta_{max} = 25.3°$
φ and ω scans	$\theta_{min} = 2.4°$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$h = -10 \rightarrow 10$
$T_{min} = 0.710$, $T_{max} = 0.834$	$k = -16 \rightarrow 16$
13254 measured reflections	$l = -18 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.066$	H-atom parameters constrained
$wR(F^2) = 0.231$	$w = 1/[\sigma^2(F_o^2) + (0.147P)^2 + 2.2875P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.013$
3296 reflections	$\Delta\rho_{max} = 1.47$ e Å^{-3}
193 parameters	$\Delta\rho_{min} = -0.33$ 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 > 2sigma(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	0.64485 (8)	0.01038 (5)	0.10349 (5)	0.0575 (3)
C1	0.8655 (4)	0.1314 (2)	0.0466 (3)	0.0705 (14)
C2	0.9625 (5)	0.1411 (3)	−0.0101 (3)	0.093 (2)

H2	0.9766	0.0902	−0.0465	0.112*
C3	1.0384 (5)	0.2267 (4)	−0.0124 (4)	0.124 (3)
H3	1.1033	0.2332	−0.0503	0.148*
C4	1.0173 (6)	0.3027 (3)	0.0420 (4)	0.146 (4)
H4	1.0681	0.3600	0.0404	0.175*
C5	0.9204 (6)	0.2931 (3)	0.0987 (4)	0.128 (3)
H5	0.9063	0.3439	0.1351	0.153*
C6	0.8445 (5)	0.2074 (3)	0.1010 (3)	0.0848 (17)
C7	0.9436 (7)	−0.0871 (3)	0.2500 (4)	0.0640 (12)
C8	0.7500 (9)	0.2027 (5)	0.1635 (4)	0.098 (2)
H8	0.7466	0.2568	0.1986	0.117*
C9	0.5841 (12)	0.1325 (5)	0.2457 (5)	0.117 (3)
H9A	0.5629	0.1977	0.2592	0.140*
H9B	0.6451	0.1027	0.3030	0.140*
C10	0.4299 (12)	0.0775 (6)	0.2049 (7)	0.125 (3)
H10A	0.3826	0.0616	0.2535	0.150*
H10B	0.3571	0.1147	0.1574	0.150*
C11	0.4148 (7)	−0.0916 (5)	0.1681 (4)	0.0801 (16)
H11	0.3420	−0.0952	0.2011	0.096*
C12	0.4489 (4)	−0.1778 (2)	0.1251 (2)	0.0686 (13)
C13	0.4001 (5)	−0.2635 (3)	0.1534 (3)	0.0921 (19)
H13	0.3496	−0.2641	0.1994	0.110*
C14	0.4266 (6)	−0.3482 (2)	0.1127 (3)	0.106 (2)
H14	0.3939	−0.4055	0.1316	0.128*
C15	0.5020 (5)	−0.34726 (18)	0.0439 (3)	0.0937 (19)
H15	0.5197	−0.4040	0.0167	0.112*
C16	0.5508 (4)	−0.2616 (2)	0.0156 (2)	0.0723 (14)
H16	0.6013	−0.2610	−0.0304	0.087*
C17	0.5243 (4)	−0.17685 (18)	0.0563 (2)	0.0592 (11)
N1	0.6693 (7)	0.1302 (3)	0.1756 (3)	0.0799 (13)
N2	0.4777 (6)	−0.0108 (3)	0.1639 (3)	0.0737 (12)
N3	0.8165 (6)	−0.0691 (4)	0.2100 (4)	0.0823 (13)
O1	0.7880 (4)	0.0494 (3)	0.0418 (3)	0.0692 (9)
O2	0.5682 (4)	−0.0941 (2)	0.0227 (2)	0.0574 (8)
S1	1.11942 (18)	−0.11754 (13)	0.30794 (13)	0.0894 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0669 (5)	0.0504 (5)	0.0598 (5)	0.0061 (3)	0.0259 (4)	−0.0011 (3)
C1	0.057 (3)	0.066 (3)	0.080 (3)	−0.005 (2)	0.005 (2)	0.012 (3)
C2	0.061 (3)	0.089 (4)	0.127 (6)	−0.007 (3)	0.023 (3)	0.022 (4)
C3	0.076 (4)	0.120 (7)	0.159 (8)	−0.037 (4)	0.010 (4)	0.042 (6)
C4	0.117 (7)	0.112 (7)	0.162 (9)	−0.061 (6)	−0.034 (6)	0.028 (6)
C5	0.133 (7)	0.085 (5)	0.123 (6)	−0.041 (5)	−0.029 (5)	0.002 (4)
C6	0.091 (4)	0.068 (3)	0.075 (4)	−0.012 (3)	−0.009 (3)	−0.001 (3)
C7	0.080 (3)	0.051 (3)	0.066 (3)	0.006 (2)	0.029 (3)	0.010 (2)
C8	0.130 (6)	0.064 (4)	0.071 (4)	0.009 (4)	−0.015 (4)	−0.016 (3)

C9	0.190 (9)	0.082 (5)	0.090 (5)	0.030 (5)	0.058 (5)	−0.015 (4)
C10	0.169 (8)	0.110 (6)	0.130 (6)	0.039 (6)	0.098 (6)	−0.011 (5)
C11	0.079 (3)	0.105 (5)	0.067 (3)	0.013 (3)	0.037 (3)	0.023 (3)
C12	0.061 (3)	0.079 (3)	0.066 (3)	0.000 (2)	0.018 (2)	0.020 (3)
C13	0.090 (4)	0.102 (5)	0.084 (4)	−0.019 (4)	0.025 (3)	0.030 (4)
C14	0.111 (5)	0.073 (4)	0.124 (6)	−0.021 (4)	0.017 (5)	0.035 (4)
C15	0.090 (4)	0.058 (3)	0.126 (6)	0.000 (3)	0.021 (4)	0.010 (3)
C16	0.070 (3)	0.053 (3)	0.093 (4)	0.003 (2)	0.021 (3)	0.005 (2)
C17	0.055 (2)	0.054 (2)	0.068 (3)	0.001 (2)	0.017 (2)	0.006 (2)
N1	0.114 (4)	0.061 (3)	0.061 (3)	0.016 (3)	0.020 (2)	−0.006 (2)
N2	0.085 (3)	0.079 (3)	0.070 (3)	0.015 (2)	0.043 (2)	0.006 (2)
N3	0.085 (3)	0.078 (3)	0.082 (3)	0.016 (3)	0.020 (3)	0.011 (2)
O1	0.069 (2)	0.060 (2)	0.084 (2)	−0.0027 (16)	0.0313 (18)	−0.0004 (17)
O2	0.0661 (19)	0.0491 (16)	0.0641 (18)	0.0026 (14)	0.0302 (15)	0.0026 (14)
S1	0.0697 (9)	0.0979 (12)	0.1010 (12)	0.0079 (8)	0.0256 (8)	0.0270 (9)

Geometric parameters (Å, °)

Mn1—O1	1.874 (3)	C9—N1	1.469 (9)
Mn1—O2	1.902 (3)	C9—C10	1.552 (13)
Mn1—N1	1.979 (4)	C9—H9A	0.970
Mn1—N2	1.990 (5)	C9—H9B	0.970
Mn1—N3	2.181 (5)	C10—N2	1.503 (8)
Mn1—O2[i]	2.557 (3)	C10—H10A	0.970
C1—O1	1.339 (4)	C10—H10B	0.970
C1—C2	1.390	C11—N2	1.280 (8)
C1—C6	1.390	C11—C12	1.447 (7)
C2—C3	1.390	C11—H11	0.930
C2—H2	0.930	C12—C13	1.390
C3—C4	1.390	C12—C17	1.390
C3—H3	0.930	C13—C14	1.390
C4—C5	1.390	C13—H13	0.930
C4—H4	0.930	C14—C15	1.390
C5—C6	1.390	C14—H14	0.930
C5—H5	0.930	C15—C16	1.390
C6—C8	1.439 (9)	C15—H15	0.930
C7—N3	1.155 (7)	C16—C17	1.390
C7—S1	1.627 (6)	C16—H16	0.930
C8—N1	1.295 (9)	C17—O2	1.371 (4)
C8—H8	0.930		
O1—Mn1—O2	94.95 (14)	N1—C9—H9B	110.2
O1—Mn1—N1	92.1 (2)	C10—C9—H9B	110.2
O1—Mn1—N2	170.90 (17)	H9A—C9—H9B	108.5
O1—Mn1—N3	93.94 (18)	N2—C10—C9	104.1 (6)
O1—Mn1—O2[i]	88.62 (15)	N2—C10—H10A	110.9
O2—Mn1—N1	165.40 (19)	C9—C10—H10A	110.9
O2—Mn1—N2	89.51 (17)	N2—C10—H10B	110.9
O2—Mn1—N3	96.85 (17)	C9—C10—H10B	110.9

O2—Mn1—O2[i]	80.14 (14)	H10A—C10—H10B	109.0
N1—Mn1—N2	81.9 (2)	N2—C11—C12	124.6 (5)
N1—Mn1—N3	95.4 (2)	N2—C11—H11	117.7
N1—Mn1—O2[i]	87.29 (16)	C12—C11—H11	117.7
N2—Mn1—N3	93.4 (2)	C13—C12—C17	120.0
N2—Mn1—O2[i]	84.35 (17)	C13—C12—C11	117.6 (3)
N3—Mn1—O2[i]	176.24 (17)	C17—C12—C11	122.3 (3)
O1—C1—C2	117.4 (3)	C12—C13—C14	120.0
O1—C1—C6	122.4 (3)	C12—C13—H13	120.0
C2—C1—C6	120.0	C14—C13—H13	120.0
C3—C2—C1	120.0	C13—C14—C15	120.0
C3—C2—H2	120.0	C13—C14—H14	120.0
C1—C2—H2	120.0	C15—C14—H14	120.0
C2—C3—C4	120.0	C14—C15—C16	120.0
C2—C3—H3	120.0	C14—C15—H15	120.0
C4—C3—H3	120.0	C16—C15—H15	120.0
C5—C4—C3	120.0	C17—C16—C15	120.0
C5—C4—H4	120.0	C17—C16—H16	120.0
C3—C4—H4	120.0	C15—C16—H16	120.0
C4—C5—C6	120.0	O2—C17—C16	117.5 (2)
C4—C5—H5	120.0	O2—C17—C12	122.4 (2)
C6—C5—H5	120.0	C16—C17—C12	120.0
C5—C6—C1	120.0	C8—N1—C9	120.8 (6)
C5—C6—C8	116.3 (4)	C8—N1—Mn1	124.9 (4)
C1—C6—C8	123.6 (4)	C9—N1—Mn1	114.2 (4)
N3—C7—S1	177.1 (5)	C11—N2—C10	122.0 (6)
N1—C8—C6	126.1 (5)	C11—N2—Mn1	124.0 (4)
N1—C8—H8	117.0	C10—N2—Mn1	114.0 (5)
C6—C8—H8	117.0	C7—N3—Mn1	151.3 (5)
N1—C9—C10	107.5 (6)	C1—O1—Mn1	130.4 (3)
N1—C9—H9A	110.2	C17—O2—Mn1	120.8 (2)
C10—C9—H9A	110.2		

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

Fig. 1