

C(6)	0.467 (1)	0.810 (1)	0.3359 (6)	3.9 (4)
C(7)	0.588 (1)	0.653 (2)	0.3228 (6)	5.3 (5)
C(8)	0.383 (2)	0.403 (1)	0.2852 (7)	7.9 (7)
C(9)	0.226 (1)	0.515 (2)	0.2837 (7)	9.4 (7)
C(10)	0.387 (2)	0.597 (1)	0.2449 (6)	4.3 (4)
C(11)	0.455 (2)	0.564 (2)	0.2140 (8)	6.3 (6)
C(12)	0.486 (2)	0.623 (2)	0.1761 (9)	10.4 (8)
C(13)	0.439 (2)	0.707 (2)	0.1679 (9)	13.4 (6)
C(14)	0.377 (2)	0.746 (2)	0.1976 (9)	12.4 (8)
C(15)	0.350 (1)	0.687 (1)	0.2353 (7)	5.2 (5)
C(16)	0.523 (1)	0.814 (1)	0.5019 (7)	4.2 (4)
C(17)	0.479 (1)	0.847 (1)	0.4606 (6)	3.8 (4)
C(18)	0.537 (1)	0.918 (1)	0.4396 (7)	4.5 (4)
C(19)	0.614 (1)	0.932 (1)	0.4719 (8)	5.7 (5)
C(20)	0.608 (2)	0.864 (1)	0.5086 (7)	5.3 (5)
C(21)	0.669 (1)	0.599 (1)	0.4337 (7)	4.5 (4)
C(22)	0.740 (1)	0.654 (1)	0.4095 (7)	4.5 (4)
C(23)	0.785 (1)	0.714 (2)	0.4437 (8)	5.6 (5)
C(24)	0.739 (1)	0.697 (1)	0.4890 (8)	5.7 (5)
C(25)	0.669 (2)	0.627 (1)	0.4798 (7)	6.0 (5)
Cp(1)†	0.552	0.875	0.476	
Cp(2)	0.720	0.658	0.451	

† Cp(1) and Cp(2) represent the centroids of the C(16)–C(20) and C(21)–C(25) cyclopentadienyl rings, respectively.

Table 2. Selected geometric parameters (Å, °)

W–Nb	4.679 (2)	W–C(4)	1.99 (2)
W–P(1)	2.610 (4)	W–C(5)	2.00 (2)
W–P(2)	2.524 (5)	Nb–Cp(1)	2.06
W–C(2)	1.95 (2)	Nb–Cp(2)	2.07
W–C(3)	2.00 (2)	Nb–P(1)	2.668 (4)
P(1)–W–P(2)	97.7 (1)	C(2)–W–C(5)	88.3 (6)
P(1)–W–C(2)	176.1 (6)	C(3)–W–C(4)	177.2 (7)
P(1)–W–C(3)	91.9 (5)	C(3)–W–C(5)	87.9 (6)
P(1)–W–C(4)	90.3 (5)	C(4)–W–C(5)	93.8 (6)
P(1)–W–C(5)	88.8 (5)	P(1)–Nb–C(1)	87.3 (5)
P(2)–W–C(2)	85.4 (5)	Cp(1)–Nb–Cp(2)	139.4
P(2)–W–C(3)	87.6 (5)	W–P(1)–Nb	124.9 (2)
P(2)–W–C(4)	90.4 (5)	W–P(1)–C(6)	108.4 (6)
P(2)–W–C(5)	172.1 (4)	W–P(1)–C(7)	110.4 (7)
C(2)–W–C(3)	90.7 (7)	Nb–P(1)–C(6)	106.1 (6)
C(2)–W–C(4)	87.2 (7)	Nb–P(1)–C(7)	105.1 (6)

SDP (Enraf–Nonius, 1985) was used to solve and refine the structure.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: PA1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Mononuclear Manganese(III) Schiff Base Complex, [Mn(C₁₄H₁₀N₂O₂)-(C₈H₇O₃)(CH₄O)]

SOMNATH DUTTA AND VADIVELU MANTIVANNAN

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

LINGAMALLU GIRI BABU AND SAMUDRANIL PAL*

School of Chemistry, University of Hyderabad, Hyderabad 500 134, India

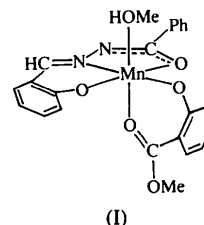
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Abstract

In the title compound, [2-(α -hydroxybenzylidenehydrazonomethyl)phenolato(2-)-*N,O,O'*](methanol-*O*)-(methyl salicylato-*O,O'*)manganese(III), [Mn(BHS)-(MS)(CH₃OH)], the manganese(III) ion is surrounded by an O₅N coordination sphere. The tridentate 2-(α -hydroxybenzylidenehydrazonomethyl)phenolate (BHS²⁻) ligand (H₂BHS is the benzoyl hydrazone of salicylaldehyde) binds the metal ion meridionally and the methyl salicylate (MS⁻) ligand is bidentate. The sixth position is occupied by a methanol molecule. There is a significant tetragonal elongation due to a Jahn–Teller effect.

Comment

Our interest in polynuclear manganese complexes has led us to obtain mononuclear manganese complexes with coordinated solvent molecules. We intend to use these mononuclear complexes as precursors in the synthesis of polynuclear species of desired nuclearity by replacing the solvent molecules with various bridging groups such as oxo, hydroxo, acetato, etc. Herein we report the structure of a new mononuclear manganese(III) complex containing a coordinated methanol molecule, (I).



A view of the [Mn(BHS)(MS)(CH₃OH)] molecule with the atom-labelling scheme is presented in Fig. 1. The manganese(III) ion has an O₅N coordination sphere.

The meridional tridentate ligand BHS²⁻ is bound to the metal ion through the phenolate O, the imine N and the amide O atoms. The bidentate MS⁻ ligand is coordinated to the manganese ion *via* the phenolate O and the keto O atoms of the ester function. The sixth position is occupied by the O atom of the CH₃OH solvent molecule. As expected, the chelate bite angle in the five-membered ring [79.0(1)°] formed by the tridentate BHS²⁻ ligand is smaller than that in the six-membered ring [90.5(1)°]. For the MS⁻ ligand, which also forms a six-membered ring, the corresponding angle is 85.2(1)°.

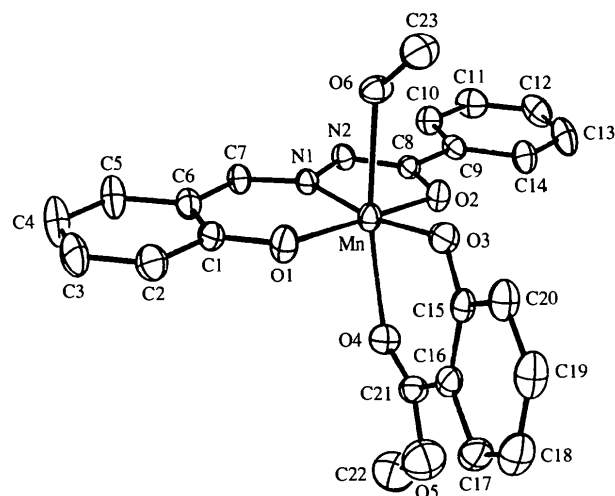


Fig. 1. The structure of [Mn(BHS)(MS)(CH₃OH)] depicting 30% probability displacement ellipsoids and the atom-labelling scheme. H atoms are omitted for clarity.

Bond distances between the Mn and phenolate-O atoms found in this complex are comparable with those of other structurally characterized Mn^{III} Schiff base complexes (Oki & Hodgson, 1990; Gohdes & Armstrong, 1992). The bond length [1.931(2) Å] between the Mn and amide-O atom is also unexceptional (Mangia, Nardelli, Pelizzi & Pelizzi, 1973). Significant tetragonal elongation of the MnO₅N octahedron is observed due to a Jahn–Teller effect. This type of distortion is very common in high-spin 3d⁴ systems such as manganese(III) (Oki & Hodgson, 1990; Larson, Lah, Li, Bonadies & Pecoraro, 1992, and references therein). The O atom of the methanol molecule [Mn—O 2.269(3) Å] and the keto O atom [Mn—O 2.234(3) Å] of the ester function of the MS⁻ ligand are coordinated along the Jahn–Teller axis. The large deviation of the O(4)—Mn—O(6) angle [169.3(1)°] from 180° is possibly due to the small chelate bite angle [85.2(1)°] of the MS⁻ ligand.

Experimental

To a methanolic solution (20 ml) of H₂BHS (240.3 mg, 1 mmol), solid KOH (115 mg, 1.02 mmol) was added and the mixture was stirred at room temperature until a clear yellow solution was obtained. To this yellow solution, 245.1 mg (1 mmol) of Mn(O₂CCH₃)₂·4H₂O dissolved in 10 ml of methanol was added followed by 0.13 ml (153 mg, 1.01 mmol) of methyl salicylate. The mixture was stirred in air at room temperature for 2 h. The dark microcrystalline solid which separated was collected by filtration and washed with ice-cold methanol and finally dried in air [yield 415 mg (87%)]. Analysis found: C 58.19, H 4.48, N 6.02%. Analysis calculated for MnC₂₃H₂₁N₂O₆: C 57.99, H 4.44, N 5.88%. Solid-state magnetic moment, $\mu_{\text{eff}} = 4.99\mu_B$ at 300 K.

Crystal data

[Mn(C₁₄H₁₀N₂O₂)(C₈H₇O₃)(CH₄O)]

$M_r = 476.4$

Triclinic

$P\bar{1}$

$a = 7.595(5) \text{ \AA}$

$b = 10.146(6) \text{ \AA}$

$c = 15.005(10) \text{ \AA}$

$\alpha = 77.28(5)^\circ$

$\beta = 75.93(5)^\circ$

$\gamma = 69.39(5)^\circ$

$V = 1038.2(12) \text{ \AA}^3$

$Z = 2$

$D_x = 1.524 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 5\text{--}15^\circ$

$\mu = 0.680 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Parallelepiped

$0.60 \times 0.53 \times 0.48 \text{ mm}$

Data collection

Nicolet R3m/V diffractometer

ω scans

Absorption correction:

none

3958 measured reflections

3654 independent reflections

3060 observed reflections

[$F > 6\sigma(F)$]

$R_{\text{int}} = 0.011$

$\theta_{\text{max}} = 25^\circ$

$h = -8 \rightarrow 9$

$k = -11 \rightarrow 12$

$l = 0 \rightarrow 17$

2 standard reflections

monitored every 98

reflections

intensity decay: none

Refinement

Refinement on F

$R = 0.0470$

$wR = 0.0595$

$S = 0.90$

3060 reflections

289 parameters

$w = 1/[\sigma^2(F_o) + 0.0008F_o^2]$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.82 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Mn	0.2395 (1)	0.9368 (1)	0.7976 (1)	0.036 (1)
O(1)	0.1111 (3)	1.0893 (2)	0.7164 (1)	0.050 (1)
O(2)	0.3803 (3)	0.8103 (2)	0.8911 (1)	0.042 (1)
O(3)	0.2799 (3)	0.7963 (2)	0.7252 (1)	0.045 (1)
O(4)	0.5188 (3)	0.9568 (2)	0.7151 (1)	0.048 (1)

O(5)	0.7659 (6)	0.9210 (5)	0.5946 (3)	0.095 (2)
O(6)	-0.0231 (3)	0.8748 (3)	0.8745 (2)	0.050 (1)
N(1)	0.1795 (3)	1.0629 (2)	0.8909 (2)	0.034 (1)
N(2)	0.2495 (3)	0.9969 (2)	0.9740 (2)	0.036 (1)
C(1)	0.0199 (4)	1.2242 (3)	0.7268 (2)	0.041 (1)
C(2)	-0.0630 (5)	1.3164 (4)	0.6529 (2)	0.055 (1)
C(3)	-0.1609 (6)	1.4584 (4)	0.6601 (3)	0.066 (1)
C(4)	-0.1814 (7)	1.5135 (4)	0.7389 (3)	0.074 (2)
C(5)	-0.1008 (6)	1.4248 (3)	0.8122 (3)	0.062 (1)
C(6)	0.0015 (4)	1.2804 (3)	0.8070 (2)	0.041 (1)
C(7)	0.0828 (4)	1.1960 (3)	0.8859 (2)	0.040 (1)
C(8)	0.3539 (4)	0.8652 (3)	0.9650 (2)	0.034 (1)
C(9)	0.4460 (4)	0.7729 (3)	1.0428 (2)	0.037 (1)
C(10)	0.4278 (5)	0.8210 (3)	1.1252 (2)	0.048 (1)
C(11)	0.5114 (6)	0.7274 (4)	1.1968 (2)	0.060 (1)
C(12)	0.6133 (6)	0.5874 (4)	1.1865 (3)	0.065 (2)
C(13)	0.6344 (6)	0.5395 (4)	1.1058 (3)	0.068 (2)
C(14)	0.5529 (5)	0.6321 (3)	1.0324 (2)	0.051 (1)
C(15)	0.3723 (4)	0.7814 (3)	0.6399 (2)	0.040 (1)
C(16)	0.5250 (4)	0.8332 (3)	0.5958 (2)	0.042 (1)
C(17)	0.6194 (5)	0.8053 (4)	0.5049 (2)	0.058 (1)
C(18)	0.5629 (6)	0.7301 (4)	0.4590 (2)	0.066 (2)
C(19)	0.4118 (6)	0.6799 (4)	0.5020 (3)	0.062 (2)
C(20)	0.3162 (5)	0.7048 (3)	0.5900 (2)	0.052 (1)
C(21)	0.5955 (4)	0.9121 (3)	0.6407 (2)	0.044 (1)
C(22)	0.8524 (9)	0.9968 (7)	0.6320 (4)	0.096 (3)
C(23)	-0.0962 (6)	0.7768 (5)	0.8567 (3)	0.068 (2)

Table 2. Selected geometric parameters (Å, °)

Mn—O(1)	1.875 (2)	Mn—O(2)	1.931 (2)
Mn—O(3)	1.876 (3)	Mn—O(4)	2.234 (3)
Mn—O(6)	2.269 (3)	Mn—N(1)	1.967 (3)
O(1)—Mn—O(2)	168.1 (1)	O(1)—Mn—O(3)	95.6 (1)
O(1)—Mn—O(4)	89.6 (1)	O(1)—Mn—O(6)	95.7 (1)
O(1)—Mn—N(1)	90.5 (1)	O(2)—Mn—O(3)	95.6 (1)
O(2)—Mn—O(4)	87.3 (1)	O(2)—Mn—O(6)	89.3 (1)
O(2)—Mn—N(1)	79.0 (1)	O(3)—Mn—O(4)	85.2 (1)
O(3)—Mn—O(6)	85.1 (1)	O(3)—Mn—N(1)	170.3 (1)
O(4)—Mn—O(6)	169.3 (1)	O(4)—Mn—N(1)	102.4 (1)
O(6)—Mn—N(1)	86.9 (1)		

The structure was solved by Patterson and Fourier methods. The model was then refined by full-matrix least-squares procedures. All non-H atoms were refined using anisotropic displacement parameters. H atoms were included in the structure-factor calculations at idealized positions with fixed displacement parameters, but were not refined.

All calculations for data reduction, structure solution and refinement were performed on a MicroVAX II computer using the *SHELXTL-Plus88* (Sheldrick, 1988) package. Data collection and cell refinement were performed using Nicolet P3 diffractometer software. Molecular graphics were prepared using *SHELXTL-Plus88*.

The data were collected at the National Single Crystal Diffractometer Facility at the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta. Financial support received from the Department of Science and Technology, New Delhi, is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1150). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Aquachloro[bis(5-chlorosalicylidene)-ethylenediaminato]manganese(III)

COLIN P. HORWITZ

Department of Chemistry, Carnegie Mellon University,
4400 Fifth Avenue, Pittsburgh, PA 15213-3890, USA

GREGORY C. DAILEY AND FOOK S. THAM

Department of Chemistry, Rensselaer Polytechnic
Institute, Troy, NY 12180-3590, USA

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Abstract

The title compound [systematic name: aquachloro{5,5'-dichloro-2,2'-[1,2-ethanediy]bis(nitrimethylidene)}diphenolato-*N,N',O,O'*}manganese(III)], [MnCl(C₁₆H₁₂Cl₂N₂O₂)(H₂O)], has the Mn^{III} center in a pseudo-octahedral environment where the four donor atoms of the Schiff base ligand define the equatorial plane [Mn—O 1.874 (3) and 1.883 (2), Mn—N 1.973 (3) and 1.986 (2) Å] with a water molecule [Mn—O 2.319 (3) Å] and a chlorine [Mn—Cl 2.572 (1) Å] occupying the axial positions.

Comment

In general, Mn^{III} Schiff base complexes with tetradentate ligands have metal centers that are six-coordinate in solution with the additional ligands being either anions or solvent molecules. This ligation phenomenon is observable by spectroscopic (Boucher & Day, 1977) and electrochemical means (Horwitz, Ciringh, Liu & Park, 1993). Solid-state structures of the same Mn^{III} Schiff base complexes are found with five-coordinate (Gohdes & Armstrong, 1988; Pecoraro & Butler, 1986) and six-coordinate (Davies, Gatehouse & Murray, 1973; Matsumoto, Takemoto, Ohyosi & Okawa, 1988; Ashmawy, Beagly, McAuliffe, Parish & Pritchard, 1990) metal centers. Subtle differences in either the solvent