

Crystal Structure of Diaqua[*N,N'*-bis(3-methoxysalicylidene)propane-1,2-diaminato]manganese(III) nitrate monohydrate

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The title compound, a hydrogen-bonded linear chain of pseudodimers, $\text{Mn}(\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2[\text{NO}_3]\cdot\text{H}_2\text{O}$, (I), has been determined. The complex affords an elongated octahedral MnN_2O_4 coordination environment, geometry with the four donor atoms of the tetradentate Schiff base in the equatorial plane and with two aqua ligands in axial positions with $\text{Mn-O} = 2.238(4)$ and $2.256(3)\text{\AA}$.

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Much recent interest in the coordination chemistry of manganese with N and/or O containing ligands has been driven by the important roles in metalloenzymes and highly valuable catalysts in olefin epoxidation,¹ optical and magnetic materials.^{2,3} In particular, manganese derivatives from tetradentate Schiff-base ligands have a clear tendency to form infinite linear or helical chains, due to the predisposition of these ligands to occupy a planar configuration in octahedral coordination geometry, leaving the axial positions free to develop polymerization through bidentate bridges.⁴ Recently, part of our research program has focused on Schiff-base Mn^{III} complexes.^{2,3} As an extension of the research on the structural characterization of Mn^{III} complexes, here the crystal structure of the title compound, which is a hydrogen-bonded linear chain of pseudodimers Schiff-base Mn^{III} complex having elongated axial Mn-O bonds to two aqua ligands, is reported.

The ligand was prepared by the reaction of 1,2-diaminopropane (1 mmol) with 3-methoxysalicylaldehyde (2 mmol) in hot ethanol (100 mL). A yellow compound was precipitated from the solution upon cooling. The title compound was prepared by the addition of manganese(III) nitrate dihydrate (1 mmol) in 70 mL of hot ethanol to the ligand (1 mmol) in 100 mL of hot methanol. The resulting solution was stirred for 10 min. A deep-green solution was obtained, which was allowed to stand at room temperature. Several weeks of standing led to the

growth of deep-green crystals of the title compound, suitable for X-ray analysis. *Anal.* Calcd for $\text{C}_{19}\text{H}_{25}\text{MnN}_3\text{O}_{10}$: C, 44.71; H, 4.94; N, 8.23%. Found: C, 44.50; H, 5.02; N, 8.35%.

Diffraction measurements were made on three-circle CCD diffractometers using graphite-monochromated $\text{Mo-K}\alpha$ radiation at 100 K. The intensity data were integrated using the SAINT program. The structure was solved by direct methods, and refined using full-matrix least squares against F^2 using SHELXTL. All non-hydrogen atoms were refined anisotropically. The 1,2-diaminopropane portion of the ligand is disordered over two positions, which manifests itself as a terminal methyl group (atoms C19A or C19B) being attached to either C17 or C18, with 67% and 33% occupancy, respectively. The water molecule O10 is disordered over two positions (O10a/O10b) with occupancies of 0.4/0.6. The positions of the water H atoms were located from difference Fourier maps. The O-H distances were restrained to $0.80(2)\text{\AA}$, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

In complex (I), the molecule comprises a manganese(III) centre coordinated by the nearly planar Schiff-base ligand [the

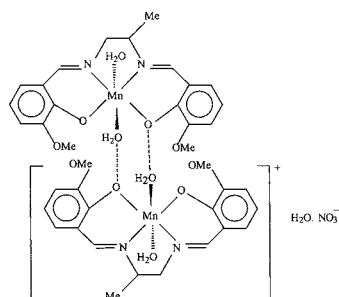


Fig. 1 Schematic diagram of the title compound.

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Table 1 Crystal and experimental data

CCDC	669006	
Formula	$\text{C}_{19}\text{H}_{25}\text{MnN}_3\text{O}_{10}$	
Formula weight	510.36	
Crystal system	triclinic	
Space group	$P\bar{1}$	
	$Z = 2$	
Unit cell dimensions	$a = 8.983(7)\text{\AA}$	$\alpha = 112.542(12)^\circ$
	$b = 11.643(9)\text{\AA}$	$\beta = 107.445(13)^\circ$
	$c = 12.661(10)\text{\AA}$	$\gamma = 93.419(13)^\circ$
Volume	$1143.7(15)\text{\AA}^3$	
D_x	1.482 g/cm^3	
No. of reflections used	2242	
θ range for data collection	1.86 to 27.57° with $\text{Mo K}\alpha$	
μ	0.636 mm^{-1}	
R	0.0551	
Largest diff. peak and hole	0.392 and $-0.625\text{ e}\text{\AA}^{-3}$	
Measurement	Bruker SMART APEX CCD area detector	
Program system	SAINT	
Structure determination	SHELXTL	
Refinement method	full-matrix least-squares on F^2	

Table 2 Selected geometric parameters [\AA , $^\circ$]

Mn(1)-N(1)	1.967 (4)	Mn(1)-O(2)	1.890 (3)
Mn(1)-N(2)	1.981 (4)	Mn(1)-O(5)	2.256 (3)
Mn(1)-O(1)	1.885 (3)	Mn(1)-O(6)	2.238 (4)
O(1)-Mn(1)-O(2)	94.29 (12)	N(1)-Mn(1)-O(5)	90.14 (14)
O(1)-Mn(1)-N(1)	91.41 (14)	N(2)-Mn(1)-O(5)	89.73 (14)
O(2)-Mn(1)-N(2)	91.91 (14)	O(2)-Mn(1)-O(6)	87.55 (13)
O(2)-Mn(1)-N(1)	174.09 (14)	O(1)-Mn(1)-O(5)	88.80 (12)
O(1)-Mn(1)-N(2)	173.66 (14)	N(1)-Mn(1)-O(6)	90.51 (14)
N(1)-Mn(1)-N(2)	82.43 (15)	N(2)-Mn(1)-O(6)	87.92 (15)
O(2)-Mn(1)-O(5)	91.55 (12)	O(5)-Mn(1)-O(6)	177.45 (12)
O(1)-Mn(1)-O(6)	93.65 (14)		

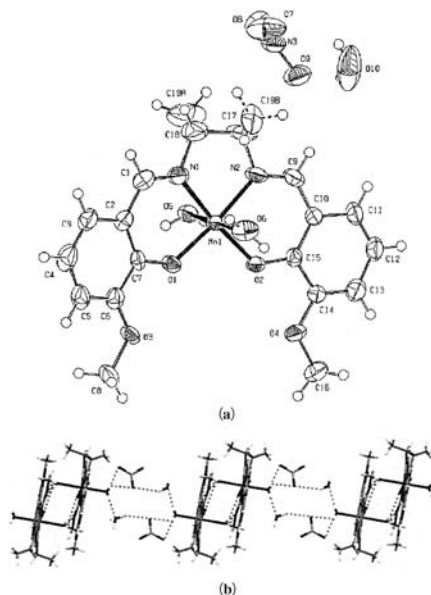


Fig. 2 (a) ORTEP drawing of the title compound with atom labeling; (b) Stick representation of the hydrogen-bonded (dashed lines) linear chain of pseudodimers formed in (I).

angle between the least-squares planes of the aromatic rings of the ligands is 11.53° with Mn-O_{phenol} bond lengths of 1.885(3) \AA and 1.890(3) \AA , together with Mn-N_{imin} bond lengths of 1.967(4) \AA and 1.981(4) \AA . The coordination sphere of the manganese centre is completed by two water molecules [Mn-O_{water} = 2.238(4) \AA , 2.256(3) \AA]. The central Mn^{III} ion adopts an elongated octahedral coordination geometry, with the displacement of the Mn1 ion from the O1/N1/N2/O2 least-squares plane being 0.002(2) \AA . In the crystal structure of (I), adjacent molecules are linked by hydrogen bonds [O5...O1ⁱ = 2.875 \AA , O5...O2ⁱ = 2.941 \AA , O5...O3ⁱ = 2.934 \AA and O5...O4ⁱ = 3.003 \AA ; symmetry code: (i) $-x+1, -y, -z$], to form hydrogen-bonded pseudo-dimers, with additional face-to-face π - π stacking interactions between the benzene groups (C7...C15 = 3.681 \AA

Table 3 Hydrogen bonding geometry [\AA , $^\circ$]

D-H...A	D-H	H...A	D...A	D-H...A
O10B-H10B...O7	0.77 (5)	2.52 (4)	3.099 (9)	133 (4)
O5-H5A...O1 ⁱ	0.80 (4)	2.29 (5)	2.875 (5)	131 (5)
O5-H5B...O2 ⁱ	0.79 (5)	2.27 (5)	2.941 (5)	144 (5)
O5-H5A...O3 ⁱ	0.80 (4)	2.18 (4)	2.934 (5)	157 (5)
O5-H5B...O4 ⁱ	0.79 (5)	2.31 (5)	3.003 (5)	147 (5)
O6-H6B...O8 ⁱⁱ	0.78 (4)	2.35 (4)	3.126 (5)	171 (4)
O6-H6B...O9 ⁱⁱ	0.78 (4)	2.30 (5)	2.893 (6)	134 (4)
O6-H6A...O10B ⁱⁱⁱ	0.78 (4)	1.89 (4)	2.670 (8)	177 (8)

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z$.

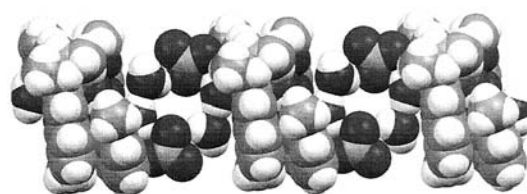


Fig. 3 Spacefill representation of the hydrogen-bonded linear chain of pseudodimers formed in (I).

and C6...C10 = 3.825 \AA); symmetry code: (i) $[-x+1, -y, -z]$. Moreover, intermolecular hydrogen bonds [O6...O8 = 3.126 \AA and O6...O9 = 2.893 \AA ; symmetry code: (ii) $x+1, y, z$, and O6...O10B = 2.670 \AA (iii) $-x+1, -y+1, -z$] between these pseudo-dimers and nitrate counterions result in hydrogen-bonded linear chains.

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