

## Research Article

# Synthesis and Crystal Structure of [Mn<sup>III</sup>(5-Br-salpn)(DMF)<sub>2</sub>][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]

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The title compound was synthesized by the reaction between a manganese(II) carboxylate and the tetradentate Schiff base ligand, 5-Br-salpnH<sub>2</sub> [*N,N'*-bis(5-Br-salicylidene)-1,3-diaminopropane] produced *in situ*. The complex crystallizes in the *P2<sub>1</sub>/c* space group with unit cell dimensions *a* = 12.37980(10), *b* = 12.60990(10), *c* = 28.9438(3),  $\alpha$  = 90.00,  $\beta$  = 102.0130(10), and  $\gamma$  = 90.00. The manganese(III) ion is in a distorted octahedral environment with longer axial bonds.

## 1. Introduction

Recent advances in the coordination chemistry of manganese has been intimately connected to diverse fields such as, asymmetric catalysis [1, 2], molecular magnetism [3–5], and bioinorganic modeling [6–8]. With its accessible oxidation states of (II), (III), (IV), and (V), manganese plays several important roles in biological systems like the oxygen-evolving complex (OEC) of photosystem II [9, 10] and enzymes like superoxide dismutase, catalase, and arginase [11, 12]. Active sites of most of these systems contain manganese ligated mainly by N and O-donor atoms from the amino acid residues of the metalloproteins. Inorganic model complexes have made significant contributions to the progress in delineating the structural and functional aspects of the active sites of these systems [13–16]. Ligands such as aliphatic, cyclic Schiff bases, polypyridyl systems, and carboxylic acids can stabilize manganese in its various oxidation states [17, 18]. Schiff base ligands with nitrogen and oxygen donor atoms may provide a chemical environment which can mimic the coordination spheres of manganese in biological systems better than any other ligand type. A whole host of manganese Schiff base complexes have been reported in this context during the last few decades [19–27]. Among these, there is a sizeable number of complexes of the salpn [salpnH<sub>2</sub> = *N,N'*-bis(salicylidene)-1, 3-diaminopropane]

and substituted salpn ligands [19–22]. We have been interested in the coordination chemistry of higher oxidation states of manganese for some time, and herein, we report the isolation of a new manganese(III) complex, [Mn<sup>III</sup>(5-Br-salpn)(DMF)<sub>2</sub>][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>].

## 2. Experimental

**2.1. Materials and Physical Measurements.** All chemicals were purchased from E-Merck and used without further purification. IR spectrum was recorded on a Nicolet 6700 spectrophotometer (KBr pellets, 4000–400 cm<sup>-1</sup>) while UV-Vis spectrum was taken on a Cary 100 Bio UV-Vis spectrophotometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHNS analyzer.

**2.2. Synthesis of [Mn<sup>III</sup>(5-Br-salpn)(DMF)<sub>2</sub>][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>].** The starting material, [Mn<sub>2</sub>(Hsal)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>], was prepared as reported earlier or alternatively by mixing hot aqueous solutions of sodium salicylate and manganese(II)chloride (2:1 molar ratio), which gave pale pink crystals of the compound in yields greater than 80% in a day's time [28]. To a solution of [Mn<sub>2</sub>(Hsal)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>] (1.00 g, 2.19 mmol), 5-bromosalicylaldehyde (0.88 g, 4.38 mmol) and sodium tetraphenylborate (0.75 g, 2.19 mmol) in methanol/DMF

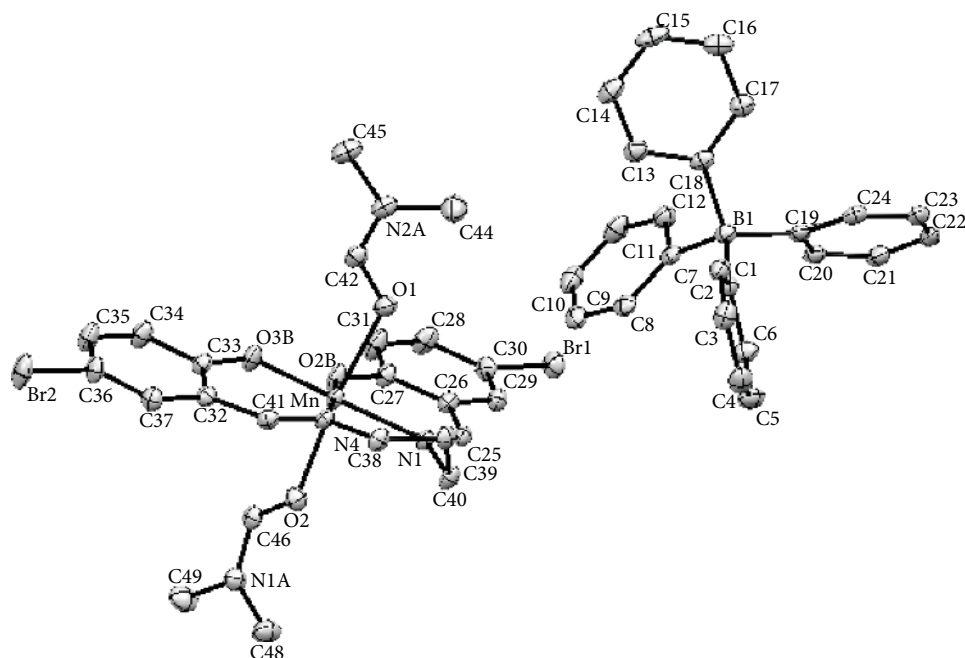


FIGURE 1: Molecular structure of  $[\text{Mn}^{\text{III}}(5\text{-Br-salpn})(\text{DMF})_2][\text{B}(\text{C}_6\text{H}_5)_4]$ . Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

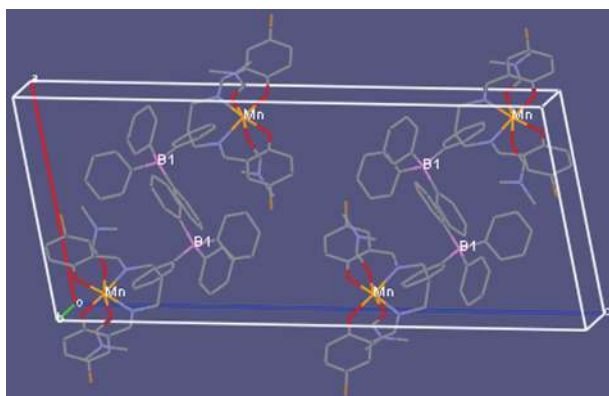


FIGURE 2: Crystal structure of  $[\text{Mn}^{\text{III}}(5\text{-Br-salpn})(\text{DMF})_2][\text{B}(\text{C}_6\text{H}_5)_4]$  showing the close packing of the cationic Mn(III) complex and the counter ions.

mixture (20 mL, 1:1 v/v), 1,3-diaminopropane (0.16 g, 2.19 mmol) was added. The solution was stirred for a few minutes, filtered, and left to be evaporated in an open conical flask. Dark green crystals were deposited in 4-5 days. These were collected by filtration, washed with diethylether, and dried in air. Anal. calc. for  $\text{C}_{47}\text{H}_{48}\text{BBr}_2\text{MnN}_4\text{O}_4$ : C, 58.84; H, 5.00; N, 5.84; Mn, 5.73. Found: C, 58.12.; H, 4.94; N, 5.29; Mn, 5.38%. IR (KBr pellet):  $\bar{\nu}/\text{cm}^{-1} = 3122 \text{ w}, 3031 \text{ w}, 1623 \text{ s}, 1579 \text{ s}, 1345 \text{ m}, 1295 \text{ w}, 1278 \text{ w}, 1261 \text{ m}, 1152 \text{ w}, 999 \text{ w}, 964 \text{ m}, 798 \text{ s}, 452 \text{ m}$ . UV-Vis (methanol):  $\lambda/\text{nm} = 232$  ( $\epsilon_{\text{max}} = 10136 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ), 474 ( $\epsilon_{\text{max}} = 341 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ).

2.3. X-Ray Crystallography. Data were collected on a Bruker APEX II diffractometer, equipped with a CCD area detector

(Cu-K $\alpha$  radiation, graphite monochromator,  $\lambda = 1.54178 \text{ \AA}$ , at 100(2) K). The crystal structure was solved by direct methods and refined by full-matrix least-squares methods based on  $F^2$  values against all reflections including anisotropic displacement parameters for all non-H atoms, using SHELXS97 and SHELXL97 [29]. All the nonhydrogen atoms were located from a Fourier map and refined anisotropically. Hydrogen site locations were inferred from neighbouring sites and were treated by a mixture of independent and constrained refinement. The molecular graphics were done with MERCURY 2.0 [30]. Crystal data and parameters for data collection are listed in Table 1.

### 3. Results

3.1. Crystal Structure of  $[\text{Mn}^{\text{III}}(5\text{-Br-salpn})(\text{DMF})_2][\text{B}(\text{C}_6\text{H}_5)_4]$ . The complex crystallizes in the monoclinic space group,  $P2_1/c$ . Molecular structure of  $[\text{Mn}(5\text{-Br-salpn})(\text{DMF})_2]\text{BPh}_4$  is depicted in Figure 1. The cation,  $[\text{Mn}(5\text{-Br-salpn})(\text{DMF})_2]^+$ , is monomeric and octahedral. The 5-Br-salpn ligand, with its  $\text{N}_2\text{O}_2$  donor set, holds the manganese(III) ion in an approximate square plane.

The  $\text{Mn}-\text{O}_{\text{phenol}}$  bonds [ $\text{Mn}-\text{O}2\text{B} = 1.8852(12) \text{ \AA}$  and  $\text{Mn}-\text{O}3\text{B} = 1.8955(12) \text{ \AA}$ ] are slightly stronger than the  $\text{Mn}-\text{N}_{\text{imine}}$  bonds [ $\text{Mn}-\text{N}1 = 2.0259(14) \text{ \AA}$  and  $\text{Mn}-\text{N}4 = 2.0459(14) \text{ \AA}$ ]. Oxygen atoms of the DMF solvent molecules coordinate with the manganese(III) ion and occupy the *trans* coordination positions of the complex. Jahn-Teller distortion causes an elongation of these axial bonds [ $\text{Mn}-\text{O}2 = 2.2119(12) \text{ \AA}$ ,  $\text{Mn}-\text{O}1 = 2.2282(13) \text{ \AA}$ ]. Selected bond angles and bond lengths of  $[\text{Mn}(5\text{-Br-salpn})(\text{DMF})_2]^+$  are given in Table 2. The  $[\text{BPh}_4]^-$  counter ions form helical chains

TABLE 1: Crystal data and parameters for data collection for  $[\text{Mn}^{\text{III}}(5\text{-Br-salpn})(\text{DMF})_2][\text{B}(\text{C}_6\text{H}_5)_4]$ .

Empirical formula	$\text{C}_{47}\text{H}_{48}\text{BBr}_2\text{MnN}_4\text{O}_4$
Formula weight	958.46
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 12.3798(1)$ Å $\alpha = 90^\circ$ $b = 12.6099(1)$ Å $\beta = 102.013(1)^\circ$ $c = 28.9438(3)$ Å $\gamma = 90^\circ$
Volume	$4419.41(7)$ Å <sup>3</sup>
Z	4
Density (calculated)	$1.441$ mg/m <sup>3</sup>
Absorption coefficient	$4.924$ mm <sup>-1</sup>
$F(000)$	1960
Crystal size	$0.48 \times 0.22 \times 0.08$ mm
$\theta$ range for data collection	$3.12\text{--}67.31^\circ$
Limiting indices	$-14 < h < 14, -15 < k < 15, -34 < l < 33$
Reflections collected	36039
Independent reflections	7606
Absorption correction	SADABS
Refinement method	full-matrix least-squares on $F^2$
Data/restraints/parameters	7606/0/537
Goodness-of-fit on $F^2$	1.096
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0610, wR_2 = 0.0240$
R indices (all data)	$R_1 = 0.0615, wR_2 = 0.0248$

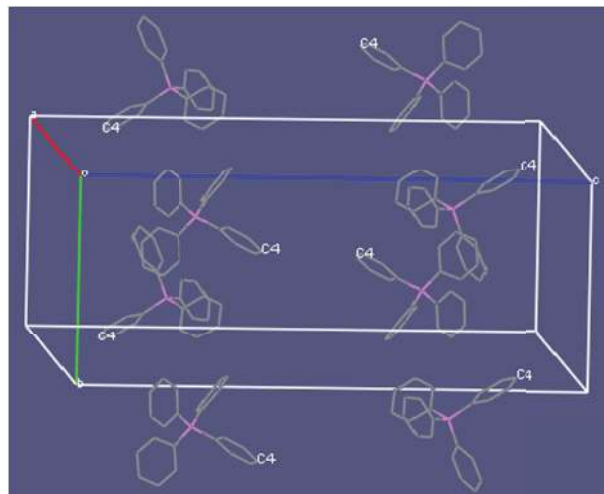
$$R_1 = \frac{\sum(|F_o| - |F_c|)}{\sum(|F_o|)}, wR_2 = \left\{ \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)]} \right\}^{1/2} w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 2.7747P], \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

TABLE 2: Selected bond distances (Å) and bond angles ( $^\circ$ ) of  $[\text{Mn}^{\text{III}}(5\text{-Br-salpn})(\text{DMF})_2]^+$ .

Mn–O2B	1.8852(12)	Mn–N4	2.0459(14)
Mn–O3B	1.8955(12)	Mn–O2	2.2119(12)
Mn–N1	2.0259(14)	Mn–O1	2.2282(13)
O2B–Mn–O3B	84.32(5)	N1–Mn–O2	86.02(5)
O2B–Mn–N1	90.08(5)	N4–Mn–O2	83.99(5)
O3B–Mn–N1	174.39(5)	O2B–Mn–O1	94.76(5)
O2B–Mn–N4	174.61(5)	O3B–Mn–O1	92.88(5)
O3B–Mn–N4	90.62(5)	N1–Mn–O1	87.72(5)
N1–Mn–N4	94.97(5)	N4–Mn–O1	87.34(5)
O2B–Mn–O2	94.50(5)	O2–Mn–O1	168.83(5)
O3B–Mn–O2	94.25(5)		

Symmetry transformations:  $-x, 1/2 + y, 1/2 - z; -x, -y, -z; x, 1/2 - y, 1/2 + z$ .

about a screw axis ( $2_1$ ) and extend parallel to the (010) plane (Figures 2 and 3).

FIGURE 3: Section of the crystal structure of  $[\text{Mn}^{\text{III}}(5\text{-Br-salpn})(\text{DMF})_2][\text{B}(\text{C}_6\text{H}_5)_4]$  showing the helical array of  $[\text{B}(\text{C}_6\text{H}_5)_4]^-$  ions about a screw axis ( $2_1$ ) parallel to the (010) plane.

## 4. Conclusions

The present work investigated a single-step reaction for the synthesis of a Schiff base complex of manganese(III) from a manganese(II) carboxylate. X-ray diffraction analysis of the complex has shown that the high spin  $d^4$  manganese(III) ion is in octahedral environment and displays an elongation along the axial bonds on account of Jahn-Teller effect. Other structural features are similar to that of the reported structures of complexes with symmetrical  $\text{N}_2\text{O}_2$  donor set ligands. See Supplementary Material available online at doi: 10.1155/2013/153023.

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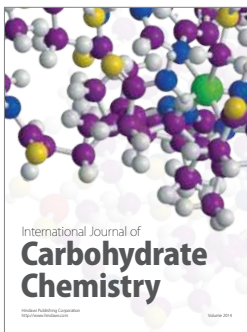
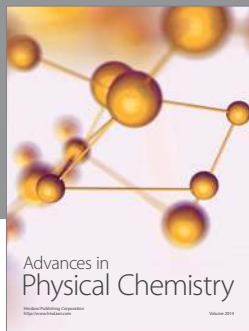
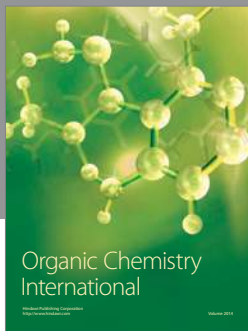
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