



# A new hydrogen-bonded pseudo-dimer Mn(III) Schiff base complex. The synthesis, X-ray structure and spectroscopic studies

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## ABSTRACT

A new hydrogen-bonded pseudo-dimer,  $[\text{Mn(III)L1}(\text{CH}_3\text{CH}_2\text{OH})_2](\text{ClO}_4)$  (**1**) (L1 = *N,N*-bis(2-hydroxy-1-naphthalideno)-1,2-diaminopropane) has been synthesized and characterized by UV–vis, IR, elemental analysis and crystal structure analysis. The single crystal X-ray diffraction reveals that the structure affords an elongated octahedral  $\text{MnN}_2\text{O}_4$  coordination environment, geometry with the four donor atoms of the tetradentate Schiff base in the equatorial plane and with two ethanol molecule in axial positions with Mn–O = 2.265(2) and 2.266(2) Å.

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## 1. Introduction

Recently, Schiff base Mn(III) complexes have been of great interest because of their important role in the development of coordination chemistry as well as catalysis [1], optical materials [2] and the application in industrial catalysis, for example epoxidation [3], bleaching [4] and paint drying [5]. Dimeric manganese(III) Schiff base complexes are of current interest from a variety of viewpoints, including molecular magnetic materials and bioinorganic chemistry. These complexes have shown a polymeric array in their solid state supramolecular structure due to  $\pi$  stacking and hydrogen bonding, involving the phenyl rings of the Schiff base, the coordinated solvent molecules and even the perchlorate counterions [6]. In the area of magnetism, these complexes generally exhibit an antiferromagnetic or ferromagnetic intra-dimer interaction [7]. Ferromagnetic dimers afford an unusual  $S=4$  ground spin state making themselves appealing candidates for a building block to design new magnetic materials such as single-molecule magnets (SMMs) [8]. In the area of bioinorganic chemistry, these complexes are very well studied because these species may be used as synthetic models of the active site of various nonheme manganese proteins and enzymes such as catalases [9], liver arginase [10], manganese ribonucleotide reductase (RNR) [11]. Synthetic chemists are also very interested in Schiff base Mn(III) complexes as model compounds for the active site of cytochrome P-450, since they have features in common with metalloporphyrins with respect to their

electronic structure and catalytic activity. The electronic and steric nature of the metal complex can be tuned by introducing electron-withdrawing and electron-releasing substituents and bulky groups in the ligand [12]. The behaviour of these manganese complexes is mainly dependent on the structure and coordination mode of the ligands in addition to the oxidation state of manganese.

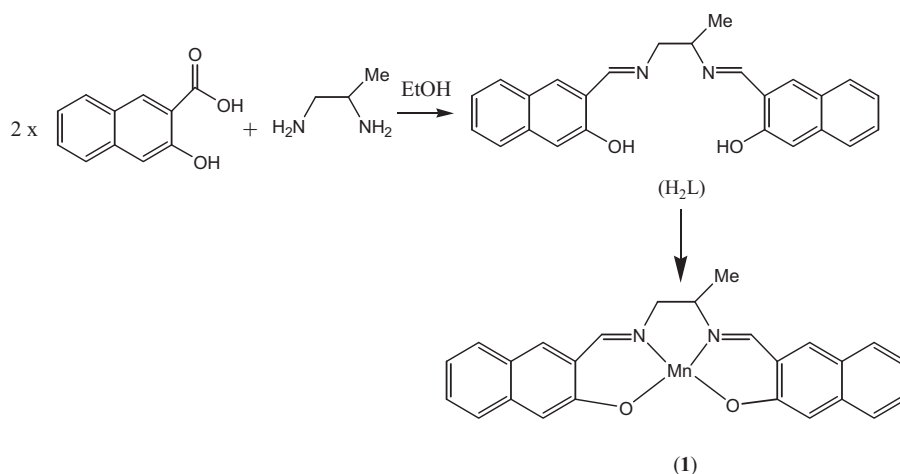
Recently our research group and others have reported the structural and magnetic characterization of mono- and binuclear manganese(III) complexes containing tetradentate Schiff base ligands with O, N, N, O, donor set [6,7,13]. In view of the importance of manganese(III) compounds and our interest in the chemistry of coordination compounds involving chelating Schiff bases, we report here the synthesis, spectral and crystallographically investigations of new hydrogen-bonded pseudo-dimer manganese(III) Schiff base complex having elongated axial Mn–O bonds to two ethanol molecule.

## 2. Experimental

### 2.1. Materials and physical measurements

All chemical reagents and solvents were purchased from Merck or Aldrich and used without further purification. Elemental (C, H, N) analyses were carried out by standard methods with a LECO, CHNS-932 analyzer. UV–vis spectra were carried out at 20 °C on a Perkin Elmer Lambda 25 UV–vis spectrometer. FT-IR spectra were measured with a Perkin-Elmer Model Bx 1600 instrument with the samples as KBr pellets in the 4000–400  $\text{cm}^{-1}$  range. The synthetic route of the ligand and complex are outlined in Scheme 1.

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**Scheme 1.** The synthetic route of the ligand **L1** and complex **1** evaluated in this study.

## 2.2. Synthesis of **1**

**Caution:** Although no problems were encountered in the present work, perchlorates are potentially explosive and should be treated in small quantities with care.

The quadridentate Schiff base ligand, **L1**, was prepared by reaction of 1,2-diamino propane (1 mmol, 0.074 g) with 2-hydroxy-1-naphthaldehyde (2 mmol, 0.344 g) in hot ethanol (100 mL). The yellow compound was precipitated from solution on cooling. Complex **1** was prepared by addition of manganese(III) acetate dihydrate (1 mmol, 0.268) in 70 mL of hot ethanol to the ligand (1 mmol, 0.384 g) in 140 mL of hot methanol. The resulting mixture was stirred for 10 min. After the mixture was filtered, sodium perchlorate monohydrate (1.71 mmol, 0.240) in 10 mL of methanol was added to the filtrate. The mixture was warmed to 50 °C, 20 mL of hot water was added and this mixture was filtered rapidly. A deep-brown solution was obtained and then allowed to stand at room temperature. Several weeks of standing have been led to the growth of crystals of the title compound suitable for X-ray analysis.

- (1) **L1**. Yellow crystals, yield 80%; Calcd.: C, 78.10; H, 6.29; N, 7.29. Found: C, 70.04; H, 6.27; N, 7.23.  
 (2) **1**. Brown crystals, yield 70%; Calcd.: C, 55.56; H, 5.14; N, 4.47. Found: C, 55.61; H, 5.07; N, 4.43.

## 2.3. X-ray structure determination

Diffraction measurements were made on a Bruker ApexII kappa CCD diffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 100 K. The intensity data were integrated using the APEXII program [14]. Absorption corrections were applied based on equivalent reflections using SADABS [14]. The structures were solved by direct methods and refined using full-matrix least-squares against  $F^2$  using SHELXL [14]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were included in idealised positions with isotropic displacement parameters constrained to 1.5 times the  $U_{\text{equiv}}$  of their attached carbon atoms for methyl hydrogens, and 1.2 times the  $U_{\text{equiv}}$  of their attached carbon atoms for all others. There is disorder in the perchlorate anion, which is a commonly observed phenomenon in the X-ray structures of perchlorate salt due to its spherical nature. The perchlorate was modelled using the SHELXTL program. The O6 atom was splitted into the O6A and O6B with 63% and 37% occupancy, respectively. The O5 atom was splitted into the O5A and O5B with 70% and 30% occupancy, respectively. Residual density is located 1.015  $\text{\AA}$  from

atom C28. The peaks indicate that there is a slight disorder of this C28 atom, which has not been allowed for.

## 3. Results and discussion

### 3.1. X-ray structure

The crystallographic data, conditions used for the intensity data collection and some features of the structure refinement are listed in Table 1. Complex **1** adopted an axially elongated octahedral  $\text{MnN}_2\text{O}_4$  coordination geometry with the four donor atoms of the tetradentate Schiff base forming the equatorial plane and ethanol molecules occupying the axial sites (Fig. 1). The displacement of Mn1 from the O1/N1/N2/O2 least-squares plane was 0.007 (2)  $\text{\AA}$ . The  $\tau$  value, which measures the degree of distortion of the  $\text{MnN}_2\text{O}_4$  chromophore, is 0.850, where  $\tau = R_S/R_L$ , the ratio of equatorial and axial mean bond lengths undergoing the Jahn–Teller effect [15]. The Mn–O<sub>phenol</sub> bond distances are Mn1–O2 = 1.879(2)  $\text{\AA}$ , Mn1–O1 = 1.904(2)  $\text{\AA}$  and the Mn–N<sub>imin</sub> bond distances are Mn1–N1 = 1.973(2) and Mn1–N2 = 1.952(3)  $\text{\AA}$  (Table 2). These are in agreement with the average Mn–O and Mn–N bond distances seen in the corresponding bonds in the monomeric  $[\text{Mn}(\text{vanen})(\text{H}_2\text{O})_2]_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $[\text{Mn}(3\text{-OMe}, 5\text{-Br-salpn})(\text{EtOH})(\text{H}_2\text{O})]\text{ClO}_4$  complexes [6b,16]. The axial Mn–O

**Table 1**  
Crystal data and structure refinement for complex **1**.

Empirical formula	$\text{C}_{29}\text{H}_{32}\text{ClMnN}_2\text{O}_8$
Formula weight	626.96 $\text{g mol}^{-1}$
Temperature	100(2) K
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 8.546(2) \text{ \AA}$ , $\alpha = 65.98(3)^\circ$ $b = 13.131(3) \text{ \AA}$ , $\beta = 74.70(3)^\circ$ $c = 14.081(3) \text{ \AA}$ , $\gamma = 77.98(3)^\circ$
Volume	1383.0(5) $\text{\AA}^3$
Z	2
Density (calculated)	1.506 $\text{g cm}^{-3}$
Absorption coefficient	0.629 $\text{mm}^{-1}$
$\theta$ range for data collection	1.86–27.49°
Index ranges	$-11 \leq h \leq 11$ , $-17 \leq k \leq 17$ , $-18 \leq l \leq 18$
Reflections collected	15,778
Independent reflections	6322 [ $R_{\text{int}} = 0.0376$ ]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	6322/2/398
Goodness-of-fit on $F^2$	$S = 1.024$
R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0556$ , $wR_2 = 0.1325$
Largest diff. peak and hole	1.066 and $-0.636 \text{ e\AA}^{-3}$

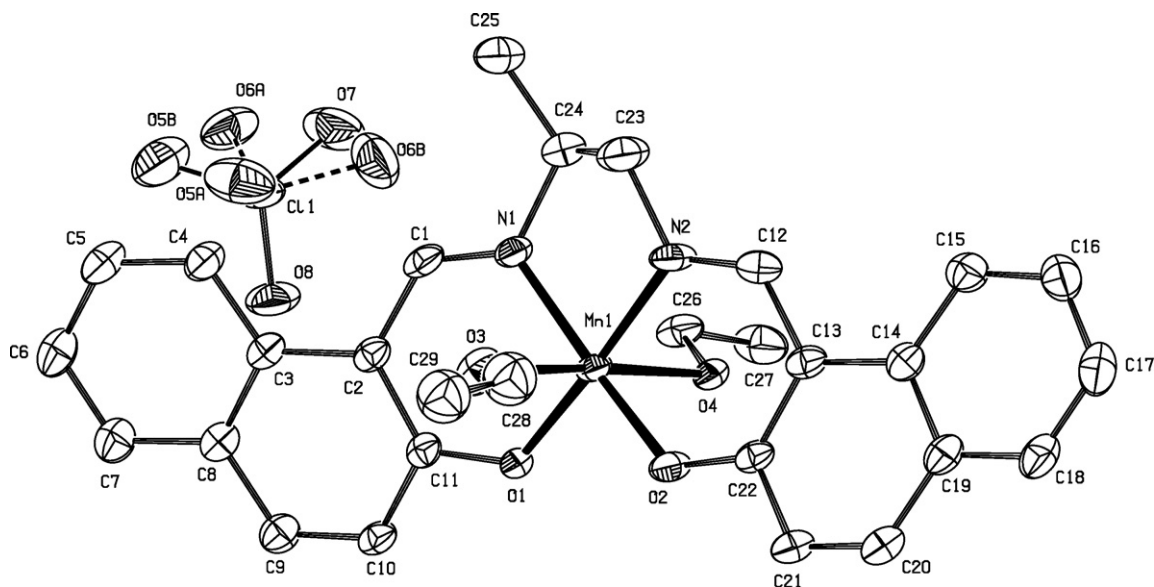


Fig. 1. ORTEP drawing of complex **1** with atom labelling (the hydrogen atoms were omitted for clarity).

Table 2

Some selected bond lengths [Å] and angles [°] for complex **1**.

Mn(1)–O(1)	1.904(2)	Mn(1)–N(2)	1.952(3)
Mn(1)–O(2)	1.879(2)	Mn(1)–O(3)	2.265(2)
Mn(1)–N(1)	1.973(2)	Mn(1)–O(4)	2.266(2)
O(1)–Mn(1)–O(3)	92.77(10)	O(2)–Mn(1)–N(1)	170.99(10)
O(1)–Mn(1)–O(4)	85.75(9)	O(2)–Mn(1)–N(2)	90.38(10)
O(1)–Mn(1)–N(1)	90.85(10)	N(1)–Mn(1)–O(3)	86.95(10)
O(1)–Mn(1)–N(2)	171.89(10)	N(1)–Mn(1)–O(4)	96.28(10)
O(2)–Mn(1)–O(1)	96.29(9)	N(2)–Mn(1)–O(3)	92.15(11)
O(2)–Mn(1)–O(3)	87.21(10)	N(2)–Mn(1)–O(4)	89.68(10)
O(2)–Mn(1)–O(4)	89.75(9)	N(2)–Mn(1)–N(1)	82.98(11)
O(3)–Mn(1)–O(4)	176.46(8)		

bond distances are Mn1–O3=2.265(2) and Mn1–O4=2.266(2) Å which are longer than the equatorial Mn–O bond distance in the same complex. The elongated octahedral geometry of the Mn(III) ion can be explained by Jahn–Teller distortions. The  $3d^4$  ion of manganese(III) gives  $^5E_g$  ground term in octahedral ligand fields. This phenomenon is also observed in other manganese(III) complexes containing the Schiff base ligand [17]. The 1,2-diamino propane group adopts a  $\lambda$  configuration, with torsion angle N1–C24–C23–N2 = 39.24°. The dihedral angle between the least-squares planes of the benzene rings of the ligands (C2–C11 and C13–C22) is 28.66°. The angles between the O1/N1/N2/O2 and C2–C11 planes and between the O1/N1/N2/O2 and C13–C22 planes are 26.44 and 20.07°, respectively. In the crystal structure of complex **1**, adjacent molecules were linked by hydrogen bonds O4...O1<sup>i</sup> = 2.806 Å; [*i* = –*x*+1, –*y*+1, –*z*+1], to form hydrogen-bonded pseudo-dimers, with additional face-to-face  $\pi$ – $\pi$  stacking interactions between the benzene groups (C13...C10 = 3.627 Å and C9...C14 = 3.807 Å). Moreover, hydrogen bonds [O3–O8 = 2.839 Å] and [O3–O6b = 3.083 Å] were formed between the axial ethanol ligand and the perchlorate ion (Fig. 2, and Table 3).

Table 3

Hydrogen bond geometry for complex **1**.

D–H...A	D–H	H...A	D...A	D–H...A
O3–H3A...O8	0.794	2.054	2.839	170.12
O3–H3A...O6B	0.794	2.545	3.083	126.34
O4–H4A...O1 <sup>i</sup>	0.787	2.021	2.806	175.81

Symmetry codes: (i) [–*x*+1, –*y*+1, –*z*+1].

### 3.2. FTIR spectroscopy

The IR spectra of **L1** and **1** provide information about the metal–ligand bonding. The Schiff base ligand **L1** shows strong absorption band at 1627  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  (cyclic). This band is shifted to 1630  $\text{cm}^{-1}$ , in **1**, which can be attributed to the coordination of the C=N nitrogen atom to the metal ion [18]. The  $\nu(\text{O}–\text{H})$  band at 3308  $\text{cm}^{-1}$  corresponding to the two hydroxy groups present in the Schiff base ligand **1**, which disappears in the complex **1**. This means that the Schiff base has been deprotonated and act as dianionic ligand [19]. A broad band centred at ca. 3354  $\text{cm}^{-1}$  are attributable to  $\nu(\text{O}–\text{H})$  of coordinated ethanol molecule which are linked by hydrogen bonding interactions in complex **1** [7d,20]. The bands at 1088 and 630  $\text{cm}^{-1}$  are due to the non-coordinated perchlorate counterion [6a,16,21]. Ligand coordination to the manganese centre is substantiated by bands appearing in the regions 418–477 and 468–530  $\text{cm}^{-1}$ , attributable

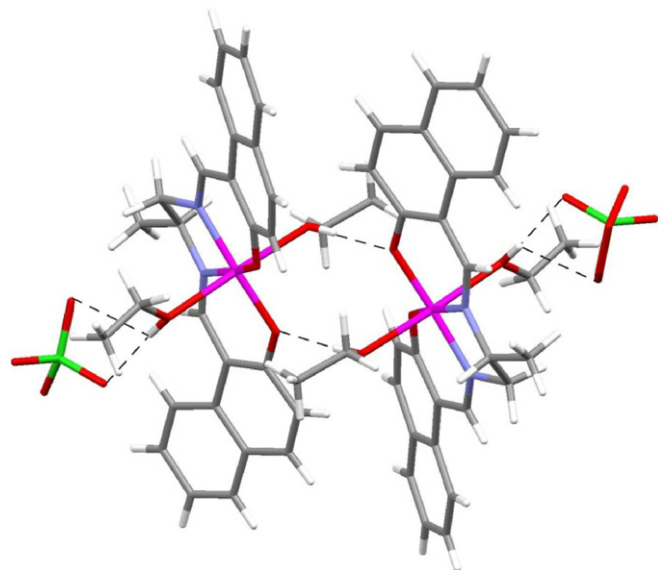


Fig. 2. Stick representation of the hydrogen-bonded (dashed lines) pseudodimers formed in complex **1**.

to  $\nu(\text{Mn}-\text{N})$  and  $\nu(\text{Mn}-\text{O})$ , respectively [7d,22]. The infrared spectrum of complex **1** is very much consistent with the structural data presented in this paper.

### 3.3. Electronic spectrum and magnetic susceptibility

The UV–vis (in DMF) spectra were recorded both for **L1** and complex **1**. Although the electronic spectrum of the manganese complexes with Schiff base ligands, in most cases, is not very good for characterization, it may help to support the structural aspects. The electronic spectrum of **L1** shows two absorption bands 242 nm and 268 nm. The absorption bands of the complex **1** are shifted to longer wavelength region 261 nm and 310 nm compared to the ligand [23]. The bands appearing at the low energy side are attributable to  $n \rightarrow \pi^*$  transitions associated with the azomethine chromophores. The bands at higher energy arise from  $\pi \rightarrow \pi^*$  transitions within the phenyl and naphthyl rings [24]. The electronic spectra of the complex **1** exhibit absorption band 665 nm suggesting an octahedral geometry, the  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}({}^4\text{G})$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}({}^4\text{G})$  transition for complex **1**. Measurements on the complex **1** reveal a room temperature magnetic moment of 4.9 B.M., which is consistent with a high-spin  $d^4$  system with no magnetic interaction between the manganese centres. Such behaviour is typical of this class of compound [25].

### Supplementary data

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk); [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk); fax: +44 1223 336033 and are available free of charge on request, quoting the Deposition No. CCDC 707914.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.saa.2011.07.038](https://doi.org/10.1016/j.saa.2011.07.038).

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