



Synthesis, crystal structure and magnetic characterization of a new phenoxo-bridged binuclear manganese(III) Schiff base complex exhibiting single-molecule-magnet behavior

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ARTICLE INFO

Article history:

Received 10 August 2008

Received in revised form 24 September 2008

Accepted 25 September 2008

Available online 6 November 2008

Keywords:

Binuclear complex

Manganese(III)

Crystal structure

Ferromagnetic exchange

Single-molecule-magnet

ABSTRACT

A new phenoxo-bridged binuclear manganese(III) Schiff base complex, $[\text{Mn}(\text{L})(\text{N}_3)]_2$ (**1**) where $\text{L} = \text{N,N}'$ -bis(salicylidene)-1,2-propanediamine has been synthesized and characterized by IR, elemental analysis, crystal structure analysis and variable temperature magnetic susceptibility measurements. The single crystal X-ray diffraction reveals that the structure is dimeric with each phenolate oxygen atom acting as a bridge between two symmetry equivalent Mn atoms. Low temperature magnetic study shows that the complex exhibits intra-dimer ferromagnetic exchange and single-molecule-magnet (SMM) behavior as well.

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1. Introduction

Exchange interaction between paramagnetic centers of a large number of binuclear complexes has already received wide attention. The investigations of magnetic properties and structural correlation of these complexes are important in the field of molecular magnetism [1–5]. In recent years, research on species having single-molecule-magnet (SMM) behavior has received considerable attention [6–11]. Due to the presence of energy barrier between spin-up and spin-down states, the SMMs may be potentially used as information storage at the molecular level. Moreover, these might be the unique systems for studying quantum spin tunneling and quantum phase interference leading to their applications in molecular electronics too [12,13].

Binuclear manganese(III) Schiff base complexes are of particular interest in the field of molecular magnetism due to the existence of paramagnetic centers in them [14–18]. These complexes are generally found to exhibit antiferromagnetic intra-dimer interaction. But reports on similar complexes with ferromagnetic interaction are scanty. The ferromagnetic dimers afford an unusual $S = 4$ ground spin state, showing sometimes the characteristic SMM behavior

which is revealed in few such recently reported complexes [19–24].

We describe here the synthesis of a new phenoxo-bridged binuclear manganese(III) complex along with its characterization, single crystal X-ray structure and low temperature magnetic study. The structure is dimeric in which two Mn^{III} ions are connected by phenolate oxygen atoms with azide as an axial ligand. Magnetic studies indicate that the complex exhibits ferromagnetic coupling between the two Mn^{III} ions and the ac magnetic susceptibility demonstrates that the complex possesses characteristic SMM behavior.

2. Experimental

2.1. Physical measurements

Elemental analyses were carried out on a Perkin–Elmer 2400-II instrument. The infrared spectrum was recorded on a Perkin–Elmer FT-IR spectrophotometer as a KBr pellet and the electronic spectrum was obtained on a Systronics 2202 spectrophotometer using methanol as solvent at 10^{-4} M concentration. Variable-temperature magnetic susceptibility measurements were carried out with a Quantum Design SQUID MPMS-XL magnetometer under an applied field of 0.1 T. The diamagnetic corrections were calculated from Pascal's constants.

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2.2. Materials

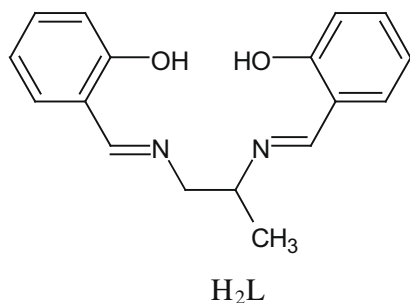
Commercially available reagent grade salicylaldehyde, 1,2-diaminopropane, manganese(II) perchlorate hexahydrate and sodium azide were used without further purification. All the solvents used were of reagent grade.

Caution: Although we did not experience any problem during the work, perchlorate and azide containing compounds being potentially explosive, should be used in small quantities and handled with great care.

2.3. Preparation

2.3.1. Synthesis of the Schiff base ligand

The tetradentate Schiff base ligand H_2L [$HOC_6H_4CHNCH_2CH(CH_3)NCHC_6H_4OH$] was obtained by refluxing a methanolic solution (40 ml) of 1,2-diaminopropane (1 mmol) and salicylaldehyde (2 mmol) for an hour. The resulting orange-red solution was kept in a desiccator for 24 h over $CaCl_2$. The thick solution left, containing the ligand, was used as such for the preparation of the complex.



2.3.2. Synthesis of the title compound $[Mn(L)(N_3)]_2$ (**1**)

2.3.2.1. Method-1. To a methanolic solution of manganese perchlorate hexahydrate (0.362 g, 1 mmol), a methanolic solution of the Schiff base (1 mmol) was added. To the resulting brown solution, an aqueous solution of NaN_3 (0.065 g, 1 mmol) was added dropwise with constant stirring. Stirring was continued for further half an hour and the solution was left for slow evaporation at room temperature. After a week, dark brown crystals of compound **1** appeared. The crystals were collected by filtration, washed with methanol and finally dried (0.250 g, 66%). *Anal. Calc.* for $C_{34}H_{32}Mn_2N_{10}O_4$: C, 54.12; H, 4.27; N, 18.56; Mn, 14.56. *Found:* C, 54.03; H, 4.21; N, 18.52; Mn, 14.53%.

2.3.2.2. Method-2. The complex was prepared by slow mixing of manganese perchlorate hexahydrate, salicylaldehyde, 1,2-diaminopropane (all in methanolic solutions) and NaN_3 (aqueous solution) together in the mole ratio of 1:2:1:1 with constant stirring and then following the same procedure as in Method-1 to obtain the pure crystals (0.270 g, 72%). *Anal. Calc.* for $C_{34}H_{32}Mn_2N_{10}O_4$: C, 54.12; H, 4.27; N, 18.56; Mn, 14.56. *Found:* C, 54.06; H, 4.22; N, 18.51; Mn, 14.52%.

2.4. Crystal structure determination and refinement

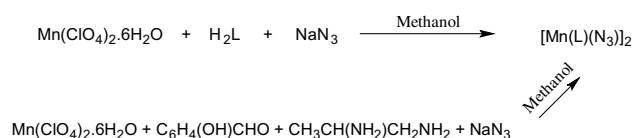
A suitable crystal of **1** was mounted on a Bruker APEX2 diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 100(2) K. The crystallographic computation, structural solution and refinement by full-matrix least-squares on F^2 were performed using SHELXL programs [25–27]. All non-hydrogen

atoms were refined with anisotropic displacement parameters. A summary of the crystallographic data, structural parameters and refinement details is presented in Table 1.

3. Results and discussion

3.1. Synthesis

Usual literature methods have been followed for the synthesis of the ligand and the Mn^{III} dimer complex. Salicylaldehyde and 1,2-diaminopropane reacted in 2:1 molar ratio to form the Schiff base. However, the same compound could also be prepared by adding the aldehyde and the amine directly to the reaction mixture thus avoiding pre-condensation to form the Schiff base ligand. It has been observed that Mn^{II} has undergone oxidation to Mn^{III} in the reaction which is probably due to aerial oxidation [19]. The relevant equations of the formation of compound **1** by the two methods are presented in the following scheme:



3.2. FTIR spectroscopy

The infrared spectrum of compound **1** exhibits a very strong and sharp absorption band at 2035 cm^{-1} corresponding to the asymmetric stretching vibrations of the terminal azide ion [$\nu_{as}(N_3)$]. The bands in the region 1616 cm^{-1} are assignable to the ν_{CN} stretches of the Schiff base ligand. Several other bands in the range of $2900\text{--}3340 \text{ cm}^{-1}$ are assigned to the characteristic absorption of CH or NH groups. All other characteristic vibrations including the phenolic C–O stretches of the metal-bound Schiff base are located in the range $600\text{--}1600 \text{ cm}^{-1}$ [28]. Thus the infrared spectrum is found to be in good agreement with the structural features of the compound.

3.3. Electronic spectrum

Although the electronic spectrum of the manganese complexes with multidentate Schiff base ligands, in most cases, is not very good for characterization, it may help to support the structural aspects. Compound **1** displays two distinct strong absorption bands in the regions 236 nm and 281 nm, which might be attributed to the charge transfer from the ligands to $Mn(III)$.

3.4. Crystal structure of $[Mn(L)(N_3)]_2$ (**1**)

The ORTEP drawing of **1** is shown in Fig. 1 and some selected bond lengths and angles are listed in Table 2. The structure is similar to those of few other dimeric Mn^{III} complexes reported earlier [19]. The compound can be described as a dimer of $[Mn(L)(N_3)]$ in which both are connected through $Mn^{III}\text{--}O$ bonding, where O. atom refers to the phenolate O-atom of the another $[Mn(L)(N_3)]$ unit. In other words, the phenolic O-atoms act as bridge between the two symmetry equivalent Mn atoms. Each Mn atom adopts a distorted octahedral geometry in which the basal plane is formed by the coordination of the two imino nitrogen (N1, N2) and two phenolic oxygen atoms (O1, O2) of the Schiff base ligand. The apical positions are occupied by one N atom of

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