



## Synthesis, characterization and pseudopolymorphism of a phenoxo-bridged binuclear manganese(III) Schiff base complex

Santanu Mandal<sup>a</sup>, Rajat Saha<sup>b</sup>, Bibekananda Mahanti<sup>a</sup>, Michel Fleck<sup>c</sup>, Debasis Bandyopadhyay<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Bankura Christian College, Bankura, West Bengal, India

<sup>b</sup> Department of Physics, Jadavpur University, Kolkata, West Bengal, India

<sup>c</sup> Institute of Mineralogy and Crystallography, Geozentrum, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria

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### ABSTRACT

Three pseudopolymorphs of a phenoxo-bridged binuclear manganese(III) complex,  $[\text{Mn}(\text{L})(\text{N}_3)]_2$  where  $\text{L} = [N,N'\text{-bis}(2\text{-hydroxyacetophenylidene})]\text{propane-1,2-diamine}$  could be synthesized using same reactants but different solvents. The syntheses of the unsolvated isomer  $[\text{Mn}(\text{L})(\text{N}_3)]_2$  (**1**) and a hydrated isomer  $[\text{Mn}(\text{L})(\text{N}_3)]_2 \cdot 3.66\text{H}_2\text{O}$  (**2**) have been achieved in acetone and methanol medium, respectively, while another previously reported complex  $[\text{Mn}(\text{L})(\text{N}_3)]_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$  (**3**) was obtained from a mixed solvent containing ethanol. The pseudopolymorphs **1**, **2** and **3** crystallize in the space groups  $P2_1/c$ ,  $P2_1/n$  and  $P2_1/n$ , respectively. Their 3D supramolecular structures have been compared to notice that the molecular building blocks are held by weak intermolecular  $\text{C-H} \cdots \pi$ ,  $\text{C-H} \cdots \text{O}$  or van der Waals interactions. While the compound **1** is an unsolvated pseudopolymorph, **2** and **3** contain water and ethanol, respectively as guest molecules in their lattices.

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### 1. Introduction

The expansion of crystal engineering as an emerging research field has been accompanied by significant interest in the nature of intermolecular interactions and their subsequent use in the formation of solid-state structures. Supramolecular chemistry and crystal engineering based on the spontaneous self-assembly of metal ions and bridging organic building blocks are of great current interest. Arrangement of a particular metal–organic framework in more than one way in the solid state may sometimes give rise to supramolecular isomerism [1–10]. The architectures of supramolecules depend greatly on the experimental conditions including the nature of solvent used in the crystallization process. During crystallization, solvent molecules take part in molecular aggregation and change the overall crystal structure in the solid state. Many solids are known to incorporate different guest/solvent molecules in their crystal structures [2,11,12] to show pseudopolymorphism. Pseudopolymorphs of a compound may exhibit different physical and chemical properties because of different arrangement of molecules in the crystal [13,14]. Increasing attention has now been paid to this aspect of molecular architectures due to its growing importance in elucidation of structure–property relationship [1–10,15–19]. Amongst various non-covalent interactions that govern

molecular arrangement in crystal structures, those involving solvent molecules have been a matter of discussion for the last few years [20–22]. Since the crystal growth of a specific pseudopolymorphic metal–organic compound with desired structure is not yet possible, variation of reaction conditions including use of different solvents is a common and effective approach [11,12,23–25] to obtain supramolecules of particular choice.

In a recent communication [26], we have reported the synthesis of complex **3** by reacting manganese perchlorate with 1,2-diaminopropane, 2-hydroxyacetophenone and sodium azide in a mixed solvent containing ethanol. The complex was characterized by single crystal X-ray diffraction analysis as well as by variable-temperature magnetic susceptibility measurements. In attempts to obtain the unsolvated form of complex **3** and to investigate further on the same synthetic system, we have performed one-pot reaction of the same reactants in the same molar ratio but with different organic media. In the present contribution, we describe the synthesis and characterization of two new dimeric manganese(III) Schiff base complexes  $[\text{Mn}(\text{L})(\text{N}_3)]_2$  (**1**) and  $[\text{Mn}(\text{L})(\text{N}_3)]_2 \cdot 3.66\text{H}_2\text{O}$  (**2**), obtained from the same reactants as in **3**, in acetone and methanol medium, respectively. The structures of both the complexes are dimeric in which two Mn(III) ions are connected by phenolate oxygen atoms with azide ion as the axial ligands.

The magnetic nature of **3** and similar other binuclear Mn(III) complexes have already been explored by many researchers including our group [26–29]. In our earlier communication [26],

\* Corresponding author. Tel./fax: +91 3242 250924.

E-mail address: dbccchem@yahoo.co.in (D. Bandyopadhyay).

the supramolecular structure of **3**, however, had not been dealt with in detail. In the present work, we have endeavored to explore the molecular architecture of the three complexes **1–3** in their solid states to conclude that they show pseudopolymorphism. During the building up of 3D networks from the binuclear complex units, supramolecular pockets containing water and ethanol as guest molecules are formed in **2** and **3**, respectively. In the solid states of the complexes, various weak attractive forces like H-bonding, C–H... $\pi$  and van der Waals interactions are operative.

## 2. Experimental

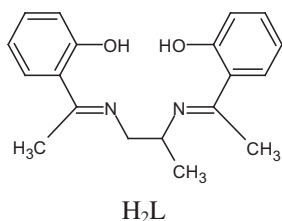
### 2.1. Physical measurements

Elemental analyses for carbon, hydrogen and nitrogen were carried out using a Perkin–Elmer 2400-II elemental analyzer. The infrared spectra were recorded on a Perkin–Elmer Spectrum 65 FT-IR spectrophotometer with KBr discs (4000–400  $\text{cm}^{-1}$ ). Room temperature solid phase magnetic susceptibilities were measured at 298 K with a PAR 155 vibrating sample magnetometer with  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as the calibrant. Molar conductances of the complexes in dry methanol were measured using a direct reading conductivity meter of Systronics (Type 304).

### 2.2. Materials

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

**Caution!** Although no problems were encountered in our work, compounds containing perchlorate and azide are potentially explosive. Therefore, only a small amount of the materials should be used at a time and handled with proper care.



### 2.3. Synthesis of the complexes

#### 2.3.1. Synthesis of $[\text{Mn}(\text{L})(\text{N}_3)]_2$ (**1**)

A solution of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.18 g, 0.5 mmol) in acetone (10  $\text{cm}^3$ ) was added slowly with constant stirring to a mixture of 1,2-diaminopropane (0.04 g, 0.5 mmol) and 2-hydroxyacetophenone (0.14 g, 1.0 mmol) taken together in 20  $\text{cm}^3$  acetone. To the resulting brown solution, an aqueous solution of  $\text{NaN}_3$  (0.03 g, 0.5 mmol) was added dropwise. Stirring was continued for further half an hour and the solution was left for slow evaporation at room temperature. After 3–4 days, dark brown shiny crystals of compound **1** appeared. The crystals were collected by filtration, washed with little acetone and finally dried. Yield: 0.12 g, 60% (based on Mn). *Anal.* Calc. for  $\text{C}_{38}\text{H}_{40}\text{Mn}_2\text{N}_{10}\text{O}_4$ : C, 56.30; H, 4.97; N, 17.28. Found: C, 56.23; H, 4.96; N, 17.22%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3067, 2980, 2038, 1598, 1579, 1536, 1435, 1326, 1304, 1231, 861, 760, 611.  $\lambda_{\text{M}}$  (MeOH,  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ): 5.  $\mu_{\text{eff}}$  (RT, BM): 6.82.

#### 2.3.2. Synthesis of $[\text{Mn}(\text{L})(\text{N}_3)]_2 \cdot 3.66\text{H}_2\text{O}$ (**2**)

The synthetic route described for **1** in Section 2.3.1 was followed in the preparation of **2** also, except that methanol was used as the solvent instead of acetone. Brown crystals of **2** appeared after a week in this case. Yield: 0.15 g, 56% (based on Mn). *Anal.* Calc. for  $\text{C}_{38}\text{H}_{47.32}\text{Mn}_2\text{N}_{10}\text{O}_{7.66}$ : C, 52.06; H, 5.44; N, 15.98. Found: C, 51.92; H, 5.35; N, 15.89%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3436, 3063, 2978, 2038, 1600, 1579, 1536, 1440, 1340, 1304, 1240, 1140, 987, 862, 754, 610.  $\lambda_{\text{M}}$  (MeOH,  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ): 7.  $\mu_{\text{eff}}$  (RT, BM): 6.79.

### 2.4. Crystal structure determination and refinement

Suitable single crystals of **1** and **2** with dimensions of  $0.07 \times 0.04 \times 0.04$  and  $0.08 \times 0.06 \times 0.04 \text{ mm}^3$ , respectively, were mounted on a Nonius kappa and a Nonius APEX diffractometer, both equipped with CCD area detector and graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The reflection data were collected and processed using the Bruker-Nonius program suites COLLECT, DENZO-SMN and related analysis software [30–32]. The structures were solved by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-square refinements on  $F^2$  using the program SHELX [33]. All atomic displacements parameters for non-hydrogen atoms have been refined with anisotropic terms. All hydrogen atoms were placed in geometrically calculated positions and refined with riding model. The clathrate water molecules in **2**, however, were modeled with the oxygen atoms only, since hydrogen atoms of those water molecules could not be located in the difference Fourier map due to their severe disorder. Refinement of hydrogen atoms placed at possible geometrical positions did not give reproducible results. Therefore, these atoms were omitted from the refinement but included in the molecular formula or all derived data. A summary of the crystallographic data, structural parameters and refinement details is presented in Table 1.

**Table 1**  
Crystallographic data for **1** and **2**.

Parameters	<b>1</b>	<b>2</b>
Formula	$\text{C}_{38}\text{H}_{40}\text{Mn}_2\text{N}_{10}\text{O}_4$	$\text{C}_{38}\text{H}_{47.32}\text{Mn}_2\text{N}_{10}\text{O}_{7.66}$
Formula weight ( $\text{g mol}^{-1}$ )	810.68	876.60
Crystal size ( $\text{mm}^3$ )	$0.07 \times 0.04 \times 0.04$	$0.08 \times 0.06 \times 0.04$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
$a$ ( $\text{\AA}$ )	7.9354(4)	10.5388(8)
$b$ ( $\text{\AA}$ )	21.5260(1)	14.8662(1)
$c$ ( $\text{\AA}$ )	21.3300(1)	12.8609(9)
$\beta$ ( $^\circ$ )	91.327(2)	89.956(2)
$V$ ( $\text{\AA}^3$ )	3642.6(3)	2014.9(3)
$Z$	4	2
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.478	1.433
$\mu$ ( $\text{mm}^{-1}$ )	0.750	0.689
$F(000)$	1680	907
$hkl$ Range	$\pm 11, -32/29, \pm 31$	$\pm 15, -14/22, -17/18$
$T$ (K)	296(2)	296(2)
$\lambda$ (MoK $\alpha$ ) ( $\text{\AA}$ )	0.71073	0.71073
Theta range for data collection ( $^\circ$ )	1.3–32.0	2.1–32.0
Reflections collected	45733	20849
Number of unique reflections	12506	6393
$R_{\text{int}}$	0.049	0.047
Observed data [ $F_o > 2\sigma(F_o)$ ]	7712	3187
Number of parameters refined	487	272
$R^a$	0.0674	0.0803
$wR^b$	0.1757	0.2189
$S$	1.10	1.15
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ( $\text{e \AA}^{-3}$ )	0.68, –0.97	1.17, –0.50

<sup>a</sup>  $R = \sum |F_o| - |F_c| / \sum |F_o|$ .

<sup>b</sup>  $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$ ,  $w = 1/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P]$ ,  $P = (F_o^2 + 2F_c^2)/3$ .

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