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# Synthesis and structural characterization of three manganese(III) complexes with N<sub>2</sub>O<sub>2</sub> donor tetradentate Schiff base ligands: Exploration of their catalase mimicking activity

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#### Abstract:

Three manganese(III) complexes,  $[Mn(L^1)(N_3)(H_2O)] \cdot CH_3OH \cdot H_2O$  (1),  $[Mn(L^2)(N_3)(H_2O)]$  (2) and  $[Mn(L^3)(H_2O)_2]ClO_4$  (3) {where  $H_2L^1 = N, N'$ -bis(3methoxysalicylidene)1,2-ethanediamine,  $H_2L^2 = N, N'$ -bis(3-methoxysalicylidene)1,2-diamino-1propene and  $H_2L^3 = N, N'$ -bis(3-methoxysalicylidene)1,2-propanediamine} have been synthesized and characterized. Single crystal x-ray diffraction analysis confirmed their structures. Weak noncovalent interactions generate extended supra-molecular assemblies in all three complexes. Catalase mimicking activities (catalytic decomposition of hydrogen peroxide into oxygen and water) of the complexes have been investigated. Complex **3** catalyzes the decomposition of hydrogen peroxide most effectively. The higher catalase mimicking efficiency of complex **3** has been related to its structure.

Keywords: Manganese(III); Crystal structure; Catalase mimicking activity.

#### 1. Introduction

Manganese(III) complexes have attracted a lot of attention because of their interesting magnetic properties (with four unpaired electrons in high spin and two unpaired electrons in low spin complexes) and structural diversities [1-5]. SOD (superoxide dismutase) and catalase are two important enzymes that help to defend the cell structure against various reactive oxygen species, e.g. hydrogen peroxide, hydrogen superoxide etc (capable of damaging different cellular components), produced naturally during oxygen metabolism [10-12]. If not destructed, these reactive oxygen species can cause oxidative stress leading to a number of human diseases [13-15]. SOD destroys hydrogen superoxide reducing it into hydrogen peroxide [16,17]. Catalase is responsible for the catalytic decomposition of hydrogen peroxide by means of its disproportionation reaction into nontoxic dioxygen and water [18-20]. Many manganese(III) complexes have also been used to mimic several enzymes, e. g. superoxide dismutase, catalase etc [6-9]. Signorella et al. reported a manganese(III) complex that can exhibit both superoxide dismutase and catalase-like activity [21]. Two manganese(II) complexes were also synthesised by the same group and both of these complexes show superoxide dismutase and catalase-like activity [22]. Britovsek et al. synthesized a bio-inspired manganese(II) complex with a linear pentadentate ligand framework containing soft sulfur donors and an alternating NSNSN binding motif which can displays excellent dual catalase/SOD-like antioxidant activity [23]. Párkányi *et* al. have reported a manganese(II) complex exhibiting similar type activity [24]. Synthesis, structural characterization and catalase-like activity of a number of manganese(II) complexes were reported by Devereux et al. [25]. A novel single site manganese(II) complex was successfully synthesized and tested in the aqueous disproportionation of hydrogen peroxide by Barszcz et al. [26]. Li et al. synthesized two new manganese(II) complexes which can

decompose hydrogen peroxide catalytically, and possess the combined functions of SOD and catalase in basic or weakly basic solutions [27].

With the specific aim to mimic catalase enzyme, we have synthesized and characterized three octahedral manganese complexes, each having [MnLXY] core, where  $H_2L$  is tetradentate Schiff base ligand occupying the equatorial positions; X and Y are monodentate ligands occupy the axial positions, as expected from considering the structures of similar Mn(III) complexes [9,28]. These monodentate ligands could be substituted by hydrogen peroxide to initiate catalase activity of the complexes (Manganese(III) is d<sup>4</sup> and labile). This special characteristic feature makes them good catalysts towards decomposition of hydrogen peroxide into dioxygen and water.

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#### 2. Experimental Section

#### 2.1. Materials

All starting materials were available from commercial suppliers and were used without further purification. Sodium azide was purchased from Merck, India. All other chemicals and solvents were purchased from Sigma–Aldrich. The reactions and all manipulations of the samples were carried out under aerobic conditions.

*Caution!!!* Although no problem was encountered during this work, perchlorate salts containing organic ligands and azide are potentially explosive. Only a minute quantity of the materials should be prepared and they must be handled with care.

#### 2.2. Preparations

2.2.1. Preparation of  $[Mn(L^1)(N_3)(H_2O)] \cdot CH_3OH \cdot H_2O$  (1)  $[H_2L^1 = N, N'-bis(3-methoxysalicylidene) - 1, 2-ethanediamine]$ 

The Schiff base ligand,  $H_2L^1$ , was synthesized by refluxing ethane-1,2-diamine (0.10 mL, ~1 mmol) with 3-methoxysalicylaldehyde (0.304 g, ~2 mmol) in methanol (20 mL) for ca. 1 h. The ligand was not isolated and a methanol solution (10 mL) of manganese(II) perchlorate hexahydrate (370 mg, ~1 mmol) was then directly added to the methanolic solution of ligand under stirring condition. An aqueous methanol solution of sodium azide (0.065 g, ~1 mmol) was then added to it and stirring was continued for further ca. 2 h. The resulting solution was then filtered and kept for slow evaporation in open atmosphere. Dark brown coloured block shape single crystals, suitable for X-ray diffraction, were obtained after few days which were collected through filtration and then dried in aerobic condition.

**Yield:** 372 mg (~76 %); based on manganese(III). Anal. Calc. for  $C_{19}H_{24}MnN_5O_7$  (FW = 489.37): C, 46.63; H, 4.94; N, 14.31 %. Found: C, 46.3; H, 5.0; N, 14.6 %. FT-IR (KBr, cm<sup>-1</sup>): 1599, 1616, ( $v_{C=N}$ ); 2035 ( $v_{N3}$ ); 2833-2970 ( $v_{C-H}$ ); 3420 ( $v_{O-H}$ ). UV-Vis,  $\lambda_{max}$  (nm), [ $\varepsilon_{max}$  (L mol<sup>-1</sup> cm<sup>-1</sup>)] (DMF), 272 (3.73 x 10<sup>4</sup>), 327 (1.73 x 10<sup>4</sup>), 426 (1.11 x 10<sup>3</sup>), 501(3.75 x 10<sup>2</sup>). Magnetic moment = 4.96µB.

2.2.2. Preparation of  $[Mn(L^2)(N_3)(H_2O)]$  (2)  $[H_2L^2 = N,N'-bis(3-methoxysalicylidene)-1,2-diamino-1-propene]$ 

In the preparation of complex **2**, propane-1,2-diamine (0.12 mL, ~1 mmol) was used instead of ethane-1,2-diamine. All other reagents were identical to that used in the preparation of complex **1**. Diffraction quality single crystals were obtained after a few days on slow evaporation of dark brown methanol solution of the complex in open atmosphere.

**Yield:** 326 mg (~72 %); based on manganese(III). Anal. Calc. for  $C_{19}H_{20}MnN_5O_5$  (FW = 453.34): C, 50.34; H, 4.45; N, 15.45 %. Found: C, 50.5; H, 4.3; N, 15.6 %. FT-IR (KBr, cm<sup>-1</sup>): 1600, 1619 ( $v_{C=N}$ ); 2828-2955 ( $v_{C-H}$ ); 3435 ( $v_{O-H}$ ). UV-Vis,  $\lambda_{max}$  (nm), [ $\varepsilon_{max}$  (L mol<sup>-1</sup> cm<sup>-1</sup>)] (DMF), 272 (3.98 × 10<sup>4</sup>), 328 (5.26 × 10<sup>3</sup>), 428 (1.94 × 10<sup>3</sup>), 508 (4.88 x 10<sup>2</sup>). Magnetic moment = 4.98µB.

2.2.3. Preparation of  $[Mn(L^3)(H_2O)_2]ClO_4$  (3)  $[H_2L^3 = N,N'-bis(3-methoxysalicylidene)-1,2-propanediamine]$ 

A methanol solution of propane-1,2-diamine (0.12 mL, ~1 mmol) and 3methoxysalicylaldehyde (0.304 g, ~2 mmol) was refluxed for ca. 1 h to prepare the tetradentate Schiff base ligand H<sub>2</sub>L<sup>3</sup>. A methanol (10 ml) solution of manganese(II) perchlorate hexahydrate (370 mg, ~1 mmol) was directly added into the methanol solution of the ligand H<sub>2</sub>L<sup>3</sup> with constant stirring. The stirring was continued for an additional ca. 2 h to get dark a dark brown resulting solution. Deep brown blocked shaped single crystals of the complex, suitable for X-ray diffraction, were obtained after a few days by slow evaporation of resulting solution in open atmosphere.

**Yield:** 394 mg (~74 %); based on manganese(III). Anal. Calc. for  $C_{19}H_{24}MnN_2O_{10}Cl$ (FW = 530.79): C, 42.99; H, 4.56; N, 5.28 %. Found: C, 42.8; H, 4.4; N, 5.4 %. FT-IR (KBr, cm<sup>-1</sup>): 1601, 1616 ( $v_{C=N}$ ); 2840-2965 ( $v_{C-H}$ ); 3430 ( $v_{O-H}$ ). UV-Vis,  $\lambda_{max}$  (nm), [ $\varepsilon_{max}$  (L mol<sup>-1</sup> cm<sup>-1</sup>)] (DMF), 270 (3.68 × 10<sup>4</sup>), 329 (4.04 × 10<sup>3</sup>), 422 (1.71 × 10<sup>3</sup>), 500 (2.81 x 10<sup>2</sup>). Magnetic moment = 5.02µB

#### 2.3. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra in KBr (4500–400 cm<sup>-1</sup>) were recorded using a PerkinElmer Spectrum Two FTIR spectrophotometer. Electronic spectra (800–200 nm) were recorded on a SHIMADZU UV-1700(E) Pharma Spec UV-Vis spectrophotometer. The magnetic susceptibility measurements were performed with a magnetic susceptibility balance, made by Sherwood Scientific, Cambridge, UK at room temperature (300 K). The corrected magnetic susceptibility,  $\chi_m$ , was calculated using the relation:  $\chi_m = \chi_{meas} - \chi_D$ . Diamagnetic susceptibilities,  $\chi_D$  were calculated using Pascal's constants [29]. Effective magnetic moments were calculated using the formula,  $\mu_{eff} = 2.828(\chi_m T)^{1/2}$ , where  $\chi_m$  was the corrected molar susceptibility. The instrument was calibrated using metallic nickel. Powder X-ray diffraction was performed on a Bruker D8 instrument with Cu-K<sub>a</sub> radiation ( $\lambda = 1.5418$  Å) generated at 40 kV and 40 mA. The powder XRD spectrum was recorded in a 20 range of 5–50° using a 1D Lynxeye detector under ambient conditions.

#### 2.4. Crystal data collection and refinement details

Suitable single crystals of all three complexes were used for data collection using a 'Bruker D8 QUEST area detector' diffractometer equipped with graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) at 273 K. Molecular structures were solved by direct method and refined by full-matrix least squares on F<sup>2</sup> using the SHELX-2014/7 package [30]. Non hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms, attached to oxygen, were located by difference Fourier maps and were kept at fixed positions. All other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on those atoms to which they were attached. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [31]. In the unit cell of complex 1, a highly disordered

water molecule was present which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules and thereby were able to produce a set of solvent-free diffraction intensities. Details about the SQUEEZE procedure are given in the CIF file. A summary of crystallographic data and refinement details of all three complexes are given in Table **S1** (Supplementary information). Selected bond lengths and bond angles are listed in Tables **1** and **2**, respectively.

#### 2.5. Hirshfeld surface analysis

Hirshfeld surfaces [32-34] and the associated two-dimensional (2D) fingerprint plots [35-37] were calculated using Crystal Explorer, [38] with bond lengths to hydrogen atoms set to standard values [39]. The details can be found in many of our previous papers [40-43].

#### 2.6. Catalase-like activity studies

Volumetric measurements of evolved dioxygen during the reactions of the manganese(III) complexes with  $H_2O_2$  were carried out as mentioned hereafter: a 50 cm<sup>3</sup> three-necked round-bottom flask containing a solution of the complexes (10<sup>-3</sup> M) in DMF (10 cm<sup>3</sup>) was placed in a water bath at 25°C. One of the necks was connected to a burette and the others were stoppered by a rubber septum. While the solution was stirring, hydrogen peroxide (30% v/v) was injected into it through the rubber septum using a microsyringe. Volumes of evolved dioxygen were measured for 5 min time intervals volumetrically.

#### 3. Results and discussion

#### 3.1. Synthesis

Schiff base ligands,  $H_2L^1$  and  $H_2L^3$ , were synthesized by the 1:1 condensation of 3methoxysalicyldehyde with ethane-1,2-diamine and propane-1,2-diamine respectively in methanol following the literature method [44,45]. On the other hand,  $H_2L^2$  was formed through oxidation of ligand,  $H_2L^3$  in reaction environment. The ligands were not isolated and were used directly for the preparation of manganese(III) complexes.

Addition of the methanol solution of manganese(II) perchlorate hexahydrate in the methanol solution of the Schiff base,  $H_2L^1$  followed by the addition of sodium azide produced a dark brown coloured complex,  $[Mn(L^1)(N_3)(H_2O)] \cdot CH_3OH \cdot H_2O$  (1). Similarly, reaction of the methanol solution of manganese(II) perchlorate hexahydrate with methanol solution of Schiff base,  $H_2L^3$  followed by the addition of sodium azide produced another dark brown coloured complex  $[Mn(L^2)(N_3)(H_2O)]$  (2). It is very interesting to note that during the reaction 1,2-diaminopropane moiety of  $H_2L^3$  is oxidized to 1,2-diamino-1-propene (1,2-pn) in reaction environment and due to this oxidative dehydrogenation a new Schiff base ligand,  $H_2L^2$  is formed. Oxidative dehydrogenation of diamine ligands coordinated to several transition metals is reported in the literature [46,47]. On the other hand, a methanol solution of manganese(II) perchlorate hexahydrate was made to react with methanolic solution of Schiff base,  $H_2L^3$  under stirring condition to prepare mononuclear complex,  $[Mn(L^3)(H_2O)_2]ClO_4$  (3). Synthetic route to all three complexes are shown in Scheme 1. Manganese(II) was converted into manganese(III) by aerial oxidation, as was observed in many previous cases [9,28].



Scheme 1: Synthetic route to the complexes.

#### 3.2. Description of the structures

#### 3.2.1. $[Mn(L^1)(N_3)(H_2O)] \cdot CH_3OH \cdot H_2O$ (1)

The structure determination reveals that complex 1 consists of a discrete mononuclear unit  $[Mn(L^1)(N_3)(H_2O)]$ . A lattice methanol molecule is also present in the asymmetric unit. Perspective view of the complex is given in Figure 1. A lattice water molecule was present which is squeezed in order to minimize the void space in the crystal structure. It crystallizes in monoclinic space group  $P2_1/c$ . The manganese(III) centre, Mn(1), has a six-coordinate pseudooctahedral geometry in which two imine nitrogen atoms [N(1) and N(2)] and two phenoxo oxygen atoms [O(1) and O(2)] of the deprotonated di-Schiff base ligand  $\{(L^1)^{2-}\}$  constitute the equatorial plane. The remaining two coordination sites of manganese(III) centre is occupied by one azide nitrogen atom [N(3)] and one water oxygen atom [O(5)] to constitute its axial plane.

The axial Mn–O(5) and Mn–N(3) distances [ 2.367(6) and 2.244(6) Å, respectively] are much longer than the basal Mn–O(1), Mn–O(2), Mn–N(1) and Mn–N(2) distances [1.873(5), 1.873(5), 1.980(7) and 1.979(7) Å, respectively] (see Table 1), which fall within the range observed for structurally characterized manganese(III) complexes [48-55]. The elongation of axial bonds indicates clear evidence of Jahn–Teller distortion, as expected for high-spin manganese(III) complexes [28]. The distortion from the perfect octahedral geometry can be easily observed from its coordinate bond angles, which deviate from the ideal values of 90° (for eis angles) or 180° (for trans angles). Mn(III)-N<sub>imine</sub> and Mn(III)-O<sub>phenoxo</sub> bond lengths in the complex are comparable to previously reported similar type manganese(III)-Schiff base complexes [48-55]. The saturated five membered chelate ring, Cg(1) [Mn(1)–N(1)–C(9)–C(10)–N(2)] in this complex shows half chair conformation with puckering parameters [56] Q = 0.319(10) Å and  $\varphi$ = 91.2(11)°. The terminal azide is quasi-linear with the N-N-N angle being 178.6(10)°, as observed in similar complexes [40,42].



Figure 1: Perspective view of complex 1 with selective atom numbering scheme. Lattice methanol molecule has been omitted for clarity.

#### 3.2.2. $[Mn(L^2)(N_3)(H_2O)]$ (2)

The X-ray crystal structure determination reveals that complex **2** crystallizes in the monoclinic space group,  $P2_1/c$ . Perspective view of the complex along with selective atomnumbering scheme is shown in Figures **2**. The manganese(III) center is in a six-coordinate distorted octahedral environment, being bonded to two imine nitrogen atoms, N(1) and N(2), and two phenoxo oxygen atoms, O(1) and O(2), of a deprotonated Schiff base ligand,  $(L^2)^-$ . The remaining two axial coordination sites of manganese(III) centre is occupied by one azide nitrogen atom, N(3) and one water oxygen atom, O(5) to complete its octahedral geometry. The coordination geometry around the metal centre is highly distorted from ideal octahedral geometry as suggested by the coordinate bond angles. The axial Mn–O(5) and Mn–N(3) bond lengths are much longer than the equatorial Mn–O(1), Mn–O(2), Mn–N(1) and Mn–N(2) bond lengths (see Table 1), which clearly indicates Jahn–Teller distortion, as expected for high-spin manganese(III) complexes [28]. The terminal azide is quasi-linear as observed in previously reported similar type complexes with the N-N-N angle being 178.2(13)° [40,42].

The most exciting observation is the oxidation of Schiff base ligand during the reaction procedure. The 1,2-diaminopropane moiety is oxidized to 1,2-diamino-1-propene (1,2-pn) via oxidative dehydrogenation reaction, which is probably catalyzed by manganese(III). The metal coordinated amine (or diamine) is oxidized by aerial oxygen to form  $\alpha$ -imine (or  $\alpha$ -di-imine) [47]. In our case, 1,2-diaminopropane moiety of the Schiff base ligand, coordinated to manganese(III) is oxidized by aerial oxygen to an  $\alpha$ -imine. The methyl group probably restricts

the formation of an  $\alpha$ -di-imine. This  $\alpha$ -imine may easily then be rearranged to form the 1,2diamino-1-propene. The C-C bond lengths of complexes **1**, **2** and **3** (oxidized part of salen-type ligands) are 1.484(13), 1.30(2) and 1.381(19), respectively. In case of complex **2**, much shorter C-C bond length confirms oxidation of Schiff base ligand.



Figure 2: Perspective view of complex 2 with selective atom numbering scheme.

#### 3.2.2. $[Mn(L^3)(H_2O)_2]ClO_4(3)$

Single crystal X-ray structure determination analysis reveals that the asymmetric unit of the complex consists of a mononuclear cation  $[Mn(L^2)(H_2O)_2]^+$  together with a non-coordinating perchlorate anion. The complex crystallizes in the monoclinic space group  $P2_1/c$ . A perspective view of the complex with selective atom-numbering scheme is shown in Figure **3**. The central manganese(III) center, Mn(1), is again in a six-coordinate octahedral environment, being bonded to two imines nitrogen atoms, N(1) and N(2) and two phenoxo oxygen atoms, O(1) and O(2), from a deprotonated Schiff base ligand  $(L^3)^-$ . Other vacant sites are coordinated by two water

oxygen atoms, O(5) and O(6), to complete its distorted octahedral geometry. The longer values of axial bonds compared to equatorial bonds (see Table 1) are indicative of tetragonal elongations as a result of the Jahn–Teller distortion, expected for high-spin manganese(III) complexes with d<sup>4</sup> configuration [9,28]. The saturated five membered ring, [Mn(1)–N(1)–C(9)– C(10)–N(2)], has an half chair conformation, with puckering parameters Q = 0.219(14) Å,  $\phi = 100(2)^{\circ}$  [56].



Figure 3: Perspective view of complex 3 with selective atom numbering scheme. Noncoordinated perchlorate anion has been omitted for clarity.

#### 3.3 Hirshfeld surface analysis

Hirshfeld surfaces of all three complexes mapped over  $d_{norm}$ , shape index and curvedness (Figure 11). The surfaces are shown as transparent to allow visualization of the molecular moiety around which they are calculated. The dominant interactions between N····H/H····C for all complexes can be seen in the Hirshfeld surfaces as red spots on the  $d_{norm}$  surface in Figure 11.

Additional visible spots in the Hirshfeld surfaces correspond to mainly C···H/H···C and H···H contacts. The tiny extent of area and light color on the Hirshfeld surfaces signify weaker and long range interactions other than hydrogen bonds. Moreover, the two dimensional fingerprint plots (Figure 12) illustrate the difference between the intermolecular interaction patterns and the relative contributions (in percentage) for the major intermolecular interactions associated with the complex. In two dimensional fingerprint plots (Figure 12) intermolecular interactions appear as distinct spikes. Complementary regions are visible in the fingerprint plots where one molecule acts as a donor ( $d_e > d_i$ ) and the other as an acceptor ( $d_e < d_i$ ).



Figure 11: Hirshfeld surfaces mapped with  $d_{\text{norm}}$  (left-side), shape index (middle) and curvedness (right-side).



**Figure 12**: Fingerprint plot: Resolved into H···H, C···H/H···C, O···H/H···O and N···H/H···N contact contributed to the total Hirshfeld Surface area of complex 1 (left), complex 2 (middle) and complex 3 (right).

#### 3.4. Spectral Analysis

Infrared spectra provide enough information to identify the way of bonding of the ligands to the metal centres. The most characteristic vibrations are selected by comparing the IR spectra of all complexes. In the IR spectra of all complexes, distinct bands as a result of the azomethine (C=N) groups around 1616 cm<sup>-1</sup> are customarily noticed [57]. The appearances of strong bands around 2032 cm<sup>-1</sup> indicate the presence of the monodentate azide coligands in complexes **1** and **2**, respectively [40,42]. Broad bands centered at around 3420 cm<sup>-1</sup> due to O–H stretching vibrations are observed in IR spectra of all complexes [58-60]. Bands in the range of 2970–2830

cm<sup>-1</sup> due to alkyl C–H bond stretching vibrations are usually noticed in IR spectra of all complexes [61].

The electronic spectra of the complexes are quite comparable to each other in DMF medium at room temperature. Intense absorption bands in the high energy region of 270 nm are assigned as intra-ligand  $\pi \rightarrow \pi^*$  transitions involving the aromatic rings. Absorption bands around 325 nm are due to  $n \rightarrow \pi^*$  transitions within the ligands. Strong absorption bands around 425 nm may be attributed to the ligand to metal charge transfer (LMCT) transitions [62]. Absorption bands with shoulders around 500 nm region are due to spin allowed d–d transitions [63,64]. Molar extinction coefficient value of d-d transition is very high may be due to the fact that LMCT band partly overlaps the d-d transition.

Formulations of all complexes as manganese(III) complexes are further supported by the room temperature solid state magnetic moment values in the region 4.96-5.02. These values are  $\mu B$  expected for discrete, high-spin (S = 2), magnetically non-coupled manganese(III) complexes having four unpaired electrons [28,65].

#### 3.5. Catalytic decomposition of hydrogen peroxide (Catalase mimicking activity) study

The catalytic activity of all three complexes towards decomposition of hydrogen peroxide has been investigated in DMF medium at 25°C temperature. In the beginning, solutions of the manganese(III) complexes were dark brown coloured but after addition of 30% (v/v) hydrogen peroxide they became fade yellow coloured or colorless and instantaneous evolution of a gas was observed for all three complexes. It can be easily understood that the evolved gas is oxygen and it comes from the catalytic decomposition of hydrogen peroxide solution. Volumetric measurements of this evolved oxygen confirmed that all three complexes are very much capable

of catalytic decomposition of hydrogen peroxide into water and oxygen but the degree of decomposition is different i.e. complex 3 is the most efficient in hydrogen peroxide decomposition followed by other two complexes. Complexes 1 and 2 have comparable efficiency. To analyze the catalytic activity four set of experiments were carried out for each complexes with different initial amount of hydrogen peroxide (10, 20, 30, 40, 50 mL 30% v/v), and a constant catalyst concentration. The measurement of the volume of evolved oxygen indicates that for constant catalyst concentration the rate of decomposition increases with increase in the initial amount of hydrogen peroxide. The volume of oxygen evolved at different initial amount of 30% v/v hydrogen peroxide for most efficient complex i.e. complex 3 is shown in Figure 13. A blank experiment in presence of 30 mL hydrogen peroxide (30% v/v) has also been performed (Figure 13). From Figure 13, it can be clearly understood that at constant catalyst concentration, decomposition of  $H_2O_2$  exhibits rate saturation kinetics. The efficiency of complex 3 at different initial amount of 30% v/v hydrogen peroxide is shown in the turnover number (TON) versus time plot in Figure 14. TON is defined as the number of moles of oxygen evolved per mole of the catalyst. Since two molecules of  $H_2O_2$  on decomposition liberates one molecule of oxygen, if  $V_t$  and  $V_{inf}$  denote the volumes of oxygen given out at any time t and at the completion of reaction, then  $(V_{inf} V_t)$  is proportional to the amount of undecomposed H<sub>2</sub>O<sub>2</sub> at time t. Now, rate constant of the reaction can be calculated from the equation: Rate constant, k =2.303/t  $\log{V_t/(V_{inf}-V_t)}$ , provided it follows first order kinetics. Substitution of experimental data (Table 3) revealed constancy in the value of rate constant (k), confirming first order kinetics. In some previously published reports, similar type tentative catalytic cycles have been proposed [9,66]. A plausible mechanistic pathway for the decomposition of hydrogen peroxide is also shown in Scheme 2. It is clear from the catalytic cycle that during the catalytic cycle,

manganese(III) is oxidised to manganese(IV) by replacing one axially coordinated ligand (water or azide) simultaneously  $H_2O_2$  is reduced to  $H_2O$ . Subsequently, molecular oxygen is generated when the catalyst regenerates to its original form. Figure 15 shows the comparison between turn over numbers of complexes 1, 2 and 3. Complex 3 seems to be the most efficient catalyst as it contains two labile solvent molecules at the axial positions of its octahedral geometry. A few mononuclear manganese(III) complexes showing catalase mimicking activity already exist in literature. Some of these previously reported complexes exhibiting catalase mimicking activity are gathered in Table 4.



Figure 13: Time dependence of oxygen evolution upon reaction of complex 3 (10<sup>-3</sup> M) with

different initial amount of hydrogen peroxide at 25 °C. A blank experiment in presence of 30 mL

H<sub>2</sub>O<sub>2</sub> has also been included.



Figure 14: Turnover number {[Evolved oxygen]/[Catalyst]) vs time for complex 3 in the

different initial amount of hydrogen peroxide at 25 °C.





(v/v) H<sub>2</sub>O<sub>2</sub> is used in each case.



Scheme 2: Plausible mechanistic pathway for the catalytic decomposition of hydrogen peroxide into water and oxygen.

In order to verify whether these complexes is capable of maintaining its structural integrity after  $H_2O_2$  decomposition process, IR spectrum of complex **3** was recorded before and after decomposition reaction. The IR spectrum of complex **3** after decomposition reaction is in excellent agreement with the IR spectrum of pure complex, confirming the structural integrity of the complex after catalytic decomposition of  $H_2O_2$ . Alternatively, we can say that the complex is chemically intact during the decomposition reaction. Figure **16** illustrates IR spectrum of complex **3** before and after the  $H_2O_2$  decomposition reaction.



Figure 16: IR spectrum of complex 3 before (blue) and after (red) the H<sub>2</sub>O<sub>2</sub> decomposition reaction.

#### 4. Conclusion

In the present work, three manganese(III) complexes derived from  $N_2O_2$  donor tetradentate Schiff base ligands were synthesized and the structures of these complexes were confirmed by single crystal X-ray diffraction technique. The solid state structures of these complexes showed the involvement of the organic ligands in several weak supramolecular interactions involving the alkoxy arms and the aromatic rings. All complexes were found to be active towards catalytic decomposition of hydrogen peroxide. Probable catalytic cycle showing the catalytic decomposition of hydrogen peroxide was also projected. During the course of hydrogen peroxide decomposition, hydrogen peroxide molecule has to coordinate the manganese(III) center by replacing the axially coordinated ligands. Since water is a neutral

molecule, it could easily be replaced by hydrogen peroxide. Alternatively, the replacement of azide coligand is probably somewhat difficult, as it is anionic in nature. The decomposition of hydrogen peroxide is, therefore, catalyzed more efficiently by complex **3** than other two complexes.

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#### Appendix A. Supplementary data

CCDC 1871955-1871957 contain the supplementary crystallographic data of complexes **1**, **2** and **3**, respectively. These data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>. The complete description on supramolecular interactions of all three complexes is given in Supplementary Information part.

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 Table 1: Selected Bond lengths (Å) of the complexes 1, 2 and 3.

	l	2	3
Mn(1)-O(1)	1.873(5)	1.913(6)	1.867(6)
Mn(1)-O(2)	1.873(5)	1.895(6)	1.865(5)
Mn(1)-O(5)	2.367(6)	2.364(7)	2.221(5)
Mn(1)-O(6)	-	-	2.373(8)
Mn(1)-N(1)	1.980(7)	1.987(9)	1.968(7)
Mn(1)-N(2)	1.979(7)	2.004(9)	1.986(8)
Mn(1)-N(3)	2.244(6)	2.191(10)	-

	1	2	3
O(1)-Mn(1)-O(2)	93.0(2)	92.2(2)	92.9(2)
O(1)-Mn(1)-O(5)	89.3(2)	88.2(3)	93.1(2)
O(1)-Mn(1)-O(6)	-	-	91.8(3)
O(1)-Mn(1)-N(1)	91.8(2)	92.5(3)	91.8(3)
O(1)-Mn(1)-N(2)	173.4(3)	171.1(3)	174.7(3)
O(1)-Mn(1)-N(3)	93.4(2)	95.3(3)	-
O(2)-Mn(1)-O(5)	92.9(2)	89.2(3)	91.4(2)
O(2)-Mn(1)-O(6)	-		90.8(3)
O(2)-Mn(1)-N(1)	174.6(3)	171.7(3)	175.0(3)
O(2)-Mn(1)-N(2)	91.6(3)	91.6(3)	92.2(3)
O(2)-Mn(1)-N(3)	94.2(2)	98.2(3)	-
O(5)-Mn(1)-N(1)	84.6(3)	84.1(3)	90.2(3)
O(5)-Mn(1)-N(2)	85.7(3)	83.7(3)	88.6(3)
O(5)-Mn(1)-N(3)	172.2(3)	171.7(4)	-
N(1)-Mn(1)-N(2)	83.4(3)	82.8(4)	83.1(3)
N(1)-Mn(1)-N(3)	88.0(3)	88.2(4)	-
N(2)-Mn(1)-N(3)	91.0(3)	92.3(4)	-
O(5)-Mn(1)-O(6)	-	-	174.5(3)
O(6)-Mn(1)-N(1)	-	-	87.2(4)
O(6)-Mn(1)-N(2)	-	-	86.3(3)

 Table 2: Selected bond angles (°) of the complexes 1, 2 and 3.

D

**Table 3**: Kinetic order for decomposition of  $H_2O_2$  {50 mL 30% (v/v)} in presence of complex 3.

Time (s)	(V <sub>t</sub> /V <sub>inf</sub> - V <sub>t</sub> )	log(V <sub>t</sub> /V <sub>inf</sub> - V <sub>t</sub> )	<mark>K (s<sup>-1</sup>)</mark>	
<mark>155</mark>	1.837209302	<mark>0.264158636</mark>	<mark>0.003924886</mark>	$\boldsymbol{\lambda}$
170	<mark>2.436619718</mark>	<mark>0.386787754</mark>	0.005239836	0
<mark>190</mark>	<mark>3.436363636</mark>	<mark>0.536099115</mark>	<mark>0.006498086</mark>	
210	<mark>5.1</mark>	0.707570176	<mark>0.007759686</mark>	

 Table 4: Maximal turnover number (TON) values for catalase mimicking activity of some

 reported mononuclear manganese(III) complexes.

Complex	Ligand donor Sites	TON	<mark>рН</mark>	<mark>Solvent</mark>	[Catalyst]	[H <sub>2</sub> O <sub>2</sub> ]	References
MnL <sup>4</sup>	N <sub>3</sub> O <sub>3</sub>	<mark>&gt;300</mark>	-	<mark>CH₃CN</mark>	6 × 10 <sup>-4</sup> M	0.1 M	[21]
Mn(X-L <sup>5</sup> )(OAc)	N <sub>2</sub> O <sub>2</sub>	<mark>2.5-</mark> 8.4	<mark>8.1</mark>	H <sub>2</sub> O	10 × 10 <sup>-6</sup> M	0.01 M	<mark>[66]</mark>
Mn(L <sup>6</sup> R)(OAc)	N <sub>3</sub> O <sub>2</sub>	<mark>4–17</mark>	<mark>7.4</mark>	H <sub>2</sub> O	10 × 10 <sup>-6</sup> M	<mark>0.05 M</mark>	<mark>[67]</mark>
Na[Mn(L <sup>7</sup> )(H <sub>2</sub> O)].5H <sub>2</sub> O	$N_2O_2$	<mark>178</mark>	<mark>8</mark>	H <sub>2</sub> O	-	-	[22]
Na[Mn(L <sup>8</sup> )(MeOH)].4H <sub>2</sub> O	N <sub>2</sub> O <sub>2</sub>	<mark>25.2</mark>	8	H <sub>2</sub> O	-	-	[22]
Mn(L <sup>9</sup> )Y;	N <sub>2</sub> O <sub>3</sub>	1200	-	DMF	-	0.0129 M	<mark>[68]</mark>
$Y = N_3 / SCN$							
MnL <sup>10</sup> (OTf) <sub>2</sub>	N₅	7	8	CH <sub>3</sub> CN/H <sub>2</sub> O	60 × 10 <sup>-6</sup> M	<mark>0.033 M</mark>	[23]
MnL <sup>11</sup> (OTf) <sub>2</sub>	N <sub>3</sub> O <sub>2</sub>	17	8	CH <sub>3</sub> CN/H <sub>2</sub> O	<mark>60 × 10<sup>-6</sup> M</mark>	<mark>0.033 M</mark>	[23]
MnL <sup>12</sup> (OTf) <sub>2</sub>	N₃S₂	<mark>39</mark>	8	CH <sub>3</sub> CN/H <sub>2</sub> O	<mark>60 × 10<sup>-6</sup> M</mark>	<mark>0.033 M</mark>	[23]
MnL <sup>13</sup> Cl <sub>2</sub>	N <sub>4</sub>	<mark>606</mark>	<mark>11.03</mark>	CH <sub>3</sub> OH/H <sub>2</sub> O	<mark>8.45 M</mark>	<mark>0.535 M</mark>	[27]
[MnL <sup>14</sup> Cl]ClO <sub>4</sub> ·MeOH	<mark>N</mark> 5	<mark>609</mark>	<mark>11.03</mark>	CH <sub>3</sub> OH/H <sub>2</sub> O	<mark>8.50 M</mark>	<mark>0.535 M</mark>	[27]
[Mn(L <sup>16</sup> )Cl <sub>2</sub> ](CH <sub>3</sub> OH)	N <sub>3</sub>	<mark>75-</mark> 83	<mark>9.6</mark>	H <sub>2</sub> O	2.11×10 <sup>−4</sup> M	<mark>0.447 M</mark>	[24]
[Mn(L <sup>17</sup> )(SO <sub>4</sub> )(H <sub>2</sub> O)] <sub>n</sub>	NO	<mark>320</mark>	7	H <sub>2</sub> O	25 × 10 <sup>-5</sup> M	0.02 mol (30% w/w)	[26]
$[Mn(L^{18})_2]_n$	N <sub>2</sub> O <sub>2</sub>	<mark>918</mark>	<mark>&gt;7</mark>	H <sub>2</sub> O + imidazole	10.3 mg (solid)	0.114 mol (35% w/w)	[25]

$[Mn(L^{19})(L^{20})_2] \cdot 4.5 H_2O$	NO <sub>2</sub> , N <sub>4</sub>	<mark>1110</mark>	<mark>&gt;7</mark>	H <sub>2</sub> O + imidazole	<mark>10 mg</mark> (solid)	<mark>0.114 mol</mark> (35% w/w)	[25]
$Mn(L^{20})(L^{21})(H_2O)$	NO <sub>2</sub> , N <sub>4</sub>	<mark>1374</mark>	<mark>&gt;7</mark>	H <sub>2</sub> O + imidazole	10.3 mg (solid)	<mark>0.114 mol</mark> (35% w/w)	[25]
$[Mn(L^{22})(CH_3OH)_2]ClO_4$	N <sub>2</sub> O <sub>2</sub>	<mark>29</mark>	-	<mark>CH₃CN</mark>	4 × 10 <sup>-6</sup> M	<mark>1.02 M</mark>	[9]

= 1-[N-(2-pyridylmethyl), N-(2-hydroxybenzyl)amino]-3-[N'-(2-hydroxybenzyl), N'-(4- $H_3^4$ methylbenzyl)amino]propan-2-ol;  $H_2L^5 = N_1N'$ -bis(salicylidene)ethane-1,2-diamine; X = phenylring substituent; R = cyclopentane-fused with ureido or acid-base catalyst auxiliary;  $H_2L^6$  =  $H_2L^7$ N,N'-bis(3-methoxysalicylidene)ethane-1,2-diamine; 1.3-bis(5sulphonatosalicylidenamino)propan-2-ol;  $H_2L^8 = 1,3$ -bis(5-sulphonatosalicylidenamino)propane; 1,4-bis(salicylidenamino)butan-2-ol;  $L^{10}$ 2,6-bis[(N-methyl(2- $H_2L^9$ pyridylmethyl)amino)methyl]pyridine;  $L^{11} = 2,6$ -bis[((2-pyridylmethyl)oxy)methyl]pyridine;  $L^{12}$ = 2,6-bis[((2-pyridylmethyl)sulpho)methyl]pyridine;  $L^{13}$  = 1-(benzimidazol-2-ylmethyl)-1,4,7triazacyclononane;  $L^{14} = 1,4$ -bis(benzimidazol-2-ylmethyl)-1,4,7-triazacyclonone);  $HL^{15} = N-(2-1)$ hydroxybenzyl)-N,N'-bis[2-(Nmethylimidazolyl);  $L^{16}$ = 1.3-bis(2) -pyridylimino)isoindolinemethyl]ethane-1,2-diamine;  $HL^{17} = 2$ -hydroxymethylpyridine;  $H_2L^{18} = 2$ -pyrazine carboxylic acid;  $L^{19} = 2,2$  bipyridine;  $H_2L^{20} = 2,6$ -pyridinedicarboxylic acid;  $L^{21} = 4$ hydroxypyridine-2,6-dicarboxylic acid;  $H_2L^{22}$ = N,N'-bis(1-(1'-hydroxy-2naphthyl)ethylidene)propane-1,3-diamine.

## **Graphical Abstract (Pictogram)**

Synthesis and structural characterization of three manganese(III) complexes with N<sub>2</sub>O<sub>2</sub> donor tetradentate Schiff base ligands: Exploration of their catalase mimicking activity

Ipsita Mondal, Kousik Ghosh, Shouvik Chattopadhyay



**Graphical Abstract (Synopsis)** 

# Synthesis and structural characterization of three manganese(III) complexes with N<sub>2</sub>O<sub>2</sub> donor tetradentate Schiff base ligands: Exploration of their catalase mimicking activity

#### Ipsita Mondal, Kousik Ghosh, Shouvik Chattopadhyay

Three manganese(III) complexes have been synthesized and characterized. The complexes were found to be active catalysts for the disproportionation of  $H_2O_2$ .

MAY