

## Article

## Synthesis of Structurally Diverse Ferrimagnetically and Antiferromagnetically Coupled MII-MnII (M=Cu, Ni) Heterometallic Schiff base Compounds with Dicyanamide Spacer and Study of Biomimetic Catalytic Activity

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Diverse

Ferrimagnetically

and

# **Synthesis** Structurally of Antiferromagnetically Coupled M<sup>II</sup>-Mn<sup>II</sup> (M=Cu, Ni) Heterometallic Schiff base Compounds with Dicyanamide Spacer and Study of **Biomimetic Catalytic Activity** Tonmoy Chakraborty,§ Abani Sarkar,§ Amit Adhikary,\*,§ Neha Chakiroy,<sup>¥</sup> Debasis Das\*,§ <sup>§</sup>Department of Chemistry, University of Calcutta, 92 A. P. C. Road, Kolkata - 700009, India. Email: dasdebasis2001@vahoo.com, aadhikarv87@gmail.com. <sup>¥</sup>Centre for Research in Nanotechnology & amp; Science (CRNTS), Indian Institute of Technology (IIT Bombay), India.

## Abstract

Two heterometallic Schiff base compounds  $\{[(CuL)Mn(N(CN)_2)_2] \cdot CH_3CN\}_{m}$  (1) and  $[(NiL)_4Mn_2(N(CN)_2)_2] \cdot (ClO_4)_2$  (2) have been synthesized using N<sub>2</sub>O<sub>2</sub> donor ligand (H<sub>2</sub>L) 2,2'-((1E,1'E)-((2,2-dimethylpropane-1,3diyl)bis(azanylylidene))bis(methanylylidene))diphenol) and a dicyanamide spacer. Single crystal X-ray structural analyses reveal that the compounds 1 and 2 have one dimensional zig-zag polymeric structure and discrete hexanuclear structure, respectively. Magnetic studies of 1 reveal the presence of intra chain ferrimagnetic coupling between Cu(II) and Mn(II) spins. Alternating interactions in an F-AF-F sequence (F: ferromagnetic; AF: antiferromagnetic) of 1 imposes the ideal situation of non-compensation in spin moments considering intra chain magnetic interactions. On the other hand, antiferromagnetic interaction between neighboring Mn(II) ions is observed for 2. ESI-MS and EPR study help to predict the solution phase structure of the two compounds. Among them, 1 dissociates to form Cu(II)-Mn(III) species with three N(CN)<sub>2</sub><sup>-</sup> and one CH<sub>3</sub>OH, making catalytically active in mimicking two well-known proteins phenoxazinone synthase and phosphatase. The calculated turnover numbers  $(k_{cat})$  for the aerial oxidation of *o*-aminophenol and hydrolysis of 4-nitrophenylphosphate (4-NPP) are 5129 h<sup>-1</sup> and 25.052 sec<sup>-1</sup>, respectively. But in solution state 2 behaves as a discrete structure which causes its inability upon the catalytic reaction. Probable mechanistic pathway has been studied by using the experimental tools such as

ESI-mass spectra, cyclic voltammetry and EPR measurements suggesting the formation of imine radical during the catalytic reaction of phenoxazinone synthase like activity.

## Introduction

Design and synthesis of heterometallic metal-organic hybrid materials are continuously pledging immense interest for their versatile application in numerous fields. The introduction of second metal centre may permit for the formation of new topologies<sup>1,2</sup> and this unusual metal environment may influence the physical properties. The close proximity between the metal thus appears to provide favorable conditions for the occurrence of enhanced the physical properties of the materials, such as their magnetic properties, catalytic properties, photo luminescent etc.<sup>3-5</sup> One of the common procedure for the synthesis of heterometallic compound initially is to prepare metalloligand of a divalent metal ion using N, O donor Schiff-base ligand<sup>6-8</sup> and then the oxygen atoms of the metalloligand coordinate to another metal ion along with the bridging ligand. The dicyanamide (dca<sup>-</sup>) ion is a versatile ligand that can coordinate to metal ions in a variety of modes, due to the flexibility and versatile coordination modes of dca<sup>-</sup>. It possesses different coordination modes such as  $\mu_{1.5}$ -dca<sup>-</sup>,  ${}^9\mu_{1.3,5}$ -dca<sup>-</sup>,  ${}^10\mu_{1.1,3,5}$ -dca<sup>-</sup>,  ${}^{11}$  and  $\mu_{1.1,3,5,5}$ -dca<sup>-</sup>.  ${}^{12}$ 

Ferrimagnetic chains belong to the most attractive phenomenon to deal with in the field of molecular magnetism due to realization of the permanent magnetization owing to the noncancellation of the antiferromagnetic coupled spins.<sup>13,14</sup> Ferrimagnetic materials are very rarely observed because the conditions for the non-compensation of the individual spin moments are very difficult to achieve.<sup>15,16</sup> Hence, experimental realization of molecular ferrimagnets is a challenging task. Structural and chemical factors largely govern the propagation of magnetic interaction. Therefore, an appropriate design strategy is needed to properly control the exchange coupling between paramagnetic centers. Heterometallic polymeric chains draw special attention in this regard because of their unusual spatial orientation of individual spins.<sup>17-19</sup>

Beside ferrimagnetic behavior, utmost focus of ongoing biomimetic and bioinspired synthetic approaches is on modeling some structural and/or functional aspect of the title metalloenzymes like catechol oxidase, phenoxazinone synthase, cytochrome c oxidase etc. Activate molecular oxygen involve great potential as catalyst for this oxidation reactions. The synthesis of newly transition metal based compounds which can act as functional model compounds for metalloenzymes with oxidase activity, are of particular interest for the development of bio-

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inspired catalysts for oxidation reactions. Most of the metalloenzymes contain multiple Cu(II) ions in their active site.<sup>20-26</sup> Phenoxazinone synthase (active site contains 5 copper ions), copper oxidase model in a biological system where *o*-aminophenol (OAP) is oxidized to aminophenoxazinone (APX).<sup>27-30</sup> Recently, we have seen that the heterometallic compounds, especially containing Mn(II) ion can catalyze such oxidase reactions with high efficiency depending upon the coordination environment around Mn(II) atom.<sup>31-34</sup>

A phosphatase is an enzyme containing transition and post transition metal ion(s) in their active sites that uses water molecule to catalyze the hydrolysis of phosphor ester bond of mono-, di-, tri-esters, fluorophosphates, fluorophosphonates, phosphoric anhydrides and many other such kind of enzymes.<sup>35-40</sup> In many biological processes, phosphatase enzymes are essential due to phosphorylation (e.g. byprotein kinases) and dephosphorylation (by phosphatases) serve diverse roles in cellular regulation and signaling,<sup>41</sup> and it also use in agriculture (removal of phosphate containing pesticides).<sup>42,43</sup> Metal ions play a major role to break the phosphate ester bond: (i) coordination environment of metal ion can be stabilized at the transition-state by hydrogen-bonding or proton-transfer, (ii) metal coordinated hydroxide that acts as a nucleophile, (iii) formation of product and regeneration of catalyst.<sup>44</sup> Recently, there is a great interest in the development of new heteronuclear metal compounds that may be used as enzymatic models of phosphatase like activity. However, a few examples have been reported in the literature.<sup>45,46</sup>

Therefore, in this contest, we prepared a tetradentate N<sub>2</sub>O<sub>2</sub> donor ligand (H<sub>2</sub>L) 2,2'-((1E,1'E)-((2,2-dimethylpropane-1,3diyl)bis(azanylylidene))bis(methanylylidene))diphenol) using 2,2dimethylpropane-1,3-diamine and salicylaldehyde. Using this ligand (H<sub>2</sub>L) and a dicyanamido spacer, two heterometallic Schiff base compounds {[(CuL)Mn(N(CN)<sub>2</sub>)<sub>2</sub>]·CH<sub>3</sub>CN}<sub>∞</sub> (1) and [(NiL)<sub>4</sub>Mn<sub>2</sub>(N(CN)<sub>2</sub>)<sub>2</sub>]·(ClO<sub>4</sub>)<sub>2</sub> (2) have been synthesized. Both the compounds have been characterized by SCXRD, FT-IR and PXRD etc. Structure of 1 is found to be one dimensional zig-zag polymeric structure and 2 is a discrete hexanuclear compound. EPR study helps to predict the oxidation state of the metal center in solution state. Compound 1 is observed to exhibit very high biomimetic oxidase activities (*e.g.*, phenoxazinone synthase like activities using *o*-aminophenol as a model substrate under aerobic conditions in methanol medium) as well as hydrolase activities (*e.g.*, phosphatase like activities using disodium salt of 4nitrophenylphosphate (4-NPP) as the model substrate in 97.5 % (v/v) *N*,*N*-dimethylformamidewater mixture), whereas 2 reveals inertness towards phenoxazinone synthase and phosphatase like activities. Probable mechanistic pathway for biomimetic oxidase and hydrolase activities has been investigated by using the experimental tools like ESI-mass spectra, cyclic voltammetry and EPR measurements. The intermediate species indicates the substrate bind to the Mn(III) center and the imine bond plays a crucial role of an electron carrier for the transformation of the *o*aminophenol to aminophenoxazinone in phenoxazinone synthase like activity with the reduction of aerial dioxygen.

## **Experimental Section**

Materials and physical methods. All reagents and chemicals were purchased from Sigma and used without further purification. Solvents used for spectroscopic studies were purified and dried by standard procedures before use. UV-Vis spectra were recorded on SHIMADZU UV-2450 spectrophotometer. Solvent N,N-dimethylformamide (DMF), Methanol were used for UV-Vis study was of spectroscopy grade. The concentration of solutions used for UV-Vis studies was kept in the range of  $\sim 5 \times 10^{-3}$  (M) in order to avoid precipitation. Samples for FT-IR study were prepared as KBr pellets, and spectra were obtained in the 400-4000 cm<sup>-1</sup> range using a Perkin-Elmer 1600 FTIR spectrometer. Temperature-dependent dc magnetic susceptibilities for powdered crystalline samples of compounds 1 and 2 were measured using a superconducting quantum interference device vibrating sample magnetometer (SOUID-VSM, Quantum Design) with an applied field of 750 Oe and 100 Oe in the temperature range 2-300 K. Cyclic voltammograms were carried out using 0.1 (M) tetrabutylamonium perchlorate (TBAP) as supporting electrolyte and  $1.0 \times 10^{-3}$  (M) of compounds in methanol solution using an Epsilon Basi-C3 Cell instrument at a scan rate of 100-400 mVs<sup>-1</sup> within the potential range of 0 to -1.80 V vs Ag/AgCl. The EPR spectra were recorded with a Bruker EMX series spectrometer operating at X-band with 100 kHz modulation frequency. DPPH (g = 2.0036) was used as a g standard. Elemental analyses were performed on a Perkin-Elmer Model 2400 analyzer. The Electrospray mass spectra were recorded on a XEVO G2 SQ-TOF mass spectrometer. 2-Hvdroxvbenzaldehvde, 2,2-dimethylpropane-1,3-diamine, (4-nitrophenyl)phosphate (Sigma-Aldrich), 2-amino phenol were purchased from commercial source and used as received. All the solvents were distilled prior to use.





Synthesis of Schiff base ligand H<sub>2</sub>L and its Copper compound [CuL]. The Schiff base ligand [H<sub>2</sub>L] and the metalloligand [CuL] were synthesized by the following procedure reported earlier.47

Synthesis of the compound {[(CuL)Mn(N(CN)<sub>2</sub>)<sub>2</sub>]·CH<sub>3</sub>CN<sub>2</sub> (1). Metalloligand [CuL] (0.369 g, 1 mmol) was dissolved in mixture of 10 mL acetonitrile-methanol (v/v 1:1) solvent, and then Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.362 g, 1 mmol) was added to the solution. The resulting solution was stirred for 10 min and finally 2 mL of a 1:1 (v/v) H<sub>2</sub>O/acetonitrile solution of sodium dicyanamide (0.178 g, 2 mmol) was added to the solution drop wise at room temperature. And the mixture was stirred for another 0.5 h. After filtration, the clear greenish brown solution was kept in a CaCl<sub>2</sub> desiccator. After few days later rectangular shaped greenish brown crystals suitable for X-ray diffraction were obtained.

Yield: 73%; Anal. Calcd. for C<sub>23</sub>H<sub>20</sub>CuMnN<sub>8</sub>O<sub>2</sub>: C (49.42%); H (3.61%); N (20.05%); Found: C (49.22%); H (3.33%); N (20.22%); FT-IR (KBr pellet): v(C=N) 1615cm<sup>-1</sup>; v(skeletal vibration) 1557 cm<sup>-1</sup>; v(C<sub>2</sub>N<sub>3</sub><sup>-</sup>) 2158 cm<sup>-1</sup>; UV/Vis (MeOH):  $\lambda_{max}(\epsilon) = 608$  nm (2,000 L mol<sup>-1</sup> cm<sup>-1</sup>), 407.11 nm (14,000 L mol<sup>-1</sup> cm<sup>-1</sup>), 341.84 nm (16,800 L mol<sup>-1</sup> cm<sup>-1</sup>), 307.84 nm (15,000 L mol<sup>-1</sup> cm<sup>-1</sup>).

**Synthesis of Nickel compound [NiL].** We prepared the Schiff base ligand H<sub>2</sub>L and the metalloligand [NiL] by following the procedure which was adopted from the literature.<sup>48</sup>

Synthesis of the compound  $[(NiL)_4Mn_2(N(CN)2)_2] \cdot (ClO_4)_2$  (2). Compound 2 was prepared by taking the 10 mL acetonitrile solution of [NiL] (0.382g, 1mmol) stirred with  $Mn(ClO_4)_2 \cdot 6H_2O$  (0.362 g, 1 mmol) for 10 mins. After that 2 mL of a 1:1 (v/v) H<sub>2</sub>O/acetonitrile solution of sodium dicyanamide (0.178 g, 2 mmol) was added to the solution drop wise at room temperature. And the mixture was stirred for another 0.5 h. After filtration brownish green solution was kept in a CaCl<sub>2</sub> desiccator. After few days later rectangular shaped deep brown crystals suitable for X-ray diffraction were obtained.

Yield: 73%; Anal. Calcd. for  $C_{80}H_{80}Cl_2Mn_2N_{14}Ni_4O_{16}$ : C (50.33%); H (4.22%); N (10.27%); Found: C (50.02%); H (4.03%); N (10.22%); FT-IR (KBr pellet): v(C=N) 1615cm<sup>-1</sup>; v(skeletal vibration) 1553 cm<sup>-1</sup>; v(C<sub>2</sub>N<sub>3</sub><sup>-</sup>) 2159, 2336 cm<sup>-1</sup>; UV/Vis (DMF):  $\lambda_{max}(\epsilon) = 361.39$  nm (17,000 L mol<sup>-1</sup> cm<sup>-1</sup>), 273.40 nm (35,600 L mol<sup>-1</sup> cm<sup>-1</sup>).

X-ray crystallographic data collection and refinement. Diffraction data for the structure reported were collected at room temperature on a Bruker Smart Apex diffractometer equipped with CCD. All the experiments were performed with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Cell refinement,<sup>49</sup> indexing and scaling of the data set were carried out using Bruker Smart Apex and Bruker Saint Packages.<sup>50</sup> The structures were solved by direct methods and subsequent Fourier

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analyses and refined by the full-matrix least-squares method based on  $F^2$  with all observed reflections.<sup>51</sup> All the calculations were performed using the WinGX System, Ver 2013.3.<sup>52</sup>

**Phenoxazinone synthase of OAP.** The phenoxazinone synthase activity of compounds 1-2 were studied using *o*-aminophenol (OAP) as a model substrate in a methanolic solution under aerobic conditions at room temperature. The reactions were carried out spectrophotometrically by monitoring the increasing the absorbance band of the amino phenoxazinone at 425 nm with 5 min time interval. For this purpose,  $1 \times 10^{-4}$  mol dm<sup>-3</sup> solutions of compounds were treated with  $1 \times 10^{-2}$  mol dm<sup>-3</sup> (100 equivalents) of *o*-aminophenol under aerobic condition. The course of the reaction was followed by UV-Vis spectroscopy. The time dependent UV-Vis spectral scan was performed in pure methanol medium. The kinetics of the OAP oxidation was determined by monitoring the increase of the product amino phenoxazinone. All the compounds showed saturation kinetics and a treatment based on the Michaelis-Menten model seemed to be appropriate. The binding constant (K<sub>M</sub>), maximum velocity (V<sub>max</sub>), and rate constant for dissociation of substrates (i.e., turnover number, k<sub>cat</sub>) were calculated for all the compounds using the Lineweaver-Burk graph of 1/V vs. 1/[S], using the equation  $1/V = \{K_M/V_{max}\} \times \{1/[S]\} + 1/V_{max}$ .

Detection of hydrogen peroxide in the catalytic reaction. To detect the formation of hydrogen peroxide during the catalytic cycle, reaction mixtures were prepared as in kinetic experiments. After 1 hour of reaction, an equal volume of water was added and OAP formed was extracted with dichloromethane. The pH of aqueous layer was fixed at 2 with H<sub>2</sub>SO<sub>4</sub>. 1 mL of 10% KI solution and three drops of 3% ammonium molybdate solution were added. In presence of hydrogen peroxide the reaction, H<sub>2</sub>O<sub>2</sub> + 2I<sup>-</sup> + 2H<sup>+</sup>  $\rightarrow$  2H<sub>2</sub>O + I<sub>2</sub> occurs, and with an excess of iodide ions, the triiodide ion is formed according to the reaction I<sub>2</sub>(aq.) + I<sup>-</sup> = I<sub>3</sub><sup>-</sup>. The reaction rate is slow but increases with increasing concentrations of acid, and the addition of an ammonium molybdate solution renders the reaction instantaneously. The formation of I<sub>3</sub><sup>-</sup> could be monitored spectrophotometrically due to the development of the characteristic I<sub>3</sub><sup>-</sup> band ( $\lambda_{max} = 353 \text{ nm}, \varepsilon = 26,000 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$ ).

**Phosphatase like activity of 4-NPP in 97.5% (v/v) DMF-H<sub>2</sub>O.** The reactions were followed by UV-Vis spectroscopy by using disodium (4-nitrophenyl) phosphate (4-NPP) hexahydrate as model substrate. The course of the catalytic reaction was monitored by the increment of the

absorption band at  $\lambda_{max}$ = 427 nm in presence of 1-2 due to the hydrolyzed product of 4-NPP i.e. 4-nitrophenolate ion in aqueous DMF ( $\epsilon$  =18500 M<sup>-1</sup>cm<sup>-1</sup>) at 25 °C. Initially, a series of solutions of the substrate, 4-NPP, having different concentrations (1×10<sup>-3</sup> to 5×10<sup>-2</sup> mol dm<sup>-3</sup>) was prepared from a concentrated stock solution of the substrate using DMF-H<sub>2</sub>O 97.5% (v/v) as solvent. Then 3 mL of this substrate solution was poured into a 1 cm quartz cell kept in the spectrophotometer to equilibrate the temperature at 25°C, 0.03 ml 5×10<sup>-3</sup> mol dm<sup>-3</sup> of compounds in DMF were quickly added and mixed thoroughly. The final A<sub>∞</sub> values for each set were obtained after one day. The determination of the initial rates, as function of the concentration of 4-NPP, reveals saturation kinetics with Michaelis-Menten like behaviour. The kinetic parameters ( $k_{cat}$ , V<sub>max</sub>,  $k_M$ ) for the hydrolysis of phosphate-ester bond were determined using Michaelis-Menten approach of enzyme kinetics.

## **Results and Discussion**

Synthesis of ligand and compounds. Here we synthesized a tetradentate  $N_2O_2$  donor Schiff base ligand  $H_2L$ , prepared *in situ* via condensation of 2-hydroxybenzaldehyde and 2,2' dimethyl 1,3 propane diamine. And then it was reacted with Cu(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O and Ni(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O to produce the metalloligand [CuL] and [NiL] respectively. By using this two metalloligand we prepared two heterometallic compound (1-2) on reaction with Mn(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O in the presence of sodium dicyanamide as a spacer, although [CuL]/[NiL]:Mn(ClO<sub>4</sub>)<sub>2</sub>:NaN(CN)<sub>2</sub> ratio was [1:1:2] (Scheme 1). The PXRD of compounds 1-2 to their respective simulated patterns are given in the supporting information (Figure S1-S2) which indicate the purity of the compounds.

**Crystal structure description.** Single crystal X-ray crystallography shows that compound 1 crystallizes in Pī space group. The structure of 1 is represented in Figure 1. The asymmetric unit contains one "metalloligand" (CuL), one Mn(II) ion and two  $\mu_{1,5}$ -dicyanamidoligands. CH<sub>3</sub>CN molecule presents as solvent of crystallization. The copper(II) is four coordinated with a square planar geometry, connected by two oxygen and two nitrogen atoms of Schiff base ligand. This four donor atoms around the Cu(1) center in the equatorial plane shows root-mean-square (r.m.s.) deviations of 0.077Å and Cu(1) atom deviated at 0.018(1)Å from the mean plane. The bond length and bond angle values are given in Table S1.



Figure 1. Ball and stick representation of crystal structure of compound 1.

The bond lengths of Cu(1)-O(1), Cu(1)-O(2), Cu(1)-N(1), Cu(1)-N(2) are 1.918(4), 1.937(4), 1.969(5) and 1.924(6) Å, respectively. And the *trans* angles of O(1)-Cu(1)-N(2), O(2)-Cu(1)-N(1) are 169.2(2)°, 170.9(2)° and dihedral angle between the two N-Cu-O planes is 6.54°, indicates slight distortion from ideal square planar geometry. The manganese(II) ion posses a hexa-coordinated octahedral geometry, coordinated by two oxygen atoms of the Schiff-base "metalloligand" and four nitrogen atoms from four dicyanamide ligands. The equatorial bond distances of Mn(1)-O(1), Mn(1)-O(2), Mn(1)-N(3), Mn(1)-N(6) are 2.134(4) Å, 2.163(4) Å, 2.136(7) Å, 2.138(7) Å and two axial bond distances of Mn(1)-N(5)<sup>a</sup>, Mn(1)-N(8)<sup>b</sup> are 2.392(7) Å and 2.193(7) Å, respectively. The axial bond angle of N(8)<sup>b</sup>-Mn(1)-N(5)<sup>a</sup> is 178(2)<sup>o</sup> and one equatorial bond angle of N(6)-Mn(1)-N(3) is 94.6(2)°, the latter being more close to the ideal octahedron but another equatorial bond angle O(1)-Mn(1)-O(2) [69.25(16)] is quite far from the ideal value (90°) that is Mn(II) center exhibits distorted octahedral geometry. However, in compound 1, the asymmetric units are connected by terminal nitrogen atom of two equatorially and axially dicyanamide ions and form distorted six member rings (Figure 2(a)). Overall structural view along b-axis is shown in Figure 2b where it looks like two distorted five member rings stacked upon another between two Mn(II) centres. The metal-metal separation of Cu(1)-Mn(1), Mn(1)-Mn(1)<sup>a</sup> and the bond angle of Mn(1)-Mn(1)<sup>a</sup>-Mn(1)<sup>b</sup> are 3.045(1) Å, 7.259(2) Å and 102.23(2)°, respectively. The polymer of 1 is simply built by translational symmetry of the crystallographic independent unit  $[(CuL)Mn(N(CN)_2)_2]$  along c-axis in Figure 2c.



**Figure 2.** (a) Distorted six-membered ring between two Mn-ions of compound 1. H-atoms have been removed for clarity, (b) View of compound 1 along b-axis and (c) one dimensional zig-zag polymeric structure along c-axis.

Single crystal X-ray crystallography reveals that compound **2** crystallizes in Pī space group. The Ball-Stick representation of **2** is depicted in Figure 3. The bond length and bond angle values are given in Table S2. The asymmetric unit contains two "metalloligand" (NiL) units (Ni1 and Ni2) and one Mn(II) unit (Mn3) which is connected to metalloligand via phenoxido oxygen atom. In asymmetric unit one perchlorate anion is present. The central Mn(3) is (six-coordinated) coordinated to two nitrogen donors from two dicyanamide ligands and four oxygen atoms from the two different "metalloligand" (NiL). In case of **2**, a centrosymmetric hexanuclear compound with a general formula of  $[{(NiL)_2Mn}_2(\mu_{1,5}-N(CN)_2)_2]^{2+}$  is formed via the bridging of two dicyanamide anions in  $\mu_{1,5}$  mode with the trinuclear asymmetric units.



Figure 3. Ball and stick representation of crystal structure of compound 2.

The bond lengths of Mn(3)-N(5) and Mn(3)-N(7)<sup>a</sup> are 2.152(6), 2.178(6) Å and the bond length of Mn(3)-O(1), Mn(3)-O(2), Mn(3)-O(3), Mn(3)-O(4) are 2.133(4), 2.272(3), 2.235(4) and 2.147(4) Å, respectively. The equatorial N(5)-Mn(3)-N(7)<sup>a</sup> bond angle involving the two cis dicyanamide groups is [89.8(2)°] and another equatorial O(1)-Mn(3)-O(3) bond angle is 89.95(14)° which are close to the angle for an ideal octahedron (90°). The axial N(7)<sup>a</sup>-Mn(3)-O(2) bond angle [165.32(17)°] is quite far from the ideal octahedron (180°) which indicates the significant distortion from the ideal octahedral geometry of Mn(II) ion. And each Ni(II) atoms are four coordinate with slightly distorted square planar geometry as all the trans angles are quite far from ideal (180°) bond angle (Figure 3), bound by two oxygen and two nitrogen atoms of Schiff-base ligand. This four donor atoms around the Ni(1) and Ni(2) centres in the equatorial plane show r.m.s. deviations of 0.198 and 0.050 Å respectively, Ni(1) and Ni(2) atoms deviated at 0.014(1), 0.006(1) Å from the mean plane.



Figure 4. Polyhedral view of compound 2 forming twelve member chair like metal core of Mn(II).

The bond lengths of Ni(1)-O(1), Ni(1)-O(2), Ni(1)-N(3), Ni(1)-N(4) are 1.869(3), 1.858(4), 1.877(5), 1.854(4) Å and the bond lengths of Ni(2)-O(3), Ni(2)-O(4), Ni(2)-N(1), Ni(2)-N(2) are 1.848(4), 1.871(4), 1.859(6) and 1.872(5) Å, respectively. And the *trans* angles of O(1)-Ni(1)-N(4), O(2)-Ni(1)-N(3), O(4)-Ni(2)-N(1), O(3)-Ni(2)-N(2) are 167.0(2)°, 166.77(18)°, 173.6(2)° and 171.0(2)° which indicate that both Ni(1) and Ni(2) undergo slight distortion from the ideal square planar geometry. This distortion is also satisfied from the calculation of dihedral angles between the two N-Ni-O planes, which are 16.69° and 4.34° for Ni(1) and Ni(2) respectively. This angle is 0° for a perfectly square planar geometry and 90° for a perfect tetrahedral geometry. From the asymmetric unit we found the metal-metal separation of Mn(3)····Ni(1), Mn(3)····Ni(2), Ni(1)····Ni(2) and Mn(3)····Mn(3)\* are 3.133(1), 3.118(1), 4.272(2) and 7.314(2) Å, respectively. The bond angle of Ni(1)-Mn(3)-Ni(2) is 86.22(3)° which indicates bent arrangement of the three metal atoms in the trinuclear mode. Figure 4 also shows twelve member chair form where two Mn(II) centres interconnected through two dicyanamide anions. Summary of SHAPE analysis of Cu<sup>II</sup>, Ni<sup>II</sup>, Mn<sup>II</sup> centres for compounds **1** and **2** is given in Table S3.

Table 1	l Crystallographic	data and	details of refinements	for compounds 1-2.
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	Compound 1	Compound 2
CCDC Number	1879134	1879135
Empirical formula	$C_{25}H_{23}CuMnN_9O_2$	$C_{80}H_{80}Mn_2Cl_2N_{14}Ni_4O_{16}$
Fw	600.00	1909.20

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System	Triclinic	Triclinic
Space group	Pī (No. 2)	Pī (No. 2)
a (Å)	11.1397(14)	9.980(2)
b (Å)	11.3454(14)	11.279(3)
c (Å)	11.7078(15)	18.546(4)
α (°)	107.327(3)	89.668(5)
β (°)	104.347(3)	84.676(5)
γ (°)	101.973(3)	85.980(5)
V (Å <sup>3</sup> )	1303.7(3)	2073.5(8)
Z	2	1
D <sub>calcd</sub> (g.cm <sup>-3</sup> )	1.528	1.529
$\mu$ (mm <sup>-1</sup> )	1.341	1.323
<i>F</i> (000)	612	982
θ range (°)	2.2 - 25.8	2.2-25.1
Collected reflections	33708	7291
Indep. Reflections	4991	7291
R <sub>int</sub>	0.185	0.000
Obs. reflections $[I \ge 2\sigma(I)]$	2533	4618
Parameters	347	546
$R_{I} [I \ge 2\sigma(I)]^{a}$	0.0673	0.0608
$wR_2 [I > 2\sigma(I)]^a$	0.1563	0.1716
GOF on F <sup>2</sup>	1.04	1.05
Residuals (e Å <sup>-3</sup> )	-0.55, 0.34	-0.73, 0.68

 $[a]R_{1} = \Sigma | F_{0}| - F_{c}| / \Sigma | F_{0}|, wR_{2} = [\Sigma w (F_{0}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{0}^{2})^{2}]^{\frac{1}{2}}$ 

**FT-IR and UV-Vis spectra of the compounds.** FT-IR spectra of compounds **1-2** (Figure S3-S4) illustrate a strong peaks at around 1615 cm<sup>-1</sup> due to the presence of -C=N stretching frequency and the bands signature of skeleton vibrations are present in the region of 1550-1560 cm<sup>-1</sup> and another strong bands near 2158 cm<sup>-1</sup> attributed for the stretching vibrations of  $(CN)_2N^-$ .

Solid state UV spectra of compounds 1 and 2 (Figure S5) show the absorption bands near 350-435 and 270-310 nm due to charge-transfer from  $p\pi$ -d $\pi$ \* and  $\pi$ - $\pi$ \* transitions involving the phenolate units of the compounds. UV-Vis study (liquid state) of 1 and 2 were performed in methanol and DMF solvent respectively, as 1 is highly soluble in methanol solvent but 2 is partially soluble in DMF solvent due to its hexanuclear compact structure. Both the compound showing absorption bands (Figure S6) near  $\lambda_{max} \sim 350-410$  nm due to charge-transfer transitions from p $\pi$  orbital of the phenolate to the d $\pi$ \* orbital of metal, and higher energy bands near 270-310 nm due to  $\pi$ - $\pi$ \* transitions involving the phenolate units of the compounds. In case of 1, another band at 608 nm (Figure S6) corresponds to the d-d band of Mn(III) but solid state UV spectra do not show any band near 608 nm (Figure S5). That is why, oxidation state of manganese centre of compound 1 changes (Mn<sup>II</sup>-Mn<sup>III</sup>) from solid to liquid state. But 2 does not exhibit such band in both solid and liquid state (inset picture of Figure S5-S6) which suggests that both in solid and solution state manganese center of 2 exists as Mn(II).

Electrospray Ionization mass spectral study. The electro spray ionization mass (ESI-MS positive) spectrum of compound 1 was recorded in acetonitrile solution (Figure S7) to access their composition in solution phase. For 1 the base peak at m/z = 765.1613 amu (calcd. m/z = 765.1034 amu) is consistent with molecular formula [C<sub>28</sub>H<sub>29</sub>CuMnN<sub>11</sub>O<sub>3</sub>+K<sup>+</sup>]+CH<sub>3</sub>CN, and another peak at m/z = 743.1729 amu (calcd. m/z = 743.0947 amu) is consistent with molecular formula [C<sub>28</sub>H<sub>30</sub>CuMnN<sub>11</sub>O<sub>3</sub>+K<sup>+</sup>]+H<sub>2</sub>O but we failed to know the solution state structure of **2** because it was not soluble in any solvent which was generally used for mass analysis.

**EPR study.** In order to verify the oxidation state of the compounds **1** and **2** in the solution phase, EPR study was performed in MeOH and DMF medium respectively. From the EPR study (Figure S8) it is revealed that **1** shows four EPR signal which is responsible for the Cu(II).<sup>53,54</sup> Therefore in solution state oxidation state of manganese centre of **1** exists as +3 (Mn(III) is EPR silent). On the another hand, six EPR spectral line of **2** corresponds to the Mn(II) present in the solution phase. EPR study helps to predict the change of the oxidation state of metal center from solid to solution state. In case of **1**, exhibits four EPR signal which implies that Cu(II)-Mn(II) changes to Cu(II)-Mn(III) in solution state and EPR spectrum of **2** indicates that both in solution and solid state Ni(II)-Mn(II) retain its geometry (Ni(II) is EPR silent and Mn(II) gives six line spectra). We also performed the conductivity study of **1-2** in MeOH and DMF medium, respectively. The molar conductance values at 298 K for **1** and **2** are 32, 156  $\Omega^{-1}$  cm<sup>2</sup> M<sup>-1</sup>, respectively. The obtained values suggest that **1** behaves as non electrolyte and **2** acts as 2:1 electrolyte. And this is the sign to retain the hexanuclear geometry of **2** in solution state.

#### Crystal Growth & Design

At 300 K,  $\chi_M T$  value for **1** is 4.56 cm<sup>3</sup>mol<sup>-1</sup>K which is close to the theoretical value of 4.75 cm<sup>3</sup>mol<sup>-1</sup>K for uncoupled one Cu<sup>2+</sup> (S = ½)and one Mn<sup>2+</sup> centre (S = 5/2), having g = 2.0. With decreasing the temperature,  $\chi_M T$  value slowly decreases upto 3.61 cm<sup>3</sup>mol<sup>-1</sup>K at 20 K. Below that,  $\chi_M T$  value abruptly increases and reached the very high value 7.5 cm<sup>3</sup>mol<sup>-1</sup>K at 8.8 K. After that  $\chi_M T$  value again sharply fall due to saturation effect and reached to the value of 5.62 cm<sup>3</sup>mol<sup>-1</sup>K at 4 K (Figure 5a). This characteristic of  $\chi_M T$  vs T plot is the feature of ferrimagnetic coupling. In order to ensure the ferrimagnetic interactions, temperature dependent field-cooled (FC) magnetization study was performed at 100 Oe and reveals spontaneous magnetization at ~ 15 K (Figure 5b). To examine the magnetic interactions,  $1/\chi_M$  vs. T was plotted in the temperature range of 50-300 K and fitted using the Curie-Weiss equation,  $1/\chi_M = (T-\theta)/C$  (Figure S9). From the fitting, C = 4.72 cm<sup>3</sup>mol<sup>-1</sup>K and  $\theta$  = -14.58 K were obtained. Value of C is consistent with the one non-interacting Cu<sup>2+</sup> and one non-interacting Mn<sup>2+</sup> centre, with g = 2.0. Negative and moderate value of  $\theta$  indicates moderate antiferromagnetic interactions dominating at higher temperature range.

 $H = -J_{I}(Cu_{1}Mn_{1} + Cu_{1}Mn_{1}) - J_{2}(Mn_{1}Mn_{1}) - g\mu_{B}H\sum_{i=1}^{4}Si$  .....(1) where  $J_{I}$  is the interaction between Cu(II)-Mn(II) centres,  $J_{2}$  is the interaction between Mn(II)-Mn(II) centres;  $S_{i}$  = individual spin.

Moreover,  $\chi_M T$  vs T plot in the temperature range of 50-300 K was fitted<sup>55</sup> using the suitable model (Figure S10) and Hamiltonian (1) and best fitting afforded  $J_I = + 2.94$  cm<sup>-1</sup>,  $J_2 = -9.11$ cm<sup>-1</sup> and g = 2.0. Usually if M-O-M (M = metal) bond angle is in the range of ~93-98°,<sup>56</sup> compound shows ferromagnetic interactions and below or above that range, antiferromagnetic interaction is expected. Here Cu-O-Mn bond angles are 97.3(2)° and 95.7(2)°. As both the bond angles fall in the range, ferromagnetic interaction is expected for  $J_I$  interaction. Indeed, from the fitting we obtained positive  $J_I$  value indicating ferromagnetic interactions. Negative  $J_2$  value suggests antiferromagnetic interactions through Mn-NCN-NCN-Mn pathway. On the basis of bond distance,  $J_I$  should have higher value than  $J_2$  interactions. However, here Cu(II) has square planar geometry where dx<sup>2</sup>-y<sup>2</sup> is magnetic orbital and Mn(II) has octahedral geometry where again dx<sup>2</sup>-y<sup>2</sup> is magnetic orbital. Hence, ferromagnetic interaction could have been strong if they belong to same plane. But as Cu(II) and Mn(II) centers exhibit in different plane (angle between two plane = 46.96°), ferromagnetic interaction is quite weak in nature (Figure S11a).<sup>57-61</sup> Besides that, both the Mn(II) centres are in same plane (Figure S11b). Therefore,  $J_2$  interaction is relatively higher.

Therefore, probable spin orientation for ferrimagnetic ordering is shown in Figure 6. Alternate ferromagnetic and antiferromagnetic interactions overall lead to ferrimagnetic chain.



Figure 5. (a) Temperature dependent molar magnetic susceptibility of compound 1 at 750 Oe Red line indicates fitting of the plot. (b) Field-cooled magnetization curve of 1 under an applied magnetic field of H = 100Oe showing ferromagnetic order at ~ 15 K.



**Figure 6.** Probable spin orientation of compound **1**. AFC: antiferromagnetic and FC: ferromagnetic.

To elucidate the origin of ferrimagnetic interaction, it is important to know the pathway of magnetic interactions. Whether the ferromagnetic interaction is through Cu-O-Mn and

antiferromagnetic interactions through Mn-(NCN)<sub>2</sub>-Mn, Cu(II) is replaced by Ni(II) because Ni(II) is square planar and it is diamagnetic in nature. Therefore, magnetic exchange interactions can only originate through Mn-(NCN)<sub>2</sub>-Mn pathway. At 300 K,  $\chi_M T$  value is 8.87 cm<sup>3</sup>mol<sup>-1</sup>K which is close to the calculated value of 8.75 cm<sup>3</sup>mol<sup>-1</sup>K for two non-interacting Mn<sup>II</sup> centres (S = 5/2 , g = 2.0) (Figure 7). Below 300 K,  $\chi_M T$  value gradually decreases with temperature probably due to antiferromagnetic interactions. Lowest value of 1.71 cm<sup>3</sup>mol<sup>-1</sup>K was obtained at 2 K. To investigate the magnetic interactions,  $\chi_M T$  vs. T plot was fitted using the dinuclear model (Figure S12) and the Hamiltonian (2). H = -  $J_I(Mn_3Mn_3') - g\mu_B H \sum_{i=1}^2 Si$  ......(2) where J is the interaction between Mn(II)-Mn(II) centres and S<sub>i</sub> = individual spin.



Figure 7. Temperature dependent molar magnetic susceptibility of compound 2. Solid line represents fitting of the plot.

From the fitting, J = -57.4 cm<sup>-1</sup> and g = 2.01 were obtained. J value indicates moderate antiferromagnetic interactions in the system. In compound **1** also antiferromagnetic interaction through Mn-(NCN)<sub>2</sub>-Mn were found. Therefore, it can be said that ferromagnetic interactions of compound **1** originates through Cu-O-Mn pathway.

**Phenoxazinone synthase studies and kinetics.** Using these two heterometallic compound we have studied phenoxazinone synthase like activity. It is an oxidase type reaction where the catalytic oxidation of *o*-aminophenol (OAP) to aminophenoxazinone (APX) is occurred shown

in scheme 2. This reaction is an oxidative dimerization type reaction where APX shows a broad absorption band near 410-425 nm in pure methanol solvent. Then we examined the catalytic activity of compounds 1-2 using *o*-aminophenol (OAP) as a model substrate in methanol solvent under an aerial atmospheric condition and we found that 1 is active towards catalytic oxidation, whereas 2 did not show any catalytic activity. Figure 8 showed the change of spectral behaviour of 1 in presence of OAP during the wavelength scan.



**Figure 8.** Increase of the APX band at around 425 nm after the addition of OAP to a methanolic solution of compounds **1** and **2**. The spectra were recorded at 5 min intervals.

After then we performed the determination of detailed kinetics studies of catalytically active compound **1** by the following procedure. For this purpose,  $1 \times 10^{-4}$  mol dm<sup>-3</sup> solutions of **1** was treated with  $1 \times 10^{-2}$  mol dm<sup>-3</sup> (100 equivalents) of *o*-aminophenol (OAP) under aerobic condition. The course of the reaction was followed by UV-Vis spectroscopy. The time dependent UV-Vis spectral scan was performed in pure methanol (MeOH) solution. The kinetics of the *o*-aminophenol (OAP) oxidation was determined by monitoring the increase of the product aminophenoxazinone (APX). The experimental conditions were same as we reported earlier. The compound **1** showed saturation kinetics and a treatment based on the Michaelis-Menten model seemed to be appropriate. The binding constant (K<sub>M</sub>), maximum velocity (V<sub>max</sub>), and rate constant for dissociation of substrates (i.e., turnover number,  $k_{cat}$ ) were calculated for all the compounds using the Lineweaver-Burk graph of 1/V vs. 1/[S], using the equation  $1/V = {K_M/V_{max}} \times {1/[S]} + 1/V_{max}$ . The Lineweaver-Burk plot and kinetics Plot of the rate vs. substrate concentration of **1** were shown in Figure S13. The kinetics parameters were obtained in Table 2.

Calculated turnover number ( $k_{cat}$  in h<sup>-1</sup>) of **1** was 5129. The value was very high ever for earlier reported homo and hetero metallic compounds, shown in the comparison Table 3.

**Table 2** Kinetic parameters for the activity of compound 1 using OAP as substrate.

Compound	$k_{\rm cat}({\rm h}^{-1})$	V <sub>max</sub>	K <sub>M</sub>	SD
1	5129	8.510×10 <sup>-4</sup>	4.760×10 <sup>-2</sup>	7.1×10 <sup>-4</sup>

It is important to detect the formation of aminophenoxazinone (APX) due to reduction of molecular di-oxygen during oxidation of *o*-aminophenol (OAP). It also helps to get an idea about the mechanistic pathway of catalytic system. There occurs the oxidation of I<sup>-</sup> to I<sub>2</sub> followed by the formation of I<sub>3</sub><sup>-</sup> as was detected in the UV-Vis spectra of the reaction mixture of *o*-aminophenol (OAP), compound **1** and KI. Therefore H<sub>2</sub>O<sub>2</sub> is released as reduced product of di-oxygen during oxidation of *o*-aminophenol (OAP) and there is a possibility to form a radical during the catalytic cycle. The band appears due to formation of I<sub>3</sub><sup>-</sup> at  $\lambda_{max} \sim 353$  nm ( $\epsilon = 26000$  L mol<sup>-1</sup> cm<sup>-1</sup>) is given in Figure S14.

**EPR Study.** Figure 9 shows the EPR spectra of compound 1 after addition of OAP recorded in methanol solvent at 77 K. It helps to find the mechanistic pathway of the catalytic cycle. From the EPR study 1 shows four line spectrum which is responsible for Cu(II) only (as Mn(III) is EPR silent). However, compound 1 in presence of OAP exhibits a new signal at  $g \approx 2.005$  (Figure 9). Comparing these two EPR spectra we can conclude that the four line spectrum of Cu(II) obtained from 1 and in addition a sharp peak of an organic free radical generated. This radical is formed due to reduction of imine bond of ligand backbone which represents the catalytic oxidation occur by the formation of imine bond radical.<sup>62,63</sup>



Figure 9. EPR spectra of compound 1 and immediately after addition of OAP in methanol solvent.

**Electrochemistry.** Cyclic voltammogram (CV) of Compound **1** has been recorded in acetonitrile medium over a potential range from -1.8 to +1.6 V. Figure S15 shows two peaks at  $E_1 = -0.7$  V and  $E_2 = -1.1$  V on a forward cathodic scan and the potential difference ( $\Delta E_{12} = E_1 - E_2$ ) between two peaks on a forward scan is -0.4 V. On the other hand, compound **1** also shows one peak at  $E_1 = -0.64$  V on a reverse scan. It suggest that the Cu(II) compound reduced to the Cu(I) state through a one-electron process. And another anodic peak at +0.96 V assigned due to for Mn(II)/Mn(III) oxidation process. After addition of OAP the peak at -1.1 V shifted to -1.19 V which is for Cu(II)/Cu(I) reduction process and a shifting of anodic peak at +0.03 V is due to for anodic stripping, consists of sudden reoxidation of metallic copper that has been deposited on the electrode surface.

Electrospray Ionization mass spectral study. ESI-MS spectra were recorded of compound 1 in a 1:1 mixture of the compound and *o*-aminophenol within 5 min of mixing in acetonitrile medium (Figure S16) to investigate the intermediate species of phenoxazinone synthase activity during the oxidative dimerization reaction of *o*-aminophenol. In this spectra, the base peak at m/z= 765.1613 amu (calcd. m/z =765.1034 amu) is observed for the dinuclear species of [Cu(L)Mn(dca)<sub>3</sub>(CH<sub>3</sub>OH)(CH<sub>3</sub>CN)+K<sup>+</sup>]<sup>+</sup>. Along with other lower intensity peaks than previous

one are observed at m/z = 772.1528 amu (calcd. m/z = 772.0643 amu) and m/z = 865.1111 amu (calcd. m/z = 865.1197 amu), attributed to the dinuclear intermediate species [Cu(L)Mn(dca)<sub>3</sub>(OAP)+K<sup>+</sup>]<sup>+</sup> and [Cu(L)Mn(dca)<sub>3</sub>(OAP)(CH<sub>3</sub>CN)+K<sup>+</sup>+Na<sup>+</sup>]<sup>+</sup>, respectively. This is probably due to the formation of compound-substrate intermediate during the catalytic oxidation reaction of o-aminophenol to phenoxazinone.

**Table 3** First-order rate constants for phenoxazinone synthase like activity by previously reported heteronuclear Schiff base compounds.

Catalyst	Substrate	Solvent	$k_{\rm cat}({\rm h}^{-1})$	Ref
$[(CuL)_2Mn(N_3)(H_2O)](ClO_4) \cdot H_2O$	OAP	МеОН	6581	31
$[\{(CuL)_2Mn\}_2(\mu_{1,5}\text{-}N(CN)_2)(CH_3CN)_2](ClO_4)_3$	OAP	MeCN	4966	32
$[{(CuL)_2Mn}_2(\mu_1-N(CN)_2)] \cdot (H_2O)_4$	OAP	MeCN	2021	32
$[\{(CuL)_2Mn\}_2(\mu_{1,5}\text{-}N(CN)_2)]_n$	OAP	MeCN	1107	32
$[(NiL)_2Mn(N_3)](ClO_4)$	OAP	MeOH	3240	34
$[(NiL)_2Mn_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2(CH_3OH)_2]$	OAP	MeOH	3360	34
$[(NiL)_2Mn(N_3)(H_2O)](ClO_4) \cdot H_2O$	OAP	MeOH	6351	64
$\{[(CuL)Mn(N(CN)2)_2] \cdot CH_3CN\}_{\infty}$	OAP	МеОН	5129	Our work

Here, OAP = *o*-aminophenol, MeCN = Acetonitrile, MeOH = Methanol solvent.

**Mechanistic insight.** The phenoxazinone synthase-like activity of some heterometallic Cu(II)-Mn(II), Ni(II)-Mn(II) compounds has been reported earlier.<sup>31-34</sup> In this content, we have synthesized two heterometallic compound Cu(II)-Mn(II) (1), Ni(II)-Mn(II) (2) with dicyanamido spacer. Here **1** is polymeric (one dimensional polymeric chain), the solution state structure of **1** (from EPR (Figure S8) and ESI-MS study (Figure S7)) containing Cu(II) and Mn(III) centres whereas manganese center coordinated with three N(CN)<sub>2</sub> and one methanol moiety. At first, a neutral species of dinuclear [Cu(L)Mn(dca)<sub>3</sub>(OAP)] is formed during the mixing of *o*aminophenol and compound **1** in methanolic solution, where hydroxyl group of *o*-aminophenol coordinated to the Mn(III) center (Scheme 2) then *o*-aminophenol releases proton to form *o*aminophenolate radical. Then this radical move their electron to the catalyst and generate imine bond radical. In the next step, the two radicals dimerize to form amino-phenoxazinone (APX) as a product, eliminated from the catalyst leaving the dinuclear [Cu(L)Mn(dca)<sub>3</sub>] species. After then

this species coordinates to o-aminophenol and enters into the next cycle. During this cycle molecular  $O_2$  is reduced to  $H_2O_2$ .



Scheme 2. Proposed mechanism for catalytic oxidation of OAP by compound 1.

**Phosphatase like activity.** Phosphatase like activity of compounds 1 and 2 were studied in aqueous DMF (DMF: water = 97.5:2.5) using disodium salt of (4-nitrophenyl)-phosphate hexahydrate (4-NPP) as model substrate. Among the compounds 1 and 2, only 1 is active towards phosphatase like activity. The hydrolytic behavior of the compounds were observed spectrophotometrically by monitoring the time evolution of p-nitrophenolate ( $\lambda_{max} = 424$  nm) through a wavelength scan from 200 to 800 nm in aqueous DMF (DMF: water = 97.5:2.5),

 where substrate catalyst ratio was 1:20 in the reaction mixture, till roughly 2% reaction conversion. The spectral change behaviour of **1-2** is shown in Figure 10.



**Figure 10.** Wavelength scan for the hydrolysis of 4-NPP in the absence and presence of (a) compound **1** and (b) compound **2** (substrate : catalyst =20:1) in 97.5% DMF recorded at 25 °C at intervals of 5 min for 1.5 h.

Kinetic Studies of the Hydrolysis of 4-NPP in 97.5% (v/v) DMF-H<sub>2</sub>O. The kinetic study of compound 1 was performed by initial slope method following the rate of increase in absorption of the band at  $\lambda_{max} \sim 427$  nm, corresponding to the rise of 4-nitrophenolate concentration in aqueous DMF solution. The initial first-order rate constants,  $V_{max}$  (sec<sup>-1</sup>) for the cleavage of 4-NPP were obtained directly from the plot of log  $[A_{\infty}/(A_{\infty}-A_t)]$  versus time which is linear. To determine the dependence of rate constants on substrate concentration, 1 was treated with five different concentrations of substrate. The kinetic parameters ( $V_{max}$ ,  $K_M$ ,  $k_{cat}$ ) for the catalyzed reactions were determined from the linear plots of 1/V versus 1/[4-NPP] values (Lineweaver-Burk plot) as per the Michaelis-Menten treatment of enzymatic kinetics. All the kinetic parameters are summarized in Table 4. The plot for enzymatic kinetic and Lineweaver-Burk plots for 1 is depicted in Figure S17. A comparison table is given in Table 5 to compare  $k_{cat}$  values with the previously reported heteronuclear Schiff base compounds.

**Table 4** First-order kinetic parameters for phosphatase activity obtained by Michaelis-Menten treatment of compound 1.

Compound	$k_{\rm cat}({\rm sec}^{-1})$	V <sub>max</sub>	K <sub>M</sub>	SD
1	25.052	12.510×10 <sup>-4</sup>	14.760×10 <sup>-4</sup>	1.2×10 <sup>-5</sup>

Electrospray Ionization mass spectral study. ESI-MS spectra were recorded of compound 1 in a 1:1 mixture of the compound and 4-NPP within 5 min of mixing in acetonitrile medium (Figure S18) to investigate the intermediate species of Phosphatase like activity during the hydrolysis of phosphate-ester bond of 4-NPP. In this spectra, the base peak at m/z = 765.1613 amu (calcd. m/zis = 765.1034 amu) observed for the dinuclear species of  $[Cu(L)Mn(dca)_3(CH_3OH)(CH_3CN)+K^+]^+$  along with another low intensity peak at m/z =900.4091 amu (calcd. m/z = 900.0507 amu), attributed to the dinuclear intermediate species  $[Cu(L)Mn(dca)_2(4-NPP)(H_2O)+K^++Na^+]^+$ , which is probably due to the formation of compoundsubstrate intermediate during the catalytic hydrolytic reaction of 4-NPP to 4-nitrophenolate ion.

**Table 5** First-order rate constants for the hydrolysis of various phosphate esters by previously

 reported heteronuclear Schiff base compounds.

Catalyst	Substrate	Solvent	$k_{\rm cat}({\rm sec}^{-1})$	Ref
[Zn <sup>II</sup> Fe <sup>III</sup> (tdmbpo)(O <sub>2</sub> AsMe <sub>2</sub> )(MeHO)](ClO <sub>4</sub> ) <sub>3</sub> · 4 MeOH·2H <sub>2</sub> O	HPNP	EtOH/ H <sub>2</sub> O	1.10×10 <sup>-3</sup>	45
[Zn <sup>II</sup> Fe <sup>III</sup> (bdmbbppo)(O <sub>2</sub> AsMe <sub>2</sub> )(MeHO)](ClO <sub>4</sub> ) <sub>3</sub> · 1.5 MeOH	HPNP	EtOH /H <sub>2</sub> O	8.33×10 <sup>-4</sup>	45
[FeMn(ICIMP)(OAc) <sub>2</sub> Cl]	BDNPP	MeCN/ H <sub>2</sub> O	-	46
$\{[(CuL)Mn(N(CN)2)_2] \cdot CH_3CN\}_{\infty}$	PNPP	DMF/ H <sub>2</sub> O	25.052	Our work

HPNP= 2-hydroxypropyl(4-nitrophenyl)phosphate, BDNPP= bis(2,4-dinitrophenyl)phosphate, PNPP= 4-nitrophenyl-phosphate.

**Mechanistic insight.** A very few heterometallic compounds have been explored earlier for phosphatase like activity. Till now only two heterometallic compounds Zn(II)-Fe(III), Fe(III)-Mn(II) have been reported.<sup>45,46</sup> Here we have synthesised two heterometallic compounds Cu(II)-Mn(II) (1) and Ni(II)-Mn(II) (2), among them only 1 shows catalytic activity whereas 2 is inactive towards phosphatase like activity. In first step of the mechanistic pathway one labile ligand (N(CN)<sub>2</sub>) gets dissociated from the Mn(III) center and simultaneously it is coordinated

one 4-NPP and in the same time nucleophile (H<sub>2</sub>O), comes from 97.5% DMF-H<sub>2</sub>O mixture<sup>62,65</sup> (Scheme 3). Then proton is abstracted form water molecule by phosphate ion to form hydroxide anion. Then attack of hydroxide anion to phosphorus center takes place which is believed to be the rate determining step. ESI-MS study helps us to identify the intermediate species where formation of 1:1 adduct between compound 1 and 4-NPP has been identified [m/z = 900.4091 amu (calcd. m/z = 900.0507 amu). Then 4-nitrophenolate ion is liberated which is monitored by UV-Vis spectroscopy. In the next step, phosphoric acid is eliminated from the catalyst leaving the dinuclear [Cu(L)Mn(dca)<sub>3</sub>(CH<sub>3</sub>OH)] species. After then this species coordinates to 4-NPP and enters into the next cycle.



Scheme 3. Proposed mechanism for catalytic cycle of compound 1 in 97.5% DMF-H<sub>2</sub>O.

## Conclusions

In this present work, we synthesized two heterometallic Schiff base compounds  $\{[(CuL)Mn(N(CN)_2)_2] \cdot CH_3CN\}_{m}$  (1) and  $[(NiL)_4Mn_2(N(CN)_2)_2] \cdot (ClO_4)_2$  (2) using H<sub>2</sub>L ligand and a dicvanamido spacer. Solid state structure of compounds 1 and 2 are one dimensional polymer of Cu(II)-Mn(II) and hexanuclear of Ni(II)-Mn(II) respectively. Magnetic studies of 1 reveal the presence of intra chain ferrimagnetic coupling between Cu(II) and Mn(II) spins and antiferromagnetic interaction was observed for 2. Only compound 1 exhibits catalytic activity towards the oxidation of o-aminophenol as well as hydrolysis of the phosphate-ester bond with very high  $k_{cat}$  value compare to the other reported heterometallic Schiff base compounds. The values reflect the facility of the heterometallic catalyst in terms of both efficiency and catalytic promiscuity for both the catalytic conversion reaction. EPR spectral analysis suggests that in solution state the oxidation state of Mn(II) of 1 changes to Mn(III) and dissociation takes place which facilitated to bind with substrate (o-aminophenol as well as 4-PNPP). O-aminophenol coordinates to the Mn(III) center and simultaneously organic imine radical that transports an electron from substrate to oxygen with the formation of H<sub>2</sub>O<sub>2</sub> during the catalytic cycle of phenoxazinone synthase like activity. The phosphatase activity of any model substrate depends on the presence of nucleophile attached to the metal center of the catalyst. In case of 1 the source of nucleophile is likely to be solvent (97.5 % DMF-H<sub>2</sub>O mixture) used for hydrolysis reaction. Probable mechanistic pathways are proposed on the basis of ESI-mass, cyclic voltammetry and EPR analyses. Formation of intermediate species has been identified with the help of mass spectral analysis. But compound 2 is managed to retain its geometry in solution state which causes its inability to form a compound-substrate intermediate during the catalytic reaction.

## **Supporting information**

PXRD pattern, FT-IR spectra, UV-Vis spectra, ESI-MS Spectra, EPR spectra,  $1/\chi_M$  vs. T plot, Kinetics plot of the rate vs. substrate concentration, Table of Coordination bond lengths (Å) and angles (°), Summary of SHAPE analysis present in the Supporting Information.

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## Notes

The authors declare no competing financial interest.

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## For Table of Contents Use Only

# Synthesis of Structurally Diverse Ferrimagnetically and Antiferromagnetically Coupled M<sup>II</sup>-Mn<sup>II</sup> (M=Cu, Ni) Heterometallic Schiff base Compounds with Dicyanamide Spacer and Study of Biomimetic Catalytic Activity

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Two heterometallic Schiff base compounds  $Cu^{II}-Mn^{II}$  (1) and  $Ni^{II}-Mn^{II}$  (2) have been synthesized. Between these, 1 having one dimensional zig-zag polymeric arrangement, revealed strong ferrimagnetic coupling at low temperature in solid phase whereas in solution state high phenoxazinone and phosphatase like activities were observed.