

# Article

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Variations of Structures and Phenoxazinone Synthase-like Activity of the Complexes Based on (Cu<sup>II</sup>)<sub>2</sub>Mn<sup>II</sup> Node and Dicyanamide Spacer

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### Abstract

Three new heterometallic Cu(II)-Mn(II) complexes,  $[{(CuL)_2Mn}_2(\mu_{1.5}-N(CN)_2)]$  $(CH_3CN)_2[(ClO_4)_3(1), [{(CuL)_2Mn}_2(\mu_1-N(CN)_2)] \cdot (H_2O)_4(2) \text{ and } [{(CuL)_2Mn}_2(\mu_{1.5}-N(CN)_2)]_n$ (3) have been synthesized using Cu(II)-metalloligand of an asymmetrically dicondensed Schiff ligand (where  $H_2L = N \cdot \alpha$ -methylsalicylidene-N'-salicylidene-1,3-propanediamine). base Complex 1 was formed when the ratio of [CuL] : Mn(ClO<sub>4</sub>)<sub>2</sub> : NaN(CN)<sub>2</sub> was 2:1:1 whereas complexes 2 and 3 were obtained with a 2: 1: 2 ratio of the same reactants on varying the reaction conditions. Single-crystal structural analyses reveal that complex 1 possesses a hexanuclear structure in which two  $(Cu^{II})_2 Mn^{II}$  units are connected by one  $\mu_{1.5}$ -N(CN)<sub>2</sub> bridge, 2 is a discrete trinuclear species with two terminally coordinated  $N(CN)_2^{-1}$  ions to the Mn(II) whereas complex 3 is a polymeric form of 2 with  $\mu_{1.5}$ -N(CN)<sub>2</sub><sup>-</sup> bridges between Cu(II) and Mn(II) centers. The thermal variations of dc magnetic susceptibilities suggest that all three complexes (1-3) are antiferromagnetically coupled with comparable exchange coupling constants (-25.4, -22.8 and -22.0 cm<sup>-1</sup>, respectively) which are expected from the Cu-O-Mn angles. All the complexes show biomemitic phenoxazinone synthase-like activity for the aerial oxidation of *o*-aminophenol to amino phenoxazinone. The turnover numbers (k<sub>cat</sub>) for the process are 4966, 2021 and 1107  $h^{-1}$  for complexes 1-3 respectively. The mass spectral evidence on intermediates suggests that the cooperative activity of the two different metal ions i.e. coordination of substrate to Mn(II) and shuttling of oxidation state of Cu between I and II is

possibly operative in the oxidation process. The highest catalytic activity of **1** is attributed to the presence of one coordinating solvent molecule to Mn(II).

# Introduction

Heterometallic polynuclear complexes of N, O donor ligands are of growing interest to the chemists mainly due to their potential applications in catalysis and in molecular magnetism.<sup>1-5</sup> The presence of different metal ions in one cluster may drastically improve catalytic activity as a result of multimetallic cooperative activities whereas the presence of unlike spin in one cluster can induce ingenious magnetic properties such as ferrimagnetism, SMM etc.<sup>6-11</sup> Various types of N, O donor ligands have been used for the synthesis of polynuclear heterometallic complexes of 3d-3d' and 3d-4f metal ions.<sup>12-17</sup> Among them, symmetrically dicondensed Schiff base ligands are arguably the most common ones, but their asymmetrically dicondensed analogues have been used only rarely. One of the common strategies for the synthesis small heterometallic clusters is to react the Cu(II) or Ni(II) chelate of the Schiff base with the salts of another 3d or 4f metal ions. The anionic part of such metal salts not only balance the charge of the resulting complex but can also coordinate to the metal ions in various ways to modulate the structures as well as the magnetic and catalytic properties of the clusters radically.<sup>18-22</sup> The anions such as N<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>, N(CN)<sub>2</sub><sup>-</sup>, RCO<sub>2</sub><sup>-</sup> etc. which have various possible coordination modes have been used to synthesize complexes with diverse structures. Among them, dicyanamide  $(N(CN)_2)$  deserves special mention as the long, bent shaped, flexible anion containing three donor N-atoms can produce complexes of varied nuclearity, shape and isomeric form.<sup>23-26</sup> Recently, we were able to isolate rather rare supramolecular isomers in the solid state with some heterometallic Cu(II)-Cd(II), Cu(II)-Co(II) and Ni(II)-Co(II) nodes of symmetrical salen type N<sub>2</sub>O<sub>2</sub> donor Schiff base ligands and N(CN)<sub>2</sub><sup>-</sup> spacers; of which isomeric Ni(II)-Co(II) species showed intriguing differences in magnetic properties.<sup>27–31</sup>

One of the most important applications of the polynuclear complexes is in the field of biomimetic catalytic model enzyme systems. A large number of homometallic complexes of some redox active metals like Cu(II), Mn(II/III), Co(II/III), Fe(II/III), Ni(II) etc. have been extensively used for catalytic oxidase type reactions e.g. catechol oxidase, phenoxazinone synthase, cytochrome *c* oxidase etc.<sup>32–37</sup> It has been shown that in those processes the activity

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and efficiency of these homometallic complexes as catalysts depend largely on the participation of metal ions into the oxidation-reduction reaction. The participation of metal ions in the oxidation process depends very subtly on the coordination number and nature of the ligands in its coordination sphere.<sup>38–42</sup> These catalytic processes have been investigated extensively by various groups but till now the catalysts that have been used in these processes are confined mostly to homometallic complexes. Recently, we have shown that the heterometallic complexes of Schiff base ligands can also show this type of biomimetic catalytic oxidase reactions.<sup>43</sup> The advantage of heterometallic complexes as catalyst lies in the fact that the cooperative effect of the metal ions in terms of coordination to the substrate and redox behavior can potentially enhance the catalytic activity.<sup>44–50</sup> In fact, recently we synthesized a heterometallic Cu<sub>2</sub><sup>II</sup>-Mn<sup>II</sup> complex of an unsymmetric Schiff base and found that it is not only catalytically activity for such oxidase reactions but its activity is the highest among all the model complexes synthesized so far.<sup>43</sup> Most of the reported synthetic functional model complexes are Cu(II) based as the naturally occurring metalloenzymes for oxidase process e. g. catechol oxidase, phenoxazinone synthase etc. contains Cu(II). The presence of redox active Mn(II) ion along with Cu(II) in a complex is expected to modify the redox behavior of the complex as a whole. Moreover, the intrinsically different coordination behavior of the metal ions can facilitate the coordination of substrate to the complex in favorable conditions.<sup>44–50</sup>

Herein, we report the synthesis and crystal structures of three heterometallic Cu(II)-Mn(II) complexes  $[{(CuL)_2Mn}_2(\mu_{1,5}-N(CN)_2)(CH_3CN)_2](ClO_4)_3$  (1),  $[{(CuL)_2Mn}_2(\mu_{1-N(CN)_2})] \cdot (H_2O)_4$  (2) and  $[{(CuL)_2Mn}_2(\mu_{1,5}-N(CN)_2)]_n$  (3) using the Cu(II) metalloligand of a unsymmetrical Schiff base ligand H<sub>2</sub>L (where H<sub>2</sub>L= *N*- $\alpha$ -methylsalicylidene-*N'*-salicylidene-1,3propanediamine). Complex 1 possesses a hexanuclear structure in which one dicyanamide ion is present per two trinuclear units whereas 2 is a discrete trinuclear species with two dicyanamide ions per trinuclear unit. The molecular formula of 3 is same as that of 2 but here the trinuclear units are connected by the  $\mu_{1,5}$ -N(CN)<sub>2</sub> ion to form a 2D polymer. Thus 2 and 3 are coordination polymerization isomers: 2 is the monomeric form of polymer 3. All three complexes exhibit model biomimetic phenoxazinone synthase like activity under aerial conditions, but their catalytic efficiencies are distinctly different. UV-Vis spectra, ESI-mass spectra analysis and cyclic voltammograms studies have been performed to determine the possible intermediates of this catalytic reaction and consequently to develop a probable mechanism. The dc magnetic susceptibility has also been measured for all these complexes.

#### **Experimental Section**

**Starting materials:** Salicylaldehyde, *o*-hydroxoacetophenone and 1,3-propanediamine were purchased from Spectrochem, India and were of reagent grade. They were used without further purification. The other metal salts and solvents were of commercially available reagent grade quality, unless otherwise stated.

*Caution!* Although not encountered during experiment, perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

Synthesis of the unsymmetrical Schiff-base ligand N- $\alpha$ -methylsalicylidene-N'-salicylidene-1,3-propanediamine (H<sub>2</sub>L) and metalloligand (CuL). The unsymmetrically di-condensed Schiff base ligand [H<sub>2</sub>L] and the metalloligand [CuL] were synthesized in our laboratory by following the methods reported earlier.<sup>43</sup>

Synthesis of the complex [{(CuL)<sub>2</sub>Mn}<sub>2</sub>( $\mu_{1,5}$ -N(CN)<sub>2</sub>)(CH<sub>3</sub>CN)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (1). Metalloligand [CuL] (0.716 g, 2 mmol) was dissolved in 20 mL acetonitrile and Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.361 g, 1 mmol) was added to the solution. The solution was stirred for 15 mins and then 4 mL 1:1 (v/v) H<sub>2</sub>O-MeCN solution of NaN(CN)<sub>2</sub> (0.089 g, 1 mmol was added drop wise to the solution at room temperature. The mixture was stirred for 20 min. A small amount of precipitate appeared during this process, which was filtered off and the filtrate was kept in a beaker inside a desiccator. The deep brown X-ray diffractable quality single crystals appeared in 3-4 days, which were collected by filtration and air dried.

**Complex 1:** Yield 0.786g (76%). Anal. Calc. for  $C_{82}H_{82}C_{13}Cu_4Mn_2N_{15}O_{20}$  (2068.06): Calculated C, 47.62; H, 4.00; N, 10.16; Found C, 47.54; H, 4.16; N, 10.01. IR:  $v_{(C=N)} = 1630$ , 1599 cm<sup>-1</sup>;  $v_{(C=O)} = 1089$  cm<sup>-1</sup> and  $v_{(N=C=N)} = 2182$ , 2242 and 2322 cm<sup>-1</sup>.

Synthesis of the complex  $[{(CuL)_2Mn}_2(\mu_1-N(CN)_2)] \cdot (H_2O)_4$  (2). The complex was synthesized following a similar procedure as for the synthesis of 1. Only difference is that here the Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O:NaN(CN)<sub>2</sub> ratio is changed to 1:2 and methanol was used as solvent

instead of acetonitrile. The brown colored X-ray quality single crystals appeared in 2-3 days, which were separated by filtration and air dried.

**Complex 2:** Yield 0.706 (73%). Anal. Calc. for  $C_{40}H_{36}Cu_2MnN_{10}O_8$  (966.83): Calculated C, 49.69; H, 3.75; N, 14.49; Found C, 49.85; H, 3.81; N, 14.46. IR:  $v_{(C=N)} = 1628$  and 1600 cm<sup>-1</sup>;  $v_{(N=C=N)} = 2152$ , 2216 and 2265 cm<sup>-1</sup>.

Synthesis of the complex  $[{(CuL)_2Mn}_2(\mu_{1,5}-N(CN)_2)]_n$  (3). This complex was synthesized by following a similar procedure as for the synthesis of 2. Only difference is that here the solution mixture was refluxed for 1 hour and then cooled at room temperature. The cooled solution is filtered and kept in a desiccator. The deep green X-ray quality single crystals appeared at the bottom of the beaker after 4-5 days, which were collected by filtration and air dried.

**Complex 3:** Yield 0.641g (71%). Anal. Calc. for  $C_{40}H_{36}Cu_2MnN_{10}O_4$  (902.83): Calculated C, 53.21; H, 4.02; N, 15.51; Found C, 53.32; H, 4.14; N, 15.59. IR:  $v_{(C=N)} = 1628$  and 1600 cm<sup>-1</sup>;  $v_{(N=C=N)} = 2152$ , 2216 and 2265 cm<sup>-1</sup>.

# **Physical Measurements**

Elemental analyses (C, H and N) were performed using a Perkin–Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets (4000–500 cm<sup>-1</sup>) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. The electronic absorption spectra (1000–240 nm) in acetonitrile solution were collected in a Hitachi U-3501 spectrophotometer. Temperature-dependent molar susceptibility for powdered crystalline sample of compounds **1–3** were measured using a superconducting quantum interference device vibrating sample magnetometer (SQUID-VSM, Quantum Design) with an applied field 500 Oe throughout the temperature range 2–300 K. The susceptibility data were corrected by Pascal's diamagnetic contributions. Isothermal magnetization measurements were performed at 2K up to 5 Tesla magnetic fields.

#### **Electrochemical measurements**

The electrochemical measurements of all three complexes (1, 2 and 3) were performed using Epsilon Basi-C3 Cell instrument at a scan rate of 50–200 mV s<sup>-1</sup> within the potential range of 0

to -1.80 V vs. Ag/AgCl. Cyclic voltammograms were carried out using 0.1 M tetrabutylamonium perchlorate (TBAP) as supporting electrolyte and  $1.0 \times 10^{-3}$  M of complexes in acetonotrile solution which are deoxygenated by bubbling with argon. The working electrode was a glassy carbon disk (0.32 cm<sup>2</sup>) which was polished with alumina solution, washed with absolute acetone and acetonotrile, and air dried before each electrochemical run. The reference electrode was Ag/AgCl, with platinum as counter electrode. All experiments were performed in standard electrochemical cells at 25°C.

#### ESI-HRMS

Electro spray ionization mass spectrometry (ESI-MS positive) ion mass spectra were acquired using a Xevo G2-S QTof (Waters) mass spectrometer, equipped with a Z-spray interface, over a mass range of 100–1200 Da, in a continuum mode. Aqueous sodium formate was used for Q-oa-Tof calibration. L-Leucine was used as the external mass calibrant lock mass  $[M+H]^+ = 556.2771$  Da. Solutions of compounds were injected at flow rate of 5µl/min. All solutions were made in mass-spectrometric grade methanol. The concentrations of complexes 1, 2 and 3 as well as complexes + substrates in solutions were the same (10<sup>-6</sup> M) during acquisitions of mass spectra.

### X-ray Crystallographic data collection and refinement

The crystal structure data for 1, 2 and 3 were collected with MoK $\alpha$  at 150K using the Oxford Diffraction X-Calibur CCD System. The crystals were positioned at 50 mm from the CCD and 321 frames were measured with counting times of 10s. Data analysis was carried out with the CrysAlis program.<sup>51</sup> The structures were solved using direct methods with the Shelxs97 program.<sup>52,53</sup> The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Absorption corrections were carried out using the ABSPACK program.<sup>54</sup> In the structure of 1, one perchlorate was disordered over a centre of symmetry and the bridging -NCNCN was disordered around a centre of symmetry. In 2, the terminal -NCNCN was disordered and there were two water molecules both refined with 25% occupancy. The structures were refined using Shelx116-

6.<sup>53</sup> The crystallographic data of complexes **1–3** are given in Table 1. Bond distances (Å) and angles (°) parameters around the metal centers of complexes **1–3** are given in Table S1.

### Phenoxazinone synthase of OAP

The Phenoxazinone synthase activity of complex 1-3 was studied using *o*-aminophenol (OAP) as the substrate in acetonotrile solution under aerobic conditions at room temperature. The reactions were followed spectrophotometrically by monitoring the increase in the absorbance maxima of the amino phenoxazinone (APX) band at 425 nm as a function of time (time scan).

 Table 1. Crystal data and structure refinement of complexes 1, 2 & 3.

	1	2	3
Formula	$C_{78}H_{76}Cu_4Mn_2N_{13}O_8, \ 3(ClO_4), 2(C_2H_3N)$	C <sub>40</sub> H <sub>36</sub> Cu <sub>2</sub> MnN <sub>10</sub> O <sub>4</sub> ,H <sub>2</sub> O	$C_{40}H_{36}Cu_2MnN_{10}O_4$
Mol. Wt.	2068.02	920.82	902.81
Crystal System	Triclinic	Monoclinic	Monoclinic
Space Group	P-1	C2/c	C2/c
a/Å	11.1797(10)	25.517(7)	16.354(1)
b/Å	13.4481(11)	10.095(2)	10.4444(6)
c/Å	15.7107(12)	16.111(4)	24.6627(18)
<i>α</i> /°	68.133(7)	90	90
<i>β</i> /°	80.785(7)	100.15(3)	112.921(8)
γl°	77.469(7)	90	90
$V/\text{\AA}^3$	2131.7(3)	4085.0(17)	3880.0(5)
Z	1	4	4
$D_c/g \text{ cm}^{-3}$	1.611	1.497	1.546
$\mu/\text{mm}^{-1}$	1.442	1.393	1.463
F (000)	1056	1884	1844
R(int)	0.051	0.116	0.051
Total Reflections	14971	8489	8850
Unique reflections	11865	4518	4386
I>2 <i>o</i> (I)	6940	2180	3058
$R_1^a, w R_2^b$	0.0920, 0.2396	0.0719, 0.1984	0.1062, 0.2827
$\operatorname{GOF}^c$ on $\operatorname{F}^2$	1.008	0.926	1.082
R (all)	0.1520	0.1430	0.1295
Temp (K)	150	150	150

	Residual electron Density, e/Å <sup>-3</sup>	-0.918, 1.891	-0.616, 0.776	-1.065, 4.353		
${}^{7}R_{1} = \overline{\Sigma}   F_{o}  -  F_{c}   / \Sigma  F_{o} , \ {}^{b}wR_{2} (F_{o}^{2}) = [\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w F_{o}^{4}]^{\frac{1}{2}} \text{ and } {}^{c}GOF = [\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{params})]^{\frac{1}{2}}$						

# **Results and Discussion:**

#### Syntheses of the complexes

The unsymmetrical ligand,  $N-\alpha$ -methylsalicylidene-N'-salicylidene-1,3-propanediamine (H<sub>2</sub>L) and its Cu(II)-metalloligand, [CuL] were synthesized by the methods as reported earlier by us.43 The metalloligand [CuL] on reaction with Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in presence of NaN(CN)<sub>2</sub> in 2:1:1 molar ratio yielded complex [ $\{(CuL)_2Mn\}_2(\mu_{1.5}-N(CN)_2)(CH_3CN)_2$ ](ClO<sub>4</sub>)<sub>3</sub> (1) from acetonitrile solution. Complex  $[{(CuL)_2Mn}_2(\mu_1-N(CN)_2)] \cdot (H_2O)_4$  (2) was obtained by reacting the same reactants in 2:1:2 molar ratio in methanol and keeping the resulting solution at room temperature. However, when this reaction mixture was put under reflux for about 1h and the solution was left at room temperature, a different complex  $[{(CuL)_2Mn}_2(\mu_{1,5}-N(CN)_2)]_n$  (3) was produced exclucively (Scheme 1). Complex 2 is a trinuclear (CuL)<sub>2</sub>Mn species in which two terminal dicyanamide ions are coordinated to Mn(II). When the solution is refluxed, the N-atom in the other end of dicyanamide ion coordinates to the axial position of the Cu(II) atom of the neighboring trinuclear unit to yield the 2D polymer, 3. Thus 3 is the polymerized isomer of momomer 2. 3 can also be prepared by dissolving 2 in methanol and then putting the solution under reflux for 1h. The similarities of the measured powdered diffractograms of complexes 1-3with their respective simulated (from mercury 3.8) diffractograms (Figure S3–S5, ESI) show the phase purity of the complexes.

### IR spectra of complexes 1, 2 and 3.

The IR spectra of each of the complexes show two strong peaks at 1630 and 1599 cm<sup>-1</sup> for **1** (Figure S1, ESI), 1628 and 1600 cm<sup>-1</sup> for both **2** and **3** (Figure S2, ESI) due to two types of azomethine v(C=N) stretchings of the unymmetrical Schiff base.<sup>43</sup> In addition, the spectrum of complex **1** shows strong and sharp peaks at 2182, 2242, 2322 cm<sup>-1</sup> for the stretching vibrations of N(CN)<sup>-</sup> ion and at 1089 cm<sup>-1</sup> for the stretching vibrations of ClO<sub>4</sub><sup>-</sup> ion, which indicate the presence of two different anions in **1**. Compounds **2** and **3** also show similar type of strong and sharp peaks at 2152, 2216 and 2265 cm<sup>-1</sup> for  $v(N(CN)^{-})$  stretching vibrations.<sup>27-31</sup>



Scheme 1. Syntheses of complexes 1–3.

# **Description of Structures:**

The structure of 1 contains  $[Mn_2Cu_4L_4(NCNCN)(NCMe)_2]^{3+}$  dimeric cations shown in Figure 1 together with discrete perchlorate anions and a solvent NCMe, the latter refined with 50% occupancy. Of the two independent perchlorate anions, one is ordered while the other is disordered with the chlorine atom on a centre of symmetry. The overall dimensions in the three metal coordination spheres are shown in Table S1.

The trinuclear unit is formed by the chelation of the two [CuL] metalloligands to the Mn centre through the O-atoms. The two independent copper atoms are both four co-ordinate with square planar environments, each being bonded to four donor atoms of the tetradentate ligand  $L^{2^-}$ . The four atoms in the equatorial plane show r.m.s. deviations of 0.112, 0.203 Å. The two metal atoms are 0.227(4), 0.221(4) Å from the planes and the two planes intersect at 29.8(2)°. The manganese atom is six-coordinate with a distorted octahedral environment being bonded to four oxygen atoms which are bridging to copper atoms and in addition to two nitrogen atoms, N(81) from an acetonitrile and N(1) from a -NCNCN- ligand which bridges in a disordered manner around a centre of symmetry to another manganese atom. The two oxygen atoms O(31) and O(61) which are *trans* to nitrogen atoms, namely N(1) and N(81), form longer bonds to the metal atom than O(11) and O(31) which are mutually trans. Of these two long bonds, Mn(1)-O(61), trans to N(81) is longer at 2.285(4)Å than Mn(1)-O(31), trans to N(1) at 2.227(4)Å.



**Figure 1**. The structure of **1**,  $[Mn_2Cu_4L_4(NCNCN)(NCMe)_2]^{3+}$  with ellipsoids at 50% probability. Anions and solvent molecules are not shown. The -NCNCN- bridge is disordered, only one set of positions is shown.

The structure of **2**,  $MnCu_2L_2$  (NCNCN)<sub>2</sub> is shown in Figure 2 together with the atomic numbering scheme. The structure contains two-fold symmetry with the Mn(2) atom on the axis. This complex has a similar structure to many previous structures of this type.<sup>27–31</sup> The two Cu(1) atoms are four-coordinate with square planar environments while the Mn(2) atom is six-coordinate with a highly distorted octahedral environment. Cu(1) is bonded to the tetradentate ligand through O(11) at 1.904(4), N(19) at 1.994(5), N(23) at 1.939(5) and O(31) at 1.921(4)Å. The Mn(2) atom, positioned on the 2-fold axis is bonded to O(11) at 2.133(4), O(31) at 2.298(4) and N(1) at 2.144(6)Å. The disparity in the Mn-O bond lengths is due to the fact that O(31) is trans to the NCNCN ligand with an angle of 169.3(2)° while the two O(11) atoms are mutually trans, though with an angle subtended at the metal of 142.3(2)°. An interesting feature of this particular structure is that the NCNCN ligand is monodentate and terminal with N(1) bonded to the metal. The two atoms C(4) and N(5) are disordered over two sites and the latter forms weak contacts with the disordered solvent water molecules which are refined with 25% occupancy.



Figure 2. The structure of 2 with ellipsoids at 30% probability.

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The structure of **3** (Figure S6, ESI) also shows two-fold symmetry and is similar to that found in **2** as shown in Figure 2 except for the fact that the two NCNCN ligands bridge to two copper atoms in different dimers to form a 2-D polymer as shown in Figure 3.

The coordination sphere of the copper atom is a square pyramid with N(5) as the axial atom forming a Cu-N bond of 2.326(7)Å. Remaining bond lengths to copper are similar to those found in **2**, namely O11 at 1.937(4), O(31) at 1.949(6), N(19) at 2.013(9) and N(23) at 1.999(8)Å. The four atoms in the equatorial plane show an r.m.s. deviation of 0.166Å with a slight tetrahedral distortion. The metal atom is 0.178(3)Å from this plane in the direction of N(5). The coordination sphere around Mn(2) is similar to that found in **2** with unique distances to O(11) 2.127(5), O(31) 2.229(5) and N(1) 2.170(7)Å.



Figure 3. The 2D structure of 3. Hydrogen atoms are omitted for clarity.

It is worth mentioning here that we have synthesized previously a few compounds using trinuclear heterometallic nodes derived from symmetrical di-Schiff base ligand  $H_2L^1$  or  $H_2L^2$ (where  $H_2L^1 = N,N'$ -bis(salicylidene)-1,3-propanediamine and  $H_2L^2 = N,N'$ -bis( $\alpha$ methylsalicylidene)-1,3-propanediamine) and dicyanamide spacer. It is interesting to note that all these complexes of  $H_2L^2$  are discrete trinuclear with terminally coordinated dicyamanide ion. On the contrary, in all such complexes of  $H_2L^1$  dicyanamide ion is invariably bridging. Moreover, the different bridging mode ( $\mu_{1,5}$  and  $\mu_{1,3,5}$ ) and conformational flexibility of the dicyanamide ion resulted in supramolecular isomerism in the complexes ranging from 0D-to-1D-to-2D<sup>27-31</sup> and 2D-to-3D.<sup>30</sup> In the present paper, the asymmetric Schiff base ligand which is prepared by condensation of the salicylaldehyde with the -NH<sub>2</sub> group at one end of 1,3-propanediamine and of the o-hydroxyacetophenone with its -NH<sub>2</sub> group at the other end yielded complex 2 in which dicyanamide is terminally coordinated like the complexes of  $H_2L^2$  and complex 3 where dicyanamide is  $\mu_{1,5}$ -bridging like the complexes of  $H_2L^1$ . Thus, unlike its symmetrical analogues, the asymmetrically condensed di-Schiff base enables the isolation of both trinuclear monomer (2) with terminal dicyanamide and its polymer (3) with  $\mu_1$  5-bridging dicyanamide by changing the reaction conditions. It is also to be noted that complex 1 of the present paper is an unprecedented single dicyanamide bridged heterometallic hexanuclear compound. There is only one similar complex<sup>28</sup> but that one is more common double dicyanamide bridged. The single dicvanamide bridge allows the solvent acetonitrile to coordinate to the Mn(II) to complete its hexa-coordination, which makes it catalytically much more active than the other two.

# **Magnetic Properties**

The thermal variations of the molar magnetic susceptibility product with temperature  $(\chi_M T)$  of complexes **1–3** are depicted in Figure 4. The room temperature  $\chi_M T$  values are 4.61, 4.60 and 4.27 cm<sup>3</sup> K mol<sup>-1</sup> for complexes **1–3** respectively, which are lower than the value of magnetically non-interacting Cu<sub>2</sub>Mn system of 5.1 cm<sup>3</sup> K mol<sup>-1</sup> for  $g_{Mn} = g_{Cu} = 2$  at 300 K.<sup>43,55–57</sup> In all the complexes, the behavior is very similar; a progressive decrease of  $\chi_M T$  value takes place upon cooling and reaches to a plateau of *ca*. 2.10, 2.03 and 1.92 cm<sup>3</sup> K mol<sup>-1</sup> for **1–3**, respectively at the temperature range of *ca*. 8–28 K. On further cooling at very low temperature (below *ca*. 5 K), the  $\chi_M T$  value further decreases to reach a value of 1.93, 1.61 and 1.74 cm<sup>3</sup> K

mol<sup>-1</sup> for complexes 1–3, respectively at 2 K. The progressive declining nature of  $\chi_M T$  value with decrease in temperature indicates the presence of strong intramolecular antiferromagnetic interactions. The saturated molar magnetizations values (M/N $\beta$ ) at 2K are 3.30, 2.80 and 3.17  $\mu_{\rm B}$ for complexes 1-3 respectively (Figure S7-S9, ESI), which represent the non-zero spin ground states with  $S_{\rm T} = |S_{\rm Mn} - 2S_{\rm Cu}| = 3/2$ . This behavior also suggests the presence of dominant antiferromagnetic coupling between Cu(II) and Mn(II) in the complexes. In the trinuclear Cu<sup>II</sup>-Mn<sup>II</sup>-Cu<sup>II</sup> structure of the complexes 1–3, two terminal Cu atoms are connected to the central Mn atoms through either very similar (in 1) or identical (in 2 and 3) double phenoxido bridge and the two terminal Cu(II) ions are not connected *via* any bridge. Therefore, to calculate the magnetic interaction parameters, we have assumed a simple symmetrical linear trimeric model, where a central Mn(II) ion (S = 5/2) and two terminal Cu(II) ions (S = 1/2) interact through the same exchange coupling (J, Figure 5 left) and used a Hamiltonian  $H = -J[S_1S_2 + S_1S_3]$ , where  $S_1 =$  $S_{Mn}$  and  $S_2 = S_3 = S_{Cu}$ . The exchange coupling between the two terminal  $Cu^{II}$  ions can be taken as zero ( $J_{Cu-Cu} = 0 \text{ cm}^{-1}$ ) because of the large Cu....Cu distances. Simulations were carried out using the equation (I).<sup>55</sup> The best fitting data lead to the following parameters:  $J_{Mn-Cu} = -25.4 \pm 0.1$ cm<sup>-1</sup>,  $g_{Mn-Cu} = 2.13 \pm 0.10$ ,  $\theta = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1;  $J_{Mn-Cu} = -0.183 \pm 0.024$  (K), R =  $1.16 \times 10^{-6}$  for compound 1; J\_{Mn-Cu} = -0.183 \pm 0.024 (K), R =  $1.16 \times 10^{-6}$  for compound 1; J\_{Mn-Cu} = -0.183 \pm 0.024 (K), R =  $1.16 \times 10^{-6}$  (K), R = 1.122.8±0.2 cm<sup>-1</sup>,  $g_{Mn-Cu} = 2.10\pm0.12$ ,  $\theta = -0.491\pm0.028$  (K), R =  $1.43\times10^{-6}$  for compound **2**;  $J_{Mn-Cu}$  $= -22.0 \pm 0.1 \text{ cm}^{-1}$ ,  $g_{Mn-Cu} = 2.02 \pm 0.08$ ,  $\theta = -0.105 \pm 0.010$  (K), R =  $8.87 \times 10^{-6}$  for compound **3**.

$$\chi_{\rm m} = \frac{Ng^2\beta^2}{4k(T-\theta)} \times \left[\frac{10+35\,e^{5J/2kT}+35\,e^{7J/2kT}+84\,e^{6J/kT}}{2+3\,e^{5J/2kT}+3\,e^{7J/2kT}+4\,e^{6J/kT}}\right] \tag{I}$$



**Figure 4.** Thermal variations of the  $\chi_M T$  products for complexes 1–3 (left to right respectively). Solid red line represents the best fitting to the appropriate model for 1, solid blue line represents the best fitting to the appropriate model for 2 and solid pink line represents the best fitting to the appropriate model for 3.

The magneto-structural correlations of double phenoxido-bridged Mn<sup>II</sup>-Cu<sup>II</sup> reveal that the sign and magnitude of magnetic exchange coupling (J) depend mostly upon the Cu–O and Mn–O bond distances, the Cu–O–Mn bond angles and the dihedral angle in the central CuO<sub>2</sub>Mn unit. <sup>43,55–57</sup> Till date, eleven double phenoxido-bridged Cu<sup>II</sup>-Mn<sup>II</sup>-Cu<sup>II</sup> trinuclear complexes have been characterized both structurally and magnetically. Correlating the structural parameters with the J values of these complexes, it appears that the strength of the antiferromagnetic exchange increases with increasing Mn–O bond distance (Figure S10, ESI), with decreasing Cu–O bond distance (Figure S11, ESI) and with increasing Cu-O-Mn bridging angle (Figure S5 right). However, the figures (Figure S10-S11, ESI) show that although the general trends for the changes of J values with Mn–O or Cu–O bond distance are discernible, the values are highly scattered. On the other hand, barring only few points, the correlation of J with Cu–O–Mn bridging angle is quite obvious and the J values of the present complexes (1-3) having average Cu–O–Mn bridging angles of 99.16°, 99.11° and 99.61° respectively, fit well in this correlation diagram (Figure 5 right).



**Figure 5**. Basic trinuclear unit of complexes 1-3 (left). Variation of the magnetic exchange coupling (*J*) in trinuclear Cu<sup>II</sup>-Mn<sup>II</sup>-Cu<sup>II</sup> double phenoxido-bridged complexes with Cu–O–Mn angle (right).

#### Electrochemistry

The cyclic voltammograms (CV) of complexes **1–3** in acetonitrile (Figure S12 in ESI) show two waves on cathodic scan (0 to -1.8 V) for the quasi-reversible reduction process at the electrode surface. The peaks are observed at  $E_c = -0.88$  and -0.99 V for **1**;  $E_c = -0.93$  and -1.07 V for **2**;  $E_c = -0.89$  and -1.02 V for **3** on forward cathodic scan with respect to an Ag/AgCl electrode at a scan rate of 50 mV/Sec. Whereas, on reverse scan the corresponding peaks are observed at  $E_a = -0.67$ , -0.74 and -0.73 V for complexes **1–3** respectively. The peak separation values ( $\Delta E_{pc} = E_{cathodic} - E_{anodic}$ )<sup>58</sup> are -0.32, -0.33 and -0.29 V for complexes **1–3** respectively. These two peaks on forward scan indicate that presence of two types of (CuL) species in solution. The peaks at around -1.0 V are for the reduction of Cu(II) to Cu(I) of isolated metallolihand (CuL)<sup>43</sup> and another peaks at slightly lower potential (-0.9 V) are for the (CuL) in trinuclear (CuL)<sub>2</sub>Mn unit. Both the species (CuL) and (CuL)<sub>2</sub>Mn are assignable in ESI mass spectra of the complexes. The potential differences ( $\Delta E_{12} = E_1 - E_2$ )<sup>59</sup> between two peaks on forward scan are -0.11, -0.14 and -0.13 V for complexes **1–3** respectively. The similar peak separation values ( $\Delta E_{pc}$ ) and potential difference values ( $\Delta E_{12}$ ) for all the complexes **1–3** indicate that the presence of similar type of species in solution phase.

#### Phenoxazinone synthase studies and kinetics

# **Detailed Description**

All three complexes, 1-3 exibit phenoxazinone synthase-like activity. The detailed kinetic studies of this catalytic oxidase activity were performed as reported previously.<sup>43</sup> The oxidative dimerisation reaction of *o*-aminophenol to phenoxazinone is shown in Scheme 2. We have examined the phenoxazinone synthase-like activity of the complexes in acetonitrile solvent under aerobic condition.



Scheme 2. Catalytic oxidation of o-aminophenol (OAP) to phenoxazinone (APX) in acetonitrile.

For the detailed kinetic study of this reaction, we used  $5 \times 10^{-5}$  M acetonitrile solution (considering hexanuclear unit) of complex **1** and  $1 \times 10^{-4}$  M acetonitrile solution (considering trinuclear unit) of both complex **2** and **3**. The  $1 \times 10^{-2}$  M acetonitrile solution of *o*-aminophenol is used as substrate solution. During wavelength scan the change in spectral behavior of complex **1** in the presence of OAP is shown in Figure 5 (left) and **2–3** are shown in Figures S13–S14 (left). The observed rate *vs*. [substrate] and the Lineweaver–Burk plots for complex **1** is depicted in Figure 6 (right) and **2–3** are shown in Figures S13–S14 (rightt). The turnover numbers (k<sub>cat</sub> in h<sup>-1</sup>) of this catalysis are 4966, 2021 and 1107 for complexes **1–3** respectively.



**Figure 6.** Increase in the APX band at around 424 nm after the addition of OAP  $(1 \times 10^{-2} \text{ M})$  to the acetonitrile solution of complex 1 (5 × 10<sup>-5</sup> M) (left) and plot of the rate vs. substrate concentration (right). Inset shows the corresponding Lineweaver–Burk plot of 1. The UV-spectra were recorded at 5 minute intervals.

# **ESI-Mass spectrometric study**

To determine the mechanistic insight of phenoxazinone synthase activity and complex-substrate intermediate during the catalytic oxidase reaction of *o*-aminophenol, we have recorded ESI-MS spectra of all three complexes and of a 1:1 mixture (v/v) of the complex and *o*-aminophenol within 5 min of mixing in acetonitrile (Figures S15–S17, ESI). In the spectra of all the complexes **1**–**3** a base peak is observed at m/z = 380.06 (calcd. 380.05) attributable to the sodiated metalloligand species [(CuL)+Na]<sup>+</sup>. Along with this, another two peaks are observed at m/z = 358.08 (calcd. 358.07) for protonated metalloligand [(CuL)+H]<sup>+</sup> and at m/z = 737.13 (calcd. 737.12) for the sodiated dinuclear species [(CuL)<sub>2</sub>Na]<sup>+</sup> (Figure S15, ESI). Spectra of the mixture of complexes **1**–**3** and *o*-aminophenol also show three common peaks at m/z = 380.06 (calcd. 380.05), m/z = 358.07 (calcd. 358.07) and m/z = 737.13 (calcd. 737.12) (Figure S16, ESI). All of these species have been found in the mass spectra of complexes **1**–**3**, but here the base peak is the protonated species that appears at m/z = 358.08 (calcd. 358.07). Along with these peaks another two low intensity peaks are observed at m/z = 1026.32 (calcd. 1026.14) and

m/z = 1052.33 (calcd. 1052.11) (Figure S17, ESI), assignable to the trinuclear species  $[(Cu(II)L)_2Mn(OAP)_2+K]^+$  and  $[(Cu(I)L)_2Mn(OAP)_2+3Na]^+$  respectively. In addition, another two peaks are observed at m/z = 1042.51 (calcd. 1042.16) and m/z = 1096.20 (calcd. 1096.13), the presence of two dioxygen coordinated trinuclear which indicate species  $[(Cu(I)L)_2Mn(O_2)(OAP)_2+Na]^+$  and  $[(Cu(II)L)_2Mn(O_2)(CH_3CN)(OAP)_2+K]^+$  respectively. In summary, in spectra of complex substrate mixture, the appearance of the peaks due to  $[(CuL)_2Mn(OAP)_2+K]^+$  $[(CuL)_2Mn(OAP)_2+3Na]^+, [(Cu(I)L)_2Mn(O_2)(OAP)_2+Na]^+$ and  $[(CuL)_2Mn(O_2)(CH_3CN)(OAP)_2+K]^+$  is noteworthy as there can be identified as the probable intermediate species formed during the oxidative conversion of o-aminophenol to phenoxazinone by dioxygen in presence of the complexes 1-3 as catalysts.

### **Mechanistic insight**

On the basis of ESI-Mass spectra, we propose a possible mechanism for the catalytic conversion. At first, on addition of o-aminophenol into the solution of each of the complexes (1-3), a neutral trinuclear species [(CuL)<sub>2</sub>Mn(OAP)<sub>2</sub>] in which two deprotonated hydroxyl groups of two oaminophenols are coordinated to Mn(II) centre, is formed (Figure S17, ESI) (Scheme 3). In the next step, Cu(II) is reduced to Cu(I) with concomitant formation of the o-iminophenolate/oaminophenolate radical. The existence and relative stability of these intermediate species can be assigned by mass spectra (Figure S16, ESI). The areal O<sub>2</sub> then oxidizes Cu(I) centers to Cu(II) and the coordinated organic radicals to phenoxazinone. The trinuclear species which is released react again with aminophenol to enter into the next cycle. During this catalytic conversion process  $3/_2O_2$  molecules are reduced to  $3H_2O$ . The probable mechanism of this catalytic conversion is shown in Scheme 3.



Scheme 3. Proposed mechanism for catalytic oxidation of OAP by complex 1.

### Structure-Activity correlation for the observed relative performance of the catalysts

Recently, there has been growing interest in homo- and heterogeneous catalysis, based on heterometallic complexes with various combinations of metal ions.<sup>60–63</sup> However, till date only very few heterometallic catalyst are reported which show homogeneous catalytic oxidase type activities. Recently, we reported some heterometallic Cu(II)-Mn(II) and Ni(II)-Mn(II) complexes derived from salen type tetradentate Schiff base ligands, which showed almost nil to very high catalytic oxidase activities.<sup>43,64</sup> It has been proposed that catalytic efficiency as well as catalytic

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#### **Crystal Growth & Design**

promiscuity of the complexes depend very much on the coordinated solvent molecule and anionic coligands to the Mn(II) centre. Here, we present three heterometallic Cu(II)-Mn(II) complexes using the same ligand and anionic coligand, yet we found that the catalytic efficiency on phenoxazinone synthase like activity of the complexes (1-3) is distinctly different. Complex 1 in which one CH<sub>3</sub>CN solvent is coordinated to the Mn(II) center of trinuclear  $Cu_{2}^{II}Mn^{II}$  unit shows highest catalytic activity ( $k_{cat} = 4966 h^{-1}$ ), the lowest activity ( $k_{cat} = 1107 h^{-1}$ ) is recorded with the polymeric complex **3** whereas the  $k_{cat}$  (2021  $h^{-1}$ ) value of discrete trinuclear unit **2** where two dicyanamide ions are coordinated the Mn(II) is in between. The difference can be explained considering the fact that the aminophenol substrate can coordinate easily to the Mn(II) centre in 1 by replacing the labile solvent acetonitrile molecule. Replacement of the coordinated dicyanamide ligand is more difficult than acetonitrile; hence the  $k_{cat}$  value of 2 is lower than that of 1. On the other hand, the catalytically active trinuclear unit is produced on dissociation of the polymeric complex 3 making it least active. As is proposed in the mechanism the redox active Cu centers do the job of electron transfer while the Mn(II) center is coordinated by the substrate but remains redox innocent during the course of the catalytic reaction. Thus the reaction rate is controlled by the ease of coordination of the substrate to the Mn(II) centre of the trinuclear unit. It is also to be noted that the  $k_{cat}$  value of 1 is more than any of the reported homometallic model complexes reported so far for phenoxazinone synthase-like activity. There is only one reported complex ( $Cu^{II}_2$ -Mn<sup>II</sup>) showing a higher k<sub>cat</sub> value than 1 and that species is also heterometallic. Therefore, one may presume that due to the cooperative effect the heterometallic model complexes can be more efficient for such oxydase reactions than homometallic complexes.

### Conclusions

To investigate subtle structural differences on magnetic properties and catalytic activities of heterometallic complex, we have synthesized three  $Cu_2^{II}-Mn^{II}$  complexes by changing the reaction conditions and proportion of dicyanamide. The metalloligand, CuL, derived from an asymmetrically dicondensed Schiff base on reaction with Mn(II) perchlorate and N(CN)<sub>2</sub><sup>-</sup> in 2:1:1 ratio resulted in a  $\mu_{1,5}$  dicyanamide bridged hexanuclear complex, [{(CuL)<sub>2</sub>Mn}<sub>2</sub>( $\mu_{1,5}$ -N(CN)<sub>2</sub>)(CH<sub>3</sub>CN)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (1). Higher proportion of N(CN)<sub>2</sub><sup>-</sup> in the same reaction mixture replaces all the perchlorate ions to produce two isomeric complexes **2** and **3** having molecular unit [{(CuL)<sub>2</sub>Mn}<sub>2</sub>(N(CN)<sub>2</sub>)]. Complex **2**, the monomeric unit of polymer **3** has been obtained at

ambient temperature and is convertible to **3** under reflux. The unsymmetric Schiff base seems enable the isolation of these two isomeric forms. The magnetic properties of the solid complexes **1–3** show antiferromagnetic coupling as are expected from phenoxido bridging angles. All three complexes show quite high phenoxazinone synthase-like activity but their catalytic efficiency is very different. The highest catalytic activity of complex **1** can be attributed to the presence of coordinating acetonitrile solvent to the Mn(II) centre. Interestingly, the catalytic activity of monomeric unit **2** is considerably higher than that of polymer **3** indicating that the two complexes are distinguishable even in solutions. ESI-Mass spectral analyses suggest the formation of substrate coordinated [(CuL)<sub>2</sub>Mn] cluster as the radical intermediate, and reduction of Cu(II) to Cu(I) in the catalytic process for all three complexes. The turnover number of complex **1** is higher than any of the model homometallic complexes and lowers than only one model complex which is also heterometallic. The observation vindicates the efficacy of heterometallic cooperative effect in the catalytic process i.e. for the present system, Mn(II) center binds the *o*-aminophenol while Cu(II) performs the redox activity.

**Supporting Information** (see footnote on the first page of this article): IR, Mass spectra and table of bond parameters of complexes 1-3 as well as Mass spectra of complexes 1 with OAP; Catalytic activity parameter and K<sub>cat</sub> values of complexes 1-3. CCDC-1567136 (for 1), - 1567137 (for 2), and -1567138 (for 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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Variations of Structures and Phenoxazinone Synthase-like Activity of the Complexes Based on (Cu<sup>II</sup>)<sub>2</sub>Mn<sup>II</sup> Node and Dicyanamide Spacer

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Three heterometallic Cu(II)-Mn(II) complexes with different structural geometries have been synthesized using the same unsymmetrical Cu(II)-metalloligand but varying the ratios of the reagents and reaction conditions. All the complexes exhibit biomimetic catalytic oxidase activity, efficiencies of which depend upon the coordination environment around the metal centers.