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# Synthesis and characterization of three hetero-dinuclear complexes with CuO<sub>2</sub>M cores (M= Na, Hg): Exploration of their phenoxazinone synthase mimicking activity

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#### Abstract

Three new hetero-dinuclear complexes,  $[CuL^1Na(NCS)]\cdot 0.5H_2O$  (1),  $[CuL^1Na(OClO_3)]\cdot 0.25H_2O$  (2) and  $[CuL^2HgCl_2]$  (3) {where  $H_2L^1 = N,N'$ -bis(3-ethoxysalicylidene)-2,2-dimethylpropane-1,3-diamine and  $H_2L^2 = N,N'$ -bis(3-methoxysalicylidene)-2,2dimethylpropane-1,3-diamine] are  $N_2O_4$  donor compartmental Schiff bases} have been synthesized and characterized. The phenoxazinone synthase mimicking activity of each complex in acetonitrile has been investigated with the model substrate *o*-aminophenol.

**Keywords:** Hetero-dinuclear complex; Schiff Base Ligand; Phenoxazinone synthase mimicking activity.

#### 1. Introduction

Compartmental Schiff bases represent fascinating ligand systems that are very effective in preparing multimetallic complexes with s, p and d-block metals [1]. There has been enormous interest in the synthesis and characterization of these heteronuclear metal complexes for their applications in magnetism, catalysis, biological modelling experiments, molecular architectures etc [2]. They can also be used for developing molecular systems capable of mimicking naturally occurring molecules responsible for the selective transport of ions [3]. On the other hand, diverse ranges of supramolecular architectures of such complexes are reported in the literature which in turn display a range of interesting functionalities including catalysis and host-guest chemistry [4]. These complexes may also be used as biomimetic catalysts, as they can mimic natural metalloproteins [5]. Some of these metalloproteins utilize their active sites for the activation, storage, and transport of aerial dioxygen molecules in enzymatic pathways: e.g., catechol oxidase (COx), phenoxazinone synthase (PHS) etc [6].

Multinuclear complexes are important due to their potential applications in catalysis [7-8]. The presence of different metal ions in one cluster may drastically change catalytic activity as a result of multimetallic cooperative activities [9]. Positive cooperativity occurs when the affinity for binding of a substrate with multiple binding sites to a metal is increased upon fixation to another metal. Each metal centre may be specifically responsible for elementary steps/transformations contributing to the overall transformation under investigation. One may thus envisage that the sharing of electrons between the metals forming the bi- or multimetallic

system will be at the origin of the specific reactivity observed [10]. A few multinuclear complexes have also been used to mimic phenoxazinone synthase, a multicopper oxidase enzyme [11-13].

In the present work, two  $N_2O_4$  donor compartmental Schiff bases, N,N'-bis(3ethoxysalicylidene)-2,2-dimethylpropane-1,3-diamine ( $H_2L^1$ ) and N,N'-bis(3methoxysalicylidene)-2,2-dimethylpropane-1,3-diamine ( $H_2L^2$ ) (Scheme 1) have been prepared and used to synthesize three new heteronuclear complexes with CuO<sub>2</sub>M cores, where M = Na for complexes 1, 2 and M = Hg for complex 3. Single crystal X-ray diffraction analyses have confirmed their structures. All three complexes have the potential to mimic phenoxazinone synthase activity.



#### 2. Experimental Section

All other materials were commercially available, reagent grade and used as purchased from Sigma-Aldrich without further purification.

*Caution!!!* Although no problems were encountered in this work, copper(II) complexes containing organic ligands in the presence of perchlorates are potentially explosive. Only a small amount of the material should be prepared and it should be handled with care.

#### 2.1 Preparation

2.1.1 Preparation of  $H_2L^1$  [N,N'-bis(3-ethoxysalicylidene)-2,2-dimethylpropane-1,3-diamine] and  $H_2L^2$  [N,N'-bis(3-methoxysalicylidene)-2,2-dimethylpropane-1,3-diamine]

A methanol solution (10 mL) of 3-ethoxysalicylaldehyde (332 mg, 2 mmol) and 2,2dimethyl-1,3-diaminopropane (0.13 mL, 1 mmol) was refluxed for ca. 1 h to form  $H_2L^1$ .  $H_2L^1$  was prepared in a similar method except that 3-methoxysalicylaldehyde (300 mg, 2 mmol) was used instead of 3-ethoxysalicylaldehyde. The ligands were not isolated and used directly for the synthesis of complexes  $[H_2L^1$  for complexes **1** and **2**;  $H_2L^2$  for complex **3**]. The ligands are presented in scheme 1.

#### 2.1.2 Preparation of complexes

#### 2.1.2.1 Preparation of $[CuL^1Na(NCS)]$ ·0.5H<sub>2</sub>O (1)

A methanol (10 mL) solution of copper(II) acetate monohydrate (200 mg, 1 mmol) was added to the methanol solution (20 mL) of  $H_2L^1$  and the resulting solution was stirred for 15 min. A methanol (10 mL) solution of sodium thiocyanate (81 mg, 1 mmol) was then added to it. The stirring was continued for about 2 h. Crystalline form of complex **1** started to appear after three days. Single crystals, suitable for X-ray diffraction, were obtained after seven days on slow evaporation of the solution in open atmosphere.

Yield: 825 mg (75%); based on copper(II). Anal. Calc. for  $C_{48}H_{58}Cu_2N_6Na_2O_9S_2$  (FW = 1100.20): C, 51.56; H, 5.41; N, 7.52; Found: C, 51.7; H, 5.2; N, 7.6%. ESI-MS (positive ion mode, Acetonitrile) m/z: 482.10 [100%, Cu(L<sup>1</sup>)Na]<sup>+</sup>. FT-IR (KBr, cm<sup>-1</sup>): 1612 (C=N); 2070 (NCS); 3448 (O-H); 2954 (C-H). UV-VIS [ $\lambda_{max}$ (nm)] [ $\epsilon_{max}$ (Lmol<sup>-1</sup>cm<sup>-1</sup>)] (acetonitrile): 220 (3.3×10<sup>4</sup>); <sup>27</sup>6 (1.9×10<sup>4</sup>); 348 (8.9×10<sup>3</sup>); 605 (4.1×10<sup>2</sup>).

#### 2.1.2.2 Preparation of [CuL<sup>1</sup>Na(OClO<sub>3</sub>)]0.25H<sub>2</sub>O (**2**)

It was prepared in a similar method as that of complex **1** except that copper(II) perchlorate hexahydrate (370 mg, 1 mmol) and sodium azide (66 mg, 1 mmol) was used instead of copper(II) acetate monohydrate and sodium thiocyanate, respectively. Single crystals, suitable for X-ray diffraction, were obtained after seven days on slow evaporation of the solution in open atmosphere.

Yield: 407 mg (70%); based on copper(II). Anal. Calc. for  $C_{23}H_{28.5}ClCuN_2NaO_{8.25}$  (FW = 586.96): C, 47.06; H, 4.89; N, 4.77; Found: C, 47.3; H, 4.7; N, 4.9%. ESI-MS (positive ion mode, Acetonitrile) m/z: 482.11 [100%, Cu(L<sup>1</sup>)Na]<sup>+</sup>. FT-IR (KBr, cm<sup>-1</sup>): 1612 (C=N); 1100 (Cl-O); 2950 (C-H). UV-VIS [ $\lambda_{max}$ (nm)] [ $\epsilon_{max}$ (Lmol<sup>-1</sup>cm<sup>-1</sup>)] (Acetonitrile): 225 (2.9×10<sup>4</sup>); 280 (2.2×10<sup>4</sup>); 352 (1.1×10<sup>3</sup>); 598 (1.3×10<sup>2</sup>).

#### 2.1.2.3 Preparation of $[CuL^2HgCl_2]$ (3)

A methanol (10 mL) solution of copper(II) chloride dihydrate (170 mg, 1 mmol) was added to the methanol solution (20 mL) of  $H_2L^2$  and the resulting solution was stirred for 15 min. A methanol (10 mL) solution of mercury(II) acetate (348 mg, 1 mmol) was then added to it.

The stirring was continued for about 2 h. Single crystals, suitable for X-ray diffraction, were obtained after one week on slow evaporation of the solution in open atmosphere.

Yield: 506 mg, 72%. Anal. Calc. for  $C_{21}H_{24}Cl_2CuHgN_2O_4$  (FW = 703.46): C, 35.85; H, 3.44; N, 3.98. Found: C, 35.9; H, 3.2; N, 4.1%. ESI-MS (positive ion mode, Acetonitrile) m/z: 454.04 [100%, Cu(L<sup>2</sup>)Na]<sup>+</sup>, 432.06 [Cu(L<sup>2</sup>)H]<sup>+</sup>. FT-IR (KBr, cm<sup>-1</sup>): 1613 (C=N); 745 (M-Cl); 2925 (C-H). UV-VIS [ $\lambda_{max}$ (nm)] [ $\epsilon_{max}$ (Lmol<sup>-1</sup>cm<sup>-1</sup>)] (acetonitrile): 227 (3.8×10<sup>4</sup>); 273 (2.8×10<sup>4</sup>); 368 (8.1×10<sup>3</sup>); 602 (2.1×10<sup>2</sup>).

#### 2.2 Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin Elmer 240C elemental analyzer. IR spectra in KBr (4500-500 cm<sup>-1</sup>) were recorded with a Perkin Elmer Spectrum Two spectrophotometer. Electronic spectra in acetonitrile were recorded on a Perkin Elmer Lambda 35 UV-visible spectrophotometer. Powder X-ray diffraction was performed on a Bruker D8 instrument with Cu K<sub> $\alpha$ </sub> ( $\lambda$  = 1.5406 Å) radiation. In this process, the complexes were ground with a mortar and pestle to prepare fine powders which were then dispersed with alcohol onto a zero background holder (ZBH). The alcohol was then allowed to evaporate to provide a nice, even coating of powder adhered to the sample holder. Thermogravimetric Analysis (TGA) was performed in a PerkinElmer Diamond (TG/DTA) instrument using Pyris software. Mass spectra were recorded on an XEVO G2QTof spectrometer (Waters) with an electrospray ionization source.

#### 2.3 X-ray crystallography

Suitable single crystals of complexes **1** and **3** were picked, mounted on a glass fibre and diffraction intensities were measured with an Oxford Diffraction XCalibur diffractometer equipped with Mo K<sub> $\alpha$ </sub> radiation ( $\lambda$  =0.71073 Å, 50 kV, 40 mA) at an ambient temperature (150 K). Data collection and reduction were performed with the Crysalis software [14]. On the other hand, a suitable single crystal of complex **2** was used for data collection using a 'Bruker SMART APEX II' diffractometer equipped with graphite-monochromated Mo K<sub> $\alpha$ </sub> radiation ( $\lambda$  = 0.71073 Å) at 150 K. The structures of all three complexes were solved by direct methods. For all complexes, non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached with oxygen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Absorption corrections for complexes **1** and **3** were carried out using ABSPACK [15] and for complex **2** using SADABS [16]. The structures were refined by full-matrix least squares on *F*<sup>2</sup>, using the SHELXL-2016/6 package [17].

#### 3. Results and Discussion

#### 3.1 Synthesis

2,2-dimethyl-1,3-diaminopropane was refluxed separately, with 3-ethoxysalicylaldehyde and 3-methoxysalicylaldehyde, in 1:2 ratio to form two  $N_2O_4$  donor compartmental Schiff base ligands,  $H_2L^1$  and  $H_2L^2$ , following the literature method [18]. The Schiff base ligand ( $H_2L^1$ ) on reaction with copper(II) acetate monohydrate (200 mg, 1 mmol) followed by the addition of sodium thiocyanate (81 mg, 1 mmol) in methanol formed complex **1**. The same Schiff base

 $(H_2L^1)$  on reaction with copper(II) perchlorate hexahydrate (370 mg, 1 mmol) followed by the addition of sodium azide (66 mg, 1 mmol) in methanol produced complex **2**. Schiff base  $(H_2L^2)$  on reaction with copper(II) chloride dihydrate followed by the addition of mercury(II) acetate tetrahydrate in methanol produced complex **3**. Formation of all complexes is shown in Scheme



Scheme 1: Preparation of ligands and complexes.

#### 3.2 Structure description

#### 3.2.1 $[CuL^1Na(NCS)] \cdot 0.5H_2O(1)$ and $[CuL^1Na(OCIO_3)] \cdot 0.25H_2O(2)$

Single crystal X-ray diffraction analyses reveal that complex **1** crystallizes in triclinic space group  $P\overline{1}$ , whereas complex **2** crystallizes in monoclinic space group I2/a. Details of crystallographic data and refinement details are given in Table 1. Important bond lengths and bond angles are gathered in Tables S1 and S2 [Supplementary Information (SI)] respectively.

Table 1: Crystal data and refinement details of complexes 1-3.

Complex	1	2	3
Formula	$C_{48}H_{58}Cu_2N_6Na_2O_9S_2$	C <sub>23</sub> H <sub>28.5</sub> ClCuN <sub>2</sub> NaO <sub>8.25</sub>	$C_{21}H_{24}Cl_2CuHgN_2O_4$
Formula Weight	1100.20	586.96	703.46
Temperature(K)	150	150	150
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	Ρī	/2/a	<i>P</i> 2 <sub>1</sub> /c
a (Å)	8.7492(6)	16.4292(6)	12.5433(6)
b (Å)	10.6600(9)	15.1691(7)	11.6488(5)
c (Å)	13.8973(8)	21.0946(10)	16.3580(8)
α (°)	109.628(6)	(90)	(90)
β (°)	96.568(5)	106.246(3)	105.367(5)
γ (°)	94.050(6)	(90)	(90)
Z	1	8	4
Volume (Å <sup>3</sup> )	1204.56(16)	5047.2(4)	2304.69(19)
$d_{\rm calc}$ (g cm <sup>-3</sup> )	1.517	1.545	2.027
μ (mm⁻¹)	1.051	1.040	7.838

F (000)	572	2428	1356
Total Reflections	8541	16953	14634
Unique Reflections	6726	4756	6505
Observed data [I > 2 $\sigma$ (I)]	5306	3660	4315
No. of parameters	326	331	284
R (int)	0.036	0.036	0.061
R1, wR2 (all data)	0.0721, 0.1324	0.0716, 0.1798	0.1358, 0.2162
R1, wR2 [I > 2 σ (I)]	0.0541, 0.1186	0.0546, 0.1609	0.0889, 0.1958

Molecular structures of complexes **1** and **2** are built from isolated hetero-dinuclear molecules of [CuL<sup>1</sup>Na(NCS)] and [CuL<sup>1</sup>Na(OClO<sub>3</sub>)] respectively. Both complexes contain lattice water molecules with occupancies of 0.5, that in complex **2** situated on a two-fold axis. In complex **2**, the perchlorate ion is disordered with the four oxygen atoms taking two orientations which were refined with occupation parameters, x and 1-x where x refining to 0.59(1). Perspective views of complexes **1** and **2** are depicted in Figures 1 and 2, respectively. H<sub>2</sub>L<sup>1</sup> is a N<sub>2</sub>O<sub>4</sub> donor compartmental Schiff base having inner N<sub>2</sub>O<sub>2</sub> and outer O<sub>4</sub> compartments with copper(II) occupying the inner N<sub>2</sub>O<sub>2</sub> compartment and sodium occupying the outer O<sub>4</sub> compartment. In both complexes, copper(II) centres are tetracoordinated whereas sodium centres are pentacoordinated. The copper(II) centres, Cu(1), in both complexes have square planar geometry in which two imine nitrogen atoms, N(19) and N(23), and two phenoxo oxygen atoms, O(11) and O(31), of the deprotonated di-Schiff base, are coordinated around the copper(II) centres. The sum of different angles around copper(II) centre is 359.93° for complex **1** and 360.08° for complex **2**, indicating slight distortion from perfect square planar geometry.

The trans angles [O(11)-Cu(1)-N(23)] and [O(31)-Cu(1)-N(19)] are found to be 169.1(1)°, 172.6(1)° for complex **1** and 169.4(1)°, 172.1(1)° for complex **2** respectively.

The geometry around the sodium atoms is best considered as a pentagonal pyramid with one equatorial site missing. The sodium atoms are bonded to four donor atoms from the Schiff base in the equatorial plane, e.g. two phenoxo oxygen atoms [O(11) and O(31)] and two ethoxy oxygen atoms [O(13) and O(32)]. The axial site is occupied by a nitrogen atom, N(1), from a terminal thiocyanate in complex **1** and in complex **2** by a perchlorate oxygen disordered between two sites, labelled O(41A) and O(41B).

The deviations of the four coordinating atoms, O(11), O(31), O(32) and O(13), in the basal plane from the mean plane passing through them are 0.087(1), -0.045(1) -0.086(1), 0.045(1) Å respectively for complex **1** and 0.038(2), -0.036(2), 0.019(1), -0.019(1) Å respectively for complex **2**. The deviation of Na(1) from the equatorial plane is 0.384(2) Å in complex **1** and 0.262(3) Å in complex **2**. The distances between copper(II) and sodium centres are 3.380(1) Å in complex **1** and 3.371(2) Å in complex **2**. It is noteworthy that the two equatorial planes coordinated to the copper and sodium atoms are approximately coplanar, intersecting at angles of 2.67(17) and 2.69(18)° in complexs **1** and **2** respectively. The saturated six-membered chelate rings, [Cu(1)-N(19)-C(20)-C(21)-C(22)-N(23)], have envelope conformations with puckering parameters: q = 0.574(3) Å;  $\theta = 58.3(3)^\circ$ ;  $\phi = 188.4(3)^\circ$  for complex **1** and q = 0.589(5) Å;  $\theta = 61.4(4)^\circ$ ;  $\phi = 179.7(5)^\circ$  for complex **2** [19].



Fig. 1: ORTEP view of complex 1 with ellipsoids at 50% probability. Lattice water molecule has

been omitted for clarity.



**Fig. 2**: ORTEP view of complex **2** with ellipsoids at 50% probability. Lattice water molecule has been omitted for clarity. Only the major fraction of the disordered oxygen atom of perchlorate

has been shown.

3.2.2 [CuL<sup>2</sup>HgCl<sub>2</sub>] (3)

The X-ray crystal structure determination revealed that the complex crystallizes in the monoclinic space group  $P2_1/c$ . A perspective view of the complex is shown in Fig. 3. Important bond lengths and bond angles are gathered in Tables S3 and S4 [Supplementary Information (SI)] respectively.

The molecular structure is built from isolated hetero-dinuclear molecules of  $[CuL^2HgCl_2]$ . H<sub>2</sub>L<sup>2</sup> is a N<sub>2</sub>O<sub>4</sub> donor compartmental Schiff base with copper(II) occupying the inner N<sub>2</sub>O<sub>2</sub> cavity and mercury(II) occupying the outer O<sub>4</sub> cavity. The copper(II) centre, [Cu(1)] has square planner geometry, where two imine nitrogen atoms, N(19) and N(23), and two phenoxo oxygen atoms, O(11) and O(31), of the deprotonated di-Schiff base, are coordinated with the copper(II) centre. The sum of different angles around copper(II) centre is 364.8° indicating distorted square planar geometry. The trans angles [O(11)-Cu(1)-N(23)] and [O(31)-Cu(1)-N(19)] are found to be 160.6(4)° and 163.6(4)° respectively.

The mercury(II) atom is six-coordinate with a geometry best described as distorted hexagonal bipyramidal with two adjacent equatorial sites missing. In the equatorial plane there are two phenoxo oxygen atoms, O(11) and O(31) and two ethoxy oxygen atoms O(131) and O(291), of the compartmental Schiff base coordinate with the mercury(II) centre. The O(131)-

Hg(1)-O(291) angle in the equatorial plane, adjacent to the two vacant sites, is  $178.7(3)^{\circ}$  validating that the structure cannot be an octahedron.

The axial coordination sites are occupied by two chlorine atoms, Cl(1) and Cl(2). The bridging angles between the metals, Cu(1)-O(11)-Hg(1) and Cu(1)-O(31)-Hg(1) are 107.1(4)° and 108.3(3)° respectively. The dihedral angle is 2.61° indicating the Cu(1)O(11)O(31)Hg(1) core is almost planar. The distance between the metal centres [Cu(1) and Hg(1)] is 3.652(1) Å.

The deviation of all the coordinating atoms, O(11), O(31), O(131) and O(291), in the basal plane from the mean plane passing through them are -0.098(9), 0.097(8), 0.047(3) and - 0.047(3) Å respectively. The deviation of Hg(1) is -0.031(7) Å. The saturated six membered chelate ring [Cu(1)-N(19)-C(20)-C(21)-C(22)-N(23)] has an envelope conformation with puckering parameters q = 0.598(13) Å;  $\theta$  = 119.2(11)°;  $\phi$  = 351.6(14)° [19].



Fig. 3: ORTEP view of complex 3 with ellipsoids at 50% probability.

#### 3.3 IR and electronic spectra

In the IR spectra of complexes **1-3**, distinct bands due to the azomethine (C=N) groups within the range of 1610-1615 cm<sup>-1</sup> are routinely noticed [20]. A strong band at 2072 cm<sup>-1</sup> indicates the presence of terminal thiocyanate in complex **1** [21]. Sharp peak around 1100 cm<sup>-1</sup> indicates the presence of a coordinated perchlorate in complex **2** [22]. Peak around 745 cm<sup>-1</sup> indicates the presence of metal coordinated chlorine atom in complex **3** [23]. Bands around 2935 cm<sup>-1</sup> are observed due to alkyl C-H bond stretching in all complexes [24].

In the UV spectra, square planar copper(II) usually shows three transitions; viz.  ${}^{2}A_{1g} \leftarrow {}^{2}B_{1g}$ ,  ${}^{2}B_{2g} \leftarrow {}^{2}B_{1g}$ , and  ${}^{2}Eg \leftarrow {}^{2}B_{1g}$  [25]. Electronic spectra of complexes **1-3** in acetonitrile display absorption bands ~600 nm. This band may be assigned to two superimposed transitions  ${}^{2}B_{2g} \leftarrow {}^{2}B_{1g}$ , and  ${}^{2}Eg \leftarrow {}^{2}B_{1g}$  [26]. A strong ligand to metal charge transfer transition ~350 nm is observed which is characteristic of transition metal complexes with Schiff base ligands. Bands ~225 nm and ~280 nm may be assigned as  $\pi^* \leftarrow$  n and  $\pi^* \leftarrow \pi$  transitions respectively [27].

#### 3.4 X-ray diffraction of powdered samples

The experimental PXRD patterns of the bulk products are in good agreement with the simulated XRD patterns from single crystal X-ray diffraction results, indicating consistency of the bulk sample. The simulated patterns of the complexes are calculated from the single crystal structural data (Cif) using the CCDC Mercury software.

#### 3.5 Thermo-gravimetric analysis

The thermal behaviour of all complexes is studied in a dynamic nitrogen atmosphere (20 mL min<sup>-1</sup>) at a heating rate of 10°C min min<sup>-1</sup> using thermo-gravimetric (TG) technique. The

thermo-gravimetric plots for complexes 1-3 are given in Figures 4, S17 and S18 [Supplementary Information (SI)] respectively. Complex 1 is stable up to ~50°C. An elimination of a water molecule from complex 1 in the temperature range 50-100°C occurs. The second weight loss for complex 1 occurs in the temperature range 275-450°C, where a weight loss of ~29.1% is observed (calc. 29.5%). This corresponds to the loss of two metals and thiocyanate anion which converts complex 1 in to  $H_2L^1$ . An elimination of water molecule from complex 2 in the temperature range 70-100°C happens. The second weight loss for complex 2 occurs in the temperature range 295-360°C, where a weight loss of ~31.3% is observed (calc. 31.9%). This corresponds to the loss of two metals and perchlorate anion which converts complex 2 in to  $H_2L^1$ . Complex **3** is stable up to ~240°C. The first weight loss for complex **3** occurs in the temperature range 250-350°C where a weight loss of ~38.3% is observed (calc. 38.5%). This corresponds to the loss of the mercury and two chloride molecule which converts complex 3 in to copper-ligand complex. The second weight loss for complex 3 occurs in the temperature range 260-470°C whereas the same of ~14.1% is observed (calc. 14.4%). This corresponds to the loss of copper which converts complex **3** in to  $H_2L^2$ . Endothermic peaks in the DSC plots have also been found indicating total combustion of the complexes and are found to be matching with major weight loss in TGA.



Fig. 4: TGA plot of complex 1.

#### 3.6 Phenoxazinone synthase like activity

To check the ability of the complexes to oxidize *o*-aminophenol to 2-aminophenoxazine-3-one (phenoxazinone synthase mimicking activity),  $10^{-1}$  M acetonitrile solution of oaminophenol are mixed separately with  $10^{-5}$  M solution of all three complexes, and the spectra are recorded for 2 h and 30 min at room temperature. It is found that all complexes show phenoxazinone synthase mimicking activity. The time dependent spectral profiles of complexes **1-3** are shown in Figures 5, S19 and S20 [Supplementary Information (SI)] respectively. The gradual increase of peak (characteristic of the phenoxazinone absorption) intensity at ~410 nm implies the catalytic conversation of *o*-aminophenol to 2-aminophenoxazine-3-one under aerobic conditions. The spectral growth (corresponding to the formation of phenoxazinone) is negligible for bare metal {copper(II), sodium and mercury(II)} salts compared to the spectral

growth for the complexes and hence it may be concluded that the complexes act as better catalysts compared to the bare salts of these metals.



**Fig. 5:** The spectral profile showing the growth of 2-aminophenoxazine-3-one at ~410 nm upon addition of  $10^{-1}$  M *o*-aminophenol to a solution containing complex **1** ( $10^{-5}$  M) in CH<sub>3</sub>CN.

#### 3.7 Kinetic parameters and rationalization of the K<sub>cat</sub> values

The above mechanism is based upon the well-known Michaelis–Menten equation:

$$V = \frac{V_{max}[S]}{K_M + [S]}$$

Where, V = initial rate; [S] = concentration of the substrates;  $K_M = (k_2 + k_3)/k_1$ , Michaelis– Menten constant for the metal complex and  $V_{max}$  = maximum initial rate attained for a particular concentration of the metal complex in the presence of a large excess of the

substrate. One of the most widely used transformation of the above equation, is the wellknown Lineweaver-Burk Equation as follows:

$$\frac{1}{V} = \frac{K_M}{V_{max}} \frac{1}{[S]} + \frac{1}{V_{max}}$$

The Lineweaver-Burk plot is used to analyse different parameters, viz.  $V_{max}$  (Maximum reaction velocity),  $K_M$  (Michaelis constant), and  $K_{cat}$  (Turnover number). Table 2 contains all these kinetic parameters of complexes **1-3** for phenoxazinone synthase like activity. The initial rate is determined from the slope of the absorbance vs time plot. In all cases, first order dependence is observed at low substrate concentrations, whereas saturation kinetics was found at higher substrate concentrations. The initial rate versus substrate concentration plot and Lineweaver-Burk plot for complex **1** are shown in Fig. 6.



**Fig. 6:** Initial rate versus substrate concentration plot for the oxidation of *o*-aminophenol catalyzed by complex **1** in CH<sub>3</sub>CN (left). Representative Lineweaver-Burk plot for the oxidation of *o*-aminophenol catalyzed by complex **1** in CH<sub>3</sub>CN (right).

The catalytic activity depends on the interaction between substrate and catalyst. More facile interaction leads to higher K<sub>cat</sub> values (Table 6). The formal oxidation state of copper and sodium in both complexes is +2 and +1 respectively, which facilitate the approach of a negatively charged substrate to the metal centre. Due to this reason both complexes exhibit catalytic property.

**Table 2:** Kinetic parameters of complexes **1**-**3** for phenoxazinone synthase mimicking activity at 25<sup>0</sup> C in acetonitrile medium.

Complex	<i>V<sub>max</sub></i> (M min <sup>-1</sup> )	<i>К<sub>М</sub></i> (М)	K <sub>cat</sub> (min <sup>-1</sup> )
1	2.23x10 <sup>-3</sup>	1.79 x10 <sup>-2</sup>	222.9
2	3.10x10 <sup>-3</sup>	5.58 x10 <sup>-2</sup>	310.1
3	4.97x10 <sup>-3</sup>	10.6 x10 <sup>-2</sup>	497.4

Literature survey shows that several hetero-dinuclear copper(II)/sodium and copper(II)/mercury(II) complexes using similar kind of ligands have been reported by several groups [28]. All such complexes are gathered in Table 3. However, catalytic activities of these complexes have not been investigated. Complexes **1-3** are eventually the first examples of hetero-dinuclear copper(II)/sodium and copper(II)/mercury(II) complexes showing phenoxazinone synthase mimicking activity.

 Table 3: X-ray characterized copper(II)/sodium and copper(II)/mercury(II) complexes reported

 in literature.

CCDC	Complex	K <sub>cat</sub> (min⁻¹)	Ref
FOFLIX	[CuL <sup>1</sup> Na(ClO <sub>4</sub> )(CH <sub>3</sub> OH)]	Not explored	[28a]
СІКРАР	$[CuL^2Na(NO_3)(CH_3OH)]$	Not explored	[28b]
XEDBIR02	$[CuL^1Na(NO_3)(CH_3OH)]$	Not explored	[28b]
XEDBIR01	$[CuL^{3}Na(NO_{3})(CH_{3}OH)]$	Not explored	[28c]
VEYLAO	$[Cu(HL^4)Na(NO_3)(CH_3OH)]$	Not explored	[28d]
KESYOY	$[CuL^{5}Na(ClO_{4})(CH_{3}CN)]$	Not explored	[28e]
QEHGUH	[CuL <sup>1</sup> Na(NO <sub>3</sub> )(H <sub>2</sub> O)]	Not explored	[28f]
QEHGOB	[CuL <sup>1</sup> Na(N <sub>3</sub> )(CH <sub>3</sub> OH)]	Not explored	[28f]
QEHHAO	[CuL <sup>1</sup> Na(NCS)(H <sub>2</sub> O)]	Not explored	[28f]
HAXFUJ	[CuL <sup>1</sup> Na(CH <sub>3</sub> COO)(H <sub>2</sub> O)]·2H <sub>2</sub> O	Not explored	[28g]
HAMSOF	[CuL <sup>6</sup> Na(NO₃)(H₂O)]·2CH₃CN	Not explored	[28h]
HAMSUL	[CuL <sup>6</sup> NaN₃(CH₃OH)]·CH₃OH	Not explored	[28h]
HAMTAS	[CuL <sup>6</sup> Na(ClO <sub>4</sub> )(CH <sub>3</sub> CN)]·0.5CH <sub>3</sub> CN	Not explored	[28h]
HAMTEW	$[CuL^6Na(BF_4)(CH_3OH)]\cdot H_2O$	Not explored	[28h]
KEZYOF	[Cu(HL <sup>4</sup> )HgCl <sub>2</sub> ]	Not explored	[28d]
WENXIY	[(CuL <sup>7</sup> CH <sub>3</sub> )HgCl <sub>2</sub> ]	Not explored	[28i]
-	[CuL <sup>1</sup> Na(NCS)]·0.5H₂O	222.9	This work
-	[CuL <sup>1</sup> Na(OClO <sub>3</sub> )]·0.25H <sub>2</sub> O	310.1	This work

[Cul <sup>2</sup> HgCl <sub>2</sub> ]	497.4	This work
	477.4	

where,  $H_2L^1 = N,N'$ -bis(3-methoxysalicylidene)propane-1,3-diamine;  $H_2L^2 = N,N'$ -bis(3-methoxysalicylidene)-2-methylpropane-1,2-diamine;  $H_2L^3 = N,N'$ -bis(3-methoxysalicylidene)ethane-1,2-diamine;  $H_3L^4 = N,N'$ -bis(3-methoxysalicylidene)-2-hydroxy-propane-1,3-diamine;  $H_2L^5 = N,N'$ -bis(3-methoxysalicylidene)phenylene-1,2-diamine;  $H_2L^6 = N,N'$ -bis(3-ethoxysalicylidene)phenylene-1,2-diamine;  $H_2L^7 = N,N'$ -bis( $\alpha$ -methylsalicylidene)propane-1,3-diamine.

#### 4. Concluding Remarks

In summary, synthesis and X-ray characterization of three hetero-dinuclear complexes with CuO<sub>2</sub>M core (M=Na, Hg) are described in this paper. Single crystal X-ray diffraction has confirmed their structures. All complexes are found to show catalytic property towards the oxidation of *o*-aminophenol. The catalytic efficiency of all complexes has been assessed following conventional Michaelis-Menten enzyme kinetics.

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#### Appendix A. Supplementary data

CCDC 1823123-1823125 contain the supplementary crystallographic data for **1**, **2** and **3** respectively.

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# Synthesis and characterization of three hetero-dinuclear complexes with $CuO_2M$ cores (M= Na, Hg): Exploration of their phenoxazinone synthase mimicking activity

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Synthesis and characterization of three hetero-dinuclear

complexes with CuO<sub>2</sub>M cores (M= Na, Hg): Exploration of their

# phenoxazinone synthase mimicking activity

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Phenoxazinone synthase mimicking activities have been investigated in hetero-dinuclear III copper(II)/sodium and copper(II)/mercury(II) complexes with N<sub>2</sub>O<sub>4</sub> donor compartmental Schiff