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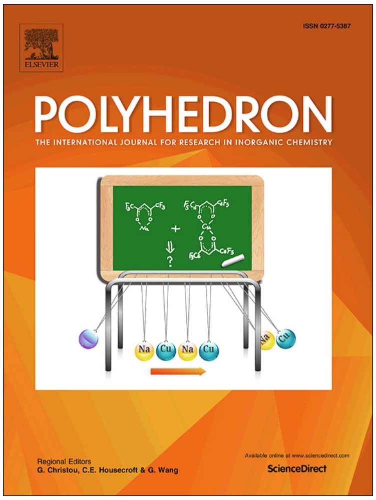

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Synthesis and characterization of a double oximato bridged dimeric copper(II) complex and its use in oxidative dimerisation of *o*-aminophenol

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Abstract

A dinuclear copper(II) complex, $[(CH_3CN)Cu(L)_2Cu](ClO_4)_2$, has been synthesized by reacting an oxime-based tridentate Schiff base ligand, 3-[2-(dimethylamino)-ethylimino] butan-2-one oxime (**HL**), with copper(II) perchlorate hexahydrate. The complex has been characterized by elemental and spectral analyses. Structure of the complex has been confirmed by single crystal X-ray diffraction technique. The complex may be used as moderate catalyst for the oxidation of *o*-aminophenol to 2-aminophenoxazine-3-one.

Keywords: Dinuclear; Tridentate Schiff base; Catalyst; Phenoxazinone synthase mimicking activity.

Introduction

Diverse catalytic activity [1-6], utility in modeling the multimetal active sites of metalloproteins [7] and potential use in material science [8-10] have attracted the attention of coordination chemists to design and synthesize homo- or hetero-polynuclear complexes of transition metals. Among them many copper(II) complexes have been synthesized to explore the

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involvement of copper active sites in several catalytic biological processes, to understand the magneto-structural correlations arising from the electronic exchange coupling among copper(II) centers, and to develop different molecular-based functional materials [11–15]. Many complexing agents have been used to prepare such complexes.

Oximes are very significant ligands in synthetic inorganic chemistry and coordination chemistry as well [16–21]. Probably, dimethyl glyoxime (H_2DMG) is the most famous in this family and is known to have the potential to detect nickel(II) in quantitative analysis by forming the rose red complex, $Ni(DMG)_2$ [22]. It is also used in gravimetric analysis of nickel since long [23]. Oxime ligands are once again topical in connection with the amazing capability of the deprotonated oximato groups to form bridges between metal ions thereby producing multinuclear complexes of various nuclearity [24-49].

Literature shows that many oximato Schiff bases have been used to prepare many copper(II) and mixed valence copper(II/I) complexes. Magnetic properties of many such complexes have been studied in detail [50-52]. DNA binding and cleavage activity of few such complexes also studied [53]. However, best to our knowledge, there is no report of phenoxazinone syntheses mimicking activity of any such complexes. Phenoxazinone synthase is a copper-containing oxidase enzyme, which is found in the bacterium, *Streptomyces antibioticus*. The oxidative condensation of various derivatives of *o*-aminophenol (two molecules) into phenoxazinone chromophore is catalyzed by this enzyme [54].

In the present work, we have synthesized a dinuclear copper(II) complex with an oximato Schiff base, 3-[2-(dimethylamino)-ethylimino]butan-2-one oxime (HL). The structure of the complex was confirmed by single crystal X-ray diffraction analysis. The complex has been

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found to be an efficient catalyst to perform the aerial oxidation of o-aminophenol to 2-aminophenoxazine-3-one and could be used as functional model for copper containing enzyme phenoxazinone synthase. The detailed kinetic study of the catalytic cycle was performed to evaluate various kinetic parameters, including the turnover number.

Experimental section

Starting materials

2,3-butanedione monoxime and N,N-dimethyl-1,2-ethanediamine were purchased from commercial sources and used as received. Copper(II) perchlorate hexahydrate was prepared by the standard laboratory method; solvents were of reagent grade and used without further purification.

Caution!!! It is very important to note hre that metal perchlorates are potentially explosive, especially when coordinated with organic ligands. Only a small amount of material should be prepared, and it should be handled with care.

Preparation of $[(CH_3CN)Cu(L)_2Cu](ClO_4)_2$

A mono-condensed Schiff base ligand, ***HL***, *3-[2-(dimethylamino)-ethylimino]butan-2-one oxime*, was synthesized by refluxing of N,N-dimethyl-1,2-ethanediamine (0.2 mL, 2 mmol) with 2,3-butanedione monoxime (~202 mg, 2 mmol) in acetonitrile solution (10 mL) for ca. 6 h and allowed to cool. The Schiff base was not isolated and purified, but was used directly for the complex formation.

An acetonitrile solution (5 mL) of copper(II) perchlorate hexahydrate (~741 mg, 2 mmol) was added to the acetonitrile solution (10 mL) of the Schiff base ligand ***HL***, with constant

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stirring for about 2h. The resulting reaction mixture was left unperturbed for slow evaporation at room temperature. After few days, green crystals, suitable for X-Ray diffraction were collected by filtration.

Yield: 496 mg (~70%, based on copper(II)). Anal. Calc. for $C_{18}H_{35}Cl_2Cu_2N_7O_{10}$ (FW: 707.53): C, 42.51; H, 6.94; N, 19.28. Found: C, 42.4; H, 6.8; N, 19.4 %. FT-IR (KBr, cm^{-1}): 1661 ($\nu_{C=N}$); 1030–1075 cm^{-1}, 620 cm^{-1} (ν_{ClO4^-}), 1140 cm^{-1} (ν_{NO}), 464 cm^{-1} ($\nu_{Cu\text{-}N}$). UV–Vis, λ_{max} (nm), [ε_{max} (L mol^{-1} cm^{-1})] (solvent): 579 ($0.30x10^2$); 418 ($0.87x10^2$); 312 ($6.84x10^2$). Crystal data for the complex: $C_{18}H_{35}Cl_2Cu_2N_7O_{10}$, M.W. = 707.53, monoclinic, space group $P2_1/n$, a (Å) = 13.428(2), b (Å) = 12.639(2), c (Å) = 17.014(3), V (cm^3) = 2887.0(8), Z = 4, d_{calc} = 1.628 g cm^{-3}, μ (mm^{-1}) = 1.719, F(000) = 1456, 57855 total reflections, 5189 unique reflections [R(int) = 0.096], 353 no of parameters, Observed data [I >2 σ (I)] = 3822, R1 = 0.0898, wR2 = 0.2097 (all data), R1 = 0.0610, wR2 = 0.1713 [I > 2 σ(I)], Temperature = 273 K.

Physical measurement

Elemental analysis (carbon, hydrogen and nitrogen) was performed using a Perkin-Elmer 240C elemental analyzer. IR spectrum in KBr (4500-500 cm^{-1}) were recorded with a Perkin-Elmer Spectrum Two spectrophotometer. Electronic spectrum was recorded on a JASCO J-630 spectrophotometer.

X-ray crystallography

A suitable single crystal of the complex was used for data collection using a 'Bruker D8 QUEST area detector' diffractometer equipped with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The molecular structure was solved by direct method and refined by full-matrix least squares on F^2 using the SHELXL-18/1 package [55]. Non-hydrogen atoms were refined

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with anisotropic thermal parameters. All hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [56].

Catalytic oxidation of *o*-aminophenol to 2-aminophenoxazine-3-one

Phenoxazinone synthase mimicking activity of the present complex was conducted at room temperature under aerobic condition for ca. 2 h. During this experiment, 10^{-4} M acetonitrile solution of the complex in acetonitrile was added to solutions with varying concentrations (10^{-3} to 10^{-2}) of substrate (*o*-aminophenol) in acetonitrile. The kinetics of the reaction was followed spectrophotometrically by observing the increase in the absorbance maxima at around 425 nm, which is characteristic of phenoxazinone chromophore. In the above case, complex: substrate ratio were ≥ 1:10 to maintain pseudo-first order condition to determine the dependence of rate on substrate concentration and various kinetic parameters. The rate of the reaction was derived from the initial rate method.

Results and discussion

Synthesis

N,N-dimethylethylenediamine was refluxed with 2,3-butanedione monoxime in a 1:1 ratio to form a N_3O donor compartmental Schiff base ligand, ***HL***, following a literature method [16]. This Schiff base (***HL***) on reaction with copper(II) perchlorate hexahydrate in acetonitrile formed the complex. Formation of the complex has been shown in Scheme **1**

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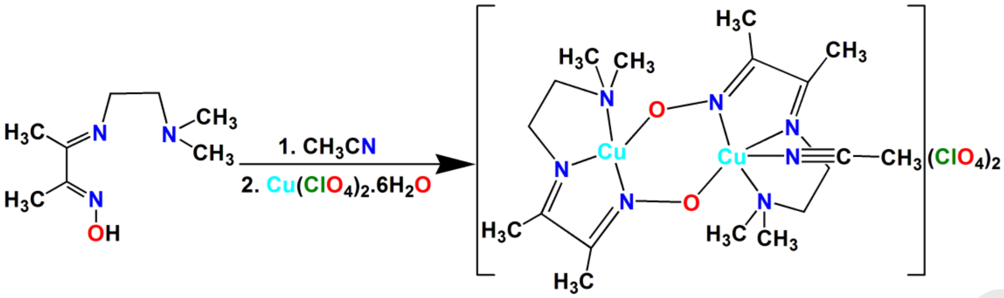

Scheme 1: Synthetic route to the complex.

Description of [(CH$_3$CN)Cu(L)$_2$Cu](ClO$_4$)$_2$

The molecular structure of the complex has been established by X-ray single crystal diffraction measurement. It reveals that the complex consists of cationic dinuclear unit of formula $[Cu_2\mathbf{L_2}^1]^{2+}$ along with two uncoordinated perchlorate anions and a coordinated acetonitrile molecule. The complex crystallizes in monoclinic space group, $P2_1/n$, with Z=4. The dinuclear unit has been shown in Fig. **1**.

The dinuclear complex contains two deprotonated Schiff bases, of which, both acts as a tridentate ligand. The coordination polyhedral around both metal centers are different: one copper centre, Cu(1), is a tetra-coordinated being bonded to N(3) (oxime nitrogen), N(2) (imine nitrogen), N(1) (amine nitrogen) of the tridentate ligand and the fourth position is occupied by O(2) (oxime oxygen) of the second ligand. The tetrahedral environment around Cu(1) is distorted as confirmed by the τ_4 index which is 1.172. The τ_4 index is defined as $\tau_4 = [360° - (\alpha+\beta)]/141°$, with α and β (in °) being the two largest angles around the central metal in the complex with $\tau_4 = 0$ for a perfect square planar and $\tau_4 = 1$ for a perfect tetrahedron. [57] On the other hand, penta-coordinated Cu(2), is either square pyramidal or trigonal bipyramidal being bonded to N(4) (oxime nitrogen), N(5) (imine nitrogen), N(6) (amine nitrogen) of the tridentate ligand and the

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fourth position is occupied by O(1) (oxime oxygen) of the second ligand. However, one of the axial position of Cu(2) is occupied by the nitrogen atom (N7) of an acetonitrile solvent at a distance of 2.303(7) Å. The distortion from the square pyramid to the trigonal bipyramid is calculated using the Addison parameter [58] The Addison parameter (τ) value for Cu(2) is 0.032, confirming the actual geometry is distorted square pyramid (dsp). The basal planes around both the copper atoms are coordinated by the three nitrogen atoms of one ligand and oxygen of a second ligand from the tridentate Schiff base ligand. The deviations of the coordinating atoms, O(2), N(1), N(2) and N(3), in the basal plane from the mean plane passing through them are -0.104(5), 0.068(5), -0.118(5) and 0.060(5) Å, respectively, whereas deviations of the coordinating atoms, O(1), N(4), N(5) and N(6), in the basal plane from the mean plane passing through them are 0.093(5), 0.011(5), 0.089(5) and 0.003(5) Å, respectively in the complex. The deviation of Cu(1) and Cu(2) from the same plane is 0.0942(7) Å and -0.195(7), respectively.

A cooperative –NO– bridged dinuclear cluster usually contains a central six-membered [Cu(1)-N(3)-O(1)-Cu(2)-N(4)-O(2)] ring in the complex is close to planarity. The average ring angle is 118.26°. The main deviation from a regular hexagonal ring shape is due to the relatively large size of the copper atoms and to the difference in the Cu-O and Cu-N bonds. The Cu(1)–O(2) and Cu(1)–N(3) bond distances are 1.878(5) and 1.991(4) Å respectively, whereas the Cu(2)–O(1) and Cu(2)–N(4) bond distances are 1.916(5) and 2.006(4) Å respectively, as expected from electronegativity considerations. The coordinated CH_3CN group appears to have little effect. Thus, the six-membered rings may be considered as pseudoaromatic systems containing sp^2 oxygen and nitrogen atoms, with the p_z orbital of each oxygen and nitrogen atom contributing an electron pair and the copper atoms each contributing one unpaired electron to make a total of ten π electrons ring system. The average ligand–Cu(1)–ligand angle is 89.9°. The

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average ligand–Cu(2)–ligand angle (ignoring the acetonitrile) is 89.14°. The copper-copper separation is 3.613(1) Å which is within the range of the reported distance separation in $\mu_{1,2}$-N,O double oximato-bridged Cu_2 complexes.[59, 60] No significant supramolecular interactions are observed.

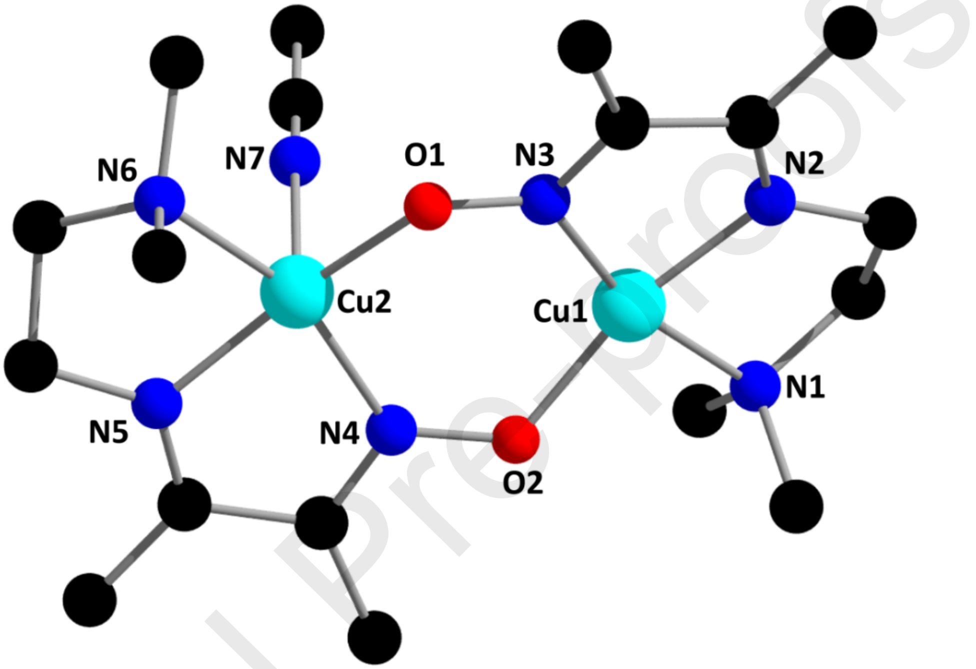

Fig. 1: Perspective view of the complex with selective atom numbering scheme. Hydrogen atoms have been omitted for clarity. The two lattice perchlorates have been omitted for clarity. Selected bond lengths (Å) and angles (°):Cu(1)–O(2) 1.878(5), Cu(1)–N(2) 1.917(5), Cu(1)–N(3) 1.992(5), Cu(1)–N(1) 2.051(5), Cu(2)–O(1) 1.916(4), Cu(2)–N(4) 2.006(5), Cu(2)–N(5) 1.946(5), Cu(2)–N(6) 2.057(5), Cu(2)–N(7) 2.304(7), O(2)–Cu(1)–N(2) 166.2(2), O(2)–Cu(1)–N(3) 104.85(19), N(2)–Cu(1)–N(3) 81.1(2), O(2)–Cu(1)–N(1) 89.62(19), N(2)–Cu(1)–N(1) 84.1(2), N(3)–Cu(1)–N(1) 165.2(2), O(1)–Cu(2)–N(5) 162.3(2), O(1)–Cu(2)–N(4) 103.07(18), N(5)–Cu(2)–N(4) 79.8(2), O(1)–Cu(2)–N(6) 90.97(18), N(5)–Cu(2)–N(6) 82.7(2), N(4)–Cu(2)–

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N(6) 160.3(2), N(4)–Cu(2)–N(7) 93.3(2), O(1)–Cu(2)–N(7) 97.9(2), N(5)–Cu(2)–N(7) 99.3(2), N(6)–Cu(2)–N(7) 98.4(2).

Hirshfeld surfaces

The Hirshfeld surface emerged from an attempt to define the space occupied by a molecule in a crystal for the purpose of subdividing the crystal electron density into molecular fragments [61]. d_{norm} is a normalised contact distance [62]. Intermolecular contacts are highlighted in the d_{norm} surface (when atoms make intermolecular contacts closer than the sum of their van der Waals radii, these contacts will be highlighted in red whereas longer contacts are blue, and contacts around the sum of van der Waals radii are white). Hirshfeld surfaces of the complex mapped over d_{norm} (range of -0.1 to 1.5 Å). Red spots on these surfaces denote the dominant interactions [N···H/H···N, O···H/H···O and C···H/H···C]. As the Hirshfeld surface defines the shape of the molecule in terms of its surrounding crystalline environment, the local shape of the surface may provide some chemical insight whereas shape index is a qualitative measure of shape and can be sensitive to very subtle changes in surface shape, particularly in regions where the total curvature (or the curvedness) is very low [63]. The 2D fingerprint plots, [64] which are used to analyze the intermolecular contacts at the same time, revealed that the main intermolecular interactions in the complex are N···H/H···N, O···H/H···O or C···H/H···C. The Hirshfeld surfaces and the corresponding 2D fingerprint plots for the complex has been shown in Fig. **2**.

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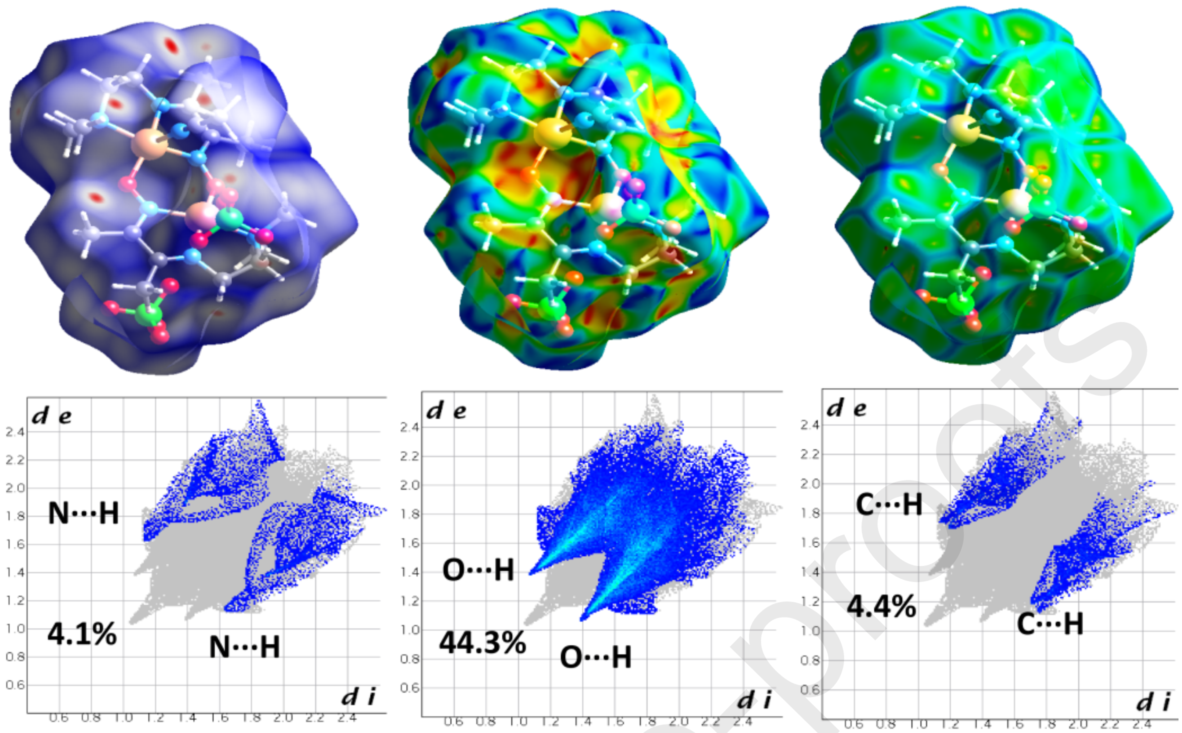

Fig. 2: Hirshfeld surfaces and fingerprint plots of the complex.

IR and electronic spectra

The IR spectrum of the complex is in a good agreement with X-ray structural data. A weak and sharp absorption band at 1661 cm^{-1} assigned to the >C=N stretching frequency of the Schiff base ligand, **HL** [65]. The coordination of the ligand to the metal center is substantiated by a band appearing at 464 cm^{-1} for the complex mainly attributed to the Cu–N stretching, [66] while a band at 1140 cm^{-1} suggests the presence of N–O bonds [33]. A characteristic band of the perchlorate anion around 1030–1075 cm^{-1} and 620 cm^{-1} in the spectrum of perchlorate complex assigned to the ionic perchlorate suggest the perchlorate group outside the coordination sphere in the complex [67]. The IR spectra of the complex and the ligand have been shown in Fig. **3** and **4** respectively.

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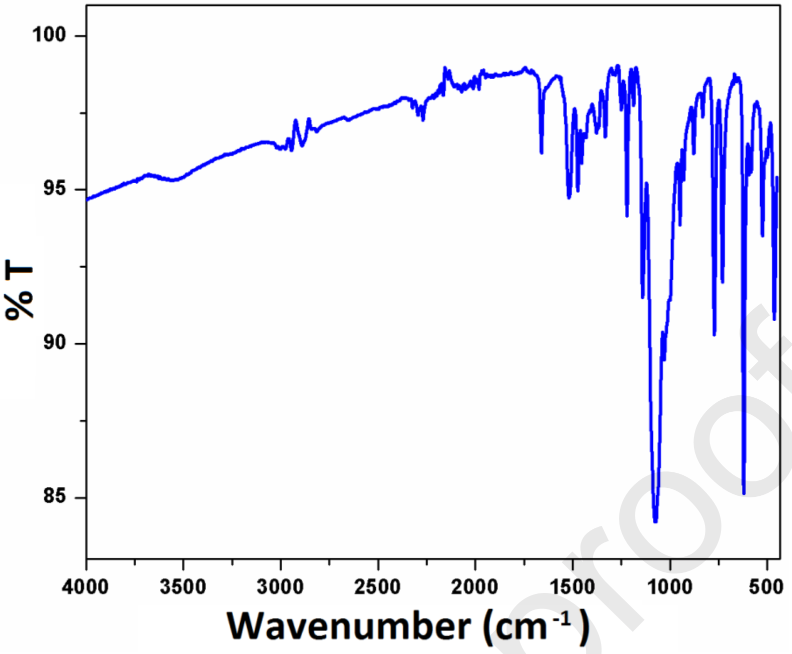

Fig. 3: IR spectrum of the complex.

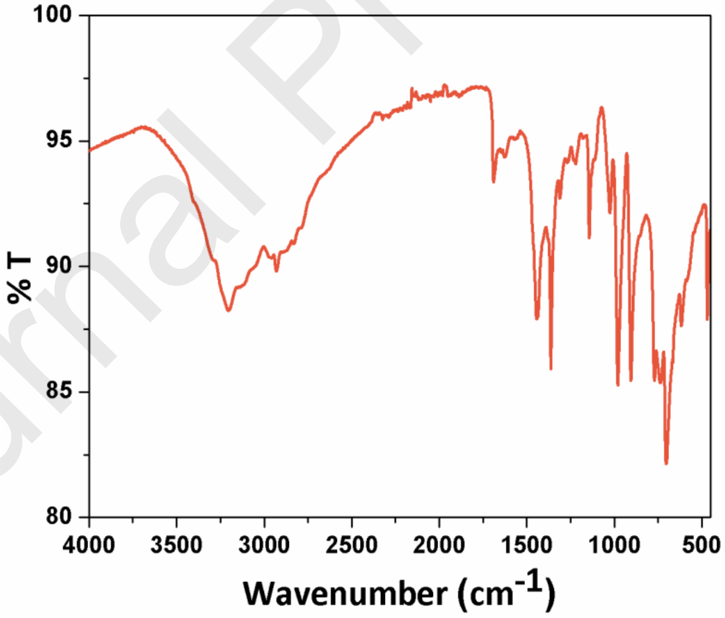

Fig. 4: IR spectrum of the ligand.

Electronic spectrum of the complex in acetonitrile displays one absorption band in the visible region at 579 nm which may be considered as ${}^2T_{2g}(D)\leftarrow{}^2E_g(D)$ transition for copper(II) in

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the square based environment [16]. In addition, A band at 418 nm may be attributed to LMCT transition from the nitrogen donor centre of Schiff base to copper(II) [68]. Moreover, absorption band at 312 may be considered as intra-ligand charge transfer transitions [16, 68]. The UV-vis spectrum of the complex has been shown in Fig. **5**.

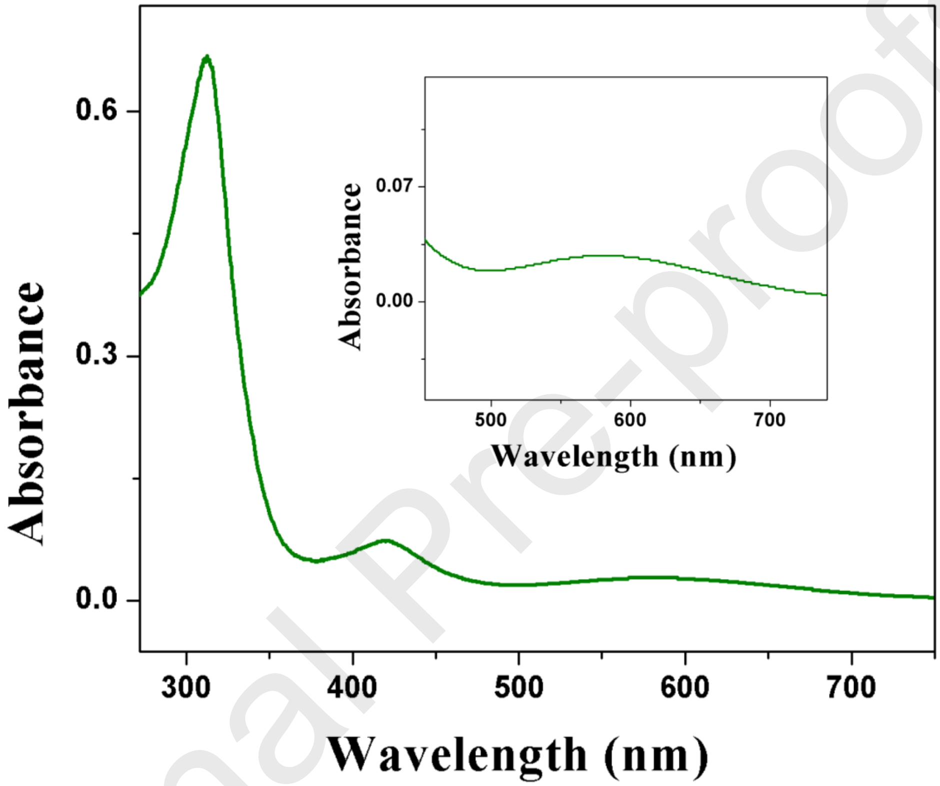

Fig. 5: UV-vis spectrum of the complex. Inset shows visible range spectrum.

Phenoxazinone synthase mimicking activity

An acetonitrile solution (10^{-2} M) of *o*-aminophenol was mixed with 10^{-4} M acetonitrile solution of the complex to check the phenoxazinone synthase mimicking activity of the complex. Kinetics of the reaction was studied spectrophotometrically and the spectra were recorded for up to ~ 2 h in aerobic condition at room temperature. No additional base was added in the reaction medium to minimise the possibility of auto-oxidation of the substrate. The time dependent

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spectral scans of the complex show gradual increase of the peak intensities at ~ 425 nm (typical for phenoxazinone chromophore), suggesting the catalytic areal oxidation of *o*-aminophenol to 2-aminophenoxazine-3-one. To prove the phenoxazinone synthase mimicking activity of the complex, comparative experiments without catalyst under identical conditions has been performed, which showed no significant growth of the spectra at λ_{max} ~ 425 nm. Also the spectral growth (corresponding to the formation of phenoxazinone) is negligible for (i) bare copper(II) perchlorate and (ii) bare copper(II) acetate compared to the spectral growth [at λ_{max} ~ 425 nm] for the complex and hence it may be concluded that the complex acts as better catalyst compared to the bare copper(II) salts. The time dependent spectral profile for a period of ~ 2 h in acetonitrile medium of the complex has been shown in Fig.**6**. The initial rate of the pseudo-first order reaction was easily calculated from the slope of the absorbance versus time plot. The same process was repeated for at least three times and the overall average value was taken. Initial rate of the reaction versus substrate concentration plot of the complex indicates rate saturation kinetics of the complex (Fig. **7a**). This observation clearly indicates that formation of 2-aminophenoxazine-3-one proceeds through a quite stable intermediate complex substrate adduct, which is formed at a pre-equilibrium stage and the irreversible substrate oxidation is the rate determining step of the catalytic cycle. K_M and V_{max} value for the complex is calculated 1.70×10^{-2} M and 1.11×10^{-3}, respectively. The turnover number (K_{cat}) value is obtained by dividing the V_{max} by the concentration of the complex used, and is found to be 11.1 h^{-1}.

It is clear that the copper(II) complex is active towards the oxidation of *o*-aminophenol in aerobic condition at room temperature. A tentative catalytic cycle for the oxidation of *o*-aminophenol to 2-aminophenoxazine-3-one may be proposed. At the first step *o*-aminophenol forms adducts with the complex by replacing the acetonitrile molecule, which results an *o*-

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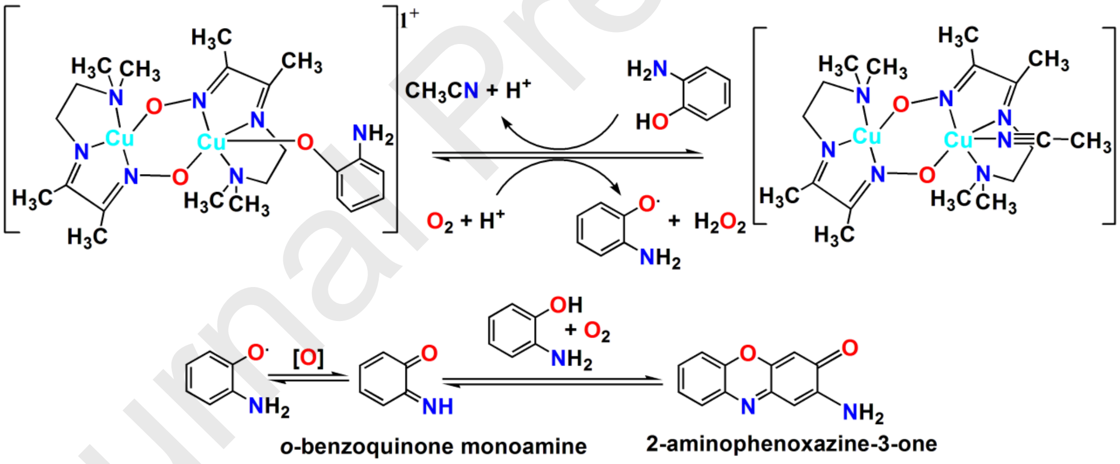
aminophenol radical by the reaction with molecular dioxygen regenerating the complex. The *o*-aminophenol radical may generate *o*-benzoquinone monoamine, which may easily be converted to 2-aminophenoxazine-3-one by the reaction with dioxygen and *o*-aminophenol (Scheme **2**).

In order to verify whether the complex is capable of maintaining its structural integrity during the phenoxazinone synthase mimicking activity, IR experiment for the complex was performed during the course of catalytic experiment. The IR experiment indicated that the pattern is nearly identical when compared with the pure complex. Hence the IR experiment imply that the complex maintains its structural integrity even after getting involved in the phenoxazinone synthase mimicking activity. IR spectra of the complex (before and after phenoxazinone synthase mimicking activity) have been shown in Fig. **8**.



Scheme 2: Probable mechanistic pathway showing the formation of 2-aminophenoxazine-3-one.

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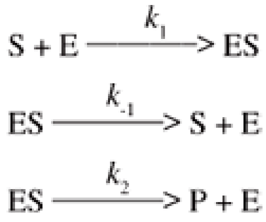
Validation of kinetic parameters

Briggs-Haldane scheme [69] was used in the kinetic study to determine kinetic parameters. This scheme considers the formation and dissociation reactions of the enzyme-substrate complex, ES and its decomposition reaction, forming the product (P) and regenerating the enzyme (E).



Applying this kinetic scheme to the steady state approximation for the concentration of the enzyme-substrate adducts, the Michaelis-Menten equation for initial reaction rate was achieved (equation 1).

$$V\ (\text{time}^{-1}) = V_{max}[S]/([S] + K_M)\ \text{- - - - - - - -}\ (\mathbf{1})$$

A double reciprocal Lineweaver–Burk plot is obtained upon linearization from Michaelis–Menten model, which is used to analyze a variety of parameters, viz. V_{max} (Maximum reaction velocity), K_M (Michaelis constant), and K_{cat} (Turnover number). The Lineweaver–Burk Equation as follows:

$$1/V = K_M/V_{max}.1/[S] + 1/V_{max}\ \text{- - - - - - - - - -}\ (\mathbf{2})$$

Plot of Eq. 1 for kinetic studies of aerobic oxidations of *o*-aminophenol catalyzed by the complex shows rectangular hyperbolic nature which finally leads to a saturation curve (Fig. **6a**). This confirms the first order rate kinetics followed by the substrates. Initial rate constants, V (min^{-1}) were obtained directly from the slope of the plot of $\log[(A_\infty - A_0)/(A_\infty - A_t)]$ vs. time which is a

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straight line passing through the origin. According to Eq. 1, the limiting rate at high substrate concentration, i.e. $[S]_0$, is designated as V_{max} ($V_{max} = k_{cat}[E]_0$)

Rearranging Eq. 1 gives Hanes equation (Eq. 3). In this case, [S]/V vs. [S] are plotted.

$$[S]/V = [S]/V_{max} + K_M/V_{max} \text{ - - - - - - - - - - } (\mathbf{3})$$

Eadie-Hofstee equation (Eq. 4) is sometimes used in biochemistry for graphical representation of enzyme kinetics. In this case, V/[S] vs. V is plotted.

$$V = V_{max} - K_M (V/[S]) \text{ - - - - - - - - - - - } (\mathbf{4})$$

Rate saturation kinetics was assessed by Eq. 1. Significant kinetic parameters, like $\mathbf{V_{max}}$**,** i.e. maximum reaction velocity, $\mathbf{K_M}$**,** i.e. Michaelis constant and $\boldsymbol{k_{cat}}$**,** i.e. turnover number, were obtained by utilizing Equations 3 and 4. Related plots of the catalytic activities of the complex are shown in Fig. **7**.

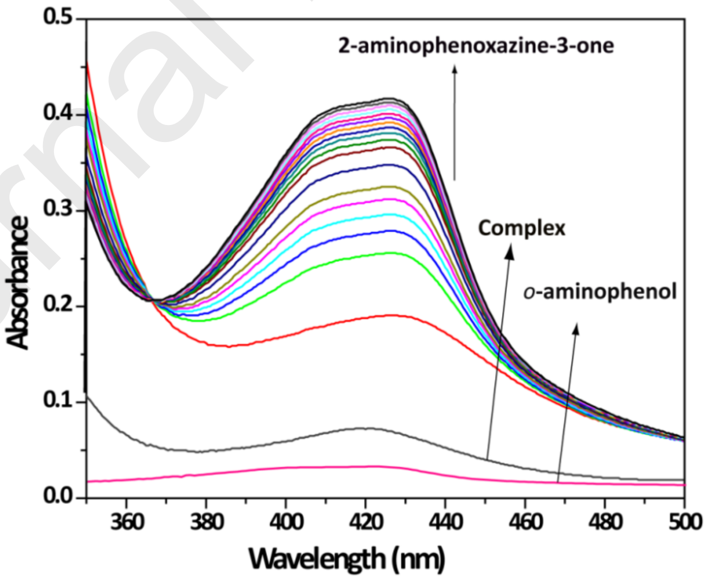

Fig.6: The UV–Vis spectral profiles indicating the increment of 2-aminophenoxazine-3-one at 425 nm upon gradual addition of 10^{-2} M *o*-aminophenol to the 10^{-4} M of the complex.

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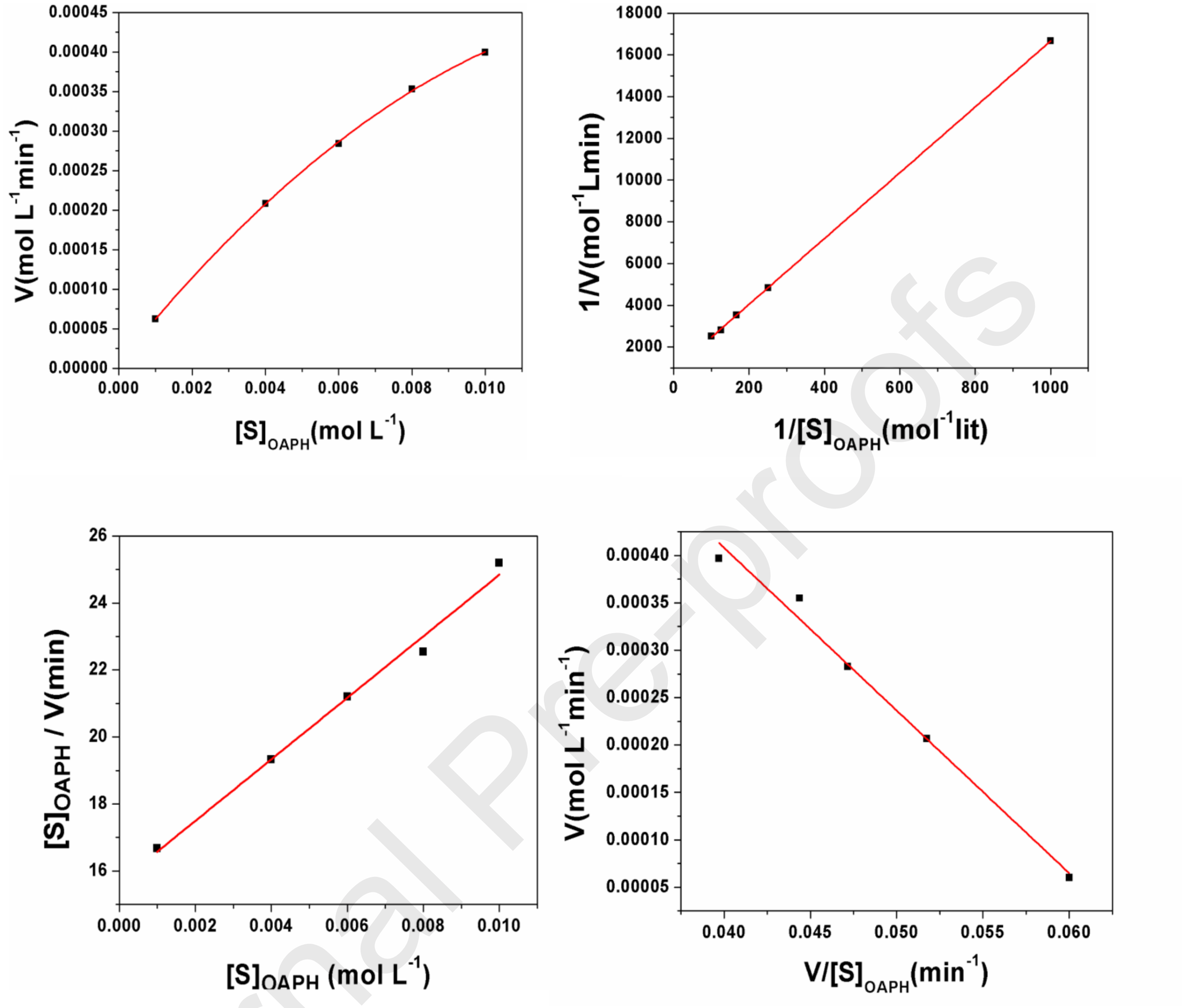

Fig. 7: (a) Initial rate vs. substrate concentration plot, (b) Linear Lineweaver–Burk plot, (c) Hanes Wolf plot and (d) Eadie Hofstee plot for the oxidation of *o*-aminophenol in dioxygen-saturated acetonitrile catalyzed by the complex at room temperature.

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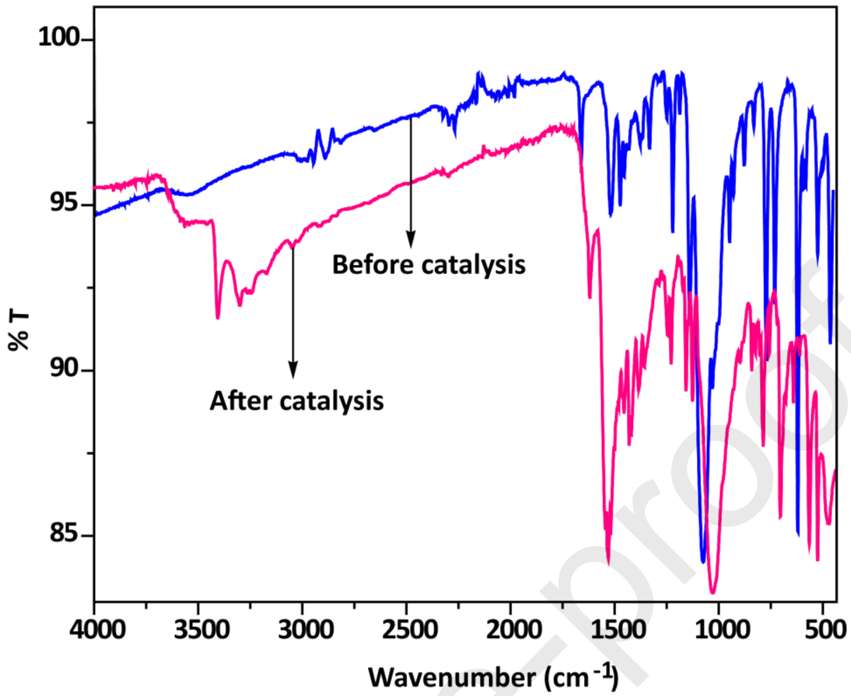

Fig. 8: IR spectra of the complex before (blue) and after (pink) the catalytic experiment.

The present complex is the first copper(II) complex of any oxime based Schiff base exhibiting phenoxazinone synthase mimicking activity. It is therefore not possible to compare its catalytic activity other similar complexes. However, catalytic properties of some di and poly-nuclear copper(II) complexes [70-73] with N_2O donor Schiff base ligands have been gathered in gathered in Table 1.

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Table 1: K_{cat} values of some X-ray characterized copper(II) complexes reported in literature.

CCDC	**Complex**	**K_{cat} (h^{-1})**	**Ref**
1572023	$[L^1Cu(\mu\text{-}Cl)_2CuL^1]$	1065 (In CH_3OH) 213 (In CH_3CN) 2844 (In CH_2Cl_2)	70
1507035	$[Cu_4(L^2)_4]$	86.3 (In CH_3OH)	71
1507036	$[Cu_4(L^3)_4]$	340.26 (In CH_3OH) 1028.9 (In DMSO)	71
1455999	$[Cu_4(L^4)_4]$	1.21 x10^5 (In CH_3OH)	72
1524680	$[Cu(\mu\text{-}Cl)(phen)Cl]_2$	1.69 x10^4 (In CH_3OH)	73
1940162	***$[(CH_3CN)Cu(L)_2Cu](ClO_4)_2$***	11.1 (In CH_3CN)	This work

L^1 = 2-(α-Hydroxyethyl)benzimidazole (Hhebmz), L^2 = (E)-4-Chloro-2-((thiazol-2-ylimino)methyl)phenol, L^3 = (E)-4-Bromo-2-((thiazol-2-ylimino)methyl)phenol, L^4 = N-(2-hydroxyethyl)-3-methoxysalicylaldimine, L^5 = 2,2'-bipyridine, L^6 = 1,10-phenanthroline, L^7 = N-(2-hydroxy-3,5-di-tert-butylphenyl)-2-aminobenzylalcohol.

Concluding remarks

We report the syntheses and structural characterization of one double oximato bridged dinuclear copper(II) complex containing oxime-based tridentate Schiff base ligand. Single crystal X-ray diffraction has confirmed the structure of the complex. Both copper(II) centrers are not residing in identical environment, as one copper(II) is penta-coordinated and is additionally

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bound to an acetonitrile molecule. The complex was found to exhibit phenoxazinone synthase like activity (i.e. conversion of *o*-aminophenol to 2-aminophenoxazine-3-one). The loosely bound acetonitrile may be replaced by *o*-aminophenol to initiate catalytic cycle. The catalytic efficiency of the complex has been assessed following conventional Michaelis–Menten enzyme kinetics. The complex may be considered as the first copper(II) complex with oxime based Schiff base ligand, which is employed as catalyst for the oxidation of *o*-aminophenol to 2-aminophenoxazine-3-one, although the catalytic efficiency of the complex is moderate.

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Appendix A. Supplementary data

CCDC 1940162 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Graphical Abstract (Synopsis)

Synthesis and characterization of a double oximato bridged dimeric copper(II) complex and its use in oxidative dimerisation of *o*-aminophenol

Tamal Dutta, Saikat Mirdya, Pritam Giri, Shouvik Chattopadhyay*

One new dinuclear copper(II) complex containing oxime-based tridentate Schiff base ligand has been synthesized and characterized. The catalytic ability of the complex in phenoxazinone synthase mimicking activity has been explored.

Graphical Abstract (Pictogram)

Synthesis and characterization of a double oximato bridged dimeric copper(II) complex and its use in oxidative dimerisation of *o*-aminophenol

Tamal Dutta, Saikat Mirdya, Pritam Giri, Shouvik Chattopadhyay*

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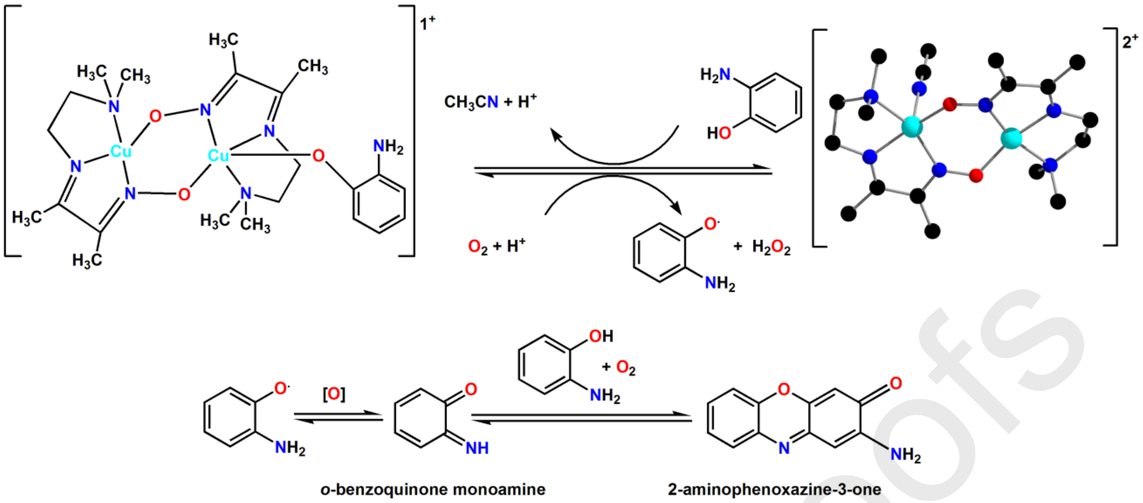

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