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Synthesis, characterization, spectral and catalytic activity of tetradentate (NNNO) azo-imine Schiff base copper(II) complexes

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Abstract

The hexadentate ligand, 2,2′-bis(salicylideneamino)azobenzene, **1** has been synthesized from 2,2'-diaminoazobenzene and salicylaldehyde in refluxing diethyl ether. Reaction of ligand **1** with Cu(II) acetate and Cu(II) perchlorate separately in methanol afforded tetradentate (N,N,N,O) Cu(II) complexes, Cu(L) & [Cu(HL)]ClO$_4$ respectively [where H$_2$L represent the one imine moiety cleavage product of ligand 1 (H represents the dissociable amino and phenolic protons)]. These were characterized by microanalytical data and spectroscopic studies. In addition, the crystal structures of the ligand **1** and complexes Cu(L) & [Cu(HL)]ClO$_4$ were determined by X-ray diffraction analysis. The diffraction analysis revealed that the ligand (H$_2$L) binds Cu(II) centers in (N,N,N,O) tetra dentate fashion in distorted square planer geometry. In complex [Cu(HL)]ClO$_4$ the apical position of copper center is weakly coordinated with one perchlorate ion. The dimeric structure of the molecule [Cu(HL)]ClO$_4$ is stabilized through NH$_2$···O hydrogen bonds. The fluorescence and redox property of ligand 1 and complexes Cu(L) & [Cu(HL)]ClO$_4$ were studied. Preliminary DFT calculations were carried out using crystallographic coordinates to understand the electronic spectra and redox properties of the ligand and complexes. The complex Cu(L) shows very good catalytic activities towards oxidation of benzyl alcohol to benzaldeyhde (under solvent-free condition) and organic thioethers to sulfoxide and sulfones using H$_2$O$_2$ as the oxidant.

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1. Introduction

Transition metal complexes incorporating Schiff base ligands work as active catalysts in homogeneous and heterogeneous reactions and their reactivity varies from metal to metal, nature of ligands and coordination sites [1-10]. Copper(II) complexes with tetradentate ligands are of considerable interest due to their structural, catalytic and magnetic properties, in addition to being potential models for several important biological systems [1-4, 11-14]. The copper complexes of tetradentate Schiff bases have been used as catalysts during the last decades in many reactions such as; epoxidation of olefins [15-18], alkylation [19], arylation [20], asymmetric Henry reaction [21-22], alcohol oxidation [23-26], nitroaldol reaction [27], asymmetric aziridination [28-29], asymmetric sulfoxidation [30-32], enantioselective ring opening polymerization [33-34] and oxidation of organic compound that has attracted a vast attention in the field of academic and industrial study [1-4, 10, 35-36].

The selective oxidation of organic molecules catalyzed by transition metal complex is one of the most successful and smooth processes for the oxo functionalization of organic substrates [10, 15-18, 23-26, 30-32, 35-36]. The oxidation of alcohols to aldehydes or ketones and organic thioethers to sulfoxides and sulfones are the important reactions in synthetic organic chemistry and fine chemical synthesis [23-26, 30-32]. Conventional methods for performing such transformations generally involve the use of stoichiometric amounts of inorganic oxidants which generate environmentally hazardous or toxic byproducts [37-38]. From environmental standpoints there is a strong need for the establishment of efficient and selective catalytic systems using green oxidant. Hydrogen peroxide is found to be a superior oxidizing agent for the oxidation of alcohols and thioethers as it is efficient and yield water only the byproduct [39-40]. Many catalytic systems for the hydrogen peroxide oxidation of alcohols and thioethers have been developed [23-26, 30-32], the interest is growing continuously in the search for new efficient metal catalysts in this purpose.

Herein, we describe the synthesis and characterization of hexadentate ligand, 2,2′-bis(salicylideneamino)azobenzene, **1**. The reactions of ligand **1** with Cu(OAc)$_2$.H$_2$O and Cu(ClO$_4$)$_2$.6H$_2$O (1:1) separately in methanol afforded Cu(II) complexes (Cu(L) & [Cu(HL)]ClO$_4$), have been described. The complexes have been characterized by the spectroscopic data. The crystal structures of the complexes (Cu(L) & [Cu(HL)]ClO$_4$) were determined by X-ray diffraction analysis. The fluorescence and redox property of ligand **1** and complexes (Cu(L) & [Cu(HL)]ClO$_4$) were studied. Probable explanations of redox orbitals and electronic spectra have been co-related on the basis of single point DFT calculations. The oxidation of benzyl alcohol to benzaldeyhde and organic thioethers to sulfoxide and sulphone has been examined in the presence of catalytic amounts of Cu(L) and using H$_2$O$_2$ as oxidant.

2. Experimental

2.1. Materials

The solvents used in the reactions were of reagent grade (E. Marck, Kolkata, India) and were purified and dried by general procedure [41]. Methyl iodide, ethyl bromide, allyl chloride, benzyl chloride, salicylaldehyde were purchased from E. mark, India. 4-methylbenzyl alcohol, 2-methylbenzyl alcohol, 4-methoxybenzyl alcohol, thiophenol, copper acetate monohydrate, copper perchlorate hexahydrate were purchased from Sigma-Aldrich. 2,2'-diaminoazobenzene and alkyl thiophenol were prepared by following reported procedures [42-43].

2.2. Physical measurements

Microanalysis (C, H, N) was performed using a Perkin-Elmer 2400 C, H, N, S / O series II elemental analyzer. Infrared spectra were recorded on a Perkin Elmer BX-1 FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1800 PC spectrophotometer. ^{1}H NMR spectra were obtained on Bruker 400 NMR spectrometers in CDCl$_3$ using TMS as the internal standard. Emission spectra were recorded with a Perkin Elmer

LS-55 Luminescence Spectrometer. Electrochemical measurements were made under dinitrogen atmosphere using a CH instruments model 600D potentiostat. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

2.3. Syntheses

2.3.1. Synthesis of ligand 1

To a solution of 2,2'-diaminoazobenzene (0.4 g, 1.88 mmol), in 50 mL diethyl ether was added salicylaldehyde (0.465 g, 3.81 mmol). The resulting mixture was then heated to reflux for 5 h. It was kept undisturbed for 1 h to obtain solid crystals of 1. The solid product was then filtered and washed with diethyl ether. Yield: 1, 95%. Anal. Calc. for $C_{26}H_{20}N_4O_2$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.03; H, 4.52; N, 13.57%. UV/VIS (λ_{max} / nm (ε / dm^2 mol^{-1}), dichloromethane): 290 (28740), 235 (28970). IR (KBr, cm^{-1}): 1615 v(C=N), 1473 v(N=N), 1283 v(O-C). ^{1}H NMR (400 MHz, CDCl$_3$): 6.87 (ArH, t, 1H, J = 8 Hz), 7.00 (ArH, d, 1H, J = 8 Hz), 7.19-7.35 (ArH, m, 5H), 7.47 (ArH, t, 1H, J = 8 Hz), 7.75 (ArH, d, 1H, J = 8 Hz), 8.60 (CH, s, 1H), 13.58 (OH, s, 1H).

2.3.2. Synthesis of complex Cu(L)

A solution of 1 (0.15 g, 0.36 mmol) in 10 mL methanol was added to a solution of Cu(OAc)$_2$.H$_2$O (0.071 g, 0.36 mmol) in 10 mL methanol. The mixture was stirred for 1 h. The pink violet solid precipitate was separated by filtration and the solid mass was dissolved in dichloromethane. After the evaporation of the solvent, a pink-violet solid of pure Cu(L) was obtained. Yield: 75%. Anal. Calc. for $C_{19}H_{14}CuN_4O$: C, 60.39; H, 3.73; N, 14.83. Found: C, 60.65; H, 3.93; N, 14.61%. UV/VIS (λ_{max}/nm (ε/ dm^2 mol^{-1}), dichloromethane): 560 (11560), 530 (14100), 420 (18250), 380 (21480), 315 (28530), 240 (44960). IR (KBr, cm^{-1}): 3328 v(NH), 1609 v(C=N), 1439 v(N=N), 1313 v(O-C).

2.3.3. Synthesis of complex [Cu(HL)]ClO$_4$

A solution of **1** (0.15 g, 0.36 mmol) in 10 mL methanol was added to a solution of $Cu(ClO_4)_2.6H_2O$ (0.132 g, 0.36 mmol) in 10 mL methanol. The mixture was stirred for 1 h. The colour of the solution immediately changed to pink-violet. The resulting solution was then filtered and allowed to stand at room temperature. After slow evaporation of the solvent at room temperature, a pink violet coloured needle shape crystals suitable for x-ray analysis were obtained. Yield: 70%. Anal. Calc. for $C_{19}H_{15}ClCuN_4O_5$: C, 47.71; H, 3.16; N, 11.71. Found: C, 47.46; H, 3.05; N, 11.79%. UV/VIS (λ_{max} / nm (ε / dm^2 mol^{-1}), dichloromethane): 560 (9360), 530 (11340), 420 (14230), 380 (15590), 320 (19970), 240 (34500). IR (KBr, cm^{-1}): 3421, 3328 $\nu(NH_2)$, 1608 $\nu(C=N)$, 1429 $\nu(N=N)$, 1313 $\nu(O-C)$, 1091 $\nu(Cl-O)$.

2.4. General procedure for catalytic oxygenation of thioethers

To the catalyst Cu(L) (0.014 mmol) dissolved in 10 mL dichloromethane-methanol (8:2) mixed solvent, 3 mmol of sulfide and 1.5 mL of 50% H_2O_2 were all inserted in a 25 mL round-bottom flask at 0^0C. The mixture was stirred for 6 h. After the completion of the reaction the mixture was evaporated to dryness, water was added and the product was extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, filtered. The products were separated and purified by preparative TLC using hexane–ethyl acetate (2:1) mixed solvent. The yields of the products obtained from all the reactions were determined after isolation, and characterized by ^{1}H NMR and IR spectra.

2.5. Procedure for catalytic oxidation of benzyl alcohol

To a solution of benzyl alcohol (5 mmol), catalyst Cu(L) (0.012 mmol), and 50 % H_2O_2 5 mL was added and the mixture was vigorously stirred at 75^0C for 2 h. After that the mixture was poured into water and the product was extracted with dichloromethane and dried over Na_2SO_4. The product was passed through silica column (60-120 mesh) and the complex remains trapped. Upon removal of the solvent, pure product was obtained. The yields of the products obtained from all the reactions were determined after isolation, and characterized by ^{1}H NMR and IR spectra.

2.6. Crystallography

Single crystals of 1, [Cu(HL)]ClO$_4$ were grown by slow evaporation of ether and methanol solution at 25^{0}C and Cu(L) was grown by slow evaporation of dichloromethane-methanol mixed solvent at room temperature. Data were collected by ω- scan technique on a Bruker Smart CCD diffractometer with Mo-K$_α$ radiation monochromated by graphite crystal. Structure solution was done by direct method with SHELXS–97 program [44-45]. Full matrix least square refinements on F^2 were performed using SHELXL–97 program [44-45]. All non-hydrogen atoms were refined anisotropically using reflections I > 2σ (I). The C-bound hydrogen atoms were included in calculated positions and refined as riding atoms and O, N-bound hydrogen atoms were assigned and refined. Data collection parameters and relevant crystal data are collected in Table 1.

Please insert Table 1 here

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3. Results and discussion

3.1. Synthesis

The ligand **1** used in this work, synthesized by the condensation of 2,2'-diaminoazobenzene and salicylaldehyde (1:2) in diethyl ether. The ligand was isolated as brown-red solid crystals on cooling. The preformed ligand **1** upon reaction with copper(II) acetate monohydrate and copper(II) perchlorate hexahydrate separately in methanol afforded pink violet azo aldimine Cu(II) complexes of composition (Cu(L) and [Cu(HL)]ClO$_4$) by the reductive cleavage of one N=CHC$_6$H$_4$OH bond of ligand **1**, where the ligand (H$_2$L) offers (N,N,N,O) coordination mode (Scheme 1). Presumably methanol is the source of electrons and protons for the cleavage of imine function which is supported by the observation that no reaction is observed when ligand **1** with copper(II) acetate monohydrate and copper(II) perchlorate hexahydrate are separately in refluxing CH$_2$Cl$_2$ in presence of triethyl amine base. In complex Cu(L) the ligand binds in tetradentate (N,N,N,O) bianionic fashion through deprotonated amino nitrogen, azo nitrogen, imino nitrogen and deprotonated

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phenolato oxygen atom forming two six membered and one five membered ring. Whereas, in complex [Cu(HL)]ClO$_4$ the ligand binds in tetradentate (N,N,N,O) monoanionic fashion through amino nitrogen, azo nitrogen, imino nitrogen and deprotonated phenolato oxygen and one perchlorate ion satisfy the charge of Cu(II) ion.

Please insert Scheme 1 here

3.2. UV-Vis and Fluorescence spectra

Ligand 1 and complexes Cu(L) & [Cu(HL)]ClO$_4$ are soluble in common organic solvents, such as methanol, acetone, chloroform, dichloromethane, etc., producing intense orange-red and pink-violet colours respectively. Electronic spectra of the ligand 1 and complexes were recorded in dichloromethane solutions (Fig. 1). Spectral data are collected in experimental section. Ligand 1 display an intense broad band at 290 nm characteristic of the overlapping n→π* transitions of azo (N=N) and aldimine (N=CH) function [46-48]. Complexes Cu(L) & [Cu(HL)]ClO$_4$ shows several intense absorptions within the 240-560 nm range. The high energy absorptions in ultraviolet region are majorly due to intra ligand π−π* charge transfer transitions [49-50]. A Characteristic low energy absorption band for Cu(L) & [Cu(HL)]ClO$_4$ at 415 nm is assigned as mixed metal ligand charge transfer [46-47]. To gain insight into the nature of the absorptions in the visible region, DFT calculations were performed on both the complexes. Surface plots of the molecular orbitals (HOMO & LUMO) of 1, Cu(L) and [Cu(HL)]ClO$_4$ are shown in Fig S5 (Supplementary Materials). From the orbital diagrams it appears that the HOMO and LUMO of complexes Cu(L) and [Cu(HL)]ClO$_4$ both are metal ligand mixed orbitals.

Please insert Fig. 1 here

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The fluorescence properties of ligand **1** and complexes Cu(L) and [Cu(HL)]ClO$_4$ were investigated in dilute chloroform solution at room temperature (Fig. 2). The ligand **1** exhibited a low intensity emissions bands at 450 nm upon excitation at 380 nm. Whereas complexes Cu(L) and [Cu(HL)]ClO$_4$ exhibited very high intensity emissions bands at 440 nm upon excitation at 385 nm [though coordinated ligand (H$_2$L) is little different from ligand **1**]. Quenching of fluorescence of a ligand by particular transition metal ions during complex formation is a common fact and it explained by photoinduced electron transfer process. But in this case the photoinduced electron transfer is prevented by stable complex formation after Cu(II) and ligand (H$_2$L) interaction, fluorescence intensity greatly enhanced due to metal ligand chelation effect and the overall process is referred as "CHEF" [51].

Please insert Fig. 2 here

3.3. IR and ^{1}H-NMR

The characteristic stretching frequency of the azomethine ν(HC=N) group in the free ligand 1615 cm^{-1} shifted to 1609 & 1608 cm^{-1} in the complexes due to coordination to the metal ion [37,46,52-53]. The phenolic C–O band of the ligand 1283 cm^{-1} have been shifted to higher frequency in the complex 1313 cm^{-1} indicating the coordination through the phenolic oxygen atom [46,53]. Similarly the ν$_{N=N}$ band (1473 cm^{-1}) of the ligand shifted to lower frequency (1439 & 1429 cm^{-1}) in the complexes, consistent with coordination of the azo nitrogen [42,47-48]. New bands, at 3328 cm^{-1} and 3421 & 3328 cm^{-1}, in the IR spectra of the complexes Cu(L) & [Cu(HL)]ClO$_4$ unlike the ligand **1**, has been attributed to NH and NH$_2$ groups which is formed after cleavage of one of the aldimine function from the ligand **1** upon complexation. A very strong and split broad band near 1091 cm^{-1} and a split strong band near 622 cm^{-1} are observed in the IR spectrum of the [Cu(HL)]ClO$_4$ complex, which could be due to the antisymmetric stretching and bending of perchlorate ions, respectively [46,53]. Spectral data are collected in experimental section.

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Free Schiff base ligand **1** has been characterized by ^{1}H-NMR spectrum. The ligand **1** show highly resolved ^{1}H-NMR spectrum, which is in complete agreement with the X-ray structure of the ligand. The centrosymmetric ligand **1** contains eight aromatic protons which show five distinct set of aromatic signals in the range 6.86-7.75 ppm. Two triplets 6.86 & 7.46 ppm and two doublets 7.00 & 7.75 ppm are assigned for those of aromatic proton of rings adjacent to azo function. One multiplate in the range 7.19-7.35 ppm is assigned for four protons of aldehydic ring. The phenolic –OH and azomithine (―C=N―) protons appeared as a sharp singlet at 13.58 ppm and 8.60 ppm respectively [37,46,52].

3.4. X-ray crystallography

The crystal structure of ligand 1 and complex Cu(L) & [Cu(HL)]ClO$_4$ were determined by single crystal X-ray diffraction method. The crystallographic and measurement data are shown in Table 1. Ligand 1 and complex Cu(L) are orthorhombic, complex [Cu(HL)]ClO$_4$ is triclinic and are crystallized in the space group Pbca, P2$_1$2$_1$2$_1$ and P-1 with Z = 8, 4 and 2 respectively.

The crystal structure of ligand **1** is shown in Fig. 3. Selected bond lengths and bond angles are given in Tables 2. The centrosymmetric structure of **1** reveals the planar geometry of the ligand with intra molecular hydrogen bonding between phenolic proton and imine nitrogen [O(1)-H….N(1) and O(2)-H….N(4)]. All the non-hydrogen atoms of ligand **1** make a good plane (mean deviation 0.135Å). The O(1)-C(1), N(1)-C(7), N(1)-C(8), and N(2)-C(13) bond lengths 1.349(2), 1.273(2), 1.406(2) and 1.426(2) Å are in agreement with the reported values, whereas the N(2)-N(3) azo distance (1.246(19) Å) is comparatively shorter [16,42,48].

Please insert Fig. 3 and Table 2 here

The crystal structure of Cu(L) is shown in Fig. 4 along with the atom labels. Hydrogen atoms are omitted for the clarity. Selected bond lengths and bond angles are listed in Table 3. The

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Please insert Fig. 4 and Table 3 here

Ligand (H_2L) is coordinated with Cu(II) in a dianionic (L^{2-}) tetra dentate (N,N,N,O) mode, forming two six membered chelate ring and one five membered ring. The X-Ray crystal structure of Cu(L) exhibits a copper(II) ion within a nearly square planar environment. All the non-hydrogen atoms of Cu(L) make a good plane (mean deviation 0.241Å). The metal centre is coordinated to imine nitrogen N1, azo nitrogen N2, amido nitrogen N4 and phenolate oxygen O1. The Cu-O1, Cu-N1, Cu-N4 and Cu-N2 bond distances are 1.844(3), 1.848(3), 1.862(3) and 1.850(3) Å respectively. They are in agreement with previously reported structures [16,18,24-25,32,54-55]. The N2-N3 azo distance in Cu(L) is longer (1.302(6) Å) than that of ligand **1**. The O1-Cu-N1, N1-Cu-N2, N2- Cu-N4 and O1-Cu-N4 angles are (differ only slightly from 90°) 90.89(16), 84.31(15), 93.54(15) and 91.35(16)° respectively, and the O1-Cu- N2 (174.16^0), N1-Cu- N4 (177.35^0) angles are close to 180°.

The crystal structure of [Cu(HL)]ClO$_4$ is shown in Fig. 5 along with the atom labels. Hydrogen atoms, perchlorate ion are omitted for the clarity. Selected bond lengths and bond angles are listed in Table 4. The molecular structure of the Cu(II) complex consists of one Cu(II) atom,

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Please insert Fig. 5 and Table 4 here
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one monoanionic ligand unit, and one weakly coordinated perchlorate molecule. The ligand (H_2L) is coordinated with Cu(II) in a monoanionic (HL$^-$) tetra dentate (N,N,N,O) mode, forming two six membered chelate ring and one five membered ring. The environment of the Cu(II) atom could be best described as a slightly distorted square-pyramidal ($\tau = 0.038$) geometry with the metal atom being penta-coordinated [56]. One phenolic oxygen atom (O1), one amine nitrogen, one imine nitrogen atom (N1) and one azo nitrogen of the monoanionic ligand unit constitute the basal plane (Cu–O(1), 1.903(4); Cu–N(4), 1.983(6); Cu–N(1), 1.930(5) and Cu–N(2), 1.985(4) Å), and one O atom (O(2)) of the coordinated perchlorate molecule is occupying the axial position (Cu–O(2),

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2.580(5) Å). It is clear that the axial bond length Cu–O(2) is elongated (due to the Jahn-Teller effect of copper(II)) [43,57]. The bond lengths of Cu–N and Cu–O are similar as those of analogous Cu(II) complexes of salen ligands [16,18,24-25,32]. The dimeric packing structure of [Cu(HL)]ClO$_4$ is stabilized through three-dimensional NH$_2$···O hydrogen bonds to form chair like arrangement (Fig. 6) and crystal packing contains very weak pi-pi interaction (Fig S6).

Please insert Fig. 6 here

3.5. Electrochemistry

The electrochemical behavior of ligand **1** and complexes Cu(L) and [Cu(HL)]ClO$_4$ were investigated in dichloromethane acetonitrile mixed solvent (0.1 M TBAP) by cyclic voltammetry with a scan rate of 0.1 V s^{-1} (Fig. 7) vs. SCE. The cyclic voltammogram of the ligand **1** and complexes (Cu(L) & [Cu(HL)]ClO$_4$) [though coordinated ligand (H$_2$L) is little different from ligand **1**] displayed nearly identical one electron quasi reversible oxidative response at 1.26 V, 0.90 and 0.89 V, respectively. The identical nature of the cyclic voltamogram indicates that oxidation may be ligand centered which is well in agreement with the DFT result.

Please insert Fig. 7 here

According to the DFT results the frontier orbitals of HOMO-1, HOMO, LUMO and LUMO+1 (Fig. S5) of complexes Cu(L) & [Cu(HL)]ClO$_4$ are mostly ligand character signifying the oxidation to be ligand centric.

3.6. Oxidation of thioethers

Catalytic oxidation of sulfides into corresponding sulfoxides and sulfones is an important area in current chemical research [30, 58]. These are generally used as synthetic intermediates for the production of various chemically and biologically significant molecules [59-60], as well as for the synthesis of drugs and natural products [59, 61-62]. Initial investigation of aerobic oxidation

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was carried out using alkyl phenyl sulfide as substrates with (0.014 mmol) catalyst Cu(L) and H_2O_2 under 0°C in dichloromethane methanol (8:2) mixed solvent. Two oxidation products sulfoxide and sulfone are given in scheme 2. The oxidation of phenyl methyl sulfide, as a standard substrate, by aqueous 50% H_2O_2 has been carried out using Cu(L) as catalyst to achieve the optimized reaction conditions. In order to get optimum reaction conditions, amount of catalyst and oxidant were varied while carrying the reaction at 0^0C. Three different amount of catalyst (0.005, 0.014, 0.02 mmol) were used for 3 mmol of phenyl methyl sulfide under above mentioned reaction conditions have been studied. When increasing the catalyst amount from 0.005 to 0.014 mmol the conversion increased (yield 45% to 80%) and nearly the same results were obtained with catalyst 0.02 mmol. It is clear from the above observation 0.014 mmol catalyst is enough to give ~80% conversion in 6 h of reaction time. Similarly, the effect of different H_2O_2 concentration (2, 4, 6 eqv.) on the oxidation of phenyl methyl sulfide have been studied and 4 eqv 50% H_2O_2 is the most appropriate for this oxidation reactions. The products were isolated after separation and characterized by IR spectra. The results of the oxidation products were shown in Table 5. The conversions were calculated on the basis of isolated yields.

Please insert Table 5 & Eq. 1 here

3.7. Oxidation of benzyl alcohol

Oxidation of benzyl alcohol to benzaldehyde is an important organic transformation both at a laboratory and industrial scale [63]. Benzaldehyde is a very essential chemical which has vast applications in perfumery, dyestuff and agro chemical industries [64-65]. In the present study we report the oxidation of four benzyl alcohols having different substituents in the aromatic ring under atmospheric pressure and in absence of any additive other than the substrate, benzyl alcohol, H_2O_2 (50%) and catalyst Cu(L) (Scheme 3). Before detailed study on the catalytic oxidation of substituted benzyl alcohols, initially we first optimized the reaction conditions by choosing benzyl

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alcohol as the model substrate. It was observed that nearly the same yields of benzaldehyde were obtained with catalyst amounts varying from 0.012 - 0.02 mmol. The influence of temperature was studied from 25^0C-100^0C, to obtain the optimum temperature for the oxidation reaction. The oxidation of benzyl alcohol by H_2O_2 at room temperature was very slow (yield ~20%) for 5h. The conversion of benzaldehyde increased above 50^0C. Above 90^0C, there was no significant change in the conversion of benzaldehyde due to the decomposition of H_2O_2 at high temperature. Hence, 75^0C was selected as the optimum temperature. The influence of H_2O_2 concentration on the oxidation reaction was analysed by keeping the other parameters constant. The best yield of benzaldehyde was obtained during the oxidation of benzyl alcohol, with (5 eqv.) 50% H_2O_2 for 2 h. The products were isolated after separation and characterized by IR spectra. The results of the oxidation studies were shown in Table 6. The conversions were calculated on the basis of isolated yields.

Please insert Scheme 3 and Table 6 here
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4. Conclusion

Newly designed multidentate azo ligand has been synthesized by the condensation between 2,2'-diaminoazobenzene and salicylaldehyde. Tetradentate (NNNO) Cu(II) complexes were formed after cleavage of one imine function of the ligand 1. The characterization of the ligand and complexes were accomplished by analytical and spectral data. X-ray crystallographic studies confirmed the coordination mode of the ligand to the metal through NNNO donor and reveal the square planar and square-pyramidal geometry around the copper centers. The redox property and emission behavior of both the ligand and complexes were examined. Plausible descriptions of redox orbitals and electronic spectra have been ascribed on the basis of DFT calculations. Fluorescence intensity of Cu(L) & [Cu(HL)]ClO$_4$ is greatly enhanced due to the formation of stable complexes of Cu(II) ion with ligand. The prepared catalyst gave excellent catalytic activity towards the oxidation

of benzyl alcohol to benzaldeyhde (under solvent-free condition) and organic thioether to sulfoxides and sulfones in presence of H_2O_2 as oxidant under atmospheric condition.

Appendix A. Supplementary data

Figures S1–S3 shows the IR spectra of the ligand and complexes and Figure S4 ^{1}H NMR spectrum of the ligand. CCDC 1572763, 1572729 and 1572762 contains the supplementary crystallographic data for compounds 1, Cu(L) & [Cu(HL)]ClO$_4$. 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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Scheme 1
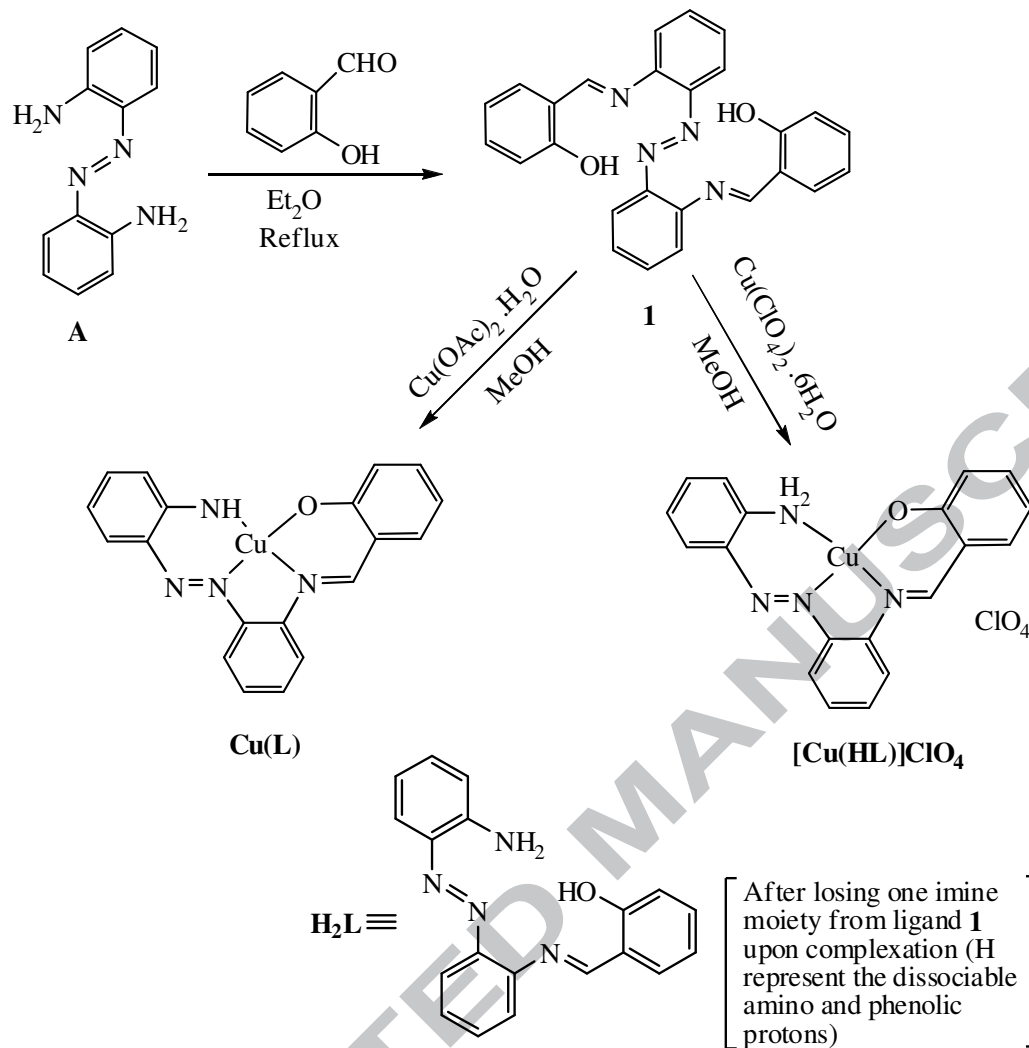
Scheme 1. Synthesis of ligand and copper(II) complexes

Scheme 2
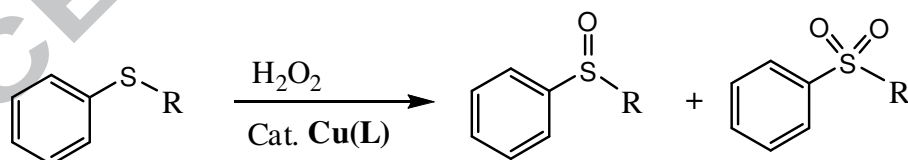
Scheme 2. Catalytic conversion of sulfide to sulfoxide and sulfone

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Scheme 3
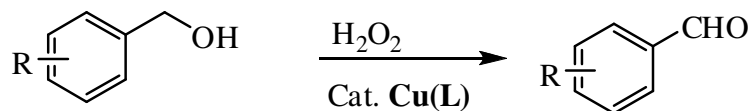
Scheme 3. Catalytic conversion of benzyl alcohol to benzaldehyde

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Table 1

Crystallographic data for **1**, **2a** and **2b**

Parameter	1	Cu(L)	[Cu(HL)]ClO$_4$
Chemical formula	C$_{26}$H$_{20}$N$_4$O$_2$	C$_{19}$H$_{14}$N$_4$OCu	C$_{19}$H$_{15}$N$_4$OCu, ClO$_4$
Formula weight	420.46	377.88	478.34
Crystal system	Orthorhombic	Orthorhombic	Triclinic
space group	P b c a	P 21 21 21	P -1
a/Å	16.5940(4)	5.0203(3)	8.5878(10)
b/Å	11.4449(3)	16.7586(9)	9.6911(11)
c/Å	21.2748(5)	18.4571(12)	12.3511(13)
α/deg	90	90	91.935(6)
β/deg	90	90	95.994(5)
γ/deg	90	90	110.762(5)
λ /Å	0.71073	0.71073	0.71073
V /Å^3	4040.44(17)	1552.85(16)	953.14(19)
F(000)	1760	772	486
Crystal Size [mm]	0.08x0.30x0.44	0.60x0.020x0.010	0.50x0.28x0.040
Z	8	4	2
T/K	180(2)	180(2)	180(2)
D/mg/m^{-3}	1.382	1.616	1.667
μ /mm^{-1}	0.090	1.421	1.328
Theta Min-Max [deg]	2.888, 27.898	2.431, 27.968	2.254, 25.966
Reflections measured	28548	33911	19487
Unique reflections (Rint)	4816	3738	3604
No. of reflections used [I> 2σ(I)]	3307	3056	2450
R1,wR2(all data)	0.0785, 0.1166	0.0592, 0.1123	0.0945, 0.1559
R1, wR2[I> 2σ(I)]	0.0493, 0.1027	0.0424, 0.1053	0.0543, 0.1306
GOF	1.019	1.054	1.070

Table 2

Selected Bond Distances (Å) and Angles (deg) for Compound **1**.

Distances			
O(1)-C(1)	1.349(2)	N(2)-N(3)	1.2460(19)
O(2)-C(22)	1.351(2)	N(3)-C(14)	1.426(2)
N(1)-C(8)	1.406(2)	N(4)-C(20)	1.276(2)
N(1)-C(7)	1.273(2)	N(4)-C(19)	1.410(2)
N(2)-C(13)	1.426(2)	C(6)-C(7)	1.444(2)
Angles			
N(3)-C(14)-C(15)	123.54(14)	C(7)-N(1)-C(8)	123.35(14)
N(3)-N(2)-C(13)	114.33(13)	C(19)-N(4)-C(20)	123.77(14)
N(2)-N(3)-C(14)	114.28(13)	O(1)-C(1)-C(6)	121.71(15)
N(4)-C(19)-C(18)	124.82(14)	N(1)-C(7)-C(6)	120.74(15)
N(4)-C(20)-C(21)	120.94(15)	O(2)-C(22)-C(21)	121.55(15)
N(1)-C(8)-C(13)	116.50(13)	N(3)-C(14)-C(19)	116.27(13)

Table 3

Selected Bond Distances (Å) and Angles (deg) for Compound **Cu(L)**.

Distances			
Cu-O(1)	1.898(3)	N(2)-N(3)	1.302(6)
Cu-N(1)	1.939(4)	N(2)-C(13)	1.416(6)
Cu-N(2)	1.938(3)	N(3)-C(14)	1.429(7)
Cu-N(4)	1.910(4)	N(4)-C(19)	1.292(6)
O(1)-C(1)	1.316(7)	C(1)-C(6)	1.446(7)
N(1)-C(7)	1.285(6)	C(6)-C(7)	1.349(7)
N(1)-C(8)	1.420(6)	C(8)-C(13)	1.399(7)
C(14)-C(19)	1.433(7)		
Angles			
O(1)-Cu-N(1)	90.89(16)	N(1)-Cu-N(4)	177.35(14)
O(1)-Cu-N(2)	174.16(18)	N(2)-Cu-N(4)	93.54(15)
O(1)-Cu-N(4)	91.35(16)	N(1)-C(8)-C(13)	115.1(5)
N(1)-Cu-N(2)	84.31(15)	Cu-O(1)-C(1)	127.9(3)
Cu-N(1)-C(7)	130.8(3)	N(2)-C(13)-C(8)	115.1(4)
Cu-N(1)-C(8)	112.6(3)	Cu-N(2)-N(3)	126.0(3)
Cu-N(2)-C(13)	112.8(3)	Cu-N(4)-C(19)	127.8(3)
N(1)-C(7)-C(6)	121.3(4)	N(2)-N(3)-C(14)	124.0(5)

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Table 4

Selected Bond Distances (Å) and Angles (deg) for Compound [**Cu(HL)]ClO₄**.

Distances			
Cu-O(1)	1.903(4)	Cu-N(1)	1.930(5)
N(3)-C(14)	1.407(7)	O(1)-C(1)	1.321(7)
Cu-O(2)	2.580(5)	Cu-N(2)	1.985(4)
N(2)-N(3)	1.259(7)	N(4)-C(15)	1.438(8)
Cu-N(4)	1.983(6)	Cl-O(3)	1.418(5)
Cl-O(2)	1.433(5)	Cl-O(4)	1.421(4)
N(1)-C(8)	1.420(6)	Cl-O(5)	1.396(5)
N(1)-C(7)	1.286(7)	N(2)-C(13)	1.426(7)
C(14)-C(15)	1.400(7)	C(1)-C(6)	1.408(8)
C(6)-C(7)	1.419(7)	C(8)-C(13)	1.402(8)
Angles			
O(1)-Cu-N(1)	95.21(16)	O(1)-Cu-O(2)	84.53(16)
O(1)-Cu-N(2)	176.81(18)	O(2)-Cu-N(1)	92.68(18)
O(1)-Cu-N(4)	90.26(18)	O(2)-Cu-N(2)	98.17(17)
O(1)-C(1)-C(6)	124.2(4)	O(2)-Cu-N(4)	87.4(2)
N(1)-Cu-N(2)	83.01(18)	N(2)-Cu-N(4)	91.5(2)
N(1)-Cu-N(4)	174.52(19)	O(2)-Cl-O(3)	107.5(3)
N(1)-C(7)-C(6)	125.6(5)	Cu-O(1)-C(1)	125.4(3)
N(1)-C(8)-C(13)	115.3(5)	Cu-O(2)-Cl	118.3(3)
Cu-N(1)-C(7)	124.7(3)	Cu-N(1)-C(8)	114.2(3)
Cu-N(2)-N(3)	132.0(4)	Cu-N(2)-C(13)	112.7(3)
N(2)-N(3)-C(14)	119.6(5)	Cu-N(4)-C(15)	120.9(4)

Table 5

Oxidation of sulfides catalyzed by **Cu(L)** in dichloromethane methanol (8:2) mixed solvent
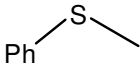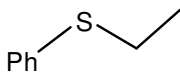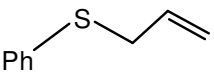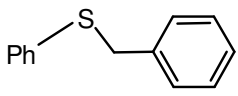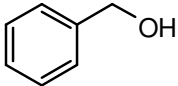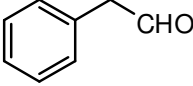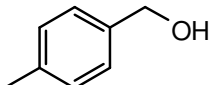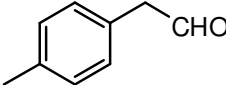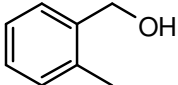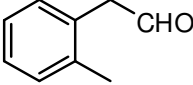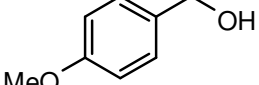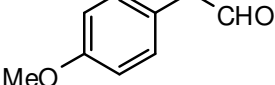
Entry	Equiv H_2O_2 (50%)	Time (h)	Yield (%)	
			Sulfoxide	Sulfone
Ph–S–CH₃	4	6	40	35
Ph–S–CH₂CH₃	4	6	36	42
Ph–S–CH₂CH=CH₂	4	6	38	42
Ph–S–CH₂–C₆H₅	4	6	32	45

Table 6

Oxidation of alcohol catalyzed by **Cu(L)**

Entry	Product	Equiv H_2O_2 (50%)	Time (h)	Yield (%)
benzyl alcohol	phenylacetaldehyde (CHO)	5	2	90
4-methylbenzyl alcohol	4-methyl CHO	5	2	85
2-methylbenzyl alcohol	2-methyl CHO	5	2	87
4-methoxybenzyl alcohol (MeO)	4-methoxy CHO (MeO)	5	2	78

Fig. 1 UV-Vis spectra of **1** (—), **Cu(L)** (—) and **[Cu(HL)]ClO₄** (—) in dichloromethane
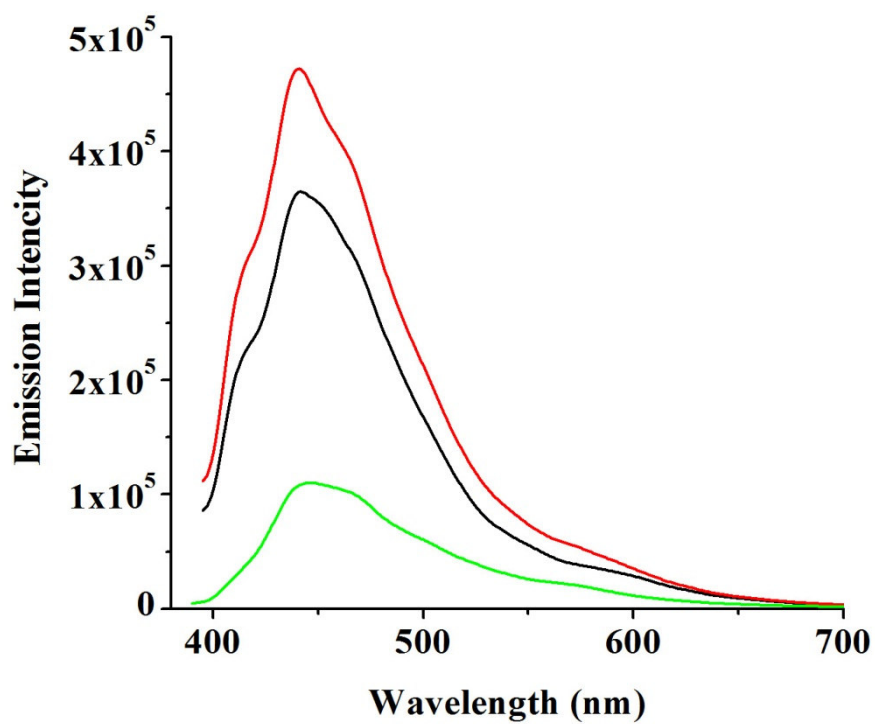
Fig. 2 Emission spectra of **1** (—), **Cu(L)** (—) and **[Cu(HL)]ClO₄** (—) in chloroform.
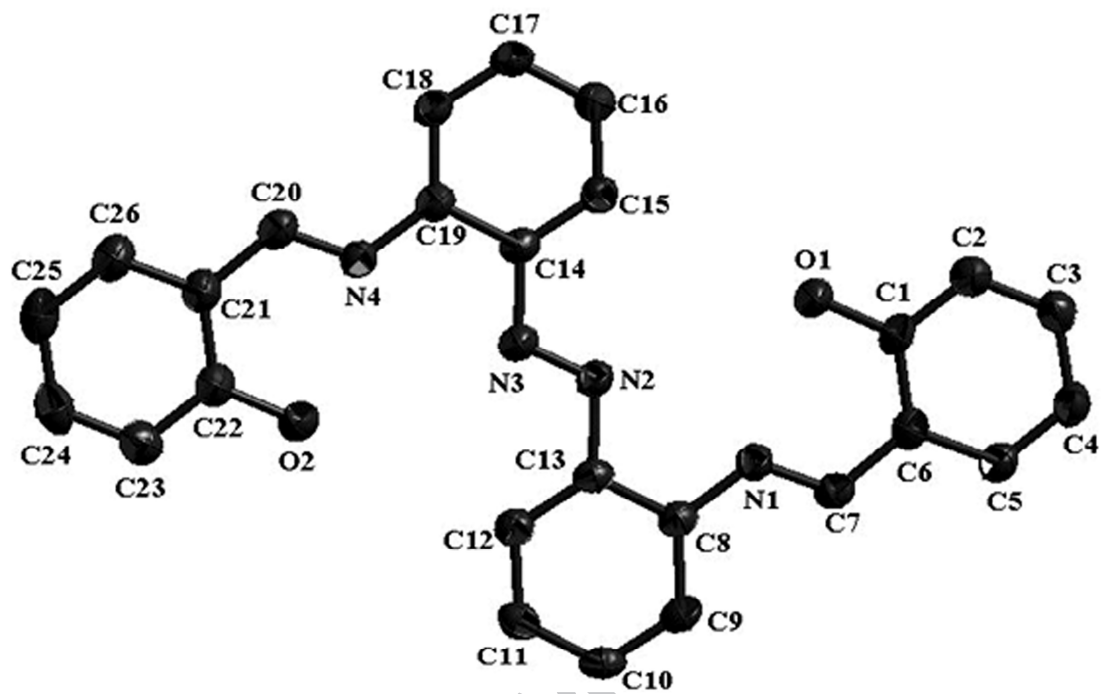
Fig. 3 Molecular structure of **1** (40% probability ellipsoids) with atom numbering scheme. Hydrogen atoms are omitted for clarity.
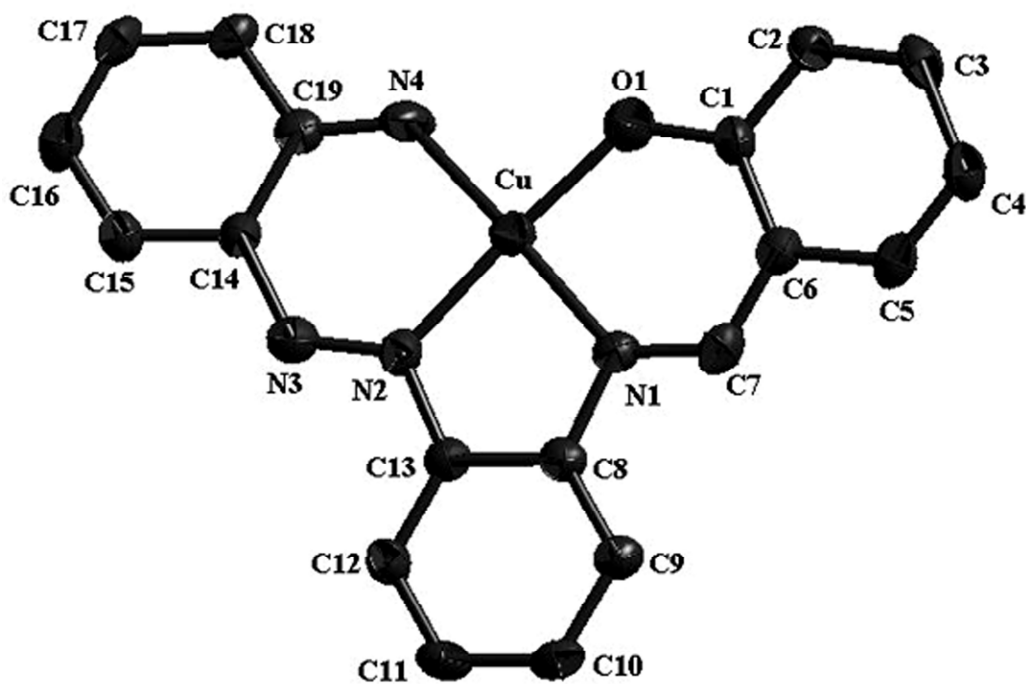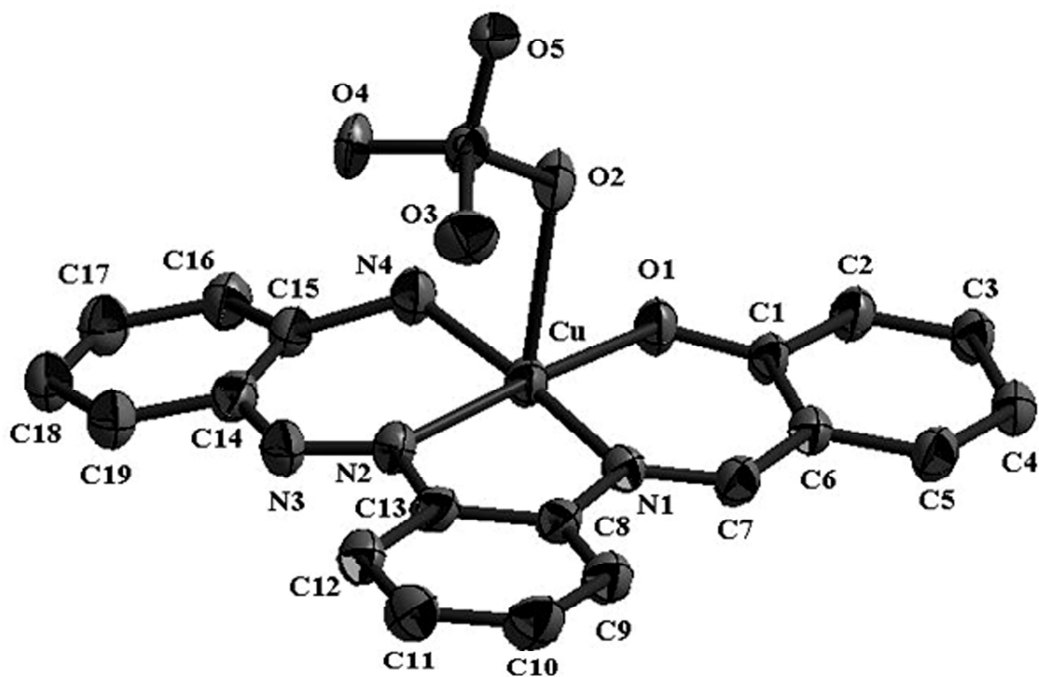
Fig. 4 Molecular structure of **Cu(L)** (40% probability ellipsoids) with atom numbering scheme. Hydrogen atoms are omitted for clarity.

Fig. 5 Molecular structure of [**Cu(HL)**]**ClO₄** (50% probability ellipsoids) with atom numbering scheme. Hydrogen atoms are omitted for clarity.
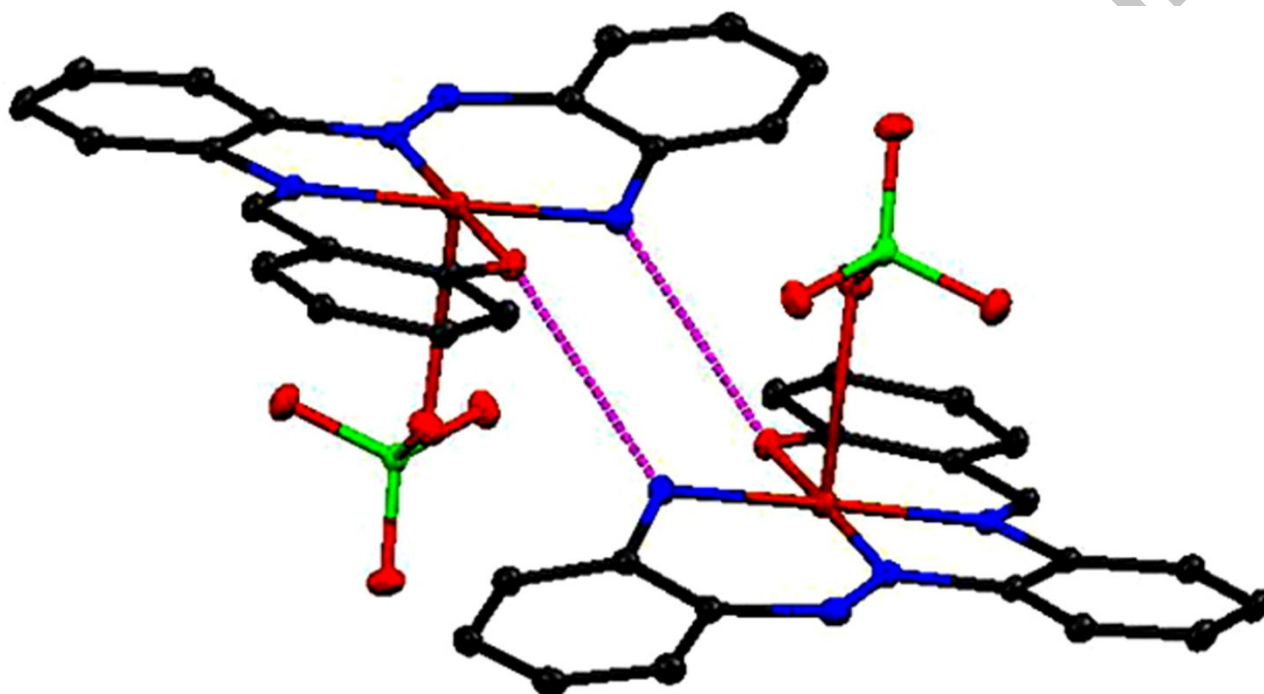
Fig. 6 Dimeric hydrogen bonded structure of [**Cu(HL)]ClO₄**. (····) Lines indicate Hydrogen bonds.
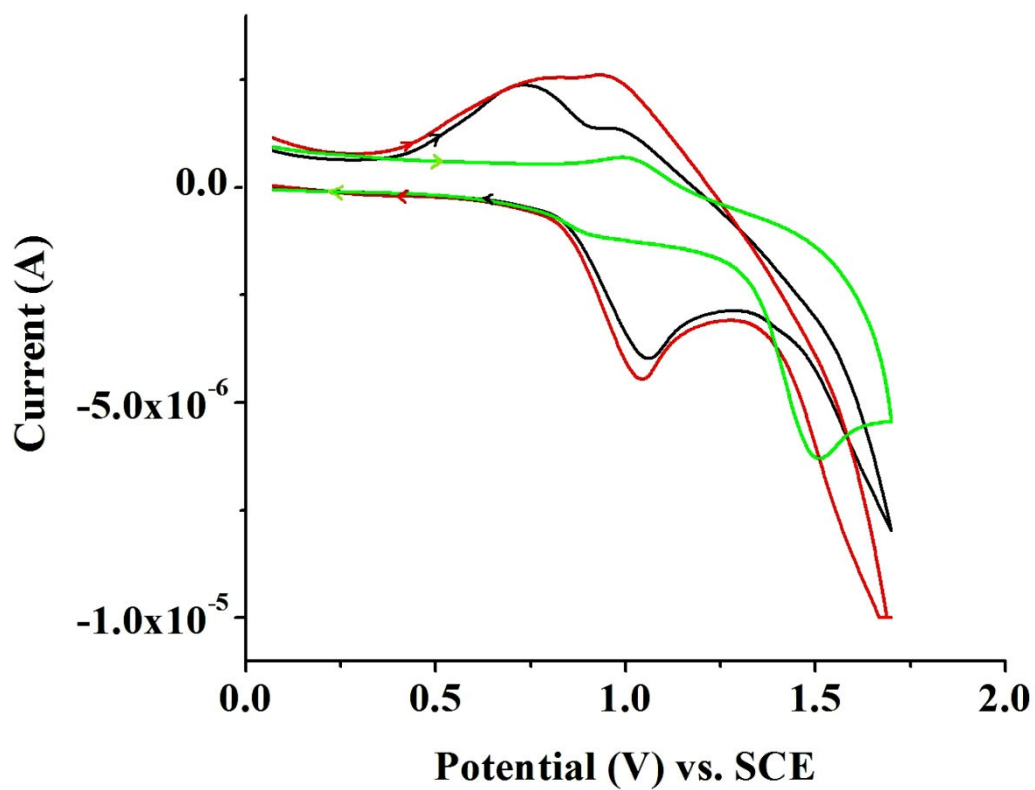
Fig. 7 CV of **1** (—),**Cu(L)** (—) and **[Cu(HL)]ClO₄** (—) in dichloromethane acetonitrile mixed solvent.

Graphical Abstract Synopsis

Synthesis, characterization, spectral and catalytic activity of tetradentate (NNNO) azo-imine Schiff base copper(II) complexes

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[a]Department of Chemistry, Kandi Raj College, Murshidabad 742137, India

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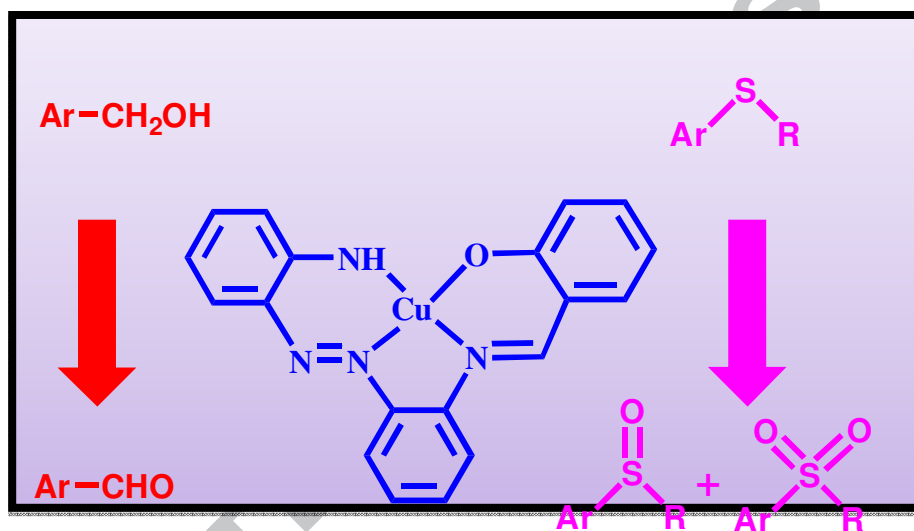
Synthesis of newly designed multidentate ligand and its copper(II) complexes. The fluorescence and redox property of both the ligand and complex were examined. Tetradentate azosalophen type Cu(II) complexes were formed after cleavage of one imine function of ligand. The complex **Cu(L)** exhibited an excellent catalytic activity toward oxidation of organic thioethers to sulfoxide and sulphone and benzyl alcohol to benzaldeyhde.

Research Highlights

1. Synthesis of a new multidentate azo Schiff base ligand.

2. Isolation, characterization and structure of new azo-aldimine complexes of Copper(II).

3. The emission and redox properties of both the ligand and complex.

4. Catalytic activity of complex Cu(L) toward H_2O_2 induced oxidation of benzyl alcohol to benzaldeyhde and organic thioethers to sulfoxide and sulfones.

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