

Synthesis and structure of copper(II) complexes: Potential cyanide sensor and oxidase model

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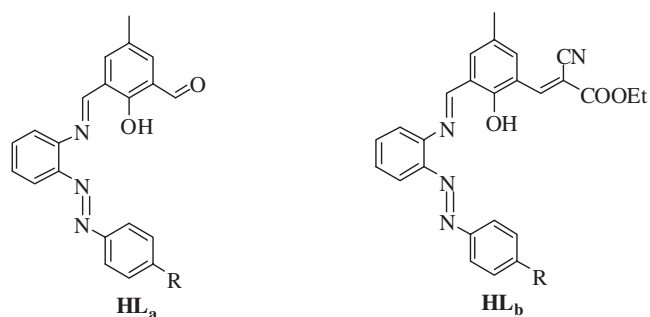
MS received 9 October 2015; revised 5 January 2016; accepted 17 February 2016

Abstract. The new complexes of compositions $[(L_a)_2Cu]$ and $[(L_b)_2Cu]$ were prepared by treating with 2-hydroxy-5-methyl-3-(2-aryldiazenyl)phenylimino) methyl) benzaldehyde (HL_a) and ethyl-2-cyano-3-(2-hydroxy-5-methyl-3-(2-aryldiazenyl) phenylimino) methyl) phenyl) acrylate (HL_b) ligands [where aryl is phenyl for HL_a^1 and HL_b^1 ; *p*-methyl phenyl for HL_a^2 and HL_b^2 ; and *p*-chloro phenyl for HL_a^3 and HL_b^3] with $Cu(OAc)_2 \cdot H_2O$, respectively. Both the bis copper(II) complexes consist of tridentate (N,N,O) anionic ligands, L_a^- or L_b^- . X-ray structures of the representative complexes $[(L_a^1)_2Cu]$ and $[(L_b^2)_2Cu]$ were determined to confirm the molecular species unequivocally. The molecular structure of copper complexes exhibited tetragonally distorted (Jahn-Teller) geometry consistent with the d^9 configuration of Cu(II) metal ion. Oxidation of benzyl alcohols using the newly synthesized complexes as catalyst has been studied. Photoluminescence properties of $[(L_a^2)_2Cu]$ and $[(L_b^2)_2Cu]$ were exploited for selective cyanide recognition. The $[(L_b)_2Cu]$, complexes displayed antibacterial activity toward gram positive and gram negative bacteria.

Keywords. 2-hydroxy-5-methyl-3-(2-aryldiazenyl)phenylimino) methyl) benzaldehyde; ethyl-2-cyano-3-(2-hydroxy-5-methyl-3-(2-aryldiazenyl)phenylimino) methyl) phenyl) acrylate, X-ray structure; tridentate (N,N,O); photoluminescence.

1. Introduction

The chemistry of transition metal complexes incorporating azo ligands have been explored considerably during the last few decades.^{1–19} Several chemical properties of copper complexes have been attributed to easy accessibility to Cu(I), Cu(II) and Cu(III) oxidation states.^{3,20–38} Although a few studies on the coordination chemistry of copper using several kinds azo ligands have been reported^{3,39–45} but azo ligands have never been used for the synthesis of copper complexes targeting the oxidase models. The necessity to make progress in developing copper oxidase models requires synthesis of appropriate copper complexes to rationalize the functions of such oxidases unequivocally.^{46–52} Therefore, to study the coordination chemistry of Cu(II) incorporating the new azo ligands,⁵³ HL_a and HL_b , with the fidelity of oxidase models, is expected to be interesting.



Structures of HL_a and HL_b

In addition, the chemistry of copper complexes incorporating azo-salen ligands, such as HL_a and HL_b , is hitherto unknown. Amongst the natural copper containing metalloenzymes having oxidase activity, the notable examples are tyrosinase or galactose oxidase (GO) that are involved in physiological oxygenation or the electronic oxidations of substrates respectively.^{54–57} One of the functions played by GO is the oxidation of 1°- alcohols to produce aldehydes in homogenous media under aerobic condition where dioxygen is the oxidant.^{54,55,58}

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The copper complexes under N_2O_2 coordination sphere where the ligands had *ortho* or *para* alkyl sulfanyl substituent as spectator, in terms of coordination to the metal centre, and both the O-donors were phenolato oxygen and both the N-donors were aldimino-N had exhibited GO activity.⁵⁹ Encouraged by these, HL_a and HL_b , were expected to be a potential ligands for the synthesis of copper complexes having catalytic property to oxidize primary alcohol to aldehyde since they are potential N,O donor ligands having substituents at the *ortho* position with respect to phenolic group.

Recently, we have shown that the Ni(II) complexes of HL_a and HL_b ligands can be the utilized for the selective recognition of cyanide ion.⁵³ Therefore, we were also motivated to assess the emission properties of new copper complexes for screening the cyanide recognition property.

Herein, the synthesis and structure of a new family of Cu(II) complexes incorporating HL_a and HL_b ligands have been described. The new copper complexes, $[(L_a^2)_2Cu]$ and $[(L_b^2)_2Cu]$, have been screened to examine the catalytic activity toward oxidation of benzyl alcohols, cyanide recognition property and antibacterial activity of $[(L_b^2)_2Cu]$ against gram positive and gram negative bacteria.

2. Experimental

2.1 Materials and methods

The solvents used for all the reactions were of reagent grade (E.Merck, India) and were purified and dried by reported procedure.⁶⁰ 2-(Arylazo) anilines were prepared according to the reported procedure.⁶¹ Copper acetate monohydrate was purchased from Sisco Research Laboratories (SRL), India. The ligands were prepared following the reported procedure.⁵³ 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 Parkin-Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1800 PC spectrophotometer.

2.2 Syntheses of $[(L_a)_2Cu]$ complexes

The complexes $[(L_a^1)_2Cu]$, $[(L_a^2)_2Cu]$, and $[(L_a^3)_2Cu]$, were prepared by similar procedure a representative example for $[(L_a^1)_2Cu]$, given below.

2.2a $[(L_a^1)_2Cu]$: To a methanolic solution of copper acetate (0.058 g, 0.29 mmol), the ligand HL_a^1 (0.002 g, 0.58 mmol) was added and the mixture was then stirred

for 3 h. Brownish precipitate was obtained. The precipitate was dissolved in dichloromethane to form deep brown color and layered with hexane. After evaporating the solvent, fine crystals were obtained. The yield was 180 mg (40%). Anal. Calc. (%) for $C_{42}H_{32}CuN_6O_4$ (748): C 67.42, H 4.28, N 11.23. Found (%): C 67.35, H 4.35, N 11.30. UV/Vis spectrum (CH_2Cl_2) λ_{max} (ϵ , $M^{-1}cm^{-1}$): 432 (7681), 291 (65201), 236 (29430). IR (KBr, cm^{-1}): $\nu = 1619$ s, 1446 s, 1665 s.

2.2b $[(L_a^2)_2Cu]$ and $[(L_a^3)_2Cu]$: The $[(L_a^2)_2Cu]$ and $[(L_a^3)_2Cu]$ complexes were prepared following similar procedure as described for $[(L_a^1)_2Cu]$ using HL_a^2 and HL_a^3 in place of HL_a^1 ligand. Yield: 0.185 g (42%) and 0.175 g (40%), respectively. Anal. Calc. (%) for $C_{44}H_{36}CuN_6O_4$ (776): C 68.07, H 4.67, N 10.13. Found (%): C 68.10, H 4.62, N 10.15. UV/Vis spectrum (CH_2Cl_2) λ_{max} (ϵ , $M^{-1}cm^{-1}$): 433 (9376), 310 (39075), 235 (42535). IR (KBr pellets, cm^{-1}): $\nu = 1618$ s, 1446 s, 1664 s. Anal. Calcd. (%) $C_{42}H_{30}CuN_6O_4Cl_2$ (817): C 61.72, H 3.67, N 10.28. Found (%): C 61.85, H 3.45, N 10.50. UV/Vis spectrum (CH_2Cl_2) λ_{max} (ϵ , $M^{-1}cm^{-1}$): 435 (9406), 312 (39086), 238 (42555). IR (KBr, cm^{-1}): $\nu = 1619$ s, 1436 s, 1671 s.

2.3 Syntheses of $[(L_b)_2Cu]$ complexes

The complexes, $[(L_b^1)_2Cu]$, $[(L_b^2)_2Cu]$, and $[(L_b^3)_2Cu]$, were prepared by similar procedure used for the representative example $[(L_b^1)_2Cu]$, described below.

2.3a $[(L_b^1)_2Cu]$: A 5 mL methanolic solution of $Cu(OAc)_2 \cdot H_2O$ (0.045 g, 0.23 mmol), 10 mL methanol solution of HL_b^1 (0.002 mg, 0.456 mmol) was added and the mixture was stirred for 2 h. Dark brown product was precipitated which was collected by filtration and was washed with petroleum ether and hexane. The precipitate was then recrystallized from a dichloromethane-hexane solvent mixture. Yield: 0.180 g (42%). Anal. calc. (%) for $C_{52}H_{42}CuN_8O_6$ (938): C, 66.55; H, 4.51; N, 11.94. Found (%): C, 66.52; H, 4.54; N, 11.90. UV/Vis spectrum (CH_2Cl_2) λ_{max} (ϵ , $M^{-1}cm^{-1}$): 475 (5740), 293 (16380), 230 (15800), IR (KBr, cm^{-1}): $\nu = 1616$ s, 1476 s, 1692 s, 2220 s.

2.3b $[(L_b^2)_2Cu]$, and $[(L_b^3)_2Cu]$: Complexes $[(L_b^2)_2Cu]$, and $[(L_b^3)_2Cu]$ were synthesized following the same procedure as for complex $[(L_b^1)_2Cu]$ using HL_b^2 and HL_b^3 in place of HL_b^1 respectively. Yield: 0.210 g (50%) and Yield: 0.215 g (51%), respectively. Anal. calc. (%) for $C_{54}H_{46}CuN_8O_6$ (967): C, 67.10; H, 4.80; N, 11.59. Found (%): C, 67.12; H, 4.76; N, 11.55. UV/Vis spectrum (CH_2Cl_2) λ_{max} (ϵ , $M^{-1}cm^{-1}$): 474

(5270), 296 (16850), 238 (11240), IR (KBr, cm^{-1}): $\nu = 1617\text{ s}, 1475\text{ s}, 1674\text{ s}, 2219\text{ s}$.

Anal. calc. (%) for $\text{C}_{52}\text{H}_{40}\text{Cl}_2\text{CuN}_8\text{O}_6$ (1005): C, 62.00; H, 4.00; N, 11.12. Found (%): C, 61.98; H, 3.95; N, 11.15. UV/Vis spectrum (CH_2Cl_2) λ_{max} (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 476 (5330), 309 (18700), 240 (10400), IR (KBr, cm^{-1}): $\nu = 1616\text{ s}, 1474\text{ s}, 1703\text{ s}, 2220\text{ s}$.

2.4 X-ray structure determination of $[(L_a^1)_2\text{Cu}]$ and $[(L_b^2)_2\text{Cu}]$

Single Crystals of $[(L_a^1)_2\text{Cu}]$ and $[(L_b^2)_2\text{Cu}]$ were grown by slow diffusion of hexane in dichloromethane solution at 25°C . Data were collected on a Bruker SMART CCD diffractometer using Mo- $\text{K}\alpha$ monochromator ($\lambda = 0.71073$). Structure solutions were performed using Shellx 97 PC version program.⁶² Full matrix least square refinements on F2 were performed using SHELXL-97 program.⁶³ All the non-hydrogen atoms were refined anisotropically using full-matrix least squares method. Hydrogen atoms were included for structure factor calculations after placing them at calculated positions. Atomic coordinates and isotropic thermal parameters of $[(L_a^1)_2\text{Cu}]$ and $[(L_b^2)_2\text{Cu}]$ are given in table 1.

2.5 Procedure for the catalytic oxidation of benzyl alcohol

A mixture of benzyl alcohol (0.5 mmol), catalyst $[(L_a^1)_2\text{Cu}]$ (4 mol%) or $[(L_b^2)_2\text{Cu}]$ (4 mol%) and 30% H_2O_2 (5 equiv.) was taken in 10 mL acetonitrile solvent

in a round bottom flask. The mixture was vigorously stirred at 70°C for 1 h. The reaction was monitored by TLC. After completion of the reaction, the solvent was removed, the organic phase was separated and dried over Na_2SO_4 and the product was purified by column chromatography (hexane/ethyl acetate). Yields were determined by weighing the isolated product, which was characterized by ^1H NMR and IR spectroscopy.

2.6 General procedure for Photoluminescence studies

Stock solutions of the complexes ($[(L_a^1)_2\text{Cu}]$ and $[(L_b^2)_2\text{Cu}]$) were prepared in CH_3CN (mixed with 0.1-0.2% DMSO) solvent in the concentration range $\sim 10^{-5}$ M. Stock solutions of tetra butyl ammonium anions (F^- , Cl^- , Br^- , I^- , CN^- , ClO_4^- , OAc^- , HSO_4^- and H_2PO_4^-) were prepared in the same solvent in the concentration range $\sim 10^{-3}$ M. For each measurement 2 mL solution was taken in the cuvette. Solutions of anions, in μL , were added to these 2 mL solutions to study the effect of anion.

2.7 Microbial activity

The metal Complex $[(L_b^2)_2\text{Cu}]$ and a reference commercial antibiotic (antibacterial drug) viz. Chloramphenicol were tested *in vitro* to assess their growth inhibitory activity against human pathogenic two Gram positive bacteria, viz. *Bacillus subtilis* (MTCC 441), *Staphylococcus aureus* (MTCC 2522) and three Gram negative bacteria viz. *Pseudomonas aeruginosa* (MTCC 741), *Shigella dysenteriae* (Clinical isolate) and *Escherichia*

Table 1. Crystallographic data for $[(L_a^1)_2\text{Cu}]$ and $[(L_b^2)_2\text{Cu}]$.

	$\text{C}_{42}\text{H}_{32}\text{CuN}_6\text{O}_4$	$\text{C}_{54}\text{H}_{46}\text{CuN}_8\text{O}_6$
Chemical formula	$\text{C}_{42}\text{H}_{32}\text{CuN}_6\text{O}_4$	$\text{C}_{54}\text{H}_{46}\text{CuN}_8\text{O}_6$
Formula weight	748.29	1006.56
Crystal system	Triclinic	monoclinic
space group	P-1(No. 2)	C2/c (No. 15)
$a/\text{\AA}$	7.4448(5)	19.934(4)
$b/\text{\AA}$	10.1717(7)	15.387(3)
$c/\text{\AA}$	12.8503(8)	15.768(3)
α/deg	97.7210(10)	90
β/deg	106.8260(10)	97.961(4)
γ/deg	109.9320(10)	90
$\lambda/\text{\AA}$	0.71073	0.71073
$V/\text{\AA}^3$	845.78(10)	4789.8(16)
F(000)	387	2092
Z	1	4
T/K	293	293
$D/\text{mg}/\text{m}^{-3}$	1.469	1.396
μ/mm^{-1}	0.701	0.521
R1(all data)	0.0330	0.0609
wR2[$I > 2\sigma(I)$]	0.0936	0.1959
GOF	1.04	0.98

coli (MTCC 443). All the bacterial strains except *Shigella dysenteriae* were obtained from the Institute of Microbial Technology, Chandigarh, India. The antibacterial tests were carried out by disc diffusion method⁶⁴ using 100 μ L of the suspension containing 10^8 CFU/mL of bacteria (turbidity of 0.5 MacFarland standards) on nutrient agar. The discs (6 mm in diameter) were impregnated with 60 μ g/disc placed on the inoculated agar. Negative controls were prepared using 100% DMSO. Chloramphenicol (10 μ g per disc) was used as positive reference standard to determine the sensitivity of each bacterial species tested. The inoculated plates were incubated at 37°C for 24 h. The antibacterial activity was evaluated by measuring the zone of inhibition, the diameters of these zones being measured in millimeters against the test organisms.

The minimal inhibitory concentration (MIC) values were followed with the bacteria strains sensitive to the metal complex in the disc diffusion assay. The MIC was defined as the lowest concentration of the compound to inhibit the growth of microorganisms. The metal complex was dissolved in 10% DMSO, first diluted to the highest concentration (1000 μ g/mL) to be tested, and then serial twofold dilutions were made in order to obtain a concentration range from 3.9 to 1000 μ g/mL in 10 mL sterile test tubes containing the nutrient broth. MIC values of the metal complex against bacterial strains were determined based on the micro well dilution method as previously described.⁶⁵ Each plate was covered with a sterile plate sealer and then incubated at the appropriate temperature 37°C for 24 h. The bacterial growth was determined by absorbance measured at 600 nm using the ELx 800 universal microplate reader (Biotek Instrument Inc., Winooski, USA).

3. Results and Discussion

3.1 Syntheses

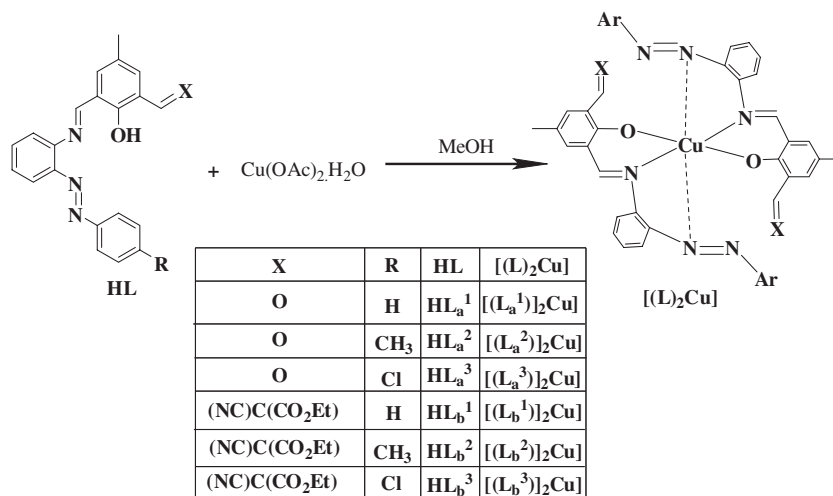
The reactions of the new HL_a and HL_b ligands with Cu(OAc)₂·H₂O in methanol afforded brown complexes of compositions [(L_a)₂Cu] and [(L_b)₂Cu], respectively (scheme 1). Both the complexes were paramagnetic matching with one unpaired electron as expected for Cu(II) metal ions. The suitable crystals of [(L_a¹)₂Cu] and [(L_b²)₂Cu] complexes for x-ray studies were grown from dichloromethane-hexane solvent mixture.

3.2 Characterization

The electronic spectra of [(L_a)₂Cu] and [(L_b)₂Cu] are distinctly different from the ligand HL_a and HL_b where the lowest energy absorption appeared near 432 nm and 475 nm, respectively.⁵³ Representative UV-Vis spectra of HL_a¹, HL_b², [(L_a¹)₂Cu] and [(L_b²)₂Cu] are shown in figure 1. Spectral data are given in the Experimental section.

The $\nu_{C=N}$ of [(L_a)₂Cu] complexes appear in the lower range (1618–1620 cm^{-1}) compared to the ligand signifying the coordination to the metal centre. The $\nu_{N=N}$ band of the ligand ($\sim 1468 \text{ cm}^{-1}$) shifts to lower frequency after formation of the [(L_a)₂Cu] complex (1446 cm^{-1}), consistent with coordination with azo nitrogen. The UV-Vis spectra of [(L_a)₂Cu] and [(L_b)₂Cu] are given in Supplementary Information (figures S1–S6).

The characteristic stretching frequencies of the $\nu_{C=N}$ in [(L_b)₂Cu] shifted to lower values at 1616 cm^{-1} compared to the ligand ($\sim 1620 \text{ cm}^{-1}$) due to coordination



Scheme 1. Preparation and structure of Complexes.

to the metal centre. The $\nu_{N=N}$ of complex $[(L_b)_2Cu]$ was shifted at 1476 cm^{-1} with respect to ligand ($\sim 1480\text{ cm}^{-1}$) indicating coordination of azo nitrogen. The relevant IR data are collected in experimental section. The IR spectra of $[(L_a)_2Cu]$ and $[(L_b)_2Cu]$ are given in Supplementary Information (figures S7–S12).

3.3 X-ray structure of $[(L_a^1)_2Cu]$ and $[(L_b^2)_2Cu]$

Suitable crystals of $[(L_a^1)_2Cu]$ and $[(L_b^2)_2Cu]$ were grown by slow diffusion of hexane into dichloromethane solution. The X-ray structure of $[(L_a^1)_2Cu]$ and $[(L_b^2)_2Cu]$ were determined and described below.

The perspective views of $[(L_a^1)_2Cu]$ and $[(L_b^2)_2Cu]$ complexes are shown in figures 2a and 2b. Selected bond parameters of $[(L_a^1)_2Cu]$ and $[(L_b^2)_2Cu]$ complexes are listed in table 2 and table 3, respectively.

In each complex, the Cu centre is coordinated by two phenolato oxygens (O1 or O_{ph}), two azomethine

nitrogen (N3 or N_{im}) and two distal azo nitrogen (N2 or N_{azo}) signifying the tetragonally distorted octahedral geometry around copper(II) consistent with the Jahn-Teller distortion in d^9 ion.^{66–68} The elongated bond distances are given in structure I below. The asymmetric unit of both the complexes consist of half molecule where Cu(II) occupies the special position. Considering tridentate mode of coordination of the deprotonated anionic ligands, $(L_a^1)^-$ and $(L_b^2)^-$, are facially oriented forming *bis* complexes. Cu-N_{im} ($1.977(1)\text{ \AA}$ for $[(L_a^1)_2Cu]$ and $1.960(3)\text{ \AA}$ for $[(L_b^2)_2Cu]$) and Cu-O_{ph} ($1.921(2)\text{ \AA}$ for $[(L_a^1)_2Cu]$ and $1.938(4)\text{ \AA}$ for $[(L_b^2)_2Cu]$) distances are within the normal range.^{69,70} Although the disordered methanol solvent (Oxygen is in special position and disordered as well) for $[(L_b^2)_2Cu]$ could not be refined satisfactorily but that did not cause much difficulty toward unequivocal characterization of the complex.

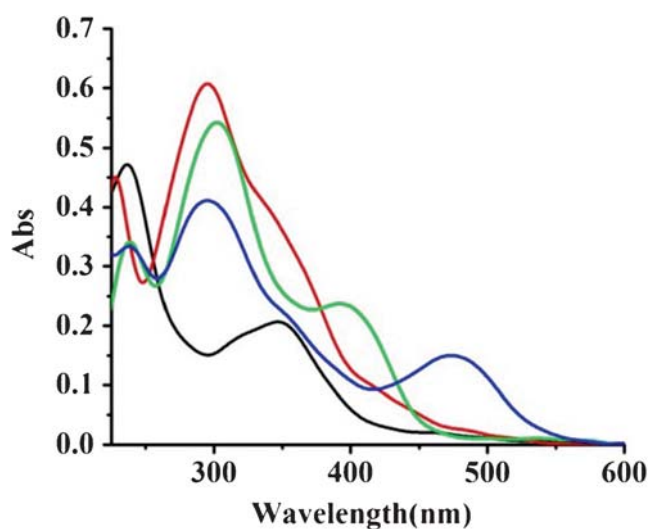
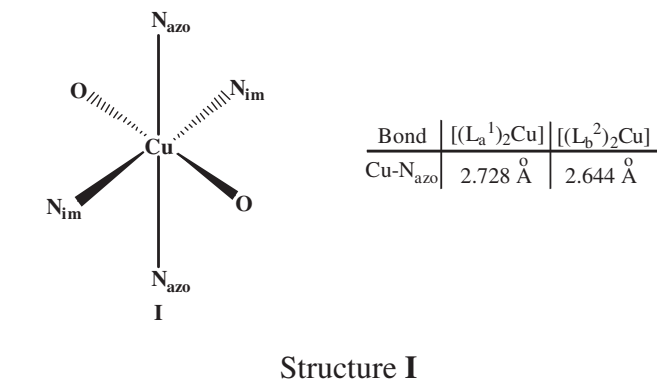
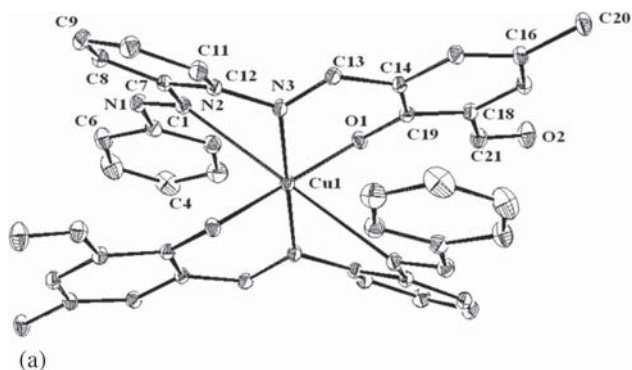


Figure 1. UV-Vis spectra of HL_a^1 (—), HL_b^2 (—), $[(L_a^1)_2Cu]$ (—) and $[(L_b^2)_2Cu]$ (—).



3.4 Selective oxidation of Benzyl alcohol

One of the important activity of Galactose Oxidase (GO) involves the oxidation of alcohols to carbonyl compounds (aldehyde or ketones).^{59,71} Several Cu(II)

Figure 2. Perspective view of (a) $[(L_a^1)_2Cu]$ and (b) $[(L_b^2)_2Cu]$ with atom numbering scheme. The hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound $[(L_a^1)_2Cu]$.

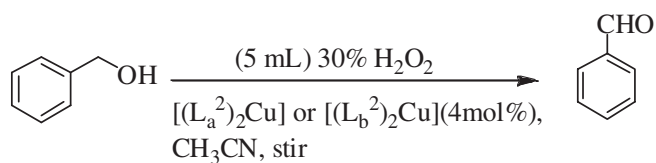
Distances			
Cu1-N2	2.7277(15)	N1-C1	1.420(2)
Cu1-N3	1.9770(14)	N2-C7	1.429(2)
Cu1-O1	1.9212(10)	N3-C12	1.423(2)
O1-C19	1.2991(17)	N3-C13	1.2883(19)
C1-C2	1.396(2)	C14-C15	1.3988(19)
C1-C6	1.392(2)	C14-C19	1.431(2)
C2-C3	1.382(3)	C18-C19	1.423(2)
C5-C6	1.383(3)	C18-C21	1.466(2)
N1-N2	1.2516(19)	O2-C21	1.215(2)
Angles			
O1-Cu1-N2	105.67(5)	N2-C7-C12	116.35(14)
O1-Cu1-N3	89.33(5)	C13-C14-C19	121.45(12)
N2-Cu1-N3	67.99(5)	O1-C19-C18	120.28(14)
Cu1-O1-C19	120.86(10)	O1-C19-C14	123.35(14)
Cu1-N2-N1	140.25(12)	N1-N2-C7	113.27(14)
Cu1-N2-C7	99.38(9)	C12-N3-C13	118.64(14)
N2-N1-C1	114.71(14)	N1-C1-C2	125.35(14)
Cu1-N3-C12	119.27(9)	N1-C1-C6	114.22(15)
Cu1-N3-C13	122.07(12)	C2-C1-C6	120.36(16)
N2-C7-C8	123.79(14)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound $[(L_b^2)_2Cu]$.

Distances			
Cu1-N2	2.644(3)	N1-N2	1.253(4)
Cu1-N3	1.960(3)	N3-C9	1.422(5)
Cu1-O1	1.938(3)	N3-C14	1.289(5)
O1-C20	1.307(4)	N4-C24	1.135(6)
O2-C25	1.218(5)	C8-C9	1.398(5)
O3-C25	1.335(5)	C14-C15	1.441(6)
O3-C26	1.450(5)	C15-C20	1.438(5)
N2-C8	1.443(5)	C19-C20	1.424(6)
Angles			
O1-Cu1-N2	102.41(11)	N2-C8-C9	115.2(4)
O1-Cu1-N3	88.93(12)	N2-C8-C13	124.4(3)
N2-Cu1-N3	69.16(11)	N3-C9-C8	117.7(3)
Cu1-N2-N1	138.1(2)	N3-C9-C10	122.5(3)
Cu1-N2-C8	99.6(2)	N3-C14-C15	123.3(4)
Cu1-N3-C9	118.7(2)	C14-C15-C20	121.4(3)
Cu1-N3-C14	121.3(3)	O1-C20-C15	122.3(4)
Cu1-O1-C20	117.2(2)	O1-C20-C19	120.0(3)

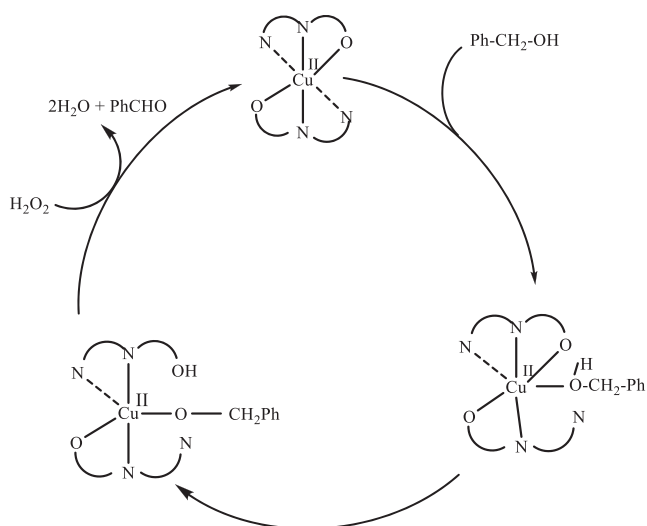
complexes, mimicking the GO models, have been used as catalyst for the oxidation of 1°-alcohols to aldehyde.^{58,72} Selective oxidation of alcohols to the corresponding carbonyl compounds (aldehyde or ketones) is an important and widely used reaction in laboratory scale organic synthesis as well as in large scale in chemical industry.⁷³⁻⁷⁶ These background information prompted us to examine the oxidase activity of $[(L_a^2)_2Cu]$ and $[(L_b^2)_2Cu]$. Oxidation of benzyl alcohol to benzaldehyde by the oxidant H_2O_2 (30%) in the presence of catalytic amount of $[(L_a^2)_2Cu]$ or $[(L_b^2)_2Cu]$

complex have been studied Eq. (1). The optimization of the oxidation has been done by varying the relative



(1)

proportions of hydrogen peroxide with respect to the catalysts and also by varying the reaction time and



Scheme 2. Probable mechanism for oxidation of alcohols to carbonyl compounds.

temperature. The isolated yields after one hour of reaction time were 60% and 80% using $[(L_a^2)_2Cu]$ or $[(L_b^2)_2Cu]$ catalyst, respectively. A plausible pathway of catalytic process is shown in scheme 2.

3.5 Photoluminescence properties and cyanide recognition

The ligands HL_a^2 and HL_b^2 exhibited photoluminescence near 505 and 585 nm on excitation at 300 nm (figure 3). These emissions are attributed to the keto form of the ligands.^{50,53}

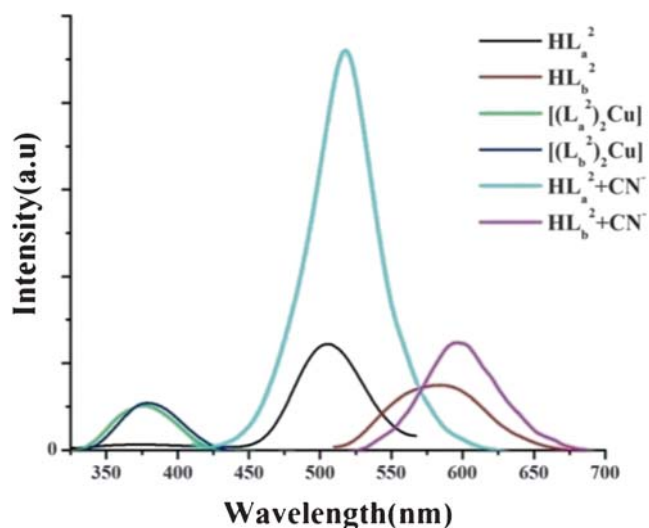


Figure 3. Emission spectra of HL_a^2 ($c = 1 \times 10^{-5}$ M) (—), HL_b^2 ($c = 1 \times 10^{-5}$ M) (—), $[(L_a^2)_2Cu]$ ($c = 2.6 \times 10^{-5}$ M) (—), $[(L_b^2)_2Cu]$ ($c = 3.9 \times 10^{-5}$ M) (—), $[HL_a^2+CN^-]$ ($c = 1.4 \times 10^{-3}$ M) (—) and $[HL_b^2+CN^-]$ ($c = 1.4 \times 10^{-3}$ M) (—) in CH_3CN containing 0.2% DMSO.

On the other hand, the $[(L_a^2)_2Cu]$ and $[(L_b^2)_2Cu]$ complexes displayed emissions of lower intensity than the ligands (figure 3). The emission behavior of $[(L_a^2)_2Cu]$ and $[(L_b^2)_2Cu]$ were measured upon addition of several anions and the results are shown in figures 4 and 5 (spectral changes are given in figures S13 and S14 in Supplementary Information). Significant increase of emission intensity on addition of Tetra butyl ammonium cyanide (TABCN), the source of CN^- , prompted us to realize the selectivity for cyanide ion. Augmentation of emission intensities of free HL_a^2 and HL_b^2 ligands were also noticed upon addition of cyanide ions as shown in figure 3.

The changes in emission spectra of $[(L_a^2)_2Cu]$ and $[(L_b^2)_2Cu]$ were recorded by increasing the cyanide concentration gradually (figures 6 and 7).

No significant peak shifts (375 nm for $[(L_a^2)_2Cu]$ and 375 nm for $[(L_b^2)_2Cu]$) occurred whereas the intensities increased considerably. The emission intensities of HL_a^2 and HL_b^2 increased upon addition of cyanide ion near 510 and 590 nm respectively.⁵³ Since the emission peak of $[(L_a^2)_2Cu]$ did not shift to 505 nm for (HL_a^2) or 510 nm for $(HL_a^2+CN^-)$ upon addition of cyanide,

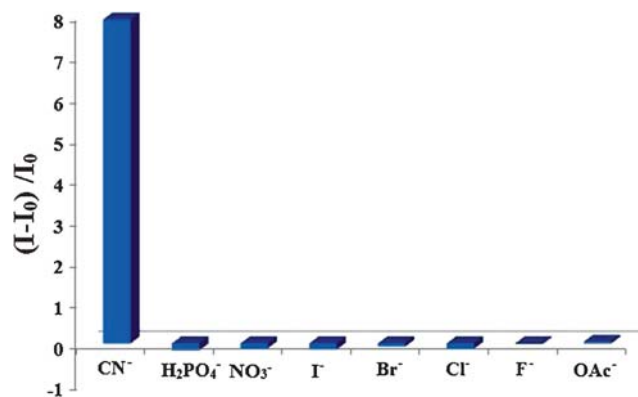


Figure 4. The $[(I - I_0) / I_0]$ values for $[(L_a^2)_2Cu]$ at 370 nm upon addition of 4 equivalent amount of respective anions in CH_3CN containing 0.2% DMSO.

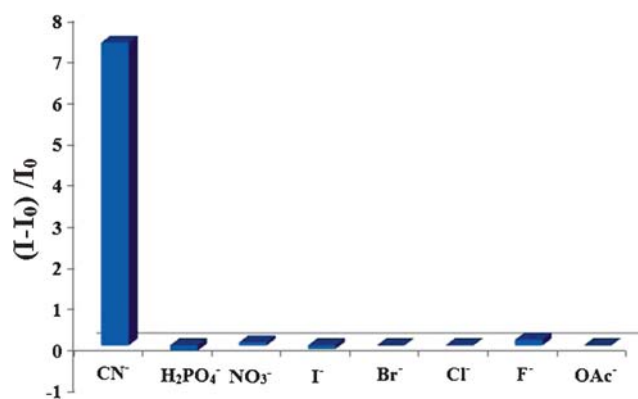


Figure 5. The $[(I - I_0) / I_0]$ values of $[(L_b^2)_2Cu]$ at 380 nm upon addition of 4 equivalent amount of respective anions in CH_3CN containing 0.2% DMSO.

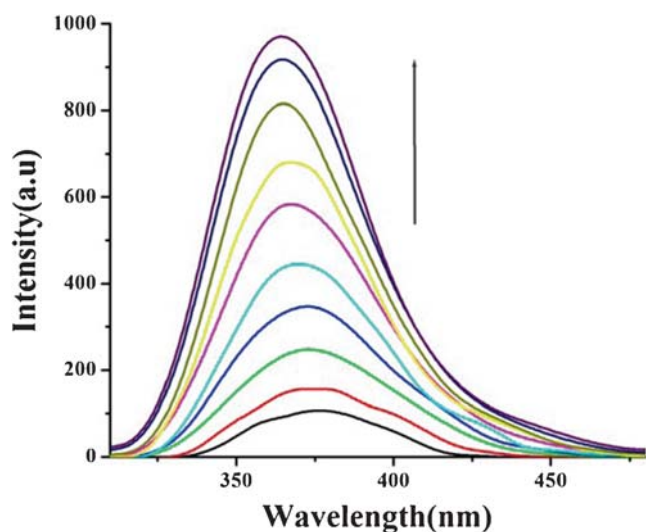


Figure 6. Increment of emission intensity of $[(L_a^2)_2Cu]$ solution in CH_3CN containing 0.2% DMSO mixed solvent upon gradual addition of TBACN upto 4 equivalent amount.

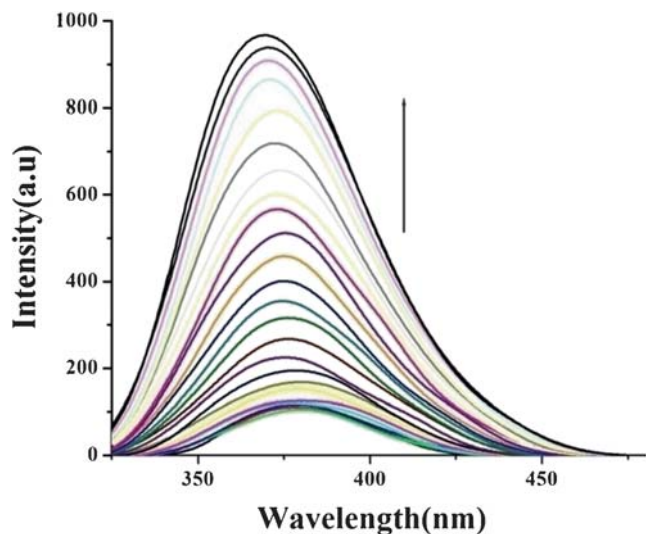


Figure 7. Increment of emission intensity of $[(L_b^2)_2Cu]$ upon gradual addition of 4 equiv. amounts of TBACN in CH_3CN containing 0.2% DMSO.

therefore it was assumed that the ligand dissociation did not take place upon addition of cyanide rather it was due to the cyanation at the free aldehyde substituent of $[(L_a^2)_2Cu]$.⁵³ Similarly, it was speculated that the enhancement of emission intensity of $[(L_b^2)_2Cu]$ upon addition of TBACN was a consequence of cyanation at olefinic carbon (C22 of figure 2b; see above).⁵³ The sensitivity toward selective cyanide recognition were $2.6 \times 10^{-5} M$ for $[(L_a^2)_2Cu]$ and $3.9 \times 10^{-5} M$ for $[(L_b^2)_2Cu]$ (figures S15 and S16). Previously reported Ni(II) complexes exhibited better sensitivity toward cyanide recognition.⁵³ Since the demetallation did not occur for $[(L_a^2)_2Cu]$ and $[(L_b^2)_2Cu]$ upon addition of cyanide ions, therefore our proposal of cyanation on the nucleophilic carbon at the ligand backbone has been further supported.

3.6 Antibacterial activity

The activity results of the metal complex $[(L_b^2)_2Cu]$ with control are shown in table 4 and compared with the results of standard antibiotic chloramphenicol. The results indicated that the synthesized metal complex is more effective in case of gram negative bacteria than the gram positive bacteria. The metal complex showed highest inhibition zone (26 mm) on gram negative bacteria *Pseudomonas aeruginosa*.

The Minimum Inhibitory Concentrations (MIC) of the metal complexes and chloramphenicol against two gram positive and three gram negative bacteria are presented in table 5. The results of the antibacterial screening indicate that both the compounds exhibit broad spectrum antibacterial activity against all the chosen reference bacteria. These results indicate that the $[(L_b^2)_2Cu]$ complex was more sensitive against gram negative bacteria than gram positive bacteria. The chloramphenicol shows lowest MIC ($3.9 \mu g mL^{-1}$) on gram positive bacteria *B. Subtilis*, whereas, the

Table 4. Screening of antibacterial activity against the metal complex and chloramphenicol.

Microorganisms	Inhibition zone in diameter (mm) around the discs		
	Metal complex (60 μg /disc)	Chloramphenicol (10 μg /disc)	Control (100% DMSO)
<i>Bacillus subtilis</i> (MTCC 441)	18	26	–
<i>Staphylococcus aureus</i> (MTCC 2522)	15	13	–
<i>Pseudomonas aeruginosa</i> (MTCC 741)	26	13	–
<i>Shigella dysenteriae</i> (Clinical isolate)	23	18	–
<i>Escherichia coli</i> (MTCC 443)	19	24	–

Table 5. Antibacterial activity of metal complex and reference drug, evaluated by their MIC.

Microorganisms	Minimum inhibitory concentration ($\mu\text{g mL}^{-1}$)		
	Metal complex	Chloramphenicol	Control (100% DMSO)
<i>Bacillus subtilis</i> (MTCC 441)	31.2	3.9	–
<i>Staphylococcus aureus</i> (MTCC 2522)	31.2	7.8	–
<i>Pseudomonas aeruginosa</i> (MTCC 741)	7.8	15.6	–
<i>Shigella dysenteriae</i> (Clinical isolate)	15.6	15.6	–
<i>Escherichia coli</i> (MTCC 443)	15.6	7.8	–

$[(L_b^2)_2Cu]$ complex shows lowest MIC ($7.8 \mu\text{g mL}^{-1}$) on gram negative bacteria *P. aeruginosa* which is much less than the MIC ($15.6 \mu\text{g mL}^{-1}$) of chloramphenicol.

4. Conclusions

Two kinds of Cu(II) complexes have been synthesized and structurally characterized. The copper(II) centers possess tetragonally distorted octahedral geometry with two axially elongated bonds. The new copper complexes not only exhibited benzyl alcohol oxidase activity but also good selectivity as cyanide sensors. The recognition of cyanide was monitored by measuring the change in photoluminescence behaviour. Antimicrobial activity of the complexes displayed better sensitivity toward gram negative bacteria.

Supplementary Information (SI)

CCDC1409893 and CCDC1409894 for $[(L_a^1)_2Cu]$ and $[(L_b^2)_2Cu]$ contain the supplementary crystallographic data, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Figures S1–S6: UV-Vis spectra of $[(L_a)_2Cu]$ and $[(L_b)_2Cu]$, Figures S7–S12: IR spectra of $[(L_a)_2Cu]$ and $[(L_b)_2Cu]$, Figures S13 and S14: Emission spectra of $[(L_a)_2Cu]$ and $[(L_b)_2Cu]$, Figure S15: Detection limits of $[(L_a^2)_2Cu]$ ($c = 7.30 \times 10^{-6} \text{ M}$) at 370 nm for TBACN ($1.4 \times 10^{-3} \text{ M}$) in CH_3CN containing 0.2% DMSO. Figure S16: Detection limits of $[(L_b^2)_2Cu]$ ($c = 4.59 \times 10^{-5} \text{ M}$) at 380 nm for TBACN ($1.4 \times 10^{-3} \text{ M}$) in CH_3CN containing 0.2% DMSO. Are given in Supplementary Information. Supplementary data associated with this article can be found, in the online version, at www.ias.ac.in/chemsci.

Acknowledgments

S.P.P. thanks the CSIR (New Delhi) for research fellowship (09/106(0112)2009-EMR-I). P.P. is thankful to the DST (New Delhi) for funding under DST-WOS-A scheme (No. SR/WOS-A/CS-140/2011). The necessary laboratory and infrastructural facility are provided by the Department of Chemistry, University of Kalyani. The support of DST under FIST and PURSE program and UGC-SAP to the Department of Chemistry, University of Kalyani are acknowledged.

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