

Synthesis, structure and, photophysical and catalytic properties of a copper(II) complex containing bidentate (N,O) Schiff base ligand

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The bidentate ligand (5-chloro-2-(2-hydroxynaphthalen-1-yl)methyleneamino)phenyl(phenyl)methanone HL, was prepared by the condensation of 2-naphthaldehyde with 2-amino-5-chlorobenzophenone. The reaction of HL with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ afforded the new complex of composition $[(\text{L})_2\text{Cu}]$. The ligand HL binds the Cu^{II} centre in bidentate (N,O) fashion being uninegative anion by the way of phenolic proton dissociation during chelation. The complex was characterized by spectroscopic studies. X-Ray structures of $[(\text{L})_2\text{Cu}]$ was determined to confirm the molecular species unequivocally. The photoluminescence properties of the ligand and complex were studied. Oxidation of benzyl alcohol using the newly synthesized complex as catalyst has been studied.

Keywords: Copper(II) complex, X-ray structure, fluorescent properties, ESIPT, oxidation reactions.

Introduction

The chemistry of transition metal complexes incorporating Schiff base ligands have been explored considerably during the last few decades due to their multifunctional properties in luminescence¹⁻³, magnetism⁴⁻⁷, catalysis⁸⁻¹⁰ and electro-chemistry^{11,12}, host-guest chemistry¹³, sensors¹⁴ and biological activity¹⁵. Schiff bases have been significantly active in metal coordination chemistry over the years due to their facile syntheses. The high affinity for the complexation of the Schiff base ligands towards the transition metal ions, especially copper ions, is utilized in preparing their complexes. The chemistry of copper complexes is of interest due to their significance in biological and industrial processes^{16,17}. The copper complexes derived from Schiff base ligands has received enormous attention due to their wide application in the field of catalyst^{18,19} including asymmetric epoxidations, oxidation of sulphides and Lewis acid assisted organic transformation. The biological relevance of transition metal complexes containing imine-nitrogen donor ligands and the rich catalytic activity of copper complexes encouraged us to prepare the Cu^{II} complexes of the Schiff base ligands²⁰⁻²⁷. Herein, we report the synthesis of the bidentate ligand HL and its mononuclear bis copper complex $[(\text{L})_2\text{Cu}]$. The ligand

and complex have been characterized by spectroscopic techniques. The crystal structure of complex $[(\text{L})_2\text{Cu}]$ has been determined, confirming the molecular structure. The fluorescence properties of both the ligand and the complex have been studied. The catalytic oxidation of benzyl alcohol to benzaldehyde has been investigated using H_2O_2 as oxidant.

Experimental

Materials and methods:

The solvents used for all the reactions were of reagent grade (E. Merck, India) and were purified and dried by reported procedure²⁸. Copper acetate monohydrate was purchased from Sisco Research Laboratories (SRL), India. 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 L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1800 PC spectrophotometer.

Syntheses of ligands HL:

2-Naphthaldehyde (200 mg, 1.28 mmol) and 2-amino-5-chlorobenzophenone (296 mg, 1.28 mmol) were heated to reflux in ethanol (40 ml) for 4 h. The bright yellow solid prod-

uct was obtained as micro crystals which were collected by filtration and thoroughly washed with ethanol and diethyl ether and dried under vacuum. Yield: 370 mg (75%). Anal. Calcd. $C_{24}H_{16}ClNO_2$ (385): C, 74.71; H, 4.18; N, 3.63. Found: C, 74.81; H, 4.25; N, 3.58%; UV-Vis spectrum (CH_3CN) λ_{max} (ϵ , $M^{-1} cm^{-1}$): 385 (695094), 326 (50635); IR: $\nu_{C=N}$ 1621, $\nu_{C=O}$ 1658; 1H NMR $CDCl_3$: δ 13.94 (s, -OH, 1H), 9.31 (s, HC=N, 1H), 8.07 (d, 1H), 7.85 (d, 2H), 7.77–7.68 (q, 2H), 7.58 (d, 2H), 7.48 (t, 4H), 7.38 (d, 2H), 7.00 (d, 1H).

HRMS (ESI-TOF): m/z Calcd: 385.0870, Found: 385.9864 $[M+H^+]$.

Synthesis of $[(L)_2Cu]$ complex:

5 ml methanolic solution of 45 mg (0.247 mmol) $Cu(OAc)_2 \cdot H_2O$, 10 ml methanol solution of 200 mg (0.519 mmol) of HL 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 then recrystallized from a dichloromethane-hexane solvent mixture. Yield: 180 mg (73%). Anal. Calcd. $C_{48}H_{30}Cl_2CuN_2O_4$ (833): C, 69.19; H, 3.63; N, 3.36. Found: C, 69.25; H, 3.67; N, 3.42%; UV-Vis spectrum (CH_3CN) λ_{max} (ϵ , $M^{-1} cm^{-1}$): 410 (86712), 316 (127491); IR: $\nu_{C=N}$ 1616, $\nu_{C=O}$ 1659.

X-Ray structure determination of $[(L)_2Cu]$:

Single crystals of $[(L)_2Cu]$ was grown by slow diffusion of hexane in dichloromethane solution at 25°C. Data were collected on a Bruker SMART CCD diffractometer using Mo-K α monochromator ($\lambda = 0.71073$). Structure solutions were performed using Shelx 97 PC version program²⁹. Full matrix least square refinements on F2 were performed using SHELXL-97 program³⁰. 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 $[(L)_2Cu]$ are given in Table 1.

Procedure for the catalytic oxidation of benzyl alcohol:

To an acetonitrile solution of benzyl alcohol (5 mmol), the catalyst $[(L)_2Cu]$ (4 mol%) or and 30% H_2O_2 (5 equiv.) were added and the mixture was vigorously stirred at 70°C for 1 h. The reaction was monitored by TLC. After completion of the

Table 1. Crystallographic data for $[(L)_2Cu]$

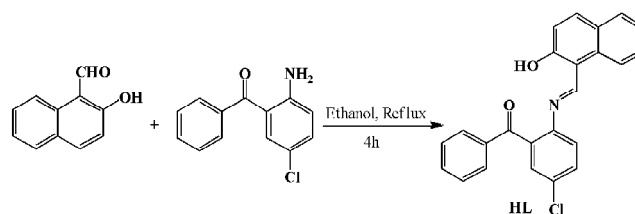
Chemical formula	$C_{48}H_{30}Cl_2CuN_2O_4$
Formula weight	833.19
Crystal system	Triclinic
Space group	P-1
a (Å)	14.7980(7)
b (Å)	10.7176(6)
c (Å)	24.7174(13)
α (deg)	90.013(4)
β (deg)	100.772(4)
γ (deg)	89.993(4)
λ (Å)	0.71073
V (Å ³)	3851.1(4)
$F(000)$	1832.0
Z	4
T (K)	296
D (mg/m ⁻³)	1.437
μ (mm ⁻¹)	0.756
R1 (all data)	0.0695
wR2 [$I > 2\sigma(I)$]	0.2252
GOF	0.931

reaction, the mixture was poured into water and the product was extracted with dichloromethane and dried over Na_2SO_4 . The solvent was removed and the product was purified by column chromatography. Yields were determined by weighing the isolated product. The product was characterized by IR and 1H NMR spectra.

Results and discussion

Synthesis of ligand and complex:

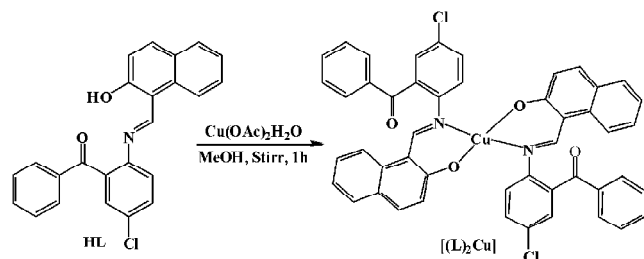
The HL, ligand was prepared by the condensation reaction of 2-naphthaldehyde with 2-amino-5-chlorobenzophenone in 1:1 M ratio in refluxing ethanol (Scheme 1).



Scheme 1. Synthesis of ligand HL.

The reaction of the HL ligand with $Cu(OAc)_2 \cdot H_2O$ in methanol afforded brown complex of composition $[(L)_2Cu]$

(Scheme 2). The complex $[(L)_2Cu]$ was paramagnetic matching with one unpaired electron as expected for Cu^{II} metal ion. The suitable crystal of $[(L)_2Cu]$ complex for X-ray studies were grown from dichloromethane-hexane solvent mixture.



Scheme 2. Synthesis of $[(L)_2Cu]$ complex.

The synthesized ligand and complex were well characterized by IR, 1H NMR, HRMS (ESI-TOF) techniques (Figs. S1-S7)

Characterization:

The UV-Vis spectra of $[(L)_2Cu]$ is distinctly different from the ligand HL the lowest energy absorption appeared near 385 nm and 410 nm, respectively³¹. Representative UV-Vis spectra of HL and $[(L)_2Cu]$ are shown in Fig. 1. Spectral data are given in the Experimental section.

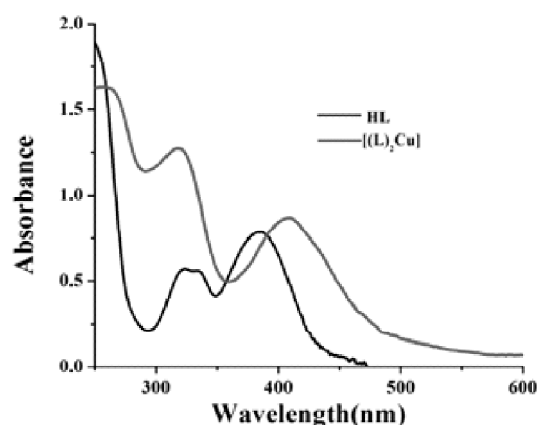


Fig. 1. UV-Vis spectra of the ligand HL and complex in acetonitrile.

The $\nu_{C=N}$ of $[(L)_2Cu]$ complex appear in the lower range (1616 cm^{-1}) compared to the ligand signifying the coordination to the metal centre. The $\nu_{C=O}$ band of the ligand ($\sim 1658\text{ cm}^{-1}$) almost remain similar after the formation of the $[(L)_2Cu]$

complex (1659 cm^{-1}), that clearly indicating that carbonyl group did not coordinated. The relevant IR data are collected in Experimental section. The IR spectra of HL and $[(L)_2Cu]$ are given in Supplementary Information (Figs. S1-S2). The ligand HL afforded satisfactory 1H NMR spectral data in $CDCl_3$. The sharp singlet near δ 13.9 was assigned to phenolic (-OH) proton for the ligand HL. The 1H NMR spectra of HL showed resonances of proton belonging to the Schiff base group at δ 9.32. The 1H NMR spectral features for the aromatic protons of the ligand HL matched well with the composition and structure. The 1H NMR spectra of HL are given in Supplementary Information (Fig. S3). The electrospray mass spectrum of HL exhibited the most significant peak at m/z 385.9864 which was consistent with the molecular MH^+ ion.

X-Ray structure of $[(L)_2Cu]$:

Suitable crystals of $[(L)_2Cu]$ was grown by slow diffusion of hexane into dichloromethane solution. The X-ray structure of $[(L)_2Cu]$ was determined and described below. The perspective view of $[(L)_2Cu]$ complex is shown in Fig. 2. Selected bond parameters of $[(L)_2Cu]$ complex is listed in Table 1 and Table 2, respectively. In the $[(L)_2Cu]$ complex, the Cu centre is coordinated by two phenolato oxygens ($O1$ or O_{ph}),

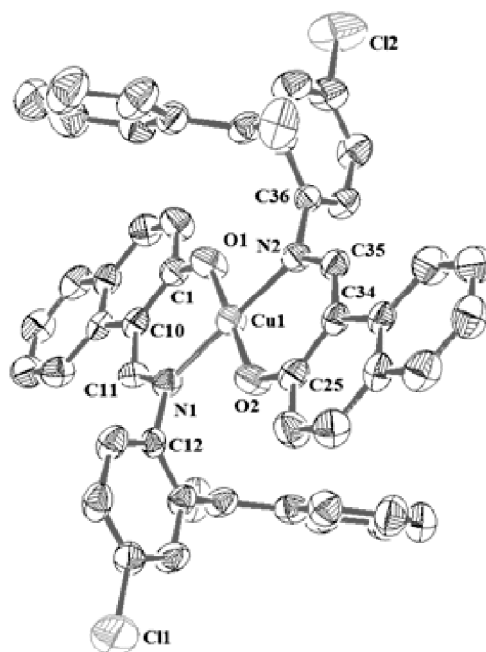


Fig. 2. ORTEP and atom-numbering scheme for $[(L)_2Cu]$ complex. Hydrogen atoms are omitted for clarity.

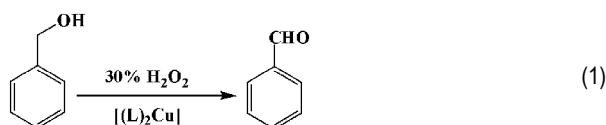
Table 2. Selected bond distances (Å) and angles (deg) for $[(L)_2Cu]$

Distances			
Cu1-N1	1.981(4)	C10-C11	1.428(7)
Cu1-N2	1.977(5)	C25-C34	1.397(8)
Cu1-O1	1.880(3)	C34-C35	1.406(7)
Cu1-O2	1.875(3)	N1-C11	1.306(6)
O1-C1	1.301(6)	N1-C12	1.449(7)
O2-C25	1.309(6)	N2-C35	1.309(6)
C1-C10	1.396(8)	N2-C36	1.447(7)
Angles			
O1-Cu1-N1	90.6(2)	Cu1-N1-C11	125.6(3)
O1-Cu1-N2	89.9(2)	Cu1-N1-C12	120.4(3)
O2-Cu1-N1	88.9(2)	C1-C10-C11	120.9(4)
O2-Cu1-N2	90.7(2)	N1-C11-C10	126.7(5)
Cu1-O1-C1	130.6(4)	N2-C35-C34	127.3(4)

two imine nitrogen (N_{im}). The central Cu^{II} ion in this complex is four-coordinate and is slightly distorted square planar geometry. The asymmetric unit of $[(L)_2Cu]$ complex consist of half molecule where Cu^{II} occupies the special position. The Cu-O and Cu- N_{im} distances are 1.873(2) Å and 1.297(4) Å and consistent with the coordination of phenolato oxygen to Cu^{II} square planar³¹.

Selective oxidation of benzyl alcohol:

Selective oxidation of benzyl alcohols to the benzaldehyde is a significant and widely used reaction in laboratory scale organic synthesis as well as in large scale in chemical industry^{32–35}. The complex $[(L)_2Cu]$ have been scrutinized for the per oxidative oxidation of benzyl alcohol with H_2O_2 (30%) as the oxidant in aqueous acetonitrile mixture [eq. (1)].



The reaction has been optimized by varying the relative proportions of hydrogen peroxide with respect to the catalyst and also by varying the reaction time and temperature. The isolated yield of the benzaldehyde after one hour of reaction time was 60% using $[(L)_2Cu]$ catalyst.

Fluorescence spectral:

The photoluminescence properties of the ligand HL and

the $[(L)_2Cu]$ complex were investigated in acetonitrile (Fig. 3).

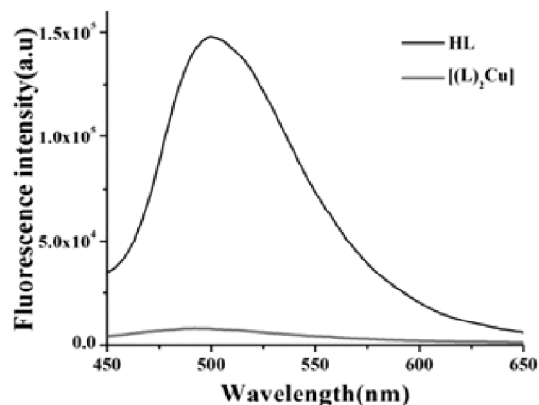
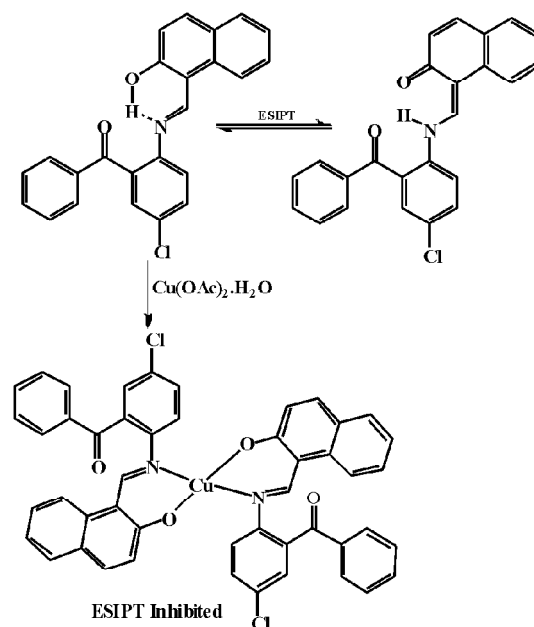


Fig. 3. Emission spectra of HL and HL_2 , $[(L)_2Cu]$ in CH_3CN .

The ligand HL exhibited moderate intensity emission near 500 nm upon excitation at 385 nm. The peak at 595 nm arises due to the excited state intramolecular proton transfer (ESIPT) followed by excited state intramolecular charge transfer (ESICT) from the phenol -OH to the imine nitrogen atom (Scheme 3)^{36–38}.

On the other hand, $[(L)_2Cu]$ complex exhibited quenched



Scheme 3. Possible emission mechanism of HL to Cu^{2+} .

emission at 500 nm in acetonitrile. Coordination of Cu²⁺ involving the imine nitrogen atom inhibits the ESIPT which resulted in decrease in the emission at 500 nm.

Conclusions

In summary, we have successfully synthesized and characterized Schiff base copper(II) complex incorporating N,O donor ligand. The structure of the complex [(L)₂Cu] was confirmed by X-ray crystallography. As application, the synthesized [(L)₂Cu] complex have been used as catalyst in the oxidation of benzyl alcohol to benzaldehyde. In addition we have also examined the fluorescence properties of the ligand and complex. The ligand exhibited photoluminescence property due to the excited state intramolecular proton transfer (ESIPT).

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Appendix A. Supporting Information (ESI)

X-Ray crystallographic file in CIF format for [(L)₂Cu] complex; CCDC reference number 1815667. Figs. S1-S4 is provided as electronic supplementary materials in Supporting Information.

Notes

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