

## Syntheses and Characterisation of Fluorescent Schiff Bases and Their Copper Complexes from Salicylaldehyde

A.K. Surabhi, K. Pradeepkumar

Research Department of Chemistry, PRNSS College, Mattanur, Kannur, Kerala, 670702, India

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**Abstract:** Synthesized and characterized two Schiff bases  $L^1$  and  $L^2$  by the condensation reaction between 2,6-diaminopyridine and salicylaldehyde. Their Cu(II) complexes have been synthesized by the reaction of these ligands with Cu(II) acetate monohydrate. Characterization of the compounds has been done using the techniques like elemental analyses, magnetic moment measurement, conductance measurement, thermogravimetry and IR, UV, NMR, EPR and mass spectroscopy. The compounds exhibit luminescence property. The antibacterial properties of the ligands and complexes have been screened.

**Keywords:** Mono Schiff base, bis Schiff base, 2,6-diaminopyridine, fluorescence and antibacterial.

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### I. Introduction

Schiff bases find immense potential applications in chemical biology [1-4]. Availability of different bonding sites in heterocyclic compounds containing rings like pyridine, thiophene, furan, etc., prompted researchers to synthesize Schiff bases from them. Pyridine ring contains hetero atom nitrogen with a localized pair of electrons. Hence numerous ligands and their transition metal complexes containing pyridine ring have been synthesized and tested for their activity in various fields [5-9]. But only a few studies have been carried out with diaminopyridines as a part of the ligands [10-13]. It is observed that on exciting with 320 nm radiation, 2,6-diaminopyridine exhibits fluorescence emission. Furthermore, this diamine shows enhanced fluorescence activity in Schiff bases and their corresponding copper complexes synthesized from it. This behavior is very useful in biological imaging, DNA sequencing, tracking the uptake of drugs by the cell by visualizing the fluorescent tag, etc., which are some of the superior biological applications of fluorescent compounds. This observation motivated us to prepare novel Schiff base ligands from 2,6-diaminopyridine. In this paper, the synthesis and characterization of two ligands and their copper complexes are reported. The antibacterial activity of the synthesized compounds has been investigated.

### II. Experimental

#### Materials and reagents

All the chemicals used are of analytical grade. 2,6-diaminopyridine was purchased from Across Organics. 2-hydroxybenzaldehyde and Cu(II) acetate monohydrate were supplied by Sigma-Aldrich. All solvents were of analytical grade and were used as such.

#### Instruments

Elemental analyses (CHN) were performed on an Elementar Model Vario ELIII CHNS Analyser. Metal estimation was done by the standard gravimetric method. Magnetic measurements were conducted using a Sherwood Scientific model Mag way MSB MK1 magnetic susceptibility balance. Molar conductance values of the solutions of complexes in DMSO ( $\sim 10^{-3}$ M) were obtained from a Deluxe conductivity meter, Model 601E. IR measurements of the compounds in the 4000-400 $\text{cm}^{-1}$  range were carried out by the KBr pellet method using a Thermo Nicolet AVATAR 370 DTGS model FT IR Spectrophotometer. Mass spectra of the ligands and complexes were recorded in a JMS-T100LC, Accu TOF (DART-MS) mass spectrometer. Thermogravimetric analysis (TG-DTG) was performed using NETZSCH STA 449F3 JUPITER TG-DSC analyser in an atmosphere of nitrogen gas at a heating rate of 10 K/min.  $^1\text{H}$  NMR spectra of the ligands were recorded using FT NMR Bruker Avance III, 400MHz model spectrophotometer with DMSO as the solvent. Solution state electronic spectral measurements of the ligands and complexes in DMSO solvent in the range 200-900 nm were carried out with the help of Systronics-2201 model spectrophotometer. Solid state UV spectral measurements were conducted using Varian Carry 5000 model UV-Visible-NIR Spectrophotometer. Fluorescence spectra were recorded using a LS 55 model Perkin Elmer spectrofluorimeter.

#### Synthesis of mono Schiff base ligand $H_2$ DapyMHB [ $L^1$ ]

##### (2E)-N2-[(2-methylphenyl)methylidene]pyridine-2,6-diamine

2,6-diaminopyridine (0.109g, 1mmol) and 2-hydroxybenzaldehyde (0.122g, 1mmol) were dissolved separately in ethanol (ratio 1:2) and the latter is poured to the former with constant stirring. The mixture was refluxed for

three hours and the resulting yellow solution was concentrated by evaporation. The yellow precipitate of mono Schiff base was filtered, washed with ethanol and dried.

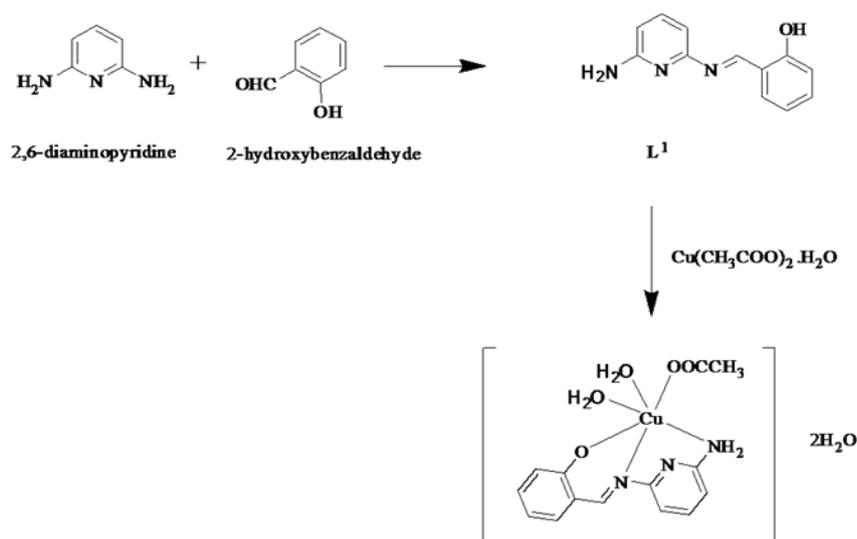
**Synthesis of bis Schiff base ligand (*H<sub>2</sub>DapyBHB*) [*L<sup>2</sup>*]**

**(1*E*)-1-(2-methylphenyl)-N-{6-[(*E*)-[(2-methylphenyl)methylidene]amino]pyridine-2-yl}methanimine**

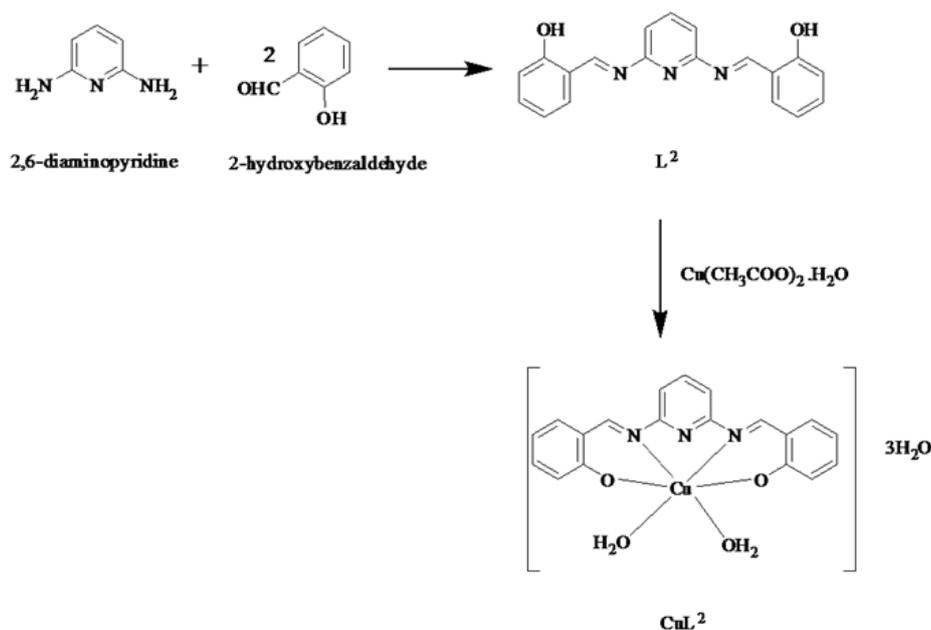
2,6-diaminopyridine (0.109g, 1mmol) and 2-hydroxybenzaldehyde (0.244g, 2mmol) were dissolved separately in ethanol (ratio 1:2) and the latter is poured to the former with constant stirring. The mixture was refluxed for three hours and the resulting orange solution was concentrated by evaporation. The orange precipitate of bis Schiff base was filtered, washed with ethanol and dried.

**Synthesis of metal complexes**

A general procedure was employed for the synthesis of metal complexes. The Schiff base ligand was dissolved in sufficient quantity of DMF and 10 ml of ethanol, followed by the dropwise addition of equimolar amount of ethanolic solution of Cu(II) acetate monohydrate. The mixture was refluxed for three hours. The refluxed solution was concentrated by evaporation and the black precipitate obtained was filtered, washed successively with ethanol and ether and dried (scheme 1 and 2).



**Scheme 1.** Molecular structure of the Ligand *L*<sup>1</sup> and complex CuL<sup>1</sup>



**Scheme 2.** Molecular structure of the Ligand *L*<sup>2</sup> and complex CuL<sup>2</sup>

### Invitro antibacterial property

The invitro antibacterial activity of the Schiff bases and their complexes has been tested against the gram negative bacteria species, Escherichia Coli and gram positive species, Staphylococcus Aureus, by Agar well diffusion method standardised by NCCLS, 1993. The experiments have been performed using nutrient agar as medium and streptomycin as control. Each of the compounds was dissolved in DMSO and solutions of different concentrations (25, 50 and 100 ppm) were prepared separately. In the typical procedure, nutrient agar medium was prepared and autoclaved at 15 lbs pressure at 121°C for 15 minutes. The autoclaved medium was mixed well and poured in to 100 mm petriplates (25-30ml/plate) while molten.

Petriplates containing 20ml Nutrient Agar Medium were inoculated with bacterial strain E. coli or S. Aureus (growth of culture adjusted according to McFards Standard). Wells of approximately 10 mm was bored using a well cutter and samples of 25, 50, and 100 ppm concentrations were added. The plates were then incubated at 37 °C for 24 hours. During this period, the test solutions seeded are allowed to diffuse out into the medium and interact with the test organisms in the freshly seeded plate affecting its growth. The resulting zones of inhibition will be uniformly circular as there is a confluent lawn of growth. The diameter of zone of inhibition can be measured in centimeters. The antibacterial activity of the compounds was assayed by measuring the diameter of the inhibition zone formed around the well [NCCLS 1993].

### III. Results and discussion

The analytical and physical data of the ligands and their copper complexes are presented in Table 1. All the compounds are partially soluble in ethanol and completely soluble in polar organic solvents like chloroform, DMF, DMSO, etc. The two octahedral complexes differ in their stoichiometry. Schiff base complex  $CuL^1$  is assumed to have a structure in which one monobasic tridentate ligand is coordinated to the Cu(II) ion along with one acetate ion. While complex  $CuL^2$  is formed by the coordination of one dibasic tetradentate ligand to the Cu(II) ion in  $N_2O_2$  fashion. The octahedral coordination sphere in both complexes is expected to be completed by the coordination of water molecules.

Conductivity measurements of the complexes in DMSO ( $10^{-3}M$ ) indicate that  $CuL^1$  and  $CuL^2$  are nonelectrolytes in DMSO. The magnetic moments of the two complexes  $CuL^1$  and  $CuL^2$  calculated from magnetic susceptibility measurements and using the diamagnetic corrections are 1.8 and 2.1 B.M., respectively, indicating the presence of two unpaired electrons.

**Table 1.** Analytical and physical data of the Schiff bases and their metal complexes

Compound	Mp °C	M.Wt	Colour (% yield)	C% found (calc.)	H% found (calc.)	N% found (calc.)	M% found (calc.)	$\mu_{eff}$ BM	$\Delta_M$ Ohm <sup>-1</sup> mol <sup>-1</sup> cm <sup>2</sup>
$C_{12}H_{11}N_3O$ (L <sup>1</sup> )	110	213	Yellow90%	67.4 (67.6)	5.8 (5.1)	18.9 (19.7)		–	–
$C_{19}H_{15}N_3O_2$ (L <sup>2</sup> )	135	317	Brownish yellow 93%	70.8 (71.9)	4.9 (4.7)	12.8 (13.2)		–	–
$[Cu(C_{12}H_{10}N_3O)_2] \cdot H_2O$ $[CuL^1OAc] \cdot 4H_2O$	>300	406.5	Black 80%	42.2 (41.4)	4.5 (5.1)	10.6 (10.3)	15.8 (15.6)	1.8	3.4
$[Cu(C_{19}H_{13}N_3O_2) \cdot 2H_2O] \cdot 3H_2O$ [CuL <sup>2</sup> ·2H <sub>2</sub> O]·3H <sub>2</sub> O	>300	468.5	Black 81%	47.8 (48.6)	4.4 (4.9)	8.9 (8.9)	13.5 (13.5)	2.1	2.6

### Infrared and <sup>1</sup>H NMR spectroscopy

**Table 2.** Infrared spectral data of the Schiff bases and their metal complexes

compound	$\nu(C=N)$	$\nu(O-H)$	$\nu(C-N)$	$\nu(C-O)$	$\nu NH_2$	$\nu(COO^-)$	$\nu(M-N)$ cm <sup>-1</sup>	$\nu(M-O)$ cm <sup>-1</sup>
L <sup>1</sup>	1617	3382	1446	1270	3444(asy), 3210(sym),	-	-	-
$[CuL^1OAc] \cdot 4H_2O$	1608,	3357	1444	1278	3437(asy), 3205(sym)	1531(asy), 1322(sym)	455	414
L <sup>2</sup>	1618	3434	1488, 1430	1270(asy), 1226(sym)	-	-	-	-
$[CuL^2(H_2O)_2] \cdot 3H_2O$	1609(asy), 1531(sym),	3432	1440	1284(asy), 1234(sym)	-	-	457	412

The important IR bands of Schiff base ligands and their metal complexes are listed in Table 2. The IR spectra of the complexes are compared with those of the ligands to determine the involvement of different sites in chelation. The ligand L<sup>1</sup> exhibits a sharp band at 1610 cm<sup>-1</sup> which can be attributed to (C=N) stretching vibration of newly formed azomethine group [14]. A singlet at  $\delta$  8.122 ppm (1H) of the azomethyl proton in the

$^1\text{H}$  NMR spectrum confirms its formation. The two sharp and strong bands at  $3444$  and  $3210\text{ cm}^{-1}$  are respectively due to the asymmetric and symmetric stretching vibrations of free  $\text{NH}_2$  group of 2,6-diaminopyridine moiety [15]. In the magnetic spectrum, peak corresponding to amino group is observed as a doublet at  $\delta$  6.688 (2H). The presence of hydroxyl group is evident from a broad and strong band in IR spectrum at  $3382\text{ cm}^{-1}$  and a singlet at  $\delta$  10.912 ppm (1H) in the NMR spectrum. Broadness may be due to the intermolecular hydrogen bonding. A medium band at  $751\text{ cm}^{-1}$  and a weak one at  $618\text{ cm}^{-1}$  can be assigned to the out of plane and in plane pyridyl ring deformation respectively. In the complex  $\text{CuL}^1$ , the band due to  $\nu(\text{C}=\text{N})$  motion is found shifted to  $1608\text{ cm}^{-1}$ , which indicates the coordination of azomethine nitrogen [16]. The asymmetric and symmetric stretching vibrations of free  $\text{NH}_2$  group of 2,6-diaminopyridine moiety were also shifted to lower frequency in the complexes showing the coordination of that nitrogen atom. The complex displays a medium strong band at  $3357\text{ cm}^{-1}$  which may be due to O-H stretching vibrations of lattice water [17]. The bands for the out of plane and in plane pyridyl ring deformation in the ligand are not changed abruptly in the complexes indicating that pyridine N is not involved in coordination. The C=O stretching vibration of the phenolic group is evident from the band at  $1270\text{ cm}^{-1}$  in the ligand is found raised in the complex  $\text{CuL}^1$  to  $1282\text{ cm}^{-1}$  pointing that phenolic oxygen is bonded to metal after oxidation [18]. The bands for  $\nu_{\text{asy}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$  with a difference above  $200\text{ cm}^{-1}$  confirms the coordination of acetate ion in monodentate fashion [19]. The non-ligand bands in between  $500\text{-}400\text{ cm}^{-1}$  can be assigned to M-N and M-O bond vibrations.

The IR spectra of ligand  $\text{L}^2$  and its complex (Fig. 2) show distinguishable bands. In the ligand  $\text{L}^2$ , the two sharp bands at  $1618\text{ cm}^{-1}$  and  $1567\text{ cm}^{-1}$  can be assigned to stretching vibrations of newly formed azomethine group and that of pyridine ring. The proton on the two azomethine carbons appear at  $\delta$  7.674 ppm (1H) and  $\delta$  7.669 ppm (1H) in the NMR spectrum (Fig. 1). A sharp band at  $3434\text{ cm}^{-1}$  may be that of  $\nu$  (O-H) stretching vibration. The presence of hydroxyl group is confirmed from the singlet at  $\delta$  10.25 ppm (2H). The asymmetric and symmetric stretching vibrations of the two pyridine ring carbon – azomethine nitrogen groups (C-N) appear respectively at  $1488$  and  $1430\text{ cm}^{-1}$ . The multiplets found in the  $\delta$  6.984 - 6.944 ppm (3H) and  $\delta$  7.654 – 7.005 ppm (8H) can be assigned respectively to pyridyl and phenyl protons. In the complex  $\text{CuL}^2$ , the bands corresponding to stretching vibration of azomethine group is found at  $1609\text{ cm}^{-1}$  indicating the coordination of both imino nitrogens. The broad band at around  $3432\text{ cm}^{-1}$  in the complex may be due to hydrogen bonded lattice and coordinated water. The two phenolic groups in the ligand exhibit a single band for (C-O) stretching vibration at  $1270\text{ cm}^{-1}$  while the complex shows two bands at  $1284$  and  $1234\text{ cm}^{-1}$ . It can be attributed to asymmetric and symmetric vibration, possible due to the peculiar structure of the complex, in which metal atom is coordinated to the hydroxyl group after deprotonation [18]. The complex exhibits a single band for  $\nu(\text{C}=\text{N})$  due to the symmetric structure at  $1446\text{ cm}^{-1}$ . The bands for pyridine ring stretching and bending vibrations are found unchanged, which rules out the possibility of coordination of ring nitrogen. The bands in between  $500\text{-}400\text{ cm}^{-1}$  can be assigned to M-N and M-O bond vibrations [19]. The paramagnetic and the monomeric nature of the metal ion is clear from the absence of peaks in NMR spectra.

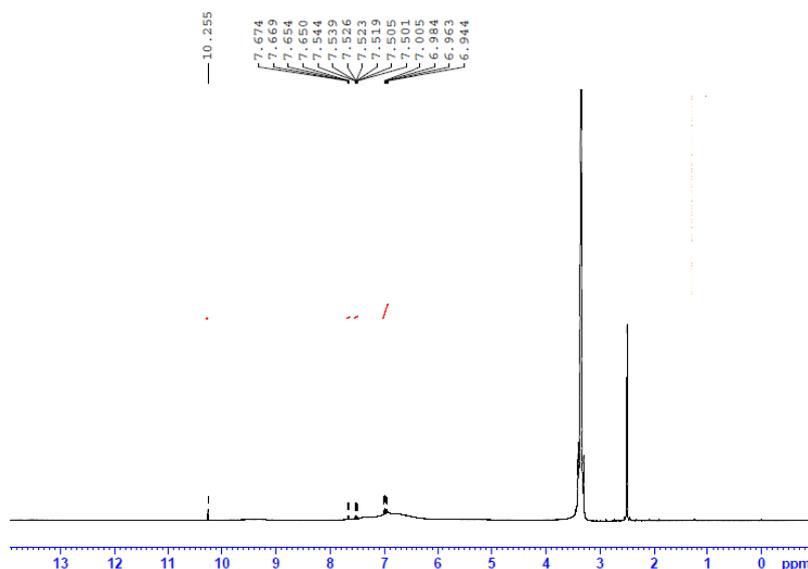


Fig. 1.  $^1\text{H}$  NMR spectrum of the ligand  $\text{L}^2$

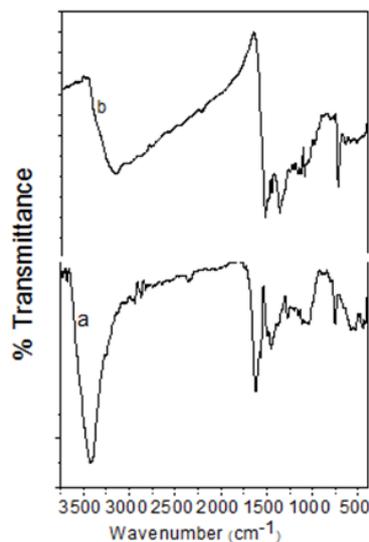


Fig. 2. IR spectra of (a) ligand  $L^2$  and (b)  $CuL^2$

### Mass Spectra

Being an excellent tool for getting molar mass, mass spectrum of the compounds were recorded and from the mode of fragmentation obtained, the exact structure of the compounds are deduced. The characteristic fragments can be given as  $m/z$  (%). The molecular ion peak of ligand  $L^1$  is observed at 211 (8) amu (calc.212) although the relative intensity is very small. The spectrum exhibits peaks at 169 (5) amu (calc.169) corresponding to the removal of  $CH_2=CH-CH_3$  from benzaldehyde moiety of the ligand. The base peak is observed at 120 (100) amu (calc.122) corresponding to benzaldehyde.

The molecular ion peak of the complex  $CuL^1$  is observed at 332 (10) amu (calc.333). It implies the formation of a species by removing two molecules of water of hydration from the compound. The existence of ligand molecule is indicated by the peak at 211 (20) amu (calc.212). The mass spectrum exhibits peaks at 279 and 120 amu corresponding to the removal of acetate and diaminopyridine moieties. The base peak observed at 120 (100) amu (calc.120) signifies the formation of benzaldehyde molecule ion.

The molecular ion peaks of ligand  $L^2$  and complex  $CuL^2$  are observed at 317 (8) amu (calc.317) and 467 (8) amu (calc.468) with very small relative intensities. The ligand and the complex exhibit peaks at 110, 139, 169, 279 and 293 amu corresponding to the fragment ions  $C_5H_6N_3^+$ ,  $C_7H_8O_3^+$ ,  $C_{10}H_7N_3^+$ ,  $C_{16}H_{13}N_3O_2^+$  and  $C_{17}H_{12}N_3O_2^+$  in the spectra. The base peak is observed at 138 (100) amu (calc.138) corresponding to hydrated molecule of benzaldehyde.

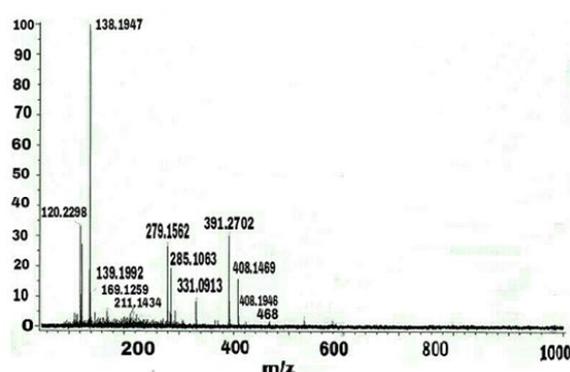
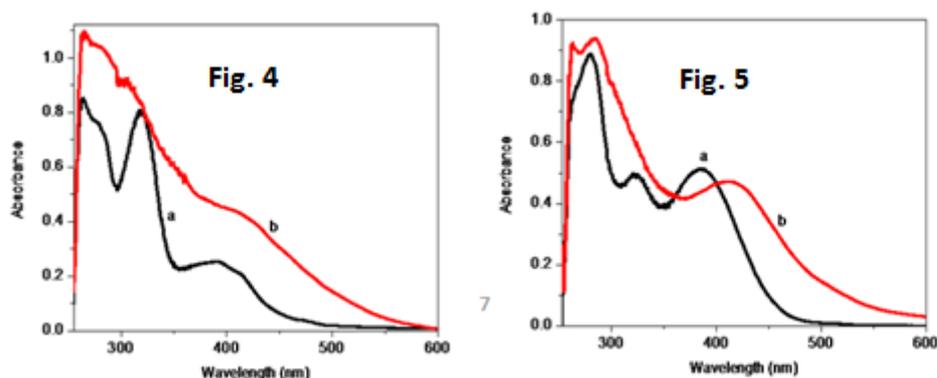


Fig. 1. Mass spectrum of complex  $CuL^2$

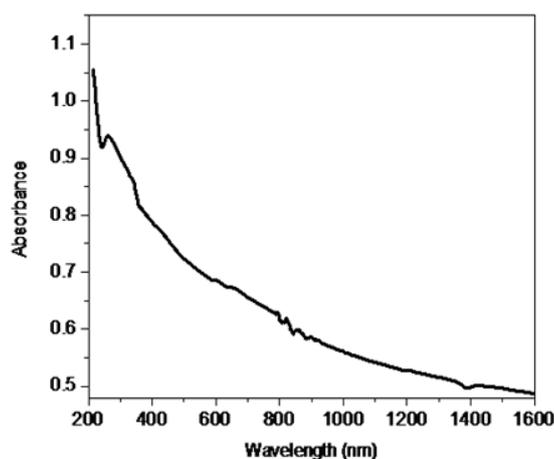
### UV Spectroscopy

The structural information in solution has been obtained from the electronic spectral studies. The solution state electronic spectrum of the compounds has been recorded in solvent DMSO, in the 200-900 nm range (Table 3). The absorption bands at 264, 320 and 392 nm in the spectrum of ligand  $L^1$  (Fig. 4a) can be assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions of the phenyl ring, azomethine group and pyridine ring. In complexes, these bands exhibit slight blue and red shift and found at 308 and 416 nm respectively, indicating the formation of complex. All the three bands of  $L^2$  is found blue shifted in the spectrum of  $CuL^2$  (Fig. 5), which

can be explained by the decrease in conjugation due to the drift of electrons from two nitrogen and two oxygen atoms in the ligand to metal ion. The solid state electronic spectra of the complexes betray a broad band with a shoulder at 843-880 nm reveal the formation of an octahedral complex (Fig. 6). This is in consistent with the other spectral assignments and affirms octahedral structure to the complexes [20].



**Fig. 4.** Electronic spectra of the compounds. (a) L<sup>1</sup>, (b) CuL<sup>1</sup>.  
**Fig. 5.** Electronic spectra of the compounds. (a) L<sup>2</sup> and (b) CuL<sup>2</sup>.



**Fig. 6.** Solid state electronic spectrum of the complex, CuL<sup>1</sup>.

**Table 3.** Electronic spectral data of the ligands and complexes

Compound	$\pi-\pi^*$ (nm)	n- $\pi^*$ (nm)
L <sup>1</sup>	263	320, 392
L <sup>2</sup>	280	324, 389
CuL <sup>1</sup>	265	308, 416
CuL <sup>2</sup>	261	285, 413

### Thermo gravimetric analysis

The thermal studies of the metal complexes has been carried out using the thermogravimetric technique (TG) and differential thermogravimetry in order to get more idea about the structure of the complexes. Thermogravimetric analysis of the complex CuL<sup>1</sup> reveals three step decomposition process. First stage decomposition with a 17.2% weight loss corresponds to the loss of four molecules of water of crystallization. Second stage of decomposition of 16% corresponds to the removal of acetate molecule and some part of the ligand and the last stage up to 1300 °C corresponds to the removal of ligand molecule. Yet the decomposition is found incomplete even at this temperature indicating the high thermal stability. The percentage of weight loss agrees well with the proposed formula. The thermal decomposition of complex CuL<sup>2</sup> proceeds through three stages. The first stage of decomposition starts at 53 °C and ends at 287 °C with a mass loss of 40.26%. This can be explained by the removal of five molecules of water in the molecule and some parts of ligand. The next stage

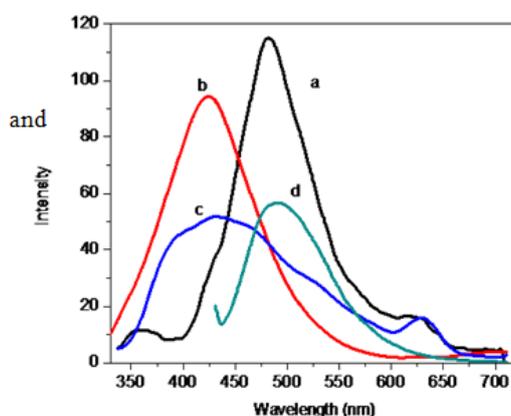
of decomposition extends from 287 °C to 550 °C corresponding to a mass loss of 43.3%. The third stage of mass loss reveals the formation of metallic residue at 890 °C

**Fluorescence spectra**

The emission properties of the ligands and complexes have been studied by passing UV radiation of appropriate wavelength through these compounds in solution state (~ 10<sup>-3</sup> M DMSO solution). The excitation wavelength is selected in between 340-370 nm. The results are given in Table 4. The ligand L<sup>1</sup> exhibit the emission at a wavelength 481 nm which is found changed to 424 nm in the complex CuL<sup>1</sup> with a decrease of intensity. The decrease in intensity would have been due to the presence of quenching groups like acetate in the complex [21]. The fluorescence maxima in the ligand L<sup>2</sup> and complex CuL<sup>2</sup> are 431 and 491 nm, respectively. The complex formation follows a slight increase in intensity. The nature of fluorescence emission of the compounds is clear from Fig. 7.

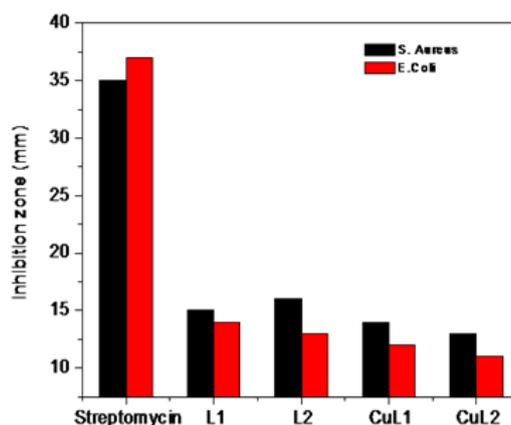
**Table 4.** Fluorescence spectral data of the ligands and complexes in nm

Compound	λ <sub>excitation</sub>	λ <sub>emission</sub>
L <sup>1</sup>	354	497
L <sup>2</sup>	328	424
CuL <sup>1</sup>	312	436
CuL <sup>2</sup>	370	494



**Fig. 7.** Fluorescence spectra of the ligands and complexes (a) L<sup>1</sup>, (b) CuL<sup>1</sup>, (c) L<sup>2</sup> and (d) CuL<sup>2</sup>.

**Invitro antibacterial property**



**Fig. 8.** Antibacterial activity of the ligands and complexes with streptomycin as the control.

The antibacterial activity of the parent Schiff base ligands and their metal complexes against *S. aureus* (G +) and *E. coli* (G -) bacteria was tested by the agar well-diffusion method [22]. The analysis results are given in Fig. 8. The tested compounds exhibit moderate antibacterial activity compared with the control. The ligands show comparatively higher activity than the complexes. Among the ligands, L<sup>2</sup> is more efficient and the antibacterial effect is maximum with microorganism *S. Aureus*. On comparing the antibacterial property of the ligands and their metal complexes with the standard streptomycin (antibacterial agent), it is concluded that

- (1) the antibacterial activity of ligands are moderate in comparison with the standard used
- (2) the complexes have a lower activity in comparison with their corresponding ligands
- (3) the metal complexes have similar activity in comparison with the ligands.

#### IV. Conclusion

Interaction of two novel Schiff bases  $L^1$  and  $L^2$  with cupric acetate monohydrate salt resulted in the formation of two novel complexes. The spectroscopic studies of the synthesized compounds revealed the structural arrangements. The ligands and their complexes showed interesting fluorescence properties which opens up the utility of them in the field of chemical biology. Ligands and complexes showed moderate antibacterial activity. Thermal analysis measurements showed a high thermal stability of the complexes.

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