



ISSN: 0975-833X

RESEARCH ARTICLE

SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF COPPER (II)
COMPLEXES CONTAINING MIXED LIGANDS, SCHIFF BASES
AND 1, 10-PHENANTHROLINE

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ARTICLE INFO

Article History:

Received 01st June, 2015
Received in revised form
28th July, 2015
Accepted 30th August, 2015
Published online 30th September, 2015

Key words:

Synthesis, Spectral characterization, Mixed
ligands, Schiff bases, Copper (II)
complexes, Antimicrobial studies.

ABSTRACT

Copper (II) complexes containing mixed ligands, Schiff bases (L_1 =(2-carboxyphenyl)-pyridine-2-ylethyleneamine; L_2 =5-Br-(2-carboxyphenyl)-pyridine-2-ylethyleneamine and L_3 =5-NO₂-(2-carboxyphenyl)-pyridine-2-ylethyleneamine) and 1, 10-phenanthroline has been synthesized by conventional methods. These copper (II) complexes has been characterized by elemental analysis, molar conductance, magnetic moment, FT-IR, electronic spectra, ESR spectra, electrochemical analysis, fluorescence spectra and thermal analysis. On the basis of these spectral studies, it is revealed that all the complexes exhibited 1:1 (metal:ligand) ratio with the coordination number 6. The antimicrobial analysis showed that copper (II) complexes containing mixed ligands, Schiff bases (L_1 , L_2 and L_3) and 1, 10-phenanthroline is more active than only ligands.

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Citation: Shrimant V. Rathod, Smita S. Giri and Sandip D. Maind, 2015. "Synthesis, spectral characterization and antimicrobial studies of copper (II) complexes containing mixed ligands, schiff bases and 1, 10-phenanthroline", *International Journal of Current Research*, 7, (9), 20556-20565.

INTRODUCTION

In 21st century the whole world is looking surprisingly towards coordination chemistry as the frontier of chemistry due to its architecturally designed mixed ligand Schiff base complexes and fascinating advances in structural, spectral, non-linear optics, photochemical, electrochemical and biochemical properties. The study of mixed ligand Schiff's base coordination compounds has emerged as one of the major center of attraction for the inorganic chemist and covers a comprehensive range of fascinating and theoretical applications. In synthetic work they continue to provide a challenge in the laboratory. In industry mixed ligand Schiff base coordination compounds play key roles in homogeneous (Kitajima *et al.*, 1988; Sheldon *et al.*, 1981; Bajaj *et al.*, 1988) & heterogeneous (Crubbs and Kroll, 1971; Cernia and Graziani 1974; Wohrle *et al.*, 1991) catalysis, purification of water (Schwoyer, 1981), analytical chemistry (Vogel, 1978), solvent extraction (Aggett and Richardson, 1970), photography (Karas and Ellis, 1980), metallurgy & electro-chemistry (Landau *et al.*, 1982).

They are also used as dyes and also used for the formulation (Harikumar *et al.*, 1989) and pharmaceuticals (May and Bulman, 1983). They are essential in many life processes such as oxygen transfer and metal ion control (Taylor and Vatz, 1973). The rapidly developing field of bioinorganic chemistry is centered on the presence of metal complexes in the biological systems (Jones *et al.*, 1979). Moreover, the study of mixed ligand Schiff base coordination compounds has enabled the inorganic chemist to make significant progress in refining the concept of chemical bonding and to explain the influence that bonding has on the various properties of the compounds (Coleman and Taylor, 1980). Majority of the mixed ligand Schiff base coordination compounds are those of transition metal ion.

Synthesis, structure and biochemical activity of copper (II) complexes of tridentate Schiff base ligands which was prepared from 2-Acetyl pyridine containing N₃ donor set along with terminal NNN- or SCN- ligand is reported (Niederhoffer *et al.*, 1984). The transition metal complexes having oxygen and nitrogen donor Schiff base possess unusual configuration, structural liability and are sensitive to molecular environment. The environment around the metal center as co-ordination geometry, number of coordinated ligands and their donor groups are the key factors for metallic proteins to carry out

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specific physiological functions (Cotton and Wilkinson, 1988). Copper (II) Schiff base complexes with pseudohalides are well known for their preparational accessibilities, exhibiting the flexibility of the coordination geometry around the metal center (Lin, 2009). Metal complexes of 1, 10-phenanthroline and its derivatives are of increasing interest because of their versatile role in chemistry (Haiju Rahaman *et al.*, 2005). The mixed ligand complexes of copper (II) with phen, 2- methyl lactate was reported which play an important role in biological process (Hosny, 2007). The copper (II) complexes of 2-acetyloxybenzoic acid (aspirine), a ligand used as an analgesic are reported to be more significantly active as an anti-inflammatory agent than the un co-ordinated ligand (Samanta *et al.*, 2007). The complexes containing mixed ligands, Schiff bases, and 1,10-phenanthroline have good microbial activities compared to the ligands and have significant potential as antimicrobial agents.

In the present paper, we report the synthesis, spectral characterization, antimicrobial studies of copper (II) complexes containing mixed ligands, Schiff bases, (L_1 =(2-carboxyphenyl)-pyridine-2-ylethyleneamine; L_2 =5-Br-(2-carboxyphenyl)-pyridine-2-ylethyleneamine and L_3 =5-NO₂-(2-carboxyphenyl)-pyridine-2-ylethyleneamine) (Fig. 1) and 1,10-phenanthroline.

MATERIALS AND METHODS

Materials

All chemicals used were of the analytical reagents grade (AR) and of highest purity available. 2-aminobenzoic acid, 2-amino-5-bromobenzoic acid, 2-amino-5-nitrobenzoic acid, 2-acetylpyridine (Lanchester) was purchased from the respective concerns and was used as received.

Methods

Copper was analyzed by titrimetric method. Elemental analysis (C, H and N) were performed on a Thermo Finnigan FLASH EA-112 CHNS analyzer. Molar Conductance (Λ_M) was measured on the ELICO (CM-185) conductivity bridge using ca 10^{-3} M solution in DMF. Magnetic susceptibility was measured on Gouy balance at room temperature using Hg (Co(SCN)₄) as calibrant. Infrared spectra were recorded on Perkin Elmer FT-IR spectrometer as KBr pellets in the 4000-400 cm^{-1} spectral range. ¹H NMR spectra of ligands were recorded on Bruker 400 MHz spectrometer using DMSO as a solvent. Electronic spectra were recorded on a Shimadzu UV-visible NIR spectrophotometer. ESR spectra of the complexes were recorded at room temperature on Varian E-112 spectrometer using TCNE as the standard. Cyclic voltammetry measurements were performed with a CH-400A Electrochemical Analyzer. A standard three electrode system, consisting of Pt disk working electrode, Pt wire counter electrode and Ag/AgCl reference electrode containing aqueous 3M KCl were used. All potentials were converted to SCE scale. Tetrabutyl ammonium perchlorate (TBAP) was used as supporting electrolyte and all measurements were carried out in DMF solution at room temperature with scan rate 50 mVs^{-1} . Florescence spectra were recorded using JASCO F.P.750

fluorescence spectrophotometer equipped with quartz cuvette of 1 cm^3 path length at room temperature. Thermal analysis (TG and DTA) measurements of the complexes were recorded on a Perkin Elmer thermal analyzer, under nitrogen atmosphere with a heating rate of 10°C min^{-1} in the temperature range R.T.-1000°C.

Antimicrobial analysis

The synthesized complexes were screened for their antimicrobial activity *in vitro* against Gram-positive (*Staphylococcus aureus*, *Staphylo cocci fecalis* and *Bacillus s.p.*), Yeast (*Fungus Candida*) and Gram-negative (*Eschi coli*, *Klebsiella* and *Pseudemonus curusin*) microorganism by disk diffusion (Bauer- Kirby) susceptibility test and were compared with standard drug.

Media and reagents

Bacterial isolate from an infectious process. Nutrient broth (soybean-caein digest broth is recommended) for growth of the inoculums. McFarland 0.5 standard for adjusting the turbidity of the inoculums. Vortex mixer for suspension of the inoculums. View box for comparison of broth with standard. A photometer used and satisfactory results are documented. Mueller-Hinton 150-mm agar plates from a lot that produces satisfactory quality control results. The pH must be 7.2 to 7.4 and the depth must be approximately 4mm. Calipers, ruler, or template for measuring the diameters of inhibitory zones.

Procedure

For Inoculums developments, with a wire loop or Dacron-tipped swab, touch the tops of four or five similar appearing, well-isolated colonies on an agar plate culture. The growth was transfred to a tube that contains 4 to 5 ml of a suitable broth medium. The culture was allowed to incubate at 35 degree until it matches the turbidity of the standard prepared in the foregoing and vigorously agitate the standard on a mechanical vortex mixer immediately before use. Adequate light was used to read the tube against a white background ith a contrasting black line. Sterile or broth if necessary was added to obtain turbidity visually comparable with that of the standard. Alternatively a direct broth or saline suspension of colonies from an 16 to 24 hour agar plate may be adjusted to the standard. In that case, the bacteria must have been growth on a nutrient, nonselective medium such as blood agar. Commercially available devices to standardize the inoculum without adjustment of turbidity and without pre-incubation in broth media have also performed acceptably. After 15 minutes of adjusting the turbidity of the inoculum suspension to that of the standard, a sterile nontoxic cotton swab was dipped into the inoculum suspension and rotate the swab several times with firm pressure on the inside wall of the tube to remove excess fluid. Inoculate the dried surface of a Muelier-Hinton agar plate that has been brought by room temperature by streaking the swab three times over the entire agar surface rotating the plate approximately 60 degree to ensure an even distribution of the inoculum. The lid of the dish was replaced and allowed for 3 to 5 minutes, but no longer than 15 minutes for the surface of the agar to dry before adding the antibiotic disks. In an alternative

inoculum preparation, a direct saline or broth suspension of colonies from a nutrient nonselective agar plate that has been incubated for 18 to 24 hours. Adjusted the inoculum to the standard density as before. This method is recommended for *haemophilus* species, *Neisseria gonorrhoea*, *Streptococcus pneumoniae* and *Staphylococcus* species.

Synthesis of Schiff base ligands (L₁/L₂/L₃)

The Schiff base ligands (2-carboxyphenyl)-pyridine-2-ylethyleneamine (L₁), 5-Br-(2-carboxyphenyl)-pyridine-2-ylethyleneamine (L₂) and 5-NO₂-(2-carboxyphenyl)-pyridine-2-ylethyleneamine (L₃) were synthesized by mixing a solution of 2-Acetyl-pyridine (0.121 g, 1 mmol) in 10 ml of ethanol with solution of 2-aminobenzoic acid (0.137 g, 1 mmol) / 2-amino-5-bromobenzoic acid (0.319 g, 1 mmol) / 2-amino-5-nitrobenzoic acid (0.285 g, 1 mmol) which was dissolved in 10 ml of absolute ethanol while stirring. The resulting mixture was refluxed at 60°C until the completion of reaction (checked by TLC). The resultant brown-coloured liquid was concentrated and kept for air evaporation.

Synthesis of (CuL(phen)Cl)Cl (L= L₁/L₂/L₃)

To a ethanolic solution of CuCl₂·2H₂O (0.170 g, 1 mmol), a ethanolic solution of L₁/L₂/L₃ (0.240 g / 0.319 g / 0.285 g; 1 mmol) was added followed by the addition of 1,10-phenanthroline (0.181 g; 1 mmol) as secondary ligand with constant stirring. Resulting solution was refluxed for 2 hr. The resulting solid green product was filtered, washed with ethanol and dried over CaCl₂.

Synthesis of (CuL(phen)ClO₄)ClO₄ (L= L₁/L₂/L₃)

To a ethanolic solution of CuClO₄·6H₂O (0.370 g, 1 mmol), a ethanolic solution of L₁/L₂/L₃ (0.240 g / 0.319 g / 0.285 g; 1 mmol) was added followed by the addition of 1,10-phenanthroline (0.181 g; 1 mmol) as secondary ligand with constant stirring. Resulting solution was refluxed for 2 hr. The resulting solid green product was filtered, washed with ethanol and dried over CaCl₂.

Synthesis of (CuL(phen)N₃)N₃ (L= L₁/L₂/L₃)

To a ethanolic solution of Cu(NO₃)₂·6H₂O (0.241 g, 1 mmol) a ethanolic solution of L₁/L₂/L₃ (0.240 g / 0.319 g / 0.285 g; 1 mmol) was added followed by 1,10-phenanthroline (0.181 g; 1 mmol) as secondary ligand then the ethanolic solution of sodium azide (0.065 g, 1 mmol), added with constant stirring. Resulting solution refluxed for 2 hr. The resulting solid green product was filtered, washed with ethanol and dried over CaCl₂.

Synthesis of (CuL(phen)NCS)NCS (L= L₁/L₂/L₃)

To a ethanolic solution of Cu(NO₃)₂·6H₂O (0.241 g, 1 mmol) a ethanolic solution of L₁/L₂/L₃ (0.240 g / 0.319 g / 0.285 g; 1 mmol) was added followed by 1,10-phenanthroline (0.181 g; 1 mmol) as secondary ligand then the ethanolic solution of ammonium thiocyanate (0.076 g, 1 mmol) added with constant stirring. Resulting solution refluxed for 2 hr. The resulting solid

green product was filtered, washed with ethanol and dried over CaCl₂.

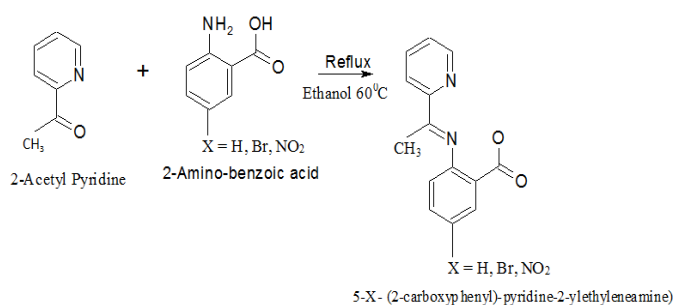
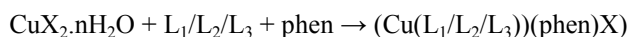


Fig.1. Synthesis and structure of the ligands (L₁, L₂ and L₃)

RESULTS AND DISCUSSION

The three Schiff bases could coordinate to the metal atoms through the phenolate oxygen, imine nitrogen, and amine nitrogen atoms. The copper (II) complexes adopt octahedral geometry by following synthesis procedure.



Elemental Analysis

Calculated value of Cu, C, H and N in ligands and all complexes is given in Table 1. It is observed that the experimental value of Cu was close agreement with calculated value and it gives an idea, that all complexes were maintained their required stoichiometry.

Molar conductance

The metal complexes were dissolved in DMF and the molar conductivities of 10⁻³M of their solutions at room temperature were measured to establish the charge of the metal complexes. The conductance data, shown in Table 1 indicate that, all the metal complexes having conductivity values in the range characteristic of the non-electrolytic nature suggesting that these complexes are neutral.

Magnetic Moment

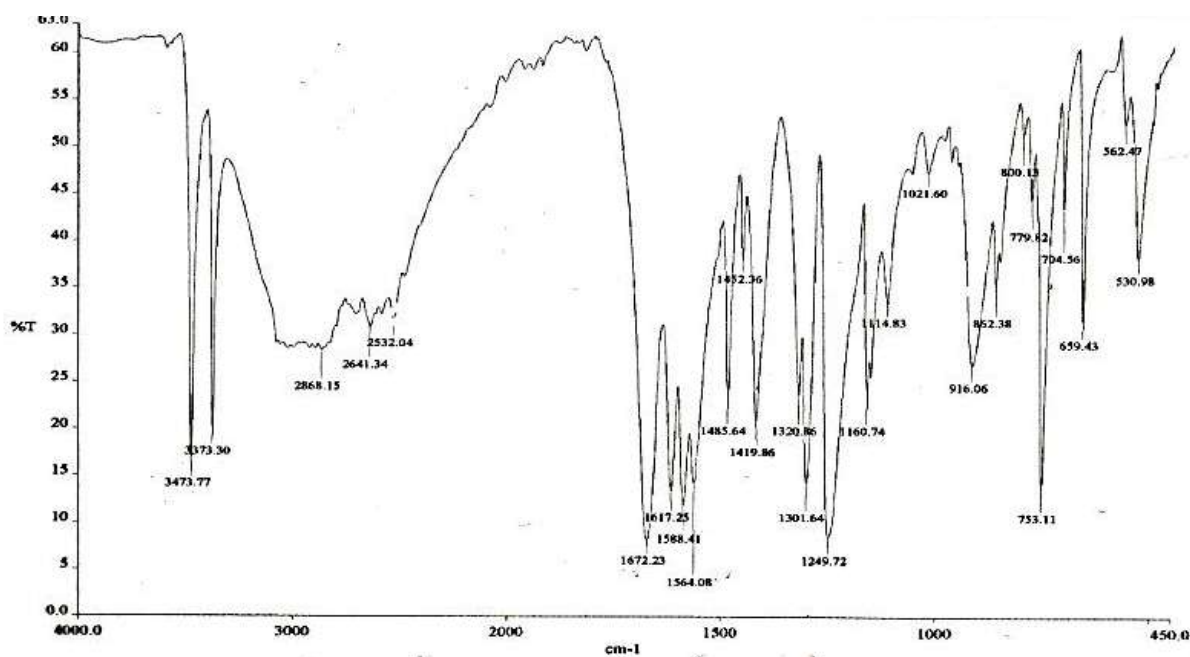
Magnetic moments of the metal complexes are listed in Table 1. The octahedral geometry of copper (II) ion in all complexes is confirmed by the measured magnetic moment values in the range 1.73μ_B -1.90μ_B which is in harmony with the reported value.

IR Spectra

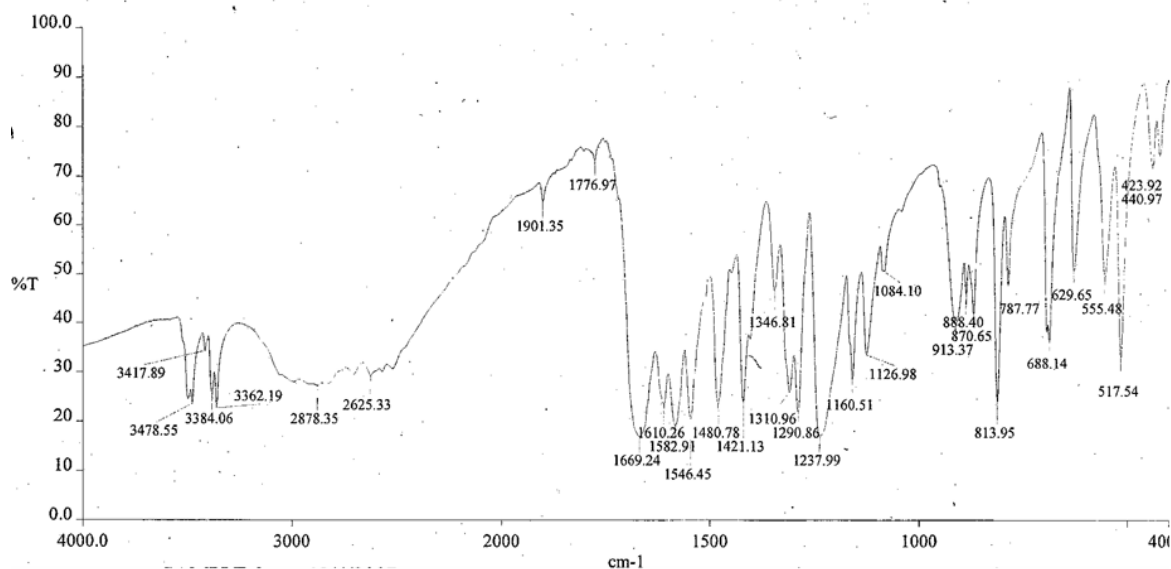
IR data of ligands and complexes is given in Table 2. Typical IR spectra of ligands L₁, L₂ and L₃ is shown in Fig. 2. The IR spectra of Schiff base ligands L₁, L₂ and L₃ show bands at 1669-1677 cm⁻¹, may be assigned to the νC=O (carboxylic group), However, the spectra of all complexes show absence of this band accompanied by the appearance of two characteristic bands at 1625-1605 and 1409-1374 cm⁻¹ attributed to asymmetric and symmetrical stretching of the carboxylic group respectively, indicating the involvement of the carboxylic oxygen atom in the complex formation.

Table 1. Analytical and physico-chemical data of the ligands and copper (II) complexes

Ligands and Copper (II) Complexes	M. F.	Mol. wt.	Color	Yield (%)	M.P. (°C)	Analytical data % found (calculated)				$\Lambda_M(\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$	μ_{eff}
						Cu	C	H	N		
L ₁	C ₁₄ H ₁₂ N ₂ O ₂	240.25	golden brown	72							
[CuL ₁ (phen)Cl] Cl	C ₂₆ H ₁₉ N ₄ O ₂ Cl ₂ Cu	617.714	green	70	>300	10.28	50.55	3.10	9.10	52.58	1.74
[CuL ₁ (phen)ClO ₄] ClO ₄	C ₂₆ H ₁₉ N ₄ O ₁₀ Cl ₂ Cu	682.202	green	65	>300	9.31	45.77	2.8	8.21	109.9	1.73
[CuL ₁ (phen)N ₃] N ₃	C ₂₆ H ₁₉ N ₁₀ O ₂ Cu	567.02	green	68	>300	11.2	50.07	3.37	24.7	55.77	1.87
[CuL ₁ (phen)NCS] NCS	C ₂₈ H ₁₉ N ₆ O ₂ S ₂ Cu	599.153	green	74	>300	10.6	56.13	3.19	14.02	61.35	1.97
L ₂	C ₁₄ H ₁₁ N ₂ O ₂ Br	319.091	dark brown	70							
[CuL ₂ (phen)Cl] Cl	C ₂₆ H ₁₈ N ₄ O ₂ Cl ₂ BrCu	696.618	green	52	>300	9.12	44.82	2.58	8.04	50	1.82
[CuL ₂ (phen)ClO ₄] ClO ₄	C ₂₆ H ₁₈ N ₄ O ₁₀ Cl ₂ BrCu	761.1061	green	62	>300	8.34	40.7	2.36	21.02	105	1.83
[CuL ₂ (phen)N ₃] N ₃	C ₂₆ H ₁₈ N ₁₀ O ₂ BrCu	645.924	green	66	>300	9.83	48.34	2.78	21.68	57	1.81
[CuL ₂ (phen)NCS] NCS	C ₂₈ H ₁₈ N ₆ O ₂ S ₂ BrCu	678.057	green	72	>300	9.37	49.59	2.65	10.32	59	1.98
L ₃	C ₁₄ H ₁₁ N ₃ O ₄	285.192	orange brown	76							
[CuL ₃ (phen)Cl] Cl	C ₂₆ H ₁₈ N ₅ O ₄ Cl ₂ Cu	599.451	green	63	>300	11.04	54.29	3.32	11.04	49.40	1.75
[CuL ₃ (phen)ClO ₄] ClO ₄	C ₂₆ H ₁₈ N ₅ O ₁₂ Cl ₂ Cu	726.938	green	67	>300	8.74	42.95	2.49	9.63	113.14	1.76
[CuL ₃ (phen)N ₃] N ₃	C ₂₆ H ₁₈ N ₁₁ O ₄ Cu	612.018	green	62	>300	10.38	51.62	2.96	25.17	58.16	1.87
[CuL ₃ (phen)NCS] NCS	C ₂₈ H ₁₈ N ₇ O ₄ S ₂ Cu	644.15	green	66	>300	9.86	52.2	2.81	15.22	61.35	1.97



(a)



(b)

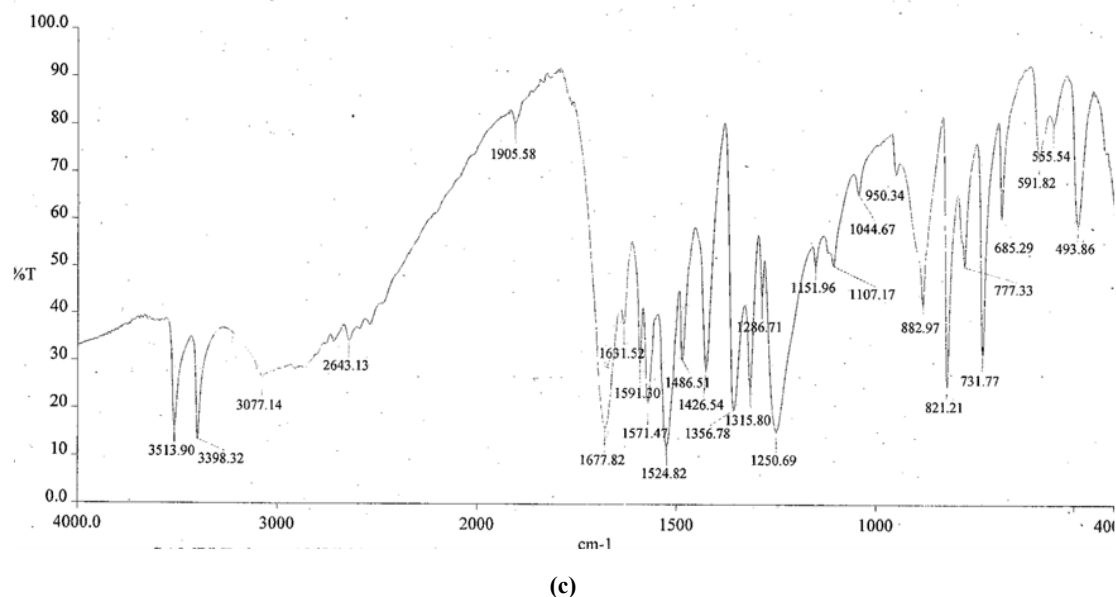
Fig. 2. IR spectra of (a) L₁ (b) L₂ and (c) L₃

Table 2. Infrared spectral data of the ligands and copper (II) complexes

Ligands and Copper (II) Complexes	vC=N	COO ⁻	1, 10- phenanthroline	Cl-/ClO ₄ ⁻ /N ₃ ⁻ /NCS ⁻	Py-N
L ₁	1617	1672			659
[CuL ₁ (phen)Cl] Cl	1614	1591, 1325	1538,1409,869,717		644
[CuL ₁ (phen)ClO ₄] ClO ₄	1606	1551, 1386	1524,1430,849,722	1087,736	623
[CuL ₁ (phen) N ₃] N ₃	1620	1572,1380	1526,1425,849,725	2066	644
[CuL ₁ (phen) NCS] NCS	1606	1582, 1383	1528,1425,844,718	2097	646
L ₂	1610	1669			669
[CuL ₂ (phen)Cl] Cl	1620	1595,1377	1544,1430,856,723		640
[CuL ₂ (phen) ClO ₄] ClO ₄	1618	1593, 1374	1535,1431,896,736	1091,730	633
[CuL ₂ (phen) N ₃] N ₃	1620	1595,1377	1555,1426,827,740	2066	654
[CuL ₂ (phen) NCS] NCS	1606	1595,1377	1555,1426,866,735	2097	646
L ₃	1631	1677			591
[CuL ₃ (phen)Cl] Cl	1626	1542,1384	1542,1428,845,721		574
[CuL ₃ (phen) ClO ₄] ClO ₄	1625	1544, 1350	1544,1426,849,722	1110,730	566
[CuL ₃ (phen) N ₃] N ₃	1626	1543,1384	1543,1426,823,722	2066	573
[CuL ₃ (phen) NCS] NCS	1604	1580,1340	1518,1426,843,718	2095	571

Table 3. Electronic spectral data of the ligands and copper (II) complexes

Ligands and Copper (II) Complexes	$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions and charge transfer transitions (nm)	d \rightarrow d transitions (nm)
L ₁	252, 275, 345	
[CuL ₁ (phen)Cl] Cl	250, 275	650, 730
[CuL ₁ (phen)ClO ₄] ClO ₄	250, 270	615, 730
[CuL ₁ (phen) N ₃] N ₃	252, 280, 336	664
[CuL ₁ (phen) NCS] NCS	260, 275, 380	650,725
L ₂	272, 332	
[CuL ₂ (phen)Cl] Cl	250, 290	650,730
[CuL ₂ (phen) ClO ₄] ClO ₄	255, 265	640 730
[CuL ₂ (phen) N ₃] N ₃	255, 280, 386	685
[CuL ₂ (phen) NCS] NCS	260, 275, 385	650. 725
L ₃	276, 332, 410	
[CuL ₃ (phen)Cl] Cl	260, 275, 410	650,725
[CuL ₃ (phen) ClO ₄] ClO ₄	260, 275, 410	666,725
[CuL ₃ (phen) N ₃] N ₃	260, 275, 385	680
[CuL ₃ (phen) NCS] NCS	260, 275, 410	650,725

Table 4. ESR spectral assignments for ligands and copper (II) Spin Hamiltonian parameters of polycrystalline complexes

Copper (II) Complexes	g	g _⊥	g _{av}	A ^a	A _⊥ ^a	A _{av} ^a	G	α^2	β^2	γ^2	K	K	K _⊥	f ^b
L ₁														
[CuL ₁ (phen)ClO ₄] ClO ₄	2.1409	2.044	2.076	129.037	26.791	57.537	3.1810	0.781	0.786	0.950	0.21	0.612	0.741	165.00
L ₂														
[CuL ₂ (phen)ClO ₄] ClO ₄	2.229	2.067	2.121	130.90	28.051	62.334	3.4171	0.8173	0.8467	0.966	0.28	0.691	0.789	170.28
L ₃														
[CuL ₃ (phen)ClO ₄] ClO ₄	2.351	2.091	2.177	139.60	30.297	66.731	3.8510	0.8640	0.9597	0.976	0.28	0.828	0.843	168.40

Expressed in units of cm⁻¹ multiplied by a factor of 10⁻⁴

The mode of coordination of carboxylate group has often been deduced from the magnitude of the observed separation between the ν_{sy} (COO-) and ν_{asy} (COO-). The separation value (Δ) between ν_{asy} (COO-) in metal complexes was more than 200 cm^{-1} (270 cm^{-1} -205 cm^{-1}) suggests the coordination of carboxylate group in all metal complexes in a monodentate fashion. The azomethine $\nu(\text{C}=\text{N})$ bands in the IR spectra of the ligands appear in the range 1610 cm^{-1} -1635 cm^{-1} , shifting of this band towards the lower frequency region by 15 cm^{-1} -25 cm^{-1} in complexes indicates involvement of azomethine nitrogen in coordination with metal ion. The pyridine ring deformation mode at $\sim 620 \text{ cm}^{-1}$ in these spectra of the free ligands is shifted to higher wave numbers in the spectra of the complexes indicating coordination of the complexes indicating coordination of the pyridine ring nitrogen atom to the copper (II). (CuL(phen)ClO₄) ClO₄ (L= L₁/L₂/L₃) exhibit band around 1087 cm^{-1} -1110 cm^{-1} and 625 cm^{-1} assignable to the asymmetry Cl-O stretching mode and the asymmetric Cl-O bending mode respectively, both show considerable splitting due to a reduced symmetry of the coordinated species suggesting some interaction of the ClO₄⁻ anion with the metal. (CuL(phen)N₃) N₃ (L= L₁/L₂/L₃) exhibit a strong sharp stretch corresponding to $\nu(\text{N}_3)$ at 2066 cm^{-1} . (CuL(phen)NCS)NCS (L= L₁/L₂/L₃) exhibit $\nu(\text{NCS})$ at 2117 cm^{-1} . These spectral features support azido and thiocyanato structures in respective complexes. The 1, 10-phenanthroline bands at 722 cm^{-1} shows their involvement in the complexes.

NMR spectra

The ¹H NMR data of ligands L₁, L₂ and L₃ is as follows; L₁ - δ 2.4 (s, H₃C-C=N) ; δ 6.5-8.3 (m<ArH) δ 8.5(s, -C=N), L₂- δ 2.1 (s, H₃C-C=N) ; δ 6.5-8.4 (m<ArH) δ 8.5(s, -C=N), L₃- δ 2.3 (s, H₃C-C=N) ; δ 6.5-8.3 (m<ArH) δ 8.4(s, -C=N).

Electronic spectra

Electronic spectral data of ligands and complexes is given in Table 3. The electronic spectra of the free ligands L₁/L₂/L₃ shows two weak bands at 330 nm – 270 nm and 410 nm – 325 nm which are assigned to the $n \rightarrow \pi$, $\pi \rightarrow \pi^*$ transitions respectively. The broad band centered at 655 nm – 725 nm appearing as an envelope in the copper (II) complexes assigned to the ²E_g and ²T_{2g} transition reveals the octahedral geometry. The ²E_g and ²T_{2g} states of the octahedral copper (II) (d⁹) split under the influence of tetrahedral distortion and distortion can be such as to cause three transition ²B_{1g} → ²B_{2g}, ²B_{1g} → ²E_g and ²B_{1g} → ²A_{1g} to remain unresolved in the spectra.

ESR spectra

ESR data of (CuL(phen)ClO₄)ClO₄ (L= L₁/L₂/L₃) is given in Table 4. To obtain further information about the stereochemistry and the site of the metal ligand bonding and to determine the magnetic interaction in the metal complexes, the X-band ESR spectra of copper (II) perchlorate complexes have been recorded in the polycrystalline state at room temperature and in DMF solution at LNT using 9.5 GHz field modulation and the g factors were quoted relative to the standard marker TCNE (g = 2.00277). EPR spectral assignments of the copper (II) perchlorate complexes along with the spin Hamiltonian

parameters and orbital reduction parameters were calculated and are summarized in Table 4. The EPR spectra of the complexes show typical axial behavior with slightly different g_{||} and g_⊥ values. The geometric parameter G, which is measure of exchange interaction between the copper centers in polycrystalline compound, is calculated using the equation $G = (g_{||} - 2.0023) / (g_{\perp} - 2.0023)$. If $G > 4$, the exchange interaction between copper (II) centers is negligible and if $G < 4$, a considerable exchange interaction is indicated in the solid complex. In all the copper (II) complexes $g_{||} > g_{\perp} > 2.0023$ and G values within the range 2.60 and 4.95 are consistent with $d_{x^2-y^2}$ ground state. The EPR spectra of all the copper (II) complexes in DMF solution at LNT are axial and $g_{||} > g_{\perp} > 2.0023$, corresponding to the presence of an unpaired electron in the $d_{x^2-y^2}$ orbital. For a copper (II) perchlorate complex, g_{||} is a parameter sensitive enough to indicate covalence. The EPR parameters g_{||}, g_⊥, g_{av}, A_{||} and A_⊥ and the energies of the d-d transitions were used to evaluate the bonding parameters α^2 , β^2 and γ^2 , which may be regarded as measures of covalency of the in-plane σ -bonding, in-plane π -bonding and out of plane π -bonding, respectively. The value of α^2 and β^2 were estimated from the following expressions where $\alpha^2 = 1.0$ indicates complete ionic character, whereas $\alpha^2 = 0.5$ denotes 100% covalent bonding, with the assumption of negligibly small values of the overlap integral.

$$\alpha^2 = - (A_{||} / 0.036) + (g_{||} - 2.0023) + 3/7 (g_{\perp} - 2.0023) + 0.04 \quad (1)$$

$$\beta^2 = (g_{||} - 2.0023) E / -8\lambda\alpha^2 \quad (2)$$

The following simplified expressions were used to calculate the bonding parameters.

$$K_{||}^2 = (g_{||} - 2.00277) E_{d-d} / -8\lambda \quad (3)$$

$$K_{\perp}^2 = (g_{\perp} - 2.00277) E_{d-d} / -2\lambda \quad (4)$$

where $K_{||}^2 = \alpha^2\beta^2$ and $K_{\perp}^2 = \alpha^2\gamma^2$, K_{||} and K_⊥ are orbital reduction factors and λ_0 represents the one spin-orbit coupling constant which equals -828 cm^{-1} . According to Hathaway, $K_{||} \approx K_{\perp} \approx 0.77$ for pure in-plane σ -bonding and $K_{||} < K_{\perp}$ for in-plane π -bonding, while for out of plane π -bonding $K_{||} > K_{\perp}$. In all the copper (II) complexes, it is observed that $K_{||} < K_{\perp}$ which indicates the presence of significant in-plane π -bonding. The values of bonding parameters α^2 , β^2 and $\gamma^2 < 1.0$ indicate significant in-plane σ -bonding and in plane π -bonding. The Fermi contact hyperfine interaction term K may be obtained from following expression;

$$K = A_{av} / P\beta^2 + (g_{av} - 2.00277) / \beta^2 \quad (5)$$

where P is the free ion dipolar term and its value is 0.036. K is dimensionless quantity, which is a measure of the contribution of s electrons to the hyperfine interaction and is generally found to have a value of 0.30.

The K values obtained for all the complexes are in agreement with those estimated by Assour, Abragam and Pryce.

Cyclic voltammetry

The electrochemical properties of the ligands and its copper (II) complexes has been examined by using cyclic voltammeter in 10^{-3} M DMF solution containing 0.05M n-Bu₄NClO₄ as supporting electrolyte and redox potentials are expressed with reference to Ag/AgCl. All the measurements were carried out in the potential range +1.5 V to -1.5 V with scan rate 50 mV s⁻¹. The potentials are summarized in Table 5. The free ligand displayed waves at E_{pa} values -0.55 V to -0.19 V and E_{pc} value -0.49 V to -0.10 V corresponding to irreversible reduction of the L₁-L₃. The electrochemical potentials of the copper (II) complexes were characterized by well-defined waves in anodic region. Since the ligands used in this work are not reversibly oxidized or reduced in the applied potential range, the redox processes are assigned to the metal centres only. In anodic region, the complexes exhibit two quasi-reversible peaks characteristics for Cu (II)/Cu(I) (E_{pc} = -0.40 V to -0.12 V) and Cu(I)/Cu(0) (E_{pc} = -0.8 V to -0.04 V) reduction. During reverse scan the peaks at (E_{pa} = -0.59 V to -0.43 V and -0.90 V to -0.03 V) corresponding to Cu(0)/Cu(I) and Cu(I)/Cu(II) are observed. The redox processes are quasi-reversible with large peak to peak separation (ΔE_p) of 230 V to 640 V. Further the redox process for the copper (II) complex of L₃ appear at more positive potential as compared to those for corresponding copper (II) complexes of L₁ and L₂.

Table 5. Electrochemical data of ligands and copper (II) complexes

Ligands and Copper (II) Complexes	Reduction Potentials(V)			
	E _{pa} (V)	E _{pc} (V)	ΔE_p (V)	E _{1/2} (V)
L ₁				
[CuL ₁ (phen)Cl] Cl	-0.12	-0.442	0.322	-0.281
[CuL ₁ (phen)ClO ₄] ClO ₄	-0.25	-0.525	0.275	-0.387
[CuL ₁ (phen)N ₃] N ₃	-0.255	-0.544	0.290	-0.417
[CuL ₁ (phen)NCS] NCS	-0.2805	-0.550	0.265	-0.399
L ₂				
[CuL ₂ (phen)Cl] Cl	-0.20	-0.52	0.27	-0.360
[CuL ₂ (phen)ClO ₄] ClO ₄	-0.27	-0.525	0.25	-0.306
[CuL ₂ (phen)N ₃] N ₃	-0.18	-0.432	0.28	-0.397
[CuL ₂ (phen)NCS] NCS	-0.210	-0.460	0.25	-0.333
L ₃				
[CuL ₃ (phen)Cl] Cl	-0.35	-0.596	0.004	-0.473
[CuL ₃ (phen)ClO ₄] ClO ₄	-0.319	-0.541	0.23	-0.277
[CuL ₃ (phen)N ₃] N ₃	-0.354	-0.585	0.231	-0.380
[CuL ₃ (phen)NCS] NCS	+0.03	-0.585	0.64	-0.310

For the most electron withdrawing substituents (R=NO₂) the reduction of the metal ion occurs at the highest potential. As the σ -bonding ability of the N-atom decreases with the increasing electron withdrawing ability of substituents, the Cu (II)/Cu (I) reduction becomes more difficult.

Thermal analysis

The thermal decomposition studies of copper (II) complexes of L₁ except (CuL₁(phen)ClO₄) ClO₄ were carried in the temperature range of 20°C to 1200°C. The complex (CuL₁(phen)ClO₄) ClO₄ was not studied by thermal analysis for safety reasons. The complex (CuL₁(phen)Cl)Cl undergoes decomposition in three steps. There is no mass loss up to 190°C revealing the absence of either water or solvent molecules in this complex. The first stage takes place in the 170°C to 270°C range with DTG peak at 230°C corresponding to mass loss 6.36% may be attributed to the decomposition of chlorine molecule (calculated mass loss=6.84%). The second stage takes place in 270°C to 440°C range corresponding to mass loss 34 % to 96 % may be attributed to the decomposition of 1, 10-phenantroline molecule (calculated mass loss=34.74%) with one broad DTG peak at 380°C to 1195°C with weak endothermic peak 980°C corresponding to the decomposition of Schiff base leaving anhydrous CuCl₂, 14.6% and calculated loss 15.3% molecule in which the DTA endothermic peaks at 660°C and 1025°C with weak multiplets at 960°C & 990°C. The Typical TG, DTG and DTA curves of (CuL₁(phen)N₃) N₃ is presented in Fig. 3. The complex (CuL₁(phen)N₃) N₃ undergoes decomposition in two steps. There is no mass loss up to 210°C range with DTG peak at 290°C corresponding to mass loss 61.32 % may be attributed to the decomposition of azide, 1,10-phenantroline and half of the ligand molecule 'L₁' (calculated mass loss = 62.15 %). The DTA curve gives an endothermic peak at 297°C. The second stage takes place in 320°C to 1051°C range with DTG peak 1010°C corresponding to the mass loss 24.11% may be attributed to the decomposition of the remaining half of the ligand molecule of 'L₁' (calculated mass loss = 25.93 %) leaving anhydrous CuO residue. The DTA curve gives weak endothermic multiplets in the 420°C to 1051°C. The complex (CuL₁(phen)NCS)NCS undergoes decomposition in three steps. There is no mass loss up to 170°C revealing the absence of either water or solvent molecule.

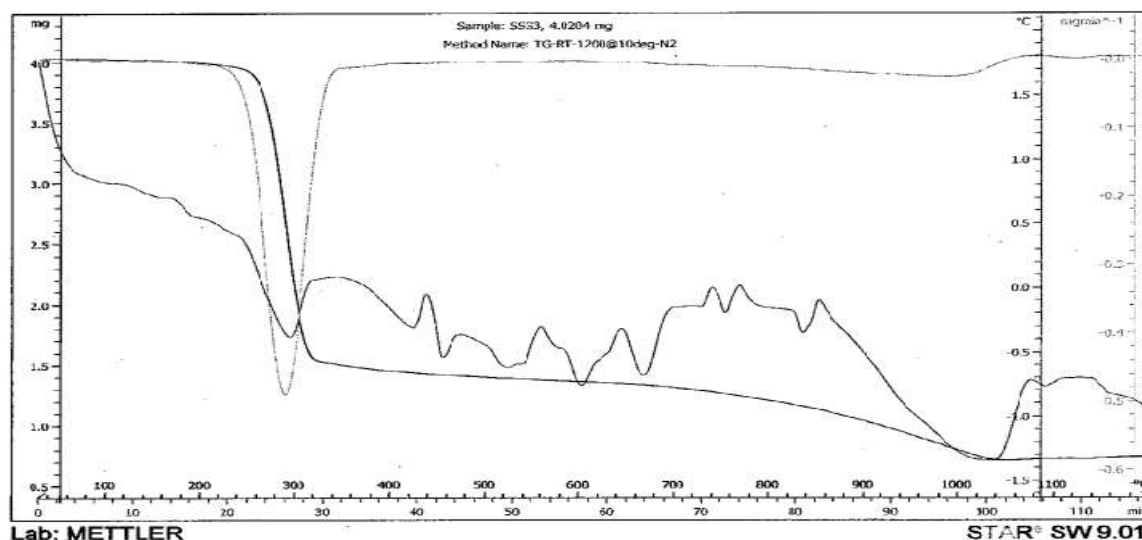


Fig. 3. Typical TG, DTG and DTA curve of [CuL₁(phen)N₃] N₃

The first stage takes place in the 170°C to 270°C range with weak DTA peak at 177°C corresponding to the mass loss 10.90% may be attributed to the decomposition of NCS ion which is in agreement with a calculated mass loss of 10.73 %. The second stage takes place in the 270°C to 480°C range. The DTA curve gives a sharp exothermic peak at 277°C corresponding to mass loss of 33.30 % attributed to the decomposition of 1,10-phenanthroline molecule. The third stage takes place in the 480°C to 1190°C range, corresponding to the mass loss 45 % may be attributed to the decomposition of Schiff base and leaving anhydrous CuO at 14.2% (calculated mass loss 14.67 %)

exhibit photoluminescence with an emission at 411 nm and 413 nm upon excitation at 282 nm and 288 nm. The ligand L₃ does not exhibit photoluminescence. The Cu (II) complexes show strong fluorescence with high quantum yield in DMF. The excitation of molecules at 360 nm to 363 nm, gives an emission at 411 nm to 510 nm with high intensity 5.701 to 659.12. It can be seen that the emission intensity of copper (II) complexes is found to be higher than that of corresponding free ligands. The enhanced fluorescence efficiency of the complexes is attributed to the co-ordination of the ligands to the copper (II) which effectively increases rigidity of ligands and reduces the loss of energy by thermal vibration decay.

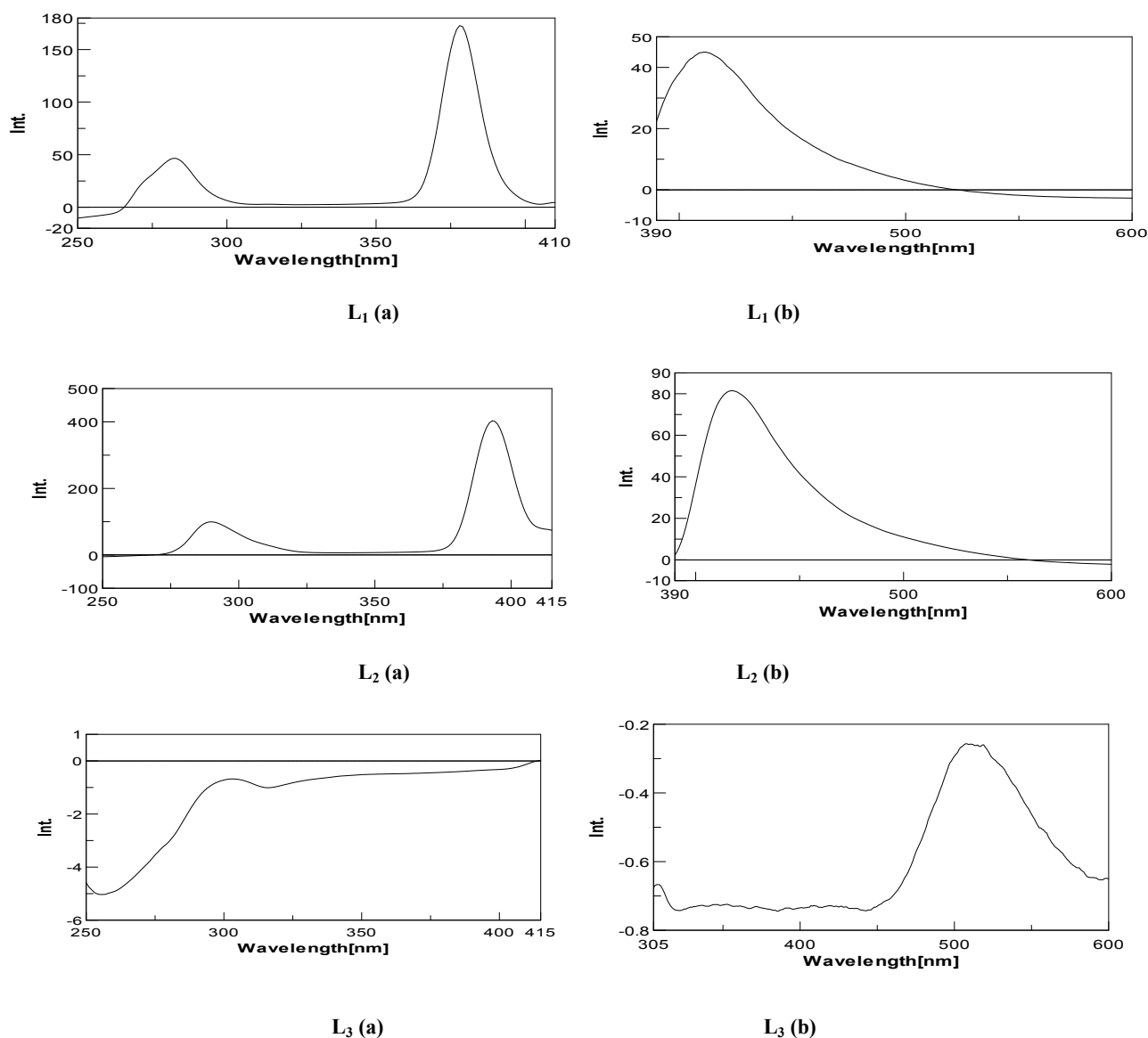


Fig. 4. The photoluminescence spectra of ligands L₁, L₂, L₃ (a) Excitation spectra, (b) Emission spectra

Fluorescence spectra

The photoluminescence spectra of ligands L₁, L₂ and L₃ are shown in Fig. 4. The photoluminescence data of ligands and complexes is given in Table 6. The photoluminescence properties of ligands L₁, L₂, L₃ and their copper (II) complexes studied at room temperature in DMF. The ligands L₁ and L₂

Antimicrobial analysis

For antimicrobial analysis, Cefprofloxacin was taken as standard for Gram-positive. It was activated by 2 mg/ml. (CuL₃(phen)ClO₄) ClO₄ complex is more active than standard for Gram-positive. For antimicrobial analysis, Fluconazole was taken as standard for Gram-negative. It was activated by 1 mg/ml.

Table 6. Photoluminescence properties of ligands and copper (II) complexes

Ligands and Copper (II) Complexes	Excitation wavelength (nm)	Emission maxima (nm)	quantum yield Φ
L ₁	282	408	
[CuL ₁ (phen)Cl] Cl	352	417	0.05
[CuL ₁ (phen)ClO ₄] ClO ₄	363	413	0.04
[CuL ₁ (phen)N ₃] N ₃	363	424	0.01
[CuL ₁ (phen)NCS] NCS	350	413	0.09
L ₂	288	413	
[CuL ₂ (phen)Cl] Cl	357	417	0.04
[CuL ₂ (phen)ClO ₄] ClO ₄	363	424	0.03
[CuL ₂ (phen)N ₃] N ₃	358	421	0.02
[CuL ₂ (phen)NCS] NCS	358	420	0.02
L ₃			
[CuL ₃ (phen)Cl] Cl	357	510	0.04
[CuL ₃ (phen)ClO ₄] ClO ₄	362	508	0.02
[CuL ₃ (phen)N ₃] N ₃	363	416	0.01
[CuL ₃ (phen)NCS] NCS	350	414	0.01

Table 7. Biological activity of ligands and copper (II) complexes

Ligands and Copper (II) Complexes	Gram Positive			Yeast	Gram Negative		
	<i>Staphylo coccus aureus</i>	<i>Staphylo cocci fecalis</i>	<i>Bacillus s.p.</i>	<i>Fungus Candida</i>	<i>Eschi coli curusin</i>	<i>Klebsiella</i>	<i>Pseudomonus</i>
L ₁							
[CuL ₁ (phen)Cl] Cl	100	008	016	008	250	025	016
[CuL ₁ (phen)ClO ₄] ClO ₄	016	004	008	004	125	016	008
[CuL ₁ (phen)N ₃] N ₃	025	025	025	250	025	025	025
[CuL ₁ (phen)NCS] NCS	025	025	025	100	025	025	012
L ₂							
[CuL ₂ (phen)Cl] Cl	100	002	002	050	125	004	016
[CuL ₂ (phen)ClO ₄] ClO ₄	016	001	001	R	125	002	008
[CuL ₂ (phen)N ₃] N ₃	250	025	250	250	100	250	500
[CuL ₂ (phen)NCS] NCS	100	100	012	225	250	500	025
L ₃							
[CuL ₃ (phen)Cl] Cl	100	004	004	100	025	004	008
[CuL ₃ (phen)ClO ₄] ClO ₄	001	002	02	008	016	002	004
[CuL ₃ (phen)N ₃] N ₃	050	025	050	100	025	050	100
[CuL ₃ (phen)NCS] NCS	100	050	050	025	025	050	100

Results showed that all complexes were more active than ligands. *Candida* was taken as a standard for Yeast and Fungus and was activated by 16 mg/ml. Complex (CuL₁(phen)ClO₄) ClO₄ and (CuL₃(phen)ClO₄) ClO₄ were more. The concentration of the standard and complexes were used 5 mg/ml for antimicrobial analysis and the duration was 3 weeks. Cyrofloxin was taken as standard for antibiotic. When the concentration was 10 mg/ml, it was activated at 22-25 mg/ml & concentration was 5 mg/ml, it was activated at 16-18 mg/ml. The bactericidal investigation data of the complexes are summarized in Table 7. Moreover, all the complexes are moderately active as compared to the standard bactericide (Streptomycin). A comparative study of the ligands and their copper (II) complexes indicates that the complexes are more active than their respective ligands. The activity increases upon coordination. The increased activity of the metal chelates than those of the ligands can be explained on the basis of Overton's concept and Chelation theory. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of the π -electrons over the whole chelating ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms. There are other factors also, which increase the activity viz. stability constant, solubility,

molar conductance, magnetic moment, lipophilicity and hydrophilicity, M-L bond length etc.

Conclusion

In this work, the coordination chemistry of the three Schiff base ligands (L₁=(2-carboxyphenyl)-pyridine-2-ylethyleneamine; L₂ = 5-Br - (2-carboxyphenyl)-pyridine-2-ylethyleneamine and L₃ = 5-NO₂ - (2-carboxyphenyl)-pyridine-2-ylethyleneamine) and their copper (II) complexes with Cl-/ClO₄-/N₃-/NCS- and 1,10-phenanthroline as secondary ligand were synthesized, described and characterized. The three Schiff base ligands act as monobasic tridentate, coordinated to the metal ions in a tridentate manner with ONN donor sites of the carbonyl oxygen, azomethine nitrogen, and pyridine nitrogen along with anion and two nitrogen of 1, 10-phenanthroline in the complex formation and in ligands, the coordination mode of carboxylate group is unidentate mode, correlating the experimental data, one can suggest the octahedral geometry for the prepared metal complexes. All the copper (II) complexes exhibit redox potential corresponding to Cu(II)/Cu(I) and Cu(I)/Cu(0), and the redox potential copper (II) complexes increases more positive by increasing electron withdrawing capacity. The copper (II) complexes showed high intensity fluorescence with high quantum yield in DMF solvent than the corresponding ligands. All the copper (II) complexes

are more active than the ligands and can be act as a significant potential antimicrobial agent.

Acknowledgements

The authors are thankful to (CMET) Pune, (IIT) Mumbai, (ISSC) Bangalore, University of Mumbai, ISI Standard Nikhil Analytical Laboratory, Sangli for Characterization and antimicrobial analysis. The authors are very much thankful to principal Dr. (Mrs.) Medha J. Gupte for their administrative support, cooperation and help.

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