



Synthesis, characterisation and biological activities of copper(II) complexes with semicarbazones and thiosemicarbazones

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ABSTRACT

Cu(II) complexes containing ligands 2-formyl pyridine semicarbazone (L_1), 2-formyl pyridine thiosemicarbazone (L_2), 5-methyl-2-formyl pyridine semicarbazone (L_3) and 5-methyl-2-formyl pyridine thiosemicarbazone (L_4) have been synthesised. The ligands were characterised on the basis of elemental analyses, IR, ¹HNMR and mass spectral studies while that of the complexes were characterised by elemental analyses, molar conductance, magnetic moment, IR, electronic and EPR spectral studies. On the basis of elemental analyses and molar conductance data the complexes were found to have general composition $[Cu(L)_2X_2]$ (where $L=L_1, L_2, L_3$ and L_4 , $X = Cl^-$, $\frac{1}{2}SO_4^{2-}$, NO_3^-). On the basis of IR, electronic and EPR spectra of complexes, tetragonal distorted octahedral geometries were found with planar coordination of the ligand around Cu^{2+} ion and the anions occupies axial position.

Keywords : Tetragonal bidentate, Copper(II) complexes.

INTRODUCTION

The coordination chemistry has been considerably enriched due to the synthesis of metal complexes, in which the metal is coordinated through sulphur, nitrogen and oxygen. Metal complexes with ligands containing N, O or S donors have been found to be useful as potential drugs and fungicidal agents [1,2]. The semicarbazones and thiosemicarbazones usually behave as chelating ligands and usually react with metallic cations giving complexes. These are versatile ligands in both neutral and anionic forms. Metal complexes of semicarbazones and thiosemicarbazones have gained special attention due to their importance in medicine and biological system [3]. The main interest to synthesise and characterise the transition metal complexes of these ligands is due to their pharmacological activities. Copper (II) complexes with semicarbazides and thiosemicarbazide have received much attention due to their wide range of applications as an antibacterial [4-7] antifungal [8-11], chemical sensor [12-14], antiviral [15-17] agent and catalyst [18-20]. In addition, they have also been used in the treatment of a number of tumors, including Hodgkin's disease.

In this paper we report the synthesis, spectral and biological investigations of Cu(II) complexes with semicarbazide and thiosemicarbazide based ligands : 2-formyl pyridine semicarbazone (L_1), 2-formyl pyridine thiosemicarbazone (L_2), 5-methyl-2-formyl pyridine semicarbazone (L_3), 5-methyl-2-formyl pyridine thiosemicarbazone (L_4).

These ligands were synthesised by the reactions as represented below (Fig.1)

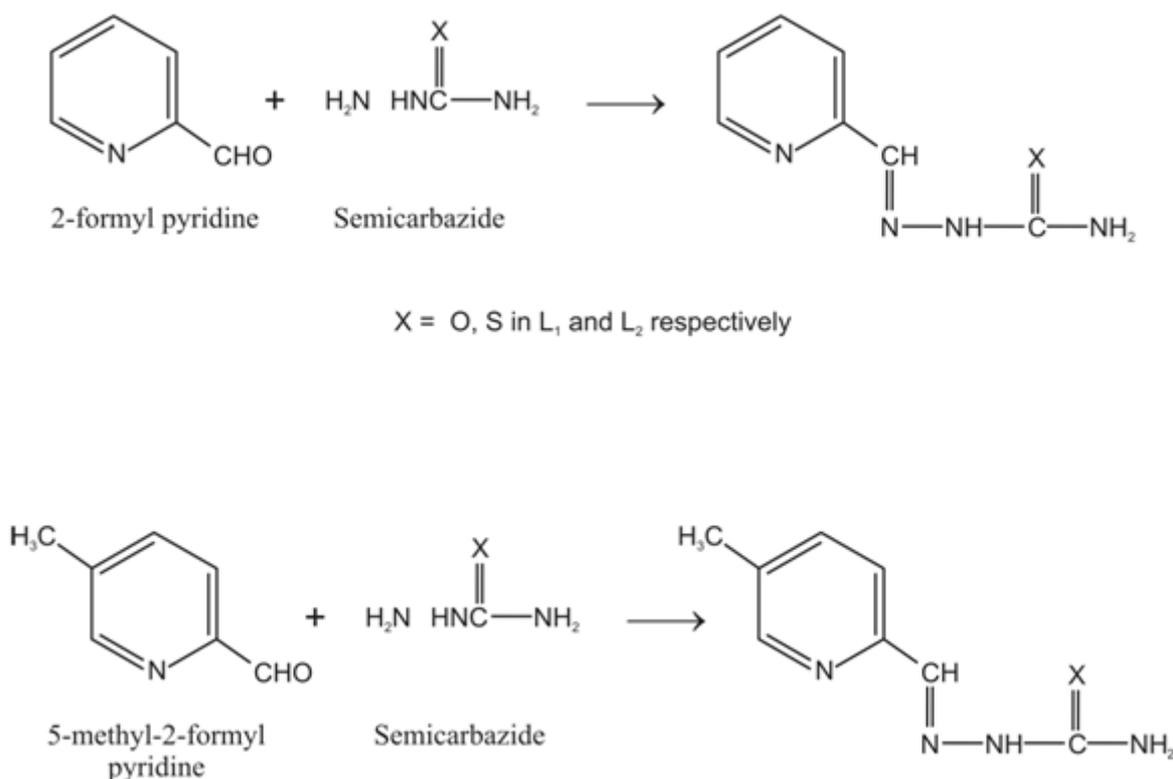


Fig.1 : Synthesis of ligand

EXPERIMENTAL SECTION

Materials

All the chemicals used were of Anala R grade and procured from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and were used as received. All solvents used were of standard/spectroscopic grade.

Synthesis of ligands

To a hot aqueous solution of semicarbazide hydrochloride and 0.02 g sodium acetate a hot ethanolic solution (20 mL) of 2-formyl pyridine (2.0g, 0.02 mol) was added. Mixture was refluxed on water bath for an hour at around 80°C. On cooling at $\approx 0^\circ\text{C}$ ligand is precipitated out. It was filtered and washed with hot water and dried over P₄O₁₀.

Thiosemicarbazide (.02 mol) and 2-formyl pyridine (.02 mol) were taken in a round bottom flask. 20 mL ethanol and 1 mL of acetic acid was added and mixture was refluxed at around 80°C till clear solution is obtained. On cooling at $\approx 0^\circ\text{C}$ ligand is precipitated out. It was filter, washed with ethanol and dried P₄O₁₀.

Synthesis of metal complexes

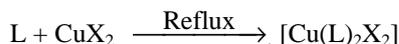
A hot ethanolic solution (20 mL) of ligand L₁, L₂, L₃ and L₄ (0.001 mol) and hot ethanolic solution (20 mL) of corresponding metal salt (0.002 mol) were mixed together with constant stirring. The mixture was refluxed for 4 hours at 80-85°C. On cooling a complex was precipitated out. It was filtered, washed with cold ethanol and dried under vacuum over P₄O₁₀.

Physical measurements

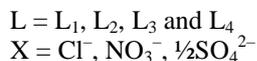
C, H and N were analysed on a carlo-Erba 1106 elemental analyser. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using CuSO₄.5H₂O as calibrant. ¹HNMR spectra was recorded at room temperature on a Bruker Advance DPX-300 spectro meter using DMSO-d₆ as a solvent. IR spectra (KBr) were recorded on FTIR spectrum BX-11 spectrophotometer. The electronic spectra were recorded in DMSO on a Shimadzu UV mini-1240 spectrophotometer. EPR spectra were recorded as polycrystalline samples and in a DMSO solution at liquid nitrogen temperature (LNT) and room temperature (RT) on an E₄-EPR spectrometer using DPPH as a g-marker.

RESULTS AND DISCUSSION

The formation of the complexes can be represented by the following reaction:



Where



On the basis of elemental analysis, the complexes were assigned to possess the composition as shown in Table 1.

Table 1 : Elemental Analysis and molar conductance data of Cu(II) complexes

Complexes	Molar Conductance $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	Colour	m.p $^{\circ}C$	Yield%	Elemental Analysis data calculated / (found)			
					M	C	H	N
[Cu(L ₁) ₂ Cl ₂] CuC ₁₄ H ₁₆ N ₈ O ₂ Cl ₂	19	Green	266	66	13.7 (13.5)	36.32 (36.30)	3.45 (3.40)	24.21 (24.19)
[Cu(L ₁) ₂ SO ₄] CuC ₁₄ H ₁₆ N ₈ SO ₆	18	Light Blue	276	65	13.03 (13.05)	34.45 (34.43)	3.28 (3.30)	22.97 (22.99)
[Cu(L ₁) ₂ (NO ₃) ₂] CuC ₁₄ H ₁₆ N ₁₀ O ₈	17	Dark Green	265	59	12.32 (12.30)	32.55 (32.60)	3.10 (3.09)	27.15 (27.13)
[Cu(L ₂) ₂ Cl ₂] CuC ₁₄ H ₁₆ N ₈ S ₂ Cl ₂	20	Light Green	255	59	12.84 (12.80)	33.97 (33.98)	3.23 (3.20)	22.64 (22.63)
[Cu(L ₂) ₂ SO ₄] CuC ₁₄ H ₁₆ N ₈ S ₃ O ₄	15	Dark Blue	232	60	12.23 (12.20)	32.33 (32.30)	3.07 (3.05)	21.55 (21.53)
[Cu(L ₂) ₂ (NO ₃) ₂] CuC ₁₄ H ₁₆ N ₁₀ S ₂ O ₉	21	Green	260	68	10.66 (10.64)	28.20 (28.23)	2.68 (2.67)	23.50 (23.53)
[Cu(L ₃) ₂ Cl ₂] CuC ₁₆ H ₂₀ N ₈ O ₂ Cl ₂	20	Green	288	67	12.95 (12.93)	39.14 (39.12)	4.07 (4.05)	22.83 (22.80)
[Cu(L ₃) ₂ SO ₄] CuC ₁₆ H ₂₀ N ₈ SO ₆	21	Light Green	285	70	12.32 (12.30)	37.24 (37.23)	3.87 (3.86)	21.72 (21.73)
[Cu(L ₃) ₂ (NO ₃) ₂] CuC ₁₆ H ₂₀ N ₁₀ O ₈	19	Blue	270	72	11.69 (11.67)	35.32 (35.30)	3.67 (3.66)	25.35 (25.77)
[Cu(L ₄) ₂ Cl ₂] CuC ₁₆ H ₂₀ N ₈ S ₂ Cl ₂	16	Green	286	69	12.15 (12.14)	36.74 (36.76)	3.84 (3.85)	21.43 (21.40)
[Cu(L ₄) ₂ SO ₄] CuC ₁₆ H ₂₀ N ₈ S ₃ O ₄	17	Green	296	70	11.60 (11.63)	35.06 (35.08)	3.65 (3.63)	20.45 (20.43)
[Cu(L ₄) ₂ (NO ₃) ₂] CuC ₁₆ H ₂₀ N ₁₀ S ₂ O ₆	20	Brown	289	65	11.04 (11.06)	33.35 (33.37)	3.47 (3.43)	24.32 (24.30)

The molar conductance data 15-21 $\Omega^2 \text{ cm}^2 \text{ mol}^{-1}$ of all the complexes in dimethylsulphoxide (DMSO) indicates that these are non-electrolyte in nature. These complexes may be formulated as [Cu(L)₂X₂] [Where L = L₁, L₂, L₃ and L₄, X = Cl⁻, NO₃⁻, $\frac{1}{2}$ SO₄²⁻]

Magnetic moment

Magnetic moments of all the Cu(II) complexes recorded at room temperature lie in the range 1.80-2.01 B.M. (Table 2) corresponding to one unpaired electron.

Table 2 : Magnetic moment and electronic spectral data of Cu(II) complexes

Complexes	μ_{eff} (B.M.)	λ_{max} (cm ⁻¹)
[Cu(L ₁) ₂ Cl ₂]	1.92	14125, 19600, 22410
[Cu(L ₁) ₂ SO ₄]	1.90	14230, 19560, 22445
[Cu(L ₁) ₂ (NO ₃) ₂]	1.89	14356, 19667, 22510
[Cu(L ₂) ₂ Cl ₂]	2.01	14450, 19508, 22400
[Cu(L ₂) ₂ SO ₄]	1.80	14339, 19565, 22335
[Cu(L ₂) ₂ (NO ₃) ₂]	1.83	14430, 19640, 22430
[Cu(L ₃) ₂ Cl ₂]	1.88	14140, 19510, 22392
[Cu(L ₃) ₂ SO ₄]	1.87	14305, 19621, 22550
[Cu(L ₃) ₂ (NO ₃) ₂]	1.88	14229, 19710, 22568
[Cu(L ₄) ₂ Cl ₂]	1.82	14501, 19670, 22350
[Cu(L ₄) ₂ SO ₄]	1.90	14420, 19600, 22364
[Cu(L ₄) ₂ (NO ₃) ₂]	1.89	14399, 19588, 22502

The data show the absence of antiferromagnetic interactions between copper pairs. All the complexes may be considered to have tetragonal geometries with planar coordination of the ligand around Cu^{2+} ion and the axial positions are occupied by anions.

IR spectra of Complexes

The important IR bands and their assignments of semicarbazide and thiosemicarbazide based ligands and their Cu(II) complexes are listed in Table 3.

Table 3 : Important IR bands and assignments of semicarbazide and Thiosemicarbazide based ligands and their Cu(II) complexes

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{NH})$	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O}/\nu(\text{M}-\text{S}))$
Ligand (L_1)	1582s	1687s	3371m-		-	-
$[\text{Cu}(L_1)_2\text{Cl}_2]$	1574m	1661s	3291m	-		
$[\text{Cu}(L_1)_2(\text{SO}_4)]$	1508	1668m	3364m-	-	-	-
$[\text{Cu}(L_1)_2(\text{NO}_3)_2]$	1529s	1656s	3306s	-	-	-
Ligand (L_2)	1531s	-	3263s	801s	-	-
$[\text{Cu}(L_2)_2\text{Cl}_2]$	1560s	-	3161s	786m	-	428m
$[\text{Cu}(L_2)_2(\text{SO}_4)]$	1419m	-	3307s	699m	-	-
$[\text{Cu}(L_2)_2(\text{NO}_3)_2]$	1420m	-	3468s	794m	-	-
Ligand (L_3)	1599s	1685m	3304s	-	-	-
$[\text{Cu}(L_3)_2\text{Cl}_2]$	1561s	1603m	3337m	-	-	451m
$[\text{Cu}(L_3)_2(\text{SO}_4)]$	1512s	1596m	3435m	-	-	-
$[\text{Cu}(L_3)_2(\text{NO}_3)_2]$	1439m	1656m	3425m	-	-	-
Ligand (L_4)	1533s	-	3374s	804m	-	-
$[\text{Cu}(L_4)_2\text{Cl}_2]$	1515m		3307m	746m	-	459m
$[\text{Cu}(L_4)_2(\text{SO}_4)]$	1437s	-	3308s	745m	-	459m

Abbreviations ; vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, br = broad, sh = sharp

With ligand L_1 : The position of ligand band due to $\nu(>\text{C}=\text{N})$, 1582 cm^{-1} [21] is shifted towards lower side by $10\text{-}80\text{ cm}^{-1}$ on complexation. The position of ligand band due to $\nu(>\text{C}=\text{O})$, 1687 cm^{-1} is also shifted to lower wave number by $10\text{-}30\text{ cm}^{-1}$. This indicates that the coordination takes place through the nitrogen atoms of the imine groups and oxygen atom of the $>\text{C}=\text{O}$ group. Thus it is implied that ligand L_1 behaves as bidentate.

With Ligand L_2 : The position of ligand band 1531 cm^{-1} due to $\nu(>\text{C}=\text{N})$ is shifted towards lower side by $10\text{-}20\text{ cm}^{-1}$ [22] on complexation. This indicates that the coordination takes place through the nitrogen atoms of the imine groups and the shifting of $\nu(>\text{C}=\text{S})$ 801 cm^{-1} towards lower side by $20\text{-}30\text{ cm}^{-1}$ suggest the involvement of sulphur in coordination. Thus, it is implied that ligand L_2 behaves as bidentate.

With Ligand L_3 : The position of ligand band due to $\nu(>\text{C}=\text{N})$, 1598 cm^{-1} [23] is shifted towards lower side by $10\text{-}20\text{ cm}^{-1}$ on complexation and the position of ligand band due to $\nu(>\text{C}=\text{S})$ 1685 cm^{-1} is also shifted wave number by $10\text{-}30\text{ cm}^{-1}$. This indicates that the coordination takes place through the nitrogen atoms of the imine groups and oxygen atom of the $>\text{C}=\text{O}$ group. Thus it is implied that ligand L_3 behaves as bidentate.

With Ligand L_4 : The position of ligand band 1533 cm^{-1} due to $\nu(>\text{C}=\text{N})$ is shifted towards lower side by $10\text{-}100\text{ cm}^{-1}$ on complexation. This indicates that the coordination takes place through the nitrogen atoms of the imine groups and the shifting of $\nu(>\text{C}=\text{S})$ 801 cm^{-1} lower side by $20\text{-}30\text{ cm}^{-1}$ suggest the involvement of sulphur in coordination. Thus it is implied that ligand L_4 behaves as bidentate.

IR Spectral bands due to Anions

IR spectra of the nitrate complexes

The IR spectra of all the complexes show absorption bands in the region of $1382\text{-}1384$ (ν_5), $\nu_a(\text{NO}_2)$ $1155\text{-}1198$ (ν_1), $\nu_s(\text{NO}_2)$ and $792\text{-}825\text{ cm}^{-1}$ (ν_2) $\nu(\text{NO})$. This indicates that nitrate group coordinates in unidentate manner [24].

IR spectra of the sulphato complexes

The sulphate complexes show two absorption bands ν_1 and ν_3 . The splitting of ν_3 band into two bands in the region $1056\text{-}1083\text{ cm}^{-1}$ corresponds to unidentate nature of sulphate group [25].

Electronic spectra

The electronic spectra of the complexes, under study having molecular formula $[\text{Cu}(L)_2X_2]$ [Table 2] (where $L = L_1, L_2, L_3,$ and $L_4, X = \text{Cl}^-, \text{NO}_3^-, \frac{1}{2}\text{SO}_4^{2-}$) show three bands in range of $14025\text{-}16891$, $22779\text{-}25445$ and $33112\text{-}38167\text{ cm}^{-1}$ [Figs. 6.13-6.24] corresponding to tetragonal geometry, which can be assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, and ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$

transitions, respectively. In all cases the transition ${}^2B_{1g} \rightarrow {}^2B_{2g}$ is usually not observed as a separate band in the tetragonal field. In some cases, a band above $30,000\text{ cm}^{-1}$ has been observed. This may be due to charge transfer which could arise from the transfer of an electron from an orbital largely belonging to a central atom. The splitting of the 2E_g state is a measure of the planar and axial field. Since the IR spectra indicate that SO_4^{2-} acts as unidentate, therefore five-coordinated geometry has been suggested.

Electronic Paramagnetic spectra

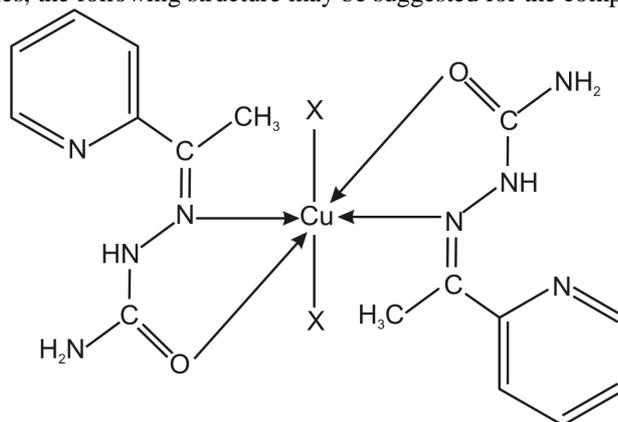
The EPR spectrum of the Cu(II) complexes were recorded as polycrystalline sample in DMSO solution. Spectra for polycrystalline sample exhibit absorptions typical for the mononuclear species with axial symmetry. The absence of Cu-Cu interaction can be explained by proposing transitions i.e. $\Delta M_s = \pm 2$ between two paramagnetic centres is negligible [26].

Table 4 : EPR spectral data of Cu(II) complexes

Complexes	g_{\parallel}	g_{\perp}	g_{iso}	G
$[\text{Cu}(\text{L}_1)_2\text{Cl}_2]$	2.201	2.0197	2.0801	10.20
$[\text{Cu}(\text{L}_1)_2(\text{NO}_3)_2]$	2.214	2.0192	2.0841	11.14
$[\text{Cu}(\text{L}_2)_2\text{Cl}_2]$	2.205	2.0194	2.0812	10.56
$[\text{Cu}(\text{L}_2)_2(\text{NO}_3)_2]$	2.215	2.0198	2.0848	10.85
$[\text{Cu}(\text{L}_3)_2(\text{NO}_3)_2]$	2.210	2.0196	2.0830	10.71
$[\text{Cu}(\text{L}_4)_2\text{Cl}_2]$	2.207	2.0193	2.0818	10.72
$[\text{Cu}(\text{L}_4)_2(\text{NO}_3)_2]$	2.209	2.0195	2.0826	10.71

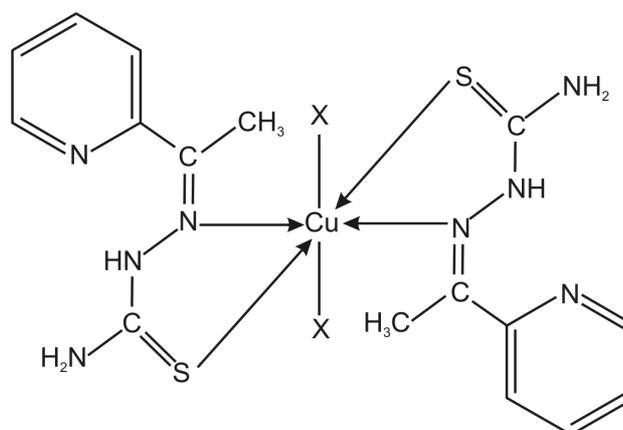
The analysis of spectra gave $g_{\parallel} = 2.201\text{--}2.215$ and $g_{\perp} = 2.0192\text{--}2.0198$. The values $g_{\parallel} > g_{\perp}$ indicates that the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving ${}^2B_{2g}$ as the ground state.

On the basis of spectral studies, the following structure may be suggested for the complexes Fig 2 – 5.



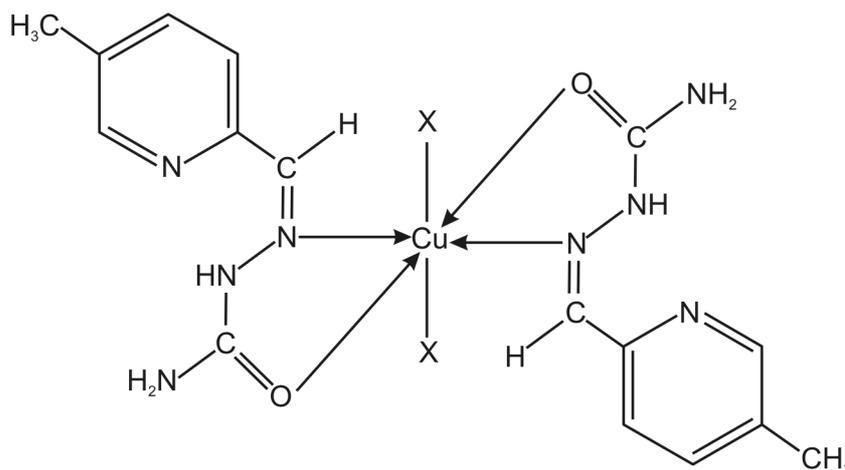
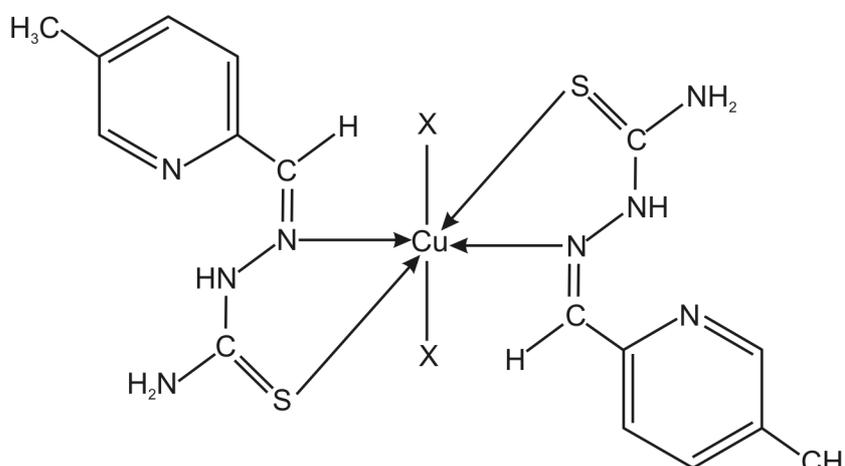
(Where X = Cl^- , NO_3^-)

Fig. 2 : Cu(II) complexes with ligand L₁



(Where X = Cl^- , NO_3^-)

Fig. 3 : Cu(II) complexes with ligand L₂

(Where X = Cl⁻, NO₃⁻)**Fig. 4 : Cu(II) complexes with ligand L₃**(Where X = Cl⁻, NO₃⁻)**Fig. 5 : Cu(II) complexes with ligand L₄****Table 5 : Antibacterial activity of ligand L₂, L₄ and their Cu(II) complexes**

S. No.	Compounds	Zone of Inhibition (mm) (conc. in ppm)					
		<i>Escherichia coli</i>			<i>Staphylococcus aureus</i>		
		250	500	1000	250	500	1000
1.	L ₂	-	6	16	-	5	7
2.	[Cu(L ₂) ₂ Cl ₂]	7	11	9	6	7	6
3.	[Cu(L ₂) ₂ SO ₄]	6	10	5	7	8	3
4.	Ciprofloxacin	-	21			18	
5.	L ₄	-	7	10	-	5	14
6.	[Cu(L ₄) ₂ Cl ₂]	9	10	12	6	8	7
7.	[Cu(L ₄) ₂ SO ₄]	9	7	8	7	7	10
8.	Ciprofloxacin		22			19	

Antibacterial Screening

Two ligands L₂ and L₄ and their Cu(II) complexes were screened for determining antibacterial activities in vitro by using filter paper disk technique at concentrations of 100 and 200 g/mL against Gram-negative bacteria viz. *Escherichia coli* and *Staphylococcus aureus* using nutrient agar media. The results have been compared with known standard drug ciprofloxacin. The activity against bacteria was evaluated by the Disc Diffusion Method [27]. 1.0 g of beef extract, 5.0 g of peptone, 5.0 g of sodium chloride and 2.0 g of yeast extract were dissolved in 1000 mL of distilled water by heating. This mixture was cooled, adjusted to pH ≈ 7.0 ± 0.2 and 15 g of agar-agar was added. The content was sterilized by autoclaving. 50 mL of stock solutions was applied on the 10 mm diameter sterile disc. After evaporating the solvent, the discs are placed on the inoculated plates. The petriplates are sealed with help of parafilm and first placed at low temperature for two hours and then incubated at suitable optimum temperature (2.0 ± 2°C) for

30-36 hours. After the expiry of the incubation period, clear zone of the inhibition associated with treated disc was measured in mm. The data (**Table 5**) reveal that the activity of ligands enhanced upon complex formation with metal ions. The highest activities of ligand L₂ and their complexes may be incorporated due to presence of pyridine ring and sulphur atom respectively. The ligand L₄ and their complexes also show the moderate activity due to the presence of pyridine ring.

In ligands L₁ and L₃ the shifting of the position of ligand band due to $\nu(>C=N)$ and $\nu(>C=O)$ towards lower wave number on complexation indicates that the coordination takes place through the nitrogen atoms of the imine groups and oxygen atom of the $>C=O$ group.

With ligands L₂ and L₄ the position of ligand band due to $\nu(>C=N)$ and $\nu(>C=S)$ is shifted towards lower wave number on complexation. This indicates that the coordination takes place through the nitrogen atom of the imine group and the involvement of sulphur in coordination.

Thus, it is implied that all four ligand behave as bidentate.

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