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Synthesis, Characterization, Antibacterial Studies of Co(II), Ni(II), Cu(II) and Zn(II) Complexes of Some Schiff Base Ligands

Abhishek Sharma[1]
Sulekh Chandra[2,*]

Authors Affiliation:
[1]Department of Chemistry Mewar University Gangrar, Chittorgarh, Rajasthan 312901, India
[2]Zakir Husain Delhi College (University of Delhi), JLN Marg, New Delhi 110002, India

***Corresponding address:**
Sulekh Chandra,
Zakir Husain Delhi College (University of Delhi), JLN Marg, New Delhi 110002, India

E-mail: schandra_00@yahoo.com

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Abstract

A series of two biologically active Schiff base ligands **HL_1** and **HL_2** have been synthesized in equimolar reaction of acetophenone derivative and different amines. The synthesized Schiff bases were used for complexation with different metal ions like Co(II), Ni(II) and Cu(II) by using a molar ratio of ligand : metal as 1:1. The characterization of Schiff bases and metal complexes was done by ^{1}H NMR, UV–Vis, IR, Mass spectrometry and molar conductivity studies. On the basis of the spectral studies an octahedral geometry has been assigned for Co(II), Ni(II) and tetrahedral for Cu(II) and Zn(II) complexes. All the synthesized compounds were studied for their *in vitro* antimicrobial activities, against four bacterial strains and two fungal strains by using serial dilution method. The data also revealed that the metal complexes showed better activity than the ligands due to chelation/coordination.

Keywords: Schiff Base, Ni(II), Co(II) and Cu(II) complexes, Spectroscopic Studies, DFT calculations, Antibacterial activity, antifungal activity

1. INTRODUCTION

Schiff bases are special class of ligands with a variety of donor atoms revealing interesting coordination modes towards numerous metals [1-5]. Schiff bases have many advantages between ligands in the coordination chemistry. They are the condensation product of an active carbonyl group as electrophile and an amino group as nucleophile. Due to their structural varieties and very unique characteristics, Schiff bases are the most versatile studied ligands in coordination chemistry. On the other hand, these compounds are an important class of organic ligands, because of their biological properties [6-7].

Due to their attractive chemical and physical properties, Schiff bases and their transition metal complexes are playing significant role in the development of coordination chemistry and have wide range of applications in numerous scientific areas [8]. A wide variety of Schiff base complexes have been studied for their biological, analytical, medicinal, pharmaceutical and other industrial applications [9-13]. Schiff bases and their complexes were also investigated for their remarkable properties, as their ability to reversibly bind oxygen, catalytic activity and photochromic properties [14–16]. Among the Schiff base derivatives, Schiff base having semicarbazide and thiosemicarbazide moiety have attracted considerable attention due to their impressive, chemical and physical

properties and biological activities [17] including their antituberculous [18] anticancer [19], antibacterial [20] and antidepressant activities [21].

In the present paper, two ligands **HL_1** and **HL_2** have been synthesized and characterized. The synthesized ligands are further used for complexation with Co(II), Ni(II) and Cu(II) ions in 1:1 molar ration

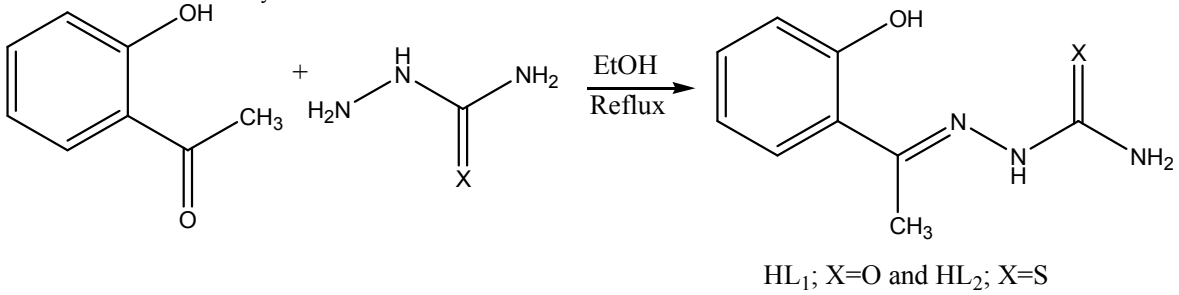
2. EXPERIMENTAL

2.1. Material and Methods

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

2.2 General procedure for the synthesis of Ligands HL_1 –HL_2

The desired Schiff base **HL_1** was synthesized by refluxing equimolar amount of 2-hydroxy acetophenone and amine derivatives taking ethanol as the solvent for 4 - 6 hr (**Scheme-1**). The progress of the reaction was monitored by TLC and after completion of the reaction, the solution was left overnight at room temperature. The solid product separated out, which was filtered, washed and recrystallized from ethanol. The structure of the synthesized Schiff bases was characterized using IR, ^{1}H NMR and their analytical data.



HL_1; X=O and HL_2; X=S

Scheme 1: Synthesis of Schiff base ligands **HL_1–HL_2**

2.3 General procedure for the synthesis of metal complexes 1–6

The metal complexes (**1–3**) of ligand **HL_1** were prepared (**Scheme -2**) by mixing hot ethanolic solution of **HL_1** (1 mmol) with ethanolic solution of salt of Co(II) (1mmol), Ni(II) (1 mmol) and Cu(II) (1 mmol). The reaction mixture was stirred for 1 hour followed by refluxing for 12–18 hours. The solvent was reduced to half and the reaction mixture was kept overnight, the product separated out, which was filtered off, washed with cold ethanol & ether and dried under vacuum over P_4O_{10}.

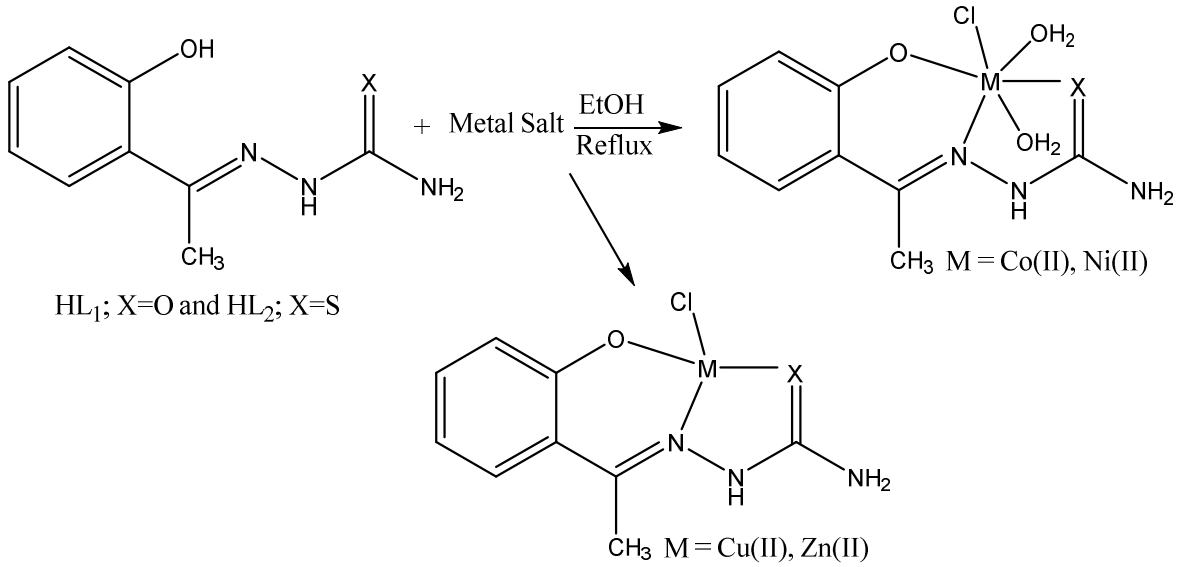
The Co(II), Ni(II) and Cu(II) complexes (**4–6**) of ligand **HL_2** were prepared by similar procedure. Physical, analytical and spectral data of ligands and metal complexes are given in **Table 1**

Table 1: Physical measurements and analytical data of the ligand (HL_1–HL_2) and metal complexes (1–6).

S.No.	Molecular mass/ molecular formula	Yield (%)	Elemental Analysis (%) found (calc.)			
			C	H	N	M[a]
HL_1	$C_9H_{11}N_3O_2$	78	55.91 (55.95)	5.72 (5.74)	16.50 (16.56)	-
HL_2	$C_9H_{11}N_3OS$	76	51.62 (51.65)	5.27 (5.30)	20.01 (20.08)	-
1	**$[CoCl(H_2O)_2(L_1)]$**	62	35.49	4.31	13.00	18.31

	$C_9H_{14}ClCoN_3O_4$		(35.51)	(4.37)	(13.02)	(18.27)
2	**$[NiCl(H_2O)_2(L_1)]$** $C_9H_{14}ClN_3NiO_4$	63	33.50 (33.53)	4.35 (4.38)	12.98 (13.03)	18.01 (18.21)
3	**$[CuCl(L_2)]$** $C_9H_{10}ClCuN_3O_2$	58	37.10 (37.12)	3.42 (3.46)	14.40 (14.43)	21.77 (21.82)
4	**$[CoCl(H_2O)_2(L_2)]$** $C_9H_{14}ClCoN_3O_3S$	65	31.90 (31.92)	4.12 (4.17)	12.35 (12.41)	17.35 (17.40)
5	**$[NiCl(H_2O)_2(L_2)]$** $C_9H_{14}ClN_3NiO_3S$	62	31.90 (31.94)	4.11 (4.17)	12.38 (12.42)	17.29 (17.34)
6	**$[CuCl(L_2)]$** $C_9H_{10}ClCuN_3OS$	64	35.13 (35.18)	3.24 (3.28)	13.60 (13.68)	20.61 (20.68)

[a] M = Co(II), Ni(II), Cu(II)



Scheme 2: Synthesis of metal complexes

2.4 Analysis

^{1}H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer and the chemical shifts were reported in ppm relative to TMS as an internal standard. IR spectra were recorded on Shimadzu IR affinity-I 8000 FT-IR spectrometer using KBr disc. UV spectra were recorded in DMSO on UV-VIS-NIR Varian Cary-5000 spectrometer. EPR spectra for the Cu (II) complexes were recorded using a JES - FA200 ESR X-band Spectrometer using TCNE as the internal reference. Elemental analysis was carried out on Perkin Elmer 2400. Magnetic moment at room temperature of the complexes were calculated by Gouy's method, using Hg $[Co(SCN)_4]$ as the calibrant. Molar conductance measurements of a 10^{-3} M solution of metal complexes in DMF were measured using a model-306 Systronics conductivity bridge.

2.5 Antibacterial Activity

All the synthesized compounds were tested for their antibacterial activity against *B. macerans* and *P. Striata* by using disc diffusion method [24] and antifungal activity was done using food poison technique [22] against the test fungi, *R.bataticola*, *A.alternata* and *F.odum*. The test compounds were dissolved in DMF in varying concentration. Streptomycin was used as a standard for antibacterial and Fluconazole for antifungal study.

3. RESULTS AND DISCUSSION

The ligands HL_1 and HL_2 were synthesized as per the procedure given in the synthesis of ligands. The crystalline solids so obtained have different shade of yellow or orange color due to the presence of chromophoric group (HC=N) in the molecule. All the metal complexes were prepared by direct reaction between Schiff base and corresponding metal salt**.** All these complexes are crystalline solids, stable in air at room temperature and the melting points of the metal complexes are much higher than that of the ligands, which indicates that these complexes are much more stable as compared to the ligands. The complexes in 10^{-3} M DMF solution have low molar conductance value (3.1–7.3 $\Omega^{-1}cm^2mol^{-1}$) indicating their non-electrolyte nature [23].

3.1 ^1H NMR Spectra

The ^1H NMR spectra have been recorded for ligand **HL_1 – HL_2** and Fig. 1 displays the ^1H NMR spectrum of HL_1. The spectra of ligand displayed azomethine (–HC=N) proton as a singlet at 9.64 ppm**.** The aromatic protons appeared as a set of doublet and triplet in the region 6.8–7.5 ppm. Two proton singlet at 6.2 ppm was due to NH_2 protons. The one proton singlet at δ 12.71 in ligand **HL_1** corresponds to –OH proton. The three protons of methyl group resonate at 2.22 ppm. A similar peak was observed in the ^1H NMR spectra of HL_1. All the peaks are found in there expected regions.

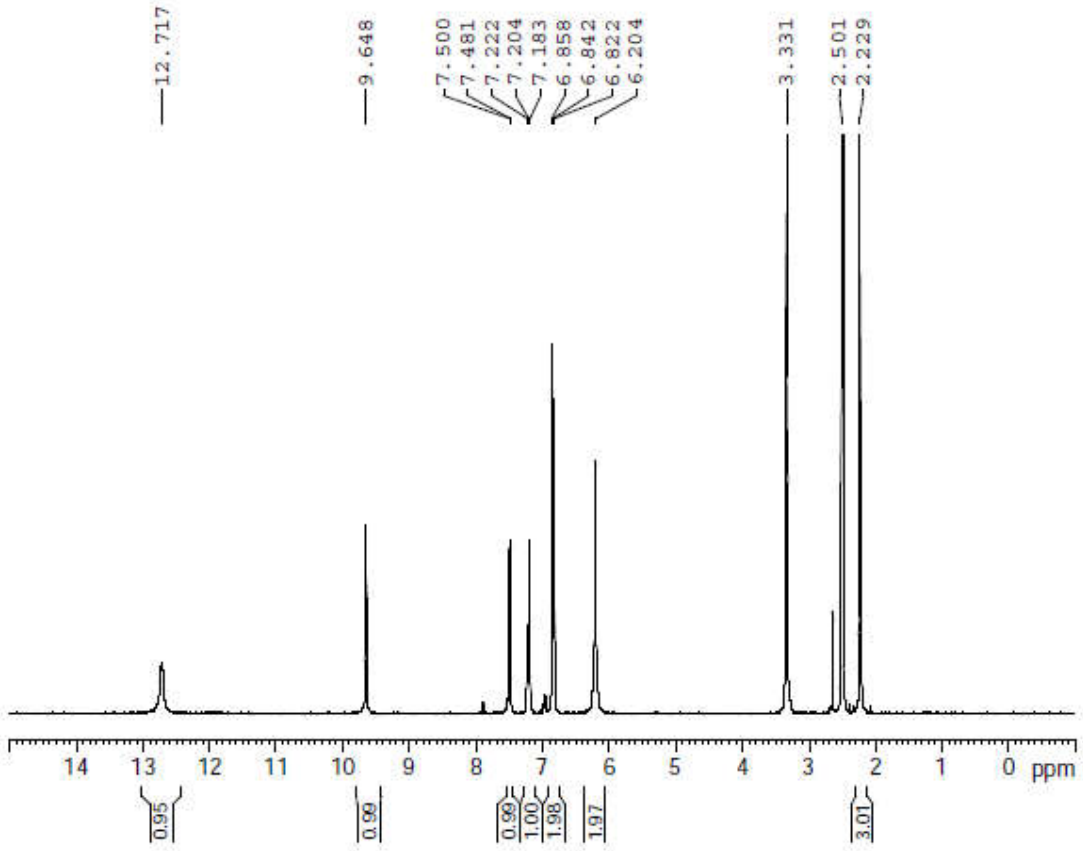


Figure 1: ^1H NMR spectra of ligand HL_1

3.2 Mass Spectrum

The ESI mass spectrum of the ligands **HL_1** & **HL_2** was done and the spectrum of HL_1 is displayed in Fig. 2. The stability of any fragment relates directly with the intensity of the corresponding peak. In

the mass spectrum of the ligands **HL_1** (**Fig. 2**) a peak corresponds to [M+1] appears at m/z value of 194.1 which confirms the proposed formula.

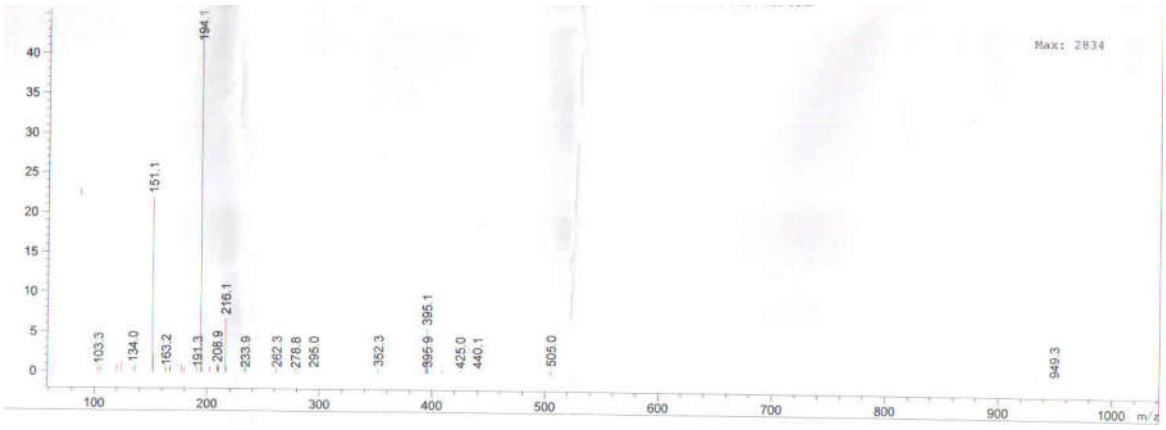


Figure 2: Mass spectrum of ligand HL_1

3.3 IR Spectra

To understand the binding mode of the ligands to the corresponding metal ions, Infrared spectral data of the ligands **HL_1–HL_2** and their metal complexes are compared. The coordination of the ligand to the corresponding metal ions was confirmed on the basis of shifts in absorption bands of various groups and absence of certain absorptions (**Table 2**). In the Infrared spectra of the ligands, the bands originally attributed to ν (C=O) of aldehyde and ν (NH_2) at 1750 and 3320, 3460 cm^{-1} respectively, of the starting materials were absent.

Table 2: Important infrared spectral bands (cm^{-1}) and their assignments

Compound	ν(HC=N)	ν(OH)	ν(M–O)	ν(M–N)
HL_1	1598	3097	-	-
1	1583	-	531	434
2	1579	-	512	418
3	1581	-	537	432
HL_2	1610	3084	-	-
4	1689	-	533	440
5	1691	-	528	431
6	1690	-	516	422

Instead, a new band appeared at 1598–1610 cm^{-1} [24] was assigned to ν(HC=N) vibration confirms the formation of Schiff base. Comparison of the IR spectral data of the ligands and the metal complexes revealed that band corresponding to ν(HC=N) vibration shifts to frequency by 20–25 cm^{-1} in all the metal complexes, which indicates the involvement of nitrogen of azomethine moiety in complexation [24]. The IR spectra of ligand HL_1 is displayed in Fig. 3.

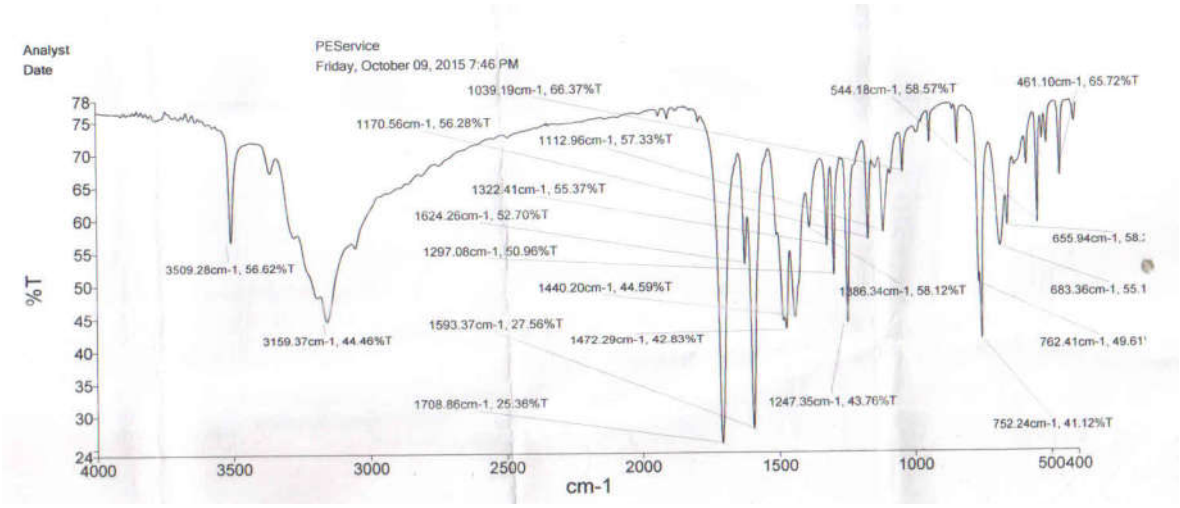


Figure 3: IR spectra of ligand HL_1

This is further supported by the appearance of a new band at 418–440 cm^{-1} due to ν(M–N) stretching [24]. A band at 3075–3159 cm^{-1} in the IR spectra of ligands was due to ν (–OH) stretching vibration and low value may be due to H-bonding between OH and nitrogen of azomethine. The absence of this band in the IR spectra of metal complexes indicates the deprotonation of phenolic OH on metal complexation and coordination through phenolic oxygen. This was further confirmed by the appearance of a weak low frequency band at 512–37 cm^{-1} due to ν(M–O) bond [24]. The presence of coordinated water molecule in complexes of Co^{2+} and Ni^{2+} metal ions was confirmed by the presence of broad band observed in the range of 3297–3324 cm^{-1} [26], while no such band was observed in Cu^{2+} and Zn^{2+} complexes.

3.4 Conductance and magnetic susceptibility measurements

The molar conductance values of metal complexes **1–6** were obtained in DMF as a solvent at room temperature and their results in ($\Omega^{-1}cm^2mol^{-1}$) are recorded. The molar conductance of the metal complexes in DMF showed values indicating that complexes **1–6** (3.1–7.3 $ohm^{-1}cm^2$ mol^{-1}) are non-electrolytes [22].

The magnetic moment (B.M.) values of all the metal complexes, **1–6** at room temperature were recorded. The magnetic moment values of Co(II) complexes were found in the range of 4.93–5.81 B.M. suggesting the Co(II) complexes in an octahedral environment [27]. Ni(II) complexes have magnetic moment values in range of 2.93–2.97 BM corresponding to two unpaired electrons, indicating a triplet ground state having octahedral geometry around metal ion [27]. The Cu(II) complexes show magnetic moment values 1.69–1.73 BM, which show the square planar arrangement around the Cu(II) ion.

3.5 Electronic Spectra

The electronic absorption spectra of the Co(II), Ni(II) and Cu(II) complexes in DMSO were recorded at room temperature and the band positions of the absorption maxima, band assignments and the proposed geometry. The electronic spectra of Co(II) complexes generally showed three absorption bands in the region at 9,923–9,571, 17,534–17,618 and 22,876–23,012 cm^{-1} assigned to transitions $^4T_{1g} \rightarrow {}^4T_{2g}(F)$, $^4T_{1g} \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g} \rightarrow {}^4T_g(P)$, showing an octahedral geometry around the Co(II) ion [35]. The electronic spectral data of Ni(II) complexes showed d-d bands in the region 10,899–10,938 15,383–16,012 and 23,110–24,135 cm^{-1}, respectively, assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, which are characteristic of Ni(II) in octahedral geometry [35]. The electronic spectra of Cu (II) complexes showed two low energy weak bands assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$

and $^2B_{1g} \rightarrow {}^2E_g$ transitions at 15187–15425 and 20054–20345 cm^{-1}, respectively [28]. A strong high energy band at 30100–30765 cm^{-1} is assigned to metal-ligand charge transfer.

3.6 EPR Spectra

The solid state X-band EPR spectra of polycrystalline solid of Cu(II) complexes recorded in powder form at RT and in DMSO at 77 K. The EPR spectra of Cu(II) complex of **HL_1** at room temperature displayed an isotropic signal having axial symmetrical line shape with two g values *i.e.* $g_\parallel = 2.27$ and $g_\perp = 2.11$ and g_{av} was computed using the relation $gav = 1/3(g_\parallel + 2g_\perp)$ table. From the observed values it is clear that $g_\parallel > g_\perp > 2.0023$ and these parameters are well consistent with related systems which suggest the square planer geometry around Cu (II) metal ion, with unpaired electron lying predominantly in the $d_{x^2-y^2}$ orbital. The $g_\parallel$ values are less than 2.3 is an indication of significant covalent bonding in Cu (II) complexes [29]. The value of exchange interaction term G calculated by using $G = (g_\parallel - 2.0023) / (g_\perp - 2.0023)$ gives idea about exchange interactions between Cu (II) centers. The value of $G < 4.0$ indicates negligible exchange interactions of Cu–Cu in the complex (Table 3).

Table 3: EPR data of Cu (II) complexes

Complex	$g_\parallel$	$g_\perp$	Gav
$[Cu(L_1)Cl]$	2.27	2.11	2.16
$[Cu(L_2)Cl]$	2.22	2.08	2.12

On the basis of the above discussion following structures can be proposed for the synthesized complexes (Fig. 4).

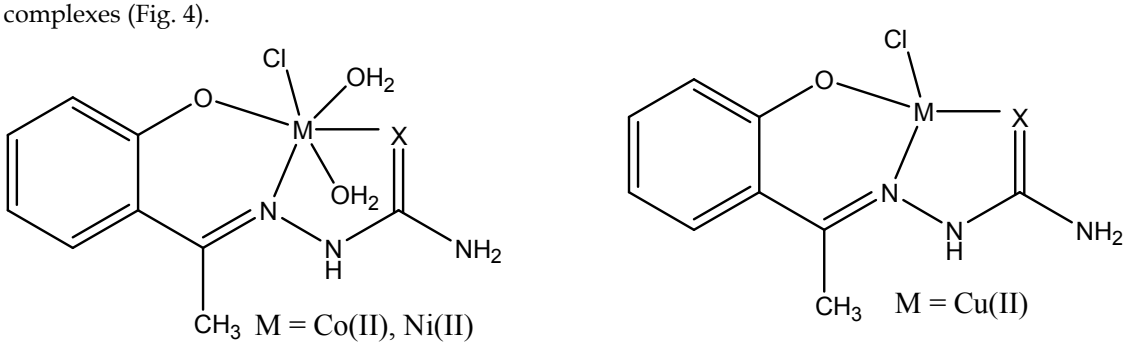


Figure 4: Proposed structures of the metal complexes

3.7 Antibacterial Activity

In vitro antibacterial activity against *Bacillus macerans* (Gram-positive) and *Pseudomonas striata* (Gram-negative) were evaluated for all synthesized compounds. Streptomycin is the standard drug used for comparison of antibacterial activity of the compounds. The antibacterial screening data (**Table 4)** show that the zone of inhibition is larger for ligand **HL_1** in comparison to HL_2. Metal complex **3** and **6** was most active against the Gram positive bacteria and Gram negative bacteria. In general an enhancement in the antibacterial activity of the ligand was observed on complexation. This increase in the activity on complexation as compare to free ligand is explained on the basis of chelation theory [30-31]. Interestingly the presence of 2D and 3D rings in the ligand also alter the activity of the compound [32]. The variation can be explained as different compounds have different impermeability in the cells of the microbes and the other factor which contributes in the degree of inhibition is the concentration of the tested compound, as activity is directly proportional to concentration of tested compounds. Fig. 5 shows the graphical representation of zone of inhibition of the tested compounds.

Table 4: Antibacterial screening data of the ligands and their metal complexes

Compounds	Diameter of inhibition zone (mm) (Conc. in µg/ml)					
	Bacillus macerans			*Pseudomonas striata*		
	250	**125**	**63.5**	**250**	**125**	**63.5**
HL_1	19	13	8	13	8	-
$[Co(L_1)Cl(H_2O)_2]$	26	20	14	16	15	4
$[Ni(L_1)Cl(H_2O)_2]$	27	18	13	21	16	5
$[Cu(L_1)Cl]$	38	29	11	41	13	9
HL_2	17	13	8	17	7	7
$[Co(L_2)Cl(H_2O)_2]$	27	17	10	26	17	11
$[Ni(L_2)Cl(H_2O)_2]$	26	19	12	29	14	10
$[Cu(L_2)Cl]$	39	26	11	32	19	11
Streptomycin (standard)	44	36	19	58	31	15

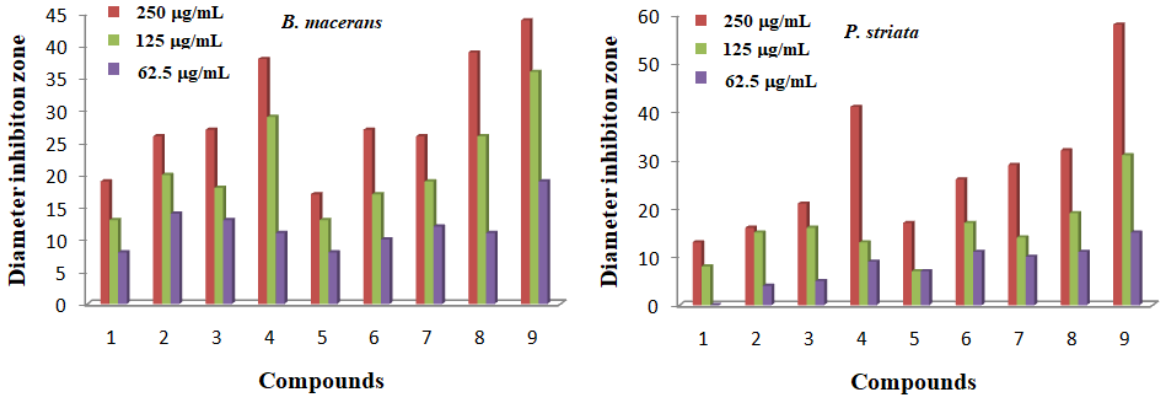


Figure 5: **Graphical representation of the *in vitro* anti bacterial activity of ligand HL_1–HL_2 and there metal complexes**

3.8 Antifungal Activity

All the synthesized compounds were screened against fungi, *Rhizoctonia batatiola*. *Alternaria alternata*, and *Fusarium odum*. Chlorothalonil is used as standard drug. The antifungal screening data is shown in **Table 5.**

Table 5: Antifungal screening data of the ligands and their metal complexes

Compounds	Mycelial Growth inhibition (%) (Conc. in µg/ml)								
	Rhizoctonia bataticola			*Alternaria alternate*			*Fusarium odum*		
	250	**125**	**63.5**	**250**	**125**	**63.5**	**250**	**125**	**63.5**
HL_1	55.4	29.1	15.2	53.7	25.8	14.6	49.1	27.0	13.4
$[Co(L_1)Cl(H_2O)_2]$	68.6	36.4	24.1	77.1	31.0	16.2	56.1	27.4	10.4
$[Ni(L_1)Cl(H_2O)_2]$	71.5	44.0	19.8	65.4	39.8	18.3	54.8	39.1	17.3
$[Cu(L_1)Cl]$	63.5	45.9	33.3	71.5	44.1	16.4	51.3	45.0	20.4
HL_2	49.7	28.1	15.9	45.4	25.9	12.8	44.8	27.3	16.1
$[Co(L_2)Cl(H_2O)_2]$	74.2	41.0	27.8	70.3	42.8	16.2	60.2	30.6	11.5
$[Ni(L_2)Cl(H_2O)_2]$	69.9	43.5	22.9	66.5	32.6	12.1	61.7	41.3	17.7
$[Cu(L_2)Cl]$	67.4	38.9	25.4	75.0	46.4	18.9	59.9	36.5	21.1
Fluconazole (standard)	91.0	79.3	46.4	97.0	83.1	47.8	87.6	71.8	45.4

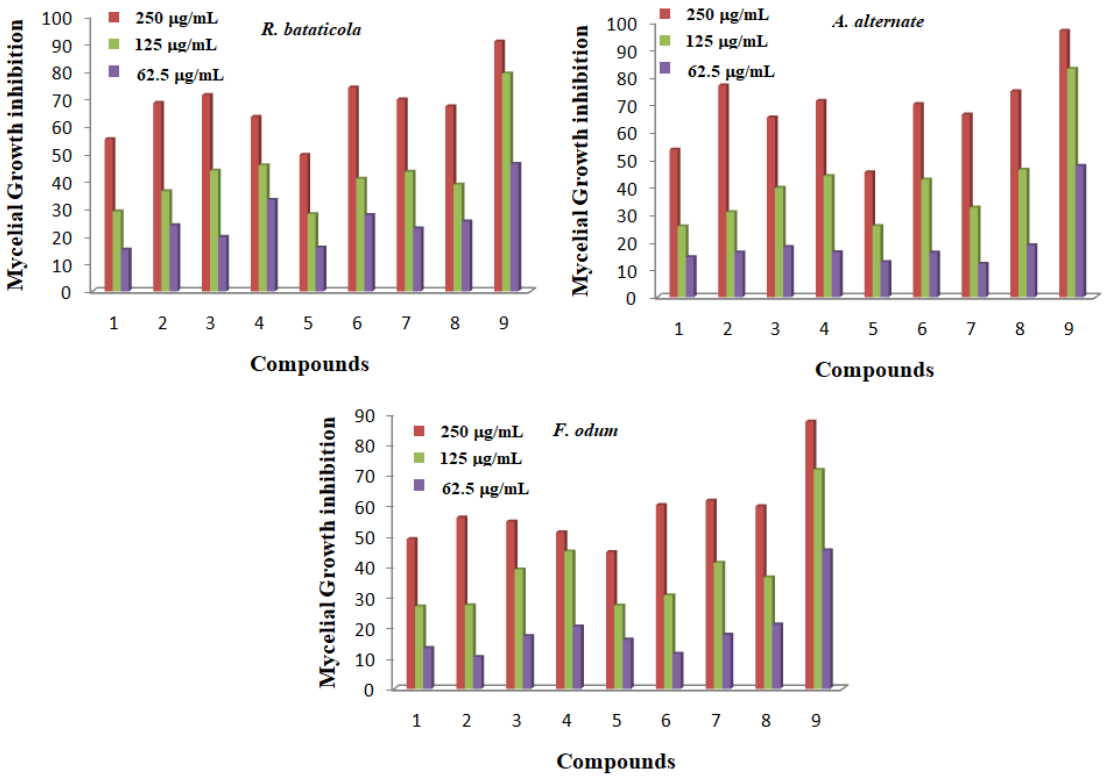


Fig. 6: **Graphical representation of the in vitro anti fumgal activity of ligand HL_1–HL_2 and there metal complexes**

From the antifungal data it may be conclude that all the compounds were moderate to significant active against the tested fungi and the metal complexes were found to be more active as compare to free ligand. Fig. 6 show the graphical representation of antifungal activity of the tested compounds.

4. CONCLUSION

The analytical and physico-chemical analyses confirmed the composition and the structure of the newly obtained complex combinations. On the basis of the spectral studies Co(II) & Ni(II) complexes were found to have a distorted octahedral geometry whereas Cu(II) complexes stabilizes in a four coordinated geometry. In all metal complexes ligands **HL_1–HL_2** coordinate in uninegative tridentate fashion. The presence of the coordinated water molecule in metal complexes was confirmed by IR data. From the antimicrobial data it may be conclude that all the compounds were moderate to significant active against the tested strains and the metal complexes were found to be more active as compare to free ligand.

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