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Antimicrobial Activities of Co(II),Ni(II),Cu(II) and Zn(II) Metal Complexes Derived from Tetradentate Schiff Base Ligands

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Abstract:
New Schiff base Co(II),Ni(II),Cu(II) and Zn(II) metal complexes have been synthesized from the tetradentate Schiff base ligands, L_1 and L_2 synthesized by the condensation of 4-aminoacetophenone, p-phenylenediamine and salicylaldehyde or 5-chlorosalicylaldehyde. [$L_1 = C_{36}H_{30}N_4O_2$ and $L_2 = C_{36}H_{28}N_4O_2Cl$]. The complexes have been characterized by elemental analysis, IR, ^{1}H NMR, UV-Vis spectra, electrochemical, molar conductance, ESR and magnetic moment studies. Elemental analysis data and molar conductance measurements revealed that the complexes are electrolytic in nature. IR spectra of the complexes show that the ligand coordinates to the metal ion through the four azomethine nitrogen atoms and the two phenolic oxygens were free from coordination. Based on the magnetic moment and electronic spectral data a square planar geometry has been approximately suggested for all the complexes. The redox behavior of the complexes was explained by cyclic voltammetry. The Schiff base metal complexes are found to have the general formula [M L_1 or L_2](OAc_2), where M = Co, Ni, Cu and Zn. Antibacterial and antifungal screening of the ligands and its metal complexes reveal that all the complexes show higher activities than the ligands. The antimicrobial studies also reveals that the complexes derived from the ligand L_2 were found to be more potent than the complexes derived from the ligand L_1.

Key words: *4-aminoacetophenone; Antimicrobial activity; Metal complexes; Schiff base ligands*

1. Introduction

In recent years a great deal of work has been done on the coordination chemistry of transition metal complexes[1,2]. Schiff base metal complexes have been widely studied due to their selective chelation to certain metal ions, stability, flexibility, structural variability and various biological applications[3,4]. Schiff bases usually act as multidentate N-N and N-O donors with the formation of mononuclear complexes. The nature of Schiff base metal complexes depends on the metal ion, the donor atoms and metal ligand interations. Salicylaldehyde and its derivatives are very useful for the synthesis of variety of Schiff bases. Additional coordinated groups attached to salicylaldehyde increase their ability to generate polynuclear complexes[5]. Schiff bases and their metal complexes are used as catalysts in various biological systems, polymers, dyes, antifertilizers and enzymeatic agents[6]. Azomethines bind to the metal ions through nitrogen, oxygen and sulphur atoms form an important class of biologically active ligands. These ligands and their metal complexes are known to function as antibacterial, antifungal, antimalarial, antitumor and antileukemec agents[7,8]. The activity of the Schiff base ligands and their metal complexes usually increases as the concentration increases. Studies show that the antimicrobial activies of the metal complexes were increased when compared with the corresponding Schiff bases[9]. The lipophilicity of the drug is increased through the formation of chelates and drug action is significantly increased due to effective permeability of the drug into the site of action. Interaction of various metal ions with antibiotics may enhance their antimicrobial activity as compared to that of free ligands[10]. The present work deals with the synthesis of new mononuclear Co(II),Ni(II),Cu(II) and Zn(II) complexes with the tetradentate Schiff base ligands L_1 and L_2 synthesized from 4-aminoacetophenone, p-phenylenediamine and salicylaldehyde or 5-chlorosalicylaldehyde, their physicochemical characterization, antibacterial, antifungal activities and comparison of the complexes synthesized from two Schiff base ligands.

2. Experimentl details

2.1. Materials and Methods

All the reagents and solvents used for the synthesis were of analar grade. 4-aminoacetophenone, p-phenylenediamine, salicylaldehyde, 5-chlorosalicylaldehyde, $Co(OAc)_2.4H_2O$, $Ni(OAc)_2.4H_2O$, $Cu(OAc)_2.H_2O$ and $Zn(OAc)_2.2H_2O$ were purchased from Loba chemie and were used without further purification. All the solvents were distilled and used according to the Literature method[11]. The C, H and N analysis were performed by using Carlo-Eraba 1106 instrument. Electronic absorption spectra were recorded on Perkin Elmer Lambda 25 UV-Vis spectrometer between 200-800 nm by using DMSO solvent. Magnetic susceptibility measurements of the complexes were carried out by Guoy method using ($Hg[Co(SCN)_4]$) as the calibrant. The IR spectra of the ligands and the complexes were recorded in KBr-pellets on a range between 400-4000 cm^{-1}. The ^1H NMR spectra was recorded on a Bruker Avance II 400 NMR spectrometer using DMSO-d_6 solvent and TMS as internal standard. The molar conductivity measurements were carried out by using Elico-CM Conductivity Bridge with 10^{-3} M DMF as solvent. Electrochemical studies were recorded in EG &G PAR model 174A polarographic analyser using three-electrode configuration in DMSO solution. 0.1 M tetrabutylammonium perchlorate was used as supporting electrolyte, platinum as working and counter electrode and their metal complexes were carried out by disc diffusion method at different concentrations.

2.2. Synthesis

The ligands and their metal complexes were synthesized based on the literature procedure with slight modification,which was reported for similar compounds[12].

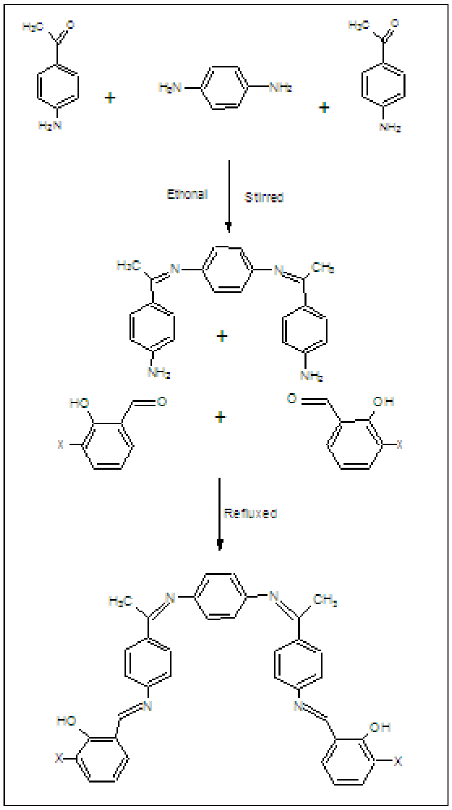
2.2.1. Synthesis of ligands

2.2.1.1. Synthesis of the Schiff base ligand L_1

To an ethanolic (25 mL) solution of p-phenylenediamine (1.0814 g, 0.01 mol), an ehtanolic (25 mL) solution of 4-aminoacetohenone (2.7034cg, 0.02 mol) was slowly added and stirred well. To the above contents an ethanolic (25 mL) solution of salicylaldehyde (2.1 mL, 0.02 mol) was added. After the addition was completed, the mixture was stirred well and refluxed for 30 min on a water bath and then cooled to room temperature. The solid product was collected by filtration, washed with cold ethanol and then dried in a desiccator.

2.2.1.2. Synthesis of the Schiff base ligand L_2

The same above procedure was adopted to synthesize the second ligand $L_{2.}$ p-phenylenediamine, 4-aminoacetohenone and 5-chlorosalicylaldehyde were used to obtain $L_{2.}$ Synthesis of the ligands L_1 and L_2 are given in Scheme1.



Scheme 1
Where, X= H for L_1 and X=Cl for L_2

2.2.2. Synthesis of Complexes

The Co(II),Ni(II),Cu(II) and Zn(II) complexes were synthesized by mixing hot ethanolic (25mL) solutions of 0.2 mmol of metal acetate solutions with the requisite amounts of the ligands (0.2mmol) under study (L_1 and L_2) in 1:1 mole ratio. The solid complexes were filtered off, washed with cold ethanol and then dried in a desiccator. The suggested structures of the complexes synthesized from ligands L_1 and L_2 are given in figure 1.

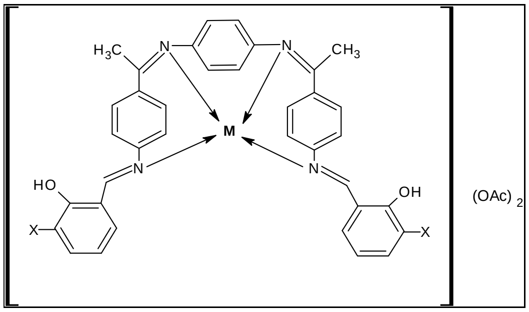


Figure.1 Where, M= Co(II) ,Ni(II), Cu(II) and Zn(II)
X= H for the complexes synthesized from ligand L_1 and X=Cl for the complexes synthesized from ligand L_2

2.3. Antimicrobial studies

The *in vitro* antibacterial activity of the tetradentate Schiff base ligands *(*L_1 and L_2) and its metal complexes were tested against the Gram +ve bacterial species such as *Staphyloccus aureus* and *Bacillus subtilis* and Gram –ve bacterial species such as *Escherichia coli* and *Klebsiella pneumoniae.* The antifungal activities were tested against the fungi *Aspergillus niger, Aspergillus flavus* and *Candida albicans* (yeast). The screening was carried out at room temperature by the disc diffusion method using the standard procedure[13,14]. *Streptomycin* was used as the standard drug for bacterial screening and *Amphotericin-B* was used as the standard drug for fungal screening. Nutrient agar medium was employed as culture media for bacterial screening and Sabouraud dextrose agar medium as culture media for fungal screening. The disc of whatmann No.1 filter paper having the diameter 5mm were soaked into the solution of the complexes dissolved in DMSO at different concentrations (50µg mL^{-1} and 75 µg mL^{-1}). After drying at room temperature, the discs were then placed on the inoculated plates containing respective medium. The plates were then incubated at 37°C for 24-48 hrs and 27°C for bacteria and fungus respectively. After the period of incubation, the antibacterial activities were recorded by measuring the diameter (mm) of the inhibitory zone and the antifungal activities were recorded as % of inhibition. The following relation was used to calculate the fungal growth inhibition:
Fungal growth inhibition (%) = (A-B) x 100 /A
Where, A is the diameter of fungal colony in control plate.
and B is the diameter of fungal colony in test plate.
The antibacterial and antifungal activities shown by the ligands and their metal complexes were compared with the standard drugs.

3. Results and Discussion

Novel Schiff base complexes were synthesized in great yield by the reaction of the Metal(II) acetates with the ligands *(*L_1 and L_2) prepared from the reactants like 4-aminoacetophenone, p-phenylenediamine and salicylaldehyde or 5-chlorosalicylaldehyde. The complexes gave satisfactory analytical data indicating 1:1 metal-ligand stoichiometry for all complexes. The analytical data for the new complexes agrees very well with the proposed mononuclear molecular formula. The synthesized ligands and their metal complexes were checked by comparing the TLC with the starting materials, which results a single spot different from the starting materials, confirms the formation and purity of the ligands and their metal complexes. All the complexes were stable to air conditions, non-hydroscopic and insoluble in water and in most of the organic solvents, but are easily soluble in DMF and DMSO. The crystals were unsuitable for single crystal X-ray structure determination and were insoluble in most common solvents. The melting points of the complexes were higher than that of the free ligands, due to chelation.

Anal. Calcd. for L_1 (%) : C,78.55; H,5.45; N,10.18. Found: C, 77.40; H, 5.50; N, 10.00; Yield: 85; m.p: 170°C. Anal. Calcd. for L_2 (%) : C,73.92: H,4.96; N,9.58; Cl,6.07. Found: C, 73.65; H, 4.89; N, 9.69; Cl, 6.13; Yield: 82; m.p: 185°C. Anal. Calcd. for $[CoL_1](OAc)_2$ (%) : C,68.29; H,5.12; N,7.97; Co,8.38. Found: C, 66.19; H, 5.18; N, 7.99; Co,8.42; Yield: 75; m.p: >300°C. Anal. Calcd. for $[NiL_1](OAc)_2$ (%) : C,68.31; H,5.12; N,7.97; Ni,8.35. Found: C, 68.42; H, 5.05; N, 7.85; Ni,8.43; Yield: 80; m.p: >300°C. Anal. Calcd. for $[CuL_1](OAc)_2$ (%) : C,67.84; H,5.09; N,7.91; Cu,8.98. Found: C, 67.91; H, 5.01; N, 7.89; Cu,8.95; Yield: 80; m.p: >300°C. Anal. Calcd. for $[ZnL_1](OAc)_2$ (%) : C,67.66; H,5.07; N,7.89; Zn,9.22. Found: C, 66.98; H, 5.12; N, 7.82; Zn,9.18; Yield: 75; m.p: >300°C. Anal. Calcd. for $[CoL_2](OAc)_2$ (%) : C,65.1; H,4.75; N,7.6; Cl,4.81; Co,8.00. Found: C, 64.96; H, 4.79; N, 7.68; Cl,4.87; Co,7.89; Yield: 75; m.p: >300°C. Anal. Calcd. for $[NiL_2](OAc)_2$ (%) : C,65.12; H,4.75; N,7.6; Cl,4.81; Ni,7.96. Found: C, 65.20; H, 4.69; N, 7.66; Cl,4.91; Ni,7.82; Yield: 75; m.p: >300°C. Anal. Calcd. for $[CuL_2](OAc)_2$ (%) : C,64.69; H,4.72; N,7.55; Cl,4.78; Cu,8.56. Found: C, 64.92; H, 4.61; N, 7.46; Cl,4.82; Cu,8.45; Yield: 80; m.p: >300°C. Anal. Calcd. for $[ZnL_2](OAc)_2$ (%) : C,65.53; H,4.71; N,7.53; Cl,4.76; Zn,8.8. Found: C, 65.49; H, 4.78; N, 7.49; Cl,4.69; Zn,8.16; Yield: 80; m.p: >300°C.

3.1. Molar conductivity studies

The electrolytic nature and stability of the complexes were determined by using molar conductivity. The molarconductance values of the mononuclear complexes were carried out in 10^{-3} M solvent of DMF at room temperature.The observed molar conductance values are listed in Table1. The molar conductivities show that the Co(II),Ni(II),Cu(II) and Zn(II) complexes are electrolytes of 1:2 type with '$\wedge_m$' in the range 142-160 Ω^{-1} cm^2 mol^{-1}. The obtained values suggest that the complexes are electrolytic in nature[15] and show the presence of acetate ion outside the coordination sphere as counter ion. Thus the charge on the complexes is neutralized by the presence of acetate ion in the outer sphere of the complexes.

Compounds	**Molecular Formula**	**Molar conductance ∧ m (Ω^{-1} cm^2 mol^{-1})**	**CV data (V)**	
			Epa	**Epc**
L_1	$C_{36}H_{30}N_4O_2$	-	-	-
$[CoL_1](OAc)_2$	$CoC_{40}H_{36}N_4O_6$	158	-0.900	-
$[NiL_1](OAc)_2$	$NiC_{40}H_{36}N_4O_6$	149	-0.690 -1.586	-0.600 +0.430
$[CuL_1](OAc)_2$	$CuC_{40}H_{36}N_4O_6$	164	+0.142 -0.592	-
$[ZnL_1](OAc)_2$	$ZnC_{40}H_{36}N_4O_6$	148	-	-
L_2	$C_{36}H_{28}N_4O_2Cl$		-	-
$[CoL_2](OAc)_2$	$CoC_{40}H_{34}N_4O_6Cl$	152	-0.950	-
$[NiL2](OAc)_2$	$CoC_{40}H_{34}N_4O_6Cl$	142	-0.690 -1.480	-0.710 +0.510
$[CuL_2](OAc)_2$	$CoC_{40}H_{34}N_4O_6Cl$	160	+0.158 -0.620	-
$[ZnL_2](OAc)_2$	$CoC_{40}H_{34}N_4O_6Cl$	144	-	-

Table 1

3.2. Infrared Spectra

The bonding of the free ligands to the metal atoms was characterized by comparison of the main infrared absorption bands of the free ligands and their complexes. Infrared spectral data for the ligands and their metal complexes are summarized in Table 2. The IR spectra of the complexes were compared with those of the free ligands. The IR spectrum of the free ligands L_1 and L_2 show a broad band in the region ~3434.78 and 3455 cm^{-1} respectively are assigned to υ(OH) stretching[16]. The band appeared in the region 3425-3445 cm^{-1} in all the complexes indicate that there is no shift in –OH stretching frequency and this shows that –OH group is free from the complexation. Strong bands observed in the free ligands around 1568 and 1590 cm^{-1} are characteristic of azomethine group[17,18]. Coordination of the Schiff base to the metal through azomethine nitrogen atom is expressed to reduce the electron density in the azomethine link and lower the azomethine group absorption frequency. In the spectra of all new complexes, the band due to azomethine group shows a negative shift to 1530-1551 cm^{-1}, indicating coordination of the azomethine nitrogen to metal center[19]. All the spectra show medium absorptions at 3041-3065 cm^{-1} due to aromatic C-H stretching. The other band appeared at 1186.13 and 1198 cm^{-1} in the IR spectrum of the ligands L_1 and L_2 are assigned to phenolic –C-O stretching. The band appeared at 1180-1189 cm^{-1} in all the complexes indicates that the two phenolic O-atom of the ligands are not coordinated to the metal ion. The IR spectrum of all the complexes show new bands appearing at 536-550 cm^{-1} which are not observed in the ligands, are assigned to stretching modes of M-N vibration [20] the wide range may be due to a relatively strong bond with the metal ions in complexes. The new bands appearing at 1146-1158 cm^{-1} and 539-599 cm^{-1} are due to an asymmetric and symmetric stretching modes respectively, indicates that acetate ion is free from complexation[21,22]. This shows that in Co(II),Ni(II),Cu(II) and Zn(II) complexes acetate ion is present as a counter ion, which was further confirmed by the molar conductance measurements. The results of IR spectral data show that the ligands behave as a tetradentate and four azomethine N-atoms are coordinated to the metal ion in all the complexes.

Compounds	**υ(OH) cm^{-1}**	**υ(C=N) cm^{-1}**	**υ(C-O) cm^{-1}**	**υ(C-H) cm^{-1}**	**υ(M-N) cm^{-1}**	**υ(-OAc) cm^{-1}**	
						1140-1190	**590-640**
L_1	3434.78	1568.05	1186.13	3050.82	-	-	-
$[CoL_1](OAc)_2$	3425.07	1530.81	1179.29	3057.53	536.20	1146.45	594.97
$[NiL_1](OAc)_2$	3428.86	1544.91	1181.74	3046.58	540	1152.92	589.28
$[CuL_1](OAc)_2$	3435.62	1520.541	180.91	3057.53	538.40	1148.03	592.10
$[ZnL_1](OAc)_2$	3425.70	1531.48	1183.63	3041.10	543.86	1149.02	592.67
L_2	3455.00	1590.00	1198.00	3055.05	-	-	-

$[CoL_2](OAc)_2$	3432.00	1545.05	1185.38	3065.02	543.00	1150.00	598.49
$[NiL2](OAc)_2$	3439.76	1551.36	1189.48	3057.28	548.81	1158.00	593.00
$[CuL_2](OAc)_2$	3443.08	1542.45	1185.00	3065.92	545.26	1154.00	597.00
$[ZnL_2](OAc)_2$	3430.56	1548.16	1186.38	3045.00	550.18	1154.78	592.00

Table 2

3.3. NMR spectrum

Evidence for the bonding mode of the ligands was provided by the ^1H NMR spectra. The chemical shifts of the different types of protons in the ^1H NMR spectra of the ligands and its Zn(II) complexes are listed in Table 3. The ^1H NMR spectrum of the Schiff base ligands L_1 and L_2 in DMSO exhibits singlet at 2.434 and 2.57 ppm respectively, are assigned to the N=C- CH_3 protons[23]. The multiplet signals at 7.3-7.6 ppm and 7.5-7.85 ppm are attributed to the aromatic ring protons. The peaks at 13.005 and 13.21 ppm are assigned to the phenolic –OH group[24]. The presence of this peak in the spectra of the Zn(II) complexes confirms that the phenolic –OH groups are not coordinated to the metal ion. Coordination of the azomethine nitrogen's in Zn(II) complexes are inferred by the downfield shift of the (CH=N) proton signal from 9.171 and 9.253 ppm[25] in the ligands to 9.462 and 9.608 ppm in the Zn(II) complexes. All these results indicate the coordination through the azomethine nitrogen atoms.

Compounds	**Chemical shift (ppm)**			
	$-CH_3$	**H-aromatic**	**CH=N**	**-OH**
L_1	2.434	7.3-7.6	9.171	13.005
$[ZnL_1](OAc)_2$	2.502	7.27-7.63	9.462	13.012
L_2	2.570	7.5-7.85	9.253	13.210
$[ZnL_2](OAc)_2$	2.610	7.58-7.91	9.608	13.250

Table 3

3.4. Magnetic susceptibility

The magnetic moment data of all the complexes were measured at room temperature in the solid state. Magnetic moment values are used to propose the structure of the complexes. The μ_{eff} values of all the complexes are given in Table 4. The magnetic moments of the mononuclear CoL_1 and CoL_2 complexes are 3.55 and 3.62 B.M. respectively, which are consistent with a square planar geometry. Similarly the magnetic moment values of the mononuclear CuL_1 and CuL_2 complexes are 1.76 and 1.79 B.M., which suggests that the Cu(II) complexes exhibits a square planar geometry . The zero magnetic moment values observed for NiL_1 and NiL_2 complexes show that the Ni(II) ions are diamagnetic, which confirms the square planar geometry. The Zn(II) complexes are also found to be diamagnetic as expected for d^{10} configuration. All these values were compared with the magnetic moment values obtained for similar complexes[12,25-27].

Compounds	**Electronic spectra λmax (nm)**				**μeff (B.M)**
	$\pi\rightarrow\pi^*$	**$n\rightarrow\pi^*$**	**L→M**	**d-d transition**	
L_1	280	380	-	-	-
$[CoL_1](OAc)_2$	270	370	420	490 $^1A_{1g}\rightarrow{}^1B_{1g}$	3.55
$[NiL_1](OAc)_2$	274	368	410	505 $^1A_{1g}\rightarrow{}^1B_{1g}$	-
$[CuL_1](OAc)_2$	278	375	400	550 $^2B_{1g}\rightarrow{}^1A_{1g}$	1.76
$[ZnL_1](OAc)_2$	276	370	390	-	-
L_2	287	385	-	-	-
$[CoL_2](OAc)_2$	275	376	425	520 $^1A_{1g}\rightarrow{}^1B_{1g}$	3.62
$[NiL2](OAc)_2$	278	373	415	514 $^1A_{1g}\rightarrow{}^1B_{1g}$	-
$[CuL_2](OAc)_2$	280	379	408	570 $^2B_{1g}\rightarrow{}^1A_{1g}$	1.79
$[ZnL_2](OAc)_2$	279	376	395	-	-

Table 4

3.5. Electronic spectra

An electronic spectrum is used to determine the geometry of the complexes. The elcectronic spectra of the ligands L_1 and L_2 and their complexes have been taken in DMSO solution between 200-800 nm at room temperature. The electronic spectral data of the tetradentate Schiff base ligands (L_1 and L_2) and their complexes are given in Table 4. In the spectra of the Schiff base ligands (L_1 and L_2), the absorption bands observed at 280 and 287 nm respectively, are assigned to $\pi\rightarrow\pi^*$ and the absorption bands at 380 and 385 nm are assigned to n→ π* transitions[28,29]. Complexation of the ligands results in a slight shift of the π → π* and n→ π* transitions, which is most notable in complexes. Coordination compounds exhibit strong CT absorptions typically in the UV and Visible portion of the spectrum. These absorptions may be more intense than d-d transitions. The spectra of all the complexes show new absorption bands in the region 390-425 nm range can be assigned to L → M Charge transfer bands. New bands at higher wave numbers support the transition of strong M-N bonds[30]. A weak band absorbed at 490 and 520 nm for the two cobalt complexes (CoL_1 and CoL_2) respectively, are assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition, indicative of the square planar or distorted square planar geometry for Co(II) ion[31]. The magnetic moment studies show that the two nickel complexes (NiL_1 and NiL_2) has diamagnetic behavior and its electronic spectrum shows absorption bands at 505 and 514 nm ascribed to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition, which supports the square planar geometry around the Ni(II) ion[32]. The electronic spectrum of the two copper complexes (CuL_1 and CuL_2) show bands in the region 550 and 570 nm respectively, are assigned to $^2B_{1g} \rightarrow {}^1A_{1g}$ transition, which are attributed to a square planar geometry for Cu(II) complexes[33]. The electronic spectral values obtained for Co(II), Ni(II) and Cu(II) complexes are in good agreement with the similar complexes synthesized [28,34]. Zn (II) belongs to d^{10} system, so the complexes which synthesized are diamagnetic in nature because of unavailability of unpaired electrons in the system. According to the empirical formula, it is proposed to have a square planar geometry[35].

3.6. Electrochemical studies

The redox behavior of all the complexes were studied by cyclic voltammetry using DMSO solvent in the potential range +2.0 - - -2.0 V. The electrochemical data such as cathodic peak potential (Epc) and anodic peak potential (Epa) are given in Table 1. The redox potential of all the metal complexes depends on factors such as coordination number, hard/soft nature of the ligand and bulkiness of the ligand. The cyclic voltammogram of mononuclear cobalt (II) complexes (CoL_1 and CoL_2) in DMSO, shows cathodic peaks at -0.9 and -0.95 V respectively, are assigned to Co(II) → Co(I) reduction. Both the complexes exhibit no oxidation peak. The CV data for the cobalt complexes reveal that an increase in bulkiness of the ligands presumably reduces the interaction of the solvent molecule with the cobalt metal, this shows that Co ion is in the +2 oxidation state. The cyclic voltammogram of mononuclear nickel(II) complexes (NiL_1 and NiL_2) in DMSO, shows cathodic peaks at -0.674, -1.586 V and -0.69, -1.48 V respectively, which were obtained due to the reduction of Ni(II) → Ni (I) and Ni(I) → Ni (0) respectively. The anodic peak observed at -0.6 and -0.71 V corresponds to the oxidation behavior of ligand moiety and at +0.43 and 0.51 V corresponds to the oxidation process of Ni(I) → Ni (II) for both the complexes respectively. The cyclic voltammogram of the mononuclear copper(II) complexes (CuL_1 and CuL_2) in DMSO , shows cathodic peaks at 0.142, -0.592 V and 0.158, -0.62 V respectively. The cathodic peaks at 0.142 and 0.15 V for CuL_1 and CuL_2 respectively, are due to the reduction of the azomethine group. The cathodic peaks at -0.592 and -0.62 V corresponds to the one electron reduction of Cu(II) → Cu(I) process followed by rapid decomposition of Cu(I) complexes. No oxidation peak was observed for these complexes. The cyclic voltammogram of mononuclear zinc(II) complexes (ZnL_1 and ZnL_2) in DMSO, shows no reduction (or) oxidation peaks, because of its invariable oxidation state i.e. +2. All these peak values are similar to the behavior observed for related complexes[36].

3.7. ESR Spectra

The ESR spectra of the complexes were recorded in the solid state at room temperature and in DMSO at the temperature of liquid nitrogen using DPPH free radical as the ‘g’ marker. The ESR spectrum of the metal complexes provides information about hyperfine and super hyperfine structures which are important in studying the geometry and the covalent character of the metal-ligand bond. In tetragonal and square-planar geometry the unpaired electrons lies in the $dx^2\text{-}y^2$ orbital with $^2B_{1g}$ as the ground state and also $g_\parallel > g_\perp > 2$[37]. The observed ESR spectral data of the Cu(II) complex showed that $g_\parallel = 2.25$ and $g_\perp = 2.06$ from the observed values, it is clear that $g_\parallel = 2.25 > g_\perp = 2.06 > 2$ and the ESR parameters of the complexes coincide with the related systems which suggest that the complex has a square-planar geometry and axially symmetric[38]. According to Hathaway[39], $G = (g_\parallel - 2)/(g_\perp - 2)$, and if G>4, the exchange interaction is negligible, where as when G<4, a considerable interaction is indicated in the solid complex. For the Cu(II) complex, the G value is 4.17. Thus the spectral parameters indicated approximately square-planar co-ordination around the Cu(II) ion[40,41]. The ESR spectra of the solid Co(II), Ni(II) and Zn(II) complexes at room temperature do not show ESR signal because the rapid spin lattice relaxation of the Co(II), Ni(II) and Zn(II) broadness the lines at high temperatures[12].

3.8. Antimicrobial activity

The antimicrobial activity of the tetradentate Schiff base ligands (L_1 and L_2) and its metal complexes were tested against more than one test organism to increase the chance of antibiotic principles in the tested materials. The ligands and their metal complexes have been tested for their antimicrobial activity against the bacterial species *Staphyloccus aureus* ,*Bacillus subtilis, Escherichia coli* and *Klebsiella pneumonia* and fungi such as *Aspergillus niger, Aspergillus flavus* and *Candida albicans* (yeast), which were evaluated by disc diffusion methods. The *in vitro* antimicrobial activities of the ligands and their complexes in diameter of growth of inhibition zone (mm) are given in Table 5. and in figures 2 (a) and 2(b). The *in vitro* antifungal activities in percentage inhibition of growth are given in Table 6. and figure 3. The concentrations used to study the antibacterial and antifungal activities were 50μg mL^{-1} and 75 μg mL^{-1}. The zones of inhibition formed were measured with calipers. The antibacterial activities of the compounds are represented by size of the diameter in mm. An inhibition zone diameter over 8mm indicated that the tested compounds are active against Gram +ve and Gram –ve bacteria, than the parent tetradentate Schiff base ligands and the standard *Streptomycin. S.aureus* used in this study displayed more resistance to the complexes than the species *B.subtilis* among Gram +ve, similarly *K. pneumonia* was more potent than *E.coli* among Gram –ve bacteria. However, some of the complexes were less effective against the yeast *Candida albicans*. The antifungal activities are represented by percentage growth of inhibition. All the complexes were found to be more effective against the fungi *Aspergillus niger* and *Aspergillus flavus*. The antibacterial and antifungal activities of the Schiff base ligands and their metal complexes arise due to the presence of hydroxyl groups and azomethine groups. The activity of the ligands and their complexes increases as the concentration increases. The metal complexes are found to be more active than that of the ligands, due to the chelation of the ligands with metal ions. Such increased activity of the metal chelates can be explained on the basis of chelation theory[42-44]. Chelation makes the Schiff base complexes to act as more powerful and potent bacteriostatic agents, thus inhibits the growth of bacteria and fungi more than that of the parent Schiff bases. The metal complexes restrict the growth of the organisms by disturbing the respiration process of the cell[12,45,46] and thus block the synthesis of proteins. The variation in the activity of the metal complexes against the organisms depends on the impermeability of the cells of the microbes. The complexes may involve in the formation of hydrogen bond though azomethine group with the active centers of the cell, resulting in interference with the normal cell prosess. It is well known that chelation is not the only criterion for antimicrobial activity. Some important factors such as the nature of the ligand, the concentration, hydrophilicity, lipophilicity and the presence of co-ligands have a considerable influence on the antimicrobial activity. The ligands and their complexes exhibit various degrees of inhibitory effects on the growth of the tested bacteria and fungi. Antibacterial and antifungal activities of the complexes synthesized from L_2 were found to be more than the complexes synthesized from the Schiff base ligand L_1. This is due to the presence of an electron withdrawing group (Cl) in the ligand (L_2). The inhibition zone values (mm) of the ligands and the matal complexes show that the biological activity of the complexes follow the order: Cu(II)> Co(II)>Zn(II) >Ni(II)> L_2> L_1. Higher antimicrobial activity of the Cu(II) complex is due to the smaller size of Cu(II) ion with high electronegativity compare to other metal ions[47]. Thus the microbial activity of all the complexes is higher than that of the free ligands. This means that metal chelates significantly increases the antimicrobial activities of the complexes.

Compounds	**Diameter of growth of inhibition zone (mm)**									
	a		**b**		**c**		**d**		**e**	
	Concentration (µg mL^{-1})									
	50	**75**	**50**	**75**	**50**	**75**	**50**	**75**	**50**	**75**
Standard	7[f]	12[f]	8[f]	11[f]	8[f]	13[f]	9[f]	13[f]	6[g]	10[g]
L_1	8	12	10	15	7	11	9	14	3	8
$[CoL_1](OAc)_2$	11	17	12	18	9	14	10	15	5	12
$[NiL_1](OAc)_2$	9	14	9	14	8	12	8	12	4	10
$[CuL_1](OAc)_2$	12	18	12	18	10	15	13	20	6	11
$[ZnL_1](OAc)_2$	10	15	10	15	9	14	12	18	5	9
L_2	9	14	12	18	8	12	10	15	4	7
$[CoL_2](OAc)_2$	12	18	13	20	10	15	12	18	7	11
$[NiL2](OAc)_2$	12	18	10	15	9	14	10	15	5	9
$[CuL_2](OAc)_2$	14	21	13	20	12	18	13	20	8	13
$[ZnL_2](OAc)_2$	10	15	9	14	9	14	10	15	6	11

Table 5

a- Staphyloccus aureus, b-Bacillus subtilis, c- Klebsiella pneumonia, d-Escherichia coli
, e-Candida albicans, [f]- Streptomycin, [g] Amphotericin-B,

Compounds	**Fungal growth of inhibition (%)**			
	A.niger		**A.flavus**	
	Concentration (µg mL^{-1})			
	50	**75**	**50**	**75**
Standard[h]	33	37	31	36
L_1	24	27	20	26
$[CoL_1](OAc)_2$	45	49	41	44
$[NiL_1](OAc)_2$	35	39	37	40
$[CuL_1](OAc)_2$	49	55	48	54
$[ZnL_1](OAc)_2$	40	43	39	45
L_2	29	33	25	31
$[CoL_2](OAc)_2$	49	55	46	51
$[NiL2](OAc)_2$	43	47	40	42
$[CuL_2](OAc)_2$	57	64	54	59
$[ZnL_2](OAc)_2$	44	49	41	45

Table 6

h-Amphotericin- B

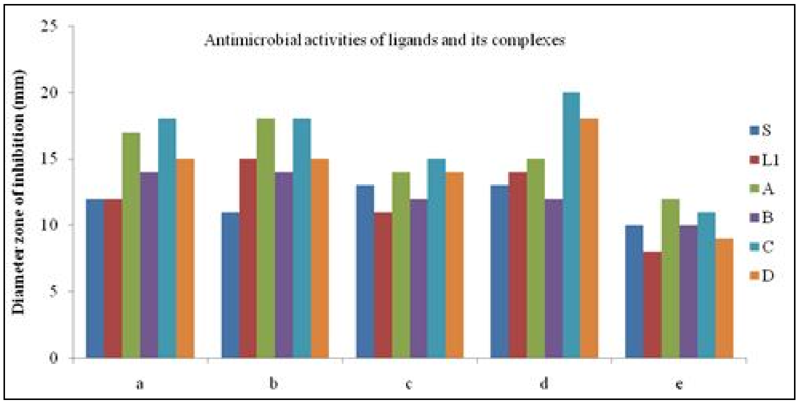


Figure 2(a) S= Streptomycin for bacteria and Amphotericin- B for fungi,
L_1- Ligand 1, A-$[CoL_1](OAc)_2$, B-$[NiL_1](OAc)_2$, C- $[CuL_1](OAc)_2$, D-$[ZnL_1](OAc)_2$.
a-Staphyloccus aureus, b-Bacillus subtilis, c- Klebsiella pneumonia, d-Escherichia coli, e-Candida albicans

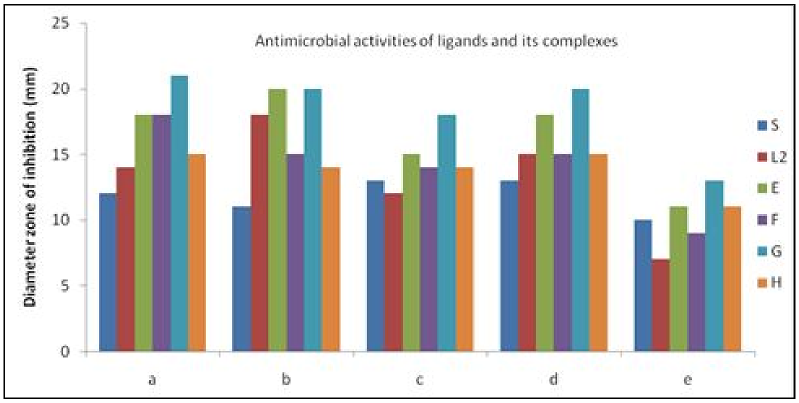


Figure 2(b) S= Streptomycin for bacteria and Amphotericin- B for fungi,
L_2- Ligand 2, E-$[CoL_2](OAc)_2$, F-$[NiL_2](OAc)_2$, G- $[CuL_2](OAc)_2$, H-$[ZnL_2](OAc)_2$.
a-Staphyloccus aureus, b-Bacillus subtilis, c- Klebsiella pneumonia, d-Escherichia coli, e-Candida albicans

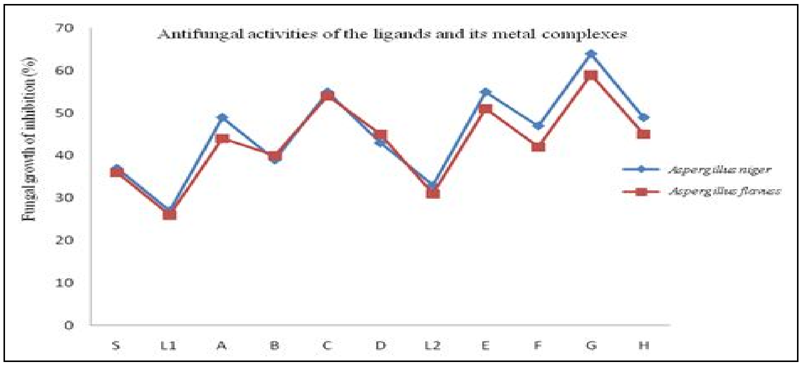


Figure.3 L_1- Ligand 1, A-$[CoL_1](OAc)_2$, B-$[NiL_1](OAc)_2$, C- $[CuL_1](OAc)_2$, D-$[ZnL_1](OAc)_2$, L_2- Ligand 2,
E-$[CoL_2](OAc)_2$, F-$[NiL_2](OAc)_2$, G- $[CuL_2](OAc)_2$, H-$[ZnL_2](OAc)_2$

4. Conclusion

Co(II),Ni(II),Cu(II) and Zn(II) complexes have been synthesized successfully from the tetradentate Schiff base ligands (L_1 and L_2) and the acetate salts of the corresponding metals in alcoholic medium with high yields. All the complexes were soluble in DMF and DMSO, but insoluble in common organic solvents. The metal-ligand ratio of 1:1 has been arrived at by the elemental analysis data. The molar conductivity data of the complexes indicate that all the complexes were electrolytic in nature and show the presence of acetate ion outside the coordination sphere as counter ion, which was further supported by IR spectra. IR spectra of the complexes indicate that the nitrogen of azomethine group was coordinated to the metal ion. The presence of –OH stretching bands in all the complexes shows the presence of free –OH groups. The IR spectra of the complexes also confirm the presence of acetate ions as counter ions. Coordination of the azomethine nitrogen atoms in Zn(II) complexes was confirmed by the ^{1}H NMR spectrum. The magnetic moment values and electronic spectral data of all complexes suggest a square planar geometry for all the complexes. Electrochemical studies shows that Co(II) and Cu(II) complexes exhibit reduction waves, which could be related to the reduction process of the cobalt and copper ions. The antimicrobial activity results reveal that the antibacterial and antifungal activity lf the complexes derived from the tetradentate ligands L_2 were more than that of the complexes derived from the Schiff base ligand L_1, due to the presence of an electron withdrawing group present in the former. Thus, the spectral data and antimicrobial activity of the metal complexes derived from the Schiff base ligands L_2, differs from the complexes derived from the Schiff base ligand L_1, due the presence of –Cl (an electron withdrawing group) in the ligand L_2.

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6. References

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