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Synthesis, Spectral, Redox and Antimicrobial Investigation of some Schiff Base Transition Metal Complexes

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Abstract: Some novel ternary NNO type Schiff bases and their Cu(II) a.nd Zn(II) chelates were synthesized in ethanol using curcuminyl-4-aminoantipyrine and aniline/substituted aniline (p-Cl, p-NO_2 and p-CH_3). They have been characterized by elemental analysis, magnetic susceptibility, Mass, IR, UV- Visible, ^{1}H-NMR and ESR spectral techniques. All the complexes exhibit square planar geometry. The monomeric and non-electrolytic natures of the complexes are evidenced by their magnetic susceptibility and low conductance data respectively. The ESR spectra of copper complexes in MeCN solution were recorded at 300 K and 77 K and their salient features are reported. The redox behavior of the copper complexes in MeCN solution at 298 K was well studied. The antimicrobial activity of the ligands and their metal chelates was tested against the bacteria such as *Staphytococcus aureus, Escherichia coli, Pseudomonas aeroginosa, Salmonella typhi, Starptococci* and the fungi such as *Aspergillus niger* and *Candida albicans*. It suggested that metal chelates have more antimicrobial activity than their parent Schiff bases.

Keywords: Schiff base, Curcuminyl-4-aminoantipyrine, Cyclic voltammogram, ESR spectra, Antimicrobial activity.

INTRODUCTION

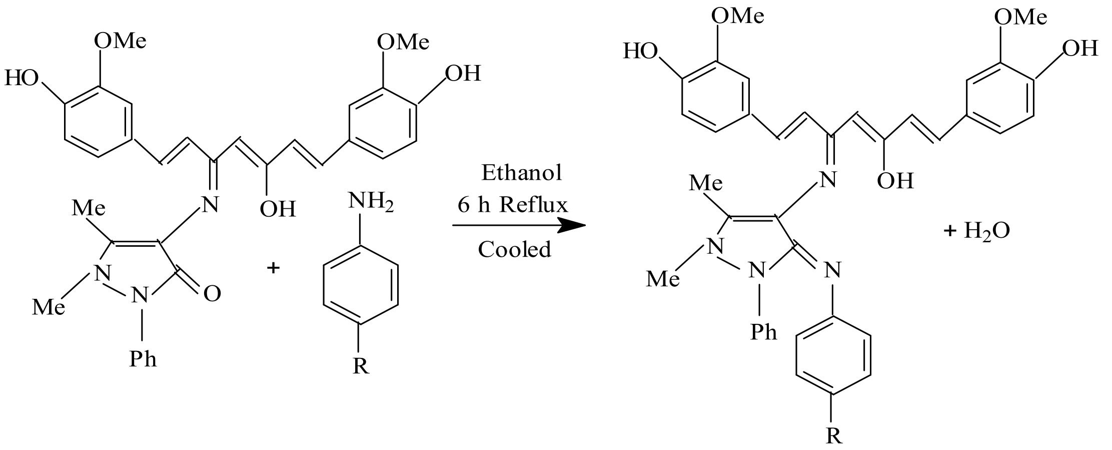
From the past five decades, the chelating behavior of β-diketones in metal chelates gives more information about the structural and spectral properties[1-6]. The coordinating property of 4-aminoantipyrine has been modified into a flexible ligand system by condensation it with β-diketones and amines[7-9]. In recent years, a number of research articles have been published on transition metal complexes derived from 4-aminoantipyrine derivatives with aza or aza-oxo donor atoms[10-15]. We were interested in examining the biological activities of Schiff bases and their transition metal complexes. Thus, in this article, we report the antimicrobial activities and structural investigation of some tridentate NNO type Schiff bases and their copper and zinc complexes derived from curcuminyl-4-aminoantipyrine and aniline/substituted aniline.

EXPERIMENTAL

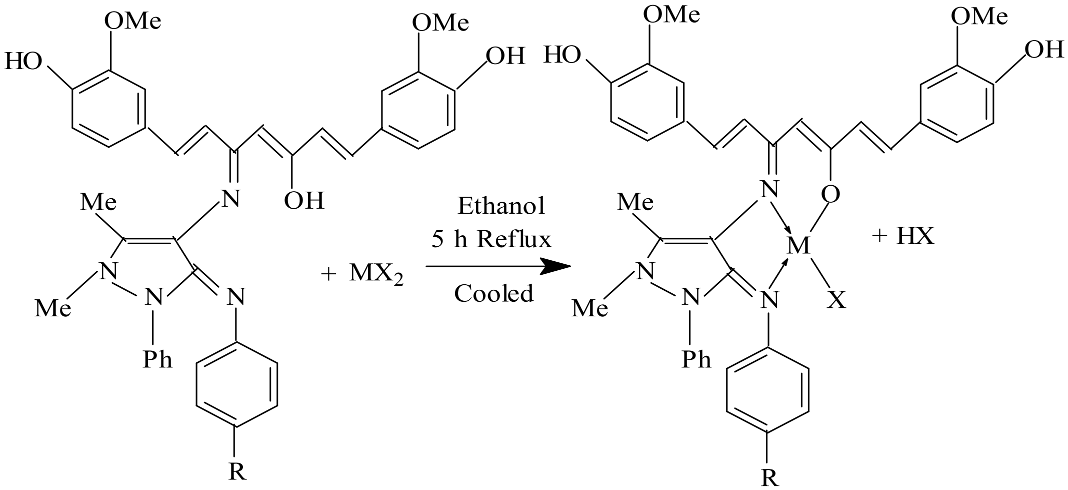
All the chemicals used for the synthesis of ligands and complexes were of Merck products and used as supplied. Spectroscopic grade solvents were used for spectral and cyclic voltammetric measurements. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer, using m-nitrobenzyl alcohol as a matrix, at Indian Institute of Chemical Technology, Hyderabad. Elemental analyses (C, H, N) were carried out with Thermofinger –Flash CA 1112 series at Sophisticated Analytical Instrumentation facility, Indian Institute of Technology, Mumbai. The molar conductance of the complexes in 10^{-3} M MeCN solution was measured using a 305 type systronic conductivity bridge with a dip type cell. H^1-NMR spectra of the Schiff bases and their zinc complexes were recorded in $CDCl_3$ solution on a Brucker 300 MHz FT-NMR spectrometer using TMS as internal standard at Madurai Kamaraj University, Madurai. The UV-Visible spectra of the compounds were recorded on a Shimadzu UV-1601 spectrophotometer. The IR spectra were recorded on a FT-IR 8400S Shimadzu spectrophotometer in the 4000 – 400 cm^{-1} range using KBr as solvents. Cyclic voltammogram of the copper complexes was recorded in MeCN solution at 300 K using a BAS CV50 electrochemical analyzer. The three electrode cell contains a reference Ag/AgCl electrode, Pt wire auxiliary electrode and glassy carbon working electrode. Tetra butyl ammonium bromide (TBAB) was used as supporting electrolyte. The X-band ESR spectra of the copper complexes in MeCN solution at 300 K and 77 K were recorded on a Varian E-112 ESR spectrometer using TCNE (Tetra cyanoethylene) as the g – marker at Sophisticated Analytical Instrumentation facility, IIT, Mumbai.

Synthesis of the Schiff bases

An ethanolic solution (50 ml) of curcuminyl-4-aminoantipyrine (0.01 mol) and aniline/substituted aniline (0.01 mol was refluxed on a water bath for 6 h. The resulting solution was concentrated to 10 ml and cooled. Then the concentrate was stirred with 10 ml of petroleum ether (40 – 60°C). The solid product obtained was collected by filtration and recrystallized from ethanol. The proposed reaction for the synthesis of Schiff bases is given in Scheme 1.



Scheme 1 Synthesis of the Schiff bases, Where, [R = H (aniline), L = L^1; R = CH_3 (*p*-Toludine), L = L^2; R = Cl (*p*-chloroaniline), L = L^3; R = NO_2 (p-nitroaniline), L = L^4]



Scheme 2 Synthesis of the complexes, Where, M = Cu(II)/Zn(II) and [R = H (aniline), L = L^1; R = CH_3 (*p*-Toludine), L = L^2; R = Cl (*p*- chloroaniline), L = L^3; R = NO_2 (p-nitroaniline), L = L^4]

Synthesis of the complexes

A solution of $CuCl_2$ or $ZnCl_2$ (0.05 mol) in ethanol was refluxed with an ethanolic solution of Schiff base (0.05 mol) for 5 h. Then the solution was reduced to 10 ml on a water bath and cooled at room temperature. The solid complex precipitated was filtered, washed and recrystallised with ethanol. The proposed reaction for the synthesis of complexes is given in Scheme 2.

Antimicrobial activity

The *in-vitro* biological screening effects of the investigated compounds were tested against the bacteria (*Escherichia coli, Salmonella typhi, Staphylococcus aureus, Starptococci,* and *Pseudomonas aeruginosa)* and fungi such as *Aspergillus niger* and *Candida albicans* by disc diffusion method using nutrients agar as the medium. The stock solutions were prepared by dissolving the compounds in MeCN and the solutions were serially diluted in order to find the MIC values. All the blank discs were moistened with the solvent. For disc assays, the compounds containing discs (6 mm) with various concentrations were placed on the surface of the nutrients agar plate previously spread with 0.1 ml of overnight culture of microorganisms and the plates were incubated at 37°C. During this period, the test solutions were diffused through the medium and the growth of micro-organisms was affected. The inhibition zones were developed, at which the concentration was noted.

RESULTS AND DISCUSSION

The analytical data for the ligands and their complexes together with some physical properties are summarized in Table 1. The analytical data of the complexes correspond well with the general formula ML, where M = Cu(II) and Zn(II); L = Deprotonated Schiff bases. The magnetic susceptibility data of the copper complexes at room temperature were consistent with square planar geometry around the central metal ion. The lower conductivity values of the chelates support their non-electrolytic nature[16]. The FAB mass spectra of Schiff bases and their complexes are in good agreement with the proposed molecular formula for the complexes.

Table 1 Physical characterization, analytical, molar conductance and magnetic susceptibility data of the Schiff bases and their complexes

Compound	Molecular formula	Formula weight	m/z values	Colour	Yield (%)	Melt./ Decomp. Point (^oC)	Found (Calcd) (%) M	C	H	N	Λ_M x 10^{-3} (mho cm^2 mol^{-1})	$\mu_{eff.}$ (B.M.)
HL^1	$C_{38}H_{36}N_4O_5$	620	620	Orange	65	125	-	73.18 (73.55)	5.71 (5.81)	7.54 (7.74)	-	-
$[CuL^1]$	$[CuC_{38}H_{35}N_4O_5Cl]$	718	717	Brown	85	180	8.96 (8.85)	63.93 (63.51)	4.73 (4.87)	6.68 (6.69)	1.62	1.86
$[ZnL^1]$	$[ZnC_{38}H_{35}N_4O_5Cl]$	720	719	yellow	90	152	8.98 (9.13)	63.43 (63.33)	4.62 (4.86)	6.64 (6.67)	3.42	-
HL^2	$C_{39}H_{38}N_4O_5$	634	634	Red	70	132	-	73.86 (73.82)	5.62 (5.99)	7.54 (7.57)	-	-
$[CuL^2]$	$[CuC_{39}H_{37}N_4O_5Cl]$	732	731	Brown	82	154	8.72 (8.68)	63.93 (63.93)	4.98 (5.05)	6.28 (6.56)	2.14	1.81
$[ZnL^2]$	$[ZnC_{39}H_{37}N_4O_5Cl]$	734	733	Brown	86	160	8.78 (8.95)	63.62 (63.76)	4.89 (5.04)	6.38 (6.36)	2.72	-
HL^3	$C_{38}H_{35}N_4O_5Cl$	655	654	Red	80	115	-	69.72 (69.67)	5.40 (5.35)	7.54 (7.33)	-	-
$[CuL^3]$	$[CuC_{38}H_{34}N_4O_5Cl_2]$	753	752	Green	88	144	8.36 (8.44)	60.16 (60.56)	4.46 (4.52)	6.41 (6.38)	3.06	1.92
$[ZnL^3]$	$[ZnC_{38}H_{34}N_4O_5Cl_2]$	755	755	Brown	90	132	8.62 (8.70)	60.63 (60.40)	4.62 (4.64)	6.42 (6.36)	2.84	-
HL^4	$C_{38}H_{35}N_5O_7$	673	673	Orange	75	140	-	67.72 (67.76)	5.40 (5.20)	10.54 (10.40)	-	-
$[CuL^4]$	$[CuC_{38}H_{34}N_5O_7Cl]$	771	770	Brown	90	186	8.32 (8.24)	60.13 (59.14)	4.54 (4.41)	9.24 (9.08)	2.32	1.93
$[ZnL^4]$	$[ZnC_{38}H_{34}N_5O_7Cl]$	773	772	Red	70	162	8.46 (8.50)	59.26 (58.98)	4.63 (4.53)	9.32 (9.06)	2.11	-

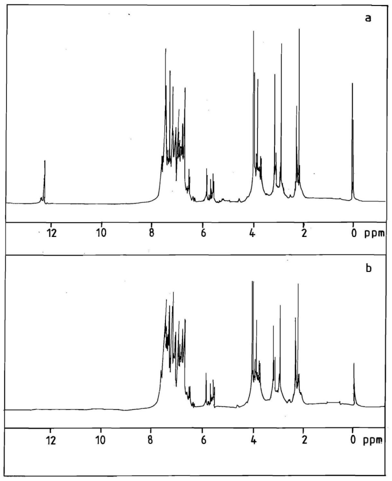


Fig. 1 ^{1}H-NMR spectra of the Schiff base (HL^1) and [ZnL^1] complex in $CDCl_3$ solution

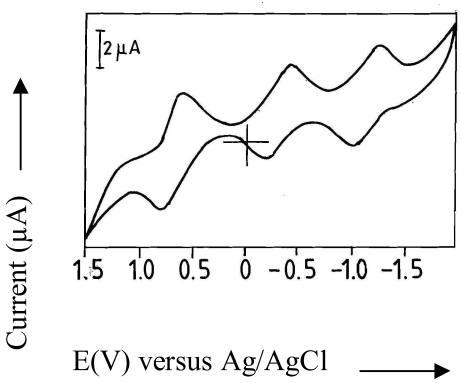


Fig. 2. The cyclic voltammogram of [CuL^3] complex in MeCN (0.1 M TBAB) solution at scan rate 100 mVs^{-1}.

H^1- NMR spectra

H^1-NMR spectra of the Schiff bases and their zinc complexes were recorded in $CDCl_3$ solution (Fig.1). The Schiff bases show their characteristic enolic -OH group of curcumin moiety peak at around 12 ppm. Absence of these peaks in the zinc complexes which indicates the loss of enolic -OH proton due the coordination with zinc ion. A slight down field shift was noted in the all other signals in the zinc complexes. The peaks at 6.2 and 6.9 ppm in all Schiff bases and the complexes are assignable to two phenolic – OH group of curcumin moiety which suggested that they are present as such and not involved in coordination.

IR Spectra

IR spectra provide the valuable information about the nature of the binding mode and functional group attached to the metal ion. In order to study the binding mode of the Schiff base to the metal in complexes, the IR spectrum of the free ligand was compared with the spectrum of the complex. The IR spectra of the ligands show a weak broad band at 3200- 2950 cm^{-1} which are assigned to enolic –OH group of curcumin moiety. The weak and broadness of these peaks are mainly due to intra-molecular hydrogen bonding between the enolic –OH group with azomethine nitrogen atom of pyrazolone ring. Existence of this enolic –OH group in all the ligands are possible only due to stabilization of –OH group by the conjugation present the curcumin system. Disappearance of this band in all complexes indicates the deprotonation of the enolic carbonyl group upon coordination. IR spectra of all compounds shows a strong band at 3600 - 3300 cm^{-1} region which are assigned to phenolic -OH group of curcumin moiety. It indicates that there is a free existence of phenolic – OH group and not involved in coordination with metal ion. In the spectra of all the Schiff bases show a strong bands at 1630 cm^{-1} and 1615 cm^{-1} region are attributable to -C=N groups. On chelation, due to possible drift of the lone pair electron density towards the metal ion, the azomethine -C=N band is expected to absorb at lower frequency in the complex. These bands are observed at 1591 - 1512 cm^{-1} region in complexes indicates the coordination of azomethine nitrogen to the metal ion. IR spectra of all the complexes also show some new peaks at 520 - 510 cm^{-1}, 460 - 470 cm^{-1} and 430 cm^{-1} region are assignable to M-N, M-O and M-Cl bonds respectively[17], which are newly formed bonds due to chelation.

UV-Visible Spectra

The UV–Visible spectra of Schiff bases and their copper complexes were recorded in MeCN solution at 300 K. All the copper complexes shows a d-d bands at *ca.* 19000 cm^{-1} - 20600 cm^{-1} region that strongly favours the square planar geometry around the metal ion . The broadness of the band can be taken as an indication of distortion from perfect square planar geometry. This is further supported by the magnetic susceptibility values (1.81 - 1.93 B.M). The absorption regions, assignments and proposed geometry of the copper complexes are presented in Table 2. These values are comparable with other reported complexes[18-20].

Table 2 Electronic spectral data of the Schiff bases and their copper complexes

Compound	Absorption region (nm)	Band assignment	Geometry
HL^1	27778, 23256	INCT	-
$[CuL^1]$	29070, 24155	INCT	
	20284	$^2B_1g \rightarrow {}^2B_2g$	Square planar
	11843	$^2B_1g \rightarrow {}^2A_1g$	
HL^2	30303, 23753	INCT	-
$[CuL^2]$	29851, 27981	INCT	
	19048	$^2B_1g \rightarrow {}^2B_2g$	Square planar
	12225	$^2B_1g \rightarrow {}^2A_1g$	
HL^3	27322, 23585	INCT	-
$[CuL^3]$	27748, 22989	INCT	
	19646	$^2B_1g \rightarrow {}^2B_2g$	Square planar
	12804	$^2B_1g \rightarrow {}^2A_1g$	
HL^4	28902, 23419	INCT	-
$[CuL^4]$	30864, 24331	INCT	
	20576	$^2B_1g \rightarrow {}^2B_2g$	Square planar
	12887	$^2B_1g \rightarrow {}^2A_1g$	

Table 3 Redox potential for the copper complexes in MeCN solution containing 0.1 M TBAB at 300 K

Complex	Peak	Ep_a(V)	Ep_c(V)	Ip_a(μA)	Ip_c (μA)
$[CuL^1]$	Cu(II)/Cu(III)	+0.61	+0.50	- 3.8	3.2
	Cu(II)/Cu(I)	- 0.63	- 0.72	- 3.0	2.2
$[CuL^2]$	Cu(II)/Cu(III)	+0.47	+0.40	- 2.0	1.8
	Cu(II)/Cu(I)	- 0.55	- 0.67	- 2.4	2.6
\					
$[CuL^3]$	Cu(II)/Cu(III)	+0.70	+0.65	- 3.8	3.2
	Cu(II)/Cu(I)	- 0.13	- 0.28	- 2.2	3.0
	Cu(I)/Cu(0)	- 1.05	- 1.13	- 2.0	2.6
$[CuL^4]$	Cu(II)/Cu(III)	+0.64	+0.56	- 3.4	3.2
	Cu(II)/Cu(I)	- 0.54	- 0.67	- 3.6	4.2

Redox Studies

The redox behavior of copper complexes is studied with the help of cyclic voltammetry. Cyclic voltammogram of the copper complexes was recorded in MeCN solution at 300 K using TBAB as supporting electrolyte and the data are summarized in Table 3. The cyclic voltammogram of [CuL^1], [CuL^2] and [CuL^4] complexes in MeCN solution shows a quasi reversible peak for the couple Cu(II)/Cu(III) in the positive region. These complexes also show another one quasi reversible peak for the couple Cu(II)/Cu(I). The single - electron transfer of this process was established by the comparison of Ip_c and Ip_a values[21&22].

The cyclic voltammogram of the [CuL^3] complex (Fig.2) in MeCN solution shows a well defined redox process corresponding to the formation of Cu(II)/Cu(III) couple at $Ep_a = 0.70$ V and the associated cathodic peak at $Ep_c = 0.65$ V. This couple was found to be reversible. This complex also shows two quasi reversible peak in the negative region characteristics for Cu(II/ Cu(I) and Cu(I)/Cu(0)[23].

ESR Spectra

The X-band ESR spectra of copper complexes in DMSO at a concentration of ca. 0.1 mol was recorded at 300 K and 77 K. The typical ESR spectra of [CuL^1] complex at 300 K and 77 K are shown in Fig. 3. The ESR parameters of the copper complexes were calculated and are summarized in Table 4.

The spectra of all the copper complexes at 300 K show one intense band in the high field region, which are isotropic due to tumbling motion of the molecules. However, all the copper complexes at 77 K show well-resolved four peaks with low intensities in the parallel region and one intense peak in perpendicular region. The absence of a half field signal at 1600 G corresponding to the $\Delta Ms = \pm 2$ transition, rules out any Cu-Cu interaction[24&25].

The g tensor values of the copper complexes can be used to derive the ground state. In square planar complexes, the unpaired electron lies in the $dx^2\text{-}y^2$ orbital giving ^2B_1g as the ground state with $g_{II} > g_{\perp} > 2$, while the unpaired electron lies in the $d_z{}^2$ orbital giving ^2A_1g as the ground state with $g_{\perp} > g_{II} > 2$. From the observed values, it is clear that $A_{II} > A_{\perp}$ and $g_{II} > g_{\perp} > 2$ which suggest that all the complexes are square planar geometry and the system is axially symmetric[26]. Furthermore, this conclusion is also supported by the fact that the unpaired electron lies predominantly in the $dx^2\text{-}y^2$ orbital, which was evident from the value of the term G = 5.3 – 4.5. It also suggests that the local tetragonal axes are aligned parallel or slightly misaligned.

The ESR parameters and d-d transition energies were used to evaluate the bonding parameters α^2, β^2 and γ^2 for the Cu(II) ion in various ligand field environments which may be regarded as measures of the covalence of the in-plane σ-bonds (α^2), in-plane π-bonds (β^2) and out-of-plane π-bonds (γ^2) respectively[27&28]. The observed values of α^2 indicate that complexes have some covalent character while the β^2 and γ^2 values indicate that there is substantial interaction in the out-of-plane π-bonding, whereas the in-plane π-bonding is completely ionic.

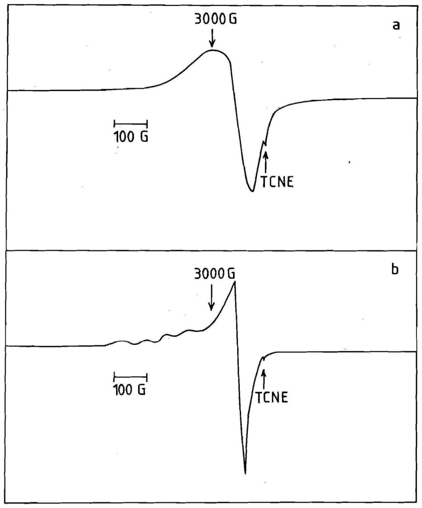


Fig. 3. The ESR spectra of [CuL^1] complex at 300 K (a) and 77 K (b) in MeCN solution

Table 4 The ESR parameters of the copper complexes in MeCN solution at 300 K and 77 K

Complex	$A_{\parallel}$	$A_{\perp}$	A_{iso}	$g_{\parallel}$	$g_{\perp}$	g_{iso}	G	α^2	β^2	γ^2
[CuL^1]	158	72	95	2.31	2.059	2.14	5.25	0.79	1.19	0.88
[CuL^2]	142	63	90	2.27	2.054	2.12	5.00	0.72	1.07	0.99
[CuL^3]	144	67	94	2.29	2.064	2.14	4.5	0.75	1.17	0.96
[CuL^4]	151	59	88	2.37	2.078	2.18	4.7	0.84	1.13	1.02

Table 5 Antimicrobial activities of ligands and their metal complexes (MIC in mg)

Compound	*Escherichia coli*	*Salmonella typhi*	*Pseudomonas aeruginosa*	*Staphylococcus aureus*	*Starptococci*	*Aspergillus niger*	*Candida albicans*
HL^1	50	50	55	50	45	60	45
[CuL^1]	45	40	40	45	40	55	40
[ZnL^1]	40	35	35	40	40	40	35
HL^2	60	70	65	50	45	55	55
[CuL^2]	55	50	50	45	40	45	45
[ZnL^2]	40	45	40	35	45	35	40
HL^3	35	35	40	35	40	55	35
[CuL^3]	30	25	30	25	30	40	25
[ZnL^3]	20	20	15	20	20	20	15
HL^4	40	40	45	40	35	50	35
[CuL^4]	35	35	30	35	30	35	30
[ZnL^4]	20	15	20	15	25	15	25

Antimicrobial Studies

The *in-vitro* biological screening effects of the investigated compounds were tested against the bacteria ((*Escherichia coli, Salmonella typhi, Staphylococcus aureus, Starptococci,* and *Pseudomonas aeruginosa)* and fungi such as *Aspergillus niger* and *Candida albicans* by disc diffusion method using nutrients agar as the medium. The minimum inhibition concentration values of the compounds against the growth microorganisms are summarized in the Table 5.

A comparative study of the ligands and their metal complexes indicate that the metal chelates exhibit higher antimicrobial activity than the ligands. Such increased activity of the metal complexes can be explained on the basis of Overtone's concept and the Tweedy chelation theory[29]. According to the Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid-soluble materials, due to which liposolubility is an important factor that controls antimicrobial activity. On chelation, the polarity of the metal ion will be reduced due to the overlap of the ligand orbital. Furthermore, it increases the delocalization of π-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms[30]. Due to the presence of more functional groups (hydroxyl groups and azomethine group), which form hydrogen bonding with proteins present in the cell walls of the organisms, resulting in interference with the normal cell process[31-33]. Comparatively, zinc complexes show higher activity than copper complexes because of their higher lipid solubility[34].

CONCLUSIONS

It is concluded that, Cu(II) and Zn(II) chelates have been prepared in ethanol using Schiff bases derived from curcuminyl-4-aminoantipyrine and aniline/substituted aniline (p-Cl, p-NO_2 and p-CH_3). Elemental analysis, magnetic susceptibility, FAB-Mass, IR, UV-Visible, NMR and ESR spectral techniques were used to confirm the structure of the chelates and ligands. All the complexes exhibit square planar geometry. The *in-vitro* biological screening effects of the investigated compounds were tested against the bacteria ((*Escherichia coli, Salmonella typhi, Staphylococcus aureus, Starptococci,* and *Pseudomonas aeruginosa)* and fungi such as *Aspergillus niger* and *Candida albicans* by disc diffusion method using nutrients agar as the medium. The metal chelates exhibited higher antimicrobial activity than free ligands. Comparatively, zinc complexes show higher activity than copper complexes.

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