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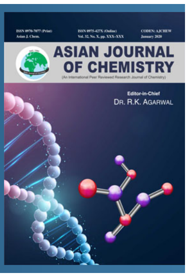

Synthesis, Spectroscopic and Antimicrobial Studies of Co(II), Cu(II) and Ni(II) Complexes of Schiff Base Derived from Citral and L-Histidine

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A new series of $[M(L)Y]X{\cdot}nH_2O$ (M = Co(II) and Cu(II), where Y = H_2O, X= NO_3^-, $n = 3$), M = Ni(II), where Y = H_2O, X = NO_3^-, $n = 2$) complexes with new Schiff base ligand (L) were synthesized by the condensation of citral and L-histidine. The ligand and its M(II) complexes were characterized based on elemental analysis, spectroscopic studies like FT-IR, electronic, ^1H NMR, ^{13}C NMR, ESR data, also accompanied with thermal studies, magnetic susceptibility and molar conductance measurements. In the light of these results, distorted square planar geometry were proposed for the M(II) complexes in which the M(II) centres are present in NNO coordination sphere. To evaluate the biological properties of the Schiff base ligand (L) and its metal complexes, they were screened for their antibacterial and antifungal activities and the results indicate that the complexes exhibit the significant activity.

Keywords: Citral, L-Histidine, Schiff base, Metal complexes, Antimicrobial activity.

INTRODUCTION

Metal-Schiff base complexes play an essential role in the field of the coordination chemistry of biological importance. Owing to the versatile behaviour of Schiff base, they flexibly coordinated to metal ions *via* donor sites to form the metal encapsulated organic sphere. In general, the chelation of organic ligands to metal ions causes drastic changes in the pharmacological activity of such compounds [1-3]. In recent years, many Schiff base transition metal complexes have been reported to possess significant and diverse biological activities such as antifungal, antibacterial, antioxidant and antimicrobial activities [4-12]. Mainly, a notable interest has emerged in transition metal complexes with Schiff base derived from amino acids, considered as excellent chelating agents since Schiff base possess amino acid moiety which has multiple donor groups (N, O and S) [13,14]. L-Histidine is one of the heterocyclic nitrogen-containing amino acid; it possesses three potential donor sites; carboxylato O atom, imidazole N and amino N atom, which make L-histidine as excellent metal ion binder [15,16].

Citral is bioactive monoterpene aldehyde, naturally imparts lemon-like aroma, to be used as lead molecule for the treatment of several diseases and ailments caused by bacteria, fungi and protozoa. Citral is used as flavours, fragrances, cosmetics, perfumery and pharmaceuticals [17-19]. A growing number of reports published on bioactivities of citral and citral rich essential oils have reflected their rapidly increasing medicinal and pharmacological significance. Since the citral is not enough explored in the field of Schiff base coordination chemistry, in the view of interest in pharmaceutical properties of citral and L-histidine; we have introduced an azomethine (-C=N-) linkage between citral and L-histidine with the concern that it may permit remarkable changes in pharmacological properties of above compounds.

To the best of our knowledge, there is no report on citral-L-histidine Schiff base and its transition metal complexes. Hence in this work, we report the synthesis and characterization of new Cu(II), Co(II) and Ni(II) complexes with Schiff base derived from citral and L-histidine. The antimicrobial properties of the ligand and its metal complexes also analyzed in the present work.

EXPERIMENTAL

All the chemicals used in the experiment were of analytical reagent grade. They included L-histidine and citral provided by Sigma-Aldrich, $Cu(NO_3)_2\cdot 3H_2O$, $Co(NO_3)_2\cdot 6H_2O$ and $Ni(NO_3)_2\cdot 6H_2O$) were from Merck, the organic solvents ethanol, diethyl ether and DMSO were of the highly purified form (A.R. grade). Deionized water was used in all the preparations. The elemental analysis were estimated using FLASH EA 1112 analyzer. IR spectra were recorded (KBR disk) on a Perkin Elmer-spectrum one FT-IR Spectrometer in the range 500-4000 cm^{-1}. The electronic absorption spectra were recorded in DMSO solvent in the range of 200-800 nm on Perkin Elmer Lambda-950 UV/VIS spectrometer. ^1H NMR and ^{13}C NMR spectra of Schiff bases were recorded on Bruker 500 MHz and 125 MHz spectrometer, respectively. Magnetic susceptibility measurements were carried out for solid complexes using Gouy balance at room temperature. Molar conductance measurements were made in DMSO solvent using digital conductivity meter (model MK-509). ESR spectrum of Cu(II) complex was recorded at Liquid Nitrogen Temperature (LNT) at solid state on JES-FA200 ESR spectrometer. TG/DTA analysis were performed on Perkin Elmer Diamond TG/DTA analyzer using heat programme RT-800 °C at 10 °C min^{-1} under N_2 atmosphere.

Synthesis of Schiff base ligand (L): A mixture of L-histidine (0.5 mol, 0.775 g) and KOH (0.25mol) dissolved in 20 mL distilled water was stirred under reflux for 30 min. To the hot homogenous mixture, citral (0.5 mol, 0.863 mL) in ethanol (10 mL) was added gradually and the entire mixture was further refluxed for 4-5 h. The opaque reddish-brown solution was obtained, which kept aside for 8 days at room temperature afforded dark reddish brown sticky nature residue. The precipitate was repeatedly washed with diethyl ether and dried. The yield of the isolated ligand was found to be 65 %. Anal. calcd. for $C_{16}H_{23}N_3O_2K$ (%): C, 58.41; H, 6.99; N, 12.69. Found (%): C, 58.50; H, 7.06; N, 12.79. FT-IR (cm^{-1}): 3399 (OH), 1637 (C=N), 1590 $\nu_{asy}(COO^-)$, 1401 $\nu_{sy}(COO^-)$, 1249 (C-O), 1380 imidazole C-N. ^1H NMR (DMSO ppm): -CH=N- (1H, S, 8.54), imidazole NH (1H, S, 11.83). ^{13}C NMR ($CDCl_3$ ppm): COO^- (179.52), -CH=N- (164.23). λ_{max} in DMSO (nm): 248, 305 and 342.

Preparation of metal(II) complexes: The complexes were prepared by adopting the *in situ* method. The aqueous solution of corresponding metal(II) nitrates (0.5 mol) were gradually added to the hot ethanolic reddish-brown solution of Schiff base in a 1:1 molar ratio. The mixture was refluxed with constant stirring giving a clear coloured solution in 30 min; refluxing was continued for 2-5 h. The resulting coloured solutions were allowed to cool in room temperature and afforded the coloured complexes. The compounds were repeatedly washed well with ethanol followed by diethyl ether and dried.

$[Co(L)H_2O]NO_3\cdot 3H_2O$ (1a): Yield: 88 %; dark brown solid. Anal. calcd. for $C_{16}H_{30}N_4O_9Co$ (%): C, 38.84; H,6.12; N, 11.58. Found (%): C, 39.92; H, 6.28; N, 11.64. FT-IR (cm^{-1}): 3415 (OH), 1617 (C=N), 1641 $\nu_{asy}(COO^-)$, 1390 $\nu_{sy}(COO^-)$, 1222 (C-O), 1353 imidazole C-N, 585 (M-N), 527 (M-O). λ_{max} in DMSO (nm): 327, 540 and 794. μ_{eff} 2.59 BM. Λ_m (ohm^{-1} cm^2 mol^{-1}): 110.

$[Cu(L)H_2O]NO_3\cdot 3H_2O$ (1b): Yield: 82 %; dark green solid. Anal. calcd. for $C_{16}H_{30}N_4O_9Cu$ (%): C, 38.51; H,6.19; N, 11.50. Found (%): C, 39.54; H, 6.22; N, 11.53. FT-IR (cm^{-1}): 3430 (OH), 1617 (C=N), 1652 $\nu_{asy}(COO^-)$, 1393 $\nu_{sy}(COO^-)$, 1232 (C-O), 1301 imidazole C-N, 561 (M-N),513 (M-O). λ_{max} in DMSO (nm): 335, 403 and, 713. μ_{eff} 1.92 BM. Λ_m (ohm^{-1} cm^2 mol^{-1}): 77.

$[Ni(L)H_2O]NO_3\cdot 2H_2O$ (1c): Yield: 89 %; yellowish-green solid. Anal. calcd. for $C_{16}H_{28}N_4O_8Ni$ (%): C,40.91; H, 5.94; N, 11.89. Found (%): C, 41.50; H, 6.09; N, 12.10. FT-IR (cm^{-1}): 3430 (OH), 1617 (C=N), 1641 $\nu_{asy}(COO^-)$, 1384 $\nu_{sy}(COO^-)$, 1216 (C-O), 1321 imidazole C-N, 561 (M-N),513 (M-O). ^1H NMR (DMSO ppm): -CH=N- (1H, S, 9.76), imidazole NH (1H, S, 11.92) λ_{max} in DMSO (nm): 329 and, 730. μ_{eff} 2.28 BM. Λ_m (ohm^{-1} cm^2 mol^{-1}): 53.

Antimicrobial activity: Agar well diffusion method was used to evaluate the antibacterial activity of the synthesized compounds. Autoclaved 15-20 mL of Mueller-Hinton agar was poured on glass petri plates and allowed to solidify. Standardized inoculum of the four investigated organisms such as Gram-positive bacteria; *Bacillus substilis, Staphylococcus aureus*, Gram-neagtive bacteria*: Escherichia coli, Klebsiella pneumoniae* were uniformly spread on the surface of these plates using sterile cotton swab. Four wells with a diameter of 8 mm (20 mm apart from one another) were punched aseptically with a sterile cork borer in each plate. Compound solution (40 μL) at desired concentration from 10 mg/mL stock was added to one well and other wells with gentamycin as positive control and compound solvent as negative control. Then, the agar plates were incubated under 37 °C for 24 h. After incubation, clear zone was observed. Inhibition of the bacterial growth was measured in mm.

Well diffusion assay antimicrobial susceptibility testing was done using the well diffusion method to detect the presence of antifungal activities of the compound samples. A sterile swab was used to distribute fungal culture (*Candida albicans*) evenly over the PDA agar medium. The plates were allowed to dry for 15 min before use in the analysis. Compound solution (40 μL) at desired concentration from 10 mg/mL stock was added to one well and other wells with clotrimazole as positive control and compound solvent as negative control. The plates were incubated at room temperature for 3 days after which they were examined for inhibition zones.

RESULTS AND DISCUSSION

Characterization of Schiff base ligand (L): The 1.1 molar condensation reaction of citral with L-histidine had led to the formation of reddish-brown Schiff base ligand. The reaction was carried out in the EtOH-water medium. The ligand was soluble in methanol, ethanol and DMSO solvents.

The FT-IR spectrum of the ligand shows the broad band in the range 3500-3080 cm^{-1} centred at 3399 cm^{-1} was due to intramolecular hydrogen bond between protonated azomethine nitrogen and carboxylate oxygen [20]. The ligand also shows bands at region 1637, 1584, 1401 and 1380 cm^{-1} were owed to azomethine ν(–C=N–), $\nu_{asy}(COO^-)$, $\nu_{sy}(COO^-)$ of carboxylate group and imidazole –C=N– stretching, respectively. The bands observed at 1496, 1461 ad 1313 cm^{-1} were probably associated with stretching of the imidazole ring. Also bands at 1146, 1059 and 774 cm^{-1} are assigned to an in-plane C–H deformation, in-plane N–H deformation of imidazole ring and C–H out of plane bend vibrations of aromatic ring, respectively [21]. The bands associated with methyl/methylene group of citral moiety are appeared at 2970, 2925 and 2854 cm^{-1}. The first two bands are assigned to ν_{as}(C–H) of stretching frequencies and the other band is owing to ν_s(C–H) stretch, respectively [22].

The electronic spectrum (Fig. 1) of Schiff base ligand shows adsorption bands at region 248, 305 and 342 nm are owing to $\pi\rightarrow\pi^*$ transition of citral moiety, $\pi\rightarrow\pi^*$ transition of hetero-aromatic moiety and $n\rightarrow\pi^*$ transition of azomethine group, respectively [23].

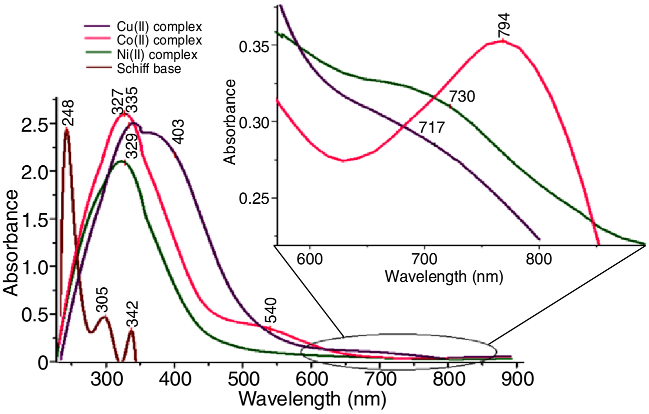


Fig. 1. Electronic spectra of Schiff base and its metal(II) complexes

The ^{1}H NMR spectrum of ligand was recorded in DMSO. The spectrum displays important downfield signal at δ 13.52 ppm is assigned to intramolecular hydrogen-bonded NH···O proton [24]. The other characteristic signals observed at δ 11.83 ppm and, δ 8.54 ppm were assigned to imidazole NH and azomethine protons, respectively. The peaks around δ 8.33, 7.39 are assigned to imidazole ring C-H protons of histidine unit. The peaks evolved at δ 5.46 and 6.68 ppm, pertaining to the -C=CH- protons of citral moiety [25]. The peaks around δ 2.89, 2.38 -2.52 ppm and at δ 1.29- 2.05 ppm were corresponds to $-CH_2-$ (histidine unit), $-CH_2-$ and $-CH_3-$ protons of citral unit, respectively..

The ^{13}C NMR spectrum of ligand was recorded in $CDCl_3$. The spectrum shows azomethine carbon and carboxylate carbon signals at δ 179.52 and δ 164.23 ppm, respectively [26]. The resonance signals observed at δ 133.32 and 136.13 ppm are owing to the carbon atoms of imidazole ring. The signals at δ 152.34 and 124.12 ppm are attributed to alkene carbon atoms of citral moiety. The –CH– (αC) and $–CH_2–$ (βC) signals of histidine moiety are observed at δ 57.66 and δ 25.30 ppm, respectively. Moreover the signals of $–CH_2–$ and $–CH_3–$ of citral appeared at δ 40.77 and 17.58- 18.06 ppm, respectively.

Characterization of metal(II) complexes: All the metal(II) complexes were obtained upon reaction between Schiff base and metal(II) ions at 1:1 molar ratio (L:M) *via in situ* method. All the metal complexes are coloured, stable at room temperature and soluble in DMSO and DMF. The elemental analysis and molar conductance data were in good agreement with the proposed stoichiometry of the complexes. The observed molar conductance of metal complexes solutions in DMSO was in consistence with the electrolytic nature (53-110 ohm^{-1} cm^2 mol^{-1}), which indicates that nitrate anion is present outside of the coordination sphere [27].

IR spectra: The mode of coordination of Schiff base to metal ions is identified by comparison of IR spectra of Schiff base ligand with those of its complexes. The relevant IR spectral data are listed in Table-1.

The presence of the broad band in all complexes at 3550-3000 cm^{-1} were owed to the ν(OH) stretch of coordinated water molecules. The broadness of the band also points the presence of hydrogen bonded water molecules and carboxylato O in their structures, which were further supported by the new peak, emerged at ~2450 cm^{-1} [28]. The sharp band appeared at 1637 cm^{-1} are assigned to ν(–C=N–) stretch of ligand, in the spectra of all complexes the band is found to be shifted to lower wave number ~1617 cm^{-1}, indicates the participation of azomethine N atom in coordination to metal ions.

The ligand spectrum exhibited the bands at 1584 and 1401 cm^{-1}, which were assigned to $\nu_{asy}(COO^-)$ and $\nu_{sy}(COO^-)$ stretching vibrations, respectively. In all the complexes, these bands were found to be shifted to higher wavenumber (1652-1641 cm^{-1}) and lower wavenumber (1384-1382 cm^{-1}), respectively. The differences between the above stretching vibrations of carboxylato group are 251-257 cm^{-1} which was higher than >200, indicated the monodentate coordination with metal(II) ions. The carboxylato C–O stretching was shifted from 1249 cm^{-1} (ligand) to lower frequencies (1253-1226 cm^{-1}) in all the complexes, which further supports the coordination of carboxylato group [29,30].

The imidazole –C=N– stretching vibration of Schiff base at 1380 cm^{-1} was found to be shifted to 1354-1326 cm^{-1} in all the complexes, indicated the coordination of imidazole N with metal ions. Also, the bands that appeared at 3127 and 1461 cm^{-1} were assigned to imidazole N–H and imidazole ring stretches of ligand which were shifted to higher wavenumbers of 3137-3135 cm^{-1} and lower wavenumber of 1440-1436 cm^{-1}, respectively for the metal complexes. This further supports the imidazole N coordination with metal(II) ions [21].

TABLE-1
IR SPECTRAL DATA (cm^{-1}) OF METAL(II) COMPLEXES WITH LIGAND (L)

Compounds	ν(OH)/ H_2O	ν(C=N)	ν_{asv} (COO^-)	ν_{sv} (COO^-)	Δν (COO^-)	ν(C-O)	Imidazole ν(N-H)	Imidazole ν(C-N)	ν(M-N)	ν(M-O)	Free NO_3^-
L	3399	1637	1590	1401	189	1249	3125	1380	–	–	–
$[Co(L)H_2O]NO_3\cdot3H_2O$	3415	1617	1641	1390	251	1222	3135	1353	585	527	1762, 1384
$[Cu(L)H_2O]NO_3\cdot3H_2O$	3430	1617	1652	1393	259	1232	3137	1326	561	513	1762, 1384
$[Ni(L)H_2O]NO_3\cdot2H_2O$	3430	1617	1641	1384	257	1216	3156	1321	559	527	1384

The assignments of proposed coordination sites (M-N & M-O) were corroborated by the appearance of medium bands at 600-550 and 527-500 cm^{-1}. The FT-IR results showed that the Schiff base ligand acted as uni-negative tridentate chelating ligand as it coordinated to metal ions through N of azomethine group, O of carboxylato group and N of the imidazole ring. The fourth position in the coordination sphere was occupied by water molecules. Along with broad band at ~ 3400 cm^{-1}, new peak evolved ~ 875 cm^{-1}, indicates the coordination of water molecule in all the complexes [31]. The observed molar conductance are in consistence with electrolytic nature of the complexes which showed that the nitrate groups were present in outer side of the coordination sphere, it is corroborated *via* new sharp peaks that appeared at 1762 and 1384 cm^{-1} [4].

Electronic spectra: The electronic spectral data are used for assigning the ligand field around the metal ions in the complexes based on the positions and number of transition peaks. The electronic spectra of Schiff base and its Co(II), Cu(II) and Ni(II) complexes were recorded in DMSO solvent in the range 200-800 nm. The assignments for the ligands and their metal complexes are given in Table-2. The absorption spectrum of the free Schiff base ligand showed absorption bands at 248, 305 and 345 nm due to $\pi\rightarrow\pi^*$ transition of citral moiety, $\pi\rightarrow\pi^*$ of hetero-aromatic moiety and $n\rightarrow\pi^*$ transition of azomethine group, respectively. In the metal complexes these separate bands are disappeared and obtained as single high intense $n\rightarrow\pi^*$ band at 327 nm (**1a**), 335 nm (**1b**) and 329 nm (**1c**). These bands demonstrate the coordination of Schiff base ligand to metal ions. Together with $n\rightarrow\pi^*$transitions the *d-d* transitions also showed by the metal complexes, except **1b** which exhibit additional LMCT transition. The **1a** exhibits two *d-d* transition at position of 540 and 794 nm are assigned to $^2B_{2g}\rightarrow{}^2A_{1g}$ and $^2B_{2g}\rightarrow{}^2E_g$ [32]. The **1b** shows the bands at 403 nm and 717 nm attributed to LMCT and $^2B_{1g}\rightarrow{}^2A_{1g}$ (*d-d*) transitions, respectively [33]. While **1c** shows *d-d* transition at position 730 nm is assigned to $^1A_{1g}\rightarrow{}^1B_{2g}$. The *d-d* transitions are strongly favoured the square planar geometry around metal(II) ions [34].

Magnetic moment: The magnetic susceptibility measurement of metal(II) complexes were carried out at 300 K. For Co(II) complex the magnetic moment value is 2.59 BM, which lie in the typical range of reported low spin square planar Co(II) complexes (2.0-2.7 BM). This value is higher than the calculated spin-only value 1.73BM, which indicates the presence of spin-orbit coupling effect. The Cu(II) complex have magnetic moment of 1.92 BM; the value is in agreement with those reported square planar Cu(II) complexes. The obtained value is slightly higher than spin only value (1.73 BM), due to the influence of spin-orbit coupling effect. The magnetic moment for Ni(II) complex is 2.28 BM and the value is too small for high-spin (S=1/2) and too large for low-spin (S=0) Ni(II) complexes. The anomalous value may arise from spin equilibrium between square planar-tetrahedral conformations. From the magnetic moment and electronic spectral data it was concluded that metal(II) complexes adopt the distorted square planar environment [32-34].

ESR spectrum of Cu(II) complex: The $[Cu(L)H_2O]NO_3\cdot 3H_2O$ (**1b**) complex was recorded in DMSO at 77 K (Fig. 2). The ESR parameters were calculated and summarized in Table-3. The orbital reduction factors and covalent parameters are summarized in Table-4. The Cu(II) complex (S = 3/2) exhibit four hyperfine splitting in low field region and one peak in high field region and absence of half field signal indicates the monomeric nature of the complex. The g tensor values can be used to derive the ground state of the complex. The observed g values $g_{\parallel}$ (2.34) > $g_{\perp}$ (2.08) > 2.00 and $A_{\parallel}$ (157) > $A_{\perp}$ (20), indicates that the complex is in square planar environment and the unpaired electron lie in the $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as the ground state. According to Massacesi *et al.*, $g_{\parallel} = 2.4$ for Cu-O bonds and 2.3 for Cu-N bonds. For the present complex, $g_{\parallel} = 2.34$, which is between 2.3-2.4 and thus in conformity with the presence of mixed Cu-O and Cu-N bonds in the chelates [35]. The g values are related to exchange interaction coupling constant (G) by the expression $G = g_{\parallel}-2.0027/g_{\perp}-2.0027$. For the present Cu(II) complex G = 4.25, which is slightly higher than 4, suggesting local tetragonal axes are slightly misaligned.

Molecular orbital coefficients α^2 (covalent in-plane σ-bonding) and β^2 (covalent in-plane π-bonding), are calculated by using the following equations:

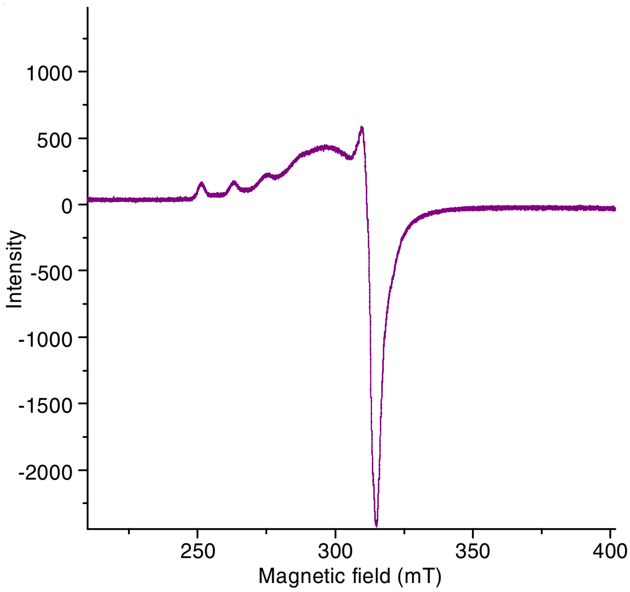


Fig. 2. EPR spectra of Cu(II) complex (**1b**)

TABLE-2
ELECTRONIC SPECTRAL ASSIGNMENTS (nm) AND MAGNETIC DATA OF M(II) COMPLEXES WITH LIGAND (L)

Compound	$\pi\rightarrow\pi^*$	$n\rightarrow\pi^*$	LMCT	*d-d*	*d-d* Band assignments	Proposed geometry	Magnetic moment (μ_{eff}) (BM)
L	248, 305	342	–	–	–	–	–
$[Co(L)H_2O]NO_3\cdot 3H_2O$	–	327	–	540, 794	$^2B_{2g}\rightarrow{}^2A_{1g},\ {}^2B_{2g}\rightarrow{}^2E_g$	Distorted square planar	2.59
$[Cu(L)H_2O]NO_3\cdot 3H_2O$	–	335	403	713	$^2B_{1g}\rightarrow{}^2A_{1g}$	Distorted square planar	1.92
$[Ni(L)H_2O]NO_3\cdot 2H_2O$	–	329	–	730	$^1A_{1g}\rightarrow{}^1B_{2g}$	Distorted square planar	2.28

TABLE-3
ESR PARAMETERS OF Cu(II) COMPLEX IN DMSO AT 77 K

Compound	$g_{\parallel}$	$g_{\perp}$	g_{iso}	$A_{\parallel}$ (G)	$A_{\perp}$ (G)	A_{iso} (G)	$g_{\parallel}/A_{\parallel}$ (cm)
$[Cu(L)H_2O]NO_3\cdot3H_2O$	2.34	2.08	2.16	157	20	65	162

$g_{iso} = (g_{\parallel} + 2g_{\perp})/3$ and $A_{iso} = (A_{\parallel} + 2A_{\perp})/3$

TABLE-4
ORBITAL REDUCTION FACTORS AND COVALENCY PARAMETERS OF Cu(II) COMPLEX

Compound	G	$K_{\parallel}^2$	$K_{\perp}^2$	K	α^2	β^2
$[Cu(L)H_2O]NO_3\cdot3H_2O$	4.2	0.71	0.67	0.32	0.85	0.84

$$\alpha^2 = (A_{\parallel}/0.034) + (g_{\parallel} - 2.0027) + 3/7\,(g_{\perp} - 2.0027) + 0.04$$

$$\beta^2 = (g_{\parallel} - 2.0027)\ E/\text{-}8\lambda\ \alpha^2$$

The calculated values for α^2 and β^2 are 0.85 and 0.84, respectively (less than unity), indicates the covalent bonding in the present complex. This is also further confirmed by orbital reduction factors. The orbital reduction factors are calculated using the following equations:

$$K_{\parallel}^2 = (g_{\parallel} - 2.0027)\ E/\text{-}8\lambda$$

$$K_{\perp}^2 = (g_{\perp} - 2.0027)\ E/\text{-}2\lambda$$

$$K^2 = K_{\parallel}^2 + K_{\perp}^2/3$$

where E is the electronic transition of ${}^2B_{1g}\rightarrow{}^2A_{1g}$, λ is spin-orbit coupling constant (-828) for the free Cu(II) ion. For the present complex, the observed order $K_{\parallel}$ (0.71) > $K_{\perp}$ (0.67) implies a greater contribution from out-of-plane π-bonding than in-plane π-bonding in metal-ligand π-bonding. K (0.46) value, which is less than unity indicates that the complex covalent character in the ligand environment [36]. The $g_{\parallel}/A_{\parallel}$ is used to detect the presence of distortion in the complex, the $g_{\parallel}/A_{\parallel}$ value is 148 cm^{-1} for the present complex, which is higher than 140 cm^{-1} (90-140 cm^{-1} for square planar), indicates that complex have moderate distortion hence distorted square planar geometry is proposed for the Cu(II) complex.

^{1}H NMR spectrum of Ni(II) complex: The ^{1}H NMR spectrum of Ni(II) complex was recorded in DMSO solution and compared with the Schiff base ligand, is in consistent with the proposed structure. The ligand exhibit a signal at δ 11.83 ppm belongs to imidazole NH proton. Upon complexation this peak was shifted to downfield region at δ 11.92 ppm, suggest the participation of one of imidazole N in coordination with Ni(II) ion. The free Schiff base shows imidazole C-H protons peaks around δ 8.33 and 7.39 ppm, which is shifted to δ 8.30 and 7.68 ppm in Ni(II) complex is a supportive evidence for coordination of imidazole-N. The important signal appeared at δ 9.76 ppm, which is found shifted from δ 8.54 ppm (ligand) indicates the coordination of azomethine nitrogen with Ni(II) ion. The peaks evolved at δ 5.46 and 5.58 ppm, pertaining to the -C=CH- protons of citral moiety of Schiff base ligand respectively. The peaks around δ 4.06, 2.32-2.51 ppm and at δ 1.57-2.12 ppm are corresponds to -CH- (histidine unit), $-CH_2-$ and $-CH_3-$ protons of citral unit, respectively.

Thermal analysis: The simultaneous TG/DTA analysis of the Co(II), Cu(II) and Ni(II) metal complexes was studied from 30 to 800 °C under a nitrogen atmosphere. The results show there is good agreement in the mass loss % between the proposed and calculated formulae.

The thermogram of the Co(II) complex exhibits multiple decomposition steps. The first step from 30-120 °C with a mass loss of 11.2 % (calcd. 11.22 %) accompanied by an endothermic peak at 80 °C on the DTA curve, is attributed to the elimination of three hydrated water molecules. The second step, from 120-234 °C with a mass loss of 3.7 % (calcd. 3.61 %) corresponds to the removal of one coordinated water molecule. For this step, a broad endothermic peak is observed at 203 °C. The third step from, 200-274 °C with a mass loss of 13.1 % (13.4 %) corresponds to removal of one nitrate molecule, which accompanied with endothermic peak in the DTA at 265 °C. The fourth step from, 270-743 °C with a mass loss of 58.8 % (calcd. 60.3 %) indicates that complete decomposition of the complex that ended with formation of CoO. In DTA, this step is accompanied by the exothermic peak at 399 °C (partial decomposition of ligand) and a broad exothermic peak at 735 °C.

$$[Co(L)H_2O]NO_3\cdot3H_2O \xrightarrow{80\,°C} [Co(L)H_2O]NO_3 \xrightarrow{203\,°C}$$
$$[Co(L)]NO_3 \xrightarrow{265\,°C} [Co(L)] \xrightarrow{735\,°C} CoO$$

The thermogram of the Cu(II) complex shows a mass loss of 11.4 % (calcd. 11.13 %) in the temperature range 30-135 °C and an endothermic DTA peak at region 125 ºC, indicates the loss of three hydrated water molecules. The second step, from 126-208 ºC with a mass loss of 15.89 % (16.32 %) corresponds to the removal of one water molecule followed by elimination of one nitrate molecule. For this step, DTA shows two crowded endothermic peaks at 162 ºC and 192 ºC. The third step, from 210-700 ºC with mass loss of 56.1 % (calcd. 58.4 %) indicates that complete decomposition of the complex that ended with formation of CuO. In DTA, this step is accompanied by the sharp exothermic peak at 408 ºC (partial decomposition of ligand) and a broad endothermic peak at 700 ºC.

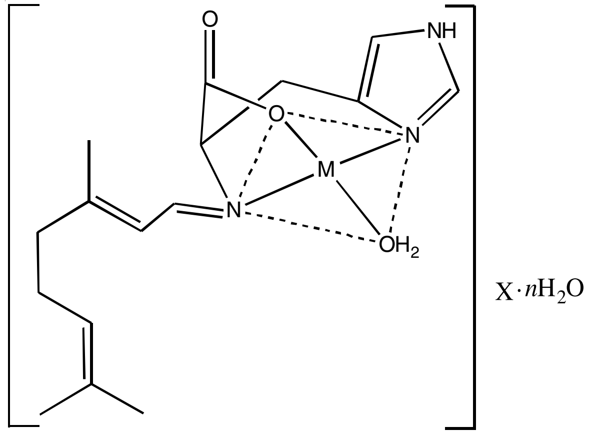
$$[Cu(L)H_2O]NO_3\cdot3H_2O \xrightarrow{125\,°C} [Cu(L)H_2O]NO_3 \xrightarrow{162\,°C}$$
$$[Cu(L)]NO_3 \xrightarrow{192\,°C} [Cu(L)] \xrightarrow{700\,°C} CuO + \text{Organic residues}$$

On the TG curve of Ni(II) complex, the first step shows the mass loss was 7.4 % (calcd. 7.79 %) at the temperature between 30-152 ºC indicating the removal of two hydrated water molecules. A broad endothermic peak at 85 °C on DTA curve corresponds to the dehydration step. The second step shows the mass loss 16.8 % (calcd. 17.1 %) In the range 135-274 ºC and the broad endothermic peak in DTA at 250 ºC indicates the removal of one coordinated water molecule and one nitrate anion from the complex. The anhydrous complex shows mass loss of 60.6% (calcd. 62%) implies the complete decomposition of the complex that ended with formation of

NiO. In DTA, this step is accompanied by a broad endothermic peak at 390 ºC (partial decomposition of ligand) and a broad exothermic peak at 735 ºC.

$$[Ni(L)H_2O]NO_3{\cdot}2H_2O \xrightarrow{85\,°C} [Ni(L)H_2O]NO_3$$
$$\xrightarrow{250\,°C} [Ni(L)] \xrightarrow{735\,°C} NiO$$

On the basis of characterization data, a tentative geometry of Cu(II), Co(II) and Ni(II) complexes is proposed in Fig. 3.



M = Co(II) & Cu(II); X= NO_3 , *n* =3

M = Ni(II); X= NO_3 , *n* =2

Fig. 3. Proposed structure of Schiff base metal(II) complexes

Antimicrobial activity: The antimicrobial screening of the Schiff base and its Cu(II), Ni(II) and Co(II) complexes (Table-5) were tested against two Gram-positive bacteria, namely, *Staphylococcus aureus* and *Bacillus subtilis and* two Gram-negative bacteria, namely, *Klebsiella pneumonia* and *Escherichia coli* and one fungus, namely, *Candida albicans,* using agar well diffusion method. The compounds were tested using the concentration of 0.4 mg mL^{-1} in DMSO solvent and compared with known antibiotics: gentamycin and clotrimazole. The result shows that the metal complexes are more active than the free ligand and starting compound citral. The citral and Schiff base ligand shows no antimicrobial activity against all tested organisms. The citral shows antimicrobial activity against *E. coli* and *C. albicans*, whereas the Schiff base ligand exhibit activity against *S. aureus* and *E. coli* strains. The Cu(II) complex **(1b)** shows the hyper inhibition activity against *B. subtilis, S. aureus* and *E. coli* and moderate inhibition activity against *K. pneumonia* and *C. albicans* strains. The Ni(II) complex (**1c**) shows moderate activity against all screened organisms except *K. pneumonia.* The Co(II) complex (**1a**) exhibits higher activity against *C. albicans* and moderate activity against *B. subtilis* and *E. coli*. Generally, the higher biological activity of metal complexes than that of the ligand (L) can be explained based on Overtone's concept and Tweedy's chelation theory. On chelation, metal ion polarity is reduced to a greater extent due to the overlapping of the ligand orbital and partial sharing of positive charge of the metal ion with donor groups. Further, the delocalization of the π-electrons is increased over the whole chelate sphere and enhances the lipophilicity of the complex. The increase in chelation rings around central metal ion increases the antibacterial activity. Based on spectral assignment, the synthesized complexes are chelated *via* N,N and O donors of Schiff base ligand. It is assumed that distorted four coordinated metal(II) complexes with tridentate ligand highly influence the lipophilic character and favour its penetration through the lipid layers of the bacterial membrane and also block the synthesis of the proteins thereby disturbing the respiration process of the cell which further restricts the growth of the organisms. The variation in the effectiveness of the compounds against different organisms depends on the variation in ribosomes of microbial cells and impermeability of the cells of the microbes [16]. The bioactivity of the citral, ligand and its complexes is found to be in the following order:

Cu(II) > Ni(II) > Co(II) > L > citral

Conclusion

In the present work, a new Schiff base NNO donor ligand (L) and its Co(II), Cu(II) and Ni(II) complexes were synthesized. The formation of the compounds has been confirmed by the analytical data, FT-IR, electronic, ^{1}H NMR, ^{13}C NMR, ESR spectral data, thermal studies, magnetic susceptibility and molar conductance data. The analytical and spectroscopic data reveal that the Schiff base acts as uninegative tridentate ligand that binds with metal ions through azomethine nitrogen, imidazole nitrogen and carboxylato oxygen. Also these coordination sites lead to form distortion from regular square planar geometry of the complexes. Molar conductance data indicates thal all the complexes are electrolytic in nature. The *in vitro* antimicrobial activity of ligand and its complexes reveals that the metal complexes show higher antimicrobial activity than the free ligand. It has been assumed that NNO coordinated distorted square planar metal(II) geometry of the complexes is one of the reason for higher antimicrobial activity of metal complexes.

TABLE-5
ANTIMICROBIAL ACTIVITY OF SCHIFF BASE AND ITS METAL(II) COMPLEXES

Compound	Zone of inhibition (mm)				
	Bacteria				Fungi
	Gram-positive		Gram-negative		
	B. subtilis	*S. aureus*	*E. coli*	*K. pneumonia*	*C. albicans*
Citral	–	–	10	–	11
L	–	10	12	–	–
1a	15	–	13	–	26
1b	22	20	25	13	15
1c	12	12	15	-	16
Standard	30	20	29	24	28

Bacteria (standard) = Gentamycin; Fungal (standard) = Clotrimazole

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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