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SYNTHESIS AND SPECTRAL CHARACTERIZATION OF SCHIFF BASE TRANSITION METAL COMPLEXES, DNA CLEAVAGE AND ANTIBACTERIAL ACTIVITY STUDIES

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ABSTRACT

A new string of transitional metal complexes of Cu(II), Zn(II) and Ni(II) have been synthesized from the Schiff base ligand derived from 2,4-dihydroxybenzaldehyde and p-aminobenzoic acid. Structural studies were obtained by their elemental analysis, magnetic susceptibility, molar conductance, IR, UV-Visible, ^{1} H-NMR and ESR spectral studies. The data shows that the complexes have a composition of ML type. The UV-Visible, magnetic susceptibility and ESR spectral data of the complexes proposed square planar geometry about the metal ion except for zinc complex. The redox behavior of the complexes was studied by cyclic voltammetry. An antimicrobial screening test shows good results in the presence of metal ion than in the ligand.

Keywords: Schiff base, 2,4-dihyroxybenzaldehyde, p-aminobenzoic acid, Antimicrobial activity, DNA cleavage

INTRODUCTION

The pasture of Schiff base complexes was the first budding version of the broad multiplicity of potential structures for the ligands depending upon the aldehyde and amines. Transition metal ions are vital to countless biological systems in natural history[1]. Metal ions are concerned in a large no of chemical reactions by the good feature of their capability to harmonize to simple or polymeric donor groups. The compounds have much curiosity because they habitually crop up in natural products and are organically important[2]. They have many applications both in the qualitative and quantitative analysis[3,4]. A tiny work has been carried out on the complexing performance of Schiff bases derived from 2,4-dihydroxybenzaldehyde and P-Aminobenzoic acid with a variety of metal ions. The antibacterial behavior exposes that the metal complexes can be dynamic in opposition to the elected bacterial strains. Virtually, all of the compounds may ensemble glowing for drug rescue playing field past inspection of their toxicology deeds in a meticulous manner and show admirable catalytic commotion in an assortment of chemical reactions. DNA cleavage studies of metal complexes showed further high-flying action in the existence of H_2O_2 compared to that in the deficiency of H_2O_2. The ability of transition metal complexes to cleave nucleic acids efficiently with a high level of selectivity for a sit or sequence offers many applications for the manipulation of genes and development of novel therapeutics.

EXPERIMENTAL

All the chemicals 2,4-dihydroxy benzaldehyde, p-aminobenzoic acid and metal salts [acetate of Cu(II), Ni(II) and Zn(II)] used in the modern work were of analytical grade. The solvents like ethanol, methanol, DMSO, DMF etc were purified by ordinary methods.

Physical Measurements

UV-Visible absorption spectra study was measured on Hewlett Packard 8425A spectrometer. Elemental analysis was performed on an elemental vario EL 111 Carlo Erba 1108 analyzer. Molar conductance measurement was conducted using 10^{-3} M solutions of the complexes in DMF on Elico – CM82 Conductivity Bridge at room temperature. Magnetic susceptibility measurement was carried out on a

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Gouy balance at room temperature. FT-IR spectra study was recorded in KBr medium on a Perkin Elmer RXI spectrophotometer in wave number region 4000-400 cm^{-1}

Synthesis of Schiff Base Ligands

The preliminary material was prepared according to the literature survey [5]. An ethanolic solution of newly prepared 2,4-dihyroxybenzaldehyde was mixed with gradually stirring ethanolic solution of p-aminobenzoic acid. The mixture was refluxed at 70^0C for 2 hr. On cooling yellow colored precipitate was alienated out, filtered, washed with ethanol and dried in vacuum[6].The Schiff base ligand is shown in figure 1. Yield 70% Elemental analysis:$C_{14}H_{11}NO_4$, Calculated C-65.36%, H-4.28%, N-5.44% ; Found C-65.33%, H-4.25%, N-5.42% ν (C=N),1619 cm^{-1}, ν (C=C),1542 cm^{-1}, UV Vis (Λ_{max}) , DMF $\pi \rightarrow \pi^*$ - 274 nm, n→ π^* - 315 nm.

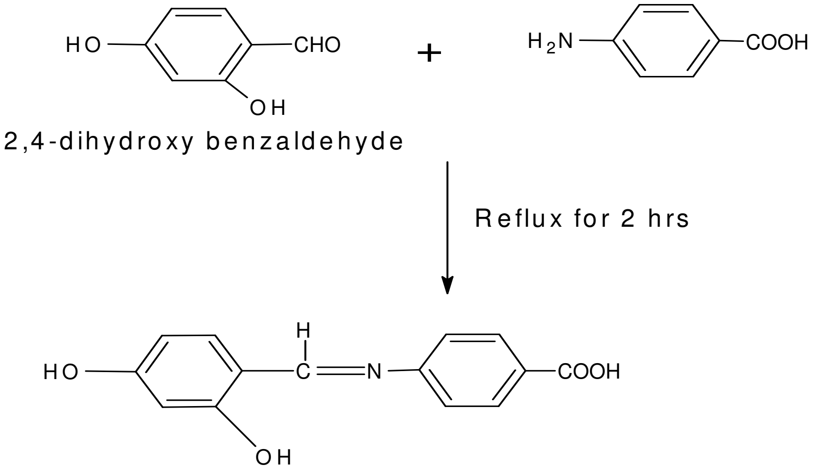

Fig.-1: Synthesis of Schiff base Ligand (L)

Synthesis of Complexes

The various complexes were prepared by addition of 5mM of $Cu(CH_3COO)_2H_2O$, $Zn(CH_3COO)_2H_2O$ and $Ni(CH_3COO)_2H_2O$ which were dissolved in about 20-30 ml of deionized distilled water, were dissolved in about 20-30 ml of water, into a hot methanolic solution of 5mM of the ligand (1:1) molar ratio. The color of the complexes changes in a few minutes. The mixture was then refluxed for 2 hrs. The precipitated solids were filtered and washed with methanol and followed by drying at 50^0C overnight[7]. The Schiff base complexes were shown in Fig.-2.

Cu(II) Complex

Yield 64% Elemental Analysis: $C_{28}H_{20}N_2O_8Cu$ Caculated C-58.33%, H-3.47%, N- 4.86 %, Cu 11.11 % ; Found C-58.30%, H-3.45%, N-4.85 % Cu 11.12 % , Λ_m– 15.25 ($ohm^{-1}cm^2mol^{-1}$) , ν (C=N),1594 cm^{-1}, ν (M-N)-456 cm^{-1}, ν (M-O),514 cm^{-1} 'UV Vis (Λ_{max}) , DMF: d → d 614 nm

Zn(II) Complex

Yield 60% Elemental Analysis: $C_{28}H_{20}N_2O_8Zn$ Caculated C-58.23%, H-3.46%, N-4.85 %, Zn=11.25% ; Found C-58.25%, H-3.44%, N-4.85 % , Zn=11.26% , Λ_m– 13.56 ($ohm^{-1}cm^2mol^{-1}$) , ν (C=N),1598 cm^{-1}, ν (M-N)-478 cm^{-1}, ν (M-O),512 cm^{-1} 'UV Vis (Λ_{max}) , DMF: d → d not observed

Ni(II) Complex

Yield 68% Elemental Analysis: $C_{28}H_{20}N_2O_8Ni$ Caculated C-58.94%, H-3.50%, N-4.91 %, Ni=10.17% ; Found C-58.95%, H-3.55%, N-4.92 %, Ni=10.19% , Λ_m– 14.5 ($ohm^{-1}cm^2mol^{-1}$) , ν (C=N),1590 cm^{-1}, ν (M-N)-412 cm^{-1}, ν (M-O),513 cm^{-1} 'UV Vis (Λ_{max}) , DMF: d → d 513,658 nm

RESULTS AND DISCUSSION

The Schiff base complexes have been synthesized by condensation of Schiff base ligand with a metal salt solution. All the complexes were crystalline in character gloomy colored solid, stable at room temperature and soluble in DMF or DMSO. The ligand can be confirmed by ^1H – NMR. All the complexes gave agreeable elemental analysis outcome with the anticipated structure of the complexes. The creation and their geometry were further confirmed by IR, UV-Visible, magnetic, EPR spectral studies. The ligand and their metal complexes were also screened for antibacterial activity against bacteria species.

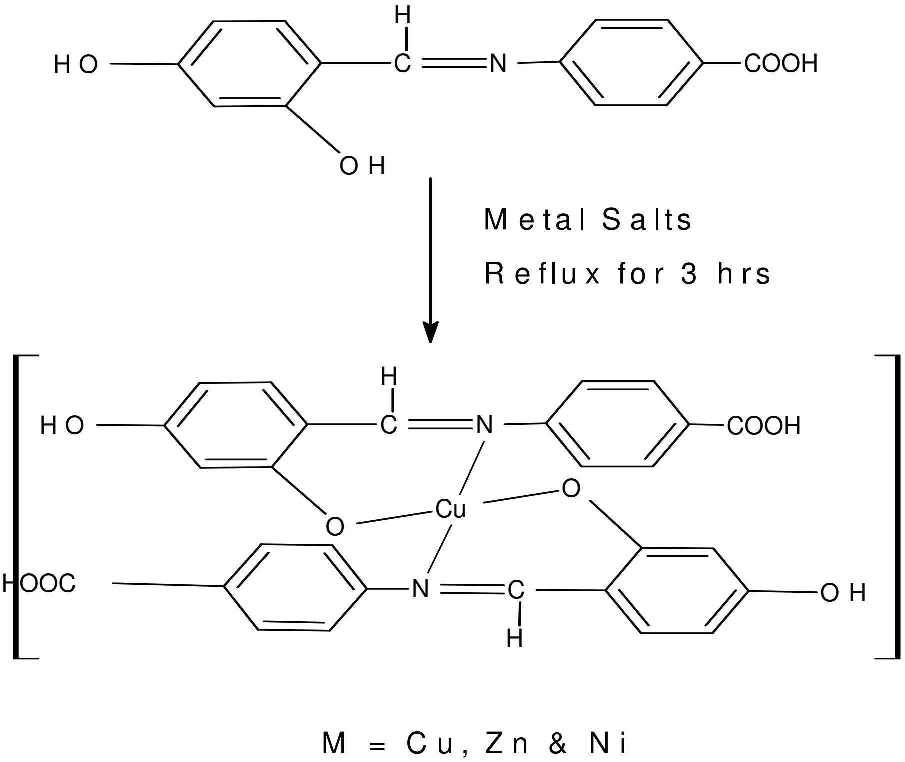

Fig.-2: Synthesis of Schiff base Complex derived from L

^{1}H-NMR Spectra of Schiff Base Ligand

^1H-NMR spectra of the compound were carried out in d6 – DMSO at room temperature using TMS as an internal standard. The Schiff base shows peaks at 7.0 and 7.1 ppm which are attributable to the aromatic protons, peak at 13.6 ppm which is attributable to the phenolic OH proton, while free azomethine proton was observed in the range of 8.51 ppm. The development of azomethine group in Schiff base was established by ^1H-NMR spectrum as shown in Fig.-3.

Electronic Absorption Spectra

The electronic absorption spectra of the Schiff bases, Cu(II) , Ni(II) and Zn(II) complexes were recorded at 300 k. The absorption region, assigned and the proposed geometry of the complexes are given in the Table-1**.** These values are comparable with that of the reported complexes[8-11]. Based resting on the exceeding factors, the planned structures of the Schiff base complexes are given in the Fig.- 4 and 5.

Magnetic Properties

The magnetic moments of the solid state complexes were measured at room temperature. The measured magnetic moments of mononuclear Cu(II) complex 1.70 BM. Magnetic susceptibility measurement showed that this complex is paramagnetic , which corresponds to the + 2 oxidation state of Cu(II) complex. This indicates that Cu(II) complex [12 -13] exhibits square planar geometry.The Ni(II) complex has diamagnetic property using Gouy balance. The observed zero magnetic moment also confirms the square planar environment for the Ni(II) complex, it conventionality with the verity that all the known square planar complex of Ni(II) complex is diamagnetic[12]. The Zn(II) complex are diamagnetic having a d^{10} system which is tetrahedral as per anticipated

EPR Spectral Studies

The EPR spectra study was recorded at room temperature in DMF solution. The Cu(II)Complex provides one broad isotopic signal the free electron g-value (2.0023) pragmatic g-value is 2.1936.The lengthening of spectra most likely is due to spin relaxation[14]. In square planar complexes, the unpaired electron lies in the d x^2-y^2 orbital giving $g_{\parallel} > g_{\perp} > 2$. From the experimental value, the complex of square planar geometry is shown in Fig.- 6.

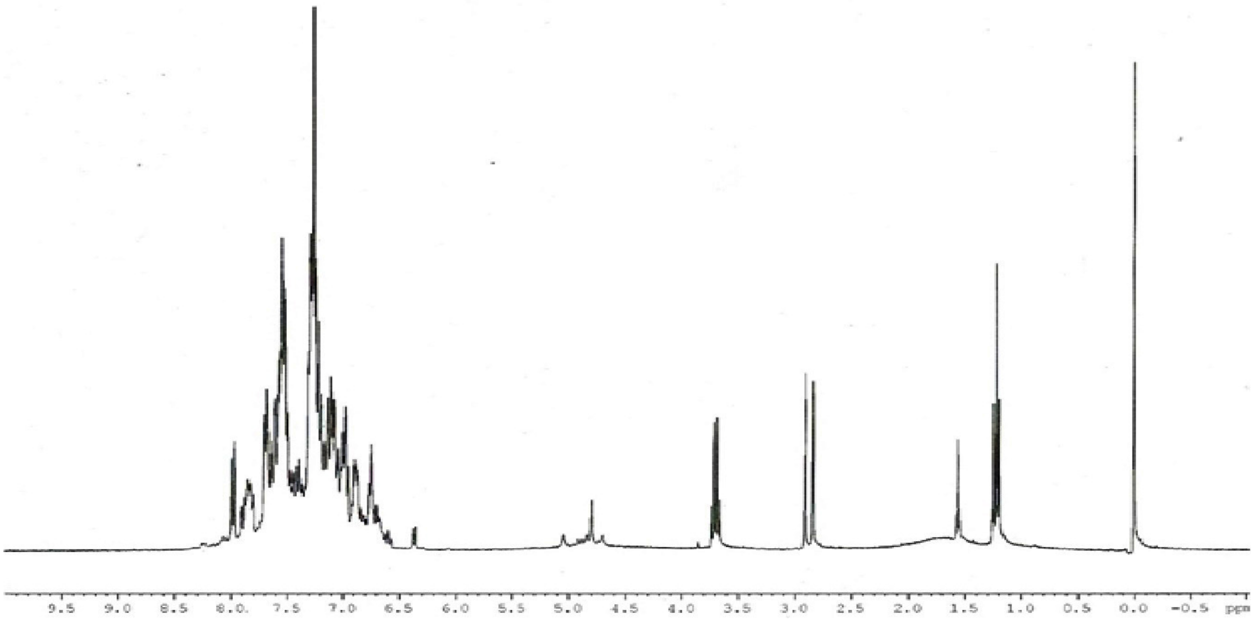

Fig.-3: H^1 –NMR spectrum of the ligand

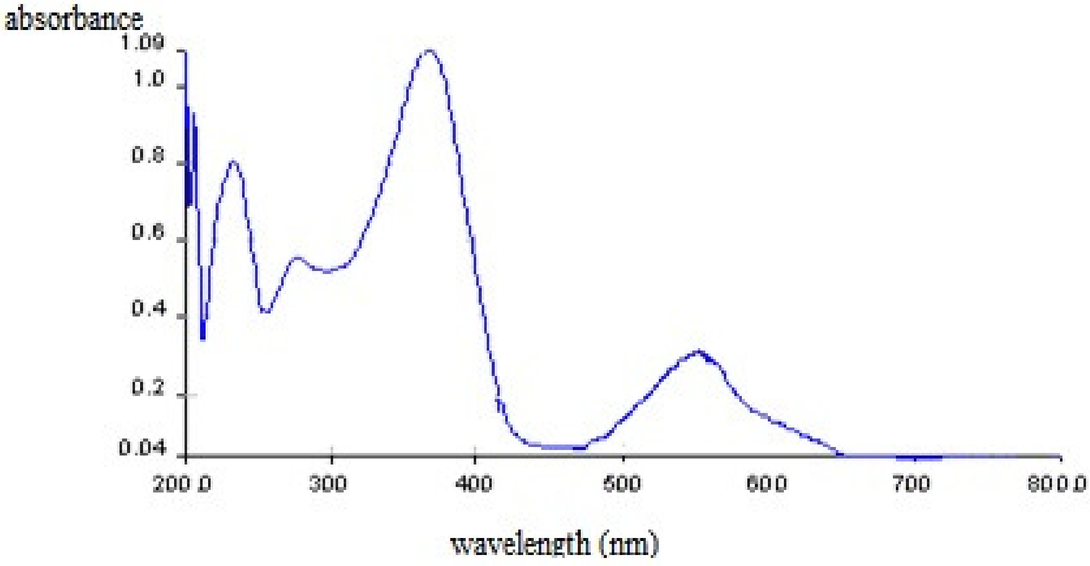

Fig.-4: Electronic spectrum of Cu(L)

Table-1: Electronic absorption spectral data of ligand and its metal complexes.

Compound	Complexes	Solvent	Absorption	Band Assignment	Geometry
L	$C_{14}H_{11}NO_4$	EtOH	274 315 415	$\pi\rightarrow\pi^*$ - $n\rightarrow\pi^*$ L→M	-
Cu(L)	$C_{28}H_{20}N_2O_8Cu$	DMF	256 310 413 625	$\pi\rightarrow\pi^*$ - $n\rightarrow\pi^*$ L→M $^2B_{1g}\rightarrow{}^2A_{1g}$	Square planar
Ni(L)	$C_{28}H_{20}N_2O_8Ni$	DMF	287 348 469 513,658	$\pi\rightarrow\pi^*$ - $n\rightarrow\pi^*$ L→M $^1A_{1g}\rightarrow{}^1A_{2g}$ $,{}^1A_{1g}\rightarrow{}^1B_{1g}$	Square planar

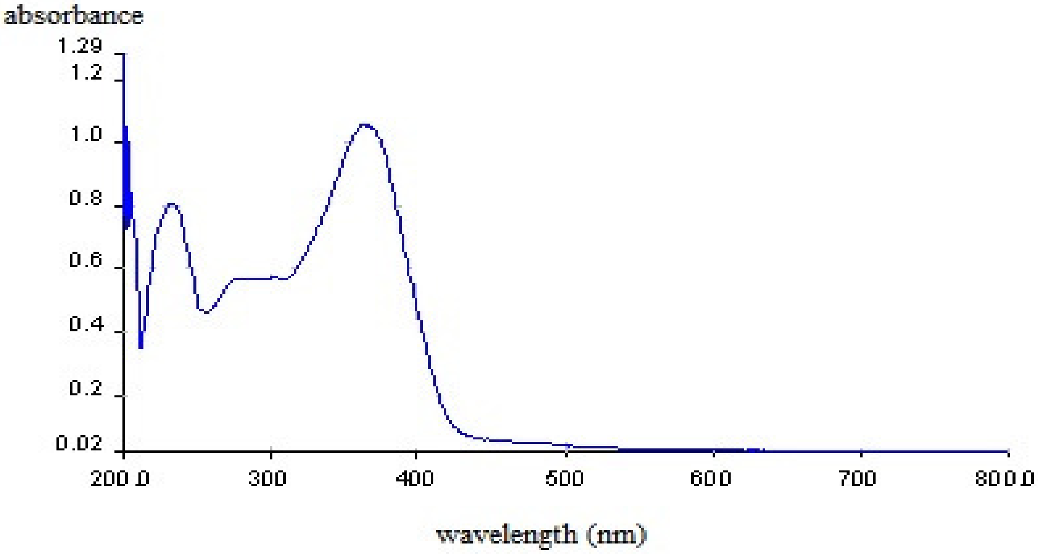

Fig.-5: Electronic spectrum of Ni(L)

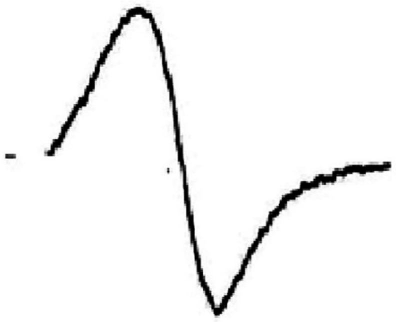

Fig.-6: EPR Spectra of Cu(II) Schiff Base Metal Complex

Cyclic Voltametry

Cyclic voltammogram of the Cu(II), Ni (II) complexes was recorded in aqueous solution with $NaClO_4$ as the sustaining electrolyte. The voltammogram of the complex is shown in Fig.-7. The cyclic voltammogram of the above complex showed two quasi – redox complex, shown in the Table-2. The electrochemical properties of the Cu(II) and Ni(II) complex exposed the quasi-reversible one electron transfer redox process.

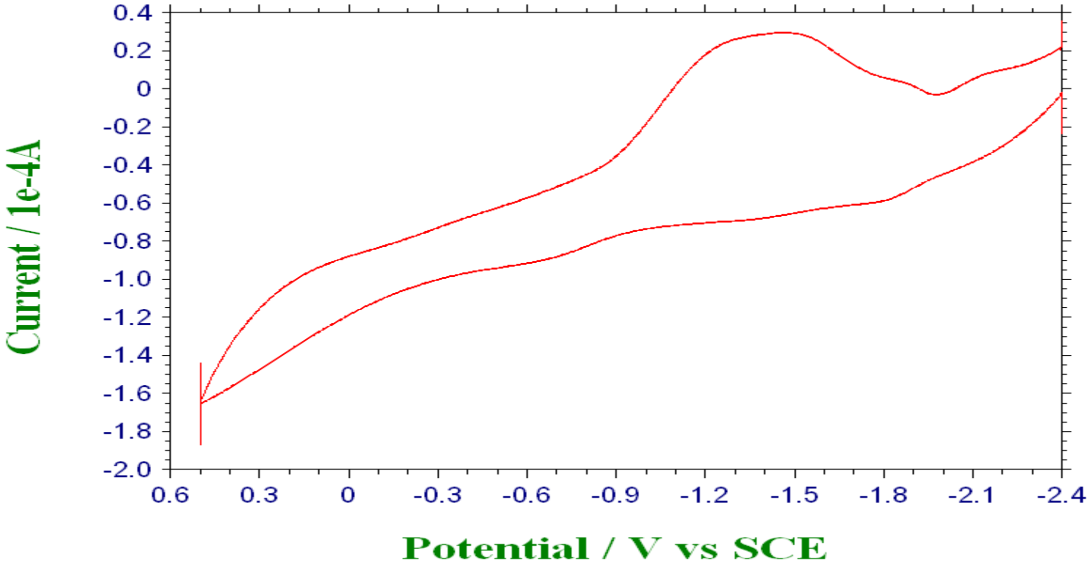

Fig.-7: Cyclic voltammogram of the Cu(L)

Table-2: Ep_a, Ep_c, ΔEp and $E_{1/2}$ data of the compounds

Complex	Ep_a (V)	Ep_c (V)	ΔEp (V)	$E_{1/2}$(V)
Cu(II) complex	0.24	0.12	0.12	0.18
	-1.3	-1.8	- 0.5	-1.55
Ni(II) complex	0.45	0.23	0.22	0.34
	-1.32	-1.84	-0.52	-1.58

Thermo Gravimetric Analysis

The energetic TGA with the percentage mass loss at dissimilar steps has been recorded. The thermal decay of the Cu(II) complex with molecular formula [$CuC_{28}H_{20}N_2O_8$] proceeded with only one main degradation step is shown in Fig.-8. The first step took place within the temperature range 180 -652°C with an expected mass loss of 43.72% [calculated mass loss = 44.61%], which is practically accounted for the loss of aromatic ligand group and an amine group. In the temperature range 300 -600°C, the mass loss was in advancement. The result of the thermal analysis showed good concord with the theoretical formula recommended from the elemental analysis[15-16].

DNA Cleavage Studies

The cleavage effectiveness of the complexes to that of the control was due to their capable DNA-binding ability. The metal complex was intelligent to convert super coiled DNA (Form- I) into open circular DNA (Form –II).The general oxidative mechanism proposed report of DNA cleavage by hydroxyl radicals via, abstraction of a hydrogen atom from sugar units and forecast the release of precise residue arising from transformed sugars, depending on the location from which the hydrogen atom is detached[17]. The cleavage was repressed by the free radical scavengers implying that hydroxyl radicals or peroxy derivatives restrained the cleavage reaction. The reaction was modulated by a metallo complex bound hydroxyl radical or peroxo species generated from the co-reactant H_2O_2.In the present study, the CT – DNA gel electrophoresis experiment was conducted at 35°C by the synthesized complex in the occurrence of H_2O_2 as an oxidant. As can be seen from the results in figure 9, at very low concentration, Nickel complex exhibits nucleus movement in the presence of H_2O_2. Control experiments using DNA alone do not show any major cleavage of CT –DNA even no longer disclosure time. From the observed results, it is calculated, that the nickel complex cleaves DNA as compared to control DNA. Further, the presence of a smear in the gel diagram indicates the presence of radical cleavage[18].

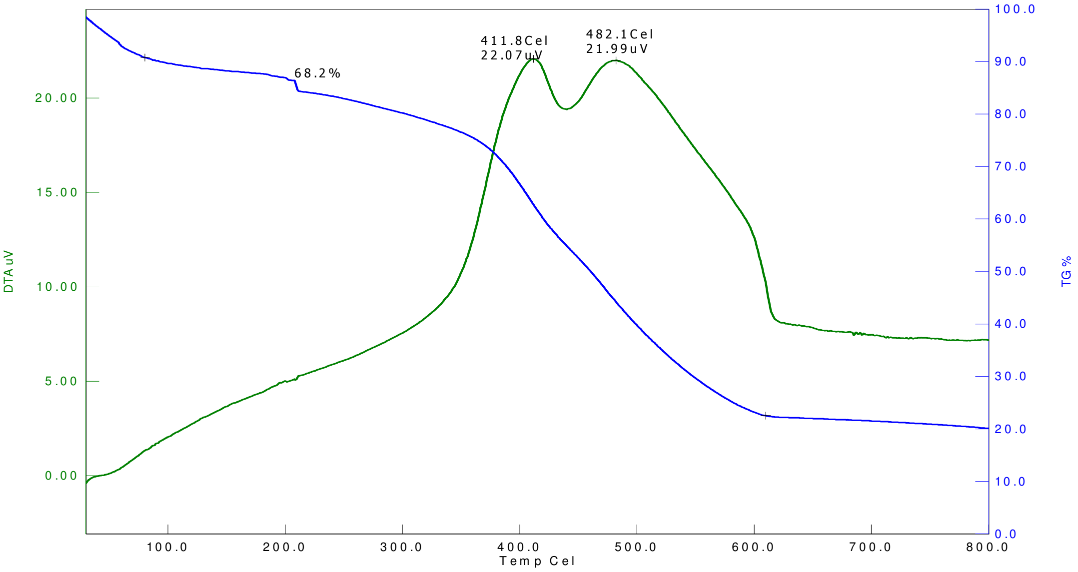

Fig.-8: Thermal Analysis of Cu(L)

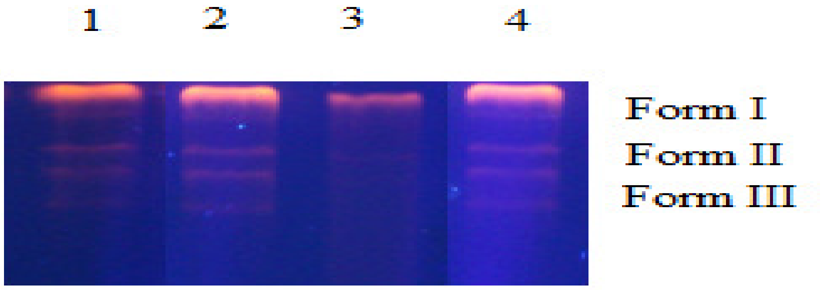

Fig.-9: DNA Cleavage studies of Ni(L) Schiff base metal complexes.
Lane 1 - DNA alone, Lane 2 - DNA + Ni(II) complex
Lane 3 - Ni (II) complex + H_2O_2 , Lane 4 - DNA + Ni(II) complex + H_2O_2

Antimicrobial Assay

Antimicrobial activity of the ligand and its complexes have been carried out against staphtylococcus, Bacillus sp, E.coli and pseudomonas by well – diffusion method using DMF as solvent as shown in Table-3.The cram of MIC values of the Schiff base and its complexes designate that the metal complexes showed the evidence of higher antibacterial activity than that of the free ligands. This was most likely due to the superior lipophilic nature of the complexes such as enlarged activity of the metal chelates can be explained on the basis of overtones concept and chelation theory. According to overtone's concept of cell permeability the lipid membrane that ambiance the cell favored the passage of only lipid soluble material due to which liposolubility is an important reason which controls the antimicrobial activity. On chelation, the polarity of the metal ion will be condensed to a better extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal ion with donor groups. Further, it increased the delocalization of π – electrons over the whole chelate ring and enhances the lipophilicity of the complex.

The increased lipophilicity enhanced the incursion of the complexes into lipid membrane[17] and blocked the metal binding sites on enzymes of microorganisms. Schiff base compounds have been shown to be hopeful leads for the intend of more proficient antimicrobial agents.

Table-3: Antibacterial activity of the Schiff base metal complexes

Compounds	E.Coli (mm)	Bacillus sp (mm)	Pseudomonas (mm)	Staphylococcus (mm)
L^6	5	3	6	5
$Cu(L^6)$	17	16	19	18
$Zn(L^6)$	13	12	13	14
$Ni(L^6)$	10	9	8	12

CONCLUSION

The monodentate Schiff base ligands have been prepared and were engaged to synthesize a novel sequence of Cu (II) and Ni (II) complexes. The spectral results propose the existence of square planar geometry for Cu (II) and Ni (II) complexes. The molar conductance measurements of the complexes showed their non – electrolytic nature. Further, these complexes were screened for antimicrobial activity and the results suggest that mixed ligand complexes have advanced antibacterial activity than the free ligand. Schiff bases are very imperative in medicinal and pharmaceutical fields. Gel electrophoresis experiment suggests that all the transition metal complexes have activity than the control CT – DNA.

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