

Exploration of new Mononuclear Schiff Base Cu (II), Ni (II) and Co (II) Complexes using Physicochemical methods

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Abstract: Reaction of 2-hydroxy-naphthalene-1-carbaldehyde, furfurylamine and M(II) salts in ethanol solution gave mononuclear Schiff base complexes, which was characterized by various spectroscopic methods. Upon complex formation, the ligand behaves as a dibasic hexadentate species with the involvement of the nitrogen and oxygen atoms of furfurylamine, azomethine and phenolic oxygen in coordination for all complexes. These studies revealed octahedral geometries for Co(II), Ni(II), and Cu(II) complexes of general formulae ML where $M = Co(II), Ni(II), \text{ and } Cu(II)$ and $L = 1-[(Furan-2-ylmethylimino)-methyl]-naphthalen-2-ol$. The conductivity data for all the complexes are consistent with one expected for non electrolyte. The stereochemistry of the complexes has been proposed on the basis of electronic data. The magnetic and EPR studies indicates the proposed structure for the synthesized complexes. The DNA cleavage capabilities of the complexes was investigated by agarose gel electrophoresis. The results suggest that mononuclear Schiff base complexes cleave pUC18 DNA. In order to evaluate the biological activity, the Schiff bases and their new metal complexes have been analysed for their antibacterial activity against bacterial species like- *Bacillus subtilis*, *Staphylococcus aureus* (as Gram-positive bacteria) and *Klebsilla pneumonia* and *Escherichia coli* (as Gram-negative bacteria).
Keywords: Mononuclear complexes, pUC18DNA, Antibacterial activity.

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I. Introduction

The development of some new biologically active mononuclear Schiff base metal complexes with the same ligating environments has undergone an inspiring growth and significant attention in recent years to study the inorganics of these metal centers for small molecule activation in biological process. The relative nature of the metal centers and the ligand environment are key issues that resolve their physical and chemical behavior of the complexes. Schiff base complexes derived from heterocyclic compounds have found to be enlarged interest in the context of bioinorganic chemistry [1-2]. Not only they have played a influential role in the development of modern coordination chemistry, but they can also a key point in the development of inorganic chemistry [3]. Heterocyclic compounds from 2-hydroxy-naphthalene-1-carbaldehyde, furfurylamine and related molecules are good ligands due to the presence of one or more ring nitrogen and oxygen atoms with a localized pair of electrons. The application potential has led to the pattern of series of novel Schiff base compounds with a wide range of reactivity and stability, physical, chemical and biological properties [4]. The synthesis and spectral characterizations of mononuclear metal complexes are of recent interest. The present work deals with the synthesis and characterization of 1-[(Furan-2-ylmethylimino)-methyl]-naphthalen-2-ol derived from 2-hydroxy-naphthalene-1-carbaldehyde, furfurylamine and their mononuclear Cu^{2+}, Co^{2+} and Ni^{2+} complexes.

II. Experimental

C, H and N analyses were carried out using a Perkin-Elmer 2400-II elemental analyzer. FT-IR data were recorded as KBr disc using Thermo Nicolet, Avatar 370 model spectrometer in the range 4000-400 cm^{-1} . UV-Vis spectra were obtained in DMF on a Perkin-Elmer Lambda 40(UV-Vis) spectrometer in the range 200-800 nm. Molar conductances of the complexes in DMF were measured using an Elico model conductivity meter. Magnetic susceptibility measurements were approved out by employing the Gouy method at room temperature. NMR signals were obtained from Bruker Avance III, 400MHz model spectrometer. EPR spectra of compounds were analysed on an E-112 ESR Spectrometer with X band microwave frequency (9.5 GHz).

Synthesis of 1-[(Furan-2-ylmethylimino)-methyl]-naphthalen-2-ol

To an ethanolic solution of 2-hydroxy-naphthalene-1-carbaldehyde (1mmol), ethanolic solution of furfurylamine (1 mmol) was added. The mixture was stirred until complete dissolution. After the addition of the equimolar amount of 2-hydroxy-naphthalene-1-carbaldehyde and furfurylamine, the mixture was stirred for 3 hrs at room temperature and a dark solution was formed [5]. After evaporating the solution, a dark yellow product was formed.

Synthesize of Mononuclear Schiff base metal complexes

A mixture of synthesized 1-[(Furan-2-ylmethylimino)-methyl]-naphthalen-2-ol (2 mmol) was added to ethanolic solution of solid metal acetate salt (1 mmol). The reaction mixture was stirred for 3 hrs at room temperature [6]. The precipitate was filtered, washed with diethyl ether and the collected solid was air dried overnight and then dried, whereupon dark color precipitate was formed. The structure of complexes was deep-rooted by spectroscopic techniques.

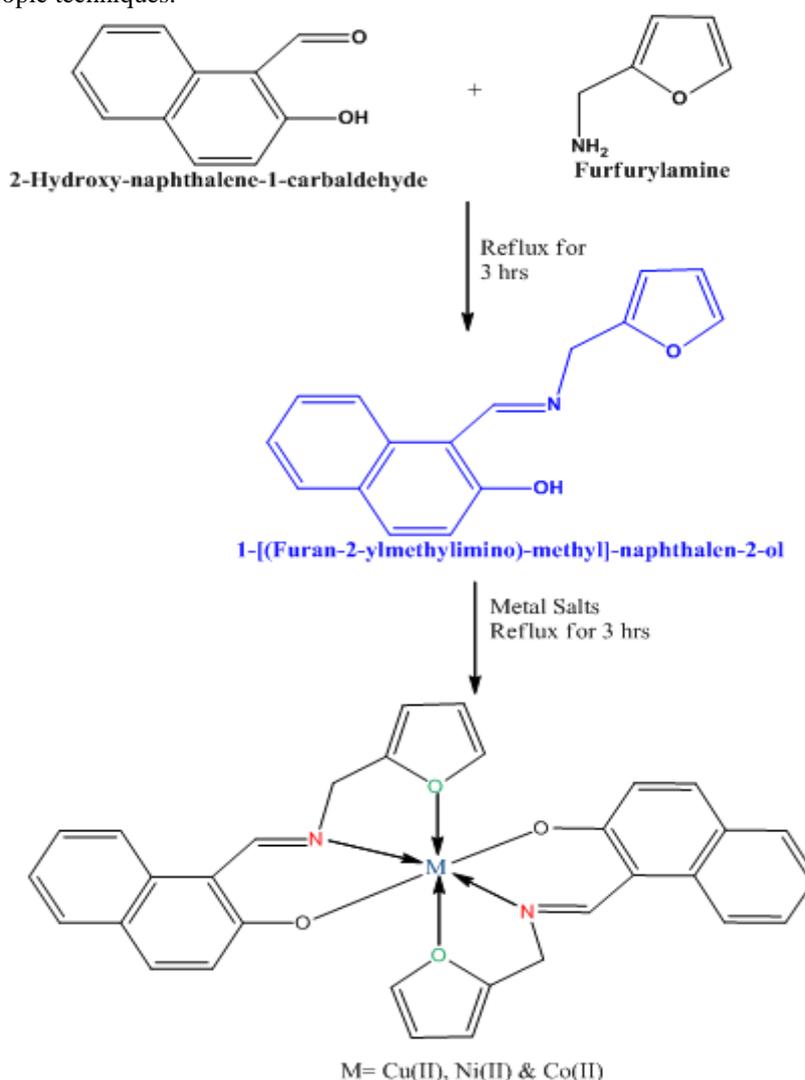


Fig. 1: Synthesis pathway for Schiff Base ligand and its Mononuclear Schiff base metal complexes

Antibacterial assay

The standard disc diffusion method was followed to find the antibacterial activity of the synthesized compounds against the organism *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis* and *Klebsilla pneumonia* [7]. The tested compounds were dissolved in DMF (Which have no inhibition activity). A disc of Whatmann no.4 filter paper having the diameter 8.00 mm were soaked in the solution of compounds in DMF. Uniform size filter paper disks were impregnated by equal volume from the specific concentration of dissolved tested compounds and carefully placed on incubated agar surface. After incubation for 36 hrs at 27 °C in the case of bacteria, inhibition of the organism which evidenced by clear zone surround each disk was measured and used to calculate mean of inhibition zones.

DNA cleavage experiments

For gel electrophoresis experiments, supercoiled pUC18 DNA was treated with the title complexes in Tris buffer (50 μ M H₂O₂ in Tris-HCl buffer pH 7.2), and the solution was irradiated at room temperature with a UV lamp (365 nm, 10 W). After being incubated at 37 °C for 2 hrs, electrophoresis was carried out at 50 V for 2 h in Tris-acetic acid- EDTA buffer. Electrophoresis was carried out and bands were visualised by UV light and photographed to establish the extent of DNA cleavage from the intensities of the bands [8]

III. Results And Discussion

Table 1: Analytical data of the Schiff base ligand and its mononuclear metal complexes

Compounds	M.Wt	Colour	M.Pt	Molar conductivity $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Elemental analysis			
					C	H	N	M
L (C ₁₆ H ₁₃ NO ₂)	251.28	Yellow	130	--	76.48 (76.40)	5.21 (5.17)	5.57 (5.57)	-
CuL (C ₃₂ H ₂₄ N ₂ O ₄ Cu)	564.09	Dark Green	260	7.4	68.07 (68.03)	4.25 (4.22)	4.96 (4.94)	11.16
CoL (C ₃₂ H ₂₄ N ₂ O ₄ Co)	559.48	Brown	220	5.8	68.63 (68.61)	4.28 (4.25)	5.00 (4.99)	10.54
NiL (C ₃₂ H ₂₄ N ₂ O ₄ Ni)	559.24	Brown	272	8.5	68.66 (68.62)	4.29 (4.26)	5.00 (4.98)	10.37

IR spectra

The IR spectrum of the ligand (L) shows a $\nu(\text{C}=\text{N})$ peak at 1638.67 cm^{-1} , and the absence of a $\nu(\text{C}=\text{O})$ peak around 1700 cm^{-1} (Table 2). These observations confirm the condensation of 2-hydroxy-naphthalene-1-carbaldehyde, furfurylamine. The IR spectra of the complexes show $\nu(\text{C}=\text{N})$ bands at 1602.35– 1612.10 cm^{-1} and is found that the $\nu(\text{C}=\text{N})$ bands in the complexes are shifted to lower energy regions compared to that in the free ligand (L). This phenomenon appears to be due to the coordination of azomethine nitrogen to the metal ion [9]. The ν OH band of the ligand is at 3439.15 cm^{-1} and its absence in the complexes is due to the involvement of the phenol O in bonding to the metal ions. Further support for this coordination were indicated by the appearance of new bands 563.22-581.03 and 445.35-490.59 cm^{-1} in the infrared of the complexes are assigned to M-O and M-N stretching vibration, respectively. The above discussion reveals that the metal ions form coordination complexes through carbonyl oxygen and azomethine nitrogen atoms.

Table 2: Infrared spectroscopic data of the Schiff base ligand and its mononuclear metal complexes

Compounds	$\nu(\text{O-H})$ (cm^{-1})	$\nu(\text{C}=\text{N})$ (cm^{-1})	$\nu(\text{C-C})$ (cm^{-1})	$\nu(\text{C}=\text{C})$ (cm^{-1})	$\nu(\text{M-O})$ (cm^{-1})	$\nu(\text{M-N})$ (cm^{-1})
C ₁₆ H ₁₃ NO ₂	3439.15	1638.67	1268.30	1591.27	--	--
C ₃₂ H ₂₄ N ₂ O ₄ Cu	--	1612.10	1318.50	1510.47	557.50	490.59
C ₃₂ H ₂₄ N ₂ O ₄ Co	--	1605.11	1302.11	1555.20	581.03	458.21
C ₃₂ H ₂₄ N ₂ O ₄ Ni	--	1602.35	1290.23	1580.62	563.22	445.35

Electronic spectra and Magnetic Moment

The electronic spectra of the complexes in DMF solution and the spectrum of Schiff base ligand, L exhibits band at 285 nm, 340 nm attributable to $\pi-\pi^*$ transitions of aromatic benzene ring and imino group and $n-\pi^*$ transitions of imino group [10]. In the complexes these bands are shifted to longer wavelengths due to outcome of coordination when binding with metal, thus confirming the formation of Schiff base metal complexes. C₃₂H₂₄N₂O₄Cu complex gave only one band due to ${}^2\text{E}_g \rightarrow {}^2\text{T}_2g$ transition at 645 nm and charge transfer transition was observed in the range of 445 nm. This electronic spectral data conclude the suggested octahedral geometry for the C₃₂H₂₄N₂O₄Cu complex. The magnetic moment for Cu(II) complex is 1.57 B.M. this clearly shows that there is no major spin interactions [11]. These bands are shifted when compared to the ligand, indicating the involvement of imine and oxygen nitrogen in coordination with copper atom. The octahedral geometry for the dark coloured complex of C₃₂H₂₄N₂O₄Co as confirmed by magnetic moment 4.82 B.M the observation of two bands in the visible region. The Ni(II) complex shows bands at 560, 675 nm respectively corresponds to ${}^6\text{A}_1g \rightarrow {}^4\text{E}_g(4\text{D})$, ${}^6\text{A}_1g \rightarrow {}^4\text{T}_2g(4\text{G})$ transitions which are compatible to an octahedral geometry around manganese(II) ion [12].

ESR Studies

The ESR spectrum of metal Cu(II) complex provides information about the geometry and nature of the ligating sites of the Schiff base and the metal. The X-band ESR spectrum of the Schiff base copper complex recorded at 77 K shows two different g -values, indicating the magnetic anisotropy in the complex. In octahedral complex, the unpaired electron is in the $d_{x^2-y^2}$ orbital. In the present copper complex, the observed g values are $g_3(2.256) > g_2(2.052) > g_1(2.002)$, which suggest that this complex has a distorted octahedral geometry [13] (Fig. 2).

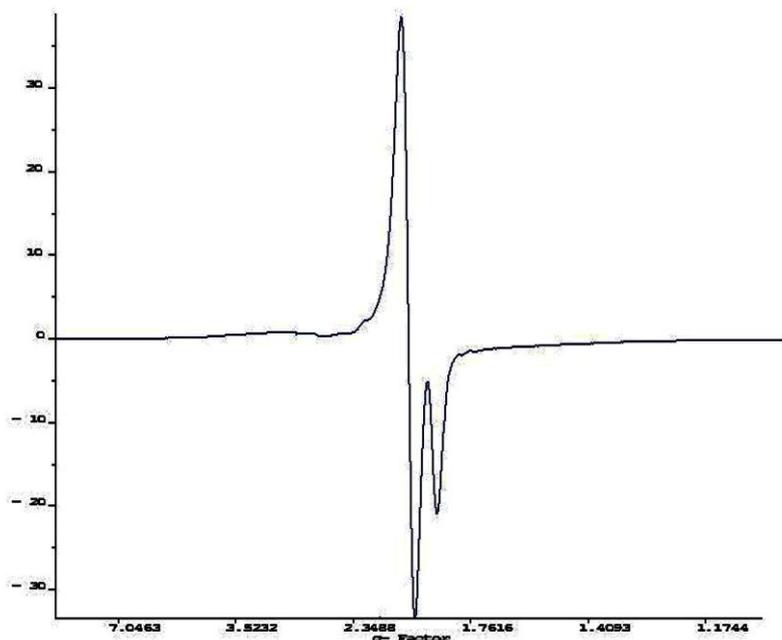


Fig. 2: ESR Spectrum of $C_{32}H_{24}N_2O_4Cu$ complex

¹H NMR spectra

The ¹H NMR Schiff base was recorded in $CDCl_3$ at room temperature. Three different type of protons were identified i) due to phenolic –OH protons around 10.21 ppm [14], ii) due to azomethine proton in the Schiff base appears at 8.562 ppm was observed and iii) signals in the region 6.66–7.73 ppm due to aromatic protons. All these observations support the infrared conclusions (Fig. 3).

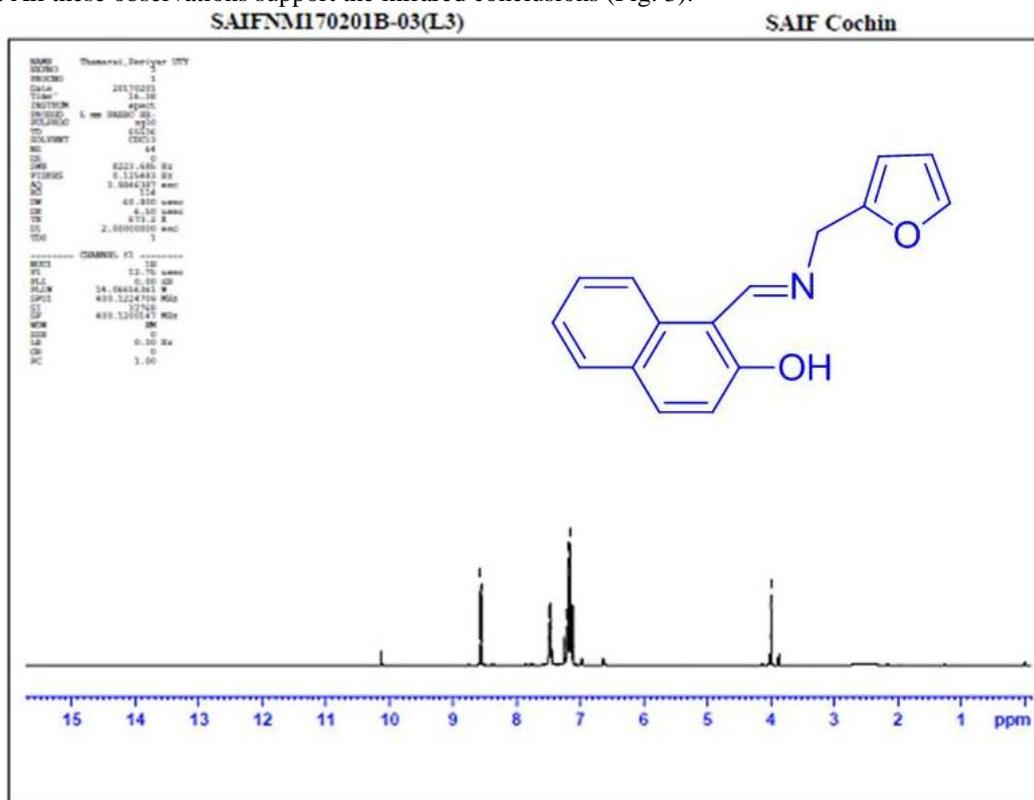


Fig. 3: ¹H-NMR Spectrum of Schiff base ligand

Powder XRD

Powder X-ray diffraction pattern of Schiff base metal complexes (Cu(II), Co(II) and Ni(II)) are carried out in the range of $2\theta = 10-80^\circ$ using XPERT-PRO diffractometer in Cu anode material [K-Alpha1 (\AA)1.54060]. The powder X-ray diffraction analysis of the metal complexes, exhibit sharp crystalline peaks indicating their crystalline nature. (Fig. 4) The crystallite size (dXRD) of the complexes was calculated using Scherer's formula [15]. The calculated average grain size values for Cu(II), Co(II) and Ni(II) are 1.53, 1.56 and 28.33 nm support that the nanocrystalline nature of metal complexes.

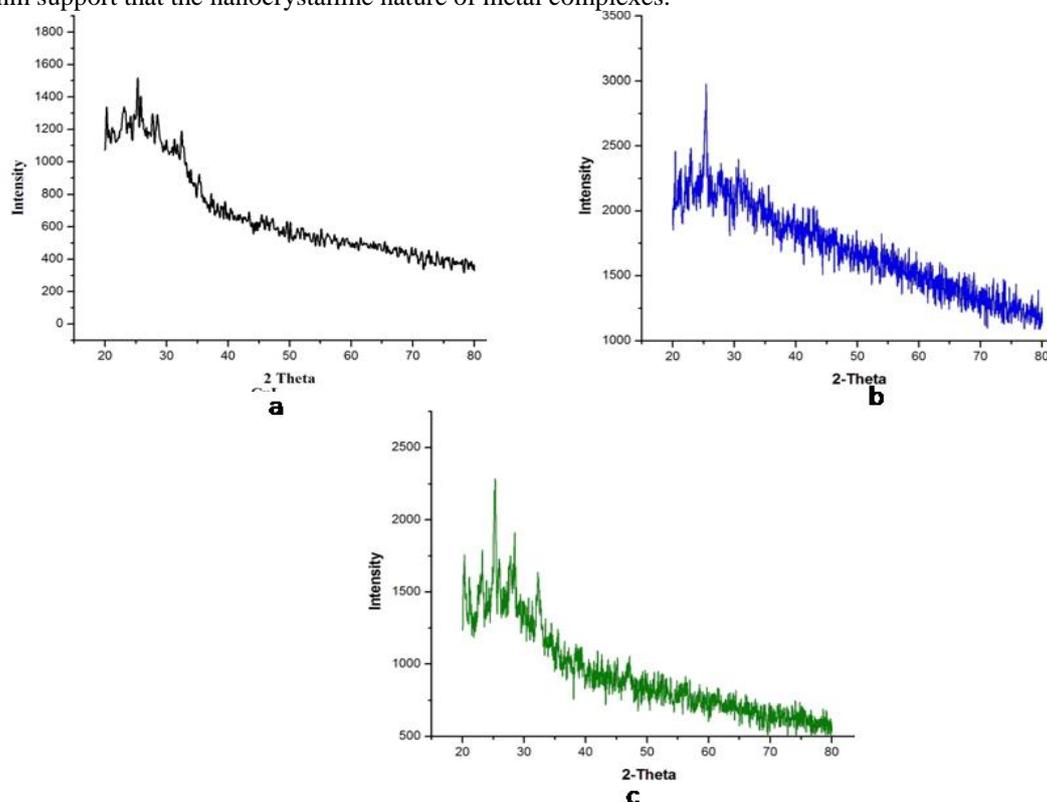


Fig. 4: P-XRD for Schiff base metal complexes (a-Cu(II); b-Co(II); C-Ni(II))

Antibacterial screening

The antibacterial screenings of the free ligand and the complexes were tested for their effect on certain bacteria. Current studies reveal that higher electronegativity and large atomic radius decreases the effective positive charges on the metal complex molecules and it results to higher antimicrobial activity [16]. From Fig.5-8, the zone of inhibition area shows to be much larger for metal chelates than that for the ligand but lesser than standard. Such increased activity of the metal chelates can be explained on the basis of chelation theory [17]. On chelation, the polarity of the metal ion will be reduced to a great extent due to the overlap of the ligand orbital. Further, it increases the delocalization of p-electrons over the whole chelate ring and enhances the lipophilicity of the complexes [18]. This increased lipophilicity leads to breakdown of the permeability barrier of the cell and thus retards the normal cell processes.

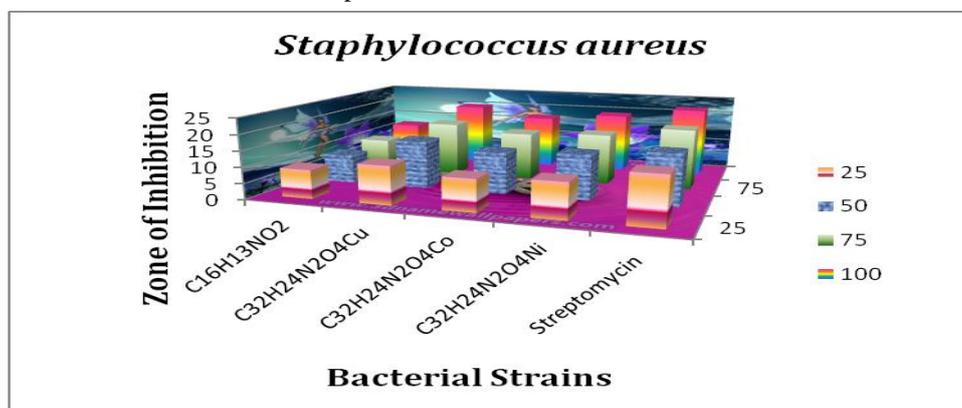


Fig. 5: Antibacterial activity of Schiff base ligand and its mononuclear Schiff base metal complexes against *Staphylococcus aureus*

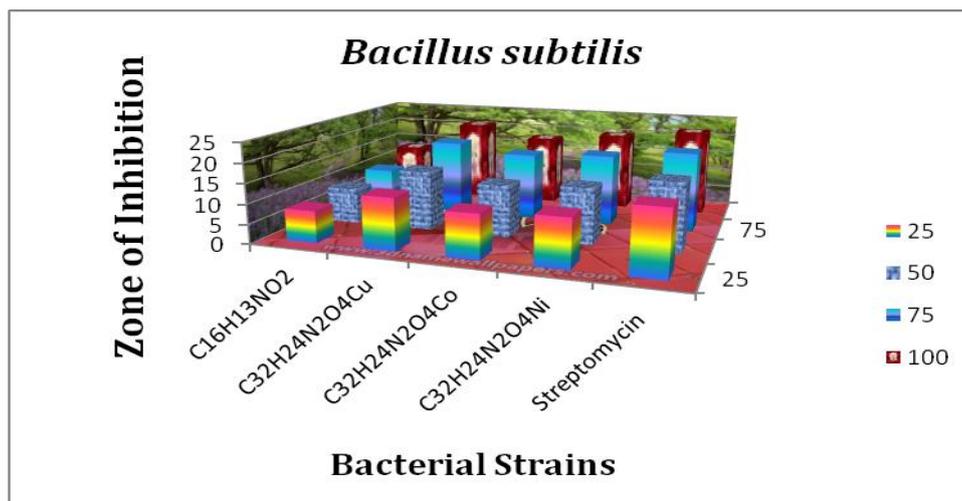


Fig. 6: Antibacterial activity of Schiff base ligand and its mononuclear Schiff base metal complexes against *Bacillus subtilis*

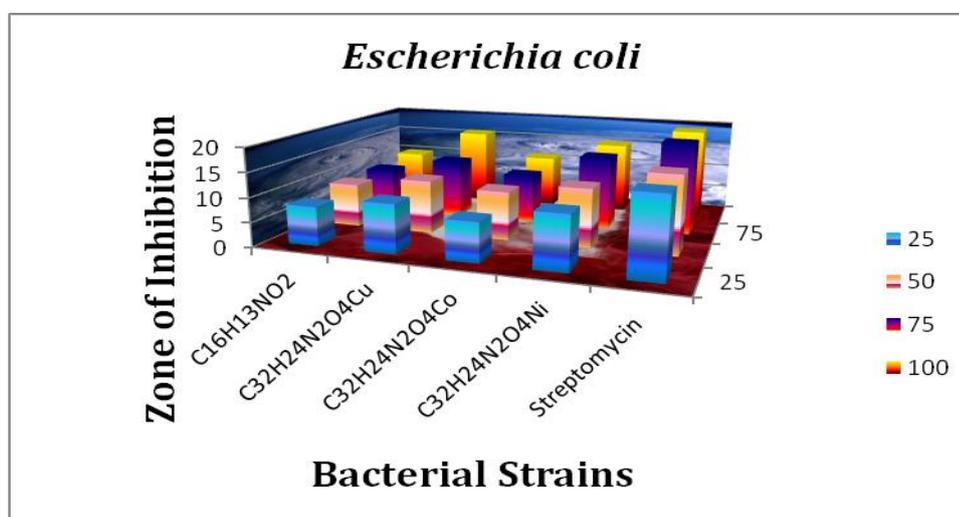


Figure 7: Antibacterial activity of Schiff base ligand and its mononuclear Schiff base metal complexes against *Escherichia coli*

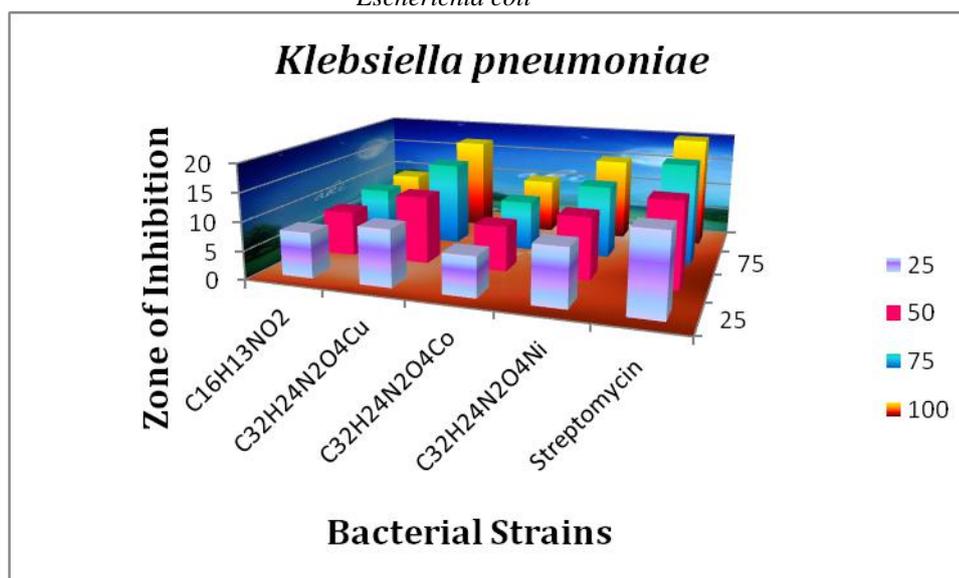


Fig. 8: Antibacterial activity of Schiff base ligand and its mononuclear Schiff base metal complexes against *Klebsiella pneumoniae*

DNA cleavage activity studies

Deoxyribonucleic acid (DNA) is the target molecule for most of the anticancer and antiviral therapies. Gel electrophoresis works on the migration of DNA under the influence of electric potential. The Co(II), Ni(II), and Cu(II) complexes were studied for their DNA cleavage activity by agarose gel electrophoresis method against pUC18DNA and the gel picture showing DNA cleavage in Fig. 9.

From figure it is evident that copper complexes cleave DNA more effectively in the presence of oxidant which may be due to hydroxyl radical (OH^\cdot) reaction with DNA. This is consistent with the increased production of hydroxyl radicals by cuprous ions similar to the well known Fenton reaction. The different DNA-cleavage efficiency of the complexes was due to the different binding affinity of the metal complexes to DNA, which has been observed in other cases [19]. From these results, we infer that the Co(II), Ni(II), and Cu(II) complexes act as a potent nuclease agents.

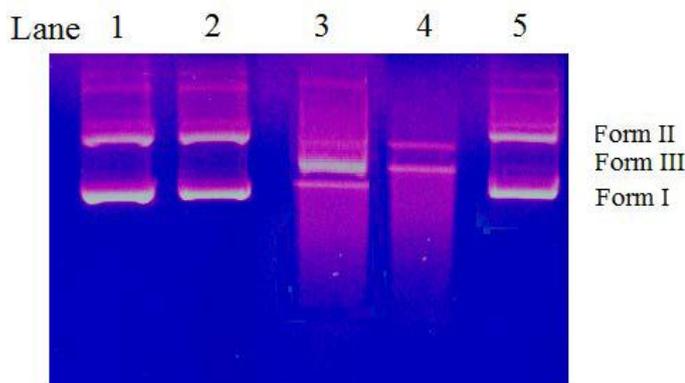


Fig. 9: Changes in the agarose gel electrophoretic pattern of pUC18DNA induced by H_2O_2 and metal complexes. Lane 1-DNA alone; Lane 2- DNA alone + H_2O_2 ; Lane 3-DNA + $\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_4\text{Cu}$ + H_2O_2 ; Lane 4-DNA + $\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_4\text{Co}$ + H_2O_2 ; Lane5-DNA + $\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_4\text{Ni}$.

IV. Conclusion

Here, we have explored the synthesis and coordination chemistry of some mononuclear complexes derived from 1-[(Furan-2-ylmethylimino)-methyl]-naphthalen-2-ol. The ligand behaves as a dibasic hexadentate species upon complexation with the involvement of phenolic oxygen and the nitrogen atoms of azomethine group in coordination for all the complexes. The newly synthesized Schiff base and its metal complexes have been confirmed by the analytical data, IR, UV-Visible, ^1H NMR, ESR spectral data, molar conductance and magnetic moment, studies. P-XRD data's shown that the metal complexes are nanocrystalline in nature. The antibacterial activity results shows that all complexes have been found to be more potent than its ligand due to the process of chelation dominantly affects the overall biological behavior of the complexes. The DNA cleavage studies revealed that the metal complexes showed good efficiency towards DNA cleavage. Based on the analytical and spectral studies, we propose octahedral geometry to all the complexes.

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