

MONOMETALLIC COMPLEXES OF 4-METHOXY-*N*² THIOPHEN-2-YL METHYLENE-BENZENE-1, 2-DIAMINE- 2-VINYL-FURAN AS A POTENTIALLY HEXADENTATE LIGAND: SYNTHESIS, SPECTRAL AND ANTIMICROBIAL PROPERTIES

P. Maheswaran ¹, E. Akila ², M. Usharani ², and R. Rajavel ^{2*}

¹ Professor, Science and Humanities, PGP College of Engineering
and Technology, Namakkal.

² Department of Chemistry, Periyar University, Salem-636 011, Tamil Nadu, India.

*Corresponding author. Mobile: +91 9865094324; Fax: +91 04272345124

ABSTRACT

Cu(II), Ni(II), Co(II) and Mn(II) complexes with newly synthesized heterocyclic Schiff base ligands derived from 2- thiophenecarboxaldehyde, 4-methoxyphenylenediamine, furfuraldehyde and 2, 2' bipyridyl. The binding manner of the ligand to the metal, composition and geometry of the metal complexes were examined by various physicochemical methods like elemental analysis, conductivity measurements, magnetic moments, IR, electronic spectral, ¹H-NMR, CV and ESR studies. The molar conductance data reveal that the chelates are electrolytes. UV–Vis spectra, ESR and magnetic moments have suggested distorted octahedral stereochemistry for Cu(II), Ni(II), Co(II) and Mn(II) complexes. The pUC18 DNA cleavage study was monitored by gel electrophoresis method. From this study, it was found that the Schiff base metal complex cleaves pUC18 DNA in presence of the oxidant H₂O₂. The Schiff base ligand and their mononuclear metal complexes were also evaluated for their antibacterial activity and was found to be energetic and inhibits the bacterial growth of *Bacillus subtilis*, *Staphylococcus aureus* (as Gram-positive bacteria) and *Klebsilla pneumonia* and *Escherichia coli* (as Gram-negative bacteria).

Keywords: 4-methoxyphenylenediamine, Gram-positive bacteria, pUC18 DNA and octahedral.

1. INTRODUCTION

The designing and synthesis of a new ligand was perhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity due to electron donor, electron acceptor properties, structural, functional groups and the position of the ligand in the coordination sphere. This may be the factor for different studies [1, 2]. Schiff base complexes derived from heterocyclic compounds have found to be augmented interest in the context of bioinorganic chemistry [3-5]. Not only they have played a seminal role in the development of modern coordination chemistry, but they can also a key point in the development of inorganic biochemistry [6]. Heterocyclic compounds such as 2-thiophenecarboxaldehyde, furfuraldehyde and related molecules are good ligands due to the presence of one or more heteroatoms atoms with a localized pair of electrons. The application potential has led to the formation of series of novel Schiff base compounds with a wide range of reactivity and stability, physical, chemical and biological properties. Though anionic Schiff base ligands have been exploited for complexation, those with neutral Schiff base ligands have not been adequately studied.

In continuation of our series of investigations, we attempted to widen the scope of derivatization by providing more flexibility through Schiff base formation with 2-thiophenecarboxaldehyde, 4-methoxyphenylenediamine, furfuraldehyde and 2, 2' bipyridyl and in conclusion complexation with metal ions to form potentially active mononuclear Schiff base complexes. The Schiff base structure affords a greater choice and flexibility, and complexation with a metal ion adds to the stability and versatility of the compounds.

2. EXPERIMENTAL

2.1. *Materials and physical measurements*

All the chemicals used were chemically pure and AR grade. Solvents were purified and dried according to standard procedures. Metal salts were purchased from Merck.

2- thiophenecarboxaldehyde, 4-methoxyphenylenediamine, furfuraldehyde and 2, 2' bipyridyl were obtained from Aldrich. Ethanol, DMSO and DMF were used as solvents purchased from Merck and Loba Chemie Pvt. Ltd. The purity of metal complexes was tested by TLC.

The elemental analysis were carried out with a Carlo- Erba 1106-model 240 Perkin Elmer analyzer. The solution conductivity measurements were performed to establish the charge type of the complexes. The complexes were dissolved in DMF and molar conductivities of 10^{-3}M of their solutions at 29°C were measured with ELICO CM 185 conductivity Bridge. Electronic absorption spectra in the UV-Visible range were recorded on Perkin Elmer Lambda -25 between 200-800 nm by using DMF as the solvent. Magnetic susceptibility measurements were carried out by employing the Gouy method at room temperature. Infrared spectra were recorded on the Perkin Elmer FT-IR- 8300 model spectrometer using KBr disc and Nujol mull techniques in the range of $4000\text{-}400\text{ cm}^{-1}$. EPR spectra of compounds were recorded on an E-112 ESR Spectrometer with X-band microwave frequency (9.5 GHz).

2.2. Synthesis of Schiff base

The Schiff base ligand was synthesized by adding 2- thiophenecarboxaldehyde (1 mM) in 20 ml of ethanol, 4-methoxyphenylenediamine (1 mM) in 20 ml of ethanol and furfuraldehyde (1 mM) in 20 ml ethanol. The mixture was refluxed for 2-3 hrs. Then solution of the ligand was kept for slow evaporation and coloured precipitate was collected and dried in air [7].

2.3. Synthesis of Mononuclear Schiff base Metal complexes

The ethanolic solution of synthesized ligand (1 mM) was added dropwise stirring to an ethanolic solution of the metal salt (1 mM) with constant stirring, followed by the addition

of 2, 2' bipyridyl (1 mM) and the mixture was boiled under reflux for 5 hrs (Fig. 1). Then, the volume of the reaction mixture was reduced by evaporation. The precipitated complexes were filtered off, washed with ethanol and then dried in *vacuo* [8].

2.4. The *in vitro* Antibacterial activity

The *in vitro* antibacterial activity of the ligand and the complexes were tested against the bacteria *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis* and *Klebsilla pneumonia* by well diffusion method using nutrient agar as the medium [9]. *Streptomycin* was used as standard component. The stock solution was prepared by dissolving the compound in DMF and the solution was serially diluted to find minimum inhibitory concentration (MIC) values. In a typical procedure, a well was made on the agar medium with microorganisms in a petri plate. The well was filled with the test solution and the plate was incubated for 24 h for bacteria at 35 °C. During the period, the test solution diffused and the growth of the inoculated micro-organisms was affected. The inhibition zone was developed, at which the concentration was noted.

2.5. Agarose Gel Electrophoresis

Cleavage products were analysed by agarose gel electrophoresis method. Test samples were prepared in DMSO. The gel electrophoresis experiments were performed by incubation of the samples containing 40 µM pUC18 DNA, 50 µM metal complexes and 50 µM H₂O₂ in tris-HCl buffer (pH 7.2) at 37°C for 2 h. After incubation, the samples were electrophoresed for 2 h at 50 V on 1% agarose gel using tris-acetic acid-EDTA buffer (pH 7.2). The gel was then stained using 1 µg cm⁻³ ethidium bromide (EB) and photographed under ultraviolet light at 360 nm. All the experiments were performed at room temperature [10].

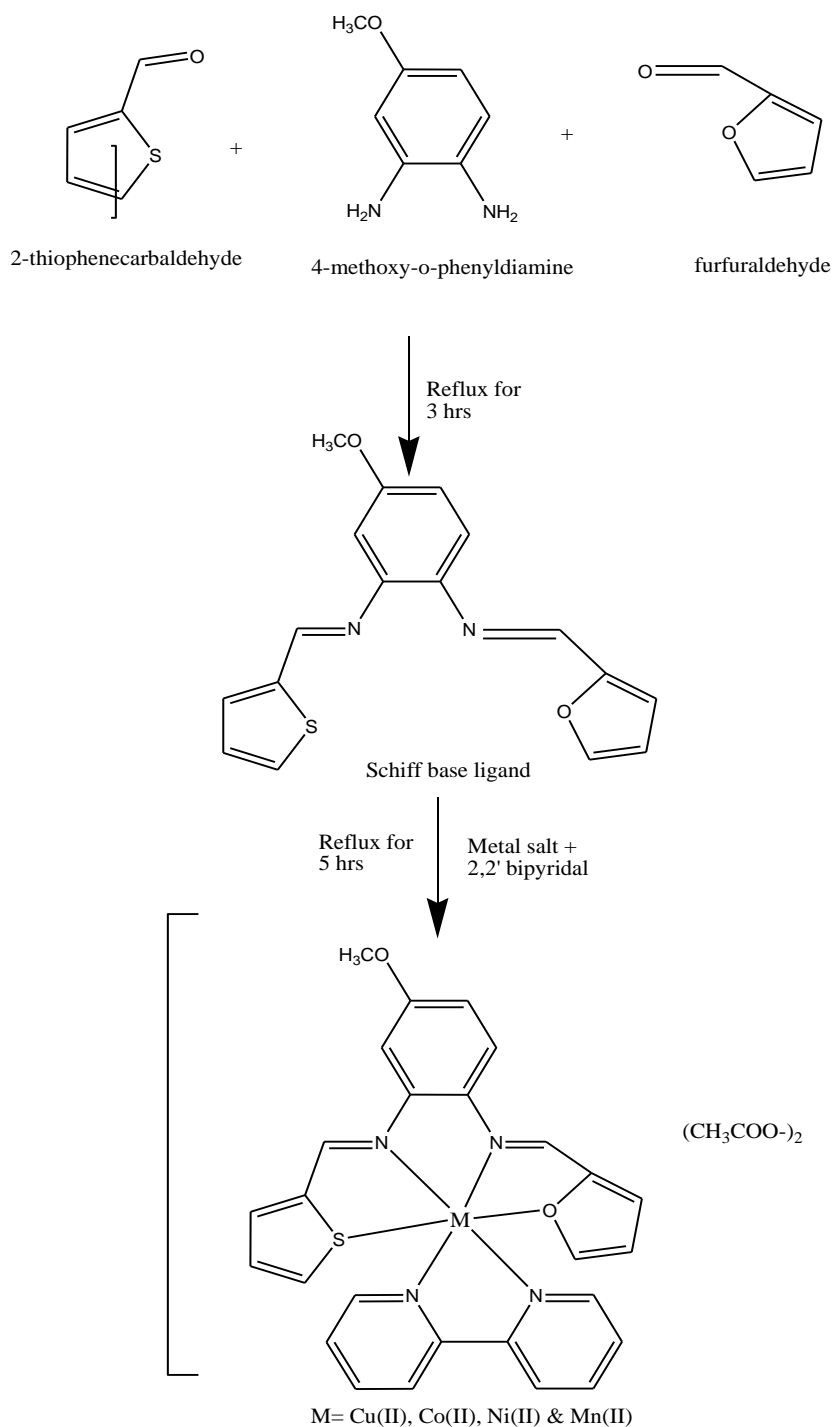


Fig 1. Synthesis of Heterocyclic Schiff base ligand and its metal(II) complexes

3. RESULTS AND DISCUSSION

$C_{17}H_{16}N_2O_2S$, $[Cu(C_{31}H_{30}N_4O_6S)]$, $[Ni(C_{31}H_{30}N_4O_6S)]$, $[Co(C_{31}H_{30}N_4O_6S)]$ and $[Mn(C_{31}H_{30}N_4O_6S)]$ mononuclear Schiff base metal complexes were synthesized by using 2-thiophenecarboxaldehyde, 4-methoxyphenylenediamine, furfuraldehyde and 2, 2'- bipyridyl. All the synthesized mononuclear Schiff base complexes are non hygroscopic stable in air. All the complexes are insoluble in water and common organic solvents but soluble in DMF and DMSO.

3.1. Elemental Composition

The results of elemental analysis were in good agreement with those required by the proposed formulae given in Table 1.

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

Molecular Formula	color	Yield %	Melting Point (°)	% of Nitrogen		% of Metal		Molar conductance Δ_m (ohm ⁻¹ cm ² mol ⁻¹)
				Cal	Exp	Cal	Exp	
$C_{17}H_{16}N_2O_2S$	Dark Yellow	80	136	8.96	8.95	-	-	-
$[Cu(C_{31}H_{30}N_4O_6S)]$	Brown	80	>200	8.61	8.59	9.76	9.74	146
$[Ni(C_{31}H_{30}N_4O_6S)]$	Black	75	>200	8.67	8.65	9.09	9.07	138
$[Co(C_{31}H_{30}N_4O_6S)]$	Brown	70	>200	8.67	8.68	9.05	9.04	152
$[Mn(C_{31}H_{30}N_4O_6S)]$	Black	75	>200	8.72	8.70	8.55	8.52	150

Where L= Ligand, Y= 2, 2' bipyridyl and Z = acetate ion.

3.2. Molar Conductivity

The solution conductivity measurements were performed to establish the charge type of the complexes. The complexes were dissolved in DMF and the molar

conductivities of 10^{-3} M of their solutions at 29 °C were measured. The observed molar conductance values are given in Table 1. The values of molar conductance suggest that complexes are electrolytes in nature [11]. The electrolytic nature of these complexes is due to the presence of counter ions outside the coordination sphere.

3.3. Infrared Spectra

The infrared spectra of the reported heterocyclic mononuclear metal complexes were measured as KBr disk and the important IR-spectral feature along with their tentative assignments are shown in Table. 2.

In all the complexes, the (C=N) group absorption shifts to lower frequencies when compare with ligand and appears in $1598\text{-}1618\text{ cm}^{-1}$ region indicating coordination of imine nitrogen atoms of the Schiff base [12].

New vibrations at $535\text{-}561\text{ cm}^{-1}$, $405\text{-}422$ and $408\text{-}417\text{ cm}^{-1}$ which are not present in the free Schiff base are attributed to the existence of ν (M-O), (M-S) and ν (M-N). The results show that ν (C-O) modes occur at $1262\text{-}1334\text{ cm}^{-1}$ respectively. The shifting of (C-O) towards higher frequency as compared to the ligand (1262 cm^{-1}) is due to the conversion of hydrogen bonded structure into a covalent metal bonded structure. The band at 1448 cm^{-1} and 1512 cm^{-1} were due to symmetric stretching frequency and asymmetric frequency of acetate ion. This result predicts that the acetate ions were coordinated outside the coordination sphere [13].

The IR spectra show the presence of metal-nitrogen, metal-oxygen, metal -sulphur and the presence of ionic acetate for the complexes.

Table 2. Infrared Spectroscopic data of the heterocyclic Schiff Base Ligand and its mononuclear metal complexes

Compounds	(C=N) (cm ⁻¹)	(C-S) (cm ⁻¹)	(C-O) (cm ⁻¹)	(M-N) (cm ⁻¹)	(M-O) (cm ⁻¹)	(M-S) (cm ⁻¹)
C ₁₇ H ₁₆ N ₂ O ₂ S	1618	732	1262	--	--	--
[Cu(C ₃₁ H ₃₀ N ₄ O ₆ S)]	1608	728	1322	462	535	405
[Ni(C ₃₁ H ₃₀ N ₄ O ₆ S)]	1604	738	1308	484	542	417
[Co(C ₃₁ H ₃₀ N ₄ O ₆ S)]	1605	744	1334	478	556	412
[Mn(C ₃₁ H ₃₀ N ₄ O ₆ S)]	1598	756	1318	492	561	408

3.4. ELECTRONIC SPECTRA

The spectra of the Heterocyclic Schiff base ligand and their metal complexes were recorded in DMSO solutions. The various bands observed were assigned to interligand and charge transfer of $n \rightarrow \pi^*$ transitions according to their energies and intensities. The band in the 355–375 nm region is ascribed to an $n \rightarrow \pi^*$ transition due to molecular orbitals originating in the $-N=C$ moiety. In the ligand, the band appears in the 258–278 nm range, which is assigned to the azomethine chromophore $\pi \rightarrow \pi^*$ transition. This band shifts to a lower wavelength in the spectra of complexes and appears at 10 ± 5 nm in the complexes.

The octahedral Cu(II) split under the influence of the distortion and the distortion can be such as to cause the three transitions ${}^2B_{1g} \rightarrow {}^2B_{2g}$; ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ in the range of 610, 590, 575 nm [14]. The electronic spectrum of the Ni(II) complex showed three bands at 642, 590, 540 nm assignable to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F) (ν_1), ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2) and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3) transitions, respectively [15]. The electronic spectrum of Co(II) complex exhibited three bands in the region of 605, 550, 536 nm which were tentatively assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (F) (ν_1), ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (F) (ν_2) and ${}^4T_{1g} \rightarrow {}^4T_{1g}$ (P) (ν_3) transitions, respectively [16].

Table 3. Electronic Spectral data of heterocyclic Schiff base ligand and its complexes.

S. No	Compound	Electronic spectra (nm)				Geometry of the complex
		$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$L \rightarrow M$	d-d	
1	C ₁₇ H ₁₆ N ₂ O ₂ S	278	375	-	-	-
2	[Cu(C ₃₁ H ₃₀ N ₄ O ₆ S)]	262	362	456	610, 590, 575	Distorted
3	[Ni(C ₃₁ H ₃₀ N ₄ O ₆ S)]	258	368	452	642, 590, 540	
4	[Co(C ₃₁ H ₃₀ N ₄ O ₆ S)]	266	370	460	605, 550, 536	
5	[Mn(C ₃₁ H ₃₀ N ₄ O ₆ S)]	270	355	432	615, 545, 530	Octahedral

3.4.¹ *H* NMR SPECTRA

The ^1H NMR spectra of all Schiff base $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ ligand were recorded in DMSO-d_6 at room temperature as shown in Figure 2. The ligand was prepared by dissolution in DMSO-d_6 and the chemical shifts were recorded with respect to TMS. Two different type of protons were identified i) characteristic resonance due to azomethine proton in the Schiff base appears at 8.23 ppm was observed and ii) the other signals in the region 6.40– 7.90 ppm exhibits due to aromatic protons [18].

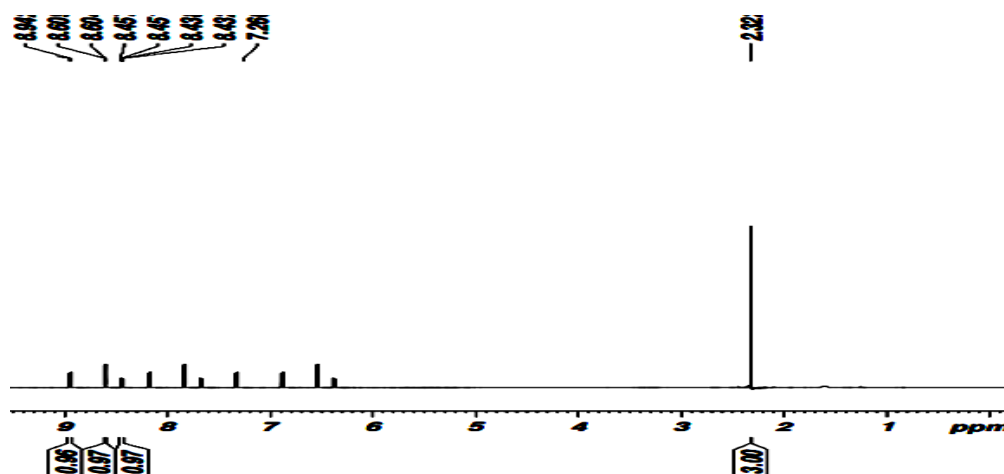
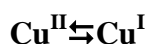


Fig. 2. ^1H NMR spectra of $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$

3.5. CYCLIC VOLTAMMETRY

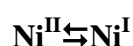
The electrochemical properties of heterocyclic mononuclear metal complexes were studied by cyclic voltammetry in DMF containing 0.1 M tetra(n-butyl)ammonium perchlorate. All the complexes undergo both reduction and oxidation in cathodic and anodic potentials, respectively. The electrochemical data are summarized in Table. 4 and 5.

The cyclic voltammogram of $[\text{Cu}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ complexes shows that the ΔE_p values falls in the range of 190 mV which shows quasireversible reduction waves. The $E_{1/2}$ values falls in the range of -0.58 V indicate that each couple corresponds to one electron transfer process. Controlled potential electrolysis was carried out at 100 mVs^{-1} and the experiment reports that each couple corresponds to one electron transfer process. So, the processes are assigned as follows.



The Cu(II) complexes show a quasireversible oxidation waves, which is assigned as a Cu(I)/ Cu(II) couple. The ΔE_p values falls in the range of 140 mV are suggest the each couple was quasireversible. The $E_{1/2}$ values falls in the range of 0.28 V indicate that each couple corresponds to one electron transfer process [19].

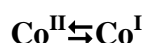
The cyclic voltammogram of $[\text{Ni}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ complex shows that the ΔE_p values of Ni(II) falls in the range of 140 mV which shows quasireversible reduction waves. The $E_{1/2}$ values falls in the range of -0.28 V indicate that each couple corresponds to one electron transfer process. Controlled potential electrolysis was carried out at 100 mVs^{-1} and the experiment reports that each couple correspond to one electron transfer process. So, the processes are assigned as follows.



The Nickel(II) complexes show a quasireversible oxidation waves, which is assigned as a Ni(II)/ Ni(III) couple. The ΔE_p values falls in the range of 190 mV are suggest the each couple

was quasireversible. The $E_{1/2}$ values falls in the range of 0.62 V indicate that each couple corresponds to one electron transfer process [20].

The $[\text{Co}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ complexes exhibit one electron quasi reversible transfer process with a peaks at ΔE_p values falls in the range of 200 mV and The $E_{1/2}$ values falls in the range of -0.60 V corresponding to reduction waves . This gives evidence for quasi reversible Co(II)/Co(I) couple. Also, ΔE_p values falls in the range of 150 mV and the $E_{1/2}$ values falls in the range of 0.32 V corresponding to oxidation waves [21].



The $[\text{Mn}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ complex exhibit one electron quasi reversible transfer process with a peaks at ΔE_p values falls in the range of 170 mV and the $E_{1/2}$ values falls in the range of -0.36 V corresponding to reduction waves . This gives evidence for quasi reversible Mn(II)/ Mn(I) couple . Also, ΔE_p values falls in the range of 120 mV and The $E_{1/2}$ values falls in the range of 0.74 V corresponding to oxidation waves [22].

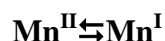


Table 4. Electrochemical data of heterocyclic Mononuclear Schiff base metal(II) complexes in DMF medium (Reduction)

S. No.	Complexes	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)	ΔE_p (mV)
1.	$[\text{Cu}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$	-0.68	-0.49	-0.58	190
2.	$[\text{Ni}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$	-0.35	-0.21	-0.28	140
3.	$[\text{Co}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$	-0.70	-0.50	-0.60	200
4.	$[\text{Mn}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$	-0.45	-0.28	-0.36	170

Table 5. Electrochemical data of heterocyclic Mononuclear Schiff base metal(II) complexes in DMF medium (Oxidation)

S. No.	Complexes	E _{pc} (V)	E _{pa} (V)	E _{1/2} (V)	ΔE _p (mV)
1.	[Cu(C ₃₁ H ₃₀ N ₄ O ₆ S)]	0.21	0.35	0.28	140
2.	[Ni(C ₃₁ H ₃₀ N ₄ O ₆ S)]	0.53	0.72	0.62	190
3.	[Co(C ₃₁ H ₃₀ N ₄ O ₆ S)]	0.25	0.40	0.32	150
4.	[Mn(C ₃₁ H ₃₀ N ₄ O ₆ S)]	0.68	0.80	0.74	120

3.6. MAGNETIC PROPERTIES

The magnetic moment values are useful in the evaluation of structural investigations. The magnetic moments of the solid-state complexes were measured at room temperature. The magnetic moment of 1.74 B.M. falls within the range normally observed for distorted octahedral Cu(II) complexes. The value of magnetic moment was 5.22 B.M. which indicates the presence of Co(II) complex in distorted octahedral geometry. The value of magnetic moment was 3.77 B.M; therefore distorted octahedral geometry is suggested for this nickel complex. The Mn(II) complex show magnetic moments is 5.55 B.M. at room temperature corresponding to five unpaired electrons which suggest distorted octahedral geometry [23-26]

3.7. EPR STUDIES

The EPR spectra of complexes provide information of importance in studying the metal ion environment. The ESR spectrum of Cu(II) complexes were recorded on X-band at frequency 9.1 GHz at room temperature. The spectra exhibited a single anisotropic intense sharp signal at room temperature with no hyperfine splitting as shown in Figure 3. This suggests that copper ions are in mononuclear environment.

The EPR spectrum of the $[\text{Cu}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ complexes show a broad signal with g_{iso} at 2.0001 which is consistent with an distorted octahedral geometry [27].

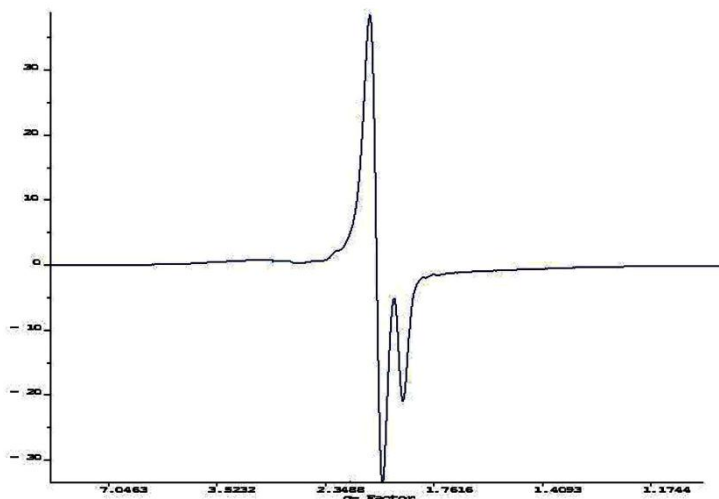


Fig. 3. EPR spectra of $[\text{Cu}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ complex

3.8. DNA CLEAVAGE STUDIES

It is well known that deoxyribonucleic acid (DNA) plays an important role in the life process since it contains all the genetic information for cellular function. $[\text{Cu}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$, $[\text{Ni}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$, $[\text{Co}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ and $[\text{Mn}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ complexes were studied for their DNA cleavage activity by agarose gel electrophoresis method. Plasmid DNA mainly has a closed-circle supercoiled form (Form I), as well as nicked form (Form II) and linear form (Form III) as small fractions. Intercalation of synthesized complexes to plasmid DNA can loosen or cleave the supercoiled form DNA, which decreases its mobility rate and can be separately visualized by agarose gel electrophoresis method. The relatively fast migration is the intact supercoil form (Form I) and the slower moving migration is the open circular form (Form II), which was generated from supercoiled. The heterocyclic mononuclear Schiff base metal complexes are able to perform cleavage of pUC18 DNA in the lane 3, 4, 5, and 6 and Figure 4. The supercoiled SC (Form I) gradually converted to nicked form NC (Form II). The OH^\bullet free radicals participate in the oxidation of the deoxyribose moiety, followed by

hydrolytic cleavage of a sugar phosphate back bone. The increase in hydroxyl radical leads to the pronounced nuclease activity in the presence of oxidant H_2O_2 . Control experiments using DNA alone do not show any significant cleavage of pUC18 DNA even on longer exposure time. From the observed results, it is concluded that the $[\text{Cu}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ complexes effectively cleave the DNA as compared to control DNA [28].

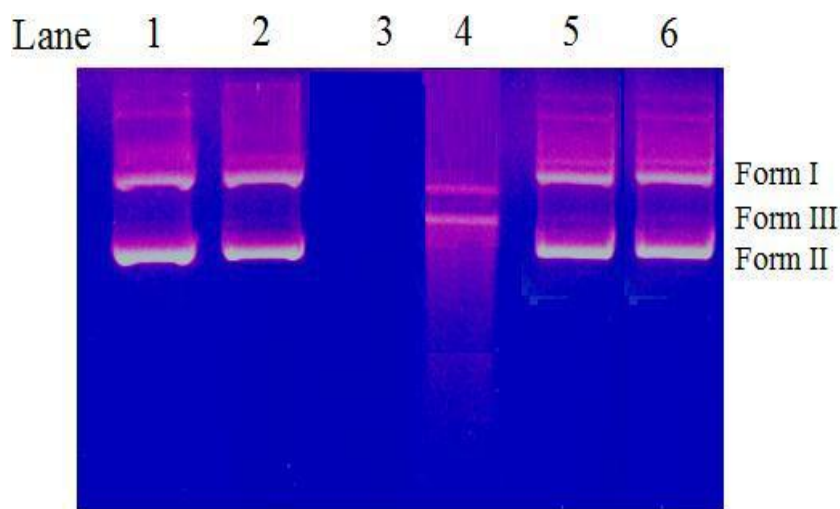


Fig. 4. Changes in the agarose gel electrophoretic pattern of pUC18DNA induced by H_2O_2 and metal complexes. Lane 1-DNA alone; Lane 2- DNA alone + H_2O_2 ; Lane 3-DNA + $[\text{Cu}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ + H_2O_2 ; Lane 4-DNA + $[\text{Co}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ + H_2O_2 ; Lane5-DNA + $[\text{Ni}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$; Lane 6-DNA+ $[\text{Mn}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ + H_2O_2 .

3.9. ANTIBACTERIAL STUDIES

The synthesized ligand and its heterocyclic mononuclear metal complexes were tested for their in vitro antibacterial activity. Significant inhibitory data was observed in the screening Table 6. The susceptibilities of certain strains of bacteria (*Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis* and *Klebsilla pneumonia*) cultures to Schiff base and their complexes were evaluated by measuring the size of the bacteriostatic diameter. This enhancement in the activity may be to the structures of Schiff base ligand by possessing an azomethine ($\text{C}=\text{N}$) linkage. The toxic activity of the complexes with the ligand can be

ascribed to the increase in the lipophilic nature of the complexes arising from chelation. The mode of action of complexes involves the formation of hydrogen bonds with the imino group by the active sites leading to interference with the cell wall synthesis. This hydrogen bond formation damages the cytoplasmic membrane and the cell permeability may also be altered leading to cell death. The higher activity of $[\text{Cu}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ complex can be explained as, on chelation the polarity of $[\text{Cu}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ ion is found to be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the copper ion with donor groups. Therefore, $[\text{Cu}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ ions are adsorbed on the surface of the cell wall of microorganisms. The adsorbed $[\text{Cu}(\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{S})]$ ions disturb the respiratory process of the cells, thus blocking the synthesis of proteins and this, in turn, restricts further growth of the organisms [29].

Table 6. Antibacterial activity for heterocyclic Schiff base ligands and its mononuclear metal complexes

Compounds	Zone of inhibition (mm)															
	Gram positive bacteria								Gram negative bacteria							
	<i>Staphylococcus aureus</i>				<i>Bacillus subtilis</i>				<i>Escherichia coli</i>				<i>Klebsiella pneumoniae</i>			
	Concentration (µg/mL)															
	25	50	75	100	25	50	75	100	25	50	75	100	25	50	75	100
C ₁₇ H ₁₆ N ₂ O ₂ S	7	7	8	9	7	7	9	9	6	6	7	8	7	8	8	9
[Cu(C ₃₁ H ₃₀ N ₄ O ₆ S)]	10	11	12	14	10	9	12	13	9	9	10	11	10	12	15	17
[Ni(C ₃₁ H ₃₀ N ₄ O ₆ S)]	9	8	10	12	9	8	11	12	6	7	7	9	9	8	9	10
[Co(C ₃₁ H ₃₀ N ₄ O ₆ S)]	10	9	12	13	10	11	12	14	8	9	9	11	9	10	11	12
[Mn(C ₃₁ H ₃₀ N ₄ O ₆ S)]	8	9	9	10	8	9	9	10	7	8	9	9	7	8	9	10
Streptomycin	16	17	20	22	14	15	17	20	12	13	16	20	13	14	16	18

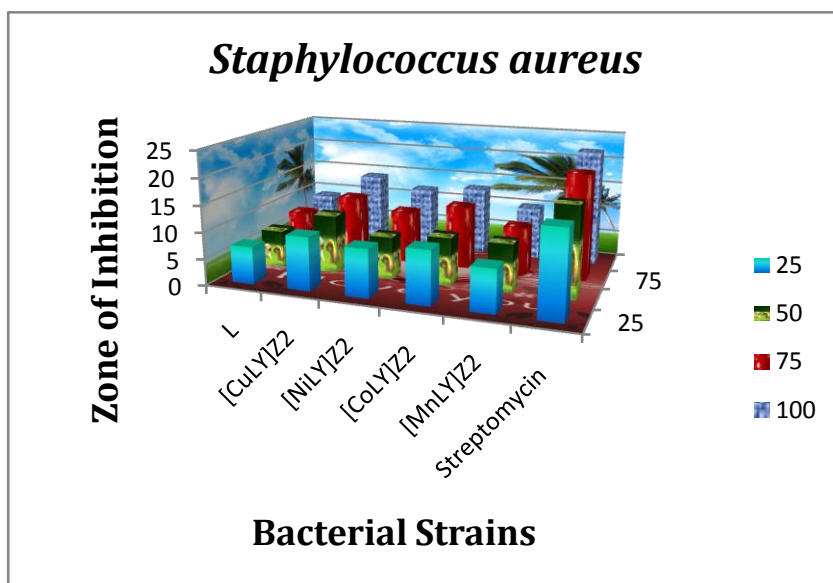


Fig. 5. Antibacterial activity of Schiff base ligand and its complexes against *Staphylococcus aureus*

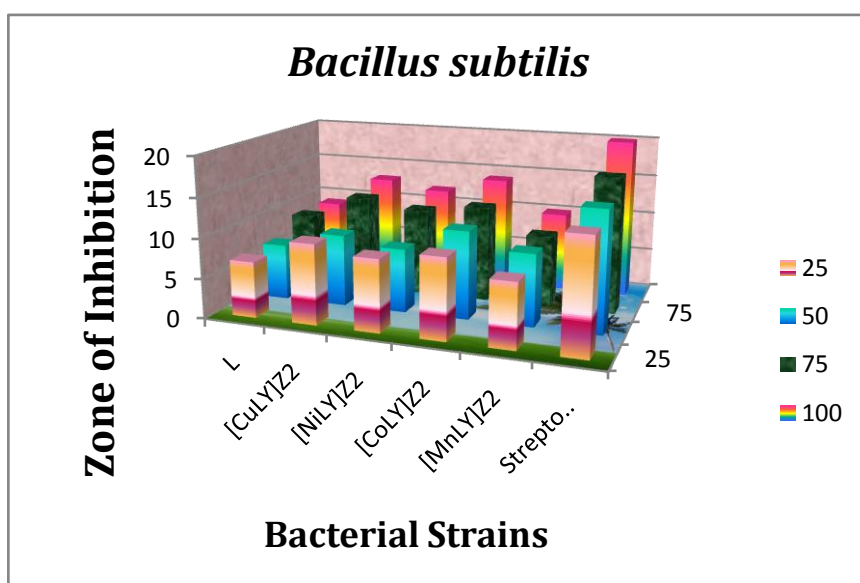


Fig. 6. Antibacterial activity of Schiff base ligand and its complexes against *Bacillus subtilis*

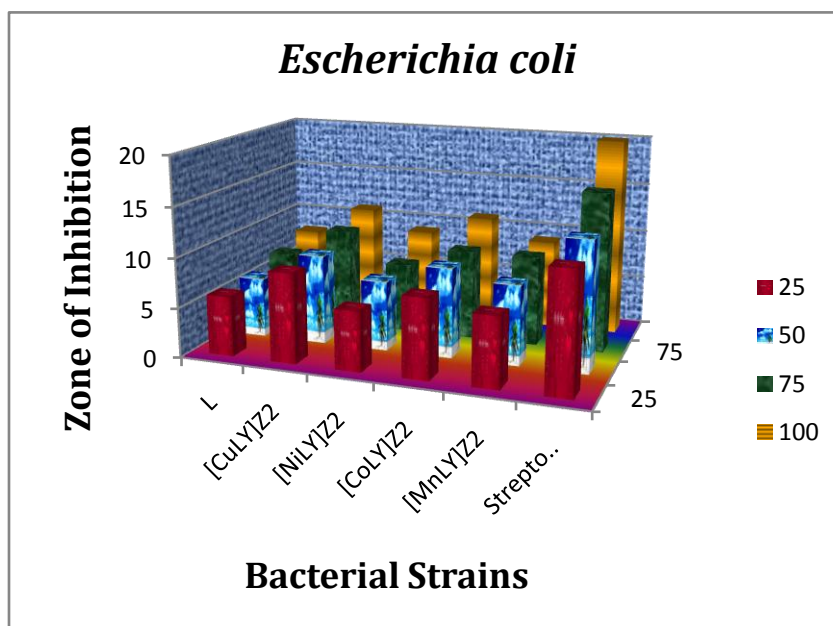


Fig. 7. Antibacterial activity of Schiff base ligand and its complexes against *Escherichia coli*

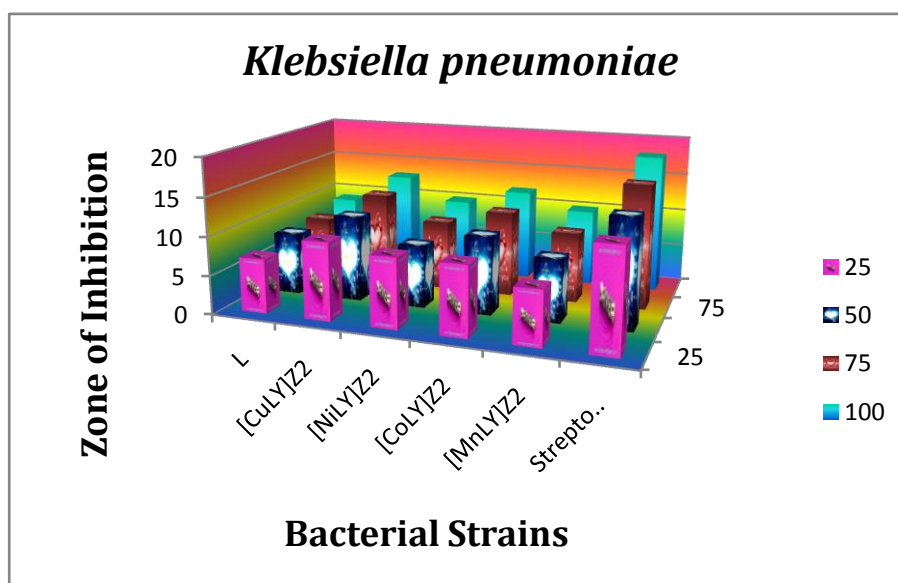


Fig. 8. Antibacterial activity of Schiff base ligand and complexes against *Klebsiella pneumoniae*

3.10. CONCLUSION

The design and synthesis of mononuclear Cu(II), Ni(II), Co(II) and Mn(II) Schiff base complexes have been demonstrated in this report. All the four complexes were synthesized

from 2- thiophenecarboxaldehyde, 4-methoxyphenylenediamine, furfuraldehyde and 2, 2' bipyridyl containing N₄OS donors set in different environments. They were characterized by spectral and analytical data. The molar conductance values indicate that the complexes were electrolytic in nature. FT-IR spectra reveal that the azomethine stretching frequency observed for all the complexes suggesting the complex formation and far IR spectra indicate that the chloride ion bonded to the metal ion. The UV-Vis, magnetic susceptibility and EPR spectral data of the complexes suggest a distorted octahedral geometry. The DNA cleavage studies reveals that the [Cu(C₃₁H₃₀N₄O₆S)] complex cleaved DNA was more effectively as compared other complexes and ligand. The antibacterial activity of the [Cu(C₃₁H₃₀N₄O₆S)] complex are higher than the ligand and other complexes.

Acknowledgement

We are thankful to our Supervisor and professors of department of chemistry, Periyar University - Salem for their encouragement and support.

References

1. Balsells J, Mejorado L, Phillips M, Ortega F, Aguirre G, Somanathan R, Walsh P J, Tetrahedron Asymm., 9, **1998**, 4135.
2. Sima J, Crao. Chem. Acta., 74, **2001**, 593.
3. Chaviara A T, Cox P J, Repana K H, Papi R M, Papazisis K T, Zambouli D, Kortsaris A H, Kyriakidis D A, Bolos C A, J. Inorg. Biochem., 98(8), **2004**, 1271.
4. Ciller J A, Seoane C, Soto J L, Yruretagoyena B, J. Heterocyclic. Chem., 23(5), **2009**, 1583.
5. Agarwal B V, Hingorani S, Synth. React. Inorg. Met-Org.Chem., 20, **1990**, 123.
6. Prakash A, Singh B K, Bhojak N, Adhikari D, Spectrochim. Acta., 76(3), **2010**, 356.
7. Akila E, Usharani M, Ramachandran S, Velraj G, Jayaseelan P and Rajavel R, Arabian Journal of Chemistry., <http://dx.doi.org/10.1016/j.arabjc.2013.11.031>.

8. Akila E, Usharani M, and Rajavel R, International Journal of Medicine and Pharmaceutical Sciences., 3(2), **2013**, 95.
9. Mohamed G G, Omar M M and Ibrahim A A., Spectrochim. Acta. A., 75, **2010**, 678.
10. Shahabadi N, Kashanian S & DarabiEuro F., J. Med. Chem., 45, **2010**, 4239.
11. Prasad R, Thankachan P P, Thomas M T and Pathak R., J. Ind. Chem. Soc., 78, **2001**, 28.
12. Hiremath C, Qureshi Z S, Reddy K M and Halli M B., Indian J. Chem. Soc., Sec A, 30, **1991**, 293.
13. Wahab Z H and Mashaly M M., Chem. Pap., 59, **2005**, 25.
14. Cotten F A, Wilkinson G, Murillo C A, Bochmann M., Adv.Inorg. Chem., 6th edn., Wiley, NewYork, **1999**.
15. Mohammad Shakir, Yasser Azim, Hamida-Tun-Nisa Cbishti, Shama Praveen, Spectrochimica Acta Part A., 65, **2006**, 490.
16. Joshi K T, Pancholi A M, Pandyaand K S, Thakar A S., J. Chem. Pharm. Res., 3(4), **2011**, 741.
17. Mustafa Dolaz, Vickie McKee, Ays, egül Gölcü, & Mehmet Tümer. Spectrochim. Acta Part A, 71, **2009**, 1648.
18. Kumar N R S, Nethiji M. and Patil K C., Polyhedron, 10, **1991**, 365.
19. Prasad R, Thankachan P P, Thomas M T and Pathak R., J. Ind. Chem. Soc. 78, **2001**, 28.
20. Kumar N R S, Nethiji M, Patel K C., Polyhedron 10, **1991**, 365.
21. Sulekh Chandra and Amit Kumar Sharma. Research Letters in Inorganic Chemistry., Article ID 945670, **2009**.

22. Chandra S, Gupta L K and Sangeetika., Synth. React. Inorg. Met.-Org. Chem. 34, **2004**,154.
23. Ranford J D, Vittal J J and Wang Y M, Inorg. Chem., 37, **1998**, 1226.
24. Agarwal R K, Sharma D, Shing L and Agarwal H, Bioinorg. Chem. Appl., doi. 10.1155/BCA/2006/29234, **2006**.
25. Aurkie R, Banerjee S, Sen S, Butcher R J, Rosair G M and Garland M T, Struct. Chem., 19, **2008**, 209.
26. Baran E J, J. Coord. Chem., 54, **2001**, 215.
27. Thirumavalavan M, Akilan P and Kandaswamy M, Supramol. Chem., 16, **2004**, 504.
28. Jayaseelan P, Akila E, Usharani M. and Rajavel R., Journal of Saudi Chemical Society, <http://dx.doi.org/10.1016/j.jscs.2013.07.001>
29. Vaghasia Y, Nair R, Soni M, Bahja S. and Chandra S., J. Serb. chem joc 69, **2004**, 991.