

## Synthesis, characterization, deoxyribonucleic acid interaction and antimicrobial studies of Schiff base binuclear transition metal complexes

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In this paper, the ligand was prepared by using the organic compounds 3, 3'-dihydroxy benzidine and 3-amino coumarin. We have synthesised binuclear Schiff base complexes using the ligand and chloride salts of copper(II), nickel(II), manganese(II), zinc(II) and chromium(III). The type of the complexes was  $[MLCl_4]$ . The synthesized binuclear Schiff base complexes were characterized by elemental analysis, molar conductance, cyclic voltametry, UV-visible, IR, electron paramagnetic resonance and nuclear magnetic resonance spectra. Gel electrophoresis was used to study deoxyribonucleic acid cleavage. Copper and nickel binuclear complexes fully degraded the supercoiled plasmid deoxyribonucleic acid. The antibacterial activity of the binuclear metal complexes against the microbes *Escherichia coli*, *Klebsiella pneumoniae* and *Staphylococcus aureus* was studied by the disc diffusion method.

**Keywords:** 3, 3'-dihydroxy benzidine, 3-amino coumarin, infrared spectra, ultraviolet-visible spectra, electron paramagnetic resonance spectra, deoxyribonucleic acid

### INTRODUCTION

Inorganic chemistry plays a vital role in electronics, pharmaceuticals, nuclear reactors, fertilisers, pesticides, polymers, semiconductors, solar cells, nano composites, photo catalysis, etc. The first-row transition metals such as copper, nickel, manganese, zinc and chromium show biological activity. In the 20<sup>th</sup> century, platinum complexes were used as anticancer agents. The ability of a metal complex to act as therapeutic agent is already discussed. Transition metals are used in bio synthesis. Complexes of transition metals show antitumor activity. Because of selective permeability, accumulation of transition metals in tumors is possible. In the past decade, a number of mononuclear complexes and their interaction with deoxyribonucleic acid were analyzed.

We have synthesized a novel Schiff base of the first row transition metal complexes which has many advantages compared with mononuclear complexes. Schiff base complexes are famous because of simple synthesis and formation of stable complexes with many transition metals. The intention of this study is to synthesize Schiff base transition metal complexes with organic ligands of the NNO type. Synthesized binuclear complexes play a vital role as anticancer [1,2], antimicrobial [3], antioxidant [4], antibacterial [5], antifungal [6], and anthelmintic [7] agents. Deoxyribonucleic acid interaction study is an important source to the development of reagents in biotechnology and

biomedical engineering. Transition metal complexes are cleaving deoxyribonucleic acid and can be used as therapeutic agents [8-10]. Ligands having nitrogen and oxygen can behave as effective chelating agents for transition metal ions [11, 12]. Antibacterial activity against microbes such as *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Escherichia coli* was analysed [13].

### EXPERIMENTAL

#### *Description of equipment, materials, methods*

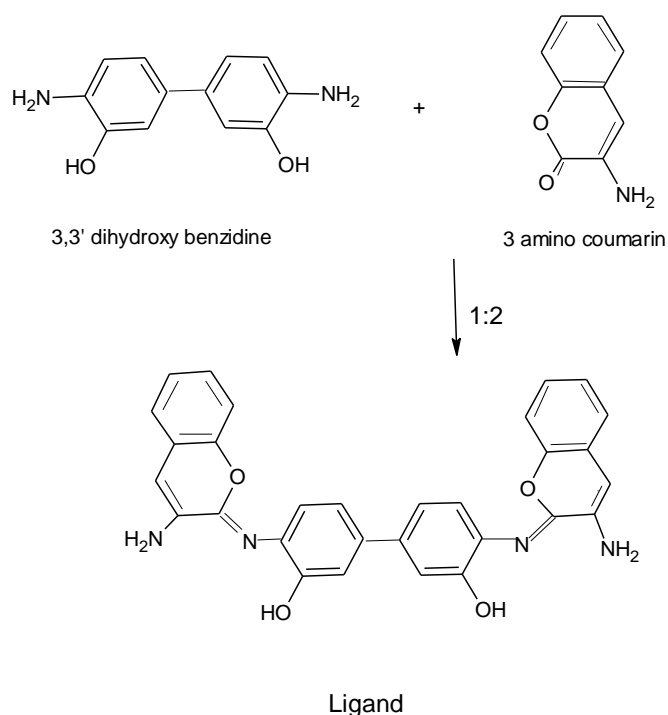
3,3'-Dihydroxy benzidine and 3-amino coumarin were obtained from Aldrich. Ethanol, DMSO and DMF solvents were used. Elemental analysis was performed by using a Carlo-Erba 1106 instrument. Molar conductances were calculated by using ELICO CM 185 conductivity bridge. The infrared spectra were collected on a Perkin Elmer FT-IR-8300 model spectrometer. Electronic absorption spectra in the UV-visible range were recorded on a Perkin Elmer Lambda-25 spectrometer between 200-700 nm. The voltammetric experiment was carried out with a CHI60 electrochemical analyzer. Electron paramagnetic resonance spectra were obtained on a Varian JEOL-JES-TE100 EPR spectrometer. The NMR spectrum was recorded on a Bruker Avance III HD nanobay spectrometer. The DNA interaction was monitored by the gel electrophoresis method. The disc diffusion technique was used for the antibacterial activity studies.

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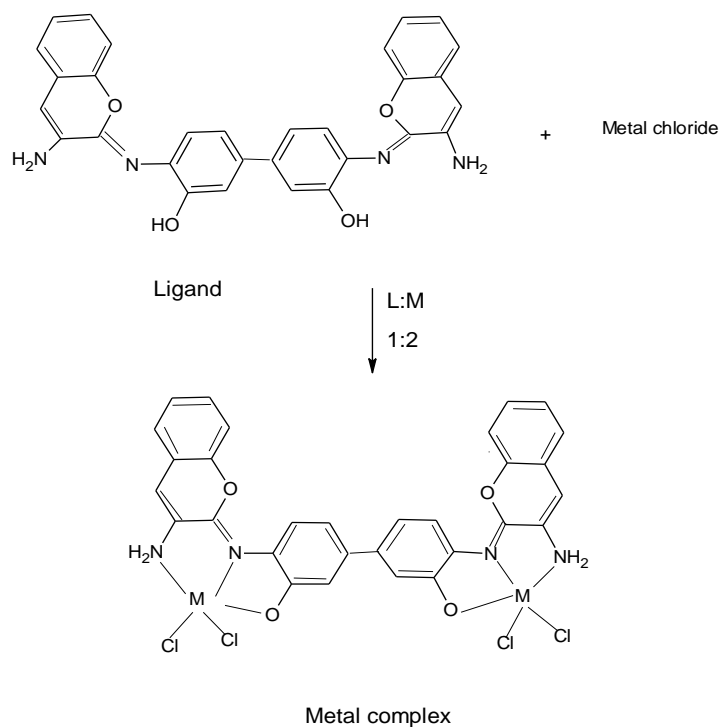
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3,3'-Dihydroxy benzidine and 3-amino coumarin were mixed slowly with uniform stirring. Ethyl alcohol was used as a solvent. The organic

compounds were heated in a round-bottom flask fitted with condenser for two hours. Precipitate was collected after cooling at 36°C. It was filtered, washed with ethanol and desiccated (Scheme 1).



Scheme 1. Preparation of ligand



Scheme 2. Synthesis of binuclear metal complexes

Ligand and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  were mixed and refluxed for 2 hours. The mixture was chilled to  $36^\circ\text{C}$ . The prepared metal complex was collected, filtered and desiccated over fused  $\text{CaCl}_2$ . Metal complexes of nickel(II), manganese(II), zinc(II) and chromium(III) were prepared in a similar way (Scheme 2).

## RESULTS AND DISCUSSION

### Elemental analysis

The results of the elemental analysis of the complexes are shown in Table 1. The 2:1 [M:L] ratio was confirmed from the data. The formula was  $\text{ML}$ , where M represents copper(II), nickel(II), manganese(II), zinc(II) and chromium(III) ions, while L represents ligand. Theoretical values and experimental values were more or less the same.

### Molar conductance study

The binuclear complexes were dissolved in dimethyl formamide. Molar conductance values are presented in Table 1. It is confirmed that the molar conductivity of copper(II), nickel(II), manganese(II), zinc(II) and chromium(III) complexes was lying in the range of  $12.26 - 15.74 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  (Table 1). Binuclear complexes are of non-ionic nature, i.e. chloride ions are not present inside the sphere.

### Infrared (IR) spectra

The IR spectral bands in the range  $3325-3335 \text{ cm}^{-1}$  belonged to  $\nu(\text{N-H})$  of the coordinated amine group, which was further confirmed by the bands obtained in the range  $470-488 \text{ cm}^{-1}$  corresponding to binding of metal and ligand, i.e.  $\nu(\text{M-N})$ . The bands obtained in the range  $1592-1598 \text{ cm}^{-1}$  confirmed the presence of azomethine  $\nu(\text{C=N})$  in all metal complexes. The far IR bands obtained in the range  $344-355 \text{ cm}^{-1}$  were due to  $\nu(\text{M-Cl})$  vibration [14]. The IR data are given in table 2.

**Table 1.** Elemental analysis of the metal complexes

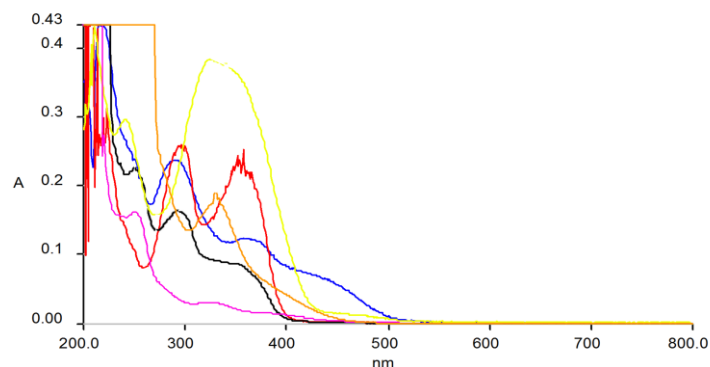
Ligand/ Complexes	Mol. Weight	% C		% H		% N		$\mu_{\text{eff}}$ (B.M)	$\Lambda_{\text{M}}$ ( $\text{Ohm}^{-1}$ $\text{cm}^2 \text{ mol}^{-1}$ )
		Calc.	Exp.	Calc.	Exp.	Calc.	Exp.		
$(\text{C}_{30}\text{H}_{22}\text{O}_4\text{N}_4)$	502.84	71.71	71.80	4.41	4.52	11.14	11.08		
$[\text{Cu}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	769.76	46.85	46.94	2.62	2.73	7.28	7.35	1.56	12.26
$[\text{Ni}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	760.04	47.44	47.54	2.66	2.76	7.37	6.25	2.64	13.42
$[\text{Mn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	752.54	47.92	47.85	2.68	2.59	7.45	7.40	5.60	15.74
$[\text{Zn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	773.42	46.62	46.70	2.61	2.70	7.25	7.35		
$[\text{Cr}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	746.66	48.30	48.25	2.70	2.80	7.51	7.60		

**Table 2.** IR spectra of the binuclear complexes

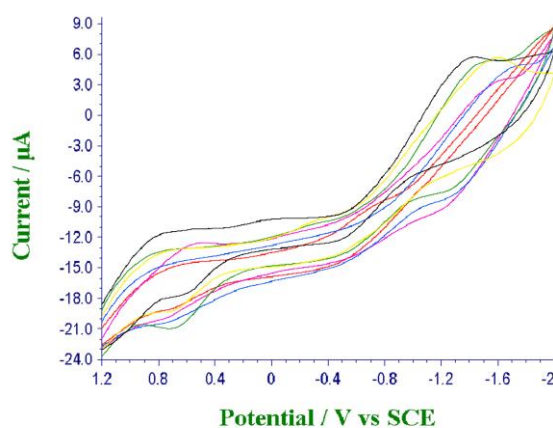
Complex	(C=N) ( $\text{cm}^{-1}$ )	$\text{NH}_2$ ( $\text{cm}^{-1}$ )	(C=C) ( $\text{cm}^{-1}$ )	(M-N) ( $\text{cm}^{-1}$ )	(M-Cl) ( $\text{cm}^{-1}$ )
$[\text{Cu}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	1592	3335	1515	470	344
$[\text{Ni}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	1598	3325	1518	473	347
$[\text{Mn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	1597	3330	1522	477	350
$[\text{Zn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	1594	3328	1526	482	352
$[\text{Cr}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	1595	3332	1530	488	355

**Table 3.** UV spectra of the Schiff base and its complexes

Binuclear Complexes	$\pi-\pi^*$ (nm)	$n-\pi^*$ (nm)	L-M CT (nm)	d-d (nm)
$[\text{Cu}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	276	325	412	659
$[\text{Ni}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	282	328	410	660
$[\text{Mn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	287	312	382	640
$[\text{Zn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	289	330	370	
$[\text{Cr}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$	292	334	368	



**Fig. 1.** UV spectra of the binuclear complexes. Yellow -  $[\text{Mn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$ , Red -  $[\text{Cu}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$ , Indigo -  $\text{Cr}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)$ ; Blue -  $(\text{C}_{30}\text{H}_{22}\text{O}_4\text{N}_4)$ , Black -  $[\text{Ni}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$ , Pink- $[\text{Zn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$



**Fig. 2.** Cyclic voltammograms of the Schiff base and its complexes. Black -  $[\text{Cr}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$ , Green -  $[\text{Mn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$ , Yellow -  $[\text{Zn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$ , Pink- $[\text{Cu}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$ , Red- $(\text{C}_{30}\text{H}_{22}\text{O}_4\text{N}_4)$ , Blue -  $[\text{Ni}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$

#### Ultraviolet-visible (UV-vis) spectral studies

The UV spectra are often very helpful in structural investigation. UV spectra of all complexes were obtained and show three main features. DMF medium was used. The intraligand charge transfer transition ( $\pi \rightarrow \pi^*$ ) was confirmed by one or two peaks obtained in the range of 276–292 nm. The ligand-to-metal charge transfer transition was responsible for the peak in the range of 368–412 nm. Electronic spectra of the mononuclear nickel (II) complex show d-d transitions corresponding to Ni (II)- $d^8$  system in an octahedral field. The mononuclear copper (II) complex exhibits a distorted octahedral geometry because of low absorption peak at 530 nm and d-d transition and. Only one broad absorption peak obtained in the binuclear copper (II) and nickel(II) complex in the region 510–650 nm, which is due to one more metal ion present in a our synthesised complexes [15]. The UV spectral data was given in table 3.

#### Cyclic voltammetry (CV)

Metal character and deoxyribonucleic acid binding ability of the metal complexes were confirmed by an electrochemical method. Cyclic voltammetric technique was used to study the interaction between copper (II) complexes with DNA. The cyclic voltammograms (CV) of the complexes  $[\text{Cu}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$ ,  $[\text{Ni}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$ , and  $[\text{Mn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$  were obtained in DMF solution at a scan rate of  $0.1 \text{ Vs}^{-1}$ . The potential was fixed from 1.2 to  $-2.0 \text{ V}$ . The cathodic wave (reduction) of the binuclear copper complex (Figure 2) gives redox properties to the own units. Thus, there was reduction of central Cu(II) to Cu(I) at  $-0.7920 \text{ V}$  and irreversible copper reduction at  $-1.4832 \text{ V}$ . The support of two one-electron reduction is observed for the binuclear copper complex, suggesting that the two copper ions have some sort of interaction with each other. Same results are obtained for the complexes  $[\text{Ni}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$  and  $[\text{Mn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$  [16–18].

### Electron paramagnetic resonance (EPR) spectra

The  $[\text{Cu}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$  complex was dissolved in DMF solvent. The solution was used in the EPR study. The EPR spectra of the  $[\text{Cu}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$  complex recorded in X-band frequency at room temperature and LNT with microwave frequency of 9.1 Ghz and magnetic field of 300 mT revealed the presence of Cu(II) ion. This spectrum confirms that a Cu(II) complex was formed. The spectrum has a g value of 2.32 mT. The shape of the spectrum and the g value indicates that Cu(II) complex structure is a cubically

distorted octahedral structure. There is no change in the LNT. The  $[\text{Mn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$  complex was dissolved in DMF solvent. The solution was used in the EPR study. The EPR spectra of the  $[\text{Mn}_2(\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_4)]$  complex recorded at LNT in X-band with microwave frequency of 9.1 Ghz and magnetic field of 300 mT revealed the presence of Mn(II) ion. This spectrum confirms the formation of the Mn(II) complex. The spectrum has a g value of 2.01 mT. The shape of the spectrum and the g value indicate that Mn(II) complex structure is octahedral. No spectrum was obtained at 36°C [19, 20].

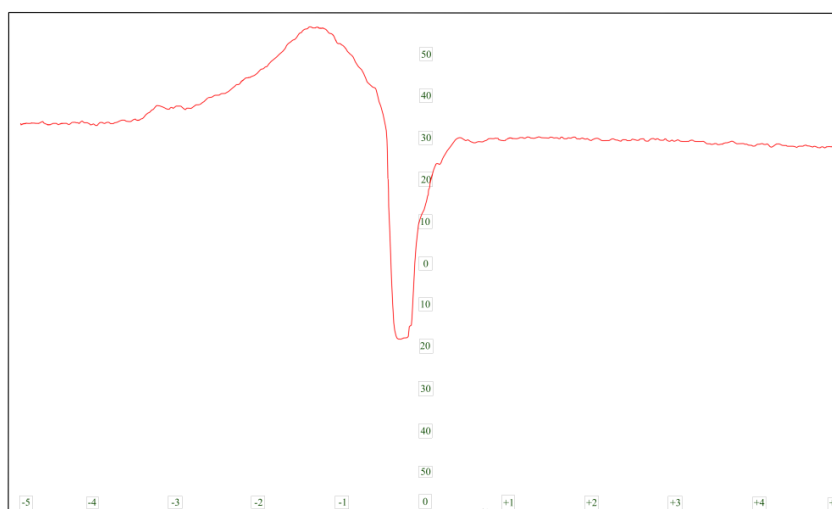


Fig. 3. EPR spectrum of the copper complex

### $^1\text{H-NMR}$ spectrum and $^{13}\text{C NMR}$ spectrum

The  $^1\text{H}$  and  $^{13}\text{C-NMR}$  spectra were recorded on Bruker Avance III HD nanobay. DMSO- $d_6$  was used as a solvent. The spectrum of the uncomplexed Schiff base ligand was compared with that of the corresponding zinc complex. Expected signals were seen in the spectra. The spectra of the ligand were dependable with the proposed structure. A singlet corresponding to a single proton was observed in the range of  $\delta$  9.01 ppm attributed to the azomethine proton ( $-\text{HC}=\text{N}$ ). The multiplet related to values  $\delta$  6.57 to 6.80 confirmed the presence of Ar-H. The study of the  $^{13}\text{C NMR}$  spectrum of the zinc (II) complex confirmed that the resonances due to the carbon

atoms of the 3, 3'-dihydroxy benzidine and 3-amino coumarin showed irrelevant changes of complex formation. Expected signals are shown in the spectrum. The values of  $\delta$  39.29 to 40.55 confirmed the presence of amine (C-N). The presence of carbon-carbon double bond (C=C) is confirmed by the values of  $\delta$  112.33 to 117.24. The values of 130.28 to 144.67 were attributed to the presence of benzene ring (C-C). It was confirmed that coordination proceeded through the carbonyl oxygen and amino group to form azomethine. NON donor set donated electrons to zinc metal to form a coordination bond [21, 22]. Because of paramagnetic effects, no spectrum was obtained for other transition metal complexes.

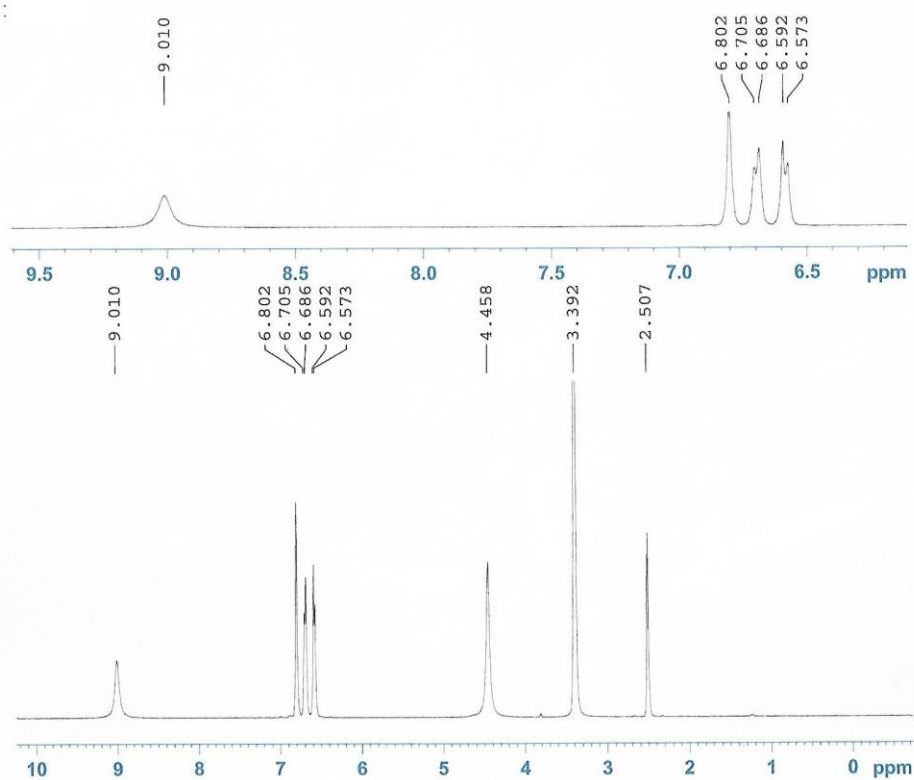


Fig. 4. <sup>1</sup>H NMR spectrum of the ligand

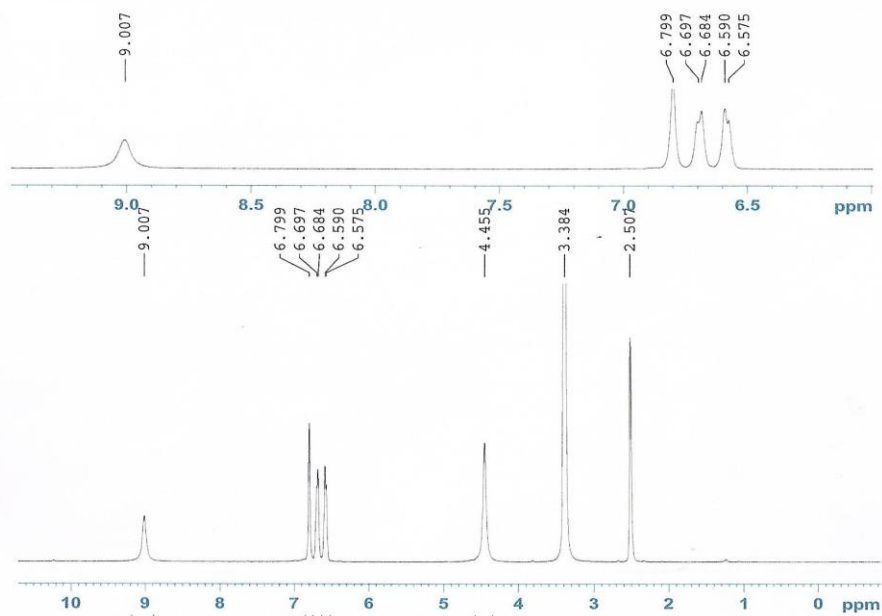


Fig. 5. <sup>1</sup>H NMR spectrum of the zinc complex

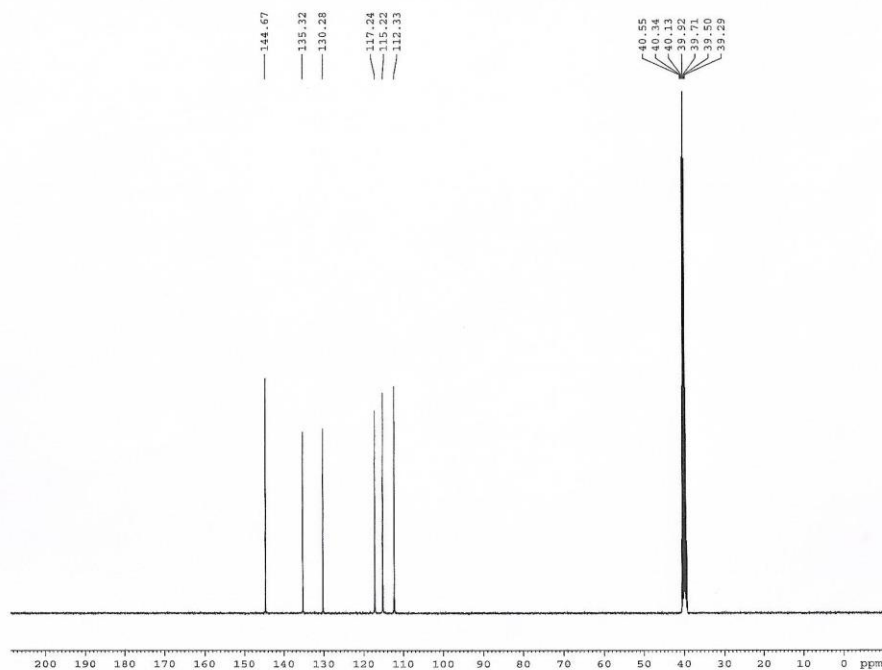


Fig. 6.  $^{13}\text{C}$  NMR spectrum of the ligand

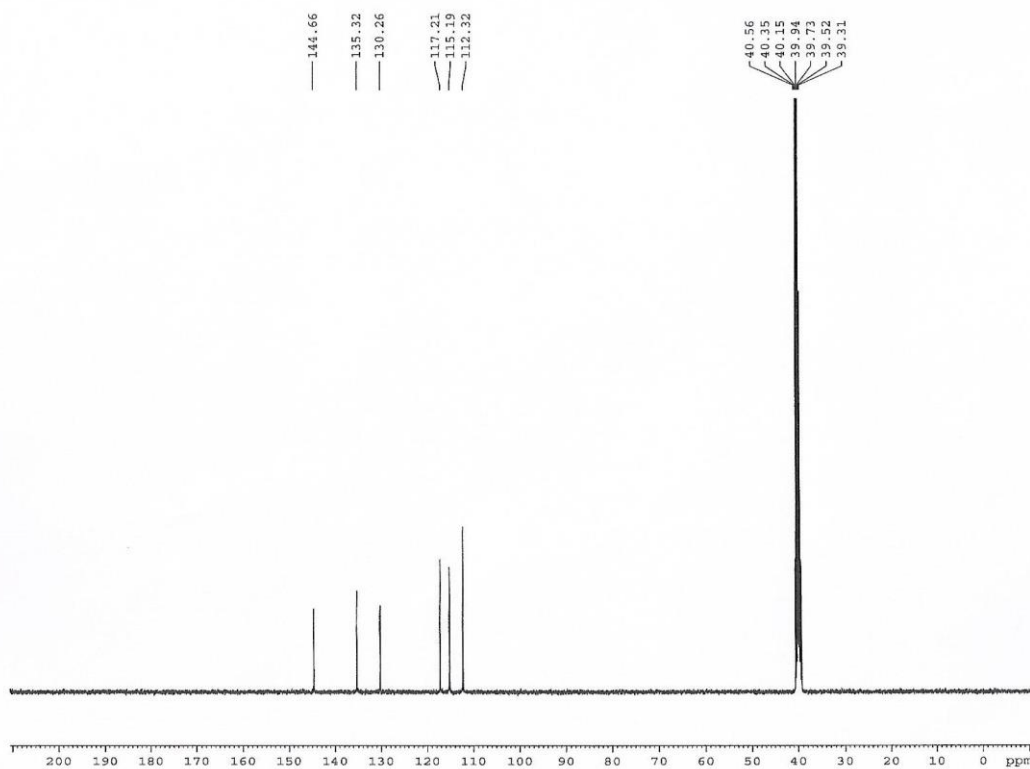
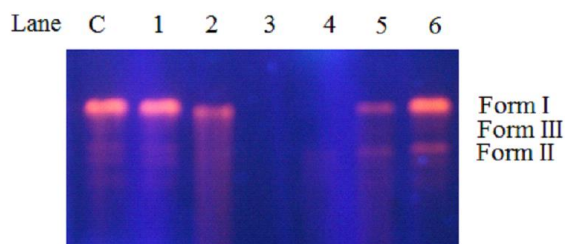


Fig. 7.  $^{13}\text{C}$  NMR spectrum of the zinc complex

### Deoxyribonucleic acid (DNA) cleavage study



**Fig. 8.** Gel electrophoretic pattern of pUC18DNA induced by hydrogen peroxide and binuclear complexes: lane C: pUC18DNA alone; lane 1: ligand + hydrogen peroxide; lane 2: pUC18DNA + Mn binuclear complex + hydrogen peroxide; lane 3: pUC18DNA +Cu binuclear complex + hydrogen peroxide; lane 4: pUC18DNA +Ni binuclear complex + hydrogen peroxide; lane 5: pUC18DNA +Zn binuclear complex + hydrogen peroxide; lane 6: pUC18DNA +Cr binuclear complex + hydrogen peroxide.

**Cleavage of plasmid pUC18 DNA.** DNA cleavage study was analyzed by the electrophoresis method (Figure 8). While conducting electrophoresis for plasmid DNA, the migration for super coiled form was fastest (Form I). Supercoils became slower moving open circular forms if one strand was cleaved (Form II). A linear nicked form was generated and migrated in between if both strands were cleaved (Form III). The different binding affinity of the complex to DNA was the main factor for DNA cleavage efficiency of the complex. Purified DNA ligase was inhibited by metal chlorides [23]. There was no significant cleavage of DNA for ligand (lane 1) even though on long exposure time. Manganese binuclear complex (lane 2) in the presence of hydrogen peroxide at higher concentration showed cleavage activity. Super coiled DNA (Form I) was cleaved and converted to open circular form (Form II) by the manganese binuclear complex. When compared with other binuclear metal complexes, higher cleavage activity is shown by copper and nickel binuclear complexes in the presence of  $H_2O_2$  (lanes 3&4). Copper and nickel binuclear complexes fully degraded the supercoiled plasmid DNA. If concentration was increased, it caused degradations. Formation of a redox couple of the metal ions and its behavior led to this degradation. The functional group -OH can cleave the DNA by combining with the hydrogen atom present in the deoxyribose sugar. Copper ions and  $H_2O_2$  produced diffusible hydroxyl radical ( $-OH$ ). It may damage DNA through Fenton type chemistry. Cleavage activity was shown by zinc and chromium binuclear complexes in the presence of  $H_2O_2$ . Zinc and

chromium binuclear complexes in the presence of  $H_2O_2$  (lanes 5&6) showed cleavage activity. Hence, supercoiled DNA (Form I) was converted to open circular form (Form II) [24].

### Antimicrobial activity

**Antimicrobial assay.** Antibacterial activity of copper(II), nickel(II), manganese(II), zinc(II) and chromium(III) complexes was determined by the disc diffusion method. Streptomycin was used as the standard antibiotic. The prepared binuclear Schiff base complexes were tested against bacteria like *Staphylococcus aureus*, *Escherichia coli* and *Klebsiella pneumoniae* bacteria. Glass plates were initially sterilized in an autoclave and were kept inside an air purifier. The respective microbial culture was swabbed into the nutrient agar plates. Then the glass plates were kept inside the incubator at 36 °C for 25 h and the diameter was measured. Metal chelates displayed higher activity compared with the standard. The minimum inhibitory concentration (MIC) values of the synthesized complexes are indicated in table 4. From the results we understood that copper(II) and nickel(II) complexes exhibit high activity towards all microorganisms [25]. The order of bacterial growth inhibition capacity was:  $Cu(II) > Ni(II) > Mn(II) > Zn(II) > Cr(III)$ . The binuclear complexes had larger MIC values against growth of microorganisms compared with the standard. Chelation theory can be used to explain the improvement of activity of the copper binuclear complex. [26]. Low concentration of the compound (500 ppm) is good enough to bring out an effective inhibition against the chosen bacteria [27]. The activity of the complexes depends on size, charge distribution, shape of the metal ions. Mn(II) metal complexes showed moderate antibacterial property [28]. The Zn(II) complex exhibited low activity against the species [29]. The Cr(III) complex exhibited lower activity against microbes compared with the other metals [30].

### CONCLUSION

From the molar conductance measurements, IR, UV, CV, EPR, and NMR spectra of the binuclear complexes, the above mentioned structure can be confirmed and complexes are octahedral. The molar conductance measurements revealed that the synthesized complexes are non-electrolytic in nature.



**Table 4.** Antibacterial activity of the binuclear complexes

Compounds	<i>K. pneumonia</i> (mm)				<i>E. coli</i> (mm)				<i>S. aureus</i> (mm)			
	Concentration ( $\mu\text{g/ml}$ )											
	25	50	75	100	25	50	75	100	25	50	75	100
[Cu <sub>2</sub> (C <sub>30</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub> Cl <sub>4</sub> )]	11	14	16	19	12	12	16	18	11	14	18	19
[Ni <sub>2</sub> (C <sub>30</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub> Cl <sub>4</sub> )]	11	12	15	18	12	14	15	17	10	12	17	18
[Mn <sub>2</sub> (C <sub>30</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub> Cl <sub>4</sub> )]	12	13	14	17	11	14	14	16	11	13	16	17
[Zn <sub>2</sub> (C <sub>30</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub> Cl <sub>4</sub> )]	10	11	12	14	11	12	12	14	11	12	13	14
[Cr <sub>2</sub> (C <sub>30</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub> Cl <sub>4</sub> )]	10	10	11	13	10	11	11	13	10	11	13	13

The novel copper(II), nickel(II), manganese(II), zinc(II) and chromium (III) binuclear complexes were synthesized from 3,3'-dihydroxy benzidine and 3-amino coumarin containing NON donors set in different environments. The antibacterial activity of the binuclear Schiff base metal complexes against microbes *Escherichia coli*, *Klebsiella pneumoniae* and *Staphylococcus aureus* was studied by the disc diffusion method. Binuclear copper(II) and nickel(II) complexes have got higher cleavage activity when compared to manganese(II), zinc(II) and chromium (III) binuclear Schiff base metal complexes.

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