

## **Synthesis, Characterization, And Biological Activity Of Schiff Base Complexes Of Cu(II) , Co(II) And Ni(II) Derived From Di-A-Formyl Methoxybis(3pentadecenylphenyl) Methane [DFMPM] And N-Butylamine**

A.Anusha<sup>1</sup>, Isac Sobana Raj \*C<sup>2</sup>., Allen Gnana Raj G<sup>3</sup>.

\*Research Scholar, Department of Chemistry and Research, N.M.C. college, Marthandam-629165 INDIA

\*\*Department of Chemistry and Research, N.M.C.College, Marthandam-629165,INDIA

\*\*\*Department of Chemistry and Research, Scott Christian College(Autonomous), Nagercoil-629003,INDIA

Corresponding Author: A.Anusha

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**ABSTRACT:** The Cu(II) ,Co(II) and Ni(II) -di a -formylmethoxy bis(3-pentadecenylphenyl)methane (DFMPM) and n- Butylamine complex were synthesized and characterized by elemental analysis, conductivity measurements, electronic, infrared, <sup>1</sup>HNMR spectral measurements, biological studies and DNA cleavage . The conductance measurements indicate that all the complexes are non-electrolytes. The infrared spectra indicate the coordination of imino nitrogen, M-N and M-O bonds. UV visible spectra could not provide structural details of these complexes. <sup>1</sup>HNMR data are consistent with IR spectral data. The results indicate that both Cu(II) Co(II) and Ni(II) ions are octa coordinated and have moderate biological activity.

**KEYWORDS:** n-butylamine , Cardanol, Epichlorohydrin, Formaldehyde, Schiffbase.

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### **I. INTRODUCTION**

Schiff base complexes have been studied extensively because of their attractive chemical and physical properties and wide range of application in numerous scientific areas. The design and synthesis of macrocyclic Schiff base complexes are currently attracting considerable attention since they can be used as supra molecular devices and sensors and contrast agents in magnetic resonance imaging. DFMPM is prepared from cardanol using formaldehyde, epichlorohydrin and sodium periodate in three stages. DFMPM formed Schiff base ligand with aniline. The present investigation involves the synthesis and characterisation of the Schiff base complexes of Cu(II),Co(II) and Ni(II) with Schiff base ligand. The results indicate that both Cu(II) ,Co(II) and Ni(II) complexes are octa coordinated having moderate biological activity.. XRD and SEM analysis indicates the complexes are nano crystalline in nature.

#### **1.1 Materials and physical measurements**

Cardanol was obtained from M/S Satya Cashew, Chennai, India. Formaldehyde (37% solution) hydrochloric acid, epichlorohydrin, 2-aminothiophenol, sodium hydroxide and other chemicals used were of AR grade quality obtained from Merk Chemicals. All the solvent used was purified by standard method. The micro analytical data (C, H, N) were collected using Perkin Elmer 2400 instrument. The metal ion intake were estimated by standard methods.

IR spectra were obtained using PE IR spectrum instrument model : system 2000. <sup>1</sup>HNMR spectra were obtained using AMX-300 MHz, FT NMR Spectrometer. Conductance measurements were obtained using systronics-305 conductivity meter. Electronic spectra of the ligands and its complexes was obtained using Perkins Elmer Lamda-25 UV-visible spectrometer in the range of 200-1100 nm. Surface morphological studies was obtained using JSM-5610 scanning electron microscope.HT-29(colon cancer) cell line was initially procured from National Centre for cell sciences, Pune.

#### **1.2 Preparation of Schiff base Ligand(L) with DFMPM with n- butylamine**

The Schiff base Ligand(L) were prepared by mixing equimolar ethanolic solution of DFMPM and 1,4-diaminobutane in ethanol and refluxed for 2 hours and then cooled the mixture and Schiff base was separated and recrystallized from ethanol and washed thoroughly with diethyl ether. [fig 1]

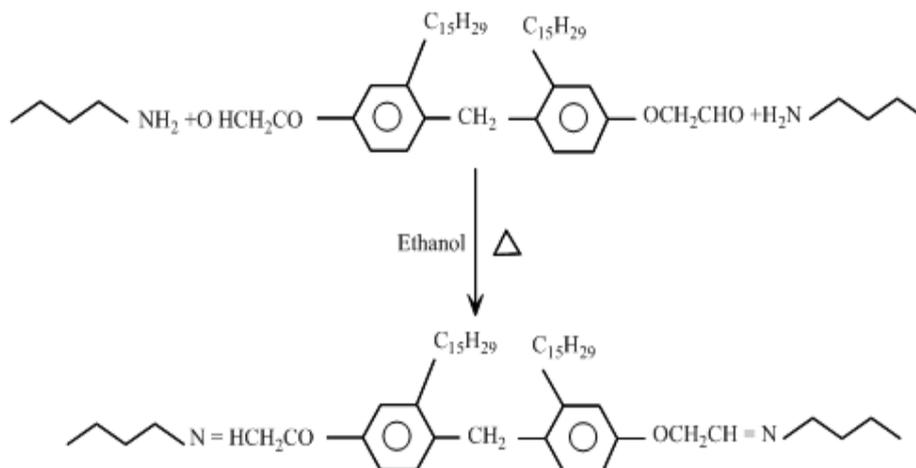


Fig 1 preparation of Schiff base ligand

### 1.3 Preparation of Schiff base metal complexes.

Schiff base complexes of Ligand(L) were prepared by the addition of hot ethanolic solution (60°C) of Ligand(L) and aqueous solution nitrates of Cu(II), Co(II) and Ni(II) ions in drop by drop in 2:1 molar ratio. The mixture was stirred for 12 hours the resulting solution was concentrated on a water bath and allowed to cool. The solid product formed was separated by filtration and washed thoroughly by ethanol and then by diethyl ether. The solid complexes were dried in vacuum.[1-3]

## II. RESULTS AND DISCUSSION

All the metal complexes prepared above are coloured and are stable towards air and have high melting point. The complexes are insoluble in water and common organic solvents but are soluble in DFM and DMSO.

### 2.1 Elemental analysis

The analytical data suggested that all the complexes are mononuclear with the ligand coordinated to the central metal atom. The metal to ligand ratio in all the complexes was 1:2. The details are given in table 1.

Table 1 Physical characteristics and analytical data of the complexes.

Ligand/ complexes	colour	Yield	Empirical formula	Molecular weight	Melting point	Elemental analysis		
						C	H	N
Ligand(L) C <sub>55</sub> H <sub>106</sub> N <sub>2</sub> O <sub>2</sub>	Brown	65	C <sub>55</sub> H <sub>106</sub> N <sub>2</sub> O <sub>2</sub>	826	225	79.90 (79.88)	12.83 (12.53)	4.56 (4.24)
[Cu(L)(NO <sub>3</sub> ) <sub>2</sub> ]	Light blue	59	CuC <sub>110</sub> H <sub>106</sub> N <sub>6</sub> O <sub>10</sub>	1839.54	>250	71.77 (71.10)	11.52 (11.25)	4.56 (4.10)
[Co(L)(NO <sub>3</sub> ) <sub>2</sub> ]	Brown	62	CoC <sub>110</sub> H <sub>106</sub> N <sub>6</sub> O <sub>10</sub>	1834.9	>250	71.93 (71.88)	11.55 (11.42)	4.57 (4.25)
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ]	Brown	57	NiC <sub>110</sub> H <sub>106</sub> N <sub>6</sub> O <sub>10</sub>	1834.69	>250	71.93 (71.75)	11.55 (11.28)	4.58 (4.29)

### 2.2 Molar conductivity

The molar conductivity values are given in Table 2. The molar conductivity values were in the range of 14 – 25 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. It showed that all the complexes are non electrolytes because their conductivity values were low.[4,5]

Table 2 Molar conductance data of ligand and its complexes

Ligand/ complexes	Molar conductivity Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	Nature
Ligand(L) C <sub>55</sub> H <sub>106</sub> N <sub>2</sub> O <sub>2</sub>	19	Non - electrolyte
[Cu(L)(NO <sub>3</sub> ) <sub>2</sub> ]	17	Non - electrolyte
[Co(L)(NO <sub>3</sub> ) <sub>2</sub> ]	16	Non - electrolyte
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ]	14	Non - electrolyte

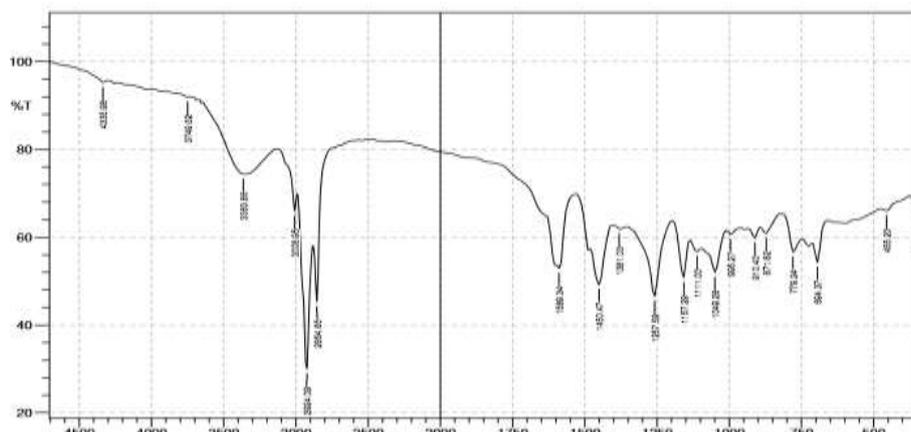
### 2.3 IR Spectral studies of Ligand(L) and its complexes

The IR spectral data of the Ligand(L) and its complexes given in Table 3 and the respective spectra. Comparison of IR spectra of Schiff base ligand with that of its metal complexes has been adopted to determine

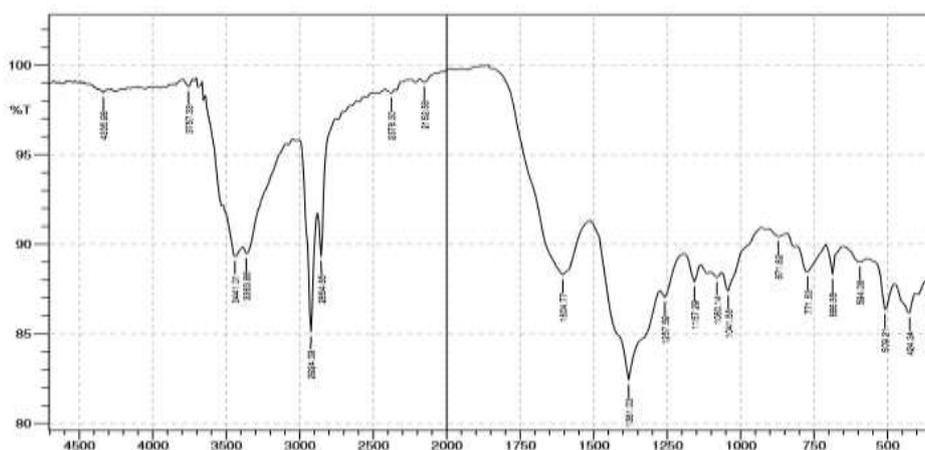
the coordinating atoms of the ligand to metal ion.[6,7] The strong band at  $1589\text{ cm}^{-1}$  is characteristics of the azomethin nitrogen present in the Schiff base Ligand(L). This was shifted to  $1604\text{ cm}^{-1} - 1627\text{ cm}^{-1}$  in the complexes which indicates the coordination of the metal to the azomethine nitrogen. The metal complexes showed broad bands at  $3371\text{ cm}^{-1} - 3441\text{ cm}^{-1}$  which is absorption of  $\nu_{(\text{O-H})}$  vibration. This indicates that the coordinated is lattice water. The spectrum of the Schiff base ligand showed a strong band its  $2924\text{ cm}^{-1}$  which was assigned to  $\nu_{(\text{C-H})}$  stretching vibration. This was shifted to  $2924\text{ cm}^{-1} - 2931\text{ cm}^{-1}$  region in all the complexes. The spectrum of Schiff base ligand showed a absorption band at  $2854\text{ cm}^{-1}$  which was assigned to  $\nu_{(\text{C-O})}$  vibration. This was shifted to  $2792\text{ cm}^{-1} - 2854\text{ cm}^{-1}$  region in all the complexes that the oxygen atom  $\nu_{(\text{M-O})}$  and  $\nu_{(\text{M-N})}$  were observed in the Far infrared region. These bands are absent in the spectra of the Schiff base ligand. The imine peak in the metal complexes change in Schiff's compared to the ligand indicating coordination of the imine nitrogen atom to the metal ion due to coordination. The coordinated nitrate group with the central metal atom  $617\text{ cm}^{-1} - 771\text{ cm}^{-1}$  is assigned to  $\nu_{(\text{M-N})}$  band and  $354\text{ cm}^{-1} - 509\text{ cm}^{-1}$  is assigned to  $\nu_{(\text{M-O})}$  bond.

**Table 3 Selected FT-IR frequencies ( $\text{cm}^{-1}$ ) of the Ligand(L) and its complexes**

Ligand/complex	$\nu_{\text{O-H}}(\text{H}_2\text{O})$	$\nu_{(\text{C-O})}$	$\nu_{(\text{C-H})}$	$\nu_{(\text{C=N})}$	$\nu_{(\text{M-N})}$	$\nu_{(\text{M-O})}$
Ligand(L) $\text{C}_{55}\text{H}_{106}\text{N}_2\text{O}_2$	3008	2854.6	2924	1589.34	-	-
$[\text{Cu}(\text{L})(\text{NO}_3)_2]$	3441.01	2854.65	2924.09	1604.77	771	509
$[\text{Co}(\text{L})(\text{NO}_3)_2]$	3394.72	2792.93	2931.8	1627.92	686	424
$[\text{Ni}(\text{L})(\text{NO}_3)_2]$	3371.57	2854.65	2931.8	1658.78	617	354



**Fig 2 FT-IR Spectrum of Schiff base Ligand(L)**



**Fig 3 FT-IR Spectrum of Cu(II) complex of Ligand(L)**

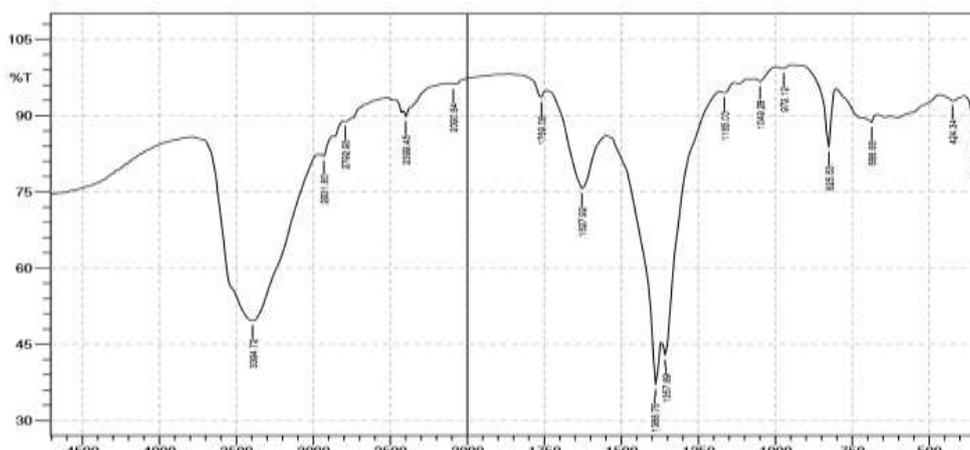


Fig 4 FT-IR Spectrum of Co(II) complex of Ligand(L)

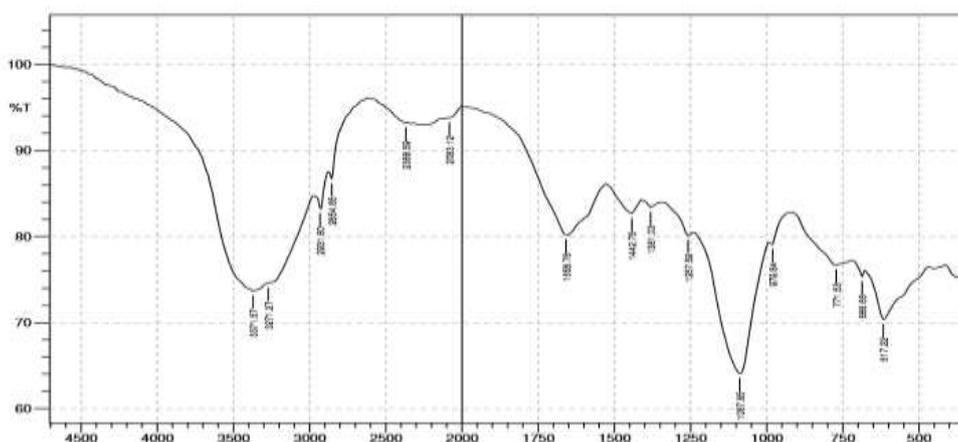


Fig 5 FT-IR Spectrum of Ni(II) complex of Ligand(L)

## 2.4 Electronic Spectra

The electronic spectral data are given in Table 8.5 and the respective spectra and showed a broad band at 231 nm which is assigned to  $\pi - \pi^2$  transition of the C = N chromophore. On complexation this band was shifted to lower wave length suggesting the coordination of imine nitrogen with central metal ion. The uv-visible spectra of Cu(II) complex showed absorption bands at 259 nm, 272 nm and 278 nm giving an octahedral geometry with field transition  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \rightarrow {}^2E_{2g}$  respectively. The broadness and position of the band favours distorted octahedral geometry for Cu(II) complex due to Jahn-Teller effect. The uv-visible spectrum of Co(II) and Ni(II) complexed showed absorption bands at 275 nm, 285 nm, 297 nm, 212 nm, 222 nm and 252 nm respectively suggesting octahedral geometry for the complexes.[8-10]

## 2.5 ${}^1\text{H}$ NMR spectra

The  ${}^1\text{H}$ NMR spectrum of Schiff base Ligand(L) and respective spectra shown in the (Fig 6). The  ${}^1\text{H}$ NMR spectra of the ligand shows a peak at ( $\delta = 8.32$  ppm) is due to the azomethine protons of the CH = N group. A multiplet signal at ( $\delta = 6.51$  ppm – 6.532 ppm) is due to substituted aromatic ring protons. The multiplet at ( $\delta = 5.096$  ppm – 5.157 ppm) and ( $\delta = 3.520$  ppm – 3.746 ppm) olefinic protons of the side chain and O-CH<sub>2</sub> group is respectively.[11]

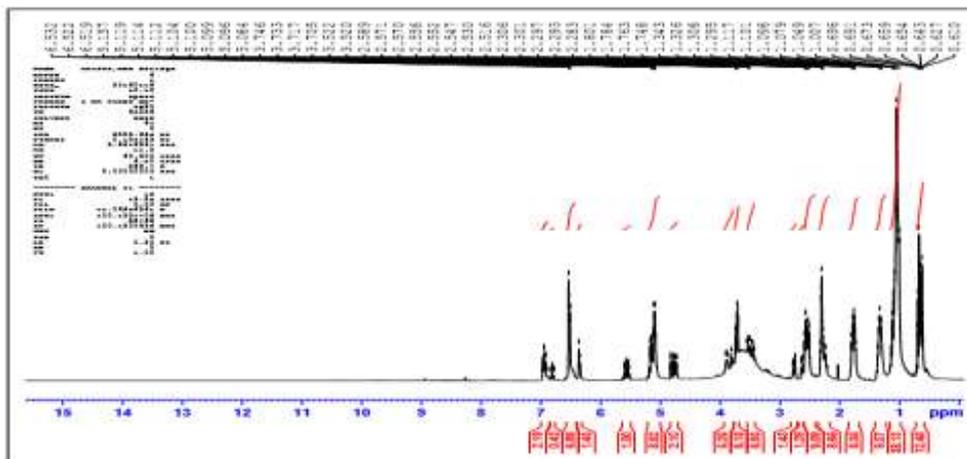


Fig 6 <sup>1</sup>H NMR Spectrum of Schiff base Ligand(L)

The <sup>1</sup>H NMR spectrum of Cu(II) complex of Ligand(L) shows the (Fig 7). The <sup>1</sup>H NMR spectra of the Cu(II) complex peak at ( $\delta = 8.20$  ppm) is due to the azomethine protons of the CH = N group. A multiplet signal at ( $\delta = 6.736$  ppm – 6.804 ppm) is due to substituted aromatic ring protons. A signal at ( $\delta = 5.346$  ppm – 5.380 ppm) and ( $\delta = 4.150$  ppm) olefinic protons of the side chain and O-CH<sub>2</sub> group is respectively. The signal in the range ( $\delta = 0.894$  ppm – 0.949 ppm) were due to the presence of saturated –CH<sub>2</sub> –CH<sub>2</sub>- group of both ligand and its complexes.[12]

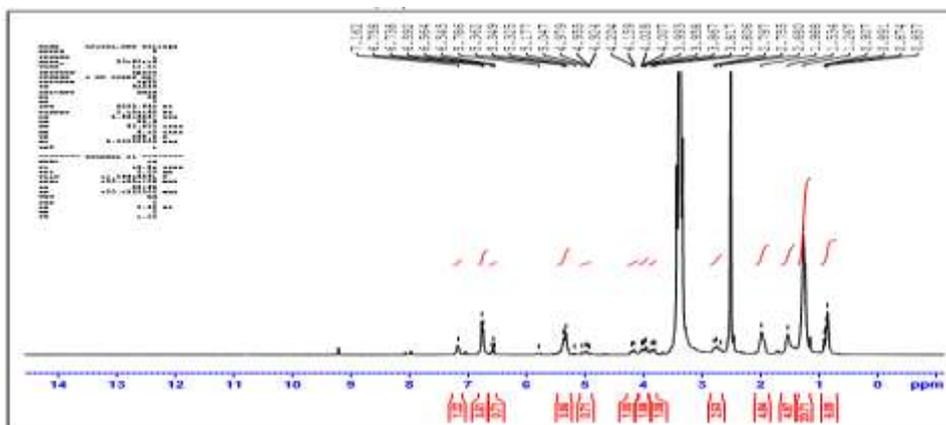


Fig 7 <sup>1</sup>H NMR spectrum of Cu(II) complex of Ligand(L)

Based on the observations in elemental analysis, IR spectra, uv-visible spectra and <sup>1</sup>H NMR spectral studies, the proposed structure of metal Schiff base Ligand and complexes. [M(L)(NO<sub>3</sub>)<sub>2</sub>] are given in (Fig 8)

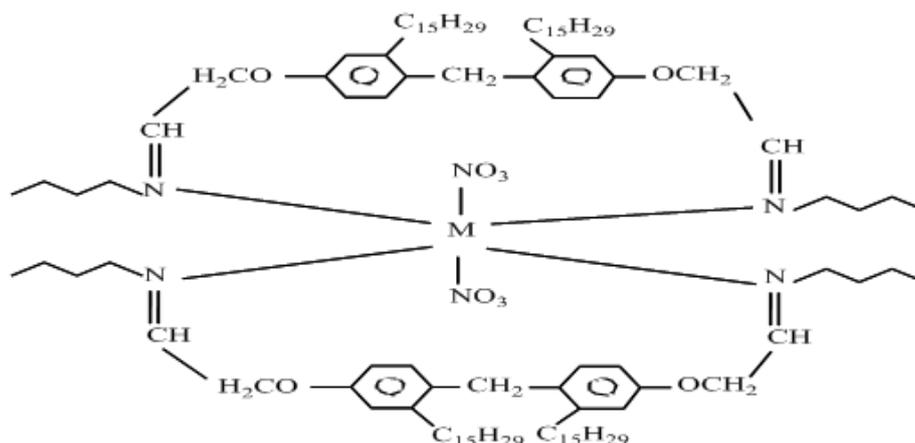


Fig 8 General Structure of Schiff base complexes of Cu(II), Co(II) and Ni(II)  
M = Cu(II), Co(II) and Ni(II)

## 2.6 XRD Analysis

The powder XRD for the Cu(II) complexes were performed. The XRD data are the respective diffractogram for the complexes are given in (Fig 9). It is evident that the strong broad peaks confirm the complexes formation and the appearance of large feeble peaks indicate the complexes to be micro crystalline. The grain size of the complexes was calculated using Scherrer's formula. The calculated grain size of the complexes is in the range of 1.72nm. These values suggested that the complexes are in nano crystalline state.[13]

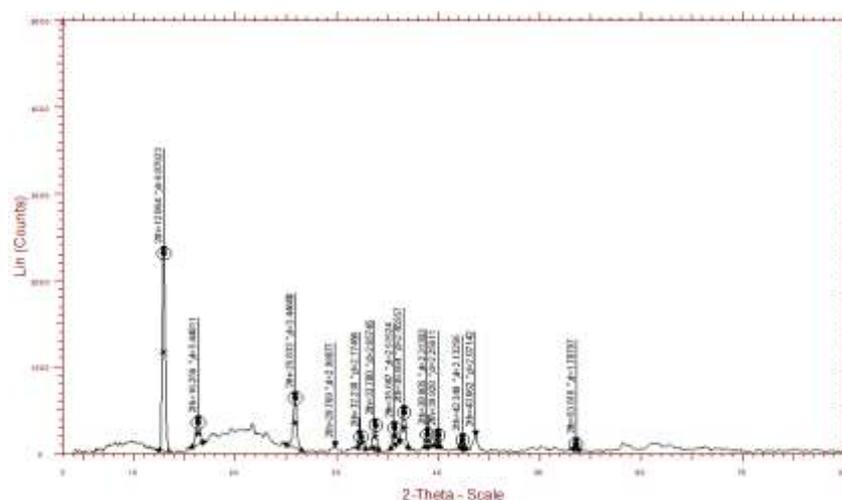


Fig 9 XRD spectrum of Cu(II) complex of Ligand(L)

## 2.7 SEM Analysis

The surface morphology of the complexes was studied using JSM 5610 scanning electron microscope. The SEM image of Cu(II) complex is given (Fig10). The SEM image showed that the complexes is nanocrystalline in nature. Careful examination of the single crystal of the complexes. The SEM images showed that all the complexes are nanocrystalline in nature showed rough, granular and pitted surface.

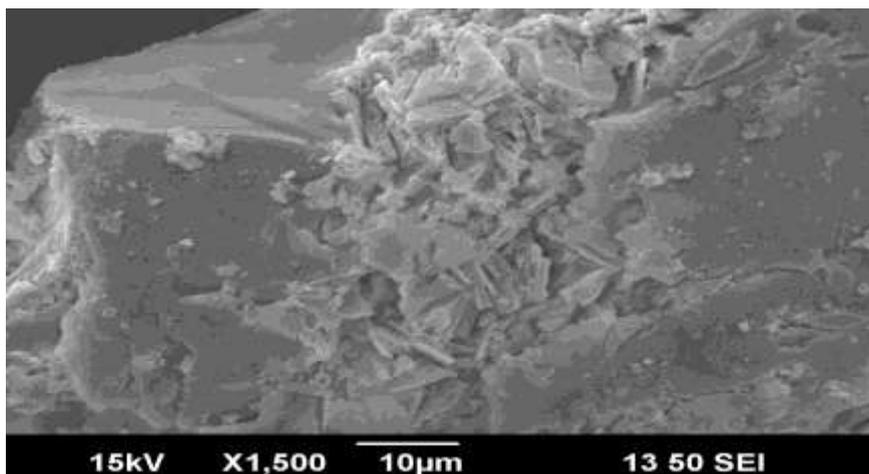


Fig 10 SEM image of Cu(II) complex of Schiff base Ligand(L)

## III. BIOLOGICAL SCREENING

### 3.1 Antimicrobial activity

The results of antibacterial activity substantiate the findings of earlier researchers that biologically active compounds become active and less biologically active compounds become more active upon coordination. Such enhancement in biological activity of metal complexes can be explained on the basis of Overtone's concept and chelation theory. The antimicrobial activity significantly increased on coordination. The present investigation suggest that all the metal complexes of the ligand bearing metal ion, have comparatively more biological activity. This antibacterial activity serves as a basis for the chemical modification directed towards the development of new class of antimicrobial agents.[14-15]

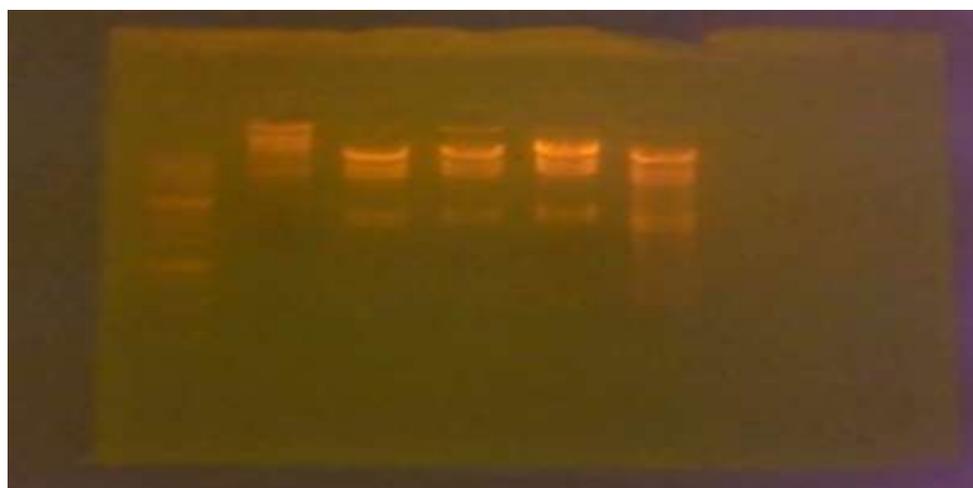
**Table 4 Antimicrobial activities of standard Ligand(L) and complexes**

Ligand/complexes	Media	Antibacterial activity(mm)				Antifungal activity(mm)	
		Staphylococcus aureus	Streptococcus mutans	E.coli	Klebsilla pneumonia	Aspergillus niger	Aspergillus flavus
Ligand(L) C <sub>55</sub> H <sub>106</sub> N <sub>2</sub> O <sub>2</sub>	Muller Hinton Agar Bacteria/ Antimytotic Agar for Fungi	7	7	7	7	7	7
[Cu(L)(NO <sub>3</sub> ) <sub>2</sub> ]		8	8	7	7	14	17
[Co(L)(NO <sub>3</sub> ) <sub>2</sub> ]		13	13	17	15	7	7
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ]		7	8	7	7	7	7
PC(Chloram Phenicaol)		16	16	15	22	-	-

### 3.2 DNA cleavage studies

The DNA cleavage ability of the complexes is monitored by gel electrophoresis. All the metal complexes are able to convert super coiled DNA in to open circular DNA. The results of DNA cleavage are given in Fig 12.

This result revealed the damage of DNA in Co(II) complex could be attributed to the cleavage of DNA. The DNA cleavage activity of the complex is Co(II) with lamda DNA on the basis of results, it is concluded that prominent DNA cleavage activity was observed in the presence of an oxidizing agent H<sub>2</sub>O<sub>2</sub>.



**Fig 11 Gel electrophoresis diagram of the complexes of Ligand (L)**

Lane 1 : DNA + Cu(L) + H<sub>2</sub>O<sub>2</sub>  
Lane 3 : DNA + Ni(L) + H<sub>2</sub>O<sub>2</sub>  
Lane 5 : Marker

Lane 2 : DNA + Co(L) + H<sub>2</sub>O<sub>2</sub>  
Lane 4 : Control DNA  
Lane 6 : DNA + L + H<sub>2</sub>O<sub>2</sub>

### IV. CONCLUSION

Schiff base metal complexes of Cu(II), Co(II) and Ni(II), were synthesized from DFMPM using L-alanine were clearly described and characterized on the basis of analytical and spectral data. The XRD, SEM analysis indicate that the crystals of Schiff base metal complexes of nanocrystalline in nature. . Antibacterial study showed that the complexes of Cu(II), Co(II), and Ni(II). The more active than the complex of Cu(II) complexes. Antifungal activity showed that the complexes of Cu(II), Co(II) and Ni(II) The more active than the complex of Co(II) when compared to other complexes. The DNA cleavage activity of complexes is in the order Cu(II) > Co(II) > Ni(II) > with lamda- DNA.

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