



**SYNTHESIS OF 14-MEMBERED TETRAAZAMACROCYCLIC COMPLEXES
AND THEIR PHYSICO-CHEMICAL CHARACTERIZATIONS
AND BIOLOGICAL SCREENING.**

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ABSTRACT

Complexes of Co(II), Ni(II), and Cu(II) containing macrocyclic tetradentate nitrogen donor (N₄) ligand have been synthesized from the template condensation reaction between substituted benzil and ethylenediamine(EDA) The newly synthesized ligands [N₄L¹] and [N₄L²] and its complexes have been characterized by elemental analyses, molar conductance measurement, magnetic susceptibility measurements, FTIR, electronic and EPR spectral. The spectral data suggested hexa co-ordinated state for these complexes. Conductivity data suggested that they behave as non-electrolytes. Based on spectral studies, an octahedral geometry has been proposed for Co(II), Ni(II) complexes but a distorted octahedral geometry for Cu(II) complexes respectively. The ligand and their complexes have been screened *in vitro* against pathogenic fungi and bacteria to assess their growth inhibiting potential.

KEYWORDS: complexes; N₄- Macrocyclic Schiff bases; Antimicrobial studies.



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INTRODUCTION

During the past few decades macrocyclic chemistry has attracted the attention of both inorganic and bioinorganic chemists. The synthesis of macrocyclic complexes has been a fascinating area of research and growing at a very fast pace owing to their resemblance with naturally occurring macrocycles and analytical, industrial, and medical applications¹⁻³. In view of the above discussion we report in the present paper, a new series of macrocyclic complexes of Co(II), Ni(II), and Cu(II) obtained by template condensation reaction of diamines and substituted benzil has been reported. These complexes were also tested for their *in vitro* antimicrobial activities. Some complexes showed remarkable antibacterial activities.

EXPERIMENTAL

Reagents

All chemicals used were of AR grade, and procured from Sigma-Aldrich. Metal salts were purchased from E-Merck and were used as received.

Preparation of Schiff base N_4 - Macrocyclic Ligand, N_4L^1 ; 2,8-Diphenyl-3,9-di(4-methoxy phenyl)-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene

A mixture of ethylenediamine (0.60g, 0.01mole) in ethanol (40ml) and ethanolic solution of methoxy benzil (2.10g, 0.01mole) and a few drops of conc. HCl were refluxed at 60-70 °C for 2 hours. The completion of reaction was confirmed by the TLC. The resulting solution was kept overnight at room temperature when a light yellow crystalline compound separated out. This was filtered washed with ethanol and dried over P_4H_{10} (yield 80%); M.P. 185-187 °C. Element chemical analysis data are shown in Table 1

Preparation of Schiff base N_4 - Macrocyclic Ligand, N_4L^2 : 2,9-Diphenyl-3,10-di(4-methoxy phenyl)-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene

This ligand was synthesized by refluxing a solution of methoxy benzil (10.5g 0.05mol) in

40ml ethanol with ethanolic solution of 1, 3 diaminopropane (0.60g, 0.05mol.) in the presence of a few drops of conc. HCl for two hours. On cooling the contents overnight a light brown crystalline compound separated out. This was filtered, washed with ethanol and dried P_4H_{10} found 96% yield 1.8g (80%); MP 210-212 °C

Preparation of Metal Complexes

A hot ethanolic solution (30ml) of the required metal salts (0.01mol) was mixed with a hot ethanolic solution (30ml) of the required ligand (0.01mole). This reaction mixture was continuously stirred and refluxed for 3hrs at 60-80 °C. On cooling, a colored complexes separated out, which was filtered, washed with cold ethanol and dried under vacuum over P_4O_{10} .

Physical measurements

The C, H and N were analyzed on Carlo-Erba 1106 elemental analyzer. The Nitrogen and chlorine of the complexes were estimated by Kjeldahl's⁴ and Volhard's⁴ method, respectively. Metal were estimated as metal-oxide gravimetrically⁵. Conductivity measurements in dry dimethylformamide were performed with a conductivity Bridge type ELICO (CM82T). Magnetic susceptibilities were measured at room temperature on a Gouy balance using $CuSO_4 \cdot 5H_2O$ as a calibrante. Diamagnetic corrections were made by using Pascal's constant⁵. Electronic spectra were recorded in DMF on shimadzu UV mini-1240 spectrophotometer. EPR spectra of the Cu (II) complexes were recorded as polycrystalline sample at room temperature E_4 -EPR spectrometer using the DPPH as the g-marker. Infrared spectra of the ligand and corresponding complexes were recorded in the range 4000-200 cm^{-1} with the help of Nicolet - Magna FTIR-500 spectrophotometer as KBr pellets. ¹H NMR spectra were recorded in DMSO- d_6 using TMS as standard on a JEOL FX-90Q spectrometer. The molecular

weights of the complexes were determined by the Rast Camphor Method⁴.

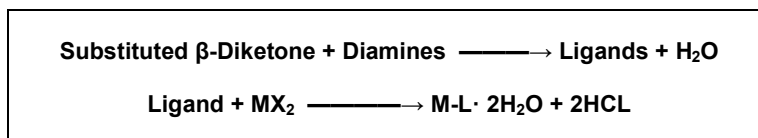
Biological activity

The results of the antibacterial and antifungal study are given in Table-5. The concentration of the compound used for testing was 01mg/ml in DMF (inactive). Grisofulvin and Norfloxacin were the standards used against fungi and bacteria respectively. In a typical procedure, a well was made on the agar medium inoculated with micro-organisms. The well was filled with the test solution using a micropipette and the plate was incubated at 37 °C for 48hrs. During this period, the test solution diffused and the growth of micro-organisms was affected. The antimicrobial activity was estimated on the basis of size of inhibition zone around the cups⁶.

RESULTS AND DISCUSSION

Preparation of ligand

The formation of ligand may be represented as



IR spectra

The IR spectrum of the free ligand was compared with the spectra of the metal complexes. The IR spectrum of N₄L¹ and N₄L² showed a strong intensity band at 1620–1630cm⁻¹ in the free ligand was assigned to the $\nu_{(C=N)}$ stretch of the azomethine group⁸. This band shifted to the lower wave number side in all of the complexes by about 15–25cm⁻¹ (1595–1615cm⁻¹) suggesting the participation of azomethine nitrogen in bonding with metal ions⁹. In the present case $\nu_{(C=C)}$, and $\nu_{(C-H)}$ stretch was observed at 1500–1565cm⁻¹ and 2900–2940cm⁻¹, remaining unaltered in the metal complexes. Metal ligand vibration are generally observed in the far IR region and usually nonligand bands observed in the complexes in the regions of 510–550cm⁻¹ and 400–440cm⁻¹ were assigned to $\nu_{(M-O)}$, $\nu_{(M-N)}$

The analytical data showed that all of the complexes had 1:1 stoichiometry (Table–1). The molar conductance values were too low to account for any dissociation of the complexes in DMF, indicating the nonelectrolytic nature of the complexes⁷. The ligand behaves as a tetradentate co-ordinate through nitrogen donor atoms (Figure 2). All the cobalt(II), nickel(II) and copper (II) complexes are paramagnetic in nature. The analytical data, electronic spectra and magnetic susceptibility agree well with the proposed composition of formed complexes. All the complexes have shown good solubility in the organic solvents, but they were found insoluble in water, benzene, and acetone. Thus, the complexes may be formulated as M[N₄L¹].2H₂O and M[N₄L²].2H₂O (where M= Co(II), Ni(II) and Cu(II); N₄L¹ and N₄L²).

stretching vibrations respectively^{10–13}. Bands at 520–525cm⁻¹ were $\nu_{(O-H)}$ strong evidence for the participation of water molecule in co-ordination¹⁴.

¹H-NMR spectra of ligands N₄L¹ and N₄L²

The ¹H NMR spectra of the compounds were obtained in d₆-DMSO at room temperature using TMS as an internal standard. The ¹H-NMR, spectrum of both the ligands N₄L¹ and N₄L² are presented in Table-6. The spectrum gave no signal corresponding to primary amine protons. This suggests the derivatization of carbonyl groups. A multiplet in the δ range 7.29–7.62ppm (m, 5H) is assigned to aromatic ring proton, 6.80–7.51(m, 4H), for substituted (OCH₃) aromatic protons, 3.73ppm(s, 6H) for –OCH₃, and another singlet

3.91ppm (s, 4H) to $-\text{CH}_2-\text{CH}_2-$ and 3.55(m, 6H) to $-\text{CH}_2\text{CH}_2\text{CH}_2-$

Visible spectra of the metal complexes

The electronic spectra of the Co(II), Ni(II) and Cu(II) complexes were recorded in DMF solvent (10^{-3}) at RT and the spectral data are given in Table-1

Cobalt(II) complexes

The macrocyclic cobalt(II) complexes appeared in the range expected for the three unpaired electrons. The electronic spectra¹⁵ of Co(II) complexes gave three bands in the regions 8635-8680 cm^{-1} , 16393-16977 cm^{-1} and 19960-20000 cm^{-1} which may be ascribed to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})\nu_1$, ${}^4\text{T}_{2g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})\nu_2$, and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})\nu_3$ transitions respectively, consistent with an a high-spin octahedral geometry around the cobalt(II) ion^{16,17}.

Nickel(II) complexes

The macrocyclic complexes of nickel(II) complexes shows three distinct bands, consistent with the spectral features of octahedral nickel(II) complexes. The broad band around 11904-12135 cm^{-1} and two intense bands around 17301-17985 cm^{-1} and 26666-27027 cm^{-1} may reasonably be assigned to ${}^3\text{T}_{2g}(\text{F}) \rightarrow {}^2\text{A}_{2g}(\text{F})\nu_1$, ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{A}_{2g}(\text{F})\nu_2$, and ${}^3\text{T}_{1g}(\text{P}) \rightarrow {}^3\text{A}_{2g}(\text{F})\nu_3$ transitions respectively. These transitions reveal that the nickel complexes possess an octahedral geometry and D_{4h} symmetry¹⁸

Copper(II) complexes

The electronic spectra of macrocyclic copper (II) complexes of both the ligands show a broad band maximum (Table 2) in the region 19047-19417 cm^{-1} with a shoulder in the region¹² 16129-16339 cm^{-1} which can unambiguously be assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}\nu_2$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_{2g}\nu_3$ transition. The broadness of the band may be due to Jahn-Teller distortion¹⁹. These observations suggest that the complexes have distorted octahedral structures (Fig. - 2)

Magnetic susceptibility measurements

The magnetic moment value of Cu(II) complexes is 1.91-1.92BM which suggests a distorted octahedral arrangement²⁰ around the metal ion. The magnetic moment of Co(II) complexes is 4.93-4.95BM which suggests the high spin co-ordinated octahedral arrangement²¹ of ligand molecules around the metal ion. The Ni(II) complexes has magnetic moment values in range 2.97-3.15 BM indicating a spin free octahedral²² configuration.

Ligand field parameter

Various ligand field parameters were calculated for Co(II) and Ni(II) complexes and listed in Table-2. The values of Dq and B were calculated by using Orgel diagram²³. The ratio of ν_2/ν_1 was considered for the calculation of B. The nephelauxetic parameter β was readily obtained by using the relation $\beta = B_{(\text{complex})} / B_{(\text{free ion})}$. Where B(Free ion) for Ni(II) is 1041 cm^{-1} and Co(II) is 971 cm^{-1} . The β values lying in the range of 0.56-0.61 indicate the appreciable covalent character of metal ligand "σ" bond²⁴.

Electron paramagnetic spectra

The X-band EPR spectrum of the polycrystalline copper complex recorded at room temperature shows a well resolved hyperfine splitting and exhibits two different g-values indicating the magnetic anisotropy in the complex. The absence of a half field signal, observed in the spectrum at 3200G due to $M_s = \pm 2$ transitions, ruling out any Cu-Cu interaction²⁵. In the present copper complexes the observed g-tensor values are $g_{\parallel} = 2.391-2.17$, $g_{\perp} = 2.084-2.035$ (Table-4), which suggest that this complex has a distorted octahedral geometry. The EPR parameters of the complex also coincide well with related systems for which it was suggested that the complexes have a distorted octahedral geometry and that the systems are axially. $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ which measured the exchange interaction between the metal centers in a polycrystalline solid, has been calculated. According to Hathaway²⁶ if the $G > 4$, the

exchange interaction is negligible but, $G < 4$ indicate considerable exchange interaction in the solid complex. Presently, the copper(II) complexes the G values are in range 4.7—4.8 which suggest that the local tetragonal axes are aligned parallel or are slightly misaligned and are consistent with a $d_{x^2-y^2}$ ground state.

ANTIMICROBIAL SCREENING

Antibacterial and antifungal activity

The antimicrobial screening data show that the compounds exhibit antimicrobial properties, and it is important to note that the metal chelates exhibit more inhibitory effects than the parent ligands. From Table-5 it is clear that the zone of inhibition is much larger for metal complexes against the gram positive bacteria (*E. Coli*) and gram negative bacteria (*S. Aureus*). The increased activity of the metal chelates can be explained on the basis of chelation theory²⁷. It is known that chelation tends to make the ligand act as more powerful and potent bactericidal agents, thus killing more of the bacteria than the ligand. It is observed that, in a complex, the positive

charge of the metal is partially shared with the donor atoms present in the ligands, and there may be n-electron delocalization over the whole chelating²⁸. This increases the lipophilic character of the metal chelate and favors permeation through the lipid layer of the bacterial membranes. There are other factors which also increase the activity, which are solubility, conductivity, and bond length between the metal and the ligand. The results of fungicidal screening show that Cu(II) and Ni(II) complexes were highly active than the free ligand against fungi. The mode of action may involve the formation of a hydrogen bond through the azomethane nitrogen atom with the active centers of the cell constituents, resulting in interference with the normal cell process. The variation in the effectiveness of different compounds against different organisms depends either on the impermeability of the cells of the microbes or the difference in ribosomes of microbial cells²⁹. It has also been proposed that concentration plays a vital role in increasing the degree of inhibition; as the concentration increases, the activity increases.

Table-1
Analytical data for the Ligands $[N_4L^1]$, $[N_4L^2]$
and its Co(II), Ni(II) and Cu(II) complexes

Compounds	Mol. Wt	Yield (%)	MP (°C)	Analysis found(calculated %)				Molar conductance $\Omega^{-1}cm^2 mol^{-1}$	μ_{eff} BM
				C	H	N	M		
N_4L^1	546.32	60	185	74.70 (74.72)	9.15 (9.16)	10.25 (10.29)	-	-	
N_4L^2	574.34	65	219	75.23 (75.25)	9.4 (9.42)	9.68 (9.7)	-	-	
$Co[N_4L^1]2H_2O$	641.23	69	>300	63.68 (63.7)	8.42 (8.45)	8.68 (8.7)	9.19 (9.2)	18.2 4.95	
$Ni[N_4L^1]2H_2O$	640.99	72	298	63.69 (63.70)	7.78 (7.80)	8.71 (8.73)	9.13 (9.15)	16.15 3.15	
$Cu[N_4L^1]2H_2O$	645.84	63	275	63.18 (63.2)	8.32 (8.34)	8.67 (8.69)	9.83 (9.85)	9.8 1.92	
$Co[N_4L^2]2H_2O$	669.25	81	>300	64.6 (64.62)	8.66 (8.68)	8.33 (8.35)	8.92 (8.94)	11.2 4.93	
$Ni[N_4L^2]2H_2O$	669.01	54	285	64.55 (64.57)	8.05 (8.07)	8.35 (8.37)	8.75 (8.77)	16.4 2.97	
$Cu[N_4L^2]2H_2O$	673.86	76	299	64.15 (64.17)	8.6 (8.62)	8.31 (8.32)	9.38 (9.4)	16.3 1.91	

Table- 2
Electronic spectral band with ligand field parameters of the Co(II), Ni(II) and Cu(II) complexes in DMF(10⁻³) solvent

Complexes	Absorption (cm ⁻¹) bands	Assignments	Dq cm ⁻¹	B cm ⁻¹	β cm ⁻¹	v ₂ /v ₁	LFSE KJ mol ⁻¹
Co[N ₄ L ¹] ₂ H ₂ O	8680, 16977,	⁴ T _{1g} (F) → ⁴ T _{2g} (F)v ₁	829.7	731.8	0.75	1.95	14.22
	20000	⁴ T _{2g} (F) → ⁴ A _{2g} (F)v ₂					
		⁴ T _{1g} (F) → ⁴ T _{1g} (P)v ₃					
Ni[N ₄ L ¹] ₂ H ₂ O	12135, 17985,	³ T _{2g} (F) → ² A _{2g} (F)v ₁	1213.5	573.8	0.56	1.48	20.80
	27027	³ T _{1g} (F) → ³ A _{2g} (F)v ₂					
		³ T _{1g} (P) → ³ A _{2g} (F)v ₃					
Cu[N ₄ L ¹] ₂ H ₂ O	16339, 19047	² B _{1g} → ² B _{2g} v ₂	1633.6	-	-	-	28.02
	25665	² B _{1g} → ² E _{2g} v ₃					
Co[N ₄ L ²] ₂ H ₂ O	8635, 16393,	⁴ T _{1g} (F) → ⁴ T _{2g} (F)v ₁	775.8	696.5	0.71	1.89	13.30
	19960	⁴ T _{2g} (F) → ⁴ A _{2g} (F)v ₂					
		⁴ T _{1g} (F) → ⁴ T _{1g} (P)v ₃					
Ni[N ₄ L ²] ₂ H ₂ O	11904, 17301	³ T _{2g} (F) → ² A _{2g} (F)v ₁	1190.1	550.3	0.53	1.45	20.41
	26666	³ T _{1g} (F) → ³ A _{2g} (F)v ₂					
		³ T _{1g} (P) → ³ A _{2g} (F)v ₃					
Cu[N ₄ L ²] ₂ H ₂ O	16129, 19417	² B _{1g} → ² B _{2g} v ₂	1612.8	-	-	-	27.65
	25626	² B _{1g} → ² E _{2g} v ₃					

Table -3
Diagnostic i.r. bands(Cm⁻¹)in [N₄L¹],[N₄L²] Ligands and its complexes.

Compound	Assignments						
	v(C=N)	v(C=C)	v(O-H)	v(C-H) _{aliphatic}	v(M-N)	v(M-O)	v(C-H) _{aromatic}
N ₄ L ¹	1620s	1545m	-	2954m	-	-	3038m
Co[N ₄ L ¹] ₂ H ₂ O	1601s	1540m	3561b	2954m	370m	870w	3043m
Ni[N ₄ L ¹] ₂ H ₂ O	1599s	1500w	3652b	2950m	345m	862w	3040m
Cu[N ₄ L ¹] ₂ H ₂ O	1605s	1580w	3650b	2953m	360m	869w	3039m
N ₄ L ²	1630s	1550w	-	2951m	-	-	3040m
Co[N ₄ L ¹] ₂ H ₂ O	1595s	1560m	3653b	2954m	355m	871w	3041m
Ni[N ₄ L ²] ₂ H ₂ O	1610s	1540m	3650b	2953m	352w	868w	3042m
Cu[N ₄ L ²] ₂ H ₂ O	1615s	1560m	3653sh	2953m	358m	860w	3043m

Abbreviations: s-strong, b-broad, m-medium, w-weak, sh-shoulder

Table-4.
EPR spectral data of the Cu(II)

Complexes	Polycrystalline sample			
	g	g ₊	g _{iso}	G
Cu[N ₄ L ¹] ₂ H ₂ O	2.391	2.084	2.185	4.76
Cu[N ₄ L ²] ₂ H ₂ O	2.17	2.035	2.08	4.85

Table-5
Antimicrobial screening data of $[N_4L^1]$, $[N_4L^2]$ and its complexes*

Compounds	Antibacterial results		Antifungal results	
	S. Aureus	E. Coli	Niger	P. Notalum
	(SA)	(EC)	(AN)	(PN)
$[N_4L^1]$	++	++	++	++
$Co[N_4L^1]2H_2O$	++	+	+++	+++
$Ni[N_4L^1]2H_2O$	+++	++	++	++
$Cu[N_4L^1]2H_2O$	++++	++++	+++	+++
$[N_4L^2]$	++	++	++	++
$Co[N_4L^2]2H_2O$	++	++	++	++
$Ni[N_4L^2]2H_2O$	+++	++	+	+
$Cu[N_4L^2]2H_2O$	++++	++++	++++	++++
Grisofulvin	-	-	+++	+++
Norfloxacin	+++	+++	-	-

*(-)No inhibition zone= inactive; 1-5mm(+)=Less active;
6-10mm(++)=Moderately active; 11-15mm(+++)=highly active;

Table-6
 1H NMR spectra of the N_4L^1 and N_4L^2 Ligands in D_6 -DMSO(Δ .PPM)

Compound	OCH ₃	Aroma. H	CH ₂ -CH ₂	-CH ₂ CH ₂ CH ₂ -
N_4L^1	3.73(s, 6H)	6.80-7.68(m, 4H)	3.91(s, 4H)	--
N_4L^2	3.73(s, 6H)	6.80-7.52(m, 4H)	--	3.55(m, 6H)

s-singlet, m-multiplet

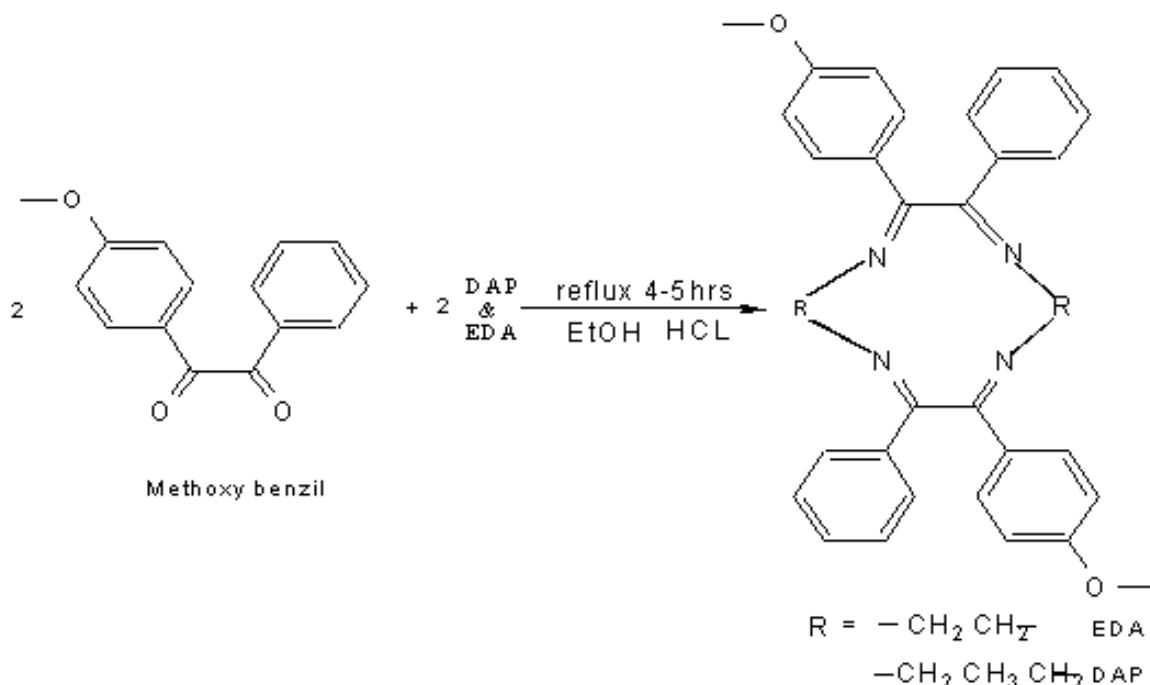


Figure 1
SCHEME FOR THE SYNTHESIS OF LIGANDS

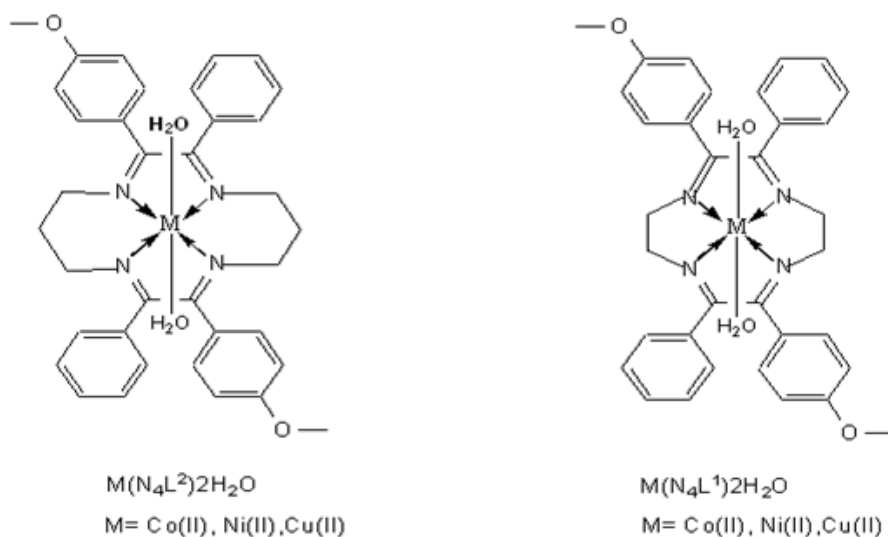
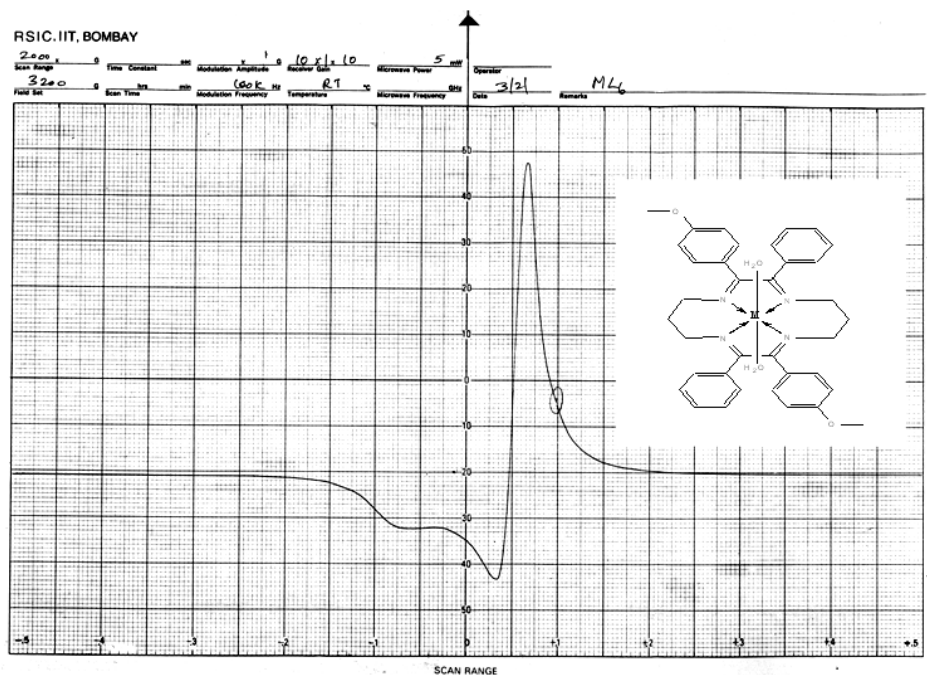


Figure 2
PROPOSED STRUCTURES OF METAL COMPLEXES



CONCLUSION

Based on the analytical data, IR, conductivity, magnetic properties and spectral studies we assigned the possible structures for all the complexes. Co(II), Ni(II) and Cu(II) complexes are octahedral in

nature. The Schiff base and its metal complexes have been screened for their antimicrobial activities. The results show that some of the complexes exhibit good activity as compared to the ligand.

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