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DESIGNING, SYNTHESIS AND SPECTROSCOPIC STUDIES OF Co(II), Ni(II) AND Cu(II) TRANSITION METAL COMPLEXES WITH NITROGEN DONOR TETRADENTATE, NOVEL MACROCYCLIC SCHIFF'S BASE LIGAND

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ABSTRACT

The macrocyclic Schiff base complexes of the [M(L)X_2], (where M = Co(II), Ni(II) and Cu(II); X=Cl^-, CH_3COO^-, ½ SO_4^{2-} and L= Ligand) have been synthesized with a macrocyclic Schiff base ligand L (3,11-dibromo-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene). The Ligand obtained by the condensation of 1,3-diaminopropane and bromomalonaldehyde. The Schiff base Ligand was characterized on the basis of elemental analysis, IR, ^{1}H NMR, EI Mass spectra, while the Co(II), Ni(II) and Cu(II) complexes were characterized by elemental analysis, magnetic susceptibility measurements, molar conductance measurements, IR, electronic and EPR spectral studies. All the macrocyclic Schiff base complexes are non-electrolyte in nature. On the basis of spectral study octahedral geometry has been assigned for Co(II) and Ni(II) complexes and tetragonal geometry proposed for Cu(II) complexes but [Cu(L)SO_4] proposed five coordinated trigonal bipyramidal geometry.

KEYWORDS: Macrocyclic ligand; transition metal complexes; spectral characterization.

INTRODUCTION

The design and synthesis of macrocyclic Schiff base ligand having tetradentate nitrogen donor atoms have been increased significant interest. There is an emerging interest in the synthesis of macrocyclic Schiff base ligands and their transition metals complexes.[1] Macrocyclic Schiff base complexes contain azo and azomethine groups. The azo group possesses excellent donor properties and is important in coordination chemistry.[2-3] The macrocyclic ligand and their transition metal complexes have received a considerable attention in last many years, due to their interesting characteristics in industrial and synthetic processes such as catalysis, photochemistry and biological systems, dyes and pigments[4], models for biologically important proteins and enzymes[5-6] biological field.[7-8] In azomethine derivatives, the -C=N- linkage was essential for biological activities like antibacterial, antifungal, antitumor, antiviral, anticancer, antimalarial, anti-inflammatory, and antioxidant etc.[9-18] They also have been used as drugs and are reported to possess a wide variety of biological activities against bacteria, fungi and a certain type of tumors and also are the useful model for bioinorganic processes.[19-20] DNA binding and cleavage, studies of transition metal complexes have become very important in the development of DNA probes[21] and chemotherapeutics. In the present research paper deals with synthesis, spectral studies of Cu(II), Ni(II), and Co(II) complexes with a tetradentate ligand, which were derived from L (3,11-dibromo-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene). These complexes were characterized with the help of various physicochemical techniques like elemental analysis, magnetic susceptibilities, and molar conductance measurements, IR, UV-Visible, and EPR Spectra.

MATERIALS AND METHODS

Materials

All chemicals used in this research were commercial products and used as supplied. Bromomalonaldehyde, 1,3-diaminopropane were of AR grade and procured from Alfa Aesar, Heysham, England and Sigma Aldrich, Bangalore, India. Metal salts were purchased from E. Merck, India and were used as received. All used solvents were of the spectroscopic grade.

Synthesis of Schiff's base ligand

A hot ethanolic solution (25 mL) of bromomalonaldehyde (0.002mol, 0.302g.) and a hot ethanolic solution (15 mL) of 1, 3-diaminopropane (0.002 mol, 0.17mL) were mixed slowly with constant stirring. The mixture was refluxed for 14 hrs at 78-80 ^{0}C. It was allowed to stay at room temperature and kept in the refrigerator overnight. On cooling, the colored solid product was precipitated out. It was filtered off, washed several times with cold ethanol and then dried in vacuum over P_4O_{10}. The physical properties of the ligand are given in Table 1. Synthesis of macrocyclic Schiff's base ligand is given in Fig. 1.

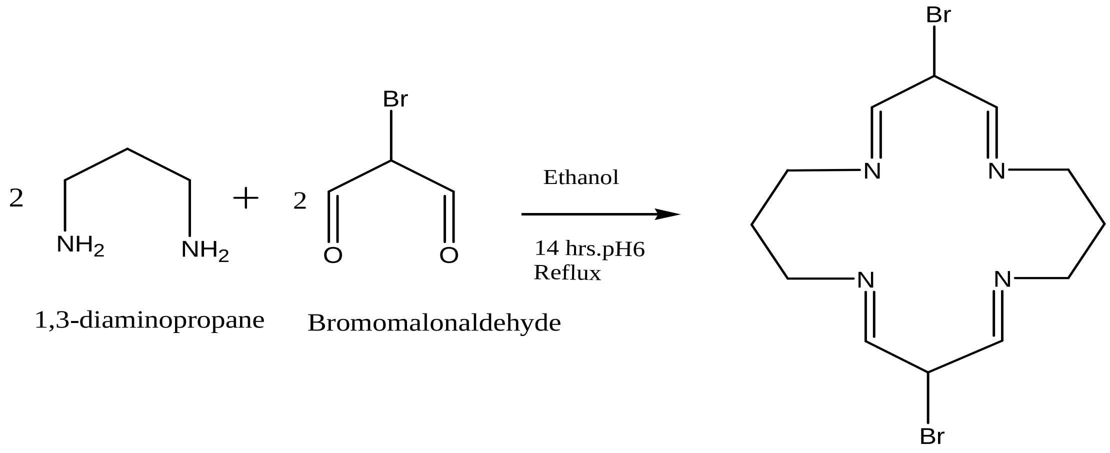


Fig. 1: 3, 11-dibromo-1, 5, 9, 13-tetraazacyclohexadeca-1, 4, 9, 12-tetraene.

Synthesis of transition metal complexes

A hot ethanolic solution of the corresponding metal salt (0.001 mol), (except $CoCI_2.6H_2O$, $Co(CH_3COO)_2$, $NiCl_2.6H_2O$, $Ni(CH_3COO)_2.4H_2O$, $CuCI_2.2H_2O$, $Cu(CH_3COO)_2.H_2O$ and $CuSO_4$ were mixed separately) with hot ethanolic solution of Schiff's base ligand (0.001 mol in 20 ml of absolute ethanol) mixed together with constant stirring. The mixture was refluxed for 14–16 hours at temp. 80^0C pH (5–7) was adjusted by adding of 2–3 drops of aqueous ammonia. On cooling, solid colored complexes were precipitated out. The corresponding colored complexes were separated out by filtration, washed thoroughly with ethanol, and dried under vacuum over P_4O_{10}. Physical data and elemental analysis for all synthesized complexes are shown in Table 1. The color was noted, the melting point was determined and yield of the complexes was calculated.

Analytical and physical measurements

Elemental study (CHN) was analyzed on Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibilities were measured at room temperature on a Gouy balance using $CuSO_4.5H_2O$ as calibrant. IR spectra were recorded on FT-IR spectrum BX spectrophotometer in KBr pellet. ^{1}H-NMR spectrum was recorded on a Bruker Advanced DPX-300 spectrometer using DMSO-d_6 as a solvent at IIT Delhi. The electronic impact mass spectrum of the ligand was recorded on JEOL, JMS-DX-303 mass spectrometer. The electronic spectra were recorded in DMSO on Shimadzu UV-visible mini 1240 spectrophotometer. EPR spectra of all complexes were recorded at room temperature (RT) on E_4-EPR spectrometer using the DDPH as the g-marker at SAIF, IIT Bombay.

RESULTS AND DISCUSSION

On the basis of elemental analysis, the complexes were found to have the general compositions [M(L)X_2], where M = Co(II), Ni(II), Cu(II), L= macrocyclic Schiff‟s base ligand, X = Cl^-, CH_3COO^-, ½ SO_4^{2-}). The molar conductance value of all complexes were found 14-25 Ω^{-1} cm^2 mol^{-1} respectively, which is show the non-electrolytic in nature of the complexes. On the basis of molar conductance values, all complexes might be formulated as [Mn(L)X_2] The physical and the analytical data of ligand and its metal complexes were listed in Table 1.

Table 1: Analytical and physical data of ligand and its transition metal complexes.

Compound/ Complexes	**Mol. Wt.**	**Yield (%)**	**Colour**	**Melting Point (^{0}C)**	**Molar Conductance (Ω^{-1}cm^2 mol^{-1})**	**Elemental analysis (%) found (calculated)**			
						M	**C**	**H**	**N**
Ligand (L)	377.84	48	Light reddish brown	178	--	--	38.12 (38.15)	4.76 (4.73)	14.82 (14.89)
[Co(L)Cl$_2$] **$CoC_{12}H_{18}N_4Br_2Cl_2$**	507.73	48	Black	>300	17	11.61 (11.62)	28.36 (28.40)	3.55 (3.60)	11.03 (11.10)
[Co((L)(OAc)$_2$] **$CoC_{16}H_{24}N_4Br_2O_4$**	562.73	50	Rust Red	299	22	10.47 (10.50)	34.12 (34.09)	4.26 (4.24)	9.95 (9.99)
[Ni(L)Cl$_2$] **$NiC_{12}H_{18}N_4Br_2Cl_2$**	507.4	54	Dirty grey	290	24	11.55 (11.62)	28.40 (28.41)	3.55 (3.50)	11.04 (11.10)
[Ni((L)(OAc)$_2$] **$NiC_{16}H_{24}N_4Br_2O_4$**	554.4	50	Brown	>300	25	10.57 (10.50)	34.63 (34.09)	4.32 (4.24)	10.10 (9.99)
[Cu(L)Cl$_2$] **$CuC_{12}H_{18}N_4Br_2Cl_2$**	512.3	49	Mehanadi	>300	21	12.40 (12.45)	28.11 (28.17)	3.51 (3.44)	10.93 (10.90)
[Cu((L)(OAc)$_2$] **$CuC_{16}H_{24}N_4Br_2O_4$**	559.3	55	Green	>320	23	11.35 (11.38)	34.33 (34.48)	4.29 (3.32)	10.01 (11.14)
[Cu((L)SO$_4$] **$CuC_{12}H_{18}N_6Br_2O_4S$**	537.0	46	Green	>300	14	11.82 (11.77)	26.82 (26.85)	3.35 (3.40)	10.13 (10.07)

CH_3COO is written as OAc

Characterization of ligand

IR spectra

IR spectrum of the synthesized macrocyclic ligand [L=3,11-dibromo-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene] has been depicted in Fig. 2. The IR spectrum of macrocyclic ligand displays bands in the region 3397- 2924 cm^{-1},1599 cm^{-1}. These bands correspond to the aromatic C-H stretching and formation of azomethine group ν(C=N) stretching vibration respectively.[23-24]

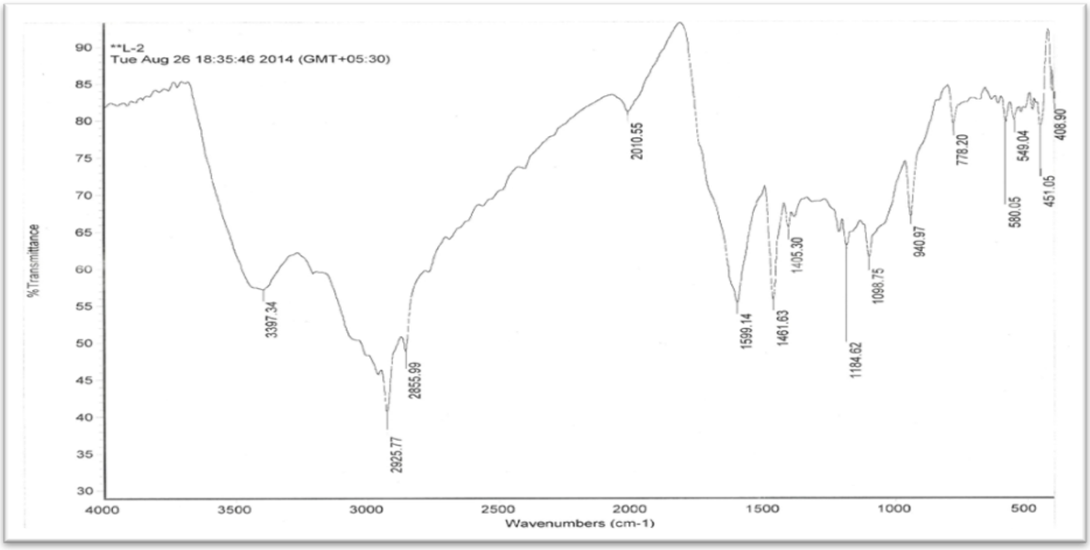


Fig. 2: IR spectrum of Ligand.

^{1}H-NMR Spectra of Ligand

The ^{1}H-NMR spectrum of Macrocyclic Schiff's base ligand presented in Fig.3, was operated at 400 MHz using DMSO-d_6 as a solvent. ^{1}H-NMR Spectrum of ligand indicates that different values of the applied field.[25-26] These are discussed below (chemical shift in ppm).

(a) A quartet found at 1.085 ppm is due to (-CH=N-CH_2-CH_2-) protons.

(b) A singlet was found at 2.010 ppm is due to (-CH=N-CH_2-) protons.

(c) A singlet was found at 3.582 ppm due to (-CHBr) protons

(d) A singlet was found at 8.130 ppm is due to azomethine (-HC=N) protons.

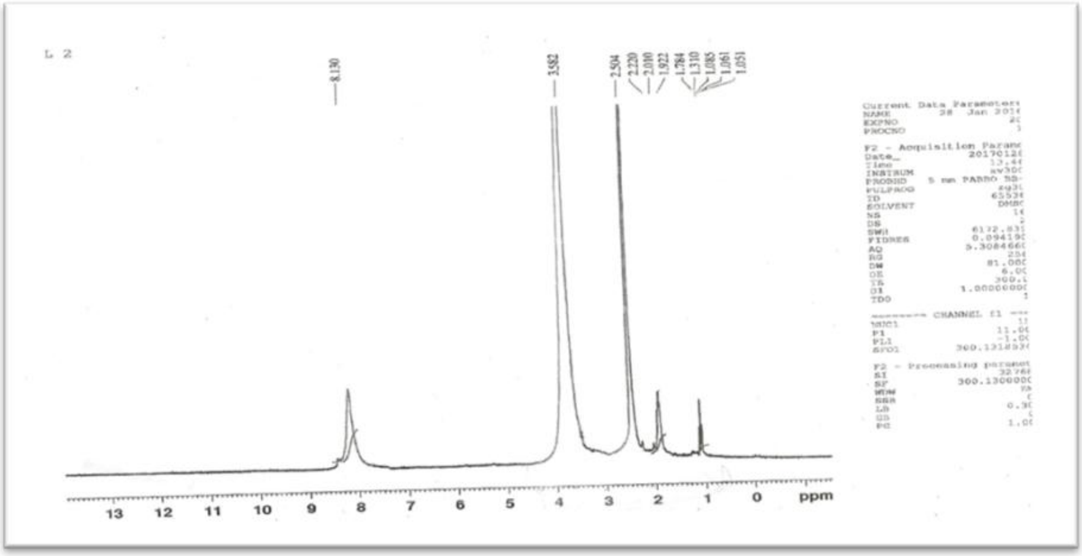


Fig. 3: ^{1}H-NMR spectrum of Ligand.

Mass Spectrum

Mass spectrum of macrocyclic Schiff's base ligand showed a molecular ion peak at m/z = 376 amu corresponding to $[M+1]^+$ which confirms the proposed molecular formula. It shows a series of peaks which correspond to the various fragmentation of ligand. Observed peaks are found at position 297, 217, 204, 177, 135, 108, 95, 68, 26 amu. The intensities of these peaks give the idea of the stabilities of the fragments. Maas spectrum of ligand is given in Fig. 4.

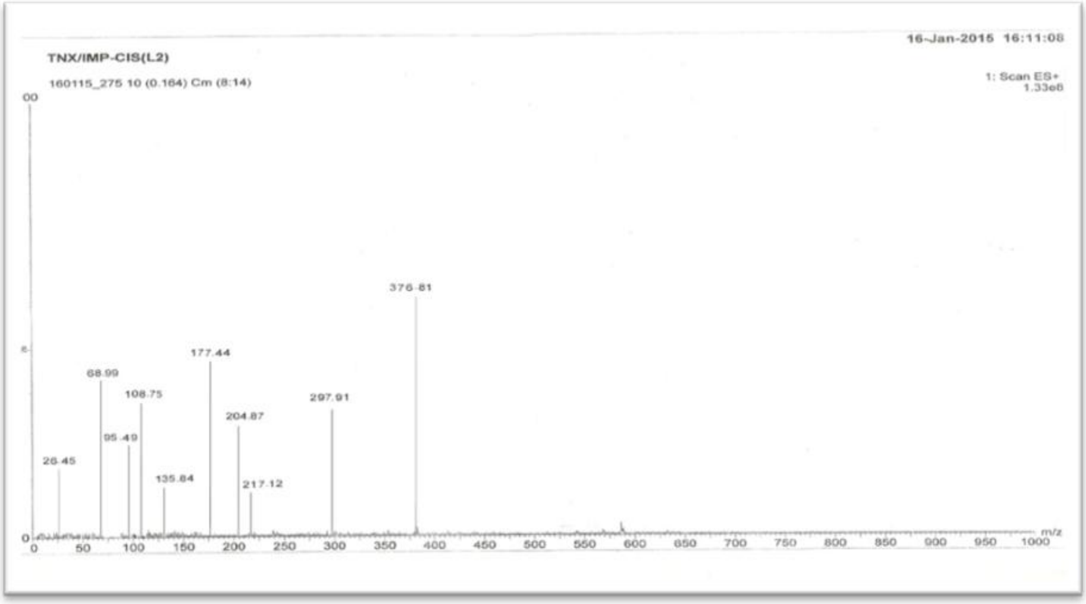


Fig. 4: Mass spectrum of Ligand.

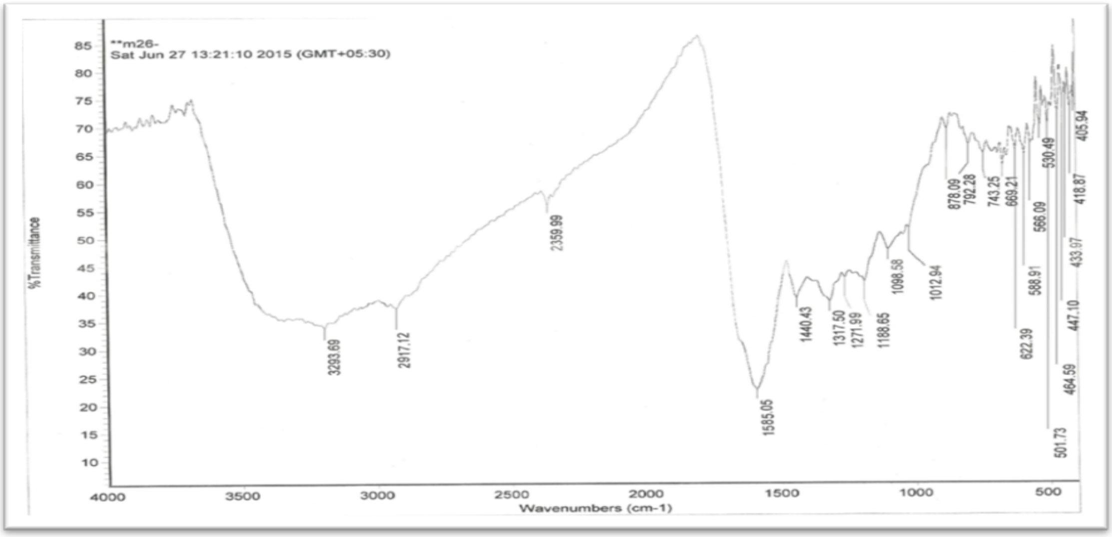
Characterization of transition metal complexes

Infrared spectra

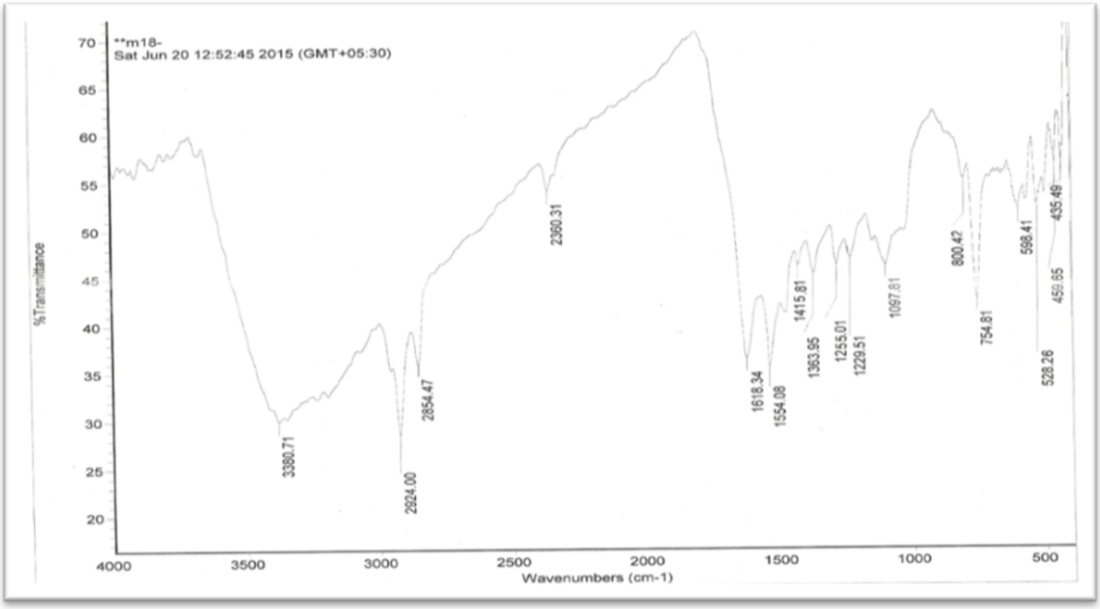
The important IR bands of macrocyclic Schiff's base ligand and metal complexes, along with their assignments are given in Table 2. The IR spectrum of ligand does not show any band corresponding to carbonyl and free primary amine, which suggest the complete condensation of an amino group with the keto group.[27] The position of ν(-C=N-) band of ligand appeared at 1599 cm^{-1}, is shifted towards lower wave number in the complexes indicating coordination via the azomethine nitrogen.[28] This is also confirmed by the appearance of bands in the range of 458–502cm^{-1}, assigned to the ν(M−N).[29] The chloro complexes show the IR bands in the region 342-358cm^{-1} due to ν(M-Cl).[30] This discussion suggests that the ligand coordinates to the metal atom in tetradentate fashion (N4).

Bands due to anions

IR spectra of the acetate complexes of Co(II), Ni(II), and Cu(II) bands lie at 1440, 1415, 1415cm^{-1} (v_2) and 1271, 1249, 1249 cm^{-1} (v_1) and the Δv i.e.166 cm^{-1} the respective suggests the unidentate nature of acetate ions.[31] It is strongly supported that both acetate ions are coordinated to the metal ion in a unidentate fashion.[32–33] The Spectrum of sulphate complex of Cu(II) showed that IR band v_3 split at 1121 and 1052 while v_1 at 981cm^{-1}, which indicating unidentate nature of sulphate ion respectively.[34-35] Shown in Fig. 5: (a), (b) and (c).



(a)



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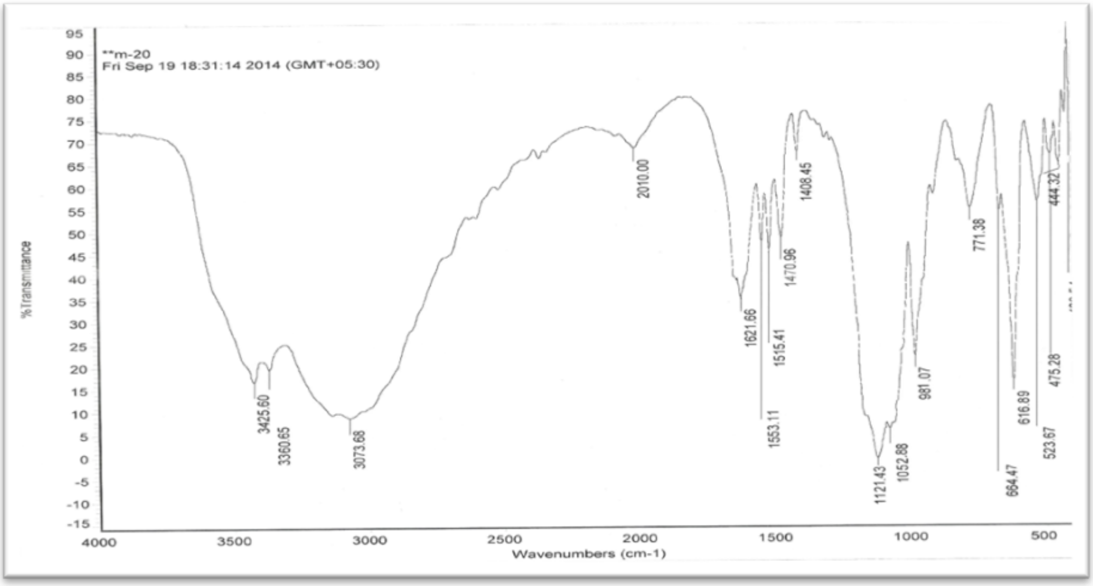


(c)

Fig. 5: IR spectra of: (a) Co(L)(OAc)$_2$],(b) Ni(L)(OAc)$_2$] And (c) [Cu(L)(SO$_4$)$_2$].

Table 2: Important infrared spectral bands of macrocyclic Ligand (cm^{-1}) and their assignments.

Compound/ Complexes	**Assignments**				**Bands due to anions**
	ν(N-H)	**ν(C-H)**	**ν(C=N)**	**ν(M-N)**	
Ligand (L)$C_{12}H_{18}N_4Br_2$	3397	2924	1599	-	-
[Co(L)Cl$_2$] $CoC_{12}H_{18}N_4Br_2Cl_2$	3217	2921	1590	502	-
[Co((L)(OAc)$_2$] $CoC_{16}H_{24}N_4Br_2O_4$	3293	2917	1585	501	ν_{as}(OAc)=1440,ν_1=1271, $\Delta\nu$=166cm^{-1}indicating monodentate nature of acetate group
[Ni(L)Cl$_2$] $NiC_{12}H_{18}N_4Br_2Cl_2$	3354	2915	1568	466	-
[Ni((L)(OAc)$_2$] $NiC_{16}H_{24}N_4Br_2O_4$	3384	2925	1592	494	ν_{as}(OAc)=1415,ν_1=1249,$\Delta\nu$=166 cm^{-1}indicating monodentate nature of acetate group
[Cu(L)Cl$_2$] $CuC_{12}H_{18}N_4Br_2Cl_2$	3345	3191	1580	458	-
[Cu((L)(OAc)$_2$] $CuC_{16}H_{24}N_4Br_2O$	3360	3073	1554	486	ν_{as}(OAc)=1415,ν_1=1255, $\Delta\nu$=160 cm^{-1}indicating monodentate nature of acetate group
[Cu((L)SO$_4$] $CuC_{12}H_{18}N_6Br_2O_4S$	3380	2924	1554	475	ν_3 splitted at 1121, and 1052 while ν_1 at 981cm^{-1} indicating unidentate nature of SO_4^{2-}

Magnetic susceptibility

The observed magnetic moments of Co(II), Ni(II) and Cu(II) complexes of macrocyclic Ligand are given in Table 3. The Co(II) complexes showed magnetic moments well within the expected range 4.79-4.97 BM corresponding to the presence of three unpaired electrons, for octahedral complexes.[36] The magnetic moment of the Ni(II) complexes lies in the range of 2.89– 2.95 BM, which is consistent with the octahedral stereochemistry of the complexes, corresponding to the presence of two unpaired electrons. At room temperature magnetic moment of the Cu(II) complexes lies in the range of 1.92–1.98 BM, corresponding to one unpaired electron. Whatsoever the geometry of Cu(II) is, its complexes always show magnetic moment corresponding to one unpaired electron.[37-38]

Electronic spectra

Cobalt(II) complexes

The electronic spectra of all the Co(II) complexes of macrocyclic Ligand were recorded using DMSO as a solvent and are shown in **Fig 6(a).** The electronic spectral data of complexes are presented in **Table 2**. The absorption bands displayed in the range of 9727-11904, 14125-14705, 18832-23529 and 33222-37568 cm^{-1} suggest high spin d^7system. These transitions may be assigned to the $^4T_{1g}$ (F) $\rightarrow ^4T_{2g}$ (F) (υ_1), $^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F) (υ_2), and $^4T_{1g}$ (F) $\rightarrow ^4T_{1g}$ (P) (υ_3). The energy differences of (υ_1- υ_2) are exactly equal to 10 Dq. υ_2 transition is usually very weak and rarely unequally observed.[39] It is difficult to make the assignments for the fourth band and it may be considered as a charge transfer band. The transitions were corresponding to the octahedral geometry of the Co(II) complexes.[40-41]

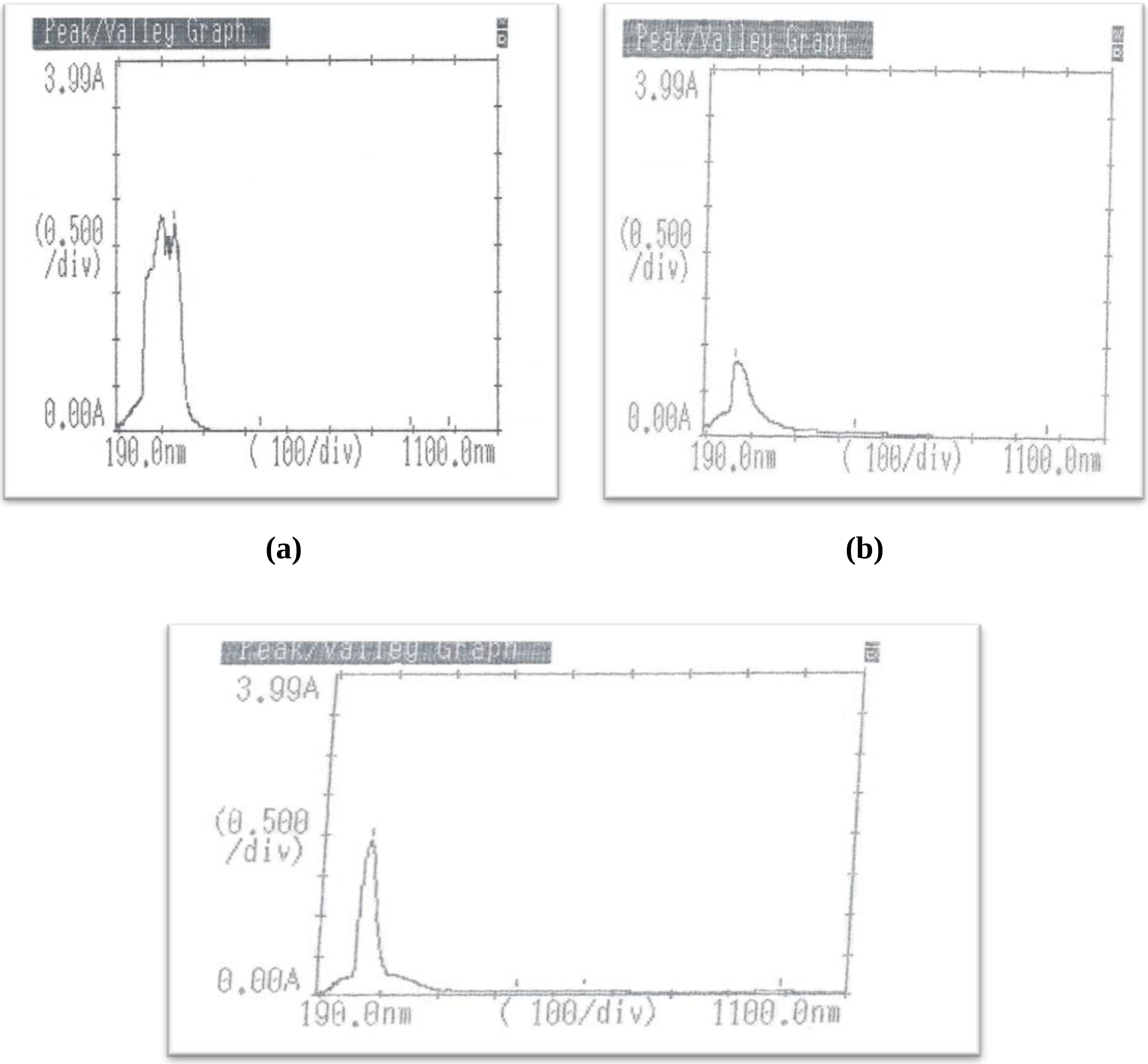
Nickel(II) complexes

The electronic spectra of Ni(II) complexes of macrocyclic Schiff's base ligand was recorded in DMSO as a solvent. The electronic spectral data of complexes are presented in Table 3. All complexes displayed three absorption bands in the range of 9865-10905 cm^{-1}, 11415-18621 cm^{-1}, and 22675-2770 cm^{-1} shown in Fig 6(b). The ground state Ni(II) in an octahedral coordination is $3A_2g$. Thus, these bands may be assigned to three spin-allowed transitions: ^3A_2g(F) $\rightarrow ^3T_2g$(F)(v_1), ^3A_2g(F) $\rightarrow$ ^3T_1g(F)(v_2) and ^3A_2g (F) $\rightarrow ^3T_1g$(P) (v_3), respectively. The position of bands indicates that the complexes have six coordinated octahedral geometries.[42]

Copper(II) complexes

The electronic spectra of Cu(II) complexes of Ligand were recorded in DMSO displayed bands in the range of 9794 - 12787 cm^{-1}, 14064 - 18348 cm^{-1} and 22624 - 28405 cm^{-1} Table

3. These bands correspond to the transitions $^2B_1g\rightarrow{}^2A_1g$ ($dx^2-y^2\rightarrow dz^2$) v_1, $^2B_1g\rightarrow{}^2B_2g$ ($dx^2y^2\rightarrow dzy$) v_2 and $^2B_1g\rightarrow{}^2Eg$ ($dx^2-y^2\rightarrow$ dxy, dyz) v_3, respectively. Therefore, the complexes may be considered to possess a tetragonal geometry.[43] The energy level sequence will depend on the amount of tetragonal distortion due to ligand field and John Teller effects.[44] The electronic spectrum of the sulphato complex showed bands at 11,690 cm^{-1}, 18,710 $cm^{-1}$and third band at 37,010 cm^{-1}. The third band appeared due to charge transfer. This complex may possess either square-pyramidal or trigonal bipyramidal geometry, shown in Fig. 6(c).



(a) **(b)**

(c)

Fig.6: UV-Vis. spectra of (a) $[Co(L)Cl_2]$ (b) $[Ni(L)(OAc)_2]$ And (c) $[Cu(L)Cl_2]$

Table 3: Magnetic moment and electronic spectral bands of Co(II), Ni(II) and Cu(II) complexes.

Complexes	**Magnetic Moment μ_{eff} (B.M.)**	**Electronic Spectral Data λ_{max}(cm^{-1})**
[Co(L)Cl$_2$] $CoC_{12}H_{18}N_4Br_2Cl_2$	4.79	9784, 14619, 18832, 33222
[Co((L)(OAc)$_2$] $CoC_{16}H_{24}N_4Br_2O_4$	4.91	9727, 14705, 22727, 37568
[Ni(L)Cl$_2$] $NiC_{12}H_{18}N_4Br_2Cl_2$	2.96	10905, 18621, 22675
[Ni((L)(OAc)$_2$] $NiC_{16}H_{24}N_4Br_2O_4$	2.87	9865, 14574, 25800
[Cu(L)Cl$_2$] $CuC_{12}H_{18}N_4Br_2Cl_2$	1.79	9794, 14064, 28405
[Cu((L)(OAc)$_2$] $CuC_{16}H_{24}N_4Br_2O$	1.98	12787, 18348, 22624
[Cu((L)SO$_4$] $CuC_{12}H_{18}N_6Br_2O_4S$	1.92	11690, 18710, 37010

Ligand field parameters

Various ligand field parameters were calculated using the procedure given by Drago.[45] Various ligand field parameters, i.e. Dq, B, β, and LFSE were calculated for Co(II), Ni(II) and Cu(II) complexes and reported in Table 4. The Dq values were evaluated using the Orgel diagram. The ratio v_1/v_2 was considered for the calculation of B. The Nephelauxetic parameter β was readily obtained by using the relation: β = B(complex)/B(free ion), the value for B(free ion) for Co(II) and Ni(II) metal ions are 1120 cm^{-1} and 1041 cm^{-1} respectively. The parameter B was calculated by the relation: $B = \upsilon_2 + \upsilon_3 - 3\upsilon_1/15$. The values of β for Co(II) complexes lie in the range of 0.245-0.491 and 0.549-0.695 for Ni(II) complexes, indicating an appreciable covalent character in the complexes.[46]

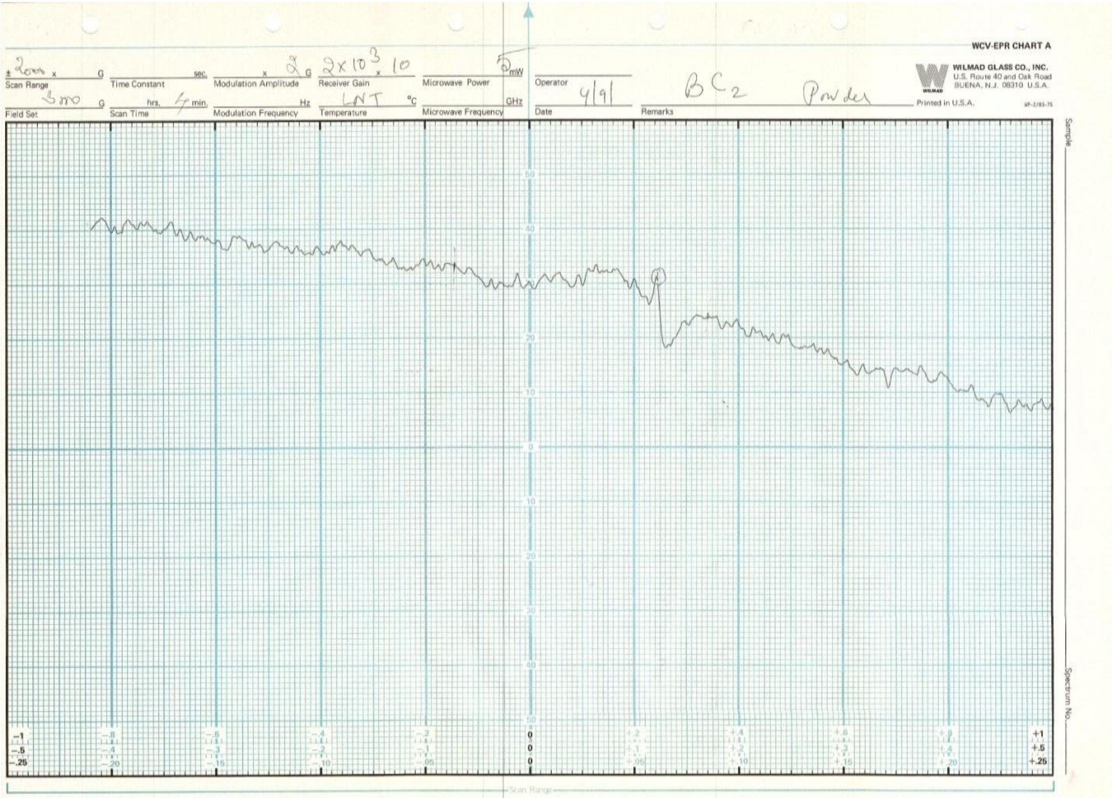
Table 4: ligand field parameters of the Co(II), Ni(II) and Cu(II) complexes.

Complexes	**Dq (cm^{-1})**	**B (cm^{-1})**	**β**	υ_2/υ_1	**LFSE (Jk/mole^{-1})**
[Co(L)Cl$_2$] $CoC_{12}H_{18}N_4Br_2Cl_2$	978	273	0.245	1.494	116.99
[Co((L)(OAc)$_2$] $CoC_{16}H_{24}N_4Br_2O_4$	972	550	0.491	1.512	116.28
[Ni(L)Cl$_2$] $NiC_{12}H_{18}N_4Br_2Cl_2$	1090	571	0.549	1.708	130.38
[Ni((L)(OAc)$_2$] $NiC_{16}H_{24}N_4Br_2O_4$	986	718	0.695	1.477	117.94
[Cu(L)Cl$_2$] $CuC_{12}H_{18}N_4Br_2Cl_2$	979	-	-	-	-
[Cu((L)(OAc)$_2$] $CuC_{16}H_{24}N_4Br_2O$	1278	-	-	-	-
[Cu((L)SO$_4$] $CuC_{12}H_{18}N_6Br_2O_4S$	1169	-	-	-	-

The EPR spectra

The EPR spectra of the cobalt(II) complexes were recorded as polycrystalline samples Fig.7(a) at liquid nitrogen temperature (LNT), because the rapid spin -lattice relaxation of Co(II) broaden the lines at higher temperatures. The g_{iso} values lay in the range 2.05 - 2.14. Table 5.[47]

The X-band EPR spectra of Cu(II) complexes of macrocyclic Ligand were recorded at room temperature in polycrystalline form at the frequency of 9.1GHz under the magnetic-field strength of 3000G and are depicted in Fig. 7 (b) After analysis of spectra, the spectral value of $g_{||}$, $g_{\perp}$ and G were calculated [$g_{||}$ = 2.33–2.37 and $g_{\perp}$ = 2.10–2.14 and G = 2.65–3.92] Table 4. The values of $g_{||}$ and $g_{\perp}$ were less than 2.38, consistent with distorted tetragonal geometry. The trend $g_{||} > g_{\perp} > 2.0023$ observed for the complexes under study indicated that unpaired d-electrons were in the dx^2-y^2 orbital of Cu(II) ion.[48] Thus, a tetragonal geometry is confirmed for the aforesaid complexes.[49] The G factor defined as $G = (g_{||} - 2)/(g_{\perp} - 2)$, which measures the exchange interaction between the metal centers in a polycrystalline solid, has been calculated. According to Hathaway, if G is greater than 4, the exchange interaction is negligible and G less than 4 indicate considerable exchange interaction in the solid complexes. The complexes reported in this paper, the “G” value, was found to be less than 4; suggesting that there was exchange interaction in solid complexes. The IR spectrum of [Cu(L)(SO_4)] complex suggested five coordinated geometry. Two basic structures were possible for five coordinated geometry i.e. trigonal bipyramidal or square pyramidal, which was characterized by the ground states dx^2-y^2 or dz^2, respectively. EPR spectrum of this complex provided an excellent basis for distinguishing between these two ground states. For this system, parameter R is calculated [$R = (g_2 - g_1)/(g_3 - g_2)$]. If the value of ‘R’ is greater than one, the ground state is predominantly as dz^2. On the other hand, the value of ‘R’ is less than one; the ground state is predominantly as dx^2-y^2. EPR spectrum of the [Cu(L)(SO_4)] complex shows three g values. The values of g_1, g_2, g_3, and R were 2.19, 2.18, 2.30, and 0.67 respectively. As the value of ‘R’ was less than one, ground state was predominantly dx^2-y^2 which were consistent with a square pyramidal geometry Fig.7(c).[50]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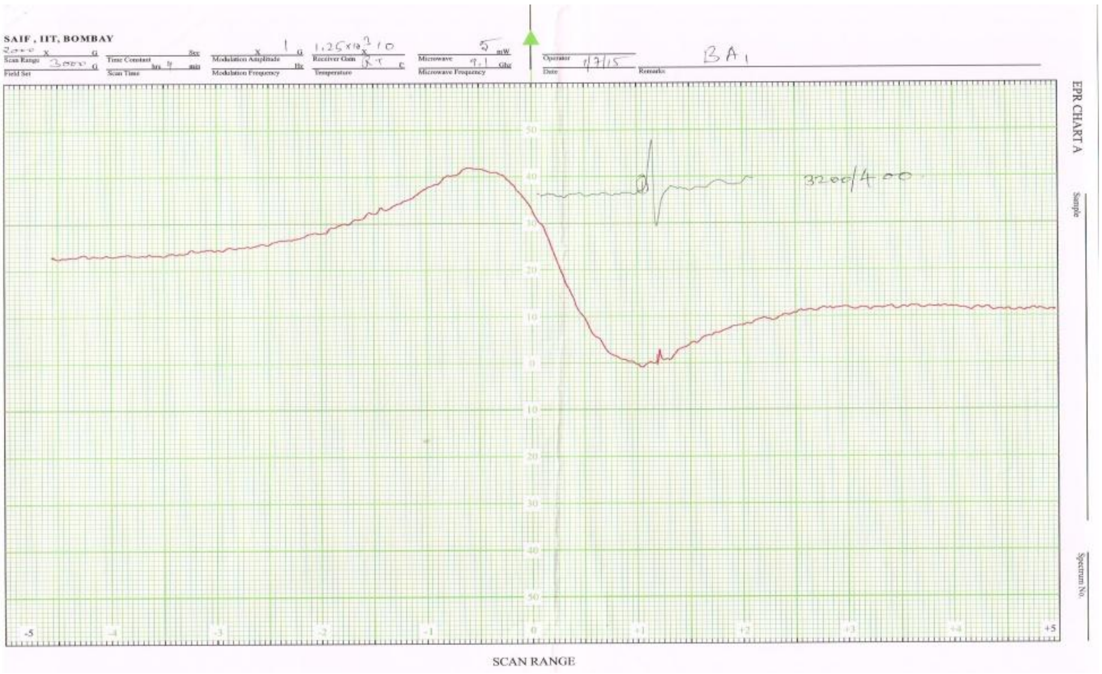
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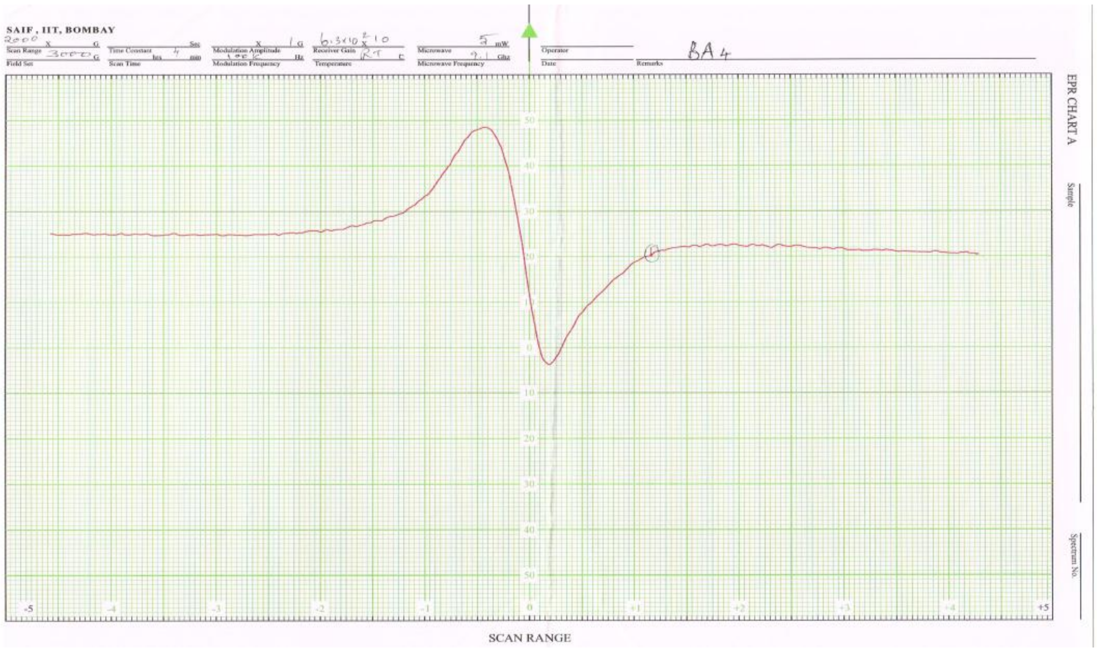
BA₁
3200/400
EPR CHART A
Sample
Spectrum No.
-5
-4
-3
-2
-1
0
+1
+2
+3
+4
+5
SCAN RANGE

(b)



(c)

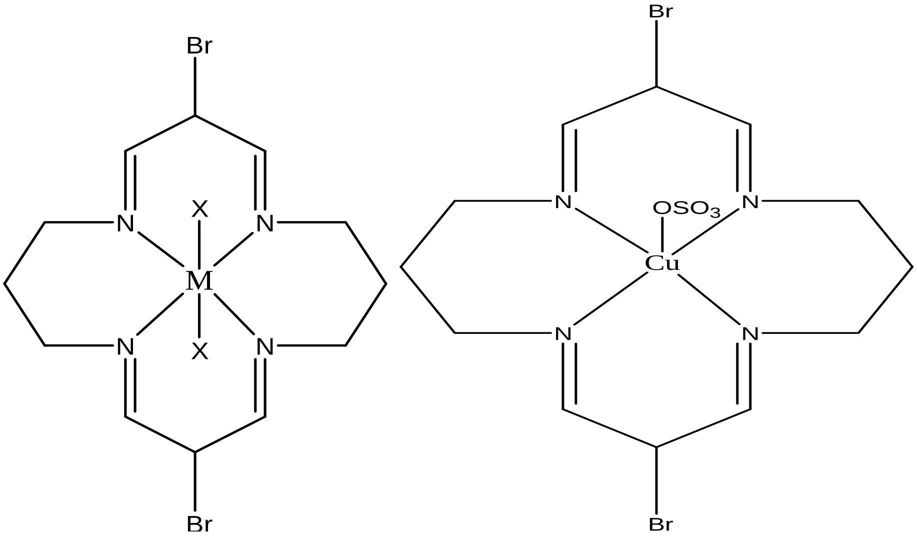
Fig.7: EPR spectra of (a) $[Co(L)Cl_2]$ (b) $[Cu(L)Cl_2]$ And (c) $[Cu(L)(SO_4)]$.

Table 5: EPR spectral data of Co(II) and Cu(II) complexes with Macrocyclic Schiff's base ligand.

Complexes	$g_\parallel$	$g_\perp$	g_{iso}	g_1	g_2	g_3	**R**	**G**
$[Co(L)Cl_2]$ $CoC_{12}H_{18}N_4Br_2Cl_2$	2.21	1.97	2.05	-	-	-	-	-
$[Co((L)(OAc)_2]$ $CoC_{16}H_{24}N_4Br_2O_4$	2.27	2.07	2.14	-	-	-	-	-
$[Cu(L)Cl_2]$ $CuC_{12}H_{18}N_4Br_2Cl_2$	2.33	2.10	2.14	-	-	-	-	3.30
$[Cu((L)(OAc)_2]$ $CuC_{16}H_{24}N_4Br_2O$	2.37	2.11	2.24	-	-	-	-	3.92
$[Cu((L)SO_4]$ $CuC_{12}H_{18}N_6Br_2O_4S$	-	-	2.15	2.10	2.18	2.30	0.67	-

Structure of the complexes

On the basis of elemental analysis, molar conductance measurement, magnetic susceptibility, IR, electronic and EPR spectral data and the subsequent discussion given above the following structures may be proposed for all the Co(II), Ni(II) and Cu(II) complexes Fig. 8.



[Cu(L)SO_4]

Fig. 8: Proposed structure of complexes with Macrocyclic Schiff's base ligand

Where M = Co(II), Ni(II), Cu(II) and X = Cl^-, and OAc= CH_3COO^-

CONCLUSION

Synthesized a tetraaza macrocyclic Schiff's base ligands has been synthesized and characterized using various techniques. We have also reported the study of the complexation capability towards chloride, acetate salts of Co(II), Cu(II) and Ni(II), and [Cu(L)(SO_4)] of metal ions. The coordination take place through four nitrogen donor atoms of the azomethine groups in [N_4] fashion. Characterization data revealed six coordinated octahedral geometry for all the synthesized Co(II), Ni(II) and Cu(II) complexes and square pyramidal geometry for [Cu(L)(SO_4)] complex.

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