



SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION OF Mn(II), Co(II), Cu(II) AND Ni(II) COMPLEXES WITH MACROCYCLIC LIGAND (L)

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ABSTRACT

Mn(II), Co(II), Cu(II) and Ni(II) complexes of new tetradentate nitrogen donor [N₄] macrocyclic ligand (L) i.e. 3,10-dibromo-1,5,8,12-tetraaza-6,7:13,14-dibenzocyclotetradeca-1,4,8,11-tetraene were synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, various spectroscopic techniques such as electronic, IR, Mass, ¹H NMR, EPR and UV-Vis spectral Studies. The molar conductance values indicated that all the metal complexes were non-electrolytic in nature, in dimethylformamide (DMSO). Metal complexes possessed general composition [M(L)(X)₂] where M = Mn(II), Cu(II), Co(II), Ni(II) and L = Ligand and X = Cl⁻, NO₃⁻ and ½SO₄²⁻. On the basis of IR Spectral study, it was concluded that ligand contains nitrogen donor [N₄] atoms and these donor atoms coordinate with metal ions to form metal complexes. Co(II), Mn(II) and Ni(II), complexes possess octahedral geometry, whereas Cu(II) complexes show tetragonal geometry and [Cu(L)SO₄] possess five coordinated trigonal bipyramidal geometry.

KEYWORDS: Magnetic Moment, IR, ¹H NMR, Mass, Electronic, EPR spectral Studies.

INTRODUCTION

The formation of macrocyclic complexes depends significantly on the dimension of the internal cavity, on the rigidity of the macrocycle, on the nature of its donor atoms and on the complexing properties of the counter ion. Macrocyclic Schiff's bases and their transition metal complexes were playing an important role in the development of coordination chemistry.^[1,2] Schiff's base metal complexes were studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas.^[3,5]

Schiff bases are compounds containing an azomethine group (-HC=N-), have drawn attention for many years ago. They are capable of forming co-ordinate bonds with many metal ions through azomethine group and phenolic group.^[6,7] Their metal complexes have been studied, with a variety of transition metal ions, since they frequently exhibit unusual structural properties. These properties resulted in wide applications in the biological fields like antifungal^[8,10], antiviral^[11], antibacterial^[12], antimalarial, antitumor^[13,14] antamoebic radio protective, trypanocidal anti-inflammatory activities and anti-carcinogenic properties.^[15,19] Some Schiff base complexes are also used as model molecules for biological catalysts^[20], agrochemicals, antimicrobial agents, oxygen carrier systems as well as having applications in analytical fields.^[21,24]

In the present study the complexes were prepared by the condensation of bromomalonaldehyde with *o*-phenylenediamine and the transition metals like Mn(II), Co(II) Cu(II) and Ni(II) chloride, nitrate and sulphate salts to afford the corresponding macrocyclic Schiff base complexes. These complexes were characterized with the help of various physicochemical techniques like IR, UV-Visible, magnetic susceptibilities, elemental analysis, conductance measurements and EPR Spectra.

MATERIALS AND METHODS

Materials: All the chemicals used were of Analytical grade and were procured from Sigma-Aldrich, and Alfa Aesar. Metal salts were purchased from E. Merck, India and were used as received. All used solvents were of standard/spectroscopic grade.

Synthesis of Schiff's base ligand

3,10-dibromo-1,5,8,12-tetraaza-6,7:13,14-dibenzocyclotetradeca-1,4,8,11-tetraene was synthesized using hot ethanolic solution (20 mL) of diketone i.e. bromomalonaldehyde (0.002 mol, 0.302 g) and hot ethanolic solution (20 mL) of diamine i.e. *o*-phenylenediamine (0.002 mol, 0.216 g). These were mixed slowly with continuous stirring and the reaction solution was refluxed for 18 h at 76-80°C. It was allowed to stay at room temperature and kept in 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 a desiccator which contains moisture absorbent silica gel. The physical properties and IR spectral data of the ligand is given in

Table 1. Synthesis of macrocyclic ligand (L) is given in **Fig.1**.

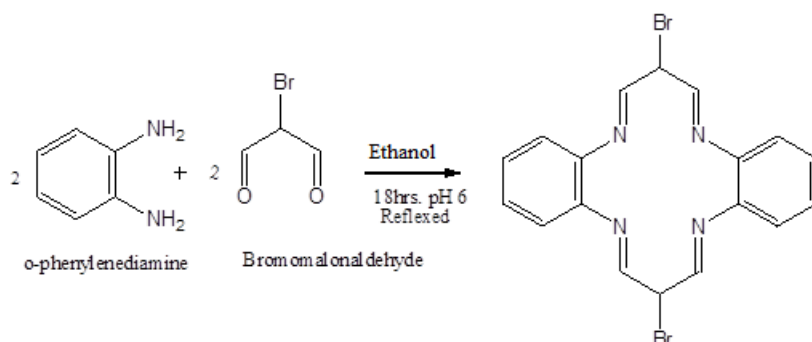


Fig. 1: Syntheses of Macrocyclic Schiff's base ligand (L).

Synthesis of transition metal complexes

A hot ethanolic solution of the corresponding metal salt (0.001mol) e.g. $[\text{MnCl}_2 \cdot 4\text{H}_2\text{O}]$, $[\text{CoCl}_2 \cdot 6\text{H}_2\text{O}]$, $[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}]$, $[\text{NiCl}_2 \cdot 6\text{H}_2\text{O}]$, $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$, $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$ and $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ were mixed separately with ethanolic solution of the corresponding ligand (0.001mol in 20 ml of absolute ethanol) e.g. L (3,10-dibromo-1,5,8,12-tetraaza-6,7:13,14-dibenzocyclotetradeca-1,4,8,11-tetraene (0.001mol, 0.445g) then mixed together with constant stirring. The mixture was refluxed for approximately 17-18 hours at 80°C at pH 6-7 was adjusted by adding 2-3 drops of aqueous ammonia. On cooling solid colored complexes were precipitated out. The solid precipitate was filtered off, washed several times with ethanol and dried in a desiccator using silica gel as moisture absorbent. Physical data and elemental analysis for all synthesized complexes are shown in **Table 1**. Color was noted, melting point was determined and yield of the complexes was calculated.

Analytical and Physical measurements

Elemental study (CHN) was analyzed on a Carlo- Erba-1106 elemental analyzer. Magnetic susceptibility was measured at room temperature on a Gouy balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a calibrant. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Electron impact mass spectra were recorded on a JEOL, JMS, and DX-303 mass spectrometer. ^1H NMR spectra was recorded on a Bruker Advanced DPX-300 spectrometer using DMSO-d_6 as a solvent at IIT Delhi. IR spectra were recorded using a FT-IR spectrum BX-II spectrophotometer in KBr pellets. The electronic spectra were recorded in DMSO on Shimadzu model UV-visible mini-1240 spectrophotometer in the wavelength region 1100–200 nm. EPR spectra of all complexes were recorded as polycrystalline sample and in DMSO at liquid nitrogen temperature on E4-EPR spectrometer using the DPPH as the g-marker at SAIF, IIT Bombay.

RESULTS AND DISCUSSION

Metal complexes were synthesized by mixing the hot ethanolic solution of ligand with ethanolic solution of the corresponding metal salt in 1:1 ratio. The macrocyclic Schiff's base ligand behaved as a tetradentate ligand and coordinated to metal ion through nitrogen of imine. All complexes were highly soluble in DMF and DMSO. In other common organic solvents they were sparingly soluble. The molar conductance values of all the complexes were found to be $10\text{-}25 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. These values corresponded non-electrolytic nature of the complexes.^[25] Thus the complexes may be formulated as $[\text{M}(\text{L})\text{X}_2]$ (where $\text{M} = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Cu}(\text{II}), \text{Ni}(\text{II})$, L = Schiff's base ligand and $\text{X} = \text{Cl}^-, \text{NO}_3^-, \frac{1}{2}\text{SO}_4^{2-}$). The physical and analytical data of ligand and its metal complexes were listed in **Table 1**.

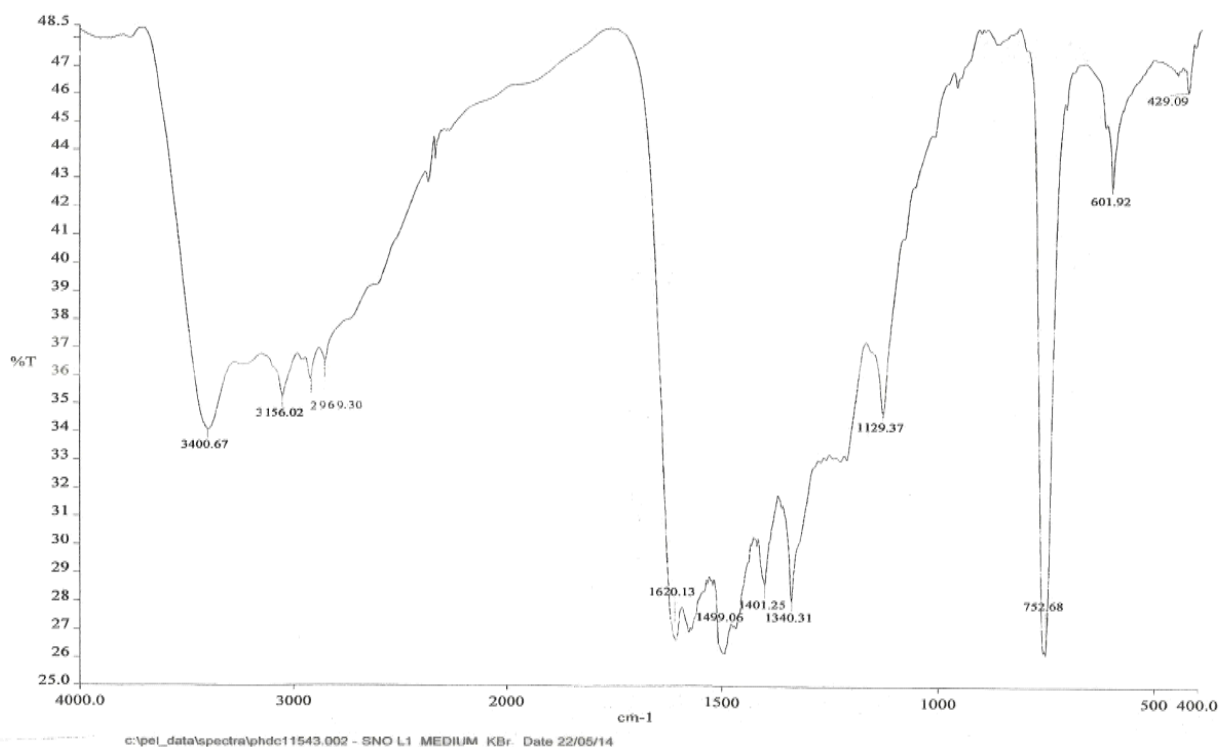
Table 1: Analytical and physical data of synthesized ligand and its metal complexes.

Ligand and Complexes	Color	Molecular Weight	Yield (%)	Melting Point (°C)	Molar Conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Elemental analysis Calculated(Found)			
						M	C	H	N
Ligand	Brown	445.8	50	240	-	-	48.45 (48.44)	3.14 (3.12)	12.56 (12.54)
[Mn(L)Cl ₂] MnC ₁₈ H ₁₄ N ₄ Br ₂ Cl ₂	Light brown	571.73	55	>300	15	9.61 (9.65)	37.78 (37.80)	2.45 (2.46)	9.61 (9.65)
[Co(L)Cl ₂] CoC ₁₈ H ₁₄ N ₄ Br ₂ Cl ₂	Greenish Yellow	575.73	46	>300	22	10.23 (10.26)	37.52 (37.54)	2.43 (2.47)	10.23 (10.26)
[Co(L)(NO ₃) ₂] CoC ₁₈ H ₁₄ N ₆ Br ₂ O ₆	Black	628.73	52	>320	12	9.37 (9.35)	34.35 (34.38)	2.23 (2.25)	9.37 (9.35)
[Cu(L)Cl ₂] CuC ₁₈ H ₁₄ N ₄ Br ₂ Cl ₂	Brown	580.3	48	>300	25	10.94 (10.85)	37.22 (37.20)	2.41 (2.48)	10.94 (10.85)
[Cu(L)(NO ₃) ₂] CuC ₁₈ H ₁₄ N ₆ Br ₂ O ₆	Dark Brown	633.3	45	>290	10	10.02 (10.00)	34.10 (34.22)	2.21 (2.36)	10.02 (10.00)
[Cu(L)SO ₄] CuC ₁₈ H ₁₄ N ₄ Br ₂ O ₄ S	Green	605.3	50	>320	15	10.49 (10.52)	35.68 (35.55)	2.31 (3.59)	9.25 (11.19)
[Ni(L)Cl ₂] NiC ₁₈ H ₁₄ N ₄ Br ₂ Cl ₂	Brown	575.4	48	>300	14	10.20 (10.24)	37.53 (37.51)	2.43 (2.40)	10.20 (10.24)
[Ni(L)(NO ₃) ₂] NiC ₁₈ H ₁₄ N ₆ Br ₂ O ₆	Green	628.4	40	>290	16	9.40 (9.38)	34.59 (34.64)	2.24 (2.28)	9.40 (9.38)

Characterization of ligand IR Spectra

An IR spectrum of the synthesized ligand has been depicted in **Fig. 2**. The IR spectrum of macrocyclic

ligand displays bands in the region 3256-2964 cm^{-1} , 1620 cm^{-1} . These bands corresponded to the aromatic C-H stretching and formation of azomethine group $\nu(\text{C}=\text{N})$ stretching vibration respectively.^[26]

**Fig. 2: IR spectrum of Schiff's base Ligand(L).**

¹H NMR spectrum of ligand

The ¹H NMR spectrum of Macrocyclic Schiff's base ligand [3,10-dibromo-1,5,8,12-tetraaza-6,7:13,14-dibenzocyclotetradeca-1,4,8,11-tetraene] was recorded in

DMSO-d₆ and is depicted in **Fig.3**. Indicates different values of applied field.^[27] These are discussed below:
(a) The sharp multiplet found at 7.6762 ppm is due to the aromatic protons (-HC=C-).

(b) A singlet observed at 8.618 ppm is due to azomethine (-HC=N-) protons.

(c) Another singlet at 3.530 ppm is due to protons near bromine (-CHBr).

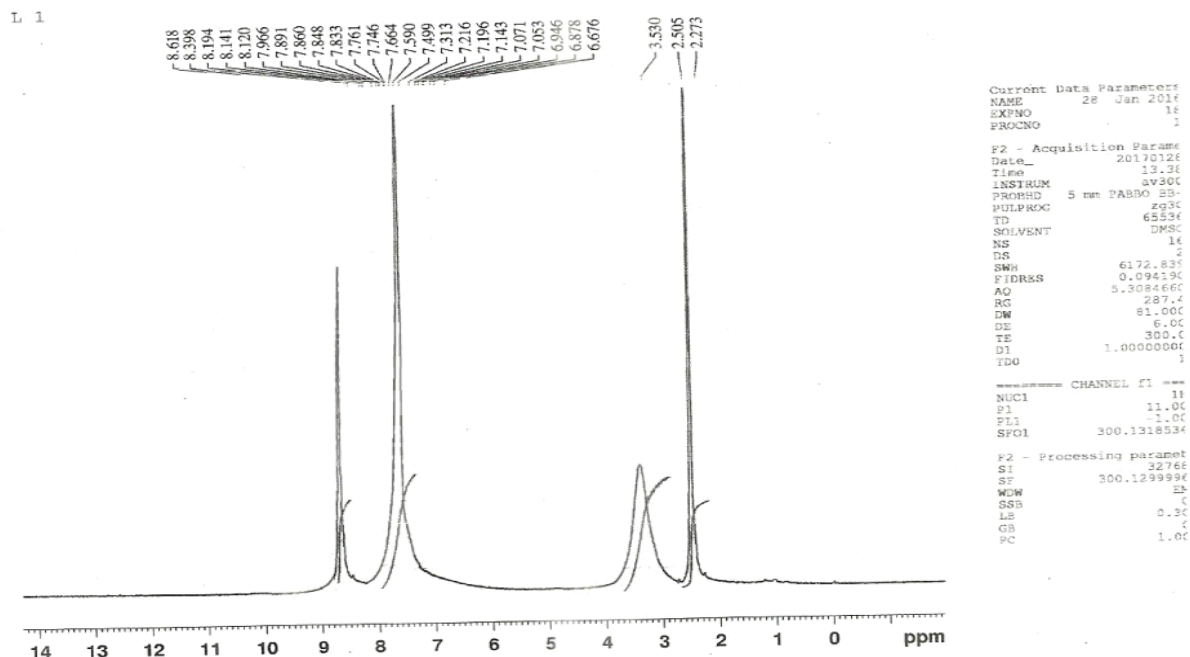


Fig. 3. ^1H NMR spectrum of Schiff's base ligand (L).

Mass spectrum

The electronic impact mass spectrum of the macrocyclic Schiff's base ligand confirmed the proposed formula by showing a molecular ion peak at $m/z = 445$ amu, corresponds to species $[\text{M}]^+$ which confirms the proposed molecular formula. It also showed a series of peaks i.e.

365, 286, 273, 246, 219, 143, 116, 103 and 76 amu corresponding to various fragmentation of ligand. The intensity of these peaks gave an idea of the stabilities of ligand. The fragmentation path of the ligand is given in Fig. 4.

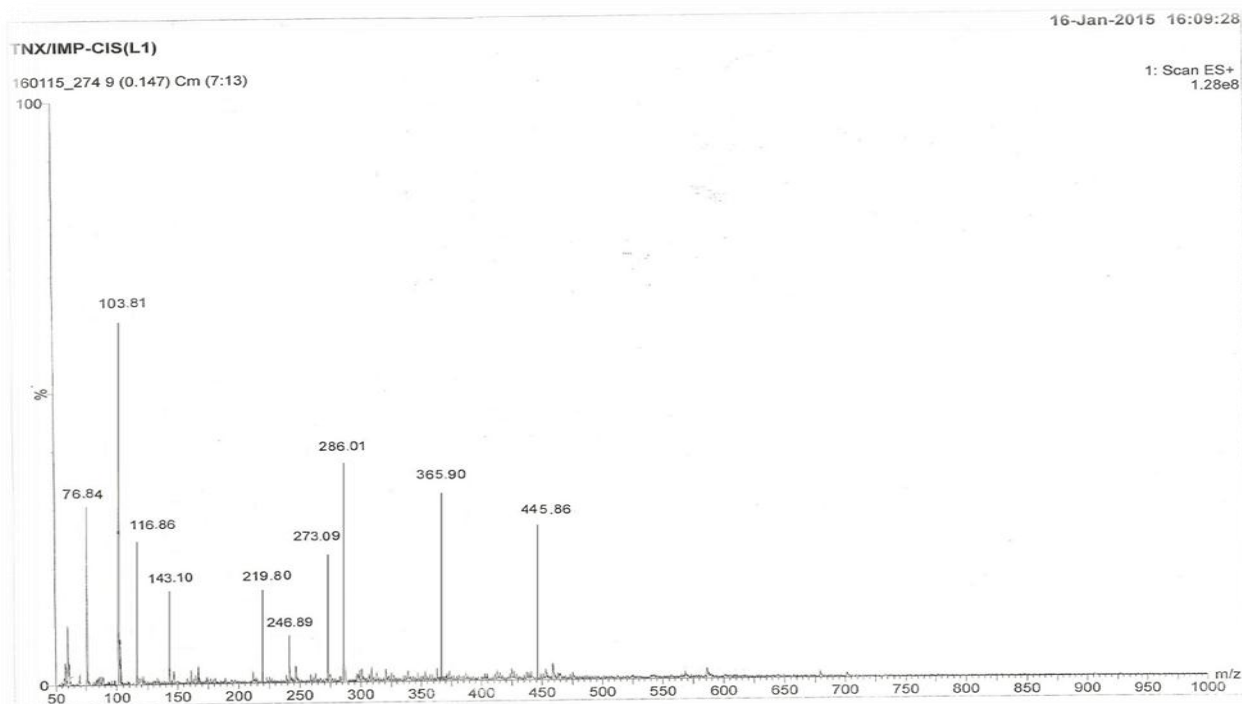


Fig. 4. Mass spectrum of Schiff's base Ligand (L).

Characterization of Transition Metal Complexes Infrared spectral studies

The important IR bands of 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 suggests the complete condensation of amino group with the keto group.^[28] The position of $\nu(\text{C}=\text{N})$ band of ligand appeared at 1620 cm^{-1} is shifted towards lower wave number in the complexes indicating coordination via the azomethine nitrogen.^[30] This is also confirmed by the appearance of bands in the range of $444\text{--}498\text{ cm}^{-1}$, which has been assigned to the $\nu(\text{M}-$

$\text{N})$.^[29] This discussion suggests that the ligand coordinates to metal atom in tetradentate fashion (N_4).

Bands due to anions

IR spectra of the $\text{Cu}(\text{II})$, $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ shows new absorption bands at $1406\text{--}1422$, $1312\text{--}1326$ and $1014\text{--}1091\text{ cm}^{-1}$ in nitrate complexes suggest that both nitrate groups are coordinated to the central metal ion in a unidentate fashion.^[30] Spectrum of sulphate complex of $\text{Cu}(\text{II})$ shows that band ν_3 got split at 1130 cm^{-1} , 1020 cm^{-1} and 988 cm^{-1} which suggests to unidentate behavior of sulphate ion.^[35] **Fig.4 (a) and (b)**.

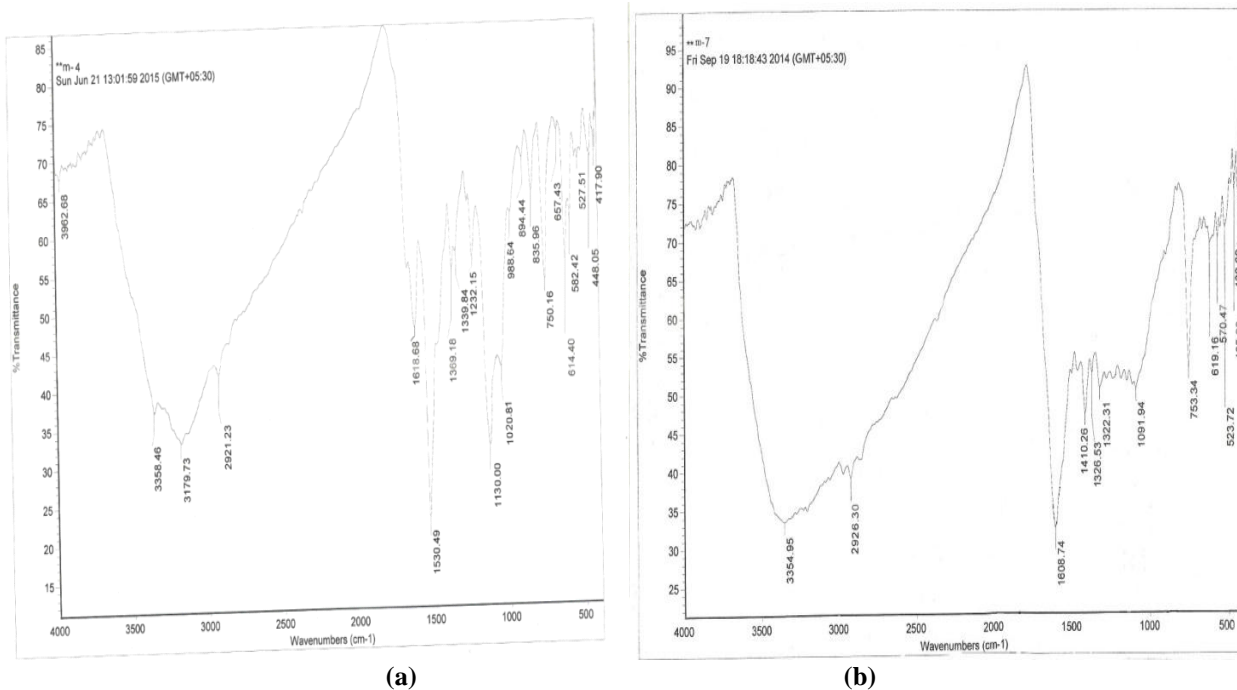


Fig. 5: IR spectra of (a) $[\text{Cu}(\text{L})(\text{SO}_4)]$ and (b) $[\text{Ni}(\text{L})(\text{NO}_3)_2]$ complex.

Table 2: Characteristic IR bands (cm^{-1}) of schiff's base and its metal complexes.

Compounds	Assignments				Bands due to anions
	$\nu(\text{N-H})$	$\nu(\text{C-H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{M-N})$	
L $\text{C}_{18}\text{H}_{14}\text{N}_4\text{Br}_2$	3256	2965	1620	-	-
$[\text{Mn}(\text{L})\text{Cl}_2]$ $\text{MnC}_{18}\text{H}_{14}\text{N}_4\text{Br}_2\text{Cl}_2$	3227	2931	1599	444	-
$[\text{Co}(\text{L})\text{Cl}_2]$ $\text{CoC}_{18}\text{H}_{14}\text{N}_4\text{Br}_2\text{Cl}_2$	3363	2925	1529	496	-
$[\text{Co}(\text{L})(\text{NO}_3)_2]$ $\text{CoC}_{18}\text{H}_{14}\text{N}_6\text{Br}_2\text{O}_6$	3370	2931	1523	498	$\nu_5=1422$, $\nu_1=1318$, $\nu_2=1014$, $\Delta\nu(\nu_5-\nu_1)=104\text{ cm}^{-1}$ indicating unidentate nature of nitrate group
$[\text{Cu}(\text{L})\text{Cl}_2]$ $\text{CuC}_{18}\text{H}_{14}\text{N}_4\text{Br}_2\text{Cl}_2$	3180	2948	1576	506	-
$[\text{Cu}(\text{L})(\text{NO}_3)_2]$ $\text{CuC}_{18}\text{H}_{14}\text{N}_6\text{Br}_2\text{O}_6$	3296	3044	1579	459	$\nu_5=1406$, $\nu_1=1312$, $\nu_2=1056$, $\Delta\nu(\nu_5-\nu_1)=94\text{ cm}^{-1}$ indicating unidentate nature of nitrate group
$[\text{Cu}(\text{L})\text{SO}_4]$ $\text{CuC}_{18}\text{H}_{14}\text{N}_4\text{Br}_2\text{O}_4\text{S}$	3358	2921	1530	448	ν_3 splitted at 1130, and 1020 while ν at 988 cm^{-1} indicating unidentate nature of SO_4^{2-}
$[\text{Ni}(\text{L})\text{Cl}_2]$ $\text{NiC}_{18}\text{H}_{14}\text{N}_4\text{Br}_2\text{Cl}_2$	3366	2918	1605	499	-
$[\text{Ni}(\text{L})(\text{NO}_3)_2]$ $\text{NiC}_{18}\text{H}_{14}\text{N}_6\text{Br}_2\text{O}_6$	3354	2926	1608	465	$\nu_5=1410$, $\nu_1=1326$, $\nu_2=1091$, $\Delta\nu(\nu_5-\nu_1)=84\text{ cm}^{-1}$ indicating unidentate nature of nitrate group

Magnetic Moments and Electronic Spectra

Magnetic Moments

Mn(II) complex in DMSO solution shows magnetic moment, 5.92 B.M at room temperature. This value indicates the presence of five unpaired electrons. Co(II) complexes showed magnetic moment value in the range 4.80-4.92 B.M. corresponding to three unpaired

electrons.^[31,32] The magnetic moments of Ni(II) complexes lies in the range 2.96-2.97 B.M. These values indicate the presence of two unpaired electrons. At room temperature Cu(II) complexes show magnetic moment in the range 1.88-1.98 BM corresponding to one unpaired electron (**Table 3**).

Table 3: Magnetic moment and electronic spectral data of the complexes.

Complexes	Magnetic Moment μ_{eff} (B.M.)	Electronic Spectral Data λ_{max} (cm ⁻¹)
[Mn(L)Cl ₂] MnC ₁₈ H ₁₄ N ₄ Br ₂ Cl ₂	5.92	15870, 21682, 24785, 36214
[Co(L)Cl ₂] CoC ₁₈ H ₁₄ N ₄ Br ₂ Cl ₂	4.80	9668, 17491, 20604, 37385
[Co(L)(NO ₃) ₂] CoC ₁₈ H ₁₄ N ₆ Br ₂ O ₆	4.92	9415, 17390, 20418, 38825
[Cu(L)Cl ₂] CuC ₁₈ H ₁₄ N ₄ Br ₂ Cl ₂	1.98	10302, 18722, 37272
[Cu(L)(NO ₃) ₂] CuC ₁₈ H ₁₄ N ₆ Br ₂ O ₆	1.91	10460, 16286, 38485
[Cu(L)SO ₄] CuC ₁₈ H ₁₄ N ₄ Br ₂ O ₄ S	1.88	11680, 18535, 36201
[Ni(L)Cl ₂] NiC ₁₈ H ₁₄ N ₄ Br ₂ Cl ₂	2.97	9465, 14874, 22625
[Ni(L)(NO ₃) ₂] NiC ₁₈ H ₁₄ N ₆ Br ₂ O ₆	2.96	9675, 14395, 25702

Electronic Spectrum of Mn(II) complex

The electronic spectra of the complexes were recorded by using DMSO as solvent. The electronic spectrum of Mn(II) complex displayed four spectral bands in the range of 15870 cm⁻¹, 21682 cm⁻¹, 24785 cm⁻¹ and 36214 cm⁻¹ **Table 3**. These spectral bands may be assigned the following transitions ⁶A_{1g} → ⁴T_{1g}, ⁶A_{1g} → ⁴E_g, ⁶A_{1g} → ⁴E_g and ⁶A_{1g} → ⁴T_{1g}.^[33] corresponding to an octahedral geometry.

Electronic Spectra of Co(II) complexes

The electronic spectra of Co(II) complexes were recorded using DMSO as a solvent. The electronic spectral data of complexes are presented in **Table 3**. For high spin d⁷ systems, bands are observed in the range of 9415-9668 cm⁻¹, 17490-17391, 20604-20418 cm⁻¹ and 38825-37385 cm⁻¹, respectively. These bands are corresponding to the following transitions: ⁴T_{1g} (⁴F) → ⁴T_{2g} (⁴F) (v₁), ⁴T_{1g} (⁴F) → ⁴A_{2g} (⁴F) (v₂), ⁴T_{1g} (⁴F) → ⁴T_{2g} (⁴P) (v₃). The energy differences of (v₁- v₂) are exactly equal to 10 Dq. v₂ transition is usually very weak and rarely unequally observed.^[34] Fourth band is due to charge transfer.

Electronic Spectra of Ni(II) complexes

The electronic spectra of Ni(II) complexes displayed three absorption bands (**Table 3**) in the ranges of 9675-9465 cm⁻¹, 14895-14874 cm⁻¹ and 25702-22625 cm⁻¹. The ground state nickel(II) in an octahedral coordination is ³A_{2g}. Thus, these bands may be assigned to three spin-allowed transitions: ³A_{2g} (F) → ³T_{2g} (F) (v₁), ³A_{2g} (F) → ³T_{1g} (F) (v₂) and ³A_{2g} (F) → ³T_{1g} (P) (v₃), respectively. The

position of bands indicated that the complexes have six coordinated octahedral geometries.^[35]

Electronic Spectra of Cu(II) Complexes

In electronic spectra of chloro, nitrate and sulphato complexes of Cu(II), bands appeared in the range of 10302-11680 cm⁻¹ and 16286-18722 cm⁻¹ may be assigned to the transitions, ²B_{1g} → ²A_{1g}(v₁), ²B_{1g} → ²B_{2g}(v₂) respectively. The third band at 36201-38485 cm⁻¹ may be due to charge transfer. Therefore, the complexes may be considered to possess a tetragonal geometry.^[40,41] The electronic spectrum of the sulphato complex showed bands at 11,680 cm⁻¹, 18,535 cm⁻¹ and third band at 36,201 cm⁻¹. Third band was appeared due to charge transfer. Thus complex may possess either square-pyramidal or trigonal bipyramidal geometry.^[36]

Ligand field parameters

Mn(II) complex

Various ligand field parameters were calculated for the Mn(II) complex and listed in **Table 4**. The values of Dq and B were calculated by using Orgel diagram. The ratio v₂/v₁ was considered for the calculation of B. The Nephelauxetic parameter β was readily obtained by using the relation: β = B(complex)/B(free ion), where B (free ion) for Mn(II) was 786 cm⁻¹ Slater Condon-Shortly parameters F₂ and F₄ are related to the Racah inter-electronic repulsion parameters B and C, as follows: B = F₂ - 5F₄ and C = 35F₄. The calculated value of β is 0.70 in the present complex, this is less than one, indicates the appreciable covalent character of metal ligand "σ" bond.^[37]

Co(II) complexes

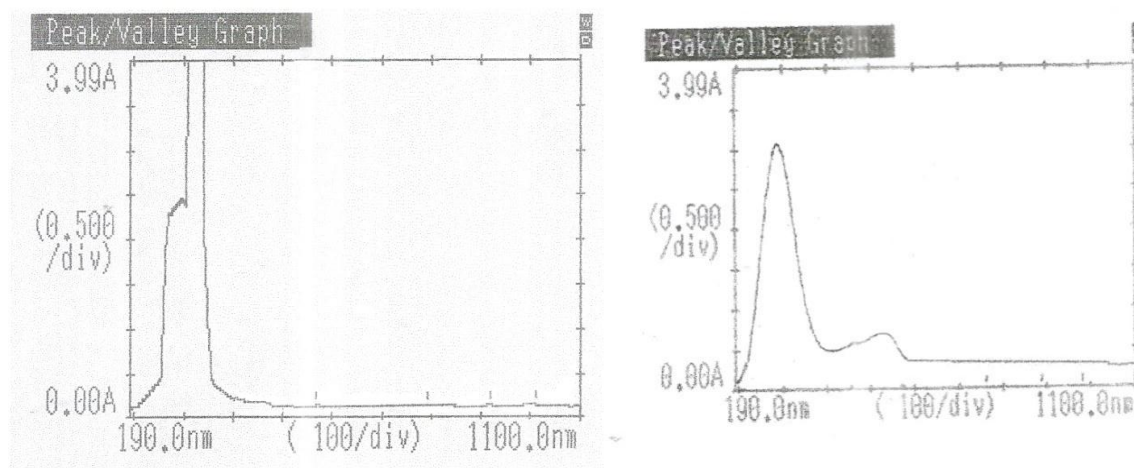
Various ligand field parameters were calculated for the Co(II) complexes and are listed in **Table 4**. The values of Dq and B were calculated by using Orgel diagram. The ratio ν_2/ν_1 was considered for the calculation of B. The Nephelauxetic parameter β was readily obtained by using the relation: $\beta = B(\text{complex})/B(\text{free ion})$, where B (free ion) for Co(II) was 1120 cm^{-1} . The parameter B was calculated by the relation: $B = \nu_2 + \nu_3 - 3\nu_1/15$. The values of β for Co(II) complexes lie in the range of 0.54-0.57, which indicate an appreciable covalent character in the Co(II) complexes.^[37]

Ni(II) complexes

Various ligand field parameters, like Dq, β , B and LFSE were calculated for Ni(II) complexes and are listed in **Table 4**. The value of Dq and B were calculated by using first and third transitions. The value for B (free ion) for Ni(II) metal ion is 1041 cm^{-1} . The parameter B was calculated by the relation: $B = \nu_2 + \nu_3 - 3\nu_1/15$.^[38] The values of β for Ni(II) complexes lie in the range of 0.58-0.74 which indicate an appreciable covalent character in the Ni(II) complexes.

Table 4: Ligand field parameters of complexes.

Complexes	Dq (cm ⁻¹)	B (cm ⁻¹)	β	ν_2/ν_1	C	F ₂	F ₄	hx	LFSE (KJ/mole ⁻¹)
[Mn(L)Cl ₂] MnC ₁₈ H ₁₄ N ₄ Br ₂ Cl ₂	1597	553	0.70	0.74	3230	1012	93	4.3	229
[Co(L)Cl ₂] CoC ₁₈ H ₁₄ N ₄ Br ₂ Cl ₂	966	606	0.54	1.81	–	–	–	–	138
[Co(L)(NO ₃) ₂] CoC ₁₈ H ₁₄ N ₆ Br ₂ O ₆	941	637	0.57	1.85	–	–	–	–	135
[Ni(L)Cl ₂] NiC ₁₈ H ₁₄ N ₄ Br ₂ Cl ₂	946	607	0.58	–	–	–	–	–	136
[Ni(L)(NO ₃) ₂] NiC ₁₈ H ₁₄ N ₆ Br ₂ O ₆	967	771	0.74	–	–	–	–	–	138



(a) (b)
Fig.6. Electronic Spectra of (a)[Mn(L)Cl₂] (b)[Cu(L)(NO₃)₂]

**Electronic Paramagnetic Resonance Spectra (E.P.R.)
 Electronic Paramagnetic Spectrum of Mn(II) complex**

The EPR spectrum of Mn(II) complex was recorded at room temperature as polycrystalline sample on X-band at frequency 9.1 GHz under the magnetic field strength 3000 Gauss. The polycrystalline spectra give an isotropic signal centered at 2.06. The spectra recorded in DMSO solution gives well resolved six line spectra due to the hyperfine interaction between the unpaired electrons with the ⁵⁵Mn nuclear ($I = 5/2$).

Electronic Paramagnetic Spectra of Co(II) complexes

The EPR spectra of the Co(II) complexes were recorded at liquid nitrogen temperature (L.N.T.) in polycrystalline form. The line shaped EPR spectrum of Co(II) complexes with $g_{\text{iso}} = 2.14-2.17$ (**Table 5**) correspond to the octahedral symmetry around the Co(II). As a consequence of the fast spin-relaxation time of high-spin cobalt (II) ion, the signals are observed only at low temperature. The polycrystalline powder EPR signals for the Co(II) complex are broad. The spectrum is consistent with an $S = 3/2$ spin state. No hyperfine splitting of the transitions is detected since it is difficult to resolve this splitting in non- magnetically diluted Co(II) complex.

The line shapes are mostly dominated by the unresolved hyperfine interactions and by a distribution of E/D, where E and D describe the axial and rhombic Zero field splitting (ZFS) constants, respectively. The spread of E/D results in a spread of g-value (g-strain). The dominant broadening effect is realized when the g-strain is converted in <B-strain> with the relation $\Delta B = - (h\nu/\beta)(\Delta g/g^2)$, where the parameters have their usual definitions. Thus, the largest and smallest g-values of the S = 3/2 spectrum have field widths that differ by an order of magnitude, rationalizing why the high field features of the spectra are so broad.^[39,40]

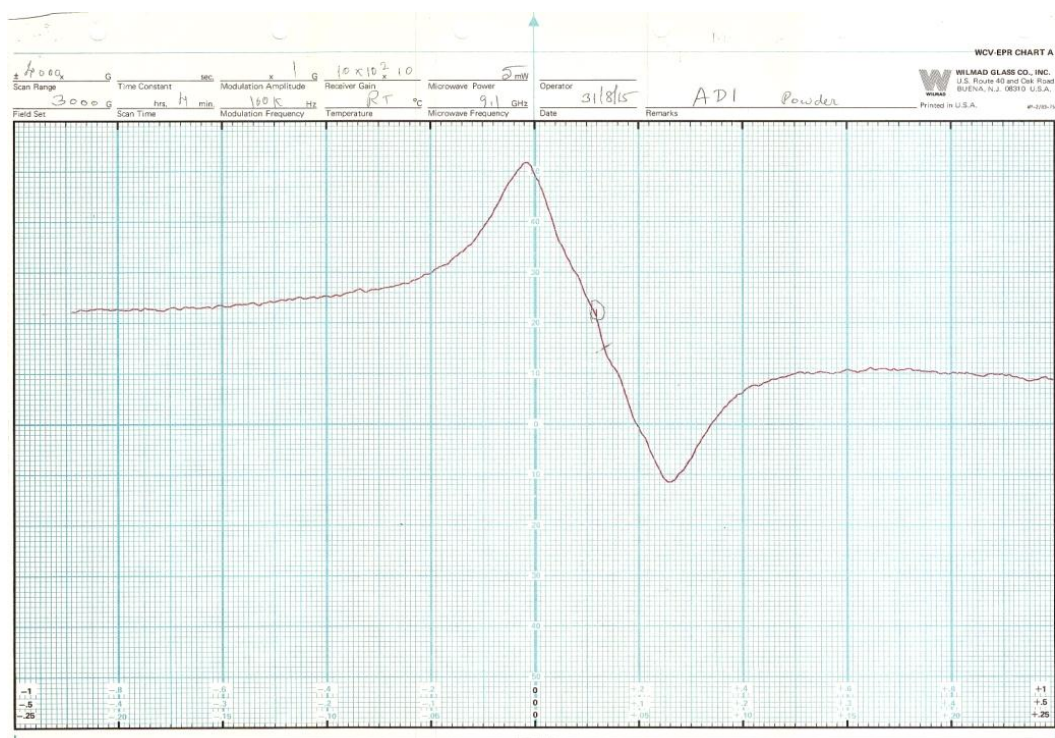
Electronic Paramagnetic Spectra of Cu(II) complexes

The EPR spectra of the Cu(II) complexes were recorded, at room temperature as polycrystalline sample, on the X-band at 9.1 GHz under the magnetic field range 3000 G. The analysis of spectrum of Cu(II) complex gives $g_{||}$

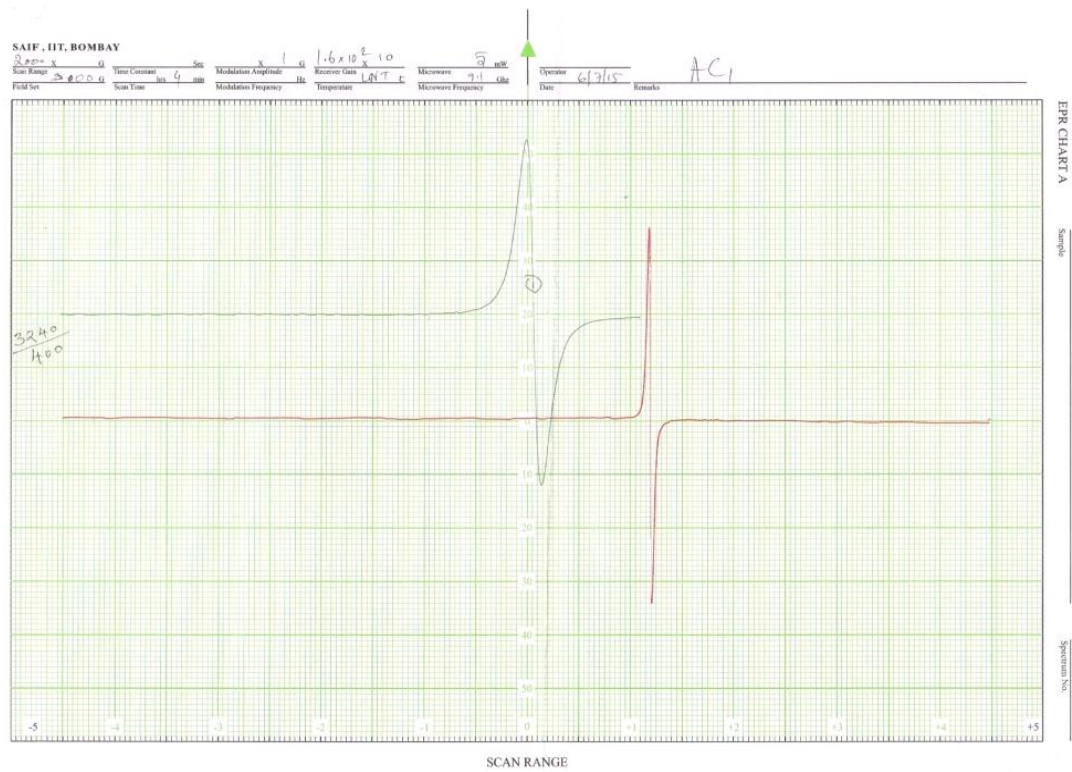
2.23 – 2.43 and g_{\perp} 2.03-2.13. The trend $g_{||} > g_{\perp} > 2.0023$, observed for the complex, under study, indicate that the unpaired electron is localized in the dx^2-y^2 orbital of the Cu(II) ion and the spectral figures are characteristic for the axial symmetry. Tetragonally elongated geometry is thus confirmed for the afore-said complex^[41], $G = (g_{||} - 2)/(g_{\perp} - 2)$, which measure the exchange interaction between the metal centers in a polycrystalline solid has been calculated. According to Hathaway, if $G > 4$, the exchange interaction is negligible, but $G < 4$ indicates considerable exchange interaction in the solid complexes.^[42] The “G” value for Cu complexes reported in this paper, is <4 indicating the exchange interaction in solid complexes. On the basis of above discussion, the structures of complexes are given in **Figure 6.**^[43-44]

Table 5: EPR spectral data of Mn(ii), Co (ii) and Cu (ii) complexes.

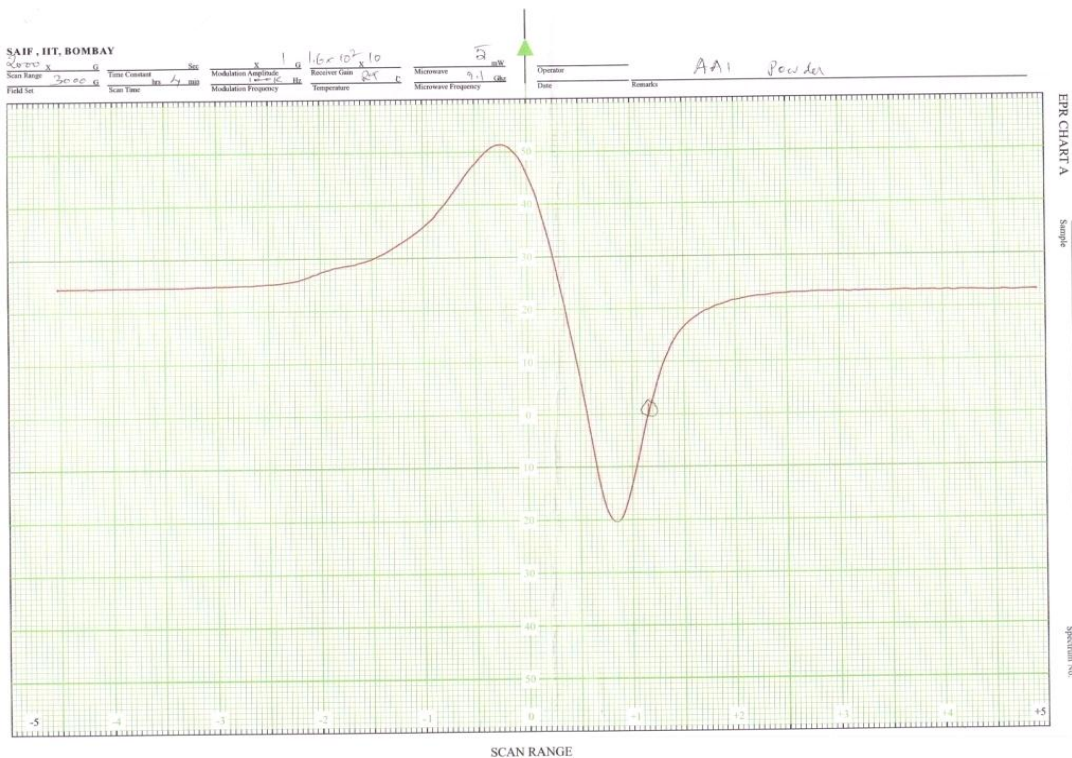
Complexes	$g_{ }$	g_{\perp}	g_{iso}	G
[Mn(L)Cl ₂]	-	-	2.06	-
[Co(L)Cl ₂]	2.26	2.09	2.17	-
[Co(L)(NO ₃) ₂]	2.26	2.08	2.14	-
[Cu(L)Cl ₂]	2.34	2.11	2.18	3.09
[Cu(L)(NO ₃) ₂]	2.23	2.03	2.09	3.89
[Cu(L)SO ₄]	2.43	2.13	2.23	3.41



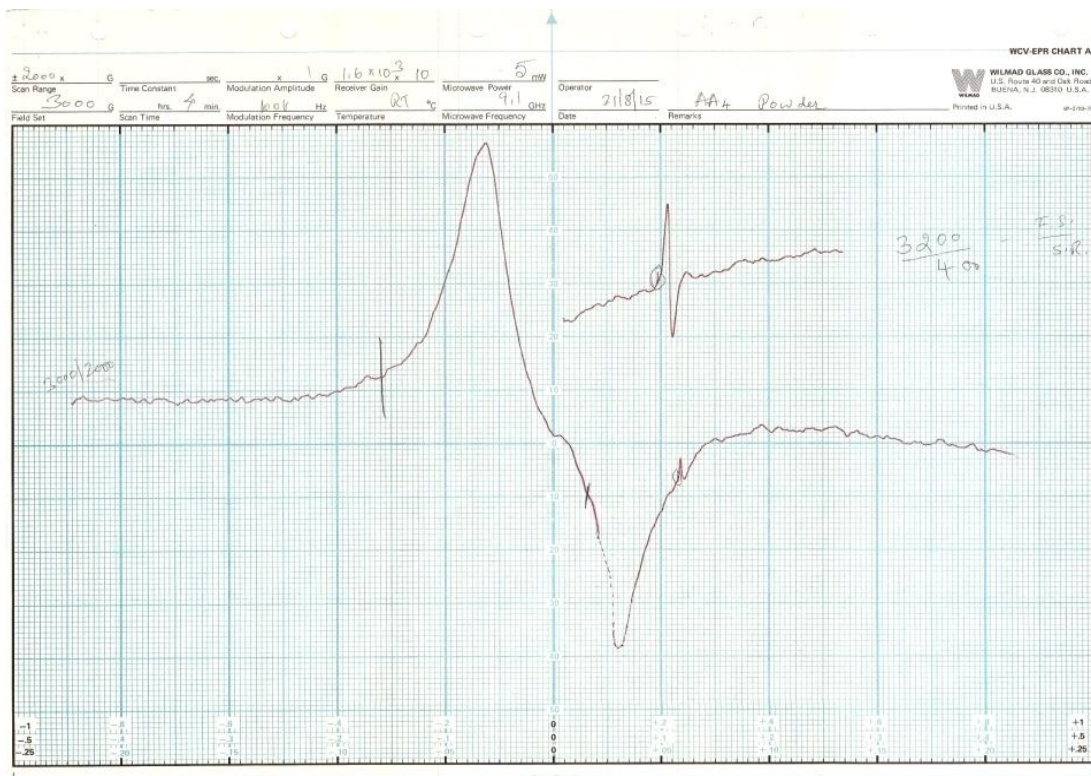
(a)



(b)

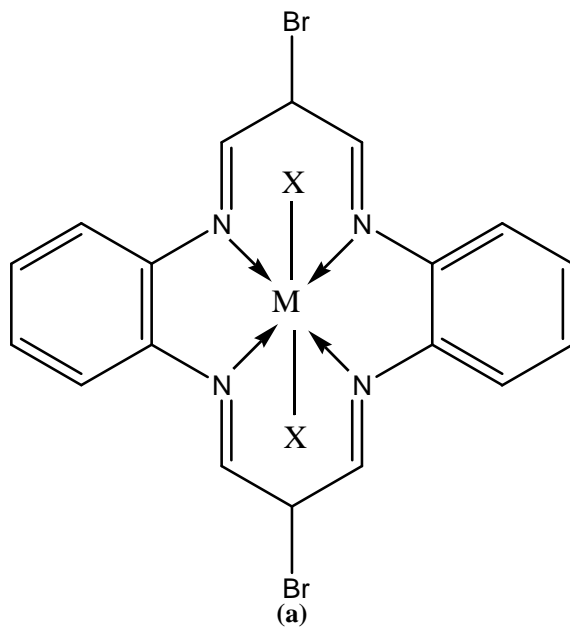


(c)



(d)

Fig. 6: ESR Spectra of (a) $[Mn(L)Cl_2]$, (b) $[Co(L)Cl_2]$, (c) $[Cu(L)Cl_2]$, and (d) $[Cu(L)SO_4]$.



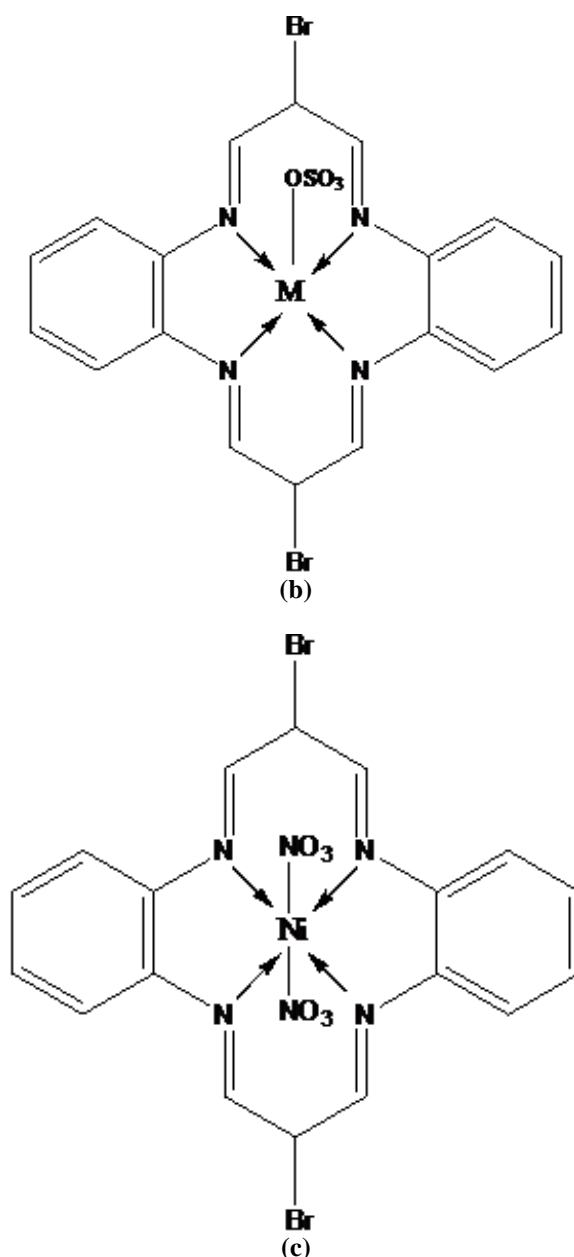


Fig. 7: Proposed structure of complexes (a) $[M(L)Cl_2]$, (b) $[Cu(L)SO_4]$, And (c) $[Ni(L)(NO_3)_2]$ where $M = Mn(II)$, $Co(II)$, $Ni(II)$ and $Cu(II)$ $X = Cl^{-1}$, NO_3^{2-}

CONCLUSION

The macrocyclic Schiff base ligand i.e. 3,10-dibromo-1,5,8,12-tetraaza-6,7:13,14-dibenzocyclotetradeca-1,4,8,11-tetraene, characterized on the basis of above observations i.e. elemental analysis, molar conductivity, UV-Visible, magnetic moment, IR and EPR, it is possible to determine the type of coordination of ligand to $Mn(II)$, $Co(II)$, $Cu(II)$ and $Ni(II)$ metal ions. The spectral study data showed that ligand exist as tetradentate (NNNN) type by bonding to metal ion through the nitrogen donor atoms. The proposed study of complexes indicates octahedral geometry for $Mn(II)$, $Co(II)$ and $Ni(II)$ complexes and tetragonal geometry for $Cu(II)$ complexes, as shown in **Fig.7**.

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