

SPECTROSCOPIC APPROACH IN CHARACTERIZATION OF MONONUCLEAR MANGANESE (II), NICKEL (II) AND COPPER (II) COMPLEXES WITH A NITROGEN DONOR TETRADENTATE MACROCYCLIC SCHIFF'S BASE LIGANDA. Rajput^{*1,2}, S. Gautam², S. Chandra² and S. P. Sati¹¹SDM Govt. (P.G.) College Doiwala, Dehradun, Garhwal, Uttarakhand.²Department of Chemistry Zakir Husain Delhi College University of Delhi, J. L. N. Marg New Delhi-110002, India.***Corresponding Author: A. Rajput**

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ABSTRACT

A tetradentate nitrogen donor [N₄] macrocyclic Schiff's base ligand, (L), has been synthesized. Mn(II), Ni(II) and Cu(II) complexes of this ligand have been synthesized and characterized by elemental analyses, molar conductance measurements, magnetic susceptibility measurements, mass, ¹H-NMR (Ligand), IR, U and EPR UV-Vis. spectral studies. On the basis of molar conductance the Mn(II), Ni(II) and Cu(II) complexes may be formulated as [M(L)X₂] where X = Cl⁻, CH₃COO⁻, NO₃⁻, SO₄²⁻ due to their non-electrolytic nature in dimethylformamide (DMSO). All the complexes are of the high spin type and characterization study revealed six coordinated octahedral geometry but tetragonal in case of Cu (II) complexes due to distortion.

KEYWORDS: Macrocyclic Ligand, Metal Complexes, Spectral Characterization, Six Coordinated Geometry.**INTRODUCTION**

Nowadays chemistry of macrocyclic ligands is a growing area of research in inorganic as well as in bioinorganic chemistry taking into accounts of its biological impact.^[1-2] The studies of macrocyclic have undergone incredible growth in recent years and their complexation chemistry with a wide variety of metal ions has been extensively studied.^[3-4] Chemistry of macrocyclic Schiff's base ligands and their transition metal complexes is developed very rapidly because of they can be tuned to force metal ions to assume unusual coordination geometrical structure.^[5-6] Transition metal macrocyclic Schiff's base complexes have received much attention as an active part of metalloenzymes and as biomimic model complexes.^[7] It is due to their resemblance with natural proteins.^[8] The chemistry of macrocyclic compounds in particular is also important due to their catalytic^[9] and biological applications.^[10] Their application in biological part are as such i.e. these compounds are used as antifungal, antibacterial, anticancer, antiviral, anti tumour, DNA binding and DNA cleavage, antioxidant etc.^[11-14] In view of invention of novel macrocyclic Schiff's base ligands and their transition metal complexes, we report the synthesis and characterization study of Mn(II), Ni(II) and Cu(II) complexes of macrocyclic Schiff's base ligand.

All chemicals used were commercial products and used as supplied. 2,3-diaminopyridine and di-benzoylmethane 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 spectroscopic grade.

Analytical and physical measurements: IR spectra were recorded on FT-IR spectrum BX spectrophotometer in KBr pellet. Mass spectrum of ligand was recorded with a model Bruker Compass micro OTOF-Q instrument. Elemental study (CHN) was analyzed on Carlo-Erba1106 elemental analyzer. ¹H-NMR spectrum was recorded on a Bruker Advanced DPX-300 spectrometer using DMSO-d₆ as a solvent at IIT Delhi. The electronic spectra were recorded in DMSO on Shimadzu UV-visible mini 1240 spectrophotometer. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. EPR spectra of all complexes were recorded at room temperature (RT) on E₄-EPR spectrometer using the DDPH as the g-marker at SAIF, IIT Bombay. Magnetic susceptibilities were measured at room temperature on a Gouy balance using CuSO₄.5H₂O as calibrant.

Synthesis of macrocyclic Schiff's base ligand: A hot ethanolic solution (20 mL) of diamine i.e. 2,3-diaminopyridine (0.02 mol) and a hot ethanolic solution (20 mL) of diketone i.e. di-benzoylmethane (0.02 mol) were mixed slowly with constant stirring. The mixture was refluxed at 85°C for 10 hrs. On cooling the reaction mixture, a solid yellow precipitate formed, was filtered,

washed with cold ethanol and dried under vacuum over P_4O_{10} .

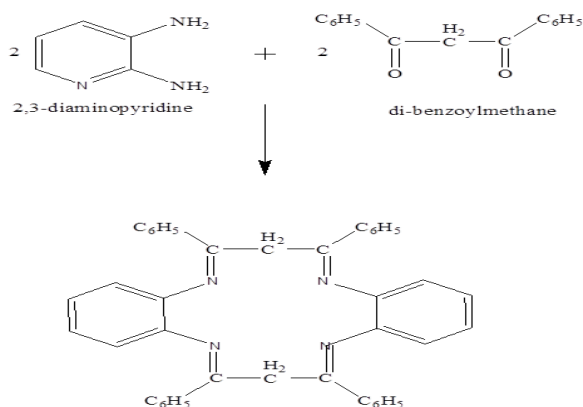


Fig. 1: Synthesis of macrocyclic Schiff's base ligand (L).

Synthesis of transition metal complexes

Table 1: Analytical, Elemental analyses and Molar Conductance Data of Mn(II), Ni(II), Cu(II) Complexes

Sl. No.	Complexes	Yield (%)	Colour	Molecular Weight (M.Wt.)	M.P. ($^{\circ}C$)	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Elemental Analyses calculated (Found)			
							M	C	H	N
1	MSB Ligand (L)	61	Light Yellow	644	$80^{\circ}C$	25		85.71	1.33	8.69
2	[Mn(L)Cl ₂]	52	Light Pink	770	$>280^{\circ}C$	27	7.14	71.68	4.67	7.27
3	[Mn(L)(OAc) ₂]	48	Pink	817	$>250^{\circ}C$	31	6.73	67.56	4.40	6.85
4	[Mn(L)(NO ₃) ₂]	45	White	823	$>300^{\circ}C$	35	6.68	67.07	4.37	6.80
5	[Ni(L)Cl ₂]	50	Green	773.69	$>250^{\circ}C$	32	7.58	71.34	4.65	7.23
6	[Ni(L)(OAc) ₂]	55	Mehndi green	820.69	$>250^{\circ}C$	27	71.5	67.26	4.38	6.82
7	[Cu(L)Cl ₂]	51	brown	778.85	$>280^{\circ}C$	22	8.15	70.90	4.62	7.19
8	[Cu(L)(OAc) ₂]	46	Dark green	825.5	$>300^{\circ}C$	20	7.69	66.86	4.36	6.78

Characterization of Macrocyclic Schiff's base ligand

IR: IR spectra were recorded on FT-IR spectrum BX-II spectrophotometer in KBr pellets. The IR spectrum of macrocyclic ligand L displayed bands in the region 3190-

A hot EtOH solution of the ligand (0.82 g, 0.002 mol) was mixed with an EtOH solution of corresponding metal salt (0.001 mol), with constant stirring and boiled under reflux for 5-10 hrs. at $80-90^{\circ}C$ (± 5). The completion of reaction was confirmed by IR spectra of Mn (II), Ni(II) and Cu(II) complexes with nitrogen donor [N₄] macrocyclic Schiff's base ligand (L).

RESULTS AND DISCUSSION

Possessed compositions and physical data of macrocyclic Schiff's base ligand and its transition metal complexes have been shown in Table 1. The molar conductance value for the mononuclear Mn(II), Ni(II) and Cu(II) complex in DMSO solution suggest that the complex are nonelectrolytes in nature.^[15] Thus, the general formula of the complexes may be given as [M(L)X₂] where M = Mn(II), Ni(II) and Cu(II). In IR spectra of the complexes the most useful vibrational bands of the complexes for establishing the mode of coordination are present.

3010 cm^{-1} , 1589 cm^{-1} Fig. 2. These bands were corresponded to the aromatic C-H stretching, azomethine group $\nu(C=N)$ stretching vibration.^[16]

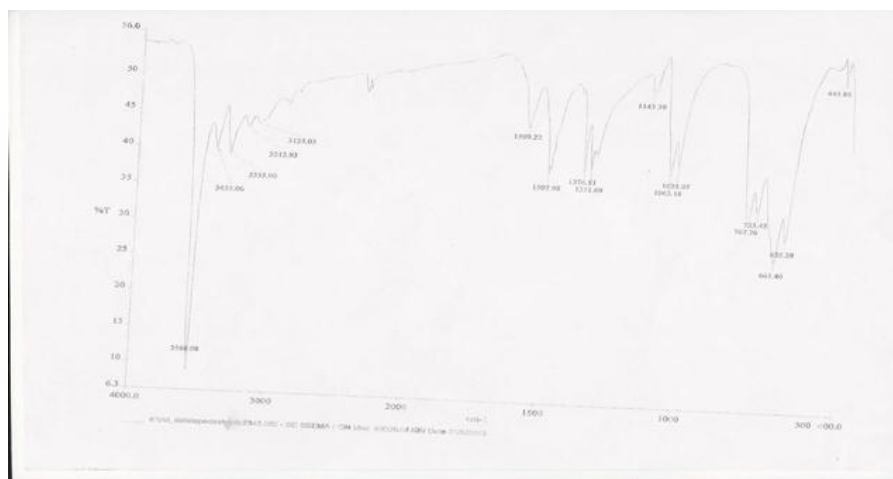


Fig. 2: IR spectrum of macrocyclic Schiff's base Ligand.

¹H-NMR: ¹H-NMR spectrum was recorded with a model Bruker Advance DPX-300 spectrometer operating at 400

MHz using DMSO-d₆ as a solvent and TMS as internal standard. ¹H-NMR Spectrum of L exhibited following

signals: These signals indicated that two different type of protons were present in ligand L. A signal at δ 8.73 ppm

and δ 3.45 ppm were corresponded to protons of aromatic ring (8H, m, Ar-H)^[17] Fig. 3.

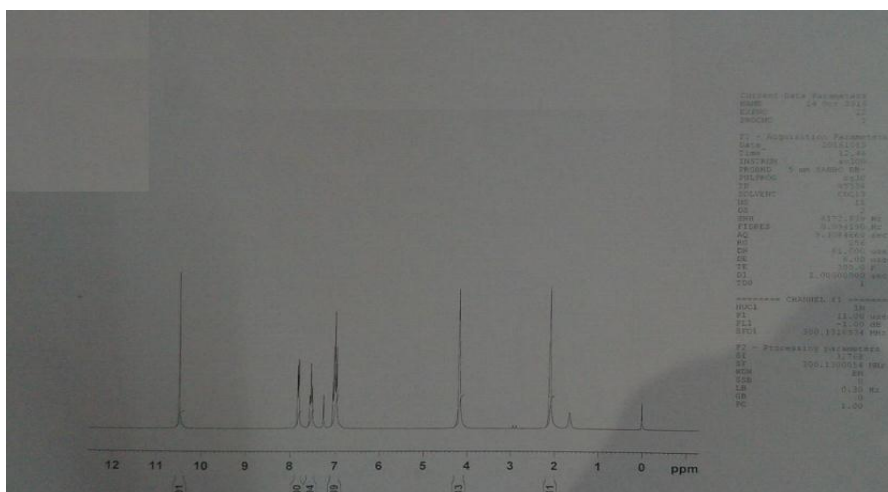


Fig. 3: ¹H-NMR spectrum of macrocyclic Schiff's base Ligand

Mass Spectrum

Mass spectrum of ligand was recorded with a model Bruker Compass micrOTOF-Q instrument. Mass spectrum showed a molecular ion peak at $m/z = 643$ 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 588, 511, 434, 357, 280, 204, 177, 165, 138, 62, 35 amu Fig. 4. Intensity of these peaks shows the stability of peaks.

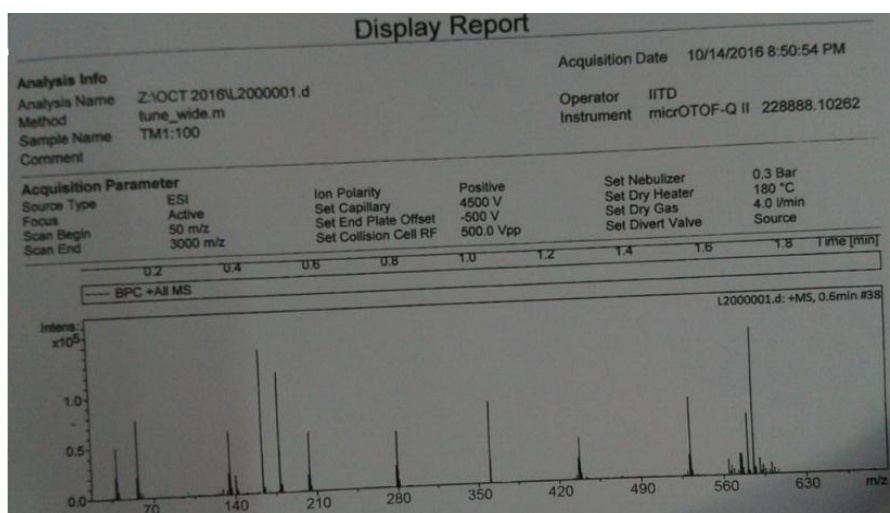


Fig. 4: Mass spectrum of macrocyclic Schiff's base Ligand

IR SPECTRA OF METAL COMPLEXES

All IR spectra of the complexes exhibits medium to strong bands at ca. 1578-1592 cm^{-1} and absence of absorption around 3400 cm^{-1} indicates that amino group of the diamine has reacted completely with the diketone.^[18] Coordination of the imine nitrogen is indicated by a decrease in energy of the IR band, which derives considerable intensity from 408-430 cm^{-1} , indicating the presence of $\nu(\text{M}-\text{N})$ ^[19] bonding. In the far IR spectra a band is observed in the range 310-320 cm^{-1} assignable to $\nu(\text{M}-\text{Cl})$ mode.^[20] These IR spectra data reveal to suggest that the ligand is tetradentate coordinating through nitrogen donor atoms $[\text{N}_4]$.

$(\text{NO}_3)_2$: The appearance of new bands at 1417-1426, 1374-1396, 1110-1121 cm^{-1} in the spectra of nitrate complexes of indicate the monodentate nature of the nitrate group. This indicates that the nitrate group coordinates to metal ion in unidentate manner Fig. 5.^[21]

$(\text{CH}_3\text{COO})_2$: The presence of absorption bands in range of 1556-1566 cm^{-1} , 1409-1452 cm^{-1} , 1339-1344 cm^{-1} in spectrum of the acetate complexes macrocyclic Schiff's base shows that both the acetate ions are coordinated to metal ion in unidentate mode.^[22]

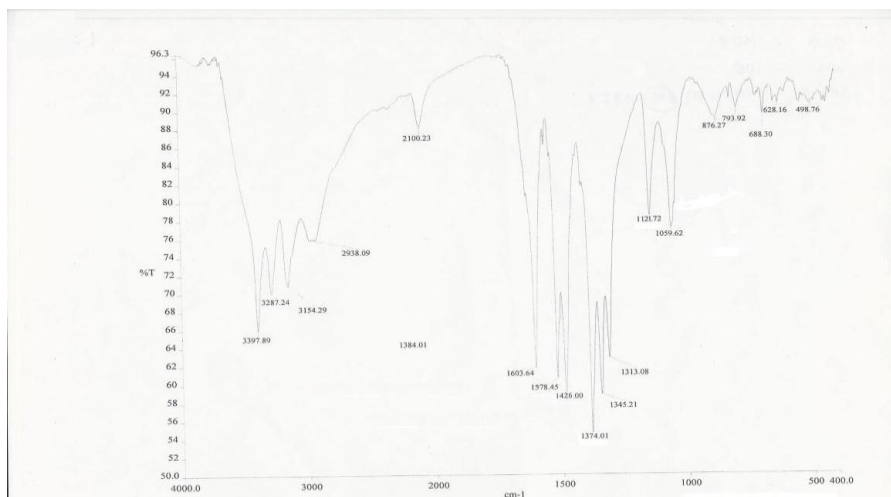


Fig. 5: IR spectra of metal complexes of $[\text{Mn}(\text{L})(\text{NO}_3)_2]$

Magnetic susceptibility

The observed magnetic moments for Mn(II), Ni(II) and Cu(II) complexes are given in Table 2. The observed values of magnetic moment for complexes are generally diagnostic of the coordination geometry about the metal ion. The room temperature magnetic moment of the manganese(II) complexes lies in the range 5.88-5.93 BM corresponding to five unpaired electrons.^[23] The magnetic moment observed for the Ni(II) complexes lies in the range of 2.91–2.94 BM which is consistent with the octahedral stereochemistry of the complexes.^[24] Room temperature magnetic moment of the Cu(II) complexes lies in the range of 1.93–1.96 BM, corresponding to one unpaired electron. Whatsoever the geometry of Cu(II) is, its complexes always show magnetic moment corresponding to one unpaired electron.^[25]

Electronic spectra

Electronic spectra of Mn(II) complexes exhibit four intensity absorption bands in the range 18,180-18,354, 22,883-24,169, 26,778-26,936, and 31,250-35087 cm^{-1} . These bands may be assigned to the transitions: ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$, ${}^4\text{A}_{1g}$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$, respectively. The electronic spectrum of the Nickel(II) complex shows three spectral bands at 9,488-9,653, 10,878-12,130 and 23,744-23950 cm^{-1} , which may be assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions, respectively. This suggests an octahedral environment around the Ni(II) ion Fig.6.^[26] The electronic spectrum of Cu(II) chloride complex displayed bands at 10,947-11792, 18,622-18,690 and 27,069-27,887 cm^{-1} . The band at 32258-33445 cm^{-1} may be due to charge transfer. Therefore, the complexes may be considered to possess a tetragonal geometry.^[27]

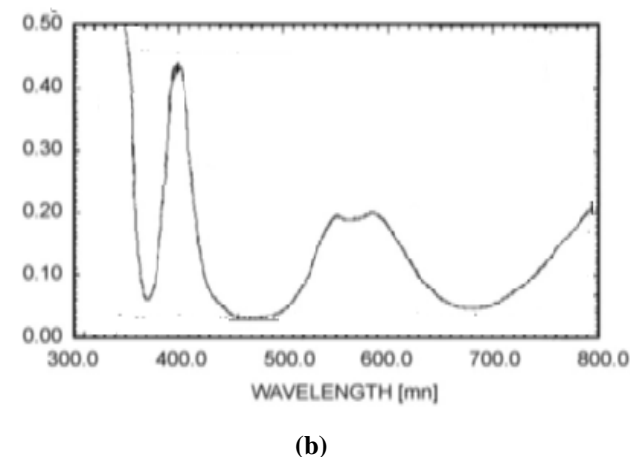
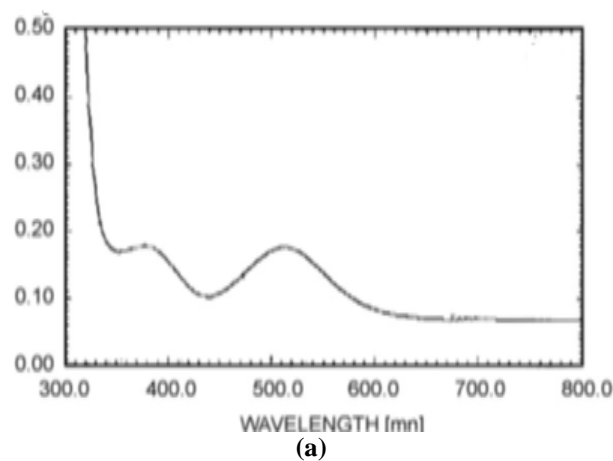


Fig. 6: Electronic spectra of the complexes (a) $[\text{Ni}(\text{L})\text{Cl}_2]$ (b) $[\text{Cu}(\text{L})(\text{OAc})_2]$

Table 2: Magnetic moment and electronic spectral bands of Mn(II), Ni(II) and Cu(II) complexes with MSB ligand

Sl. No.	Complexes	electronic spectral bands (cm ⁻¹)				μ_{eff} (B.M.)
		ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)	ν_4 (cm ⁻¹)	
1	[Mn(L)Cl ₂]	18180	22838	26778	31250	5.88
2	[Mn(L)(OAc) ₂]	18354	23763	26936	35087	5.90
3	[Mn(L)(NO ₃) ₂]	18244	24169	28910	32850	5.93
4	[Ni(L)Cl ₂]	9488	10878	23744	-	2.94
5	[Ni(L)(OAc) ₂]	9653	12130	23950	-	2.91
6	[Cu(L)Cl ₂]	11792	18622	27069	32258	1.93
7	[Cu(L)(OAc) ₂]	10945	18690	27885	33445	1.96

Ligand field parameters

Various ligand field parameters have been calculated for the complexes and are given in Table 3.

The ligand field parameter B and C values have been calculated by using the transitions, ${}^6A_{1g} \rightarrow {}^4E_g$, ${}^4A_{1g}(4G)$ and ${}^6A_{1g} \rightarrow {}^4E_g(4D)$. This is due to the fact that the energies of these two transitions are independent from the crystal field splitting energy^[28] and depends only on the parameters B and C . The calculated value of B and C are 786 and 3156 cm⁻¹, respectively. The value of Dq has been evaluated with the help of curve transition energies vs. Dq by Orgel using the energy due to the transition ${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$. Parameters B and C are linear combination of certain Coulomb exchange integral and are generally treated as empirical parameters obtained

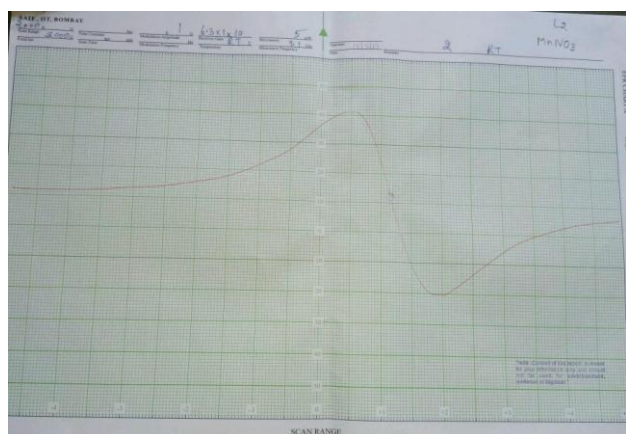
from the spectra of the free ions. Slater Condon–Shortly parameters F_2 and F_4 are related to the Racah inter-electronic repulsion parameters B and C , as follows: $B = F_2 - 5F_4$ and $C = 35F_4$. By using these values of Racah parameters B and C , the values for the parameters F_2 and F_4 have been calculated and found to be 1236.85 and 90.17, respectively. The electron-electron repulsion in the complex is less than the free ion, resulting the increased distance between electrons and thus, an effective increase in the size of the orbital will take place. On increasing delocalization, the value of β decreases. That is why the calculated value of β in the present complex is less than one. This indicates that the complex under study has appreciable covalent character in metal ligand (M-L) bond.

Table 3: Ligand field parameters of Co(II) and Ni(II) complexes with MSB ligand

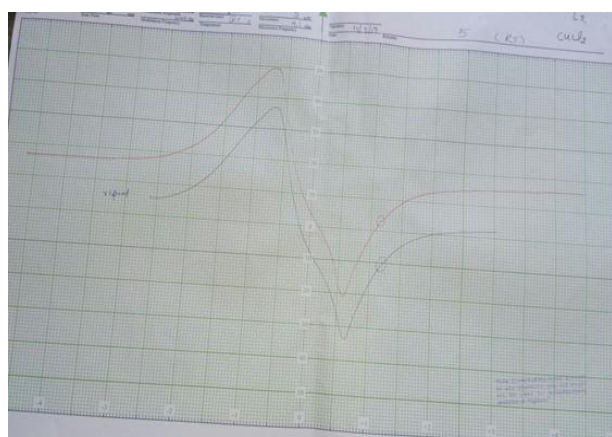
Sl. No.	Complexes	Dq (cm ⁻¹)	B (cm ⁻¹)	β	LFSE	ν_2/ν_1	F_2	F_4	C	hx
1	[Mn(L)Cl ₂]	1818	412.21	0.52	-	1.25	945.41	106.94	3743	6.8
2	[Mn(L)(OAc) ₂]	1835	844.33	0.70	-	1.29	828.03	187.54	3063	1.0
3	[Mn(L)(NO ₃) ₂]	1824	561.15	0.71	-	1.32	851.05	658.47	3094	4.1
4	[Ni(L)Cl ₂]	954	273.53	0.62	114.13	1.65	-	-	-	-
5	[Ni(L)(OAc) ₂]	947	768.46	0.73	113.38	1.33	-	-	-	-

The EPR spectra: The EPR spectrum of a polycrystalline sample gives one broad isotropic signal centered at 1.9924, characteristic for octahedral environment around the Mn(II) ion Fig. 7. EPR spectra of Cu(II) complexes were recorded at room temperature as polycrystalline sample, on X band at frequency of 9.1 GHz under the magnetic-field strength of 3000G. The analysis of spectra of Cu(II) chloride complex gives $g_{\parallel} = 2.196$, $g_{\perp} = 2.064$ Table 4. The observed g_{\parallel} values for the complex are less than 2.3 in agreement with the covalent character of the metal ligand bond. The trend $g_{\parallel} > g_{\perp} > 2.0023$ observed for the complex indicates that unpaired electron is localized in $d_{x^2-y^2}$ orbital of the Cu(II) ion and the spectral features are a characteristic of axial symmetry. Thus, a tetragonal geometry is confirmed for the aforesaid complex.^[29]

**(a)**



(b)



(c)

Fig. 7: Electronic spectra of the complexes (a) [Mn(L)Cl₂], (b) [Mn(L)(NO₃)₂], (c) [Cu(L)Cl₂]

Table 4: EPR data of Mn(II) and Cu(II) complexes with MSB ligand

Sl. No.	Complexes	g_{\parallel}	g_{\perp}	g_{iso}
1	[Mn(L)Cl ₂]	-	-	2.00
2	[Mn(L)(OAc) ₂]	-	-	1.93
3	[Mn(L)(NO ₃) ₂]	-	-	1.97
4	[Cu(L)Cl ₂]	2.68	2.21	-
5	[Cu(L)(OAc) ₂]	2.36	2.14	-

CONCLUSION

This research paper describes synthesis and characterization of novel macrocyclic Schiff's base ligand and its Mn(II), Ni(II) and Cu(II) complexes based on 2,3-diaminopyridine moiety. The synthesis procedure is simple and efficient. The complexes were non-electrolytic in nature on the basis of molar conductance analyses. On the basis of the physicochemical and spectral data, we assume that macrocyclic Schiff's base ligand behaves as tetradentate [N₄] ligand and coordinate to metal ion through its nitrogen donor atoms and anions (Cl⁻, OAc⁻, NO₃⁻). In the light of above IR, electronic and e.p.r. spectral studies we proposed an octahedral geometry for Mn(II) and Co(II) and tetragonal geometry for Cu(II) complexes.

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