

DESIGNING, SYNTHESIS AND SPECTROSCOPIC STUDIES OF Co(II), Ni(II) AND Cu(II) TRANSITION METAL COMPLEXES WITH [N₄] DONOR MACROCYCLIC SCHIFF'S BASE LIGAND DERIVED FROM 2,6-DIAMINO-4-CHOLROPYRIMIDINEA. Rajput^{1,2}, S. Gautam², S. Chandra*² and S.P. Sati¹¹Hemvati Nandan Bahuguna Garhwal University, Shri Nagar (Garhwal) Uttarakhand-246174.²Department of Chemistry Zakir Husain Delhi College University of Delhi, J.L.N. Marg New Delhi-110002, India.***Corresponding Author: S. Gautam**

Department of Chemistry Zakir Husain Delhi College University of Delhi, J.L.N. Marg New Delhi-110002, India.

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ABSTRACT

A novel tetradentate nitrogen donor [N₄] macrocyclic Schiff's base ligand which was synthesized by condensation reaction of diamine and diketone i.e. 2,6-diamino-4-cholropyrimidine and glutaric anhydride, respectively. Condensation reaction was carried out in 2:2 ratios in ethanolic medium and ligand was characterized by using analytical and spectral techniques (mass, ¹H-NMR, IR). Co(II), Ni(II) and Cu(II) complexes of this synthesized ligand were also prepared and characterized by elemental analyzes, molar conductance measurements, magnetic susceptibility measurements, electronic and EPR spectral studies. On the basis of molar conductance complexes were non electrolytic in nature. On the basis of IR, electronic and EPR spectral studies an octahedral geometry has been approved to synthesized Co(II) and Ni(II) complexes but tetragonal geometry for Cu(II) complexes.

KEYWORDS: Macrocyclic, Schiff's base, complexes, spectral, octahedral, tetragonal.**INTRODUCTION**

The scientific interest in macrocyclic Schiff's base (MSB) ligands and their metal complexes depends on the fact that not only their chemical structure resemble to the structure of naturally macrocyclic molecules but also their functional features also similar.^[1-2] Due to the above significance role of macrocyclic compounds, the study of metal complexes of these ligands appears to be interesting in view of the possibility to obtain coordination compound. The formation of macrocyclic complexes depends on the size of the macrocyclic ligand cavity, as well as on the nature of its donor atoms and also on the complexation performance of anions which involve in coordination to metal ion.^[3-5] Macrocyclic ligands are also of theoretical interest since they are capable of furnishing an environment of controlled geometry and ligand field strength.^[6] Moreover, macrocyclic Schiff's base nitrogen donor ligands have received special attention because of their hard-soft donor character and versatile coordination behavior.^[7-10] It has been well established that transition metal complexes are of biological importance due to their therapeutically activity and interest in bioinorganic chemistry.^[11] In biological field, macrocyclic transition metal complexes have received a great attention because of their antitumor, antibacterial, antiviral, antifungal and anti-carcinogenic activities.^[12-16] The complexes of metal ions in combination to macrocyclic ligands are significant, as these resemble with natural system like

porphyrin and cobalamine. The therapeutically action of metal complexes is due to their interface with nuclear DNA.^[17] The present paper deals with synthesis, spectral studies and biological evaluation of Co(II), Ni(II) and Cu(II) complexes, which were derived from diamine 2,6-diamino-4-cholropyrimidine and diketone glutaric anhydride.

MATERIALS AND METHODS

All chemicals used were commercial products and used as supplied. 2,6-diamino-4-cholropyrimidine and glutaric anhydride 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.

Synthesis of Schiff's base ligand

Chemical synthesis procedure of macrocyclic Schiff's base ligand has been presented in Fig. 1. A hot ethanolic solution (20 mL) of diamine i.e. 2,6-diamino-4-cholropyrimidine (0.02 mol) and a hot ethanolic solution (20 mL) of diketone i.e. glutaric anhydride (0.02 mol) were mixed slowly with constant stirring. The mixture was refluxed at 75-80°C for 10 hrs. On cooling the reaction mixture, a solid yellow precipitate was formed. This precipitate was filtered off, washed with cold ethanol and dried in a desiccator which contains moisture absorbent silica gel.

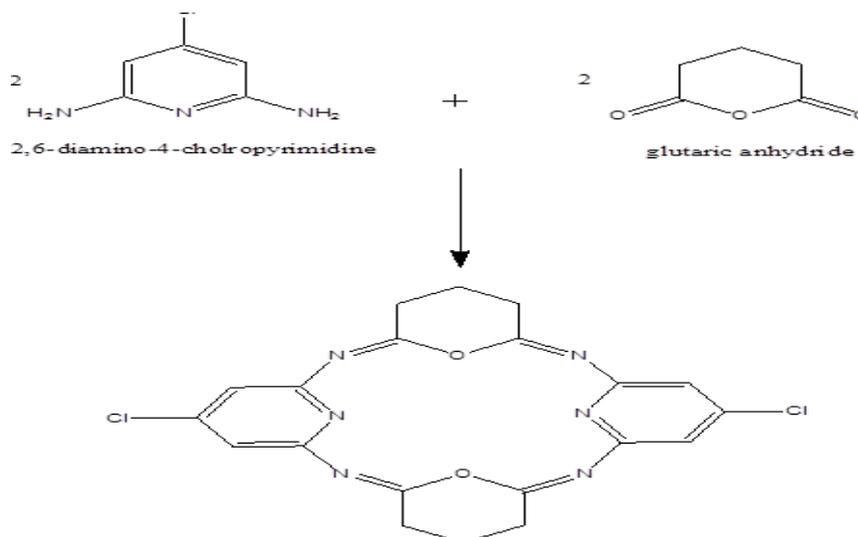


Fig. 1: Synthesis of MSB ligand

Synthesis of transition metal complexes

A hot ethanolic solution of the corresponding metal salts i.e. Cl^- , CH_3COO^- (0.001 mol) was mixed with hot ethanolic solution of macrocyclic Schiff's base ligand (0.001 mol) and content refluxed for 10-12 h at temp. $85-90^\circ\text{C}$ at pH 6-7. pH was adjusted by adding of 2-3 drops of aqueous ammonia. The synthesized corresponding colored complexes were separated out by filtration, washed thoroughly with ethanol, distilled water and dried in a desiccator.

Analytical and physical measurements

Elemental study (CHN) was analyzed on Carlo-Erba 1106 elemental analyzer. IR spectra were recorded on FT-IR spectrum BX spectrophotometer in KBr pellet. $^1\text{H-NMR}$ spectrum was recorded on a Bruker Advanced DPX-300 spectrometer using DMSO-d_6 as a solvent at IIT Delhi. Mass spectrum of ligand was recorded with a model Bruker Compass micro OTOF-Q instrument. The

electronic spectra were recorded in DMSO on Shimadzu UV-visible mini 1240 spectrophotometer. Magnetic susceptibilities were measured at room temperature on a Gouy balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant. 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.

RESULTS AND DISCUSSION

On the basis of elemental analysis complexes were found to have the general composition MLX_2 where $\text{M} = \text{Co(II)}$, Ni(II) , Cu(II) $\text{L} = \text{MSB ligand}$ $\text{X} = \text{Cl}^-$, CH_3COO^- . The molar conductance value of these complexes in dimethylsulphoxide (DMSO) corresponding to non-electrolytic nature.^[18] On the basis of molar conductance values all complexes might be formulated as $[\text{M}(\text{L})\text{X}_2]$ **Table 1.**

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

Sl. No.	Complexes	Color	Yield (%)	M.P. ($^\circ\text{C}$)	Molecular Weight (M.Wt.)	Molar Conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Elemental Analyses calculated (Found)			
							M	C	H	N
1	MSB Ligand (L)	Light Yellow	57%	196	445	-	-	53.93 (53)	4.04 (4.01)	18.87 (17.79)
2	$[\text{Co}(\text{L})\text{Cl}_2]$	Light Brown	57	$>270^\circ\text{C}$	574	17	10.19 (10.00)	41.79 (41.25)	3.13 (3.02)	14.61 (14.44)
3	$[\text{Co}(\text{L})(\text{OAc})_2]$	Brown	50	$>250^\circ\text{C}$	623	25	9.39 (9.31)	46.15 (46.01)	3.84 (3.42)	13.46 (13.44)
4	$[\text{Ni}(\text{L})\text{Cl}_2]$	Green	55	250°C	574	20	10.21 (10.09)	41.76 (41.68)	3.13 (3.10)	14.61 (14.56)
5	$[\text{Ni}(\text{L})(\text{OAc})_2]$	Dark Green	62	$>250^\circ\text{C}$	623	18	9.41 (9.20)	46.17 (46.07)	3.84 (3.79)	13.46 (13.34)
6	$[\text{Cu}(\text{L})\text{Cl}_2]$	Dark Green	60	$>260^\circ\text{C}$	579	25	10.87 (10.84)	41.41 (41.38)	3.10 (3.02)	14.49 (14.37)
7	$[\text{Cu}(\text{L})(\text{OAc})_2]$	Mehndi Green	51	$>250^\circ\text{C}$	628	23	10.02 (9.98)	45.82 (45.80)	3.81 (3.74)	13.36 (13.30)

Characterization of ligand**IR**

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

bands in the region $3213\text{--}3080\text{ cm}^{-1}$, 1673 cm^{-1} . These bands are corresponded to the aromatic C-H stretching and formation of azomethine group $\nu(\text{C}=\text{N})$ stretching vibration.^[19-20]

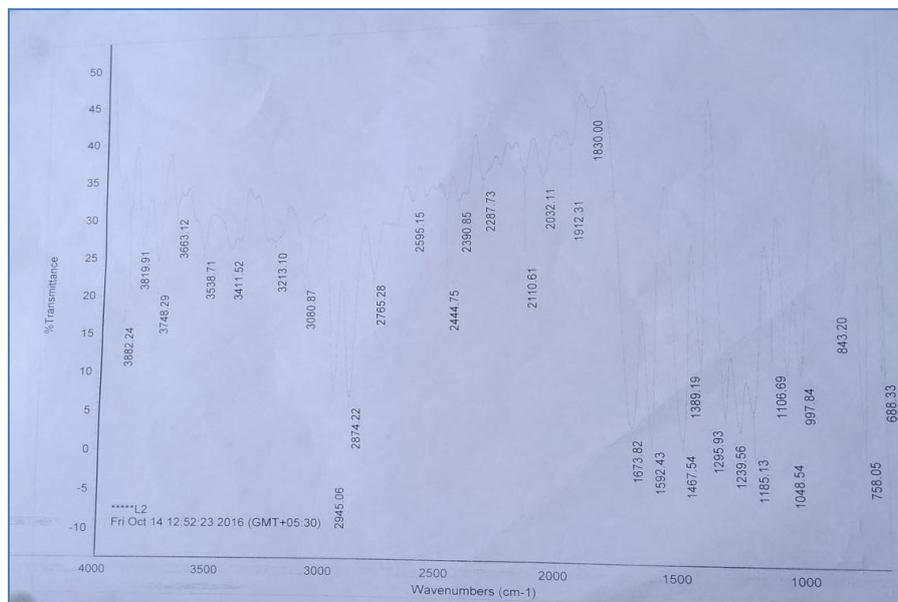


Fig. 2: IR spectrum of MSB Ligand

 $^1\text{H-NMR}$

$^1\text{H-NMR}$ spectrum presented in Fig. 3 was operated at 400 MHz using DMSO-d_6 as a solvent and TMS as internal standard. $^1\text{H-NMR}$ Spectrum of ligand exhibited

signals: these signals indicate that two different types of protons are present in ligand. A signal at δ 6.98-7.93 ppm correspond to protons of aromatic ring (8H, m, Ar-H).^[21]

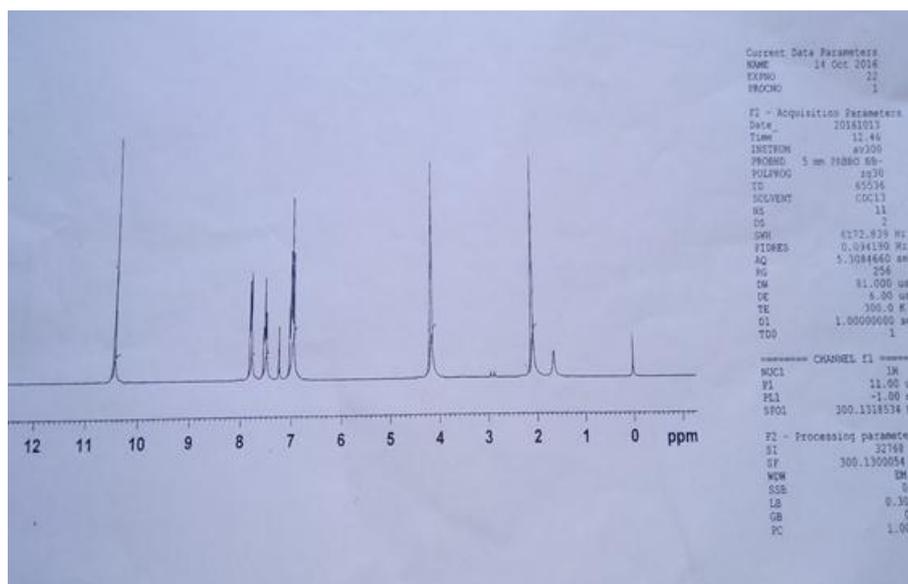


Fig. 3: $^1\text{H-NMR}$ spectrum of Ligand MSB

Mass Spectrum

Mass spectrum of ligand is given in Fig. 4. Mass spectrum showed a molecular ion peak at $m/z = 444$ amu corresponding to $[\text{M}^{+1}]^+$ 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 409, 374, 298, 201, 187, 99 amu. Intensity of these peaks shows the stability of peaks.

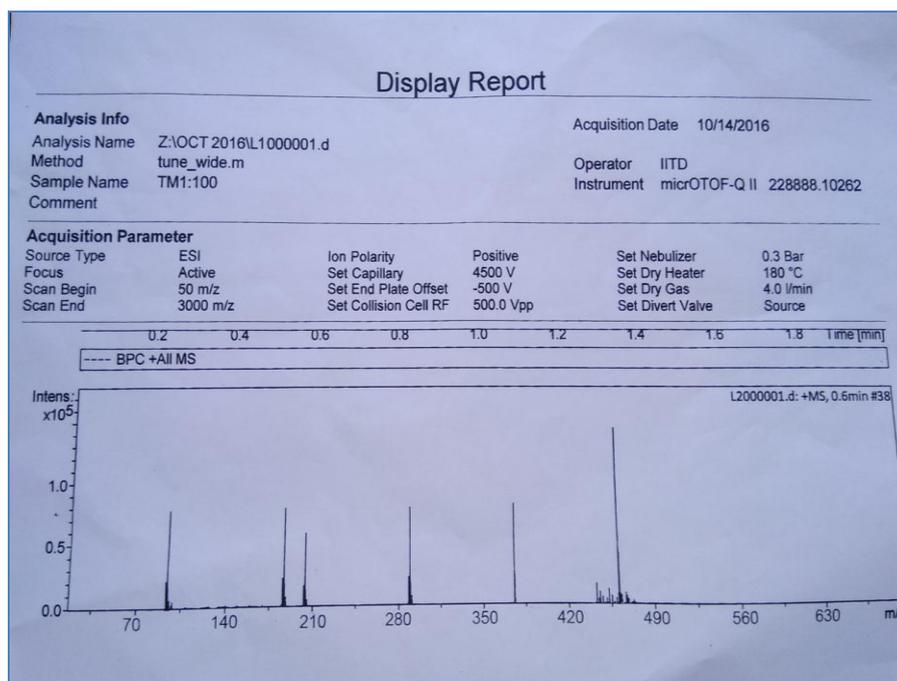


Fig. 4: Mass spectrum of MSB Ligand

Characterization of transition metal complexes IR

In the IR spectra of the complexes the band corresponding to imine group $\nu(\text{C}=\text{N})$ present in IR spectra of L_1 at position 1673 cm^{-1} shifted downward.^[22] This shifting indicated that the donor atoms coordinate to metal ion.^[23] Band at position $1658\text{-}1620 \text{ cm}^{-1}$ also suggest that coordination took place through N atoms.^[24] The chloro complexes spectra with Macrocyclic Schiff's base ligands, displayed bands in the range of $338\text{-}345 \text{ cm}^{-1}$, the presence of these bands indicated that the chloride ions coordinated to metal ion.^[25-26] The acetato complex with ligand show the IR bands in the range of $1340\text{-}1453 \text{ cm}^{-1}$ and $1248\text{-}1315 \text{ cm}^{-1}$ due to $\nu_{\text{as}}(\text{OAc})$ and $\nu_{\text{s}}(\text{OAc})$ stretching vibrations. Differences between $\nu_{\text{as}}(\text{OAc})$ - $\nu_{\text{s}}(\text{OAc})$ were found in the range of $92\text{-}138 \text{ cm}^{-1}$. The presence of these bands indicated that acetate group was coordinated to metal ion in monodentate nature.^[27]

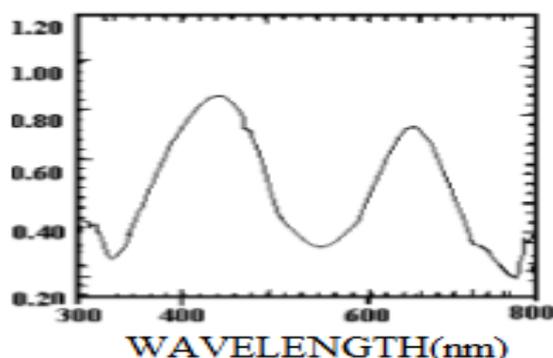
Co(II) Complexes

In the present study Co(II) complexes with all ligands show magnetic moment in the range of 4.57-4.69 BM at

room temperature corresponding to three unpaired electrons.^[28-29] The electronic spectra of Co(II) complexes were recorded using DMSO as a solvent and are shown in Fig 4(a). The electronic spectral data of complexes are presented in Table 2. For high spin d^7 systems. These bands are observed in the range of $9374\text{-}9850 \text{ cm}^{-1}$, $16000\text{-}16100$ and $20120\text{-}20400 \text{ cm}^{-1}$ respectively. These bands are corresponding to the following transitions: ${}^4T_{1g}({}^4F) \rightarrow {}^4T_{2g}({}^4F) (v_1)$, ${}^4T_{1g}({}^4F) \rightarrow {}^4A_{2g}({}^4F) (v_2)$, ${}^4T_{1g}({}^4F) \rightarrow {}^4T_{2g}({}^4P) (v_3)$. The energy differences of $(v_1 - v_2)$ are exactly equal to $10 Dq$. v_2 transition is usually very weak and rarely unequally observed.^[30]

EPR

The EPR spectra of the Co(II) complexes were recorded as polycrystalline samples at liquid nitrogen temperature (LNT), because the rapid spin lattice relaxation of Co(II) broaden the lines at higher temperatures. The g values lies in the range 2.305-2.826 Table 3 Fig. 4(b).



(a)

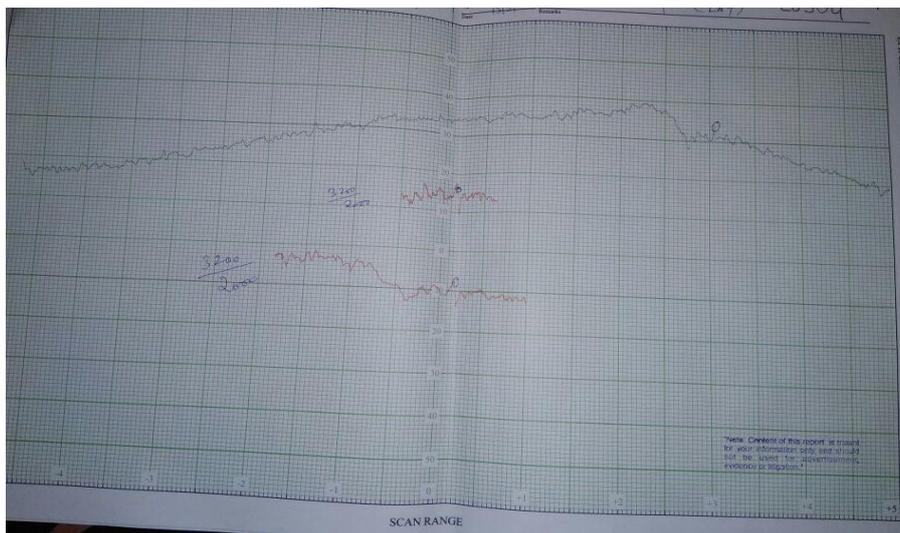
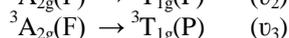
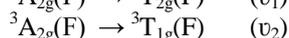
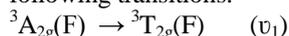


Fig. 4: (a) Electronic spectrum of [Co(L)Cl₂] (b) EPR spectrum of [Co(L)(OAc)₂]

Nickel(II) complexes

Magnetic moment of the Nickel(II) complexes at room temperature lie in the range 2.96-2.98 BM. These values are in tune with a high spin configuration and show the presence of an octahedral environment around the Ni(II) ion in the complexes Table 2.

The electronic spectra of Ni(II) complexes show three bands in the range of 9479-9542, 10799-12642 cm⁻¹ and 21930-27322 cm⁻¹ Fig. 5. These bands assign to the following transitions:



There is no splitting has been found in band v_1 , which is generally observed in D_{4h} symmetry. Thus all Ni(II) complexes possess octahedral geometry^[31]

Copper(II) complexes

The magnetic moment measurements of the Cu(II) complexes at room temperature lie in the range 1.94-1.97 BM Table 2 corresponding to one unpaired electron. Electronic spectra of the copper complexes recorded in DMSO possess absorption bands in the range of 10373-10695, 18,622-19066 cm⁻¹ which can be assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions respectively. ${}^2B_{1g} \rightarrow {}^2B_{2g}$ is usually not observed as a separate band in the tetragonal field. The energy level sequence will depend

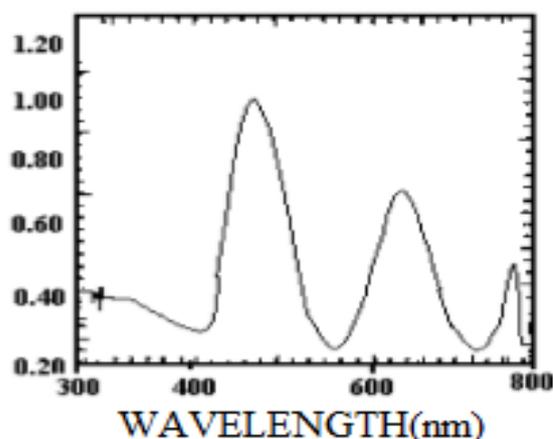


Fig. 5: Electronic spectrum of [Ni(L)Cl₂]

on the amount of tetrahedral distortion due to ligand field and Jahn-Teller distortion effect.^[32]

EPR

The X-band EPR spectra of Cu(II) complexes were recorded at room temperature in polycrystalline form and are depicted in Fig. 6(a-b)

b). In addition there is exchange-coupling interaction between the two copper centers explained by Hathaway.^[33] The calculated epr values are ($g_{\parallel} = 2.124-2.211$ and $g_{\perp} = 2.097-2.226$) given in Table-3.

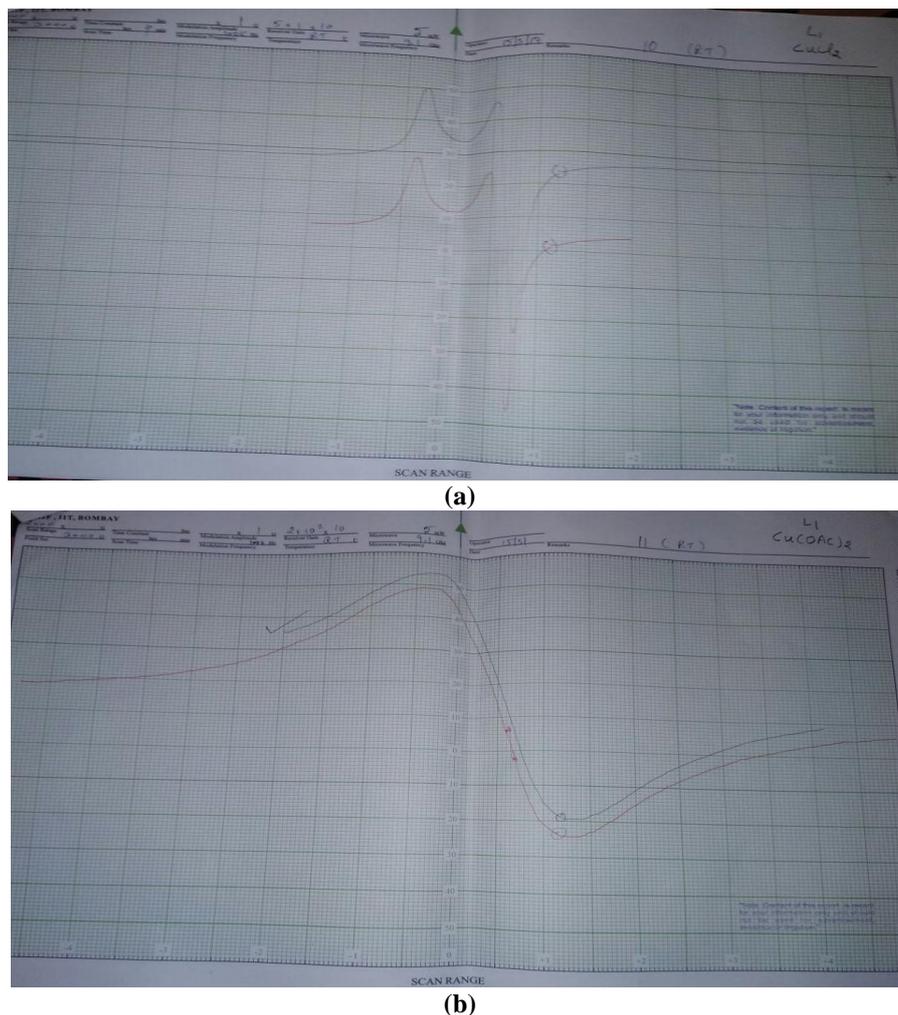


Fig. 6: EPR spectra of (a) $[\text{Cu}(\text{L})\text{Cl}_2]$ (b) $[\text{Cu}(\text{L})(\text{OAc})_2]$

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

Sl. No.	Complexes	electronic spectral bands (cm^{-1})				$\mu_{\text{eff}}(\text{B.M.})$
		$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$	$\nu_3(\text{cm}^{-1})$	$\nu_4(\text{cm}^{-1})$	
1	$[\text{Co}(\text{L})\text{Cl}_2]$	9374	16000	20400	32028	4.69
2	$[\text{Co}(\text{L})(\text{OAc})_2]$	9850	16100	20120	32895	4.57
3	$[\text{Ni}(\text{L})\text{Cl}_2]$	9542	10799	21930	37453	2.96
4	$[\text{Ni}(\text{L})(\text{OAc})_2]$	9479	12642	27322	35714	2.98
5	$[\text{Cu}(\text{L})\text{Cl}_2]$	10695	19066	27919	38023	1.97
6	$[\text{Cu}(\text{L})(\text{OAc})_2]$	10373	18622	24496	36364	1.94

Table 3: EPR data of Co(II) and Cu(II) complexes with MSB ligand

Sl. No.	Complexes	g_{\parallel}	g_{\perp}
1	$[\text{Co}(\text{L})\text{Cl}_2]$	2.305	2.167
2	$[\text{Co}(\text{L})(\text{OAc})_2]$	2.317	2.826
5	$[\text{Cu}(\text{L})\text{Cl}_2]$	2.211	2.097
6	$[\text{Cu}(\text{L})(\text{OAc})_2]$	2.124	2.226

Ligand field parameters

Various ligand field parameters, i.e. Dq , B , β and LFSE were calculated for Co(II) and Ni(II) complexes and reported in Table 4. The Dq values were evaluated using the Orgel diagram. The value for $B_{(\text{free ion})}$ for Co(II) and Ni(II) metal ions are 1120 cm^{-1} and 1041 cm^{-1} . The

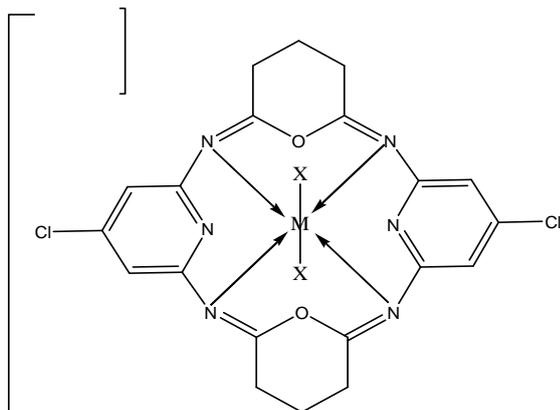
parameter B was calculated by the relation: $B = \nu_2 + \nu_3 - 3\nu_1/15$. The values of β for Co(II) complexes lie in the range 0.397-0.492, and for Ni(II) complexes 0.262-0.738 which indicate an appreciable covalent character in the complexes.^[34]

Table 4: Ligand field parameters of Co(II) and Ni(II) complexes with MSB ligand

Sl. No.	Complexes	Dq (cm ⁻¹)	B (cm ⁻¹)	β	LFSE	v ₂ /v ₁
1	[Co(L)Cl ₂]	937.4	551.86	0.492	89.70	1.70
2	[Co(L)(OAc) ₂]	985	444.66	0.397	94.25	1.63
3	[Ni(L)Cl ₂]	954.2	273.53	0.262	114.13	1.65
4	[Ni(L)(OAc) ₂]	947.9	768.46	0.738	113.38	1.33

Structure of the complexes

On the basis of elemental analysis, molar conductance measurement, magnetic moment, IR, electronic and EPR spectral data, following structure may be proposed for the Co(II), Ni(II) and Cu(II) complexes Fig. 7.

**Fig. 7: Proposed structure of complexes with MSB ligand**

Where M = Co(II), Ni(II), Cu(II) and X = Cl⁻, CH₃COO⁻

CONCLUSION

The present study revealed that synthesized macrocyclic Schiff's base (MSB) ligand act in tetradentate manner and coordination take place through four nitrogen donor atoms of the azomethine groups in (NNNN) [N₄] fashion. Characterization study data suggested six coordinated octahedral geometry for the all synthesized Co(II), Ni(II) and Cu(II) complexes.

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