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Synthesis and Characterization of Schiff Base from 3, 5-Di Chloro Salicylaldehyde with 4-Bromoaniline and 4-Aminobenzoic Acid and Its 1st Row Transition Metal Complexes

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Abstract:

Metal complexes have been prepared by using the schiff base ligand of 3,5-dichloro salicylaldimino-4-bromoaniline and 3,5-dichloro salicylaldimino-4-amino benzoic acid have been prepared and characterized by elemental analysis, magnetic and spectroscopic measurements (infrared, X-ray powder diffraction and scanning electron microscopy). Elemental analysis of the metal complexes was suggested that the stoichiometry is 1:2 metal-Ligand ratio. The following first row transition metals are used in our study, namely Co(II), Cu(II), Mn(II) and Zn(II). The coordination of metals was identified by Fourier transform infrared spectroscopy. The geometry of complexes was detected by the electronic spectroscopy. The proposed geometry for L₁ and L₂ of Zn complexes are distorted octahedral and tetrahedral geometry, but L₁ and L₂ of Mn complexes are octahedral geometry, L₁ of Cu and L₂ of Co complexes are tetrahedral geometry.

Keywords: Schiff base, transition metals, spectral studies, characterization.

1. Introduction

Multi-component ligand with flexible backbone is useful in constructing and interesting network structure^[1]. Such class of ligand is the reduced Schiff base derived from aldehyde and amine^[2]. Schiff base also known as imine or azomethine, named after Hugo Schiff was reported in 19th century by Schiff^[3]. Schiff bases are considered as a very important ligand of organic compound which have wide applications in many biological aspects. The imine nitrogen is basic and exhibits π -acceptor properties. The ligands are typically derived from aromatic amines and aromatic aldehydes^[4]. Aromatic aldehyde especially with an effective conjugation system, from stable Schiff bases, where as aliphatic aldehyde are unstable and readily polymerizes. Schiff base ligand obtained aldehyde with amine is formed more readily than with ketone. A wide range of Schiff base compound and their behavior studied because these compounds have very flexible and diverse structure. The presence of transition metal in human blood plasma indicates their importance in the mechanism for accumulating storage and transport of transition metal in living organism^[5]. Extensive research has been carried out on transition metal complexes of symmetrical Schiff base ligand in 1:2 molar ratios^[6]. Metal complexes of Schiff bases have played a centered role in the development of coordination chemistry. Most vital application in food and dye industry, analytical chemistry, catalysis, polymers, anti fertility, agro-chemicals, anti-inflammatory activity, anti-radical activity and biological systems as enzymatic agents^[7]. Our present work to prepare the 3,5-dichlorosalicylaldimino-4-amino benzoic acid and 3,5-dichlorosalicylaldimino-4-bromoaniline as a schiff base compound to coordinate with their 1st row transition metal complexes [Co(II), Cu(II), Mn(II) and Zn(II)] were prepared and its Physical properties and characterization by using the FT-IR, electronic spectroscopy and surface area studied by scanning electronic microscopy. The nature of metal complexes studied by Powder X-ray diffraction.

2. Experimental Methods

2.1. Chemicals

All the chemicals and solvents were used as AnalaR grade. All the reagents used for the preparation of the Schiff bases were obtained from Sigma Aldrich. The electronic spectra of the ligand and their complexes have been recorded viz., Shimadzu UV-visible 1800 in DMSO solvent in the range of 200-800 nm. FT-IR spectra recorded using KBr pellets in Shimadzu FT-IR 8201 spectrometer ($4000-400\text{ cm}^{-1}$). The XRD pattern of the complex was recorded on a XPERT-PRO diffraction using Cu- K_{α} -radiation ($\lambda = 1.54\text{ \AA}$). The surface morphology of the complexes were studied using VEGA 3 TESCAN Scanning electronic microscope.

2.2. Synthesis of 3, 5-dichlorosalicylaldimino-4-amino benzoic acid (L_1)

3, 5-dichloro Salicylaldehyde (20mmol) dissolved in ethanol was added to 4-amino benzoic acid (20mmol) was dissolved in ethanol. The solutions were mixed and then one drop of dilute acetic acid was added and the mixer refluxed for 5 hours, with constant stirring using magnetic stirrer. On cooling, a solid product was formed which was ethanol and then with ether and dried. The product was recrystallized from hot ethanol.

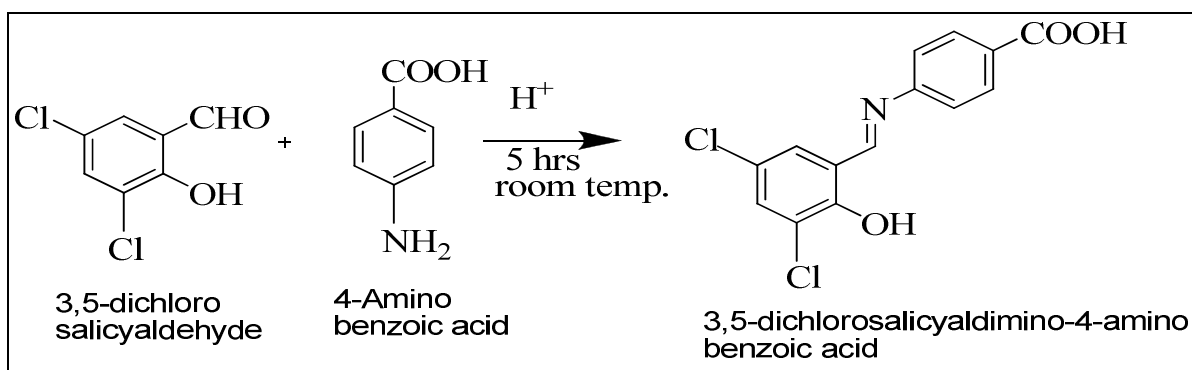


Figure 1: Synthesis of 3, 5-dichlorosalicylaldimino-4-amino benzoic acid (L_1)

2.3. Synthesis of 3, 5-dichlorosalicylaldimino-4-bromoaniline (L_2)

3, 5-dichloro Salicylaldehyde (20mmol) dissolved in ethanol was added to 4-bromo aniline (20mmol) was dissolved in ethanol. The solutions were mixed and then one drop of dilute acetic acid was added and the mixer refluxed for 5 hours, with constant stirring using magnetic stirrer. On cooling, a solid product was formed which was washed with ethanol and then dried. The product was recrystallized from hot ethanol. The ligands were bi-dendative nature.

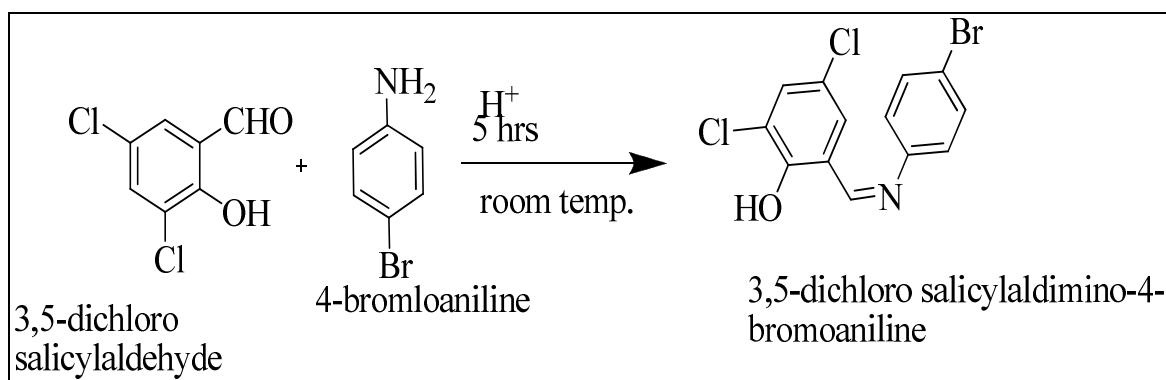


Figure 2: Syntheses of 3, 5-dichlorosalicylaldimino-4-bromoaniline (L_2)

2.4. Synthesis of Metal Complexes

A warm ethanol solution of 10mL, L_1 (0.226g, 20mmol) and L_2 (0.24g, 20mmol) was added to the 5ml of Metal chloride solution [Co (II), Cu (II)], Zn (II) and Mn (II) (20mmol) in distilled water. The metal-ligand ratio is 1:2. The mixer was refluxed for 2 hrs. with constant stirring using magnetic stirrer and then cooled with crushed ice, a solid precipitates was formed, and that can be filtered off and washed with ethanol, and dried in an air oven. Crystallization from aqueous ethanol gave pure crystals of metal complexes.

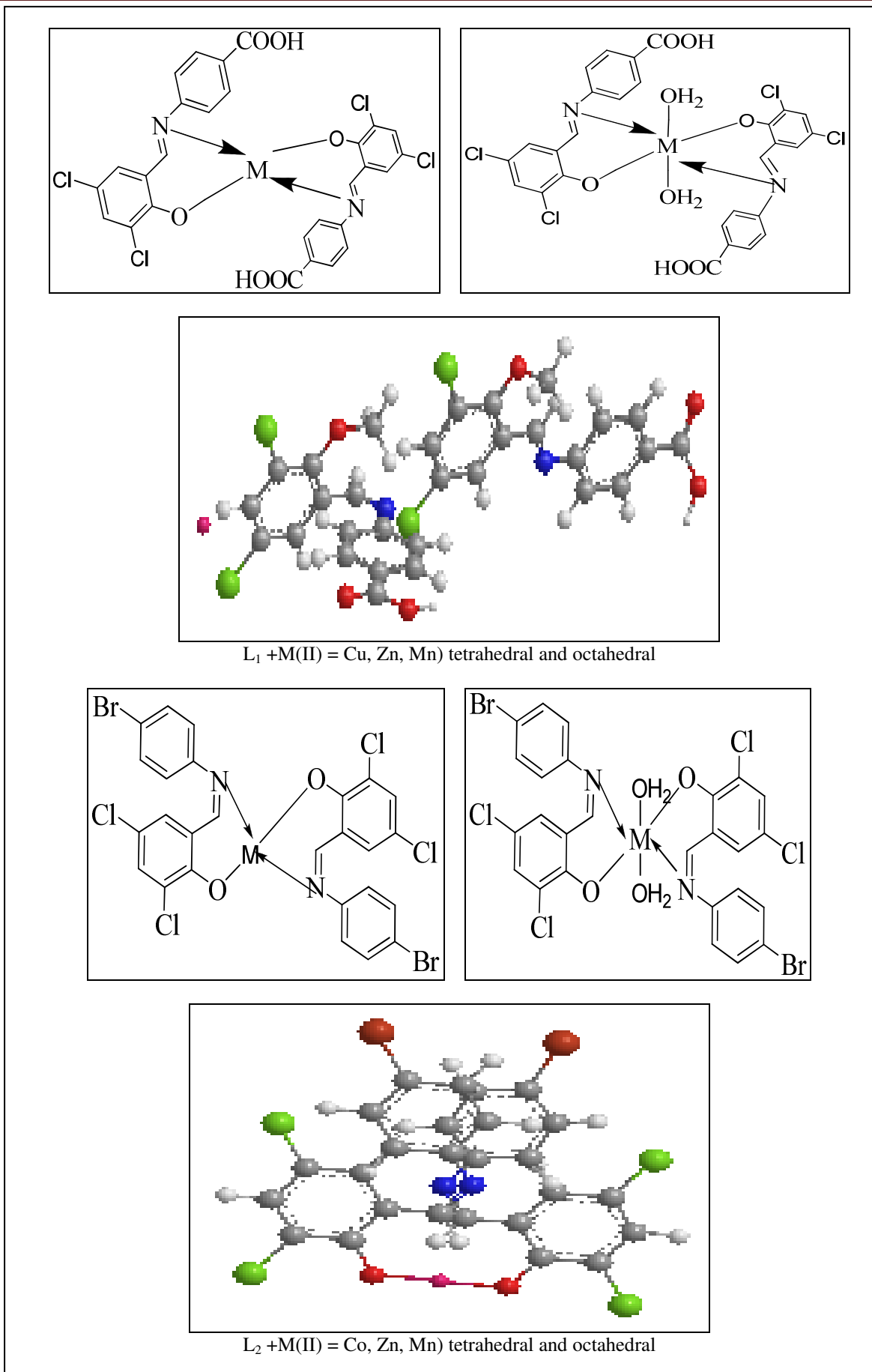


Figure 3: syntheses of metal complexes from L_1 and L_2

3. Result and Discussion

3.1. Physical Properties

The ligands and the metal complexes [Co (II), Cu (II), Mn (II), & Zn (II)] are stable in air and moisture stable. They are insoluble in ethanol, acetone but soluble in DMF, DMSO and other organic solvents. The melting points determined by using Biochem melting point apparatus and capillaries and the values are approximately.

S.No	Compound	Color	MeltingPoint(⁰ C)	Mol.Wt.(Calc.)
1.	C ₁₄ H ₉ NO ₃ Cl ₂ (L ₁)	Light orange	157	310.1351
2.	Cu(II)C ₂₈ H ₁₆ N ₂ O ₆ Cl ₄	Green	253	681.7980
3.	Zn(II)C ₂₈ H ₁₆ N ₂ O ₆ Cl ₄	Light orange	215	683.6328
4.	Mn(II)C ₂₈ H ₁₆ N ₂ O ₆ Cl ₄	Light orange	224	673.1908
5.	C ₁₃ H ₉ NO ₂ BrCl(L ₂)	Orange	165	322.5810
6.	Co(II) C ₂₆ H ₁₆ N ₂ O ₄ Br ₂ Cl ₂	Light yellow	241	710.0796
7.	Zn(II) C ₂₆ H ₁₆ N ₂ O ₄ Br ₂ Cl ₂	Light green	226	716.5264
8.	Mn(II)C ₂₆ H ₁₆ N ₂ O ₄ Br ₂ Cl ₂	Light yellow	220	706.0844

Table 1: Physical properties of ligands and metal complexes

3.2. Spectrum Analysis

3.2.1. UV-Visible Spectral Data

The UV-Visible electronic spectra (200-800 nm) is recorded by UV 1800 series () double beam spectrophotometer. The Schiff base ligand shows two type of transition, $n - \pi^*$ and $\pi - \pi^*$ respectively these transition were existed also in the spectra of the complexes, but they shifted to lower intensity, conforming the co-ordination of the ligand to the metal ion. In UV-Visible spectra the weak band at 400 to 500 nm are due intra ligand charge transfer band in the complexes, which is absent in the free Ligand spectra.

The lower wavelengths for the Schiff bases have a range between 215nm to 230nm. These values assigned to $n - \pi^*$ transition of Schiff base (C=N). These have the molar extinction co-efficient values are $0 < 100$. The longer wavelength for the range between 260 nm to 295 nm. These value are due to $\pi - \pi^*$, so they have higher λ_{max} are greater to the transition and $0 > 1000$. The electronic absorption spectral bands of the complexes [Cu (II), Co(II),Zn(II) and Mn(II)] were recorded over the range 200-800 nm in DMSO and their λ_{max} values together with tentative assignments are summarized in Table-2 are discussed in detail. The transition for Cu (L₁)₂ complex in tetrahedral geometry is spin allowed transition for ${}^3T_1 \rightarrow {}^3T_2$ (33898 cm⁻¹), ${}^3T_1 (F) \rightarrow {}^3T_1 (P)$ (35714 cm⁻¹) and ${}^3T_1 (F) \rightarrow {}^3A_2$ (44247 cm⁻¹). Mn (L₁)₂ and Mn (L₂)₂ for Octahedral geometry is spin forbidden and symmetry forbidden transition for ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (29411 cm⁻¹), ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ (34482 cm⁻¹), ${}^6A_{1g} \rightarrow {}^4E_g$ (36363 cm⁻¹), ${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$ (38461 cm⁻¹) and ${}^6A_{1g} \rightarrow {}^4E_g (D)$ (45454 cm⁻¹). Co (L₂)₂ for tetrahedral ${}^3T_1g (F) \rightarrow {}^3T_2g$ (33898 cm⁻¹), ${}^3T_1g \rightarrow {}^3A_2g$ (44247 cm⁻¹). Zn (L₁)₂ for Distorted Octahedral and Zn (L₂)₂ for distorted tetrahedral geometry.

S.No	Compound	λ_{max} value		Geometry
		nm	cm ⁻¹	
1	Free ligand(L ₁)	220 ^a	45454	-----
		275 ^b	36363	
2	Cu(L ₁) ₂	226 ^a	44247	Tetrahedral
		280 ^b	35714	
		295 ^c	33898	
3	Zn(L ₁) ₂	220 ^a	45454	Distorted Octahedral
		275 ^b	36363	
4.	Mn(L ₁) ₂	220 ^a	45454	Octahedral
		260 ^b	38461	
		275 ^b	36363	
		290 ^b	34482	
5.	Free ligand (L ₂)	223 ^a	44843	-----
		270 ^b	37073	
		229 ^a	43668	
6.	Co(L ₂) ₂	280 ^b	35714	Tetrahedral
		345 ^c	28985	
		215 ^a	46511	
7.	Zn(L ₂) ₂	275 ^b	36363	Distorted Tetrahedral
		230 ^a	43478	
8.	Mn(L ₂) ₂	260 ^b	38461	Octahedral
		345 ^c	28985	
		230 ^a	43478	

Table 2: UV-Visible Spectrum Data for Ligand & Metal Complexes (^a $n \rightarrow \pi^*$, ^b $\pi \rightarrow \pi^*$ and ^c $d \rightarrow \pi^*$).

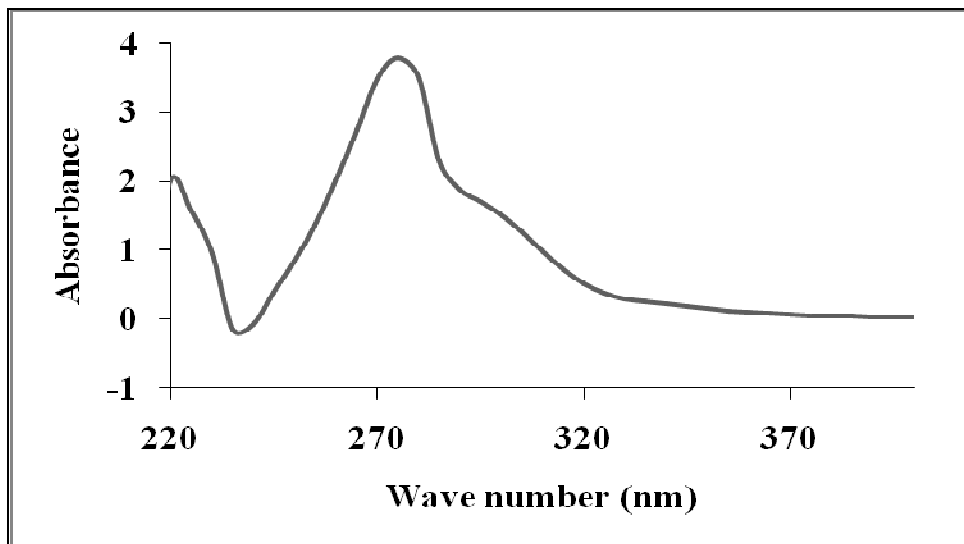


Figure 4: UV- Visible spectrum of L_1

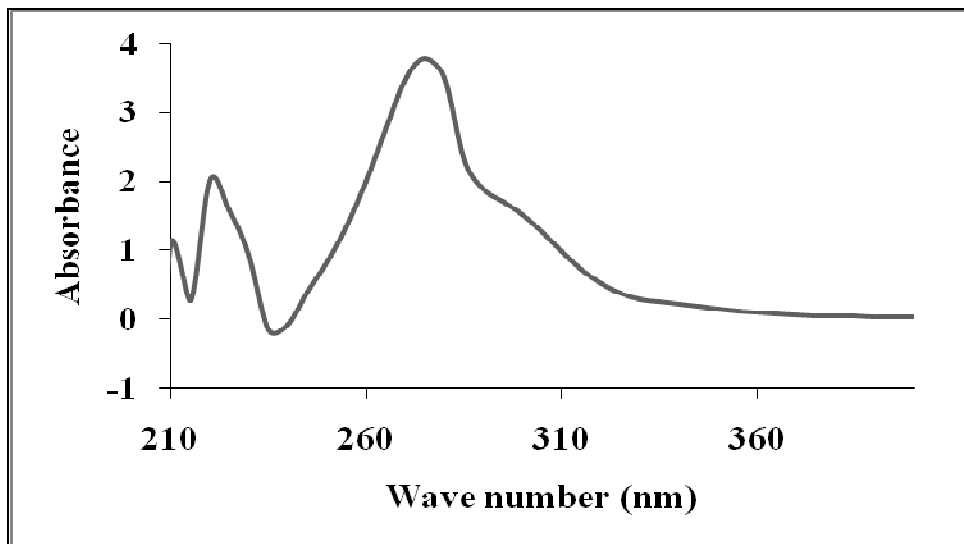


Figure 4a: UV-Visible spectrum of $Cu(L_1)_2$

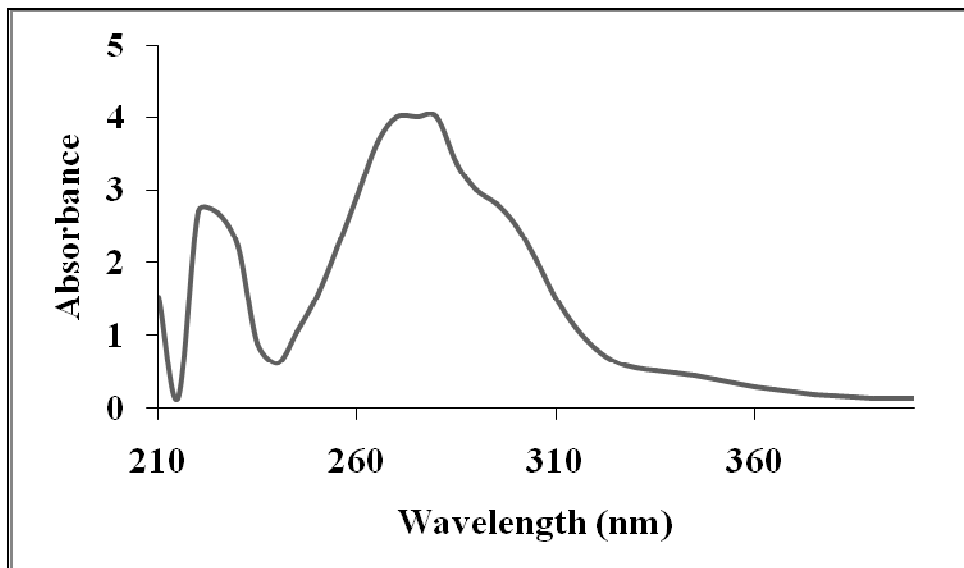


Figure 4b: UV-Visible spectrum of $Zn(L_1)_2$

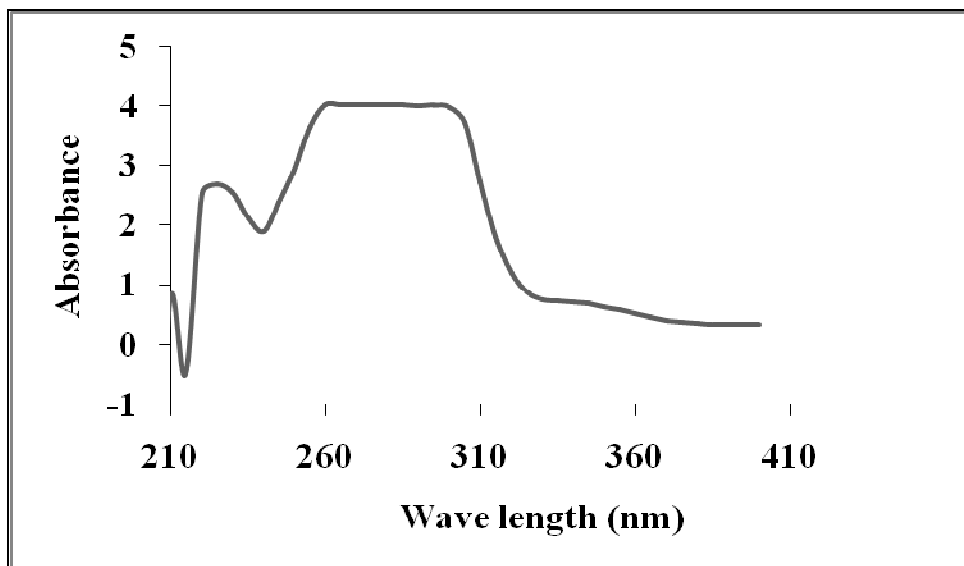


Figure 4c: UV-Visible spectrum of Mn (L₁)₂

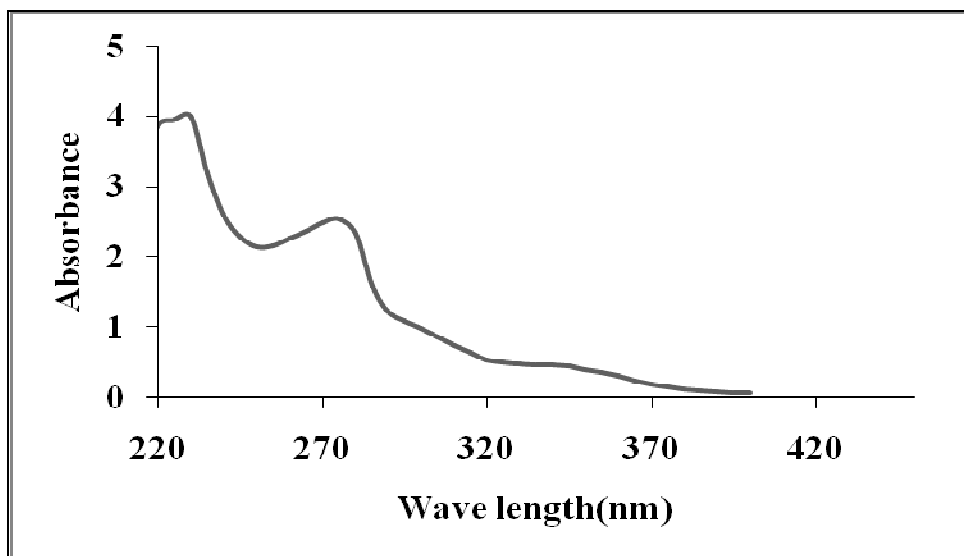


Figure 5: UV- Visible spectrum of L₂

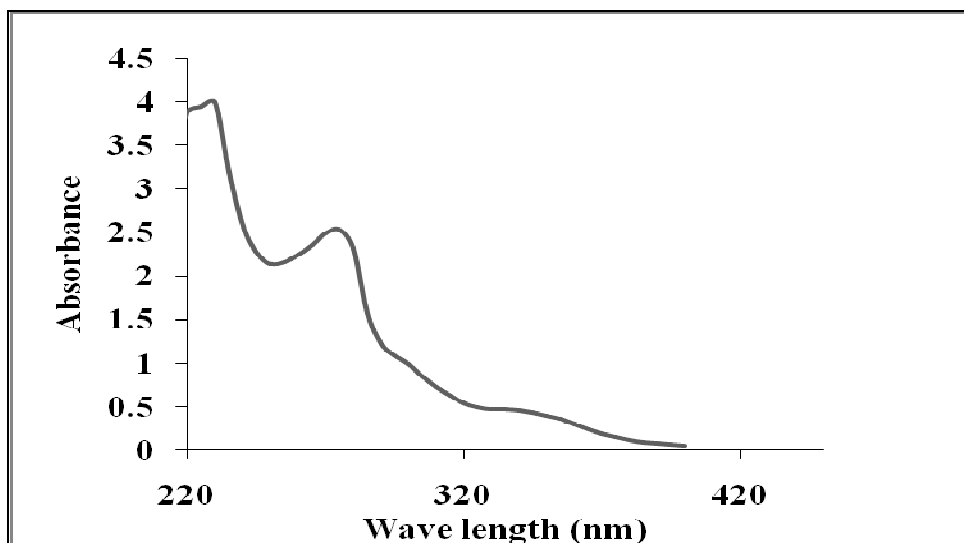


Figure 5a: UV-Visible spectrum of Co (L₂)₂

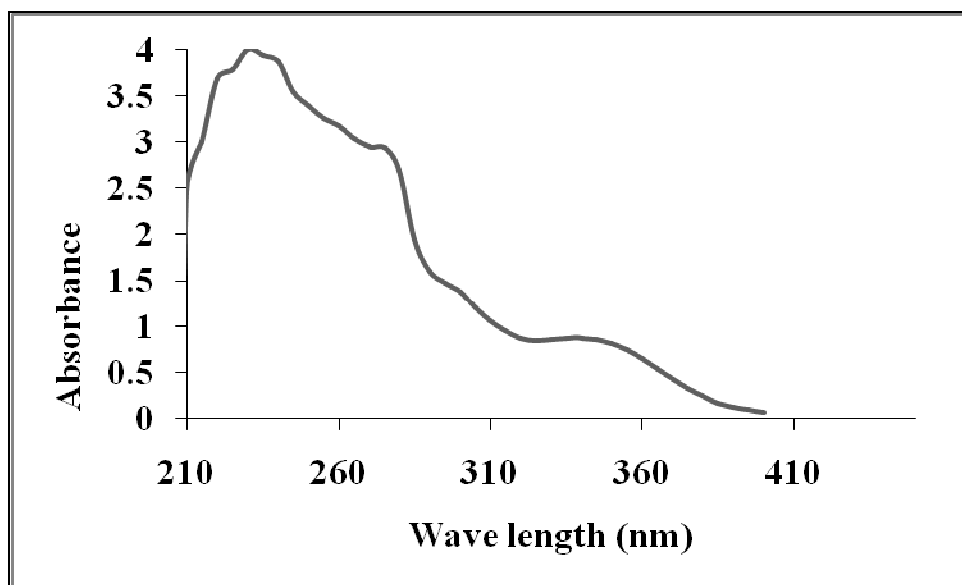


Figure 5b: UV-Visible spectrum of Zn (L_2)₂

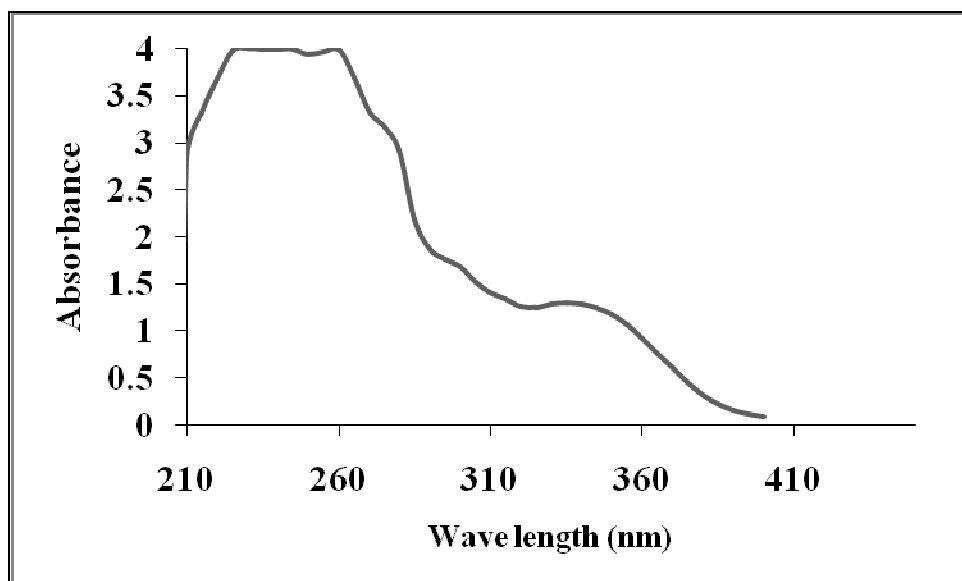


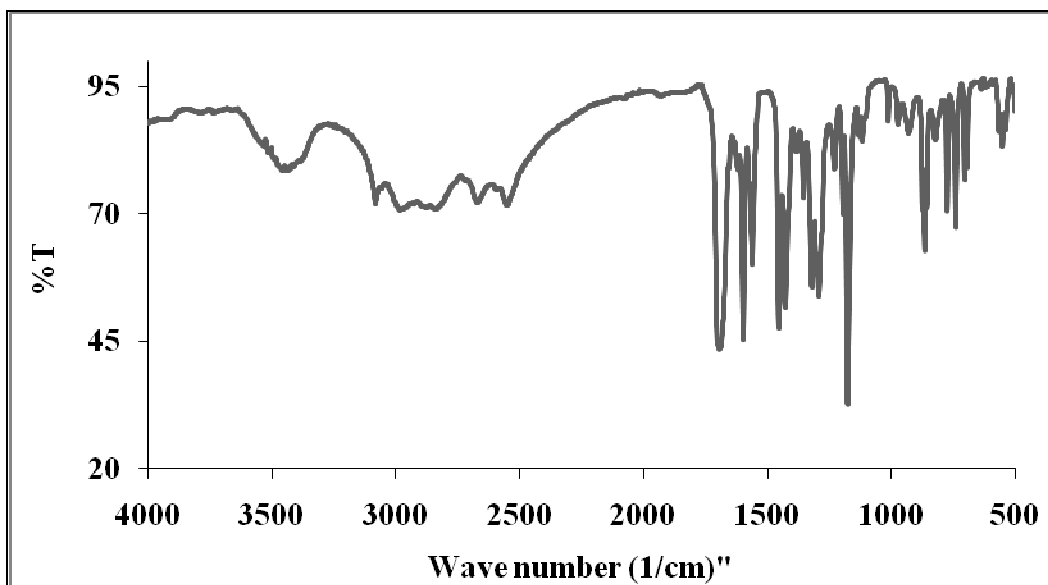
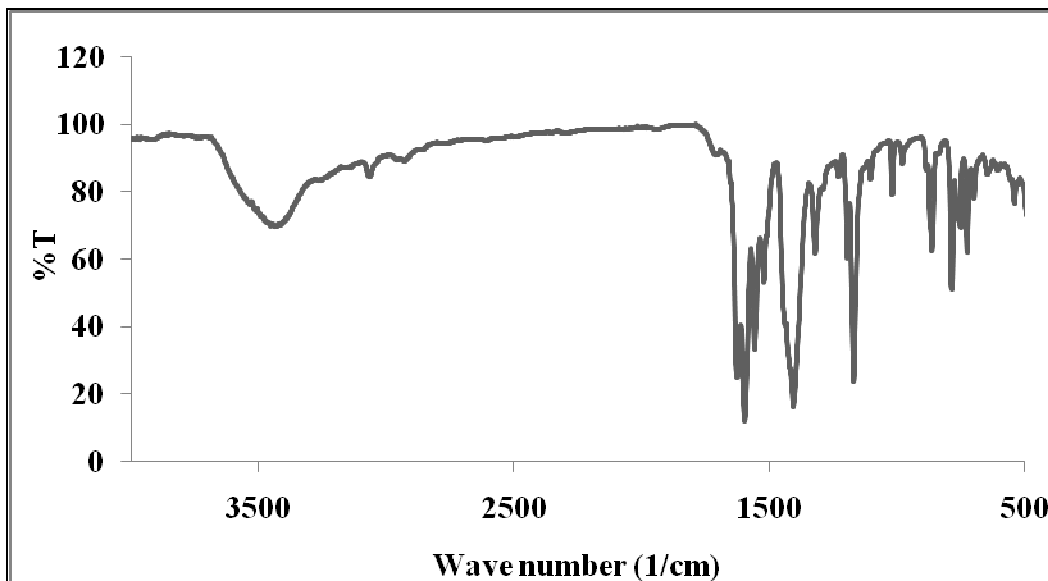
Figure 5c: UV-Visible spectrum of Mn (L_2)₂

3.2.2. IR-Spectrum Data

The IR spectra were recorded in KBr pellets using shimadzu FT-IR spectrometer ($4000-400\text{ cm}^{-1}$). The Schiff base showed the absence of bands at 1735 cm^{-1} and 3420 cm^{-1} due to carbonyl (C=O) and NH_2 Stretching vibrations and instead appearance of a strong new band at the range of ($1550-1618\text{ cm}^{-1}$) but observed data at 1614.47 cm^{-1} assigned to the azomethine (HC=N) linkage. It suggested that amino and aldehyde moieties of the starting reagents are absent and have been converted into the azomethine moiety. The comparison of the IR spectra of the Schiff bases and their metal chelates indicated that the functional group present in the metal complexes. ligands are acting in a bidentative manner. The band appearing at 1612.49 cm^{-1} due to the azomethine was shifted to lower frequency by $20-35\text{ cm}^{-1}$ indicating partition of the azomethine nitrogen in the complexation. The significant IR bands for the ligands as well as its Metal Complexes assignments are compiled and presented in the Table (3). In the IR Spectrum of the Schiff base ligand (L_1) a sharp band observed at 1612.19 cm^{-1} is assigned to the $\nu(\text{C}=\text{N})$ mode of the azomethine group. This shifts to lower wave numbers, 1560.4 cm^{-1} in all the complexes suggesting the co-ordination of the azomethine nitrogen to the metal centers. This is further substantiated by the presence of a new band around $549-710\text{ cm}^{-1}$ assignable to $\nu(\text{M}-\text{N})$. A band at 1228.66 cm^{-1} due to $\nu(\text{C}-\text{O})$ phenolic group was also observed in the ligand. L_1 contain the carboxylic group present in the frequency of C=O in 1693.50 cm^{-1} and the frequency of carboxylic -OH group present in 3059.1 cm^{-1} . The disappearance of phenolic $\nu(\text{OH})$ band at 3408.22 cm^{-1} in the Complexes suggests the co-ordination by the phenolic oxygen after deprotonation to coordinate with the metal ions. Due to the absorption is further supported by the shifting of $\nu(\text{C}-\text{O})$ Phenolic band to lower wave numbers 1226.73 cm^{-1} in the metal complex.

S. No	Compound	IR frequency range observed in cm^{-1}			
		$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
1	$\text{C}_{14}\text{H}_9\text{NO}_3\text{Cl}_2(\text{L}_1)$	1618.28	1292.31	-----	-----
2	$\text{Cu}(\text{II})\text{C}_{28}\text{H}_{16}\text{N}_2\text{O}_6\text{Cl}_4$	1556.55	1228.66	489.92	540.07
3	$\text{Zn}(\text{II})\text{C}_{28}\text{H}_{16}\text{N}_2\text{O}_6\text{Cl}_4$	1560.41	1228.66	549.56	499.56
4	$\text{Mn}(\text{II})\text{C}_{28}\text{H}_{16}\text{N}_2\text{O}_6\text{Cl}_4$	1560.41	1292.31	549.71	468.70
5	$\text{C}_{13}\text{H}_9\text{NO}_2\text{BrCl}(\text{L}_2)$	1614.62	1168.86	-----	-----
6	$\text{Co}(\text{II})\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_4\text{Br}_2\text{Cl}_2$	1556.00	1180.44	742.59	499.59
7	$\text{Zn}(\text{II})\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_4\text{Br}_2\text{Cl}_2$	1560.42	1226.73	709.80	548.54
8	$\text{Mn}(\text{II})\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_4\text{Br}_2\text{Cl}_2$	1560.41	1354.03	561.29	489.92

Table 3: FT-IR Data for Ligand & Metal Complexes

Figure 6: FT-IR spectrum of L_1 Figure 6a: FT-IR spectrum of $\text{Cu}(\text{L}_1)_2$

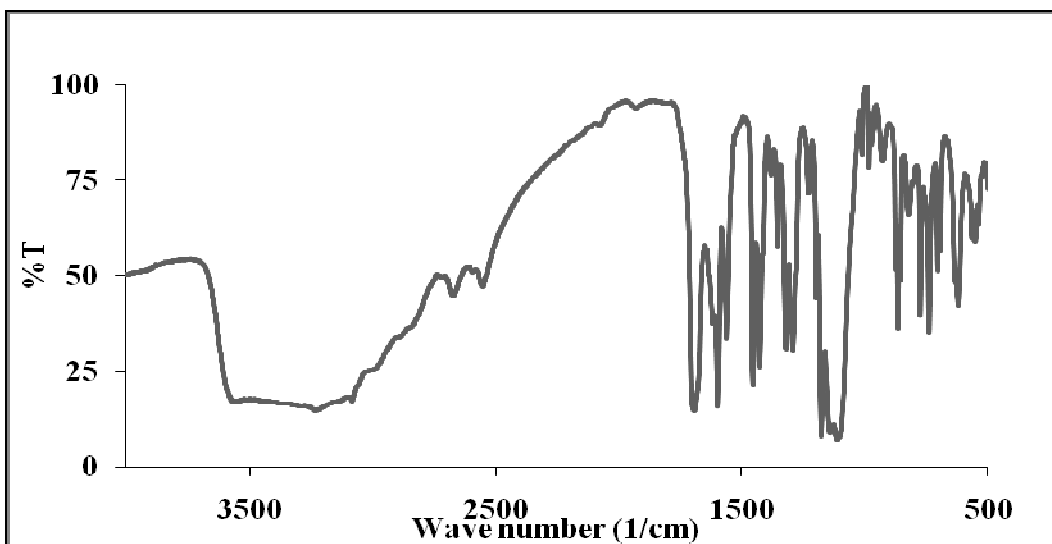


Figure 6b: FT-IR spectrum of Zn (L₁)₂

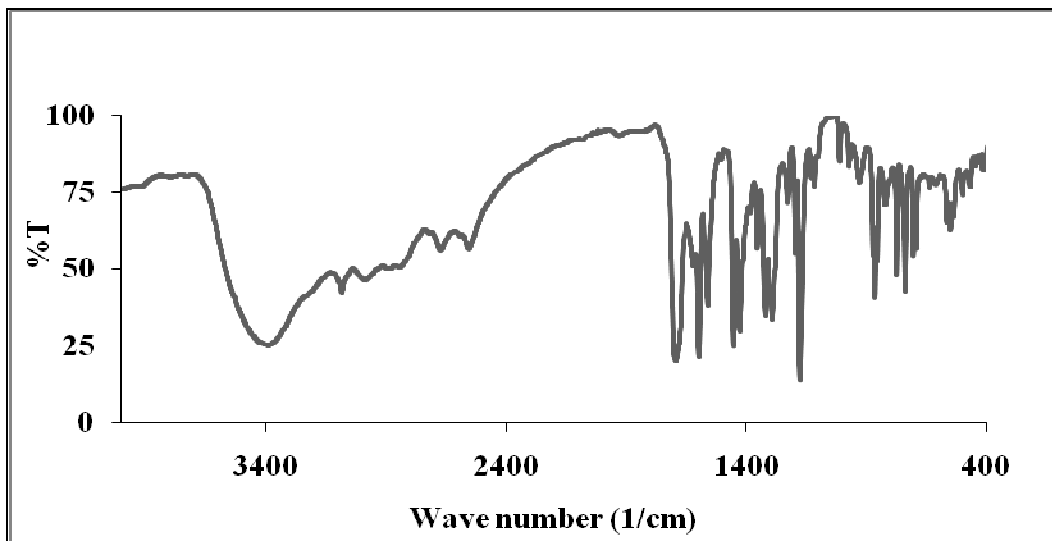


Figure 6c: FT-IR spectrum of Mn (L₁)₂

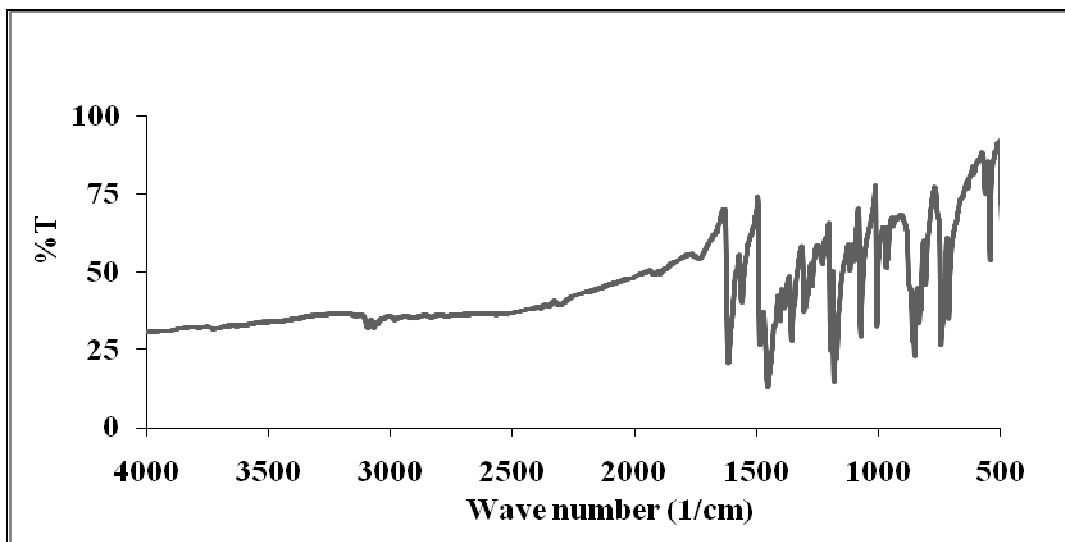


Figure 7: FT-IR spectrum of L₂

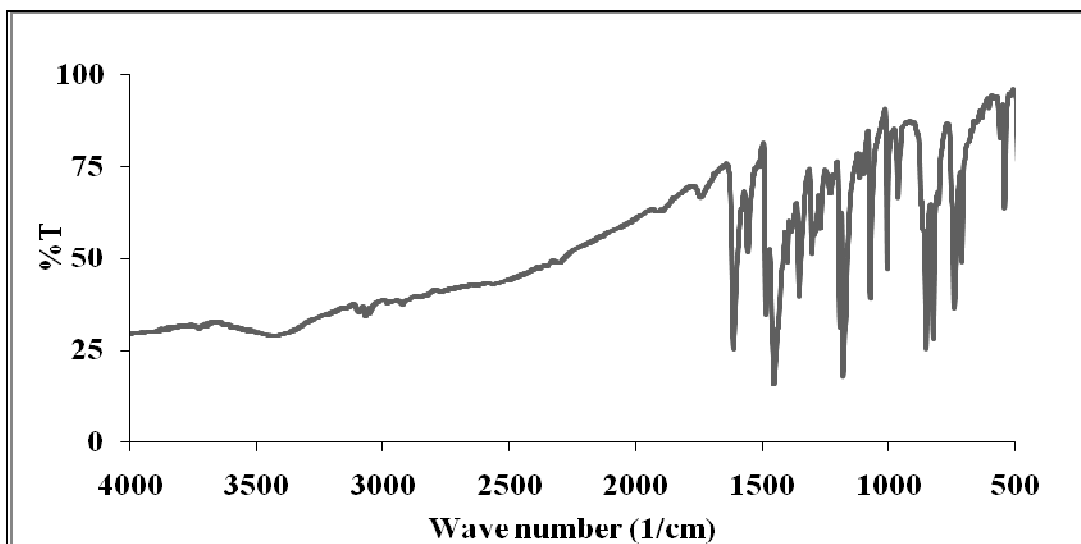


Figure 7a: FT-IR spectrum of $\text{Co}(\text{L}_2)_2$

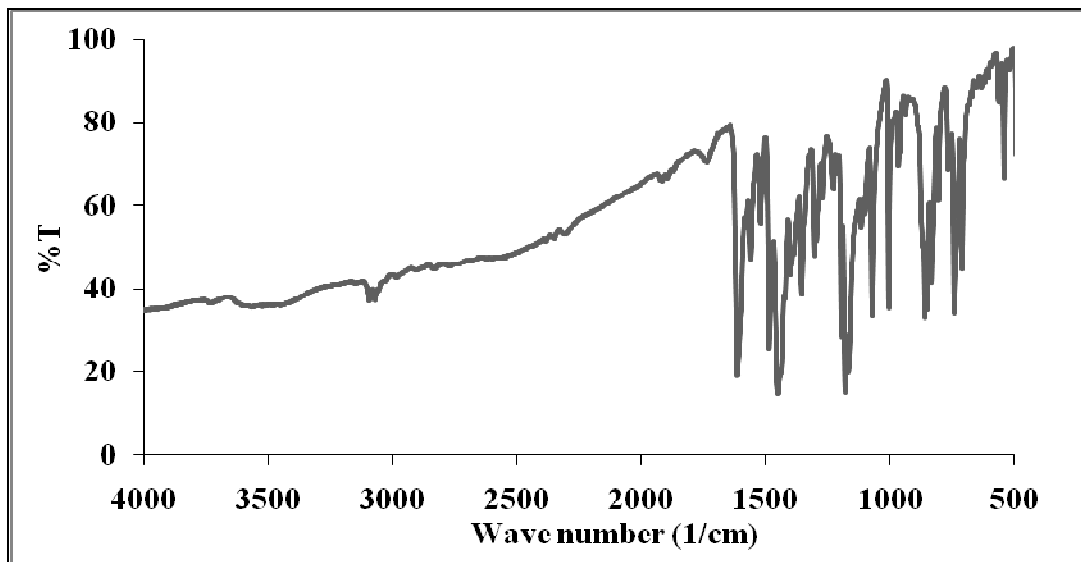


Figure 7b: FT-IR spectrum of $\text{Zn}(\text{L}_2)_2$

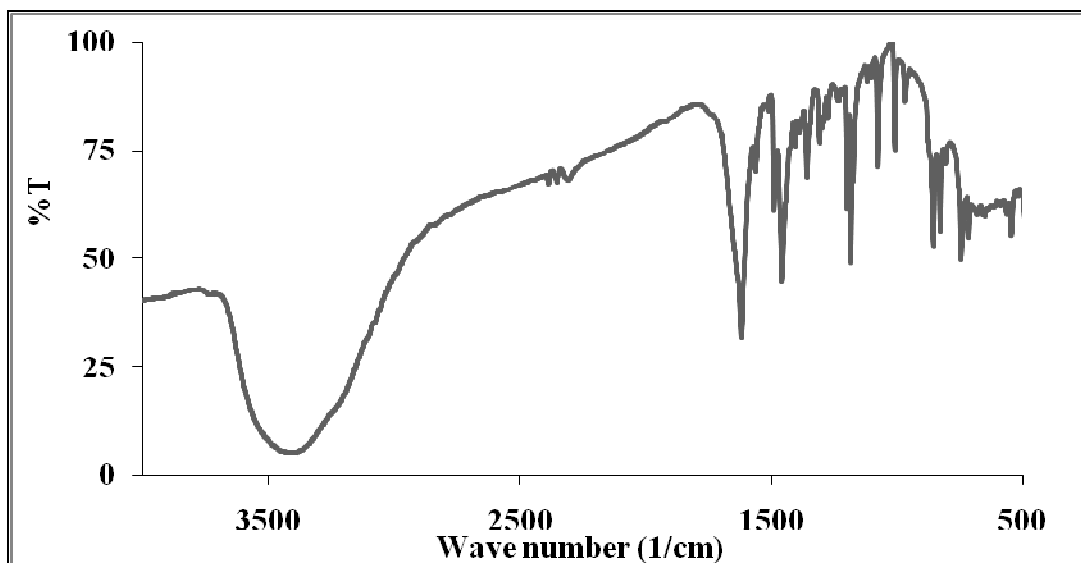


Figure 7c: FT-IR spectrum of $\text{Mn}(\text{L}_2)_2$

3.2.3. SEM (Scanning Electronic Microscopy)

SEM data is widely used to study the morphological features and surface characteristics of the metal complexes [8, 9]. The surface nature of the metal complexes has been studied via SEM, where the complexes are microcrystalline nature shown by the Figure-8.

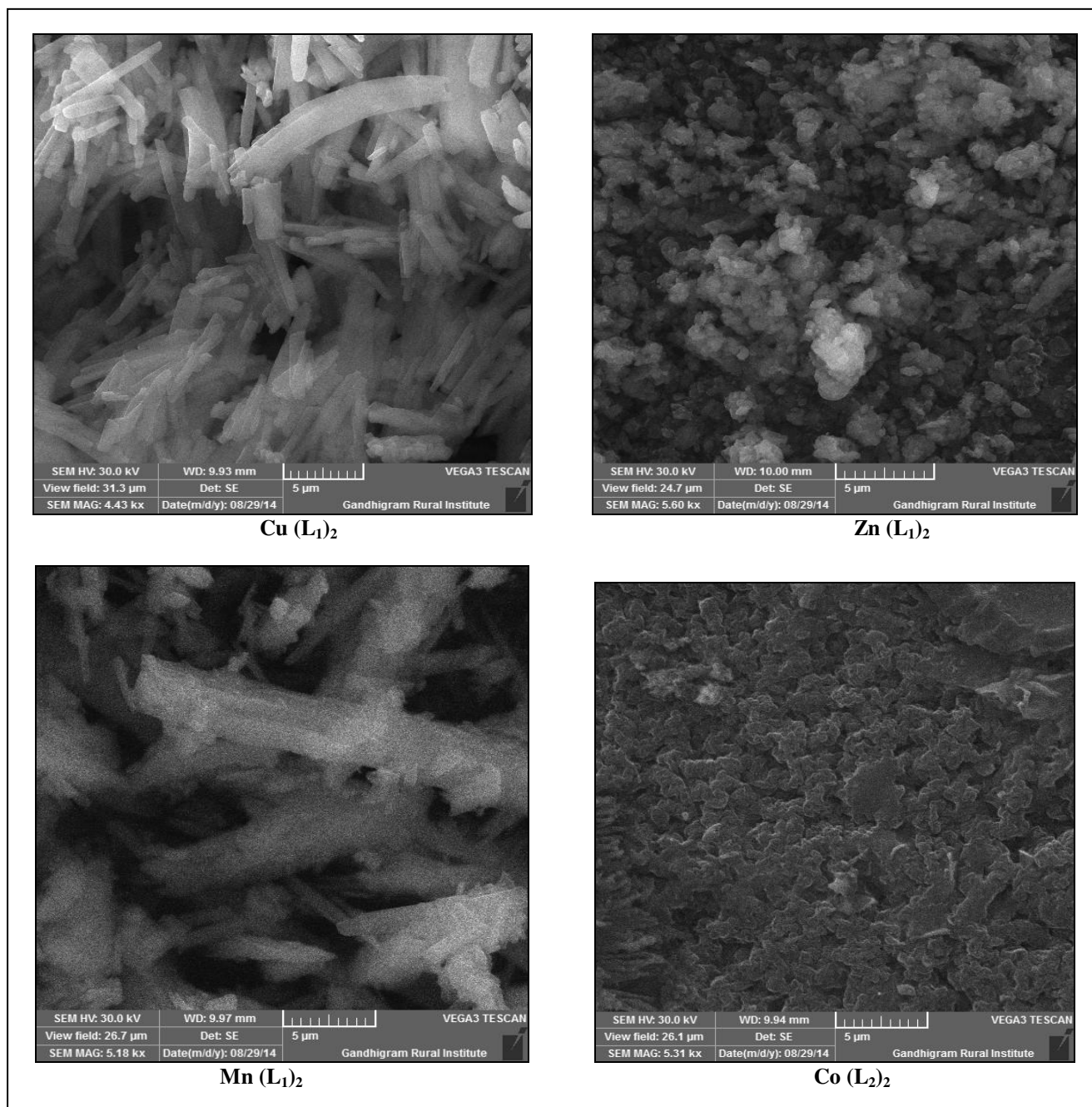


Figure 8: SEM of $\text{Cu}(\text{L}_1)_2$, $\text{Zn}(\text{L}_1)_2$, $\text{Mn}(\text{L}_2)_2$ and $\text{Co}(\text{L}_2)_2$ complexes

3.2.4. EPR Spectrum (Electron Proton Resonance)

The EPR spectrum of the complexes exhibits g values ($g_{\parallel} = 2.303$, $g_{\perp} = 2.08$). The $\text{Cu}(\text{L}_1)_2$ and $\text{Co}(\text{L}_2)_2$ complexes are tetrahedral. The value of $G = (g_{\parallel} - 2 / g_{\perp})$ which measure the exchange interaction between the metal centers in a polycrystalline solid has been calculated. The g value between 2.3-2.5 which is confirms the presence of mixed M-N and M-O bond in metal complexes [10]. The shown in Figure-9a and 8b for the spectrum of $\text{Cu}(\text{L}_1)_2$ and $\text{Co}(\text{L}_2)_2$ complexes respectively.

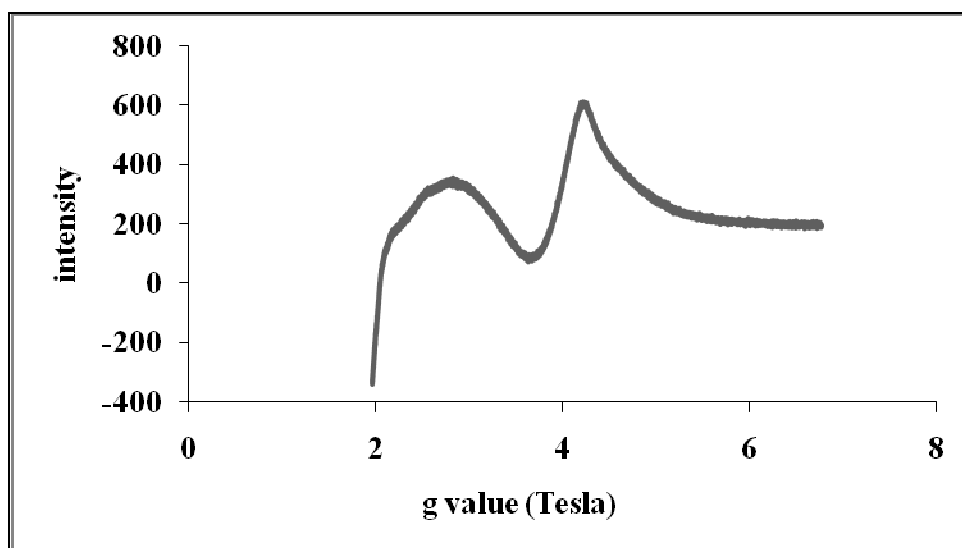


Figure 9a: EPR spectrum for $Cu(L_1)_2$

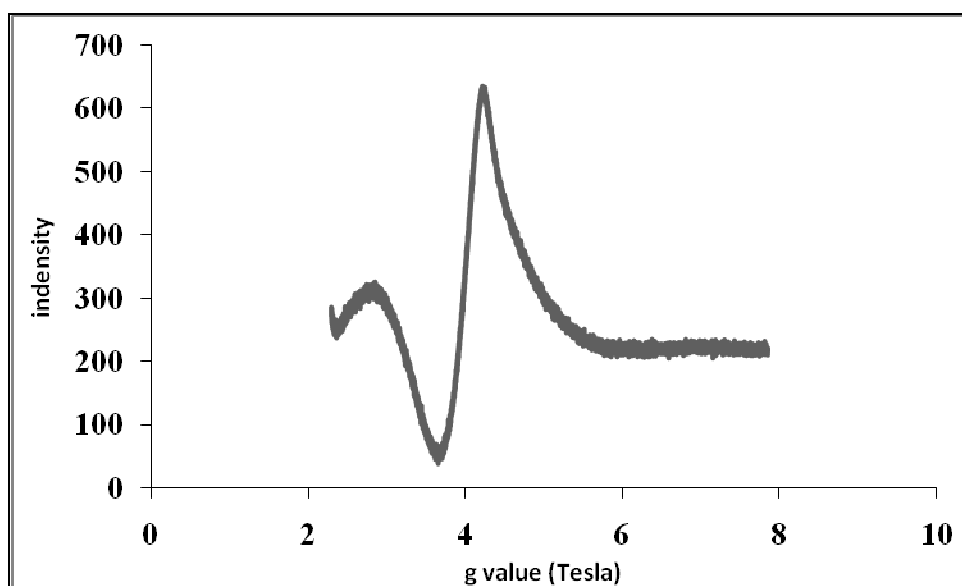


Figure 9b: EPR spectrum for Co

4. Conclusion

Synthesis of Schiff base L_1 and L_2 derived from 3, 5-dichloro Salicylaldehyde with 4-amino benzoic acid and 4-bromo aniline and their transition metal complexes of Cobalt (II), Copper (II), Zinc (II) and Manganese (II). The ligand and complexes have been characterized by spectral (UV- visible, FT-IR) techniques. Based on the spectral data which can be used to assign the coordination of the metal complexes and their geometry are Tetrahedral and Octahedral. Zn (II) complexes are distorted Octahedral and tetrahedral geometry. Which confirm the EPR spectrum one unpaired electron present in the Cu(II) complexes are tetrahedral geometry. The SEM analysis for nature of metal complexes. These studies can be helpful to further studies of DNA binding, anti-micro bacterial and anti-fungal activity of Schiff base metal complexes.

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