



Synthesis Spectral Characterization of Schiff Base and Its Metal Complexes

KEYWORDS

Bidentative ligand, Characterization, Metal Complexes.

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ABSTRACT Cobalt(II) and Copper(II) complexes of bi-dentative Schiff Base ligand, synthesized via condensation of 4-Fluro aniline and salicylaldehyde. The ligand and its metal complexes (II) are characterized on the basis of Electronic spectra, FT-IR spectra and Electronic Spin Resonance spectra. The surface morphology of metal complexes is characterized by Scanning electronic microscopic. The amounts of elements present in metal complexes are identified by EDX. To find the nature of complexes are mentioned by using XRD data.

1 Introduction

A Schiff base is formed from the simple condensation process. The condensation of aldehyde or ketone with amine [1]. Aromatic aldehyde especially with an effective conjugation system, form stable Schiff bases, where as those aliphatic aldehydes are unstable and readily polymerize. Schiff base ligands with aldehyde are formed more readily than with ketone (carbonyl carbon). Schiff bases have very flexible and different structures. The production of these compounds in complex or sensitive reactions have studied by various workers.[2-4],Metal complexes [Co(II), Cu(II) and Zn(II) ions] of Schiff base having played a central role in the development of co-ordination chemistry. It have been widely studied for their antimicrobial and anticancer properties. [5]

Transition metal complexes have attracted curiosity due to DNA binding and cleavage properties under physiological conditions. Applications of metal complexes as chemical nucleases are the focus of current research. It has been demonstrated that inorganic complexes can be used in foot printing studies[6] as sequence specific DNA binding agents, as diagnostic agents in medicinal applications and for genomic research.

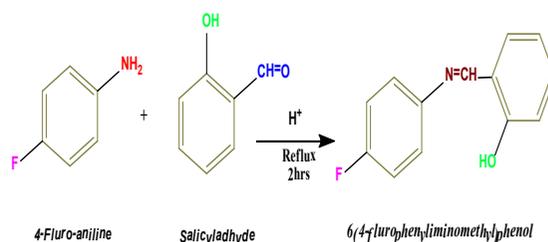
2. Experimental

All the chemicals and solvents were used as AR 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 Shimadzu UV -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 cm^{-1}). The XRD pattern of the complex was recorded on a XPERT-PRO diffraction using $\text{Cu-K}\alpha$ -radiation ($\lambda = 1.54 \text{ \AA}$).The surface morphology of the complexes were studied using VEGA3 TESCAN Scanning electron microscope. Paramagnetic behavior of metal complexes studied by Electron Spin Resonance spectroscopy (Bruker instrument).

2.1 Synthesis of ligand (L1)

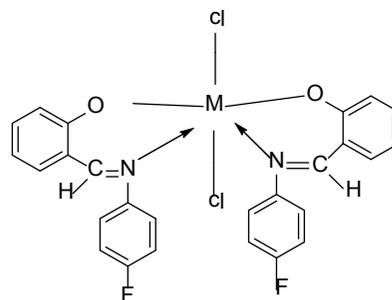
Salicylaldehyde (20 mmol) dissolved in ethanol was added to 4-fluro-Aniline was dissolved in ethanol (1:1) ratio. The solutions were mixed and then one drop of $\text{dil.H}_2\text{SO}_4$ was added and the mixer refluxed for 2 hrs, with constant

stirring using magnetic stirrer. On cooling, a solid product was formed which was filtered, washed with ethanol and ether. The product was recrystallization from hot ethanol gave (L_1).



2.2 Synthesis of metal complexes

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



M - {Co (II) & Cu (II)}

3. Results and discussion

The melting point determined by using Biochem melting point apparatus and capillaries and the values are approximately.

TABLE -3a Physical properties of ligand & metal complexes

Sl.no	Compound	Color	MeltingPoint (in °C)
1	C ₁₃ H ₁₀ NOF (L ₁)	Yellow	126
2	Co(II)C ₃₉ H ₃₀ N ₃ O ₃ F ₃	Brown	132
3	Cu(II)C ₃₉ H ₃₀ N ₃ O ₃ F ₃	Green	240

3.1 Electronic spectra

The electronic absorption spectral bands of the complexes [Cu(II), Co(II)] were recorded over the range 200-800 nm in DMSO and their λ max values together with tentative assignments are summarized in Table(3.1a) are discussed in detail. The spectral profiles below 350 nm are similar and the ligand centered transitions (intra ligand $\pi-\pi^*$ and $n-\pi^*$) of benzene and non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base complexes.

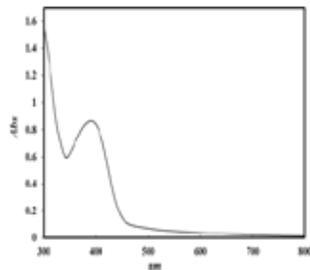
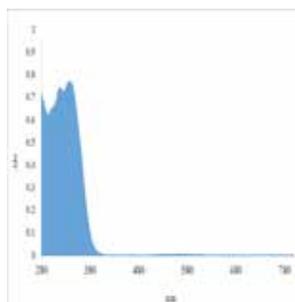
Table -3.1a Electronic absorption spectral data

S.No	Compound	λ max value		geometry	Spin & Magnetic moment
		position in nm	Position in cm ⁻¹		
1	Free ligand(L ₁)	240 ^a	-----	-----	-----
		347 ^b	-----		
2	Co(L ₁) ₂	318	31446	Octahedral	Low spin
		337 ^c	29673		
3	Cu(L ₁) ₂	280	35714	Octahedral	High spin 1.9
		389 ^e	25706		

^a- $\pi \rightarrow \pi^*$, ^b- $n \rightarrow \pi^*$ and ^c- $d \rightarrow \pi^*$.

In the figure (3.1a) Cu (II) complex shows $d-\pi^*$ Metal-Ligand Charge Transfer (MLCT) transitions in the region 380-440 nm which can be assigned to the combination of ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions in a Octahedral environment .

For Co(II) complex [figure(3.1b)] the assigned bands at about 330-400 nm to $d-\pi^*$ Metal-Ligand Charge Transfer (MLCT) transitions assignable to the combination of ${}^2B_{1g} \rightarrow {}^1A_{1g}$ and ${}^1B_{1g} \rightarrow {}^2E_g$ transitions which also supports Octahedral geometry.

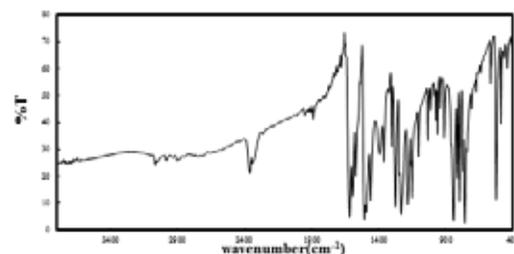
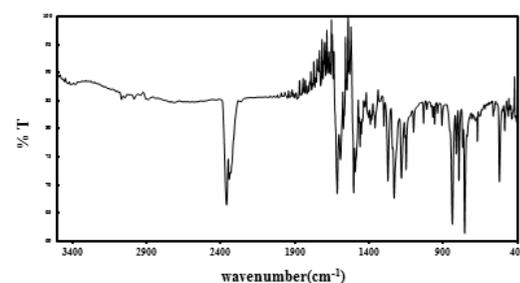
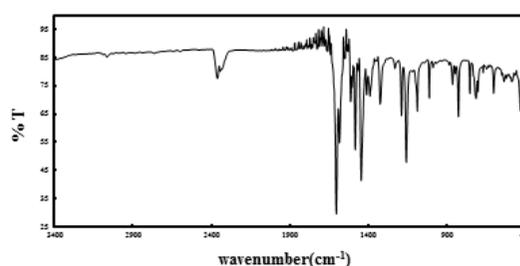
Figure-3.1a UV spectra for copper complex**Figure-3. 1b UV spectra for cobalt complex****3.2 FT-IR Spectra**

In the IR spectrum of the Schiff bases ligand (L₁) a sharp band observed at 1614 cm⁻¹ is assigned to the $\nu(C=N)$ mode of the azomethine group. This shifts to lower wave numbers, 1590-1602 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 403-436 cm⁻¹ assignable to $\nu(M-N)$. A band at 1273cm⁻¹ due to $\nu(C-O)$ phenolic group was also observed in the ligand which shown in the table 3.2.1. [7]

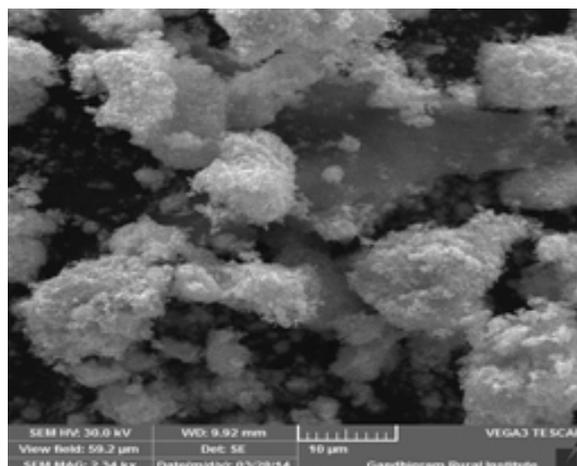
The disappearance of phenolic $\nu(OH)$ band at 3430-3464cm⁻¹ in all the complexes suggests the co-ordination by the phenolic oxygen after deprotonation to coordinate with the metal ion. This is further supported by the shifting of $\nu(C-O)$ phenolic band to lowers wave numbers 1230 cm⁻¹ in the metal complex. The appearance of a new non-ligand band around 500-543 cm⁻¹ in all the complexes due to $\nu(M-O)$ substantiates.

Table-3.2.1 FT-IR Data For Ligand & Metal Complexes

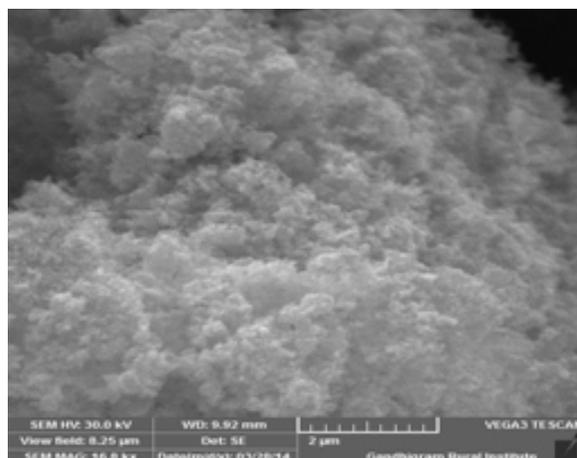
S. No	Compound	IR frequency range observed in cm ⁻¹			
		$\nu(C=N)$	$\nu(C-O)$	$\nu(M-N)$	$\nu(M-O)$
1	C ₁₃ H ₁₀ NOF(L ₁) (free ligand)	1614	1230	-----	-----
2	Co(II)C ₂₆ H ₂₀ N ₂ O ₂ F ₂	1591	1214	484	520
3	Cu(II)C ₂₆ H ₂₀ N ₂ O ₂ F ₂	1602	1205	486	536

Figure-3.2 a FT-IR spectra for [L₁]**Figure -3.2 b FT-IR spectra for Co (II) complex****Figure- 3.2 c FT-IR spectra for Cu (II) Complexes****3.3 Scanning electronic microscopy (SEM)**

SEM is analytical device to analyse the morphological and surface characteristics of carbon. The surface morphology of Co (II) and Cu (II) complex was studied using SEM and the images were shown in fig- 3.3a & 3.3b. The Cu (II) complex showed sphere like appearance on 10,000 magnification at 30 Kv. The surface area different from 2µm & 10µm level magnification for Co (II)& Cu (II) Complexes

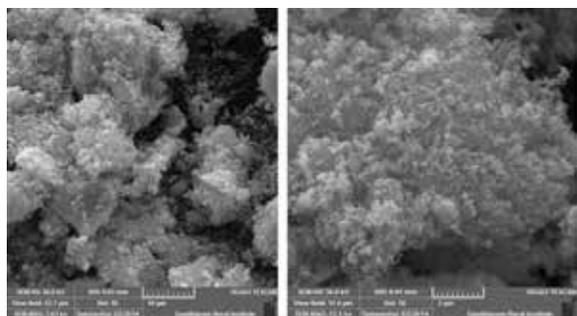


(i) higher magnification(10µm)



(ii) lower magnification(2µm)

Fig-3.3a SEM of Co (II) complex



(i) higher magnification(10µm)

(ii) lower magnification(2µm)

Fig-3.3b SEM for Cu (II) complex

3.4 XRD Analysis:

The powder XRD analysis of Co & Cu (II) complexes was carried out to find the crystalline or amorphous nature

of the complex. The diffractogram was given in Fig- 3.4a&3.4b. The strong and broad peak confirms the complex formation and the large peaks indicates that the complex is microcrystalline [8]. The powder size of the complex is calculated using Scherer's formula.

$$\text{Particle size (d)} = K\lambda / \beta \cos\theta$$

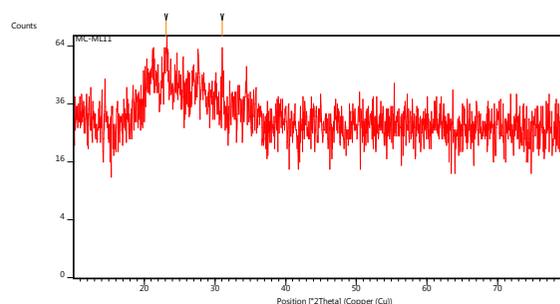


Figure-3.4a XRD for Co metal complexes

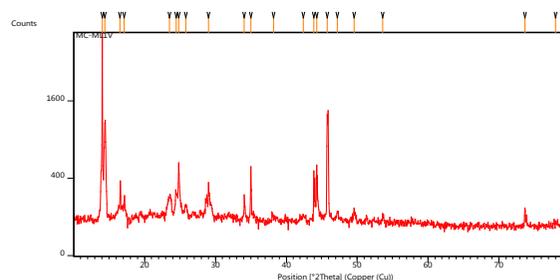


Figure-3.4 b XRD for Cu metal complexes

3.5 ESR SPECTRA

A typical ESR spectra of Co & Cu (II) complexes shown in the below figure. The spectra of complexes exhibit a set of four well-resolved signals at low field and one or two signals are high field corresponding to g_{\parallel} and g_{\perp} respectively. The g_{\parallel} and g_{\perp} values are computed from the spectrum using the tetracyano ethylene free radical as the 'g' marker. Kivelson and Nieman [9] have reported that g_{\parallel} value is less than 2.3 for covalent character and is greater than 2.3 for ionic character of the metal ligand bond. The trend $g_{\parallel} > g_{\perp} > 2.0023$, suggest that the unpaired electron lies predominantly in the dx^2-dy^2 orbital characteristic of octahedral geometry of Co & Cu(II) complexes [10]. The g average value for these complexes is greater than 2 indicating the covalent character of metal-ligand bond [11]. The ESR parameters g_{\parallel} and g_{\perp} of the complexes and the energies of d-d transitions are used to evaluation the dipolar interaction [12-14]

If G values less than 4 indicates considerable exchange interaction in the solid complexes. The above reported complex showed G values less than 4 indicating the exchange interaction in complexes. Furthermore, Masci et al [15] reported that g_n is 2.4 for copper oxygen bonds and 2.3 for copper-nitrogen bonds. For the complexes reported here, g_{\parallel} values between 2.3-2.4 which further confirms, the presence of mixed copper-nitrogen and copper-oxygen bonds in these chelates complexes.

Figure 3.5a ESR spectrum of Cu(II) complex

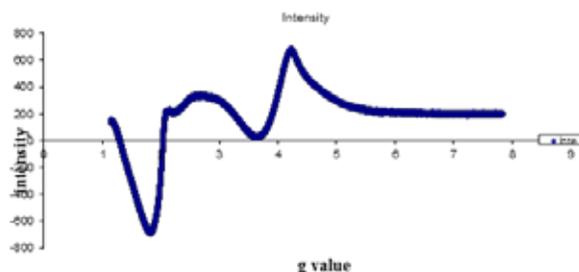
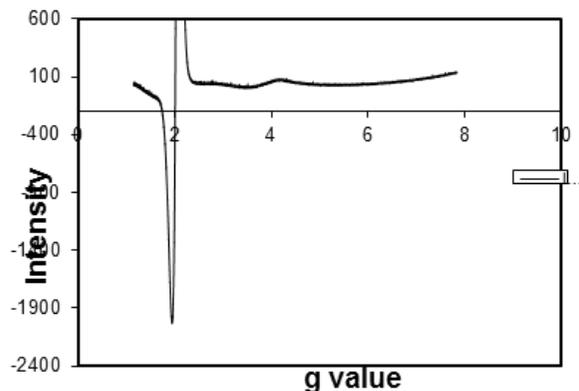


Fig- 3.5 b ESR spectrum of Co(II) complex



3.6 EDX spectra :

EDX spectra is used to calculate the percentage level of the elements present in the metal complexes like C,O,Cl,Al,Mg, are present in the Co(II) complexes shown in the fig-3.6a Similarly the elements like Cu,Cl,O,Al,Cu are present in Cu(II) complexes shown in the fig-3.6b

Fig-3.6a EDX spectrum for the Co(II) complex

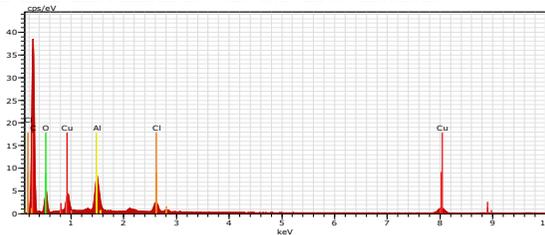
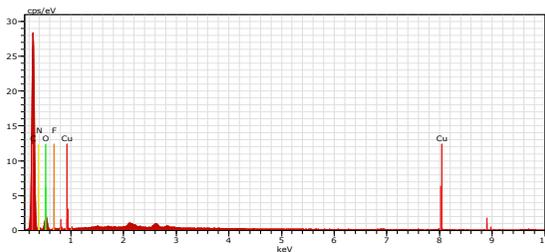


Fig 3.6b EDX spectrum for the Cu(II) complex



4 Conclusion

Schiff base ligand derived from 4-fluoro-aniline and salicylaldehyde and their transition metal complexes of Cobalt (II) and Cu (II). The ligand and complexes have been characterized by spectral (UV, FT-IR) techniques. The surface of metal complexes characterized by SEM. The amount of elements present in percentage level of the metal complexes was identified by EDX data. Based on the spectral data which can be used to assign the coordination of the metal complexes and geometry of the complexes are Octahedral and also this 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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