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Schiff base and its transition metal complexes

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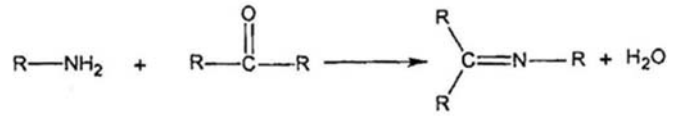
Abstract
This study to prepare new bidentative ligand of imine 2, 4-dibromo-6-4-Cholro phenyl imino phenol by using 4-Chloro aniline with di-bromo salicylaldehyde and its metal complexes (M=CO (II) & Zn (II) have been synthesized. All the complexes ML ratio 1:2. They adopt octahedral geometry. The characterization of metal complexes have been confirmed by UV-Visible, FT-IR, elemental analysis like SEM, EDX, EPR and powdered XRD.

Keywords: Metal complexes, characterization of ligand and complexes

1. Introduction

Schiff bases derived from an amine and any aldehyde are a class of compounds which co-ordinates to metal ions via the azomethine nitrogen [1]. Metal complexes of Schiff bases derived from substitiuted salicyladehydes and various amines have been widely investigated [2,3] because of their wide applications[4-9].Chelating ligands containing O and N donor atoms show broad biological activities and are special interest because of the variety of ways in which they are bonded to metal ions[10].Transition metal complexes of Schiff bases have drawn considerable attention due to their remarkable antifungal, antibacterial, antitumour and other activities.[11].

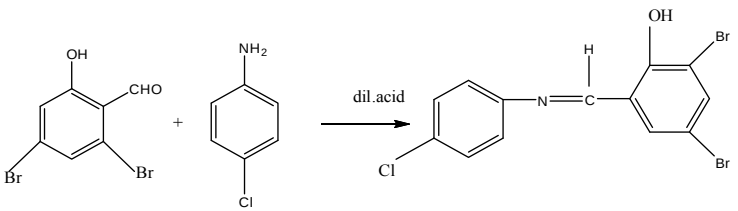


2. Experimental

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 Cu-K_α-radiation (λ= 1.54 A^0).The surface morphology of the complexes were studied using VEGA3 TESCAN Scanning electon microscope.Para magnetic behavior of metal complexes studied by Electron Spin Resonnace spectroscopy (Bruker instrument).

2.1 Synthesis of Ligand (L_1)

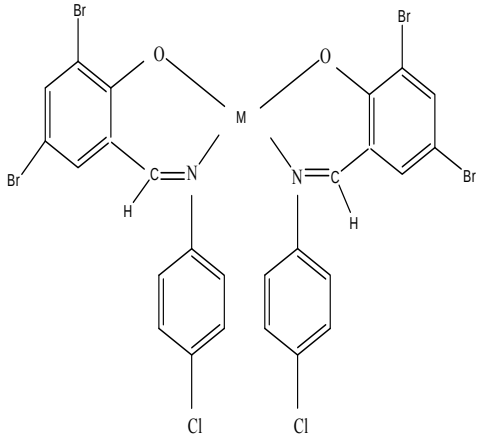
A solution of 4-chloro aniline in alcohol was added to di-bromo Salicylaldehyde in 20 ml alcohol. The mixture was refluxed for about 4hrs. The mixture was cooled in ice. The resulting precipitate was filtered and then washed with ethanol and dried in an air oven. The product was recrystallization from hot ethanol gave (L_1).



di-bromosalicyaldehyde 4-chloro aniline Schiff base

2.2 Synthesis of Schiff base metal complexes (L_1)

To add ethanolic solution of the Schiff Base Ligand L_1 with an ethanolic solution of the metal chloride was added in a molar ratio (1:1). The mixture was refluxed for about 6hrs, cooled in ice, a solid precipitate were formed, it can be filtered off and washed with ethanol, dried in air oven. Crystallization of metal complexes carried out using pure ethanol.



M -{Co(II), Zn(II)}

3. Result and Discussion

The metal complexes are insoluble in water and soluble in DMSO,
DMF, $CHCl_3$ and acetone and slightly soluble in methanol and ethanol. The physical properties of the ligands and complexes are presented in Table-1.The data are consistent with the calculated results from the empirical formula of each compound. Cobalt complexes have a very low molar conductance 45 $ohm^{-1}cm^{-1}$ mol^{-1}.The above molar conductance value confirm that the cobalt complexes are non electrolytes.

Table I

Complex	Empirical formula	Colour	Meltingpoint(^{0}c)
Ligand(L_1)	$C_{13}H_8NOBr_2Cl$	Pale yellow	80
CO-complex	$Co[C_{26}H_{14}N_2O_2Br_4Cl_2]$	Dark brown	140
Zn-complex	$Zn[C_{26}H_{14}N_2O_2Br_4Cl_2]$	Yellow	110

3.1 UV-Visible spectra

The electronic spectral measurements were used for assigning the stereo chemistry of metal ions in the complexes based on the positions and number of *d–d* transition peaks. The electronic absorption spectra of the Schiff base and its Co (II), and Zn (II) complexes were recorded at room temperature using DMSO as solvent. The spectral profiles below 350 nm are similar and are ligand centered transitions (intra ligand) π-π * and n-π * of benzene and non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base complexes.

In general the electronic spectrum of the Schiff base ligand, the two essential absorption bands were observed at 310 nm, and 360 nm and assigned to the transitions n → π*, π → π*, respectively. These transitions were existed also in the spectra of the complexes, but they shifted to different lower intensities, confirming the coordination of the ligand to the metal ions.

For Co (II) complexes the assigned bands at about 390-448 nm to d-π* (Metal-Ligand Charge Transfer transitions) assignable to the combination of $^2B_{1g} \rightarrow {}^1A_{1g}$ and $^1B_{1g} \rightarrow {}^2E_g$ transitions which also supports square-planar geometry. The absorption spectra for zinc complex shows intense bands about (291-345) nm, which may be related to ligand filed. The absorption peaks in the range (315-360 nm) for these complexes are due to charge transfer. Since it belongs to d^{10} configuration and doesn't have d-d transition. The zinc (II) complex showed band at
316 nm, assigned to intra-ligand charge transfer transitions which is diamagnetic in nature.

The electronic spectrum of the Co (II) complex displays three bands at 13,655, 15,155 and 25,008cm-1. These bands may be assigned to following transition $^4T_1g \rightarrow {}^4T_2g$ (F), $^4T_1g \rightarrow {}^4A_2g$ (F), $^4T_1g \rightarrow {}^4T_1g$ (P), respectively.

Table 2: UV spectra data for ligand and its metal complexes

Compound	Absorbance (nm)	*v*/cm^{-1}	Geometry	Magnetic moment(BM)
$C_{13}H_8NOBr_2Cl$ (Free ligand)	360	27777	----	----
$Co(II)C_{26}H_{14}N_2O_2Br_4Cl_2$	344 315	29069 31746	Square planar	4.56
$Zn(II)C_{26}H_{14}N_2O_2Br_4Cl_2$	316	31645	Square planar	----

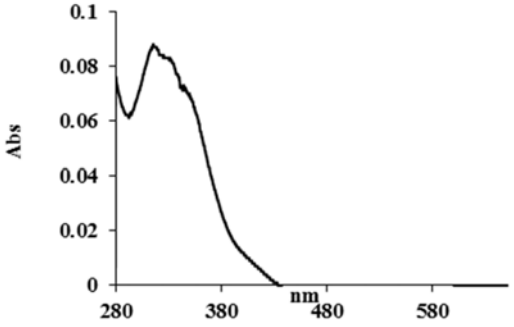


Fig 3.1a: UV-Visible spectra for cobalt (II) complex

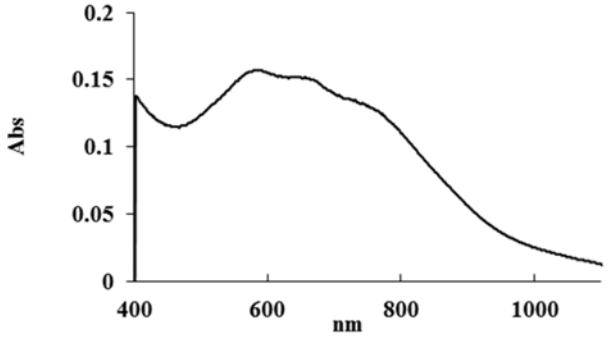


Fig 3.1b: UV-Visible spectra for zinc (II) complex

3.2 Infrared Spectra

The FT-IR spectra were recorded in KBr pellets using Shimadzu FT-IR spectrometer (4000 – 400 cm^{-1}). The significant IR bands for the ligand as well as its Co (II)

complex and their dentative assignments are complied and presented in table(I). In the IR spectrum of the Schiff bases ligand (L_1) a sharp band observed at 1612 cm^{-1} is assigned to the ν(-C=N-H) mode of the azomethine group. This shifts to lower wave numbers, 1604 cm^{-1} in all the complexes suggesting the co-ordination of the azomethine nitrogen to the metal centres. This is further substantiated by the presence of a new band around 480 cm^{-1} assignable to ν (M-N).

A band at 1454 cm^{-1} due to ν(C-O) phenolic group was also observed in the ligand. The disappearance of phenolic ν (OH) band in all the complexes suggested that co-ordination by the phenolic oxygen after deprotonation with metal ion. This is further supported by the shifting of ν(C-O) phenolic band to higher frequency 1487 cm^{-1} in the metal complex. The appearance of a ligand band around 513 cm^{-1} in all the complexes due to ν(M-O). In the IR spectra of the complexes, the stretching vibration of the free ligands *ν*(O-H), (3430-3464 $cm^{-1)}$ is not observed, suggesting deprotonation of the hydroxyl group and formation of M–O bonds.

The FT-IR spectra data for the ligand and zinc complex are presented in table-III.

The spectrum of the ligand shows the disappearance N-H bands, which suppose the complete combination of keto group with amino group. So the strong band appeared at 1610 cm^{-1} can be attributed to imine group - C=N-H while the band at 1440 cm^{-1} can be assigned to C-O. In the case of the complexes the bands of -C=N-H and C-O shifted to lower frequency. The shifting which may be due to (HOMO →LUM O), (where HOMO: Highest Occupied Molecular Orbital, LUM O: Lowest Unoccupied Molecular Orbital) confirmed the coordination of ligand through nitrogen and oxygen atoms. The band at 536cm^{-1} assigned to *ν*(M-O) for complex. The bands at 487 cm^{-1} were assigned to υ (M –N) for complex indicating that the imine nitrogen is involved in coordination with metal ions.

Table 3: FT-IR spectra data for ligand and its metal complexes:

Complex	*V*(C=N)	*V*(C-O)	*V*(M-N)	*V*(M-O)
Ligand (L_1)	1612 cm^{-1}	1454cm^{-1}	---	---
$CO(II)(L_1)_2$	1604cm^{-1}	1487cm^{-1}	480cm^{-1}	513cm^{-1}
$Zn(II)(L_1)_2$	1610cm^{-1}	1440cm^{-1}	487cm^{-1}	536cm^{-1}

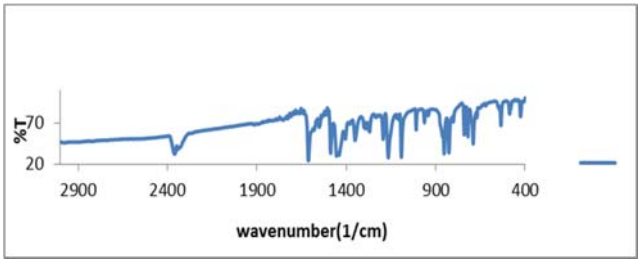


Fig 3.2a: FT-IR Spectra for ligand (L_1)

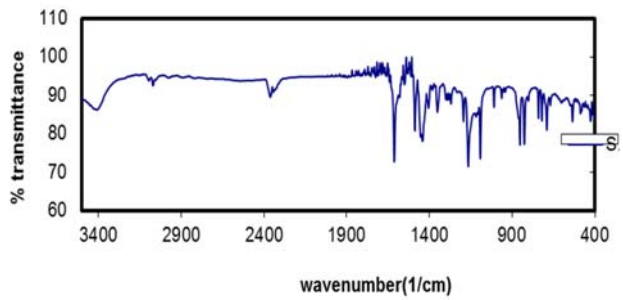


Fig 3.2b: FT-IR Spectra for Zinc (II) complex

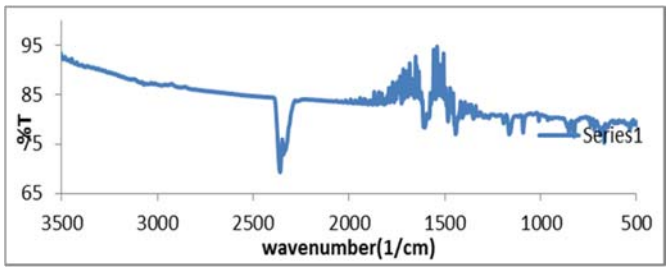


Fig-3.2c: FT-IR Spectra for cobalt (II) complex

3.3 EPR Spectra

EPR measurements have been made for Cobalt (II) and Zn (II) complexes using powder sample at room temperature, which could provide only value of g_{iso} and doesn't give g parallel and g perpendicular values. The magnetic moments of Cobalt (II) and Zinc (II) is 4.14 and 5.10 B.M. respectively which almost equal to the total spin only value. The pairing of electron is prevented by greater distance between two metal centers [12].

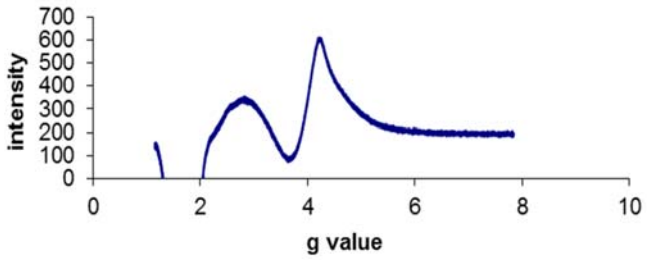


Fig 3.3a: ESR Spectra for Co (II) Complexes

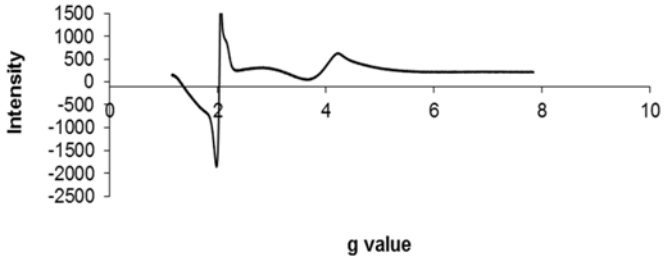


Fig-3.3b: ESR Spectra for Zn (II) Complexes

3.4 EDX spectra

EDX spectra is used to calculate the percertage 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-8. Similarly the elements like Cu,Cl,O,Al,Cu are present in Zn(II) complexes shown in the fig-9.

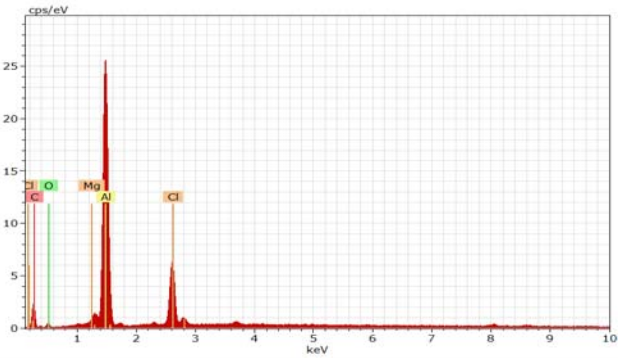


Fig- 3.4a: EDX- Co (II) metal complexes

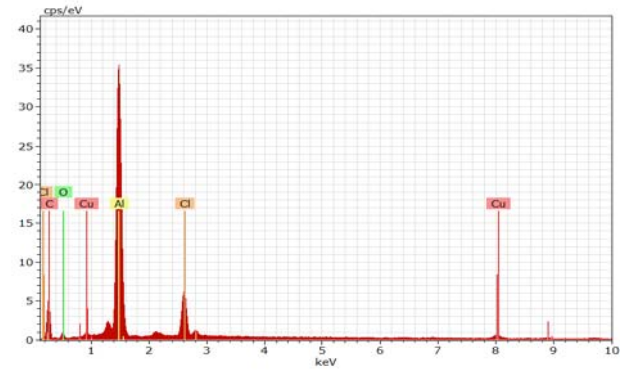


Fig 3.4b: EDX- Zn (II) metal complexes

3.5 XRD Spectra

The powdered XRD analysis of Zn (II) and Co (II) complexes was carried out to find the crystalline or amorphous nature of the complexes. The diffractogram was given in the fig-3.5a&3.5b. The strong and broad peak confirms the complex formation and the appearance of large feeble peaks indicates that the complex is macro size crystalline structure. The size of the complex is calculated using Scherer's formula.

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

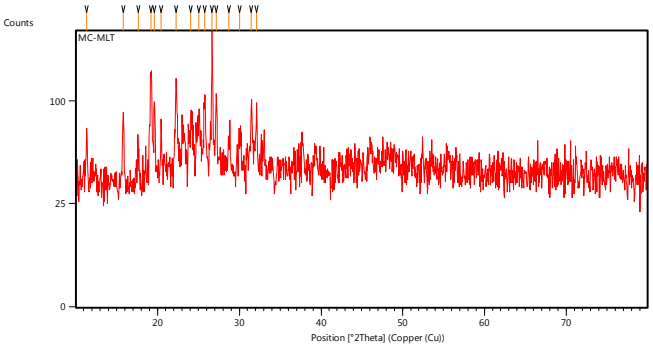


Fig -3.5a: XRD-Zn (II) complexes

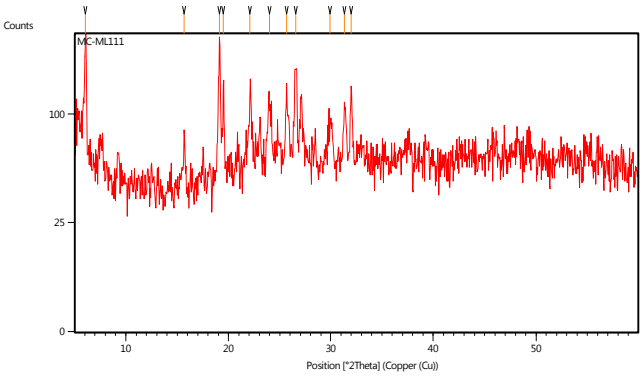
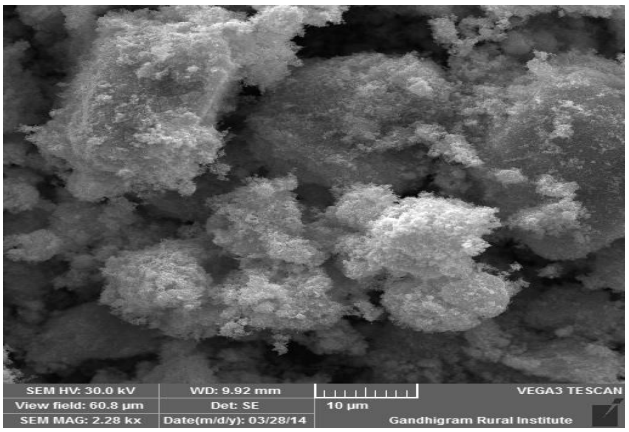


Fig 3.5b: XRD-Co (II) complexes

3.6 SEM Analysis

The surface morphology of Zn (II) and Co(II) complex was studied using SEM and the images were shown in fig-10&11. The Zn (II) and Co (II) complexes is microcrystalline in nature. The Zn(II) complexes showed cocoon like appearance on higher magnification. Lower mangnification showed cloudy liked appearance. Similarly the the Co(II) complexes showed pear fruit like appearance on higher magnification. Lower mangnification showed powered liked appearance.



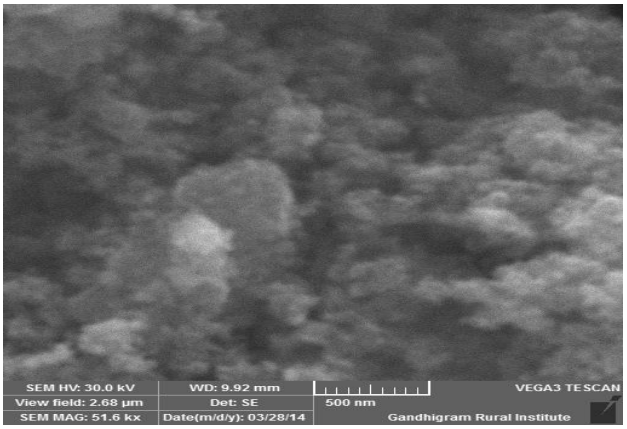
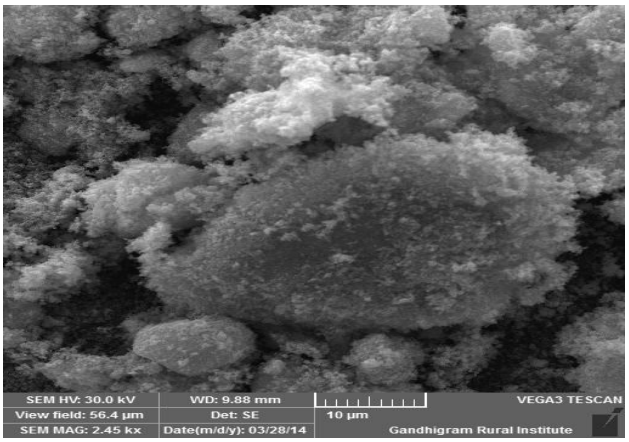


Fig-3.6a: SEM-Zn (II) complexes



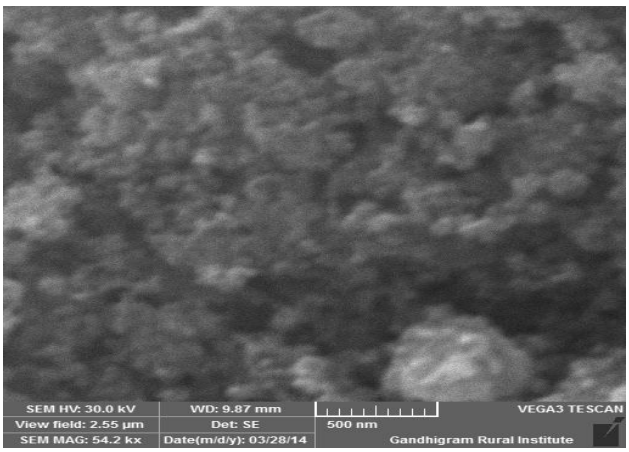


Fig-3.6b: SEM-Co (II) complexes

4. Conclusion

Schiff base ligand derived from 4-chloro aniline and di-bromosalicylaldehyde and its Co (II) and Zn (II) complexes have been synthesized. The metal chelates of ligand have been structurally characterized by spectral and analytical data. Based on these data square planar geometry has been assigned to the Co (II) and Zn (II) complex. The elements present in metal complexes were identified by EDX. From the EPR spectra the unpaired electron were indentified. XRD spectra analysed the complexed were microcrystalline structure.SEM analysis have shown the surface morphology of the metal complexes.

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