

## Synthesis and Characterization of Schiff Base Metal Complexes Derived from 3-Ethoxysalicylaldehyde and 2-Amino-4-Chlorobenzoic Acid

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### Introduction

Schiff base ligands are considered as “privileged ligands” because they are easily prepared by condensation between aldehydes and amines. These ligands are able to co-ordinate with many different metal ions. The chemistry of transition metal complexes with Schiff bases has played a vital role in the development of co-ordination chemistry as a whole<sup>1-2</sup>.

A number of authors studied different aspects of physical characterizations, spectroscopic and potentiometric investigation of several M(II) complexes including Mn, Fe, Zn, Cu, Co and Ni with Schiff base derived from 2-amino-benzoic acid and salicylaldehyde<sup>4-7</sup>.

Maihub *et.al* synthesized Fe(III) and Os(III) complexes with Schiff base derived from unsubstituted salicylaldehyde and 2-aminobenzoic acid and characterized them by various methods like IR, NMR, UV etc. Morad *et.al* synthesized Ni(II) complex with salicylaldehyde and 2-aminobenzoic acid and characterized it by various methods and also studied its antibacterial activity.

These results motivated us to prepare the complexes and characterize then making the present paper that deals the preparation of Schiff base ligand and its metal complexes characterize by the elemental analysis, magnetic susceptibility, molar conductivity measurements, electronic spectra, infrared, <sup>1</sup>HNMR, <sup>13</sup>CNMR spectrum to determine the mode of co-ordination and geometry.

### Material and methods

All chemicals like 3-ethoxysalicyl-aldehyde, 2-amino-4-chlorobenzoic acid, metal chloride salts and solvents used were reagent grade (Alfa aesar/Avra/spectrum) products and were used as such without further purifications. The percentage composition of C, H, N of complexes were measured Flash EA 112 series. Infrared spectra were measured using KBr pellets with Perkin Elmer RX1, Spectrophotometer in conventional range of 4000-400 cm<sup>-1</sup>. The electronic absorption spectra of the complexes were recorded using a Perkin Elmer Lambda 35 Spectrophotometer in the range of 350 nm-800 nm. Magnetic susceptibility measurements on powder samples were carried out by Gouy method. The diamagnetic correction were made by Pascal's constant and Hg[Co(SCN)<sub>4</sub>] was used as calibrant. The molar conductance measurements were carried out in DMSO (10<sup>-3</sup> M) using Digisun Electronic digital conductivity meter DI-909 Having dip-type cell calibrated with KCl. The

$^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectra were recorded on Mercury Plus 300 MHz NMR spectrometer by employing TMS on internal standard.

### Synthesis of Schiff base (EAP)

The Schiff base was prepared by condensation of 3-ethoxysalicylaldehyde (0.01 mol) with 2-amino-4-chlorobenzoic acid (0.01 mol) and the mixture was refluxed for 2-3hrs. The resulting solution was kept under  $0^\circ\text{C}$ . The product was obtained and collected by filtration washed several times with ethanol and recrystallized from hot ethanol and dried in a vacuum desiccator. The melting point of the ligand was found to be  $157^\circ\text{C}$ . The color is red.

### Preparation of the complexes

The complexes of Co(II), Ni(II), Cu(II), Zn(II) were prepared by refluxing respective metal chloride in ethanolic solution of ligand (1:1). The resulting mixture was refluxed for 2-4 hr at  $70\text{--}80^\circ\text{C}$ . On cooling colored solid product was collected by filtration and then washed several times with diethylether until the washing become colorless. The product was dried in air and stored in desiccators over anhydrous  $\text{CaCl}_2$  under vacuum.

### Results and discussion

The reactions of appropriate metal (II) chloride with the Schiff base ligand derived from 3-ethoxysalicylaldehyde and 2-amino-4-chlorobenzoic acid, acting as a tridentate ligand in methanol solution gave transition metal complexes. The formulations were in accordance with data of elemental analysis and physico-chemical measurements. The molar conductance of metal complexes are measured using  $10^{-3}\text{M}$  DMSO solvent, the obtained values (Table 1) suggests the presence of a non-electrolyte in nature.

**Table 1: Analytical data and physical data of the ligand and its complexes**

Compound	Molecular formula	Mol. Wt	Color	Melting point	Elemental analysis Calculated/(Observed)			$\Omega$ $\text{cm}^{-1}$
					C	H	N	
Ligand	$\text{C}_{16}\text{H}_{14}\text{ClNO}_4$	319	Red	157	60.18 (59.20)	4.41 (4.30)	4.38 (4.32)	-
EAB.CoCl <sub>2</sub>	$\text{C}_{16}\text{H}_{15}\text{Cl}_3\text{CoNO}_4$	467	Light brown	> 300	41.19 (41.08)	3.24 (3.18)	3.00 (2.95)	32
EAB.NiCl <sub>2</sub>	$\text{C}_{16}\text{H}_{15}\text{Cl}_3\text{NiNO}_4$	466	Light green	> 300	41.12 (40.98)	3.24 (3.18)	3.00 (2.82)	24
EAB.CuCl <sub>2</sub>	$\text{C}_{16}\text{H}_{15}\text{Cl}_3\text{CuNO}_4$	471	Olive green	278	40.78 (40.54)	3.21 (3.08)	2.97 (2.85)	38
EAB.ZnCl <sub>2</sub>	$\text{C}_{16}\text{H}_{15}\text{Cl}_3\text{ZnNO}_4$	473	Light yellow	234	40.62 (40.54)	3.20 (3.05)	2.96 (2.78)	42

### Infrared spectra of the Schiff base and its complexes

The infrared spectra provide valuable information regarding the nature of the functional group attached to the metal atom. In order to study the bonding mode of Schiff base to the metal complexes, IR spectrum of the free ligand was compared with the spectra of the complexes. The main infrared bands and their assignments are listed in (Table 2).

- The Infrared band assignment of all metal complexes exhibit broad band in the 3400 to 3350  $\text{cm}^{-1}$  indicating the presence of co-ordinated water molecule<sup>9</sup>.
- The spectrum of free Schiff base ligand show strong absorption at 1625 $\text{cm}^{-1}$  assigned for the  $\gamma_{\text{C=N}}$  of azomethine group. In the spectra of analyzed complexes the absorption band have been shifted to lower region by 27-45  $\text{cm}^{-1}$  which confirms the co-ordination of azomethine group through N-atom<sup>10</sup>.
- The band at 1694  $\text{cm}^{-1}$  attributed to  $\gamma_{\text{C=O}}$  vibration also shifted to lower frequency, which indicates the involvement of oxygen atom from C=O group in bonding with metal ion<sup>11</sup>.
- New bands were observed between 800-400  $\text{cm}^{-1}$  region in complexes which were absent in the spectrum of ligand. The bands between 600-680  $\text{cm}^{-1}$  were assigned to stretching frequencies of  $\gamma_{\text{(M-O)}}$ , the band between 475-580  $\text{cm}^{-1}$  has been assigned to the stretching frequencies  $\gamma_{\text{(M-N)}}$  respectively<sup>12</sup>.
- The  $\gamma_{\text{(C-O)}}$  (phenolic) stretching frequency of ligand is seen at 1376  $\text{cm}^{-1}$  which gets shifted to a lower frequency region in the complexes in the range of 1372-1326  $\text{cm}^{-1}$  and this is indicative of bonding through phenolic oxygen.
- The presence of -OH of this acid group in the spectra of the complexes, absence symmetric and asymmetric stretch of carboxylate ion and presence of anion (Chloride) in the complex suggest that the acid group is not ionized and the shift  $\gamma_{\text{(C=O)}}$  stretch to lower frequency in the spectrum of the complexes suggest that the carbonyl oxygen of COOH group in co-ordinated to metal ion.

**Table 2: Infrared spectra of the Schiff base and its complexes**

Compound	$\gamma_{\text{OH}}$	$\gamma_{\text{C=N}}$	$\gamma_{\text{C=O}}$	$\gamma_{\text{C-O}}$	$\gamma_{\text{M-N}}$	$\gamma_{\text{M-O}}$
Ligand (EAB)	3382	1625	1694	1376	-	-
EAB.CoCl <sub>2</sub>	3302	1589	1606	1365	656	432
EAB.NiCl <sub>2</sub>	3301	1591	1624	1358	671	434
EAB.CuCl <sub>2</sub>	3343	1596	1634	1354	566	416
EAB.ZnCl <sub>2</sub>	3295	1584	1656	1348	661	427

### Electronic spectra

- The spectrum of Co(II) complex showed absorptions  $22,222\text{ cm}^{-1}$  assigned to and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  transitions respectively. The cobalt (II) complex shows a magnetic moment of 4.52BM at room temperature. This high value suggests that the magnetic moment and co-ordination number six for the central cobalt(II) ion and octahedral geometry<sup>13</sup>.
- The electronic spectra of the Nickel(II) complex exhibit absorption bands at  $21,834\text{ cm}^{-1}$  assigned to  ${}^3\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$  transitions respectively in an octahedral geometry<sup>14,15</sup>. The value of magnetic moment 3.1 BM may be taken as additional evidence for its octahedral structure.
- The electronic spectra of Copper(II) complex exhibit absorption band at  $22,123\text{ cm}^{-1}$  mainly due to  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$  transition suggesting octahedral geometry 1.74 BM suggestive octahedral nature of the complex<sup>16</sup>.
- The Zinc(II) complex shows no d-d band as is expected for a  $d^{10}$  system and was found to be diamagnetic in nature. On the basis of analytical, conductance and spectral data Zinc(II) complex was assigned on octahedral geometry.

**Table 3: Electronic data of Schiff base and its complexes**

Compound	UV-Visible bands ( $\text{cm}^{-1}$ )	$\mu_{\text{eff}}$ (BM)
Ligand (EAB)	-	-
Co(II) complex	22,222	4.52
Ni(II) complex	21,834	3.10
Cu(II) complex	22,123	1.74
Zn(II) complex	-	-

### <sup>1</sup>HNMR and <sup>13</sup>CNMR spectra

The <sup>1</sup>HNMR spectrum of the ligand in DMSO shows the following signals given in Table 5. The sharp singlet at 7.7 ppm attributed to azomethine proton confirms the formation of the ligand<sup>17,18</sup>.

Another singlet corresponding to one proton is observed in 14.8 ppm is due to phenolic proton. The <sup>13</sup>CNMR spectrum of the ligand is recorded in CDCl<sub>3</sub>. It shows the following signals given in the Table 4. Azomethine carbon is observed at 151.11 ppm and phenolic carbon is observed at 190.48 ppm. Peak in the region 110-147 ppm were due to aromatic carbon.

### Zn and <sup>1</sup>HNMR spectrum

The peak of azomethine proton in ligand is shifted to downfield signal at 7.2 ppm, confirms co-ordination of nitrogen atom to Zn(II) ion. The COOH and OH proton also shifted to downfield which confirms co-ordination.

**Table 4:  $^{13}\text{C}$ NMR of the Schiff base ligand**

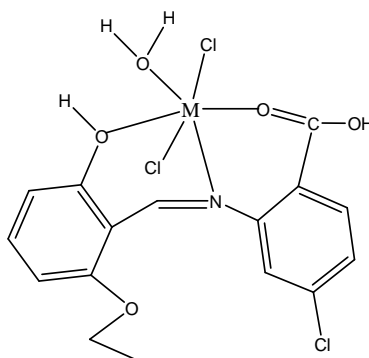
$\delta$ ppm	Functional group assigned
110-147	Aromatic carbons
151	Azomethine carbon
194	Carboxylic carbon
13.56	Methyl carbon
63.51	Methylene carbon

**Table 5:  $^1\text{H}$ NMR of the Schiff base and its Zn(II) complexes**

Compound	-CH=N ( $\delta$ ppm)	Aromatic protons ( $\delta$ ppm)	-OH ( $\delta$ ppm)	COOH ( $\delta$ ppm)	CH <sub>3</sub> ( $\delta$ ppm)
Ligand	7.7	6.6-7	14.8	10.4	1.5
Zn-complex	7.2	6.6-7	14.0	10.0	1.5

### Conclusion

The EAB ligand and its metal complexes of Co(II), Ni(II), Cu(II), Zn(II) were synthesized and characterized. The structural data established on the basis of elemental analysis (C, H, N), infrared, ultra-violet,  $^1\text{H}$ NMR,  $^{13}\text{C}$ NMR, magnetic susceptibility of complexes were recorded and discussed.

**Structure of metal complexes**

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