

# Synthesis and Characterization of 4-(3-bromo-5-chloro-2-hydroxybenzylidimino) Benzoic Acid and its Transition Metal Complexes

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**Abstract:** Metal complexes using the schiff base ligand of 3-bromo-5-chloro salicylaldimino-4-amino benzoic acid have been prepared and characterized by elemental analysis, magnetic and spectroscopic measurements viz., (infrared and <sup>1</sup>H-NMR). An elemental analysis of the metal complexes was suggested that the stoichiometry of metal-Ligand ratio is 1:2. The following first row transition metals are used in our studies namely Co (II), Cu(II), and Mn(II). The coordination of metals with ligand were identified by Fourier transform infra red spectroscopy. The geometry of complexes were detected by the electronic spectroscopy. The proposed geometry for Mn-L<sub>2</sub> complexes is octahedral geometry. Other Co (II) and Cu (II) complexes are distorted octahedral geometry.

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

## 1. Introduction

A Schiff base was first reported by Hugo Schiff in the year 1864, Schiff base is a compound with a functional group that contains carbon-nitrogen double bond with nitrogen connected to either an aryl or alkyl group but not hydrogen. Schiff base is the product yield from the condensation reaction of primary amines with carbonyl compounds (R-CO or R-CHO). The general formula of Schiff base is R<sub>1</sub>R<sub>2</sub>C=NR where R represents aryl or alkyl group which is more stable. The chemistry of the carbon-nitrogen double bond plays a significant role in the progresses of chemical science. The common Schiff bases are crystalline solids, which are feebly basic but at least some form insoluble salts with strong acids [1,2]. Schiff bases are used as intermediates for the synthesis of amino acids or as ligands for preparation of metal complexes having a series of different structures. Schiff base compounds are widely applicable in medical science. Recent study reveals that, multi-dentate complexes of iron and nickel showed high activities of ethylene oligomerization and polymerization [3]. A Schiff base behaves as a Flexi-dentative ligand and commonly co-ordinates through O atom of the de-protonated phenolic group and the N atom of azomethine group. In Schiff base azomethine N and other donor atoms like oxygen play a vital role in co-ordination chemistry [4].

Transition metal complexes with Schiff bases had expanded enormously and embraced wide and diversified subject comprising vast areas of bio-organic compounds. Many studies have been done on transition metal complexes of Schiff base due to the fact that Schiff bases offer opportunities for inducing substrate chirality, tuning metal centered electron factor, enhancing the solubility and stability of either homogenous or heterogeneous catalyst as well as stabilizing. The presence of transition metal in human blood plasma indicates their importance in the mechanism for accumulating storage and transport of Oxygen in living organism [5]. Schiff base ligands are able

to coordinate many different metals and stabilize them in various oxidation states. Transition metal complexes of O-donor ligands have been found to have promising antibacterial, antifungal and anti-inflammatory activities. Transition metal complexes of N-donor ligands (Schiff bases) showed anti-*Candida* activities. The first row transition metal complexes such as Co (II), Ni (II), and Cu (II) have been found to exhibit fungicidal, bactericidal and antiviral activity. These complexes are most important due to their ability to serve as polymeric ultraviolet stabilizers, as laser dyes and molecular switches in logic or memory circuits. 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 search. It has been demonstrated that in-organic complexes as chemical nucleases are the focus of current research. It has been demonstrated that inorganic complexes can be used in foot printing studies of an amino acid sequence as a specific DNA binding agents, as diagnostic agents in medicinal applications and for genomic research [6, 7].

## 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 cm<sup>-1</sup>). The <sup>1</sup>H NMR records in DMSO solvent by Bruker 300MHz.

## 2.2. Synthesis of 4-(3-bromo-5-chloro-2-hydroxybenzylidimino) benzoic acid ( $L_1$ )

3-bromo-5-chloroSalicylaldehyde (0.4709g, 20 mmol) dissolved in ethanol was added to 4-amino benzoic acid (0.274g, 20mmol) was dissolved in ethanol. The solutions

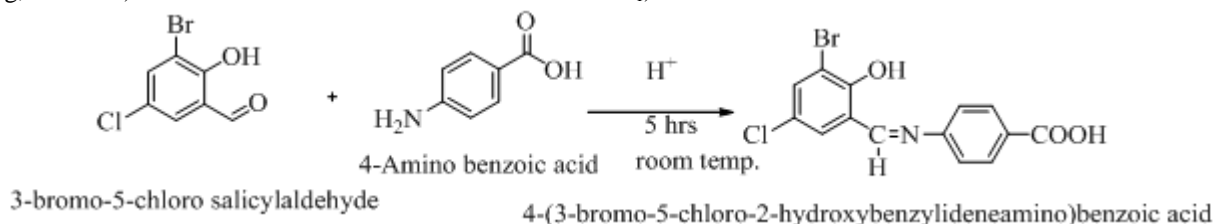


Figure 1: a- Synthesis of 4-(3-bromo-5-chloro-2-hydroxybenzylidimino) benzoic acid ( $L_1$ )

## 2.3. Synthesis of metal complexes of Schiff base ( $L_1$ )

A warm ethanol solution (10 mL) of  $L_1$  (0.708g, 20mmol) was added to the 5ml of Metal chloride solution [Co (II), Mn (II)] and acetate solution of Cu(II) (0.475g, 0.395g, 0.399g in 20mmol respectively) in distilled water. The contents refluxed for 6 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.

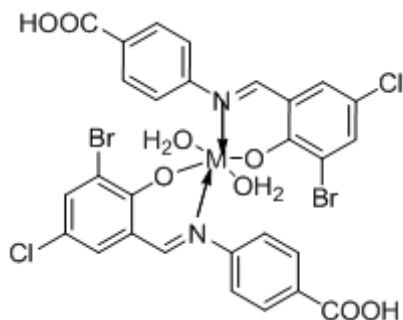


Figure 1: b- M=Mn (II), Co(II) & Cu(II).

were mixed and then one drop of diluted acetic acid was added and then refluxed for 6 hrs, with constant stirring using magnetic stirrer. On cooling, a solid product was formed which was filtered, washed with ethanol and dried. The product was recrystallization from hot ethanol gave ( $L_1$ ).



Figure 1: c- Structure and molecular modeling of Metal complexes

## 3. Result and Discussion

### 3.1. Physical Properties

All metal complexes [Co (II), Mn (II) and Cu (II)] are stable in air and moisture. They are insoluble in ethanol, acetone but soluble in DMF and DMSO. The melting points determined by using Biochem melting point apparatus the values are given below.

Table 1: Physical Properties, FT-IR and electronic spectrum data of the Ligand and its complexes

S. No	Compound	Color	M.pt. °C	M.Wt. (Calc.)	IR frequency range observed in $cm^{-1}$				$\lambda_{max}$ value (nm)		d-d transition (nm)	Geometry
					$\nu(C=N)$	$\nu(C-O)$	$\nu(M-N)$	$\nu(M-O)$	$n-\pi^*$	$\pi-\pi^*$		
1.	$C_{14}H_9NO_3$ BrCl ( $L_1$ )	Orange orange	157	310.13	1595.13	1290.38	-	-	225	270	-	-----
2.	Co(II) $C_{28}H_{16}N_2O_6$ $Br_2Cl_2$	Green	253	681.79	1573.91	1228.66	495.71	545.85	220	285	345	Distorted Octahedral
3.	Mn (II) $C_{28}H_{16}N_2O_6$ $Br_2Cl_2$	Light orange	215	683.63	1556.55	1228.66	453.29	561.29	225	280	345	Octahedral
4.	Cu(II) $C_{28}H_{16}N_2O_6$ $Br_2Cl_2$	Light orange	224	673.19	1558.48	1228.66	408.91	536.21	225	295	345	Distorted Octahedral

### 3.2. FT-IR spectrum

The IR spectra were recorded in KBr pellets using Shimadzu FT-IR spectrometer (4000 -400  $cm^{-1}$ ). The Schiff base showed the absence of carbonyl bands ( $C=O$ ) at 1735  $cm^{-1}$  and  $NH_2$  3420  $cm^{-1}$  due to stretching vibrations and instead appearance of a strong new band at the range of (1550-

1635 $cm^{-1}$ ) but observed data at 1595.13 $cm^{-1}$  assigned to the azomethine ( $HC=N$ ) linkage. It is suggested that amine 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 Schiff bases were coordinated to the metal ions in three ways, representing the

ligands acting in a bi-dentative manner. The band appearing at  $1595.13\text{ cm}^{-1}$  due to the azomethine was shifted to lower frequency by  $20\text{--}35\text{ cm}^{-1}$  indicating partition of the azomethine nitrogen in the complexation band at  $1573.91\text{ cm}^{-1}$ . The significant IR bands for the ligands as well as their {Co (II), Mn (II) & Cu (II)} complexes and the values presented in Table-1. This shifts to lower wave numbers,  $1552\text{--}1573\text{ cm}^{-1}$  in all the complexes suggesting that co-ordination of the azomethine nitrogen to the metal centers. This is further substantiated by the presence of a new band around  $403\text{--}495\text{ cm}^{-1}$  assignable to  $\nu(\text{M-N})$ . A

band at  $1290\text{ cm}^{-1}$  due to  $\nu(\text{C-O})$  phenolic group was also observed in the ligand. The disappearance of phenolic  $\nu(\text{OH})$  band at  $3415\text{--}3464\text{ cm}^{-1}$  in all the complexes suggests the co-ordination by the phenolic oxygen after deprotonation to coordinate with the metal ions. This is further supported by the shifting of  $\nu(\text{C-O})$  phenolic band to lower wave numbers  $1290.38\text{ cm}^{-1}$  in the metal complex to  $1228\text{ cm}^{-1}$ . The appearance of a new band around  $500\text{--}560\text{ cm}^{-1}$  in all the complexes due to  $\nu(\text{M-O})$  substantiates. Shown below the Fig-1d for FT-IR spectrum details.

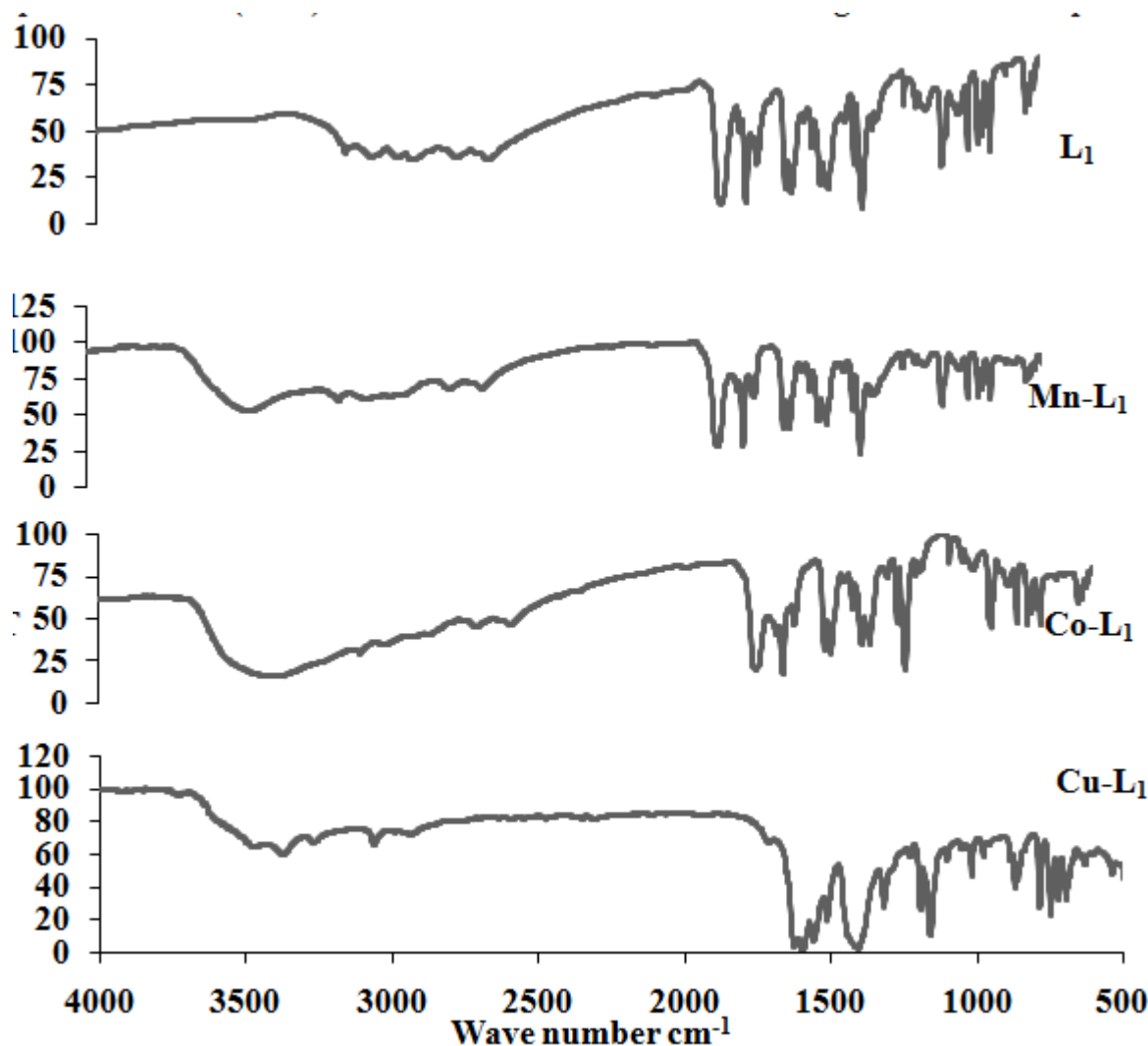


Figure 1d: FT-IR Spectrum of  $L_1$  and Metal complexes

### 3.3. UV spectra

The UV-Visible electronic spectra ( $200\text{--}800\text{ nm}$ ) is recorded by UV 1800 series double beam spectrophotometer. The Schiff base ligand shows two type of transition,  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  respectively these transition were existed 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 should be at  $400$  to  $500\text{ nm}$  are due to intra ligand charge transfer band in the complexes, which is absence in the ligand. The lower wavelengths for the Schiff bases have a range between  $270\text{ nm}$  to  $290\text{ nm}$ . These values assigned to  $n \rightarrow \pi^*$  of Schiff base ( $\text{C}=\text{N}$ ) and aromatic nature of Schiff bases [8]. These have the molar extinction co-efficient values is 0

$<100$ . The longer wavelength for the range between  $310\text{ nm}$  to  $330\text{ nm}$ . This values are due to  $\pi \rightarrow \pi^*$ , so they have higher  $\lambda_{\text{max}}$  are greater to the transition and  $0 > 1000$ . The electronic absorption spectral bands of the complexes [Cu (II), Co (II) and Mn (II)] were recorded over the range  $200\text{--}800\text{ nm}$  in DMSO and their  $\lambda_{\text{max}}$  values together with tentative assignments are summarized in Table-1 are discussed in detail. The spectral profiles below  $350\text{ nm}$  are similar and ligand centered transitions (intra ligand (L)  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$ ) of benzene and non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base complexes [9]

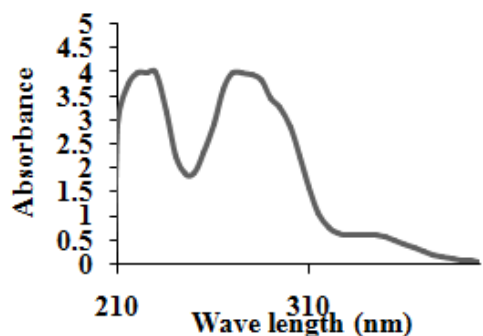


Figure 2: UV spectra for  $L_1$

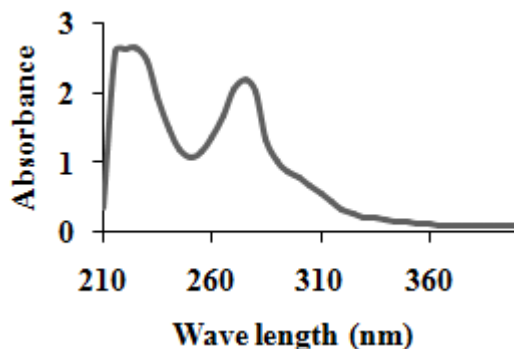


Figure 2 (a): UV spectra for Cu (II) ( $L_1$ )<sub>2</sub> complex

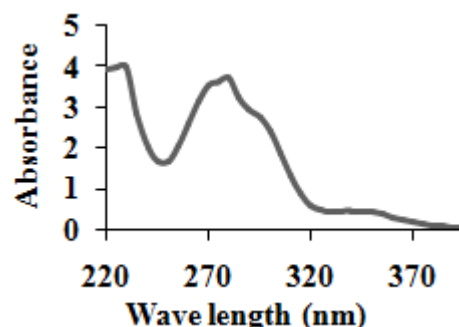


Figure 2 (b): UV spectra for Co (II) ( $L_1$ )<sub>2</sub> complex

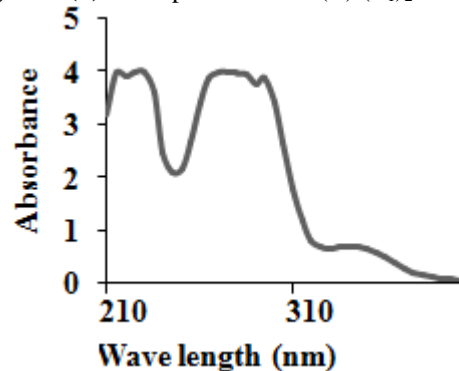


Figure 2 (c): UV spectra for Mn (II) ( $L_1$ )<sub>2</sub> complex

### 3.4. $^1\text{H}$ -NMR spectra for $L_1$

The  $^1\text{H}$ -NMR shows conformation of Ligand structure. The chemical shift value of proton in predicted in the Figure-3. The NMR value OH (s, 5.35), OH (s, 11.0), imine  $-\text{CH}$  (s, 8.64).

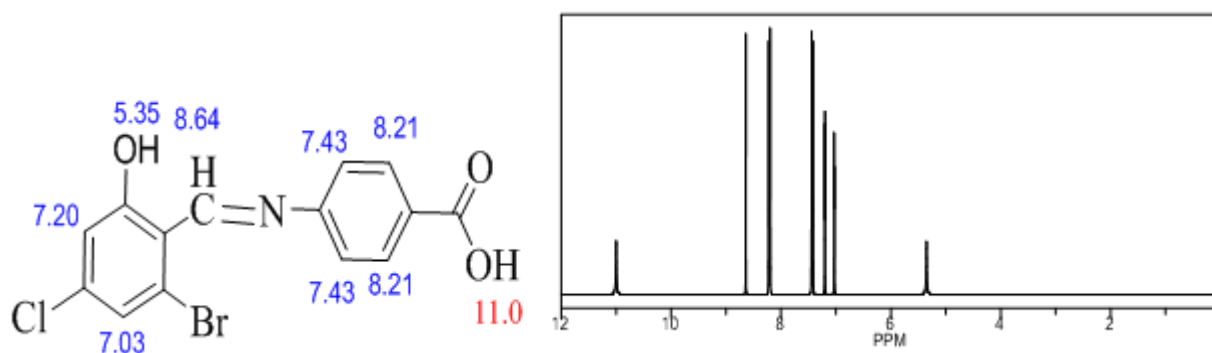


Figure 3:  $^1\text{H}$ -NMR spectrum and the predict structure for  $L_1$

### 3.5. EPR Spectrum (Electron paramagnetic resonance)

The EPR spectrum of Cu complex exhibits g value ( $g_{\parallel} = 2.303$ ,  $g_{\perp} = 2.08$ ). The Cu- $(L_1)_2$  complex is distorted Octahedral. The g value between 2.3 to 2.5 which confirm the presence of mixed M-N and M-O bond in metal complex [10]. The shown in Figure-4 for the spectrum of Cu- $(L_1)_2$  complex.

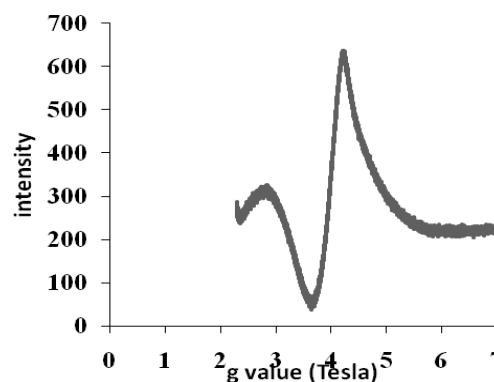


Figure 4: EPR Spectrum for Cu- $(L_1)_2$

#### 4. Conclusion

Schiff base ligand ( $L_1$ ) derived from 4-aminobenzoic acid with 3-bromo-5-chlorosalicylaldehyde respectively and their transition metal complexes of Co (II), Cu (II) and Mn (II). The ligands and their complexes have been characterized by spectral studies like (UV, FT-IR,  $^1\text{H-NMR}$  and EPR) and also analytical techniques. Based on the spectral data which can be used to assign the coordination of the metal complexes Mn(II) Octahedral and Co(II) and Cu(II) distorted Octahedral should be discussed. Which confirm the EPR spectrum one unpaired electron present in the Cu (II) complex is distorted octahedral geometry and also this study can be helpful to further studies of DNA binding, anti-microbial and anti-fungal activities of Schiff base metal complexes.

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