

Metal complexes of Schiff base derived from 3-bromo, 5-chloro Salicyldehyde with Alanine: characterization, molecular modeling and antibacterial activity study

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Abstract - Biologically active tridentate Schiff base ligand derived from 3-bromo-5-chloro salicyldehyde with alanine(DL-Alanine) and their Fe(II), Co(II), Ni(II) and Cu(II) complexes have been synthesized and characterized by physical and spectroscopic techniques. The vibrational spectrum suggests that the Schiff base ligand coordinated to the metal ions in a tridentate manner with ONO donor sites of the nitrogen atom of the imine group, oxygen atom of carboxaloto group and with phenolic oxygen to give an octahedral geometry. TOF-Mass spectrum explains the successive degradation of the molecular species and justified ML₂ complex. Electronic spectra and magnetic properties of the complexes are consistent with the proposed octahedral geometry. The structure optimization by MM2 calculation supports an octahedral geometry of the complexes. The preliminary *in vitro* antibacterial activity of all the complexes at two different concentrations was screened against four bacterial pathogens namely, *Streptococcus*, *Salmonella typhi*, *Staphylococcus aureus* and *Escherichia coli* showed moderate activity and slightly higher compared to the ligand.

Index Terms - Antibacterial activity, Metal complexes, Molecular modeling, Schiff base, Spectral studies.

1.INTRODUCTION

Schiff bases derived from an amino and carbonyl compound are important class of ligands that coordinate to metal ions via azomethine nitrogen played a significant role in the development of coordination and bioinorganic chemistry and are considered remarkable responsible for antibacterial, antitumor, antifungal, anticancer, diuretic and herbicidal activities[1]. It has been widely used as dyes and pigments, catalysts, polymer stabilizers [2],

luminescence chemo sensors [3] and intermediates in organic synthesis [4]. Schiff base can also be used as corrosion inhibitors for different metal–electrolyte systems, since they adsorb and form a corrosion-mitigating surface film through their electron-rich centers, including the imine moiety, this moiety can offer strong bonding with metallic ions because of its π -acceptor properties [5]. Moreover, several studies addressed the tribological activities of Schiff bases and their role as biolubricant additives [6]. Additionally, the use of Schiff bases as catalysts in fixation of CO₂ to mitigate its accumulation in the atmosphere has been widely studied [7].

The improved biological properties of metal complexes over their precursor ligands, chelation leads to formation of a more stable metal organic framework, since chelation improves the lipophilicity of the compounds [8]. The choice of metal connectors and the bridging ligands permits the utilization of these materials in areas, heterogenous and biomimetic catalysis; sensor technologies; luminescence; drug delivery and proton conductivity [9]. Bioinorganic chemistry also focus upon, the function of inorganic substances in living systems, including the transport mechanism, speciation and mineralization of inorganic materials and also the use of pharmacotherapy and diagnosis. These substances can be metal ions composite ions, coordination complexes or inorganic molecules [10]. The chelating property of Schiff bases plays a significant role in its antioxidant activity and this could be helpful in the development of compounds with anticancer activity in transition metal complexes [11].

Schiff base ligands containing nitrogen and oxygen donor atoms are considered structural models of

complicated biological processes and coordinate with metal ions to form complexes with variant geometries and flexible redox property. The influence of Iron(II), Cobalt (II), Nickel (II) and Copper (II) ions on the biological activity of these compounds and their intrinsic chemical interest as multidentate ligands has prompted a considerable increase in the study of their coordination behavior. The present work deals with the synthesis and spectral characterization of tridentate salicylaldehyde schiff base transition metal complexes. Molecular modeling has become useful tool for theoretical calculation studies on metal complexes to predict the stereo chemical structures. The biological evaluation of the synthesized compounds was also carried out to study their sensitivity towards variety of organisms.

2. EXPERIMENTAL

2.1. General and instrumental

All the reagents, starting materials as well as solvents used were of analytical grade, purchased commercially and used without any further purification. Melting point of the synthesized compounds was recorded on an OMEGA melting point apparatus. Elemental C, H and N analysis were carried out on a Elementar vario EL III(Germany) model. Shimadzu flame atomic absorption spectrophotometer was used to estimate metal content by decomposing the complex in hot concentrated nitric acid. Bruker Advance 400MHz instrument was used for recording ^1H NMR spectra. The solid state Fourier transform infrared (FTIR) spectra were recorded on Perkin Elmer FTIR spectrophotometer in the range of $4000\text{-}400\text{ cm}^{-1}$ and $400\text{-}100\text{ cm}^{-1}$ in potassium bromide and polyethylene pellets respectively. The Ultraviolet-Visible spectra were recorded using Shimadzu 160A ultraviolet spectrometer in the range of $1100\text{-}100\text{nm}$. EPR spectrum of copper complex was recorded on a Varian E-112 spectrometer with a variable temperature liquid nitrogen cryostat. Mass spectra (TOF-MS) were recorded on waters(USA)KC-455 model with ES^+ mode. Magnetic susceptibility measurements at RT were carried out in the powder state on a vibrating sample magnetometer PAR 155 with 5000G field strength. Computational analysis of the proposed structure of the complexes was performed using *HyperChem* professional version 7.51 program package. *In vitro* antibacterial screening

activity of the synthesized compounds against *Streptococcus*, *Salmonella typhi*, *Staphylococcus aureus* and *Escherchia coli* bacteria were carried out by inhibition zone method using agar diffusion method[12]. In this method a standard 6.35 mm diameter sterilized filter paper disc impregnated with the synthesized compound(100 and 200 $\mu\text{g/ml}$ in DMSO) was placed on an agar plate seeded with the test bacterial strains. The plates were incubated for 24 hours at 40°C . The activity was determined by measuring the diameter of inhibition zone (in mm) and Chloramphenicol was used as the standard control.

2.2 Synthesis of ligand and complexes:

2.2.1 Synthesis of ligand

Schiff base ligand was prepared from the reaction of 3-bromo-5-chloro salicylaldehyde (0.01mol), alanine(0.01mol) in ethanol solvent and KOH solution. Deprotonation of ligand becomes easier for the addition of KOH. The reaction mixture was refluxing for 3h. The hot reaction mixture was cooled and poured on crushed ice. When a lemon yellow solid mass separated out, the resulting solid mass was filtered, washed first with distilled water and then with cold ethanol and finally dried in a vacuum desiccators. The dried mass was recrystallized from ethanol to deliver the pure compound (m.p.159 $^\circ\text{C}$)(Figure 1: Proposed structure of the ligand).

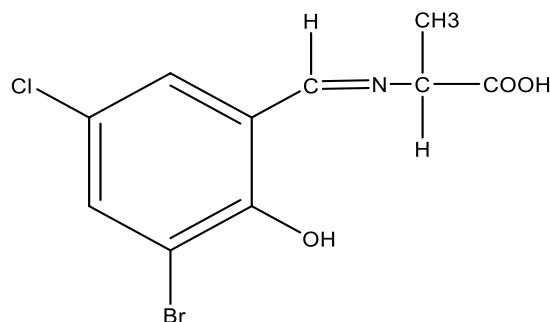


Figure 1: Proposed structure of the ligand

2.2.2 Synthesis of metal complexes:

The newly synthesized ligand 3-bromo-5-chloro salicylaldehyde alanine Schiff base (5 m mol) in 20 ml of absolute ethanol was added dropwise to a solution containing $\text{MCl}_2 \cdot x\text{H}_2\text{O}$ (2.5 m mol) [$\text{M(II)} = \text{Fe(II)}$, Co(II) , Ni(II) , Cu(II)] in absolute ethanol(20 ml) with constant stirring. Stirring was continued with heating 60°C for 4h, after which the volume was reduced on a water bath. On cooling at room temperature the

colored precipitate was filtered washed with cold ethanol and dried over P₄O₁₀ *in vacuo*. The dried mass was recrystallized from ethanol to obtain the pure product(Figure 2: Proposed structure of complexes).

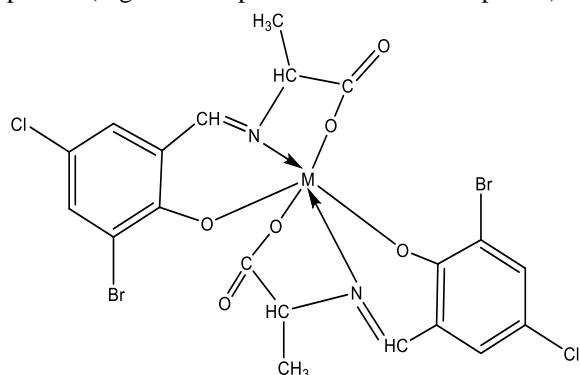


Figure 2: Proposed Structure of complexes [M= Fe(II), Co(II), Ni(II), Cu(II)]

3. RESULTS AND DISCUSSION

The micro-elemental analysis as well as molecular weight of the synthesized compounds was in agreement with the predicted formula. On the basis of elemental analysis data (Table1), the complexes have the general composition ML₂, where M = Fe(II), Co(II), Ni(II) and Cu(II); Ligand = 3-bromo-5-chloro salicylaldehyde alanine Schiff base. The complexes were obtained in powder form and were found to be sufficiently soluble in Acetone and DMSO for spectral measurements.

Table 1: Analytical and electronic spectral data of the ligand and their metal complexes

S No	Compound/complex (Empirical formula)	Color	MP (°C)	Yield (%)	Analysis: found (Calculated) (%)					μ _{eff} (BM)
					C	H	O	N	M	
1	Ligand (C ₁₀ H ₉ O ₃ NBrCl)	Lime yellow	159	87	76.08 (76.13)	7.50 (7.55)	5.96 (5.92)	10.43 (10.50)	-	-
2	Complex I [Fe(C ₂₀ H ₁₄ O ₆ N ₂ Br ₂ Cl ₂)]	Peach	17	86	68.31 (68.29)	6.02 (6.08)	5.35 (5.39)	9.37 (9.43)	10.94 (10.98)	5.20
3	Complex II [Co(C ₂₀ H ₁₄ O ₆ N ₂ Br ₂ Cl ₂)]	Lalic	298	89	63.10 (63.18)	5.58 (5.50)	4.96 (4.99)	8.69 (8.72)	17.44 (17.46)	4.70
4	Complex III [Ni(C ₂₀ H ₁₄ O ₆ N ₂ Br ₂ Cl ₂)]	Green	287	85	62.70 (62.68)	5.53 (5.55)	4.91 (4.96)	8.60 (8.57)	18.24 (18.29)	3.10
5	Complex IV [Cu(C ₂₀ H ₁₄ O ₆ N ₂ Br ₂ Cl ₂)]	Greenish Blue	273	84	5.20 (55.26)	4.87 (4.91)	4.33 (4.40)	7.57 (7.60)	28.02 (27.99)	1.85

3.1 Spectroscopic studies and magnetic studies

¹H NMR spectrum of the Schiff base ligand (Figure 3) exhibit signals at 1.61 ppm due to CH - CN, 3.71 ppm due to -CO-CH₃, and 9.80 ppm due to Ar-CH=N. A sharp multiplet signals between 7.25 – 7.76 ppm are due to Ar-H. A singlet corresponding to one proton observed at 11.60 ppm is due to Ar-OH. The metal complexes are paramagnetic in nature so it gives rise to special effects shown by a wide chemical shift range and broadened signals. Due to paramagnetism, it diminishes the NMR spectrum resolution to the extent that coupling is rarely resolved.

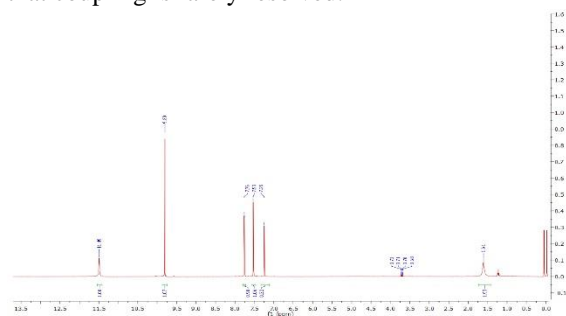


Figure 3: ¹H NMR spectrum of the ligand

A comparative study of the FTIR spectra of ligand and its metal complexes discloses the coordination modes and sites of the ligand to the metal ions. The significant infrared bands of the Schiff base and their metal complexes are represented in table 2.

Table 2 :IR spectral data (cm⁻¹) of the ligand and metal complexes

Frequen cy	Ligan d	Comple x I	Comple x II	Comple x III	Comple x IV
ν (OH)	3280 (s)	2990 (w)	2999(s)	2985 (m)	2980 (m)
ν (C=N)	1660 (s)	1643 (w)	1650 (m)	1640 (s)	1630 (s)
ν (M-O)	-	520 (s)	510 (m)	518 (s)	530 (s)
ν (M-N)	-	410 (s)	420 (m)	416 (s)	408 (m)
ν (CH ₃)	1300 (s)	1348 (s)	1357 (w)	1350 (s)	1365 (s)
ν (C ₆ H ₅)	1280 (s)	1260 (s)	1250 (m)	1260 (m)	1370 (w)
ν (C-O)	1390 (s)	1380(s)	1375 (s)	1273 (s)	1379 (s)
δ (CH)	2880 (m)	2840 (w)	2870 (s)	2872 (w)	2870 (w)

s: strong; m: medium; w: weak

Figure 4a: Infrared spectrum of the ligand, shows a broad band between 3200-3600 cm^{-1} , which can be attributed to $\nu(\text{Ph-OH})$ [13]. This band is either disappears or shifted to lower frequency in complexes, which can be attributed to deprotonation of phenolic OH group during coordination. This has been further confirmed by the shift of $\nu(\text{Ar-C-O})$ stretching band observed at 1390 cm^{-1} in the free ligand to a lower frequency to the extent 10-20 cm^{-1} , suggests the weakening of $\nu(\text{Ar-C-O})$ and formation of stronger M-O bond [14]. The free Schiff base ligand exhibited characteristic strong band at 1660 cm^{-1} , attributed to the azomethine ($-\text{HC}=\text{N}$) group, which were shifted to lower frequencies (1650-1630 cm^{-1}) in the complexes due to the chelation of the imine nitrogen to the metal ions (Fig. 4b-e: Infrared spectrum of complexes). Coordination of the Schiff base to the metal through the nitrogen atom is expected to withdrawing the electron density in the azomethine link and causing lower shift of the $\nu(\text{C}=\text{N})$ absorption frequency [15]. The strong absorptions at 1570-1615 cm^{-1} and 1450-1520 cm^{-1} are observed for $\nu_{\text{as}}(\text{COO})$ and $\delta_{\text{s}}(\text{COO})$. These bands are shifted by certain pattern, which reveals the ligand is involved in the coordination through carboxyl group and acts as monodentate. The separation between anti-symmetric and symmetric stretching is $\sim 120 \text{ cm}^{-1}$, suggesting the covalent nature of M-O bond in complexes. Metal ligand bond is further confirmed by the appearance of a medium intensity band in the range 420-480 cm^{-1} and 520-545 cm^{-1} in the spectra of the complexes allotted to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ bond formation respectively. The stretching vibrations of $-\text{OH}$, $-\text{C}=\text{N}$, $-\text{COO}$ and Ar-C-O bonds of complexes are different because the backbones are influenced by metal ion and the structure of amino acid residue [16].

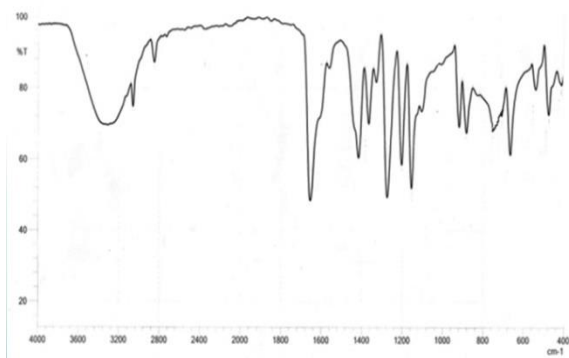


Figure 4a: IR spectrum of the ligand

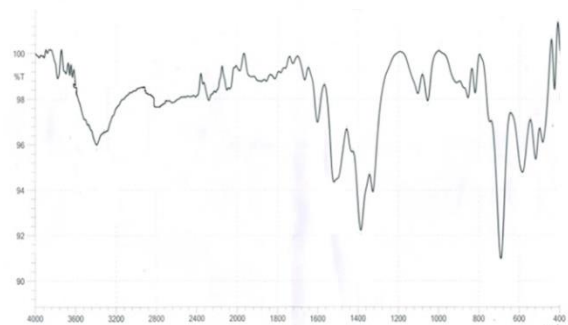


Figure 4b: IR spectrum of complex I



Figure 4c: IR spectrum of complex II



Figure 4d: IR spectrum of complex III

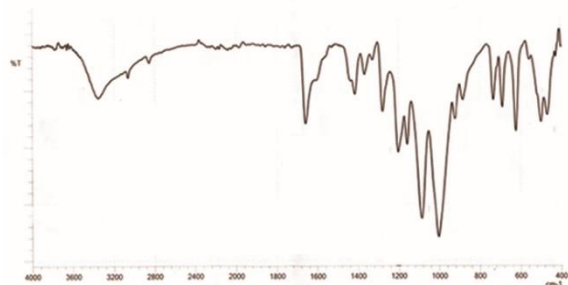


Figure 4e: IR spectrum of complex IV

The UV-visible spectra of Schiff base ligand exhibited two bands at 325 and 370 nm attributed to benzene $\pi \rightarrow \pi^*$ and azomethine $n \rightarrow \pi^*$ transition respectively. In complexes these two bands due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions were also observed but the band due to azomethine $n \rightarrow \pi^*$ transition has shifted to lower wavelength due to lone pair donation from nitrogen atom to metal ions. The Fe(II) complex showed d-d transition bands at 613 and 810 nm which were

assigned to ${}^5T_{2g} \rightarrow {}^5B_{1g}$ and ${}^5T_{2g} \rightarrow {}^5B_{1g}$ transitions respectively. The remaining bands at 338 and 365 nm also obtained were assigned to charge transfer, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively. The magnetic susceptibility measurements for Fe(II) complex were 5.20 BM indicates d^6 configuration having octahedral geometry. The Co(II) complex exhibits two distinct bands of high wavelength spectrum at 465 and 540 nm were assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition, confirming octahedral geometry of the complex[17]. The magnetic susceptibility value (4.70BM) further supports octahedral geometry around the Co(II) ions. The high energy bands for this complex were observed at 320 and 360nm, assignable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ charge transfer transitions, respectively. The spectrum of Ni(II) complex showed three band in the regions 450,552 and 765 nm were assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transitions, in an octahedral geometry. This was validated by magnetic susceptibility value 3.10BM confirms high spin octahedral complex. The remaining bands in the ultraviolet region at 327 and 358 nm also obtained in Ni(II) complex were assigned to charge transfer, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively. The spectrum of Cu(II) exhibited a single absorption band in visible region at 652 nm consistent with ${}^2B_{1g} \rightarrow {}^2E_g$ transition and charge transfer bands at 330 and 366 nm were typically octahedral geometry. The magnetic susceptibility value (1.85 BM) validating the mononuclear octahedral complex having d^9 configuration [18].

The EPR spectrum of Cu(II) complex has been studied at room temperature (Figure 5: EPR spectrum of Cu(II) complex). The spectrum of the complex showed axial in nature having $g_{\parallel} (2.0205) > g_o (2.0144) > g_{\perp} (2.0114) > g_e (2.0023)$, indicates that unpaired electron most likely reside in dx^2-y^2 (or less likely d_{xy}) ground state orbital, Here $g_o = 1/3(g_{\parallel} + 2g_{\perp})$. The g_{\parallel} value for Cu(II) complex is less than 2.3 shows noticeable covalent character of the Cu(II) – Ligand bond[19]. The geometric parameter, G is a measure of degree exchange character $= (g_{\parallel} - g_e) / (g_{\perp} - g_e) = 2$, measures the exchange interaction between copper centers in the polycrystalline compound, indicates axial nature of the Cu(II) complex having considerable exchange interaction in solid state. The shape of the ESR spectrum indicates that the Cu(II) complex possesses distorted octahedral structure.

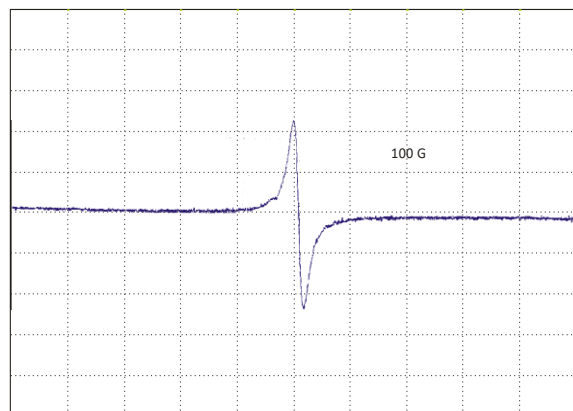


Figure 5: EPR spectrum of complex IV

The mass spectrum of the ligand, a molecular ion peak was observed at m/z 307 corresponding to its molecular weight in agreement with elemental composition suggested by CHN analysis result confirms purity of the ligand. The spectrum also exhibited various fragments of the ligand. The molecular formulas calculated from micro analytical data for the complexes have been supported by the TOF-mass studies. The metal complexes initial fragmentation pattern is similar, a binuclear nature for these complexes $[M(L_2)]^+$ can be deduced (Fig 6a-d: TOF Mass spectrum of the complexes). The mass spectrum of the complexes having a molecular ion peaks at m/z 665 (Fe(II) complex), m/z 668 (Co(II) complex), m/z 668 (Ni(II) complex) and m/z 673 (Cu(II) complex) respectively, further confirming the purity of the complexes. In the spectrum of the ligand the peaks at m/z 304, 288 and 273 were due to loss of $2H^+$, O, CH_3 moieties. The prominent peak at m/z 304 in all the complexes are degradation to $[C_{10}H_7NOBrCl]^+$ molecule which are result of demetallation and subsequently a partial intramolecular hydrogen bonding[20].

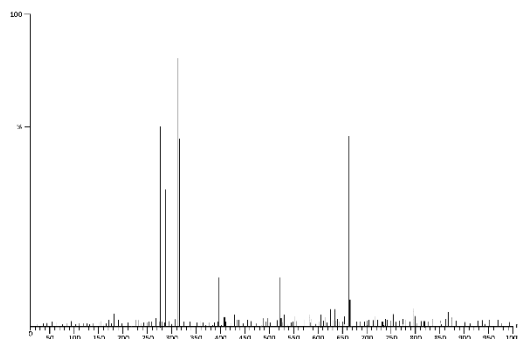


Figure 6a: TOF mass spectrum of complex I

gradient 0.913926 converged with 79 cycles 177 points, respectively. The energy minimization values for Iron complex has minimum than Copper complex than nickel complex than Cobalt complex which has maximum energy. It indicates Iron complex has maximum stability than other metal complexes.

3.3 Biological studies

The anti-bacterial results of the Schiff base ligand and their metal complexes indicate that the synthesized compounds had activity against *Streptococcus*, *Salmonella typhi*, *Staphylococcus aureus* and *Escherichia coli* bacteria. Two different concentrations (100 and 200µg/ml) of the compounds have been considered for antibacterial studies. The ligand bears activity even better than reference chlorophinacol. The Iron complex shows lowest level of activity as it is not active against *Salmonella typhi* at two different concentrations measured. The cobalt complex was not active against *Salmonella typhi* at low concentration but has significant activity against high concentration. Nickel complex shows significant activity against all microorganisms, but it was active with *Staphylococcus aureus* with higher concentration. The copper complex exhibited greatest activity in the entire microorganism tested at two different concentrations. In general, the activity of the ligand and complexes increases with increases as their concentrations. Moreover, the complexes deliver better antibacterial activity at their higher concentration. The ligand and complexes exhibit high activity against *Escherichia coli* and shows less effective against *Salmonella typhi* bacteria. The enhanced activity of the metal complexes may be attributed to chelation of Schiff base that provide stability and more susceptibility against microorganism. The Schiff base having (C=N) bond with oxygen and nitrogen donor ability inhibit enzyme activity due to their deactivation by metal chelation. This permits their efficient permeation through lipid layer organism and destroys their bioactivity[21].

CONCLUSION

The Schiff base 3-bromo-5-chloro salicyldehyde alanine and its Fe(II), Co(II), Ni(II) and Cu(II) complexes have been prepared and characterized by spectroscopic and magnetic studies. From the analytical and spectral data the ligand acts as tridentate and coordinate to the metal ions through azomethine

nitrogen, phenolic oxygen and oxygen atom of the hydroxyl group of carboxylic group to give an octahedral geometry. The infrared spectra displayed the proper chelation of the Schiff base towards the metal ions and the electronic absorption spectroscopy exhibited the existence of $n \rightarrow \pi^*$ (azomethine) and $\pi \rightarrow \pi^*$ (phenyl) transitions in the complexes. Absence of signals in $^1\text{H NMR}$ spectra of complexes inferred its paramagnetic behavior that has been confirmed by magnetic susceptibility measurements. Molecular modeling studies helps to determine the energy minimization of optimized structure of the complexes and bond energy, bond length values have been noted. *In vitro* antibacterial study indicated that the complexes showed moderate activity against tested microorganism and slightly higher activity than ligand. The Cu(II) complexes is the most active against all the tested microorganism at two different concentrations.

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