

**Mn(II), Co(II), Ni(II), AND Cu(II) COMPLEXES OF AMINO ACID DERIVED SCHIFF
BASE LIGAND: SYNTHESIS, CHARACTERIZATION AND *IN-VITRO*
ANTIBACTERIAL INVESTIGATIONS**

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ABSTRACT. Four complexes of Mn(II), Co(II), Ni(II) and Cu(II) with Schiff base ligand (H₃L) derived from 2-amino-3-methylbutanoic acid and acetylacetonate were synthesized. All complexes were characterized by elemental analysis, Fourier-transform infrared spectroscopy and electronic spectroscopy. The results confirmed the coordination of the ligand to metals in tridentate fashion via the hydroxyl oxygen, the azomethine nitrogen and the enolic acetylacetonate oxygen. Antimicrobial activities were established for all complexes, free ligand and ciprofloxacin for comparison. Both the ligand and its metal complexes were active against Gram-positive and negative bacterial strains. The Cu(II) complex, showed highest antibacterial activity among the complexes screened. Other complexes displayed considerable antibacterial activity. Octahedral geometry was proposed for the metal(II) complexes with the Schiff base.

KEY WORDS: Schiff base, Amino acid, Metal Complexes, Antibacterial agents

INTRODUCTION

Microbial resistance to antibiotics has become an issue of worldwide concern, which requires concerted efforts to address it [1, 2]. The infections caused by bacterial resistance to current available antibiotics are responsible for the alarming increasing high rate of mortality annually [3]. These antibiotic-resistant infections affect lives everyday causing a threat to health similar to influenza, tuberculosis and HIV combined [4-6]. Bacteria usually developed different resistance mode to overcome the extended spectrum of antibiotics [7], and the mechanism through which this resistance evolved as acknowledged by microbiologists, include enzymatic degradation by the lactamases, destruction of lactam ring and its re-configuration [8]. This has resulted to series of research which aimed at increasing the efficacy of the anti-microbial agent against the resistance micro-organisms. As a result, the necessity to design new agents for combating this resistance is of top most priority [9]. Transition metals ions have inherent advantages over the more common organic-based drugs. They can provide a wide range of coordination geometries, various redox states, ‘tunability’ of kinetics and thermodynamics of ligand substitution [10, 11]. Metal-based drugs play an essential role in medicine for the treatment of various diseases.

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Amino acids are versatile bio-ligands for complex formations because they contain an important combination of carboxylic and amine groups. They are also a very good candidate for the Schiff bases condensation reactions, with an array of carbonyl compounds due to the presence of amine groups. These reactions have been shown to stabilize when aldehydes and amino acids can form two five membered rings chelated to the metal ion. It was suggested that atoms of amino acid will hold in the plane of the aromatic ring when they are coordinated to the metal ions [12]. Metal complexes derived from amino acids have attracted much more attention because of its inorganic and biological importance [13-15]. They show wide applications as anti-cancer, anti-tumor, anti-bacterial, anti-fungal, and anti-inflammatory agents [15-17]. The majority of work of amino acids Schiff-bases has been carried out on the aromatic aldehyde and its derivatives [18, 19].

In this manuscript, the synthesis, spectral characterization and antibacterial investigations of the new Mn(II), Co(II), Ni(II) and Cu(II) complexes of 2-amino-3-methylbutanoic acid (valine) and acetylacetone have been described.

EXPERIMENTAL

All the solvents and reagents were of analytical grade and were used as purchased from commercial sources. The metal chlorides were used as hydrated salts. CHN analyzer (Perkin-Elmer 2400 model) was used to obtain the carbon, hydrogen and nitrogen contents. Fourier transform infrared spectra were measured on a Mattson 5000 FTIR spectrophotometer in the 4000–400 cm^{-1} range using KBr pellets. Electronic spectra were recorded using JENWAY 6405 UV-Vis spectrophotometer between 200-1100 nm by using suitable solvent. The MPA100 Optimelt Automated Melting Point System (SRS) was used to obtain the melting points of the compounds. The antibacterial activities of the ligand and its metal complexes were carried out by well-diffusion method. The data obtained were analyzed using GraphPad Prism 8 (GraphPad Software Inc., San Diego, California, USA). Data are recorded as means of duplicate \pm standard deviation (SD).

Preparation of Schiff base

The Schiff base ligand (**H₃L**) was prepared by condensation of 2-amino-3-methylbutanoic acid (0.06 mmol) with acetylacetone (0.06 mmol) in 20 mL of H₂O/ethanol and the mixture was stirred for 4-5 h. K₂CO₃ (0.1% w/v in ethanol) was added to adjust the pH of the solution at 7-8. The precipitate was filtered, washed with ethanol and then ether to remove unreacted ligands, and then dried. The purity of ligand was checked by TLC and was then recrystallized from ethanol to obtain pale yellow crystalline solid (Figure 1).

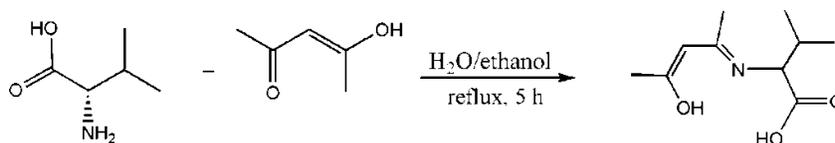


Figure 1. Synthetic route for the preparation of the Schiff base.

Synthesis of metal(II) complexes

The metal(II) complexes were prepared from four hydrated metal salts. 0.05 mol of ligand (**H₃L**) in 20 mL of ethanol, was added to the 0.05 mmol of MCl₂.xH₂O (where, M = CuCl₂.2H₂O, NiCl₂.6H₂O, CoCl₂.6H₂O and MnCl₂.4H₂O) in ethanol solution. The mixture was stirred for 3-5 h and the precipitated colored complexes were filtrated, washed with water, ethanol and kept dry in a vacuum desiccator over anhydrous calcium chloride (Figure 2).

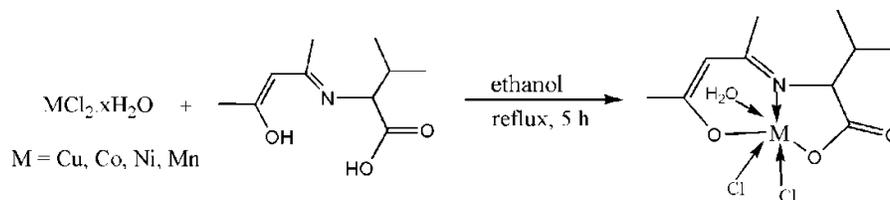


Figure 2. Synthetic route for the preparation of the Schiff base metal complexes.

Antibacterial studies

The synthesized Schiff base and metal complexes were tested *in-vitro* using clinical isolates of two Gram-negative (*Escherichia coli* and *Staphylococcus aureus*) and two Gram-positive (*Klebsiella pneumonia* and *Pseudomonas aeruginosa*) bacterial strains with sterile Muller–Hinton nutrient agar as the medium. A 5 mm diameter well for each was dug in Muller Hinton agar using a cork borer. The ligand and complexes were dissolved separately in DMSO to have different concentrations (25 and 50 µg) per disc. The solution was carefully introduced into each well. The plates were incubated at 37 °C for 24 h. The clear inhibition zone around the well was determined and results measured (in mm). Ciprofloxacin was used as standard drug.

RESULTS AND DISCUSSION

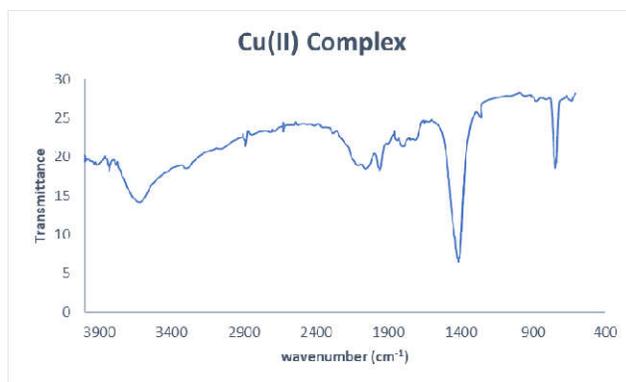
A new series of Schiff base complexes, $[M(H_3L)(H_2O)Cl_2]$, (Mn(II), Ni(II), Co(II) and Cu(II)) have been derived from the reaction of 2-amino-3-methylbutanoic acid and acetylacetonate in presence of respective metal salts. The compounds were stable in air and soluble in DMSO (dimethylsulfoxide) and DMF (dimethylformamide). Melting point values for the derived complexes ranges between 220–242 °C when compared to a relatively lower value of 204 °C for the ligand (Schiff base). The increased melting points can be due to the coordination of the ligand to the metal ions. The low values of molar conductance of the complexes in DMSO indicate the complexes are non-electrolyte nature, and are in affirmation of a neutral metal complex derived from dianionic ligand [20]. The complexes were all coloured which is a major characteristics of transition metal compounds. The results of the elemental analyses were in close agreement with the calculated values and hence confirm the stoichiometry of the compounds. The absorption peaks of electronic spectroscopy and characteristics bands of the infrared analysis, further ascertain the formation and geometry of the complexes.

Table 1. Empirical formula, molecular weight, elemental analysis data, melting point and colour.

Compound	Molecular weight found (calc.)	Elemental analysis found (calc.)			Melting point (°C)	Colour	Molar conductivity ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)
		%C	%H	%N			
Schiff base $C_{10}H_{17}NO_3$	199.25 (199.12)	51.46 (51.48)	8.20 (8.21)	6.02 (6.00)	204	Off white	22.2
Cu(II) complex $C_{10}H_{17}Cl_2NO_4Cu$	347.98 (349.20)	34.35 (34.22)	4.90 (4.84)	4.01 (4.15)	220	Dark green	21.4
Co(II) complex $C_{10}H_{17}Cl_2NO_4Co$	343.99 (345.09)	34.80 (34.62)	4.97 (4.96)	4.06 (4.10)	242	Blue	20.6
Ni(II) complex $C_{10}H_{17}Cl_2NO_4Ni$	344.85 (342.98)	34.83 (35.13)	4.98 (5.12)	4.06 (4.08)	228	Gray	24.2
Mn(II) complex $C_{10}H_{17}Cl_2NO_4Mn$	341.09 (339.89)	35.21 (34.88)	5.02 (5.15)	4.11 (4.18)	238	Yellow	23.5

Infrared spectra of Schiff base metal complexes

The infrared spectra of Schiff base and metal complexes are shown in Figure 3. The infrared data of the Schiff base and complexes are recorded in Table 2. The comparison of the ligand and complexes spectra serves as the basis of determining the coordination sites of the metal complexes [21]. The spectra bands $\nu_{as}(\text{NH}_2)$, $\nu_s(\text{NH}_2)$ of 2-amino-3-methylbutanoic and $\nu(\text{C}=\text{O})$ of acac, were not present in the complexes, while there is presence of new band for the azomethine group $\nu(\text{C}=\text{N})$. The azomethine band seen indicates condensation of the starting ligands. The metal complexes spectra display bands of carbonyl groups at 1722 and 1716 cm^{-1} from acac. The bands seen in range $1595\text{--}1546\text{ cm}^{-1}$ were new and are assigned to $\nu(\text{CH}=\text{C})$ vibration [14]. The Schiff base behaves as a tridentate as the results indicates, coordinating to the central metals through the enol form of the acac oxygen, azomethine nitrogen and carboxylate oxygen (Figure 2). The assignments of the various bands in all the samples have been done in relation to similar compounds. The spectra are different from each other. The participation of the carboxylate group in bonding is supported by presence of bands observed at 665 and 582 cm^{-1} [21]. Bands of the metal complexes shown in the regions $752\text{--}738$ and $623\text{--}605\text{ cm}^{-1}$ were ascribed to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$, respectively [22].



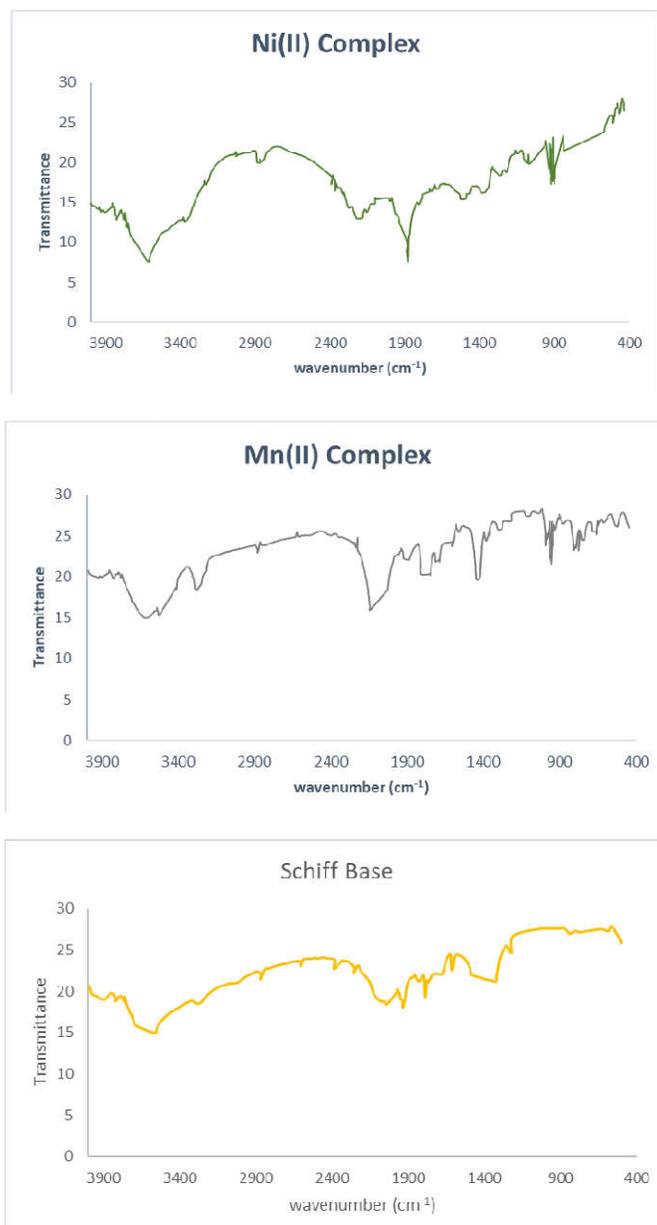


Figure 3. Infrared spectra of Schiff base and metal complexes.

Table 2. Infrared frequencies (in cm^{-1}) of Schiff base ligand and complexes.

Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\nu(\text{OH})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
Schiff Base	3307	1654	1632	1584	1366	1055	-	-
Cu(II) complex	3379	1625	1614	1546	1384	1051	740	621
Co(II) complex	3361	1652	1616	1595	1319	1074	752	605
Ni(II) complex	3312	1635	1614	1568	1386	1010	738	621
Mn(II) complex	3305	1631	1618	1556	1325	1026	751	623

The involvement of deprotonated carboxylate and enolic carbonyl oxygen as well as the azomethine nitrogen in coordination is supported by the above findings.

Electronic spectra of Schiff base metal complexes

The UV-Vis electronic spectra are shown in Figure 4 and absorption data of all complexes are listed in Table 3. The Schiff base ligand showed two absorption bands in the UV regions. The absorptions at 270 nm and 290 nm ascribed to the $\pi \rightarrow \pi^*$ transition is attributed for the intraligand of aromatic system while the bands at 320 nm and 319 nm were respectively assigned to the $n \rightarrow \pi^*$ transition for nitrogen atom of $-\text{NH}_2$ and imine $-\text{N}=\text{C}$ -group [28]. The electronic changes of these peaks which correspond to the Schiff base interaction with the metal ions are listed in Table 3. The peaks at 601 nm, 512 nm and 457 nm assigned to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions, respectively, in an octahedral geometry around Mn(II) ion in manganese(II) complexes were observed in spectra for **1** [23]. The Co(II) complex **2**, exhibits peaks at 607 nm, 511 nm, 447 nm attributed to the transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{E}_{2g}(\text{F})$, and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$, respectively, suggesting an octahedral geometry [29]. Also the complex of Ni(II) present absorption peak at 629 nm which is expected for the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ transition, also the observed peak at 551 nm, is related to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$, and signal at 467 nm is due to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transition indicating octahedral geometry [24]. Copper(II) complex showed broad peak at 614 nm assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transition suggesting an octahedral geometry [25].

Table 3. Electronic spectra data of the Schiff base and its complexes.

Compound	λ_{max} (nm)	Assignment
Schiff base	255	$\pi \rightarrow \pi^*$
	355	$n \rightarrow \pi^*$
Cu(II) complex	250	$\pi \rightarrow \pi^*$
	371	$\pi \rightarrow n^*$
	604	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$
Co(II) complex	268	$\pi \rightarrow \pi^*$
	353	$\pi \rightarrow n^*$
	511	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$
	614	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{E}_{2g}(\text{F})$
Ni(II) complex	292	$\pi \rightarrow \pi^*$
	350	$n \rightarrow \pi^*$
	467	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$
	551	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$
	629	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$
Mn(II) complex	245	$\pi \rightarrow \pi^*$
	353	$n \rightarrow \pi^*$
	457	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$
	512	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$
	601	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$

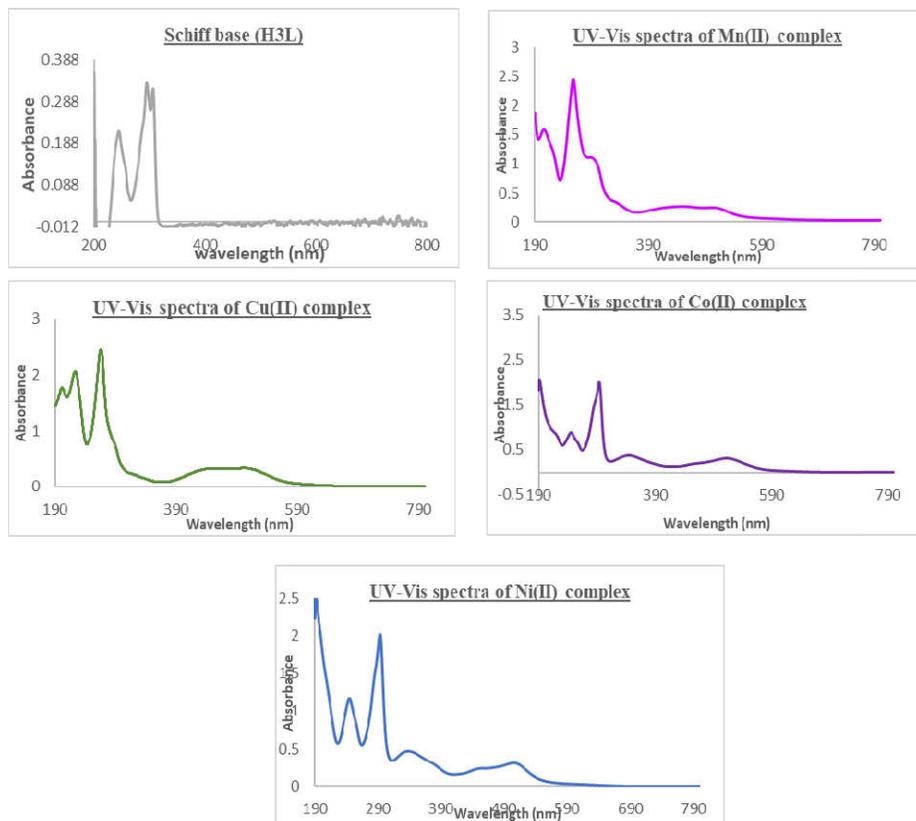
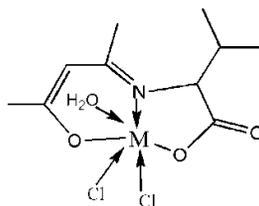


Figure 4. Electronic spectra of the ligand and its metal complexes.

The data from spectral and analytical data suggests the modelled structure for the prepared complexes (Figure 5).



M = Cu, Co, Ni, Mn

Figure 5. Proposed structure for the prepared complexes.

Antimicrobial studies of Schiff base metal complexes

The disc diffusion method was employed in screening the antibacterial potential of the Schiff base and metal complexes against clinical isolates of *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa* and *Klebsiella pneumoniae*. The results from the antibacterial studies of the prepared complexes are given in Table 4. The solvent and metal salt used showed no growth inhibition, suggesting they do not mediate in the antimicrobial activity of the synthesized complexes.

Table 4. Results of antimicrobial screening of ligand and metal complexes.

Compound	Inhibition zone diameter (mm)							
	<i>S. aureus</i>		<i>E. coli</i>		<i>P. aeruginosa</i>		<i>K. pneumoniae</i>	
	Concentrations (mg/L)							
	25	50	25	50	25	50	25	50
Ciprofloxacin	18	20	20	22	22	22	18	18
Ligand (H ₃ L)	12	12	14	14	12	14	12	14
[CuCl ₂ (H ₃ L)(H ₂ O)]	14	16	16	16	16	18	14	16
[CoCl ₂ (H ₃ L)(H ₂ O)]	12	12	14	16	12	14	14	16
[NiCl ₂ (H ₃ L)(H ₂ O)]	12	14	14	14	14	16	12	14
[MnCl ₂ (H ₃ L)(H ₂ O)]	12	14	12	14	12	12	12	14

The complexes showed moderate to good antibacterial activity against the tested isolates as compared to the Schiff ligand and ciprofloxacin. As the concentration of the compounds increases there was increase in inhibitory activity. The activity of the ligand is enhanced upon complex formation, as shown by the data. The presence of the azomethine linkage is suggested on the basis of the structures of H₃L which is significant in explaining the transamination and resamination reactions mechanism in biological system. Ligands with oxygen and nitrogen donor systems have been known to possibly inhibit enzyme production, since they require these groups for their activity to appear more prone to deactivation by the metal ions upon coordination [26, 27]. Thus, we infer that complexation increases the antimicrobial activity.

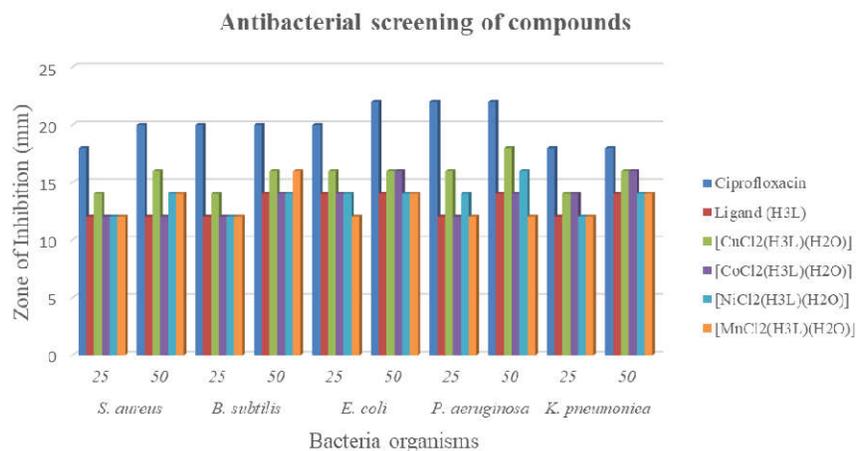


Figure 6. Chart showing the inhibition zones of Schiff base and metal complexes.

CONCLUSION

A Schiff base ligand derived from acetylacetone and 2-amino-3-methylbutanoic acid and a series of its metal(II) complexes have been prepared and characterized by microanalysis and spectroscopic techniques. The prepared Schiff bases behaves as a tridentate ligand. The data from characterization studies confirm that the metal ions are coordinated to the hydroxyl and carbonyl oxygens and azomethine nitrogen atoms. The ligand and metal complexes were screened *in vitro* against five bacterial strains. All the compounds exhibited significant antibacterial inhibitory potential. The Cu(II) complex showed the best inhibitory activity against the bacterial *P. aeruginosa* when compared with other samples. Extended work could study the antioxidant and anticancer potentials of the prepared complexes in future.

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