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Synthesis, characterization and antimicrobial activity of transition metal complexes with Schiff base derived from 1, 2-diphenylethane-1, 2-dione with o-phenylenediamine and benzophenone

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Abstract:

Novel Schiff base ligand (L1) was derived from 1,2-diphenylethane-1,2-dione with O-phenylenediamine and benzophenone and their metal complexes with the transition metals Co (II), Cu (II) and Zn (II) have been prepared by using a molar ratio of ligand: metal as 1:1. These metal complexes were characterised by the various sophisticated techniques like FTIR, UV-Visible, NMR, and Mass spectrophotometry. These characterizations have concluded that the Schiff base ligand formed acts as a tetradentate ligand and coordinates with the transition metals involved through the four azomethine nitrogen atoms. The structure and bonding nature of all the compounds showed that all complexes possessed an octahedral geometry except the Cu (II) complexes which showed a distorted octahedral geometry. Mass spectrum explains the successive degradation of the molecular species in solution. All the synthesized compounds were studied for their in vitro antibacterial, and antifungal activities, against Staphylococcus aureus, Bacillus subtilis, *Escherichia coli, Klebsiella pneumoniae and Salmonella typhi bacterial strains and against five fungal strains Aspergillus niger, Fusarium solani, Curvularia lunata, Rhizoctonia bataicola and Candida albicans by using agar-well diffusion method. It has been shown that all the synthesized compounds showed moderate to significant antibacterial activity against one or more bacterial strains.*

Key words: Synthesis, characterization, antimicrobial activity, transition metal complexes

Introduction

Coordination Chemistry gave the beautiful chance to Schiff bases and their metal complexes to emerge as a diverse field of chemistry. Now-a-days these metal complexes play an important role in the development and progress of coordination chemistry [1–3]. The literature clearly shows that the study of this diverse ligand system is linked with many of the key advances made in inorganic chemistry [4, 5]. Although the magnetic, spectroscopic and catalytic properties of these Schiff-base complexes are well documented [6, 7]. Presently, the coordination chemistry of structurally modified bio-ligands and the transition metal complexes with potential biological activity are the focus of extensive investigations in front of inorganic chemists. Schiff base ligands have received special attention because of their mixed softhard donor character, versatile coordination behaviour [8]. Structural factors such as ligand rigidity, the types of donor atoms and their disposition have shown to play significant roles in determining the binding features of these ligands toward metal cations. The chelating ability of Schiff bases gives them the place in the coordination chemistry and are used as chelating agents [9-11], in catalysis, anti-oxidative activity, medicine as antibiotics, anti-inflammatory agents and in industry for anti-corrosion properties [12-15]. A considerable number of Schiff-base complexes have potential biological interest and are used as more or less successful models of biological compounds [16]. The research field dealing with Schiff base metal complexes is very broad due in part to their potential interest for a number of interdisciplinary areas that include bioinorganic chemistry, catalysis, and magneto chemistry [17–21]. The preparation of Schiff bases containing >C=N groups with potential ligating ability has drawn a lot of attention because of their use as chelating agents, analytical reagents, metal indicators in complexometric titrations and calorimetric reagents, in addition to biochemical research [22]. The behaviour of the >C=N bond is strongly dependent on the structure of the amine moiety, which in turn controls the efficiency of the conjugation and may incorporate structural elements able to modulate the steric crowding around the coordination [23]. In view of above applications, in this present paper we report synthesis and characterization of Co (II), Cu (II) and Zn (II) complexes derived from 1,2-diphenylethane-1,2-dione, o-phenylenediamine and benzophenone. Besides the characterization of complexes by standard technique like IR, NMR, elemental analyses, magnetic susceptibility and conductance measurements, the biological activities of the synthesized complexes have been examined against some antimicrobial strains for evaluation of antibacterial and antifungal activities of the synthesized chemical compounds. The results obtained were compared with standard drugs: Fluconazole and Kanamycin.

Experimental protocols

Reagents and instruments

Laboratory reagent grade O-phenylenediamine and 1, 2-diphenylethane-1,2-dione were obtained from E Merck (Germany), benzophenone from Aldrich. The analytical grade metallic salts $CoCl_2 \cdot 6H_2O$, $CuCl_2.6H_2O$ and $ZnCl_2.4H_2O$ were obtained from E Merck (Germany). Absolute alcohol was obtained from E Merck (Germany) and methanol from Sd-Fine Chemicals (India).Hydrochloric acid was obtained from E Merck

(Germany). Double distilled water was used in all experimental work. All chemicals were used without further purification. ^1H NMR spectra were recorded with a Bruker Advance II spectrometer operating at 400 MHz using $CDCl_3$ as internal standard for ligand L1 and DMSO for its metal complexes ML. FTIR spectra were recorded in the range of 4000 - 400 cm^{-1} on Perkin-Elmer FTIR spectrometer, using KBr pellets. The elemental analysis (C, H and N) of the complexes were performed using Elementar vario EL III (Germany) model. The molar conductance at 10^{-3}M dilution was measured by Elico-Conductometer Bridge. The UV–visible spectra were recorded in methanol on Beckman DU-64 spectrophotometer with quartz cells of 1 cm path length. Antimicrobial studies have been done at Center of Research for Development, University of Kashmir.

Preparation of Schiff's Base.

Preparation of N^1-(diphenylmethylene) benzene-1, 2-diamine (L)

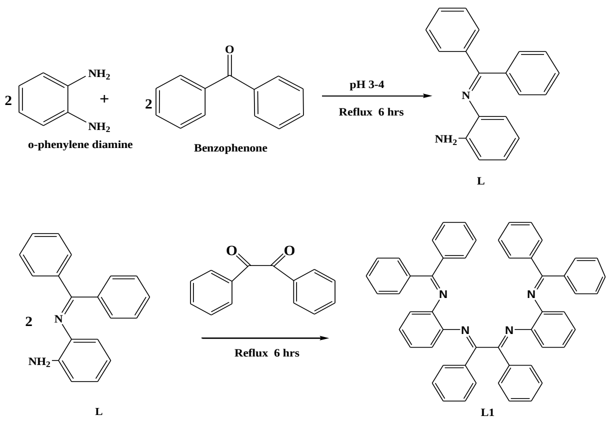
O-phenylenediamine (4.55g, 0.025mol) in ethanol solution (30ml) was added to magnetically stirred ethanolic solution (30 ml) of benzophenone (2.70g, 0.025 mol) and mixture was refluxed for 6 hours through monitoring by TLC. After completion of the reaction, the resultant mixture was cooled to room temperature, filtered and reduced nearly half of its volume by rotary evaporator. It was then allowed to stay at room temperature for 3 h which resulted in the solid product. It was filtered, washed with methanol and recrystallized with a mixture of ethanol: methanol (1:1). The crystalline product obtained was dried over fused calcium chloride in desiccators.

L: Yield: 68%. Anal. Calc. for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29 (%); Found: C, 79.5; H, 4.5; N, 10.1 (%). IR (KBr pellet, cm^{-1}): 1632 υ(–C=N);, 3204, υ(–N–H str;). ^1H NMR (d): (aromatic) 7.2–8.2 (m); (aromatic–C–NH),4.0 (s).

Preparation of (E)-N_1-(diphenylmethylene)-N_2-((E)-2-(2 (diphenylmethyleneamino) phenylimino)-1, 2-diphenylethylidene) benzene-1, 2-diamine (L1)

A hot ethanolic solution (25 mL) of N^1-(diphenylmethylene) benzene-1, 2-diamine (L) (5.25 g, 0.050 mol), and a hot ethanolic solution (25 mL) of 1, 2-diphenylethane-1,2-dione (2.62 g, 0.025 mol) were mixed slowly with constant stirring. The mixture was refluxed at 75 °C for 8–10 h in presence of few drops of concentrated HCl. On cooling, a crystalline product was formed, which was filtered, washed with cold ethanol, and dried under vacuum over P_4O_{10} (Scheme 1).

L1. Yield: 63%. Anal. Calc. for $C_{52}H_{38}N_4$: C, 86.88; H, 5.33; N, 7.79; Found: C, 88.3; H, 5.28; N, 7.60 (%). IR (KBr pellet, cm^{-1}) 1638 υ (–C=N); 1525 υ(–HC=C). ^{1}H NMR (δ, ppm): (aromatic) 7.0–8.0 (m). MS m/z (%): 719 $[M+1]^+$. λmax (cm^{-1}) in EtOH, 26,666-28,237 cm^{-1}.



Scheme 1: Synthesis of the ligand

Preparation of Ligand−Metal Complexes.

Complexation of ligand L1 was carried out separately with the metal salts $CoCl_2.6H_2O$, $CuCl_2.4H_2O$ and ZnCl2 by refluxing with continuous stirring (1:1 molar ratio) of ligand and metal salts dissolved in ethanol for 3 h. The crystalline products thus obtained were filtered, washed with aqueous methanolic solution and finally dried over fused calcium chloride in desiccators. The color of the L1−$CoCl_2$ complex was Pink and that of the L1−$CuCl_2$ complex was Green. A similar procedure was followed for complexing ligand L1 separately with $ZnCl_2$. In this case refluxing with stirring was done for 3−4 h. and the color of the complex was Pale brown.

[CoL1Cl$_2$]. Yield: 60%. Anal. Calc. for $C_{52}H_{38}N_4CoCl_2$: Co, 6.94; C, 73.59; H, 4.51; N, 6.60(%); Found: Co, 6.92; C, 73.58; H, 4.50; N, 6.59 (%). IR (KBr pellet, cm^{-1}): 1608 υ(–C=N); 1497 υ(–HC=C); 1472, 1306, 423 (M–N). MS m/z (%): 849 $[M+1]^+$. Λ_M 10^{-3} (ohm^{-1} cm^2 mol^{-1}) = 5.5. UV–Vis (DMF, 10^{-3} M) λmax (cm^{-1}), 16,146– 18,416

[CuL1Cl$_2$]. Yield: 61%. Anal. Calc. for $C_{52}H_{38}N_4CuCl_2$: Cu, 7.45; C, 73.19; H, 4.49; N, 6.57; Cl,8.31 Found: Cu, 7.44; C, 60.9; H, 4.6; N, 5.8 (%). IR (KBr pellet, cm^{-1}): 1608 υ(C=N); 1507 υ(–HC=C); 437 (M–N). MS m/z (%): 853 $[M+1]^+$. Λ_M 10^{-3} (ohm^{-1} cm^2 mol^{-1}) = 9.2. UV–Vis (DMF, 10^{-3} M) λ_{max} (cm^{-1}), 22,552 - 26,659 cm^{-1}

[ZnL1Cl$_2$]. Yield: 59%. Anal. Calc. for $C_{52}H_{38}N_4ZnCl_2$: Zn, 7.65; C, 73.19; H, 4.49; N, 5.6; Found: Zn, 7.55; C, 72.9; H, 4.45; N, 5.5 (%). IR (KBr pellet, cm^{-1}): 1612 υ(–C=N); 1522 υ(–HC=C); 441 (M–N). MS m/z (%): 852 $[M+1]^+$. Λ_M 10^{-3} (ohm^{-1} cm^2mol^{-1}) = 4.3. UV–Vis (DMF, 10^{-3} M) λmax (cm^{-1}), 28,460-31,950cm^{-1}

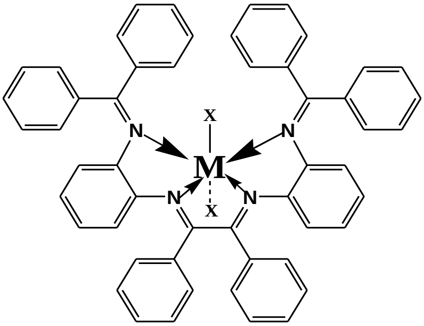


Fig. 1. Proposed structure of synthesized complexes where M = Co (II), Cu (II), and Zn (II) and Where X = Cl^-

Evaluation of antimicrobial activity

Qualitative determination of antimicrobial activity was done using the disc diffusion method. The biological activities of synthesized Schiff base and its metal complexes were studied for their antibacterial and antifungal activities in DMF solvent against bacterial and fungi species. Suspensions in sterile peptone water from 24 h cultures of microorganisms were adjusted to 0.5 McFarland. Muller–Hinton petri discs of 90 mm were inoculated using these suspensions. Paper discs (6 mm in diameter) containing 10 µL of the substance to be tested were placed in a circular pattern in each inoculated plate. DMF impregnated discs were used as negative controls. Toxicity tests of the solvent, DMF, showed that the concentration used in antibacterial activity assays did not interfere with the growth of the microorganisms.

Determination of MIC

The in vitro antimicrobial activity was performed against Gram positive bacteria: *Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Klebsiella pneumoniae* and *Salmonella typhi* bacterial strains and against five fungal strains *Aspergillus niger, Fusarium solani, Curvularia lunata, Rhizoctonia bataicola and Candida albicans*. The standard and test samples were dissolved in DMF to give a concentration of 100 µg/mL. The minimum inhibitory concentration (MIC) was determined by broth micro dilution method [24]. Dilutions of test and standard compounds were prepared in nutrient broth (bacteria) or Sabouraud dextrose broth (fungi) [25]. The samples were incubated at 37°C for 24 h (bacteria) and at 25°C for 48 h (fungi), respectively, and the results were recorded in terms of MIC (the lowest concentration of test substance which inhibited the growth of microorganisms).

Results and discussion

The spectral and analytical data show the formula of the Co (II), Cu(II) and Zn(II) complexes as [CoL1Cl$_2$] , [CuL1Cl$_2$ and [ZnL1Cl$_2$]. All the Co(II), Cu(II) and Zn(II) complexes are colored, stable in air and non-hygroscopic solids. They are sparingly soluble in all organic solvents. The elemental analyses show that the Co(II), Cu(II) and Zn(II) complexes have a 1:1 stoichiometry of the type M:L. The molar conductance values at 10^{-3} M concentration are too low to account for any dissociation of the complexes in DMF. Hence, the Co(II), Cu(II) and Zn(II) complexes may be regarded as non-electrolytes. The spectroscopic and magnetic studies conclude an octahedral geometry for the Co(II) and distorted octahedral for Cu(II) complexes and a six coordinated octahedral geometry for the Zn(II) complexes.

Infrared spectra

The coordination mode and sites of the ligand to the metal ions were investigated by comparing the infrared spectra of the free ligand with its metal complexes. The band found in the region of 1638–1631 cm^{-1} is the characteristic of the ʋ(C=N) stretching mode [26–28] indicates the formation of the Schiff base compound containing (–C=N) group in the compound L. The presence of the bands 1625 cm^{-1} in the compound L1 indicates the formation of azomethine group .The shifting of this band to lower frequency by ca. 30 cm^{-1} on complexation compared to free ligands indicates the involvement of the azomethine nitrogen in chelation with the metal ion, the coordination of the nitrogen to the metal ion would be expected to reduce the electron density of the azomethine link and thus causes a shift in the ʋ(C=N) group [29]. Coupled with this, the absence of a band around 1680–1710 cm^{-1} [30], characteristic of ʋ(–C=O) in 1,2-diphenylethane-1,2-dione, suggests that the condensation of the keto groups is complete. Conclusive evidence of the bonding is also shown by the observation that new bands appear in the spectra of all metal complexes in the low frequency regions at 420–447 and 360–389 cm^{-1} characteristic for M–N and M–Cl vibrations, respectively, which are not observed in the spectra of free ligands.

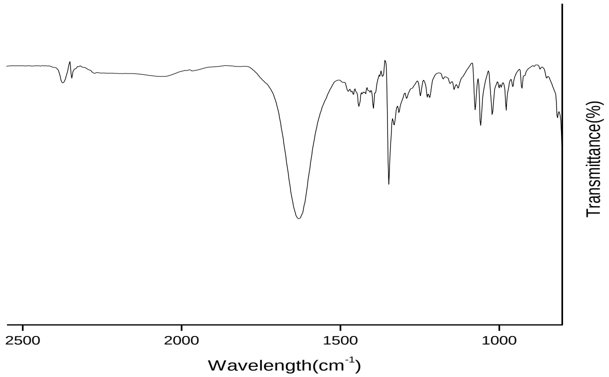


Fig. 2 FT-IR spectrum of L1

Molar conductivity

The complexes are found to be non-electrolytic nature in 10^{-3} M DMF solution, implying the coordination of chloride anion to the central metal ion. The lower conductance values (3.7–9.2 $\Omega^{-1}cm^{-2}mol^{-1}$) of the complexes support their non-electrolytic nature. The elemental analysis results of the metal complexes also agree with the calculated values, showing that the complexes have 1:1 metal/ligand ratio.

Magnetic moments and electronic spectra

The geometry of the metal complexes has been deduced from electronic spectra and magnetic data of the complexes. The electronic spectra of the complexes were recorded in solution. The free ligands exhibit two intense bands in 44,754–40,546 and 28,261– 26,139 cm^{-1} region due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [31], respectively. In all the metal complexes, the absorption bands at 28,539–34,161 cm^{-1} are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions that are observed in the spectra of the free ligand L1. These transitions are shifted to blue or red frequencies due to the coordination of the ligand with metal ions. The electronic spectra of Co(II) complexes show broad, intensity bands in the visible region, around 16,146– 17,416 cm^{-1}, which are assigned to the combination of $^2B_{1g}\rightarrow{}^2A_{1g}$ and $^2B_{1g}\rightarrow{}^2E_g$ transitions respectively. The electronic spectral data suggest a octahedral around the Co(II) ion. The observed magnetic moment of the Co(II) complexes (1.81–1.87 B.M) at room temperature indicates the non-coupled mononuclear complexes of magnetically diluted d^9 system with S = 1/2 spin-state. The electronic spectrum of the copper (II) complex shows bathochromic shifts in the absorption frequencies azomethine chromophore. The band structure observed between 26,666 - 28,237 cm^{-1} in free ligand spectrum appears to shift to 22,552 - 26,659 cm $^{-1}$. This is a consequence of the involvement azomethine functions in chelation. The electronic absorption spectra of the diamagnetic Zn(II) complexes show the bands at 28,460-31,950cm^{-1} which are assigned to intra-ligand charge transfer transitions.

NMR spectra of zinc complexes

In ^1H NMR, the aromatic region is a set of multiplets in the range of 7.0–8.2 ppm for all the ligands and their complexes. There is no appreciable change in all other signals of the complex. (Fig. 3a-3c)

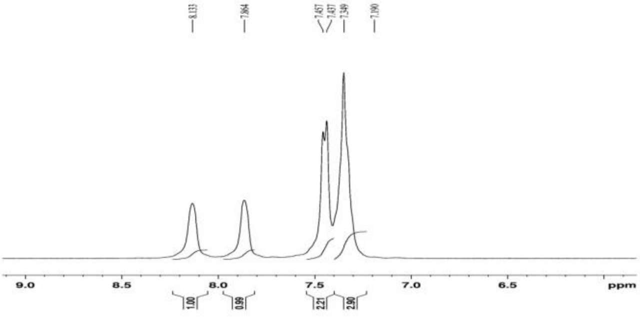


Fig. 3a NMR of [$CoL1Cl_2$].

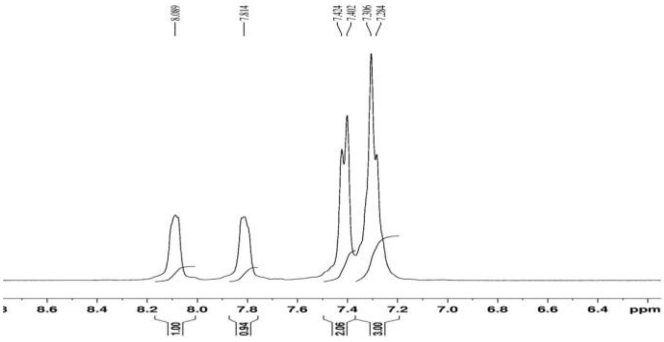


Fig. 3b NMR of [CuL1Cl$_2$].

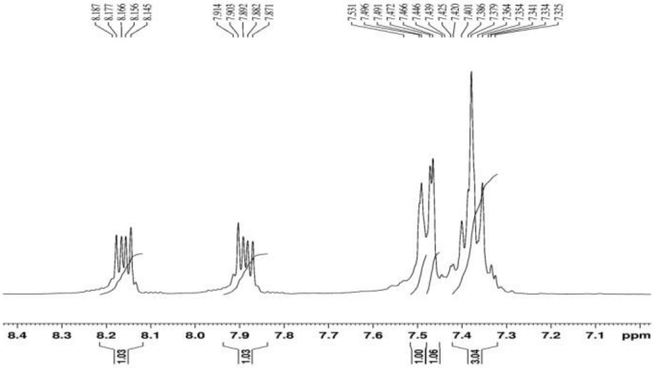


Fig.3c NMR of [ZnL1Cl$_2$].

Thermogravimetric studies

The thermal behaviors of Co^{2+} complexes have been studied, as a function of temperature. The thermal decomposition of [Co (L1)Cl$_2$] complexe took place in two step as indicated by DTG peaks around 370°C and 540°C respectively corresponding to the mass loss of organic moiety. Hence, finally the metal complexes decompose gradually with the formation of metal oxide above 540°C.

Mass spectra

The ESI-mass spectra of synthesized ligands and their complexes were recorded and the obtained molecular ion peaks confirm the proposed formulae. The mass spectrum of L1 ligand shows M+1 peak at m/z 719 (86.4%) corresponding to **$[C_{52}H_{38}N_4]^+$ ion**. The mass spectrum of $[CuL1Cl_2]$ shows peaks at m/z 753 with 63.9% abundances. The strongest peaks (base beak) at m/z 719 represent the stable species $C_{52}H_{38}N_4$. The m/z of all the fragments of ligands and their complexes confirm the stoichiometry of the complexes as $[MLCl_2]$. The observed peaks are in good agreement with their formulae as expressed from micro analytical data. Thus, the mass spectral data reinforce the conclusion drawn from the analytical and conductance values.

Antimicrobial activity

The minimal inhibitory concentrations of tested schiff base metal complexes against certain bacteria and fungi are shown in Tables 1 and 2. The ligand (L1) and their metal complexes were prepared and tested for their in vitro antimicrobial activity against the five strains of bacteria (gram negative and gram positive), and five strains of fungi. Few metal complexes showed high in vitro antimicrobial activity. All the Co(II) and Cu(II) metal complexes showed significant antibacterial and antifungal activities compared to free ligands, But the activity was lesser than the standard drugs. It is clearly depicted in Figs.5a and 5b. Such increased activity of the complexes can be explained on the basis of Overtone's concept [33] and the Tweedy's Chelation theory [34].The nature of metal ion also plays a decisive role in determining antimicrobial properties. In the present study, the order of the antimicrobial activity of the synthesized compounds (based on the metal atom present) follows: Co > Cu > Zn > L1. The mode of action of the compounds may involve the formation of a hydrogen bond through the azomethine group with the active centres of cell constituents, resulting in interferences with the normal cell process [35, 36].

Table 1 Minimum inhibitory concentration of the synthesized compounds against growth of bacteria (µg/mL).

Compound	Minimum inhibitory concentration (MIC) (x 10^4 µM)				
	Staphylococcus aureus	*Bacillus subtilis*	*Escherichia coli*	*Klebsiella pneumoniae*	*Salmonella typhi*
L1	9.1	9.5	10	9.7	9.2
[CoL1Cl2]	5.5	5.1	4.9	5.5	5.3
[CuL1Cl2]	6.1	6.5	6.1	6.8	6.5
[ZnL1Cl2]	7.2	7.8	7	7.3	7.5
Kanamycina	1.5	2.5	1.2	2	2.2

[a] Kanamycin is used as the standard.

Table 2 Minimum inhibitory concentration of the synthesized compounds against the growth of fungi (µg/mL).

Compound	Minimum inhibitory concentration (MIC) (x10^4 µM)				
	Aspergillus niger	*Fusarium solani*	*Curvularia lunata*	*Rhizoctonia bataicola*	*Candida albicans*
L1	8.2	8.5	8	8	8.2
[CoL1Cl2]	6.5	6.2	6	6.8	6.1
[CuL1Cl2]	5.9	5.8	6.2	6.3	6.5
[ZnL1Cl2]	8.5	8.9	8	8.3	8.5
Fluconazole[a]	1.3	1.6	1.1	1.4	1.7

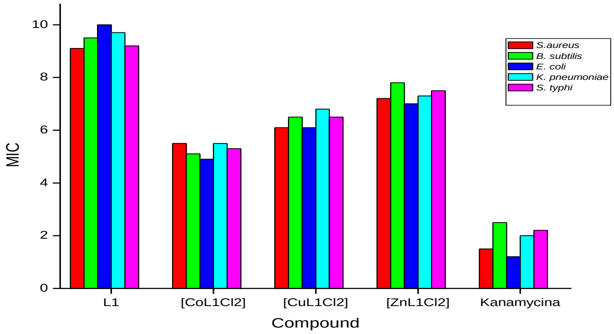


Fig. 5a. Minimum inhibitory concentration of the synthesized compounds against the growth of bacteria (µg/mL).

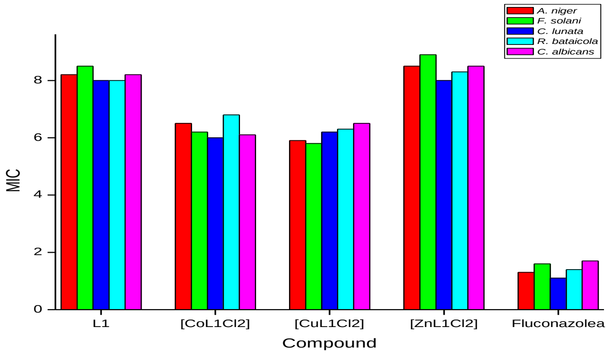


Fig.5b. Minimum inhibitory concentration of the synthesized compounds against growth of fungi (µg/mL).

Conclusion

In this paper, few novel Schiff bases and their Co(II) ,Cu(II) and Zn(II) complexes have been synthesized and characterized by sophisticated techniques and analytical data. The IR, electronic transition and g tensor data lead to the conclusion that the central metal ion assumes a octahedral geometry. We have evaluated in vitro the antibacterial and antifungal of newly synthesized Schiff base ligands and their metal complexes. The cobalt (II) complex of L1 has higher potency against Gram-positive bacteria than Gram-negative bacteria.

Acknowledgments

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