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SYNTHESIS, SPECTRAL AND BIOLOGICAL ACTIVITY OF MIXED LIGAND SCHIFF BASE COMPLEXES DERIVED FROM SALICYLALDEHYDE

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Abstract

New mixed ligand complexes of the transition metal ion Cu(II), Co(II), and Mn(II) with salicylaldehyde and various aniline derivatives have been synthesized. The characterization of these newly synthesized mixed ligand complexes were done by elemental analysis, conductivity measurements, infrared spectra, cyclic voltammetry and UV-Visible spectra. Their electrical conductance values indicate that all the complexes are non-electrolyte. The antibacterial and antifungal activities of the complexes have been studied against some pathogenic bacteria and fungi.

Keywords: Salicylaldehyde, 4-chloroaniline, 4-bromoaniline, 4-nitroaniline and biological studies.

Introduction

The branch of inorganic chemistry that deals with the study of coordination compounds is called coordination chemistry. In recent years a considerable amount of work has been done on the coordination chemistry of transition metal complexes with Schiff bases ligands to model the physical and chemical behavior of biological process [1, 2]. In coordination chemistry, Schiff bases have a significant role as ligands still a century after their discovery [3]. Schiff base ligands are considered “privileged ligands” because they are easily prepared by the condensation between aldehydes and amines. Schiff base ligands are able to coordinate many different metals and to stabilize them in various oxidation states. The Schiff base complexes have been used in catalytic reactions [4] and as models

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for biological systems [5]. During past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors [6]. This may be attributed to their stability, biological activity [7] and potential applications in many fields such as oxidation catalysis [8], electrochemistry [9]. The complexes make these compounds effective and stereospecific catalysts for oxidation, reduction and hydrolysis and they show biological activity, and other transformation of organic and inorganic chemistry. It is well known that some drugs have higher activity when administrated as metal complexes than as free ligands [10]. The complexes containing O, N donor atoms are very important owing to their significant antibacterial and anticancer activity [11]. Recently, we have synthesized and characterized some Schiff base metal complexes and their *in vitro* antibacterial activities have been investigated [12]. Many metal complexes have powerful antimicrobial activities and are already in common day-to-day use in medicinal field [13]. In the present paper, we report the results on the synthesis, characterization and antimicrobial activities of mixed ligand complexes derived from salicylaldehyde and various aniline derivatives.

Experimental

All the reagents were Merck products and were used as supplied. The IR spectra of the complexes were recorded on a Shimadzu spectrophotometer in range of 400-4000 cm^{-1} using KBr pellets. The UV-Vis spectra were recorded on a Shimadzu spectrophotometer using DMF as solvent. Electrochemical studies were carried out using a tetrabutylammonium perchlorate (TBAP) used as supporting electrolyte. The molar conductance of the complexes was measured using a Systronic conductivity bridge.

Synthesis of Unsymmetrical mixed ligands

The Schiff bases are prepared by refluxing a mixture of equimolar amounts of aldehydes with corresponding amines in ethanolic medium [14]. The Schiff base ligand (L_1) was prepared by mixing an ethanolic solution of 4-chloro aniline with that of ethanolic solution of salicylaldehyde (1:1 molar ratio). The resulting solution was stirred continuously for one hour. The reaction mixture was cooled at room temperature and the bright yellow crystalline solid was obtained. Then the solid was filtered off and dried [15]. The preparation of ligand L_2 and L_3 follows the

same procedure which discussed above. L₂ ligand is obtained from bromoaniline and salicylaldehyde where as L₃ from nitroaniline and salicylaldehyde.

Synthesis of Unsymmetrical mixed ligand complexes

The unsymmetrical Schiff base mixed ligand complexes were prepared according to the literature procedure [16]. To a hot ethanolic solution of copper(II) acetate pentahydrate, hot ethanolic solution of ligand (L₁) is added drop wise followed by the addition of ligand (L₂). The reaction mixture was kept on a water bath for refluxation. It was refluxed for 3hrs. The precipitated complexes were filtered off and dried. Similar procedure was adopted for the synthesis of mixed ligand complexes ML₁L₃ and ML₂L₃. The elemental analysis indicates that all the metal complexes have 1:1:1 stoichiometry with respect to L₁:L₂: M where M = Cu(II), Co(II), and Mn(II).

Result and Discussion

The synthesized ligand and its complexes were characterized by physicochemical techniques. Satisfactory results of elemental analysis and spectral studies revealed that the synthesized mixed ligand complexes were of good purity. Various attempts to obtain the single crystals have so far been unsuccessful. The complexes were insoluble in water, partially soluble in ethanol but soluble in DMF and DMSO.

Conductivity measurements

The nature and stability of the complexes are determined by using Molar conductivity studies. Conductivity values were used to identify the charge type of the mixed ligand complexes. The stoichiometry of the metal complexes can be confirmed by conductometric titration [17]. The conductances were measured for synthesized mixed ligand complexes using 10⁻³ M DMF solvent. The values are in the range of 10-50 ohm⁻¹mol⁻¹cm² these values are too low to account for any dissociation of the mixed ligand complexes in DMF. Hence these complexes can be regarded as non-electrolyte [18].

IR Spectra

IR Spectra provide valuable information regarding the nature of the functional groups, structure of the mixed ligand and the mode of coordination of it to the metal ion in the complexes. IR spectra for the Schiff base ligands such L₁, L₂, L₃ shows a broad band at around 3410-3422 cm⁻¹ due to the phenolic hydroxyl group respectively in free

ligands, which disappeared in spectra of their complexes indicating probably the coordination through phenolic oxygen moiety[19]. The Schiff base ligands L₁, L₂ and L₃ register $\nu(\text{C}=\text{O})$ at about 1271, 1280 and 1271 cm^{-1} which is shifted to higher region at around 1300-1390 cm^{-1} respectively indicating the coordination through phenolic oxygen atom[20]. In the Schiff base $\nu(\text{C}=\text{N})$ stretching band appears at about 1610-1614 cm^{-1} . This band shifts to lower energy in case of complexes around the region 1568-1606 cm^{-1} which indicates coordination through the azomethine nitrogen [21]. Conclusive evidence of the bonding is also shown by the observation that new bands in the spectra of the metal complexes appears at 522-590 cm^{-1} and 372-501 cm^{-1} these are assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ stretching vibrations and are not observed in the spectra of the ligand [22].

Electronic Spectra

The electronic spectra of the ligand and their complexes have been measured in DMF solution between 200-800 nm at room temperature. In the spectra of the Schiff base ligand, the absorption band observed at 280 nm is assigned to a benzene $\pi-\pi^*$ transition and the band at 390 nm is assigned due to $n-\pi^*$ transition associated with the azomethine chromophore ($-\text{C}=\text{N}$) [23]. The new bands observed near 390-450 nm can be assigned to L \rightarrow M charge transfer band. The newly synthesized Schiff base mixed ligand gives colored complexes with metal ions that have a series of overlapping absorption bands in the UV part of the spectrum as well as in the visible part. In such cases the d-d transition may be completely overwhelmed and essentially impossible to observe [24]. Mostly d-d transition occurs in the region of 420-550 nm.

Cyclic Voltammetry

The Redox behavior of these complexes has been investigated by cyclic voltammeter in DMF using 0.1 M Tetrabutylammoniumperchlorate (TBAP) as supporting electrolyte. The electrochemical data obtained at a glassy carbon electrode in DMF solution are recorded. The copper complexes are redox active and show a cyclic voltammetric response in the potential range 0.7- 1.7 V [25] assigned to the Cu (II)/ Cu (I) couple. The non-equivalent current intensity of cathodic and anodic peaks ($i_c/i_a = 0.6$ V) indicates a quasi reversible behavior [26]. It has been shown that the formal redox potential of Cu (II)/ Cu (I) couple is dependent on factors such as coordination number, hards/ soft nature of the ligands and bulkiness of the ligands [27]. The cobalt complexes exhibit one

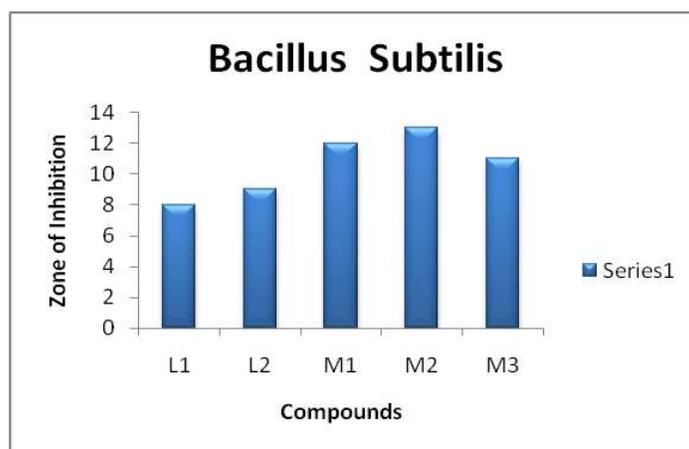
electron quasi reversible transfer process with a peaks at $E_{pa} = 0.6$ V, $E_{pc} = 1.6$ V and $\Delta E_p = 1$ V. This gives evidence for quasi reversible Co(II)/Co(I) couple. The one electron cyclic response for Manganese complexes were observed at $E_{pc} = 1.8$ V and $E_{pa} = 0.5$ V. Manganese(III) is expected to undergo reduction to Mn(II)/Mn(I) and oxidation to Mn(IV). The forward is due to the reduction and reverse peak is due to oxidation. The redox system is quasi-reversible in nature. The CV data also shows the redox nature of the other Schiff base mixed ligand complexes.

Antibacterial activity

The antibacterial activity of mixed ligand complexes were tested against some bacteria and were determined by paper disc diffusion method. In testing the anti-bacterial activity of these compounds we used more than one test organism to increase the chance of detecting the antibiotic potential and other anti-microbial agents was determined by the assay plates, which were incubated at 37°C for 1 day (Bacteria). All of these tested compounds showed a remarkable biological activity against different types of Gram positive and Gram negative bacteria [28]. The diameters of inhibition zone of various complexes are recorded in the Table.1. From the table, it is concluded that all the metal complexes exhibit moderate and higher antimicrobial activity than the free ligand. The activity increases with increase of concentration of test solution containing new complexes. On comparing the biological activity of Schiff bases and its metal complexes with standard, the following results are obtained: In various combinations of mixed ligand complexes such as ML_1L_2 , ML_2L_3 , and ML_1L_3 in which the complexes formed from the combination of ML_2L_3 shows a higher antibacterial activity towards all the gram +ve and gram -ve bacteria when compared to other combinations of ML_1L_2 , ML_1L_3 . On the other hand, the complexes formed from the combination of ML_1L_3 will show a higher activity towards bacteria next to that of ML_2L_3 combination. The complexes from ML_1L_2 combinations will show a slightly less antibacterial activity towards bacteria when compared to ML_2L_3 , ML_1L_2 combinations. The antibacterial activity of mixed ligand Schiff base complexes and its ligand are shown in figures 1.1-1.8.

Table.1. Antibacterial activities of ligand and complexes

S.NO	Compounds	S. Aureus (mm)	B. Subtilis (mm)	E.coli (mm)
L ₁	Salca	7	8	9
L ₂	Salba	8	9	11
L ₃	Salna	9	10	12
M ₁	[CuL ₁ L ₂]	10	2	13
M ₂	[CoL ₁ L ₂]	14	12	10
M ₃	[MnL ₁ L ₂]	16	11	9
M ₄	[CuL ₂ L ₃]	12	14	15
M ₅	[CoL ₂ L ₃]	11	13	15
M ₆	[MnL ₂ L ₃]	13	15	16
M ₇	[CuL ₁ L ₃]	17	14	16
M ₈	[CoL ₁ L ₃]	15	19	18
M ₉	[MnL ₁ L ₃]	17	19	20

**Fig.1.1: (1) Activity of Schiff base ligand and Schiff base mixed complexes against Bacillus Subtilis**

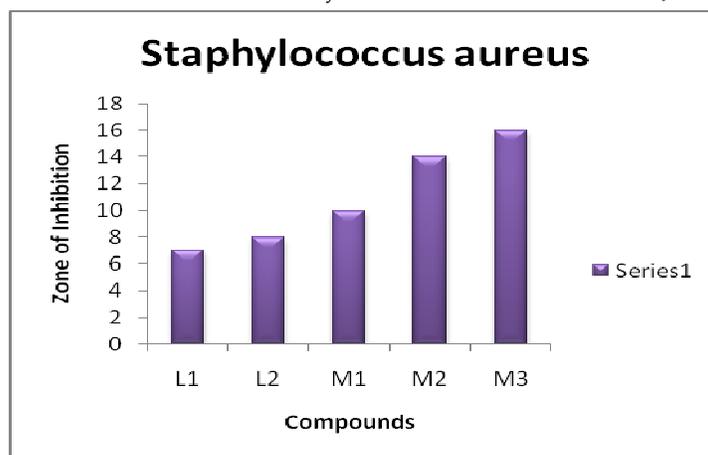


Fig.1.2: (2) Activity of Schiff base ligand and Schiff base mixed complexes against Staphylococcus aureus

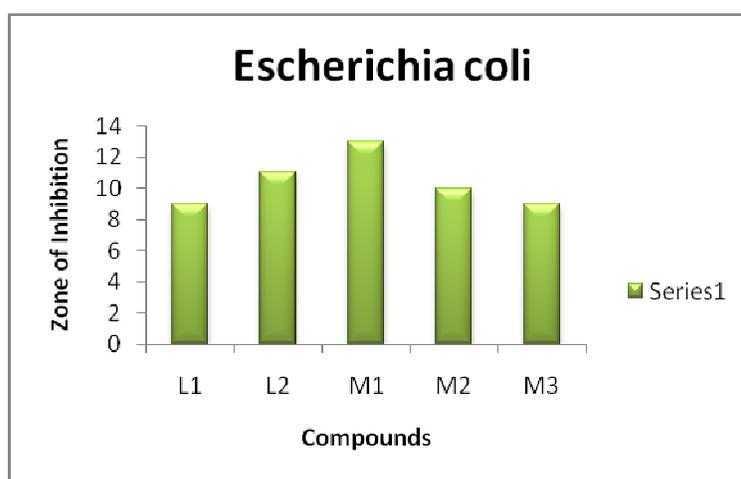


Fig.1.3: (3) Activity of Schiff base ligand and Schiff base mixed complexes against Escherichia Coli

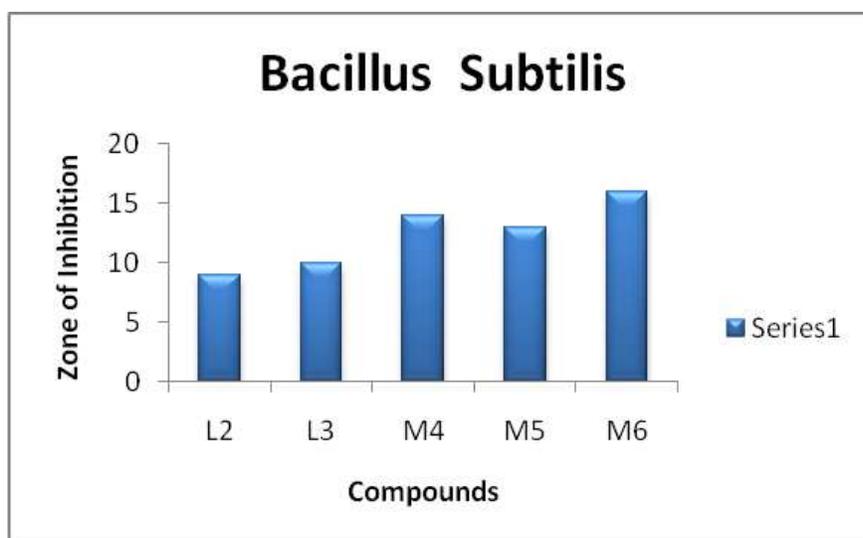


Fig.1.3: (1a) Activity of Schiff base ligand and Schiff base mixed complexes against Bacillus Subtilis

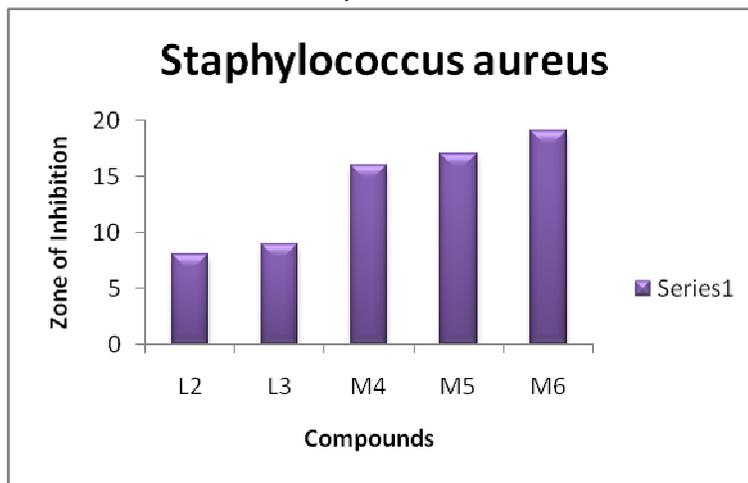


Fig.1.4: (2a) Activity of Schiff base ligand and Schiff base mixed complexes against Staphylococcus aureus

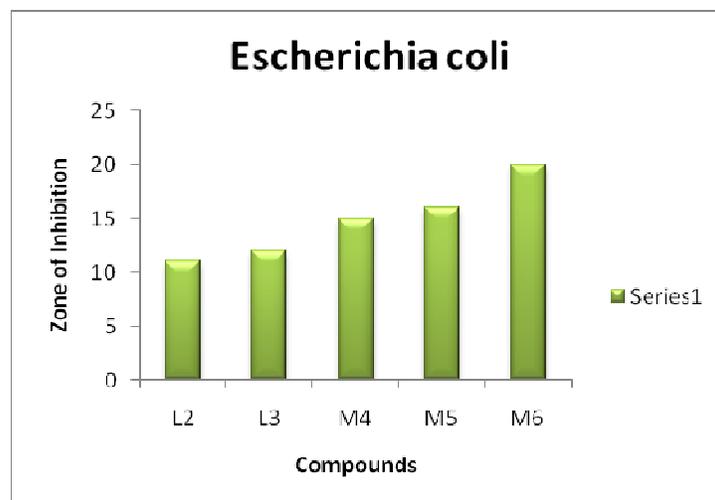


Fig.1.5: (3a) Activity of Schiff base ligand and Schiff base mixed complexes against Escherichia Coli

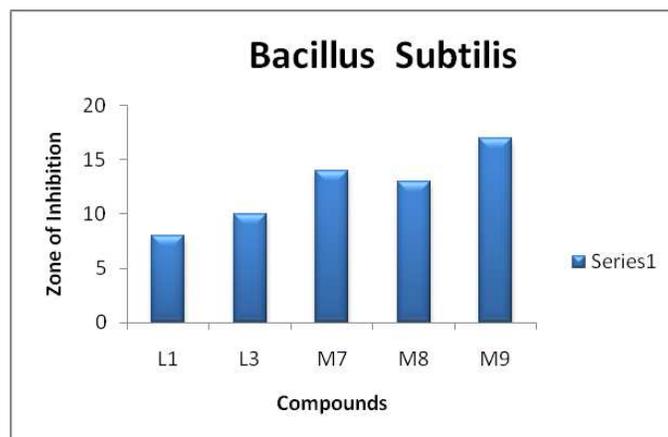


Fig.1.6: (1b) Activity of Schiff base ligand and Schiff base mixed complexes against Bacillus Subtilis

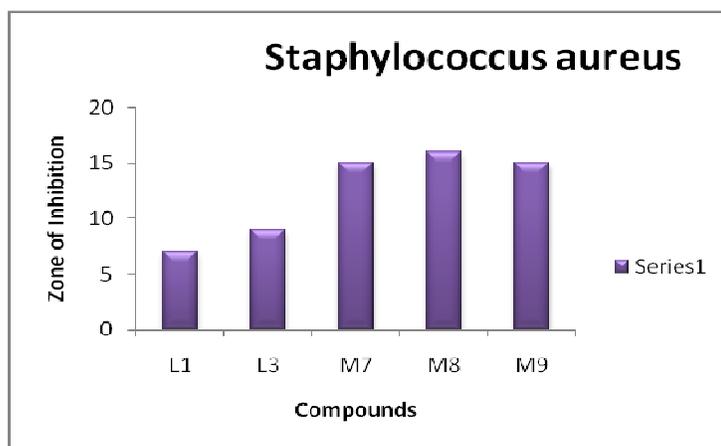


Fig.1.7: (2b) Activity of Schiff base ligand and Schiff base mixed complexes against Staphylococcus aureus

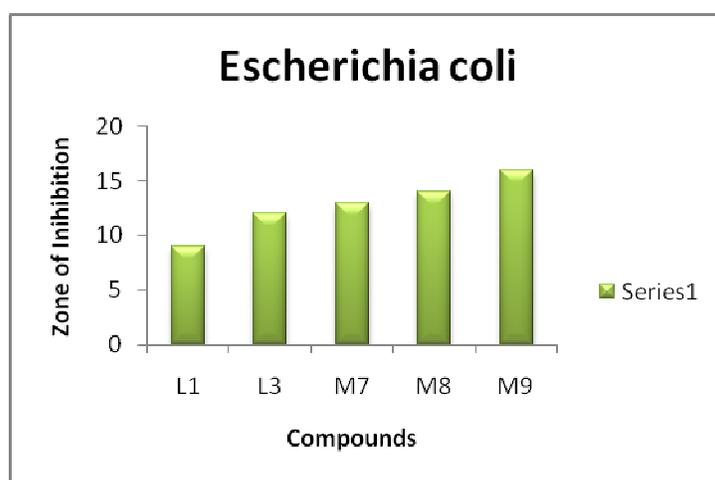


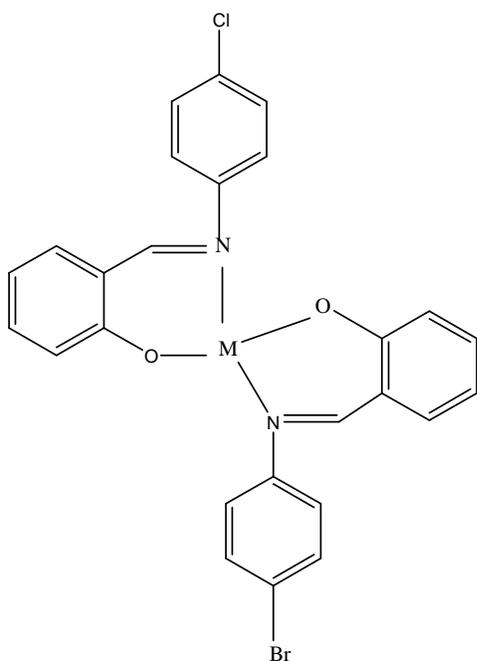
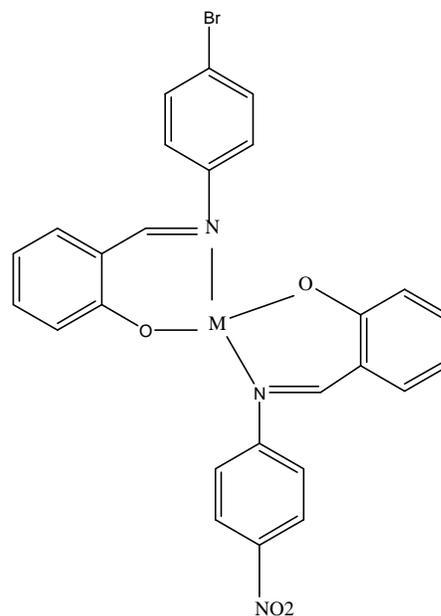
Fig.1.8: (3b) Activity of Schiff base ligand and Schiff base mixed complexes against Escherichia Coli

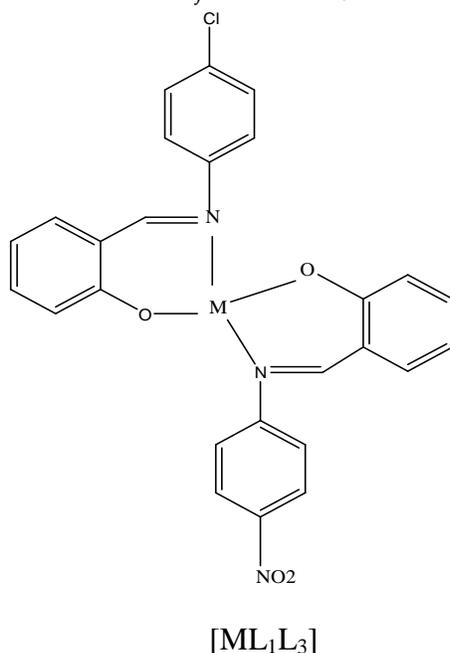
From the above result, the antimicrobial data reveal that the complexes are more bioactive than the free ligands; the enhanced activity of the metal complexes may be ascribed to the increased lipophilic nature of the complexes arising due to chelation. On chelation [29], the polarity of the metal ion is reduced to a greater extent due to overlap of ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. It increases the delocalization of π - electrons around the whole chelate ring and inhibits the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of micro organisms. The complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of organisms.

Conclusion

In this paper, we have synthesized and structurally characterized a mixed ligand metal (II) Schiff base complexes. The spectral results suggest the presence of square planar geometry around the metal. The molar conductivity measurements reveal that the complexes are non- electrolytic in nature. The electronic absorption spectral data of the isolated complexes confirmed the electronic transition and the chemical structures. Electrochemical studies shows the redox potential for Cu(II), Co(II) and Mn(II) ions, thus confirming the presence of these metal ions in the mononuclear complexes. Further, these complexes were screened for antimicrobial activity and results suggest that mixed ligand complexes have higher antibacterial activity than the free ligands. The complex which has nitro group in it will posses higher activity than the complex containing chloro and bromo group in it, because nitro group is electron withdrawing group.

Proposed Structures

[ML₁L₂][ML₂L₃]



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