International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.11 No.02, pp 12-17, 2018

Synthesis, Characterization and Biological Activities of Copperchloride (II) Complex Derived From 4 – Amino Antipyrine, Furfural and DL Cysteine

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Abstract : Schiff base which than form chelate complex with metal ions. These types of Schiff bases are important for their significant biological activity. The 4 – Amino antipyrine, Furfural and dl cysteineare a group of highly reactive compounds that form potentially active. They also show interesting structural properties on complexation with metal ions. It was characterized by using ^{1}H'NMR, FT-IR spectroscopy and the antibacterial activity of the compound was evaluated against Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli) bacteria.

Keywords : Characterization ,Biologicalactivites, Complexation, Antimicrobial activity.

Introduction

Bioinorganic chemistry is a field that urbanized the role of metals in biology. It includes the study of both natural phenomena such as the concert of metalloproteinase as well synthetically introduced metals, including those that are non-essential, in remedy and toxicology. Many biological processes counting respiration, large amount of metabolism, photosynthesis, nitrogen fixation, muscle contraction, nerve transmission, signal transduction and protection against toxic nature, mutagenic agents etc.The inorganic elements, particularly metal ions play an important role in biology, which has lead to the development of huge quantity of metal complexes with varied therapeutic activity. Based on the virtual concentrations in the biological systems, the metals are divided into: (1) Macronutrients (relatively large amounts) - Na, K, Mg, Ca, S, P, Cl& Fe 2) Micronutrients (trace elements) - Mn, Co, Ni, Cu, Zn, V, Cr, Mo, Se, F, I, Al, Pb, Sn, Si etc., which are present in low concentration and are used for biocatalysts [2]. Schiff base ligands have been important in bio inorganic chemistry catalogue for over 150 years. Schiff bases are usually regarded as easily prepared excellent ligands. Their instantaneous and continuing attractiveness undeniably stem from the ease of their synthesis, perplexing adaptability and wide ranging complexing ability once formed [3]. Hugo German chemist developed a new class of organic compounds in 1864 [4]. It is prepared by condensing amine, with carbonyl compound generally by refluxing in alcohol. Schiff bases are capable of forming coordinate bonds with many of metal ions through both azomethine group and phenolic group or via its azomethine or phenolic groups. The bonding ability of the ligands depends on the nature of atoms that act as coordination site, their electronegativity and steric factors. Presence ofa lone pair of electrons in an sp^{2}hybridisedorbital of nitrogen

International Journal of ChemTech Research, 2018,11(02): 12-17.

DOI= http://dx.doi.org/10.20902/IJCTR.2018.110202

atom of the azomethine group is of extensive chemical importance and impart excellent chelating ability especially when used in combination with one or more donor atoms close to the azomethine group. Imine or azomethine groups are present in various natural, naturally derived and non- natural compounds .The availability of different types of amines and carbonyl compounds enabled the synthesis of Schiff bases with diverse structural features. Schiff base ligands readily co-ordinate with a range of metal ions yielding stable complexes, which exhibit interesting physical, chemical, biological and catalytic properties. The Schiff bases are widely studied because of increasing recognition of their role in biological systems. Their complexes are used in chemical processes as catalyst and as biological models for understanding the structure of biomolecules. They serve as a model to the activity of metallo proteins. Schiff bases are useful ligands because of their synthetic accessibility, diversity and structural varieties. The co-ordination chemistry of Schiff bases derives from salicylaldehyde has been the subject of many studies and a number of them are used as oxygen carriers to mimic complicated biological systems . They are also efficient reagents in trace analysis of some metal cations. Schiff base ligands have an affinity for transition metals such as Cu, Mn, Co and Fe. Some of these complexes have been studied in great deal for their various structures, steric effects and their co-ordination chemistry. The thermodynamic, theoretical and catalytic aspects of this class of compounds have been extensively investigated. Complexes containing Schiff base ligands and its derivatives play important roles in oxidation chemistry. The properties of Schiff base metal complexes stimulated much interest for their contributions to single molecule-based magnetism, material science, catalysis of many reactions like carbonylation, hydroformylation, oxidation, reduction and epoxidation their industrial applications and complexing ability towards some toxic metals. The high affinity for the chelation of the Schiff bases towards the transition metal ions are utilized in preparing their solid complexes. Schiff base complexes containing nitrogen and oxygen as donor atoms play an important role in biological systems and represent models for metalloproteins and metalloenzymes that catalyse the reduction of nitrogen and oxygen.Tetradentateschiff base complexes of copper afford two main differences relative to macrocyclic ligands, easier access to mixed donor environments and an open equatorial ring, the whole size of which can in principle accommodate more easily the expected changes in metal size upon oxidation or reduction. The co-ordination chemistry of copper metal complexes with salen-type ligands had achieved a special status,because of their very interesting oxygen binding reactivity, redox chemistry, unusual magnetic and structural properties, as well as their usage as catalysts for the oxidation and epoxidation reactions[6-8].

In view of these finding, this work has devoted with the aim to synthesize some transition metals complexes with symmetrical Schiff base ligands, (3,5-dichloro-2-hydroxy acetophenone, 4-chloro-o-phenylenediamine)and to examine their physical properties involving spectral behaviours, the electrical conductance values and to determine the efficiency of the synthesized complexes against pathogenic bacteria. Schiff bases derived from an amino and carbonyl compound are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively1. In azomethine derivatives, the C=N linkage is essential for biological activity, several azomethine has been reported to possess remarkable antibacterial, antifungal, anticancer and antimalarial activities 2-3. The complexes of copper with Schiff bases have wide applications in food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical, anti-inflammable activity, antiradical activities and biological activities4. Schiff-base complexes are considered to be among the most important stereo chemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety5. Copper (II) complexes show distorted octahedral and tetrahedral symmetries due to d9 configuration (Jahn- Teller effect). The distortion is usually seen as axial elongation consistent with the liability and geometric flexibility of the complex. Therefore, typical Cu (II) complexes have square planar or square pyramidal geometries with weakly associated ligands in the axial position (s), but some copper (II) complexes possess trigonalbipyramidal geometry [9-12].. The fundamental role of copper and the recognition of its complexes as important bioactive compounds *in vitro* and *in vivo* aroused an ever-increasing interest in these agents as potential drugs for therapeutic intervention in various diseases.

In the present work, the **4** – Amino antipyrine, Furfural and dl cysteineare a group of highly reactive compounds that form potentially active Schiff base which than form chelate complex with metal ions. These types of Schiff bases are important for their significant biological activity. They also show interesting structural properties on complexation with metal ions. Still no one compound using this molecule for this complexation. The complexation of this compound tested against antibacterial activity of *E. coli*, a gram negative bacterium and *S. aureus*, a gram positive bacterium.

Materials and Methods:

4 – Amino antipyrine, Furfural and dl cysteine, copper(II) chloride, ethanol were purchased from sigma Aldrich.The solvents were analar grade.

Characterization

FT-IR spectra were recorded on a FT-IR 1650 Shimadzu Spectrometer in the range of 4000-400 cm^{-1}using KBr disks. Electronic spectra of the ligand and its complexes were recorded at room temperature on a Schimadzu UV–3101PC UV-VIS NIR scanning spectrophotometer. ^{1}H-NMR spectra is carried out in $CDCl_3$ at room temperature on a 500 MHz Bruker advanced DPX spectrophotometers with chemical shifts reported relative to TMS.

Synthesis of Schiff Base Ligand and Mononuclear Complex:

Ligand $L^1$is synthesized by refluxing an ethanolic solution of 1mmol of 4 – Amino antipyrine (0.2032g), Furfural (0.0960g) and dl cysteine (0.1210g). The solution was kept for slow evaporation and Orange coloured precipitate was collected. The precipitate was washed with ethanol and then dried in air.Mononuclear Cu(II) complex is synthesized by refluxing an ethanolic solution of 2mmol of ligand-1 with ethanolic solution of 1mmol of copper (II) chloride. The reflux ate is kept overnight. The resulting light brown coloured precipitate was collected and dried in air.

Antimicrobial Activity

The agar disc diffusion method was followed to determine the *in vitro* antibacterial activity of the mononuclear complex was tested against two bacterial strains *E. coli* and *S. aureu,s bacillus*. The inocula of the selected bacterial species were prepared from the fresh overnight broth cultures (Tripton soy broth with 0.6% yeast 20 extract - Torlak, Serbia) that were incubated at 37 ºC with constant stirring and were then used for the diffusion studies. The diffusion technique was carried out by forming 4 mm thick layers pouring agar into Petri dishes and adding dense inoculua of the test organisms of two bacterial strains in order to obtain better growth. Petri plates were kept for 10 min in the laminar air flow and after that, discs (6 mm) were prepared from Whatman no.3 filter paper, immersed into different volumes of (5, 10 (µg/mL)) metal complexes, placed at equal distances and then incubated at 37˚C for overnight in a bacteriological incubator. After incubation the width of zone of inhibition (mm) around the disc which was produced by the ligand and metal complexes against the two bacterial strains were measured calculated the mean of inhibition zones.

Result and Discussion:

Synthesis and Characterisation of Mononuclear Schiff Base Complex:

Ligand $L^1$is synthesized by refluxing an ethanolic solution of 1mmol of 4 – Amino antipyrine (0.2032g), Furfural (0.0960g) and dl cysteine (0.1210g). The solution was kept for slow evaporation and Orange coloured precipitate was collected. The precipitate was washed with ethanol and then dried in air. Mononuclear Cu(II) complex is synthesized by refluxing an ethanolic solution of 2mmol of ligand-1 with ethanolic solution of 1mmol of copper (II) chloride. The refluxate is kept overnight. The resulting light brown coloured precipitate was collected and dried in air.

The FT-IR analysis of Ligand (HL), mono nuclear (Cu-L) was carried out and the corresponding spectra are shown in the Fig –1.

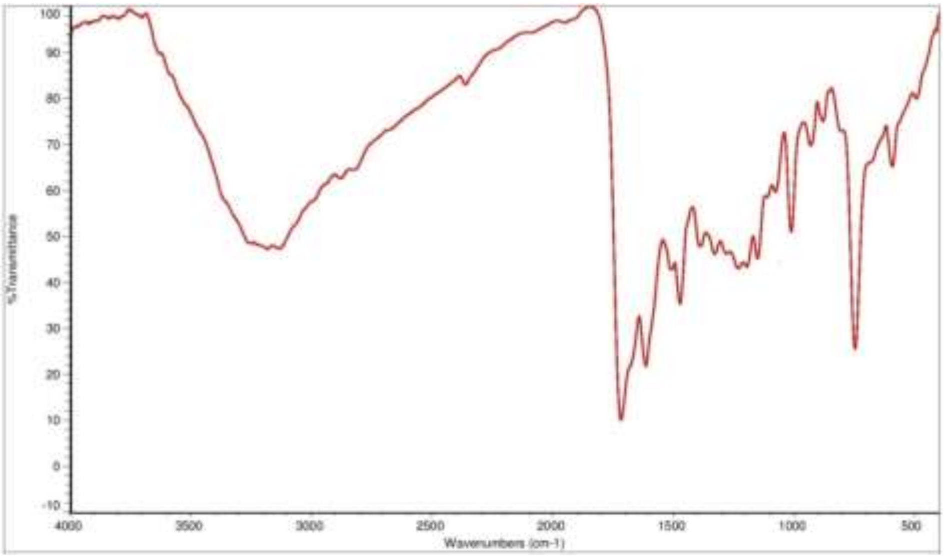

Fig. 1: FTIR Spectrum of Shiffbase compound

In IR spectrum of the ligand, the –O-H stretching vibration band was observed at 3252 cm $^{-1}$, as well as the C-N band at 1070 cm^{-1}, the C=O sharp band at 1715 cm^{-1}, and the C-O band at 1200 cm^{-1}. The spectrum of mono nuclear complex (Cu-L) shows the C=N sharp band, the C-N and the C-O band at 1000 cm^{-1}, 1040 cm^{-1}, and 1690 cm^{-1} and NH shows band at 1580 cm^{-1} respectively . The 1H NMR spectrum of the free Schiff-base shows singlet peaks at δ = 7.543 ppm assigned to - CH=N (imine) protons. In addition, the chemical shift for the SH group was observed at 1.615 ppm Themultiplet at δ = 6.950 – 7.543 ppm is assigned to protons of aromatic ring. Hence confirms the structure of the synthesized Schiff base ligand. The above NMR data are given by confirm the structure of newly prepared Schiff base ligand. In H^1 NMR Spectrum shows RN=CH peak at δ = 9.851 ppm. The additional peak acid as carboxylic acid at δ = 10.925 ppm (Fig.2).

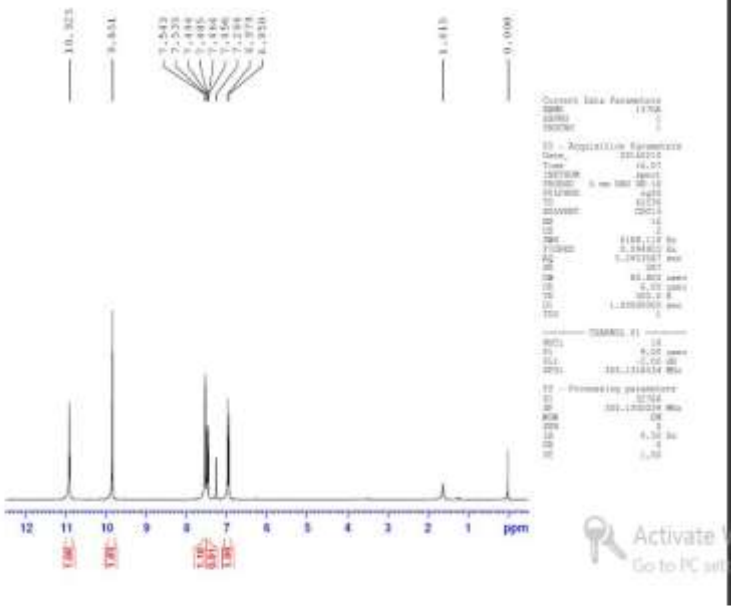

Fig. 1: ^{1}HNMR Spectrum of Shiffbase compound

Antibacterial Activity:

In particular the complex showed excellent activity against *E. coli* which is due to the differences in the cell wall structure. The cell wall of the gram-positive bacteria is made of a thick layer of peptidoglycan, consisting of linear polysaccharide chains leading to difficult penetration compared to the gram-negative bacteria where the cell wall possesses thinner layer of peptidoglycan. Therefore, changes in the membrane structure of bacteria follows in the increased anti-bacterial activity for the coatings against *E. coli*. From the results it is well evident that the mononuclear complex not only retards the bacterial adhesion, but also effectively kills the adhered bacteria suggesting effective and long lasting antibacterial activity against both *E. coli* and *S. aureus*(Fig.3)

Fig.3. The zone of inhibition of the samples against (a) S.aureus bacteria (b) E.coli bacteria

Conclusion:

The **4 – Amino antipyrine, Furfural and dl cysteine** are a group of highly reactive compounds that form potentially active Schiff base which than form chelate complex with metal ions. These types of Schiff bases are important for their significant biological activity. They also show interesting structural properties on complexation with metal ions. Still no one compound using this molecule for this complexation. The complexation of this compound is very effective against antibacterial activity of *E. coli*, a gram negative bacterium and *S. aureus*, a gram positive bacterium.

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