SYNTHESIS, SPECTRAL CHARACTERIZATION AND BIOCIDAL EVALUATION OF SCHIFF BASE METAL(II) COMPLEXES FROM AMINO ACIDS

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ABSTRACT

A novel ligand (E)-2-(2-hydroxy-3-methoxybenzylideneamino)-3-hydroxybutanoic acid (HMA-HBA) and its metal nitrate complexes of Cu(II), Ni(II) and Co(II) were synthesized and characterized by infrared, electronic spectra, elemental analysis, magnetic susceptibility and molar conductivity. The analytical and electronic spectral data suggest a 6-coordinate octahedral structure and 1:1 stoichiometry for all the prepared metal (II) complexes. Molar conductance studies revealed the electrolytic behavior of the newly prepared complexes. The free Schiff base ligand and their metal complexes were also screened for the selected bacterial and fungal species by disc diffusion technique.

Keywords: Schiff base, Metal complexes, Disc diffusion, Antibacterial, Octahedral Geometry.

INTRODUCTION

Coordination Chemistry has become more and more fascinating after the recent advances in bioinorganic chemistry. The Schiff bases from aromatic aldehydes are known to exhibit potent antibacterial, anti-inflammatory, anticonvulsant activities. After realizing the importance of the coordination phenomenon in the biological process, several metal-containing ligands and their role in the biological systems have been studied. In general metal, chelates are found to be more antimicrobial than the chelating agent. Threonine, being the essential amino acid is not synthesized by the human body and has to be supplied through diet. Threonine has innumerable biological importance which supports the central nervous system, cardiovascular, immune system functioning, mainly eliminates the accumulation of fat in the liver thereby smooth functioning of the digestive and intestinal tracts. A survey of the literature reveals that several substituted aldehydes from Schiff bases with amino acids have been prepared and studied. However, no work has been done with the present Cu(II), Ni(II) and Co(II) complexes of Schiff base derived from 2-hydroxy-3-methoxy benzaldehyde and L-Threonine. Hence the present study consists of the synthesis of Schiff base (E)-2-(2-hydroxy-3-methoxybenzylideneamino)-3-hydroxybutanoic acid (HMA-HBA) formed by the condensation of 2-hydroxy-3-methoxy benzaldehyde and L-Threonine, its M(II) complexes and their characterization by different analytical techniques. Their antibacterial activity have also been compared.

EXPERIMENTAL

Materials

Chemicals 2-hydroxy-3-methoxy benzaldehyde and L-Threonine (Sigma Aldrich) and reagents were of analytical grade (E. Merck). Nitrate salts of Cu(II), Ni(II) and Co (II) ions were taken. Sodium hydroxide, ethanol, DMSO, DMF, diethyl ether solvents were used.

Instrumentation

The FT-IR bands in the range of 400-4000 cm⁻¹ were recorded using Thermo Nicolet. UV spectra were obtained using Varian, Cary 5000 spectrophotometer in the range of 200-800 nm. The electrochemical analysis was determined using the Elementar analyzer Vario EL III. All these recordings have been done at STIC, CUSAT Cochin. The magnetic moment values of the complexes were determined using Guoy balance. Molar conductivity measurements were recorded by conductivity bridge (Elico CM-82T) using
DMSO solvent. The microbial species used for biological analysis were brought from (MTCC) Gene Bank Chandigarh.

**Synthesis of Ligand (HMA-HBA)**
The Schiff base HMA-HBA was prepared by using equimolar amounts of 2-hydroxy-3-methoxy benzaldehyde (0.304 g, 0.1 m mol) in ethanol and an aqueous solution of L-Threonine (0.230 g, 0.1 m mol) with continuous stirring. The mixture was refluxed and heated for 6 hours at 65 °C. A yellow-colored solid mass that separates was isolated by filtration, purified with diethyl ether, dried and can be stored using desiccator. The purity of the ligand was tested using TLC. The ligand is soluble in DMF, ethanol, methanol and DMSO. (Scheme-1).

**Synthesis of Metal (II) Complexes**
An aqueous nitrate salt solution 20 ml of Cu(II), Ni(II) and Co(II) metal ions were separately added to a hot ethanolic solution of Ligand (0.1 mmol) with continuous stirring. The reaction mixture was heated for 3 hours at 65 °C. 0.1 mmol of NaOH 4-5 drops are added to adjust the pH and heated for 1 hour. The solid metal complexes were precipitated. The obtained products were filtered, washed with diethyl ether, dried, and stored in a desiccator.

**RESULTS AND DISCUSSION**

**IR Spectra**
The synthesized complexes exhibit a sharp band at 1634 - 1641 cm$^{-1}$ which is stretching vibration for azomethine group (-CH=N-) shifted to lower wavenumbers from ligand at 1647 cm$^{-1}$ after complexation confirms the bonding of azomethine-N to the M(II) ions$^3$. A broad peak at 3430 cm$^{-1}$ of the ligand may be due to hydrogen-bonded ν(-OH) stretching vibration$^4$. The ν(C-O) at 1240-1256 cm$^{-1}$ for the complexes undergoing a downshift when compared to ligand at (1273 cm$^{-1}$) confirms the coordination of phenolic oxygen in C-O-M with metal ion$^5$. This is further confirmed by two weak bands ν(M-O) and (M-N) found near 575-648 cm$^{-1}$ and 411-465 cm$^{-1}$$^6$$^7$$^8$. After complexation, the ν$_{as}$(COO$^-$) and ν$_{s}$(COO$^-$) display reasonable shifts to higher wavenumbers 1581-1601 cm$^{-1}$ and 1351-1353 cm$^{-1}$ compared to those of ligand 1542cm$^{-1}$ and 1325 cm$^{-1}$ whose ∆ν = >200 cm$^{-1}$ suggest monodenticity of the carboxylate group$^9$. The steep broadband observed at 3360-3400 cm$^{-1}$ in the complexes is due to coordinated water molecules$^{10}$ and the weak band near 835-843 cm$^{-1}$ corresponds to the rocking vibration mode of water. An additional band in the Ni(II) complex at 1432 cm$^{-1}$ and 1352 cm$^{-1}$ implies unidentate coordination of the nitrate group. Ionic nitrate in complexes$^{11}$ gives a strong band at 1384 cm$^{-1}$(Fig.-1).

**UV- Visible Spectra**
The ligand HMA-HBA displays electronic waves at 272 and 357 nm due to π-π$^*$ transitions of phenyl ring and n-π$^*$ transition of azomethine group. The Cu(II) complex displays band at 281nm, 345nm and 608 nm giving d-d transition $^2$E$_g$$\rightarrow$$^2$T$_2g$, preferring octahedral geometry$^{12}$. The Ni(II) complex has a band at 271nm, 355nm and 606 nm, the assigned d-d transition is $^3$A$_{2g}$(F)$\rightarrow$ $^3$T$_{1g}$(F) taking octahedral geometry$^{13}$. The band present in the electronic spectrum of Co(II) complex at 271nm, 365nm, 408 nm reveals transition $^4$T$_{1g}$(F)$\rightarrow$$^4$T$_{1g}$(P)$^{14,15}$ owing to octahedral geometry(Fig.-2).
Fig. 1: IR Bands (cm⁻¹) of Complexes

Fig. 2: UV Spectra of Complexes
Magnetic Susceptibility
The magnetic moment was determined using Guoy balance and the values are 1.71, 3.1 and 4.2 B.M. for Cu(II), Ni(II) and Co(II) complexes respectively. These values confirm octahedral geometry.\(^{16-18}\)

Molar Conductance Measurements
The observed values of molar conductance 122, 58, 84 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) at concentration 10\(^{-3}\) M with DMSO solvent of Cu\(^{II}\), Ni\(^{II}\) and Co\(^{II}\) complexes respectively. These values are high due to the displacement of NO\(_3^-\) ions by DMSO and reveals that all the three Metal (II) complexes are electrolytes.

Biological Activity
The Schiff base Ligand and metal (II) complexes are screened against some selected bacteria namely *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Staphylococcus aureus* and Fungal species *Aspergillus niger*, *Aspergillus flavus*, *Saccharomyces cerevisiae* respectively at a concentration of 0.1g/1ml in DMSO and their results are displayed in Table-1. Antibiotic Gentamycin is used as a standard for bacteria and Flucanazole is used as a standard for Fungal screening. Ni(II) complex is found to be most active against *P. aeruginosa*, *B. subilis*, *A. niger*, *A. flavus* while compared to the Ligand and other metal complexes. The Ligand and Cu(II) complex show zero activity against *A. flavus*, but in this case Co(II) and Ni(II) exhibits equal moderate activity. The increased activity can be explained by Chelation Theory.\(^{19,20}\) Increased activity increases liphophilicity of the complexes\(^{21}\) and sometimes results in the breakdown of the permeability barrier of the cell.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Inhibition Zone ( diameter in mm)</th>
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<tbody>
<tr>
<td><strong>Bacterial species</strong></td>
<td><strong>P. aeruginosa</strong></td>
</tr>
<tr>
<td>HMA- HBA</td>
<td>11</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>--</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>13</td>
</tr>
<tr>
<td>Co(II)</td>
<td>8</td>
</tr>
<tr>
<td>Gentamycin</td>
<td>30</td>
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<tr>
<td>Flucanazole</td>
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CONCLUSION
Thus the Ligand HMA-HBA is linked to the metal(II) ion in a tridentate ONO fashion and the linkage sites are phenolic-O, imino-N and carboxylate-O atoms. All the metal complexes prefer octahedral geometry and the Ligand to metal composition is in 1:1 ratio. The molar conductance data indicates the electrolytic nature of the metal complexes. The antibacterial activity of the tested complexes follows the trend Control >Ni(II) > HMA-HBA > Co(II) > Cu(II).

ACKNOWLEDGEMENT
Authors gratefully acknowledge CUSAT- Cochin, Inbiotics- Nagercoil for providing the analysis results and also thankful to the Management, Principal and HOD of Chemistry for providing Research Lab facilities.
REFERENCES


[RJC-5531/2020]