Synthesis and binding mode of N, N'-bis(4-methoxybenzylidene)ethan-1,2-diamine with Co(II), Ni(II) and Hg(II)

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Abstract
The Schiff base ligand, N, N’-bis(4-methoxybenzylidene)ethan-1,2-diamine and its metal complexes of Co(II), Ni(II) and Hg(II) have been successfully synthesized and characterized physicochemically and infrared spectroscopically. The ligand was obtained in excellent yield of 90.38 % whereas the complexes showed low yield (29.54 – 32.95 %). The ligand and complexes were solid, air and moisture stable with high melting points (180 -320 °C) which further proved their thermostability. The low values of their molar conductance indicate non-electrolytic nature. The infrared spectroscopic data shows appearance of the azomethine peak at 1623.89 cm⁻¹ in the spectrum of the Schiff base which shifted to lower wave number by 33-55 cm⁻¹ in the spectra of the complexes indicating inferentiality of bidenticity of the Schiff base upon interaction with the metal ions having the two azomethine nitrogen atoms as the coordination sites. The empirical formula determination revealed the formation of the complexes in 1:2:2 metal-ligand-chloride ratio which could be represented as [ML₂Cl₂].nH₂O (where M=Co²⁺, Ni²⁺ or Hg²⁺, n= 2, 6, 4 for the complexes respectively). An octahedral structure has been proposed for the complexes.

Keywords: thermostability, octahedral, bidenticity, infrared spectra, non-electrolyte

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1. Introduction
The condensation of a carbonyl moiety RR'C=O (R, R' = alkyl or aryl group for ketones, R' = H for aldehydes) with a primary amine R"NH₂ (R" = alkyl or aryl group) forms an iminic group RR'C=NR" bond which is referred to as azomethine or secondary aldimine when R"= H [1]. The term Schiff base is now commonly applied to these compounds since the first report by Hugo Schiff more than one and half century ago, and the lone pair of the iminic nitrogen makes Schiff bases popular as ligands for metal centres [2]. Schiff bases that contain aryl substituents having effective conjugation are substantially more stable and more readily synthesized, while those which contain alkyl substituents are relatively unstable [3]. Two symmetrical Schiff bases, N, N-bis(2-hydroxybenzylidene)ethylene diamine and N,N-bis (2,4-dimethoxybenzylidene)ethylene diamine, have been prepared by the condensation of ethylenediamine with benzaldehyde derivatives; 2-hydroxybenzaldehyde and 2,4-dimethoxybenzaldehyde, as well as Fe(III) complexes with mentioned Schiff bases. The Schiff base ligands and their iron complexes were characterized by elemental analysis, ultraviolet visible spectroscopy (UV-Vis.), proton nuclear magnetic resonance (¹H NMR) and infrared (IR) Spectroscopy [4]. In recent years, concerted efforts have been made in the synthesis of Schiff bases derived from ethylene diamine and its metal complexes [5-9]. Similarly, lot of work has been reported on Schiff base metal complexes containing 4-methoxybenzaldehyde [10-12]. For example; Co(II), Ni(II) and Zn(II) complexes of Schiff bases derived from condensation of 4-anisaldehyde with anisidine, (AAN) or 2,4-dinitrophenylhydrazine, (ADN) have been prepared in 1:2 molar ratio (metal:ligand). The compounds have been characterized using elemental analysis, electronic spectra, infrared with molar conductance measurements [13].

Search into the available literature reveals paucity of information on the synthesis of Schiff base derived from 4-methoxybenzaldehyde and ethylene diamine and its metal(II) complexes, hence this research work on the synthesis and complexation behaviour of the ligand towards metal(II) ions.

2. Materials and methods
2.1. Physical measurements
All measurements were carried out using Electronic balance Metra, Model = XY2002C, No = 15055 15. Water of crystallization was determined using thermostat oven: DHG-93030A. The electrical conductivity was recorded using LIDA instrument model DDS-307 conductivity meter. The IR spectrum for each compound was obtained using the Fourier transform infrared (FT-IR) spectrophotometer BUCK Scientific model 530 in the range 600-4000 cm⁻¹ and the results were recorded at the Department of Chemistry, Yobe State University, Damaturu, Nigeria. Melting point was recorded on melting point apparatus at the Faculty of Pharmacy, University of Maiduguri. The metal content was gravimetrically determined subsequent to acid decomposition of the complexes [14].
2.2. Synthesis of N, N’-bis(4-methoxybenzylidene)ethan-1,2-diamine

The ligand was prepared by modification of the procedure reported in the literature [15]. This was achieved by addition of 2.44 ml (0.03 mol) of ethylenediamine to 60 ml ethanolic solution of 4-methoxybenzaldehyde (7.29 ml, 0.06 mol) and then few drops of NaOH. The resultant mixture was magnetically stirred under reflux at 70 °C for 3 hours. The reaction is depicted in figure 1.

![Diagram of synthesis of N, N’-bis(4-methoxybenzylidene)ethan-1,2-diamine](image)

**Figure 1.** Schematic Depiction of synthesis of N, N’-bis(4-methoxybenzylidene)ethan-1,2-diamine

2.3. Generic Procedure for Synthesis of Metal(II) Complexes

To 1.788 g (0.006 mol) of the synthesized ligand dissolved in 50 ml of ethanol, an equivalent of 0.003 mol of the metal salts (NiCl₂·6H₂O, 0.7131 g; CoCl₂·6H₂O, 0.7139 g; HgCl₂, 0.543 g) was added and heated on water bath for 2 hours at 70 °C. The resultant solution was allowed to stand for 48 hours; thence the products formed were filtered, washed several times and dried in vacuum over calcium chloride [16]. The formation of the complexes is depicted in equation 1:

\[ \text{MCl}_2\cdot n\text{H}_2\text{O} + 2\text{L} \rightarrow \text{ML}_2\cdot y\text{H}_2\text{O} + 2\text{HCl} \] (1)

Where M = Co(II), Ni(II) or Hg(II); n = 0 or 6 and y = 2, 4 or 6
2.4. Estimation of Water of Crystallization

The water of hydration was determined by separately placing 0.2 g of each of the complexes on a watch glass of known weight, which was placed in an oven at 110 °C until constant weight was obtained. The net weight loss was recorded after cooling as weight of water of hydration. The percentage of water of hydration was calculated using equation 2 [17]. The results are presented in Table 3.

\[
\% \text{ of water of hydration} = \frac{\text{weight loss}}{\text{weight of sample taken}} \times 100
\]  

(2)

2.5. Molar Conductance Measurements

The 0.001 mol of each of the complex was dissolved in 10 ml of ethanol and the corresponding conductance value was recorded using LIDA instrument model DDS-307 conductivity meter at 33±1 °C. From the observed conductance recorded, the specific conductance and the molar conductance of the metal complexes were calculated using equations 3 and 4 respectively [18]. The results obtained are shown in Table 1:

Specific Conductance = Observed conductance × Cell constant × Correction factor

Molar conductance = \[ \frac{1000 \, K}{\text{Molar concentration}} \]

where \( k \) = specific conductance

2.6. Fourier transform infrared spectroscopy

In the absence of a powerful technique such as X-ray crystallography, IR spectroscopy is the most suitable technique to obtain information in order to elucidate the nature of the binding of the ligand to the metal ions [24].

3. Results and discussion

3.1. Physicochemical Data

The molecular formulae, weights, colours, percentage yields, melting points and molar conductance values of the synthesized compounds are shown in Table 1. The milk crystalline Schiff base, N, N’-bis (4-methoxybenzylidene)ethan-1,2-diamine was afforded in excellent yield of 90.38 % via the condensation reaction between 4-methoxybenzaldehyde and ethylenediamine in 2:1 ratio in ethanolic medium. The Schiff base has a melting point of 180 °C. This sharp value is indicative of the high purity of the synthesized ligand [19,20]. Moreover, the interaction of the Schiff base with Co(II), Ni(II) and Hg(II) chlorides gave orange, silver and canary coloured metal(II) complexes respectively, with percentage yield range 29.54 – 32.95 %. The colour of the complexes is due to the electronic excitation from \( t_{2g} \) to higher \( eg \) by absorption of visible light [21,28]. The decomposition temperatures
of the complexes were found to be in the range 300-320 °C, their values indicate that the metal complexes are thermostable [22] and are in good agreement with values of similar metal complexes [4,13,16].

**Table 1.** Analytical Data of the Schiff Base and its Metal(II) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight (g/mol)</th>
<th>Colour</th>
<th>Yield (%)</th>
<th>M.P/D. T (°C)</th>
<th>Molar conductance (Ω·cm²·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand</td>
<td>296.40</td>
<td>Milk</td>
<td>90.38</td>
<td>180</td>
<td>-</td>
</tr>
<tr>
<td>Co(L)₂Cl₂.6H₂O</td>
<td>830.73</td>
<td>Orange</td>
<td>31.81</td>
<td>300</td>
<td>5.19</td>
</tr>
<tr>
<td>[Ni(L)₂]Cl₂.2H₂O</td>
<td>758.49</td>
<td>Silver</td>
<td>29.54</td>
<td>310</td>
<td>21.58</td>
</tr>
<tr>
<td>[Hg(L)₂]Cl₂.4H₂O</td>
<td>936.39</td>
<td>Canary</td>
<td>32.95</td>
<td>320</td>
<td>*</td>
</tr>
</tbody>
</table>


3.2. Solubility Profile of the Synthesized Compounds

The solubility of the synthesized Schiff base and metal(II) complexes was tested in common polar and non-polar solvents. The results are shown in **Table 2.** The Schiff base was found soluble in all the solvents used including water. Similarly, Ni(II) and Co(II) complexes showed solubility or slight solubility in ethanol, methanol and tetrachloromethane. This signifies that there is an interaction between the metal chelates and these solvents.

**Table 2.** Results of the Solubility Test

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D. H₂O</td>
</tr>
<tr>
<td></td>
<td>C  H  C  H</td>
</tr>
<tr>
<td>L</td>
<td>SS  S  S  S</td>
</tr>
<tr>
<td>[Co(L)₂]Cl₂.6H₂O</td>
<td>SS  SS  S  S</td>
</tr>
<tr>
<td>[Ni(L)₂]Cl₂.2H₂O</td>
<td>SS  S  SS  S</td>
</tr>
<tr>
<td>[Hg(L)₂]Cl₂.4H₂O</td>
<td>IS  IS  IS  IS</td>
</tr>
</tbody>
</table>

Keys: L = C₁₈H₂₀N₂O₂, IS=Insoluble, S=Soluble, SS=slightly soluble, C=Cold, H=Hot

Therefore, it is assumed that the chemical structure of the metal complexes compose partly of hydrophobic and hydrophilic portions [29]. Their solubility in both polar and non-polar solvent is due to the fact that the complexes have low polarities and similar attractive forces therefore dissolved in the mentioned solvents which have both polar and non-polar ends [23]. In contrast, the Hg(II) complex was
insoluble in all the solvents used including DMF. The insolubility and very high decomposition temperature could be due to the strong coordinate bond as a result of chelate formation [30]. The metal content of the complexes has been gravimetrically determined. The observed values are in good harmony with calculated values consistent with 1:2 metal-ligand ratio. The water of crystallization has been determined and expressed as percentage. The observed percentages for the Ni(II), Co(II) and Hg(II) complexes were 4 %, 13 % and 8 % respectively. These experimental percentages are in good agreement with calculated values. It could be inferred that metal(II) complexes under investigation are hydrated with 2, 6 and 4 water molecules respectively (Table 3).

Table 3. Results of metal content and water of Crystallization in the Metal(II) Complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Molar mass (g/mol)</th>
<th>% Found (Calculated)</th>
<th>Equivalent Number of H2O Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(L)2]Cl2.6H2O</td>
<td>830.73</td>
<td>6.86(7.09)</td>
<td>7.94(8.54)</td>
</tr>
<tr>
<td>[Ni(L)2]Cl2.2H2O</td>
<td>758.49</td>
<td>7.23(7.74)</td>
<td>9.73(9.41)</td>
</tr>
<tr>
<td>[Hg(L)2]Cl2.4H2O</td>
<td>936.39</td>
<td>21.89(21.42)</td>
<td>7.16(7.58)</td>
</tr>
</tbody>
</table>

3.3. Infrared Spectral Data of the Synthesized Compounds

The selected bands of the Schiff base ligand and its metal(II) complexes are presented in Table 4, and spectra as figures 2-5. In the spectrum of the Schiff base ligand, the strong band at 1623.89 cm\(^{-1}\) is due to the (C=\(\text{N}\)) stretching vibration [25]. No peak related to unreacted primary amine or carboxyl groups were observed in the spectrum of the Schiff base. On complex formation, the IR band due to azomethane group got shifted to lower wave number by 33- 55 cm\(^{-1}\), indicating coordination through the nitrogen atom of the azomethine group to the metal ions [16,24]. Furthermore, the band appearing at 800.84 - 814.63 cm\(^{-1}\) in the spectra of the complexes supported the coordination through the azomethine nitrogen atom [15].

Table 4. Selected IR Spectra (cm\(^{-1}\)) of the Schiff Base and its Metal(II) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(\text{OH})\text{H}_2\text{O})</th>
<th>(\nu(\text{C=(\text{N})}))</th>
<th>(\nu(\text{M-N}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand</td>
<td>-</td>
<td>1623.89s</td>
<td>-</td>
</tr>
<tr>
<td>Co(L)2Cl2.6H2O</td>
<td>3212.92b</td>
<td>1571.70s</td>
<td>802.53s</td>
</tr>
<tr>
<td>[Ni(L)2]Cl2.2H2O</td>
<td>3288.04b</td>
<td>1568.53 s, sh</td>
<td>814.63w</td>
</tr>
<tr>
<td>[Hg(L)2]Cl2.4H2O</td>
<td>3188.74b</td>
<td>1590.91m</td>
<td>800.84w</td>
</tr>
</tbody>
</table>

\(\text{L} = \text{C}_{18}\text{H}_{30}\text{N}_2\text{O}_2\), S=strong, sh= sharp, b= broad, m=medium, w= weak
Figure 2. IR Spectrum of Schiff Base Ligand

Figure 3. IR Spectrum of Co(II) Complex
The spectra of the complexes showed broad bands in the region 3188.74 - 3288.04 cm⁻¹ arising due to water lattice in the complexes [26,27]. The coordinated chloride ions could not be detected since they occur out of scale of the instrument used [19]. Silver nitrate test only gave white precipitate when acid-
digested solution of the complexes where used indicated that the chloride ions are inside the coordination sphere as supported by molar conductance values [12]. From the results and information from the literature [13, 24] the structure of the complexes is proposed as shown in figure 6.

![Proposed geometric structure of the Metal(II) Complexes](image)

Where M = Ni(II), Hg(II) or Co(II) and n = 2, 4 or 6 respectively

**Figure 6: Proposed geometric structure of the Metal(II) Complexes**

**Conclusion**

The Schiff base ligand, N, N’-bis(4-methoxybenzylidene)ethan-1,2-diamine and its transition metal complexes of Ni(II), Co(II) and Hg(II) have been successfully synthesized and characterized physicochemically as well as spectroscopically. The ligand and complexes characterized as solid, air and moisture stable with high melting point which further proof their thermostability. The complexes were non-electrolytic in nature. From the data collected from IR, the Schiff base ligand displayed bidenticity upon interaction with the metal ions with the two azomethine nitrogen atoms being the donor sites. The empirical formulae of the synthesized complexes were [ML₂Cl₂].nH₂O. The complexes possess six coordinate octahedral geometry.

**Conflict of Interest**

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

**References**


