Synthesis and physicochemical study on Ni(II) complex of Schiff base derived from 4-methoxybenzaldehyde and o-aminobenzoic acid

Abubakar Abdullahi AHMED*, Hassan Usman ALI, Abdullahi Idi MOHAMMED

Department of Pure and Applied Chemistry, Faculty of Science, University of Maiduguri, P.M.B. 1069, Maiduguri, Borno State, Nigeria

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ABSTRACT
Nickel(II) complex of a Schiff base derived from 4-methoxybenzaldehyde and 2-aminobenzoic acid has been synthesized. The Schiff base ligand and the metal complex were appropriately characterized by melting point, solubility, conductance measurement, water content and infrared spectroscopy. Both the Schiff base ligand and complex were solid, air, and moisture stable. The ligand melted at 210°C whereas the complex showed high thermally stability with decomposition temperature > 340°C. The recorded molar conductance of 18.15 Ω cm² mol⁻¹ revealed non-electrolytic nature of the complex. The FT-IR spectra revealed the coordination of the Schiff base via azomethine nitrogen and deprotonated hydroxyl oxygen of the carboxyl group, hence rendering the ligand monobasic bidentate with ON type of coordination sites. Moreover, the FT-IR and thermo-analytical data confirmed the presence of water lattice in the complex. Accordingly, a square planar structure is probable for the complex.

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Keywords: 4-methoxybenzaldehyde, Square planar, Thermostability, Bidentate, ON donor, o-aminobenzoic acid.

1. Introduction:
Schiff bases are the products of a chemical reaction of a primary amine with an aldehyde or a ketone under a given set of conditions. Structurally, oxygen of the carbonyl functional (C=O) in an aldehyde and/or a ketone is replaced with nitrogen leading to the formation of imine or azomethine (C=N) functionality with liberation of a water molecule [1]. Transition metal complexes with Schiff bases have expanded enormously and embraced wide and diversified subject comprising vast area of organometallic compounds and various aspects of bio-coordination chemistry [2]. The transition metal complexes of Schiff base ligands have attracted the attention of inorganic chemists for over two decades because of vast application in pharmaceutical and industrial fields. Due to their simple synthesis and versatility, Schiff base complexes continue to be important and a popular area of research as such complexes persistently play a very significant role in understanding the various aspects of coordination chemistry of transition metals. Schiff base and its complexes of both transition and inner transition metals ions are extensively used in the study of structure and bonding in coordination complexes [3].

Over the past few years, many Schiff base metal complexes of o-aminobenzoic acid have been reported. Gayathri et al. [4] synthesized and characterized oxovanadium VO(IV) and Cu(II) complexes with a tridentate Schiff base derived from benzoin and 2-aminobenzoic acid. The structures of the compounds were deduced from elemental and thermal analyses, UV-visible, FTIR and ESR spectral analysis cum magnetic susceptibility and molar conductivity measurements. On the basis of electronic spectra and magnetic moment, an octahedral geometry have been assigned for both complexes with [VOL(H₂O)₃] and [CuL(H₂O)₃] formulation. Govindaraj et al. [5] reported synthesis and characterization of Ni(II) complexes with two Schiff base: L₁, 2-((2-hydroxy-3-methoxybenzylidene)amino)benzoic acid obtained by condensation

(*) Corresponding author:
Tel.: +2348034568942
E-mail address: abubakarabdullahiamed28@gmail.com
of o-vanillin and 2-aminobenzoic acid and L2, 2-((2-hydroxybenzylidene)amino)benzoic acid obtained by the condensation of salicylaldehyde and 2-aminobenzoic acid. The ligands and complexes were characterized by a number of spectral and analytical techniques. The data show the composition of the complexes to be [(NiL−2H)(H2O)]2H2O or [(NiL−2H)(H2O)]2H2O. Ali et al. [6] prepared a Schiff base ligand from 2-furancarboxaldehyde and 2-aminobenzoic acid and its complexes with Cu(II), Ni(II), Co(II), Cd(II), and Ni(II) ions. and were characterized based on microanalysis, IR, 1H NMR, solid reflectance, magnetic susceptibility as well as molar conductance measurements and thermogravimetric analyses (TG and DTG). The data suggest the variable formulation of the complexes. The molar conductance data of the chelates revealed non-electrolytic nature. Thermal analysis indicated the presence of water of hydrations. Ahmed and Aliyu [7] reported synthesis of a Schiff base ligand derived from 4-(N,N-dimethylamino)benzaldehyde and 2-aminobenzoic acid with its Mn(II) complex; and characterized by solubility test, determination of water of hydration, melting point/decomposition temperature, infrared spectroscopy, elemental analysis, atomic absorption spectroscopy, molar conductivity and magnetic susceptibility measurements. The complex was coral red solid, air stable and soluble in most of the organic solvents used. The molar conductance value suggests its non-electrolytic nature. The melting point of the Schiff base was found to be 177 °C while the decomposition temperature of the complex was 202 °C suggesting its thermal stability. The atomic absorption spectroscopy and elemental analysis data revealed the formation of the complex in 1:2 Metal–ligand ratio. The determination of water of hydration showed that the complex is hydrated. The infrared spectral data indicate that the Schiff base ligand exhibits bidentate nature coordinated to the metal ion via the nitrogen atom of the azomethine (C=N) and deprotonated carboxylate oxygen (COO−). On the basis of magnetic susceptibility, a four – coordinate tetrahedral geometry was proposed for the complex. Uba et al. [8] reported the complexes of Co(II), Mn(II) and Ni(II) with Schiff base derived from condensation of pentane-2,4-dione and 2-aminobenzoic acid. The synthesized compounds were characterized by molar conductivity, infrared and elemental analyses. The solubility study revealed that the compounds are soluble in most organic solvents except chloroform and diethyl ether. The molar conductance measurement values of the complexes were small suggestive of their non-electrolytic nature. Biological studies showed the non-electrolytic nature of the complexes. The compounds were assayed for antibacterial activity and were found to have good activity except Ni(II) complex. Hussein et al. [9] reported a bidentate Schiff base, 4(1H-imidazoleyl)acetoephononeanthranilic acid by combination of equimolar amounts of imidazoleacetoephonene and 2-aminobenzoic acid under reflux. Air stable complexes were obtained by interacting the Schiff base with Co(II), Cd(II) and Ni(II) ions. For structure elucidation, several analytical and spectral techniques were used viz: IR, UV-visible, 1H-NMR, mass spectra as well as magnetic susceptibility measurements, elemental and thermogravimetric analyses. Magnetic moments of 3.4 and 3.8 B.M. were respectively found for the Ni(II) and Co(II) suggestive of octahedral geometry. Molar conductance measurements showed that the complexes are non-electrolyte. In continuation of their work, Ahmed and co-workers [10,11] reported the synthesis of a Schiff base ligand obtained by condensation reaction of 2-aminobenzoic acid and 4-(N,N-dimethylamino)benzaldehyde in 1:1 molar ratio. Refluxing the Schiff base ligand with metal(II) chloride salts afforded the corresponding complexes. The Schiff base and its complexes were characterized by melting point/decomposition temperature determination, solubility test, estimation of water of crystallization, elemental analysis, infrared spectral analysis, molar conductance and magnetic susceptibility measurements. The ligand and the complexes were coloured, non-hygrosopic, air stable solids which were found soluble in most of the organic solvents used. The elemental analysis data showed their formation in 1:2 metal - ligand ratio.

In order to get an insight into the behaviour of Schiff bases, the imine linkage (−N = CH−) is a significant feature that makes Schiff base ligands interesting for biological activities as well as coordination with the metal ions. The interaction between these metal ions and ligands provides complexes of different structural features. We therefore, synthesize Schiff base from 4-methoxybenzaldehyde and o-aminobenzoic acid, coordinate Ni(II) to the Schiff base, and characterize the Schiff base and its complex on the basis of solubility, melting point, FT-IR spectroscopy, water of hydration and Conductivity measurements.

2. Material and methods:

2.1. Materials:

Chemicals used in the work like 4-methoxybenzaldehyde, o-aminobenzoic acid (BDH), NiCl2.6H2O, ethanol, chloroform, methanol, acetone were of analytical grade. All preparations were carried out using distilled water.

2.2. Physical measurements:

Melting points and decomposition temperatures were measured using an electrothermal melting point apparatus at the Faculty of Pharmacy, and Electrical conductivity measurements of the synthesized complex was carried out at room temperature using 10−3 M solutions of the sample in DMF using LIDA DDS-307 Conductivity meter with k = 0.994 cm−1 at the Department of Pure and Applied Chemistry, University of Maiduguri, Nigeria. Infrared spectra were recorded using FT-IR BUCK scientific model 530 infrared spectrophotometer in the range 4000-600 cm−1 at Yobe State University, Nigeria.
Thermo-analysis for determination of water of crystallization was carried out using Thermostat oven DHG-9030A, Pec medical using the procedure previously reported [11]. All weightings were carried out using Electronic balance Metra, Model XY2002C No. 1505515.

2.3. Synthesis of Schiff base:
The Schiff base was synthesized by dissolving 4-methoxybenzaldehyde (0.06 mol; 7.30 ml) and same moles of o-aminobenzoic acid (8.22 g) in ethanolic solution (50 ml). The obtained mixture was heated and stirred magnetically for 2 hours. Crystals were formed after 10 days, then filtered, washed and dried in vacuum [12]. The schematic representation of the reaction is depicted in figure 1.

\[
\text{MeO-CO-CHO + H}_2\text{N-CH}_2\text{COOH (50 ml) } \rightarrow \text{MeO-CO-N(CH}_2\text{COOH) + H}_2\text{O (11.22 g) + MeO-CO-N(CH}_2\text{COOH) + H}_2\text{O (12.22 g).}
\]

![Figure 1. Schematic representation of synthesis of Schiff base ligand.](image)

2.4. Synthesis of Ni(II) complex:
The complex was obtained by interaction of 30 ml ethanolic solution of the Schiff base (5 mmol, 1.276 g) with isovolumic amount of NiCl\(_2\).6H\(_2\)O (2.5 mmol, 0.594 g). The mixture magnetically stirred under reflux at 70°C for 3 hours. The complex precipitated out overnight, washed with ethanol and isolated by filtration, dried in a vacuum over calcium chloride as absorbent. The yield was recorded and percentage yield calculated [12]. Equation (1) depicts the chemical reaction.

\[
\text{NiCl}_2\cdot6\text{H}_2\text{O} + 2\text{HL} \rightarrow \left[\text{NiL}_2\right]3\frac{1}{2}\text{H}_2\text{O} + 2\text{HCl} + 2\frac{1}{2}\text{H}_2\text{O (1)}
\]

2.5. Solubility test:
The solubility of the compounds was determined using the following solvents: Distilled H\(_2\)O, DMF, ethanol, diethyl ether, Benzene, chloromethane and acetone. 0.2 g each of the prepared compounds were taken in a separate clean test tube and the solvent was added drop-wise then in excess while shaking and then observed for any visible change or reaction [13].

2.6. Determination of melting point:
The powdered ligand and the complex were separately filled into one-side opened capillary tube and placed in the melting point apparatus fitted with thermometer. The apparatus was switched on and the temperature was noted when the compound first just began to melt to clear liquid or decompose [14].

3. Results and discussion:
3.1. Physicochemical properties:
The Schiff base (HL) was successfully synthesized in excellent yield of 94 % by condensation of 4-methoxybenzaldehyde and o-aminobenzoic acid. The recorded yield was 34.92 % [14]. The colour of Schiff base is yellow while the Ni(II) complex was pale yellow. The colour may be due to d-d transition. The Schiff base ligand was reasonably thermostable with melting point of 210°C. This sharp melting point indicates that it was obtained in pure form [15,16]. The decomposition temperature of the Ni(II) complex was found to be >340 °C, exceeding the instrument’s limit. This very high temperature presumes good thermal stability of the complex due to the formation of large ring [7,17].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Weight (g/mol)</th>
<th>Colour</th>
<th>Yield (%)</th>
<th>M.P (°C)</th>
<th>% H(_2)O Found</th>
<th>% H(_2)O Calculated</th>
<th>No. Of water molecules</th>
<th>Λm (Ω(^{-1})cm(^2) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>255.29</td>
<td>Yellow</td>
<td>74.17</td>
<td>210</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[\text{NiL}_2]3\frac{1}{2}\text{H}_2\text{O}</td>
<td>630.27</td>
<td>Pale yellow</td>
<td>34.92</td>
<td>&gt;340</td>
<td>10.00</td>
<td>9.99</td>
<td>3\frac{1}{2}</td>
<td>18.15</td>
</tr>
</tbody>
</table>

Table 1. Physicochemical properties of Schiff base ligand and its Ni(II) Complex.

L = C\(_{15}\)H\(_{16}\)NO\(_2\)
3.2. Solubility:
The Solubility of the Schiff base ligand and Ni(II) complex was tested in different polar and non-polar solvents. The results revealed that the ligand is soluble in hot distilled water, acetone, benzene, ethanol, chloromethane and DMF but insoluble in hot and cold diethyl ether whereas the Ni(II) complex was soluble in hot distilled water and DMF but insoluble in other organic solvents used. The results are presented in Table 2.

Table 2. Solubility of the Schiff base ligand and its Ni(II) Complex.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Distilled H$_2$O</th>
<th>Acetone</th>
<th>Benzene</th>
<th>Ethanol</th>
<th>Chloromethane</th>
<th>Diethyl ether</th>
<th>DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>[NiL$_2$].3½H$_2$O</td>
<td>IS</td>
<td>IS</td>
<td>IS</td>
<td>IS</td>
<td>IS</td>
<td>IS</td>
<td>S</td>
</tr>
</tbody>
</table>

Keys: C = Cold, H=Hot, S = Soluble, IS = Insoluble, SS = Slightly Soluble, L = C$_{15}$H$_{12}$NO$_2$.

3.3. Molar conductivity measurement:
The molar conductance of 10$^{-3}$ M Ni(II) complex was measured in DMF solvent at room temperature. The molar conductivity value was 18.15 Ω$^{-1}$ cm$^2$ mol$^{-1}$. This value is too low to account for any dissociation of the complex in the solvent and the obtained value was taken as evidence for non-electrolytic nature of the complex [18].

3.4. Fourier Transform infrared spectroscopy:
In order to study the bonding mode of the ligand to metal ion in the complex, the FT-IR spectrum of the free ligand Schiff base was compared with that of the complex. Some important IR vibrational band of the ligand and its complex with their assignments are presented in Table 3 and the spectra are shown as Figures 2 and 3. The IR spectrum of the metal complex exhibits broad band at 3322 cm$^{-1}$ indicating the presence of water lattice [19]. The band at 1619 cm$^{-1}$ in the ligand is ascribed to ν(C=N) vibration. The shifting of this band to lower wavenumber by 36 cm$^{-1}$ suggests the Coordination of the Nickel ion via nitrogen atom of the azomethine ν(C=N). It is expected that coordination of nitrogen to the metal atom would reduce the electron density in the azomethine link, thus lowers the -HC=N absorption [20]. A band at 1728 cm$^{-1}$ in the ligand was assignment to ν(C=O) stretching vibration of the COOH group. This band shifted to lower frequency of 1678 cm$^{-1}$ in the complex indicating the participation of oxygen atom of the hydroxyl group in coordination [21]. New bands in the region 779 cm$^{-1}$ and 684 cm$^{-1}$ have been assigned to ν(Ni-N) and ν(Ni-O) stretching vibrations respectively, confirming the coordination through nitrogen and oxygen [22]. Therefore, the Schiff base ligand showed monobasic bidentate behaviour with NO type having the nitrogen of the azomethine and oxygen of the hydroxy of the carboxyl group as bonding sites.

Table 3. The main IR spectra of the Schiff base ligand ad its Ni(II) Complex.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(OH) H$_2$O</th>
<th>ν(OH) Carboxylic</th>
<th>ν(C=O) Carboxylic</th>
<th>ν(C=N)</th>
<th>ν(C-O)</th>
<th>ν(Ni-N)</th>
<th>ν(Ni-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>_</td>
<td>3463w</td>
<td>1728s</td>
<td>1619m</td>
<td>1289s</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td>[NiL$_2$].3½H$_2$O</td>
<td>3322b,w</td>
<td>-</td>
<td>1678w</td>
<td>1583s</td>
<td>1266m</td>
<td>779w</td>
<td>684w</td>
</tr>
</tbody>
</table>

Keys: m = medium, s = strong, w = weak, b = broad, L = C$_{15}$H$_{12}$NO$_2$.

Figure 2. FT-IR spectrum of the Schiff base ligand.
3.5. Determination of number of water molecules of crystallization:
The percentage of the anhydrous complex was obtained by subtracting the % of water crystallization from 100 %. The obtained percentage was used to calculate the empirical formula as presented in Table 4. The result showed that the mole ratio of the anhydrous complex to the water of crystallization is 1: 3½. It is concluded that the complex is hydrated.

Table 3. Empirical formula determination of the complex.

<table>
<thead>
<tr>
<th>Species</th>
<th>Anhydrous Complex</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>% composition by mass</td>
<td>90 %</td>
<td>10 %</td>
</tr>
<tr>
<td>Mole Ratio</td>
<td>1</td>
<td>3½</td>
</tr>
</tbody>
</table>

On the basis of physicochemical and FT-IR data as well as information from other related works, a square planar geometry is proposed for the complex (Fig. 4).

4. Conclusion:
The following main conclusions are drawn from the present study:
- The Schiff base ligand and its Ni(II) complex were successfully synthesized in good yield and characterized using various physical and FT-IR spectroscopic techniques.
- The sharp melting point and FT-IR data confirmed the formation of the Schiff base ligand.
- The synthesized compounds have high thermostability.
- The metal complex is hydrated.
- The Schiff base acted as monobasic ligand coordinated to the Ni(II) ion bidentately with ON donor sites from azomethine nitrogen and deprotonated hydroxyl oxygen of the carboxyl group, indicating square planar geometry.
References:


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