Synthesis and characterization of Co (II), Ni (II) and Cu (II) complexes with unsymmetrical tetradentate Schiff base ligand

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Abstract
A novel series of cobalt (II), nickel (II) and copper (II) complexes of unsymmetrical Schiff base ligand 1-(2-hydroxynaphthalideneimino)-2-(5 methoxysalicylidene imino)-4 chlorobenzene-1,2-diamine was synthesised by condensation reaction of 1:1:1 molar ratio of 2-hydroxynaphthalene-1-carbaldehyde, 4-chlorobenzene-1,2-diamine and 5-methoxysalicyldiethyde in alcoholic medium. The synthesised ligand and its metal complexes were characterised by elemental analysis, molar conductance measurements, magnetic susceptibility measurements, UV-Vis and infrared spectral data. The molar conductance of synthesised metal complexes in DMSO solution indicates their non-electrolytic nature.

The analytical data show the general formula for the complexes to be [M(L)₂] where L = Schiff base ligand and M = Co (II), Ni (II) and Cu (II). The spectral data and magnetic moment suggested that Schiff base behaves as a tetradentate ligand, coordinating through azomethine nitrogen and phenolic oxygen atoms to the metal ion. Magnetic susceptibility measurements, UV-Vis and infrared spectral data show metal complexes having square planar geometry.

Keywords: Unsymmetrical Schiff base, 2-hydroxynaphthalene-1-carbaldehyde,5-methoxy salicyldiethyde, metal complexes.

Introduction
Schiff bases are azomethine functional group versatile compounds synthesized from the condensation reaction of a primary amine with carbonyl compounds under variable conditions of solvents, temperature and pH. Due to effective conjugation and less polymerization, Schiff bases of aromatic carbonyl compounds are more stable than aliphatic. The stability, reactivity and biological activity of Schiff bases and their metal complexes depend on azomethine or imine group of ligands. Schiff base ligand and its metal complexes play a versatile role in analytical chemistry, catalysis, antibacterial, antifungal, antiviral, anticancer, antimalarial, anti-inflammatory and antioxidants. Benzene-1,2-diamine is used in polymer industry and removal of sulphur from mining ores. Unsymmetrical tetradentate Schiff base ligands contain donor atoms nitrogen and oxygen which play a central role in coordination chemistry for analysis, biochemistry, catalysis and material chemistry.

In the present study, we report the synthesis and characterization of Co (II), Ni (II) and Cu(II) complexes with unsymmetrical tetradentate ligand derived from 2-hydroxynaphthalene-1-carbaldehyde, 4-chlorobenzene-1,2-diamine and 5-methoxysalicyldiethyde in alcoholic medium.

Material and Methods
All the solvents and chemicals used in present research were of Anal-R grade and were used without further purification. The reagents used in the synthesis of Schiff base ligand were obtained from Sigma Aldrich. Metal salts of cobalt, nickel and copper were obtained from Loba Chemie. The elemental analysis of investigated compounds was obtained on Carlo Erba 1108 analyzer. The molar conductivity of the synthesised metal complexes was measured on Elico-CM 82 conductivity meter used 10⁻³ M solution in DMSO as solvent.

The IR spectra of the synthesized Schiff base and its metal complexes were recorded on Perkin Elmer 577 spectrophotometer using KBr pellets in the range 4000 – 400 cm⁻¹. The magnetic susceptibility of metal (II)complexes at room temperature was measured by Gouy method using Hg [Co (SCN)₄] as calibrant. The UV-Vis spectra of investigated metal complexes were recorded by using Hitachi-320 spectrophotometer.

Synthesis of Schiff base ligand (HL): The unsymmetrical tetradeinate Schiff base ligand (HL) was prepared in two steps. In the first step, the monocondensed half-unit was prepared by 1:1 molar ratio of the condensation of 4-chlorobenzene-1,2-diamine (2.85g,0.02mol) with 2-hydroxynaphthalene-1-carbaldehyde (3.44 g, 0.02 mol) in ethanolic medium and stirred for 3 h. In the second step, the monocondensed half-unit was refluxed with ethanolic solution of 5-methoxysalicyldiethyde (3.04 g, 0.02 mol). The orange precipitate was formed at room temperature upon cooling the solution. The solid precipitate was collected, filtered, washed with ether and recrystallized with ethanol and dried under reduced pressure over anhydrous CaCl₂ in a desiccator. The melting point of the Schiff base ligand was found to be 178°C.

Synthesis of metal complexes: A ethanolic solution of Schiff base ligand (0.01 mol) was mixed with ethanolic solution of metal salts (0.01mol) and refluxed on water bath for 3-4 h in presence of 0.01 mol of sodium carbonate. A
coloured product appeared when resulting solution was cooled at room temperature. The precipitate was washed with water and then with ethyl alcohol. The resulting compound was recrystallized and dried in vacuo.

**Results and Discussion**

The analytical data of synthesized Schiff base and its metal complexes are presented in table 1. All the metal (II) complexes are non-hygrosopic and stable at room temperature. The molar conductivity data of metal complexes are listed in table 2. The lower values of molar conductance of investigated metal complexes in DMSO revealed their non-electrolytic nature. The analytical and spectral data revealed that metal complexes have 1:1(metal: ligand) stoichiometry and mononuclear nature.

![Figure 1: Structure of Schiff base ligand](image)

**Table 1**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Colour</th>
<th>M.P(0°C)</th>
<th>Elemental analysis (% found / calcd.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>HL(C_{25}H_{19}N_{2}O_{3}Cl)</td>
<td>Orange</td>
<td>178°C</td>
<td>69.63 (69.68)</td>
</tr>
<tr>
<td>[Co(C_{25}H_{17}N_{2}O_{3}Cl)]</td>
<td>Brown</td>
<td>240°C</td>
<td>61.48 (61.55)</td>
</tr>
<tr>
<td>[Ni(C_{25}H_{17}N_{2}O_{3}Cl)]</td>
<td>Red</td>
<td>208°C</td>
<td>61.53 (61.58)</td>
</tr>
<tr>
<td>[Cu(C_{25}H_{17}N_{2}O_{3}Cl)]</td>
<td>Pale brown</td>
<td>234°C</td>
<td>60.87 (60.98)</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Solvent</th>
<th>Molar conductance (Ω⁻¹ cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(C_{25}H_{17}N_{2}O_{3}Cl)]</td>
<td>DMSO</td>
<td>16.4</td>
</tr>
<tr>
<td>[Ni(C_{25}H_{17}N_{2}O_{3}Cl)]</td>
<td>DMSO</td>
<td>11.2</td>
</tr>
<tr>
<td>[Cu(C_{25}H_{17}N_{2}O_{3}Cl)]</td>
<td>DMSO</td>
<td>12.6</td>
</tr>
</tbody>
</table>
Electronic spectra and magnetic moment: The magnetic moment and electronic absorption spectra data of metal complexes in DMSO solution are listed in Table 3. The electronic absorption spectra of Co(II) complex in DMSO show a single d-d transition band at 24978 cm\(^{-1}\) and charge-transfer band at 30020 cm\(^{-1}\). The magnetic moment value supported square-planar geometry for Cu(II) complex.

Conclusion
The unsymmetrical tetradentate Schiff base ligand and its Co(II), Ni(II) and Cu(II) complexes were synthesized and characterized by elemental analysis, conductance measurements, magnetic susceptibility measurements, UV-Vis and infrared spectral data. The analytical data show the general formula of the complexes to be \([\text{M(L)}_2]\) where \(\text{L} = \text{Schiff base ligand and M = Co(II), Ni(II) and Cu(II)}.\) The lower values of molar conductance of synthesized metal complexes indicates their non-electrolytic nature.

The analytical and spectral data revealed that metal complexes have 1:1 (metal: ligand) stoichiometry and mononuclear nature. The spectral data suggested that Schiff base ligand behaves as tetradentate coordinating through nitrogen atoms of azomethine and oxygen atoms of phenolic group to metal ion. On the basis of magnetic susceptibility measurements, UV-Vis and infrared spectral data metal (II) complexes were proposed to be of square planar geometry.

References
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3. Anjum A., Paswan S., Kumar M., Ali H. and Dubey R.K., Synthesis, characterization and DFT studies of Some cobalt(II) and 

Table 3

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(\mu_{eff}/(B.M.))</th>
<th>Spectral bands(cm(^{-1}))</th>
<th>Transitions</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(C}_2\text{H}_7\text{N}_2\text{O}_3\text{Cl}])</td>
<td>2.23</td>
<td>24978 30020</td>
<td>CT</td>
<td>Square planar</td>
</tr>
<tr>
<td>([\text{Ni(C}_2\text{H}_7\text{N}_2\text{O}_3\text{Cl}])</td>
<td>Diamagnetic</td>
<td>20150 25872 30370</td>
<td>(^1\text{A}_g \rightarrow ^1\text{B}_g), (^1\text{A}_g \rightarrow ^1\text{E}_g)</td>
<td>Square planar</td>
</tr>
<tr>
<td>([\text{Cu(C}_2\text{H}_7\text{N}_2\text{O}_3\text{Cl}])</td>
<td>1.81</td>
<td>22980 30230</td>
<td>(^2\text{B}_g \rightarrow ^2\text{E}_g)</td>
<td>Square planar</td>
</tr>
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</table>

Table 4

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(\nu(\text{O} - \text{H}))</th>
<th>(\nu(\text{C} = \text{N}))</th>
<th>(\nu(\text{C} - \text{O}))</th>
<th>(\nu(\text{M} - \text{N}))</th>
<th>(\nu(\text{M} - \text{O}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{HL(C}_2\text{H}_6\text{N}_2\text{O}_3\text{Cl}])</td>
<td>3380</td>
<td>1621</td>
<td>1315</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Co(C}_2\text{H}_7\text{N}_2\text{O}_3\text{Cl}])</td>
<td>-</td>
<td>1612</td>
<td>1340</td>
<td>476</td>
<td>569</td>
</tr>
<tr>
<td>([\text{Ni(C}_2\text{H}_7\text{N}_2\text{O}_3\text{Cl}])</td>
<td>-</td>
<td>1605</td>
<td>1345</td>
<td>481</td>
<td>560</td>
</tr>
<tr>
<td>([\text{Cu(C}_2\text{H}_7\text{N}_2\text{O}_3\text{Cl}])</td>
<td>-</td>
<td>1598</td>
<td>1338</td>
<td>498</td>
<td>562</td>
</tr>
</tbody>
</table>

IR Spectra: The infrared spectra of synthesized Schiff base and its Co(II), Ni(II) and Cu(II) complexes are listed in Table 4. A sharp and broad band at 1621 cm\(^{-1}\) in free ligand due to azomethine \(\nu(\text{C} = \text{N})\) vibration has shifted to lower frequency 1598 – 1612 cm\(^{-1}\) in the complexes, indicating the bond formation of azomethine nitrogen to the metal ion. The Schiff base ligand shows a broad band at 3380 cm\(^{-1}\) due to \(\nu(\text{O}-\text{H})\) vibration. These spectral bands are absent in the metal complexes indicating deprotonation of the phenolic group and coordination of phenolic oxygen to the metal ion which is also supported by the shift of phenolic \(\nu(\text{C} - \text{O})\) vibration at 1315 cm\(^{-1}\) in the free Schiff base to 1338 – 1345 cm\(^{-1}\) in the complexes. The appearance of weak intensity bands for the complexes in the region 560 – 569 cm\(^{-1}\) and 476 – 498 cm\(^{-1}\) was assigned to \(\nu(\text{M} - \text{O})\) and \(\nu(\text{M} - \text{N})\) respectively which also supported the coordination of azomethine nitrogen atoms and phenolic oxygen atoms to metal ion.

The electronic spectra of Co(II) complex show a broad unsymmetrical band at 22980 cm\(^{-1}\) assigned to \(^3\text{B}_g \rightarrow ^3\text{E}_g\) transition and one intense band at 30230 cm\(^{-1}\) assigned as intra-ligand or charge -transfer transition. The observed magnetic moment of Cu(II) complex was found to be 1.81 B.M. The electronic spectral data and magnetic moment value supported square-planar geometry for Cu(II) complex.\(^{12}\)


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