Research Article

Solvent Free Synthesis and Characterization of Few Metal Complexes of Schiff Base Derived from 2-Amino-5, 6-dimethyl Benzimidazole and Syringaldehyde

Mahesh G. Undegaonkar1*, Sadashiv N. Sinkar2, Vijay N. Bhosale3, Sunil R. Mirgane4

1Department of Chemistry, ASC College Badnapur, Jalna, Maharashtra, India
2Department of Chemistry, MSS'S Arts, Science and Commerce College, Ambad, Maharashtra, India
3Shivaji Arts, Commerce and Science College Kannad, Aurangabad, Maharashtra, India
4Department of Chemistry, JES College Jalna, Jalna, Maharashtra, India

ABSTRACT

A solvent-free synthesis of bidentate Schiff base ligand was carried out by treating 2-Amino-5, 6-dimethyl benzimidazole with Syringaldehyde in 1:1 molar proportion in a scientific microwave oven. The excellent yield was obtained after purification. Few metal complexes of Schiff base were synthesized by using Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Ag(I) metal salts in microwave oven under solvent-free condition. All metal complexes showed distinct color at the end of the reaction, and the melting point of each complex preliminary confirmed the formation of the product. A detailed characterization of both Schiff base and its representative metal complexes was carried out by several analytical and spectral techniques, including elemental analysis, Infrared (IR) spectroscopy, 1HNMR spectroscopy, liquid chromatography–mass spectrometry (LCMS), UV spectroscopy, and TGA. The spectroscopic analysis supports the predicted structure of the parent Schiff base ligand. Bioactivity of Schiff base & respective metal complexes was studied against Escherichia coli, Staphylococcus aureus and Salmonella typhi showing significant bioactivity of the metal complexes and Schiff base ligand.

INTRODUCTION

Schiff bases are chemically imine molecules with common structural formula R1R2C=NR3 where R1, R3 ≠ H. Hugo Schiff in 1864 synthesized such kind of molecule first time and then this class of compounds named as Schiff base.[1,2] Schiff bases further treated with many metal salts yields metal complexes, and both these Schiff bases and their metal complexes have vast applications in drug synthesis.[3] The azomethine group present in Schiff base can form highly stable complexes with transition metal ions. The 'N' atom in the azomethine group has lone pair of electrons, which enables stable transition metal complexes by occupying vacant d orbitals of metal ions.[4,5] Present work fundamentally focuses on solvent free synthesis of Schiff base and its metal complex using the scientific micro oven. It is observed that Microwave-assisted synthesis is low cost, less pollutant emitting, and time-consuming method.[6,7] Microwave-assisted synthesis also has the advantage of higher yield, low accident probability, and environmentally safe.[8-10] Schiff base and their metal complexes show significant biological activities like antiviral, antipolio, antibiotic, anticancer, antituberculastic, fungicidal, insecticidal, etc.[11-15] The principal pharmaceutical advantage of the present study is that the heterocyclic Schiff bases and their metal complexes can be structurally modified to

*Corresponding Author: Mr. M.G.Undegaonkar
Address: Flat No. 16, Onkar Residency [Phase II], Tuljabhavani nagar, Darga Road, Jalna-431203, Dist. – Jalna, Maharashtra, India
Email: undegaonkar@gmail.com 9284525010
Tel.: +91-9284525010

Relevant conflicts of interest/financial disclosures: 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.

Copyright © 2021 M. G. Undegaonkar et al. This is an open access article distributed under the terms of the Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License which allows others to remix, tweak, and build upon the work non-commercially, as long as the author is credited and the new creations are licensed under the identical terms.
Solvent Free Synthesis and Characterization of Schiff Base Metal Complexes

anticancer agent, characteristic antimicrobial agents being remarkable pharmacophores and precursors of drug molecules.

**MATERIALS AND METHODS**

**Material Methods**

All chemicals were purchased from Sigma Alderich, Loba Chem, and Merck. In addition, 2-Amino-5, 6-dimethyl benzimidazole, syringaldehyde were purchased from Sigma Alderich and metal nitrates from Loba Chem and Merck. All chemicals were used as received. Parent Schiff base ligand was synthesized by condensing 2-Amino-5, 6-dimethyl benzimidazole, and syringaldehyde in the 1:1 molar ratio in a scientific microwave oven. After ligand synthesis, metal complexes were synthesized by treating ligand with transition metal salts in a same scientific microwave oven.

**Techniques**

All syntheses were carried out in a scientific oven, 2450 MHz frequency, 800 W. All melting points were recorded on digital melting point apparatus. The electronic absorption spectra were recorded in the wavelength range 200 to 800 nm in DMSO solution using UV-VIS spectrophotometer. The IR spectra were recorded on a Schimadzu Dr-8031 instrument. The TGA was carried out in dynamic nitrogen atmosphere (30 mL/min) with a heating rate of 10/min using Shimadzu TGA–50H thermal analyser. Thin layer chromatography (TLC) analyses were performed on pre-coated aluminium plates with silica gel. TLC spots were visualized in UV chamber.

**Synthesis of New Parent Schiff Base Ligand**

The parent Schiff base ligand was prepared by the reaction between 2-amino-5, 6-dimethyl benzimidazole [1.62gm, 0.01 mol], and syringaldehyde [1.82 gm, 0.01mol] under solvent-free condition. The reaction mixture was first mixed in a grinder and then irradiated about 20 minutes periodically at 750 W in a microwave oven. The irradiated microwave product was then kept at room temperature and then washed with dry ether. The final product was then recrystallized using absolute ethanol to give brown crystals. The yield obtained was 3.10 gm (95%) and the melting point recorded was 120. The product’s advancement and pureness was examined using TLC, and a solvent mixture used was n-hexane + ethyl acetate (7:3) (Table 1).

**Syntheses of Metal Complexes**

The metal complexes were also prepared by the same microwave method under solvent free conditions. First, the appropriated metal salt was mixed with the required amount of parent ligand, (E)-4-((5, 6-dimethyl-1-H-benzo[d]imidazole-2-ylimino)methyl)-2, 6-dimethoxyphenol, in a grinder to mix thoroughly. Then the mixture was irradiated for few seconds to minutes at 750 W. The product obtained was washed and recrystallized with hot ethanol, then dried at room temperature. The melting point of each complex was recorded. The metal salts used were MnCl₂, Fe(NO₃)₃.9H₂O, Co(NO₃)₂.6H₂O, Ni(NO₃)₂.6H₂O, Cu(NO₃)₂.3H₂O, Zn(NO₃)₂.6H₂O, Cd(NO₃)₂.4H₂O and AgNO₃ (Fig. 1 & Table 2).

**RESULT AND DISCUSSION**

A few important facts were observed at the end of the microwave-assisted solvent-free synthesis of Schiff
base and its metal complexes, like shorter reaction time and higher yield. In this method, homogeneity of the reaction mixture was raised by a rotating reactor keeping tray. The results obtained were confirmed by repeating the procedure twice. The entire procedures were completed within a few seconds to a few minutes, and higher yield nearly and above 90%. The metal complexes obtained show absolute color and sharp melting points. All the synthesized complexes were found stable and in a solid-state at room temperature. The synthesized complexes were found insoluble in a common organic solvent but were soluble in Dimethylsulfoxide (DMSO) and Drug Master File (DMF). The parent ligand and its eight metal complexes exhibit significant biological activity.

**Elemental Composition Analysis and Physical Properties**

**Infrared Spectra Analysis**

Analysis of parent Schiff base ligand: The IR spectra of parent Schiff base ligand showed a most characteristic band at 1674.21 cm$^{-1}$ due to azomethine, $\nu$(C=N),$^{[16]}$ stretching. Also, a band at 3452.58 cm$^{-1}$ showed due to NH stretching of benzimidazole moiety.$^{[16,17]}$ The parent ligand spectrum showed bands at 3774.69 cm$^{-1}$ and 1348.24 cm$^{-1}$ due to stretching and deformation of phenolic OH, whereas the band at 1126.43 cm$^{-1}$ showed due to phenolic $\nu$(C-O).$^{[17,18]}$ These bands confirmed the formation of the parent ligand.

Analysis of metal complex (L-Ni): The IR spectrum of L-Ni complex showed a shift in frequency of azomethine, $\nu$(C=N), stretching from 1674.21 to 1681.93 cm$^{-1}$ as compared to parent ligand.$^{[19-21]}$ Also, band due to phenolic OH stretching shifted from 3774.69 to 3610.74 cm$^{-1}$ and phenolic $\nu$(C-O) stretching moved from 1126.43 to 1033.85 cm$^{-1}$. The most distinguishing bands of this metal complex are that of M-N. The M-N band was detected at 482.2 cm$^{-1}$. These bands confirmed the formation of a stable (L-Ni) metal complex.$^{[22-27]}$ The weaker bands detected at 779.24 and 842.89 cm$^{-1}$ are caused by OH wagging mode of vibrations suggesting the presence of coordinated water (OH$^-_2$) molecules in the metal complex.$^{[28-30,38]}$ These bands are lacking in IR spectrum of the parent ligand.

The IR data of both metal complexes showed the bidentate nature of parent ligand. The IR data of both parent Schiff base ligand and its metal complexes is summarized in Table 3.

**$^1$HNMR Spectral Studies**

The peaks observed in $^1$HNMR spectra of parent Schiff base ligand are as follows. The most characteristic peak at 8.99 ppm (s, 1H, N=CH) was observed due to H-from azomethine group. The peaks observed at 6.96–7.68 ppm showed owing to H-from both aromatic rings. The peak observed at 5.01 ppm (s, 2H, OH, and NH) attributable to H from phenolic -OH and imidazole –NH. The peak was observed at 3.33 ppm (s, 6H) due to two methoxy methyl groups, whereas peaks were observed at 2.51 ppm (s, 6H) caused by two methyl groups attached to the aromatic ring.

**Mass Spectral Studies**

The mass spectrum study of the parent Schiff base ligand showed a significant peak at m/z 327 (M$^+$), which corresponds to the molecular weight of the parent Schiff base ligand, i.e., 325.

**Electronic Spectra**

The electronic spectrum of both metal complexes (L-Ni, L-Zn) was recorded in the wavelength region 200 nm to 800 nm in DMSO solution. The electronic spectral data of both complexes are summarized in Table 5.

---

**Table 3:** Selected Infrared Frequencies (cm$^{-1}$) of parent ligand and its complexes

<table>
<thead>
<tr>
<th>Ligand / Complex</th>
<th>$\nu$(C=N) Azomethine</th>
<th>$\nu$(OH) Phenolic</th>
<th>$\nu$(C-O) Phenolic</th>
<th>$\nu$(M-N)</th>
<th>$\nu$(H$_2$O) wagging</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{10}$H$</em>{18}$O$_2$N$_2$</td>
<td>1674.21</td>
<td>3774.69</td>
<td>1126.43</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[(C$<em>{10}$H$</em>{18}$O$_2$N$_2$)$_2$(H$_2$O)$_2$]Ni</td>
<td>1681.93</td>
<td>3640</td>
<td>1033.85</td>
<td>482.20</td>
<td>709.2, 825</td>
</tr>
<tr>
<td>[(C$<em>{10}$H$</em>{18}$O$_2$N$_2$)$_2$(H$_2$O)$_2$]Zn</td>
<td>1753.29</td>
<td>3610.74</td>
<td>1033.85</td>
<td>495.71</td>
<td>779.24, 842.89</td>
</tr>
</tbody>
</table>

**Table 4:** Observed $^1$HNMR Peaks (in ppm) of Parent Schiff base ligand

<table>
<thead>
<tr>
<th>Compound</th>
<th>H-from azomethine group</th>
<th>H-from aromatic group</th>
<th>H-from phenolic and imidazole</th>
<th>H-from methoxy methyl group</th>
<th>H-from 5, 6 dimethyl group</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{10}$H$</em>{18}$O$_2$N$_2$</td>
<td>8.99</td>
<td>6.96–7.68</td>
<td>5.01</td>
<td>3.33</td>
<td>2.51</td>
</tr>
</tbody>
</table>
Solvent Free Synthesis and Characterization of Schiff Base Metal Complexes

Table 5: Electronic spectral data and probable geometries for the metal complexes

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Complex</th>
<th>UV Vis major bands absorption maxima cm⁻¹ (nm)</th>
<th>Assignment</th>
<th>Proposed geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[(C₁₈H₁₅O₄N₃)₃(H₂O)₂]Ni</td>
<td>32320.62 (309.4)</td>
<td>³A₂g(F) → ³T₂g(F)</td>
<td>Octahedral</td>
</tr>
<tr>
<td>2</td>
<td>[(C₁₈H₁₅O₄N₃)₃(H₂O)₂]Zn</td>
<td>32341.53 (309.2)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>34411.56 (290.6)</td>
<td>³A₂g(F) → ³T₁g(F)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>44274.79 (226)</td>
<td>³A₂g(F) → ³T₁g(P)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49067.71 (203.8)</td>
<td>Charge transfer</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6: Thermogravimetric analytical data of metal complexes

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compound</th>
<th>Weight loss (%)</th>
<th>Temperature (°C)</th>
<th>Weight loss (%)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[(C₁₈H₁₅O₄N₃)₃(H₂O)₂]Ni</td>
<td>0</td>
<td>27.23</td>
<td>0</td>
<td>30.2</td>
</tr>
<tr>
<td>2</td>
<td>[(C₁₈H₁₅O₄N₃)₃(H₂O)₂]Zn</td>
<td>10</td>
<td>173.83</td>
<td>10</td>
<td>89.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>249.53</td>
<td>20</td>
<td>194.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>284.02</td>
<td>30</td>
<td>266.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>303.10</td>
<td>40</td>
<td>326.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>343.06</td>
<td>50</td>
<td>379.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>380.23</td>
<td>60</td>
<td>463.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>385.01</td>
<td>70</td>
<td>486.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>416.73</td>
<td>74.024</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Total wt. loss)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>87.151</td>
<td>475</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 2: Projected structure of Metal complexes

[M = Mn²⁺ / Fe³⁻ / Co²⁺ / Ni²⁺ / Cu²⁺ / Zn²⁺ / Cd²⁺ / Ag⁺]

The electronic spectrum of the Ni (II) complex reveals major bands at 49067.71 cm⁻¹ (203.8 nm), 44274.79 cm⁻¹ (226 nm), 34411.56 cm⁻¹ (290.6 nm) and 32320.62 cm⁻¹ (309.4 nm). The band at 49067.71 cm⁻¹ is due to charge transfer proving the coordination of the ligand to Ni (II).

The electronic spectrum of the Zn (II) complex reveals major bands at 49067.71 cm⁻¹ (203.8 nm), 44274.79 cm⁻¹ (226 nm), 34411.56 cm⁻¹ (290.6 nm) and 32320.62 cm⁻¹ (309.4 nm). However, the last three correspond to ³A₂g(F) → ³T₂g(F), ³A₂g(F) → ³T₁g(F), ³A₂g(F) → ³T₁g(P) transitions respectively. The electronic transition shown in the spectrum supports octahedral geometry of the complex. The major bands also conform to π → π* and n → π* transitions.

The major bands in the electronic spectrum of the Zn (II) complex exposes major bands at 32341.53 cm⁻¹ (309.2 nm), 34411.56 cm⁻¹ (290.2 nm), 44274.79 cm⁻¹ (226 nm), 49067.71 cm⁻¹ (203.8 nm), 44274.79 cm⁻¹ (226 nm), 34411.56 cm⁻¹ (290.6 nm) and 32320.62 cm⁻¹ (309.4 nm). However, the last three correspond to ³A₂g(F) → ³T₂g(F), ³A₂g(F) → ³T₁g(F), ³A₂g(F) → ³T₁g(P) transitions respectively. The electronic transition shown in the spectrum supports octahedral geometry of the complex. The major bands also conform to π → π* and n → π* transitions.

Table 7: Antibacterial activity of ligand and their metal complexes

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compounds</th>
<th>Minimum Inhibition Concentration (μg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₁₈H₁₅O₄N₃</td>
<td>E. Coli: 100</td>
</tr>
<tr>
<td>2</td>
<td>[(C₁₈H₁₅O₄N₃)₃(H₂O)₂]Fe</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>[(C₁₈H₁₅O₄N₃)₃(H₂O)₂]Mn</td>
<td>250</td>
</tr>
<tr>
<td>4</td>
<td>[(C₁₈H₁₅O₄N₃)₃(H₂O)₂]Co</td>
<td>250</td>
</tr>
<tr>
<td>5</td>
<td>[(C₁₈H₁₅O₄N₃)₃(H₂O)₂]Ni</td>
<td>250</td>
</tr>
<tr>
<td>6</td>
<td>[(C₁₈H₁₅O₄N₃)₃(H₂O)₂]Cu</td>
<td>250</td>
</tr>
<tr>
<td>7</td>
<td>[(C₁₈H₁₅O₄N₃)₃(H₂O)₂]Zn</td>
<td>250</td>
</tr>
<tr>
<td>8</td>
<td>[(C₁₈H₁₅O₄N₃)₃(H₂O)₂]Cd</td>
<td>500</td>
</tr>
<tr>
<td>9</td>
<td>[(C₁₈H₁₅O₄N₃)₃(H₂O)₂]Ag</td>
<td>500</td>
</tr>
</tbody>
</table>

The last three correspond to ³A₂g(F) → ³T₂g(F), ³A₂g(F) → ³T₁g(F), ³A₂g(F) → ³T₁g(P) transitions respectively. The electronic transition shown in the spectrum supports octahedral geometry of the complex. The major bands also conform to π → π* and n → π* transitions.

The thermal data extracted from the thermogram of both the metal complexes (L-Ni, L-Zn) were carried with in the temperature range from room temperature to 500. The heating was carried in the dynamic nitrogen atmosphere with a linear heating rate of 10 min⁻¹. The nitrogen flow rate was kept at 30 mL min⁻¹. The thermal data extracted from the thermogram of both complexes are summarized in Table 6.

Thermal Analysis of Metal Complexes

The TGA of both the metal complexes (L-Ni, L-Zn) were carried with in the temperature range from room temperature to 500. The heating was carried in the dynamic nitrogen atmosphere with a linear heating rate of 10 min⁻¹. The nitrogen flow rate was kept at 30 mL min⁻¹. The thermal data extracted from the thermogram of both complexes are summarized in Table 6.
The L-Ni complex thermogram clearly shows a total weight loss of 87.151%, which may be observed in steps shown in Table 6. At first, the water of crystallization was lost in the range of 27 to 150 and 10% weight loss was found at 173.83. This is followed by loss of methyl, methoxy, hydroxyl and remaining organic moiety resulting in total weight loss of 87.151% (cal. 91%) up to 475. A stable curve above 475 indicates the formation of stable metal oxide (Ni-O).[25, 31-33]

The L-Zn complex thermogram, evidently, exhibits a total weight loss of 74.024%, which may be seen in steps shown in Table 6. At first, the water of crystallization was lost in the range of 30 to 80 and 10% weight loss was found at 89.62. This is followed by loss of methyl, methoxy, and remaining organic moiety resulting in total weight loss of 74.024% up to 500. A constant curve at 500 indicates the formation of stable metal oxide (Zn-O).[33, 34]

Bioactivity Study

The biological activity was measured in terms of % of inhibition in vitro. The assay was carried according to the micro-assay protocol of Rieckmann and co-workers with minor modifications.[39, 40] The antimicrobial activity of synthesized Schiff base ligand and its metal complexes were screened against Escherichia Coli, staphylococcus Aureus and Salmonella Typhi grew at 37 overnight. The Micro Broth Dilution method measured the minimum inhibition concentration using streptomycin as a reference drug at wavelength 475 nm. The test samples were prepared using DMSO solvent in the concentration range between 4 µg/mL to 100 µg/mL.

The MIC data summarized in Table 7 clearly shows that the parent ligand and its Fe (III) complex show excellent activity against Escherichia Coli compared to the rest of the metal complexes. The Co (II) complex and Cd (II) complex show excellent activity against S. Aureus compared to the parent ligand and the rest of the metal complexes. The Mn (II) complex shows excellent activity against Salmonella Typhi compared to the parent ligand and the rest of the metal complexes.

Conclusion

In the present work, solvent-free syntheses of new bidentate Schiff base ligand, (E)-4-((5, 6-dimethyl-1-H-benzo[d] imidazole-2-yliino) methyl)-2, 6-dimethoxyphenol, and its metal complexes were performed using the microwave method. All the synthesized compounds were characterized by different analytical and spectral methods, which support the projected structure of the new Schiff base ligand and its corresponding metal complexes. The main advantages of this method are a decrease in reaction time and an increase in yield. The method also supports the green synthesis concept and very easy to conduct.

Acknowledgment

The authors are thankful to Shivaji Arts, Commerce and Science College Kannad, Aurangabad, Maharashtra, India and JES College Jalna, Maharashtra, India, for their support.

References

Solvent Free Synthesis and Characterization of Schiff Base Metal Complexes


