Synthesis and Spectroscopic Studies of Metal Complexes with Schiff Bases Derived from 2-[5-(Pyridin-2-Ylmethylene)-Amino] 1,3,4-Thiadiazol-2-Yl-Phenol

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Abstract
Herein, we show the preparation and the characterization of new metal complexes by using a Schiff base ligand 2-[5-(Pyridin-2-ylmethylene)-amino] 1,3,4-thiadiazol-2-yl-phenol (L) with the metals Co(II), Ni(II), Cu(II) and Zn(II). This Schiff base ligand was synthesized via condensing [2-pyridine carboxaldehyde] with [2-amino-5-phenyl-1,3,4-thiadiazol] in an alcoholic solution. For preparing complexes, two tetradeutate Schiff bases ligand were employed with two metal ions of Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ as dinuclear formula M₂L₂. The synthesized ligand and its metal complexes were well characterized using FTIR, UV-Vis absorption, elemental analysis, thermal analysis, ¹H-NMR, and mass spectroscopy. Based on these characterizations, the chemical structures of the ligand and the metal complexes were confirmed. Furthermore, the electronic and magnetic properties of the prepared metal complexes were clearly understood.

[DOI: 10.22401/ANJS.001.05]

Keywords: Thiadiazol, Schiff base, Complexes, Microwave irradiation.

Introduction
There have been great implementations of Schiff bases synthesized by using aromatic amines and aldehydes in various scientific domains, e.g., biological, inorganic and analytical chemistry, [1-3]. Over the last century, there have been high demands for synthesizing Schiff bases based ligands due to their significant importance especially in clinical applications. This importance stems from the fact that these ligands possess electron rich atoms such as nitrogen and oxygen as anchors which in turn enhanced the importance of nitrogen and oxygen donor organic compounds and the significant role as coordination sites if reacted with metals, [4-6].

Novel complexes of type M₂(HL)₂. 4H₂O(M=Co(II), Ni (II) and Cu (II)) were synthesized via exploiting the ligand (HL)=2-[(1H-Pyrrol-2-ylmethylene)]-5-(2-hydroxy-phenyl)-[1,3,4-thiadiazol]. These ligands were synthesized by condensing [1H-Pyrrole-2-carbaldehyde] with [2-amino-5-(2-hydroxy-phenyl-1,3,4-thiadiazole] in alcohol environment. The synthesized complexes have been identified using ¹H-NMR, FTIR, UV-vis and mass spectra. Further identification has been achieved via measuring magnetic susceptibility, and some thermal analyses, [7].

The plethora of reports have showed that different kinds of isomers especially 1,3,4-thiadiazol derivatives exhibited a very wide range of biological implementations [8]. Additionally, many protocols for the preparation of 1,3,4-thiadiazol have been established, [9-10]. Those implementations are ascribed to the presence of the −N=C−O group, [11]. An important class of organic compounds has been formed from Pyridin; thiadiazol and its derivatives due to their outstanding applications as analgesic, antipyretics and anti-inflammatory, [12]. Furthermore, pyridin can be exploited to form some Schiff bases which have been reported as important reagents in biological, and clinical applications, [13,14]. Along with our work on the metal complexes of Schiff bases, we report here the study of some new, Co(II), Ni (II), Cu (II) and Zn (II) complexes of Schiff bases derived from Pyridin and 2-amino-5-(2-hydroxy-phenyl-1,3,4-thiadiazol). The synthesis and characterization of these metal-based complexes with series of Schiff bases are discussed here. Where, L is a Schiff base of 2-amino-5-(2-hydroxy-phenyl-1,3,4-oxadiazol with pyridin-based metal.
complexes with some oxygen and nitrogen donor ligands, [15].

**Experimental Material and Methods:**

All chemical were supplied from sigma Aldrich and Fluka (HPLC grade) and used as received without purification.

The FTIR spectra were collected within the range (4000-400) cm\(^{-1}\) on KBr disc via using FTIR instrument 4200 Jasco Spectrophotometer. Additionally, the UV-Visible spectra were obtained using Shimadzu UV-Vis. 160 Spectrophotometer in the spectral range of 200-1000 nm. Magnetic properties of metal complexes were determined via measuring the magnetic susceptibility at 25 °C using (Magnetic Susceptibility Balance) Johnson Mathey Catalytic Systems Division. To determine the melting point for all of the synthesized compounds, a melting point apparatus Gallenkamp M.F600.010 F was used. Elemental microanalysis was performed using elemental analyzer model 550 Carlo-Erba Instruments (Italy) microwave moulinex Model-MW-83 (France).

1)-Synthesis of [2-amino-5-(2-hydroxyphenyl)-1,3,4-thiadiazol][A], [12]

This ligand was synthesized via reproducing the established protocol in [16]. In short, a mixture of salicylic acid (0.1 mol 12.2 g), thiosemicarbazide (0.1 mol 9.1 g) and (40 ml) of POCl\(_3\) was heated gently for 3 hours followed by cooling via adding 250 mL of ultrapure water, and then refluxed for 4 hours as depicted in Scheme.1. Thereafter, the mixture was cooled, and filtered. The supernatant neutralized with KOH and recrystallized using ethanol as a solvent. Melting point (m.p.), yield, and elemental analysis data are summarized in Table (1).

2)-Synthesis of 2-{5-(Pyridin-2-ylmethylen)-amino} 1,3,4-thiadiazol-2-ylphenol [L]

Method (1): A mixture of [2-pyridine carboxaldehyde] and the [2-amino-5-(2-hydroxyphenyl-1,3,4-thiadiazol) at 1:1 mole ratio was made in 99.99% ethanol (25 ml) with adding (3) few drops of glacial acetic acid, and then refluxed for 4 hours. Thereafter, the mixture was left to get cool down to room temperature. The resulting mixture was filtered, dried, and recrystallized using a mixture of methanol and ethanol as solvents (1:1) to give yellow powder.

Method (2): A mixture of [2-pyridine carboxaldehyde and the (2-amino-5-(2-hydroxy-phenyl-1,3,4-thiadiazol) at 1:1 mole ratio was prepared and well grinded using a mortar, then dried and irradiated by a microwave of 240 W for a period of 7 minutes. Thereafter, the reaction mixture was left to cool down and the product was recrystallized 2 times using a mixture of methanol and ethanol (1:1) to give a yellow powder. The yield and the elemental analysis data are also displayed in Table (1).

![Scheme (1) The synthesis protocols of (A) and (L) ligands.](image)

**Preparation of Metal Complexes**

**Method (1):** A set of solutions of Co(II), Ni(II), Cu(II) or Zn(II) was made, and then being added to the ligand solution 1:1 mole ratio. These mixtures were stirred for 2 hours with heating up to 50 °C. Colored crystalline were obtained at room temperature. The obtained solutions were filtered, washed with ultrapure water, recrystallized, and finally dried at 50 °C.

**Method (2):** The metal complexes were prepared exactly as in method (1), except that stirring was substituted by sonication for 60 minutes. The elemental analysis data for complexes obtained from method (1) and (2) are summarized in Table (1).

**Results and Discussion**

As mentioned earlier in the experimental section, the ligand (A) was successfully synthesized according to a reported procedure and then ligand (L) was synthesized and well characterized.
The (L) ligand was involved in complexation reactions with Co (II), Ni (II), Cu (II), and Zn (II).

The metal: ligand proportion in these complexes was determined by Job methods and mole ratio. The outcome results from these methods were very consistent and revealed that 2:2 ratio was dominant in all metal aforementioned complexes. Regarding the stability of these complexes, we observed that (A) and (L) ligands and the latter complexes were decomposed at their intrinsic melting points. The decomposition points (melting), color and other absorption characteristics of ligands and their complexes are shown in Table (1 and 2). These bands were further categorized into three main groups: The intermolecular transitions which were spotted in the UV region, charge transfer from ligand to metal, and d-d transitions represented in the UV-Visible region (200-900) nm.

Back to the synthesized L, the chemical structure of was confirmed via conducting FTIR and 1H-NMR spectral measurements.

The FT-IR spectrum showed the absence of the two absorptive bands of (−NH2) stretching vibrations (symmetric and asymmetric). Furthermore showed all the suggested bonds for olefinic groups (C−H), (C=C) aromatic, endocyclic (C=N) and exocyclic imine group. Stretching vibrations in addition to bending that be observed in substituted aromatic ring. stretching band near the region (1206-1277cm⁻¹) was observed to the all prepared compounds (Schiff bases) that attributed to (=N−N=C−) cyclic group; 3441 cm⁻¹ (υ OH Stretching), a band at 1439 cm⁻¹ due to (vibration of Pyridin ring), 1601 cm⁻¹ (υ C=N Stretching of amine), All the spectroscopic characteristics for other remaining compounds are listed in Table (3).

1H-NMR spectrum of ligand [L] Fig. (1), shows the following characteristic chemical shift, (CDCL₃-d₆) ppm. The four aromatic ring protons (δ 6.124 -8.085) ppm, (m,8 H, Ar and pyridin), the signal at (δ 9.669) assigned to (N=C−H) proton (azomethine), the signal at δ=11.870 (s, 1H, OH), δ 1.571 (solvent).

The positive ion mass spectral analysis of (L) was located at m/z 282.4. (M+1) Fig.(2), confirmed the predicted molecular weight which is (282.6).
The characterization data of the prepared compounds/Found (calculated).

<table>
<thead>
<tr>
<th>Compound Formula</th>
<th>Yield (%)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>Cl</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>A C₆H₂N₂O₂</td>
<td>70%</td>
<td>49.70 (49.73)</td>
<td>3.62 (3.65)</td>
<td>21.77 (21.75)</td>
<td>8.28 (8.28)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>L C₁₂H₁₀N₄O₂</td>
<td>78%</td>
<td>59.80 (59.56)</td>
<td>3.45 (3.57)</td>
<td>19.67 (19.85)</td>
<td>11.44 (11.36)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Co₂ (L)₂ (H₂O)₄] Cl₂</td>
<td>75%</td>
<td>40.84 (40.12)</td>
<td>3.18 (3.73)</td>
<td>13.61 (12.93)</td>
<td>7.79 (7.11)</td>
<td>8.61 (9.11)</td>
<td>14.31</td>
</tr>
<tr>
<td>[Ni₂ (L)₂(H₂O)₄] Cl₂</td>
<td>76%</td>
<td>40.86 (40.33)</td>
<td>3.18 (3.55)</td>
<td>13.62 (12.87)</td>
<td>7.79 (7.98)</td>
<td>8.62 (8.86)</td>
<td>14.26</td>
</tr>
<tr>
<td>[Cu₂ (L)₂(H₂O)₄] Cl₂</td>
<td>75%</td>
<td>40.39 (40.55)</td>
<td>3.15 (3.27)</td>
<td>13.46 (12.96)</td>
<td>7.70 (7.89)</td>
<td>8.52 (8.93)</td>
<td>14.26</td>
</tr>
<tr>
<td>[Zn₂ (L)₂(H₂O)₄] Cl₂</td>
<td>69%</td>
<td>40.21 (40.61)</td>
<td>3.13 (3.09)</td>
<td>13.40 (13.89)</td>
<td>7.67 (8.09)</td>
<td>8.48 (8.65)</td>
<td>15.64</td>
</tr>
</tbody>
</table>

Physical and electronic information of ligand and complexes in DMF.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Dec. Point °C</th>
<th>Conductivity (OHM⁻¹.CM⁻¹.MOL⁻¹)</th>
<th>Magnetic Moment (B.M)</th>
<th>Color</th>
<th>Absorption Bands (nm)</th>
<th>Assigned Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>285d</td>
<td>–</td>
<td>–</td>
<td>White</td>
<td>215</td>
<td>π → π*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>380</td>
<td>n → π*</td>
</tr>
<tr>
<td>[Co₂ (L)₂ (H₂O)₄] Cl₂</td>
<td>285</td>
<td>136</td>
<td>4.43</td>
<td>Brawn</td>
<td>755</td>
<td>ℏ₁g → ℏ₂g</td>
</tr>
<tr>
<td>[Ni₂ (L)₂(H₂O)₄] Cl₂</td>
<td>310</td>
<td>137</td>
<td>2.9</td>
<td>Bluish green</td>
<td>585</td>
<td>ℏ₁g(Π) → ℏ₂g(Π)</td>
</tr>
<tr>
<td>[Cu₂ (L)₂(H₂O)₄] Cl₂</td>
<td>320 d</td>
<td>150</td>
<td>1.61</td>
<td>Brawn</td>
<td>940</td>
<td>ℏ₂g → ℏ₂g(Π)</td>
</tr>
<tr>
<td>[Zn₂ (L)₂(H₂O)₄] Cl₂</td>
<td>310</td>
<td>129</td>
<td>–</td>
<td>Of White</td>
<td>565, 635</td>
<td>ℏ₂g → ℏ₂g</td>
</tr>
</tbody>
</table>

Infrared spectral analysis of metal complexes

The IR spectral data of the ligands revealed a (ν O–H) (weak hydrogen bonded) located at 3441 cm⁻¹. The disappearance of this absorption band from all obtained metal-complexes spectra confirms the disappearance of the proton of the hydroxyl group of the benzene ring throughout the complexation. The narrow and high intensity band at 1595 cm⁻¹ in the ligands was assigned to νC=N (azomethine). A shift (Δν = 8-24 cm⁻¹) in νC=N (azomethine) was observed as a result of coordination suggesting that the nitrogen of azomethine group contributed in the coordination. All of the complexes showed a broad band in the region (3241-3281) cm⁻¹ which may be ascribed to the (ν O–H) band of coordinated water, [17]. In relation to the octahedral geometry of the metal complexes, the coordination of two water molecules was expected.

The absorption bands at 451 cm⁻¹ in Co(II) complexes, 463 cm⁻¹ in Ni(II) complexes, 477 cm⁻¹ in Cu(II) and 464 cm⁻¹ in Zn(II) complexes might be attributed to metal-nitrogen stretching vibration [18,19]. All of the metal complexes took part in the coordination in the ligand on its own, the band at (1478-1419) cm⁻¹ was attributed to the stretching of (C–N=N–C) thiadizole ring. Upon complexation, this band was shifted to a high frequency region. In order to rationalize this shift, it has been shown in the literature that we are ware of that this is because of reducing the bond order of the carbon-nitrogen bond as a consequence of complexation of the metal to the ligand.
transition via nitrogen in (υC=N) compared to its respective ligands. In fact, it indicates that the nitrogen atom of the ring has nothing to do with participate in the complexation process. Nonetheless, in water containing complexes, this absorption band has been observed as a broad peak with structure which is assigned with coupling of the bending mode of coordinated complex, [20-22].

Table (3)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>v(C=N)</th>
<th>v Pyridin ring</th>
<th>v(C=N≡N=C)</th>
<th>v(M−O)</th>
<th>v (H2O)</th>
<th>v(O−H)</th>
<th>v(M–N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>1601 (s)</td>
<td>1439</td>
<td>1206-1277</td>
<td>–</td>
<td>–</td>
<td>3441</td>
<td>–</td>
</tr>
<tr>
<td>[Co2 (L)2(H2O)4]Cl2</td>
<td>1613(s)</td>
<td>1417</td>
<td>1236-1286m</td>
<td>552w</td>
<td>3275</td>
<td>–</td>
<td>451w</td>
</tr>
<tr>
<td>[Ni2 (L)2(H2O)4]Cl2</td>
<td>1625(s)</td>
<td>1423</td>
<td>1255-1293m</td>
<td>533w</td>
<td>3281</td>
<td>–</td>
<td>463w</td>
</tr>
<tr>
<td>[Cu2(L)2(H2O)4]Cl2</td>
<td>1609(s)</td>
<td>1429</td>
<td>1234-1267m</td>
<td>521w</td>
<td>3241</td>
<td>3378</td>
<td>477w</td>
</tr>
<tr>
<td>[Zn2(L)2(H2O)4]Cl2</td>
<td>1611(s)</td>
<td>1419</td>
<td>1246-1271m</td>
<td>512w</td>
<td>3255</td>
<td>3295</td>
<td>464w</td>
</tr>
</tbody>
</table>

Mole Ratio Method

In this method, the concentration of the metal ions was maintained constant with enabling the ligands concentrations to be varied, [21]. A set of metal-complex solutions was prepared in ethanol with different metal:ligand ratios. The absorbances of these solutions were measured by using UV spectrophotometer at λmax of the expected complex M2L2.

All of the aforementioned spectroscopic, elemental, and magnetic measurements allowed us to suggest the following chemical structure of the metal complexes that we prepared in this effort as depicted in Fig.(3).

Fig.(3) The proposed chemical structure of the M-L complexes based on the obtained electronic and NMR data.

Conclusion

In conclusion, the ligand 2-(5-(Pyridin-2-ylmethylene)-amino)-1,3,4-thiadiazol-2-ylphenol was successfully synthesized and characterized by NMR and UV-Visible spectroscopic measurements.

The prepared metal complexes were characterized as well using UV-Visible spectrometry and the chemical structure of the coordination complexes was proposed based on the data obtained from the aforementioned technique. The information presented here will pave the way for using these metal complexes in various scientific applications.

References