Synthesis, Spectroscopic and Thermodynamic Studies of Metal Complexes with Schiff Bases Derived from 2-[5-(Pyridin-2-ylmethylene)-amino] 1,3,4-Oxadiazol-2-yl-Phenol

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Abstract
New metal complexes of the ligand 2-[5-(Pyridin-2-ylmethylene)-amino] 1,3,4-thiadiazol-2-yl-phenol (L) with the metal ions Co(II), Ni(II), Cu(II) and Zn(II) were prepared in alcoholic medium. The Schiff base was condensed [2-pyridine carboxaldehyde] with [2-amino-5-(phenyl-1,3,4-oxadiazole] in alcoholic medium. Two tetradentate Schiff bases ligand were used for complexation upon two metal ions of Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ as dineuclear formula M₂L₂. The synthesized compound and their metal complexes were characterized by FTIR Spectroscopy, electronic spectroscopy, Elemental analysis, magnetic susceptibility measurements, thermal analysis , ¹H-NMR spectra, and mass spectra. The activation thermodynamic parameters such as ΔE*, ΔΗ¹, ΔS¹ and ΔG¹ were calculated from the TGA curve using Coats-Red fern method. From the measurements, structures of the complexes were proposed.

Keywords: Schiff base, Microwave synthesis, Thermodynamic Parameters.

Introduction
A large number of Schiff base compounds derived from aromatic amines and aromatic aldehydes have a wide range of applications in many fields like biological, inorganic and analytical chemistry [1]. Increasing physiological importance of nitrogen and oxygen donor organic compounds and active role played by coordination certain metal ions to them. Have interested use in synthesizing and studying structural aspects of metal complexes with some oxygen and nitrogen donor ligands [2].

Literature survey reveals that out of various isomers particularly 1,3,4-oxadiazole derivatives exhibit wide range of biological activities [3]. Also various route for the synthesis of 1,3,4-oxadiazole have been reported[4-6]. These activities are probably due to the presence of the—N=C–O group [7]. Pyridin; oxadiazol and its derivatives form an important class of organic compounds due to their structural chemistry and biological activities as analgesic, antipyretics and anti-inflammatory [8]. In addition Pyridin can form a variety of Schiff bases are reported to be superior reagents in biological, clinical and analytical applications [9,10]. In continuation of 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-oxadiazole. Preparation and characterization of above metal ion complexes with this Schiff bases are reported here. Where, HL is a Schiff base of 2-amino-5-(2-hydroxy-phenyl-1,3,4- oxadiazol with Pyridin Matel ion complexes with some oxygen and nitrogen donor ligands[11]. From the TGA curves recorded for the successive steps in the decomposition process of these ligand and complexes it was possible to determine the following characteristic thermal parameters for each reaction step: Initial point temperature of decomposition (Ti): the point at which TG curve starts deviating from its base line. Final point temperature of decomposition (Tf): the point at which TG curve returns to its base line. Peak temperature, i.e. temperature of maximum rate of weight loss: the point obtained from the intersection of tangents to the peak of TG curve. Mass loss at the decomposition step (Dm): it is the amount of mass that extends from the point Ti up to the reaction end point Tf on the TG curve, i.e. the magnitude of the ordinate of a TG curve. The material released at each step of the decomposition is identified by attributing the mass loss (Dm) at a given step to the component of similar weight calculated from the molecular formula of the investigated complexes, comparing that with literatures of
relevant compounds considering their temperature. This may assist identifying the mechanism of reaction in the decomposition steps taking place in the complexes under study. Activation energy (E) of the composition step: the integral method used is the Coats-Redfern equation \[12\]. for reaction order \(n \neq 1\) or \(n = 2\), which when linearised for a correctly chosen \(n\) yields the activation energy from the slop:

\[
\log \left( \frac{1-(1-a)^{1-n}}{1-(1-a)^{1-1}} \right) = \log \left( \frac{Z R}{a q^E \left( \frac{1}{2RT} \right) \left( \frac{1}{E} \right)} \right) \cdot \frac{E}{2.303RT} \quad \text{……}\quad n \neq 1
\]

\[
\log \left( \frac{1-(1-a)^{1-1}}{1-(1-a)^{1-1}} \right) = \log \left( \frac{Z R}{a q^E \left( \frac{1}{2RT} \right) \left( \frac{1}{E} \right)} \right) \cdot \frac{E}{2.303RT} \quad \text{……}\quad n = 1
\]

\[
\Delta S^* = 2.303R \log(\frac{AH/K}{T_{max}}), \quad \Delta H^* = E - RT_{max}, \quad \Delta G^* = \Delta H^* - T_{max} \Delta S^* \quad \text{where:}
\]

\(a\) = fraction of weight loss, \(T\) = temperature (°K), \(n\) = order of reaction, \(A\) or \(Z\) = pre-exponential factor, \(R\) = molar gas constant, \(E\) = activation energy and \(q\) = heating rate.

Order of reaction (n): it is the one for which a plot of the Coats-Redfern expression gives the best straight line among various trial values of \(n\) that are examined relative to that estimated by the Horovitz-Metzger method \[13\].

Experimental

All chemical used were of reagent grade (supplied by either sigma Aldrich or fluka) and used as supplied. The FTIR spectra in the range \((4000-400)\) cm\(^{-1}\) cut were recorded as KBr disc on FTIR.4200 Jasco Spectrophotometer. The UV-Visible spectra were measured in ethanol using Shimadzu UV-Vis. 160 A-Ultra-violet Spectrophotometer in the range \((200-1000)\) nm. Magnetic Susceptibility measurement for complexes were obtained at room temperature using (Magnetic Susceptibility Balance) Jhnson Mattey Catalytic Systems Division. Gallencamp M.F.B600.010 F melting point apparatus were used to measure the melting point of all the prepared compounds. Elemental microanalysis was carried out using Elemental Analyzer Model 5500 Carlo-Erba Instruments (Italy) microwave monelax.

1)- Synthesis of [2-amino-5-(2-hydroxy-phenyl-1,3,4-oxadiazole)]\[14\] [A]

A-Synthesis Semicarbazone: Semicarbazide Hydrochloride (0.1 mol) and sodium acetate (0.2 mol) were added and dissolved in 15-20mL of distilled water placed in flat-bottomed flask. In a separate beaker containing required Salicylaldehyde (0.1 mol) was dissolved in absolute alcohol. This ethanolic aromatic aldehyde solution was added slowly to the solution of semicarbazide hydrochloride. The precipitate, were separated, was filtered, dried and recrystallised from 95% hot ethanol.

B-Semicarbazone (0.1 mol) and sodium acetate (0.2 mol) was dissolved in 300-400 mL of glacial acetic acid with continuous stirring. Bromine (7 mL in 50 mL of GAA) was added slowly to it. Solution was stirred for an hour and then poured on crushed ice. The resulting solid was separated, dried and recrystallised from hot ethanol (95%) yield, elemental analysis is show in Table (1).

2)-2-[5-(Pyridin-2-ylmethylene)-amino]1,3,4-oxadiazol-2-yl-phenol [L]

Method (1): A mixture of equimolar amounts (0.05 mol) of appropriate [2-pyridine carboxaldehyde] and the [2-amino-5-(2-hydroxy-phenyl-1,3,4-oxadiazole)], in absolute ethanol (25 ml) with (3) drops of glacial acetic acid was refluxed (4) hours. The reaction mixture was then allowed to cool at room temperature, and the precipitate was filtered, dried, and recrystallized from mixture (methanol and ethanol) (1:1) to give yellow powder.

Method (2): A mixture of equimolar amounts (0.05 mol) of appropriate [2-pyridine carboxaldehyde] and the (2-amino-5-(2-hydroxy-phenyl-1,3,4-oxadiazole), were ground with a mortar, mixed, dried and subjected to microwave irradiation 240W for (15) minutes, after completion the reaction mixture was cooled to room temperature the solid obtained was recrystallized twice from mixture (methanol and ethanol) (1:1) to give yellow powder, yield, elemental analysis is show in Table (1).
Preparation of complexes

Method (1): An ethanol solution of the metal salt of Co(II), Ni(II), Cu(II) or Zn(II) were added to an ethanolic solution of (L) in 1:1 (metal : ligand) molar ratios. Stirring for 2 hours with heating 70 oC, crystalline colored precipitates formed after cooling at room temperature, the resulting solids were filtered off, washed with distilled water, dried and recrystallized from ethanol and dried at 50 oC.

Method (2): An ethanol solution of the metal salt of Co(II), Ni (II), Cu (II) or Zn (II) were added to an ethanolic solution of (L) in 1:1 (metal : ligand) molar ratios. And put in ultrasonic bath heating 65 oC. After 50 mints crystalline colored precipitates formed after cooling at room temperature, the resulting solids were filtered off, washed with distilled water, dried and recrystallized from ethanol and dried at 50 oC. yield, C.H.N.S analysis are shown in Table (1).

Result and Discussion

The synthetic procedure of Schiff base ligand are presented in Scheme (1). The reactions of divalent transition metal ions viz., Co(II), Ni(II), Cu(II) and Zn(II). The composition of the complexes formed in solution has been established by mole ratio and job methods. In both cases the results reveals (2:2) metal to ligand ratio yielded the corresponding metal chelates. Shows the decomposition point, color and electronic absorption bands for ligand and complexes in Table (1, 2). The bands are classified into three distinct groups: The intermolecular transitions appear in the UV region, charge transfer from ligand to metal, and d-d transitions appear in the UV-Visible region.

1-[2-amino-5-(2-hydroxy-phenyl-1,3,4-oxadiazole) [A]

The reaction of Semicarbazide Hydrochloride with Salicylaldehyde in presence of sodium acetate/Br2 afforded 2-amino-5-phenyl-1,3,4-oxadiazole[14]. The structural assignment of the product was based on it's melting point and spectral (FT-IR and UV/Vis.) data in Table (1, 2). The FT-IR spectrum of compound (A) exhibited significant two band in the range (3402–3213)cm⁻¹ which could be attributed to asymmetric and symmetric stretching vibrations of NH₂ group. band in the (3428) cm⁻¹ stretching vibrations of (OH). Besides this, band at about (1475-1423 cm⁻¹) due to cyclic (C = N) stretching is also observed. Bands at (1518cm⁻¹) and (1484cm⁻¹) are due to the (N-H) bending and (C-N) stretching vibrations, respectively [15,16].

2) 2-[5-(Pyridin-2-ylmethylene)-amino] 1,3,4-oxadiazol-2-yl-phenol [L]

The FT-IR spectra show the disappearance of the two absorption bands due to (-NH₂) stretching of amino oxadiazole [L] showed all the suggested bonds for olefinic (C-H), (C=C) aromatic, endocyclic (C=N) and exocyclic imine group. Stretching vibrations in addition to out of plane bending of substituted aromatic ring. All the prepared compounds (Schiff bases) exhibited the stretching band near the region (1419-1478 cm⁻¹) this due to (=N-N=C-) cyclic group; 3426 cm⁻1 (υ OH Stretching), a band at 1415-1469 cm⁻¹ attributed to (vibration of Pyridin ring), 1595cm⁻¹ (υ C=N Stretching of amine), 1229 cm⁻¹, 1468 cm⁻¹ (Characteristic bands of oxadiazole ring). All the spectral data for other compounds are listed in Table (3).
$^1$H-NMR spectrum of compounds [L] Fig.(1), shows the following characteristic chemical shift, (CDCl$_3$-d$_6$) ppm. The four aromatic ring protons ($\delta$ 7.285 -8.696) (s,4H, Ar), and four Pyridin ring appeared protons at ($\delta$ 6.144 – 7.18) ppm, the signal at ($\delta$ 8.885) attributed to (N=C-H) proton (azomethine), the signal at $\delta$=10.874 (s, 1H, OH), $\delta$ 1.572 (Solvent organic).

The positive ion mass spectral analysis of (L) observe at m/z 266.4. (M+1) Fig.(2), confirms the theoretical molecular weight i.e. 266.25.

**Fig.(1): $^1$H-NMR For the ligand (L).**

**Fig.(2): LC-MS for ligand (L).**
υC=N (azomethine) is observed upon coordination indicating that the nitrogen of azomethine group is involved in coordination. All the complexes show broad band in the region (3295-3378) cm⁻¹ which may be assigned to ν O-H) of coordinated water[17]. To account for the octahedral stereochemistry of the metal complexes, the coordination of two water molecules is expected.

The bands at 541 cm⁻¹ in Co(II) complexes, 591 cm⁻¹ in Ni(II) complexe, 590 cm⁻¹ in Cu(II) complexe and 575 cm⁻¹ in Zn(II)
complex may be due to metal-nitrogen stretching vibration[18,19]. All the metal complexes involved in coordination in the free ligand, the band at (1478-1419) cm\(^{-1}\) is assigned to the stretching of (C-N=N-C) oxadizole ring. On complexation, this band was shifted to a high frequency region. This shift is probably due to the lowering of bond order of the carbon-nitrogen bond resulted from complexation of the metal to the ligand through nitrogen in (υC=N) compared to its respective ligands. This suggests that the nitrogen atom of the ring has not participated in the chelation. However, in water containing chelates, this band is observed as a broad with structure this may be due to coupling of the bending mode of coordinated [20].

Table (3)

Infrared data of Ligand and its metal complexes (cm\(^{-1}\)).

<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>1595(s)</td>
<td>1415</td>
<td>1478-1419</td>
<td>-</td>
<td>3275</td>
<td>-</td>
<td>3395</td>
</tr>
<tr>
<td>[Co2 (L)2 (H2O)4] Cl2</td>
<td>1610(s)</td>
<td>1427</td>
<td>1488-1431</td>
<td>483w</td>
<td>3275</td>
<td>-</td>
<td>541w</td>
</tr>
<tr>
<td>[Ni2 (L)2(H2O)4] Cl2</td>
<td>1617(s)</td>
<td>1427</td>
<td>1491-1433</td>
<td>534w</td>
<td>3281</td>
<td>-</td>
<td>591w</td>
</tr>
<tr>
<td>[Cu2 (L)2(H2O)4] Cl2</td>
<td>1603(s)</td>
<td>1431</td>
<td>1489-1430</td>
<td>448w</td>
<td>3241</td>
<td>3378</td>
<td>590w</td>
</tr>
<tr>
<td>[Zn2 (L)2(H2O)4] Cl2</td>
<td>1611(s)</td>
<td>1434</td>
<td>1479-1433</td>
<td>483w</td>
<td>3255</td>
<td>3295</td>
<td>575w</td>
</tr>
</tbody>
</table>

Thermal analysis

To understand thermal decomposition process, Schiff bass and its metal complexes were examined by thermo gravimetric analysis in the temperature range of 35–700 °C Fig.(3). The obtained thermo analytical results from TGA curves for all these compounds are given in Table (4). The decomposition was completed at 693 °C for all the complexes. The data from the thermo gravimetric analyses indicated that the decomposition of the complexes and the ligand proceeds in (two or three) steps. The final decomposition products were metal oxide mixture formed above 598 °C for the metal [21]. Plot log K against 1/T °K and determine the slope of the straight line relation, calculate of the values of the kinetic and thermodynamic factors (n order of reaction, Z (pre-exponential factor), (ΔS*) entropy, (ΔH*) enthalpy, (ΔG*) Gibbs free energy) from Table (4) thermal analysis (TG) curves by way Coates Radefrn Coats- Redfern.

We find that the positive values for (ΔG*) indicate that interactions is automatic (non-spontaneous) in the case of transformation. The negative values for (ΔS *) indicate that ligand have a more structured installation (more ordered structure) of the reactants and the reactions are slow more than the natural or formal. As for the positive (ΔH* values) indicate that interactions endothermic). Negative values indicate that the interactions conducive to heat and small values of the coefficient of (Z) show that the fast dissociation reactions ligand while large positive values and when the case can be classified as slow-moving reactions.
In this investigation, the concentration of the metal ions were maintained constant and the ligands concentrations were varied [21], so a series of metal-ligand aqueous ethanolic solutions were prepared with different [L]/[M] ratios. The absorptions of these solutions were measured using UV spectrophotometer at λ max of the expected complex M₂L₂.

Absorbance versus [L]/[M] curves were drawn for all complexes.

From the FTIR Spectroscopy, electronic spectroscopy, Elemental analysis, magnetic susceptibility measurements, thermal analysis suggest the following structure.

**Table (4)**

Thermodynamic parameters of the ligand and metal complexes.

<table>
<thead>
<tr>
<th>Sample (step)</th>
<th>T.range °C</th>
<th>N</th>
<th>R²</th>
<th>T.m.ax °K</th>
<th>Ea KJ mol⁻¹</th>
<th>Δ H* KJ mol⁻¹</th>
<th>ZSec x10⁻²</th>
<th>Δ S* J mol⁻¹K⁻¹</th>
<th>Δ G* KJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁(1)</td>
<td>37-380</td>
<td>1</td>
<td>0.99</td>
<td>545.50</td>
<td>70.25</td>
<td>65.53</td>
<td>16.66</td>
<td>-230.2</td>
<td>190.45</td>
</tr>
<tr>
<td>L₁(2)</td>
<td>380-700</td>
<td>0.9</td>
<td>0.99</td>
<td>840.50</td>
<td>-11.23</td>
<td>-18.11</td>
<td>4.3 x10⁻⁵</td>
<td>-375.3</td>
<td>279.21</td>
</tr>
<tr>
<td>Co₁(1)</td>
<td>37-370</td>
<td>0.9</td>
<td>0.99</td>
<td>476.4</td>
<td>31.57</td>
<td>27.62</td>
<td>7.25</td>
<td>-291.78</td>
<td>165.65</td>
</tr>
<tr>
<td>Co₁(2)</td>
<td>370-470</td>
<td>0.9</td>
<td>1</td>
<td>644.21</td>
<td>-7.92</td>
<td>-12.17</td>
<td>5.6</td>
<td>-355.84</td>
<td>214.09</td>
</tr>
<tr>
<td>Co₁(3)</td>
<td>470-700</td>
<td>0.9</td>
<td>0.99</td>
<td>766.6</td>
<td>-6.65</td>
<td>-13.282</td>
<td>6.35</td>
<td>-352.37</td>
<td>260.62</td>
</tr>
<tr>
<td>Ni₁(1)</td>
<td>37-140</td>
<td>0.9</td>
<td>0.99</td>
<td>384</td>
<td>20.45</td>
<td>16.92</td>
<td>0.00451</td>
<td>-312.457</td>
<td>136.17</td>
</tr>
<tr>
<td>Ni₁(2)</td>
<td>140-390</td>
<td>0.9</td>
<td>0.99</td>
<td>507</td>
<td>36.5</td>
<td>32.2919</td>
<td>0.017</td>
<td>-287.19</td>
<td>175.8</td>
</tr>
<tr>
<td>Ni₁(3)</td>
<td>390-700</td>
<td>0.9</td>
<td>0.99</td>
<td>775.12</td>
<td>-11.19</td>
<td>-17.62</td>
<td>35.4</td>
<td>-259.25</td>
<td>259.25</td>
</tr>
<tr>
<td>Cu₁(1)</td>
<td>37-170</td>
<td>0.9</td>
<td>0.99</td>
<td>423</td>
<td>123.9</td>
<td>46.49</td>
<td>7.68</td>
<td>-222.79</td>
<td>135.39</td>
</tr>
<tr>
<td>Cu₁(2)</td>
<td>170-400</td>
<td>0.9</td>
<td>0.99</td>
<td>554</td>
<td>54.24</td>
<td>121.04</td>
<td>0.5357</td>
<td>-101.22</td>
<td>170.56</td>
</tr>
<tr>
<td>Cu₁(3)</td>
<td>400-700</td>
<td>0.9</td>
<td>1</td>
<td>726.35</td>
<td>-5.734</td>
<td>4.91</td>
<td>-359.81</td>
<td>311.7</td>
<td></td>
</tr>
<tr>
<td>Zn₁(1)</td>
<td>37-160</td>
<td>1</td>
<td>0.99</td>
<td>525</td>
<td>8.26</td>
<td>3.9</td>
<td>4.3 x10⁻⁶</td>
<td>-352.4</td>
<td>187.67</td>
</tr>
<tr>
<td>Zn₁(2)</td>
<td>160-430</td>
<td>0.9</td>
<td>0.99</td>
<td>678</td>
<td>-10.22</td>
<td>-15.85</td>
<td>3.9 x10⁻⁶</td>
<td>-355.3</td>
<td>225.23</td>
</tr>
<tr>
<td>Zn₁(3)</td>
<td>430-700</td>
<td>0.9</td>
<td>0.99</td>
<td>810</td>
<td>-10.86</td>
<td>-17.69</td>
<td>3.4 x10⁻⁶</td>
<td>-357.9</td>
<td>279.75</td>
</tr>
</tbody>
</table>

**Molar Ratio Method**

In this investigation, the concentration of the metal ions were maintained constant and the ligands concentrations were varied [21], so a series of metal-ligand aqueous ethanolic solutions were prepared with different [L]/[M] ratios. The absorptions of these solutions were measured using UV spectrophotometer at λ max of the expected complex M₂L₂.
References


الخلاصة

حضرت معقدات جديد نوع [M_2(L)_2(H_2O)_4] Cl_2

حيث [M=Co(II), Ni(II), Cu(II) or Zn(II)]

باستخدام الليكند L والتي

1,3,4-thiadiazol-2-yl-phenol

حضرت من تفاعل 5-(2-هيدروكسى فينيل)1,3,4-

واكساديازول مع 2- برين كرووكسي الدهادى في الكحول

النتيجة، شحخت المعقدات المحضرة بتقنية أطياف الأشعة تحت الحمراء وأطياف الإلكترونية وظيف الكثافة و النتيجة

المغنطيسى البروتوني والتحليل الحراري وكانما حددت

البارامترات الترموديناميكية" G avec

باعتماد معادلة Coats-Red fern

للمركبات وذلك مرحلة من مراحل التحلل، فضلاً عن قياس

الحساسية المغناطيسية. كما استخدم التحليل العنصري