Spectroscopic and structural studies of some transition metal complexes of a synthetic ligands derived from 4-acetylpyridine

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ABSTRACT
Co(II), Ni(II) and Cu(II) complexes with novel heterocyclic ligands derived from 4-acetylpyridine and thiosemicarbazide were synthesized and characterized by elemental analysis, molar conductance, spectral methods (mid infrared, 1H-NMR, mass and UV/vis spectra) and simultaneous thermal analysis (TG and DTG) techniques. The molar conductance measurements proved that all complexes are electrolytes compared with their ligands. The IR spectra of the two ligands and their complexes are used to identify the type of bonding. The kinetic thermodynamic parameters such as: E*, ΔH*, ΔS* and ΔG* are estimated from the DTG curves. The free ligands and their complexes have been studied for their possible biological activity (antibacterial and antifungal).

KEYWORDS
4-acetylpyridine; Infrared spectra; Thermal analysis; 1H-NMR spectra; Microbiological screening.

INTRODUCTION
Metal complexes containing 4-pyridine moiety such as 1-(pyridine-4-yl) ethylidene) hydrazinecarbothioamide and 1-(pyridine-4-yl) ethylidene amino) 2-thioxoimidazolidin derivatives have aroused considerable interest in view of their industrial and biological importance.

Many of these compounds possess a wide spectrum of medicinal properties, including activity against tuberculosis, leprosy, and bacterial and viral infections. They have also been found to be active against influenza, protozoa, smallpox, psoriasis, rheumatism, trypanosomiasis, coccidiosis, malaria and certain kinds of tumors and have been suggested as possible pesticides and fungicides. Their activity has frequently been thought to be due to their ability to chelate trace metals[1-5].

The present study discuss the synthesis, spectroscopic and structural studies of some transition metal complexes of a synthetic ligands derived from 4-acetylpyridine.
scopic characterization and biological screening of heterocyclic ligands derived from 4-acetylpyridine with thiosemicarbazide towards Co(II), Ni(II) and Cu(II) ions.

**EXPERIMENTAL**

**Materials and instrumentation**

All chemicals were reagent grade and were used without further purification. 4-acetylpyridine, thiosemicarbazide and chloro acetic acid were purchased from Fluka Chemical Co., CoCl$_2$.6H$_2$O, NiCl$_2$.6H$_2$O and CuCl$_2$.2H$_2$O from (Merck Co.).

Carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer CHN 2400 in the Micro-analytical Unit at the Faculty of Science, Cairo University, Egypt. The metal content was found gravimetrically by converting the compounds into their corresponding oxides.

IR spectra were recorded on Bruker FTIR Spectrophotometer (4000-400cm$^{-1}$) in KBr pellets. The UV–vis, spectra were determined in the DMSO solvent with concentration (1.0 $\times$ 10$^{-3}$M) for the free ligands and their complexes using Jenway 6405 Spectrophotometer with 1cm quartz cell, in the range 200-800nm. Molar conductivities of freshly prepared 1.0 $\times$ 10$^{-3}$ mol/dm$^3$...
DMSO solutions were measured using Jenway 4010 conductivity meter.

1H-NMR spectrum of the two ligands (L1 and L2), Ni-L1, and Cu-L2 complexes were recorded on Varian Gemini 200 MHz spectrometer using DMSO-d6 as solvent and TMS as an internal reference. The purity of the two ligands, L1-Cu and L2-Co were checked from mass spectra at 70eV by using AEI MS 30 Mass spectrometer. Thermogravimetric analysis (TGA and DTG) were carried out in dynamic nitrogen atmosphere (30ml/ min) with a heating rate of 10 C/min using a Schimadzu TGA-50H thermal analyzer.

**Synthesis of L1 and L2**

[(2-(1-pyridin-4-yl) ethyldiene)-4-hydrazine-carbothioamide] [L1]

A mixture of 4-acetylpyridine (12.1gm, 0.1 mole), thiosemicarbazide (12gm, 0.13 mole) and methanol (100ml) was heated under reflux for 2 hr. after cooling the precipitate was filtered off, washed with methanol, crystallized from methanol to give white crystals.

[(2-(2-(1-(pyridine-4-yl) ethyldene) hydrazine-carbothioamido) acetic acid) [L2]

A mixture of (L1) (0.1 mole), and chloroethylacetate (0.1mole) was added to solution of sodium methoxide (100ml) and heated under reflux for 2 hr. after cooling the precipitate was filtered off, crystallized from methanol to give yellow crystals.

**Synthesis of the complexes**

A general method is: the desired weight of the free ligands was dissolved in 30 ml methanol and the solution was adjusted to pH 7.0 by addition of methanolic solution of ammonium hydroxide. The metal salts were dissolved in 20 ml of methanol and then the prepared solutions were slowly added to the solution of the ligand under magnetic stirring. After heating for about 1 h, the obtained precipitates were filtered off, wash with hot methanol and dried at 60°C.

**Microbiological screening**

For these investigations the hole well method was applied. The investigated isolates of bacteria were seeded in tubes with nutrient broth (NB). The seeded NB (1cm3) was homogenized in the tubes with 9cm3 of melted (45°C) nutrient agar (NA). The homogeneous suspensions were poured into Petri dishes. The holes (diameter 4 mm) were done in the cool medium. After cooling in these holes, 2 x 10⁻³ dm³ of the investigated compounds were applied using a micropipette. After incubation for 24 h in a thermostat at 25-27°C, the inhibition (sterile) zone diameters (including disc) were measured and expressed mm. An inhibition zone diameter over 7mm indicates that the tested compound is active against the bacteria under investigation.

The antibacterial activities of the investigated compounds were tested against Bacillus Subtilis, Streptococcus Penumonia, Staphylococcus aureus (as Gram Positive Bacteria), Escherichia Coli and Pesudomonas
The complexes are air-stable, hygroscopic, with higher melting points, insoluble in H₂O and most of organic solvents, but soluble in DMSO and DMF.

Condensation of 4-acetylpyridine with thiosemicarbazide readily gives rise to the corresponding L₁ and L₂, which was easily identified by its IR, ¹H-NMR and mass spectra. Bidentate complexes were obtained upon reaction between metal ions of and L₁ and L₂ ligands at 1:1 molar ratio. The ligands L₁ and L₂ on reaction with CoCl₂.6H₂O, NiCl₂.6H₂O and CuCl₂.2H₂O salts, yield complexes corresponding to the general formula [CoL₁(H₂O)]Cl (I), [NiL₁(H₂O)]Cl₂.2H₂O (II), [CuL₁(H₂O)]Cl (III), [CoL₂(H₂O)]Cl (IV),

### RESULTS AND DISCUSSION

The results of the elemental analysis and some physical characteristics of the obtained compounds are given in TABLE 1.
The newly synthesized ligands and its complexes are very stable at room temperature in the solid state. The analytical data are in a good agreement with the proposed stoichiometry of the complexes. The metal-to-ligand ratio in the Co(II), Ni(II) and Cu(II) complexes was found to be 1:1.

**Molar conductivities of the metal chelates**

The molar conductivity values for the complexes in DMSO solvent (1.0 x 10^-3 mol) were in the range (114.30-311.60) μs. The molar conductivity measurements in the range of electrolytic nature (TABLE 1). Conductivity measurements have frequently been used in structural of metal chelates (mode of coordination) within the limits of their solubility. They provide a method of testing the degree of ionization of the complexes, the molecular ions that a complex liberates in solution (incase of presence anions outside the coordination sphere), the higher will be its molar conductivity and vice versa[8]. It is clear from the conductivity data, compared with the values of free ligands that the complexes present seem to be electrolytes. Also the molar conductance values indicate that the anions may be exhibits outside or absent or inside the coordination sphere. This result was strongly supported with the chemical analysis (elemental analysis data) where Cl⁻ ions are detected by addition of AgNO₃ solution. Also the conductivity values for L₁ complexes are greater than that for L₂, where they have two chlorine atoms.

**Infrared spectra**

The main IR data of the two ligands L₁, L₂ and their complexes are summarized in TABLE 2 and IR spectra are shown in Figure 1. The presence of the broad...
### TABLE 4: Thermal data of the L₁ and L₂ complexes (I-VI)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Steps</th>
<th>Temperature range (°C)</th>
<th>DTG peak (°C)</th>
<th>TG Weight loss (%)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Calc.</td>
<td>Found</td>
</tr>
<tr>
<td><strong>[CoL₁(H₂O)][Cl]₂</strong></td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>25-250</td>
<td>150</td>
<td>22.82</td>
<td>21.85 C₅H₇N (pyridine ring)</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>250-400</td>
<td>300</td>
<td>39.19</td>
<td>39.28 C₅H₇N₃Os (organic moiety)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>37.99 38.87 CoCl₂ (residue)</td>
</tr>
<tr>
<td><strong>[NiL₁(H₂O)]₂[Cl]₂·2H₂O</strong></td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>25-100</td>
<td>75</td>
<td>18.19 17.83</td>
<td>4H₂O</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>100-225</td>
<td>175</td>
<td>19.72 19.86</td>
<td>C₅H₇N (pyridine ring)</td>
</tr>
<tr>
<td></td>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>225-400</td>
<td>315</td>
<td>29.32 29.52</td>
<td>C₅H₇N₃S (organic moiety)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>32.77 32.79 NiCl₂ (residue)</td>
</tr>
<tr>
<td><strong>[CuL₁(H₂O)][Cl]₂</strong></td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>25-200</td>
<td>125</td>
<td>22.52 22.53</td>
<td>C₅H₇N (pyridine ring)</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>200-400</td>
<td>250</td>
<td>38.67 39.29</td>
<td>C₅H₇N₃Os (organic moiety)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>38.81 38.18 CuCl₂ (residue)</td>
</tr>
<tr>
<td><strong>[CoL₂(H₂O)]₂Cl</strong></td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>25-100</td>
<td>65</td>
<td>9.43 9.51</td>
<td>2H₂O</td>
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<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>100-400</td>
<td>250</td>
<td>61.61 60.05</td>
<td>C₁₀H₁₄N₃Os (organic moiety)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>28.96 30.44 CoO (residue)</td>
</tr>
<tr>
<td><strong>[NiL₂(H₂O)]₄Cl₂H₂O</strong></td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>25-225</td>
<td>65</td>
<td>23.83 23.51</td>
<td>6H₂O</td>
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<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>225-400</td>
<td>250</td>
<td>61.61 60.05</td>
<td>C₁₀H₁₄N₃Os (organic moiety)</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>28.96 30.44 NiO (residue)</td>
</tr>
<tr>
<td><strong>[CuL₂(H₂O)]₄Cl</strong></td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>25-150</td>
<td>115</td>
<td>12.79 12.52</td>
<td>3H₂O</td>
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<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>150-400</td>
<td>300</td>
<td>59.95 59.79</td>
<td>C₁₀H₁₄N₃O₂S (organic moiety)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>27.26 27.69 CuO (residue)</td>
</tr>
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</table>

### TABLE 5: Kinetic parameters using the Coats–Redfern (CR) and Horowitz–Metzger (HM) operated for the L₁ and L₂ complexes (I-VI)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Stage</th>
<th>Method</th>
<th>E (J mol⁻¹)</th>
<th>A (s⁻¹)</th>
<th>ΔS (J mol⁻¹ K⁻¹)</th>
<th>ΔH (J mol⁻¹)</th>
<th>ΔG (J mol⁻¹)</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>CR</td>
<td>6.82 × 10⁴</td>
<td>3.87 × 10⁶</td>
<td>-1.22 × 10²</td>
<td>6.48 × 10⁴</td>
<td>1.16 × 10⁴</td>
<td>0.9954</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HM</td>
<td>7.39 × 10⁴</td>
<td>2.14 × 10⁷</td>
<td>-1.07 × 10²</td>
<td>7.04 × 10⁴</td>
<td>1.15 × 10⁴</td>
<td>0.9994</td>
</tr>
<tr>
<td></td>
<td></td>
<td>average</td>
<td>7.10 × 10⁴</td>
<td>1.26 × 10⁷</td>
<td>-1.14 × 10²</td>
<td>6.76 × 10⁴</td>
<td>1.15 × 10⁴</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>CR</td>
<td>5.46 × 10⁴</td>
<td>7.09 × 10⁵</td>
<td>-1.75 × 10²</td>
<td>5.08 × 10⁴</td>
<td>1.32 × 10⁵</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HM</td>
<td>6.50 × 10⁵</td>
<td>1.94 × 10⁵</td>
<td>-1.47 × 10²</td>
<td>6.11 × 10⁴</td>
<td>1.79 × 10⁵</td>
<td>0.9995</td>
</tr>
<tr>
<td></td>
<td></td>
<td>average</td>
<td>5.98 × 10⁴</td>
<td>1.01 × 10⁵</td>
<td>-1.61 × 10²</td>
<td>5.59 × 10⁴</td>
<td>1.55 × 10⁵</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>CR</td>
<td>2.04 × 10⁴</td>
<td>4.56 × 10⁴</td>
<td>-2.35 × 10²</td>
<td>1.69 × 10⁴</td>
<td>1.15 × 10⁤</td>
<td>0.9923</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HM</td>
<td>3.78 × 10⁴</td>
<td>3.46 × 10⁵</td>
<td>-1.99 × 10²</td>
<td>3.44 × 10⁴</td>
<td>1.18 × 10⁤</td>
<td>0.9997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>average</td>
<td>2.91 × 10⁴</td>
<td>1.95 × 10⁵</td>
<td>-2.17 × 10²</td>
<td>2.56 × 10⁴</td>
<td>1.16 × 10⁤</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>CR</td>
<td>2.84 × 10⁵</td>
<td>1.93 × 10⁷</td>
<td>2.73 × 10²</td>
<td>2.79 × 10⁴</td>
<td>1.42 × 10⁤</td>
<td>0.9992</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HM</td>
<td>3.02 × 10⁵</td>
<td>7.26 × 10⁹</td>
<td>3.22 × 10²</td>
<td>2.97 × 10⁴</td>
<td>1.35 × 10⁤</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>average</td>
<td>2.93 × 10⁵</td>
<td>3.63 × 10⁹</td>
<td>2.97 × 10²</td>
<td>2.88 × 10⁴</td>
<td>1.38 × 10⁤</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>CR</td>
<td>3.96 × 10⁴</td>
<td>2.83 × 10⁴</td>
<td>-2.01 × 10²</td>
<td>3.61 × 10⁴</td>
<td>1.21 × 10⁤</td>
<td>0.9630</td>
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<td></td>
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<td>HM</td>
<td>4.74 × 10⁴</td>
<td>5.62 × 10³</td>
<td>-1.76 × 10²</td>
<td>4.39 × 10⁴</td>
<td>1.18 × 10⁤</td>
<td>0.9975</td>
</tr>
<tr>
<td></td>
<td></td>
<td>average</td>
<td>4.35 × 10⁴</td>
<td>1.69 × 10⁴</td>
<td>-1.90 × 10²</td>
<td>4.00 × 10⁴</td>
<td>1.19 × 10⁤</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>CR</td>
<td>1.94 × 10⁵</td>
<td>2.73 × 10³</td>
<td>2.01 × 10²</td>
<td>1.91 × 10⁵</td>
<td>1.10 × 10⁤</td>
<td>0.9956</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HM</td>
<td>2.01 × 10⁵</td>
<td>4.16 × 10⁴</td>
<td>2.24 × 10²</td>
<td>1.98 × 10⁵</td>
<td>1.07 × 10⁤</td>
<td>0.9947</td>
</tr>
<tr>
<td></td>
<td></td>
<td>average</td>
<td>1.97 × 10⁵</td>
<td>2.21 × 10⁴</td>
<td>2.12 × 10²</td>
<td>1.94 × 10⁵</td>
<td>1.08 × 10⁤</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1: The FT-IR spectra of L1 and L2 and their complexes (I-VI)
Figure 2: The UV spectra of \( L_1 \) and \( L_2 \) and their complexes (I-VI)
plexes, states that the hydrogen ion in the ligand molecule is substituted by the metal ions\(^7\). The stretching asymmetric (\(\nu_{as}\)) of carboxylate group between 1500 and 1542 cm\(^{-1}\) and of the symmetric vibrations (\(\nu_s\)) at 1409-1403 cm\(^{-1}\) confirm these hypotheses. The shifting of \(\nu(C = N)\) in the spectra of the complexes indicate the sharing of this group in the formation of the complexes\(^8\). The coordination of the metal ions via nitrogen atom is confirmed by presence the \(\nu(M-N)\) bands at range 430-493 cm\(^{-1}\).

**Electronic absorption spectra**

The spectra of the two ligands and their complexes in DMSO are shown in figure 2 and the spectral data are listed in TABLE 3. There are two detected absorption bands in the spectra of the free ligands and their complexes, the first one which appears at range 205-260 nm was assigned to \(\pi-\pi^*\)\(^9\), and the second which appears at range 285-385 nm was assigned to \(n-\pi^*\) intraligand transitions\(^10,11\). These transitions also found in the spectra of the complexes, but they are shifted. There are evident that the increasing in the absorbance (hyperchromic effect) clarified in all of the spectra of the complexes attributed to the complexation behavior of two ligands.
40 Transition metal complexes of a synthetic ligands derived from 4-acetylpyridine

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Towards metal ions, confirming the coordination of the ligands to the metallic ions. The absorption bands at 448nm in the spectrum of \([\text{NiL}_2(\text{H}_2\text{O})_4]\text{Cl}.2\text{H}_2\text{O}\) which can be attributed to ligand to metal charge-transfer.

H-NMR spectra

The proton magnetic resonance spectra of the \(L_1, L_2, [\text{NiL}_1(\text{H}_2\text{O})_2]\text{Cl}.2\text{H}_2\text{O}\) (II) and \([\text{CuL}_2(\text{H}_2\text{O})_4]\text{Cl}\) (VI) complexes were analyzed (Figure 3). The signals exhibited by the free ligand \(L_1\) due to the NH group and NH\(_2\) group protons at 9.57ppm and 11.25ppm, respectively, have been disappeared and only one signal is appeared in the spectrum of the \([\text{NiL}_2(\text{H}_2\text{O})_2]\text{Cl}.2\text{H}_2\text{O}\) (II) complex at 2.11 ppm indicating the coordination of the two nitrogen atoms with the metal ion. Also, the signals exhibited by the free ligand \(L_2\) due to the NH group and carboxylate group protons at 9.57ppm and 12.42ppm, respectively, disappears in the spectrum of the \([\text{CuL}_2(\text{H}_2\text{O})_4]\text{Cl}\) (VI) complex indicating the coordination of nitrogen atom of NH group and oxygen atom (carboxylate ion) with the metal ion\(^{[12,13]}\). The aromatic signals of pyridine ring do not shift significantly, thus showing that the magnetic environment of the aromatic ring has not changed significantly with coordination.

Mass spectra

The purity of \(L_1, L_2, [\text{CuL}_1(\text{H}_2\text{O})_2]\text{Cl}\) (III) and \([\text{CoL}_2(\text{H}_2\text{O})_2]\text{Cl}\) (IV) was checked from mass spectra (Figure 4), where the spectra showed that a clearly base peaks (m/e) molecular weights and the intensity (%). The fragmentations of them are presented in Schemes...
1-4. Their is difference between the fragmentation path way of the two ligand rather than the two complexes resulted according to the place of complexation, the formation of the complexes via NH and NH₂ groups incase of L₁ and via NH and COOH groups in L₂.

Thermogravimetric analysis

Thermal analysis curves (TG and DTG) of the studies complexes are shown in figure 5. The thermoanalytical results are summarized in TABLE 4.

[CoL₁(H₂O)₂]Cl₂ (I)

The thermal decomposition of this complex occurs at two steps. The first degradation step take place in the range of 25-250°C and it corresponds to the eliminated of the pyridine ring due to a weight loss of 21.85% in a good matching with theoretical value 22.82%. The second step fall in the range of 250-400°C which is assigned to loss of C₃H₆N₃S (organic rest) with a weight loss 39.28% and the calculated value is 39.19%.

[CoL₂(H₂O)₂]Cl (IV)

This complex decomposed also in two steps, the first one occurring at 25-100°C and corresponding to the evolution of all two coordination water molecules, representing a weight loss of 9.51% and its calculated value is 9.43%. The second step occurring at 100-400°C is corresponding to the loss of C₁₀H₁₁N₄S (organic rest), representing a weight loss of 60.05% and its calculated value is 61.61%.

[CoL₁(H₂O)₂]Cl₂ (III)

The Cu(II) complex decomposed like Co(II) complex only in two steps. The first extended from 25°C to 200°C and can be assigned to the loss of pyridine ring, representing a weight loss of 22.53% and its calculated value is 22.52%. The second step occurring at 200-400°C corresponding to the loss of C₃H₆N₃S (organic moiety), representing a weight loss of 39.29% and its calculated value is 38.67%.

[CoL₂(H₂O)₂]Cl (IV)

This complex decomposed also in two steps, the first one occurring at 25-100°C and corresponding to the evolution of all two coordination water molecules, representing a weight loss of 9.51% and its calculated value is 9.43%. The second step occurring at 100-400°C is corresponding to the loss of C₁₀H₁₁N₄S (organic rest), representing a weight loss of 60.05% and its calculated value is 61.61%.

[CoL₁(H₂O)₂]Cl₂ (III)

The Cu(II) complex decomposed like Co(II) complex only in two steps. The first extended from 25°C to 200°C and can be assigned to the loss of pyridine ring, representing a weight loss of 22.53% and its calculated value is 22.52%. The second step occurring at 200-400°C corresponding to the loss of C₃H₆N₃S (organic moiety), representing a weight loss of 39.29% and its calculated value is 38.67%.

Thermogravimetric analysis

Thermal analysis curves (TG and DTG) of the studies complexes are shown in figure 5. The thermoanalytical results are summarized in TABLE 4.

TABLE 6: Antibacterial and antifungal activity data of L₁ and L₂ and their complexes (I-VI)

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>Antibacterial activity data</th>
<th>Antifungal activity data</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>L₂</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>I</td>
<td>+++</td>
<td>++</td>
</tr>
<tr>
<td>II</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>III</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>IV</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>V</td>
<td>++</td>
<td>+++</td>
</tr>
<tr>
<td>VI</td>
<td>+</td>
<td>+++</td>
</tr>
</tbody>
</table>

**TABLE 6 : Antibacterial and antifungal activity data of L₁ and L₂ and their complexes (I-VI)**

- **Antibacterial activity data**
  - **Gram positive bacteria**
    - Bacillus Subtilis
    - Streptococcus Penumonia
    - Staphylococcus Aureas
  - **Gram negative bacteria**
    - E.Coli
    - Pesudomonas Sp.

- **Antifungal activity data**
  - Aspergillus Nigaer
  - Penicillium Sp.

- **Compd. No.**
  - L₁: +++
  - L₂: +
  - I: +++
  - II: +++
  - III: +++
  - IV: +++
  - V: +++
  - VI: ++

- **Compd. No.**
  - [CoL₁(H₂O)₂]Cl₂ (I)
  - [CoL₂(H₂O)₂]Cl (IV)
  - [NiL₁(H₂O)₂]Cl₂.H₂O (II)
  - [NiL₂(H₂O)₄]Cl.2H₂O (V)

**[CoL₁(H₂O)₂]Cl₂ (I)**

The thermal decomposition of this complex occurs at two steps. The first degradation step take place in the range of 25-250°C and it corresponds to the eliminated of the pyridine ring due to a weight loss of 21.85% in a good matching with theoretical value 22.82%. The second step fall in the range of 250-400°C which is assigned to loss of C₃H₆N₃S (organic rest) with a weight loss 39.28% and the calculated value is 39.19%.

**[CoL₂(H₂O)₂]Cl (IV)**

This complex decomposed also in two steps, the first one occurring at 25-100°C and corresponding to the evolution of all two coordination water molecules, representing a weight loss of 9.51% and its calculated value is 9.43%. The second step occurring at 100-400°C is corresponding to the loss of C₁₀H₁₁N₄S (organic rest), representing a weight loss of 60.05% and its calculated value is 61.61%.

**[NiL₁(H₂O)₂]Cl₂.H₂O (II)**

The thermal decomposition of [NiL₁(H₂O)₂]Cl₂.H₂O complex completely in three steps. The first degradation step take place in the range of 25-100°C and it corresponds to the eliminated of four water molecule due to a weight loss of 17.83% in a good matching with theoretical value 18.19%. The second step fall in the range of 100-225°C which is assigned to loss of C₃H₆N₃S (organic rest) with a weight loss 29.52% and the calculated value is 29.32%.
step occurring at 225–400°C is corresponding to the loss of C_{10}H_{11}N_{4}OS (organic moiety), representing a weight loss of 10.07% and its calculated value is 9.87%. The final product resulted at 400°C was NiO.

\[[CuL_2(H_2O)_4]Cl\] (VI)

As mentioned above in the Co(II) and Ni(II) complexes, \[[CuL_2(H_2O)_4]Cl\] (VI) complex, also has two decomposition steps. The first step located in the range between 25-150°C at maximum temperature DTG$_{\text{max}}$ = 115°C and the weight loss at this step is 12.52% due to the loss of three water molecules, in agreement with the theoretical weight loss value of 12.79%. The second step occurring at 150-400°C is corresponding to the loss of the last water molecule and C_{10}H_{11}N_{4}OS (organic moiety), representing a weight loss of 59.79% and its calculated value is 59.95%. The final formed product at 400°C is CuO.

Kinetic studies

In recent years there has been increasing interest in determining the rate-dependent parameters of solid-state non-isothermal decomposition reactions by analysis of TG curves. Several equations\(^{[9-21]}\) have been proposed as means of analyzing a TG curve and obtaining values for kinetic parameters. Many authors\(^{[14-19]}\) have discussed the advantages of this method over the conventional isothermal method. The rate of a decomposition process can be described as the product of two separate functions of temperature and conversion\(^{[18]}\), using

\[
d\alpha/dt = k(T)f(\alpha)
\]

where \(\alpha\) is the fraction decomposed at time \(t\), \(k(T)\) is the temperature dependent function and \(f(\alpha)\) is the conversion function dependent on the mechanism of decomposition. It has been established that the temperature dependent function \(k(T)\) is of the Arrhenius type and can be considered as the rate constant \(k\).

\[
k = A e^{-E^*/RT}
\]

where R is the gas constant in (Jmol\(^{-1}\)K\(^{-1}\)). Substituting equation (2) into equation (1), we get,

\[
d\alpha/dT = (A/\phi e^{-E^*/RT})f(\alpha)
\]

where \(\phi\) is the linear heating rate \(dT/dt\). On integration and approximation, this equation can be obtained in the following form

\[
\ln g(\alpha) = - \frac{E^*}{RT} + \ln[AR/\phi E]
\]

where \(g(\alpha)\) is a function of \(\alpha\) dependent on the mechanism of the reaction. The integral on the right hand side is known as temperature integral and has no closed for solution. So, several techniques have been used for the evaluation of temperature integral. Most commonly used methods for this purpose are the differential method of Freeman and Carroll\(^{[14]}\) integral method of Coat and Redfern\(^{[16]}\), the approximation method of Horowitz and Metzger\(^{[19]}\).

In the present investigation, the general thermal behaviors of the \(L_1\) and \(L_2\) complexes in terms of stability ranges, peak temperatures and values of kinetic parameters, are shown in figure 6 and TABLE 5. The kinetic parameters have been evaluated using the following methods and the results obtained by these methods are well agreement with each other. The following two methods are discussed in brief.

Coats-redfern equation

The Coats-Redfern equation, which is a typical integral method, can be represented as:

\[
\int_0^\alpha \frac{d\alpha}{(1-\alpha)n} = \frac{A}{\phi} \int_{T_1}^{T_2} \exp\left(-\frac{E^*}{RT}\right) dt
\]

For convenience of integration the lower limit \(T_1\) is
usually taken as zero. This equation on integration gives;

\[ \ln\left(\frac{1-\alpha}{T^2}\right) = -\frac{E^*}{RT} + \ln\left(\frac{A}{\phi E^*}\right) \]

A plot of left-hand side (LHS) against 1/T was drawn. \( E^* \) is the energy of activation in J mol\(^{-1}\) and calculated from the slope and A in (s\(^{-1}\)) from the intercept value. The entropy of activation \( \Delta S^* \) in (JK\(^{-1}\)mol\(^{-1}\)) was calculated by using the equation:

\[ \Delta S^* = R \ln\left(\frac{Ah/k_B}{T_s}\right) \]  

where \( k_B \) is the Boltzmann constant, \( h \) is the Plank’s constant and \( T_s \) is the DTG peak temperature\(^{[22]} \).

**Horowitz-Metzger equation**

The Horowitz-Metzger equation is an illustrative of the approximation methods. These authors derived the relation:

\[ \log\left(\frac{1-(1-\alpha)^{1-n}}{1-n}\right) = E^*/2.303RT - \log 2.303 \]  

When \( n = 1 \), the LHS of equation 4 would be \( \log(-\log (1-\alpha)) \). For a first-order kinetic process the Horowitz-Metzger equation may be written in the form:

\[ \log\log\left(\frac{w}{w}\right) = E^*/2.303RT - \log 2.303 \]

where \( \theta = T - T_s \), \( w = w_{a} - w \), \( w_{a} = \) mass loss at the completion of the reaction; \( w = \) mass loss up to time \( t \). The plot of \( \log\log\left(\frac{w}{w}\right) \) vs \( \theta \) was drawn and found to be linear from the slope of which \( E^* \) was calculated. The pre-exponential factor, A, was calculated from the equation:

\[ E^*/RT = A/\phi \exp(-E^*/RT) \]

The entropy of activation, \( \Delta S^* \), was calculated from equation 3. The enthalpy activation, \( \Delta H^* \), and Gibbs free energy, \( \Delta G^* \), were calculated from; \( \Delta H^* = E^* - RT \) and \( \Delta G^* = \Delta H^* - T\Delta S^* \), respectively.

The reaction for which \( \Delta G \) is positive and \( \Delta S \) is negative considered as unfavorable or non spontaneous reactions.

Reactions are classified as either exothermic (\( \Delta H < 0 \)) or endothermic (\( \Delta H > 0 \)) on the basis of whether they give off or absorb heat. Reactions can also be classified as exergonic (\( \Delta G < 0 \)) or endergonic (\( \Delta G > 0 \)) on the basis of whether the free energy of the system decreases or increases during the reaction.

The thermodynamic data obtained with the two methods are in harmony with each other. The correlation coefficients of the Arhenius plots of the thermal decomposition steps were found to lie in the range 0.9630 to 0.9999, showing a good fit with linear function. It is clear that the thermal decomposition process of all \( L_1 \) and \( L_2 \) complexes is non-spontaneous, i.e, the complexes are thermally stable.

**Microbiological screening**

The results of antibacterial activities in vitro of the two ligands and their complexes are given in TABLE 6. From the results we can see that all the effect on the selected bacteria can be ordered as, \( \text{Bacillus Subtilis} > \text{Streptococcus Penumonia} > \text{Staphylococcus aureus} > \text{Escherichia Coli} > \text{Pseudomonas Sp} \).

Also the two ligands and their complexes have been evaluated for their antifungal activity. The minimal inhibitory concentration values listed in TABLE 6 show that all the test compounds have more effect on \( \text{Aspergillus Nigaer} \) than \( \text{Penicillium Sp} \).

**Structure of the \( L_1 \) and \( L_2 \) and their complexes**

The fact that these compounds were isolated as powders and not as single crystals means that no complete structure determination can be made. Accordingly, the above mentioned discussions using elemental analysis, molar conductance, (infrared, \(^1\)H-NMR and mass) spectra as well as thermogravimetric analysis; the sug-
gested structures of the \( L_1 \) and \( L_2 \) and their complexes can be represented in Scheme 5.

REFERENCES


