Synthesis, Characterization and Antibacterial Activity of Mixed Ligand (HL) Complexes Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) with Azide (N$_3^-$)

Jassim S. Sultan, Sajed M. Lateaf, Dhuha K. Rashid

Department of Chemistry, College of Education for pure Sciences, Ibn Al-Hiatham, University of Baghdad, Baghdad, Iraq
Email: ja.sultan@yahoo.com

Received 12 June 2015; accepted 5 October 2015; published 8 October 2015

Copyright © 2015 by authors and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY).
http://creativecommons.org/licenses/by/4.0/

Abstract

The complexes of mixed ligand (HL) as primary ligand with azide ion (N$_3^-$) as co-ligand with Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) were prepared via reaction metal (II) chloride salt with ligand (HL) and sodium azide (NaN$_3$) using 1:2:2 mole ratio in ethanol solvent, respectively. The complexes of mixed ligand (HL) were characterized by elemental microanalysis (C.H.N), atomic absorption chloride content, molar conductance, magnetic susceptibility, melting point, FTIR and UV-Vis spectral data. The anti bacterial activity with four kinds of bacteria, Staphylococcus aureus, Bacillus, Escherichia coli and Pseudomonas aureus was studied.

Keywords

4-Aminoantipyrine, Glyoxylic Acid, Sodium Azide, Schiff Base, Azido Mixed Ligand

1. Introduction

The chemistry of Schiff bases metal complexes is of interest because these species display a variety of reactivity mode and they possess catalytic and biological activity [1]. Metal complexes of nitrogen-oxygen chelating agents derived from 4-aminoantipyrine Schiff bases have been studied extensively due to their pronounced applications in biological, clinical, analytical and pharmacological areas [2]-[4].

4-Aminoantipyrine, an antipyretic agent [5] is one of the pyrazole derivatives. Numerous synthetic compounds containing pyrazole moiety have been focused in the field of medicinal chemistry [6] because of their
pharmacological, photographic, catalytic and liquid crystals applications [7] [8]. Glyoxylic acid and its derivatives play important roles in natural processes participating in the glyoxylate cycle which functions in plants and some microorganisms [9]. It has been widely used in organic synthesis for the manufacture of intermediate products in pharmaceutical [10]. The spectrophotometric methods are usually based on the reactivity of the aldehyde group [11] [12]. Azido-mixed ligand complexes particular interest has been focused on the azido ligand \( \text{N}_3^- \) not only for its efficiency in ferromagnetic or antiferromagnetic coupling but also for its diversity in coordination modes, \( \mu_1, 1 \), (end-on EO), \( \mu_1, 3 \) (end-end, EE), \( \mu_1, 1, 1 \), \( \mu_1, 1, 3 \) or still other modes and polymeric bridging network, and a large number of azido-bridged complexes with different dimensionalities and various topologies have been reported in the literature [13] [14]. Polynuclear complexes and coordination polymer in which paramagnetic metal ions are bridged by short ligands have attracted great attention in recent years. The studies focusing on better understanding fundamental magnetic applications, a large number of a zide-bridged transition metal complexes, have been reported [15].

2. Experimental

All chemicals were purchased from BDH, and used without further purifications.

2.1. Instrumentation

FTIR spectra were recorded in KBr on Shimadzu-8300 Spectrophotometer in the range of (4000 - 400 cm\(^{-1}\)). The electronic spectra in \( \text{H}_2\text{O} \) were recorded using the UV-Visible spectrophotometer type (spectra 190 - 900 nm) CECIL, England, with quartz cell of (1 cm) path length. The melting point was recorded on Gallen kamp Melting point Apparatus.

The Conductance Measurements were recorded on W. T. W. conductivity Meter. The metal contents of the complexes were determined by atomic absorption (A. A.) technique using a Shimadzu PR-5 with Orphic Printer atomic absorption spectrophotometer. Balance Magnetic Susceptibility model MSB-MLI was conducted for measuring the magnetic susceptibility.

The characterization of the new ligand (L) is achieved by \( ^1\text{H} \) and \( ^{13}\text{C} \)-NMR spectra were recorded by using a Bruker 300 MHZ (Switzerland). Chemical Shift of all \( ^1\text{H} \) and \( ^{13}\text{C} \)-NMR spectra were recorded in \( \delta \) (ppm) unit downfield from internal reference tetramethylsilane (TMS), using \( \text{D}_2\text{O} \) as a solvent. Elemental analysis for carbon, hydrogen was performed using a Euro Vector EA 3000 A Elemental Analysis (Italy).

2.2. Synthesis of Ligand and Complexes

2.2.1. Synthesis of Ligand (1,5-Diemthyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino) (HL)

A solution of (4-AAP) (0.203 g, 1 mmole) in ethanol (20 ml), and a few drop of 48% of HBr, was added to a solution of (Glyoxylic acid) (0.074 g, 1 mmol) in ethanol (10 ml). The mixture was refluxed for (6 hr) with stirring. The resulting was an orange solution allowed to cool and dried at room temperature, then washed with ethanol and re-crystallization to the precipitate with methanol/\( \text{H}_2\text{O} \) to give orange crystals during (24 hr), m.p. (128 - 132)\(^\circ\)C.

2.2.2. Synthesis of [Co(HL)\(_2\)\(\text{N}_3\)]\(_2\)\(\text{H}_2\text{O} \) Complex

A solution of (HL) (0.518 g, 2 mmole) in ethanol (5 ml) and a solution of NaN\(_3\) (0.13 g, 2 mmol) in ethanol (5 ml) were added to a stirred solution of CoCl\(_2\)\(\text{H}_2\text{O} \) (0.238 g, 1 mmol) in ethanol (5 ml). The resulting mixture was stirred for (1 hr). Then the mixture was filtered and dried then the precipitate was washed with an excess of ethanol and dried at room temperature during (24 hr). A pale green crystals were obtained, m.p. (116 - 121)\(^\circ\)C. A similar method was used to prepare of Mn(II), Ni(II), Zn(II), Cd(II) and Hg(II) mixed ligand complexes.

3. Results and Discussion

3.1. Characterization of Ligand (HL)

In this study, new Schiff base ligand (HL) type (NOO) donor atoms was synthesized according to the used method shown in Scheme 1.

Spectroscopic methods [FT-IR, UV-Vis, \(^1\text{H} \) NMR, \(^{13}\text{C} \) NMR] along with melting point and elemental micro-analysis C.H.N. were used to characterization the new ligand (HL).
3.1.1. $^1$H NMR Spectral Data
The $^1$H-NMR spectrum of ligand (HL) shows single peaks attributed to two methyl groups appeared at range ($\delta 1.06 - \delta 2.91$) ppm. The strong signal obtained at ($\delta 3.35$) ppm due to DMSO-$d_6$. The weak peak at ($\delta 8.14$) ppm was attributed to proton of azomethine group (-N=CH-). Single weak peak attributed to proton of (-COOH) appeared at ($\delta 9.30$) ppm. The multiple chemical shifts around ($6.98 - 7.47$) ppm may assigned to aromatic protons. The two weak signals at ($\delta 3.04$) and ($\delta 3.14$) ppm refer to water molecule of DMSO [16].

3.1.2. $^{13}$C NMR Spectral Data
$^{13}$C NMR spectrum of ligand (HL) shows chemical shifts at (15.54) ppm and (18.35) ppm refer to C$_5$ and C$_6$ for two CH$_3$ group respectively. The chemical shifts at (61.79) ppm and (88.32) ppm were attributed to C$_3$ and C$_4$ of C=C in 4-AAP ring respectively. Signals related to aromatic carbon (C$_7$ - C$_{12}$) were detected at range (126.04 - 130.89) ppm. The chemical shift of C$_1$ for carboxylic group appeared as expected downfield at (170.25) ppm. The two chemical shift at (165.51) ppm and (135.47) ppm were attributed to C$_2$ for azomethine group (-N=CH-) and C$_{13}$ to C=O for 4-AAP respectively. Finally, the chemical shift at (40.86) ppm is due to DMSO $d_6$ [17].

3.2. Characterization of Mixed Ligand (HL) Complexes with Azide ($\text{N}_3^-$)
The complexes of mixed ligand, (HL) as primary ligand with azide ion ($\text{N}_3^-$) as co-ligand with Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) were prepared via reaction metal (II) chloride salt with ligand (HL) and sodium azide (NaN$_3$) using 1:2:2 mole ratio in ethanol solvent respectively. The method of this synthesis shows in Scheme 2 and Scheme 3.

Spectroscopic methods [FT-IR, UV-Vis, A. A.] along with molar conductivity, elemental microanalysis C,H,N, Chloride content, magnetic susceptibility, melting point were used to characterize the prepared mixed ligand complexes. All mixed ligand complexes are stable in solution and soluble in methanol, ethanol, acetone, DMSO and DMF solvents. Some physical properties were listed in Table 1. Elemental microanalysis C,H,N, metal and chloride analysis are in a good agreement with calculated values, Table 2.

3.2.1. Molar Conductance
The molar conductance values, Table 1, of the soluble mixed ligand complexes in DMSO solvent in $10^{-3}$ M solution at room temperature refer to non-electrolytic nature [18].

3.2.2. Magnetic Susceptibility
The magnetic susceptibility for all complexes were measured at room temperature and the effective magnetic moment ($\mu_{eff}$) values [19] were listed in Table 3.

3.2.3. FT-IR Spectral Data
The IR spectra of mixed ligand complexes Co(II), Ni(II), Zn(II), Cd(II), and Hg(II), exhibited band at (1616) cm$^{-1}$, (1624) cm$^{-1}$, (1614) cm$^{-1}$, (1616) cm$^{-1}$, and (1635) cm$^{-1}$, respectively, refers to stretching frequency $\nu$C=O of 4-AAP ring, which was shifted to lower frequency when its comparison with that of the free ligand (HL), showing that the coordination between oxygen atom of this group with metal ion has happened [20]. The IR spectrum of mixed ligand complex of Mn(II), showed no change in position of the stretching frequency of $\nu$C=O ring when it compare of free ligand, indicating that the oxygen atom of (C=O) ring wasn’t involved in coordination with Mn(II). The detected bands at (1593) cm$^{-1}$, (1591) cm$^{-1}$, (1593) cm$^{-1}$, (1591) cm$^{-1}$, (1591) cm$^{-1}$, and (1591) cm$^{-1}$ in the IR spectra of all mixed ligand complexes refer to stretching frequency of imine...
Scheme 2. Synthesis route of mixed ligand complexes for Co(II), Ni(II), Zn(II), Cd(II) and Hg(II).

\[
\begin{align*}
\text{Complexes} & \quad \text{M.wt g/mol} & \text{Yield %} & \text{Colour} & \text{M. P. °C} & \text{M.C ohm}^{-1}\text{cm}^2\text{mol}^{-1} \\
[Mn(HL)₂(N₃)₂(H₂O)]·H₂O & 711 & 78 & \text{Dark green} & 100 & 12.22 \\
[Co(HL)₂(N₃)₂]·2H₂O & 697 & 91 & \text{Pale green} & 120 & 9.42 \\
[Ni(HL)₂(N₃)₂]·3H₂O & 714.7 & 92 & \text{Pale olive} & 122 & 15.58 \\
[Zn(HL)₂(N₃)₂]·3H₂O & 721.4 & 88 & \text{Pale orange} & \text{dec. 108 - 112} & 7.97 \\
[Cd(HL)₂(N₃)₂]·2H₂O & 750.4 & 89 & \text{Pale orange} & 103 & 9.21 \\
[Hg(HL)₂(N₃)₂]·3H₂O & 856.6 & 92 & \text{Pale orange} & 102 & 9.16 \\
\end{align*}
\]
Table 2. Elemental microanalysis of mixed ligand (HL) complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Found, (cal cu.)%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>[Mn(HL)₂(N₃)₂(H₂O)]·H₂O</td>
<td>(43.88)</td>
</tr>
<tr>
<td>[Co(HL)₂(N₃)₂(H₂O)₂]·H₂O</td>
<td>(44.76)</td>
</tr>
<tr>
<td>[Ni(HL)₂(N₃)₂]·3H₂O</td>
<td>(43.65)</td>
</tr>
<tr>
<td>[Zn(HL)₂(N₃)₂]·3H₂O</td>
<td>(43.24)</td>
</tr>
<tr>
<td>[Cd(HL)₂(N₃)₂]·2H₂O</td>
<td>(41.57)</td>
</tr>
<tr>
<td>[Hg(HL)₂(N₃)₂]·3H₂O</td>
<td>(36.42)</td>
</tr>
</tbody>
</table>

Table 3. Magnetic susceptibility and \( \mu_{\text{eff.}} \) (B.M) of some mixed ligand (HL) complexes.

<table>
<thead>
<tr>
<th>Complexes*</th>
<th>( X_g \times 10^6 )</th>
<th>( X_{\text{tot}} \times 10^4 )</th>
<th>( X_A \times 10^6 )</th>
<th>( \mu_{\text{eff.}} ) (B.M)</th>
<th>Suggested structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(HL)₂(N₃)₂(H₂O)₂]·H₂O</td>
<td>18.57</td>
<td>13204.65</td>
<td>12971.03</td>
<td>5.56</td>
<td>Octahedral</td>
</tr>
<tr>
<td>[Co(HL)₂(N₃)₂]·2H₂O</td>
<td>14.08</td>
<td>9815.38</td>
<td>10049.0</td>
<td>4.88</td>
<td>Octahedral</td>
</tr>
<tr>
<td>[Ni(HL)₂(N₃)₂]·3H₂O</td>
<td>4.50</td>
<td>3217.88</td>
<td>3451.50</td>
<td>2.86</td>
<td>Octahedral</td>
</tr>
</tbody>
</table>

The observed shifts and new bands in the IR spectra of the complexes were attributed to the coordination of the azide ion \( \text{N}_3^- \) to the metal ions, indicating the formation of coordination complexes. These complexes were found to be non-electrolytic as evidenced by their molar conductance values.
Table 4. The FT-IR spectral data (cm\(^{-1}\)) of ligand (HL) and its mixed complexes.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(\nu) O-H</th>
<th>(\nu) C=O ring</th>
<th>(\nu) C=O carbox.</th>
<th>(\nu) N=C imine</th>
<th>(\nu) COO(^{-}) asy.</th>
<th>(\nu) N=C(^{+}) sy.</th>
<th>(\nu) N=(\mathrm{N}_3) asy.</th>
<th>(\nu) C=(\mathrm{N}_3) sy.</th>
<th>(\nu) C=H arom.</th>
<th>(\nu) C-H aliph.</th>
<th>(\nu) M-N</th>
<th>(\nu) M-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(HL)</td>
<td>3421</td>
<td>1645</td>
<td>1724</td>
<td>1608</td>
<td>1419</td>
<td>1369</td>
<td>-</td>
<td>-</td>
<td>2123</td>
<td>2058</td>
<td>1311</td>
<td>1570</td>
</tr>
<tr>
<td>[Mn(HL)(_2)((\mathrm{N}_3))(_2)((\mathrm{H}_2)O)(_2)](\cdot)(\mathrm{H}_2)O</td>
<td>3340</td>
<td>1647</td>
<td>Overlap</td>
<td>1593</td>
<td>1417</td>
<td>1369</td>
<td>1586</td>
<td>2939</td>
<td>1197</td>
<td>2900</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Co(HL)(_2)((\mathrm{N}_3))(_2)](\cdot)(\mathrm{H}_2)O</td>
<td>3442</td>
<td>1616</td>
<td>Overlap</td>
<td>1591</td>
<td>1421</td>
<td>1371</td>
<td>2123</td>
<td>2102</td>
<td>1311</td>
<td>1573</td>
<td>Overlap</td>
<td>1197</td>
</tr>
<tr>
<td>[Ni(HL)(_2)((\mathrm{N}_3))(_2)](\cdot)3(\mathrm{H}_2)O</td>
<td>3390</td>
<td>1624</td>
<td>1735</td>
<td>1593</td>
<td>1417</td>
<td>1363</td>
<td>2121</td>
<td>2036</td>
<td>1311</td>
<td>1575</td>
<td>Overlap</td>
<td>1168</td>
</tr>
<tr>
<td>[Zn(HL)(_2)((\mathrm{N}_3))(_2)](\cdot)3(\mathrm{H}_2)O</td>
<td>3464</td>
<td>1614</td>
<td>1735</td>
<td>1591</td>
<td>1419</td>
<td>1373</td>
<td>2065</td>
<td>Overlap</td>
<td>1317</td>
<td>1560</td>
<td>3066</td>
<td>1141</td>
</tr>
<tr>
<td>[Cd(HL)(_2)((\mathrm{N}_3))(_2)](\cdot)2(\mathrm{H}_2)O</td>
<td>3446</td>
<td>1616</td>
<td>Overlap</td>
<td>1591</td>
<td>1419</td>
<td>1375</td>
<td>2065</td>
<td>Overlap</td>
<td>1317</td>
<td>1558</td>
<td>3064</td>
<td>1188</td>
</tr>
<tr>
<td>[Hg(HL)(_2)((\mathrm{N}_3))(_2)](\cdot)3(\mathrm{H}_2)O</td>
<td>3346</td>
<td>1635</td>
<td>Overlap</td>
<td>1591</td>
<td>1419</td>
<td>1369</td>
<td>2125</td>
<td>Overlap</td>
<td>1313</td>
<td>1558</td>
<td>3064</td>
<td>1188</td>
</tr>
</tbody>
</table>

Table 5. Electronic spectral data of ligand (HL) and its mixed complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda) nm</th>
<th>(\nu) (cm(^{-1}))</th>
<th>(\varepsilon_{\text{max}}) (molar(^{-1})L cm(^{-1}))</th>
<th>Electronic transition</th>
<th>Suggested structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>(HL)</td>
<td>276</td>
<td>36,231</td>
<td>1885</td>
<td>(\pi \rightarrow \pi^*)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>346</td>
<td>28,901</td>
<td>614</td>
<td>(\pi \rightarrow \pi^*)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>362</td>
<td>27,624</td>
<td>500</td>
<td>(\pi \rightarrow \pi^*)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>297</td>
<td>33,670</td>
<td>2370</td>
<td>Intra-ligand</td>
<td></td>
</tr>
<tr>
<td></td>
<td>345</td>
<td>28,986</td>
<td>2042</td>
<td>Intra-ligand</td>
<td></td>
</tr>
<tr>
<td>[Mn(HL)(_2)((\mathrm{N}_3))(_2)((\mathrm{H}_2)O)(_2)](\cdot)(\mathrm{H}_2)O</td>
<td>359</td>
<td>27,855</td>
<td>1324</td>
<td>Intra-ligand</td>
<td>Oh</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>21,053</td>
<td>208</td>
<td>(6\text{A}_1g \rightarrow 4\text{T}_2g(G))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>638</td>
<td>15,674</td>
<td>41</td>
<td>(6\text{A}_1g \rightarrow 4\text{T}_1g(G))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>794</td>
<td>12,594</td>
<td>7</td>
<td>(6\text{A}_1g \rightarrow 4\text{E}_g(D))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>286</td>
<td>34,965</td>
<td>2304</td>
<td>Intra-ligand</td>
<td></td>
</tr>
<tr>
<td></td>
<td>345</td>
<td>28,986</td>
<td>2034</td>
<td>Intra-ligand</td>
<td></td>
</tr>
<tr>
<td>[Co(HL)(_2)((\mathrm{N}_3))(_2)](\cdot)2(\mathrm{H}_2)O</td>
<td>362</td>
<td>27,624</td>
<td>1228</td>
<td>Intra-ligand</td>
<td>oh</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>15,387</td>
<td>13</td>
<td>(4\text{T}_1g \rightarrow 3\text{A}_1g)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>879</td>
<td>11,377</td>
<td>4</td>
<td>(4\text{T}_1g \rightarrow 3\text{T}_2g)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>281</td>
<td>35,587</td>
<td>2218</td>
<td>Intra-ligand</td>
<td></td>
</tr>
<tr>
<td></td>
<td>347</td>
<td>28,818</td>
<td>1152</td>
<td>Intra-ligand</td>
<td></td>
</tr>
<tr>
<td>[Ni(HL)(_2)((\mathrm{N}_3))(_2)](\cdot)3(\mathrm{H}_2)O</td>
<td>365</td>
<td>27,397</td>
<td>842</td>
<td>Intra-ligand</td>
<td>Oh</td>
</tr>
<tr>
<td></td>
<td>426</td>
<td>23,474</td>
<td>323</td>
<td>(3\text{A}_1g \rightarrow 3\text{T}_2g(P))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>792</td>
<td>15,942</td>
<td>10</td>
<td>(3\text{A}_1g \rightarrow 3\text{T}_2g)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>879</td>
<td>11,377</td>
<td>2</td>
<td>(3\text{A}_1g \rightarrow 3\text{T}_2g)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>286</td>
<td>34,965</td>
<td>2278</td>
<td>Intra-ligand</td>
<td></td>
</tr>
<tr>
<td>[Zn(HL)(_2)((\mathrm{N}_3))(_2)](\cdot)3(\mathrm{H}_2)O</td>
<td>345</td>
<td>28,986</td>
<td>1489</td>
<td>Intra-ligand</td>
<td>Oh</td>
</tr>
<tr>
<td></td>
<td>354</td>
<td>28,249</td>
<td>962</td>
<td>Intra-ligand</td>
<td></td>
</tr>
<tr>
<td></td>
<td>286</td>
<td>34,965</td>
<td>2276</td>
<td>Intra-ligand</td>
<td></td>
</tr>
<tr>
<td>[Cd(HL)(_2)((\mathrm{N}_3))(_2)](\cdot)2(\mathrm{H}_2)O</td>
<td>345</td>
<td>28,986</td>
<td>1485</td>
<td>Intra-ligand</td>
<td>Oh</td>
</tr>
<tr>
<td></td>
<td>354</td>
<td>28,249</td>
<td>960</td>
<td>Intra-ligand</td>
<td></td>
</tr>
<tr>
<td></td>
<td>286</td>
<td>35,211</td>
<td>2274</td>
<td>Intra-ligand</td>
<td></td>
</tr>
<tr>
<td>[Hg(HL)(_2)((\mathrm{N}_3))(_2)](\cdot)3(\mathrm{H}_2)O</td>
<td>345</td>
<td>28,986</td>
<td>2085</td>
<td>Intra-ligand</td>
<td>Oh</td>
</tr>
<tr>
<td></td>
<td>354</td>
<td>28,249</td>
<td>1266</td>
<td>Intra-ligand</td>
<td></td>
</tr>
</tbody>
</table>
transitions and suggested geometries. The electronic spectra for all mixed ligand complexes displayed three absorption peaks in the ultraviolet region. The first peak at range (281 - 297) nm \((\varepsilon_{\text{max}} = 2370 - \varepsilon_{\text{max}} = 2218) \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}\), the second peak at (345, 347) nm \((\varepsilon_{\text{max}} = 1152 - \varepsilon_{\text{max}} = 2278) \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}\), the third peak at (354 - 365) nm \((\varepsilon_{\text{max}} = 842 - \varepsilon_{\text{max}} = 1324) \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}\) were attributed to intra-ligand \(\pi \rightarrow \pi^*\), \(n \rightarrow \pi^*\), and \(n \rightarrow \pi^*\), respectively [25] which exhibited bath chromic shift or hypsochromic shift when it comparison with that of free ligand (HL).

3.2.5. [Mn(HL)2(N3)2(H2O)2]·H2O
The UV-Vis spectrum of Mn(II) complex, displayed three additional absorption peaks. The first peak at (475) nm \((\varepsilon_{\text{max}} = 208) \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}\), the second peak at (638) nm \((\varepsilon_{\text{max}} = 41) \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}\), the third peak at (794) nm \((\varepsilon_{\text{max}} = 7) \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}\) were attributed to (d-d) spin-forbidden electronic transition type 6A1g \(\rightarrow 4T_2\text{g}(G)\), 6A1g \(\rightarrow 4T_1\text{g}(G)\), and 6A1g \(\rightarrow 4E\text{g}(D)\), confirming octahedral geometry about Mn(II) [27].

3.2.6. [Co(HL)2(N3)2]·2H2O
The electronic spectrum of Co(II) complex, showed two additional absorption peaks. The first peak at (650) nm \((\varepsilon_{\text{max}} = 13) \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}\), and the second peak at (879) nm \((\varepsilon_{\text{max}} = 4) \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}\) were attributed to (d-d) spin-allowed electronic transition type 4T1g \(\rightarrow 4A_2\text{g}\), and 4T1g \(\rightarrow 4T_2\text{g}\), respectively, characteristic octahedral geometry around Co(II) [28].

3.2.7. [Ni(HL)2(N3)2]·H2O
The UV-Vis spectrum of Ni(II) complex, displayed three additional absorption peaks. The first peak at (426) nm \((\varepsilon_{\text{max}} = 323) \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}\), the second peak at (792) nm \((\varepsilon_{\text{max}} = 10) \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}\), the third peak at (879) nm \((\varepsilon_{\text{max}} = 2) \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}\) were due to (d-d) spin-allowed electronic transition type 3A1g \(\rightarrow 3T_1\text{g}(P)\), 3A1g \(\rightarrow 3T_1\text{g}\), and 3A1g \(\rightarrow 3T_2\text{g}\), respectively, which were a good agreement for octahedral geometry of Ni(II) complexes [29].

3.2.8. [Zn(HL)2(N3)2]·3H2O, [Cd(HL)2(N3)2]·2H2O, and Hg(HL)2(N3)2]·3H2O
The electronic spectra of Zn(II), Cd(II), and Hg(II), respectively show no absorption peaks in the visible region, indicating (d10-system) for Zn(II), Cd(II), and Hg(II), that is mean no d-d electronic transition happened [27].

3.3. Biological Activity of the Ligand (HL) and Mixed Ligand Complexes
Indicating that the new ligand and its mixed ligand complexes exhibited antibacterial activity against four kinds of bacterial: *Staphylococcus aureus*, *Bacillus*, *Escherichia coli*, and *Pseudomonad aureus* respectively, in Table 6, Figure 1 and Figure 2. The enhanced activity of the complexes can be explained on the bases of Overtone’s concept and Tweedy’s chelation theory [30] [31].

**Table 6.** Showed the inhibition circle diameter in millimeter for the bacteria after 24 hour in cubation paid (37˚C) for ligand (HL) and its mono and mated complexes.

<table>
<thead>
<tr>
<th>Compounds</th>
<th><em>E. coli</em></th>
<th><em>Pseudomonas</em></th>
<th><em>Bacillus</em></th>
<th><em>Staphylococcus</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>5</td>
<td>7</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Ligand (HL)</td>
<td>13</td>
<td>14</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>[Mn(HL)2(N3)2(H2O)2]·H2O</td>
<td>-</td>
<td>11</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>[Co(HL)2(N3)2]·2H2O</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td>[Ni(HL)2(N3)2]·3H2O</td>
<td>13</td>
<td>10</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td>[Zn(HL)2(N3)2]·3H2O</td>
<td>13</td>
<td>11</td>
<td>21</td>
<td>11</td>
</tr>
<tr>
<td>[Cd(HL)2(N3)2]·2H2O</td>
<td>16</td>
<td>16</td>
<td>32</td>
<td>18</td>
</tr>
<tr>
<td>[Hg(HL)2(N3)2]·3H2O</td>
<td>26</td>
<td>11</td>
<td>26</td>
<td>12</td>
</tr>
</tbody>
</table>
4. Conclusions and the Proposed Molecular Structure for All Prepared Complexes

According to the characterization data for new Schiff base (HL) derived from 4-aminoantipyrine with glyoxylic acid, and its mixed ligand complexes based Schiff base ligand HL primary ligand and azide ion (N\textsubscript{3}\textsuperscript{-}) (co-ligand), by FT-IR, UV-Vis, atomic absorption, \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, magnetic susceptibility, molar conductivity, elemental microanalysis, chloride content along with melting point, we found that:

1) The Schiff base (HL) in mixed ligand complexes behaved bidentate ligand through its azomethine nitrogen, oxygen atom of C=O group of five member ring with the central metal ions: Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) forming complexes with molecular formula: [M(HL)\textsubscript{2}(N\textsubscript{3})\textsubscript{2}]\textsubscript{m}H\textsubscript{2}O where: (M\textsuperscript{II} = Co, Cd; m = 2), (M\textsuperscript{II} = Ni, Zn, Hg; m = 3), except in Mn(II) complex, Schiff base (HL) behaved monodentate ligand via azomethine nitrogen forming complex with molecular formula [Mn(HL)\textsubscript{2}(N\textsubscript{3})\textsubscript{2}]\textsubscript{1}H\textsubscript{2}O.

2) The octahedral geometrical structure was suggested for all prepared complexes based on the characterization data for all technique.

3) The antibacterial study showed that the complexes were more toxic to the strain of bacteria taken under study than the Schiff base ligand (HL).

References


