Synthesis, Characterization and Thermal Studies of Cr (III), Co (II) and Ni (II) Complexes with Schiff Base

Dina A. Najeeb, Farah M. Ibrahim*

Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq

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The physiologically active compounds of Schiff bases find application in the treatment of several diseases. This biological activity of Schiff base is attributed to the formation of stable chelates with a transition metal, and they are known to exhibit a wide variety of pharmacological properties and carcinostatic activities. Cr (III), Co (II), and Ni (II) complexes of Schiff base were chosen for the present experimental work and theoretical treatment and characterized by different spectroscopies such as elemental analysis CHN, infrared, ultra visible spectroscopies, magnetic susceptibility, molar conductivity measurements, and thermal analysis. The results of this research, indicate that the complexes have a type composition [M (NL)]. Schiff base NL: derived from 2-aminobenzoic acid and Benzil, M: Cr (III), Co (II), and Ni (II) transition metal ions. Schiff base acts as a tetradentate ligand with ions through the hydroxyl groups and imine groups. The work was included theoretical calculations of NL and its complexes, which were done by the program of hyperchem8. 0.7 using semi-empirical calculations. The PM3 method used to calculate the heat of formation (\(\Delta H_f\)), binding energy (\(\Delta E_b\)), total energy (\(\Delta E_{tot}\)), and geometric properties of the compounds.

INTRODUCTION

Transition metal complexes have enticed great attention owing to their charming chemical and physical properties and their wide-ranging applications in our life (Al-Hamdani et al., 2015; Kulandaisamy and Palanimurugan, 2015). Transition metal complexes of Schiff base ligand with donor atoms like nitrogen, oxygen have applications in biological and clinical areas (Ombenga et al., 2016; Aliyu and Ado, 2010; Najeeb, 2016). The coordination studies of Schiff bases get attractive physic-chemical properties in various areas of science (Najeeb et al., 2017; Sarkar et al., 2020; Yousif et al., 2011). In recent years, these Schiff bases complexes have flagged the way to find. The chemistry of metal complexes has always been defied to chemists as it has more branches nowadays (Ommeya et al., 2020; Ibrahim, 2017; Ibrahim et al., 2014). (Ibrahim et al., 2018) The metal complexes prepared from heterocyclic ligands can be used as antifungal, anti-inflammatory, anti-HIV, anticancer, diuretic, hypoglycemic, antithyroid, and antimalarials (Kurtoglu et al., 2014; Ušcumlić and Nikolić, 2009). At present, Schiff bases complexes have been potentially investigated due to many applications as anti-corrosion and crystal engineering (Gupta and Sutar, 2008; Mounika et al., 2010). The Schiff ligands are extensively investigated the synthetic elasticity, the reactivity for the metal ion, and its structural similarities with biological compounds as there is the presence of azomethine (–N=CH–) group...
which imports in of transformation mechanism and racemization reaction biologically (Nakamoto, 2009; Chai et al., 2015). Computational chemistry is defined as the application of mathematical and theoretical principles to predict the behavior of molecules in the chemical system. The electronic structure calculations provide energetic properties of chemical compounds, spectroscopic data, and the probability of many chemical reaction pathways. The electrostatic potential is used for finding sites of reaction in a compound (Gaber et al., 2008). This work aims to prepare the Schiff base compound with three transition ions Cr (III), Co (II), and Ni (II), then characterized by different spectroscopy measurements with the theoretical study of these complexes.

MATERIALS AND METHODS

Instrumentation

Infrared spectra were measured by ALPHA FTIR Shimadzu UV-Vis 160A spectrophotometer was used for UV-Visible spectra. Molar conductivity measurements were carried by using a water bath. The precipitate was collected by filtration, and washed with ethanol and dried in an oven at 50°C and identified by FT-IR, UV-Visible spectroscopy, magnetic susceptibility measurements, in addition to thermal analysis (Mohan et al., 2013).

RESULTS AND DISCUSSION

The physical data of the NL compound and its complexes have shown in Table 1 and measured by different spectroscopies such as elemental analysis CHN, magnetic susceptibility, molar conductivity measurements. The molar conductance values of 0.001M Co (II) and Ni (II) complexes in DMF solvent reveal non-electrolytic nature (Hasan et al., 2016).

FTIR spectroscopy

Infrared data of the NL ligand and its complexes are shown in Table 2. The stretching carboxylate group of the ligand is observed at 1660.52 and 1451.55 cm⁻¹ for asymmetric and symmetric stretching modes, respectively. These bands appeared at (1657.18 -1445.88) cm⁻¹ for ν(COO) and 1366.38 cm⁻¹ for νs(COO) of Co (II) complex, Ni (II) complex has bands at 1683.75 cm⁻¹ for νas(COO) and 1465.12 cm⁻¹ for νs(COO). Also, Cr (III) complex showed bands at (1657.18 -1445.88) cm⁻¹ for νas(COO) and νs(COO), respectively, see Figure 2, Figure 3 and Figure 4. The values of Δν for all complexes appeared in the region (211.3 - 223.84) cm⁻¹, which is greater than 200 cm⁻¹ indicating the carboxylate group act as a monodentate ligand. The stretching hydroxyl groups in the complex spectra disappearing represent the coordination through the OH group. ν C=N band of ligand appears at 1583.09 cm⁻¹ was shifted due to the coordination with metal ions. (Mahboub, 2020; Akhter et al., 2017; Wang et al., 2000).

Thermal analysis

The thermo-gravimetric analysis is one of the very useful tools in chemical science, helps to investigate the structure of complexes, and can provide information about chemical and physical phenomena of a compound, data of decomposition products, shown in Table 3. (Gaber et al., 2008; Al-Hamdani et al., 2015).

Ultraviolet-visible spectroscopy and magnetic moment

The ultraviolet, visible spectrum of the ligand in chloroform solvent showed bands at 252 nm and 370 nm these transitions attributed to π → π* and
**Figure 1: Synthesis of NL**

**Figure 2: The structural formula and 3D structure of Cr (III)**

**Table 1: Physical and analytical data of the NL and its complexes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield Product</th>
<th>M.p °C</th>
<th>Elemental analysis Found%, Calc.%</th>
<th>Molar conductance, DMF solvent μs/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td></td>
<td>C % O % N % H % M %</td>
<td></td>
</tr>
<tr>
<td>NL</td>
<td>76%</td>
<td>165</td>
<td>73 13.5 6 4 - -</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>75.3 14.3 6.2 4.5 4</td>
<td></td>
</tr>
<tr>
<td>[CrNL.2H₂O]Cl</td>
<td>70%</td>
<td>278</td>
<td>62.12 11.15 5 4 9</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>62.24 11.84 5.20 4.08 9.13</td>
<td></td>
</tr>
<tr>
<td>[CoNL]</td>
<td>66%</td>
<td>265</td>
<td>65 12 5 3 11</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>66.54 12.67 5.54 3.56 11.67</td>
<td></td>
</tr>
<tr>
<td>[NiNL].H₂O</td>
<td>74%</td>
<td>234</td>
<td>66 12.1 5.36 3.43 11.34</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>66.35 12.25 5.36 3.44 11.12</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3: The structural formula and 3D structure of Co(II)

Figure 4: The structural formula and 3D structure of Ni(II)

Table 2: IR data of NL and its metal complexes, cm$^{-1}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{as}$(COO)</th>
<th>$\nu_{s}$(COO)</th>
<th>$\nu$ C=N</th>
<th>$\nu$ C-H aromatic</th>
<th>$\nu$O-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>NL</td>
<td>1660.52</td>
<td>1451.55</td>
<td>1583.09</td>
<td>3065.37</td>
<td>3320.16</td>
</tr>
<tr>
<td>[CrNL.2H$_2$O]Cl</td>
<td>1657.18</td>
<td>1445.88</td>
<td>1585.24</td>
<td>3063.31</td>
<td>-</td>
</tr>
<tr>
<td>[CoNL]</td>
<td>1590.22</td>
<td>1366.38</td>
<td>1534.28</td>
<td>3136.11</td>
<td>-</td>
</tr>
<tr>
<td>[NiNL].H$_2$O</td>
<td>1683.75</td>
<td>1465.12</td>
<td>1554.41</td>
<td>3060.0</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 3: Thermo analysis measurement for Cr (III), Co (II), and Ni (II) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temperature range, °C</th>
<th>Weight loss %</th>
<th>Decomposition part</th>
<th>Liberate part</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>Calculate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CrC$<em>{28}$H$</em>{18}$N$_2$O$_6$Cl]</td>
<td>100-150</td>
<td>5.01</td>
<td>6.03</td>
<td>-2(H$_2$O)</td>
</tr>
<tr>
<td></td>
<td>412.3- 515</td>
<td>84.21</td>
<td>78.9</td>
<td>-2(C$_6$H$_5$)</td>
</tr>
<tr>
<td>[NiC$<em>{28}$H$</em>{20}$N$_2$O$_5$]</td>
<td>125.2- 200</td>
<td>14.16</td>
<td>15.32</td>
<td>-2(CO)</td>
</tr>
<tr>
<td></td>
<td>412.3- 410</td>
<td>68.56</td>
<td>68.54</td>
<td>-2(C$_6$H$_5$)</td>
</tr>
<tr>
<td>[CrC$<em>{28}$H$</em>{18}$N$_2$O$_4$Cl]</td>
<td>128.2- 140</td>
<td>11.09</td>
<td>19.04</td>
<td>-2(H$_2$O)</td>
</tr>
<tr>
<td></td>
<td>230-300</td>
<td>70.7</td>
<td>73.01</td>
<td>-2(C$_6$H$_5$)</td>
</tr>
</tbody>
</table>

Table 4: Ultraviolet-visible and magnetic moment for Cr (III), Co (II), and Ni (II) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>Band, nm</th>
<th>Assignment</th>
<th>Suggested Structure</th>
<th>Magnetic moment, B.M</th>
</tr>
</thead>
<tbody>
<tr>
<td>NL</td>
<td>Yellow</td>
<td>258, 370</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[CrNL.2H$_2$O]Cl</td>
<td>Greenish</td>
<td>761</td>
<td>$^4$A$<em>{2g}$ (F) $\rightarrow$ $^4$T$</em>{2g}$ (F)</td>
<td>Octahedral</td>
<td>3.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$^4$A$<em>{2g}$ (F) $\rightarrow$ $^4$T$</em>{1g}$ (F)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$^4$A$<em>{2g}$ (F) $\rightarrow$ $^4$T$</em>{1g}$ (F)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>333</td>
<td>$n \rightarrow \pi^*$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[CoNL]</td>
<td>Pink</td>
<td>632</td>
<td>$^4$A$<em>{2g}$ (F) $\rightarrow$ $^4$T$</em>{1g}$ (P)</td>
<td>Tetrahedral</td>
<td>4.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>233</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650</td>
<td>$^1$A$<em>{1g}$ $\rightarrow$ $^1$B$</em>{1g}$</td>
<td>Square planar</td>
<td>Zero</td>
</tr>
<tr>
<td>[NiNL].H$_2$O</td>
<td>Gray</td>
<td>334, 258</td>
<td>$n \rightarrow \pi^*$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 5: Calculations of some energies and physical properties of compounds

<table>
<thead>
<tr>
<th>Property*</th>
<th>PM3 method*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{tot}}$ (KJ/mole)</td>
<td>-494198.13</td>
</tr>
<tr>
<td>$E_b$ (KJ/mole)</td>
<td>-26067.15</td>
</tr>
<tr>
<td>$\Delta H^o_f$ (KJ/mole)</td>
<td>272.83</td>
</tr>
<tr>
<td>$E_{\text{HOMO}}$ (ev)</td>
<td>-8.2906</td>
</tr>
<tr>
<td>$E_{\text{LOMO}}$ (ev)</td>
<td>-2.3898</td>
</tr>
<tr>
<td>[CrNL.2H$_2$O]Cl</td>
<td></td>
</tr>
<tr>
<td>$E_{\text{tot}}$ (KJ/mole)</td>
<td>-639542.69</td>
</tr>
<tr>
<td>$E_b$ (KJ/mole)</td>
<td>-31195.81</td>
</tr>
<tr>
<td>$\Delta H^o_f$ (KJ/mole)</td>
<td>-880.04</td>
</tr>
<tr>
<td>$E_{\text{HOMO}}$ (ev)</td>
<td>-7.6052</td>
</tr>
<tr>
<td>$E_{\text{LOMO}}$ (ev)</td>
<td>-0.9295</td>
</tr>
<tr>
<td>[CoNL]</td>
<td></td>
</tr>
<tr>
<td>$E_{\text{tot}}$ (KJ/mole)</td>
<td>-567911.85</td>
</tr>
<tr>
<td>$E_b$ (KJ/mole)</td>
<td>-27227.02</td>
</tr>
<tr>
<td>$\Delta H^o_f$ (KJ/mole)</td>
<td>-894.59</td>
</tr>
<tr>
<td>$E_{\text{HOMO}}$ (ev)</td>
<td>-5.3242</td>
</tr>
<tr>
<td>$E_{\text{LOMO}}$ (ev)</td>
<td>-3.0525</td>
</tr>
<tr>
<td>[NiNL].H$_2$O</td>
<td></td>
</tr>
<tr>
<td>$E_{\text{tot}}$ (KJ/mole)</td>
<td>-623639.44</td>
</tr>
<tr>
<td>$E_b$ (KJ/mole)</td>
<td>-27936.22</td>
</tr>
<tr>
<td>$\Delta H^o_f$ (KJ/mole)</td>
<td>916.47</td>
</tr>
<tr>
<td>$E_{\text{HOMO}}$ (ev)</td>
<td>-9.7086</td>
</tr>
<tr>
<td>$E_{\text{LOMO}}$ (ev)</td>
<td>-2.1738</td>
</tr>
</tbody>
</table>

*Semi-empirical calculations and PM3 method for NL and its complexes

Figure 5: 2D electrostatic potential of NL

Figure 6: 2D electrostatic potential of Co(II)

n→π* electronic transitions, respectively.

The Cr (III) complex show bands at 761,676 and 333nm, the magnetic moment of Cr$^{3+}$ (d$^3$) was 3.89 B.M. So that octahedral geometry was proposed. The band and at 632 nm assigned to d-d transition in the Co (II) complex, the magnetic moment of Co$^{3+}$ (d$^7$) was 4.62 B.M. for paramagnetic properties. Therefore the tetrahedral geometry was proposed. Ni (II) complex shows, bands assigned to metal to ligand (charge transfer) transition and d-d transition at 258,334 and 650 nm, respectively, the magnetic moment of Ni$^{2+}$ (d$^8$) was zero due to diamagnetic properties; therefore, square planar geometry.
was suggested (Aliyu and Ado, 2010; Zoubi, 2013; Hamada et al., 2016), see Table 4.

**Theoretical study**

The electrostatic potentials of the NL ligand and its complexes were calculated and plotted as 2D to know the reactive sites of the molecules Figure 5 and Figure 6. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) values were plotted as 3D contour to get more information about these compounds Figure 7, and the frontier orbitals are governing factor in different reactions (Gaber et al., 2008).

In this theoretical study, the Chemoffice program was used to draw the structure of compounds, and Chemoffice 3D used to draw the 3D structure of molecules. Hyperchem 8.0.7 program using Semi-empirical calculations and the PM3 method to characterize compounds by calculating optimized geometries, HOMO, LUMO, electrostatic potential and showed the [NiNL]. H$_2$O more stable complex, and from the theoretical data of Table 5, the stability of NL complexes follows the order: Ni (II) >Co (II) > Cr (III).

**CONCLUSION**

Experimental results obtained from this work suggest Cr (III) has an octahedral structure, while Co(II) has a tetrahedral structure and Ni (II) has a square planar structure with tetradentate Schiff base ligand, this coordination occurs by the deprotonated hydroxyl of carboxylate group and an amine group N=C. The molar conductivity of Cr(III) complex was electrolyte nature due to the chloride ion in the solution, while non-electrolytic nature for Co (II) and Ni (II) complexes. Thermal analysis of Cr (III) complex confirms the presence of a coordinated water molecule and water molecule was presented out of the coordination sphere of Ni (II) complex, as well as semi-empirical data using the PM3 method showed the [NiNL]. H$_2$O more stable complex. The electrostatic potential finds sites of the reaction between the transition metal ion and the donor atoms of the tetradentate Schiff base. The calculations showed that LUMO of transition metal ion prefers to react with the HOMO of oxygen and nitrogen of atoms of Schiff base.

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**Conflict of Interest**

The authors declare that they have no conflict of interest.

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