Physicochemical studies of Chromium II and Cadmium II complexes with Schiff base ligands derived from 2,4-dinitrophenyl hydrazine

1Kawuwa B., 2Buba M. and 3Yakubu S.

1Department of Chemical Science Federal University of Kashere Gombe, Gombe State, Nigeria.
2Department of Science Laboratory Technology, Federal Polytechnic, Mubi Adamawa State, Nigeria.

ABSTRACT
A polydentate ligand is a molecule or ion that bonds to the central atom through several of the ligand’s atoms; ligands with 2, 3, 4 or even 6 bonds to the central atom are common. The central atom or ion, together with all ligands comprises the coordination sphere. The aim of this research was to investigate physiochemical studies of chromium II, and cadmium II complexes with Schiff base ligands derived from 2,4-dinitrophenyl hydrazine. The condensation reaction of 2,4-dinitrophenylhydrazine and benzaldehyde in an ethanolic solution in 1:1 molar ratio in the presence of glacial acetic acid as catalyst yields an orange Schiff base ligand (L). The Cd(II) and Cr(II) complexes of the Schiff base ligand (benzaldehyde, 2,4-dinitrophenylhydrazone) abbreviated as BDNPH were synthesized by reaction of the metal salts with the Schiff base ligand (L) in 1:2 (M:L) molar ratio of the metal to ligand. This yield a dark brown and lemon green complexes of Cd(II) and Cr(II) respectively. The Schiff base was isolated in 83% yield while Cd(II) and Cr(II) complexes were isolated in 57% and 53% yield respectively. Cd(II) and Cr(II) complexes with Schiff base ligand derived from 2,4-dinitrophenylhydrazine were synthesized and characterized by FT-IR spectroscopy and UV-Vis. Spectroscopy. The Schiff base ligand coordinates with the metal ion through the nitrogen of the azomethine (imine) group, nitrogen of the hydrazinic band and nitrogen atom from each of the to nitrate ions for Cd(II) complex and two chlorine atoms for Cr(II) complex to complete the octahedral geometry. The Schiff base ligand behaves as a bidentate ligand.

Keywords: Ligand, Physicochemical, Chromium II, Cadmium II complexes and Schiff base

INTRODUCTION
Coordination compound consists of a central atom or ion, which is usually metallic and is called the coordination center, and a surrounding array of bound molecules or ions, that are in turn known as ligands or complexing agents. Many metal-containing compounds, especially those of transition metals, are coordination complexes [1]. Coordination complexes are so pervasive that their structures and reactions are described in many ways, sometimes confusingly. The atom within a ligand that is bonded to the central metal atom or ion is called the donor atom. In a typical complex, a metal ion is bonded to several donor atoms, which can be the same or different. A polydentate(multiple bonded) ligand is a molecule or ion that bonds to the central atom through several of the ligand’s atoms; ligands with 2, 3, 4 or even 6 bonds to the central atom are common. The central atom or ion, together with all ligands comprises the coordination sphere. The central atoms or ion and the donor atoms
comprise the first coordination sphere. Coordination refers to the "coordinate covalent bonds" (dipolar bonds) between the ligands and the central atom. Originally, a complex implied a reversible association of molecules, atoms, or ions through such weak chemical bonds. As applied to coordination chemistry, this meaning has evolved. Some metal complexes are formed virtually irreversibly and many are bound together by bonds that are quite strong [2].

The number of donor atoms attached to the central atom or ion is called the coordination number. The most common coordination numbers are 2, 4, and especially 6. A hydrated ion is one kind of a complex ion (or simply a complex), a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. If all the ligands are monodentate, then the number of donor atoms equals the number of ligands. The oxidation state and the coordination number reflect the number of bonds formed between the metal ion and the ligands in the complex ion. However, the coordination number of Pt(en)$_2^+$ is 4 (rather than 2) since it has two bidentate ligands, which contain four donor atoms in total [3]. In coordination chemistry, a ligand is an ion or molecule (functional group) that binds to a central metal atom to form a coordination complex. The bonding with the metal generally involves formal donation of one or more of the ligand’s electron pairs. The nature of metal–ligand bonding can range from covalent to ionic. Furthermore, the metal–ligand bond order can range from one to three. Ligands are viewed as Lewis bases, although rare cases are known to involve Lewis acidic "ligands". Especially in the area of organometallic chemistry, ligands are classified as L and X (or combinations of the two). The classification scheme – the "CBC Method" for Covalent Bond Classification – was popularized by M.L.H. Green and is based on the notion that there are three basic types [of ligands]... represented by the symbols L, X, and Z, which correspond respectively to 2-electron, 1-electron and 0-electron neutral ligands. Another type of ligand worthy of consideration is the LX ligand which as expected from the used conventional representation will donate three electrons if NVE (Number of Valence Electrons) required. Example is alkoxyligands (which is regularly known as X ligand too). L ligands are derived from charge-neutral precursors and are represented by amines, phosphines, CO, N$_2$, and alkenes. X ligands typically are derived from anionic precursors such as chloride but includes ligands where salts of anion do not really exist such as hydride and alkyl. Thus, the complex IrCl(CO)(PPh$_3$)$_2$ is classified as an MXL complex, since CO and the two PPh$_3$ ligands are classified as Ls. The oxidative addition of H$_2$ to IrCl(CO)(PPh$_3$)$_2$ gives an 18e$^-$ MLX$_3$ product, IrClH$_2$(CO)(PPh$_3$)$_2$. EDTA$^{4-}$ is classified as an L,X ligand, as it features four anions and two neutral donor sites. Cp is classified as an L$_2$X ligand [4].
Statement of the Problem

The synthesis of Schiff base metal complexes have grown rapidly over the years, this is due to the various applications attributed to the metal complexes. From the literature studies, only few reports are available on the Schiff base complexes derived from 2,4-dinitrophenylhydrazine. Hence, there is need to synthesize more of the Schiff base complexes derived from 2,4-dinitrophenylhydrazine.

AIM AND OBJECTIVES

Aim

The aim of this research was to investigate physiochemical studies of chromium II, and cadmium II complexes with Schiff base ligands derived from 2,4-dinitrophenyl hydrazine.

Objectives

- To determine the synthesis and characterization of chromium II and cadmium II metal complexes
- To examine the characterization of 2,4 ditrophenyl hydrazine
- To examine the computational method of ligand deformation energies

Significance of the Study

The study provides the coordination modes of new Schiff base ligand and its metal complexes that could add to new knowledge. It also reveals the stoichiometric compositions of the Schiff base ligand and its metal complexes. The structural information of these coordination compounds could be used to
expand their possible application in areas such as biological studies, chemical studies, agriculture studies, and DNA binding studies.

**Scope and Limitation**

This study is limited to the synthesis and physicochemical studies of one Schiff base ligand and two metal complexes. It is expected that other studies in the future will cover the areas not examine.

**MATERIALS AND METHODS**

**Materials**

All chemicals and solvents are of analytical grade and were used as received without further purification. All the glass wares that were used were washed thoroughly with distilled water and then dried in an oven at 80 °C. The metal salts were obtained in the form of their chloride for cadmium and chloride for cobalt.

**Equipment’s/Apparatus**

Mechanical stirrer, funnel, burette, measuring cylinder, beaker, pipette, volumetric flask, conical flask, electronic balance, capillary tube, Bibby Scientific electro-thermal melting point apparatus 9300, heating mantle/hot plate, condenser, desiccators, filter paper, Jenway 3540 conductivity meter, Jenway 6405 UV-Visible spectroscopy and Perkin Elmer, Fourier transform infrared spectroscopy.

**Chemicals/Reagents**

2,4dinitrophenylhydrazine, benzaldehyde, glacial acetic acid, cadmium (II) chloride hexahydrate, chromium (II) chloride hexahydrate, ethanol, diethyl ether, acetone, benzene, methanol, chloroform, toluene, dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), acetonitrile and ethyl acetate.

**Methods**

**Synthesis of Schiff Base (L)**

The Schiff base ligand was prepared with some modification of the method described by (Jarrahpour and Zarei, 2004). The ligand was prepared by condensation of benzaldehyde with 2,4-dinitrophenylhydrazine in 1:1 molar ratio in an alcoholic medium (ethanol). 2.8 mL, 0.25 mole of benzaldehyde was dissolved in 100 mL of ethanol. Again 5.1g, 0.25 mole of 2,4-dinitrophenylhydrazine was dissolved in 100 mL of ethanol. These two solutions were stirred vigorously and heated under reflux for 5 hours. 3 drops of glacial acetic acid were added as catalyst. The reaction mixture was allowed to cool to normal ambient temperature for 30 minutes. The orange precipitate that was formed was therefore filtered off and washed several times using cold ethanol. The crystalline solid was purified by recrystallization from hot ethanol and was dried in vacuum.
The Cd(II) metal complex was prepared with some modification of the earlier reported method described by [5]. A solution of the metal salt (0.72g, 0.1 mole) in hot ethanol (25 mL) was mixed drop wise with the solution of the Schiff base ligand (L) (1.44g, 0.2 mole) in hot ethanol (25 mL) in a molar ratio (1:2) of the metal to ligand. The resulting mixture was stirred under reflux for 3 hours. For the complex to be formed, the product was allowed to cool to a normal ambient temperature. After cooling, a dark brown precipitate was formed which was collected by filtration and then washed several times with 50% ethanol and diethyl ether. The solid product was dried in air and stored in desiccator over anhydrous calcium chloride in vacuum.

The Cr(II) metal complex was prepared with some modification of the earlier reported method described by [5]. A solution of the metal salt (0.59g, 0.1 mole) in hot ethanol (25 mL) was mixed drop wise with the solution of the Schiff base ligand (L) (1.43g, 0.2 mole) in hot ethanol (25 mL) in a molar ratio (1:2) of the metal to ligand. The resulting mixture was stirred under reflux for 3 hours. For the complex to be formed, the product was allowed to cool to a normal ambient temperature. After cooling, a lemon green precipitate was formed which was collected by filtration and then washed several times with 50% ethanol and diethyl ether. The solid product was dried in air and stored in desiccator over anhydrous calcium chloride in vacuum.

Physico-Chemical Analysis of the Schiff Base Ligand and its Metal Complexes

The physico-chemical analysis such as solubility, melting point determination and conductivity measurement of the Schiff base ligand and its metal complexes were carried out.

Solubility

The solubility of the Schiff base ligand and its metal complexes were checked by various solvents: water, diethyl ether, acetone, benzene, methanol, chloroform, toluene, ethanol, ethyl acetate, tetrahydrofuran (THF), acetonitrile, dimethylsulfoxide (DMSO) and dimethylformamide (DMF). 1g of each compound was mixed and stirred with 5 mL of each of the solvents in test tube. In each case the solubility of the compounds were recorded [6].
Melting Point Determination

The melting point was determined by placing a finely powdered sample in a capillary tube and heating by melting point apparatus and the results were recorded. The melting point of each sample was recorded after it starts to melt [7].

Conductivity

The conductivity of the complexes was measured using a conductivity meter. A finely powdered sample was dissolved in a beaker containing the solvent dimethylsulfoxide (DMSO) at the concentration of $10^{-3}$ M. The sensor on the conductivity meter was submerged into the solution being tested and the readings were taken [8].

Percentage Element Analysis

The percentage of elements in the Schiff base ligand and its metal complexes was computed using standard methods.

Characterization of the Schiff Base Ligand and its Metal Complexes

The compounds were characterized using UV-Visible spectroscopy, Fourier transform infrared spectroscopy.

Fourier Transform-Infrared (FT-IR) Spectroscopic Analysis

Infrared spectra of the samples were recorded on Perkin Elmer FT-IR/NIR spectrophotometer Frontier. All the spectra were run in the range 4000 - 550 cm$^{-1}$ at room temperature [9].

The Ultraviolet/visible (UV-Vis) Spectroscopic Analysis

The UV-Vis spectra were recorded using plastic cuvettes in the region of 250 - 800 nm. Solution of the Schiff base ligand and its metal complexes were prepared and dilute in dimethylformamide (DMF) and the readings/spectra were collected [9].

RESULTS AND DISCUSSION

Results

From the synthesis and characterization of Schiff base ligand (BDNPH) and its metal complexes, the following results were obtained:

Physico-Chemical Data

Table 1: Analytical data for the Schiff base ligand and its complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Point (°C)</th>
<th>Conductivity ($\Omega^{-1} \text{ mol}^{-1} \text{ cm}^{2}$)</th>
<th>%yield</th>
<th>% Metal (Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDNPH</td>
<td>Orange</td>
<td>190</td>
<td>-</td>
<td>83</td>
<td>-</td>
</tr>
<tr>
<td>[Cd(BDNPH)$_2$Cl$_2$]</td>
<td>Brown</td>
<td>210</td>
<td>109</td>
<td>54</td>
<td>7.69</td>
</tr>
<tr>
<td>[Cr(BDNPH)$_2$Cl$_2$]</td>
<td>Lemon Green</td>
<td>202</td>
<td>98</td>
<td>69</td>
<td>8.24</td>
</tr>
</tbody>
</table>
Table 2: Analytical data for percentage of elements (Calculated) and calculated mass of the Schiff base ligand and its metal complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>Mass (gmol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDNPH</td>
<td>54.17</td>
<td>4.17</td>
<td>19.44</td>
<td>22.22</td>
<td>288</td>
</tr>
<tr>
<td>[Cd(BDNPH)<em>{2}Cl</em>{2}]</td>
<td>37.94</td>
<td>3.16</td>
<td>29.51</td>
<td>33.72</td>
<td>759</td>
</tr>
<tr>
<td>[Cr(BDNPH)<em>{2}Cl</em>{2}]</td>
<td>41.20</td>
<td>3.43</td>
<td>32.05</td>
<td>36.62</td>
<td>699</td>
</tr>
</tbody>
</table>

Solubility Measurement

Table 3: Solubility of the Schiff base ligand and its metal complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Water</th>
<th>Ethanol</th>
<th>Methanol</th>
<th>Chloroform</th>
<th>Acetone</th>
<th>Benzene</th>
<th>Toluene</th>
<th>DMF</th>
<th>DAN</th>
<th>DMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDNPH</td>
<td>IS</td>
<td>SS</td>
<td>SS</td>
<td>SS</td>
<td>S</td>
<td>SS</td>
<td>SS</td>
<td>S</td>
<td>SS</td>
<td>S</td>
</tr>
<tr>
<td>Cd(BDNH)<em>{2}Cl</em>{2}</td>
<td>IS</td>
<td>SS</td>
<td>SS</td>
<td>S</td>
<td>SS</td>
<td>IS</td>
<td>SS</td>
<td>IS</td>
<td>IS</td>
<td>IS</td>
</tr>
<tr>
<td>Cr(BDNP)<em>{2}Cl</em>{2}</td>
<td>IS</td>
<td>SS</td>
<td>IS</td>
<td>S</td>
<td>SS</td>
<td>S</td>
<td>SS</td>
<td>IS</td>
<td>S</td>
<td>IS</td>
</tr>
</tbody>
</table>

Hint:
IS = Insoluble
SS = Slightly soluble
S = Soluble
DMF = Dimethylformamide
DMSO = Dimethylsulfoxide
THF = Tetrahydrofuran
DAN = Diacetonitrile.
Fourier Transform-Infrared (FT-IR) Spectroscopic Analysis

Table 4: Infrared spectra result for BDNPH and its metal complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(C=N)</th>
<th>$\nu$(N-N)</th>
<th>$\nu$(N-H)</th>
<th>$\nu$(M-N)</th>
<th>$\nu$(Cr-Cl)</th>
<th>$\nu$(NO$_3^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>BDNPH</td>
<td>1620</td>
<td>982</td>
<td>3288</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Cd(BDNPH)$_2$ Cl$_2$]</td>
<td>1592</td>
<td>1335</td>
<td>3450</td>
<td>537</td>
<td>-</td>
<td>1205</td>
</tr>
<tr>
<td>[Cr(BDNPH)$_2$Cl$_2$]</td>
<td>1591</td>
<td>1333</td>
<td>3436</td>
<td>529</td>
<td>549</td>
<td>-</td>
</tr>
</tbody>
</table>

Ultraviolet/visible (UV-Vis) Spectroscopic Analysis

Table 5: Results showing the UV-Vis. spectra of BDNPH and its metal complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength(nm)</th>
<th>Energies(cm$^{-1}$)</th>
<th>Assignment</th>
<th>Geometry</th>
<th>Suggested</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDNPH</td>
<td>215</td>
<td>20300</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>21400</td>
<td>$\pi \rightarrow \pi^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>18490</td>
<td>$n \rightarrow \pi^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>26540</td>
<td>$n \rightarrow \pi^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cd(BDNPH)$_2$ Cl$_2$]</td>
<td>250</td>
<td>27800</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>Octahedral</td>
<td></td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>30100</td>
<td>$\pi \rightarrow \pi^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>365</td>
<td>15750$^3$</td>
<td>$A_2g \rightarrow 3T_{1g}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>425</td>
<td>18440$^4$</td>
<td>$T_{1g} \rightarrow 4T_{1g} \text{ (P)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cr(BDNPH)$_2$Cl$_2$]</td>
<td>210</td>
<td>21500</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>Octahedral</td>
<td></td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>42200</td>
<td>$\pi \rightarrow \pi^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>330</td>
<td>19190$^3$</td>
<td>$A_2g \rightarrow 3T_{1g}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 2: Proposed Structure of [Cd(BDNPH)$_2$Cl$_2$] Complex.

Figure 3: Proposed Structure of [Cr(BDNPH)$_2$Cl$_2$] Complex.
DISCUSSION

The condensation reaction of 2,4-dinitrophenylhydrazine and benzaldehyde in an ethanolic solution in 1:1 molar ratio in the presence of glacial acetic acid as catalyst yields an orange Schiff base ligand (L). The Cd(II) and Cr(II) complexes of the Schiff base ligand (benzaldehyde, 2,4-dinitrophenylhydrazone) abbreviated as BDNPH were synthesized by reaction of the metal salts with the Schiff base ligand (L) in 1:2 (M:L) molar ratio of the metal to ligand. This yield a dark brown and lemon green complexes of Cd(II) and Cr(II) respectively. The Schiff base was isolated in 83% yield while Cd(II) and Cr(II) complexes were isolated in 57% and 53% yield respectively.

Physico-Chemical Data

The physical characteristics of the Schiff base ligand and its metal complexes are shown in Table 1 above, which shows colour, melting point, percentage yield, conductivity, percentage element analysis found (calculated) and percentage metal found (calculated) of the synthesized compounds. At ambient temperature, the Schiff base ligand and its metal complexes are soluble in polar aprotic solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF) and ethyl acetate. They are insoluble in water but slightly soluble in common organic solvents such as methanol, ethanol, acetone, benzene, toluene, chloroform, diethyl ether and acetonitrile. The solubility of the complexes in polar aprotic solvents such as dimethlyformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF) and ethyl acetate is probably due to the polar nature of the complexes and also due to the large dipole moments and large dielectric constants of polar aprotic solvents. The high polarity of these solvents allows them to dissolve charged species. The molar conductance values of the soluble complexes in dimethylsulfoxide (DMSO) (10⁻³ M) showed higher values (101 – 115 Ω⁻¹ mol⁻¹ cm²) indicating that these complexes are good electrolytes suggesting the polymeric nature and partial solvolysis of the complexes in DMSO medium. All the complexes synthesized were coloured ranging from their parent ligand to metal complex. Cd(II) complex gives a dark brown colour while Cr(II) complex gives a lemon green colour respectively. The colour of these complexes is due to d-d transition and charge transfer spectra within the ligand and the metal ion. The complexes are also non-hygroscopic solids with different melting point ranging from 199 to 211°C. All complexes have melting points higher than their respective parent ligand probably due to complexation.

Molar Conductance Measurement

The conductivity of the compounds was taken on JENWAY 3540 conductivity meter. The molar conductance values of the metal complexes are shown in Table 1 above. The molar conductance values measured in DMSO (10⁻³ M) at 25 ± 2 °C for these complexes are in the range 101 - 115 Ω⁻¹ mol⁻¹ cm². According to these results, the complexes are electrolytes.

Melting Point Measurement

The melting points of the compounds were taken on Electro-thermal melting point apparatus 9300. The melting points are presented in Table 1 above. The results obtained suggest that the melting points are sharp indicating the purity of the Schiff base ligand and its metal complexes. The complexes have higher melting points rather than the Schiff base ligand. Specifically the ligand melts around 199 – 201 °C, while for Cd(II) and Cr(II) complexes, the melting points are 211 °C and 206 °C respectively. The metal complexes shows higher melting point because the metal elements itself show higher melting point due to the closed packed structure and other metallic properties such as high melting point, solid at room temperature etc. Therefore, they have strong metallic bond and small
atomic radii thus, they need strong or more energy to break after coordination through transition metal [9].

Solubility Measurement
The solubility test for the Schiff base ligand and its metal complexes as shown in table 3 above, were done in order to identify the best solvent to be used for purification and other spectroscopic measurement. The solubility test of the Schiff base ligand and its metal complexes in water and common organic solvents carried out showed that both the Schiff base ligand and its metal complexes are insoluble in water, slightly soluble in common organic solvents such as methanol, ethanol, acetone, benzene, toluene, chloroform, diethyl ether and acetonitrile but readily soluble in polar aprotic solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF) and ethyl acetate suggesting the polar nature of the compounds [10].

Fourier Transform-Infrared (FT-IR) Spectroscopic Analysis
In order to determine the binding mode of Schiff base ligand to metal in the complexes, IR spectrum of the free ligand was compared with the spectra of the metal complexes. The IR spectra of the synthesized Schiff base ligand and its metal complexes were recorded on Perkin Elmer FT-IR/NIR Spectrometer Frontier within the region of 4000 – 550 cm\(^{-1}\). IR spectral bands of the Schiff base ligand and its metal complexes are presented in Table 4.4 above. Band at 1616 cm\(^{-1}\) in the Schiff base ligand is assigned to imine (azomethine) \(\nu(C=\text{N})\) stretching vibration. This band is shifted to lower wave number 1605-1606 cm\(^{-1}\) in the metal complexes due to the coordination of the nitrogen atom of the azomethine group to the central metal atom [11]. The characteristic hydrazinic band \(\nu(\text{N-N})\) appeared at 989 cm\(^{-1}\) in the Schiff base ligand. The absorption frequency of this band has increased to 1021 – 1025 cm\(^{-1}\). This could be due to donation of the unpaired electrons from the nitrogen to the metal (II) ion, incidentally deflating the repulsion force and subsequently, shifting the absorption frequency to a higher value. The \(\nu(\text{N-H})\) stretching at 3284 cm\(^{-1}\) in the Schiff base ligand shifted to lower frequency 3234 - 3241 cm\(^{-1}\), this also supported the involvement of hydrazinic nitrogen in coordination with the central metal. The presence of nitrate in the coordination sphere of Cd(II) metal confirmed by the \(\nu(\text{Cl})\) at 1217 cm\(^{-1}\), this indicates the possible coordination of nitrate group to Cd(II) metal. A band at 551 cm\(^{-1}\) is assigned to \(\nu(\text{Cr-Cl})\). Which indicates the coordination of chlorine to Cr(II) metal. The new bands around 671 – 682 cm\(^{-1}\) are assigned to \(\nu(M-N)\). This confirmed the coordination of benzaldehyde,2,4dinitrophenylhydrazone to the metal (II) ion. Thus, it may be concluded that the complexes are octahedral. The Schiff base ligand, benzaldehyde,2,4dinitrophenylhydrazone is bidentate. Each metal ion coordinating to the nitrogen of the azomethine (imine), nitrogen of the hydrazinic band, nitrogen atom from each of the two nitrate ions for Cd(II) complex and two chlorine atoms for Cr(II) complex to complete the octahedral structure[12].

Ultraviolet/visible (UV-Vis) Spectroscopic Analysis
The UV-Visible spectra of the synthesized Schiff base ligand and its metal complexes were recorded on JENWAY 6405 UV/Vis. spectrophotometer at the region of 250 – 800nm. UV-Visible bands of the Schiff base ligand and its metal complexes are presented in Table 4.5 above. The UV-Visible spectra of the Schiff base ligand exhibit strong absorption bands at 215, 270, 360 and 420nm which were attributed to \(\pi \rightarrow \pi^*\) and \(n \rightarrow \pi^*\) transitions respectively. The band at 420nm is due to the \(n \rightarrow \pi^*\) transitions of the non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base ligand (Erdal et al., 2016). The cadmium (II) complex exhibit 4 bands at 210, 280, 330 and
475 nm. According to Orgel diagram for d configuration, these are assigned to \( \pi \rightarrow \pi^* \), \( \pi \rightarrow \pi^* \), \( ^3A_g \rightarrow ^3T_g \), and \( ^3T_g \rightarrow ^4T_g \). The nickel (II) complex also shows 4 bands at 250, 260, 360 and 425 nm which corresponds to \( \pi \rightarrow \pi^* \), \( \pi \rightarrow \pi^* \), \( ^3A_g \rightarrow ^3T_g \) and \( ^3A_g \rightarrow ^3T_g \). These characteristics bands observed in the UV-Visible spectra suggest the octahedral configuration for all the complexes.

**CONCLUSION**

Cd(II) and Cr(II) complexes with Schiff base ligand derived from 2,4-dinitrophenylhydrazine were synthesized and characterized by FT-IR spectroscopy and UV-Vis. Spectroscopy. The Schiff base ligand coordinates with the metal ion through the nitrogen of the azomethine (imine) group, nitrogen of the hydrazinic band and nitrogen atom from each of the to nitrate ions for Cd(II) complex and two chlorine atoms for Cr(II) complex to complete the octahedral geometry. The Schiff base ligand behaves as a bidentate ligand.

**RECOMMENDATIONS**

Schiff bases have been widely explored for industrial applications. However, the chemical and biochemical activity of this class of compounds still requires further investigations. Results obtained from this research indicates that further work needs to be carried out in the following areas to fully establish the synthesis and characterization of transition metal complexes [Cd(II) and Cr(II)] with Schiff base ligand derived from 2,4-dinitrophenylhydrazine through the use and application of:

- Elemental analyzer to fully find out the exact percentage of elements in the Schiff base ligand and its metal complexes.
- H-NMR and C-NMR to be able to know the complete structures of the synthesized compounds.
- Advanced microscopic technique such as X-ray Powder Diffraction to examine the true geometry of the Schiff base ligand and its metal complexes.
- Mass spectroscopy to find out the real atomic weight of the compounds and their common framework.
- Schiff base ligand (BDNPH) and its metal complexes in catalysis.
- Schiff base ligand (BDNPH) and its metal complexes in medicine and pharmacy such as biological activity, antibacterial properties, antifungal properties, biocidal properties, antiviral properties, antimalarial properties, anticancer properties etc.
- Schiff base ligand (BDNPH) and its metal complexes in synthesis and chemical analysis such as production of pharmaceuticals and agrochemical industry.

**REFERENCES**


