Preparation and Physical Investigation of Complexes Derived from 4-Dimethylaminobenzaldehyde and 4-Aminoantipyrine Schiff Base with Ni(II), Cu(II), Rh(III), and Pt(IV) Ions

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Abstract

Four new Schiff base complexes derived from Ni(II), Cu(II), Rh(III), and Pt(IV) with 4-dimethylaminobenzaldehyde and 4-aminoantipyrine were prepared and investigated using some elemental analysis such as molar conductivity measurements, thermogravimetric analysis, magnetic moments, infrared, electronic and mass spectra. The elemental analysis for C, H, and N showed the formation of 1:1[M:L] complexes. The molar conductivity measurements revealed that the complexes are nonelectrolyte in nature. The thermogravimetric analysis data exhibited the presence of coordinated and hydrated water molecules. The magnetic moment results showed paramagnetic phenomena for nickel and copper complexes and diamagnetic phenomena for Rhodium and platinum complexes. The infrared spectral data of the prepared complexes displayed the proper coordination sites of the present Schiff base towards the metal ions. The electronic absorption spectral data of the prepared complexes confirmed the electronic transitions and the chemical structures. The mass spectra of the free Schiff base and its complex with Rh(III) exhibited an interesting fragmentations.

Keywords: 4-Dimethylaminobenzaldehyde; 4-Aminoantipyrine; Nonelectrolyte; Schiff base complexes.

Introduction

Schiff bases are characterized by the HC=N- (imine) group which is important in illustrating the mechanism of transamination and racemisation reactions in biological systems. Ni(II) chelate of the Schiff base derived from 4-dimethylaminobenzaldehyde and cysteine has been prepared and characterized by several physical techniques. Boghaei synthesized and characterized nonsymmetrical of Ni(II) and Cu(II) ions tetradeinate Schiff base complexes with N2O2 and N2O donor sites. El-ajaily et al. studied the antibacterial activities of the Schiff base derived from the Salicylaldehyde and histidine and its Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) complexes on some pathogenic bacteria. The divalent metal ions of Co(II), Ni(II) or Zn(II) have the formulae of ML2X2 and ML2 in their complexes, in which L represents benzointhiosemicarbazone and X represent halide or nitrate ions The complexes have been prepared and investigated on the basis of elemental analysis and electronic spectra.
The present work aims to synthesis and characterize the geometrical structures of Schiff base complexes.

**Experimental**

**Chemicals and reagents**

All chemicals used in this work were reagent grade materials from BDH or Aldrich including 4-dimethylaminobenzaldehyde, 4-aminoantipyrine, NiCl₂.6H₂O, Cu(CH₃COO)₂.H₂O, PtCl₄, RhCl₃.3H₂O, C₂H₅OH, CH₃OH, CHCl₃ and double distilled water.

**Measurements**

The synthesized Schiff base complexes were subjected to (C, H and N) 2400 elemental analyzer. The molar conductance measurements were carried out in DMSO solvent using conductivity meter model CMD650 digital. The thermogravimetric analysis was achieved using Schimadzu thermal analyzer (Japan). The weight losses were measured from ambient temperature to 1000°C in rate of 10°C/min. The magnetic moment measurements of the complexes were measured by using magnetic susceptibility balance Sherwood Scientific England. The Infrared spectra were obtained by using KBr disk technique on IFS-25 DPUS/Ir spectrometer (Bruker) in the range of 4000-500 cm⁻¹. The electronic absorption spectra of the complexes were measured in CHCl₃ solvent using UV-Vis-NIR3101PC Schimadzu (Japan). The mass spectra were carried out using Q1000 EXGC-MS Schimadzu spectrometer at 70eV and MA energy using a direct insertion probe at temperature range of 90-110 °C.

**Preparation of Schiff base**

The Schiff base from 4-dimethylaminobenzaldehyde and 4-aminoantipyrine was prepared by adding an ethanolic solution (30 ml) of 4-dimethylaminobenzaldehyde (1.49 g ; 0.01 mol) to an ethanolic solution of 4-aminoantipyrine (2.03 g ; 0.01 mol). The mixture was stirred for two hours, and the resulting mixture was evaporated under vacuum to remove the solvent. The obtained product was collected by filtration, washed several times with methanol and recrystallized from hot ethanol and then dried under vacuum. The melting point of the yellow crystals found to be 245 °C. The purity was confirmed by the elemental analysis and TLC techniques.

**Preparation of Schiff base complexes**

The mixtures of the Schiff base under investigation (0.01 mmol; 3.34 g) in 30 ml ethanol and metal salts [10mmol, NiCl₂.6H₂O (2.37 g), Cu(CH₃COO)₂.H₂O (1.99 g), RhCl₃.3H₂O (2.63 g) and PtCl₄ (1.50 g)] in the same amount of the same solvent were refluxed for two hours. The complexes were collected by filtration and then washed several times with hot ethanol until the mother liquors become colourless. The resulted products were dried in air and stored in a desiccator over anhydrous CaCl₂ under vacuum. Good yields of about 80% were obtained and their purity was confirmed by the elemental analysis data. They decomposed above 350 °C.
Results and Discussion

Microanalysis

The elemental analysis data of the complexes as shown in Table (1) exhibit the formation of 1:1[M:L] ratio. It was found that the theoretical values are in a good agreement with the found data. The purity of the Schiff base complexes were tested by TLC technique and C, H and N elemental analyses.

Table (1): Elemental analyses and some physical properties of Schiff base complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>M.Wt</th>
<th>Λm</th>
<th>µ BM</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni (L)(Cl)2(H2O)2].4H2O</td>
<td>71.16</td>
<td>6.75</td>
<td>16.59</td>
<td>334.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Cu(L)(Cl)2].H2O</td>
<td>71.16</td>
<td>6.75</td>
<td>16.59</td>
<td>334.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Rh(L)(Cl)3(H2O)].3H2O</td>
<td>71.16</td>
<td>6.75</td>
<td>16.59</td>
<td>334.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Pt(L)(Cl)4].2H2O</td>
<td>71.16</td>
<td>6.75</td>
<td>16.59</td>
<td>334.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Λm = molar conductance (ohm⁻¹ cm² mol⁻¹), Bold = found values

Molar conductivity

The molar conductance measurements of the prepared complexes were carried out in DMSO solvent and the obtained values (Table 1) were taken as a good evidence for the existence of a non-electrolyte nature.[8]

Thermogravimetric analysis

The thermogravimetric analysis data of Rh(III) and Pt(IV) Schiff base complexes display weigh-losses of 16.50 and 3.50% corresponding to three and two water molecules of hydration at 295 and 170 °C, respectively and the weight-loss of 7.00% is due to loss of one coordinated water molecule above 295 °C. The residual of metal oxides (Rh2O3) and (PtO2) of 26.00 and 41.00% were appeared at temperatures at 980 and 994 °C coincide fairly with the theoretical values shown in Table (2) and Figures (1 and 2).
**Table (2):** Thermogravimetric analysis data of Rh(III) and Pt(IV) Schiff base complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Water of hydration Weight loss</th>
<th>No. of Water Molecules</th>
<th>.Temp C°</th>
<th>Water of Coordination Weight loss %</th>
<th>No. of Water Molecules</th>
<th>MO Weight % loss</th>
<th>.Temp C°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(L)(Cl)₃[H₂O]·3H₂O</td>
<td>17.56 16.50</td>
<td>3</td>
<td>295</td>
<td>7.10 00.7</td>
<td>1</td>
<td>27.02 26.00</td>
<td>980</td>
</tr>
<tr>
<td>Pt(L)(Cl)₄·2H₂O</td>
<td>5.09 3.50</td>
<td>2</td>
<td>170</td>
<td>-</td>
<td>-</td>
<td>42.09 41.00</td>
<td>994</td>
</tr>
</tbody>
</table>

Bold values are Found values

**Figure (1):** Thermogravimetric analysis of Pt(IV)-L complex

**Figure (2):** Thermogravimetric analysis of Rh(III)-L complex
Infrared spectra

The infrared spectra of these complexes (Fig-3) exhibit a broad band in the range of 3323-3449 cm\(^{-1}\) due to the presence of water molecules, Table (3). The absorption bands in the range of 1620-1650 cm\(^{-1}\) are assigned to the existence of \(\nu(\text{HC=N-})\) group of the azomethine. The changing of this group to higher frequency indicates the affected of this group by complexation.\(^9\) The other coordination site, which can take a part in coordination is the (C=O) group, the strong evidence of sharing of this group can be seen from the position of the band at 1647 cm\(^{-1}\) in the spectrum of free ligand. The shifting of this band to higher frequency in the spectra of the complexes suggest the participation of (C=O) group in chelation.\(^{10}\) New bands in the range of 632-651 and 459-501 cm\(^{-1}\) which are not present in the free Schiff base are due to \(\nu(\text{M-O})\) and \(\nu(\text{M–N})\) vibrations,\(^{11}\) and the appearance of these vibrations support the involvement of nitrogen and oxygen atoms of azomethine and carbonyl groups of the free Schiff base in complexation with the metal ions under investigation.

**Figure (3):** Infrared spectra of Ni(II), Cu(II), Rh(III) and Pt(IV)-L complexes
**Electronic spectra and magnetic moments**

The electronic spectra of the Schiff base and its complexes were recorded in chloroform and their assignments are given in Table (3). The free Schiff base spectral data display three bands at 311 nm (32154 cm\(^{-1}\)), 338 nm (29586 cm\(^{-1}\)) and 364 nm (27473 cm\(^{-1}\)) attributed to \(\pi \rightarrow \pi^*\) (phenyl ring) and \(n \rightarrow \pi^*\) (HC=N) transitions.\(^{[12]}\) The spectrum of Ni(II) Schiff base complex (Figure 4) reveals absorption bands in this domain 297-426 nm (33670 - 23474 cm\(^{-1}\)) assigned to \(^3\)A\(_{2g}(F) \rightarrow ^3\)T\(_{2g}(F)\) and \(^3\)A\(_{2g}(F) \rightarrow ^3\)T\(_{1g}(P)\) transitions and an octahedral geometry was suggested.\(^{[13]}\)

For Cu(II) Schiff base complex. The spectrum shows two bands at 280-517 nm (35714-19342 cm\(^{-1}\)) due to charge transfer and \(^2\)T\(_{2g} \rightarrow ^2\)E\(_g\) transitions. The intensity of the bands suggest a square planar geometry.\(^{[14]}\) The electronic spectrum of Rh(III) Schiff base complex shows four bands at 308 nm (32468 cm\(^{-1}\)), 320 nm (31250 cm\(^{-1}\)), 384 nm (26042 cm\(^{-1}\)) and 803 nm (12453 cm\(^{-1}\)) which could be attributed to the presence of a charge transfer (L \(\rightarrow\) M) and \(^1\)A\(_{1g}\)(l) \(\rightarrow\) \(^1\)T\(_{2g}\)(l) transitions, and an octahedral geometry was proposed for this complex.\(^{[15]}\)

For the Pt(VI) Schiff base complex, the electronic spectral data exhibit four bands at 308 nm (32468 cm\(^{-1}\)), 355 nm (29851 cm\(^{-1}\)), 490 nm (20408 cm\(^{-1}\)) and 519 nm (19268 cm\(^{-1}\)) due to the presence of a charge transfer (L \(\rightarrow\) M), \(^1\)A\(_{1g}\)(l) \(\rightarrow\) \(^1\)T\(_{2g}\)(l), \(^1\)A\(_{1g}\)(l) \(\rightarrow\) \(^1\)T\(_{1g}\)(l) and \(^1\)A\(_{1g}\)(l) \(\rightarrow\) \(^1\)E\(_g\)(l) transitions, and an octahedral geometry was suggested.\(^{[16]}\) The obtained magnetic moment values (Table 1) show the presence of a paramagnetic phenomena for both Ni(II) and Cu(II) complexes and diamagnetic character for Rh(III) and Pt(IV) complexes and support the geometrical structures which confirmed by the electronic absorption spectral data.

![Figure (4): Electronic spectrum of Ni(II)-L complex](image-url)
Table (3): Infrared band assignments (cm$^{-1}$), electronic absorption bands (nm, cm$^{-1}$) and the electron paramagnetic resonance spectral data of the Schiff base complexes.

<table>
<thead>
<tr>
<th>Ligand/Complexes</th>
<th>(OH)$\nu$ (H$_2$O)</th>
<th>(\nu(C=\text{N})</th>
<th>(\nu(C=\text{O})</th>
<th>(\nu(M-N)</th>
<th>(\nu(M-O)</th>
<th>$\lambda_{\text{max}}$ nm cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-</td>
<td>1610</td>
<td>1647</td>
<td>-</td>
<td>-</td>
<td>311 (32154), 338 (29586), 364 (27473)</td>
</tr>
<tr>
<td>[Ni(L)(Cl)$_2$(H$_2$O)$_2$].4H$_2$O</td>
<td>3323</td>
<td>1625</td>
<td>1808</td>
<td>632</td>
<td>455</td>
<td>297 (33670), 338 (29586), 371 (26954), 426 (23474)</td>
</tr>
<tr>
<td>[Cu(L)(Cl)$_2$.H$_2$O]</td>
<td>3423</td>
<td>1654</td>
<td>1755</td>
<td>645</td>
<td>469</td>
<td>280 (35714), 317 (31546), 456 (21929), 517 (19342)</td>
</tr>
<tr>
<td>[Rh(L)(Cl)$_3$(H$_2$O)].3H$_2$O</td>
<td>3446</td>
<td>1620</td>
<td>1775</td>
<td>651</td>
<td>459</td>
<td>308 (32468), 320 (31250), 384 (26042), 803 (12453)</td>
</tr>
<tr>
<td>[Pt(L)(Cl)$_4$.2H$_2$O]</td>
<td>3449</td>
<td>1655</td>
<td>1776</td>
<td>638</td>
<td>501</td>
<td>308 (32468), 335 (29851), 490 (20408), 519 (19268)</td>
</tr>
</tbody>
</table>

Mass spectrum of Rh(III) Schiff base complex

The mass fragmentations of the free Schiff base and its Rh(III) complex are shown in schemes 1, 2 and figures 5,6. The base peak at m/e$^-$ 334 is corresponding to the original molecular weight of the Schiff base under investigation. Meanwhile, the base peak of 203 is analogous to the loss of C$_9$H$_{10}$N in addition to Rh(III), 3Cl$^-$ and 4H$_2$O molecules from the original molecular weight of the complex (615.31).
Scheme 1: Mass spectral fragmentation of Schiff base L

\[
\begin{align*}
\text{Scheme 2: Mass spectral fragmentation of Rh(III)-L complex } [m/e^+ = 615.31] 
\end{align*}
\]
Conclusion

From the previous mentioned chemical analysis data, we can suggest the following geometrical structures for the prepared metal complexes:

Figures: The proposed chemical structure of the prepared metal complexes
References

[16] Jarbou, A. M., "Preparation and characterization of some mixed ligand chelates of VO(IV), Cr(III) and Fe(III) ions", M.Sc Thesis; Garyounis University 2006.