Synthesis and Characterization Complexes Of Ni(II),Co(II) and Mn(II) with Schiff Base Derivatives from (2-hydroxy-benzylidene) and Urea or Thiourea

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Abstract

Complexes of the Schiff base ligands (2-hydroxy-benzylidene)- thiourea = (L₁), (2-hydroxy-benzylidene)- urea = (L₂)of these ligands with some of transition metal ions Mn²⁺, Co²⁺ and Ni²⁺ have been prepared and characterized by their (C.H.N) elemental analysis, IR, UV-VIS, atomic absorption, Molar conductivity measurements, Magnetic Susceptibility and melting points. From the result probable structures of the prepared complexes were proposed.

الخلاصة

تم تحضير معقدات قواعد شف (2-هيدروكسف بنزيليفدن- ثايويوريففا ول(ل₁, (2-هيدروكسف بنزيليفدن- يوريفففا (ل₂) للهفففال الليكنفففدات مفففح بعفففص امفففقا العنا فففر ا نتقاليفففة Mn²⁺, Co²⁺, Ni²⁺ ودراسة تراكيب الليكندات والمعقدات المحضرة منها باستخدام تقنية التحليل الدقيق للعنا ففراء (C.H.N) ومطيافية الالشعة تحت الحمراء والأشعة فوق البنفسجية وتقنية الامتصاص الذري فضلًا عن قياس الموصلية الكهربا يففة ودرجة المحضرة وقهاء المو ففلية الكهربا يففة ودرجات الالصهار للمعقدات المحضرة وعلى ضوء النتائج تم استنتاج تراكيب هذه المعقدات.
Introduction

Schiff bases have been widely used as bidentate ligands in the field of coordination chemistry \(^1\). the Schiff base complexes have been used in catalytic reaction \(^2\) and as models for biological systems \(^3\). In recent years many copper complexes of Schiff base were prepared\(^4\). It has been reported that the structure of the constituent bonded to the imino nitrogen affects the coordination geometry of the complexes \(^5\). Metal complexes of Schiff bases are extensively studied due to synthetic flexibility, selectivity and sensitivity towards a variety of metal atoms \(^6\).

In this work will investigate has been the chemistry of this urea and thiourea compound by preparing its Schiff base with 2-hydroxy-benzylidene, and study of the complexes metal (Mn\(^{2+}\), Co\(^{2+}\), and Ni\(^{2+}\)); bidentate ligands these:

\[
(2\text{-}\text{Hydroxy- benzylidene} - \text{thiourea}) \text{ (L1)}
\]

\[
(2\text{-}\text{Hydroxy- benzylidene} - \text{urea}) \text{ (L2)}
\]

Experimental

1- INSTRUMENTATION:

A pye – Unicom sp3-100 infrared spectrophotometer was used to record the IR spectra as KBr and CsI disc, UV/VIS spectra were measured by a HITACHI U-2000 spectrophotometer, Elemental Analysis (C.H.N) founded on (Carlo Erloa microanalyzier type 1106), determination of all metals
percentage by atomic absorption spectrophotometry on AA-680G (Shimadzu). Electrical conductance was measured on conductivity CDC304 (Jenway4070) Melting points determined by an electric heated block apparatus (Gallen Kamp), and were uncorrected.

2-MATERIALS:

[MnCl₂.6H₂O], [CoCl₂.6H₂O], [NiCl₂.6H₂O] were supplied by BDH, Ethanol Absolute, diethylether, DMSO, Urea, thiourea supplied by Aldrich.

A- Preparation of the ligand:

Preparation of (L₁),(L₂) were prepared according to the literature (7) The full name of the Schiff base will be replaced by a number (L₁,L₂) respectively as in shown in table (1) for the rest of this paper . The physical properties of these compounds (L₁, L₂) are listed in table (1). The characters IR bands and UV/Vis spectrum in DMSO as shown in table (2), (3).

B-General procedure for preparation of complexes :

To a hot solution of ligands (L₁ or L₂) (2 mmole) in absolute ethanol (5 ml), a hot solution of metal chloride (1 mmole) in absolute ethanol (5ml) (dissolved in dilute HCl) (8) was added (neutral medium) and the resultant mixture was stirred and refluxed for 2 hours, the color of the solution changed immediately, the reaction mixture was cooled, and the solution was evaporated in vacuum, or lefted over night at room temperature , after this time a precipitate formed . This was collected by filtration in vacuo, washed and recrystallized from absolute ethanol/ether.

The physical properties of prepared complexes are listed in table (4).

The analogous complexes were prepared in a similar manner to that described above by adding a hot solution of ligands (L₁ or L₂) (1 mmole) in absolute ethanol (5 ml) to a hot solution of metal chloride (1 mmole) in absolute ethanol (5ml).The molar ratio of the complexes was determined according to the methods (9).
Table (1): Physical properties of the Schiff's base ligand

<table>
<thead>
<tr>
<th>No.</th>
<th>Name and structure of compound</th>
<th>Yield %</th>
<th>M.P Cº</th>
<th>Elemental analysis % found (% cal.)</th>
<th>colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>L1</td>
<td>(2-Hydroxy- benzylidene ) -thiourea</td>
<td>77</td>
<td>166-168</td>
<td>53.25 (53.31)</td>
<td>4.53 (4.25)</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Schiff's base ligand L1" /></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>L2</td>
<td>(2-Hydroxy- benzylidene ) -urea</td>
<td>72</td>
<td>149-151</td>
<td>58.42 (58.53)</td>
<td>5.00 (4.91)</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Schiff's base ligand L2" /></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (2): The characteristic ir bands of the Schiff's base ligand

<table>
<thead>
<tr>
<th>No.</th>
<th>( \nu(\text{O-H}) ) phenol cm(^{-1})</th>
<th>( \nu(\text{C-H}) ) Aromatic cm(^{-1})</th>
<th>( \nu(\text{C=O}) ) cm(^{-1})</th>
<th>( \nu(\text{C=N}) ) Imine cm(^{-1})</th>
<th>( \nu(\text{C=C}) ) Aromatic cm(^{-1})</th>
<th>( \nu(\text{C=S}) ) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>3470</td>
<td>3025</td>
<td>-</td>
<td>1620</td>
<td>1580,1520</td>
<td>1240</td>
</tr>
<tr>
<td>L2</td>
<td>3470</td>
<td>3060</td>
<td>1680</td>
<td>1615</td>
<td>1580,1540</td>
<td>-</td>
</tr>
</tbody>
</table>
Table (3): UV-VISIBAL absorption of the shiff base ligand

<table>
<thead>
<tr>
<th>No.</th>
<th>complexes</th>
<th>Colour</th>
<th>ΔM μs mol⁻¹</th>
<th>M.P C°</th>
<th>UV/VIS nm</th>
<th>Elemental analysis</th>
<th>IR SPECTRA cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( % found)</td>
<td>% cal</td>
</tr>
<tr>
<td>1</td>
<td>[Mn(L1)2]Cl2</td>
<td>G.Y</td>
<td>65</td>
<td>186-188</td>
<td>280,320,400</td>
<td>11.13 (11.10)</td>
<td>14.63 (14.61)</td>
</tr>
<tr>
<td>2</td>
<td>[Co(L1)2]Cl2</td>
<td>L.B</td>
<td>75</td>
<td>190-192</td>
<td>278,315,410</td>
<td>11.86 (11.83)</td>
<td>14.51 (14.48)</td>
</tr>
<tr>
<td>3</td>
<td>[Ni(L1)2]Cl2</td>
<td>L.G</td>
<td>85</td>
<td>193-195</td>
<td>285,325,415</td>
<td>11.86 (11.84)</td>
<td>14.51 (14.49)</td>
</tr>
<tr>
<td>4</td>
<td>[Mn(L2)2]Cl2</td>
<td>G.Y</td>
<td>70</td>
<td>169-171</td>
<td>290,325,405</td>
<td>11.92 (11.89)</td>
<td>15.67 (15.64)</td>
</tr>
<tr>
<td>5</td>
<td>[Co(L2)2]Cl2</td>
<td>L.B</td>
<td>80</td>
<td>165-167</td>
<td>295,330,415</td>
<td>12.69 (12.66)</td>
<td>15.53 (15.51)</td>
</tr>
<tr>
<td>6</td>
<td>[Ni(L2)2]Cl2</td>
<td>L.G</td>
<td>75</td>
<td>170-172</td>
<td>285,320,400</td>
<td>12.69 (12.67)</td>
<td>15.53 (15.51)</td>
</tr>
<tr>
<td>10</td>
<td>[Mn(L2) Cl2H2O]</td>
<td>L.G</td>
<td>10</td>
<td>175-177</td>
<td>280,315,405</td>
<td>15.07 (15.04)</td>
<td>15.10 (15.08)</td>
</tr>
</tbody>
</table>

G.Y = green yellowish, L.B = Light Brown, L.G = Light Green
Results and Discussion

The structures of schiff base complexes were confirmed by spectroscopic techniques ir and uv/visible. Infrared spectra of the two ligands (L₁), (L₂) show the usual broad bands in the region around (3360-3475 cm⁻¹) due to the NH₂ stretching frequency (10) of the amide group of the ligands; No effect on these frequencies after complexation precludes the possibility of complexation at this group (11).

The band at 1620 and 1615 cm⁻¹ in the spectrum of (L₁)&(L₂) respectively due to υ(C=O) stretching shifted to the lower frequencies in the complexes (12) (table 4).

The negative shift generally in υ(C=O) suggested coordination to metal ions through nitrogen atom of (-C=N-) Schif’s base (13) of the ligand and on complexation indicates involvement of azomethine nitrogen (7,10) with metal ions.

The band at 1240 cm⁻¹ due to υ(C=S) stretching vibrations in (L₁), in the metal complexes this band is weakened and lowered (15) (table 4). The observations indicate the coordination of the ligand (L₁) through sulphur atom.

The carbonyl stretching frequency in (L₂) decreases to (1630-1650) cm⁻¹ compared to the free ligand at 1680 cm⁻¹, due to the charge transfer from the ligand to the metal (9).

In metal complexes a new peak is found 1265 cm⁻¹ for υ(C-O) which is very characteristic and υ(O-H) was broad (11,12) (table 4).

New bands which appeared at low frequencies in the spectra of the prepared complexes were probably due to (metal- nitrogen), (metal- sulphur), and (metal- chloride), bond vibration frequencies (table 4).

The complexes give different colour from the transition metal salts and the ligands, then this was important indication to coordinate occurrence (13), therefore these colourly complexes show different characteristic absorption band in position, intensity or together when compared with the bands of ligand and this was another indication for the coordination occurrence (14,15).

The uv/visible spectra of the two prepared ligands (L₁, L₂) at (10⁻³ M) in ethanol were showed three absorption bands (15). The first band between (380-385) nm represented (π-π*) while the second band (300-305) nm represented (π - π*) and the third band (265-270) nm is called (B-band) for phenyl group (16,17).

Electronic spectra of Co(II) complexes showed one band at approximately 410 nm assigned for the 4T₂g→4T₁g transition of 3F₄ term of d⁷ system. this may indicate an octahedral geometry for Co complexes.

The electronic spectra of the Ni(II) complexes, exhibit four bands in the range 10390, 18620, 27900 and 36200 cm⁻¹. An examination of these bands indicates that the complexes have an octahedral geometry (18). Thus, these bands may be assigned to the three spin allowed transitions 3A₂g(F)→3T₂g(F), 3A₂g(F)→3T₁g(F) and 3A₂g(F)→3T₂g(P) respectively.

The Mn(II), Co(II) and Ni(II) complexes had normal values of the magnetic moments, i.e. 2.10, 3.50 and 4.70 B.M respectively, indicating their mono nuclear. Based on the experimental evidence obtained the complexes were characterized as six coordinates with octahedral structures (19).

The measurements of the molar electrical conductivity of the complexes at (25°C) in DMSO are presented in table (4). These results show the molar conductivity are relatively high values, these complexes are electrolyte and low values refer to the complexes are non-
electrolyte, are in agreement with the proposed structures of the complexes.

The method of continuous variation mole ratio method are employed in this work molar ratio (1:1) metal to ligand for (7-12) complexes and (1:2) metal to ligand for (1-6) complexes as shown below:

According to the results obtained from ir, uv/vis, molar ratio, molar conductivity and atomic absorption measurements for the prepared complexes, the proposed molecular structure of the complexes has an octahedral structure as shown below:

\[
\begin{array}{c}
\text{Y:}\{L_1=S, \ L_2=O\} \\
\text{Complexes No. (7-12)} \\
\text{M=(Mn}^{2+}, \text{Co}^{2+} \text{and Ni}^{2+})
\end{array}
\]

\[
\begin{array}{c}
\text{Y:}\{L_1=S, \ L_2=O\} \\
\text{Complexes No. (1-6)} \\
\text{M=(Mn}^{2+}, \text{Co}^{2+} \text{and Ni}^{2+})
\end{array}
\]
References