PREPARATION AND STUDYING OF (SPECTRAL, COMPLEXATION, PHYSICAL MEASUREMENTS) OF MACRO LIGANDS WITH THEIR COMPLEXES

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ABSTRACT

The aim of this studying is preparation of new two ligands and their complexes with cadmium ion, all reactions prepared through reaction of diketone or aldehyde compounds with primary amine (aliphatic and aromatic) such as ethylene diamine, amino acid – alanine. The synthesized ligands and their complexes were characterized by (I.R, UV-Vis, H.NMR, (C.H.N) –analysis), molar conductance (M.C) and melting points (M.P) then atomic absorption (A.M). The two ligands gave good results and complexes through many studies for determination of optimal conditions of complexation with mole ratio (M:L) (1:1) and the ligand (L_1) gave tetrahedral but the ligand (L_2) gave octahedral.

Keywords: haf, rend, moh.

No: of Tables: 3 No: of Figures: 16 No: of References: 18
INTRODUCTION

Macro ligands are important types of coordination ligands in inorganic chemistry which can be synthesized from an aliphatic or aromatic amine and a carbonyl compound (aldehyde or ketone) by nucleophilic addition forming a hemiaminal, followed by dehydration to generate an imine\(^{(1-4)}\). In a typical reaction:

![Reaction Scheme]

Macro ligands from Schiff base are versatile ligands which are prepared from the condensation reaction of primary amines with carbonyl compounds. These compounds are very important in medical chemistry and pharmaceutical chemistry for their wide spectrum of biological activities. Most of them have biological activities such as antimicrobial, antifungal as well as antitumor activity. Transition metal complexes derived from the Schiff base ligands with biological activity have been widely studied\(^{(5-10)}\).

![Schiff Base]

Schiff bases are a group of organic intermediates, which are very often used in the synthesis and chemical analysis. They are exerted in the production of pharmaceutical and agrochemical industry\(^{(11-14)}\).

Experimental:

All measurements such as:

1. **Melting points** were determined in open capillary tube and were uncorrected.
2. **The I.R. spectra** were recorded in KBr-disc, Shimadzu (8300).
4. **Atomic absorption.**
5--- UV –Vis –spectra photometer ,
6 --- Molar conductance (DMSO–solvent ) ,
7--- (H.NMR )– SPECTRA in Canada .
8--- Optimal conditions .
9--- TLC - plate .

Methods :
Preparation of ligand ( L₁ ) :
The ligand (L₁) was prepared according procedures[14-16], 1,3–di (nitro phenyl) –propane -1,3–dione (0.1mole) and (0.2mole) from amino acid – alanine were heated in presence of absolute ethanol with drops of glacial acetic acid with refluxing for (4 hrs) , the precipitate filtered and dried, then re crystallized with absolute ethanol to give 80 % of macro ligand (L₁).

Preparation of ligand ( L₂ ) :
The ligand (L₂) prepared from reaction between 4- nitro-2,6 –di formal phenol (0.1mole) and (0.2mole) of ethylene diamine in presence of absolute ethanol for (5 hrs) with mechanical stirring according to studying[14-16], the precipitate was filtered and re crystallized, which (0.01mole) refluxed with (0.01mole) of 4-nitro-2,6-dibenzoyl-phenol to give 82 % of macroligand (L₂).
Preparation of Two Complexes with Ion (Cd\(^{2+}\)):
According to procedures\(^{[17,18]}\), the hot ethanolic solution of ligands [(L1) or (L2)] respectively was added to solution of ion salt of chloride (CdCl\(_2\)) in mole ratio (metal: ligand) (1:1) respectively after stirring (2 hrs) , precipitates formed , dried and re-crystallized to give (82% ,80 % ) respectively from complexes of two ligands respectively .

Results and Discussion:
Schiff bases are common ligands in coordination chemistry. The imine nitrogen is basic and exhibits pi-acceptor properties. All ligands and complexes were identified and characterization by several methods:

Studying of optimal condition of complexes:
The optimal conditions of complexes with ion Cd(II) were studied in this studying such as calibration curves of optimal concentration of Cd\(^{2+}\) (0.90 X10\(^{-4}\)m) , while concentration of ligands [ 1X10\(^{-3}\)M of ligand (L1) , 0.2X10\(^{-3}\)M of ligand (L2) ] , while optimal (PH=8) for complex of ligand (L1) and ( PH=8.5 ) for complex of ligand (L2) in base medium, and chemical identification UV-Visible . Other studies of these complexes in table (1) and
Figs (1-6).

**Fig (1): UV-Vis Spectrum of Ligand \((L_1)\)**

**Fig (2): UV-Vis Spectrum of complex \([\text{Cd}(L_1)]\)**
Fig (3): UV-Vis Spectrum of Ligand (L₂)

Fig (4): UV-Vis Spectrum of complex [Cd (L₂)]
Some physical properties were measured such as melting point, formation of complexes by job method and mole ratio method through series solutions were prepared having a constant concentration (1X10^{-3}M) of Cd salt (CdCl$_2$) and ligand, the (M:L) ratio was determined from relationship between the absorption and mole ratio (M :L) found to be (1:1) for all complexes, Table (1). All results ((mole ratio, calibration curve, stoichiometry, chemical spectra) indicate that the Cd-complexes with the two ligands were stoichiometry (metal : ligand) (1:1):

**Mole Ratio of Complexes:**

![Fig(5): Optimal PH of complex [ Cd (L$_1$) ]](image)

![Fig(6): Optimal PH of complex [ Cd (L$_2$) ]](image)
The conductivity and (C.H.N) with Atomic Absorption:
Table (1) showed all results of conductivity measurements which were (0.87, 1.28) ohm$^{-1}$mole$^{-1}$cm$^2$ of (1x10$^{-3}$M) solution in (DMSO) which indicates that the (Cd - Complexes) are non-electrolytic in nature, and other property such as melting points, uv-visible are listed in table (1):
Table (1): physical properties and UV-Visible of ligands with Complexes:

<table>
<thead>
<tr>
<th>Ligands &amp; Complexes</th>
<th>M.P (°C)</th>
<th>λ_max</th>
<th>Conductance ( \Omega^{-1} \cdot \text{Cm}^2 \cdot \text{mole}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand (L₁) ( C_{21}H_{20}N_4O_8 )</td>
<td>172</td>
<td>270</td>
<td>/</td>
</tr>
<tr>
<td>Ligand (L₂) ( C_{24}H_{26}N_6O_6 )</td>
<td>196</td>
<td>280</td>
<td>/</td>
</tr>
<tr>
<td>Complex [Cd( L₁)]</td>
<td>226</td>
<td>400</td>
<td>0.87</td>
</tr>
<tr>
<td>Complex [Cd( L₂)]</td>
<td>244</td>
<td>410</td>
<td>1.28</td>
</tr>
</tbody>
</table>

And other results such as (C.H.N) with Atomic Absorption which gave percentage % of metal ion in complexes are listed in Table (2):

Table (2): Elemental Analysis and Atomic Absorption:

<table>
<thead>
<tr>
<th>Ligands &amp; Complexes</th>
<th>Calc. / Found</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>Cd %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand (L₁) ( C_{21}H_{20}N_4O_8 )</td>
<td></td>
<td>55.26</td>
<td>4.38</td>
<td>12.28</td>
<td>/</td>
</tr>
<tr>
<td>Ligand (L₂) ( C_{24}H_{26}N_6O_6 )</td>
<td></td>
<td>58.29</td>
<td>5.26</td>
<td>17.00</td>
<td>/</td>
</tr>
<tr>
<td>Complex [Cd( L₁)]</td>
<td></td>
<td>44.49</td>
<td>3.17</td>
<td>9.88</td>
<td>19.84</td>
</tr>
<tr>
<td>Complex [Cd( L₂)]</td>
<td></td>
<td>47.64</td>
<td>3.97</td>
<td>13.89</td>
<td>18.59</td>
</tr>
</tbody>
</table>

Spectral Characterization:

I.R – spectra: shown absorption bands in ligands [(L₁), (L₂)] at (3132-2670, 3435) cm\(^{-1}\) due to hydroxyl groups\(^{15}\) of carboxylic acid in ligand (L₁) and hydroxyl group of phenol in ligand (L₂) respectively in free ligands which disappeared in spectra of their complexes indicating the coordination through phenolic oxygen moiety and oxygen of carboxyl group at bond (M–O) are (563 -576) cm\(^{-1}\). The I.R –spectra of (Schiff bases CH=N)\(^{15,16}\) respectively in ligands exhibit bands at (1626 , 1631) cm\(^{-1}\) respectively ,which have been shifted towards lower frequencies at (1614 , 1619) cm\(^{-1}\) respectively in complexes to coordination with ion (Cd\(^{2+}\))

The coordination through nitrogen of imine group (CH=N) and oxygen of hydroxyl group of phenol or hydroxyl group of carboxyl in complexes, table (3) and figs (9-12) .
Table (3) : FT.IR data (cm$^{-1}$) of ligands with complexes.

<table>
<thead>
<tr>
<th>Ligands &amp; Complexes</th>
<th>(CH=N) imine group</th>
<th>(-NO$_2$) Carbonyl of Carboxyl</th>
<th>(-OH) Carboxyl, Phenol</th>
<th>(M-N)</th>
<th>(M-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L$_1$)</td>
<td>1626</td>
<td>1347</td>
<td>1728</td>
<td>3132-2670</td>
<td>/</td>
</tr>
<tr>
<td>(L$_2$)</td>
<td>1631</td>
<td>1361</td>
<td>/</td>
<td>3435</td>
<td>/</td>
</tr>
<tr>
<td>[Cd( L$_1$)]</td>
<td>1614</td>
<td>1349</td>
<td>1717</td>
<td>/</td>
<td>489</td>
</tr>
<tr>
<td>[Cd( L$_2$)]</td>
<td>1619</td>
<td>1365</td>
<td>/</td>
<td>/</td>
<td>485</td>
</tr>
</tbody>
</table>

Fig(9): FT.IR of Ligand (L$_1$)
Fig(10): FTIR of Complex [ Cd ( L1 ) ]

Fig(11): FTIR of Ligand ( L2 )
Fig(12): FT.IR of Complex [ Cd ( L₂ ) ]

Studying of H.NMR spectra: spectra of ligands showed signals at δ (13.34, 11.08) for hydroxyl group of carboxyl and hydroxyl group of phenol (OH) in free ligands, which disappeared in their complexes as a result of coordination with (Cd²⁺). And other signals are shown in table (4) and some of figures (13, 16).

<table>
<thead>
<tr>
<th>Ligands &amp; Complexes</th>
<th>(OH) phenol</th>
<th>(OH) Carboxyl</th>
<th>Other groups ((only functional groups))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand (L₁)</td>
<td>/</td>
<td>13.34</td>
<td>(-Ph-) proton of phenyl ring: 6.98 – 7.40.</td>
</tr>
<tr>
<td>Ligand (L₂)</td>
<td>11.08</td>
<td>/</td>
<td>8.13(CH=N) : proton of imine group.</td>
</tr>
<tr>
<td>Complex [Cd(L₁)]</td>
<td>/</td>
<td>/</td>
<td>(-Ph-) proton of phenyl ring: 6.85 – 7.61.</td>
</tr>
<tr>
<td>Complex [Cd(L₂)]</td>
<td>/</td>
<td>/</td>
<td>(-Ph-) proton of phenyl ring: 6.90 – 7.67.</td>
</tr>
</tbody>
</table>
Fig (13): H.NMR of Ligand (L1)

Fig (14): H.NMR of Complex [Cd (L1)]
Fig (15): H.NMR of Ligand (L$_2$)

Fig (16): H.NMR of Complex [Cd (L$_2$)]
References


