Synthesis and Spectral Studies for new Schiff base and its Binuclear Complexes with Zn\textsuperscript{II}, Cd\textsuperscript{II} and Hg\textsuperscript{II}

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Abstract

A new ligand (H\textsubscript{4}L) and its complexes with (Zn\textsuperscript{II}, Cd\textsuperscript{II} and Hg\textsuperscript{II}) were prepared. This ligand was prepared in two steps. In the first step a solution of terephthaldehyde in methanol was reacted under reflux with 1,2-phenylenediamine to give an precursor compound which reacted in the second step with 2,4-dihydroxybenzaldehyde to give the ligand. The complexes were then synthesized by direct reaction of the corresponding metal chloride with the ligand. The ligand and complexes were characterized by spectroscopic methods FT-IR, UV-Vis, \textsuperscript{1}HNMR, and atomic absorption, chloride content, HPLC, mole-ratio determination. in addition to conductivity measurement. The data of these measurements suggest a distorted tetrahedral geometry for Zn\textsuperscript{II}, Cd\textsuperscript{II} and Hg\textsuperscript{II} complexes and that they would be presented as \([M\textsubscript{2}L(H\textsubscript{2}L)Cl\textsubscript{2}]\). The Stability Constant K and Gibbs free energy \(\Delta G\) were calculated for \([Zn\textsubscript{2}(H\textsubscript{2}L)Cl\textsubscript{2}]\) and \([Cd\textsubscript{2}(H\textsubscript{2}L)Cl\textsubscript{2}]\) complexes by using spectrophotometer method. The obtained values indicate that these complexes are stable in their solution. The biological activity for the following ligand (H\textsubscript{4}L) and complexes \([Zn\textsubscript{2}(H\textsubscript{2}L)Cl\textsubscript{2}]\) and \([Cd\textsubscript{2}(H\textsubscript{2}L)Cl\textsubscript{2}]\) was studied.

Introduction

Schiff's bases derived from aromatic amines and aromatic aldehydes and its complexes have a wide variety of applications in many fields, e.g., biological, inorganic and analytical chemistry [1-3]. Schiff's bases of o-phenylenediamine and its complexes have a variety of applications including biological, analytical [4] and clinical [5]. Metal complexes of Schiff base are extensively studied due to synthetic flexibility and sensitivity toward a variety of metal atoms [6]. They are found useful in catalysis, in medicine as antibiotics and anti-inflammatory agent and in the industry as anti-corrosion [7-10]. It has been found that all the complexes are antimicrobially active and show higher activity than the free ligand. Metal chelation affects significantly the antimicrobial/bioactive behavior of the organic ligands [11]. In this paper the synthesis and characterization of Schiff base \([4,4'-(2,2'-(1,4-phenylenebis(methan-1-yl-1-ylidene))bis(azan-1-yl-1-ylidene)bis(1,2-phenyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene) dibenzene1,3-diol)]\) ligand derived from the reaction of terephthaldehyde, o-phenylenediamine and 2,4-Dihydroxy benzaldehyde and some of its complexes with (Zn\textsuperscript{II}, Cd\textsuperscript{II} and Hg\textsuperscript{II}) are reported.

Experimental

Reagent grade terephthaldehyde and 2,4-Dihydroxy benzaldehyde obtained from Fluka and o-phenylenediamine obtained from Aldrich and used as received while ZnCl\textsubscript{2}, CdCl\textsubscript{2}, H\textsubscript{2}O and HgCl\textsubscript{2} were available from (Riedial – Dehaen, Fluka, Merck and Hopkins & William LTD) respectively. The FT-IR spectra of compounds were recorded as (KBr) disc using a shimadzu 8300 FTIR Spectrophotometer in the range (4000-400) cm\textsuperscript{-1}. Electronic spectra of prepared
compounds were measured in the region (200-900) nm for 10^-3 M solutions in (DMF) as a solvent at 25°C by using a CECIL, CE7200 spectrophotometer. While metal contents of the complexes were determined by atomic absorption (A.A) technique using a Shimadzu (AA.620) atomic absorption spectrophotometer. Electrical conductivity measurements of the complexes were recorded at 25°C for 10^-3 M solutions of the samples in (DMF) by using a (Wissenschaftlich-Techniche Werkstatten, D1820 Wilhelm LF 42) conductivity meter. Nuclear magnetic resonance spectra \(^1\)HNMR for the ligand (H\(_4\)L) were recorded via using Burker (400MHz) spectrophotometer with a tetramethylsilane (TMS) as an internal standard in DMSO-d\(_6\) in Al-Baath University, Syria. The chloride contents for complexes were determined by potentiometric titration method on (686-Tirol processor-665. Dosimat Metrohn Swiss). The melting point was measured using Stuart melting point.

**Preparation**

**Synthesis of the ligand (H\(_4\)L):** The ligand was prepared in two steps

**Step (1): preparation of the (precursor compound).**

To a solution of terephthaldehyde 0.15 g (1.12 mmole) in (5 ml) of methanol, (5) drops of glacial acetic acid were slowly added, the obtained solution was mixed with 1,2-phenylenediamine 0.241 g (2.23 mmole) (5ml) in methanol. The mixture was refluxed for (5 hrs.) with stirring. The orange solution was left to dry for (24 hrs.) in room temperature, the precipitate was washed with an excess of methanol, and was dried. An orange solid was obtained. Yield (0.26) g, (74%), m.p. (190 dec).

**Step (2): preparation of the ligand (H\(_4\)L):**

A solution of (precursor compound) 0.12 g (0.38 mmole) in methanol (5 ml) and few drops of DMF were added to 0.1 g (0.72 mmole) of 2,4-dihydroxybenzaldehyde dissolving in methanol (5ml), then five drops of glacial acetic acid were added slowly to the reaction mixture. The reaction mixture was refluxed for (5 hrs.) with continuous stirring. The brown solution was left to dry for (72 hrs.) at room temperature, the precipitate was washed with an excess of methanol, and was dried. A brown solid was obtained. Yield (0.18) g, (85%), m.p. (223 dec).

**Synthesis of complexes ions**

**Synthesis of [Zn\(_2\)(H\(_2\)L)Cl\(_2\)] (1) complex:**

5ml of methanol it solution containing 0.15 g (0.27 mmole) of (H\(_4\)L) with few drops of DMF were placed in a round bottomed flask. Then a 0.04g (0.71 mmol) of KOH in (5 ml) ethanol was added. A solution of ZnCl\(_2\) 0.074g (0.54 mmole) in (10 ml) methanol was drop wise added with stirring. The mixture was refluxed for (3 hrs.). A deep green precipitate was formed, which was filtered off, washed several times with methanol and dried at room temperature during (72 hrs.). Yield (0.051) g, (76 %), m.p. (270 dec).

**Synthesis of [Cd\(_2\)(H\(_2\)L)Cl\(_2\)] (2), [Hg\(_2\)(H\(_2\)L)Cl\(_2\)] (3)**

The method used to prepare these complexes was a similar method to that mentioned in the preparation of [Zn\(_2\)(H\(_2\)L)Cl\(_2\)] complex. Table (1) shows the stated weight of starting materials, % yield and some physical properties of the prepared complexes.

**Results and Discussion**

The preparation of the ligand (H\(_4\)L) and complexes of the general method as shown in Scheme
Scheme (1) Synthesis route of the Schiff's base ligand (H₄L) and its complexes

[where M(II)=Zn, Cd and Hg]
The $^1$HNMR spectrum of ligand (H$_4$L), Figure (2) in DMSO–d$_6$ solvent shows a singlet signal at ($\delta = 10.93$ ppm) equivalent to two protons assigned to (O–H) group of carbon (C$_{13,22}$). Two protons of (C$_5$-OH, C$_{30}$-OH) group appear as a singlet signal at ($\delta = 13.1$ ppm) [18]. Two protons of (N=C$_7$-H, N=C$_{28}$-H) imine group appear as a singlet signal at ($\delta = 8.36$ ppm). Two protons of (N=C$_{14}$-H, N=C$_{21}$-H) imine group appear as a singlet signal at ($\delta = 9.93$ ppm). The multiplet signals at ($\delta = 6.33$ ppm), (7.23), (7.33), (7.46), (7.53), (7.63), (7.95) ppm are due to aromatic hydrogen of carbon (C$_{2,33}$), (C$_{3,34}$), (C$_{6,31}$), (C$_{9,12,23,26}$), (C$_{10,11,24,25}$), (C$_{16,21}$), (C$_{19,29}$) respectively[13,14].

The FTIR spectra of the ligand and the complexes are presented in table (2) and fig (3a,3b). The spectrum of the ligand fig (3a) shows the disappearance of C=O and N-H bands, which suppose the complete condition of keto group with amino group [15,16]. So the strong band appeared at 1635 cm$^{-1}$ and 1620 cm$^{-1}$ can be attributed to imin group C=N (benz) and (tere) respectively while the band at 1238 cm$^{-1}$ can be assigned to C-O. The two bands at 3429 cm$^{-1}$ and 3140 cm$^{-1}$ are due to the ν (O-H) stretching [17,18]. In the case of the complexes (1-3) fig (3b) the bands of C=N and C-O shifted to lower frequency appearing for C=N at (1627,1604) cm$^{-1}$, (1620 , 1589) cm$^{-1}$, (1600, 1577) cm$^{-1}$ and at (1215, 1203, 1226) cm$^{-1}$ for (C-O)[19-22]. The shifting which may be due to (HOMO → LUMO), (where HOMO: Highest Occupied Molecular Orbital, LUMO: Lowest Unoccupied Molecular Orbital) confirmed the coordination of ligand through nitrogen and oxygen atoms [23]. The broad band at (3429) cm$^{-1}$ attributed to ν(OH) in the free ligand shifted to lower frequency appeared at (3329) cm$^{-1}$, (3387) cm$^{-1}$ and (3356) cm$^{-1}$ for complexes [1-3] respectively[24]. The bands at (550), (551) and (559) were assigned to ν (M–N) for compounds [1-3] respectively, indicating that the imine nitrogen is involved in coordination with metal ions [25, 26]. The bands (at 421), (470) and (497) cm$^{-1}$ were assigned to ν(M–O) for compounds (1-3) respectively indicating that the phenolic oxygen of the ligand is involved in coordination with metal ions[25,26].

The (UV-Vis) spectrum for the ligand (H$_4$L), Figure (4) exhibits three high absorption peak, the first peaks, at (282nm) (35460.99 cm$^{-1}$) ($\varepsilon_{\text{max}}$=2229 molar$^{-1}$.cm$^{-1}$), the second absorption peak at (330nm)(30303 cm$^{-1}$) ($\varepsilon_{\text{max}}$=2175 molar$^{-1}$.cm$^{-1}$) and the third peak at (348nm)(28571.4 cm$^{-1}$)($\varepsilon_{\text{max}}$= 1861 molar$^{-1}$.cm$^{-1}$), which were assigned to ($\pi$→ $\pi^*$) and (n→ $\pi^*$) transition respectively[17].

The (UV-Vis) spectra data for the complexes (1-3) are given in table (3).The absorption spectra for these complexes show intense bands about (291-345) nm, which may be related to ligand filed. The absorption peaks in the range (351-360) nm for these complexes are due to charge transfer (C.T) since they belong to d$^{10}$ configuration and they don’t have d-d transition [27,28]. From the position of the band and the value of $\varepsilon_{\text{max}}$ the tetrahedral structure may be proposed for these complexes.

The Molar conductance values for the ligand (H$_4$L) complexes are summarized in table (3). These values were found in the range (24.9 - 27.9) S.cm$^2$.mole$^{-1}$, so they correspond to non-electrolytic behavior [29].

The (HPLC) chromatograms for the compound (H$_4$L), [Zn$_2$(H$_2$L)Cl$_2$] and [Cd$_2$(H$_2$L)Cl$_2$] complexes, exhibits one sharp signal at retention time (Rt=6.877), (Rt=7.036) and (Rt=7.048) respectively, indicating the purity of the compounds.

The atomic absorption analysis and the chloride content results of the complexes are in a good agreement with the suggested formula [M$_2$(H$_2$L)Cl$_2$].

The mole-ratio (L:M) was calculated depending on the measurement the absorbance of the solutions which contain increased molar concentrations of one component (ligand) with constant concentration to the other component metal ion. The optical absorbance was measured at wave length of highest absorbance of produced complex and does not occur at the absorbance to the chelate ligand alone or to the metal ion alone. The relationship between the absorbance which
was presented as (Y) axis and the concentration of the two reactants (ligand: metal) was drawn, which was presented as (X) axis, then the rectum contiguity was drown until they intersect and from the intersection point equivalent metal was limitated as it was shown in the figures (5a) and (5b).

On the basis of these measurement the stability constant $K$ and Gibbs free energy $\Delta G$ were calculated. The stability constant $K$ and Gibbs free energy were calculated using the method shown above. The equilibrium of the complex metal ion and the ligand for 2:1 mole ratios and $K$ for this ratio is expressed by:

$$2M + L \leftrightarrow M_2L \ldots \ldots \ldots \ldots (1)$$

$$K = \frac{[M_2L]}{[M]^2[L]} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 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Table (2): FT-IR spectral data (wave number \( \nu \) cm\(^{-1} \)) for the ligand (H\(_4\)L) and its complexes

<table>
<thead>
<tr>
<th>No.</th>
<th>Compounds</th>
<th>( \nu(C=N) )</th>
<th>( \nu(O-H) )</th>
<th>( \nu(C=\text{C}) ) ( \text{arom.} )</th>
<th>( \nu(C=\text{C}) ) ( \text{arom.} )</th>
<th>( \nu(C-H) ) ( \text{aliph.} )</th>
<th>( \nu(C-O) )</th>
<th>( \nu(M-N) )</th>
<th>( \nu(M-O) )</th>
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<tbody>
<tr>
<td>1</td>
<td>[H(_4)L]</td>
<td>1635</td>
<td>3429</td>
<td>1500</td>
<td>3062</td>
<td>2927</td>
<td>1235</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>[Zn(_2)(H(_2)L)Cl(_2)]</td>
<td>1627</td>
<td>3329</td>
<td>1527</td>
<td>3066</td>
<td>2924</td>
<td>1215</td>
<td>550</td>
<td>421</td>
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<tr>
<td>3</td>
<td>[Cd(_2)(H(_2)L)Cl(_2)]</td>
<td>1620</td>
<td>3387</td>
<td>1539</td>
<td>2950</td>
<td>2924</td>
<td>1203</td>
<td>551</td>
<td>470</td>
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<tr>
<td></td>
<td>[Hg(_2)(H(_2)L)Cl(_2)]</td>
<td>1600</td>
<td>3356</td>
<td>1550</td>
<td>3089</td>
<td>2958</td>
<td>1222</td>
<td>559</td>
<td>497</td>
</tr>
</tbody>
</table>

Table (3): Electronic data and molar conductivity for the ligand (H\(_4\)L) and its Metal complexes

<table>
<thead>
<tr>
<th>No.</th>
<th>Compounds</th>
<th>( \lambda \text{ nm} )</th>
<th>( \nu \text{ cm}^{-1} )</th>
<th>Assignments</th>
<th>( \Lambda_m \text{ S.cm}^2\text{ mole}^{-1} )</th>
<th>Coordination</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>H(_4)L</td>
<td>282</td>
<td>35460.99</td>
<td>( \pi \rightarrow \pi )</td>
<td>-</td>
<td>Distorted Tetrahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td>330</td>
<td>30303</td>
<td>( \pi \rightarrow \pi^* )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>348</td>
<td>28735.63</td>
<td>( n \rightarrow \pi^* )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>[Zn(_2)(H(_2)L)Cl(_2)]</td>
<td>292</td>
<td>34246.57</td>
<td>Ligand field</td>
<td>25</td>
<td>Distorted Tetrahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td>334</td>
<td>29940</td>
<td>Ligand field</td>
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<td></td>
<td></td>
<td>351</td>
<td>28490</td>
<td>C.T</td>
<td></td>
<td></td>
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<tr>
<td>3</td>
<td>[Cd(_2)(H(_2)L)Cl(_2)]</td>
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<td>[Hg(_2)(H(_2)L)Cl(_2)]</td>
<td>292</td>
<td>34246.57</td>
<td>Ligand field</td>
<td>27.9</td>
<td>Distorted Tetrahedral</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>351</td>
<td>28490</td>
<td>C.T</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table (4) Stability constant and $\Delta G$ for the ligand (H$_4$L) complexes [Zn$_2$(H$_2$L)Cl$_2$] and [Cd$_2$(H$_2$L)Cl$_2$]

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\alpha$</th>
<th>$\alpha_m$</th>
<th>$\alpha$</th>
<th>K</th>
<th>Log K</th>
<th>1/K</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn$_2$(H$_4$L)Cl$_2$]</td>
<td>2.37</td>
<td>2.4</td>
<td>0.0125</td>
<td>1.26408090117×10$^{11}$</td>
<td>11</td>
<td>7.91×10$^{-12}$</td>
<td>-62.8</td>
</tr>
<tr>
<td>[Cd$_2$(H$_4$L)Cl$_2$]</td>
<td>1.82</td>
<td>1.83</td>
<td>0.00546</td>
<td>1.5277112135517×10$^{12}$</td>
<td>12.18</td>
<td>6.55×10$^{-13}$</td>
<td>-69.5</td>
</tr>
</tbody>
</table>

Table (5) Showed the inhibition circle diameter in millimeter for the bacteria after 24 hour incubation paid and 37°C for H$_4$L and some complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>P.S.</th>
<th>B.C.</th>
</tr>
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<tbody>
<tr>
<td>Control DMF</td>
<td>10.9</td>
<td>9.9</td>
</tr>
<tr>
<td>H$_4$L</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>[Zn$_2$(H$_2$L)Cl$_2$]</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>[Cd$_2$(H$_2$L)Cl$_2$]</td>
<td>20</td>
<td>18</td>
</tr>
</tbody>
</table>
Fig. (2) $^1$HNMR spectrum of the ligand (H$_4$L)

Fig. (3a) FT-IR spectrum for the (H$_4$L)

Fig. (3b) FT-IR Spectrum of the complex [(Zn$_2$(H$_2$L)Cl$_2$)]

Fig. (4) Electronic spectrum of the ligand (H$_4$L)
Fig. (5a) The mole-ratio curve of complex \([\text{Zn}_2(\text{H}_2\text{L})\text{Cl}_2]\) in solution \((1 \times 10^{-3} \text{ mole.L}^{-1})\) at \((\lambda=345 \text{ nm})\)

Fig. (5b) The mole-ratio curve of complex \([\text{Cd}_2(\text{H}_2\text{L})\text{Cl}_2]\) in solution \((1 \times 10^{-3} \text{ mole.L}^{-1})\) at \((\lambda=335 \text{ nm})\)
تحضير ودراسات طيفية لقاعدة شف جديدة ومعقداتها ثنائية النواة مع 

\( \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}} \) \text{and} \ \text{Hg}^{\text{II}} \\

أحمد ثابت نعّمان

قسم الكيمياء، كلية التربية ابن الهيثم، جامعة بغداد

الخلاصة

تتضمن البحث تحضير الليكائد الجديد

\(4,4'-\text{(2,2'-(1,4-phenelenebis(methan-1-yl-1-ylidene))bis(azan-1-yl-1-ylidene)bis(1,2-phenylen))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)dibenzene1,3-diol}\)

إذ حضر هذا الليكائد بخطواتين:

الخطوة الأولى مفاعلية مع (terephthaldehyde) وتكوين

\( \text{N}^1,\text{N}^1'-(1,4-phenylenediamine)dibenzene-1,2diamine \)

الخطوة الثانية مفاعلية مع

\( 2,4\text{dihydroxy benzaldehyde} \)

وتكوين الليكائد الجديد (H,L)

\(4,4'-\text{(2,2'-(1,4-phenelenebis(methan-1-yl-1-ylidene))bis(azan-1-yl-1-ylidene)bis(1,2-phenylen))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)dibenzene1,3-diol}\)

تم مفاعلية هذا الليكائد مع بعض العناصر الفلزية باستعمال الميثانول وسطا للتفاعل وبنسبة (1:2) إذ تكانت معقدات جديدة لها

الصيغة العامة 

\([\text{M}_2(\text{H}_3\text{L})\text{Cl}_2]\),

\(\text{M} = \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}} \text{and Hg}^{\text{II}}\)

وشخصت جميع المركبات بالطرق الطيفية، الأشعة تحت الحمراء، والأشعة فوق البنفسجية - المرئية، (HPLC)

مطفرية الامتصاص الذري للعناصر وتم تعين محتوى الكربون ودرجات الأنصهار مع قياس التوصيلية المولارية الكهربائية. كذلك استخدمت طريقة (mole-ratio) لتعيين نسبة الليكائد إلى الفلز وكانت النسبة 2:1. من نتائج البحث فان

الشكل الفيزيائي المقترح لمعقدات كل من الزئبق والكادميوم والزنك هو رباعي السطوح المشوهة. حسب ثابت الاستقرارية (K)

\( \Delta \text{G} \)

وطاقة جبس الحرة . أُختيرت الفعالية البيولوجية لليكائد المحضير ومعقداته.

IJPAS