Synthesis of Tetra Dentate \( \text{N}_2\text{O}_2 \) and their Complexes with \( \text{Cu}^{(II)}, \text{Zn}^{(II)}, \text{Cd}^{(II)} \) and \( \text{Hg}^{(II)} \) Ions.

Maysoon. T. Tawfiq
Ahlaam. J. Zaier
Dept. of Chemistry/ College of Education for Pure Science/ (Ibn Al-Haitham)/ University of Baghdad.
Muna . I .Khalaf
Dept . of Chemistry / College of Science / University of Baghdad

Received in: 19 March 2014, Accepted in: 29 September 2014

Abstract
A Schiff base ligand 1,2-[Bis-(1-phenyl-2-hydroxy-2-phenyl)-amino] benzene \([\text{H}_2\text{L}]\) and its complexes with \( \text{Cu}^{(II)}, \text{Zn}^{(II)}, \text{Cd}^{(II)} \) and \( \text{Hg}^{(II)} \) ions are reported. The ligand was prepared by condensation reaction of ortho-phenylenediamine in methanol under reflux with benzoin to give the mentioned ligand. Then the complexes were synthesized by adding corresponding metal salts to the solution of the ligand in methanol under reflux with 1:1 metal to ligand ratio. On the basis of molar conductance I.R., U.V-Vis, HPLC, chloride content and atomic absorption the complexes may be formulated as \( \text{K}_2[\text{M(L)Cl}_2] \)[\( \text{M}^{II} = \text{Cu}, \text{Zn}, \text{Cd} \) and \( \text{Hg} \)]. The data of these measurements suggest a tetrahedral geometry to complexes \( \text{Cu}, \text{Zn}, \text{Cd} \) and \( \text{Hg} \).

Key words: Synthesis, Schiff bases, Tetra dentate ligand.
Introduction

Schiff bases compounds are used as ligands and the bidented ligands have been among those, they are commonly used in preparing metal complexes. These ligands are described according to their donor as N,N donor and N,O donor Schiff bases[1,2]. The Schiff base complexes are used in catalytic reaction[3] and as models for biological system[4,5]. Many Schiff base ligands with a variety of donor sets, such as (N,O), (N,S) and (N,N) and (N,N) and their transition metal complexes were reported[6,7]. Also Schiff base ligands are well known to have pronounced biological activities[8]. The imino group in Schiff bases can form complexes with transition metal as CoII, CuII and CdII[9].

In 2003 chafa and Co-worker[10] prepared a Schiff kind (N 2O2) [4,4-Bis(salicylidene-imino)di-phenyl ethane (saldiphz) and its transition metal complexes with Co II, CuII and CdII]. In this paper the synthesis and characterization of new ligand 1,2-[Bis-(1-phenl-2-hydroxy-2-phenyl)-amino] benzene [H2L] and its complexes with CuII, ZnII, CdII and HgII were reported. Literature survey shows that Schiff bases complexes have wide range of applications on the industrial scale, such as dyes and pigments [11]. Another area of application of these Schiff bases is analytical chemistry where some of these compounds are used as ligand in complexometry topic [12]. For a long time tetradentate Schiff base complexes have attracted many interests in the field of coordination chemistry [17-18]. Also tetradentate Schiff bases with a N 2O2 donor atom set are well known to coordinate with various metal ions [17-18]. Schiff base of 4- aminoantipyrine and its complexes have a variety of applications in biological, clinical, analytical and pharmacological areas [19-21].

Experimental

Reagents were purchased from Fluka and Rediel-Dehenge chemical Co.IR. spectra were recorded as (KBr) discs using a Shimadzu 8400 FT-IR Spectrophotometer in the range (4000-450) cm⁻¹. Electronic spectra of the prepared compounds were measured in the region (200-900) nm for 10⁻³M solution in (EtOH) at 25°C using a Shimadzu 160 spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. Metal contents of the complexes were determined by atomic absorption (A.A.) technique using a Shimadzu A.A. 680G atomic absorption spectrophotometer. The chloride contents for complexes were determined by potentiometric titration method on (686-titro processor-665), Dosinat metrom Swiss. Electrical conductivity measurements of the complexes were recorded at 25°C for 10⁻³M solutions in (DMSO) as a solvent using a PW952 digital conductivity meter.

Synthesis of the ligand [H₂L]

A solution of (O-phenylene diamine) (2.16g ,0.02 mmol) in methanol (15mL) was added slowly to a mixture of (benzoin) (8.84g,0.04 mmol) dissolving in methanol (20mL) with (2-4) drops of glacial acetic acid. The mixture was refluxed for (5 hrs.), and allowed to dry at room temperature for (24 hrs.). A green solid was obtained. Recrystillized from ethanol. Yield (78%), (3.3g), m.p. (240 0C dec.).

Synthesis of ligand [H₂L] Complexes. Synthesis of [Cu(HL)]Cl (1)

A solution of (H₂L) (0.992g , 0.002 mmol) in (10mL) methanol dissolved in a solution of KOH (0.224 g , 0.04 mmol) (5mL) ethanol was placed in (100mL) round bottomed flask. A solution of CuCl₂.2H₂O (0.34g , 0.002 mmol) in ethanol (5mL) was added drop-wise with stirring. The mixture was refluxed at (78)C in water bath for (5 hrs.) with stirring. Then the mixture was allowed to cool at room temperature, filtered, washed with methanol. A deep green solid was formed. Recrystillized from ethanol. Yield (57%), (0.38g) , (290 0C dec.).
Synthesis of [Zn(HL)]Cl(2), [Cd(HL)]Cl(3) and [Hg(HL)]Cl(4) Complexes

The method used to prepare these complexes was similar to that mentioned in the preparation of [Cu(HL)]Cl complex. Table(1) states weight to starting materials, % yield and some physical properties of the prepared complexes.

Results and Discussion

The new ligand [H2L] was prepared in two steps according to the general method as shown in Schem-1. The IR spectrum for [H2L] (Fig.2) display a broad band at 3414 cm⁻¹ which is due to the ν(O-H) stretching of the phenolic hydroxyl group [22]. The band at 1678 cm⁻¹ is attributed to ν(C=N) stretching frequency for the imino oxime groups vibration respectively [23-25]. The sharp bands at 1261 and 1207 cm⁻¹ are attributed to ν(C-N) and ν(C-O) stretching vibration respectively. U.V-Vis spectrum of the ligand (Fig.3) showed high intense absorption peak at (312) nm, (3401.3) cm⁻¹ (Σmax.=2106 molar⁻¹.cm⁻¹) which assigned to overlap of (π→π*) and (n→π*) electronic transition[26].

Complexes

The synthesis of the complexes was carried out by the reaction of [H2L] with [MCl2×H2O][where M = CuII, ZnII CdII and HgII] in methanol under reflux (Scheme- 2). These complexes are stable in solution and electrolyte system (1:1) in DMSO (table-3). The analytical and physical data (table-1) and spectral data (table-2) are compatible with the suggested structures (Fig. 1).

The IR spectra data of complexes are presented in (table- 2). The IR spectra of the complexes show bands at 3323, 3394, 3341 and 3379 cm⁻¹ which were attributed to ν(OH…..O) stretching vibration of the hydrogen bonding. This band is shifted to lower frequency in comparison with that of the free ligand at 3414 cm⁻¹ [27-28].

The strong band in free ligand [H2L] at 1678 cm⁻¹ for the imine group (C=N) was shifted to lower frequency at 1668, 1632, 1662 and 1670 cm⁻¹ for the complexes (1), (2), (3) and (4) respectively and this due to coordination with metal ions[23-25].

The bands at 1211, 1180, 1215 and 1208 cm⁻¹ were assigned to ν(C-O) stretching vibration in the IR spectra of complexes (1), (2), (3) and (4). The bands at 642, 651, 644 and 686 cm⁻¹ were assigned to ν(M-N) for complexes (1), (2), (3) and (4) respectively indicating that the imine nitrogen is involved in coordination with metal ions[30-31]. The bands at 422, 424, 416 and 562 cm⁻¹ were assigned to ν(M-O) for compounds(1), (2), (3) and (4), indicating that the phenolic oxygen of the ligand is involved in coordination with metal ions[31-33].

Figs. (2-1), (2-2), (2-3) and (2-4) represent the (IR) spectra of [Cu(HL)]Cl, [Zn(HL)]Cl, [Cd(HL)]Cl and [Hg(HL)]Cl. The (U.V-Vis) spectra for all complexes as shown in Figs. (3-1), (3-2), (3-3) and (3-4). The absorption data for complexes are given in (table- 3). In general, the spectra showed two intense peaks in the U.V region at (301,330), (314,323), (302,335) and (301,334) nm for complexes (1), (2), (3) and (4). These peaks were assigned to ligand field and charge transfer transition respectively[34]. Electronic spectrum for complex (1) exhibited peak at 699 nm which can be attributed to (d-d) transition type (⁴B₁g→⁴B₂g). A position of this peak is a good agreement with reported for CuII distorted tetrahedral geometry[35].

The absence of (d-d) transitions in the Electronic spectra of complexes (2), (3) and (4) are arrangement with (d¹⁰) configuration [36]. The molar conductance values determined in (DMSO) solution (10⁻³M) found in the range (66-78) Am (Ω¹.cm².Mole⁻¹) (table 3) which indicated that the complexes are electrolyte (1:1) ratio[37]. The micro analysis of the (A.A.) and chloride content results for the complexes [Cu(HL)]Cl, [Zn(HL)]Cl, [Cd(HL)]Cl and [Hg(HL)]Cl, (table-1) are in a good agreement with the calculated values.
References
23. Xishi Tai, Xianhong yin, Qiang chen, and Minyuta; (2003), "Synthesis of some Transition Metal Complexes of a Novel Schiff Base Ligand Derived from 2,2-Bis (P-Methoxy phenyl amine and Salicylicaldehyde Molecules" , 8,.439-440.

Table No.(1): Some physical properties of the complexes and their reactants quantities.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>m.p °C</th>
<th>Color</th>
<th>Metal Chloride</th>
<th>Weight of Metal Chloride (g) = 0.002 mole</th>
<th>Weight of Product (g)</th>
<th>Yield %</th>
<th>Metal % Prac. (Theo.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(HL)Cl]</td>
<td>290</td>
<td>Deep green</td>
<td>CuCl₂.2H₂O</td>
<td>0.34</td>
<td>0.38</td>
<td>57</td>
<td>11.1 (11.39)</td>
</tr>
<tr>
<td>[Zn(HL)Cl]</td>
<td>257</td>
<td>Brown</td>
<td>ZnCl₂.×H₂O</td>
<td>0.27</td>
<td>0.30</td>
<td>55</td>
<td>10.2 (11.68)</td>
</tr>
<tr>
<td>[Cd(HL)Cl]</td>
<td>310</td>
<td>Deep green</td>
<td>CdCl₂.×H₂O</td>
<td>0.40</td>
<td>0.48</td>
<td>55</td>
<td>16.89 (16.53)</td>
</tr>
<tr>
<td>[Hg(HL)Cl]</td>
<td>340</td>
<td>Green</td>
<td>HgCl₂.×H₂O</td>
<td>0.54</td>
<td>0.75</td>
<td>45</td>
<td>28.31 (28.87)</td>
</tr>
</tbody>
</table>
Table No.(2): I.R Spectral data of the ligand and it's complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(O-H) phenol</th>
<th>$\nu$(O-H…O) hydrogen bonding</th>
<th>$\nu$(C=N) imine</th>
<th>$\nu$(C-N)</th>
<th>$\nu$(C-O)</th>
<th>M-O M-N</th>
<th>Others bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H$_2$L]</td>
<td>3414</td>
<td>1678</td>
<td>1261</td>
<td>1207</td>
<td>-</td>
<td>-</td>
<td>$\nu$(C=C) 1450 $\nu$(C-H) alph. 2931 $\nu$(C-H) arom. 3059</td>
</tr>
<tr>
<td>Cu(H$_2$L)Cl</td>
<td>3323</td>
<td>1668</td>
<td>1290</td>
<td>1211</td>
<td>422</td>
<td>642</td>
<td>$\nu$(C=C) 1444 $\nu$(C-H) alph. 2980 $\nu$(C-H) arom. 3058</td>
</tr>
<tr>
<td>Zn(H$_2$L)Cl</td>
<td>3394</td>
<td>1678</td>
<td>1222</td>
<td>1180</td>
<td>424</td>
<td>651</td>
<td>$\nu$(C=C) 1446 $\nu$(C-H) alph. 2927 $\nu$(C-H) arom. 3028</td>
</tr>
<tr>
<td>Cd(H$_2$L)Cl</td>
<td>3371</td>
<td>1662</td>
<td>1284</td>
<td>1211</td>
<td>416</td>
<td>644</td>
<td>$\nu$(C=C) 1396 $\nu$(C-H) alph. 2947 $\nu$(C-H) arom.3062</td>
</tr>
<tr>
<td>Hg(H$_2$L)Cl</td>
<td>3379</td>
<td>1677</td>
<td>1256</td>
<td>1205</td>
<td>562</td>
<td>686</td>
<td>$\nu$(C=C) 1352 $\nu$(C-H) alph. 2920 $\nu$(C-H) arom.3085</td>
</tr>
</tbody>
</table>

Table No.(3): Electronic spectral data, and conductance measurement for the ligand [H$_2$L] and it's complexes.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>$\lambda$ nm</th>
<th>Wave number cm$^{-1}$</th>
<th>$\epsilon_{\text{max}}$</th>
<th>Assignment</th>
<th>$\text{Am}$ (\text{cm}^{-1} \cdot \text{Mole}^{-1})</th>
<th>Propose structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>[L]</td>
<td>312</td>
<td>34013</td>
<td>2106</td>
<td>$\pi \rightarrow \pi^<em>$ $n \rightarrow \pi^</em>$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu(HL)Cl</td>
<td>301</td>
<td>3322</td>
<td>510</td>
<td>Ligand field Charge transfer</td>
<td>78</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td></td>
<td>330</td>
<td></td>
<td>440</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>699</td>
<td>1430</td>
<td>331</td>
<td></td>
<td>$^2B_1g \rightarrow ^2B_2g$</td>
<td></td>
</tr>
<tr>
<td>Zn(HL)Cl</td>
<td>314</td>
<td>3184</td>
<td>2318</td>
<td>Ligand field Charge transfer</td>
<td>66</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>30959</td>
<td>1255</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd(HL)Cl</td>
<td>302</td>
<td>3311</td>
<td>1384</td>
<td>Ligand field Charge transfer</td>
<td>69</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td></td>
<td>335</td>
<td>29850</td>
<td>1158</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg(HL)Cl</td>
<td>301</td>
<td>3322</td>
<td>1288</td>
<td>Ligand field Charge transfer</td>
<td>62</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td></td>
<td>334</td>
<td>2994</td>
<td>983</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Scheme No.(1): The Synthesis route of the Ligand [H₂L].
Scheme No. (2): Preparation of the metal complexes.

\[
\text{Scheme No. (2): Preparation of the metal complexes.}
\]
Figure NO .(1) : The suggested structure for the prepared complexes

Figure No. (2): The I.R spectrum of the ligand [H2L]
Figure No.(2-1): The I.R spectrum of \([\text{Cu(HL)}]\text{Cl}\)

Figure No. (2-2):- The I.R spectrum of \([\text{Zn(HL)}]\text{Cl}\).

Figure No.(2-3):- The I.R spectrum of \([\text{Cd(HL)}]\text{Cl}\)
Figure No. (2-4). The I.R spectrum of [Hg(HL)]Cl

Figure No. (3): The U.V spectrum of the ligand [H₂L]

Figure No. (3-1): The U.V spectrum of [Cu(HL)]Cl
Figure No. (3-2): The U.V spectrum of [Zn(HL)]Cl

Figure No. (3-3): The U.V spectrum of [Cd(HL)]Cl

Figure No. (3-4): The U.V spectrum of [Hg(HL)]Cl
تحضير ليكاند رباعي المنح نوع $\text{N}_2\text{O}_2\text{O}_2$ مع معقداته مع ($\text{Cu}^{II}$, $\text{Zn}^{II}$, $\text{Cd}^{II}$ and $\text{Hg}^{II}$)

 Mouth Samir يتقوم تحقق

 قسم الكيمياء/كلية التربية للعلوم الصرفة (إبن الهيثم) / جامعة بغداد

 منى اسماعيل خلف

 قسم الكيمياء/كلية العلوم / جامعة بغداد

أول البحث في: 19 آذار 2014، قبل البحث في: 29 ايلول 2014

الخلاصة

تضمن البحث تحضير ليكاند رباعي المنح $[1, 2-\text{Bis}(1\text{-phenyl-2-hydroxy-2-phenyl})\text{-amino})\text{benzene} \ [\text{H}_2\text{L}]]$ مع معالجة الليكاند مع أيونات ($\text{Cu}^{II}$, $\text{Zn}^{II}$, $\text{Cd}^{II}$ and $\text{Hg}^{II}$) وذلك من معالجة (ortho-phenylenediamine) مع (benzoin) تكوينت سلسلة من المعقدات (1:1) باستخدام الميثانول وسطاً للتفاعل وبنسبة $\text{KOH}$ بوجود القاعدة (1:1) و+$\text{M} = (\text{Cu}^{II}, \text{Zn}^{II}, \text{Cd}^{II}$ and $\text{Hg}^{II})$$\text{Cl}$

 شَرَفَت جميع المركبات المحضرة بوساطة التقنيات الأثاثية: الأشعة تحت الحمراء ، والأشعة فوق البنفسجية – المرنية،$

$\text{HPLC}$،$\text{كشافات التحليل}

$\text{الكيميائية}. من معطيات التحليل فأن الشكل الهرمي المفترض لمعقدات الرباعي المنح والكادميوم والزنك هو شكل رباعي السطوح$

الأعمال المفتوحة: تحضير، قواعد شيف، ليكاند رباعي السن.