Metal (II) Complexes with Tridentate N, N,O Ligand: Synthesis, Characterization and Biological Studies

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Abstract
The preparation of some new coordination compounds for nickel (II), manganese (II), copper (II), cobalt (II) and mercury (II), with ligand obtained from Benzoin and 2-amino pyridine. The ligand [6-(2-hydroxy-1,2-diphenylethylideneamino)pyridin-3-yl]ium (L) was made from reacting ethanol with metal salts in (1:1) (metal : ligand) ratio. [MLCl] was the inclusive formula of the complexes where M = Mn(II), Co(II), Ni(II), Cu(II) and Hg(II). Metal analysis by electronic spectra, atomic absorption, infrared spectra, 1H & 13C-NMR (only ligand) spectral studies, magnetic moment and molar conductance measurements used to describe the compounds. The determinations indicated that the ligand coordinates with the metal (II) ion in neutral tridentate manner through the azomethine nitrogen atom, nitrogen atom for pyridine and oxygen atom of the benzoin, all the studies reveal coordination four for the metals in all the complexes. Tetrahedral and square planar structures were suggested for metal complexes.

Key words: Schiff base, 2-amino pyridine, Characterization, Metal chelate complexes.
Introduction

Amino compounds as heterocyclic containing one or more possibilitygiver centers took asignificant assignment in the study of reaction of tridentate Schiff base system [1]. They are recognized to act ligands as bidentate or tridentate when chelated to metalon [2]. Schiff bases are a grade of significant compounds due to their broad domain of enforcements and qualities [3]. Schiff base and its complexes have presented with a lot notice because of their use as models for biological arrangement and applications as i.e. in the areas of catalysis clinical, pharmacologically and photochemical [5]. Schiff bases are reported to possess antibacterial [6], antifungal [7], anticancer [8], herbicidal anticonvulsant [9] and diuretic activities [10]. These ligands have ONO giver atom group were attracted the interest of many authors are well recognized to coordinate with various metal ions and this has [11]. In this study, Schiff base of 2-aminopyridine with benzoin has been synthesized, characterized and antibacterial activity study of the new complexes were prepared. Further more, the structures of prepared compounds were definite by spectral studies. The arrangement of the compounds is displayed in scheme (1) and (2).

Experimental

2-amino pyridine and Benzoin were purchased from Sigma Chemical Co. (USA). Glacial acetic acid reagent from" (Aldrich and Sigma). The all metal salts used were gave from (BDH).

Instrumentation

Melting point were determined on "Gallenkamp melting point Apparatus ". Elemental microanalysis C.H.N. were carried out using "Euro Vector EA 3000 A Analysis". FT-IR measurements were recorded on "Shimadzu- 8300 Spectrophotometer". Electronic spectra were recorded using "UV-Vis. spectrophotometer type CECIL". 1H and 13C-NMR spectra were recorded by using a Bruker 300 MHZ (Switzerland). Chemical shift. Conductivity measurements were obtained from WTW conductivity meter. The chloride content determined using potentiometric titration method on "686–Titro Processor –665 Dosim A– Metrohm/Swiss". Atomic Absorption of complexes were obtained from a Shimadzu PR-5. ORAPRINT or alphabetic spectrophotometer".

Synthesis of \[6-(2-hydroxy-1,2-diphenylethylideneamino)pyridin-3-ylum)] (L)

The [L] was prepared according to the method published in literature [1] scheme (1) An ethanolic solution of (30 mL) 2-aminopyridine (0.094g, 0.001 mmole) was added to an ethanolic solution of benzoin (0.21, 0.01 mmole) and three drops from glacial acetic acid. The resultant mixture was refluxed for ca. 6 h. The solid product formed was filtered and recrystallized from ethanol [2].
Synthesis of M(II) Complexes
A solution of metal (II) chlorides in ethanol (2mmole) was stirred with ethanolic solution of the Schiff base (2mmole) and three drops from KOH solution, for ca. 2 h on a magnetic stirrer at 50°C. The solid complex precipitated was filtered off and washed thoroughly with ethanol and dried in vacuo, recrystallized from a hot of (10mL) ethanol, a coloured precipitate was formed [5, 6]. The physical properties of complexes were listed in Table (1).

Results and Discussion
NMR spectrum
The \(^1\)H NMR spectrum shows signals at: 1.15 ppm singlet for 1H benzoin H atom; singlet at 2.50 ppm due to DMSO solvent; singlet signal at 3.385 for 1H hydroxylic proton, the remaining [bands multiplied] from 5.6 to 8.2 ppm belong to the three aromatic ring protons that overlap with each other [10].

The \(^{13}\)C NMR spectrum: in the spectrum the 40.8 ppm signal is due to the solvent C atoms of DMSO; 73.2 attributed to C-OH moiety; the aromatic carbon peaks appeared in the range from 124.43 to 149.88 ppm, finely the two peaks above 160 ppm, returned to the two sp\(^2\) Carbon atoms that linked with Nitrogen, the firs are for Schiff base band and the other one returns to α-imine pyridine [12].
The IR spectra for the ligand and its complexes

The important IR absorption bands for the synthesized Schiff bases are listed. In the L, the band shows at 1604 cm\(^{-1}\) that it was assigned to the \(\nu(C=N)\) stretching mode. In complexes this band was shifted to lower regions, 1598 cm\(^{-1}\), 1593 cm\(^{-1}\), 1591 cm\(^{-1}\), 1595 cm\(^{-1}\), and 1596 cm\(^{-1}\) for Mn(II), Co(II), Ni(II), Cu(II) and Hg(II) complexes respectively, suggesting the coordination of azomethine nitrogen to metal atom in complexation [13]. The (IR) spectra of the complexes showed bands at the range (1576-1581) cm\(^{-1}\) were assigned to \(\nu(C=N)\) groups for the pyridine ring in 2-amino pyridine, which shifted the frequency to a lower in comparison with that of Schiff base was showed at (1588) cm\(^{-1}\), when coordination with the metal ion referring to share of two nitrogen\(-\nu(C=N)\). The bands show at 1531 cm\(^{-1}\) and 1498 cm\(^{-1}\) were assigned to the \(\nu(C=C)\) stretching mode in the ligand. These bands prove the presence of benzene. IR spectrum of the ligand showed a broad band at 3344 cm\(^{-1}\) due to \(\nu(OH)\) stretching mode in the ligand [14]. This band was absent in the spectra of complexes, they indicate the disappearing of the alcoholic proton on complexation and involvement of alcoholic anionic oxygen in coordination [15]. Moreover, the strong band at 1187 cm\(^{-1}\) is due to \(\nu(C-O)\) (alcoholic) in the ligand. A medium band corresponding to pyridine nitrogen \(\nu(C-N)\) was observed at 1531 cm\(^{-1}\) [16,17]. The bands show at (1587) cm\(^{-1}\) and (1349) cm\(^{-1}\) were observed to be shifted to higher or lower frequencies, at 1240–1257 cm\(^{-1}\) and 1183–1198 cm\(^{-1}\). Also the bands show at (582-547) (460-482) due to \(\nu(M-O)\) and \(\nu(M-N)\), respectively. In the metal complexes indicating the involvement of nitrogen of pyridine ring and oxygen of the alcoholic group in the complex formation [18-19].

The UV Spectral Studies

The Cu(II), Co(II), Ni(II), Mn(II) and Hg(II) complexes of ligand L were subjected to their UV-Visible spectral studies at room temperature in the range of 200–1100nm by using DMF as a solvent, and the data of the ligand (L) were recording Table (5).

The U.V-Vis spectrum of Schiff base, Fig.(3) in Table (5) displayed two absorptions. The first absorption at (280) nm (35714 cm\(^{-1}\)) may be assigned to \(\pi-\sigma^*\) transition. The second peak at (312) nm (32051 cm\(^{-1}\)) was attributed to \(n-\pi^*\) electronic transition [20].

- The electronic spectrum of the Co (II) complex showed two peaks, the first peak (331) nm (30211 cm\(^{-1}\)) which was assigned to C.T transition. The second peak at (611) nm (16366) cm\(^{-1}\) was allocated to (d-d) electronic transition type \(4A_2 (F) \rightarrow 4T_1 (P)\). (5.71) B.M. is a magnetic sensibility of this complex. [21] It has been a tetrahedral environment [22].

- The U.V-Vis spectrum of the Ni (II) complex displayed two peaks, the first peak (332) nm (30120 cm\(^{-1}\)) which was assigned to C.T transition. The second peak at (770) nm (12987 cm\(^{-1}\)) was allocated to (d-d) electronic transition type \(1A_{1g} (F) \rightarrow 2E_g\). It has been as square planar configuration. Diamagnetic is a magnetic sensibility of this complex [23].

- The U.V-Vis spectrum of the Copper (II) complex showed two peaks, the first peak (327) nm (30581 cm\(^{-1}\)) which was assigned to C.T transition. The second peak at (543) nm (18416 cm\(^{-1}\)) was referred to (d-d) transition type \(1B_{1g} \rightarrow 2A_{1g}\). 1.76B.M is a magnetic moment. It has been as a square planar configuration of this complex [24].

While the absorptions of manganese (II) complex showed three bands, the first bond (335) nm (29650 cm\(^{-1}\)) which was assigned to C T transition. The second and third bands at 453 nm (12903 cm\(^{-1}\)) and 586 nm (22075 cm\(^{-1}\)) which have been assigned to \(^6A_1 \rightarrow ^4A_{1g}\) and \(^6A_1 \rightarrow ^4E\) (G) transitions respectively. 5.75B.M. is amagnetic sensibility of this complex. It has been a tetrahedral configuration [25].
The complex mercury (II) is diamagnetic giving two peaks at 334 nm ($29940\text{cm}^{-1}$) and 410 nm ($24390\text{cm}^{-1}$) were allocated to C T transitions. The peaks disappear in the visible region. It has been a tetrahedral configuration[26].

**Biological Activities**

Tridentate Schiff base ligand derived by the condensation2-amino pyridine with benzoin and its complexes showed biological activities against the type of bacterial(*Bacillus*) except[Cu(L)Cl].[27 and 28].The results indicate that the complexes showed more activity than the ligand under similar experimental conditions, table (6) DMF (which was used as a solvent and Controller) was a good solvent to prepare 1ppm of each tested sample .All compounds ligand and its complexes have good biological activity against the type of bacterial (*Escherichia coli*), (*Staphylococcus aureu*) and (*Escherichia coli*) in Fig (5).Table (6) Diameter of zone of inhibition.

**Molar conductivity**

The conductance values in DMF of the complexes show in the ambit10 to 25 ohm$^{-1}$.cm$^{2}$mol$^{-1}$ which is quite lower than that expected for an electrolyte and appear their non-electrolytic nature as in Table(5).

**Conclusion**

The new ligand (L) and all complexes were synthesis. The metal (II) ions are coordinated by one amine (H-C=N) atom ,N of pyridine and O atom of benzoin. Spectroscopic and structural data display(4)-chelate in metal complexes obtaining to the bind of tridentates ligand groups with one chelated chloride in schemes (1&2).

**References**


16. Chaurasia, M.R.; Miss P. S. and Singh N.K.;(1982) Mixed Ligand Complexes of N-6-Methyl Benzothiazol-2-yl-Salicylaldimine& 2-Methyl Benzimidazole with Cu(II),Ni(II), Co(II), Mn(II),Vo(II), Zn(II), Cd(II) and Hg(II), J. of Chem. Sci., 110-114


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And Antimicrobial Activity of N,N’-bis (2-Thiophenecarboxamido)-1,3-Diaminopropane and 
N,N’-bis (2-Furan-Carboxamido)-1,3-diaminopropane and their Cu (II), Zn (II), Co(II) 
23. A. A. Ahmed and S. A. BenGuzzi (2008); Synthesis and Characterization of Some 
Transition Metals Complexes of Schiff Base Derived From Benzidine and Acetylacetone. J. of 
Sci. and Appl., 2(1)83-90.
(II), Dioxomolybdenum (VI) and Oxovanadium (V) Complexes with Monobasic Bidentate 
27. Bukhari, I.H.; Arif, M.; Akbar, J. and Khan, A.H. ;(2005) Preparation, Characterization and 
Biological Evaluation of Schiff Base Transition Metal Complexes with Cephradine, Pak. J. 

Table (1) Some properties of prepared compounds

<table>
<thead>
<tr>
<th>Empirical Formula</th>
<th>Chemical Formula</th>
<th>Molecular Weight</th>
<th>Yield %</th>
<th>M.Pº</th>
<th>Colour</th>
<th>Calc. % Found</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>L</td>
<td>C₁₉H₁₂N₂O</td>
<td>358.43</td>
<td>60</td>
<td>140</td>
<td>yellow</td>
<td>(76.74)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(9.36)</td>
</tr>
<tr>
<td>[Co(L)Cl]</td>
<td>C₁₉H₁₂ClCoN₂O</td>
<td>380.01</td>
<td>67</td>
<td>220</td>
<td>Blue</td>
<td>(59.94)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(9.36)</td>
</tr>
<tr>
<td>[Ni(L)Cl]</td>
<td>C₁₉H₁₂CIN₂N₂O</td>
<td>380.47</td>
<td>76</td>
<td>254</td>
<td>Pule brown</td>
<td>(59.98)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(9.36)</td>
</tr>
<tr>
<td>[Mn(L)Cl]</td>
<td>C₁₉H₁₂ClMnN₂O</td>
<td>382.32</td>
<td>82</td>
<td>208</td>
<td>Greenh yellow</td>
<td>(60.58)</td>
</tr>
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<td></td>
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<td></td>
<td>(9.36)</td>
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<tr>
<td>[Cu(L)Cl]</td>
<td>C₁₉H₁₂ClCuN₂O</td>
<td>385.33</td>
<td>73</td>
<td>219</td>
<td>brown</td>
<td>(59.23)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(9.36)</td>
</tr>
<tr>
<td>[Hg(L)Cl]</td>
<td>C₁₉H₁₂ClHgN₂O</td>
<td>522.37</td>
<td>84</td>
<td>241</td>
<td>Pule brown</td>
<td>(43.69)</td>
</tr>
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</table>

Table (2)¹H-NMR Shifts for Schiff base in DMSO-d₆

<table>
<thead>
<tr>
<th>CH-OH</th>
<th>DMSO</th>
<th>OH-CH</th>
<th>Py-H</th>
<th>Ar-H</th>
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<tr>
<td>1.15</td>
<td>2.5</td>
<td>3.82</td>
<td>5.39-6.18</td>
<td>6.83-8.12</td>
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</table>

Table (3) ¹³C-NMR shifts for Schiff base in DMSO-d₆

<table>
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<tr>
<th>DMSO</th>
<th>C-OH</th>
<th>Py-C</th>
<th>Ar-C</th>
<th>Py-C=N</th>
<th>HC=N</th>
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<tr>
<td>40.80</td>
<td>73.29</td>
<td>124.70-129.61</td>
<td>130.20-141.56</td>
<td>160.39</td>
<td>164.47</td>
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### Table (4) FT-IR data for Schiff base and the complexes

<table>
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<tr>
<th>Compound</th>
<th>µ(H - O)</th>
<th>µ(H - C) aromatic</th>
<th>µ(H - C) aliphatic</th>
<th>µ(N=C)</th>
<th>λmax</th>
<th>µ(N – M)</th>
<th>µ(O – M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>3344</td>
<td>3059</td>
<td>2937</td>
<td>1604</td>
<td>1588</td>
<td>1240</td>
<td>-</td>
</tr>
<tr>
<td>[Co(L)Cl]</td>
<td>-</td>
<td>3068</td>
<td>2937</td>
<td>1595</td>
<td>1579</td>
<td>1242</td>
<td>547</td>
</tr>
<tr>
<td>[Ni(L)Cl]</td>
<td>-</td>
<td>3056</td>
<td>2924</td>
<td>1593</td>
<td>1581</td>
<td>1243</td>
<td>547</td>
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<tr>
<td>[Cu(L)Cl]</td>
<td>-</td>
<td>3076</td>
<td>2926</td>
<td>1591</td>
<td>1578</td>
<td>1241</td>
<td>549</td>
</tr>
<tr>
<td>[Mn(L)Cl]</td>
<td>-</td>
<td>3026</td>
<td>2924</td>
<td>1598</td>
<td>1576</td>
<td>1243</td>
<td>582</td>
</tr>
<tr>
<td>[Hg(L)Cl]</td>
<td>-</td>
<td>3040</td>
<td>2927</td>
<td>1596</td>
<td>1578</td>
<td>1242</td>
<td>545</td>
</tr>
</tbody>
</table>

### Table (5) UV-Vis data of Schiff base and the complexes

<table>
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<tr>
<th>Comp.</th>
<th>µeff</th>
<th>λmax</th>
<th>wave number</th>
<th>Assignments</th>
<th>Proposed</th>
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<tr>
<td>L</td>
<td>-</td>
<td>280</td>
<td>35714</td>
<td>π→π*</td>
<td>-</td>
</tr>
<tr>
<td>[Co(L)Cl]</td>
<td>5.71</td>
<td>312</td>
<td>32051</td>
<td>n→π*</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>[Ni(L)Cl]</td>
<td>Dai.</td>
<td>611</td>
<td>16366</td>
<td>^4A2(ge)→^4T1 (pe)</td>
<td>square planar</td>
</tr>
<tr>
<td>[Cu(L)Cl]</td>
<td>1.76</td>
<td>327</td>
<td>30581</td>
<td>^4T1(ge)→^2T1(g)</td>
<td>square planar</td>
</tr>
<tr>
<td>[Mn(L)Cl]</td>
<td>5.75</td>
<td>335</td>
<td>29850</td>
<td>^4A1(g)→^4T1(g)</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>[Hg(L)Cl]</td>
<td>-</td>
<td>410</td>
<td>24390</td>
<td>^6A1(g)→^4E (ge)</td>
<td>square planar</td>
</tr>
</tbody>
</table>

### Table (6) Diameter of zone of inhibition (mm)

<table>
<thead>
<tr>
<th>Compound.</th>
<th>DMF control</th>
<th>L</th>
<th>Co complex</th>
<th>Mn complex</th>
<th>Ncomplex</th>
<th>Cucomplex</th>
<th>Hgcomplex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Escherichia. Coli</td>
<td>1</td>
<td>3</td>
<td>10</td>
<td>10</td>
<td>6</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Staphylococcus aureus</td>
<td>-</td>
<td>5</td>
<td>12</td>
<td>14</td>
<td>9</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>Bacillus</td>
<td>-</td>
<td>7</td>
<td>9</td>
<td>10</td>
<td>-</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>Pseudomonas</td>
<td>1</td>
<td>6</td>
<td>8</td>
<td>13</td>
<td>10</td>
<td>14</td>
<td>12</td>
</tr>
</tbody>
</table>

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Figure (1) The IR spectrum of Schiff base

Figure (2) The IR spectrum of Ni complex

Figure (3) The UV spectrum of Schiff base

Figure (4) The UV spectrum of Ni complex
Figure (5) The $^1$H-NMR spectrum of Schiff base

Figure (6) The $^{13}$C-NMR spectrum of Schiff base

Figure (7) Effect of *Escherichia Coli* gram negative
Figure (8) Effect of *Staphylococcus aureus*

Figure (9) Effect of *Bacillus* gram

Figure (10) Effect of *pseudomonas* gram
معقدات الفلزات الثنائية مع ليكاند ثلاثي السن: 
دراسة تحضير، تشخيص وفعالية البيولوجي.

علي نبيل نصيف
قسم الكيمياء/ كلية التربية ابن الهيثم للعلوم (ابن الهيثم) / جامعة بغداد

استلم في: 22/كانون الأول/2016، قبل في: 28/حزيران/2016

الخلاصة

تحضير بعض المركبات التناسقية الجديدة للكوبالت، النحاس، المنغنيز، النيكل، النكيل والثاني (II) من ليكاند كمادة مذابة في الماء، حيث يتم التفاعل مع الأحماض الفلزية في الإيثانول كمادة منشقة في نسبة 1:1. المركبات التي لها الصيغة العامة [MLCI] حيث M = ليكاند، M = مذابة في الماء، L = الأمين، C = الكوبالت، I = النحاس، N = المنغنيز، Ni = النيكل، Cu = النكيل والثاني (II).

تم تشخيص الليكاند والمعقدات الفلزية وذلك باستخدام تحليل الفلزات عن طريق الالتصاص الذري والرنين النووي، التصوير المغناطيسي، التصوير بالرنين النووي، والرنين الذري. أطياف الأشعة تحت الحمراء، الأطياف الإلكترونية، التوصيلية الإلكترونية وقياسات الذاكرة المغناطيسية. وأشارت القياسات أن الليكاند تتفاعل مع أيون الفلز بطريقة ثلاثي السن من خلال ذرة النتروجين للإيزومور، ذرة النتروجين من البروتين من ذرة الأوكسجين من المنتجين جميع المركبات تكشف أن التناسق رباعي في جميع المركبات واقترحت بنية رباعي المسطح ومربع مستوي لمعدات الفلزية.

الكلمات المفتاحية: قاعدة شيف، 2-امينو بيريدين، تشخيص ومخالب مكشوفة، فلزية.