Preparation-and Spectroscopic Characterization of Transition Metal Complexes with Schiff base 2-[1-(1H-indol-3-yl)ethylimino) methyl]naphthalene-1-ol

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Abstract:
The ligand 2-[1-(1H-indol-3-yl)ethylimino) methyl]naphthalene-1-ol, derived from 1-hydroxy-2-naphthaldehyde and 2-(1H-indol-3-yl)ethylamine, was used to produce a new sequence of metal ions complexes. Thus ligand reactions with NiCl₂, H₂O, PdCl₂, FeCl₃, H₂O and H₂PtCl₆, H₂O were sequentially made to collect mono-nuclear Ni(II), Pd(II), Fe (III), and Pt(IV). (IR or FTIR), Ultraviolet Reflective (UV–visible), Mass Spectra analysis, Bohr-magnetic (B.M.), metal content, chloride content and molar conductivity have been the defining features of the composites. The Fe(III) and Pt(IV) complexes have octahedral geometries, while the Ni(II) complex has tetrahedral geometry and the Pd (II) complex has square planer geometry, according to these findings.

Keywords: Mass spectra, Metal Complexes, Schiff base.

Introduction:
Indole compounds can be present in a variety of natural sources, including fungal metabolites, Indole alkaloids, and aquatic organisms. The inclusion of the (-N=CH-) group, denotes antibacterial, antifungal, antimalarial, antiviral, and antipyretic properties and multifaceted applications such as organic synthesis intermediates, rewards, polymer stabilizers, coordination chemistry ligands, and dyes or colorants. Due to their ease of synthesis, structural variability, and broad range of applications, Schiff bases are regarded as important ligands for metal ion coordination complexes. Schiff bases are important in coordination chemistry because they shape stable complexes with the largest transition metal ions with ease. Numerous biologically important Schiff bases and their mineral complexes have been identified in the paper, with significant roles in anticoncorrosion, soil treatment factors, and medicinal factors, as well as agricultural, analytical, biological, therapeutic, biochemical, antimicrobial, anticancer, antibacterial, antitumor activity, and antifungal activity. Schiff bases undergo chelation with oxygen, nitrogen, and other elements. Collections of imine or azomethine can be used in a variety of natural, derivative, and non-natural compounds. Some compounds' biological activities are based on the existence of an amine group. These ligands were mostly used as polydentate ligands, and they showed excellent steric properties as well as electronic smooth tuning of their metal complexes. Schiff base complexes with two or three metal centers are ideal catalysts. It is also understood that ligand-metal ion coordination enhances the biological function of the ligand thus reducing the cytotoxic effects of the metal atom and ligand. Schiff bases are polydentate ligands and their complexes designed by chemists, and they have been used in a variety of applications. This ligand has never been seen in this type before, according to the analysis. This work investigates the synthesis and characterization of a new Schiff base ligand from the reaction of 2-(1H-indol-3-yl) ethylamine with 1-hydroxy-2-naphthaldehyde and their metal complexes. The consequences proposed that Schiff base acts like a bidentate ligand for all the prepared complexes.
Materials and Methods: Chemicals and Measurements

Chemicals were obtained from industrial sources (Sigma-Aldrich, Merck) and were not filtered prior to usage. Eurovector EA 3000A was used to conduct elemental microanalysis. Metal ions were calculated as metal oxides using a gravimetric method. The following instruments were used to calculate the molar conductivity (units) of metal complexes: Conduct meter (WTW). The chloride content of complexes was calculated using Mohr's method in the presence of potassium chromate and silver nitrate as a titrating agent. At 25°C in England, the magnetic study was calculated by the Balance of Johnson Matthey catalytic device division. MS QP50A: DI Analysis. The Shimadzu QP-2010-Plus (E170Ev) spectrometer was used to interpret mass spectra for ligands and complexes. The SHIMADZU 1800 Double Beam UV-Visible spectrophotometer was used to record electronic spectra for compounds in the (UV-Visible) range 200-1100 nm. Bruker Ultra Sheild 300 MHz NMR was used to produce H-NMR spectra. Fourier Transform Infrared (FTIR) spectra were obtained using SHIMADZU FT-IR 8400S Fourier transforms and KBr and CsI discs in the wavenumber range of 4000 to 200 cm⁻¹.

Synthesis of ligand 2-[[1(1H-indol-3-yl)-ethylinino]-methyl]-naphthalene-1-ol

The stoichiometry of both compounds 1-hydroxy-2-naphthaldehyde (0.847 g, 0.00492 mol) and 2-(1H-indol-3-yl)-ethylinino (0.788 g, 0.00492 mol) was treated by dissolving them in a methanolic solution 15 mL, applying three drops of HBr, and then enabling the mixture to reverse develop for six hours and then, purified and lifted. Yield: 89 percent, M.p. 266-268 degrees Celsius. Different peaks at = 7.838-8.257ppm (m, 10H, Ar-H) in the 1H-NMR range of Schiff base (HL) are correlated with aromatic protons. The existence of proton of amine is shown by the peak at = 9.353 ppm (s,1H, N-H). The peak at = 8.535 ppm belongs to the (s1H, N=CH) aldehyde group, the peak at = 3.337 ppm belongs to the (tetra1H, N-CH) group, and the peak at = 2.634 – 2.845 ppm belongs to the (dub late, 3H, C-CH₃) group and (2.5ppm to DMSO).

Synthesis of complexes

Metals of Schiff base were made by refluxing a 2:1 molar rate ethanolic solution of Schiff base and equivalent metal salts at 250mL in two necked flasks for three hours. Chloride salts of Pt(IV), Pd(II), Ni(II), and Fe (III) were included in the current analysis. Filtration was used to remove the strong precipitate that had accumulated in the reduced amount of origin oil. The raw material was recrystallized with ethanol, then dried and stored in vacuum desiccators scheme 1.
**Results and Discussion:**

C.H.N. Analysis was conducted and it was found that the practical results match the theory as shown in the Tab.1 Metal salts were used with ratio 2:1 reaction of ligand and metal, and the molar conductivity showed that all the complexes were of equal charge, except for the iron complex, had an ionic ratio of 1:1.

**Table 1. Results of the Elemental microanalysis as well some physical characteristic for ligand LH as well metal complexes**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Chemical Formula</th>
<th>M.Wt</th>
<th>Color</th>
<th>M.p</th>
<th>Elemental microanalysis%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C Found</td>
</tr>
<tr>
<td>LH</td>
<td>C21 H17 N2O</td>
<td>314.38</td>
<td>Brown</td>
<td>266-268</td>
<td>80.49</td>
</tr>
<tr>
<td></td>
<td>[Ni(L)2]</td>
<td>685.44</td>
<td>Green</td>
<td>Dec. &lt;300</td>
<td>81.21</td>
</tr>
<tr>
<td></td>
<td>[PtCl2 L2]</td>
<td>733.17</td>
<td>Deep</td>
<td>Brown</td>
<td>73.60</td>
</tr>
<tr>
<td></td>
<td>[FeL(H2O)2]Cl</td>
<td>754.07</td>
<td>Brown</td>
<td>Red</td>
<td>72.11</td>
</tr>
</tbody>
</table>

Electronic absorption spectra, magnetic moments, and conductivity measurements:

The ligand's electronic range (LH) shows acute absorption at (364 nm, 27473 cm⁻¹), which is assigned to n→π*, and (322 nm, 31056 cm⁻¹) which is assigned to π→ π* (Fig. 2). The electronic spectrum of the Ni(II) Complex with ligand displays many absorption bands at 262, 290, 330, 563, and 784 nm, respectively, which are allocated to π→π*, π→π*, n→π*, T1(g)→T2(g), T1(f)→T1(p) respectively (Fig. 3). The magnetic moment of the Ni(II) (d⁶) complex has also been estimated to be 2.82 B.M. All of the information presented above of the Ni(II) complex is consistent with tetrahedral geometry. The diamagnetic Pd(II) d⁶ low spin complex has absorption peaks at 248, 347, and 643 nm, which correspond to π→ π*, n→π* and 1A1g→1A1g sequentially, and another band at 572 nm, which can be chosen as 1A1g→1B1g (Fig. 4). The square planer Pd(II) complex is responsible for these assignments. The spectrum of Pt(IV) complex Tab.2 shows peaks at 320, 386, 466, and 542 nm, which are due to π→π*, n→π*, 1A1g→1T2g, and 1A1g→1T1g transitions (Fig. 5), sequentially, and suggest octahedral symmetry around Pt(IV) complex. The electrical spectrum of the Fe complex reported four peaks at 337, 374, 466 and one at 652 nm, which were attributed to the π→π*, n→π*, 6A1g→1T2g(G) and 6A1g→1T1g(G) transitions, respectively (Fig. 6); the observed magnetic moment of this complex is compatible with the octahedral geometry structure13-16.

**Table 2. Electronic spectral data from metal complexes for (LH) Ligand, molar conductivity at (DMSO 1×10⁻³ M) as well magnetic moments.**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Geometry</th>
<th>Magnetic sensitivity</th>
<th>λmax (nm)</th>
<th>ucm⁻¹</th>
<th>ABS</th>
<th>εmax L mol⁻¹ cm⁻¹</th>
<th>Assignment</th>
<th>Amax cm⁻¹ Ωmol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH</td>
<td>Dia.</td>
<td>364</td>
<td>27473</td>
<td>2.874</td>
<td>2874</td>
<td>n→π*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Dia.</td>
<td>322</td>
<td>31056</td>
<td>2.455</td>
<td>2455</td>
<td>π→π*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Ni(L)2]</td>
<td>T.d</td>
<td>262</td>
<td>38168</td>
<td>0.278</td>
<td>278</td>
<td>π→π*</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>S.p</td>
<td>290</td>
<td>34483</td>
<td>0.285</td>
<td>285</td>
<td>π→π*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Dia.</td>
<td>330</td>
<td>30303</td>
<td>0.306</td>
<td>306</td>
<td>n→π*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Dia.</td>
<td>563</td>
<td>17762</td>
<td>0.066</td>
<td>66</td>
<td>1A1g→1B1g</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>[Pd(L)2]</td>
<td>O.h</td>
<td>347</td>
<td>28818</td>
<td>0.516</td>
<td>516</td>
<td>π→π*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Dia.</td>
<td>572</td>
<td>17483</td>
<td>0.023</td>
<td>23</td>
<td>1A1g→1A1g</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[PtCl2 L2]</td>
<td>O.h</td>
<td>643</td>
<td>15552</td>
<td>0.021</td>
<td>21</td>
<td>1A1g→1A1g</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Dia.</td>
<td>320</td>
<td>31250</td>
<td>0.356</td>
<td>356</td>
<td>π→π*</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Dia.</td>
<td>386</td>
<td>25907</td>
<td>0.012</td>
<td>12</td>
<td>n→π*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[FeL(H2O)2]Cl</td>
<td>O.h</td>
<td>337</td>
<td>26252</td>
<td>2.889</td>
<td>2889</td>
<td>π→π*</td>
<td>54</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 1. $^1$H-NMR Spectrum of ligand

Figure 2. UV-Vis Spectrum of Ligand (LH)

Figure 3. UV-Vis Spectrum of Ni Complex.

Figure 4. UV-Vis Spectrum of Pd complex.
Infrared Spectra

The structural features of the Schiff base and its metal complexes, as shown in Figs. 7, 8 are proportional to all peculiar kinds of FTIR spectra. In the area 1641 cm$^{-1}$ assigned to (C=N), enough stretching vibration Tab.3 was noted. The wide bands about 3427 cm$^{-1}$ are allocated to the H-bonded –OH(alcohol) stretching vibration; a large band at 3287,3089,2920, and 2860 cm$^{-1}$ in the IR spectra of the Schiff bases is assigned to the $\nu$(N–H), $\nu$(C–H) aromatic, $\nu$(C–H) aliphatic, and $\nu$(C–H) aldehyde vibrations, sequentially. When the vibrational spectra in Tab.3 of metal complexes with the free ligand are compared, the $\nu$(C=N) is transferred to a lower wavenumber 18-15 cm$^{-1}$, the coordination nitrogen of the azomethine group to the metal ion into the imine acts in the range 1623-1629 cm$^{-1}$, and oxygen with the (O–H) aldehyde moiety acts in the range 1623-1629 cm$^{-1}$, the spectra of the complexes present weak bands in 509-580 cm$^{-1}$ and 416-467 cm$^{-1}$ which are assigned to $\nu$(M–N) and $\nu$(M–O), respectively$^{17,20}$. 

Table 3. Infrared spectral data for ligand (LH) as well complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>O-H</th>
<th>N-H</th>
<th>C-H</th>
<th>C-H</th>
<th>C-H</th>
<th>C=O</th>
<th>M-N</th>
<th>M-O</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH</td>
<td>3427</td>
<td>3287</td>
<td>3089</td>
<td>2920</td>
<td>2860</td>
<td>1641</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Ni(L)$_2$]</td>
<td></td>
<td>3288</td>
<td>3082</td>
<td>2918</td>
<td>2867</td>
<td>1623</td>
<td>540</td>
<td>416</td>
<td>-</td>
</tr>
<tr>
<td>[Pd(L)$_2$]</td>
<td>3282</td>
<td>3081</td>
<td>2915</td>
<td>2860</td>
<td>1627</td>
<td>509</td>
<td>425</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[PtCl$_2$(L)$_2$]</td>
<td>3277</td>
<td>3055</td>
<td>2920</td>
<td>2854</td>
<td>1626</td>
<td>538</td>
<td>436</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[FeL$_2$(H$_2$O)$_2$]Cl</td>
<td>3279</td>
<td>3056</td>
<td>2912</td>
<td>2859</td>
<td>1629</td>
<td>580</td>
<td>467</td>
<td>3566</td>
<td>820</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>610</td>
</tr>
</tbody>
</table>

Figure 7. FT-IR spectrum of ligand
Mass Spectra Analysis

The proposed formula corresponds to the molecular weight, Scheme 2 and figs. 9,10 show the fragmentation obtained for the complexes $^{21-24}$. 

Figure 8. FT-IR spectrum of pt complex

Figure 9. LC-Mass spectrum of (LH) ligand

Figure 10. LC-Mass spectrum of Fe complex
Conclusion:

A new Schiff base, 2-[1-(1H-indol-3-yl)ethylimino)methyl]naphthalene-1-ol, was successfully synthesized from the condensation reaction of the 1-hydroxy-2-naphthaldehyde with 2-(1H-indol-3-yl)ethylamine and its structure was characterized by elemental analysis and Mass Spectra analysis, NMR and FTIR spectra. The
ligand LH exhibited bidentate coordination behavior with the metal ions as was confirmed by the FTIR spectra and mass spectra analysis of metal complexes. Metal complexes of the ligand with Ni(II), Pd(II), Pt(IV) and Fe(III) ions have been characterized by CHN, Bohr-magnetic (B.M.), metal content, chloride content, molar conductivity, Mass Spectra Analysis, UV-visible and FTIR spectrophotometry which confirmed the structural formula of ligand: metal being 2:1 in all complexes. In addition, the complexes of Pt(IV) and Fe(III) were octahedral geometries. Ni(II) complex was tetrahedral geometry and Pd(II) complex was square planar structure.

Author’s declaration:
- Conflicts of Interest: None.
- I hereby confirm that all the Figures and Tables in the manuscript are mine. Besides, the Figures and images, which are not mine, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

References:


 تحضير وتشخيص طيفي لمعدقات العناصر الانتقالية مع قاعدة شيف-1(أندول-3-يل)إيثيل ايمينو)مثيل[نفثالين]-1-ول

رشا خضر حسين الدفاعي
قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة:
تم تحضير سلسلة جديدة من معقدات أيونات المعادن الليكانت-2-(1H-اندول-3-يل)إيثيل ايمينو)مثيل[نفثالين]-1-ول وتم تحضير معقدات أحادي النواة من طريق NiCl2.6H2O, PdCl2, FeCl3, PtCl6.6H2O وتم تشخيص المركبات عن طريق قياس الاشعة تحت الحمراء والأشعة فوق البنفسجية واطياف الBohr Magnetic(B.M.) (1HNMR). وتم تحديد محتوى الفلز ومحولى الكلور والموصلية المولية وفقا للنتائج ان الأشكال الهندسية لمعدقات الحديد الثلاثي والبلاتين الرباعي ثمانية السطوح أما الليكانت الثنائي رباعي السطوح والبلاديوم الثنائي فيكون مربع مستوي.

الكلمات المفتاحية: مطيافية الكتلة، المعقدات الفلزية، قاعدة الشيف.