Synthesis and Spectroscopic Characterization of New N\textcdot O\textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot \textcdot 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Preparation of Metal Complexes

The complexes were prepared using a general procedure\(^{11}\) in which an ethanol solution (≈15 mL) of each of metal salt were added to a solution of the ligand (≈15 mL) which dissolved in absolute ethanol. The equimolar mixture were refluxed with stirring for three hours, the resulting precipitate were filtered and washed with diethyl ether and recrystallized from hot ≈95% ethanol then dried under vacuum. The obtained metal complexes were crystalline, non-hygroscopic and stable at room temperature. Table (1) shows the physical properties of the ligand and metal complexes.

![Synthesis equation of the (HPEHB) ligand.](image-url)
Results and Discussion

The complexes were analyzed for carbon, hydrogen and nitrogen contents and their percentages. The analytical data for the ligand and the complexes are given in Table (1) above.

Metal and elemental analysis in Table (1) shows that the stoichiometry of the complexes was found to be 1:1 (M:L) and the experimental values of CHN and the metal contents are in a good agreement with the theoretical values.

UV-Visible Spectroscopy, Magnetic Susceptibility and Molar Conductivity Analyses

The electronic spectrum of the Schiff base exhibits band at \( \lambda_{\text{max}} = 312 \) nm ascribed to the n–\( \pi^* \) transitions. Table (4) shows the transitions bands of the Schiff base and its metal complexes. The electronic spectra of the Cd\(^{2+}\) and Zn\(^{2+}\) complexes displays bands at \( \lambda_{\text{max}} \) nm and \( \lambda_{\text{max}} \) nm respectively which attribute to \( \pi-\pi^* \) transitions, while the bands at \( \lambda_{\text{max}} \) nm and \( \lambda_{\text{max}} \) nm respectively assigned to n–\( \pi^* \) transitions. The bands at \( \lambda_{\text{max}} \) nm that appears in Ni\(^{2+}\) spectrum belong to ligand metal charge transfer (L-MCT) \[13\].

Conductivity measurements of complexes were carried out in 1 M dimethyl sulfoxide (DMSO) solvent. The molar conductance values are listed in the Table (4). The table reveals that the conductance values of all the metal complexes lie in the range of non-electrolytes \[12\]. The magnetic susceptibility measurements, Table (3), show that all the metal complexes have diamagnetic nature \[15\].

Table (1)
Physical properties of the new compounds.

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>Colour</th>
<th>M.P (°C)</th>
<th>Yield (%)</th>
<th>Molecular weight (g.mol(^{-1}))</th>
<th>Symbol</th>
<th>% Found(calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}<em>7 \text{H}</em>{11} \text{N}_4 \text{O}_4 )</td>
<td>Yellow</td>
<td>&gt; 300</td>
<td>( \approx ) 70.2</td>
<td>( \approx ) 186.1</td>
<td>H•L</td>
<td>( \approx ) 77.79 (77.43)</td>
</tr>
<tr>
<td>( \text{C}<em>7 \text{H}</em>{11} \text{CdN}_4 \text{O}_4 )</td>
<td>Yellow</td>
<td>&gt; 300</td>
<td>( \approx ) 77.0</td>
<td>( \approx ) 432.4</td>
<td>Cd(II) H•L•H•O</td>
<td>( \approx ) 43.77 (43.47)</td>
</tr>
<tr>
<td>( \text{C}<em>7 \text{H}</em>{11} \text{ZnN}_4 \text{O}_4 )</td>
<td>Yellow</td>
<td>&gt; 300</td>
<td>( \approx ) 78.0</td>
<td>( \approx ) 380.79</td>
<td>Zn(II) H•L•H•O</td>
<td>( \approx ) 35.34 (35.12)</td>
</tr>
<tr>
<td>( \text{C}<em>7 \text{H}</em>{11} \text{NiN}_4 \text{O}_4 )</td>
<td>Dark brown</td>
<td>&gt; 300</td>
<td>( \approx ) 75.0</td>
<td>( \approx ) 338.99</td>
<td>Ni(II) H•L•H•O</td>
<td>( \approx ) 40.54 (40.32)</td>
</tr>
</tbody>
</table>

Table (4)
Magnetic, Conductivity and Electronic data for the Ligand and the Metal Complexes in (1 M) Using DMSO solvent.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Magnetic Property ( \mu_{\text{eff.}} ) (B.M.)</th>
<th>Conductivity ( \mu \text{s.cm}^{-1} )</th>
<th>( \lambda_{\text{max}} ) (nm) ((\text{log } \varepsilon))</th>
<th>Suggested structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>H•L</td>
<td>-</td>
<td>-</td>
<td>( \approx ) 312 (3,4,1)</td>
<td>-</td>
</tr>
<tr>
<td>Cd(II) H•L•H•O</td>
<td>Diamagnetic</td>
<td>( \approx ) 7,40</td>
<td>( \approx ) 312 (4,4,1), ( \approx ) 328 (3,6,5)</td>
<td>Distorted O.H</td>
</tr>
<tr>
<td>Zn(II) H•L•H•O</td>
<td>Diamagnetic</td>
<td>( \approx ) 4,87</td>
<td>( \approx ) 328 (3,6,5), ( \approx ) 328 (3,6,5)</td>
<td>Distorted O.H</td>
</tr>
</tbody>
</table>
Mass Spectroscopy

The mass spectroscopic analysis was used to assist in determining the molecular formula of the ligand and to predict its structure through the examination of fragment ions. The relatively low intensities of the molecular ion peaks \([M]+\), is indicative of the ease of fragmentation of the compound and this has reflected the number of heteroatoms present in the structure. Fig.\(^{(1)}\) shows the mass spectrum of the ligand while the fragment ions and the mass fragmentation patterns are shown below:\(^{(1)}\)

Fragmentation of the Ligand.

**Infrared Spectral Studies**

The IR spectral data of the ligand and its metal complexes are shown in Table \((\uparrow)\); it showed that the ligand \(\text{H-L} \) behaves as a dinegatively tetradentate of the type \(\text{N-O}^\text{−} \) with two coordinating sites (\(\text{N}, \text{O} \)). This behavior was proved by the shift of \(\nu(\text{C=N})\), \(\nu(\text{C=O})\) signals to lower frequencies \((1705, 1658, 1639 \text{ cm}^{-1})\) respectively for \(\text{C=O}\) and \((1604, 1572 \text{ and } 1517 \text{ cm}^{-1})\) respectively for \(\text{C=N}\).
The simultaneous appearance of new bands in the 3092-5103 cm⁻¹ and 427-437 cm⁻¹ is due to (M-O) and (M-N) suggesting the coordination of the metal ions with the ligand via nitrogen and oxygen[15,16] 1608, 1749 cm⁻¹ respectively for (C=O) and 1642, 1717 and 1617 cm⁻¹ respectively for (C=N). The simultaneous appearance of new bands in the 3092-5103 cm⁻¹ and 427-437 cm⁻¹ is due to (M-O) and (M-N) suggesting the coordination of the metal ions with the ligand via nitrogen and oxygen[15,16].

**Table (7)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>(ν(C=O))</th>
<th>(ν(C=O))</th>
<th>(ν(N-N))</th>
<th>(ν(M-O))</th>
<th>(ν(M-N))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H·L</td>
<td>1141</td>
<td>1156</td>
<td>1127</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cd(II) H·L·H·O</td>
<td>1162</td>
<td>1156</td>
<td>1127</td>
<td>570</td>
<td>442</td>
</tr>
<tr>
<td>Zn(II) H·L·H·O</td>
<td>1112</td>
<td>1158</td>
<td>1133</td>
<td>516</td>
<td>442</td>
</tr>
<tr>
<td>Ni(II) H·L·H·O</td>
<td>1148</td>
<td>1179</td>
<td>1118</td>
<td>518</td>
<td>448</td>
</tr>
</tbody>
</table>

The suggested structures of the metal complexes are shown below where the complexes shows two vicinal nitrogen atoms coordinating a metal center due to attraction of amide hydrogen by the oxygen of carbonyl group which increase the possibility of the amide nitrogen to coordinated to the central metal as was presented by Kumar et al, [11].

**Conclusion**

New Schiff base H·L and its (M⁺) complexes were prepared and characterized using elemental analysis. The study confirmed that the ligand was coordinated to the central metal ion as di-negatively charged coordinated ligand. Based on the data obtained, the stoichiometry and the tentative structure for the metal complexes were suggested to be in distortedoctahedral.

**Suggested structures of the metal complexes.**

**References**


الخلاصة

ليكود جديد رياعي السطوح ن-1 (4-ثنائي هايدروكسي فنيل) إلى (2-ثنائي هايدروكسي بنزوهيدرازين (H, L) قد تم تحضيره بتصعيد 1 (4-ثنائي هايدروكسي فنيل) إلى (2-ثنائي هايدروكسي بنزوهيدرازين (H, L) أيون مع 2 هايدروكسي بنزوهيدرازين. ثلاثة معدات من الخلايا الانتقائية من تثبيت الكادميوم، ثنائي النيكل، وثنائي الخارشين قد تم تحضيرها مع (H, L). تشخيص جميع المركبات المحضرة قد تم انجازه باستخدم
الدراسات الطيفية لتجهيز التحليل للمانع، المطياف الكلي، الحساسية المغناطيسية، التوصيلية المولارية، فوق البنفسجية - المرئية، تحت الحمراء و الرنين المغناطسي. الدراسات تشير إلى أن المتوقع بان المعقدات تكون على شكل ثمانية السطوح المشوهة وأن الليكند ينتمي من خلال نيتروجين الأروميثان واثنين اوكسجين الفينولية بالإضافة إلى حزئتين ماء.