Synthesis and Characterization of 1,3,4- Oxadiazole derivatives with some new transition metal complexes

Ibrahim abood flifel* 
technical institute of shatra

Samah Hussein Kadhim **
Colleg of Science,University of Thi-Qar

Abstract:
A new ligands N-[(1E)-(2-bromo phenyl)methylene]-5-hydrazino-1,3,4-oxadiazol-2-amine (L1) and ethanedia[5-[(2-bromobenzylidine)amino]-1,3,4-oxadiazol-2-yl]hydrazone (L2)and its Co(II), Ni(II)and Cu(II) complexes were synthesized. The authenticity of the ligands (L1,L2). This complexes were established by elemental analysis, conductance and magnetic susceptibility measurements, as well as spectroscopic (FTIR, mass, uv-visible). The FTIR and mass spectra were corresponding as it is expected. The (L1) acts as a bidentate ligand coordinating through the oxygen atom of the oxadiazole ring and the nitrogen atom of amino group. This view is further supported by the appearance of a band corresponding to the metal-nitrogen and metal-oxygen stretching vibration at 454–688 cm⁻¹ and 314-466 cm⁻¹ in the complexes respectively. The (L2) acts as a tridentate ligand coordinating through the two oxygen atoms of the oxadiazole ring and [C=O]gruop and the nitrogen atom of shiff base [C=N]. The magnetic studies suggest an tetrahedral and octahedral geometry of the complexes. The complex of Co(III) for the (L1) have shown tetrahedral geometry, the complex of Cu(II) has shown tetrahedral geometry with (L1). The complexes of [Ni(II), Cu(II)] for the (L2) have shown tetrahedral geometry.

Keywords: 1,3,4-oxadiazol, transition metal complexes, IR spectra, mass spectra, electronic spectra.

1. Introduction
1, 3, 4-Oxadiazole derivatives are the heterocyclic that have received considerable attention during the last two decades. They found in number of pharmaceutical applications [1-4] several compounds are known as antimicrobial agents [5-7]. Some of these compounds have also analgesic, antinflammatory, anticancer, anti-HIV agent, antiparkinsonian and antiproliferative agent [8,9,10,11,12]. Some material applications of 1,3,4-oxadiazole derivatives lie in the field of liquid crystals[13]. PVC stabilizers [14-16].1,3,4-Oxadiazole derivatives are also among the most widely employed electron conducting and hole blocking (ECHB) materials in organic light-emitting diodes (LEDs). Although some types of metal complexes have found to be good emitters and or excellent electron transporters with excellent thermal properties.
2.1 Instrumentation
Elemental C, H and N analysis were carried out on a ThermoFinigan flash analyzer, the FTIR spectra in the range (4000-200) cm\(^{-1}\) were recorded as CsI discs using a Shimadzu FTIR spectrophotometer, molar conductance measurements were made in anhydrous DMSO at 25 °C using Inolabcond 720. The electronic spectra of ligand and their metal complexes have been recorded in the range of (200-900)nm by using T60 U Spectrometer the concentration of solutions 10\(^{-3}\) M using DMSO as solvent. Melting points were determined in open capillary tubes using an electro thermal melting point /SMP3I apparatus. Mass spectra were recorded in the range (0-800) m/e on a 5973 network mass selective detector.

2.2 Preparation of the ligands
The new ligands N-[(1E)-(2-bromophenyl)methylene]-5-hydrazino-1,3,4-oxadiazol-2-amine (L1) and ethanedial{5-[(2-bromobenzylidene)amino]-1,3,4-oxadiazol-2-yl}hydrazone (L2) (Scheme 1) were prepared as follows:

A mixture of Semicarbazide (7.5g, 0.1mol) and Potassium hydroxide (5.6g, 0.1mol) and CS\(_2\) (7.6 g,0.1 mol) in ethanol absolute (100mL) was refluxed in a water bath for 5 hr or H\(_2\)S gas is cease. The resultant mixture[A] was concentrated by distillation and acidified with dilute hydrochloric acid (0.1 mol) and the white solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel. Yield: 80 %, m.p. 222-224°C.

A mixture of [A](2.34g,0.02mol) ,2-bromo benzaldehyde (3.7g,0.02mol) in 100ml ethanol was refluxed in a water bath for 8 hr. The resultant mixture[B] yellow solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel. Yield: 80 %, m.p. 228-230 °C.

A mixture of [B] (5.68g,0.02mol) and hydrazine hydrate (1gm,0.02mol) dissolved in ethanol (50mL) was refluxed on a water bath for 6 hr, until the evolution of H\(_2\)S gas ceased[17-18]. The resultant mixture[L1] was concentrated and separated then filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel. Yield: 73 %, m.p.217-219°C.

A mixture[L1] (2.82g,0.01mol) and glyoxal (0.58g,0.01mol) dissolved in ethanol (50mL) was refluxed on a water bath for 3 hr, The resultant mixture[L2] was concentrated and the yellow solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel. Yield: 76 %, m.p.218°C.

Scheme (1): Synthesis of L1and L2
2.3 Preparation of complexes

2.3.1 preparation of L1 complexes

The Co(III), Cu(II) complexes were prepared by refluxing the respective hydrated metal chloride (2.73 g, 0.01 mol) and (1.7 g, 0.01 mol) in 15 ml ethanol with 50 ml of an ethanolic solution of the [L1](2.82g,0.01mol) for 4 hr. The resultant solids which separated were filtered, washed with ethanol and dried in air.

2.3.2 preparation of L2 complexes

The Ni(II), Cu(II) complexes were prepared by refluxing the respective hydrated metal chloride (2.37 g, 0.01 mol) and (1.7 g, 0.01 mol) in 15 ml ethanol with 50 ml of an ethanolic solution of the [L2](3.22g,0.01mol) for 4 hr. The resultant solids which separated were filtered, washed with ethanol and dried in air.

3. RESULTS & DISCUSSION

The purity of the ligands and its complexes were checked by TLC using silica gel-G as adsorbent.

Table (1), Melting point, magnetic susceptibility, physical properties and molar conductance of all the compounds studied are tabulated in Table (2). The calculated values were in a good agreement with the experimental values.

<table>
<thead>
<tr>
<th>NO.</th>
<th>Compound</th>
<th>Molecular formula</th>
<th>Molecular Weight</th>
<th>Λ Scm² mol⁻¹</th>
<th>Melting point</th>
<th>μeff MB</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L1</td>
<td>C₂H₈N₅OBr</td>
<td>282</td>
<td>--</td>
<td>217-219</td>
<td>-------</td>
</tr>
<tr>
<td>2</td>
<td>[Co(L1)₂Cl₂]</td>
<td>CoC₆H₈N₅OBrCl₂</td>
<td>692</td>
<td>5.3</td>
<td>128</td>
<td>3.9</td>
</tr>
<tr>
<td>3</td>
<td>[Cu (L1)Cl₂]</td>
<td>CuC₉H₉N₅OBrCl₂</td>
<td>415</td>
<td>3.5</td>
<td>209-210</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>L2</td>
<td>C₁₁H₁₀N₅O₂Br</td>
<td>322</td>
<td>--</td>
<td>218</td>
<td>-------</td>
</tr>
<tr>
<td>5</td>
<td>[Ni (L2)Cl]Cl</td>
<td>NiC₁₁H₁₀N₅O₂BrCl₂</td>
<td>416</td>
<td>34</td>
<td>170</td>
<td>2.9</td>
</tr>
<tr>
<td>6</td>
<td>[Cu (L2)Cl]Cl</td>
<td>CuC₁₁H₁₀N₅O₂BrCl₂</td>
<td>420</td>
<td>53</td>
<td>207-208</td>
<td>1.6</td>
</tr>
</tbody>
</table>

3.1 Infra-Red Spectroscopy

The FTIR spectrum for L1 shows a characteristic stretching absorption bands at 3294cm⁻¹, 1612 cm⁻¹, 1312 cm⁻¹ and 1425 assigned to υ(N-H) group,C=N of the oxadiazole ring, asymmetrical C-O-C, symmetrical C-O-C stretching respectively[19-20]. The FTIR spectrum for L2 shows a characteristic stretching absorption bands at 3226cm⁻¹, 1616 cm⁻¹, 1309 cm⁻¹ and 1448 assigned to υ(N-H) group,C=N of the oxadiazole ring, asymmetrical C-O-C, symmetrical C-O-C stretching respectively.

The C=N and N-H stretching vibrations are important to predict the bonding mode of the ligand. these bands were shifted to the high or low frequencies in the spectra of complexes compare with ligand, observed changes are the evidences of complexion had happened. The IR data of the complexes are shown in Table (3) and figure(8-11). lists the stretching frequency (υ) for some of the characteristics groups exhibited by the (L1,L2) and complexes.

Table 3: Characteristic absorption bands of (L1,L2) and its complexes

<table>
<thead>
<tr>
<th>NO</th>
<th>Compound</th>
<th>(\nu) N-H</th>
<th>(\nu)C=N</th>
<th>(\nu)C-O-C</th>
<th>(\nu)M-N</th>
<th>(\nu)M-O</th>
<th>(\nu)M-Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L1</td>
<td>3294</td>
<td>1612</td>
<td>1315</td>
<td>1425</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>[Co(L1)Cl₂]</td>
<td>3324</td>
<td>1687</td>
<td>1311</td>
<td>1406</td>
<td>688</td>
<td>466</td>
</tr>
<tr>
<td>3</td>
<td>[Cu(L1)Cl₂]</td>
<td>3272</td>
<td>1614</td>
<td>1321</td>
<td>1418</td>
<td>571</td>
<td>422</td>
</tr>
<tr>
<td>4</td>
<td>L2</td>
<td>3226</td>
<td>1616</td>
<td>1309</td>
<td>1448</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>[Ni(L2)Cl₂]</td>
<td>3232</td>
<td>1623</td>
<td>1382</td>
<td>1402</td>
<td>686</td>
<td>314</td>
</tr>
<tr>
<td>6</td>
<td>[Cu(L2)Cl₂]</td>
<td>3236</td>
<td>1618</td>
<td>1362</td>
<td>1434</td>
<td>454</td>
<td>365</td>
</tr>
</tbody>
</table>

3.2 Electronic spectra

The electronic spectra of the ligands (L1) and (L2) under study exhibit three absorption bands due to \(n\rightarrow\pi^*\), \(\pi\rightarrow\pi^*\) and \(n\rightarrow\sigma^*\) transitions in the (422-445)nm, (265-275)nm and (245-263)nm respectively[21]. The Co(III) complex exhibits bands at (14814)cm\(^{-1}\) and (24154)cm\(^{-1}\), assigned to \(^1\)A\(_{1g}\rightarrow\(^3\)T\(_{1g}\)(P) and \(^3\)A\(_{1g}\rightarrow\(^3\)T\(_{2g}\)(P), in an octahedral field [22]. The Ni(II) complex exhibits bands at (17035)cm\(^{-1}\), (23094)cm\(^{-1}\) and (37735)cm\(^{-1}\), assigned to \(^4\)A\(_{2g}\)(F)\(\rightarrow\(^4\)T\(_{2g}\)(F), \(^4\)A\(_{2g}\)(F)\(\rightarrow\(^4\)T\(_{1g}\)(F) and \(^4\)A\(_{2g}\)(F)\(\rightarrow\(^4\)T\(_{1g}\)(P) respectively, in a tetrahedral field [23]. These bands supported the octahedral geometry of Co(III) with ligand (L1) and tetrahedral geometry of Cu(II) with ligand (L1). The Ni(II) and Cu (II) complexes with ligand (L2) have shown tetrahedral geometry, as shown in (Table 4) and figures(12-15).

Table 4: Electronic Spectra of (L1,L2) and its Metal Complexes

<table>
<thead>
<tr>
<th>compound</th>
<th>(\lambda_{\text{max}}) nm</th>
<th>(\nu) cm(^{-1})</th>
<th>(\lambda_{\text{max}}) nm</th>
<th>(\nu) cm(^{-1})</th>
<th>(\lambda_{\text{max}}) nm</th>
<th>(\nu) cm(^{-1})</th>
<th>(\lambda_{\text{max}}) nm</th>
<th>(\nu) cm(^{-1})</th>
<th>(\nu) V/V (_l)</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>422</td>
<td>23696</td>
<td>265</td>
<td>37735</td>
<td>245</td>
<td>40816</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>Octahedra 1</td>
</tr>
<tr>
<td>[Co(L1)Cl₂]</td>
<td>675</td>
<td>14814</td>
<td>414</td>
<td>24154</td>
<td>278</td>
<td>35971</td>
<td>254</td>
<td>45045</td>
<td>1.63</td>
<td>Octahedra 1</td>
</tr>
<tr>
<td>[Cu(L1)Cl₂]</td>
<td>420</td>
<td>23809</td>
<td>-----</td>
<td>-----</td>
<td>266</td>
<td>37594</td>
<td>233</td>
<td>42918</td>
<td>-----</td>
<td>Tetrahedra 1</td>
</tr>
<tr>
<td>L2</td>
<td>445</td>
<td>22471</td>
<td>275</td>
<td>36363</td>
<td>263</td>
<td>38022</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>Tetrahedra 1</td>
</tr>
<tr>
<td>[Ni(L2)Cl₂]</td>
<td>587</td>
<td>17035</td>
<td>433</td>
<td>23094</td>
<td>265</td>
<td>37735</td>
<td>251</td>
<td>39840</td>
<td>1.35</td>
<td>Tetrahedra 1</td>
</tr>
<tr>
<td>[Cu(L2)Cl₂]</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>218</td>
<td>45871</td>
<td>-----</td>
<td>Tetrahedra 1</td>
</tr>
</tbody>
</table>

3.3 Mass spectra

The mass spectrum of the complex [Co(L1)Cl₂] exhibits a molecular ion peak (M)\(^+\) at m/z 692, the complex spectra shows fragment ion peak at m/z 621 due to(C\(_{18}H_{16}N_{10}O_{2}Br_{2}Co\))\(^+\). the spectra shows another peaks at m/z (128,183 and 311) due to(C\(_2\)N\(_2\)OCo)\(^+\),(C\(_7\)H\(_5\)BrN)\(^+\) and (C\(_9\)H\(_7\)N\(_3\)OBrCo)\(^+\) respectively as shown in(Fig.16).

The mass spectrum of the complex [Cu(L1)Cl₂] shows a molecular ion peak at m/z [M+1] 416, the complex spectra shows fragment ion peak at m/z 399 an 384 due to (C\(_9\)H\(_8\)Br\(_4\)O\(_2\)CuCl\(_2\))\(^+\) and (C\(_9\)H\(_7\)Br\(_3\)N\(_3\)O\(_2\)CuCl\(_2\))\(^+\) respectively, the complex spectra shows fragment ion peak with loss two chlorine atom at m/z (349,313) due to (C\(_9\)H\(_3\)Br\(_2\)N\(_2\)O\(_2\)CuCl)\(^+\) and (C\(_9\)H\(_3\)Br\(_2\)N\(_2\)O\(_2\)Cu)\(^+\) respectively. the spectra shows another peaks at m/z (70, 83 and 183) due to(C\(_2\)N\(_2\)O)\(^+\), (C\(_2\)N\(_2\)O)\(^+\) and (C\(_7\)H\(_3\)BrN)\(^+\) respectively as shown in(Fig.17).
The mass spectrum of the complex \([\text{Ni} \ (L_2) \ \text{Cl}] \text{Cl}\) shows a molecular ion peak at m/z \((M)^+\) 415, the complex spectra shows fragment ion peak at m/z 387 and 374 due to \((\text{C}_{10}\text{H}_7\text{BrN}_5\text{ONiCl})^+\) and \((\text{C}_9\text{H}_4\text{BrN}_5\text{ONiCl})^+\) Respectively. The spectrum shows another peaks at m/z 70.84, 111.183 and 211 due to \((\text{C}_2\text{N}_2\text{O})^+\), \((\text{C}_2\text{HN}_3\text{O})^+\), \((\text{C}_3\text{HN}_4\text{O})^+\), \((\text{C}_7\text{H}_3\text{BrN})^+\) and \((\text{C}_8\text{H}_6\text{BrN}_2)^+\) respectively as shown in(Fig. 18).

The mass spectrum of the complex \([\text{Cu} \ (L_2) \ \text{Cl}] \text{Cl}\) shows a molecular ion peak at m/z \((M)^+\) 420. This complex shows another a fragment ion peak with loss of chlorine atom at m/z 384, the spectrum shows another peaks at m/z 111 and 183 due to \((\text{C}_3\text{HN}_4\text{O})^+\) and \((\text{C}_7\text{H}_3\text{BrN})^+\) respectively as shown in(Fig. 19).

On the basis of the preceding discussion, the structure of the complexes suggested as follows in scheme(2)below.

![Scheme(2): Shows proposed structures of complexes](image)

Analytical and spectra data (IR, mass spectra) of all synthesized compounds were in full agreement with the proposed structure

4. conclusion

The ligands N-[(1E)-(2-bromo phenyl)methylene]-5-hydrazone-1,3,4-oxadiazol-2-amine (L1) yl]hydrazone (L2) were and ethanedial{5-[(2-bromo benzylidene)amino]-1,3,4-oxadiazol-2 successfully synthesized. The ligands were treated to different transition metal salt to afford the corresponding complexes. It may be concluded that the ligands coordinate through Nitrogen atom and oxygen atom as shown in figures (5-6). This view is further supported by the appearance of a bands corresponding to the metal-nitrogen and metal- oxygen stretching vibrations at 454-688 cm\(^{-1}\) and 314-466 cm\(^{-1}\) in the complexes respectively [24]. the Co atom leading to the formation octahedral geometry with the (L1) and Cu atom leading the formation tetrahedral geometry with the (L1). tetrahedral geometry was proposed for the (Ni (II) and Cu(II) prepared complexes with the (L2).
Fig. 1. Total charge density of L1

Fig. 2. Electrostatic potential of L1

Fig. 3. Total charge density of L2

Fig. 4. Electrostatic potential of L2
Fig. 5. L

Fig. 6. L2-Ni

Fig. 7. L1-Cu
Fig. 8. FTIR spectrum of the (L1)

Fig. 9. FTIR spectrum of the complex [Co(L1)_2Cl_2]

Fig. 10. FTIR spectrum of the (L2)
Fig. 11. FTIR spectrum of the complex [Ni (L2) Cl]Cl

Fig. 12. UV-visible spectrum of the (L1)
Fig. 13. UV-visible spectrum of the complex [Cu (L1) Cl₂]

Fig. 14. UV-visible spectrum of the (L2)

Fig. 15. UV-visible spectrum of the complex [Ni (L2) Cl]Cl
Fig. 16. Mass spectrum of the complex [Co(L1)₂Cl₂]

Fig. 17. Mass spectrum of the complex [Cu(L1)Cl₂]
Fig. 18. Mass spectrum of the complex [Ni (L2)Cl]Cl

Fig. 19. Mass spectrum of the complex [Cu (L2) Cl]Cl
References


