Synthesis and Optical Studies of the 3,4-dimethoxy Benzaldehyde [5-(2-hydroxyphenyl)-1,3,4-oxadiazol-2-y]hydrazone Metal Complexes

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Abstract—The aim of the present study is to synthesize and optical studies of 3,4-dimethoxy benzaldehyde [5-(2-hydroxyphenyl)-1,3,4-oxadiazol-2-y]hydrazone metal complexes. Firstly, the 3,4-dimethoxy benzaldehyde [5-(2-hydroxyphenyl)-1,3,4-oxadiazol-2-y] hydrazone was synthesized by the reaction of the 2-(5-hydradzino-1,3,4-oxadiazol-2-y)phenol with 2,3-dimethoxybenzaldehyde in the ethanol as a solvent. Scondly, its complexes of Cr(III), Fe(III), Co(II) and Ni (II) have been synthesized. The synthesized compounds and its metal complexes were characterized by the FTIR, Mass spectra and UV-vis absorption. The results confirmed the suggested square planar geometry of the Ni (II) complex and tetrahedral geometry of the Co(II) complex, while Cr (III), Fe(III) complexes were assigned octahedral geometrics. The optical absorption spectra of those complexes in the wavelength range from 200-900 nm were studied. The results showed that the optical absorption is due to indirect allowed transitions of the compound and its complexes, the energy gap (Eg) of these compounds decreases in the order L > Ni (II) > Fe(III) > Co(II) and > Cr(III), the absorption coefficient (α), real and imaginary parts (εr,εi), and optical conductivity (σopt) were estimated.

Keywords—Oxadiazole, Optical properties, Energy gap.

I. INTRODUCTION

One of the most interesting areas of research is the electrically conducting organometallic [Sheats.et al., 1984]. The method of producing conducting organometallic involves complexion transition metals with conjugated bridging ligands. The ability of the alter the oxidation state of the metal ion and the charge density along the ligand provides an alternative route to charge carrier creation as opposed to redox doping.

Metal complexes containing oxadiazole moiety such as 1,3,4-oxadiazole derivatives have aroused considerable interest in view of their industrial and biological importance [Farhanullah et al., 2004]. Many of these compounds possess a wide spectrum of medicinal properties, including activity against tuberculosis, leprosy, and bacterial and viral infections. It was found that these compounds are active against influenza, protozoa, smallpox, psoriasis, rheumatism, trypanosomiasis, coccidiosis, malaria and certain kinds of tumors and have been suggested as possible pesticides and fungicides. Their activity has frequently been thought to be due to their ability to chelate trace metals [Khan.et al., 1990, Khan.et al., 1991].

Optical properties such as refractive indices for certain range of wavelength between ultraviolet and near infrared and optical band gap values are becoming quite important criteria for selection of application of the fabricated films; the refractive indices of optical materials have considerable importance for applications in integrated optic devices such as switches [Zhu .et al., 2006].

The absorption coefficient near fundamental absorption edge in both of crystalline and amorphous semiconductors is dependent on the photon energy. For direct transitions, the absorption coefficient was taken on the following more general form as a function of photon energy [Hussein.et al.,2014].

\[ \alpha \ h \ v = A \ ( \alpha \ h \ v - E_g )^n \]  \hspace{1cm} (1)

And for indirect transition

\[ \alpha \ h \ v = B \ ( \alpha \ h \ v - E_g )^n \]  \hspace{1cm} (2)

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where \( \nu \) is the frequency of the incident photon, \( n \) is the number which characterizes the optical processes. \( n \) has the value 1/2 for the direct allowed transition, 3/2 for a forbidden direct allowed transition and 2 for the indirect allowed transition. \( A \) and \( B \) are constants and \( E_g \) is the optical energy gap. When the straight portion of the graph of \( (\alpha h\nu)^{-1} \) against \( h\nu \) is extrapolated to \( \alpha = 0 \) the intercept gives the transition band gap [Ezema. et al., 2005].

The optical absorption coefficient \( \alpha \) (cm\(^{-1}\)) which is a function of wavelength can be calculated from the optical absorbance spectra by using the relations [Ezema. et al., 2005].

\[
I = I_0 e^{-\alpha t}
\]

Where \( I \) is the incident intensity and \( I_0 \) is the penetrating light intensity, and \( t \) is the thicknesses of matter (cm).

The absorption coefficient can be calculated by:

\[
\alpha = 2.303 \left( \frac{A}{t} \right)
\]

The refractive index \( n \) can be expressed by:

\[
n = \left( 1 + \sqrt{R} \right) / \left( 1 - \sqrt{R} \right)
\]

The extinction coefficient \( K \) can be calculated by:

\[
k = \frac{\alpha \lambda}{4\pi} \text{ mm}
\]

The optical conductivity, \( \sigma_{opt} \), is related to light speed and can be expressed by the following equation:

\[
\sigma_{opt} = \frac{\alpha c t}{4\pi}
\]

The present study discusses the synthesis, characterization and optical conductivity of heterocyclic ligands towards Cr(III), Fe(III), Co(II) and Ni(II) ions.

### II. MATERIALS AND METHODS

All chemical compounds were used as received without purification. They were obtained from BDH, Sigma Aldrich and Fluka. All metal salts were used as chlorides.

#### A. Physical Measurement

The melting point or the decomposition temperature of the prepared ligand and its metal complexes were observed in an electro thermal melting point apparatus model (Melting SMP31). The FTIR spectra were recorded using KBr disc on Shimadzu FTIR spectrophotometer (Model: IR- affinity, Shimadzu) in the range (250-4000) cm\(^{-1}\). Mass Spectra were obtained using (Network Mass Selective Detector5973). The spectra of absorption were recorded for wavelengths 200-900 nm using UV-visible spectrophotometer model (U-V25400-38) by SHIMADZU Co. Purity of the ligand and its metal complexes were tested by Thin Layer Chromatography (TLC).

#### B. Preparation of the Ligand

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1) Synthesis of 3-hydroxybenzohydrazide (A).

A mixture of methyl 3-hydroxybenzoate (15.2ml, 0.1mol) and hydrazine hydrate (10ml, 0.2mol) was dissolved in (100 ml) ethanol. The mixture was refluxed for 8 hours, then the solvent evaporated to half. The solid product was collected and recrystallized using methanol [Zoulikha. et al., 2007, Athraa, et al., 2019]. Melting point 148°C, yield 95%.

2) Synthesis of 3-(5-mercapto-1,3,4-oxadiazol-2-yl)phenol (B)

A mixture of 3-hydroxybenzohydrazide (A) (15gm, 0.1mol) and potassium hydroxide (5.6gm, 0.1mol) in absolut ethanol 50ml, carbon disulfide (6ml 0.1mol) in 50ml ethanol was added. The mixture was refluxed until H\(_2\)S gas evaporation has been stopped. The solvent was evaporated and the mixture was acidified with HCl (25%) . The solid product formed was filtered, recrystallized from ethanol absolute [Zoulikha. et al., 2007]. The solid (B) had a white color, melting point 225°C, yield 80%.

3) Synthesis of 3-(5-hydrazinyl-1,3,4- oxadiazol-2-yl) phenol (C)

Amixture of 3-(5-mercapto-1,3,4-oxadiazol-2-yl)phenol (B) (6.5gm ,0.028 mol) and hydrazine hydrate (1.8ml ,0.057 mol) in ethanol (50 ml) was heated for 20 hours. Then the mixture was concentrated and then cooled [Saddam., et al., 2017., Samah , 2012] The solid particles were filtered and the crude product recrystallized from ethanol. The prepared crystals had a melting point of 222°C, yield 61.5%.

4) Synthesis of Compound 3-(5-(2-(2,3-dimethoxybenzylidene)hydrazinyl) 1,3,4-oxadiazol-2-yl)phenol (L1)

96
The 3-(5-(2,3-dimethoxybenzylidene)hydrazinyl) 1,3,4-oxadiazol-2-yl]phenol (D) was synthesized by a condensation reaction of the 3-(5-hydrazino-1,3,4-oxadiazol-2-yl) phenol (C) with dimethoxybenzaldehyde (1.92g, 0.01mol) (1.66 gm, 0.01mol) in ethanol (50 ml) was refluxed for 4 hours. The solid product formed was filtered with a glass funnel, then recrystallized from ethanol to get a yellow ligand, yield 80%. Figure (1) shows the prepared materials. [Athraa.et al , 2019 , Wathiq.et al., 2012 , Athraa.et al., 2012]

**C. Preparation of Complexes**

The complexes were synthesized by mix (0.001mol) from ligand L1 with salts (0.001mol) from salts [CrCl₃·6H₂O, FeCl₃·6H₂O, CoCl₂·6H₂O and NiCl₂·6H₂] both alone in (50ml) ethanol and refluxed for 3 hours (monitored by TLC). Then the precipitate was filtered and washed with ethanol or aqueous ethanol to remove unreacted salts or ligand, afterwards the precipitated complexes were dried [Ibrahim.et al., 2012]

### III. RESULTS AND DISCUSSION

#### A. FT-IR Spectra

The main FTIR data of the ligand L1 and its complexes are summarized in Table (1). The free ligand exhibited six major bands at (3525) cm⁻¹, (3218) cm⁻¹, (1614) cm⁻¹, (1536) cm⁻¹, (1245) cm⁻¹ and (1338) cm⁻¹ which refer to the following stretching vibration (υ OH), (υ NH₂), (υ C=N) imine [Redha.et al.,2014 , Dharkar , et al.,2011 , Athraa .et al.,2015 ], (υ C=N) oxa, (υ C-O-C) sym and (υ C-O-C) asy respectively. As shown below (Table 1). In the metal complexes new bands were formed attributed to the coordinated (M-N), (M-O) and (M-Cl) bonds and appeared at the region (462-532) cm⁻¹, (354-378) cm⁻¹ and (208-270) cm⁻¹ respectively. This indicates that the coordinate occurred through the (N), (O) and (Cl) atoms.

#### B. Mass Spectra

The purity of L1, [Cr(L₁) Cl₃], [Fe(L₁) Cl₃], [Co(L₁)Cl₂] and [Ni(L₁)Cl₂] was checked from mass spectra Figures (2-6), where the spectra showed that a clear base peaks (m/e) molecular weights and the intensity (%).

The mass spectrum of the ligand exhibits a molecular ion peak [M]+ at 340 m/e. The mass spectrum of the complexes [Cr(L₁) Cl₃], [Fe(L₁) Cl₃], [Co(L₁)Cl₂] and [Ni(L₁)Cl₂] shows a molecular ion peak [M]+ at (498), (502), (465) and (467) which is equivalent to the molecular mass of the complexes respectively.

### Fig. 2. Mass spectra of ligand
C. Optical Properties

Figure (7) shows the optical absorbance curve versus wavelength with a range of (200-900) nm at room temperature for ligand and its complexes thin films. There is one peak that can be seen for pure ligand at 323 nm related to \( \pi-\pi^* \), while there are two peaks that can be observed for the complexes, one at about 330-345 nm related to \( \pi-\pi^* \) and the other at around 540-567 nm, but they are shifted towards higher wavelengths (red shift). There are evident that the increase in the absorbance (hyperchromic effect) clarified in all spectra of the complexes attributed to the complexation behavior of ligand towards metal ions, confirming the coordination of the ligands to the metallic ions.

Figure (8) shows a plot of absorption coefficient versus photon energy for ligand and its complexes. The absorption coefficient of film was calculated after correction for the reflection losses according to Equation (2). The value of the absorption coefficient plays an important role to the limitation of the type of transition. It is obvious from the same figure that the value of \( (\alpha) \) is lower than 104 cm\(^{-1}\) indicating that the transition was an indirect electron transmission. According to Equation (2), the plots of \( (\alpha h\nu)^{1/2} \) versus photon energy are shown in Figure (9). The lower energy line corresponds to the phonon absorption processes, while the photon energy intercepts at \( (E_g+\Delta_p) \). The other corresponds to the phonon emission processes and photon energy intercept at \( (E_g-\Delta_p) \).

The energy gap of the ligand films decreases in the order \( L > Ni(II)/L > Fe(III)/L > Co(II)/L \) and \( > Cr(III)/L \) when the ionic radii decrease the values of indirect band gap energy \( (E_g) \) and the phonon energy \( (\Delta_p) \) are tabulated in Table (2).
Fig. 8. The relationship between absorption coefficient and photon energy for L and its complexes.

Fig. 9. The relationship between \((\alpha h\nu)^{1/2}\) and photon energy for L and its complexes.

**TABLE 2.** Indirect band gap energy \((E_g)\) and the phonon energy \((E_p)\) values for compound and its complexes

<table>
<thead>
<tr>
<th>compound</th>
<th>(E_g)</th>
<th>(E_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>2.85</td>
<td>1.1</td>
</tr>
<tr>
<td>Cr</td>
<td>1.15</td>
<td>0.45</td>
</tr>
<tr>
<td>Fe</td>
<td>1.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Co</td>
<td>1.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Ni</td>
<td>1.9</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Figures (10) and (11) show the relationship between real part \((\varepsilon_r)\) and imaginary part \((\varepsilon_i)\) of dielectric constant with photon energy for ligand and its complexes. The real and imaginary parts were computed from Equations (7) and (8), respectively. The real part is associated with how much it will slow down the speed of light in the material and the imaginary part illustrates that how a dielectric constant absorbs energy from electric field due to dipole motion. It is clearly obvious, for \((\varepsilon_r)\) that the value decreases, and \((\varepsilon_i)\) increase in the order of decrease of ionic radii as follows: Ni > Fe > Co > Cr [13].

Fig. 10. The relationship between real part and photon energy for L and its complexes.

Fig. 11. The relationship between imaginary part and photon energy for L and its complexes.

Figure (12) shows the relationship between optical conductivity and photon energy for ligand and its complexes. The optical conductivity was determined using equation (9). It is clear that there is an increase in optical conductivity as increasing in the order L < Ni (II)/L < Fe(III)/L < Co(II)/L and < Cr(III)/L. The increase in optical conductivity is due to the high absorbance of ligand with different transition metals thin film or may be due to electron excited by photon energy. Also, it may be caused by the hopping of the charge carriers between the localized states as well as due to the excitation of the charge carriers to the states in the conduction band [Doering. et al. 2006, Dharkar. et al. 2012].
IV. CONCLUSION

The ligand 3-(5-(2-(2,3-dimethoxybenzylidene)hydrazinyl)1,3,4-oxadiazol-2-yl)phenol was successfully synthesized. The FTIR, Mass spectra observations suggest the octahedral geometry for the Cr(III), Fe(III) and tetrahedral geometry was proposed for Co(II) while square planar geometry for Ni (II). The optical transmission spectrum is used to calculate the optical Parameters such as absorption coefficient, imaginary part and optical conductivity where found to be increase, while the energy gap and real parts decrease in the order of decrease of ionic radii as follows Ni > Fe > Co > Cr.

V. REFERENCES


