

Synthesis and Optical Studies of the 3,4-dimethoxy Benzaldehyde [5-(2-hydroxyphenyl)-1,3,4-oxadiazol-2-yl]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-yl]hydrazone metal complexes. Firstly, the 3,4-dimethoxybenzaldehyde [5-(2-hydroxyphenyl)-1,3,4-oxadiazol-2-yl] hydrazone was synthesized by the reaction of the 2-(5-hydrazino-1,3,4-oxadiazol-2-yl)phenol with 2,3-dimethoxybenzaldehyde in the ethanol as a solvent. Secondly, 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 geometries. 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 (E_g) 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 (ϵ_r, ϵ_i), and optical conductivity (σ_{opt}) 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 the producing conducting organometallic involves complexing 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].

$$\alpha h\nu = A (\alpha h\nu - E_g)^n \quad (1)$$

And for indirect transition

$$\alpha h\nu = B (\alpha h\nu - E_g)^n \quad (2)$$

where ν 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 $(\alpha h\nu)^n$ against $h\nu$ is extrapolated to $\alpha = 0$ the intercept gives the transition band gap [Ezema et al., 2005].

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

$$I = I_0 e^{-\alpha t} \quad (3)$$

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:

$$\alpha = 2.303(A/t) \quad (4)$$

The refractive index n can be expressed by:

$$n = (1 + \sqrt{R}) / (1 - \sqrt{R}) \quad (5)$$

The extinction coefficient K can be calculated by:

$$k = \alpha \lambda / 4\pi \quad \text{mm} \quad (6)$$

The real and imaginary complex dielectric constants can be expressed by Equation 7 and 8, respectively:

$$\epsilon' = n^2 - k^2 \quad (7)$$

$$\epsilon'' = 2nk \quad (8)$$

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

$$\sigma_{\text{opt}} = \alpha n c / 4\pi \quad (9)$$

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 Detector 5973). 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)

To 3-hydroxybenzohydrazide (A) (15gm, 0.1mol) and potassium hydroxide (5.6gm, 0.1mol) in absolute ethanol 50ml, carbon disulfide (6ml 0.1mol) in 50ml ethanol was added. The mixture was refluxed until H₂S gas evolution 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)

A mixture 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)

The 3-(5-(2-(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 (1.92gm, 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]

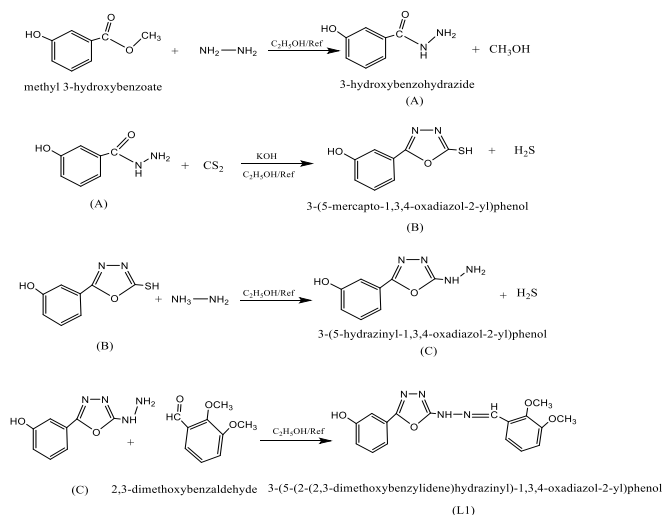


Fig. 1. Synthesis of ligand

C. Preparation of Complexes

The complexes were synthesized by mix (0.001mol) from ligand L1 with salts (0.001mol) from salts $[\text{CrCl}_3 \cdot 6\text{H}_2\text{O}]$, $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]$, $[\text{CoCl}_2 \cdot 6\text{H}_2\text{O}]$ and $[\text{NiCl}_2 \cdot 6\text{H}_2\text{O}]$ 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 $(3525) \text{ cm}^{-1}$, $(3218) \text{ cm}^{-1}$, $(1614) \text{ cm}^{-1}$, $(1536) \text{ cm}^{-1}$, $(1245) \text{ cm}^{-1}$ and $(1338) \text{ cm}^{-1}$ which refer to the following stretching vibration ($\nu \text{ OH}$), ($\nu \text{ NH}_2$), ($\nu \text{ C=N}$) imine [Redha.et al.,2014 , Dharkar , .et al.,2011 ,Athraa .et al.,2015], ($\nu \text{ C=N}$) oxa, ($\nu \text{ C-O-C}$) sym and ($\nu \text{ C-O-C}$) 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 $(462-532) \text{ cm}^{-1}$, $(354-378) \text{ cm}^{-1}$ and $(208-270) \text{ cm}^{-1}$ respectively. This indicates that the coordinate occurred through the (N), (O) and (Cl) atoms.

TABLE 1. IR Frequencies (cm^{-1}) of the Compound and their Metal Complexes

Compound	(OH)	(NH)	imine(C=N)	$\nu(\text{C=N})$	(C-O-C)	(M-N)	(M-O)	(M-Cl)
$\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_4$	3525	3218	1614	1536	1338 (Asy) 1245(sy)	---	---	---
$[\text{Cr}(\text{L}_1)_3\text{Cl}_3]$	3572	3286	1612	1535	1338(Asy) 1242(sy)	516	362	270
$[\text{Fe}(\text{L}_1)_3\text{Cl}_3]$	3550	3255	1620	1550	1350(Asy) 1244(sy)	532	359	248
$[\text{Co}(\text{L}_1)_2\text{Cl}_2]$	3487	3271	1618	1566	1296(Asy) 1240(sy)	520	378	208
$[\text{Ni}(\text{L}_1)_2\text{Cl}_2]$	3533	3101	1622	1473	1319(Asy) 1232(sy)	462	354	262

B. Mass Spectra

The purity of L1, $[\text{Cr}(\text{L}_1)_3\text{Cl}_3]$, $[\text{Fe}(\text{L}_1)_3\text{Cl}_3]$, $[\text{Co}(\text{L}_1)_2\text{Cl}_2]$ and $[\text{Ni}(\text{L}_1)_2\text{Cl}_2]$ was checked from mass spectra Figures (2-6), where the spectra showed a clear base peaks (m/e) molecular weights and the intensity (%).

The mass spectrum of the ligand exhibits a molecular ion peak $[\text{M}]^+$ at 340 m/e. The mass spectrum of the complexes $[\text{Cr}(\text{L}_1)_3\text{Cl}_3]$, $[\text{Fe}(\text{L}_1)_3\text{Cl}_3]$, $[\text{Co}(\text{L}_1)_2\text{Cl}_2]$ and $[\text{Ni}(\text{L}_1)_2\text{Cl}_2]$ shows a molecular ion peak $[\text{M}]^+$ at (498), (502), (465) and (467) which is equivalent to the molecular mass of the complexes respectively.

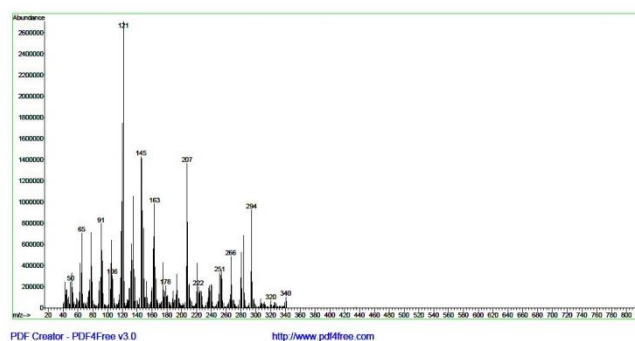


Fig. 2. Mass spectra of ligand

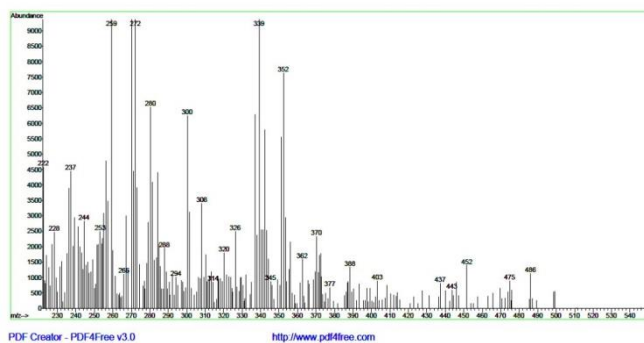


Fig. 3. Mass spectra of [Cr(L) Cl3]

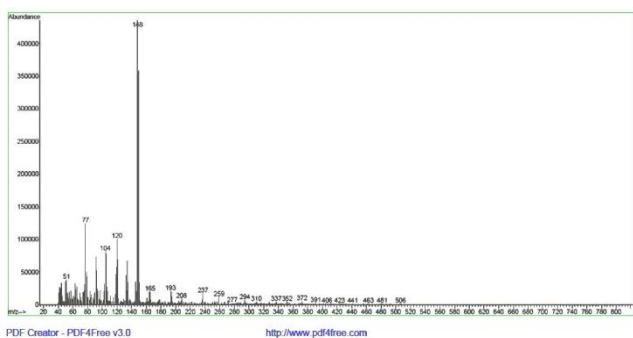


Fig. 4. Mass spectra of [Fe(L) Cl3]

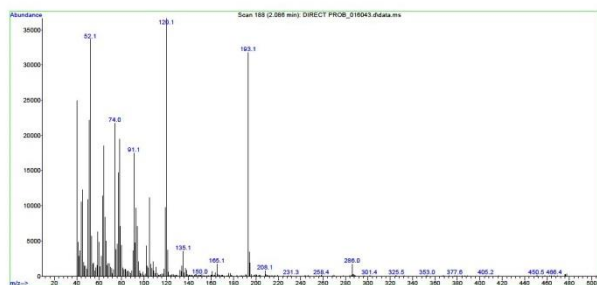
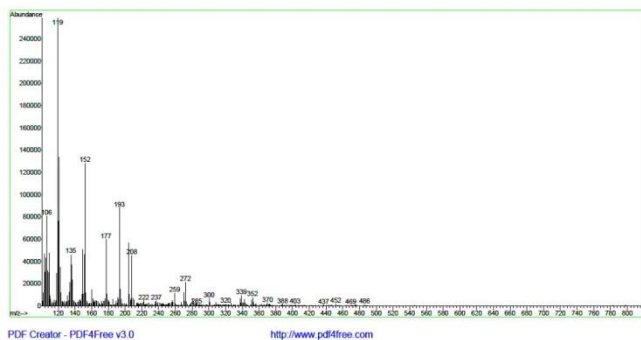


Fig. 5. Mass spectra of [Co(L)Cl2]



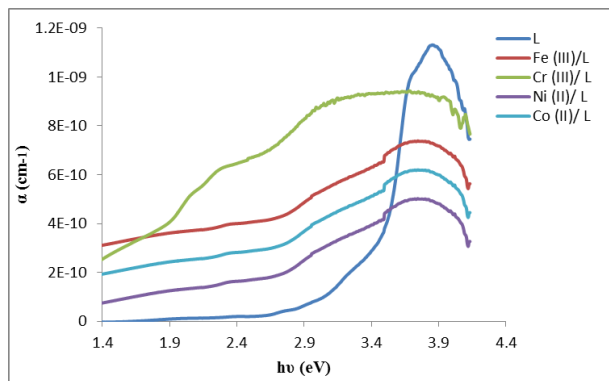


Fig. 8. The relationship between absorption coefficient and photon energy for L and its complexes.

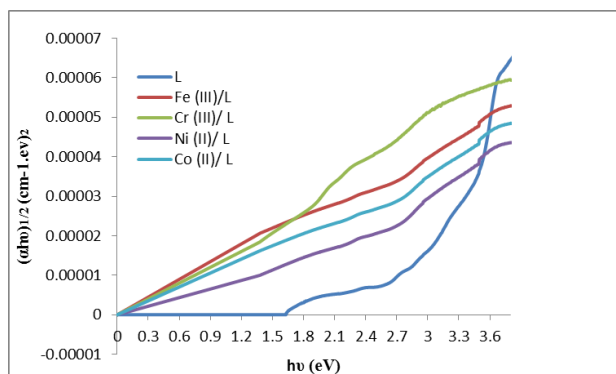


Fig. 9. The relationship between $(\alpha h\nu)^{1/2}$ and photon energy for L and its complexes.

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

compound	E_g^{ind}	E_p
L	2.85	1.1
Cr	1.15	0.45
Fe	1.5	0.7
Co	1.3	0.6
Ni	1.9	0.9

Figures (10) and (11) show the relationship between real part (ϵ_r) and imaginary part (ϵ_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 (ϵ_r) that the value decreases, and (ϵ_i)

increase in the order of decrease of ionic radii as follows: Ni > Fe > Co > Cr [13].

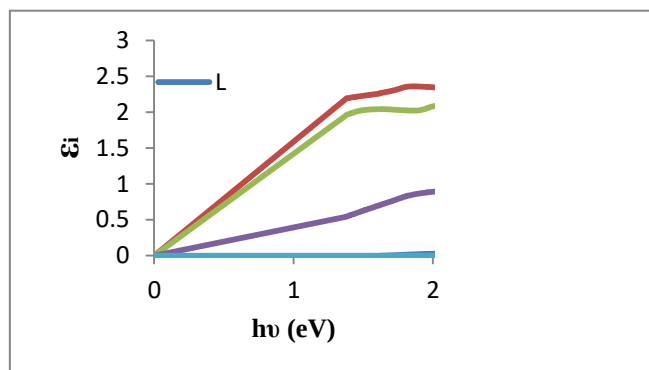


Fig. 10. The relationship between real part and photon energy for L and its complexes.

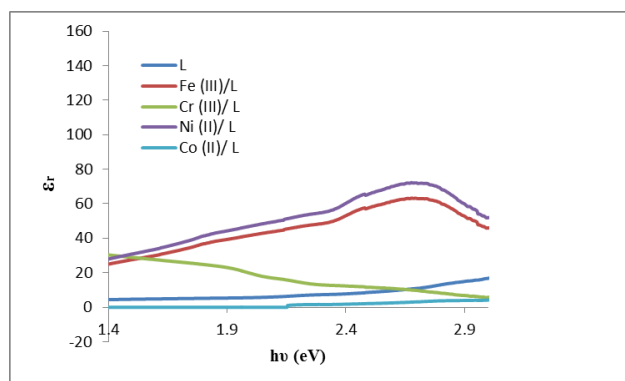


Fig. 11. The relationship between imaginary part and photon energy for L and its complexes.

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].

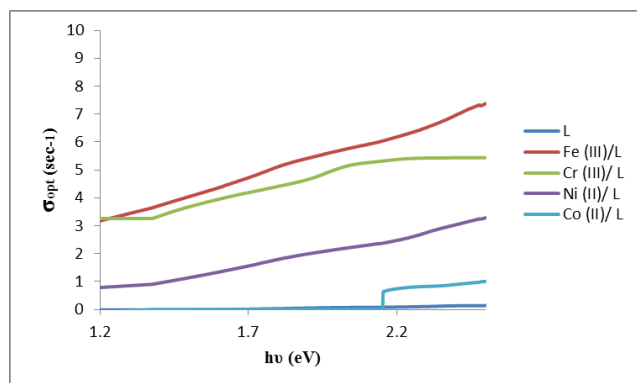


Fig. 12. The relationship between optical conductivity and photon energy for L and its complexes.

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 $\text{Ni} > \text{Fe} > \text{Co} > \text{Cr}$.

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