

# Synthesis, spectral and Electrical Conductivity Studies of 3-(5-(2(furan-2-ylmethylene)hydrazinyl)-1,3,4-oxadiazol-2-yl)phenol with some its transition metal ion complexes

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## Abstract

Schiff base complexes of Cr(III), Fe(III), Co(II) and Ni (II) synthesized 3-(5-hydrazino-1,3,4- oxadiazol-2-yl) phenol and Furfural. The ligand and its metal complexes was characterized FTIR, <sup>1</sup>HNMR and Mass spectra. From results it was suggested square planar geometry for Ni (II) complex and tetrahedral geometry for Co(II) complex, while Cr(III), Fe(III) complexes were assigned octahedral geometrics. Conductivity of the powder samples were measured by two probe method. Measured electrical conductivities of Cr(III), Fe(III), Co(II) and Ni (II) complexes of ligand are reported in this paper. The result showed that the conductivity increased with increasing temperature and is in the order L < Ni (II) < Fe(III) < Co(II) and < Cr(III), showing semi conducting behavior and activation energy of metal complexes was estimated.

**Keywords:** Schiff base, Electrical conductivity, Activation energy.

## 1. INTRODUCTION

Complexes containing Schiff bases have not only found extensive application in design and synthesis of organic molecules [1], but these compounds exhibit several of significant electrical conductivity [2], host-guest chemistry [3], sensors [4], and biological activity [5] and played an extremely vital role in the development of modern electronics; particularly in the communication and computer fields. It is because of the only software, which has made it possible to microminiaturise massive electronic gadgets. The electrical conduction mechanism of the organic semiconductors and especially of the Schiff bases is very important for the application of these materials in electronics, electro techniques and power sources. In this connection, studies were made to establish a correlation between the chemical structure and characteristics defining semi-conducting properties [6]. The electrical properties of the Schiff bases ligands and their metal complexes have been intensively studied by many of the research groups all over the world. electrical conductivity of heterocyclic ligands derived from 1,3,4-oxadiazole towards Cr(III), Fe(III), Co(II) and Ni (II) ions.

## 2. MATERIALS AND METHODS

All the chemicals and solvents used were of chemically pure grade, and commercially available. All metal salts were used as chloride.

### 2.1. Physical measurement

The melting point or the decomposition temperature of all the prepared ligand and metal complexes were observed in an electro thermal melting point apparatus model (Melting SMP31). The FTIR spectra in the rang (250-4000) cm<sup>-1</sup> were recorded as KBr disc using a Shimadzu FTIR spectrophotometer ( Model: IR- affinity, Shimadzu). Nuclear Magnetic Resonance Spectra were obtained using Burker DXR System AL500(500 MHz). Mass Spectra were obtained using (Network Mass Selective Detector 5973). Electrical conductivity measurements were carried out by using DIGIT MULTIMETER 8808A, PWS2185 DC Power supply 0-18,5A. purity of the ligand

and metal complexes was tested by Thin Layer Chromatography (TLC).

### 2.2. Preparation of the Ligand

#### Synthesis of 3-hydroxybenzohydrazide

A mixture of methyl 3-hydroxybenzoate (15.2ml, 0.1mol) and hydrazine hydrate (10ml, 0.2mol) was dissolved in (100 ml) ethanol were refluxed for 8 hours. The mixture was evaporated to half ,cooled, filtered and recrystallized in methanol [7], the solid (A) was white, melting point 148 °C, yield 95%.

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

3-hydroxybenzohydrazide (A) (15gm , 0.1mol), potassium hydroxide (5.6gm , 0.1mol) and carbon disulfide (6ml 0.1mol) were refluxed in ethanol (100 ml) ethanol. The solvent was evaporated and acidified with HCl (25%) then the precipitated was filtered and the result solid was recrystallized from ethanol absolute [8]. The solid (B) was white, melting point 225 °C, yield 80%.

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

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 as solvent (50 ml) were refluxed for 20 hours. The mixture was concentration and then cooled [9 ]. white precipitate (C) was filtered and recrystallized from ethanol. Melting point 222 °C, yield 61.5%.

#### Synthesis of Compound 3-(5-(2-furan-2-ylmethylene)hydrazinyl) 1,3,4-oxadiazol-2-yl]phenol

The ligand was synthesized by condensation of 3-(5-hydrazino-1,3,4- oxadiazol-2-yl) phenol (C) and furfural (1.92gm ,0.01mol) (0.96ml , 0.01mol) in ethanol (30 ml). Then the mixture refluxed for 4 hours. The ligand was precipitated, filtered and recrystallized from ethanol to get yellow ligand , melting point 287 °C, yield 85%.

#### Preparation of Complexes

The complexes were synthesized by mix (0.001mol) from ligand with salts (0.001mol) from salts [CrCl<sub>3</sub>.6H<sub>2</sub>O, FeCl<sub>3</sub>.6H<sub>2</sub>O, CoCl<sub>2</sub>.6H<sub>2</sub>O and NiCl<sub>2</sub>.6H<sub>2</sub>] both alone in (50ml) ethanol and refluxed for 3 hours (monitored by

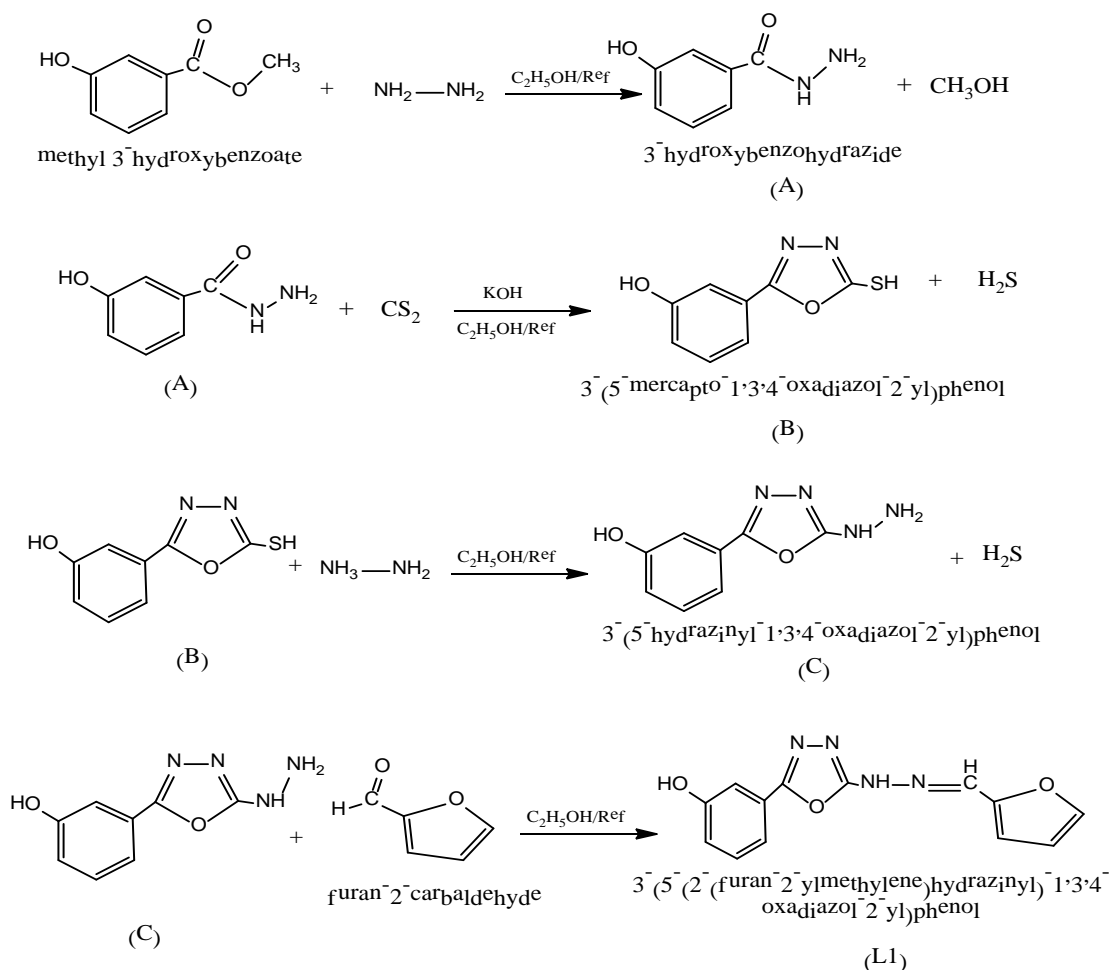
TLC) .then the precipitate was filtered and wash with ethanol or aqueous ethanol to removed unreacted salts or ligand ,then precipitated complexes was dried[10] .

### 3. RESULT AND DISCUSSION

#### 3.1 FT-IR spectra

FT-IR of the synthesized ligand and its complexes were carried out KBr disc to ligand and CsI for complexes. The free ligand exhibited six major bands at (3300) cm<sup>-1</sup>, (3194) cm<sup>-1</sup>, (1633) cm<sup>-1</sup>,(1533) cm<sup>-1</sup>, (1498) cm<sup>-1</sup>, (1321) cm<sup>-1</sup>,

(1074) cm<sup>-1</sup> which are attributable to( $\nu$  OH), ( $\nu$  NH<sub>2</sub>), ( $\nu$  C=N) imine, ( $\nu$  C=N) oxa, ( $\nu$  C-O-C) sym, ( $\nu$  C-O-C) asy and structure movement bands respectively, as shown below (table1). New bands were formed attributed to the coordinated (M-N), (M-O) and (M-Cl) bonds and appeared at the region (507) cm<sup>-1</sup>, (437) cm<sup>-1</sup> and (304) cm<sup>-1</sup> respectively. This indicates that the coordinate occurred through the (N), (O) and (Cl) atoms.



Scheme (1): Synthesis of ligand

Table 1. IR frequencies (cm<sup>-1</sup>) of the compound and their metal complexes

| No. | Compound  | $\nu$ (OH) | $\nu$ (NH) | $\nu$ (C=N) imine | $\nu$ (C=N) oxadiazole | $\nu$ (C-O-C)         | Struc. Movement | $\nu$ (M-N) | $\nu$ (M-O) | $\nu$ (M-Cl) |
|-----|---|------------|------------|-------------------|------------------------|-----------------------|-----------------|-------------|-------------|--------------|
| 1   | C <sub>13</sub> H <sub>10</sub> N <sub>4</sub> O <sub>3</sub> | 3300       | 3194       | 1633              | 1533                   | 1321(Asy)<br>1234(sy) | 1074            | -           |             |              |
| 2   | [Cr(L <sub>1</sub> ) Cl <sub>3</sub> ]                        | 3300       | 3134       | 1637              | 1535                   | 1321(Asy)<br>1242(sy) | 1016            | 507         | 366         | <b>258</b>   |
| 3   | [Fe(L <sub>1</sub> ) Cl <sub>3</sub> ]                        | 3302       | 3196       | 1637              | 1554                   | 1321(Asy)<br>1232(sy) | 1074            | 527         | 335         | <b>257</b>   |
| 4   | [Co(L <sub>1</sub> )Cl <sub>2</sub> ]                         | 3298       | 3190       | 1637              | 1535                   | 1319(Asy)<br>1232(sy) | 1076            | 505         | 343         | <b>254</b>   |
| 5   | [Ni(L <sub>1</sub> )Cl <sub>2</sub> ]                         | 3300       | 3194       | 1637              | 1533                   | 1319(Asy)<br>1232(sy) | 1074            | 504         | 304         | <b>260</b>   |

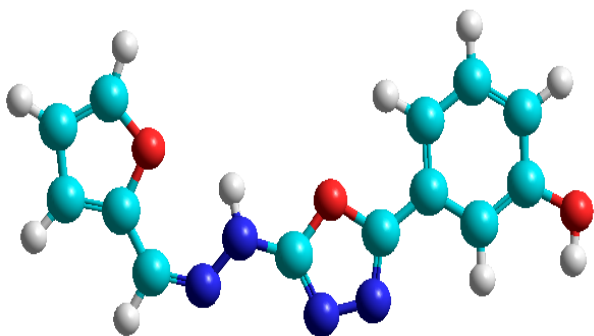


Figure 1. ligand

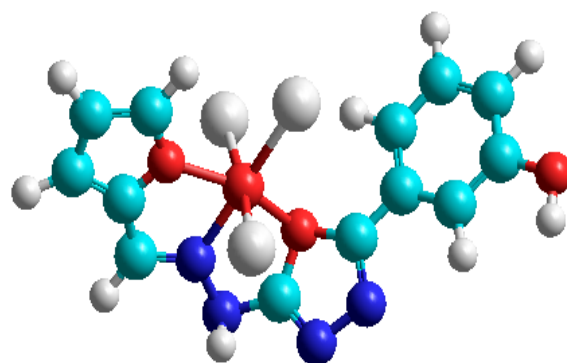


Figure 5. [Fe(L)Cl<sub>3</sub>]

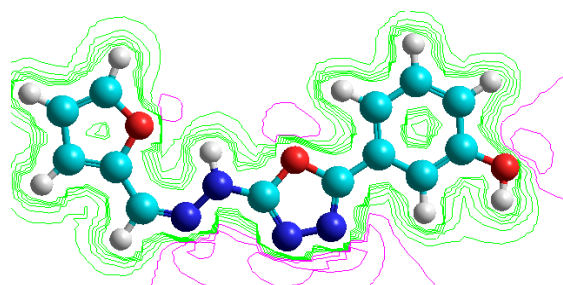


Figure 2. Electrostatic potential 2D for ligand

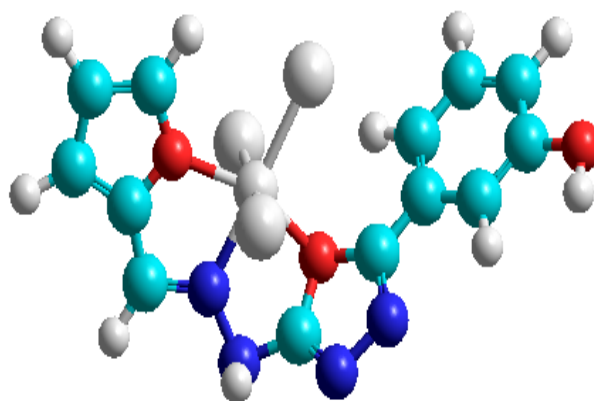


Figure 6. [Cr(L)Cl<sub>3</sub>]

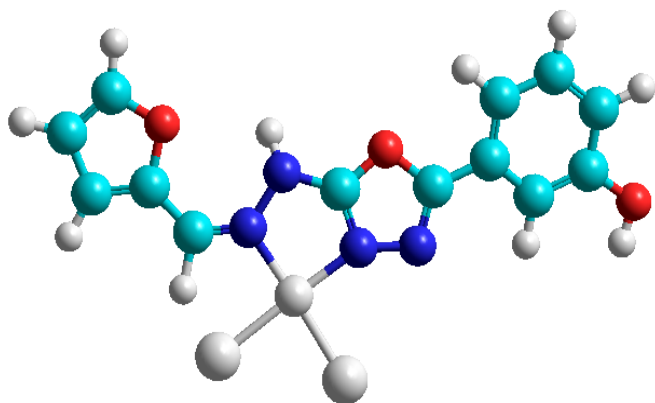


Figure 3. [Ni(L)Cl<sub>2</sub>]

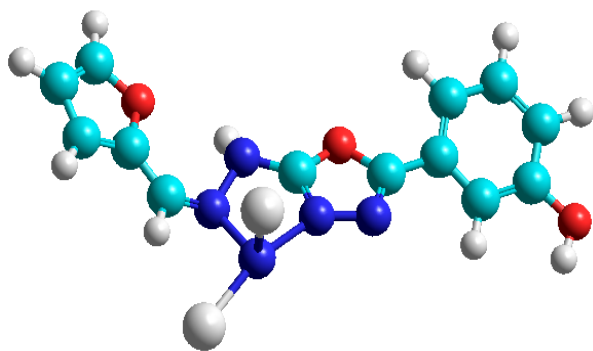


Figure 4. [Co(L)Cl<sub>2</sub>]

### 3.2 Nuclear Magnetic Resonance

The <sup>1</sup>H-NMR spectra of ligand exhibit a 14.11 (H,s,OH), 6.73-8 (7H,m, aromatic protons), 9.41(1H,s,CH=Ph),10.08(1H,s,NH), 2.5(s,DMSO). The proton NMR of the ligand shown in figure (7). <sup>1</sup>H-NMR(DMSO-d<sup>6</sup>) spectral information was given extra support for the proposition of the structure.

### 3.3 Mass spectra

The mass spectrum of the ligand exhibits a molecular ion peak [M]<sup>+</sup> at 270 m/z ,the ligand spectra shows fragments at (203,177,111,139,150,163) m/z due to {[C<sub>9</sub>H<sub>7</sub>N<sub>4</sub>O<sub>2</sub>]<sup>+</sup>, [C<sub>7</sub>H<sub>5</sub>N<sub>4</sub>O<sub>2</sub>]<sup>+</sup>, [C<sub>3</sub>H<sub>3</sub>N<sub>4</sub>O<sub>2</sub>]<sup>+</sup>, [C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>]<sup>+</sup>, [C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O]<sup>+</sup>, [C<sub>8</sub>H<sub>8</sub>NO<sub>2</sub>]<sup>+</sup>, [C<sub>9</sub>H<sub>11</sub>N<sub>2</sub>O]<sup>+</sup>} respectively as shown in figure (8).

The mass spectrum of the complex [Co(L)Cl<sub>2</sub>] shows a molecular ion peak [M]<sup>+</sup> at(404) m/z which is equivalent to molecular mass of the complex .This complex shows another a fragment ion peak with loss of chlorine atom at (334,369) due to [Co(L)Cl]<sup>+</sup> and [Co(L)]<sup>+</sup> respectively.

The mass spectrum of the complex [Ni(L)Cl<sub>2</sub>] shows a molecular ion peak [M]<sup>+</sup> (404) m/z which is equivalent to molecular mass of the complex. This complex shows another a fragment ion peak with loss of chlorine atom at (334,369) due to [Ni(L)Cl]<sup>+</sup> and [Ni(L)]<sup>+</sup> respectively.

The mass spectrum of the complex [Cr(L)Cl<sub>3</sub>] shows a molecular ion peak [M]<sup>+</sup> (432) m/z which is equivalent to molecular mass of the complex .This complex shows another a fragment ion peak with loss of chlorine atom at (362,327,397) due to [Cr(L)Cl<sub>2</sub>]<sup>+</sup>, [Cr(L)Cl]<sup>+</sup>, and [Cr(L)]<sup>+</sup>

respectively. The mass spectrum of the complex  $[\text{Fe}(\text{L})\text{Cl}_3]$  shows a molecular ion peak  $[\text{M}]^+$  (435) m/z which is equivalent to molecular mass of the complex. This complex shows another a fragment ion peak with

loss of chlorine atom at (365,330,400) due to  $[\text{Fe}(\text{L})\text{Cl}_2]^+$ ,  $[\text{Fe}(\text{L})\text{Cl}]^+$ , and  $[\text{Fe}(\text{L})]^+$  respectively. The mass spectra of the complexes shown in figures (9) - (12).

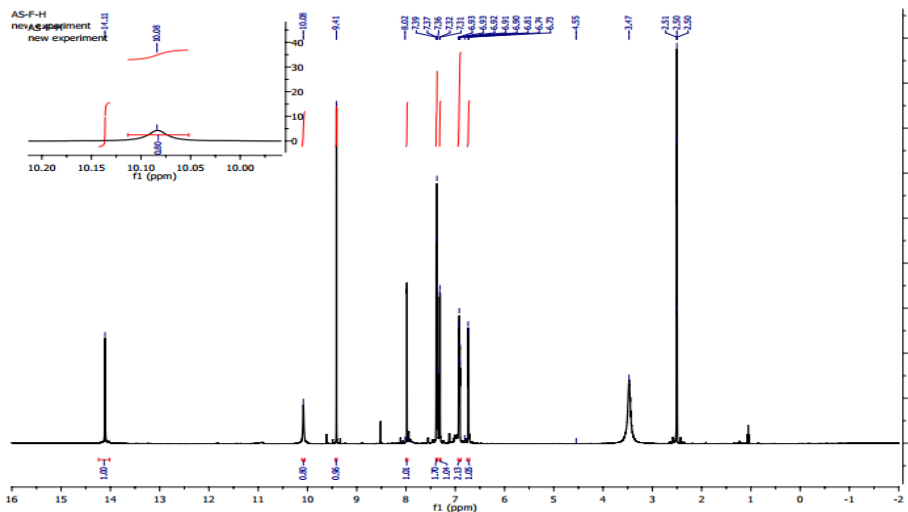


Figure 7. <sup>1</sup>H-NMR spectra of ligand

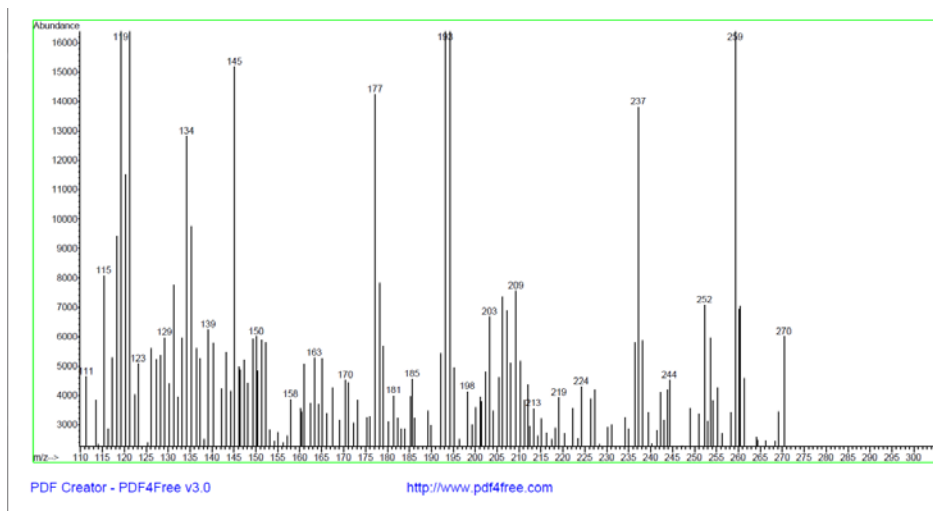


Figure 8. mass spectra of ligand

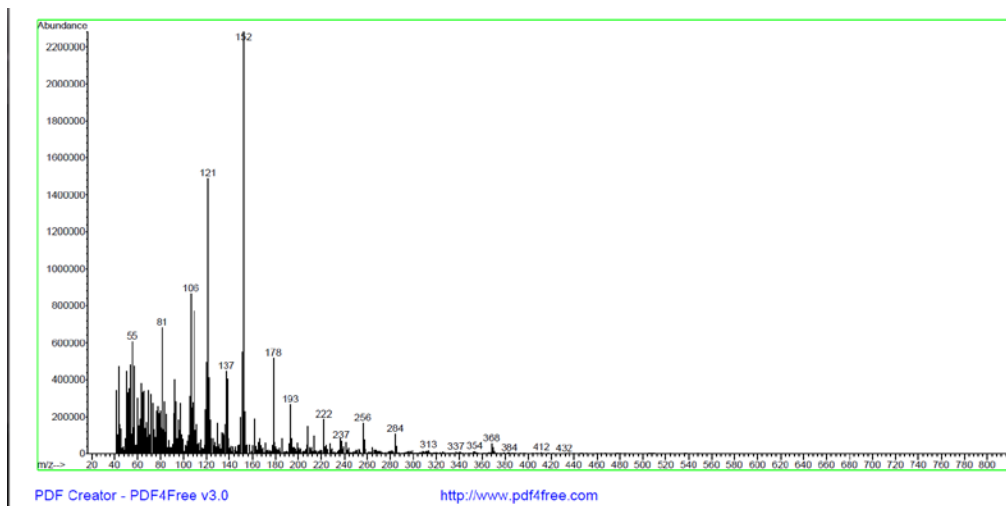


Figure 9. mass spectra of  $[\text{Ni}(\text{L})\text{Cl}_2]$

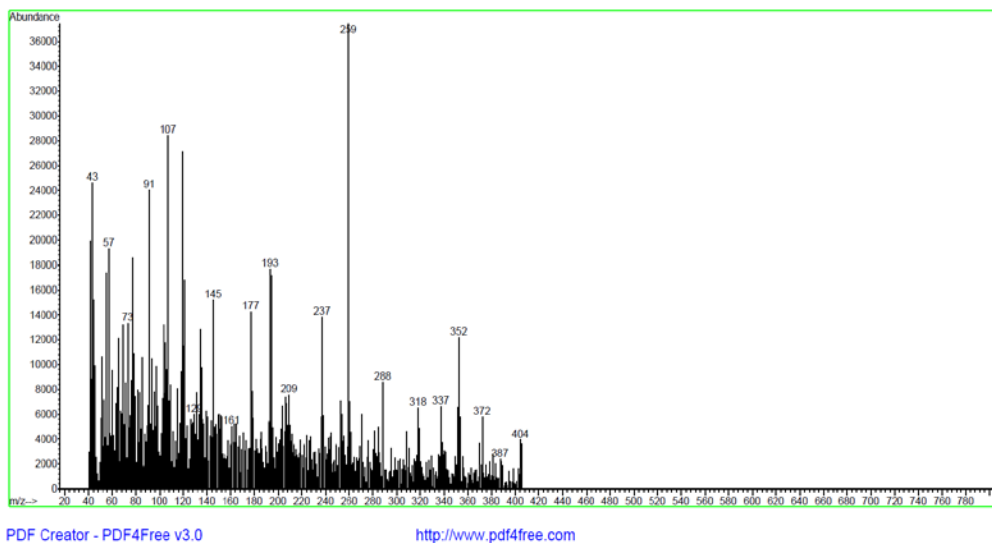


Figure 10. mass spectra of [Co(L)Cl<sub>2</sub>]

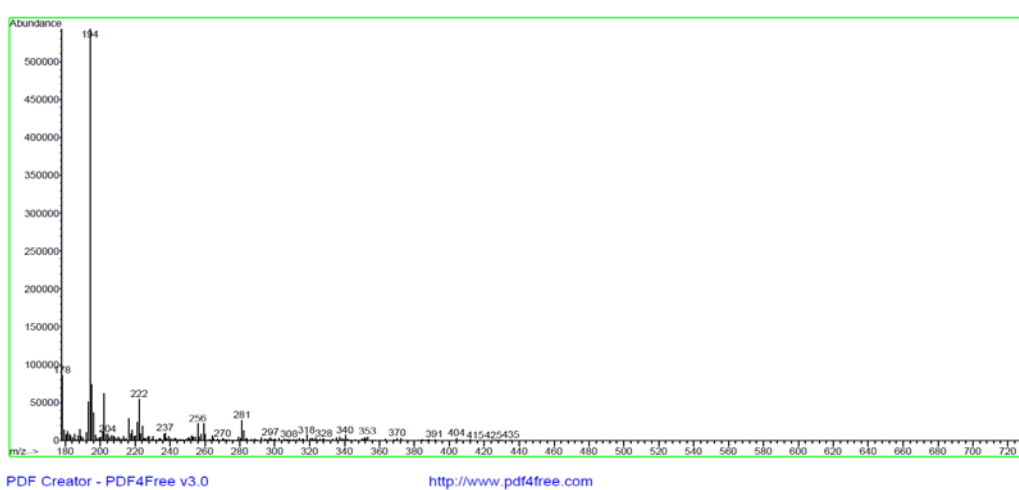


Figure 11. mass spectra of [Fe(L)Cl<sub>3</sub>]

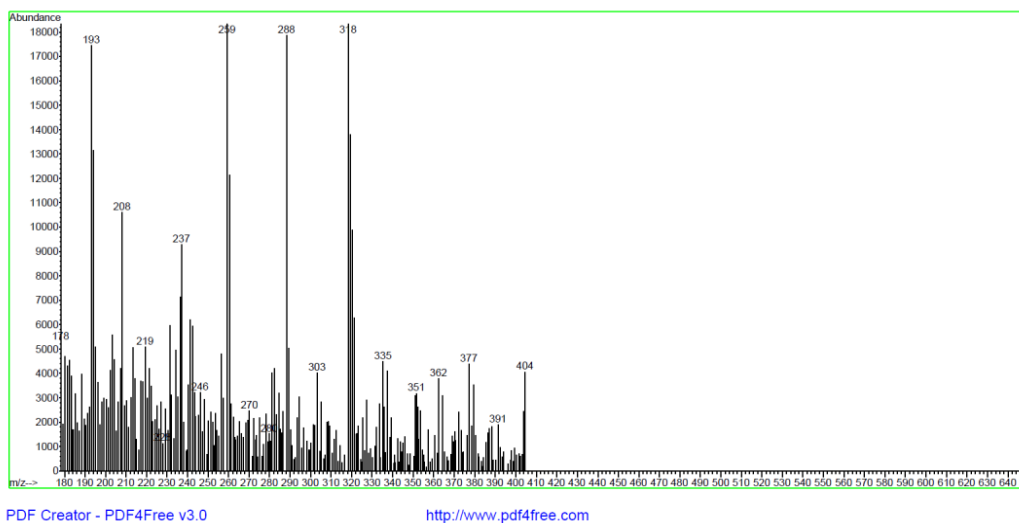


Figure 12. mass spectra of [Cr(L)Cl<sub>3</sub>]

**3.4 Electrical conductivity**

The electrical conductivity measurements  $\sigma$  on the solid state for the Cr(III), Fe(III), Co(II) and Ni(II) complexes of L and complexes in tablets form have been calculated within temperature range (313-373) K. The activation energy as well as electrical conductivities data is reported in Table(2). Upon the experimental data, the electrical conductivity data directly relationship with increasing the temperature according the following equation [11]:

$$\sigma = \sigma_0 \exp (-E_a/RT) \quad (1-1)$$

Where

$E_a$ : activation energy,  $\sigma_0$ : constant value.

Figures (13) - (17) show the relationship between current-voltage characteristics of ligand and complexes films with temperature range (303-393) K. Ohmic behavior was noticed at low voltage of less than 10V at all metals. The current increases with increasing temperature and the applied voltage is identical to the characteristics of semiconductor materials [12].

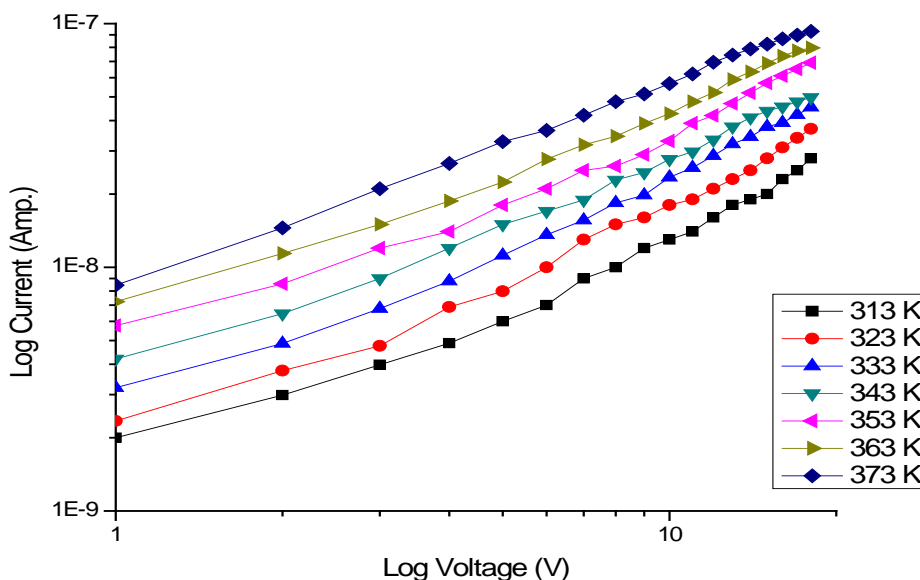
When temperature increases, more localized electrons have the energy to bridge the gap and the system becomes more ordered, then decreasing amount of localized states present allowing for more mobile of charge carriers [13]. On other hand, the molecular structure of the ligand and complexes greatly influences the charge carriers mobility according to the (I-V) characteristics.

The electrical conductivity of L and complexes increase in the order of decrease of ionic radii as follows: Ni > Fe > Co > Cr.

Figure (18) shows the relation between  $\ln \sigma$  and  $1/KT$  (eV) (equation 1) from where activation energy of ligand with complexes can be calculated from the slope of the straight line. It was found that the values of activation energy decrease with the increase of in the order Ni > Fe > Co > Cr.

**Table 2. The electrical conductivity (S/cm)and activation energy ( $E_a$ ) of L and complexes.**

| Physical parameter      | Compounds              |                       |                       |                       |                       |
|-------------------------|------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                         | L                      | Ni(II)/L              | Fe(III)/L             | Co(II)/L              | Cr (III)/L            |
| Electrical conductivity | $6.70 \times 10^{-11}$ | $5.19 \times 10^{-9}$ | $1.83 \times 10^{-8}$ | $8.74 \times 10^{-8}$ | $4.79 \times 10^{-7}$ |
| Activation energy       | 0.36                   | 0.31                  | 0.28                  | 0.26                  | 0.23                  |



**Figure 13. (I-V) Characteristics at different temperatures for ligand.**

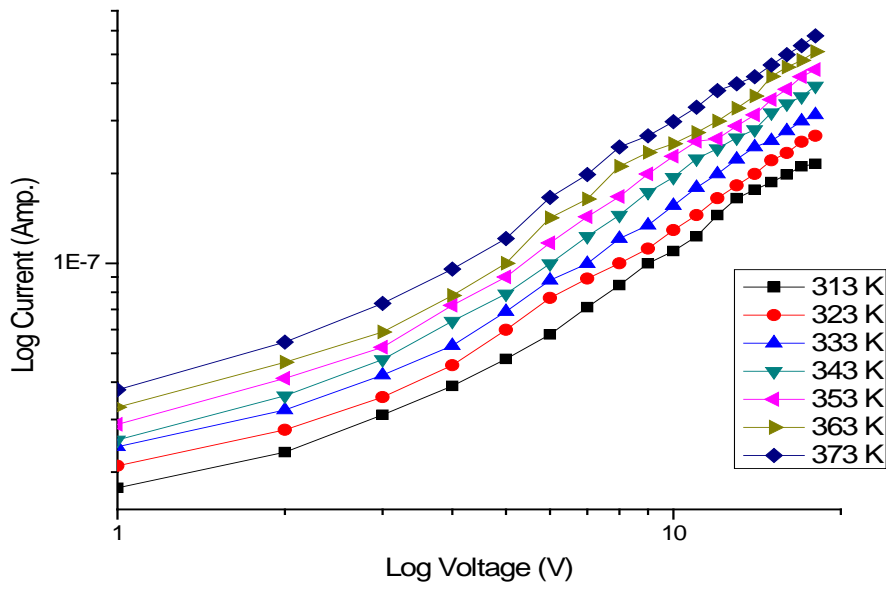


Figure 14. (I-V) Characteristics at different temperatures for [Ni(L)Cl<sub>2</sub>].

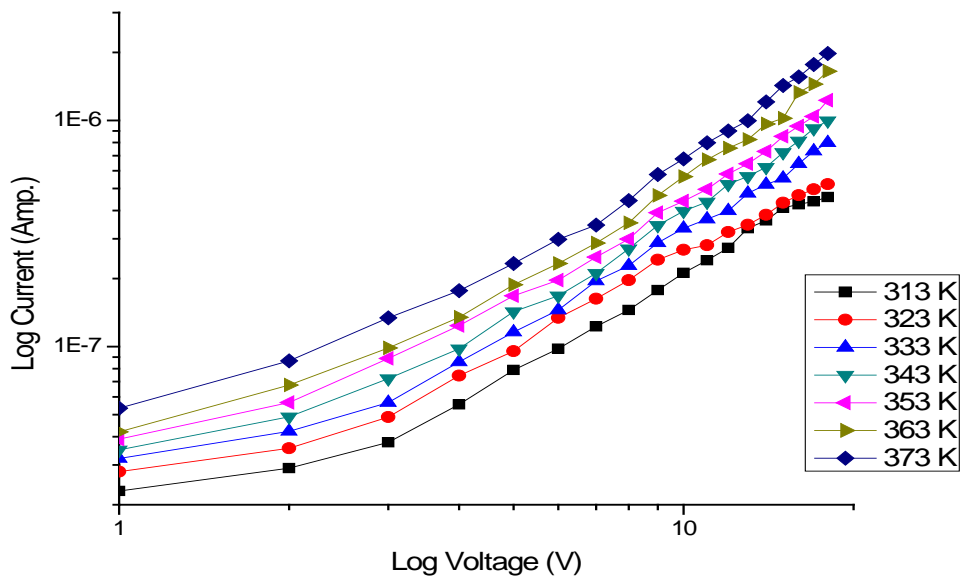


Figure 15. (I-V) Characteristics at different temperatures for [Fe(L)Cl<sub>3</sub>].

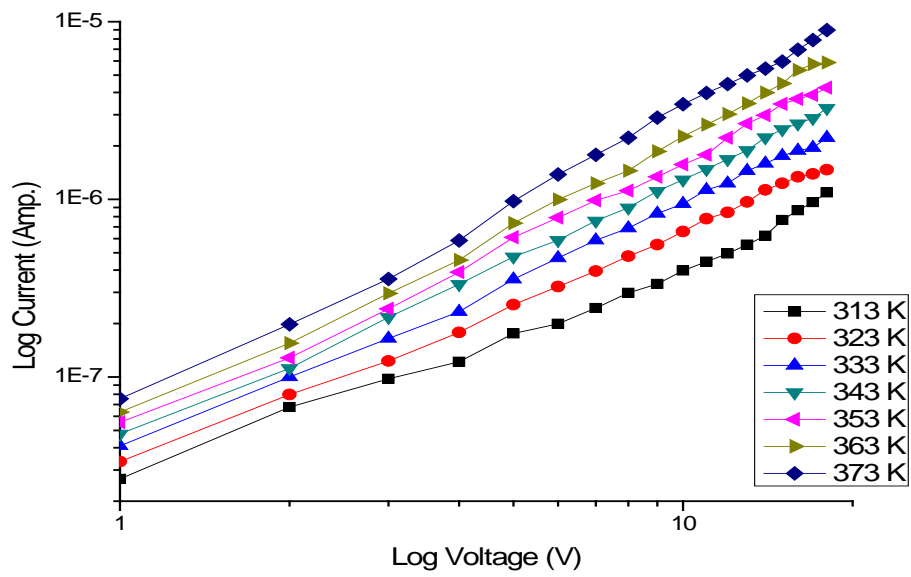


Figure 16. (I-V) Characteristics at different temperatures for [Co(L)Cl<sub>2</sub>].

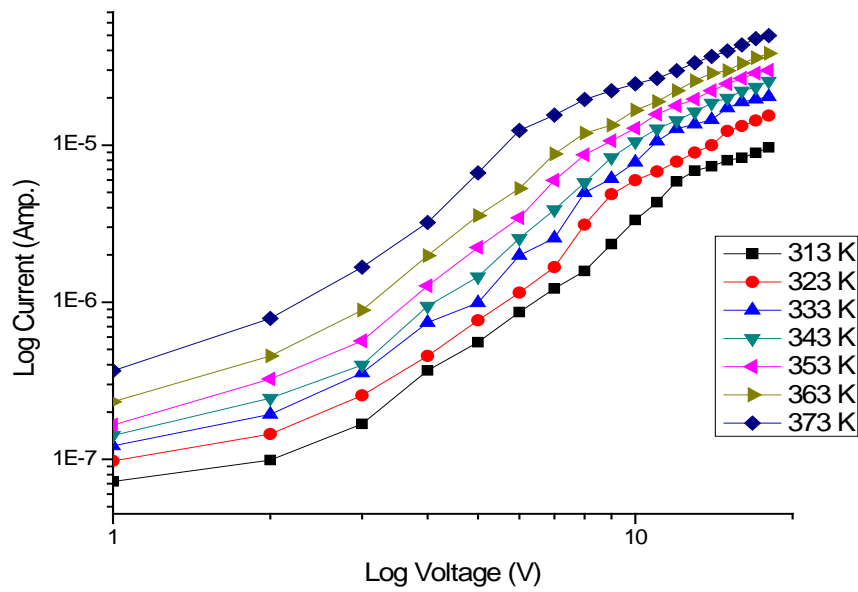


Figure 17. (I-V) Characteristics at different temperatures [Cr(L)Cl<sub>3</sub>].



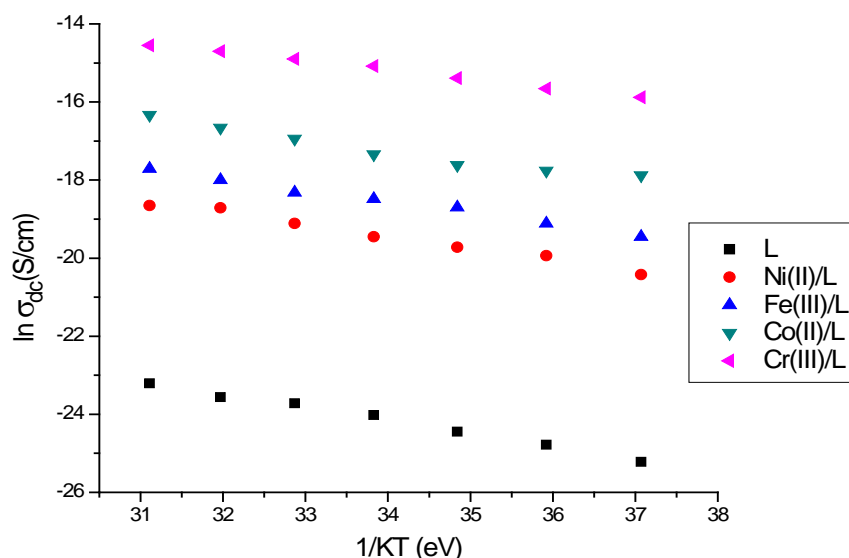


Figure 18. The relationship between  $\ln \sigma_{dc}$  and  $1/kT$  for ligand with complexes.

#### CONCLUSION

The ligand 3-(5-(2-furan-2-ylmethylene)hydrazinyl) 1,3,4-oxadiazol-2-yl]phenol was successfully synthesized. The FTIR, <sup>1</sup>HNMR and 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 conductivity increase with increasing the in the order of decrease of ionic radii as follows Ni > Fe > Co > Cr as the temperature increase the conductivity is increase too in a behavior similar to the semiconducting materials.

#### REFERENCE

1. Taylor M.K., Relinski J., Wallace D., Polyhedron 23 (2004) 3201.
2. Ermer O., Adv. Mater. 3 (1991) 608.
3. Kitazawa T., Nishikiori S., Kuroda R., Iwamoto T., J. Chem. Soc. Dalton trans. (1994) 1029.
4. Dybtsev D.N., Chun H., Yoon S.H., Kim D., Kim K., J. Am.Chem. Soc. 126 (2004) 32.
5. Pan L., Sander M.B., Huang X.Y., Li J., Smith M., Bittner E., Bochrath B., Johnson J.K., J. Am. Chem. Soc. 126(2004) 1308.
6. Gautman F and Lyons L E, Organic semiconductors, John Wiley, New York, (1967).
7. Dina A. Najeeb, J. Al-Nahrain Univ., 14.(2011)3.
8. Kishore K. et al., Eur. J. Med. Chem., 45(2010)11.
9. Derivatives P., Abdel-all M. T., El-sayed W.A., Aech. Pharm. Chem. Life Sci., 341(2008).
10. Menati S., Amiri H., Riahi M., Comptes rendus- Chem., (2015).
- 11 Harun M., Saion E., Kassim A., Hussain M., Mustafa I. and Omer M., Malaysian Polymer Journal (MPJ), 3 (2008)2.
12. Samah H. K., Athraa H. M, Global Journal of Pure and Applied Chemistry Research, 51( 2017)1.13 C.Lentz, B.Samuel, H.Foley and M.Haque, Publishing Corpoation, Journal of Nanomaterials,2011, 1, 8.