



## The Coordination chemistry and cyclic voltammetry exploration of Cu(II), Co(II), Ni(II) and Zn(II) complexes of novel (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl) benzamide ligand



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### Abstract

A novel thiosemicarbazone derivative ligand (DEHC-H), (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl) benzamide ligand was synthesized after three steps. Firstly, the reaction between acetyl pyridine with hydrazine hydrate at room temperature to obtain (E)-2-(1-hydrazonoethyl)pyridine. Secondly, 3,4-dichlorobenzoyl chloride was refluxed with potassium thiocyanate in acetonitrile solvent forming 3,4-dichlorobenzoyl isothiocyanate. The last step of the reaction is summarized by the refluxing the mixture of (E)-2-(1-hydrazonoethyl) pyridine and 3,4-dichlorobenzoyl isothiocyanate in acetonitrile solvent. A series of eight new metal complexes, Copper(II), Cobalt(II), Nickel(II) and Zinc(II) chloride and acetate complexes of the thiosemicarbazone derivative ligand (DEHC-H) were accomplished in DMF/H<sub>2</sub>O or CHCl<sub>3</sub>/CH<sub>3</sub>OH mixture solvents. The {[DEHC)CuCl], [(DEHC)CoCl], [(DEHC)NiCl], [(DEHC-H)ZnCl<sub>2</sub>], [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub>} were prepared by the reaction of the free ligand with chloride and acetate metal salts, CuCl<sub>2</sub>.2H<sub>2</sub>O, CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, ZnCl<sub>2</sub>, Cu(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O, Co(CH<sub>3</sub>COO)<sub>2</sub>.4H<sub>2</sub>O, Ni(CH<sub>3</sub>COO)<sub>2</sub>.4H<sub>2</sub>O and Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O. The preparation of the metal complexes was achieved in 1:1 and 1:2 mole ratios of (Metal salt : free Ligand). The identities of the thiosemicarbazone derivative ligand (DEHC-H) and its metal chloride and acetate complexes were characterized and confirmed by <sup>1</sup>HNMR, <sup>13</sup>CNMR, UV-visible, Infrared, mass spectroscopy, elemental analysis, solubility test, magnetic moments and conductivity measurements. The spectroscopic techniques and measurements indicate that the metal chloride complexes were formed with the neutral structural formula [(DEHC)MCl], where M= Copper(II), Cobalt(II) and Nickel(II) and with the neutral structural formula [(DEHC-H)ZnCl<sub>2</sub>] for Zinc(II) complexes in spite of two mole ratios were examined 1:1 and 1:2 (Metal : Ligand). In the other side, the acetate complexes were formed as the anionic formula [(DEHC-H)<sub>2</sub>M](CH<sub>3</sub>COO)<sub>2</sub>. The employed techniques indicate that thiosemicarbazone chloride complexes with formula [(DEHC)MCl], one tridentate [(DEHC) ligand coordinating in the thiole form with the metal ion and the fourth site was the chloride anion to form square planar geometry. While Zinc(II) complex [(DEHC-H)ZnCl<sub>2</sub>] show coordinating of the one tridentate [(DEHC-H) ligand as thione where the fourth and the fifth sites coordinating with the Zinc(II) ion to adopt a square pyramidal geometry. The characterization of the all acetate complexes [(DEHC-H)<sub>2</sub>M](CH<sub>3</sub>COO)<sub>2</sub> pointed to two moles of tridentate [(DEHC-H) ligands in thione form coordinating with the metal ions to fill six sites forming octahedral geometry as well as to two moles of acetate ions as counter ions. It is worth noting that tridentate thiosemicarbazone [(DEHC-H) ligand coordinates through the nitrogen pyridyl, thionic sulfur and the azomethine nitrogen atoms. The observed magnetic moments data exhibit diamagnetic properties of Zinc(II) chloride and acetate complexes and Nickel(II) square planar chloride complexes. While Cu(II) and Co(II) square planar chloride compounds and Copper(II), Cobalt(II) and Nickel(II) octahedral acetate complexes appeared as paramagnetic species. The electrochemical behavior of a set Copper(II), Cobalt(II) and Nickel(II) chloride and acetate complexes of (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl) benzamide ligand were recorded using cyclic voltammetry technique. The voltammetric analysis of Copper(II) chloride and acetate complexes displays a quasi-reversible one electron reduction in the range -1.0728 to -1.1439 volt versus Fc/Fc<sup>+</sup> ascribable to the Copper(II)/Copper(I) redox couple. The Co(II) and Ni(II) chloride and acetate compounds display one and two irreversible oxidation processes respectively in the range +0.419 to +0.479 in Co(II) compounds and +0.449 to +0.491 as well as to +0.656 to +0.721 volt versus Fc/Fc<sup>+</sup> in Ni(II) compounds.

**Keywords:** Thiosemicarbazone, Metal chloride and acetate complexes, Cyclic voltammetry, N, S, N' tridentate ligand, Different mole ratios.

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## 1. Introduction

Thiosemicarbazone derivatives compose an essential type of organic substances because of their owing to the privilege structural form and remarkable activity in biology field, for example their activity against bacteria and viruses. The containing of the oxygen and sulfur atoms in heterocyclic thiosemicarbazone derivatives enhances their applying in different biology fields [1-2]. In general, the various structural form, biological activities, ionic sensitivity and different probable bonding styles of thiosemicarbazones lead researchers with an increased interest concerning to thiosemicarbazones [3]. It is discovered that metal complexes have distinct properties than their free ligands by owing them different advantage and motivating chemistry [4]. The diverse and significant properties like pharmacological properties of the thiosemicarbazones metal complexes have been faced researchers to study this type of complexes [5-6]. The literatures reported that the thiosemicarbazone metal complexes exhibit different manner than the thiosemicarbazone free ligands or metal ions separately. Such as Copper(II) thiosemicarbazones complexes showed higher or lower biological activity than ion metals or free ligands [7-9]. The Cu(II) and Ni(II) compounds revealed increasing of their activities against bacteria, fungi, inflammatory and HIV as compared with the free ligand [10]. As well as thiosemicarbazone derivatives as pliable ligands are able them to relevant using in different fields in inorganic chemistry as chelating agents to form element complexes. In material science as electrochemical sensor [11], nonlinear optical species [12] and Langmuir film [13], the thiosemicarbazones complexes exhibited high activity. Thiosemicarbazone metal complexes are considered as one of the most significant category of N and S donor ligands [14] due to their extremely interesting biological [15-18], medicinal [19-22], pharmacological [23-25] chemical features [26] and in bioinorganic operations [27-28]. Different reports of acetophenone thiosemicarbazone derivatives and their Copper(II) and Nickel(II) complexes have revealed motivating structural electronic shape, bonding properties [29-31] and antimicrobial properties [32-34]. A numerous interest of NSO donor ligands has been appeared in coordination chemistry because of their amazing structural and biological characteristics [35-39]. Multidentate hetrocyclic compounds including N atom are deemed as essential species as building blocks forming of the complexes style [40-41]. Despite the importance of the thiosemicarbazone derivatives, the element complexes such as Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes of the thiosemicarbazones based on 2-acetyl pyridine still

have not been enough studied and probed. This paper in continuation of our contributions of thiourea and thiosemicarbazone derivatives [42-44], and due to wide band of probable various applications of the metal compounds of thiosemicarbazones. For all the above we investigate here substantially the synthesis and the full characterization of a set of eight complexes of Copper(II), Cobalt(II), Nickel(II) and Zinc(II) chloride and acetate complexes of a novel thiosemicarbazone derivative (DEHC-H), (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl) benzamide ligand. The major target of this paper is to explore the noteworthy role of the 2-acetyl pyridyl benzoyl thiosemicarbazone derivatives and their Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes. A simple, rapid synthesis in addition to the vast area of the potential applications are accompanying, with the distinguished motivation, the synthesis of thiosemicarbazones and their element complexes. The chemistry, synthesis and pureness of the new prepared thiosemicarbazone ligand and its element complexes were achieved and confirmed by whole the conceivable techniques. The electrochemical behavior of the novel ligand and its Copper(II), Cobalt(II) and Nickel(II) complexes were investigated by using cyclic voltammetry technique which is the else main aim of this work to probe the redox manner and knowing the oxidation state of the central ion after the complexes form. The flexible structure of a multi dentate novel thiosemicarbazone derivative ligand (DEHC-H), (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl) benzamide ligand be eligible to coordinate with metal ions in various probable geometrical shapes via N pyridyl ring, oxygen carbonyl group, sulfur C=S group, NH group and nitrogen C=N group. This is what take our attention strongly to search and progress the coordination chemistry of the thiosemicarbazone pyridyl benzoyl derivatives. The active role of the thiosemicarbazones as building components to form heterocyclic compounds and their capable activity towards bacteria, fungi and cancer was great motivate for us to their exploration.

## 2. Experimental

### 2.1 Materials

All starting materials (2-Acetyl pyridine (ALDRICH), hydrazine hydrate (THOMAS BAKER), 3,4-dichloro benzoyl chloride (SIGMA-ALDRICH) and potassium thiocyanate (HAMILTON), metal salts {CuCl<sub>2</sub>.2H<sub>2</sub>O (SIGMA-ALDRICH), CoCl<sub>2</sub>.6H<sub>2</sub>O (SIGMA-ALDRICH), NiCl<sub>2</sub>.6H<sub>2</sub>O (ALDRICH), ZnCl<sub>2</sub> (Merck), Cu(CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O (SIGMA-ALDRICH), Co(CH<sub>3</sub>COO)<sub>2</sub>.4H<sub>2</sub>O (SIGMA-ALDRICH), Ni(CH<sub>3</sub>COO)<sub>2</sub>.4H<sub>2</sub>O (ALDRICH) and

Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (Merck)} and solvents, acetonitrile (Merck), chloroform (HIMEDIA), methanol (Merck), dimethylformamide (Merck) which were utilized to synthesis thiosemicarbazone ligand and its metal complexes were used as received and purchased from different chemical companies as mentioned above. The tetra butyl ammonium hexafluoro phosphate (TBAHFP) which was employed as supporting electrolyte to study the electrochemical behaviour was procured from ALDRICH.

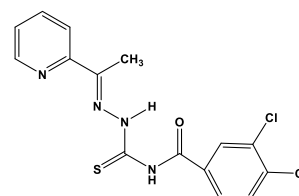
## 2.2 Instrumentation

The melting point of the free ligand (DEHC-H) and the decomposition points for all the prepared complexes were accomplished via the electro thermal VeeGo Digital model VMP-D.Jenway. Different spectroscopic techniques and valuable measurements were elucidated to characterize and confirm the identity of the free ligand (DEHC-H) and its Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes like <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FT-IR, UV-vis., mass spectroscopy, CHNS analysis, magnetic susceptibility and cyclic voltammetry technique. The Bruker 400 MHz spectrophotometer was used to measure <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the thiosemicarbazone ligand (DEHC-H) in dimethyl sulfoxide-d<sub>6</sub>. A Japanese Shimadzu model 8400S spectrometer was employed to record the FT-IR spectra of the prepared compounds in the extent 400-4000 cm<sup>-1</sup> using potassium bromide disc. A SHIMADZU UV/vis-1800 spectrometer from 200-1100 nm was elucidated to measure the electronic spectra of the prepared compounds in dimethyl sulfoxide solvent using 1 cm cell. The elemental analysis was accomplished using Perkin CE-440 elemental analyzer to indicate and confirm the structural form of the prepared compounds via C, H, N and S atoms percentage proportional to their full compounds. A Waters LCT Premier XE (oa-TOF) mass spectrophotometer was used to record the electrospray ionization mass spectra ESI-MS (m/z) % for the prepared compounds. The magnetic moments were achieved using A Johnson Matthey magnetic susceptibility balance [45] at room temperature. The molar conductivities of the prepared compounds were measured ranging (25\*10<sup>-6</sup>-1.21\*10<sup>-2</sup>) mol/L in dimethyl sulfoxide solvent via the W.T.W conductivity Master LBR meter at room temperature. The CH Instruments, USA, Digi-Ivy (Model DY2300 Seriespotentiostat/biopotentiostat, electrochemical analyzer were dedicated to study the electrochemical properties of the ligand (DEHC-H) and its Copper(II), Cobalt(II) and Nickel(II) complexes via cyclic voltammetry technique. The dimethylsulfoxide solvent was used to dissolve 0.1 mol/L of the tetra butyl ammonium hexafluoro phosphate (TBAHFP)

and 1\*10<sup>-3</sup> mol/L of the electro active compounds. The cyclic voltammograms was recorded at room temperature (25 degree centigrade) and the solutions under work were degassed through passing nitrogen gas for 15 minutes to through away undesired oxygen gas. The cyclic voltammograms were recorded by using an exceptionally three electrodes system, which is including working, auxiliary, and reference electrodes and were made from a platinum, platinum wire and a non-aqueous solution Ag/AgNO<sub>3</sub> respectively. The sand paper should be used to polish the working electrode before each measure to get effective smooth surface, which is promoting its sensitivity towards electrochemical features.

## 2.3 Synthesis of [(E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonyl)thiyl)benzamide ligand] (DEHC-H ligand) :

1-(pyridin-2-yl)ethan-1-one (1.21 g, 10 mmol) in 10 mL acetonitrile was added to hydrazine hydrate (80 %) (0.32 g, 10 mmol) in 5 mL acetonitrile. The mixture solution was stirred



at r. t. for 24 hours to get white precipitate, (E)-2-(1-hydrazonoethyl) pyridine. The acid chloride, 3,4-dichloro benzoyl chloride (2.09 g, 10 mmol) in 10 mL CH<sub>3</sub>CN was refluxed for 3 hours with KSCN (0.97 g, 10 mmol) in 5 mL CH<sub>3</sub>CN. In the end of this reaction, yellow solution was obtained (3,4-dichlorobenzoyl isothiocyanate) after removing the white precipitate which is potassium chloride. The last step to synthesis the desired ligand is concluded by refluxing for 3 hours, the (E)-2-(1-hydrazonoethyl)pyridine (1.35 g, 10 mmol) in 10 mL CH<sub>3</sub>CN with the yellow solution (3,4-dichlorobenzoyl isothiocyanate). The yellow formed precipitate was collected by filtration. Yellow crystals were yielded via recrystallization in hot acetonitrile. Yield: (1.15 g, 85%); m.p= 191-193<sup>o</sup>C, ESI-MS (m/z)(%): 366.10 [M-H] (60%); FT-IR (cm<sup>-1</sup>): ν(N-H) 3421, ν(C=O) 1663, δ(N-H)<sup>1</sup> 1586, δ(N-H)<sup>2</sup> 1532, ν(C=N) 1466, ν(C=S), 1300. UV-vis. Spectrum, λ<sub>max</sub> nm (εM, M<sup>-1</sup>cm<sup>-1</sup>): 290(13900), 347(11420); <sup>1</sup>HNMR (400 MHz, DMSO-d<sub>6</sub>), δ(ppm): 13.70 (1H, s, N-H(NHCS)), 12.08 (1H, s, N-H(NHCO)), 8.67 (1H, d, Py J<sub>HH</sub> = 5 Hz), 8.28 (1H, d, Py J<sub>HH</sub> = 3 Hz), 8.18 (1H, d, Ar J<sub>HH</sub> = 10 Hz), 7.97 (1H, s, Ar), 7.94 (1H, t, Py J<sub>HH</sub> = 5 Hz), 7.84 (1H, d, Ar J<sub>HH</sub> = 10 Hz), 7.50 (1H, t, Py J<sub>HH</sub> = 5 Hz), 2.49 (3H, s, 1CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>), δ(ppm): 177.96 (C=S), 166.99 (C=O), 157.19, 154.55, 149.31, 137.37, 136.45, 132.79, 131.74, 131.31, 131.19, 129.54, 125.26, 121.49, 12.93 (CH<sub>3</sub>), Anal. Calcd. For C<sub>15</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>4</sub>OS (%):C, 49.06; H, 3.29; N, 15.26; S,

8.73, Found (%): C, 49.38; H, 3.26; N, 15.37; S, 8.67. See Figures 1-3.

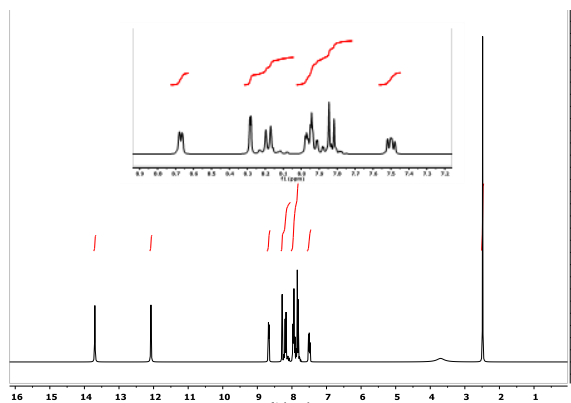


Figure 1:  $^1\text{H}$ NMR spectrum of [(E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide ligand] (DEHC-H) ligand.

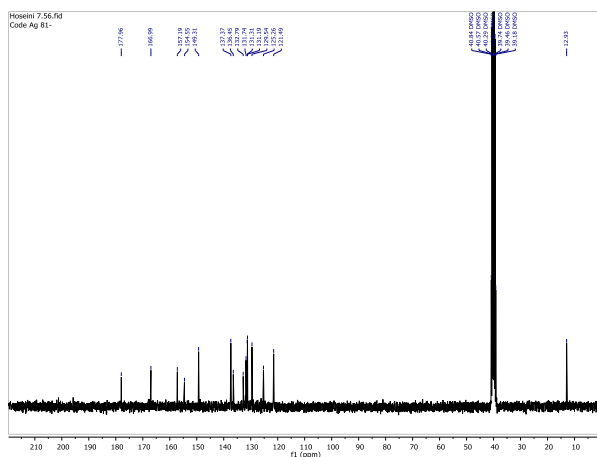


Figure 2:  $^{13}\text{C}$ NMR spectrum of [(E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide ligand] (DEHC-H) ligand.

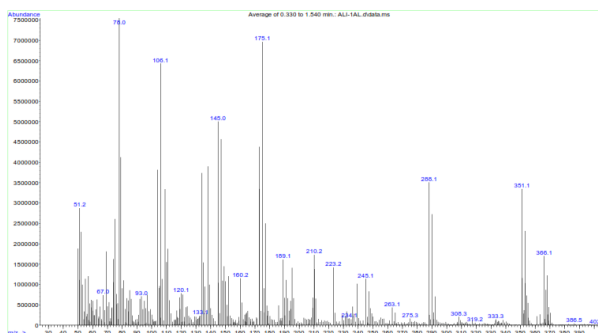
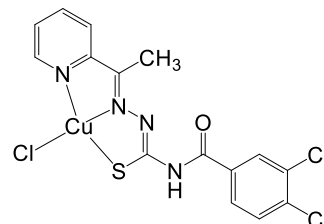


Figure 3: Mass spectrum of [(E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide ligand] (DEHC-H) ligand.

## 2.4 Synthesis of complexes [(DEHC)CuCl], [(DEHC)CoCl], [(DEHC)NiCl], [(DEHC-H)ZnCl<sub>2</sub>], [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub>

### 2.4.1. Synthesis of Mono [(E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide] mono chloro Copper(II) [(DEHC)CuCl]

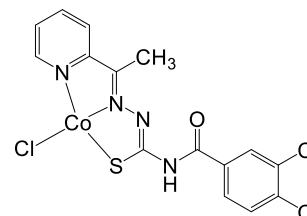
To a DMF solution (5 mL) of (DEHC-H) Ligand (0.74 g, 2 mmol) is added gradually a H<sub>2</sub>O (2 mL) of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.34 g, 2 mmol). The mixture solution keeps stirring at r. t.



for 2 hours. In the end of reaction, green precipitate was formed. To purify the prepared complex, 2 mL DMF was used to wash the complex and remove the unreacted starting material. Then dried under vacuum. Green crystals were obtained at r. t. by the diffusion of diethyl ether vapour into a CH<sub>3</sub>CN solution of it. Yield: (0.57 g, 77 %); D.p= 245<sup>o</sup>C, light green crystals; ESI-MS (*m/z*): 462.70 [M] (80%); FT-IR (cm<sup>-1</sup>):  $\nu(\text{N-H})$  3306,  $\nu(\text{C=O})$  1660,  $\delta(\text{N-H})^1$  1589,  $\nu(\text{C=N})$  1438,  $\nu(\text{Cu-S})$  444,  $\nu(\text{Cu-N})$  548; UV-vis. Spectrum,  $\lambda_{\text{max}}$  nm ( $\epsilon\text{M}$ , M<sup>-1</sup> cm<sup>-1</sup>): 293(10810), 361(8700), 595(20); Anal. Calcd. For C<sub>15</sub>H<sub>11</sub>Cl<sub>3</sub>CuN<sub>4</sub>OS (%): C, 38.73; H, 2.38; N, 12.04; S, 6.89. Found (%): C, 38.96; H, 2.49; N, 11.97; S, 6.87.

### 2.4.2. Synthesis of Mono [(E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide] mono chloro Cobalt(II) [(DEHC)CoCl]

To a CHCl<sub>3</sub> solution (5 mL) of (DEHC-H) Ligand (0.74 g, 2 mmol) is added gradually a methanol (3 mL) of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.48 g, 2 mmol). The mixture solution was refluxed

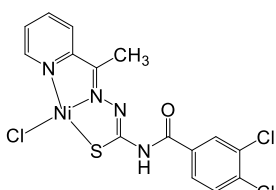


for 3 hours. In the end of reaction, green precipitate was formed. To purify the prepared complex, 2 mL CHCl<sub>3</sub> was used to wash the complex and remove the unreacted starting material. Then dried under vacuum. Green crystals were obtained at r. t. by the diffusion of diethyl ether vapour into a CH<sub>3</sub>CN solution of it. Yield: (0.51 g, 69 %); D.p= 201<sup>o</sup>C, dark green

crystals; ESI-MS ( $m/z$ )(%): 459.70 [M+H] (96%); FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{N-H})$  3383,  $\nu(\text{C=O})$  1659,  $\delta(\text{N-H})^1$  1601,  $\nu(\text{C=N})$  1439,  $\nu(\text{Co-S})$  440,  $\nu(\text{Co-N})$  517; UV-vis. Spectrum,  $\lambda_{\text{max}}$  nm ( $\epsilon\text{M}$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 295(9400), 362(8530), 607(31); Anal. Calcd. For  $\text{C}_{15}\text{H}_{11}\text{Cl}_3\text{CoN}_4\text{OS}$  (%): C, 39.11; H, 2.41; N, 12.16; S, 6.96. Found (%): C, 39.27; H, 2.56; N, 12.00; S, 6.87.

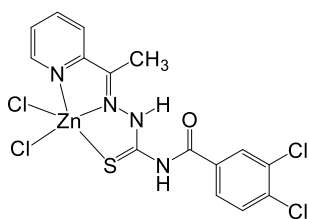
**2.4.3. Synthesis of Mono [(E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide)] mono chloro Nickel(II) [(DEHC)NiCl]**

The [(DEHC)NiCl] complex was prepared similar to [(DEHC)CoCl] complex by using:  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.48 g, 2 mmol), (DEHC-H) ligand (0.74 g, 2 mmol). Yield: (0.61 g, 83 %); D.p= 225 °C, dark brown crystals; ESI-MS ( $m/z$ )(%): 458.50 [M+H] (92.6%); FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{N-H})$  3322,  $\nu(\text{C=O})$  1660,  $\delta(\text{N-H})^1$  1566,  $\nu(\text{C=N})$  1435,  $\nu(\text{Ni-S})$  467,  $\nu(\text{Ni-N})$  538; UV-vis. Spectrum,  $\lambda_{\text{max}}$  nm, ( $\epsilon\text{M}$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 293(11320), 362(9130), 603(18); Anal. Calcd. For  $\text{C}_{15}\text{H}_{11}\text{Cl}_3\text{N}_4\text{NiOS}$  (%): C, 39.13; H, 2.41; N, 12.17; S, 6.96. Found (%): C, 39.35; H, 2.59; N, 12.22; S, 7.01.



**2.4.4. Synthesis of Mono [(E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide)] di chloro Zinc(II) [(DEHC-H)ZnCl<sub>2</sub>]**

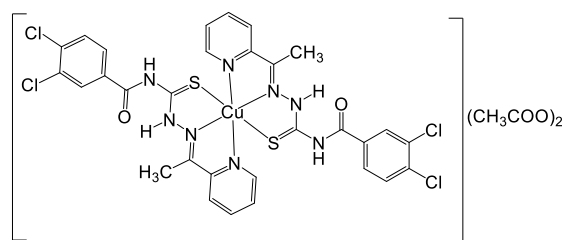
Similar procedure as mentioned above for [(DEHC)CoCl] preparation was followed using:  $\text{ZnCl}_2$  (0.28 g, 2 mmol), (DEHC-H) ligand (0.74 g, 2 mmol). Yield: (0.52 g, 70%); D.p= 238 °C, Yellow crystals; ESI-MS ( $m/z$ )(%): 501.53 [M+H] (70%); FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{N-H})$  3345,  $\nu(\text{C=O})$  1660,  $\delta(\text{N-H})^1$  1585,  $\delta(\text{N-H})^2$  1554,  $\nu(\text{C=N})$  1427,  $\nu(\text{C=S})$ , 1272,  $\nu(\text{Zn-S})$  443,  $\nu(\text{Zn-N})$  525; UV-vis. Spectrum,  $\lambda_{\text{max}}$  nm, ( $\epsilon\text{M}$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 297(12710), 368(10310); Anal. Calcd. For  $\text{C}_{15}\text{H}_{12}\text{Cl}_4\text{N}_4\text{OSZn}$  (%): C, 35.78; H, 2.40; N, 11.13; S, 6.37. Found (%): C, 35.96; H, 2.61; N, 10.94; S, 6.40.



**2.4.5. Synthesis of bis [(E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide)]Copper(II) di acetate [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>**

**2.4.6. Synthesis of bis [(E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide)]Cobalt(II) di acetate [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>**

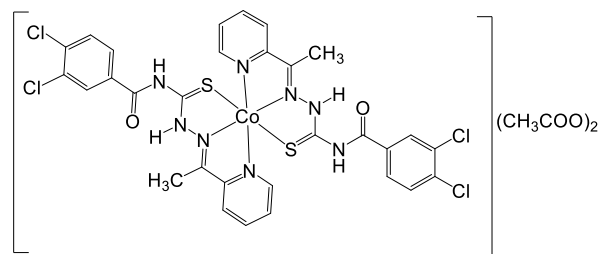
Similar procedure as mentioned above for [(DEHC)CuCl] preparation was followed using:  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.2 g, 1 mmol) instead of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , (DEHC-H) ligand (0.74 g, 2 mmol). Yield: (0.62 g, 84 %); D.p= 263 °C, Dark green crystals; ESI-MS ( $m/z$ )(%): 795.90 [M+H] (77%); FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{N-H})$  3256,  $\nu(\text{C=O})$  1663,  $\delta(\text{N-H})^1$  1589,  $\delta(\text{N-H})^2$  1555,  $\nu(\text{C=N})$  1435,  $\nu(\text{C=S})$ , 1269,  $\nu(\text{Cu-S})$  441,  $\nu(\text{Cu-N})$  542; UV-vis. Spectrum,  $\lambda_{\text{max}}$  nm ( $\epsilon\text{M}$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 292(9910), 357(8940), 625(45); Anal. Calcd. For  $\text{C}_{34}\text{H}_{30}\text{Cl}_4\text{CuN}_8\text{O}_6\text{S}_2$  (%): C, 44.58; H, 3.30; N, 12.23; S, 7.00. Found (%): C, 44.69; H, 3.27; N,



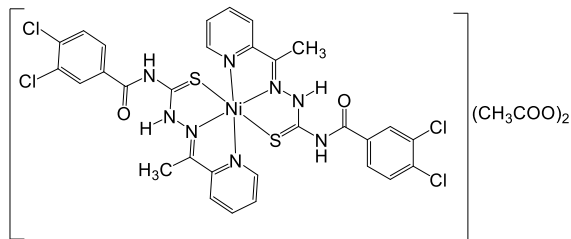
12.36; S, 7.08.

**2.4.7. Synthesis of bis [(E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide)]Nickel(II) di acetate [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub>**

Similar procedure as mentioned above for [(DEHC)CoCl] preparation was followed using:  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (0.24 g, 1 mmol) instead of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , (DEHC-H) ligand (0.74 g, 2 mmol). Yield: (0.48 g, 65 %); D.p= 212 °C, dark green crystals; ESI-MS ( $m/z$ )(%): 792.09 [M+H] (100%); FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{N-H})$  3345,  $\nu(\text{C=O})$  1663,  $\delta(\text{N-H})^1$  1593,  $\delta(\text{N-H})^2$  1532,  $\nu(\text{C=N})$  1438,  $\nu(\text{C=S})$ , 1281,  $\nu(\text{Co-S})$  451,  $\nu(\text{Co-N})$  521; UV-vis. Spectrum,  $\lambda_{\text{max}}$  nm ( $\epsilon\text{M}$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 294(10300), 362(8810), 632(38); Anal. Calcd. For  $\text{C}_{34}\text{H}_{30}\text{Cl}_4\text{CoN}_8\text{O}_6\text{S}_2$  (%): C, 44.80; H, 3.32; N, 12.29; S, 7.03. Found (%): C, 45.07; H, 3.49; N, 12.38; S, 7.06.

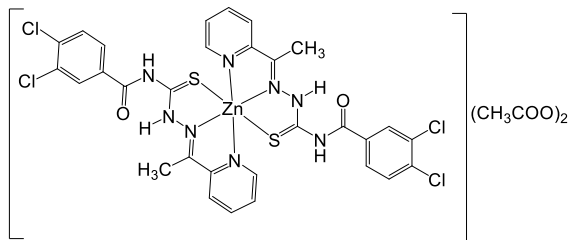


Similar procedure as mentioned above for [(DEHC)NiCl] preparation was followed using: Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.24 g, 1 mmol) instead of NiCl<sub>2</sub>·6H<sub>2</sub>O, (DEHC-H) ligand (0.74 g, 2 mmol). Yield: (0.66 g, 89 %); D.p= 231 °C, dark green crystals; ESI-MS (*m/z*)(%): 791.11 [M+H] (78%); FT-IR (cm<sup>-1</sup>): ν(N-H) 3302, ν(C=O) 1662, δ(N-H)<sup>1</sup> 1589, δ(N-H)<sup>2</sup> 1558, ν(C=N) 1412, ν(C=S), 1258, ν(Ni-S) 436, ν(Ni-N) 529; UV-vis. Spectrum, λ<sub>max</sub> nm (εM, M<sup>-1</sup>cm<sup>-1</sup>): 292(10530), 360(8910), 600(23), 960(26) ; Anal. Calcd. For C<sub>34</sub>H<sub>30</sub>Cl<sub>4</sub>N<sub>8</sub>NiO<sub>6</sub>S<sub>2</sub> (%): C, 44.81; H, 3.32; N, 12.30; S, 7.04. Found (%):C, 44.91; H, 3.15; N, 12.35; S, 7.13.



#### 2.4.8. Synthesis of bis [(E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide]Zinc(II) di acetate [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub>

Similar procedure as mentioned above for [(DEHC-H)ZnCl<sub>2</sub>] preparation was followed using: Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.22 g, 1 mmol) instead of ZnCl<sub>2</sub>, L (0.74 g, 2 mmol). Yield: (0.43 g, 59 %); D.p= 241 °C, Yellow crystals; ESI-MS (*m/z*)(%): 797.40 [M+H] (80%); FT-IR (cm<sup>-1</sup>): ν(N-H) 3318, ν(C=O) 1661, δ(N-H)<sup>1</sup> 1589, δ(N-H)<sup>2</sup> 1559, ν(C=N) 1412, ν(C=S), 1261, ν(Zn-S) 440, ν(Zn-N) 529; UV-vis. Spectrum, λ<sub>max</sub> nm (εM, M<sup>-1</sup> cm<sup>-1</sup>): 295(13140), 363(9531); Anal. Calcd. For C<sub>34</sub>H<sub>30</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>6</sub>S<sub>2</sub>Zn (%): C,44.49; H, 3.29; N, 12.21; S, 6.99. Found (%):C,44.55; H, 3.15; N, 12.25; S, 7.07.

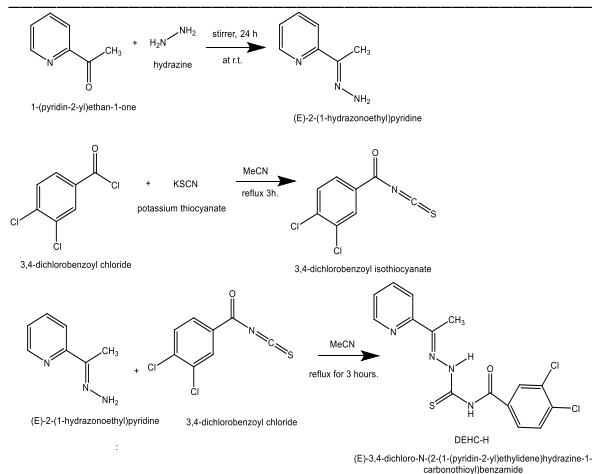


### 3. Results and discussion

#### 3.1. Synthesis of (DEHC-H) Ligand and its Copper(II), Cobalt(II), Nickel(II) and Zinc(II) transition metal complexes

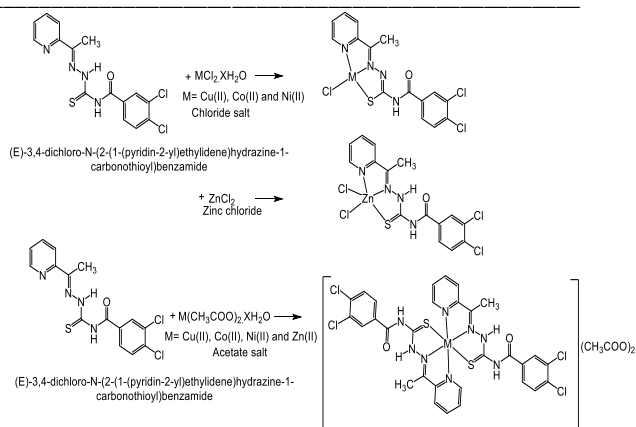
The reaction between the thiosemicarbazone ligand, (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide (DEHC-H) ligand with CuCl<sub>2</sub>·2H<sub>2</sub>O and Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O in DMF/H<sub>2</sub>O mixture solvents gave the Copper(II) complexes, [(DEHC)CuCl] and [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub> respectively. While [(DEHC)CoCl], [(DEHC)NiCl], [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> complexes were obtained from the reaction between (DEHC-H) ligand with CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, ZnCl<sub>2</sub>, Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O in CHCl<sub>3</sub>/methanol respectively. All the synthesized ligand and its complexes were gained in solid state as crystals after recrystallization in acetonitrile solution. They are collected in good yield and they have high stability in the solid and solution states. The solubility test of the chloride and acetate complexes were achieved in different polar and nonpolar solvents. All these complexes insoluble in water and the chloride complexes insoluble in polar solvents while the acetate complexes soluble in polar solvents. The synthesis method of the (DEHC-H) ligand is divided into three steps: first, the synthesis of (E)-2-(1-hydrazonoethyl)pyridine which is achieved via stirring the mixture of 1-(pyridin-2-yl)ethan-1-one and hydrazine at r. t. for 24 hours. Second: the synthesis of 3,4-dichlorobenzoyl isothiocyanate through refluxing the mixture of 3,4-dichlorobenzoyl chloride and potassium thiocyanate in acetonitrile for 3 hours. The last step is the synthesis of the desired ligand by the refluxing for 3 hours the resulted compounds from the first and second steps, of (E)-2-(1-hydrazonoethyl)pyridine and 3,4-dichlorobenzoyl isothiocyanate in acetonitrile. Finally, the yellow crystals are gained abundantly from the yellow solution and the amine group in (E)-2-(1-hydrazonoethyl)pyridine converted to thiourea component. High yield (85%) of (DEHC-H) ligand were collected after recrystallization in acetonitrile solution to result yellow crystals. **Scheme 1** concluded the synthesis steps of the thiosemicarbazone ligand (DEHC-H).

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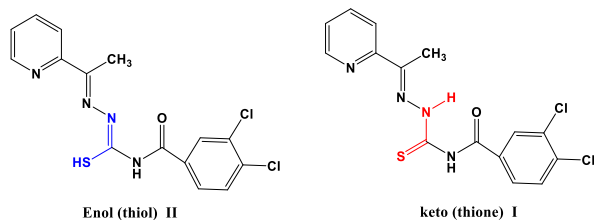
**Scheme 1: Synthetic steps of the thiosemicarbazone derivative ligand (DEHC-H), showing its synthesis conditions.**

The [(DEHC)CuCl] and [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub> copper(II) compounds were created via the stirring of (DEHC-H) ligand in dimethyl formamide solvent with CuCl<sub>2</sub>·2H<sub>2</sub>O or Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O in water solvent at room temperature for two hours to produce green precipitate of [(DEHC)CuCl] and [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub> respectively. The [(DEHC)CoCl], [(DEHC)NiCl], [(DEHC-H)ZnCl<sub>2</sub>], [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> Cobalt(II), Nickel(II) and Zinc(II) complexes were gotten by the refluxing for 2 hours the (DEHC-H) ligand in chloroform solvent with CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, ZnCl<sub>2</sub>, Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O in methanol solvent. Colored precipitate was formed for these complexes, as green precipitate of [(DEHC)CoCl], [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub> and [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub>, brown precipitate of [(DEHC)NiCl], yellow precipitate [(DEHC-H)ZnCl<sub>2</sub>] and [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> complexes. The diffusion of diethyl ether vapor in CH<sub>3</sub>CN solution for the prepared complexes formed colored crystals as mentioned in the synthesis part. The suggested geometrical shapes for all metal complexes were full characterized and confirmed via various spectroscopic techniques. **Scheme 2** shows the preparation conditions of the prepared metal complexes.



**Scheme 2: The preparation of chloride and acetate metal complexes of the thiosemicarbazone derivative ligand (DEHC-H)**

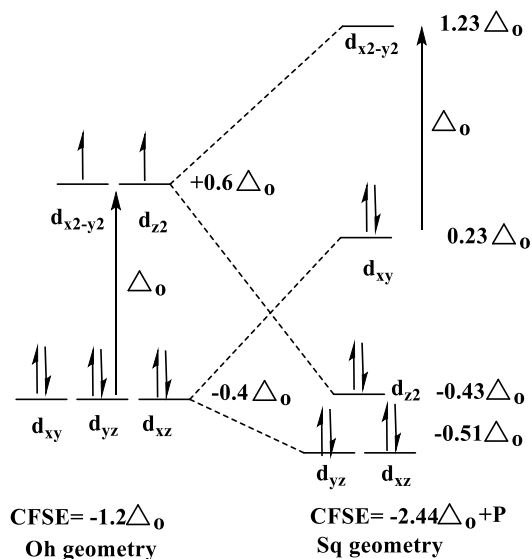
Two mole ratios were examined to prepare chloride and acetate complexes, 1:1 and 2:1 (free ligand: metal salt). Full characterization for all complexes achieved by different spectroscopic techniques and valuable measurements. They revealed that chloride complexes were formed with the neutral structural formula [(DEHC)MCl], where M= Copper(II), Cobalt(II) and Nickel(II) and with the neutral structural formula [(DEHC-H)ZnCl<sub>2</sub>] for Zinc(II) complexes in spite of using different mole ratios. While the acetate complexes were appeared as the anionic formula [(DEHC-H)<sub>2</sub>M](CH<sub>3</sub>COO)<sub>2</sub>. The employed techniques indicate that thiosemicarbazone chloride complexes with formula [(DEHC)MCl], one tridentate [(DEHC) ligand coordinating in the thione form with the metal ion and the fourth site was the chloride anion to form square planar geometry. While Zinc(II) complex [(DEHC-H)ZnCl<sub>2</sub>] show coordinating of the one tridentate [(DEHC-H) ligand as thione form with the Zinc(II) ion where the fourth and fifth sites coordinating with two chloride anions to adopt a square pyramidal geometry. The characterization of the all acetate complexes [(DEHC-H)<sub>2</sub>M](CH<sub>3</sub>COO)<sub>2</sub> pointed to two moles of tridentate [(DEHC-H) ligand in thione form coordinate with the metal ions to fill six sites forming octahedral geometry with two moles of acetate ions as counter ions. It is worth noting that tridentate thiosemicarbazone [(DEHC-H) ligand coordinates through the nitrogen pyridyl, thionic sulfur and the azomethine nitrogen atoms. Interestingly, two forms were observed and characterized in the thiosemicarbazone metal chloride and acetate complexes solutions, keto (thione) (I) and enol (thiol) (II) forms as an equilibrium mixture which is named thione-thiol tautomerism. See **Figure 4**.



**Figure 4: Thione and thiol tautomerism of thiosemicarbazone derivative (DEHC-H) ligand**

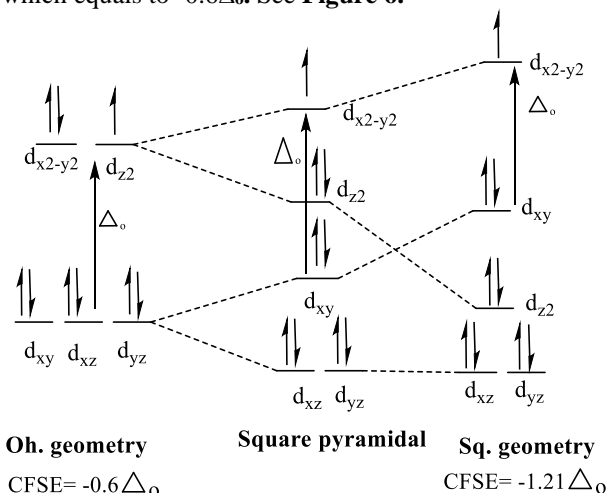
### 3.2 The preference structural forms and oxidation states of Cu, Co, Ni and Zn ions in their element complexes.

The public sight of the geometrical forms and the oxidation states of Cu, Co, Ni and Zn ions in their element complexes and their preferences to them were concluded in our contribution elsewhere [44]. As related with the oxidation states, the Copper is preferred Copper(I) and Copper(II), Nickel is adopted Nickel(II) more than Nickel(I) and Nickel(III) whereas Zinc showed Zinc(II) ions in whole its complexes. The survey is interested too with the preferences of the metal complexes to various geometrical forms. It is noticed that Ni(II) ion is appeared in its complexes to more than one coordination geometrical structure such as octahedral, trigonal pyramidal, square planar, tetrahedral and T-shaped. The octahedral geometry was the most adopted and then square planar in Ni(II) complexes due to the Crystal Field Stabilization Energy value which equals to  $-1.2 \Delta_o$  and  $-2.44 \Delta_o + P$  in octahedral and square planar geometries respectively. The  $\Delta_o$  represents the crystal field splitting parameter while P indicates to the required energy to paring electrons. Apparently, the crystal field stabilization energy (CFSE) of square planar is higher than the crystal field stabilization energy of octahedral so the square planar complexes have high stability than octahedral. In spite of the above, the complexes preference of the square planar or octahedral depends on  $\Delta_o$  (the crystal field splitting parameter) and P (the required energy to paring electrons) values which mean the complexes with higher  $\Delta_o$  tend to coordinating as square planar geometry. See **Figure 5**.



**Figure 5: The Nickel(II),  $d^8$  compounds supported via Crystal Field Theory the preference of octahedral geometry than square planar.**

The Cu(II) compounds coordinated and appeared in different coordination geometry like square planar, octahedral, square pyramidal, pyramidal trigonal bipyramidal and trigonal pyramidal. But the preference was to square planar and less to octahedral geometry and this is related to the highly structural stabilization in square planar geometry which cause higher value of the Crystal Field Stabilization Energy which equals to  $-1.21 \Delta_o$  than its value in octahedral which equals to  $-0.6 \Delta_o$ . See **Figure 6**.

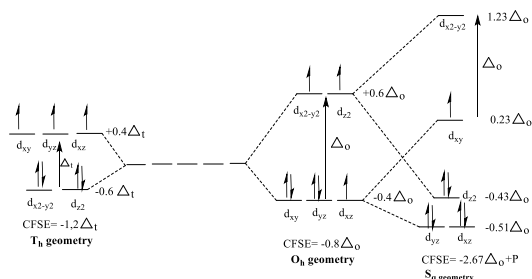


**Figure 6: The Copper(II),  $d^9$  compounds supported via Crystal Field Theory the preference of a square planar than an octahedral geometry.**

The Co(II) compounds exhibited the various styles of coordination such as the square planar, tetrahedral and octahedral geometries in the above survey. The

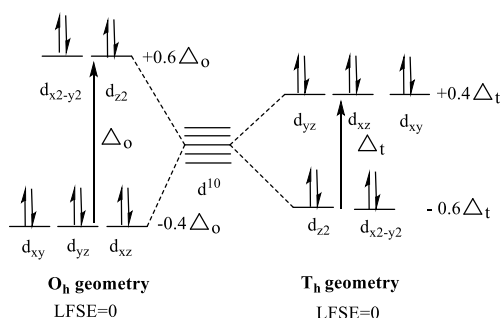


preference to a square planar is clear than a tetrahedral and an octahedral geometries due to the high value of the crystal field stabilization energy in square planar than its value in tetrahedral or octahedral. See **Figure 7**.



**Figure 7:** The Cobalt(II),  $d^7$  compounds supported via Crystal Field Theory the preference of a square planar than a tetrahedral and an octahedral geometry.

The Zn(II) compounds were also under survey, they adopted tetrahedral, trigonal pyramidal, square pyramidal, trigonal bipyramidal and octahedral geometries but the utmost widespread was tetrahedral geometry. Theoretically and according to the Ligand Field Stabilization Energy values in both the tetrahedral and octahedral geometries, there is no tendency to one from the other due to the zero value of Ligand Field Stabilization Energy in these geometries. The big preference of the Zn(II) compounds to compose tetrahedral complexes may be due to the structural form and the structural steric hindrance of the free ligand and thermochemical circumstances around the metal ions in their compounds [45-46]. See **Figure 8**.



**Figure 8:** The Zinc(II),  $d^{10}$  compounds supported via Crystal Field Theory there is no preference towards a tetrahedral or an octahedral geometry.

### 3.3. FT-IR Spectral investigation

To reach and to confirm the structural forms of the synthesized ligands and their element complexes, various techniques ought to be employed with complete characterization. The great technique is FT-IR spectroscopy which is dedicated to characterize the

functional groups and to locate the coordination mode between the metal ions and functional groups in the free ligands. The FT-IR spectral data of the thiosemicarbazone derivative, (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide (DEHC-H) ligand and its Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes are concluded in the procedural part and exhibited in **Table 1**. The FT-IR spectrum of (DEHC-H) ligand exhibited different prominent peaks like  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{S})$  which located at 1466 and 1300  $\text{cm}^{-1}$  respectively. The  $\nu(\text{N}-\text{H})$  and  $\delta(\text{N}-\text{H})^1$  bands appeared at 3421 and 1586  $\text{cm}^{-1}$  sequentially. Another significant bands were noticed in the spectrum of the (DEHC-H) free ligand which are the  $\delta(\text{N}-\text{H})^2$  and  $\nu(\text{C}=\text{O})$  bands which were observed at 1532 and 1663  $\text{cm}^{-1}$  respectively and this is a good indication to the presence of interligand hydrogen bonding [47]. As well as the FT-IR spectrum of the free ligand did not show any bands in the range 2500-2600  $\text{cm}^{-1}$  which is assigned to S-H vibration confirming the thione formula of the thiosemicarbazone free ligand [48]. As compared to the thiosemicarbazone (DEHC-H) free ligand, the FT-IR spectra of the synthesized metal complexes,  $[(\text{DEHC-H})\text{ZnCl}_2]$ ,  $[(\text{DEHC-H})_2\text{Cu}](\text{CH}_3\text{COO})_2$ ,  $[(\text{DEHC-H})_2\text{Co}](\text{CH}_3\text{COO})_2$ ,  $[(\text{DEHC-H})_2\text{Ni}](\text{CH}_3\text{COO})_2$  and  $[(\text{DEHC-H})_2\text{Zn}](\text{CH}_3\text{COO})_2$  showed a remarkable red shift of the  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{S})$  bands which appeared at (1412-1439)  $\text{cm}^{-1}$  and (1258-1281)  $\text{cm}^{-1}$  which confirm the free ligand coordinates as thione form with metal ion. But with regarding to the  $[(\text{DEHC})\text{CuCl}]$ ,  $[(\text{DEHC})\text{CoCl}]$  and  $[(\text{DEHC})\text{NiCl}]$  complexes, the C=N group was observed in the range above with the absence of the C=S band in the free ligand indicating that the free ligand coordinates as thiol form in these complexes. The nitrogen atom in C=N group and the sulfur atom in C=S group have clear properties to donate electrons to the central metal ion which is deemed electropositive group in the complexes. This would be decrease the distinctive double bond and the force constant in C=N and C=S bonds. So these bonds appeared at red shift and lower wave number as compared with the (DEHC-H) free ligand. The FT-IR spectra assignments illustrated that the C=O group did not take part in the coordination between free ligand and the metal ions because the carbonyl vibration frequency in the all synthesized complexes nearly at the same its value in the free ligand. Another important output from the FT-IR spectra of the metal complexes was the existence of the intralegand hydrogen bonds in  $[(\text{DEHC-H})\text{ZnCl}_2]$ ,  $[(\text{DEHC-H})_2\text{Cu}](\text{CH}_3\text{COO})_2$ ,  $[(\text{DEHC-H})_2\text{Co}](\text{CH}_3\text{COO})_2$ ,  $[(\text{DEHC-H})_2\text{Ni}](\text{CH}_3\text{COO})_2$  and  $[(\text{DEHC-H})_2\text{Zn}](\text{CH}_3\text{COO})_2$  complexes in the range (1532-1558  $\text{cm}^{-1}$ ) attributed to  $\delta(\text{N}-\text{H})^2$  band to confirm the coordinating of the  $[(\text{DEHC-H})$  ligand in these complexes as thion form.

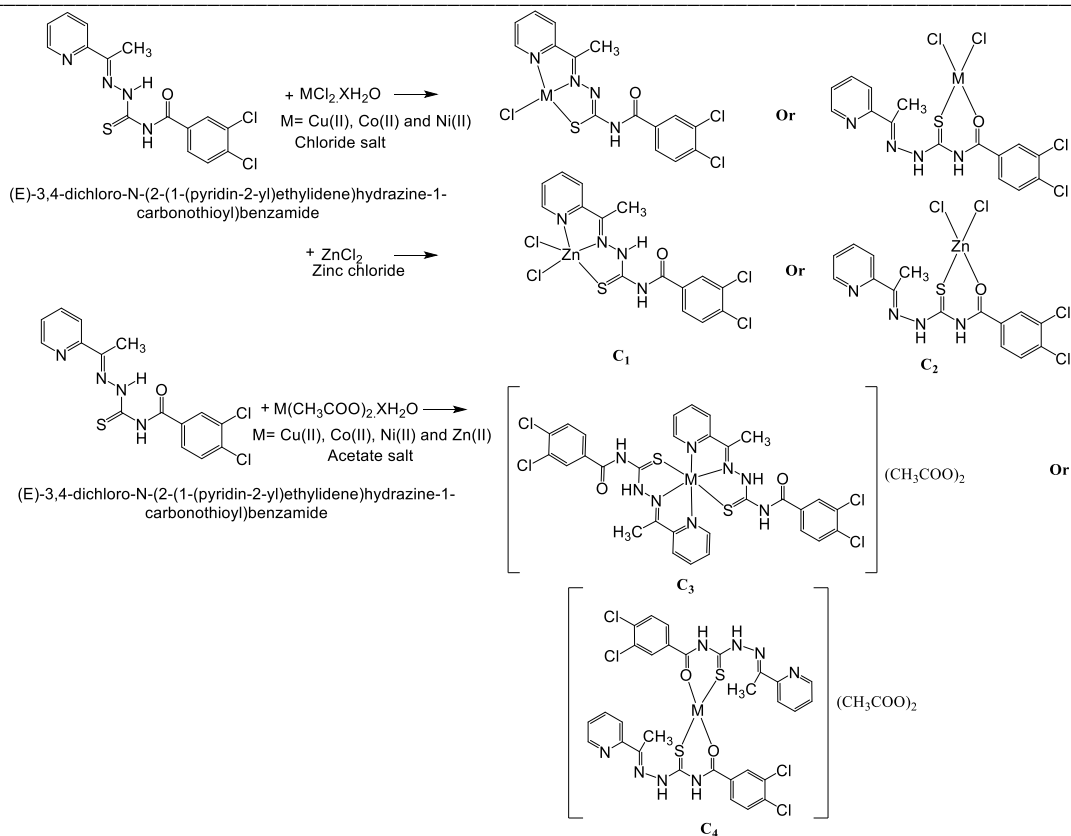
While the FT-IR spectra of the [(DEHC)CuCl], [(DEHC)CoCl], [(DEHC)NiCl] complexes showed the absence of this bond confirming the thiol form of the free ligand in their complexes. In consonance with the structure of the thiosemicarbazone (DEHC-H) ligand and its containing of different functional groups like C=N band in pyridyl moiety, C=N and N-H in the skeletal of the free ligand, C=S and C=O groups with different donor atoms such as nitrogen, sulfur and oxygen, more than one coordination forms are probable to synthesis. See **Scheme 3**. The C<sub>1</sub> or C<sub>2</sub> forms are potential to synthesis as the chloride compounds whereas the acetate complexes may be appear in the C<sub>3</sub> or C<sub>4</sub> complexes. From FT-IR spectra of the free ligand and its complexes, it is clear that the chloride and acetate complexes were created as C<sub>1</sub> and C<sub>3</sub> forms respectively due to the fixed vibration frequency of C=O group and the red shift of C=S and C=N groups in the element complexes comparing with

their (DEHC-H) ligand. All the above characterization face to and confirm the coordination between the thiosemicarbazone (DEHC-H) ligand as tridentate ligand with central metal ions via the sulfur and nitrogen atoms in C=S and C=N groups respectively while the third site is populated with nitrogen atom from the pyridyl group. Another significant evidence to confirm complexes in C<sub>1</sub> form in chloride complexes and C<sub>3</sub> form in acetate complexes was the exhibition of two new peaks in the spectra of the metal complexes at 436-467 cm<sup>-1</sup> and 517-548 cm<sup>-1</sup> that are attributed to M-S and M-N peaks. See **Figure 9**. This finding of the coordination style broadly supports our work in the previous studies in this area linking thiosemicarbazone derivatives with different metal ions like Copper(II), Nickel(II) and Zinc(II) ions via their coordination of the thiosemicarbazone ligands as tridentate ligands by the nitrogen pyridyl group, nitrogen C=N group and thio C=S group [44].

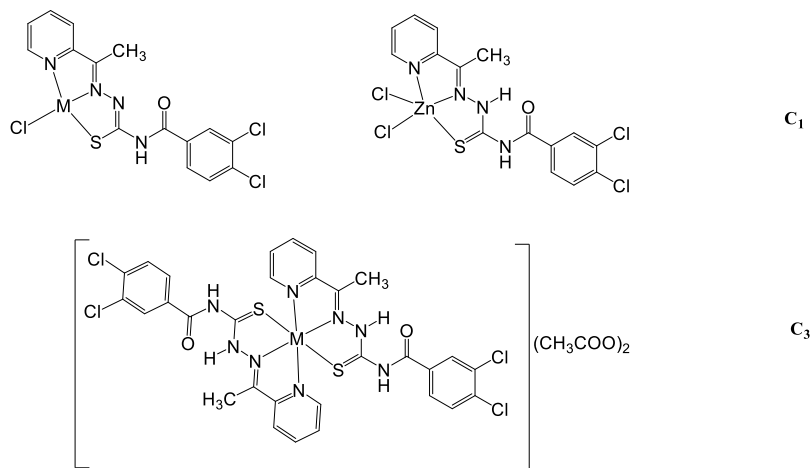
**Table 1:** FT-IR spectral identification (cm<sup>-1</sup>) of (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl) ethylidene) hydrazine-1-carbonothioyl) benzamide (DEHC-H) ligand and its Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes.

Compound.	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\delta(\text{N-H})^1$	$\delta(\text{N-H})^2$	$\nu(\text{C=N})$	$\nu(\text{C=S})$	$\nu(\text{M-S})$	$\nu(\text{M-N})$
(DEHC-H)	3421	1663	1586	1532	1466	1300	-	-
[(DEHC)CuCl]	3306	1660	1589	-	1438	-	444	548
[(DEHC-H) <sub>2</sub> Cu](AC) <sub>2</sub>	3256	1663	1589	1555	1435	1269	441	542
[(DEHC)CoCl]	3383	1659	1601	-	1439	-	440	517
[(DEHC-H) <sub>2</sub> Co](AC) <sub>2</sub>	3345	1663	1593	1532	1438	1281	451	521
[(DEHC)NiCl]	3322	1660	1566	-	1435	-	467	538
[(DEHC-H) <sub>2</sub> Ni](AC) <sub>2</sub>	3302	1662	1589	1558	1412	1258	436	529
[(DEHC-H)ZnCl <sub>2</sub> ]	3345	1660	1585	1554	1423	1272	443	525
[(DEHC-H) <sub>2</sub> Zn](AC) <sub>2</sub>	3318	1661	1589	1559	1412	1261	440	529

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**Scheme 3: The predictable complexes  $C_1$ - $C_4$  forms of chloride and acetate metal complexes of the thiosemicarbazone derivative ligand (DEHC-H).**



**Figure 9: The  $C_1$  and  $C_3$  metal chloride and acetate complexes forms of the thiosemicarbazone ligand (DEHC-H).**

### 3.4. Electronic spectral survey

The ultra-violet visible spectra of the (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide ligand and its Cu(II), Co(II), Ni(II) and Zn(II) compounds were achieved at 25°C in

N,N-Dimethylformamide (DMF) solvent. **Table 2** clarified the electronic spectral assignments in nm unit for all the synthesized compounds. The spectra of the free ligand (DEHC-H) exhibited two peaks at

290(13900) and 347 nm (11420  $M^{-1}cm^{-1}$ ) associated with the intra ligand  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions respectively of the C=C in the phenyl, C=N in the pyridyl, C=S in thione and C=O groups in the free ligand. The Zn(II) complexes, [(DEHC-H)ZnCl<sub>2</sub>] and [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> showed red shift in their intra ligand  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions to 297(12710)-295(13140) and 363(9531)-368 nm (10310  $M^{-1}cm^{-1}$ ) sequentially as compared to the free ligand (DEHC-H) itself. As expected and according to the fill d-orbital in  $d^{10}$  Zn compounds and their diamagnetic manner no  $d-d$  transitions were observed in their electronic spectra. The electronic spectra of the chloride compounds, [(DEHC)CuCl], [(DEHC)CoCl] and [(DEHC)NiCl] confirm the four coordinate square planar geometrical shape around the central metal ions Cu(II), Co(II) and Ni(II) via presence of a single broad peak at 595(20), 607(31) and 603 nm (18  $M^{-1}cm^{-1}$ ) respectively which are attributed to  $d_{xy}-d_{x^2-y^2}$  transition. See Figures 10-11. As well as, the chloride compounds revealed red shift of the intra ligand peaks at  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions to 293(10810)-295(9400) and 361(8700)-362 nm (8530  $M^{-1}cm^{-1}$ ) sequentially. The acetate complexes, [(DEHC-H)<sub>2</sub>M](CH<sub>3</sub>COO)<sub>2</sub>, M=Cu, Co and Ni revealed shift of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions to the high wavelength in comparison with the DEHC-H ligand to appear in the range 292(9910)-294(10300) and 357(8940)-362 nm (8810  $M^{-1}cm^{-1}$ ) sequentially. The remarkable peak in [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub> and [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub> complexes was located in turn at 625(45) and 632 nm (38  $M^{-1}cm^{-1}$ ) which are assigned to  $d(t_{2g})-d(e_g)$  transition emphasizing the octahedral geometry in these compounds. From Table 2 and Figure 12 it is apparent that [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> adopted octahedral geometry through the observation of two peaks at 600(23) and 960 nm (26  $M^{-1}cm^{-1}$ ) which are assigned to  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  ( $\nu_2$ ) and  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  ( $\nu_1$ ) transitions sequentially. These two peaks noticed with absence of the  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  ( $\nu_3$ ) transition in spite of Ni(II) complexes should generally reveal three peaks  $\{ {}^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1), {}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3) \}$  transitions. This is may be due to the combination between  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$  transitions to give one broad transition with high intensity. The spectrochemical parameters 10Dq, B and  $\beta$  of the octahedral [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> compound are calculated to be 1036  $cm^{-1}$ , 829  $cm^{-1}$  and 0.79 respectively. What is interesting about the data in Table 2 is that the red shift of the intra ligand peaks at  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions which appeared at high wavelength as compared to their values in the free ligand DEHC-H. This is may be attributable to the high electropositivity of metal ion which withdraw electron density from the multiple bonds like C=N and

C=S towards it and then reduce the multiple bond characteristic as well as the effect of the resonance conjugation between the aryl and the C=O groups considers main factor to present the long wavelength. These results seem to be consistent with other research, which found thiosemicarbazone derivative of Ni(II), Co(II) and Cu(II) compounds adopted octahedral geometry[49-51] and the other that revealed the square planar geometry of these metal derivatives [52-53].

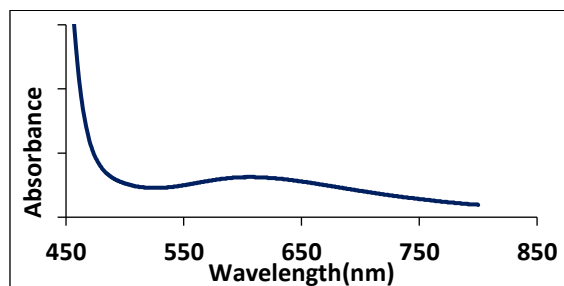


Figure 10: The ultra-violet visible spectrum of square planar [(DEHC)CuCl] compound.

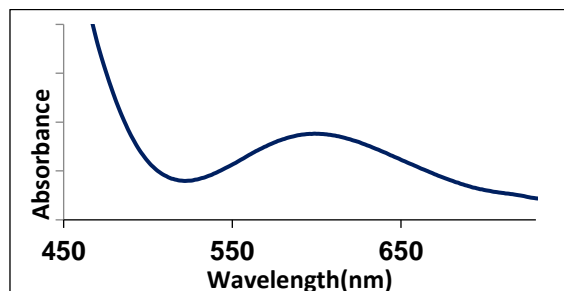


Figure 11: The ultra-violet visible spectrum of square planar [(DEHC)NiCl] compound.

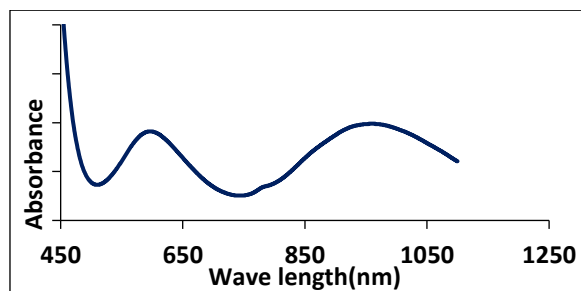


Figure 12: The ultra-violet visible spectrum of octahedral [(DEHC-H)<sub>2</sub>Ni](AC)<sub>2</sub> compound.

**Table 2: Electronic spectral assignment (nm) of the Cu(II), Co(II), Ni(II) and Zn(II) compounds of novel (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl) benzamide ligand as well as to the free ligand (DEHC-H) in DMF solvent. AC=(CH<sub>3</sub>COO<sup>-</sup>)**

Compound.	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$d_{xy} \rightarrow d_{x^2-y^2}$	$d(t_{2g}) \rightarrow d(e_g)$	${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) ( $\nu_2$ )	${}^3A_{2g} \rightarrow {}^3T_{2g}$ ( $\nu_1$ )	$\Delta$ (cm) <sup>-1</sup>	B (cm) <sup>-1</sup>	$\beta$
(DEHC-H)	290	347	---	---	---	---	---	---	---
[(DEHC)CuCl]	293	361	595	---	---	---	---	---	---
[(DEHC)CoCl]	295	362	607	---	---	---	---	---	---
[(DEHC)NiCl]	293	362	603	---	---	---	---	---	---
[(DEHC-H)ZnCl <sub>2</sub> ]	297	368	---	---	---	---	---	---	---
[(DEHC-H) <sub>2</sub> Cu](AC) <sub>2</sub>	292	357	---	625	---	---	---	---	---
[(DEHC-H) <sub>2</sub> Co](AC) <sub>2</sub>	294	362	---	632	---	---	---	---	---
[(DEHC-H) <sub>2</sub> Ni](AC) <sub>2</sub>	292	360	---	---	600	960	1036	829	0.79
[(DEHC-H) <sub>2</sub> Zn](AC) <sub>2</sub>	295	363	---	---	---	---	---	---	---

### 3.5. Magnetic moment measurements

Predominantly, the magnetic moment data are employed jointly with the assignments of UV-vis. spectra to come up with the oxidation state, oxidation number, stereochemistry and geometrical coordination forms of the metal ions in their complexes. The theoretical magnetic moment equals to  $[n(n+2)]^{1/2}$  when n= number of unpaired electrons. **Table 3** is illustrated the magnetic moment data of {[ (DEHC)CuCl], [(DEHC)CoCl], [(DEHC)NiCl], [(DEHC-H)ZnCl<sub>2</sub>], [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub>} complexes which were measured via a Johnson Matthey magnetic susceptibility balance at room temperature. The magnetic moment data refers to the paramagnetic manner of the Cu(II) complexes, [(DEHC)CuCl] and [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>, Co(II) complexes [(DEHC)CoCl] and [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub> and Ni(II) complex [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub>. While the Ni(II) complex [(DEHC)NiCl] and Zn(II) complexes [(DEHC-H)ZnCl<sub>2</sub>] and [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> owned diamagnetic behavior. The observed magnetic moment values (1.81 BM and 2.12 BM) for square planar [(DEHC)CuCl] and octahedral [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub> indicate the presence of a single unpaired electron containing d<sup>9</sup> Cu(II) ion. The [(DEHC)CoCl] and [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub> complexes exhibit the observed  $\mu_{eff.} = 2.42$  BM and 5.04 BM to confirm the square planar and high spin in octahedral geometry respectively for these d<sup>7</sup> Co(II) compounds. The magnetic moment of Ni(II)

compound [(DEHC)NiCl] equals to zero emphasizing the square planar around the Ni(II) ion and the diamagnetic properties of it whilst its value for the [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> complex was 3.23 BM confirming the octahedral geometry around the Ni(II) ion. Ultimately, the magnetic moment values were zero of d<sup>10</sup> Zn(II) complexes [(DEHC-H)ZnCl<sub>2</sub>] and [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> which asserted their diamagnetic manner. The theoretical effective moments of the Cu(II) complexes, square planar [(DEHC)CuCl] and octahedral [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub> equal to 1.73 BM and the Co(II) complexes square planar [(DEHC)CoCl] and high spin octahedral [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub> equal to 1.73 BM and 3.88 BM respectively while in the Ni(II) complex [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> equal to 2.83 BM. There is a minimum change, but under control and satisfied explanation, between the theoretical and the observed magnetic moment values due to the effect of ligand field of the square planar and octahedral geometry leading to ineffectual orbital moment quenching. The observed results are consistent with data reported in the previous studies [43-44, 54-55].

**Table 3: The magnetic data of the Cu(II), Co(II), Ni(II) and Zn(II) complexes of (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl) benzamide ligand, AC= (CH<sub>3</sub>COO<sup>-</sup>)**

No.	Complex	d orbital electronic configuration	Observed magnetic moment B.M.	Theoretical magnetic moment B.M.
1	[(DEHC)CuCl]	d <sup>9</sup> (d <sub>xz</sub> <sup>2</sup> d <sub>yz</sub> <sup>2</sup> d <sub>z<sup>2</sup></sub> <sup>2</sup> d <sub>xy</sub> <sup>2</sup> d <sub>x<sup>2</sup>-y<sup>2</sup></sub> <sup>1</sup> )	1.81	1.73
2	[(DEHC)CoCl]	d <sup>7</sup> (d <sub>xz</sub> <sup>2</sup> d <sub>yz</sub> <sup>2</sup> d <sub>z<sup>2</sup></sub> <sup>2</sup> d <sub>xy</sub> <sup>1</sup> d <sub>x<sup>2</sup>-y<sup>2</sup></sub> <sup>0</sup> )	2.42	1.73
3	[(DEHC)NiCl]	d <sup>8</sup> (d <sub>xz</sub> <sup>2</sup> d <sub>yz</sub> <sup>2</sup> d <sub>z<sup>2</sup></sub> <sup>2</sup> d <sub>xy</sub> <sup>2</sup> d <sub>x<sup>2</sup>-y<sup>2</sup></sub> <sup>0</sup> )	diamagnetic	zero
4	[(DEHC-H)ZnCl <sub>2</sub> ]	d <sup>10</sup> (d <sub>xz</sub> <sup>2</sup> d <sub>yz</sub> <sup>2</sup> d <sub>xy</sub> <sup>2</sup> d <sub>z<sup>2</sup></sub> <sup>2</sup> d <sub>x<sup>2</sup>-y<sup>2</sup></sub> <sup>2</sup> )	diamagnetic	zero
5	[(DEHC-H) <sub>2</sub> Cu](AC) <sub>2</sub>	d <sup>9</sup> (t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>3</sup> )	2.12	1.73
6	[(DEHC-H) <sub>2</sub> Co](AC) <sub>2</sub>	d <sup>7</sup> high spin (t <sub>2g</sub> <sup>5</sup> e <sub>g</sub> <sup>2</sup> )	5.04	3.88
7	[(DEHC-H) <sub>2</sub> Ni](AC) <sub>2</sub>	d <sup>8</sup> (t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>2</sup> )	3.23	2.83
8	[(DEHC-H) <sub>2</sub> Zn](AC) <sub>2</sub>	d <sup>10</sup> (t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>4</sup> )	diamagnetic	zero

### 3.6. Molar Conductance probes

The investigation of the molar conductivity values of the Cu(II), Co(II), Ni(II) and Zn(II) compounds of the thiosemicarbazone free ligand (DEHC-H), (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide in DMSO solvent were accomplished at 25°C. The used range of their concentration were 25\*10<sup>-6</sup>-1.21\*10<sup>-2</sup> M. The molar conductivity measurements have been usually employed to inspect the electrolytic manner of the synthesized element complexes and then altogether in cooperation with the other techniques it is able to reach to the structural form of the metal complexes, the style of coordination and the presence or absent of the anion groups outside the coordination sphere. The molar conductance value (Λ<sub>m</sub>) was calculated according to the equation: Λ<sub>m</sub> = 10<sup>3</sup> K̄.C<sup>-1</sup> (K̄= specific conductance and C= molar concentration of the complexes). The most striking result to emerge from the conductivity data is that the higher molar conductivity values of the (DEHC-H) acetate complexes than its corresponding chloride complexes. In which acetate complexes appeared at 1\*10<sup>-4</sup> M in the extent 77.669 -125.070 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> while chloride complexes at 10.787 - 16.398 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. These data are brilliant evidence enhancing the ionic electrolytic manner and the structural forms [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> compounds of the acetate complexes in (1:2 M:L) mole ratio. While the [(DEHC)CuCl], [(DEHC)CoCl], [(DEHC)NiCl], [(DEHC-H)ZnCl<sub>2</sub>] compounds of the chloride complexes exhibited non electrolytic behavior with (1:1 L:M) mole ratio. This finding is consistent with pertinent prior studies [56-57]. The Friedrich

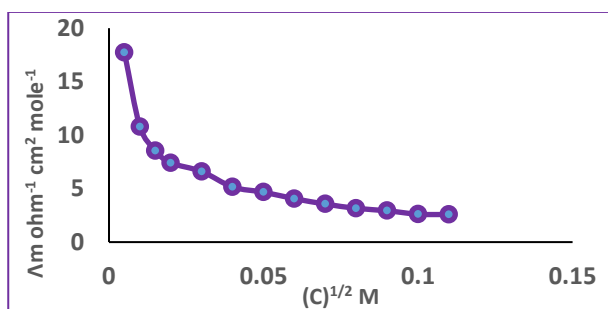
Kohlrausch equation {Λ<sub>m</sub> = Λ<sub>m</sub><sup>0</sup> - K(C)<sup>1/2</sup>, K is the Kohlrausch coefficient} was employed to find out the nature of the electrolytic compound via plot the molar conductivity values (Λ<sub>m</sub>) against the square root of the element complexes concentrations (C)<sup>1/2</sup>, see **Figures 13-14**. Another surprising obtained result is the straight-line relationship between K̄ and C and this is caused by the high concentration that cause large number of ions as well as to varied dissociation degree (α) [58]. Therefore, it is easy to notice the consistency between the straight line of the theoretical equation (C = 10<sup>3</sup> K̄.Λ<sub>m</sub><sup>-1</sup>) and the applied K̄ and C values. Interestingly, the molar conductance at zero concentration Λ<sub>m</sub><sup>0</sup> and the dissociation degree constant K<sub>d</sub> values were obtained of the element complexes via drawing the Kraos equation (Λ<sub>m</sub>.C = K<sub>d</sub>.Λ<sub>m</sub><sup>0.2</sup> (1/Λ<sub>m</sub>) - K<sub>d</sub>.Λ<sub>m</sub><sup>0</sup>). **Figures 15-16** showed the employed Kraos equation to Ni(II) complexes. **Table 4** clarified the K̄, Λ<sub>m</sub>, Λ<sub>m</sub><sup>0</sup> and K<sub>d</sub> parameters values of the prepared complexes. When we are looking in the first glance at the **Table 4**, it is easy to classify and arrange the metal complexes as the molar conductance ascending order, Ni(II) > Co(II) > Cu(II) > Zn(II) complexes. The molar conductance of the Ni(II), Co(II), Cu(II) and Zn(II) acetate compounds are found at 125.070, 108.900, 97.324 and 77.669 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> sequentially. Whereas the chloride complexes gave them at 16.398, 13.826, 11.682 and 10.787 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> sequentially. In the other side, the dissociation constant which elucidate the nature of rigidity of the bonding between the free ligand and central metal ion, is listed in **Table 4** and ordered in 3.734-8.847 mol/cm<sup>3</sup> and 36.624-79.190 mol/cm<sup>3</sup> of chloride and acetate compounds. A comparison of the K<sub>d</sub> results reveals that the chloride compounds have big rigidity bond between the thiosemicarbazone ligand, the metal ion and chloride

groups in [(DEHC)MCl], M= Cu, Co and Ni, [(DEHC-H)ZnCl<sub>2</sub>] compounds whilst the acetate compounds exhibit the comparatively weakness bond in [(DEHC-H)<sub>2</sub>M](CH<sub>3</sub>COO)<sub>2</sub>, M= Cu, Co, Ni and Zn. These are because of the strong chloride-chelating group in chloride compounds than the bigger size counter ion

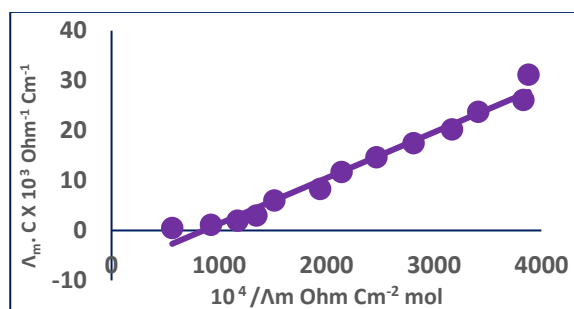
acetate, which appeared in the coordination between two molecules of free ligand and the metal ion in acetate compounds. All of the reasons mentioned above lead to the high K<sub>d</sub> obtained values in chloride compounds than acetate compounds.

**Table 4:** The specific conductance  $\bar{K}$  and Molar conductance  $\Lambda_m$  at 0.0001 mol.L<sup>-1</sup>, zero concentration  $\Lambda_0$  and dissociation constant K<sub>d</sub> values for the Cu(II), Co(II), Ni(II) and Zn(II) compounds of the thiosemicarbazone (DEHC-H) free ligand.

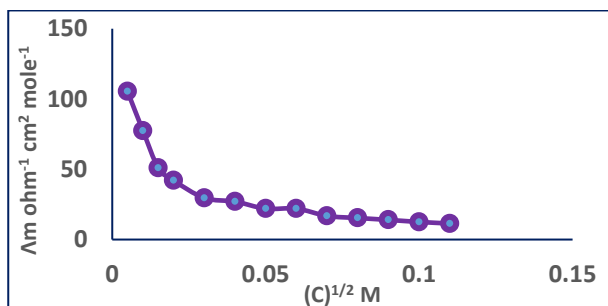
No.	Compound	$\bar{K} \cdot 10^{-6}$ (ohm <sup>-1</sup> cm <sup>-1</sup> )	$\Lambda_m$ (Ohm <sup>-1</sup> Cm <sup>2</sup> mol <sup>-1</sup> )	$\Lambda_0$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	K <sub>d</sub> X 10 <sup>-2</sup> (mol.Cm <sup>-3</sup> )
1	[(DEHC)CuCl]	1.168	11.682	37.290	5.648
2	[(DEHC)CoCl]	1.383	13.826	41.357	6.045
3	[(DEHC)NiCl]	1.639	16.398	59.058	8.847
4	[(DEHC-H)ZnCl <sub>2</sub> ]	1.076	10.787	31.349	3.734
5	[(DEHC-H) <sub>2</sub> Cu](AC) <sub>2</sub>	9.732	97.324	169.569	49.376
6	[(DEHC-H) <sub>2</sub> Co](AC) <sub>2</sub>	10.890	108.900	180.229	55.485
7	[(DEHC-H) <sub>2</sub> Ni](AC) <sub>2</sub>	12.507	125.070	213.406	79.190
8	[(DEHC-H) <sub>2</sub> Zn](AC) <sub>2</sub>	7.766	77.669	124.523	36.624



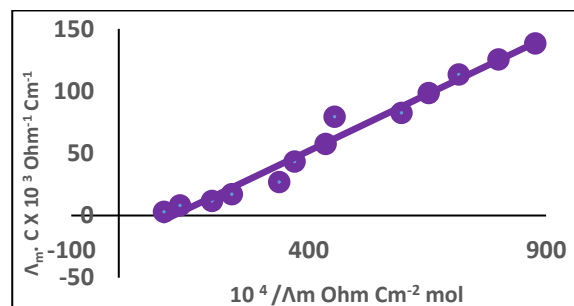
**Figure 13:** The molar conductivity  $\Lambda_m$  against  $(C)^{1/2}$  for [(DEHC-H)ZnCl<sub>2</sub>] compound.



**Figure 15:**  $\Lambda_m \cdot C \times 10^3$  against  $10^4 / \Lambda_m$  for [(DEHC-H)ZnCl<sub>2</sub>] compound.



**Figure 14:** The molar conductivity  $\Lambda_m$  against  $(C)^{1/2}$  for [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> compound.



**Figure 16:**  $\Lambda_m \cdot C \times 10^3$  versus  $10^4 / \Lambda_m$  for [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> compound.

### 3.7 Solubility check

According to the truth ‘‘like dissolves like’’ and the ability to know the polarity and the ionic and nonionic behavior of the various compounds from the results of solubility test so the solubility of the free ligand DEHC-H and their Cu(II), Co(II), Ni(II) and Zn(II)

complexes were obtained using diverse nonpolar and polar solvents. The using solvents were  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_{12}$  and  $\text{CCl}_4$  as nonpolar solvents and  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , acetone, me-CN, ethyl acetate, water, dimethyl formamide and dimethyl sulfoxide as polar solvents. The solubility test results of the free ligand and their metal complexes are given in **Table 5**. It is clear from **Table 5** as well as it is interesting to note that the chloride complexes are generally insoluble or poor soluble in polar solvents  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , acetone, me-CN and ethyl acetate but soluble or poor soluble in nonpolar solvents  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_{12}$  and  $\text{CCl}_4$ . In the other side the acetate complexes showed high solubility in polar solvents with no solubility in nonpolar solvents. These different results of the solubility test of the prepared chloride and acetate complexes lead to enhance the nonionic features with neutral structure  $[(\text{DEB})\text{MCl}]$ ,  $\text{M}=\text{Cu}$ ,  $\text{Co}$  and  $\text{Ni}$  ions and  $[(\text{DEB-H})\text{ZnCl}_2]$  of chloride complexes and ionic structure  $[(\text{DEB-H})_2\text{M}](\text{CH}_3\text{COO})_2$  of acetate complexes. Another remarkable thing that chloride and acetate complexes were completely soluble in dimethyl formamide and dimethyl sulfoxide solvents because of their high polarity as well as new complexes may be prepared as solvent-complex complexation while the free ligand and its element complexes were not soluble in  $\text{H}_2\text{O}$  at all.

### 3.8. Electrochemical investigation of the reduction/oxidation properties

The bunch of combined factors effecting on the electrochemical features of the element complexes like coordination number, charge kind, the size of chelated ring group, the swapping groups on the ring, the unsaturation allocation and the axial ligation degree [59-60]. The oxidation state of metal ions and basicity manner of the free ligands are essential factors influencing of the complexes composition. Therefore, the electrochemical probes are deemed as remarkable study due to its ability to emphasize the oxidation state of the metal ion in its complexes and to detect the spectral and structural variations joining with electron transfer. Cyclic voltammetry is considered as one of the most important technique to investigate the electrochemical properties of the metal ions. Its importance is due to the rapid reduction/oxidation data of the metal complexes can be obtained everywhere of the used potential range. The redox potential parameter is important to represent the electron transfer by the redox carrier in addition to its role as redox catalyst. The redox behavior of the free thiosemicarbazone ligand (DEHC-H) and its Cu(II), Co(II) and Ni(II) complexes,  $[(\text{DEHC})\text{CuCl}]$ ,  $[(\text{DEHC})\text{CoCl}]$ ,  $[(\text{DEHC})\text{NiCl}]$ ,  $[(\text{DEHC-H})_2\text{Cu}](\text{CH}_3\text{COO})_2$ ,  $[(\text{DEHC-H})_2\text{Co}](\text{CH}_3\text{COO})_2$  and

$[(\text{DEHC-H})_2\text{Ni}](\text{CH}_3\text{COO})_2$  have been probed via CV technique. They were accomplished in the acetonitrile solvent potential range +2.0 to -2.0 volt at gradual scan rates (100-1000 millivolts/sec) against Ag/AgCl as reference electrode and the measured solution containing  $1 \times 10^{-1}$  M of the supporting electrolyte, TBAHFP (tetra butyl ammonium hexa fluoro phosphate) and  $1 \times 10^{-3}$  M of the electro active species under investigation. Cyclic voltammograms of the free ligand and its complexes did not show any peaks identified to the free ligand but there are different observable peaks corresponding to the metal centered processes. Another important obtained data showed that the prepared complexes did not suffer from dissociation through various and frequent scan rates. **Tables 6-7** concluded the assignments of the redox couple and the observed electrochemical data of the ligand (DEHC-H) and its Cu(II), Co(II) and Ni(II) complexes respectively.

The cyclic voltammograms of Cu(II) chloride and acetate complexes  $[(\text{DEHC})\text{CuCl}]$  and  $[(\text{DEHC-H})_2\text{Cu}](\text{CH}_3\text{COO})_2$  showed a single quasireversible cathodic system related with the Cu(II)/Cu(I) redox couple process which observed at (-1.1439 volt vs  $\text{Fc}/\text{Fc}^+$ ) and (-1.0728 volt vs  $\text{Fc}/\text{Fc}^+$ ) respectively (**Table 6** and **Figures 17-18**). The obtained quasireversible behavior was confirmed via the various facts: 1) The value of ( $I_p^c / I_p^a$ ) ratio is less than one. 2) In the diverse employed scan rates, the voltage of the Cu(II)/Cu(I) peak shifted to different potentials. 3) The square root of the various scan rates connected with the peak currents as straight-line relationship. 4) The potential separation ( $\Delta E = E_p^a - E_p^c$ ) between two peaks in the same process is larger than 59 millivolts. The observed  $\Delta E$  values are 235 millivolts and 354 millivolts for  $[(\text{DEHC})\text{CuCl}]$  and  $[(\text{DEHC-H})_2\text{Cu}](\text{CH}_3\text{COO})_2$  sequentially and this deviation may be due to the structural-geometrical rearrangement accompanying the conversion Cu(II)/Cu(I) redox couple. This finding broadly supports the work of previous studies in this area linking Cu(II) complexes with the quasireversible process [61-62].

The cyclic voltammograms of chloride and acetate complexes of the Ni(II) ion,  $[(\text{DEHC})\text{NiCl}]$  and  $[(\text{DEHC-H})_2\text{Ni}](\text{CH}_3\text{COO})_2$  exhibited analogous features in the examined potential range +2.0 to -2.0 volt. Two successive easily distinguishable irreversible oxidation waves located at (+0.491 and +0.721 volt against  $\text{Fc}/\text{Fc}^+$ ) in chloride compound and at (+0.449 and +0.656 volt against  $\text{Fc}/\text{Fc}^+$ ) in the acetate compound. As compared to analogous Ni(II) complexes [63], the irreversible electrode couples authorize attribution to a single electron oxidation system Ni(I)/ Ni(II) couple and Ni(II)/ Ni(III) couple



sequentially (**Table 7**). These Ni(II) voltammograms are showed in **Figures 19** and **20**. The cyclic voltammograms of the Co(II) complexes (**Figures 21** and **22**), [(DEHC)CoCl] and [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub> revealed an irreversible anodic process in the positive range (+ 0.479 volt versus Fc/Fc<sup>+</sup>) and (+ 0.419 volt versus Fc/Fc<sup>+</sup>) respectively (**Table 7**). Which can be assigned to the redox manner of the metal ion Co(I)/Co(II) couple as compared with analogous Co(II) complexes reported earlier [64]. It is obvious from **Tables 6-7** and **Figures 17, 19 and 21** that the chloride compounds [(DEHC)CuCl], [(DEHC)NiCl] and [(DEHC)CoCl] were noticed at higher anodic potential than their corresponding acetate compounds [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>. This is relating with the behavior of chloride ions, which are presence in the chloride complexes that directly bonded with metal ion as great electron withdrawing groups and enhance the charge of the metal ion to more electropositive than its ion in acetate complexes. That means the chloride electron-withdrawing groups in chloride complexes reduce the electron density in the oxidation center. They shifted the reductive potential of the Cu(II)/Cu(I) electrode couple in Cu(II) complexes, the oxidative potential of the Ni(I)/Ni(II) and Ni(II)/Ni(III) electrode couples in Ni(II) complexes and Co(I)/Co(II) electrode couple in Co(II) complexes, to high positive value than their values in the acetate complexes. Therefore, the oxidation process in chloride complexes more difficult than acetate complexes and so it appeared at high oxidative potential in the chloride complexes.

Table 5: Solubility Check of Cu(II), Co(II), Ni(II) and Zn(II) complexes of (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide ligand.

Polar Solvents						Nonpolar Solvents				
Solvent	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	acetone	meCN	ethyl acetate	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>12</sub>	CCl <sub>4</sub>
Complex										
[(DEHC)CuCl]	Poor soluble	Non soluble	Poor soluble	soluble	Non soluble	soluble	soluble	Poor soluble	Poor soluble	Poor soluble
[(DEHC)CoCl]	Poor soluble	Non soluble	Poor soluble	soluble	Non soluble	soluble	soluble	Poor soluble	Poor soluble	Poor soluble
[(DEHC)NiCl]	Poor soluble	Non soluble	Poor soluble	soluble	Non soluble	soluble	soluble	Poor soluble	Poor soluble	Poor soluble
[(DEHC-H)ZnCl <sub>2</sub> ]	Poor soluble	Non soluble	Poor soluble	soluble	Non soluble	soluble	soluble	Poor soluble	Poor soluble	Poor soluble
[(DEHC-H) <sub>2</sub> Cu](AC) <sub>2</sub>	soluble	soluble	soluble	soluble	soluble	Non soluble	Non soluble	Non soluble	Non soluble	Non soluble
[(DEHC-H) <sub>2</sub> Co](AC) <sub>2</sub>	soluble	soluble	soluble	soluble	soluble	Non soluble	Non soluble	Non soluble	Non soluble	Non soluble
[(DEHC-H) <sub>2</sub> Ni](AC) <sub>2</sub>	soluble	soluble	soluble	soluble	soluble	Non soluble	Non soluble	Non soluble	Non soluble	Non soluble
[(DEHC-H) <sub>2</sub> Zn](AC) <sub>2</sub>	soluble	soluble	soluble	soluble	soluble	Non soluble	Non soluble	Non soluble	Non soluble	Non soluble

Table 6: Cyclic voltammety data for the quasi-reversible behavior displayed by Cu(II) compounds in acetonitrile solution, supporting electrolyte [Bu<sub>4</sub>N]<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup> (10<sup>-1</sup> M), temperature=25°C measured at 10<sup>2</sup> mv/sec.

Complex	Quasi reversible vs FC/FC <sup>+</sup>						
	E <sub>pa</sub> V	E <sub>pc</sub> V	ΔE <sub>p</sub> mv	E <sub>1/2</sub> V	I <sub>pa</sub> μA	I <sub>pc</sub> μA	I <sub>pc</sub> /I <sub>pa</sub>
[(DEHC)CuCl]	-1.1439	-1.3786	235	-1.2613	5.23	3.90	0.746
[(DEHC-H) <sub>2</sub> Cu](CH <sub>3</sub> COO) <sub>2</sub>	-1.0728	-1.4263	354	-1.2496	3.12	2.37	0.759

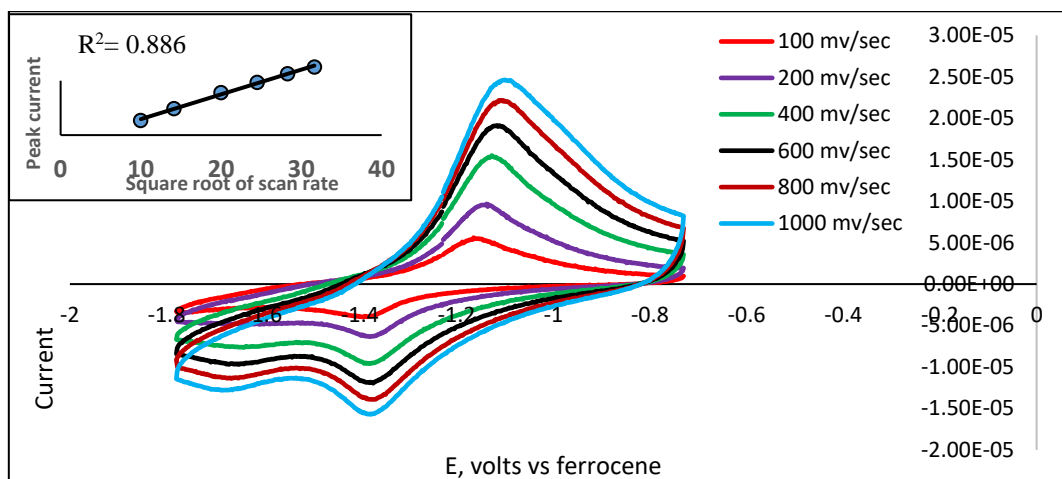


Figure 17: Cyclic voltammogram for [(DEHC)CuCl] compound exhibiting the quasireversible manner in acetonitrile solution at different scan rate 10<sup>2</sup>-10<sup>3</sup> mv/sec.

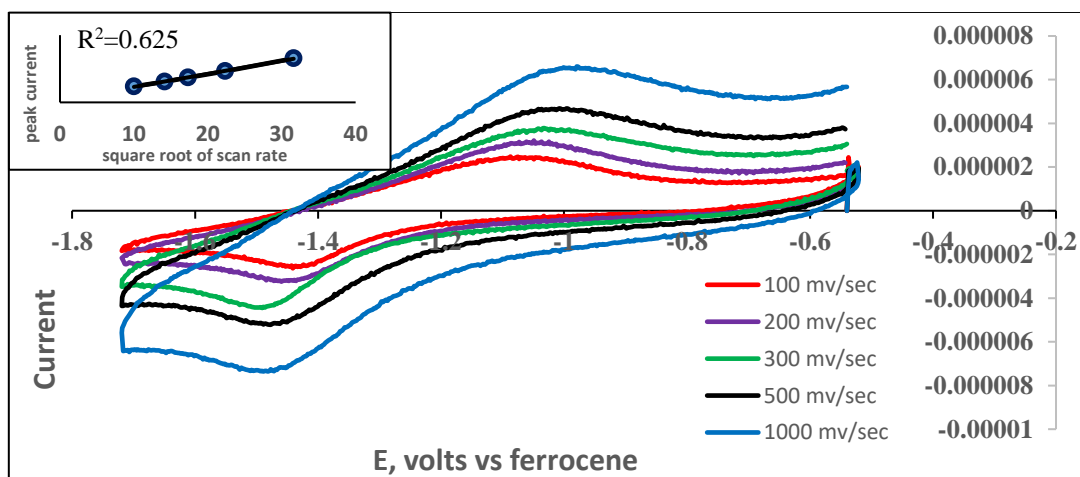
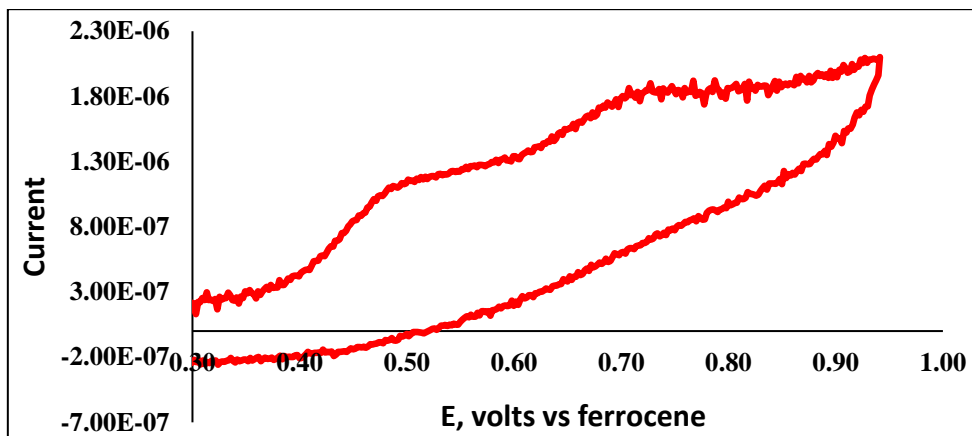


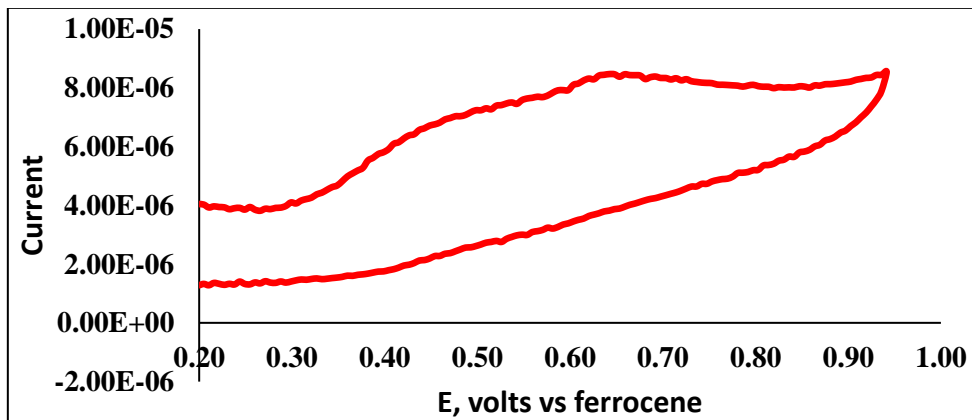
Figure 18: Cyclic voltammogram for [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub> compound exhibiting the quasireversible manner in acetonitrile solution at different scan rate 10<sup>2</sup>-10<sup>3</sup> mv/sec.

**Table 7:** Cyclic voltammetry data for the irreversible behaviour displayed by Ni(II) and Co(II) compounds in acetonitrile solution, supporting electrolyte  $[\text{Bu}_4\text{N}]^+ [\text{PF}_6]^-$  ( $10^{-1}$  M), temperature  $=25^\circ\text{C}$  measured at  $10^2$  mv/sec.

complex	$E_p/\text{V}$ vs Fc/Fc <sup>+</sup>	
	irreversible Oxidative Peaks	
$[(\text{DEHC})\text{NiCl}]$	+0.491	+0.721
$[(\text{DEHC-H})_2\text{Ni}](\text{AC})_2$	+0.449	+0.656
$[(\text{DEHC})\text{CoCl}]$	+0.479	-----
$[(\text{DEHC-H})_2\text{Co}](\text{AC})_2$	+0.419	-----



**Figure 19:** Cyclic voltammogram for  $[(\text{DEHC})\text{NiCl}]$  compound exhibiting the irreversible manner in acetonitrile solution at the scan rate  $10^2$  mv/sec.



**Figure 20:** Cyclic voltammogram for  $[(\text{DEHC-H})_2\text{Ni}](\text{CH}_3\text{COO})_2$  compound exhibiting the irreversible manner in acetonitrile solution at the scan rate  $10^2$  mv/sec.

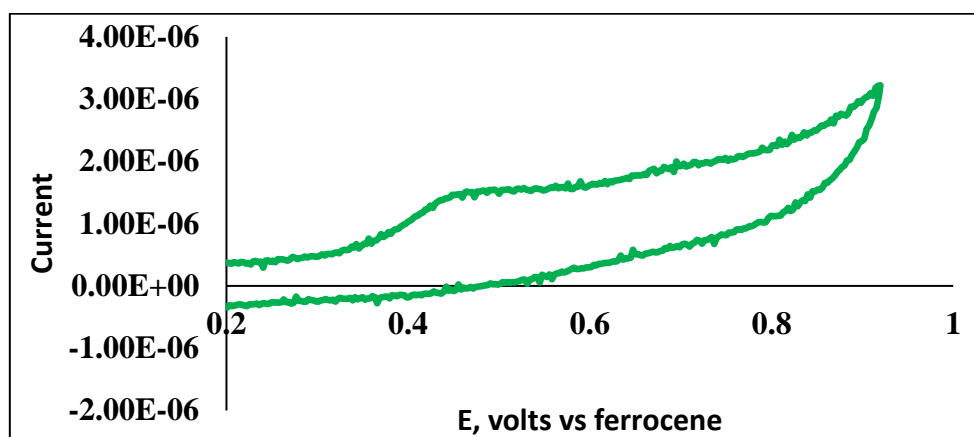


Figure 21: Cyclic voltammogram for [(DEHC)CoCl] compound exhibiting the irreversible manner in acetonitrile solution at the scan rate  $10^2$  mv/sec.

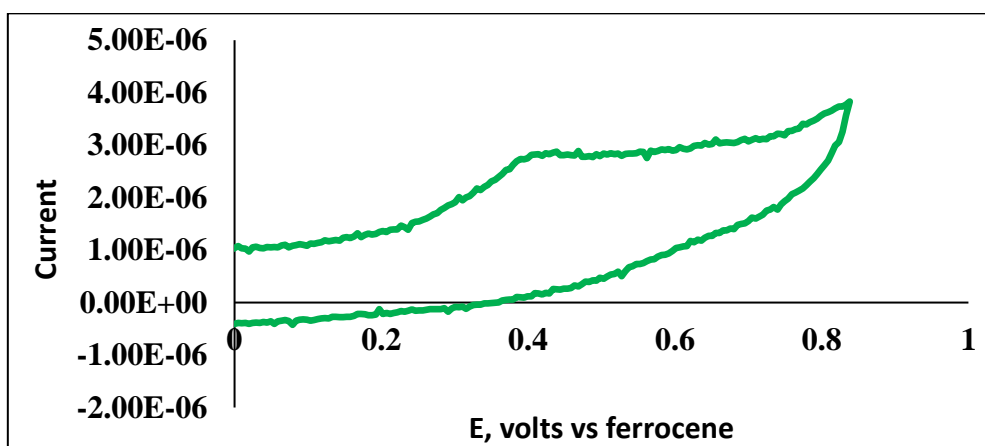


Figure 22: Cyclic voltammogram for [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub> compound exhibiting the irreversible manner in acetonitrile solution at the scan rate  $10^2$  mv/sec.

#### 4. Conclusion

This research studied the synthesis and full characterization of the new set of Cu(II), Co(II), Ni(II) and Zn(II) chloride and acetate compounds of the thiosemicarbazone derivative, (E)-3,4-dichloro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl)benzamide. Different spectroscopic techniques and worthy measurements like <sup>1</sup>H and <sup>13</sup>CNMR, FT-IR, Ultra Violet-visible, mass spectra spectroscopies and CHNS, magnetic moment, solubility probe and molar conductivity measurements were dedicated to confirm the structural formula of the free ligand (DEHC-H) and its element complexes. These complexes are formed as {[[(DEHC)CuCl], [(DEHC)CoCl], [(DEHC)NiCl], [(DEHC-H)ZnCl<sub>2</sub>], [(DEHC-H)<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, [(DEHC-H)<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [(DEHC-H)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub>]. The coordination chemistry of the (DEHC-H) ligand in its metal

complexes has been explored in detail and the used technique altogether easily emphasized its inventiveness flexible and multifaceted manner to produce stable compounds in their solid states. The full characterization methods indicated that (DEHC-H) ligand coordinated as deprotonated ligand with metal ions as square planar geometrical shape via MN<sub>2</sub>S skeletal in Cu(II), Co(II) and Ni(II) chloride complexes [(DEHC)CuCl], [(DEHC)CoCl] and [(DEHC)NiCl] respectively while Zn(II) chloride complex, [(DEHC-H)ZnCl<sub>2</sub>] adopt protonated ligand in its a square pyramidal geometry. In the prepared chloride complexes, one mole tridentate (DEHC-H) ligand coordinated through N-atom in pyridine moiety, N-atom in azomethine and S-atom in C=S bond, with metal ion. Whilst the fourth site in Cu(II), Co(II) and Ni(II) complexes is occupied by one chloro group and the fourth and the fifth sites in Zn(II) complex are filled via two chloro groups. In the other side, the acetate complexes were arranged in octahedral geometry and the free ligand adopts the

protonated form as  $[(\text{DEHC-H})_2\text{Cu}](\text{CH}_3\text{COO})_2$ ,  $[(\text{DEHC-H})_2\text{Co}](\text{CH}_3\text{COO})_2$ ,  $[(\text{DEHC-H})_2\text{Ni}](\text{CH}_3\text{COO})_2$  and  $[(\text{DEHC-H})_2\text{Zn}](\text{CH}_3\text{COO})_2$  and two moles of the tridentate  $[(\text{DEHC-H})]$  ligand are coordinating with the central ion as the same inner sites as chloride complexes. Two acetate groups as counter ions are distinguishing the acetate complexes. The most striking result to protrude from the analysis data is that the structural formula of chloride complexes is the same even if the condensation reaction between the  $[(\text{DEHC-H})]$  ligand and metal chloride perform in two moles ratio 1:1 and 2:1 (Ligand: Metal). Which they are  $[(\text{DEHC})\text{MCl}]$ ,  $\text{M} = \text{Cu(II)}$ ,  $\text{Co(II)}$  and  $\text{Ni(II)}$  and  $[(\text{DEHC-H})\text{ZnCl}_2]$ . Similar circumstances were used to prepare acetate complexes except exchange metal chloride with metal acetate to obtain the same structure  $[(\text{DEHC-H})_2\text{M}](\text{CH}_3\text{COO})_2$ ,  $\text{M} = \text{Cu}$ ,  $\text{Co}$ ,  $\text{Ni}$  and  $\text{Zn}$ . A possible explanation for this might be concern with the properties of chloro group such as tiny size and hard leaving group. This clarifies that 1:1 mole ratio gives (1:1 L:M) in addition to one or two chloro coordinated groups, so in 2:1 mole ratio it is hard to free ligand to remove chloro group and exchange it. That explains the obtained form of chloride complexes as the above formula and not to be in the form  $[(\text{DEHC})_2\text{M}]\text{Cl}_2$ . Acetate complexes displayed reverse manner to chloride complexes, it appears in the form  $[(\text{DEHC-H})_2\text{M}](\text{CH}_3\text{COO})_2$  and not as  $[(\text{DEHC-H})\text{M}](\text{CH}_3\text{COO})_2$ ,  $\text{M} = \text{Cu}$ ,  $\text{Co}$ ,  $\text{Ni}$  and  $\text{Zn}$  whether it prepares in 1:1 or 2:1 mole ratios. This is related with the features of acetate anion groups as great leaving as well as large size group. Electrochemical investigation were achieved via cyclic voltammetry technique. The cyclic voltammograms of  $\text{Cu(II)}$  compounds showed a single quasireversible cathodic system associated with the  $\text{Cu(II)/Cu(I)}$  redox couple process. The cyclic voltammograms of  $\text{Ni(II)}$  compounds exhibited double successive irreversible anodic system related with the  $\text{Ni(I)/Ni(II)}$  and  $\text{Ni(II)/Ni(III)}$  redox couple processes while  $\text{Co(II)}$  compounds presented a unique irreversible anodic system accompanying to the  $\text{Co(I)/Co(II)}$  redox couple. The finding results revealed that the thiosemicarbazone  $[(\text{DEHC-H})]$  free ligand is stabilized the  $\text{Cu(II)}$  and  $\text{Cu(I)}$  ions in the prepared  $\text{Cu(II)}$  complexes in acetonitrile solvent whilst  $\text{Ni(I)}$  and  $\text{Co(I)}$  ions are not fixed in the same solvent. The cyclic voltammograms of  $\text{Cu(II)}$  complexes enhanced their acting role as electrochemical sensors and electrocatalytic operations due to their forming of stable  $\text{Cu(II)}$  and  $\text{Cu(I)}$  ions and their cathodic potential of the quasireversible couple. The most interesting aspect of electrochemical probes is that the high potential that noticed in chloride compounds as compared to the corresponding acetate complexes and this is because

of the presence of chloro groups, which promote the electro positivity of the central ion via the great electron withdrawing manner of chloro groups. Then it needs high potential to redox process happening.

### Conflict of interests

Authors Ali A. A. Al-Riyahee, Ashwaq Shenta and Khansaa Saud would be delighted to announce that there is no conflict of interests as regard to publish this research.

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