

**Draft Manuscript for Review**

"Electrochemical Studies Of Novel 3,4-Dichloro-N-((5-ChloroPyridin-2-yl)Carbamothioyl)Benzamide Based On Its Complexes With Copper(II), Cobalt(II), Nickel(II) and Zinc(II) ions"

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Peer Review



## Electrochemical Studies Of Novel 3,4-Dichloro-*N*-((5-ChloroPyridin-2-yl)Carbamothioyl)Benzamide Based On Its Complexes With Copper(II), Cobalt(II), Nickel(II) and Zinc(II) ions



### Abstract

The synthesis of novel *N,N'*-disubstituted benzoyl thiourea ligand [3,4-dichloro-*N*-((5-chloropyridin-2-yl)carbamothioyl)benzamide] (L) is achieved in two steps. First step by refluxing KSCN with 3,4-dichloro benzoyl chloride in CH<sub>3</sub>CN solvent and the other step by the reaction of the resulting filtrate from the first step with 2-amino-5-chloropyridine. The copper(II), Cobalt(II), Nickel(II) and Zinc(II) chloride and acetate salts were coordinated with L ligand in the 1:1 and 1:2 mole ratios (M:L) in the solvent mixture of DMF/H<sub>2</sub>O or CHCl<sub>3</sub>/methanol to form the complexes with structural formulas {[LMCl<sub>2</sub>] and [L<sub>2</sub>M](CH<sub>3</sub>COO)<sub>2</sub>, M= Copper(II), Cobalt(II), Nickel(II) and Zinc(II) ions}. Two mole ratios of the starting materials, 1:1 and 1:2 (M:L) were experimented to form chloride complexes, the product was with structural formula [LMCl<sub>2</sub>] while acetate complexes with [L<sub>2</sub>M](CH<sub>3</sub>COO)<sub>2</sub> formula are resulted with the same conditions. Ligand L and its complexes [LCuCl<sub>2</sub>], [LCoCl<sub>2</sub>], [LNiCl<sub>2</sub>], [LZnCl<sub>2</sub>], [L<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>, [L<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, [L<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [(L)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> have been characterized by mass spectrometry, elemental analysis, magnetic moments, conductivity measurements, solubility test, UV-visible, FTIR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies. Electrochemical studies were probed by using cyclic voltammetry technique(CV). The data reflect the quasi-reversible reductive nature for the Copper(II) complexes with one electron transfer process while Nickel(II) and Cobalt(II) complexes exhibited two consecutive irreversible reductive nature. The observed UV-visible, elemental analysis, molar conductivity, magnetic moment measurements and solubility test revealed that the metal ion in the all prepared complexes adopted four coordinated square planar structures and [LCuCl<sub>2</sub>], [LCoCl<sub>2</sub>], [LNiCl<sub>2</sub>], [LZnCl<sub>2</sub>], are formed as neutral complexes while [L<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>, [L<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, [L<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [(L)<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> adopted anion complexes. The observed magnetic moments show diamagnetic properties of Zinc(II) and Nickel(II) complexes while Copper(II) and Cobalt(II) appeared as paramagnetic species. FT-IR analysis confirmed the coordination sites between the central metal ion with ligand L through two sites, the nitrogen atom in pyridyl ring and the sulphur atom in C=S group.

**Keywords:** Metal complexes, benzoylthiourea, N, S donor ligands, Spectral measurements, CV technique and different mole ratio.

### 1. Introduction

In general, the chemical compounds including donor sites like O, N and S atoms are massively reported [1]. Currently, their corresponding complexes derivatives played a vital role in a wide range of

different areas due to the nature of O, N, S atoms, the delocalized electrons and geometrical structure which effect directly in the behaviour of transition element complexes [2]. These compounds represent privilege chelating ligands in coordination chemistry and their transition element complexes are worthwhile and valuable in various fields such as: magnetic materials, constructional component to synthesis a large set heterocyclic compounds, homogenous catalysis, redox

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sensor, strong selective of metal complexes in liquid-liquid extraction system [3-7]. As well as, the existence of sulfur, nitrogen and oxygen atoms in organic compounds and their complexes earn them and enhance the pharmacological and biological activity as antimicrobial, antifungal, antiviral agents and so on [8-19]. There is a considerable volume of published studies describing the role of thioureas in coordination chemistry as functional chelates with metal ions through oxygen and sulfur atoms in thiourea derivatives [20]. The benzoyl thiourea derivatives are classified as significant kind of thioureas depending on their broad spectrum of applications in: extractions of different elements as Nickel, Cobalt, Silver and Palladium [21], analytical field [22-24], biological activity as insecticidal, antifungal, antithyroid, antitubercular, antibacterial, antitumor, antiviral and herbicidal [25-28]. Coordination chemistry of their complexes are supplied good information of their characteristics [29] and their catalyst activity were reported with high efficiency [30]. The main goal of this work is to investigate and show the remarkable role act by transition element complexes of pyridyl thiourea derivatives. This paper is deemed a continuation of my scientific journey in the world of thiourea derivatives when I started my PhD study to probe these derivatives and discover many facts of them and give different significant contributions [31]. The synthesis of new thiourea derivatives and preparation of their metal complexes have a distinct motivation due to their easy, fast preparation as well as a wide range of their possible applications. All possible analyzes were dedicated to investigate the chemistry, preparation and purification of the novel ligand and its complexes. Another major purpose of this study was to probe and assess the electrochemical manners of the new ligand and its complexes to explore the reduction/oxidation processes and then knowledge of the oxidation state of the metal ion which follow these complexes composition. Our interest of survey and improve the chemistry on N, N'-disubstituted benzoyl pyridyl thiourea derivative and probing its coordination chemistry is coming from its structure which has more than one functional set like carbonyl, C=S, nitrogen pyridyl and N-H amine groups that qualify these derivatives to coordinate with copper(II), cobalt(II), nickel(II) and zinc(II) ions through different potential structural geometry. Their capable using in varied areas is considered good push for us to interest in their study like: building blockers in the creation of heterocyclic derivatives, active reagents to separation of Pt-group elements and their wide range activity as antimicrobial, antifungal, anticancer and so on.

## 2. Experimental

### 2.1 Materials

Each of starting compounds, solvents and reagents which are used to prepare thioureas and their element complexes were gained from BDH, Fluka, Merck chemical companies without extra purification. While TBAHFP (Tetra butyl ammonium hexafluoro phosphate) which is used as supporting electrolyte in cyclic voltammetry experiments was bought from Aldrich Chemical Company.

### 2.2 Instrumentation

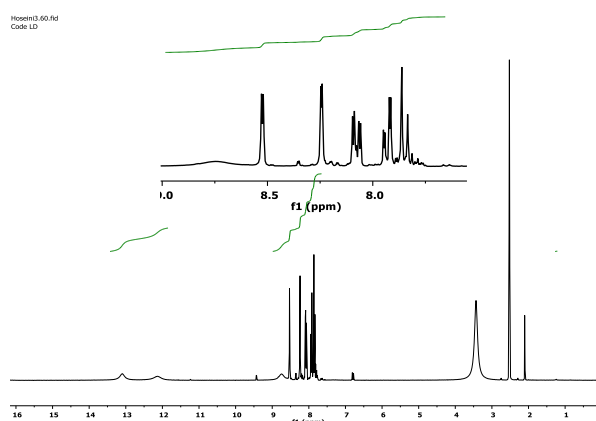
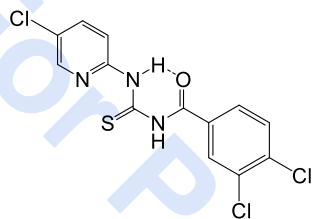
The electro thermal VeeGo Digital model VMP-D.Jenway was used to measure the melting point and decomposition point in degree Celsius of the free ligand L and its metal complexes respectively. These novel compounds were full characterized using FTIR, UV-visible,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ , elemental analysis, mass spectra, magnetic susceptibility and CV technique. FTIR spectra for all compounds were carried out in the range  $400\text{-}4000\text{ cm}^{-1}$  via a Japanese Shimadzu model 8400S spectrophotometer when samples were mixed with dry potassium bromide, then the formed disc were neatly compressed and measured. Dimethyl Sulfoxide (DMSO) solvent was employed to record the UV-vis. spectra of the compounds by using a (SHIMADZU UV/vis-1800) spectrophotometer from  $200\text{-}1100\text{ nm}$  (cell length  $1\text{ cm}$ ).  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of ligand L were accomplished on Bruker 400 MHz spectrometer by using DMSO- $d_6$  as solvent and tetra methyl silane as inner standard. The percentage of carbon, hydrogen, nitrogen in all compounds were determined by Perkin CE-440 elemental analyser while ESI-MS ( $m/z$ ) % was determined through recording the mass spectra on a Waters LCT Premier XE (oa-TOF) mass spectrometer. A Johnson Matthey magnetic susceptibility balance [33] were used to check the effective magnetic moments at room temperature ( $25^\circ\text{C}$ ). The W.T.W conductivity Master LBR meter was employed to perform the molar conductivities in the range  $25 \times 10^{-6}$  to  $1.21 \times 10^{-2}\text{ mol.L}^{-1}$  solutions of element complexes in dimethyl sulfoxide at room temperature.

The electrochemical measurements were performed and educed through cyclic voltammograms of the free ligand L and its complexes using CH Instruments, USA, Digi-Ivy (Model DY2300 Seriespotenstiosate/biopotenstiosate, electrochemical analyzer), in acetonitrile solvent with existence of  $0.1\text{ M}^{-1}$  of the supporting electrolyte tetra butyl ammonium hexa fluoro phosphate (TBAHFP) and  $0.001\text{ M}^{-1}$  of the electro active species. CV experiments are accomplished at  $25^\circ\text{C}$  with passing  $\text{N}_2$  gas on overall the solutions under study to remove oxygen gas during the experiment till the time of measurement. An

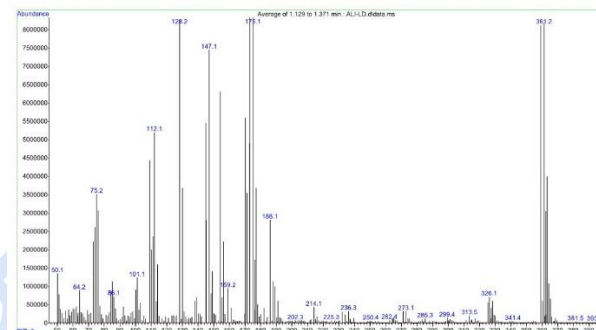
especially model three electrodes glass cell with cell cap coating by Teflon was employed to carried out CV experiment. A platinum working electrode and a platinum wire auxiliary electrode while a non-aqueous solution silver/silver nitrate as reference electrode were used to accomplish CV voltammograms. A working electrode should be polished before starting the measurement to be smooth using sand paper and obtain effective surface which enhancing the sensitive electrochemical properties.

### 2.3 Synthesis of [3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl)benzamide] (L ligand) :

An CH<sub>3</sub>CN solution (10 mL) of KSCN (0.97 g, 10 mmol) was added drop by drop to an CH<sub>3</sub>CN solution (10 mL) of 3,4-dichloro benzoyl chloride (2.09 g, 10 mmol). The mixture was refluxed for 3 hours and then filtered to obtain clear yellow solution to remove the white precipitate (KCl). The yellow filtrate was added to an acetonitrile solution (10 mL) of 2-amino-5-chloro pyridine (1.29 g, 10 mmol) and the reaction mixture was refluxed for a further 3 hours. The solution allowed to cool to room temperature and the white precipitate was gathered by filtration. Recrystallization from hot acetonitrile yielded crystals as white plates. Yield: (1.01 g, 78%); m.p= 202-204°C, ESI-MS (*m/z*)(%): 361.20 [M+H] (100%); FT-IR (cm<sup>-1</sup>): ν(N-H) 3240, ν(C=O) 1673, δ(N-H)<sup>1</sup> 1586, δ(N-H)<sup>2</sup> 1560, ν(C=N) 1528, ν(C=S), 1338; UV-vis. Spectrum, λ<sub>max</sub> nm (εM, M<sup>-1</sup>cm<sup>-1</sup>): 270(11861), 295(13616), 340(6433); <sup>1</sup>HNMR (400 MHz, DMSO-d<sub>6</sub>), δ(ppm): 13.10 (1H, s, N-H(NHCS)), 12.13 (1H, s, N-H(NHCO)), 8.74 (1H, s, Py), 8.52 (1H, s, Ar), 8.24 (1H, d, Py *J*<sub>HH</sub> = 5 Hz), 8.08 (1H, d, Ar *J*<sub>HH</sub> = 7.5 Hz), 7.93 (1H, d, Py *J*<sub>HH</sub> = 5 Hz), 7.82 (1H, d, Ar *J*<sub>HH</sub> = 7.5 Hz). <sup>13</sup>CNMR (100 MHz, DMSO-d<sub>6</sub>), δ(ppm): 178.30 (C=S), 166.43 (C=O), 150.23, 147.37, 138.42, 136.48, 131.82, 131.27, 129.45, 127.76, 126.16, 117.07, 110.26. Anal. Calcd. For C<sub>13</sub>H<sub>8</sub>Cl<sub>3</sub>N<sub>3</sub>OS (%): C, 43.30; H, 2.24; N, 11.65; S, 8.89, Found (%): C, 43.12; H, 2.20; N, 11.71; S, 8.86. See **Figures 1 and 2**.



**Figure 1:** <sup>1</sup>HNMR spectrum of [3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl) benzamide] (L ligand).

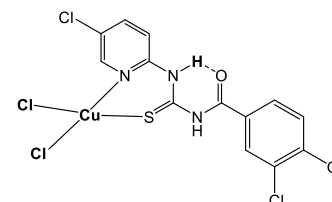


**Figure 2:** Mass spectrum of [3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl) benzamide] (L ligand).

### 2.4 Synthesis of complexes [LCuCl<sub>2</sub>], [LCoCl<sub>2</sub>], [LNiCl<sub>2</sub>], [LZnCl<sub>2</sub>], [L<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>, [L<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, [L<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [L<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub>

#### 2.4.1. Synthesis of Mono ([3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl) benzamide) di chloro Copper(II) [LCuCl<sub>2</sub>]

Ligand L (0.36 g, 1 mmol) was dissolved in DMF (4 mL) and stirred at room temperature. A H<sub>2</sub>O (3 mL) solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.17 g, 1 mmol) was added

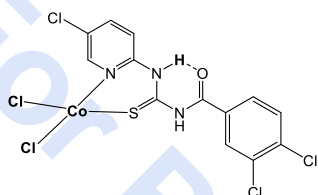


slowly to the stirred solution. The mixture was continued stirring for 1 hour. The colourless solution turned green and formed a precipitate. The green precipitate was filtered, washed with a little bit of DMF to remove unreacted ligand and dried under vacuum. Green crystals of it were grown at room temperature by the diffusion of diethyl ether vapour

into an acetonitrile solution. Yield: (0.22 g, 62 %); D.p= 278<sup>o</sup>C, green crystals; ESI-MS (*m/z*)(%): 495.40 [M] (100%); FT-IR (cm<sup>-1</sup>):  $\nu$ (N-H) 3349,  $\nu$ (C=O) 1670,  $\delta$ (N-H)<sup>1</sup> 1570,  $\delta$ (N-H)<sup>2</sup> 1531,  $\nu$ (C=N) 1485,  $\nu$ (C=S), 1315,  $\nu$ (Cu-S) 478,  $\nu$ (Cu-N) 536; UV-vis. Spectrum,  $\lambda_{\max}$  nm ( $\epsilon$ M, M<sup>-1</sup> cm<sup>-1</sup>): 273(11522), 295(12272), 344(10294), 590(24); Anal. Calcd. For C<sub>13</sub>H<sub>8</sub>Cl<sub>5</sub>CuN<sub>3</sub>OS (%) : C, 31.54; H, 1.63; N, 8.49; S, 6.48. Found (%): C, 31.32; H, 1.74; N, 8.22; S, 6.50.

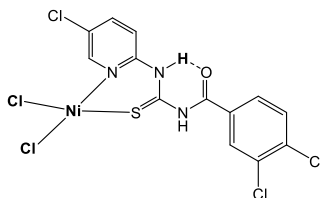
#### 2.4.2. Synthesis of Mono ([3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl) benzamide) di chloro Cobalt(II) [LCoCl<sub>2</sub>]

Ligand **L** (0.36 g, 1 mmol) was dissolved in CHCl<sub>3</sub> (3 mL) and stirred at room temperature. A CH<sub>3</sub>OH (3 mL) solution of CoCl<sub>2</sub>.6H<sub>2</sub>O (0.24 g, 1 mmol) was added gradually to the stirred solution. The mixture was refluxed for 1 hour. The colourless solution turned into light green and formed a precipitate. The precipitate was filtered, washed with CHCl<sub>3</sub> to remove unreacted ligand and dried under vacuum. Green crystals were grown at room temperature by the diffusion of diethyl ether vapour into an acetonitrile solution. Yield: (0.29 g, 80 %); D.p= 104<sup>o</sup>C, green crystals; ESI-MS (*m/z*)(%): 491.70 [M+H] (70%); FT-IR (cm<sup>-1</sup>):  $\nu$ (N-H) 3325,  $\nu$ (C=O) 1669,  $\delta$ (N-H)<sup>1</sup> 1616,  $\delta$ (N-H)<sup>2</sup> 1543,  $\nu$ (C=N) 1462,  $\nu$ (C=S), 1312,  $\nu$ (Co-S) 509,  $\nu$ (Co-N) 536; UV-vis. Spectrum,  $\lambda_{\max}$  nm ( $\epsilon$ M, M<sup>-1</sup> cm<sup>-1</sup>): 280(11822), 295(13555), 350(6277), 611(28); Anal. Calcd. For C<sub>13</sub>H<sub>8</sub>Cl<sub>5</sub>CoN<sub>3</sub>OS (%) : C, 31.84; H, 1.64; N, 8.57; S, 6.54. Found (%): C, 31.63; H, 1.46; N, 8.32; S, 6.44.



#### 2.4.3. Synthesis of Mono ([3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl) benzamide) di chloro Nickel(II) [LNiCl<sub>2</sub>]

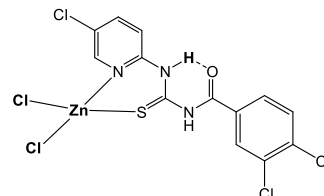
The same method as reported for [LCoCl<sub>2</sub>] was followed using: NiCl<sub>2</sub>.6H<sub>2</sub>O (0.24 g, 1 mmol), **L** (0.36 g, 1 mmol). Yield: (0.26 g, 71%); D.p= 172<sup>o</sup>C, light brown crystals; ESI-MS (*m/z*)(%): 490.50 [M] (62.6%); FT-IR (cm<sup>-1</sup>):  $\nu$ (N-H) 3325,  $\nu$ (C=O) 1669,  $\delta$ (N-H)<sup>1</sup> 1585,  $\delta$ (N-H)<sup>2</sup> 1547,  $\nu$ (C=N) 1458,  $\nu$ (C=S), 1285,  $\nu$ (Ni-S) 509,  $\nu$ (Ni-N) 540; UV-vis. Spectrum,  $\lambda_{\max}$  nm ( $\epsilon$ M, M<sup>-1</sup> cm<sup>-1</sup>): 275(11294), 295(12866), 345(10433), 601(19); Anal. Calcd. For C<sub>13</sub>H<sub>8</sub>Cl<sub>5</sub>N<sub>3</sub>NiOS (%) : C,



31.85; H, 1.64; N, 8.57; S, 6.54. Found (%): C, 32.17; H, 1.79; N, 8.42; S, 6.73.

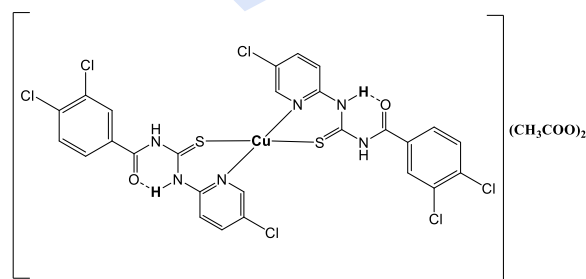
#### 2.4.4. Synthesis of Mono ([3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl) benzamide) di chloro Zinc(II) [LZnCl<sub>2</sub>]

The same method as reported for [LCoCl<sub>2</sub>] was followed using: ZnCl<sub>2</sub> (0.14 g, 1 mmol), **L** (0.36 g, 1 mmol). Yield: (0.24 g, 69%); D.p= 178<sup>o</sup>C, White crystals; ESI-MS (*m/z*)(%): 497.20 [M] (60%); FT-IR (cm<sup>-1</sup>):  $\nu$ (N-H) 3380,  $\nu$ (C=O) 1670,  $\delta$ (N-H)<sup>1</sup> 1580,  $\delta$ (N-H)<sup>2</sup> 1524,  $\nu$ (C=N) 1454,  $\nu$ (C=S), 1285,  $\nu$ (Zn-S) 508,  $\nu$ (Zn-N) 539; UV-vis. Spectrum,  $\lambda_{\max}$  nm ( $\epsilon$ M, M<sup>-1</sup> cm<sup>-1</sup>): 280(11377), 295(12911), 345(10272); Anal. Calcd. For C<sub>13</sub>H<sub>8</sub>Cl<sub>5</sub>N<sub>3</sub>OSZn (%) : C, 31.42; H, 1.62; N, 8.46; S, 6.43. Found (%): C, 31.76; H, 1.69; N, 8.66; S, 6.31.



#### 2.4.5. Synthesis of Bis ([3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl) benzamide) Copper(II) [L<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>

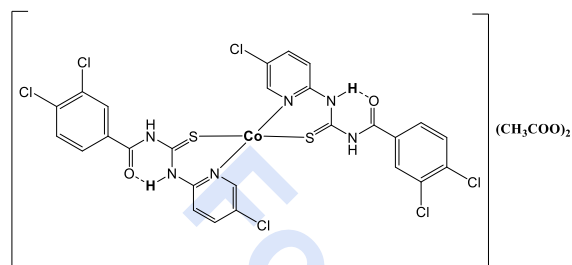
The same method as reported for [LCuCl<sub>2</sub>] was followed using: Cu(CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O (0.1 g, 0.5 mmol) instead of CuCl<sub>2</sub>.2H<sub>2</sub>O, **L** (0.36 g, 1 mmol). Yield: (0.27 g, 74 %); D.p= 284<sup>o</sup>C, Green crystals; ESI-MS (*m/z*)(%): 779.40 [M-H] (67%); FT-IR (cm<sup>-1</sup>):  $\nu$ (N-H) 3283,  $\nu$ (C=O) 1672,  $\delta$ (N-H)<sup>1</sup> 1582,  $\delta$ (N-H)<sup>2</sup> 1520,  $\nu$ (C=N) 1489,  $\nu$ (C=S), 1319,  $\nu$ (Cu-S) 478,  $\nu$ (Cu-N) 540; UV-vis. Spectrum,  $\lambda_{\max}$  nm ( $\epsilon$ M, M<sup>-1</sup>cm<sup>-1</sup>): 275(8533), 315(9222), 350(9405), 581(19); Anal. Calcd. For C<sub>30</sub>H<sub>22</sub>Cl<sub>6</sub>CuN<sub>6</sub>O<sub>6</sub>S<sub>2</sub> (%) : C, 39.91; H, 2.46; N, 9.31; S, 7.10. Found (%): C, 39.68; H, 2.59; N, 9.16; S, 7.31.



#### 2.4.6. Synthesis of Bis ([3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl) benzamide) Cobalt(II) [L<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>

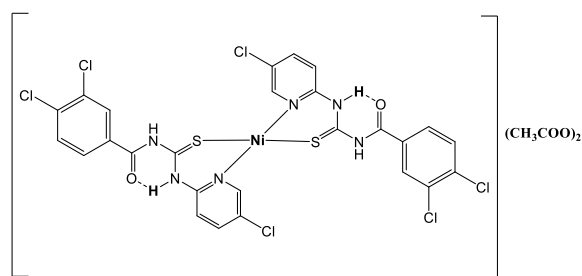
The same method as reported for [LCoCl<sub>2</sub>] was followed using: Co(CH<sub>3</sub>COO)<sub>2</sub>.4H<sub>2</sub>O (0.12 g, 0.5 mmol) instead of CoCl<sub>2</sub>.6H<sub>2</sub>O, **L** (0.36 g, 1 mmol). Yield: (0.32 g, 69 %); D.p= 110<sup>o</sup>C, dark green crystals; ESI-MS (*m/z*)(%): 777.09 [M+] (100%); FT-

IR (cm<sup>-1</sup>):  $\nu(\text{N-H})$  3345,  $\nu(\text{C=O})$  1667,  $\delta(\text{N-H})^1$  1620,  $\delta(\text{N-H})^2$  1551,  $\nu(\text{C=N})$  1485,  $\nu(\text{C=S})$ , 1288,  $\nu(\text{Co-S})$  509,  $\nu(\text{Co-N})$  537; UV-vis. Spectrum,  $\lambda_{\text{max}}$  nm ( $\epsilon\text{M}$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 275(11522), 295(13216), 335(10027), 605(22); Anal. Calcd. For  $\text{C}_{30}\text{H}_{22}\text{Cl}_6\text{CoN}_6\text{O}_6\text{S}_2$  (%): C, 40.11; H, 2.47; N, 9.36; S, 7.14. Found (%): C, 39.90; H, 2.65; N, 9.67; S, 7.24.



#### 2.4.7. Synthesis of Bis ([3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl)benz-amide] Nickel(II) $[\text{L}_2\text{Ni}](\text{CH}_3\text{COO})_2$

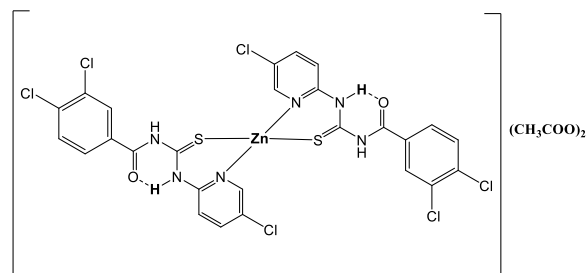
The same method as reported for  $[\text{LNiCl}_2]$  was followed using:  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (0.12 g, 0.5 mmol) instead of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , **L** (0.36 g, 1 mmol). Yield: (0.29 g, 81 %); D.p= 198 °C, dark brown crystals; ESI-MS ( $m/z$ ): 777.01  $[\text{M}^+]$  (78%); FT-IR (cm<sup>-1</sup>):  $\nu(\text{N-H})$  3322,  $\nu(\text{C=O})$  1669,  $\delta(\text{N-H})^1$  1582,  $\delta(\text{N-H})^2$  1551,  $\nu(\text{C=N})$  1458,  $\nu(\text{C=S})$ , 1288,  $\nu(\text{Ni-S})$  513,  $\nu(\text{Ni-N})$  542; UV-vis. Spectrum,  $\lambda_{\text{max}}$  nm ( $\epsilon\text{M}$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 270(9683), 293(12772), 355(10483), 599(11); Anal. Calcd. For  $\text{C}_{30}\text{H}_{22}\text{Cl}_6\text{NiO}_6\text{S}_2$  (%): C, 40.12; H, 2.47; N, 9.36; S, 7.14. Found (%): C, 40.52; H, 2.40; N, 9.09; S, 7.33.



#### 2.4.8. Synthesis of Bis ([3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl)benz-amide] Zinc(II) $[\text{L}_2\text{Zn}](\text{CH}_3\text{COO})_2$

The same method as reported for  $[\text{LZnCl}_2]$  was followed using:  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.11 g, 0.5 mmol) instead of  $\text{ZnCl}_2$ , **L** (0.36 g, 1 mmol). Yield: (0.27 g, 65 %); D.p= 280 °C, White crystals; ESI-MS ( $m/z$ ): 802.70  $[\text{M}^+\text{Na}]$  (80%); FT-IR (cm<sup>-1</sup>):  $\nu(\text{N-H})$  3290,  $\nu(\text{C=O})$  1670,  $\delta(\text{N-H})^1$  1589,  $\delta(\text{N-H})^2$  1535,  $\nu(\text{C=N})$  1458,  $\nu(\text{C=S})$ , 1292,  $\nu(\text{Zn-S})$  509,  $\nu(\text{Zn-N})$  541; UV-vis. Spectrum,  $\lambda_{\text{max}}$  nm ( $\epsilon\text{M}$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 280(12255), 290(13011), 350(10505). Anal. Calcd.

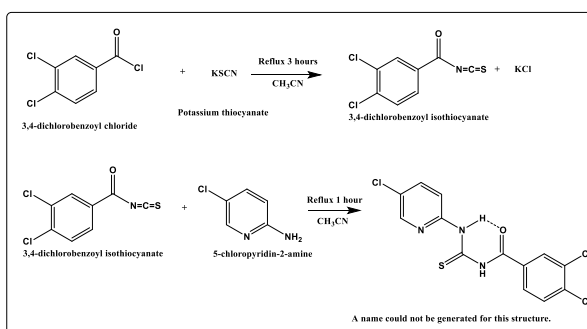
For  $\text{C}_{30}\text{H}_{22}\text{Cl}_6\text{N}_6\text{O}_6\text{S}_2\text{Zn}$  (%): C, 39.83; H, 2.45; N, 9.29; S, 7.09. Found (%): C, 40.11; H, 2.67; N, 9.64; S, 7.23.



### 3. Results and discussion

#### 3.1. Synthesis of Ligand (L) and its transition element complexes

The [3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl)benzamide] (**L**) ligand and its synthesized Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes are quite stabilized in air. When the solubility test is accomplished to check solubility of chloride and acetate complexes in different polar and nonpolar solvents, it is found that they are insoluble in  $\text{H}_2\text{O}$  and acetate complexes soluble in different polar solvents especially  $\text{CH}_3\text{CN}$  and chloride complexes insoluble in polar solvents. The  $\text{NH}_2$  group in the starting material (5-chloro-2-aminopyridine) turned into thiourea moiety by very sparingly adding of 1 equivalent of 3,4-dichloro benzoyl isothiocyanate in  $\text{CH}_3\text{CN}$  with reflux the mixture to 1 hour. This step is preceded with preparation of benzoyl isothiocyanate by refluxing 3,4-dichloro benzoyl chloride and KSCN in  $\text{CH}_3\text{CN}$  solvent. In the end of reaction, a white precipitate appeared profusely from the light yellow solution. Then, the precipitate was recrystallized in  $\text{CH}_3\text{CN}$  solvent to give white crystals in good yield (78%). **Scheme 1** illustrates the synthetic routes of free ligand **L**.



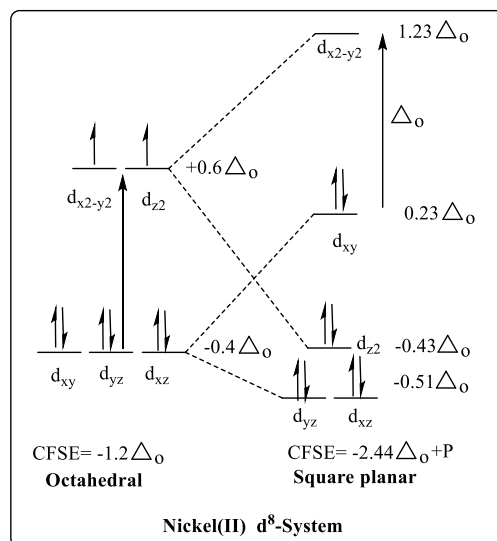
**Scheme 1: Synthetic routes of the ligand L showing the reaction conditions.**

The copper(II) complexes were prepared by the mixing the  $\text{H}_2\text{O}$  solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or

Cu(CH<sub>3</sub>COO)<sub>2</sub>·6H<sub>2</sub>O with DMF solution of ligand **L** for 1 hour at room temperature to change the colorless solution of ligand **L** to green precipitate were formed which wash with a little bit of DMF to obtain [LCuCl<sub>2</sub>] and [L<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub> respectively. The green crystals were obtained by the diffusion of diethyl ether vapor into an acetonitrile solution. The cobalt(II), Nickel(II) and Zinc(II) complexes were created by the refluxing the CH<sub>3</sub>OH solution of MCl<sub>2</sub>·2H<sub>2</sub>O or M(CH<sub>3</sub>COO)<sub>2</sub>·6H<sub>2</sub>O, M= Co, Ni and Zn with CHCl<sub>3</sub> solution of ligand **L** for 2 hours to change the colorless solution to colorful precipitate and then wash with CHCl<sub>3</sub> solvent to remove unreacted ligand. The light green and dark green precipitate were collected from [LCoCl<sub>2</sub>] and [L<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, light brown and dark brown precipitate from [LNiCl<sub>2</sub>] and [L<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub>, white precipitate from [LZnCl<sub>2</sub>] and [L<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> respectively. These complexes gave crystals by diffusion of (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O solvent into CH<sub>3</sub>CN solution. Full characterization like spectrographic analysis confirmed the suggested form for all the formed complexes.

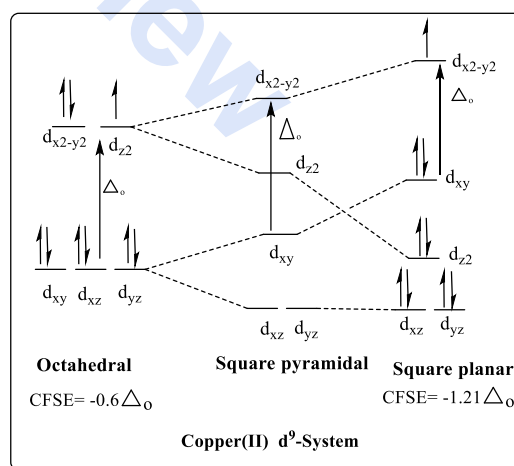
### 3.2 The preference geometrical shape and oxidation states of Copper, Cobalt, Nickel and Zinc ions in their complexes.

It is so important to take a general thought on the preference of oxidation state of Copper, Cobalt, Nickel and Zinc ions in their metal complexes as well as their geometrical shapes. In 2016, we reported our survey on the preferred oxidative states of the metal ions in their complexes [31]. We pointed Copper take two oxidation states Cu<sup>+1</sup> or Cu<sup>+2</sup> and Nickel mostly preferred Ni<sup>+2</sup> and rarely Ni<sup>+1</sup> and Ni<sup>+3</sup> while the Zinc was noticed completely Zn<sup>+2</sup> in all its complexes under survey. With regard to the geometrical shape of the metal complexes and which one more preferred of the metal ion in its complexes, the investigation showed different coordination geometry of Nickel(II) like T-shaped, tetrahedral, trigonal pyramidal, square planar and octahedral. The most preference geometries were octahedral and square planar less than it. This preference of Nickel(II) compounds to octahedral geometry than square planar is related with the -1.2 Δ<sub>o</sub> value of Crystal Field Stabilization Energy for octahedral complexes whilst its value of square planar compounds is -2.44 Δ<sub>o</sub> +P, Δ<sub>o</sub> = the proportional variety, P refers to pairing energy. Seemingly, the square planar complexes are more stable as compared to octahedral (CFSE<sub>square planar</sub> > CFSE<sub>octahedral</sub>), generally, the preferred geometry depending on Δ<sub>o</sub> contra P. So, complexes with big Δ<sub>o</sub> favor square planar shape, see **Figure 3**.



**Figure 3: Crystal Field Theory of Nickel(II) compounds showing their tendency to display an octahedral geometry against a square planar coordination geometry.**

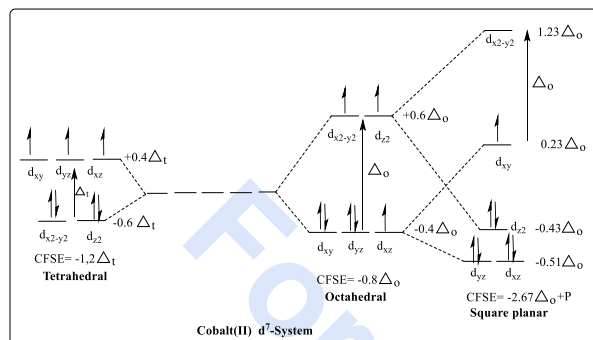
The complexes of Copper(II) adopted trigonal pyramidal, trigonal bipyramidal, pyramidal, square pyramidal, octahedral and square planar. Most of Copper(II) complexes were arranged in square planar geometry and then in octahedral. The high preference to square planar geometry than octahedral is due to the structural stabilization of square planar than octahedral shape (CFSE<sub>square planar</sub> = -1.21Δ<sub>o</sub> > CFSE<sub>octahedral</sub> = -0.6Δ<sub>o</sub>). See **Figure 4**.



**Figure 4: Crystal Field Energy of Copper(II) compounds showing their preference to a square planar against an octahedral geometry coordination geometry.**

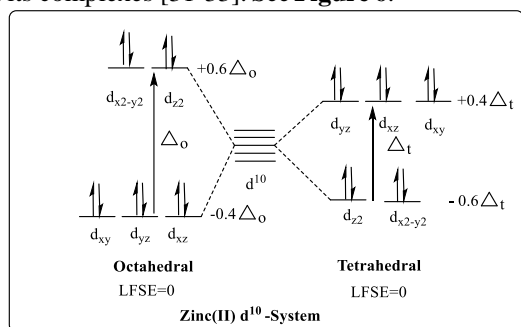
In general, Cobalt(II) complexes showed different modes of coordination like octahedral, tetrahedral and

square planar. From **Figure 5**, it is easy to notice that Cobalt(II) complexes prefer a square planar than a tetrahedral and an octahedral geometry. This depends on the value of crystal field stabilization energy CFSE, which arranges in  $(CFSE_{\text{square planar}} > CFSE_{\text{tetrahedral}} > CFSE_{\text{octahedral}})$ .



**Figure 5: Crystal Field Energy of Cobalt(II) compounds showing their preference to octahedral, tetrahedral and square planar coordination geometries.**

While  $d^{10}$  Zinc(II) complexes appeared in trigonal pyramidal, trigonal bipyramidal, octahedral and tetrahedral, the most common geometry was tetrahedral. There is no preference between octahedral and tetrahedral geometries because the values of Ligand Field Stabilization Energy are zero in all of them. The high tendency of Zinc(II) to form tetrahedral complexes could be attribute to the structural steric hindrance of the ligand and thermochemical environment around the metal center in its complexes [31-33]. See **Figure 6**.



**Figure 6: Crystal Field Energy of Zinc(II) compounds showing there is no tendency to an octahedral geometry against a tetrahedral coordination geometry.**

### 3.3. FT-IR Spectral data

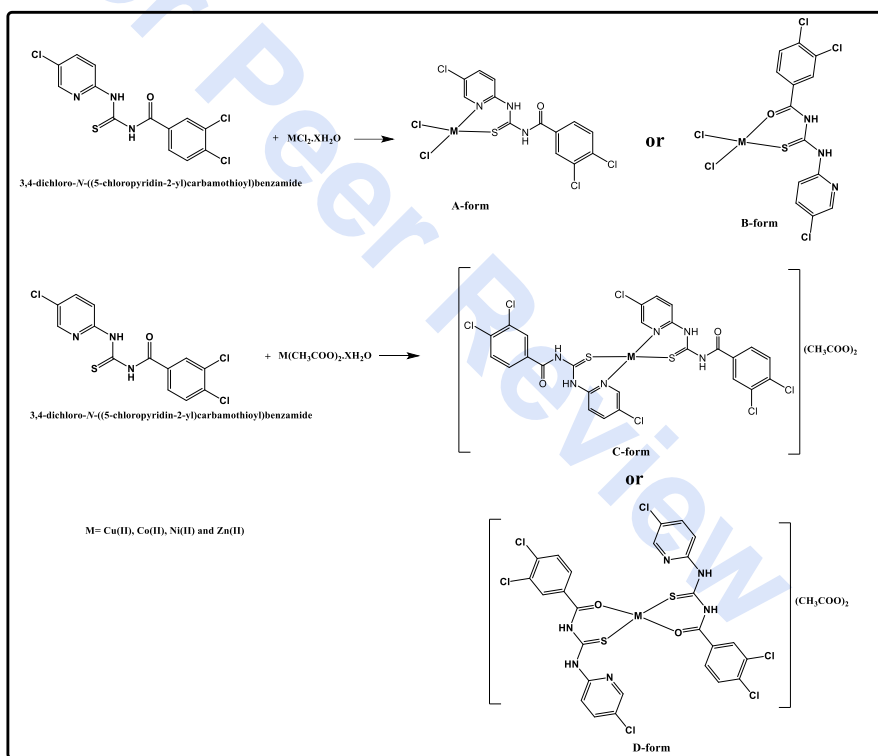
Different physical and spectral techniques should be used to confirm the structure of the prepared compounds as full characterization. IR spectroscopy technique is deemed one of the most significant technique employed to determine the style of the

coordination between central ions with free ligand. The fundamental vibrational functional bands of 3,4-dichloro-*N*-((5-chloropyridin-2-yl)carbamothioyl) benzamide ligand (**L**) and its prepared Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes are presented in the experimental part and reported in **Table 1**. The bands which appeared at 1560 and 1673  $\text{cm}^{-1}$  in the ligand **L** spectrum are attributed to  $\delta(\text{N-H})^2$  and  $\nu(\text{C=O})$  respectively [34]. This indicates to the existence of interligand hydrogen bonding. Significant bands which appeared at 1528, 1338  $\text{cm}^{-1}$  are assigned to  $\nu(\text{C=N})$  and  $\nu(\text{C=S})$  respectively. Furthermore, its FT-IR spectrum showed  $\nu(\text{N-H})$  and  $\delta(\text{N-H})^1$  at 3240 and 1586  $\text{cm}^{-1}$  too. While the FT-IR spectra of all prepared complexes exhibited a noticeable red shift (lower wavenumber as compared to free ligand) of  $\nu(\text{C=N})$  and  $\nu(\text{C=S})$  peaks at (1454-1489)  $\text{cm}^{-1}$  and (1285-1319)  $\text{cm}^{-1}$  which are confirmed the coordination between thiourea ligand **L** with metal ions through nitrogen atom in pyridyl ring and sulfur atom in thiourea moiety. The electron donating manners of nitrogen and sulfur atoms in C=N and C=S groups toward metal ions which consider more electropositive species reduce and weak the double bond characteristic in C=N and C=S bonds. Then, this reduce the force constant of the bonds which make them observable at lower wavenumber relative to free ligand **L**. The  $\nu(\text{C=O})$  in all complexes still approximately around the same its value in the free ligand and this refers to C=O group do not contribute in the coordination to form complexes and the intraligand hydrogen bonding still exist in the inner form complexes. According to the structural formula of ligand **L**, there are different possible coordination sites to form its metal complexes: nitrogen atom in C=N pyridyl group, sulfur atom in C=S group and oxygen atom in C=O group and this is allowed to more than one form to happen as showed below in **Scheme 2**. Chloride complexes are possible to create as A-form or B-form and acetate complexes could form in C-form or D-form. The red shift of C=N and C=S and the constant C=O group in the prepared complexes as compared with free ligand **L** is a decisive evidence to form A-form in chloride complexes and C-form in acetate complexes. As well as, two new bands appeared at 478-513  $\text{cm}^{-1}$  and 536-542  $\text{cm}^{-1}$  are assigned to M-S and M-N bonds in complexes which confirm A-form and C-form in chloride and acetate complexes respectively (**Scheme 3**). This mode of chelation is consistent and in good agreement with the already reported complexes benzoyl thiourea derivatives that coordinate with Copper(II), Nickel(II) and Zinc(II) ions through nitrogen C=N and sulfur C=S groups [31].

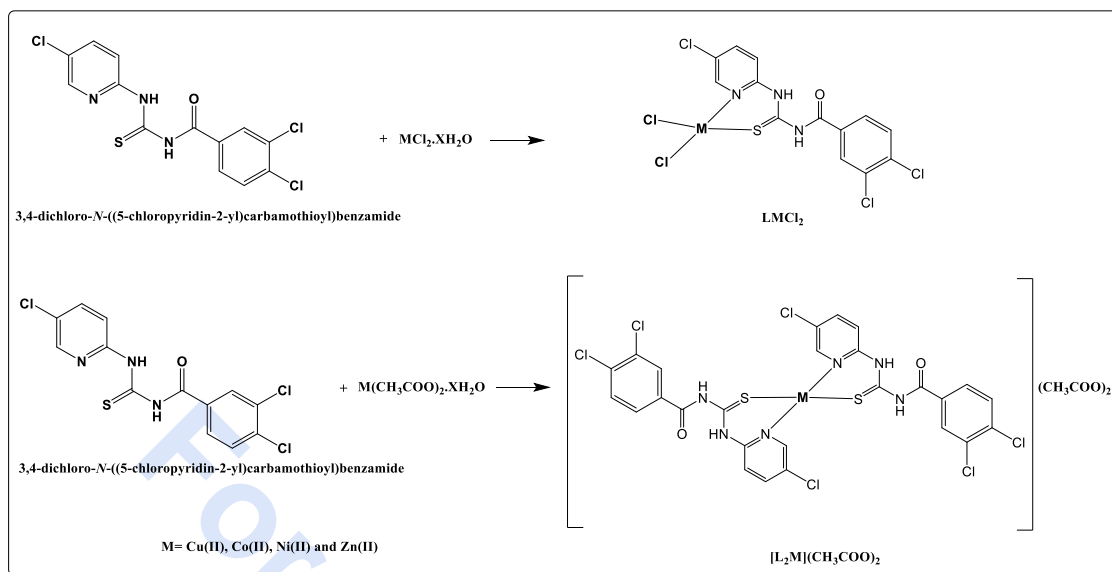


Table 1: Assignments of the IR characterization (cm<sup>-1</sup>) of 3,4-dichloro-N-((5-chloro pyridin-2-yl)carbamothioyl)benzamide (L) and its metal complexes.

Compound.	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\delta(\text{N-H})^1$	$\delta(\text{N-H})^2$	$\nu(\text{C=N})$	$\nu(\text{C=S})$	$\nu(\text{M-S})$	$\nu(\text{M-N})$
L	3240	1673	1586	1560	1528	1338	-	-
[LCuCl <sub>2</sub> ]	3349	1670	1570	1531	1485	1315	478	536
[L <sub>2</sub> Cu](CH <sub>3</sub> COO) <sub>2</sub>	3283	1672	1582	1520	1489	1319	478	540
[LCoCl <sub>2</sub> ]	3325	1669	1616	1543	1462	1312	509	536
[L <sub>2</sub> Co](CH <sub>3</sub> COO) <sub>2</sub>	3345	1667	1620	1551	1485	1288	509	537
[LNiCl <sub>2</sub> ]	3325	1669	1585	1547	1458	1285	509	540
[L <sub>2</sub> Ni](CH <sub>3</sub> COO) <sub>2</sub>	3322	1669	1582	1551	1458	1288	513	542
[LZnCl <sub>2</sub> ]	3380	1670	1580	1524	1454	1285	508	539
[L <sub>2</sub> Zn](CH <sub>3</sub> COO) <sub>2</sub>	3290	1670	1589	1535	1458	1292	509	541



Scheme 2: Potential structural formula (A-D forms) of element complexes of ligand L by using metal chloride and metal acetate.

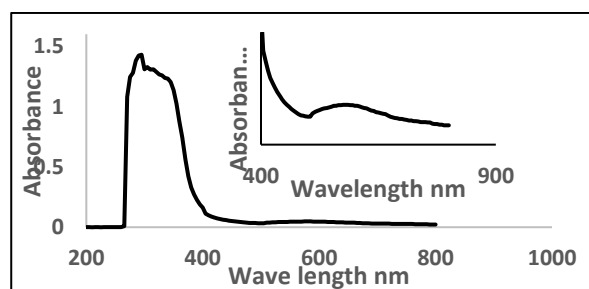


**Scheme 3:** Structural formula of the prepared Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes of thiourea ligand L by using metal chloride and metal acetate.

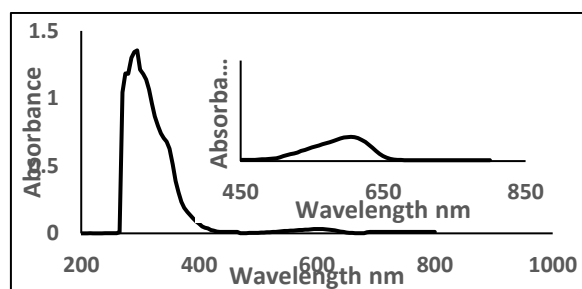
### 3.4. Electronic Spectra

The electronic spectra of free ligand 3,4-dichloro-N-(5-chloropyridin-2-yl)carbamothioyl benzamide ligand (L) and its Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes were recorded in DMSO solution at room temperature and the data are listed in **Table 2**. The UV-vis. spectrum of free ligand L showed  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  peaks at high energy 270 nm, 295 nm and 340 nm which are shifted in the range 270-280 nm, 290-315 nm and 335-355 nm respectively in Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes. A square planar four coordinated system of the Copper(II) complexes is emphasized by the appearance of  $d-d$  transitions which are noticed at 590 nm ( $24 M^{-1} cm^{-1}$ ) and 581 nm ( $19 M^{-1} cm^{-1}$ ) in the electronic spectra of their complexes,  $[LCuCl_2]$  and  $[L_2Cu](CH_3COO)_2$  respectively, for example **Figure 7**. The Cobalt(II) complexes,  $[LCoCl_2]$  and  $[L_2Co]$

$(CH_3COO)_2$  exhibited a square planar geometry. One band is observed at 611 nm ( $28 M^{-1} cm^{-1}$ ) and 605 nm ( $22 M^{-1} cm^{-1}$ ) in  $[LCoCl_2]$  and  $[L_2Co](CH_3COO)_2$  respectively relating with  $d_{xy} \rightarrow d_{x^2-y^2}$  transition, for example **Figure 8**. The spectra of Nickel(II) complexes reflected a square planar environment around the Nickel(II) ion with single  $d-d$  transition located at 601 nm ( $19 M^{-1} cm^{-1}$ ) and 599 nm ( $11 M^{-1} cm^{-1}$ ) which are attributed to  $d_{xy} \rightarrow d_{x^2-y^2}$  transition in  $[LNiCl_2]$  and  $[L_2Ni](CH_3COO)_2$  complexes. These values are in good agreement with the related compound  $[Ni(DEP)]$  which reveals a similar transition  $d_{xy} \rightarrow d_{x^2-y^2}$  at 568 nm [35,36]. The UV-visible spectra of diamagnetic  $d^{10}$  Zinc(II) complexes,  $[LZnCl_2]$  and  $[L_2Zn](CH_3COO)_2$  have similar absorptions in free ligand L by displaying intra ligand transitions ( $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$ ) with absence of  $d-d$  transitions according to expectation.



**Figure 7:** The electronic spectrum of square planar  $[LCuCl_2]$  complex.



**Figure 8:** The electronic spectrum of square planar  $[LCoCl_2]$  complex.

**Table 2: Assignments of the UV-visible characterization  $\lambda_{\text{max}}$ , nm, ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) of the free ligand (L) and its metal complexes.**

Compound.	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$d_{\text{sv}} - d_{\text{x}^2 - \text{y}^2}$
L	270(11816)	295(13616) 340(6433)	-----
[LCuCl <sub>2</sub> ]	273(11522)	295(12272) 344(10294)	590(24)
[L <sub>2</sub> Cu](CH <sub>3</sub> COO) <sub>2</sub>	275(8533)	315(9222) 350(9405)	581(19)
[LCoCl <sub>2</sub> ]	280(11822)	295(13555) 350(6277)	611(28)
[L <sub>2</sub> Co](CH <sub>3</sub> COO) <sub>2</sub>	275(11522)	295(13216) 335(10027)	605(22)
[LNiCl <sub>2</sub> ]	275(11294)	295(12866) 345(10433)	601(19)
[L <sub>2</sub> Ni](CH <sub>3</sub> COO) <sub>2</sub>	270(9683)	293(12772) 355(10483)	599(11)
[LZnCl <sub>2</sub> ]	280(11377),	295(12911) 345(10272)	-----
[L <sub>2</sub> Zn](CH <sub>3</sub> COO) <sub>2</sub>	280(12255)	290(13011) 350(10505)	-----

### 3.5. Magnetic moment measurements

The magnetic moment of the [LCuCl<sub>2</sub>], [LCoCl<sub>2</sub>], [LNiCl<sub>2</sub>], [LZnCl<sub>2</sub>], [L<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>, [L<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, [L<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [L<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> complexes were accomplished at room temperature using a Johnson Matthey magnetic susceptibility balance. The measured magnetic moment values indicate that Zinc(II) and Nickel(II) complexes are diamagnetic while Copper(II) and Cobalt(II) complexes are paramagnetic. The observed magnetic moments of Copper(II) complexes, [LCuCl<sub>2</sub>] and [L<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub> are 1.74 B.M. and 1.83 B.M. which correspond with one unpaired electron  $d^9$  configuration in Copper(II) complexes and confirming square planar geometry. The  $d^7$  Cobalt(II) complexes [LCoCl<sub>2</sub>] and [L<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub> exhibit paramagnetic behavior with observed magnetic moments 2.65 B.M. and 2.83 B.M. to emphasize the square planar coordination structure. While the effective theoretical magnetic moment value equals to value of spin only which is 1.73 B.M.. These difference is related with the ligand field of square planar geometry which cause ineffective quenching of the orbital moments. The magnetic moments of Nickel(II) complexes are zero and that enhancing the diamagnetic features and the square planar coordination geometry around the Nickel(II) ion. Finally, zero value of the observed magnetic moment of  $d^{10}$  Zinc(II) complexes confirms the diamagnetic properties of  $d^{10}$  Zinc(II) complexes. As expected. These results in agreement with previous literature data [37-39]. **Table 3** presents the observed magnetic moments of the prepared complexes.

**Table 3: Magnetic data of the Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes of 3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl)benzamide ligand.**

No.	Complex	Observed magnetic moment B.M.
1	[LCuCl <sub>2</sub> ]	1.74
2	[LCoCl <sub>2</sub> ]	2.65
3	[LNiCl <sub>2</sub> ]	Diamagnetic
4	[LZnCl <sub>2</sub> ]	Diamagnetic
5	[L <sub>2</sub> Cu](CH <sub>3</sub> COO) <sub>2</sub>	1.83
6	[L <sub>2</sub> Co](CH <sub>3</sub> COO) <sub>2</sub>	2.83
7	[L <sub>2</sub> Ni](CH <sub>3</sub> COO) <sub>2</sub>	diamagnetic
8	[L <sub>2</sub> Zn](CH <sub>3</sub> COO) <sub>2</sub>	diamagnetic

### 3.6. Molar Conductivity measurements

The molar conductance of Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes of 3,4-dichloro-N-((5-chloro pyridin-2-yl)carbamothioyl)benzamide ligand were recorded at room temperature using DiMethylSulfoxide solvent in the range  $25 \times 10^{-6}$  -  $1.21 \times 10^{-2} \text{ mol.L}^{-1}$  to investigate the electrolytic behavior of the complexes. The equation:  $\Lambda_m = 1000 \text{ K}/C$  ( $\Lambda_m$  = molar conductance,  $\text{K}$  = specific conductance,  $C$  = molar concentration of the complexes) was used to calculate the molar conductance. The most interesting finding was that the molar conductivity measurements at  $1 \times 10^{-4} \text{ mol. L}^{-1}$  exhibit high values of acetate metal complexes which fall in the range  $64.190$ - $113.700 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  and they are much higher than the values of chloride metal complexes in the range  $6.725$ - $9.110 \text{ Ohm}^{-1} \text{ Cm}^2 \text{ mol}^{-1}$  confirming good electrolytic behavior of acetate metal complexes with 1:2 (Metal:Ligand) ratio, type [L<sub>2</sub>M](CH<sub>3</sub>COO)<sub>2</sub> and the non-electrolytic nature of chloride metal complexes in a 1:1 (Metal:Ligand) ratio, type [LMCl<sub>2</sub>]. These results are agreed with previous relevant reports [40,41]. The linear relation was observed between the concentration of solutions and the specific conductance due to the higher number of ions with increasing the electrolytes concentration and the various of dissociation degree [42]. The molar conductances  $\Lambda_m$  were plotted versus the square root of the concentration for metal complexes solutions  $C^{1/2}$  according to Friedrich Kohlrausch equation. See **Figures 9** and **10** for the Nickel(II) acetate and chloride complexes to applied Friedrich Kohlrausch equation.

$$\Lambda_m = \Lambda_m^0 - K(C)^{1/2} \dots \dots \dots (1)$$

Theoretically, from equation 1, it is clear that direct and positive relation between the molar conductance and the concentration which is absolutely identical with the practical data. The Kraos equation (equation 2) was drawn with linear function to gain  $\Lambda_m^0$  and  $K_d$

values of the metal complexes. See **Figures 11 and 12** for the Nickel(II) acetate and chloride complexes to applied Kraos equation.

$$\Lambda_m \cdot C = K_d \cdot \Lambda_m^{\circ 2} (1 / \Lambda_m) - K_d \cdot \Lambda_m^{\circ} \quad (2)$$

$\Lambda_m$  is the molar conductance at a specific concentration.

$\Lambda_m^{\circ}$  is the molar conductivity at infinite dilution or at zero concentration. It is easy to record  $\Lambda_m^{\circ}$  value through applying of  $\Lambda_m$  as a function of the square of root of the solution concentration.

C is the solution concentration

$K_d$  is the dissociation degree constant even for strong concentrated electrolytes.

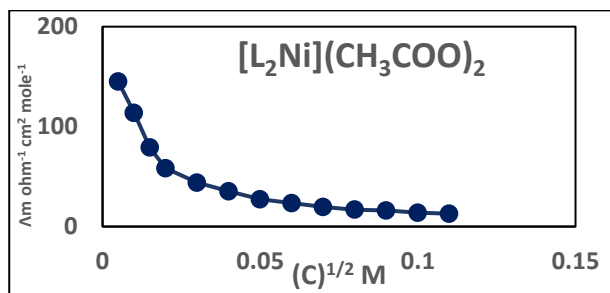
K is the Kohlrausch coefficient, which relates with the stoichiometry of the specific salt in solution.

The molar conductances ( $\Lambda_m$  and  $\Lambda_m^{\circ}$ ) and dissociation constant  $K_d$  for the metal complexes of ligand L are listed in **Table 4**. Another important finding from the molar conductivity data was that the metal complexes arranged in Nickel(II)>Copper(II)>Cobalt(II)>Zinc(II) complexes as increasing in  $\Lambda_m$  values. For example,  $\Lambda_m$  values for Nickel(II),

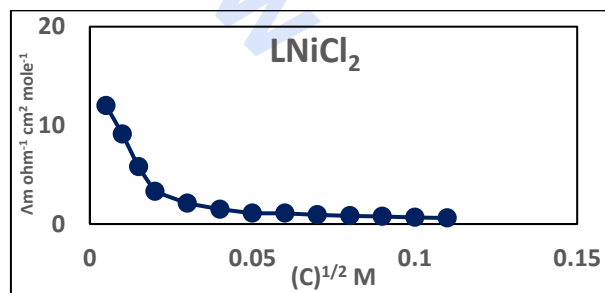
Copper(II), Cobalt(II), Zinc(II) acetate complexes were 113.700, 99.310, 90.750, 64.190  $\text{Ohm}^{-1} \text{Cm}^2 \text{mol}^{-1}$  respectively while  $\Lambda_m$  values for Nickel(II), Copper(II), Cobalt(II), Zinc(II) chloride complexes were 9.110, 8.131, 7.301, 6.725  $\text{Ohm}^{-1} \text{Cm}^2 \text{mol}^{-1}$  respectively. The dissociation constant  $K_d$  values of metal complexes describe the affinity and the strength of bound among ligand, chelating agent and metal ion. In **Table 4**,  $K_d$  values of chloride complexes arranged in 1.234 to 3.949  $\text{mol} \cdot \text{cm}^{-3}$  and acetate complexes in 25.802 to 73.499  $\text{mol} \cdot \text{cm}^{-3}$ . So, it is obvious finding that the  $K_d$  values of chloride complexes are lower than acetate complexes to show the high strength bonding in  $[\text{LMCl}_2]$  complexes between the metal ion with ligand L and two chloride groups. While high  $K_d$  of acetate complexes describes the relatively weak bonding in  $[\text{L}_2\text{M}](\text{CH}_3\text{COO})_2$  complexes. These are due to the strong chloride chelating agents in chloride complexes than acetate complexes which have big acetate counter ion and two moles of ligand chelating with the metal central ion.

**Table 4: Molar conductivity at  $1 \times 10^{-4} \text{ M}$  ( $\Lambda_m$ ), at infinite dilution ( $\Lambda_0$ ) and dissociation constant ( $K_d$ ) for Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes of 3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl)benzamide ligand.**

No.	Complex	$\Lambda_0$ ( $\text{Ohm}^{-1} \text{Cm}^2 \text{mol}^{-1}$ )	$\Lambda_m$ ( $\text{Ohm}^{-1} \text{Cm}^2 \text{mol}^{-1}$ ) at $1 \times 10^{-4} \text{ mol/L}$	$K_d \times 10^{-6}$ ( $\text{mol} \cdot \text{cm}^{-3}$ )
1	$[\text{LCuCl}_2]$	33.900	8.131	2.259
2	$[\text{LCoCl}_2]$	26.579	7.301	1.994
3	$[\text{LNiCl}_2]$	44.268	9.110	3.949
4	$[\text{LZnCl}_2]$	21.378	6.725	1.234
5	$[\text{L}_2\text{Cu}](\text{CH}_3\text{COO})_2$	164.628	99.310	65.130
6	$[\text{L}_2\text{Co}](\text{CH}_3\text{COO})_2$	153.538	90.750	48.473
7	$[\text{L}_2\text{Ni}](\text{CH}_3\text{COO})_2$	206.300	113.700	73.499
8	$[\text{L}_2\text{Zn}](\text{CH}_3\text{COO})_2$	103.769	64.190	25.802



**Figure 9: Molar conductance  $\Lambda_m$  versus  $(C)^{1/2}$  for  $[\text{L}_2\text{Ni}](\text{CH}_3\text{COO})_2$  complex.**



**Figure 10: Molar conductance  $\Lambda_m$  versus  $(C)^{1/2}$  for  $\text{LNiCl}_2$  complex.**

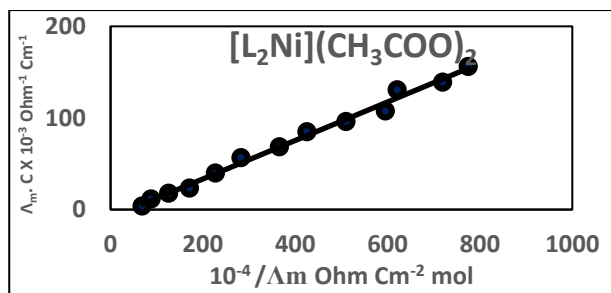


Figure 11:  $\Lambda_m \cdot C \times 10^{-3}$  versus  $10^{-4} / \Lambda_m$  for  $[L_2Ni](CH_3COO)_2$  complex.

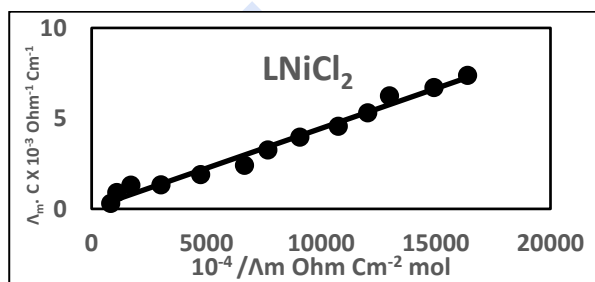


Figure 12:  $\Lambda_m \cdot C \times 10^{-3}$  versus  $10^{-4} / \Lambda_m$  for  $LNiCl_2$  complex.

### 3.7. Solubility Test

Different solvents are employed to accomplish the solubility test of Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes of 3,4-dichloro-*N*-((5-chloro pyridin-2-yl)carbamio thioyl) benzamide ligand. The used solvents are classified into two types, polar solvents like ( $H_2O$ , DMSO, DMF, methanol, absolute ethanol, acetone, acetonitrile and ethyl acetate) and nonpolar solvents like (chloroform, methylene chloride, toluene, benzene cyclohexane and  $CCl_4$ ). The solubility test is used to know the ionic and nonionic manners of complexes. Solubility test of these complexes is presented in **Table 5**. The most obvious finding to emerge from **Table 5** is that the acetate complexes are soluble in the used polar solvent like methanol, absolute ethanol, acetone, acetonitrile and ethyl acetate with quite solubility in DMF and DMSO. While acetate complexes exhibit contrary behavior towards nonpolar solvent through their no solubility in them like chloroform, methylene chloride, toluene, benzene cyclohexane and  $CCl_4$ . The good solubility of acetate complexes in polar solvents and no solubility in nonpolar solvents confirm the ionic properties of acetate complexes in the form  $[L_2M](CH_3COO)_2$ . On the other hand, chloride complexes showed opposite manner towards their solubility in polar and nonpolar solvents. They are nonsoluble or poor soluble in polar solvents and soluble or poor soluble in nonpolar solvents and these results confirm the nonionic properties and neutral

form,  $[LMCl_2]$  of chloride complexes. Another important finding was that acetate and chloride complexes were obviously soluble in DMF and DMSO solvents and this is due to very big polarity of these solvents and the possible complexation between solvent with complexes.

### 3.8. Electrochemical Measurements

The Importance of study electrochemical behavior for element complexes come through the conformation of the oxidation state of central metal ion in its complexes which considers with ligand basicity significant factors effecting on the formation of the complexes. The activity of cyclic voltammetry technique is coming from the fast knowing of the redox manner of element complexes throughout a spread potential area. The redox properties of central ion affected directly by the structure and the physical properties of the chelated ligand. The potential of reduction/oxidation process is considered as essential parameter to describe the capability of the electron transformation by reduction/oxidation centre as well as its acting as reduction/oxidation catalyst. The cyclic voltammograms of Copper(II), Cobalt(II) and Nickel(II) complexes were recorded in  $CH_3CN$  solution including  $0.1 \text{ mol.L}^{-1}$  of the supporting electrolyte, tetra butyl ammonium hexa fluoro phosphate (TBAHFP). The electrochemical data are summarized for Copper(II), Cobalt(II) and Nickel(II) complexes in **Table 6**. The cyclic voltammograms of Copper(II) complexes,  $[LCuCl_2]$  and  $[L_2Cu](CH_3COO)_2$  reveal a single quasi-reversible electron transfer process throughout the used scan rate range of  $100\text{-}1000 \text{ mv.sec}^{-1}$  at the cathodic potential at  $-0.3183$  and  $-0.3524$  volt (vs  $Fc/Fc^+$ ) respectively as showed in **Figures 13** and **14**. This potential is perfect to standard Copper(II)/Copper(I) couple. The big peak to peak splitting as compared to the internal standard peak in ferrocene and the lower than 1 value of the ratio of passing current at cathode electrode to passing current at anode electrode ( $i_{pc}$  to  $i_{pa}$ ) confirm the quasi-reversible system. The peak to peak splitting value for  $[LCuCl_2]$  and  $[L_2Cu](CH_3COO)_2$  are  $303 \text{ mv}$  and  $315 \text{ mv}$  respectively and they are probably because of the structural/geometrical rearrangement happening on the transformation between Copper(II) to Copper(I) oxidation state. From **Table 6** it is observed that the potential of chloride complex,  $[LCuCl_2]$  is lower than the potential of acetate complex,  $[L_2Cu](CH_3COO)_2$ . This is due to the existence of two chloride groups in chloride complexes which known as good electron withdrawing groups chelating with metal ion, then make metal ion more charge positivity and then appear with lower potential.

Two irreversible reduction processes are observed at (-1.1826 and -1.8305 volt vs Fc/Fc<sup>+</sup>) and (-1.2599 and -1.9223 volt vs Fc/Fc<sup>+</sup>) in the cyclic voltammograms of [LNiCl<sub>2</sub>] and [L<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> sequentially (**Table 7**). The first irreversible reduction is attributed to the couple Nickel(II) to Nickel(I) and the second irreversible process imputed to Nickel(III) to Nickel(II) system. **Figures 15** and **16** are presented the cyclic voltammograms of Nickel(II) complexes. These results are consistent with those of the report of Fawaz *et al.* who also studied Nickel(II) complex of similar thiourea derivative [bis(6-benzoylthiourea-2-pyridylmethyl)(2-pyridylmethyl) amine] which presented two irreversible reductions at -1.37 V and -1.78 V (vs Fc/Fc<sup>+</sup>) in acetonitrile solvent [44]. The Cobalt(II) complexes, LCoCl<sub>2</sub> and [L<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub> exhibit quite similar electrochemical behavior as Nickel(II) complexes. Their cyclic voltammograms of LCoCl<sub>2</sub> and [L<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub> display two consecutive irreversible processes at (-1.1735 and -1.6703 volt vs Fc/Fc<sup>+</sup>) and (-1.1955 and -1.7283 volt vs Fc/Fc<sup>+</sup>) respectively (**Table 7**). The first reductive irreversible process is assigned to Cobalt(II)/Cobalt(I) while the second process is attributed to Cobalt(III)/Cobalt(II) as compared to similar Cobalt(II) complexes [43, 44]. **Figures 17** and **18** illustrated cyclic voltammograms for the Cobalt(II) complexes. From **Table 7** and as similar behaviour to Copper(II) complexes, the chloride complexes of Nickel(II) and Cobalt(II) ions appeared in the lower potential than their corresponding acetate complexes.

**Table 5: Solubility Test of Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes of 3,4-dichloro-N-((5-chloropyridin-2-yl)carbamoyl)benzamide ligand.**

No.	polarity	Solvent	[LCuCl <sub>2</sub> ]	[LCoCl <sub>2</sub> ]	[LNiCl <sub>2</sub> ]	[LZnCl <sub>2</sub> ]	[L <sub>2</sub> Cu] (CH <sub>3</sub> COO) <sub>2</sub>	[L <sub>2</sub> Co] (CH <sub>3</sub> COO) <sub>2</sub>	[L <sub>2</sub> Ni] (CH <sub>3</sub> COO) <sub>2</sub>	[L <sub>2</sub> Zn] (CH <sub>3</sub> COO) <sub>2</sub>
1		H <sub>2</sub> O	Nonsoluble	Nonsoluble	Nonsoluble	Nonsoluble	Nonsoluble	Nonsoluble	Nonsoluble	Nonsoluble
2		DMSO	Soluble	Soluble	Soluble	Soluble	Quite soluble	Quite soluble	Quite soluble	Quite soluble
3	Polar solvent	DMF	Soluble	Soluble	Soluble	Soluble	Quite soluble	Quite soluble	Quite soluble	Quite soluble
4		methanol	Poor Soluble	Poor Soluble	Poor Soluble	Poor Soluble	Soluble	Soluble	Soluble	Soluble
5		ethanol	Poor Soluble	Poor Soluble	Poor Soluble	Poor Soluble	Soluble	Soluble	Soluble	Soluble
6		acetone	Poor Soluble	Poor Soluble	Poor Soluble	Poor Soluble	Soluble	Soluble	Soluble	Soluble
7		acetonitrile	Poor Soluble	Poor Soluble	Poor Soluble	Poor Soluble	Soluble	Soluble	Soluble	Soluble
8		ethyl acetate	Nonsoluble	Nonsoluble	Nonsoluble	Nonsoluble	Soluble	Soluble	Soluble	Soluble
9		chloroform	Soluble	Soluble	Soluble	Soluble	Nonsoluble	Nonsoluble	Nonsoluble	Nonsoluble
10		Methylene chloride	Soluble	Soluble	Soluble	Soluble	Nonsoluble	Nonsoluble	Nonsoluble	Nonsoluble
11	Non Polar solvent	toluene	Poor Soluble	Poor Soluble	Poor Soluble	Poor Soluble	Nonsoluble	Nonsoluble	Nonsoluble	Nonsoluble
12		benzene	Poor Soluble	Poor Soluble	Poor Soluble	Poor Soluble	Nonsoluble	Nonsoluble	Nonsoluble	Nonsoluble
13		cyclohexane	Poor Soluble	Poor Soluble	Poor Soluble	Poor Soluble	Nonsoluble	Nonsoluble	Nonsoluble	Nonsoluble
14		CCl <sub>4</sub>	Poor Soluble	Poor Soluble	Poor Soluble	Poor Soluble	Nonsoluble	Nonsoluble	Nonsoluble	Nonsoluble

Table 6: Electrochemical parameters for the quasi-reversible process presented by copper(II) complexes in CH<sub>3</sub>CN solvent, supporting electrolyte [Bu<sub>4</sub>N][PF<sub>6</sub>] (0.1 mol.L<sup>-1</sup>), t =25<sup>o</sup> c measured at 100 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>
[LCuCl <sub>2</sub> ]	-0.3183	-0.6209	303	-0.4696	15.6	13.6	0.871
[L <sub>2</sub> Cu](CH <sub>3</sub> COO) <sub>2</sub>	-0.3524	-0.6673	315	-0.5098	2.5	1.6	0.64

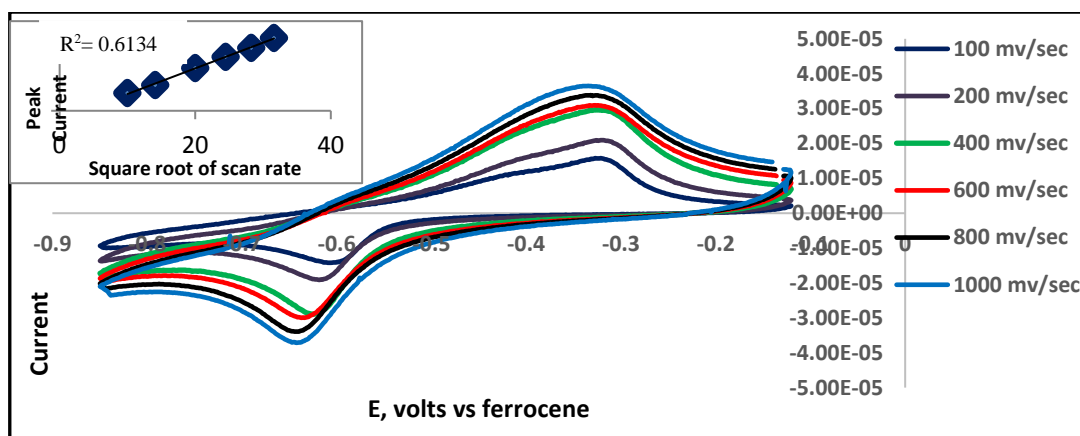


Figure 13: Cyclic voltammogram showing quasi-reversible system of [LCuCl<sub>2</sub>] complex.

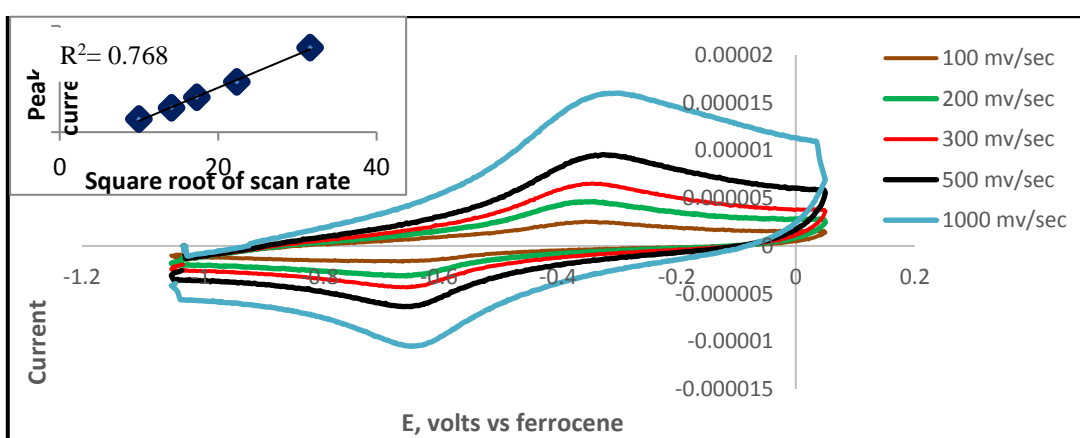


Figure 14: Cyclic voltammogram showing quasi-reversible system of [L<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub> complex.

Table 7: Electrochemical parameters for the irreversible process presented by Nickel(II) and Cobalt(II) complexes in CH<sub>3</sub>CN solvent, supporting electrolyte [Bu<sub>4</sub>N][PF<sub>6</sub>] (0.1 mol.L<sup>-1</sup>), t =25<sup>o</sup> c measured at 100 mv/sec.

complex	E <sub>p</sub> /V vs Fc/Fc <sup>+</sup> irreversible reductions	
[LNiCl <sub>2</sub> ]	-1.1826	-1.8305
[L <sub>2</sub> Ni](CH <sub>3</sub> COO) <sub>2</sub>	-1.2599	-1.9223
[LCoCl <sub>2</sub> ]	-1.1735	-1.6703
[L <sub>2</sub> Co](CH <sub>3</sub> COO) <sub>2</sub>	-1.1955	-1.7283



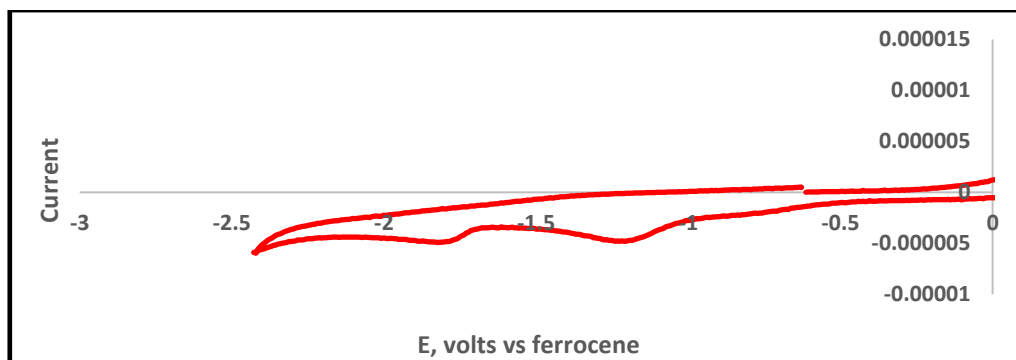


Figure 15: Cyclic voltammogram showing irreversible system of [LNiCl<sub>2</sub>] complex.

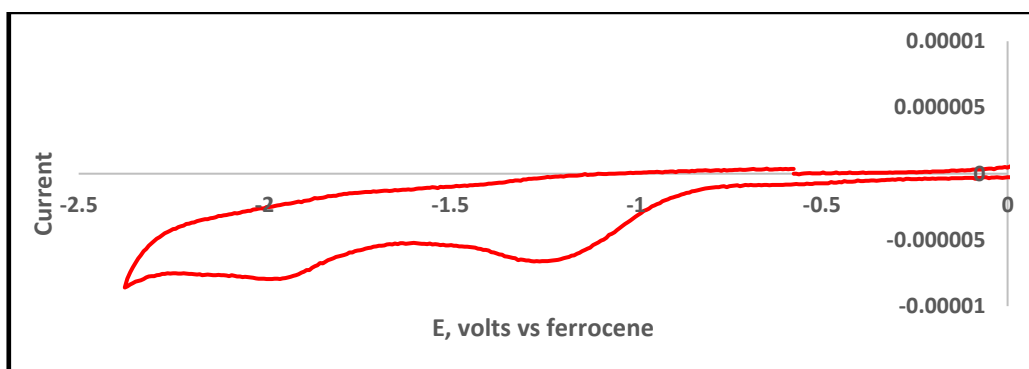


Figure 16: Cyclic voltammogram showing irreversible system of [L<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> complex.

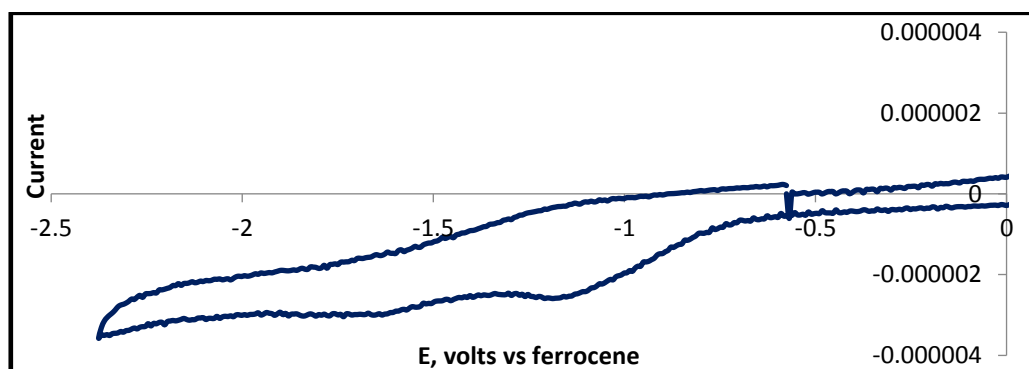


Figure 17: Cyclic voltammogram showing irreversible system of [LCoCl<sub>2</sub>] complex.

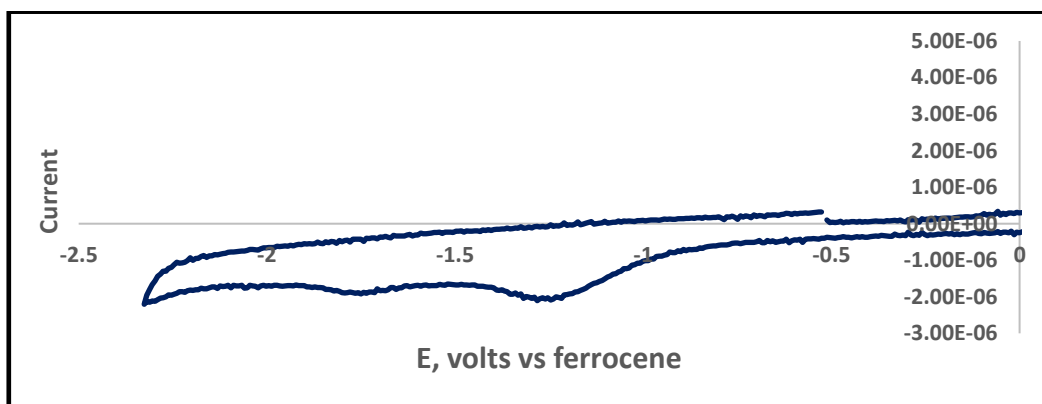


Figure 18: Cyclic voltammogram showing irreversible system of [L<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub> complex.

#### 4. Conclusion

In this study, The new N, N'-disubstituted benzoyl thiourea derivative, [3,4-dichloro-N-((5-chloropyridin-2-yl)carbamothioyl)benzamide] ligand (L) and its series of Copper(II), Cobalt(II), Nickel(II) and Zinc(II) complexes [LCuCl<sub>2</sub>], [LCoCl<sub>2</sub>], [LNiCl<sub>2</sub>], [LZnCl<sub>2</sub>], [L<sub>2</sub>Cu](CH<sub>3</sub>COO)<sub>2</sub>, [L<sub>2</sub>Co](CH<sub>3</sub>COO)<sub>2</sub>, [L<sub>2</sub>Ni](CH<sub>3</sub>COO)<sub>2</sub> and [L<sub>2</sub>Zn](CH<sub>3</sub>COO)<sub>2</sub> have been synthesized and characterized by elemental analysis, magnetic moments, conductivity measurements, solubility test, mass spectra, IR, UV-vis, <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy. The coordinaton behavior of free ligand L has been investigated and the characterization studies reveal the versatility of these ligands to form stable complexes with the transition metal ions under study. The spectrographic techniques of these complexes showed the free ligand L has a strong geometrical preference for four coordinate square planar geometry with the MN<sub>2</sub>S<sub>2</sub> skeletal in acetate complexes [ML<sub>2</sub>](CH<sub>3</sub>COO)<sub>2</sub> and two moles of ligand (L) have been found to bind as anion bidentate ligand through two sulfur atoms in two C=S groups and two nitrogen atoms in two pyridyl groups. While the metal(II) ion in MLCl<sub>2</sub> adoptting MNSCl<sub>2</sub> site and coordinates with sulfur atom in C=S and nitrogen atom in pyridyl ring, third and fourth sites are occupied with two chloride ions. The most obvious and interesting finding to emerge from the analysis and makes an attractive approach to new complexes, is that when the reaction accomplishes between ligand L and metal chlorides in 1:1 and 2:1 (L:M) mole ratio sequentially, the result is the same with LMCl<sub>2</sub> formula. While the same reactions were performed by using the same conditions as above with excepting use metal acetates instead of metal chlorides to give [ML<sub>2</sub>](CH<sub>3</sub>COO)<sub>2</sub>. The reason of these formulas is related with the nature of the chloride ion as difficult leaving group and its small size, so it is clear that it is difficult for the ligand L to displace and replace two chloride ions from MLCl<sub>2</sub> to form [ML<sub>2</sub>]Cl<sub>2</sub>. The opposite thing happens with using metal acetate, in 1:1 and 2:1 mole ratio the product is [ML<sub>2</sub>](CH<sub>3</sub>COO)<sub>2</sub> not LM(CH<sub>3</sub>COO)<sub>2</sub> and this is due the behaviour of acetate anion as good leaving and big size group. Cyclic voltammometry studies show that Copper(II) complexes give one electron transfer metal based quasi-reversible reductive process due to Copper(II)/Copper(I) redox couple while two reductive consecutive irreversible processes are observed in the cyclic voltammograms of Cobalt(II) and Nickel(II) complexes due to M(II)/M(I) and M(III)/M(II) redox couples. This indicating that free thiourea ligand stabilizes both Copper(II) and Copper(I) ions in their complexes while Nickel(I) and Cobalt(I) are not stable in CH<sub>3</sub>CN solvent. The electrochemical manners of Copper complexes, quasi-reversible process with low reductive potential and high stability of Copper(II) and Copper(I) suggest

their probable electrocatalytic and electrochemical sensor applications. Interestingly, chloride complexes is observed at low potential than acetate complexes due to the existence of two chloride groups which consider good electron withdrawing groups making metal ion more positive.

#### 5. Conflicts of interest

The authors would like to declare that there are no conflicts to publish this paper.

#### 6. Acknowledgments

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