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## **Synthesis , Characterization and physical studies of Some New Co(II), Ni(II), Cu(II) and Zn(II) Complexes with (E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl) benzamide Ligand**

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### **Abstract:**

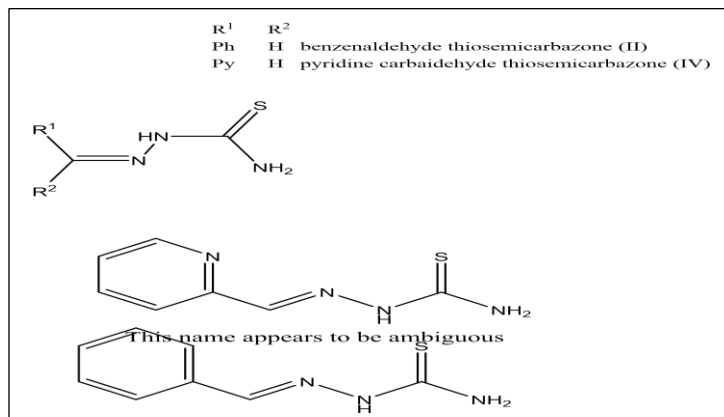
New series complexes of Cu(II), Ni(II), Zn (II) and Co(II) ions were derived from the novel thiosemicarbazone compound, (E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl) benzamide (MNEC-H) ligand was prepared in three steps. The step one the reaction between acetyl pyridine with hydrazine hydrate at room temperature to obtain (E) - 2 -(1 -hydrazonoethyl)pyridine. The Second step 3-nitro 4- methy- benzoyl chloride was refluxed with potassium thiocyanate in acetonitrile solvent forming 3-nitro 4- methy- benzoyl isothiocyanate. The third step of the reaction is summarized by the refluxing the mixture of (E) - 2 -(1 -hydrazonoethyl) pyridine and 3-nitro 4- methy- benzoyl isothiocyanate in acetonitrile solvent to form the desired free ligand (MNEC-H). Two types of the element complexes were synthesized and investigated, the chloride as well as acetate compounds through employing different mole ratios 1:1 (L:M) and 2:1 (L:M) whereas L and M represent the (MNEC-H) ligand and metal salt respectively via using metal chloride and metal acetate salts to gaining [(MNEC-H)MCl]Cl and [(MNEC-H)<sub>2</sub>M] structures. The various available spectroscopies and techniques were used to characterize and confirm the formula of the free ligand (MNEC-H) and its element compounds. <sup>1</sup>HNMR, <sup>13</sup>CNMR, IR, UV-vis, mass spectra, CHNS, magnetic effective moment, conductance values. The cyclic voltammetry of the prepared element complexes were recorded in DMSO solvent to investigate their redox behavior. The Cu(II) compounds showed quasi reversible process at the cathodic potential whereas the Co(II) and Ni(II) complexes displayed one irreversible system at the oxidative potential. All the employed techniques and measurements confirmed together that the chloride compounds arranged as tetrahedral four coordinated [(MNEC-H)MCl]Cl in neutral formula whereas the acetate compounds adopted octahedral six coordinated [(MNEC-H)<sub>2</sub>M] in neutral structure too. The Zn(II) chloride and acetate complexes were confirmed as diamagnetic species according to the effective magnetic

data. While Cu(II), Ni(II), Co(II) and Zn(II) chloride and acetate compounds appeared as paramagnetic species.

**KEYWORDS : Thiosemicarbazone; Metals (Cu(II), Ni(II), Zn(II)Co(II) Complexes; Magnetic Susceptibility; Molar Conductivity ; Cyclic Voltammetry.**

### 1-Introduction

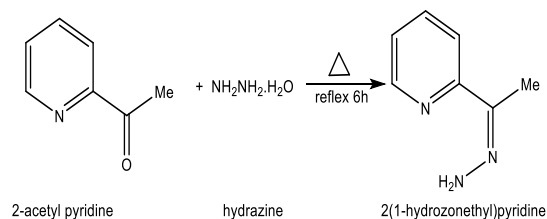
Thiosemicarbazone In organic chemistry with the formula  $H_2NC(S)NHN=CR_2$  is a derivative of imines made by a condensation reaction among a ketone or aldehyde and thiosemicarbazide. They are classified as imine derivatives as they consist from the reaction of an aldehyde or ketone with the terminal  $-NH_2$  group of semicarbazide, which behaves very alike to primary amines [1-3] Thiosemicarbazones are the analogs of the thiosemicarbazides with a sulfur atom in site of the oxygen atom. Thiosemicarbazones are made up of the condensation of an aldehyde or ketone with a thiosemicarbazide. They have high coordinative ability known they have several:potential donor atoms by which they can relation to transition metals. This coordinative ability can be increased if the R1 and R2 compensate include additional donor atoms [4-5] as the following .Scheme1.



**Scheme 1: the general method to prepare of thiosemicarbazon**

Thiosemicarbazone (hydrazine carbothioamides) are a group of compounds with high biological: activity[6]. because to their versatile biological and pharmacological efficacy, their derivatives are of specific importance. They are well intermediates for pharmaceutical and bio-active material synthesis and so, commonly used in medicinal chemistry field. They have also found that it is used in several fields in the branches of chemistry they are used commercially as dyes, photographic films;, plastic and textiles [7] In the past years, thiosemicarbazone derivatives have shown a wide-ranging of biological activity anti-fungal,anti-tumor/cancer:[8], Antimicrobial, sodium channel blocker, antiviral [9]

## 2- Experimental



### 2.1- Materials

Potassium thiocyanate (Aldrich), acetonitrile (Merck), 4-methyl , 3-nitro benzoylchloride (Aldrich), Copper chloride dehydrate (Merck), Copper acetate hydrate (Sigma Aldrich), Nickel chloride six hydrate (CDH), Nickel acetate tetra hydrate (Aldrich) ,Zinc chloride (Merck), Zinc acetate dehydrate (Merck), Cobalt chloride six hydrate (CDH), Vanadium sulfate hydrate (Merck) .

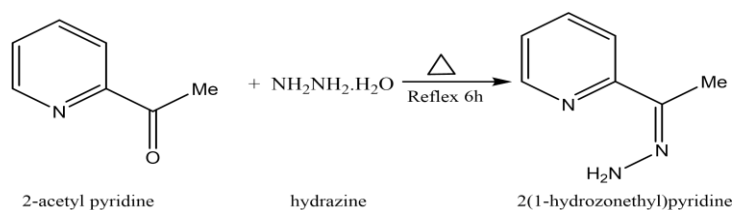
### 2.2- Physical Measurements

The melting points of compounds were recorded on VeeGO Dijital model VMP-Djenway (England), Chemistry Department, College of Sciences, University of Basrah, Iraq. (Elemental analysis CHN) The elemental analysis of all the synthesized compounds was performed by using Costech 4010 (Italy), University of Tarbiat Modares, Tehran, Iran. (Infrared Spectra FT-IR) The IR spectra of all the synthesized compounds were measured as KBr disks for solid samples in the region between (400-4000)  $\text{cm}^{-1}$  by using FT.IR 8400, Shimadazu (Japan), Chemistry Department, College of Sciences, University of Basrah, Iraq. (Ultraviolet and Visible Spectra UV-Visible) for the synthesized compounds were recorded at the Department of Chemistry, College of Science, University of Basrah by the use of Scan 80D (England) at range 200-1200 nm using DMSO as a solvents and 1cm<sup>2</sup> pathway quartz cells. Nuclear Magnetic Resonance Spectrometer (<sup>1</sup>H , <sup>13</sup>C -NMR) were recorded at Tehran University, Islamic republic of Iran by using a inova 500 MHz. Chemical shift of all <sup>1</sup>H-and <sup>13</sup>C NMR spectra were recorded in  $\delta$ (ppm) unit downfield from the internal reference tetramethylsilane (TMS), using DMSO-d<sub>6</sub> solvents. (Conductivity Measurements) Wiss-Techn. Warkstatten D812 Weilheim Mod.LBR(Germany)ChemistryDepartment, College of Sciences, University of Basrah, Iraq. (Mass spectra) for some prepared compounds were performed in Agilent Technologies Instrument by using EI Technique at ionizing potential of 70 eV, in faculty of chemistry, University of Tabriz, Iran. (Magnetic sensitivity) Balance magantic susceptibility model (MSBMKI) College of Sciences, University of mostinsraa , Iraq. (cyclic voltammetry(DY2300Series)potentiostate/Bioptentiostate (Digi-Ivy) Department of Chemistry, College of Science, University of Basrah.

## 2.3- Synthesis of compounds

### 2.3.1- General procedure for synthesis of 2-(1-hydrazonoethyl) Pyridine.

For the purpose of gaining 2-(1-hydrazonoethyl) Pyridine is defrosted 2- acetyl pyridine (0.01 mole) in methanol (25ml) follow by addition of hydrazine hydrate (0.01 mole) in methanol (10ml), The mixture was refluxed for 6hour. The formed solid product was separated by filtration, purified by crystallization from petroleum ether. Ligand as white crystales was obtaine with a yield of (89%) and M.P=119-121°C .as the following Scheme 2 [10] .



Scheme 2: Synthesis of 2-(1-hydrazonoethyl) Pyridine.

### 2.3.2 - Procedure for synthesis of (E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl) benzamide ligand (MNEC-H):

The ligand (**MNEC-H**): was created by a modification to a previously defined methods [11-12]. To a suspension of potassium thiocyanate (5mmol) in acetonitrile (10 ml) was added dropwise a solution of 3-nitro 4- methy- benzoyl chloride (5mmol) in acetonitrile (10ml). The reaction mixture was refluxed for 3h. After this timee, the mixture was a yellow solution with a white precipitat. The mixture was filtered to remove the white precipitate (KCl).A solution of 2-(1-hydrazonoethyl) Pyridine (5mmol) in acetonitrile (10ml) was added to the yellow solution and the reaction mixture was stirred for 2 hours. The solution was left to cool and filtration was used to collect the precipitate substance which was washed with acetonitrile 30ml and filtered to obtain crystals by recrystallization from chloroform: ethanol (1:1), Ligand yellow crystals was obtained. Yield: (0.2 g, 83%); m.p= 150-152<sup>0</sup>C,

### 2.3.3- Synthesis of complexes M:L (1:1) and (1:2)

[(MNEC-H)CuCl]Cl, [(MNECH)CoCl]Cl, [(MNEC-H)NiCl]Cl, [(MNEC-H)ZnCl<sub>2</sub>], [(MNEC-H)<sub>2</sub>Cu], [(DEHC-H)<sub>2</sub>Co]Cl<sub>2</sub>, [(DEHC -H)<sub>2</sub>Ni] and [(DEHC -H)<sub>2</sub>Zn].

#### 2.3.3.1- Synthesis of Mono [(E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl) ethylidene) hydrazine-1-carbonothioyl) benza mide] mono chloro Copper(II)]chloride [(MNEC-H)CuCl]Cl (1:1) M:L

The complex was prepared by adding a homogeneous solution of salt CuCl<sub>2</sub>.H<sub>2</sub>O (0.154g, 0.9mmol) using a suitable solvent (ethanol) to a homogeneous solution of the ligand (MNEC-H) (0.3g, 0.9 mmol) dissolved in a suitable solvent (DMF) and leaving the mixture stirred at room temperature for 2 h. The result green precipitate was filtered, washed with ethanol (5 ml) to remove non-reactive ligand and dried in air [11-13]. Yield: (0.280gm 90%, m.p= 84<sup>0</sup>C (Decompose) .

**2.3.3.2- Synthesis of Mono [(E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl) ethylidene) hydrazine-1-carbonothioyl) benza mide] mono chloro Cobalt (II)]chloride [(MNEC-H)CoCl]Cl (1:1)**

Compound [(MNEC-H)CoCl]Cl was prepared similar to Compound [(MNEC-H)CuCl]Cl by adding a homogeneous solution of salt  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.214g, 0.9 mmol) using a suitable solvent (DMF) to a homogeneous solution of the ligand (MNEC-H) (0.3g, 0.9 mmol) dissolved in a suitable solvent (DMF) and leaving the mixture under refluxed for 2h [14-15]. The brown precipitate was filtered, washed with ethanol (5 ml) to remove unreacted ligand and dried in air. Yield: 0.555gm, 92% m.p= 104°C (Decompose) .

**2.3.3.3- Synthesis of Mono [(E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl) ethylidene) hydrazine-1-carbonothioyl) benza mide] mono chloro nickel (II)]chloride [(MNEC-H)NiCl]Cl (1:1)**

Compound [(MNEC-H)NiCl]Cl was prepared similar to Compound [(MNEC-H)CuCl]Cl by adding a homogeneous solution of salt  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.213g, 0.9 mmol) using a suitable solvent (DMF) to a homogeneous solution of the ligand (MNEC-H) (0.3g, 0.9 mmol) dissolved in a suitable solvent (DMF) and leaving the mixture under refluxed for 2 h. The brown precipitate was filtered, washed with ethanol (5 ml) to remove unreacted ligand and dried in air. 0.449gm 60%; m.p = 220°C (Decompose)

**2.3.3.4- Synthesis of Mono [(E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl) ethylidene) hydrazine-1-carbonothioyl) benza mide] di chloro zinc (II)] [(MNEC-H)ZnCl<sub>2</sub>] (1:1)**

Compound [(MNEC-H)ZnCl<sub>2</sub>] was prepared similar to Compound [(MNEC-H)CuCl]Cl by adding a homogeneous solution of salt  $\text{ZnCl}_2$  (0.122g, 0.9 mmol) using a suitable solvent (ethanol) to a homogeneous solution of the ligand (MNEC-H) (0.3g, 0.9 mmol), and the same steps, dissolved in a suitable solvent (DMF) and leaving the mixture under refluxed for 2h. The brown precipitate was filtered, washed with ethanol (5 ml) to remove unreacted ligand and dried in air, Yield: 0.369gm 61%; m.p = 216°C (Decompose).

**2.3.3.5- Synthesis of bis [(E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl)ethylidene) hydrazine-1-carbonothioyl) benza mide] copper (II)] [(MNEC-H)<sub>2</sub>Cu] (1:2) M:L**

The complex was prepared by adding a homogeneous solution of salt  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.179g, 0.9mmol) using a suitable solvent (DMF) to a homogeneous solution of the ligand (MNEC-H) (0.6g, 1.6 mmol) dissolved in a suitable solvent (DMF) and leaving the mixture stirred at room temperature for 2h. The brown precipitate was filtered, washed with ethanol (5ml) to remove unreacted ligand and dried in air, Yield: 0.414gm 68%; m.p = 206°C (Decompose) .

**2.3.3.6- Synthesis of bis [(E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl)ethylidene) hydrazine-1-carbonothioyl) benza mide] cobalt (II)] di chloride[(MNEC-H)<sub>2</sub>Co]Cl<sub>2</sub> (1:2)**

The complex was prepared by adding a homogeneous solution of salt  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.214g, 0.9mmol) using a suitable solvent (DMF) to a homogeneous solution of the ligand (MNEC-H) (0.6g, 1.6 mmol)

dissolved in a suitable solvent (DMF) and leaving the mixture under refluxed for 2 h. The brown precipitate was filtered, washed with ethanol (5ml) to remove unreacted ligand and dried in air. Yield: 0.555gm, 92% m.p= 104°C (Decompose).

**2.3.3-7- Synthesis of bis [(E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl)ethylidene) hydrazine-1-carbonothioyl) benzamide] nickel (II)] [(MNEC-H)<sub>2</sub>Ni] (1:2)**

The complexes are prepared by adding a homogeneous solution of salt Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.223g, 0.9mmol) using a suitable solvent (DMF) to a homogeneous solution of the ligand (MNEC-H) (0.6g, 1.6 mmol) dissolved in a suitable solvent (DMF) and leaving the mixture under refluxed for 2 h. The brown precipitate was filtered, washed with ethanol (5ml) to remove unreacted ligand and dried in air, Yield: 0.511gm 83%, m.p= 191°C (Decompose) .

**2.3.3-8- Synthesis of bis [(E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl)ethylidene) hydrazine-1-carbonothioyl) benzamide] zinc (II)] [(MNEC-H)<sub>2</sub>Zn] (1:2)**

The complexes are prepared by adding a homogeneous solution of salt Zn(CH<sub>3</sub>COO)<sub>2</sub> (0.179g, 0.9mmol) using a suitable solvent (DMF) to a homogeneous solution of the ligand (MNEC-H) (0.6g, 1.6 mmol) dissolved in a suitable solvent (DMF) and leaving the mixture under refluxed for 2h. The brown precipitate was filtered, washed with ethanol (5ml) to remove unreacted ligand and dried in air. Yield: ; 0.511gm 83%, m.p= 191°C (Decompose),

**3- Results and discussion**

**3.1. FTIR spectral data**

Infrared spectroscopy is the preferred method for detecting and determining the functional groups positions in a given sample. This technique was performed to get genuine information about the vibrational origin of all the prepared compounds.

Characterization of Infrared spectroscopy was accomplished by Shimadzu FT-IR 8400S spectroscopy /Japan, as KBr disc for solid models, as the diagnostic results showed the presence of packages common to all prepared compounds showed important vibrational bands in certain regions, especially in the fingerprint and other regions.

The FTIR spectra of the prepared ligand MNEC-H as the diagnostic results showed the presence of packages in the prepared ligand and disappearance of other bends that were present in the raw materials of prepared ligand, as showed the disappearance of the stretch vibration band belonged to the isothiocyanates group N=C=S for benzoyl isothiocyanate that appear when (2100-1950) cm<sup>-1</sup> and when appearance of the packages (-NH-C=O) at 1670 cm<sup>-1</sup> and the bend of (-NH-C=S) at the range (1246) cm<sup>-1</sup>. This indicates the formation of ligand [16-17], and the bond appearance (C=N pyridine) at 1616 cm<sup>-1</sup> and (C=N imine) at 1550 cm<sup>-1</sup> plus a packages appearance (N-H amide) at (3414 , 3302) cm<sup>-1</sup>, (C-H aromatic , aliphatic) at (3074, 2977) cm<sup>-1</sup>, as the following figure1. refer to the infrared spectra of the prepared ligand [18-19]

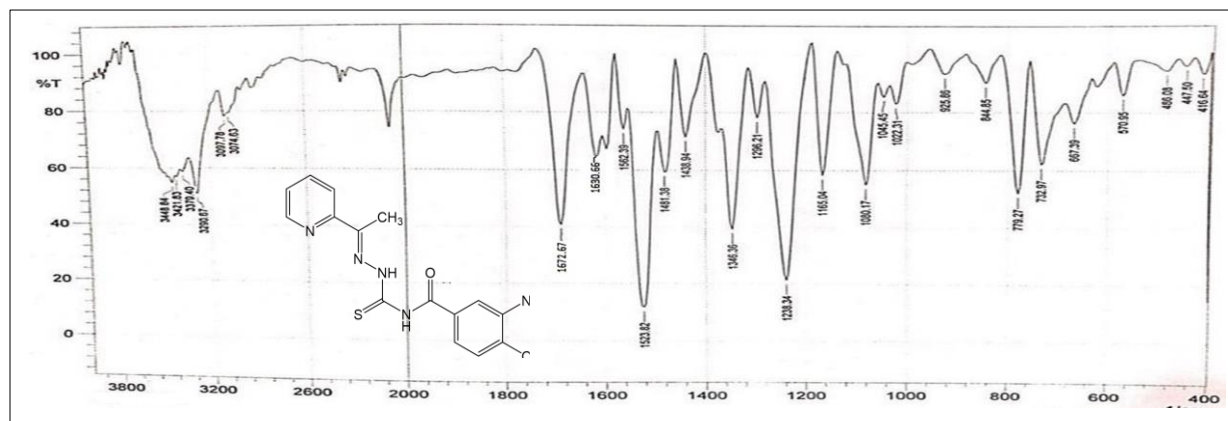


Figure 1: FT-IR Spectrum of ligand MNEC-H

The FT-IR spectra of complexes [(MNEC-H)CuCl]Cl, [(MNECH)CoCl]Cl, [(MNEC-H)NiCl]Cl, [(MNEC-H)ZnCl<sub>2</sub>], [(MNEC-H)<sub>2</sub>Cu], [(DEHC-H)<sub>2</sub>Co]Cl<sub>2</sub>, [(DEHC-H)<sub>2</sub>Ni] and [(DEHC-H)<sub>2</sub>Zn]

show clear change in stretching frequency for C=N pyridine, C=N imine and (NH-C=S) appearance of strong peaks also shifts to lower energy at (1630-1597) cm<sup>-1</sup>, (1550-1527) cm<sup>-1</sup>, (1246-1237) cm<sup>-1</sup> respectively in all prepared complexes compared to the corresponding free ligand, This indicates the coordinate of the sulfur atom of the C=S group to the metal center atom which decrease the C=S bond by the electrons donating from the sulfur atom toward the metal atom center and then decrease the bond order, The C=N stretching vibration was observed at lower frequency compared to the corresponding free ligand suggesting the coordination of the (pyridyl, imine) nitrogen atom to the metal center [20]. as well as the appearance of bands at (570-605) indicating the formation of the complex and the formation of the bond (M-N), as well as the emergence of a band at the frequency (416-432) cm<sup>-1</sup> of the formation of the bond (M-S) [21] which confirms the formation of the complex and the link of the ligand with the complex see figure (2-4), **Table 1** shows the most important bands and its frequency of the prepared compounds.

Table 1: FT-IR Spectral Data of the Synthetic compounds

Comp. Symbol	N-H amide	NH-C=O	C=N Pyridine	C=N Imine	NH-C=S	M-N(py) M-N(imine)	M-S
MNEC-H	3302	1670	1616	1550	1246	---	---
[(MNECH)CuCl]Cl	3448	1672	1630	1523	1238	570 486	416
[(MNEC-H) <sub>2</sub> Cu]	3428	1677	1628	1531	1257	570 486	420
[(MNECH)NiCl]Cl	3383	1670	1643	1527	1257	578 460	422
[(MNEC-H) <sub>2</sub> Ni]	3417	1666	1566	1531	1269	574 464	424
[(MNECH)ZnCl <sub>2</sub> ]	3348	1677	1589	1519	1234	567 455	425
[(MNEC-H) <sub>2</sub> Zn]	3414	1670	1629	1531	1238	567 447	422
[(MNECH)CoCl]Cl	3414	1675	1577	1527	1257	574 444	419
[(MNECH) <sub>2</sub> Co]Cl <sub>2</sub>	3321	1666	1600	1527	1237	547 494	429



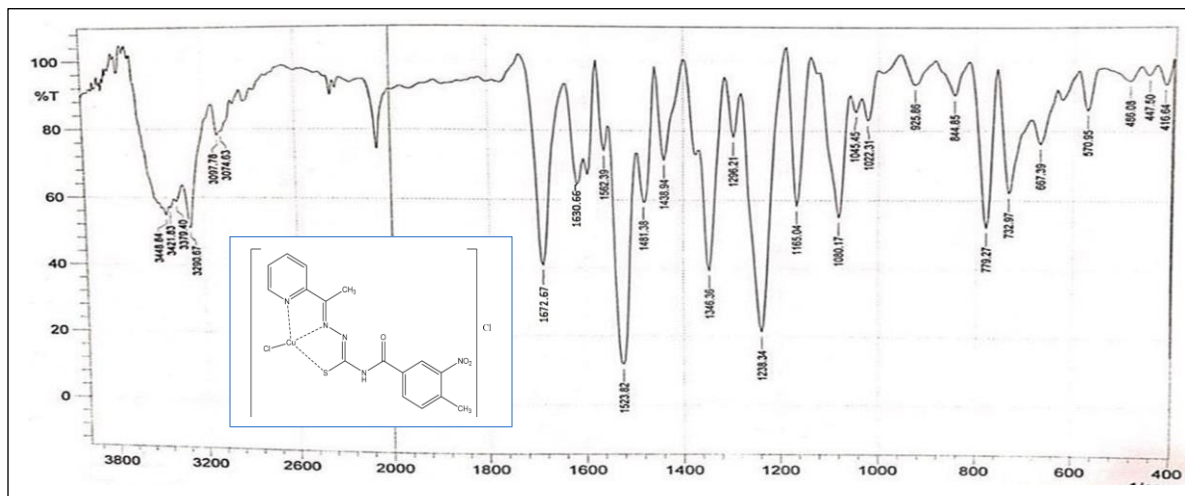


Figure 2: FT-IR Spectrum of complexes  $[(MNEC-H)CuCl]Cl$

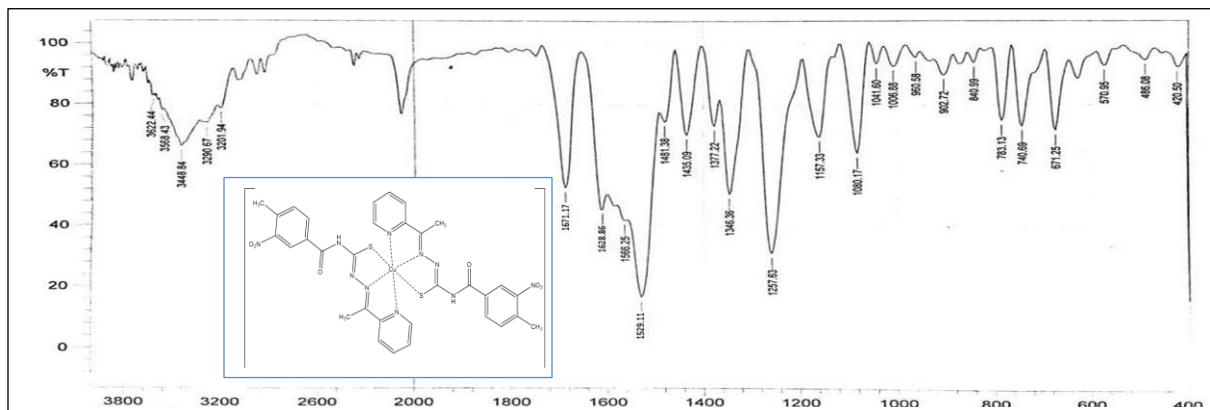


Figure 3: FT-IR Spectrum of complexes  $[(MNEC-H)_2Cu]$

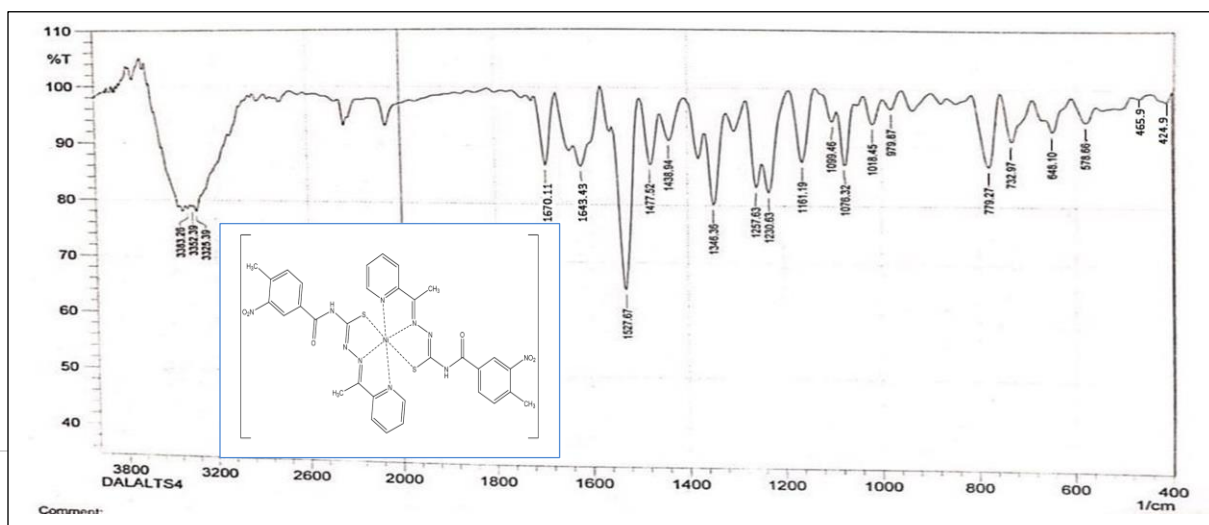


Figure 4: FT-IR Spectrum of complexes [(MNEC-H)<sub>2</sub>Ni]

### 3.2-Nuclear Magnetic Resonance (NMR)

A review of the literature revealed that NMR spectroscopy has been proven to be useful in establishing the nature and structure of compounds. The NMR spectra of the synthesized compounds were recorded in DMSO-d<sub>6</sub> solvent using tetramethylsilane (TMS) as internal standard. The <sup>1</sup>HNMR spectra of the compounds given results indicating the compatibility of the proposed structures.

#### 3.2.1- Proton Nuclear Magnetic Resonance (<sup>1</sup>HNMR) of ligands and complexes

The <sup>1</sup>HNMR spectrum of the thiosemicarbazone ligand (MNEC-H) where it shows a single signal at which is ascribed to each the proton of amine groups (NH<sub>A</sub>(NH-C=O), NH<sub>B</sub>(NC=S)) at (12.18, 11.97) ppm respectively, as such we can have observed single signal at which is ascribed to each the proton of pyridine ring (1Ha,1Hb,1Hc) at (8.65, 7.98, 7.48) ppm respectively. See Figures 5 .

In addition to the appearance of special single signals for the aromatic ring compensators (1He, 1Hf, 1Hg, 3H(CH<sub>3</sub>)) at (8.69, 8.55, 7.90, 2.65) ppm respectively, also it was observed that bundles of dimethyl sulfoxide DMSO-d<sub>6</sub> solvent in their specific locations upon displacement (2.50-2.53) ppm respectively, as the following Figure10. [22].

The <sup>1</sup>HNMR spectrum of the complexes Zn(II) (1:1) (1:2) [(MNEC-H)ZnCl<sub>2</sub>], [(MNEC-H)<sub>2</sub>Zn] that the background are zinc metal associated with thiosemicarbazone ligand (1:1), (1:2) it also possesses the same packages but they are show clear shift towards low frequencies a comparative with packages ligands this indicates the consistency of ligand ligand with metal ion[11,23] . See Figures 6-7 .

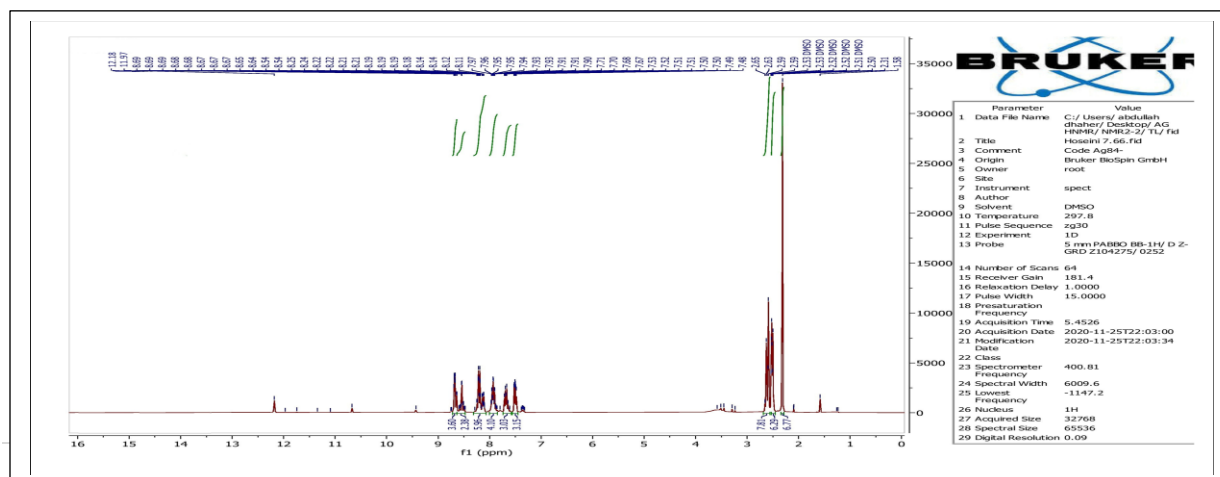


Figure 5:  $^1\text{H}$ NMR spectrum of (E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl) ethyl) dene) hydrazine-1-carbonothioyl benzamide ligand (MNEC-H)

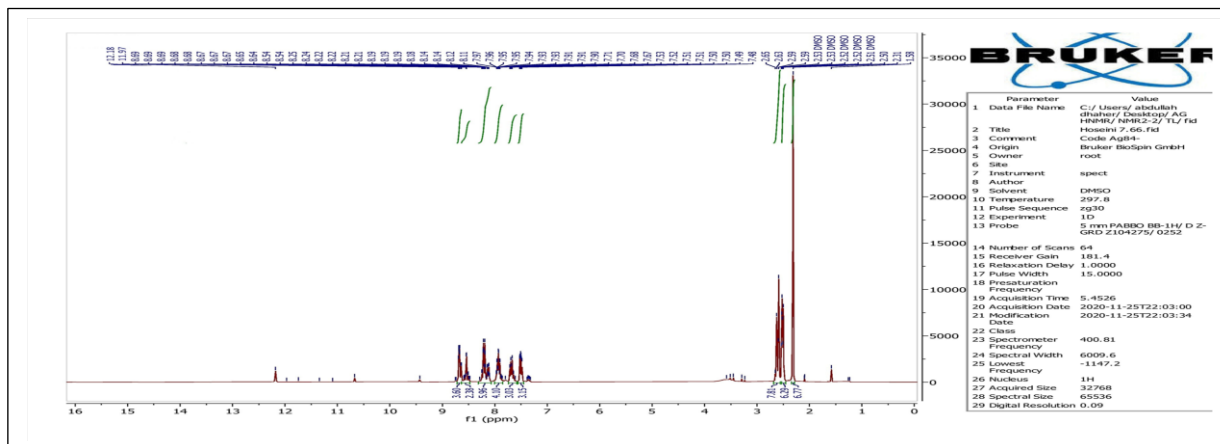


Figure 6:  $^1\text{H}$ NMR Spectrum of Complex [(MNEC-H)ZnCl<sub>2</sub>]

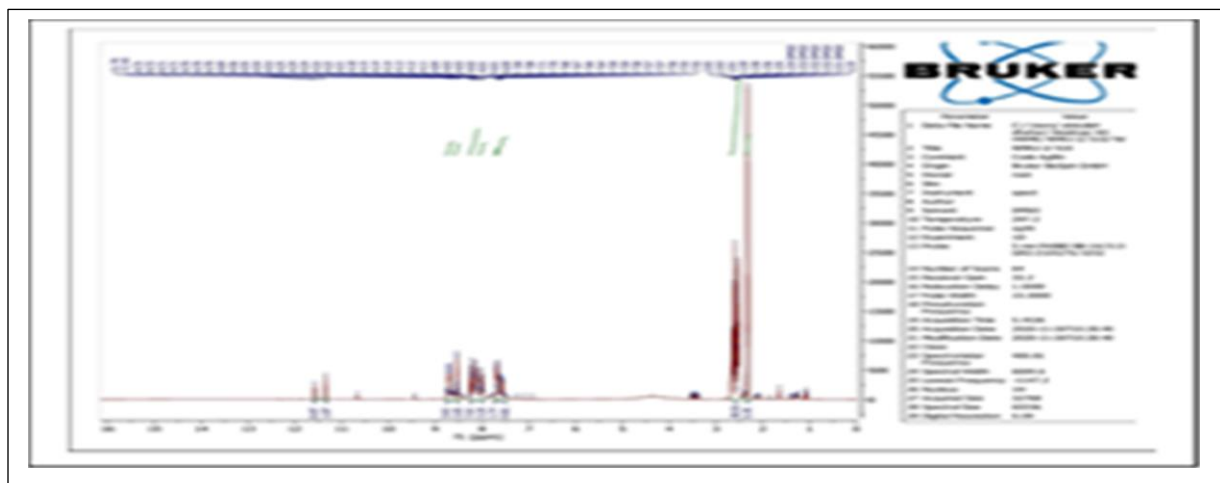


Figure 7:  $^1\text{H}$ NMR Spectrum of Complex [(MNEC-H)<sub>2</sub>Zn]

### 3.2.2- Carbon-13 Nuclear Magnetic Resonance ( $^{13}\text{C}$ NMR) of ligands and complexes.

The  $^{13}\text{C}$ NMR spectra of the new synthetic compounds Zn(II) (1:1) (1:2) [(MNEC-H)ZnCl<sub>2</sub>], [(MNEC-H)<sub>2</sub>Zn] were recorded in DMSO- $d_6$ . All these spectra showed seven peaks in the region (39-41) ppm which was due to the DMSO- $d_6$  solvent. The signals of aromatic carbon of the thiosemicarbazone ligand and synthesized compounds represented at  $\delta$  121.23- 138.52 ppm, The signals of pyridine carbon represented at  $\delta$  134.32-149.34 ppm as appear carbon thioamide and carbon amide The signals in different shift chemical according increasing the resonance contribution of  $\pi$ -bonds[24-25] while the signal of the methyl carbon observed at the range  $\delta$  20.19- 14.15 ppm in MNEC-H, [(MNEC-H)ZnCl<sub>2</sub>], [(MNEC-H)<sub>2</sub>Zn] and a sign Ar-NO<sub>2</sub> appear in range chemical shift de shielding down filed because NO<sub>2</sub>

group it has high electronegativity observed at the range  $\delta$  148- 149.96 ppm, we also notice the appearance of the signals in a location that differs from the location of their appearance in their appearance in the ligand spectrum this is an indication of the symmetry with the metallic ion [26]. See Figures 8-9 .

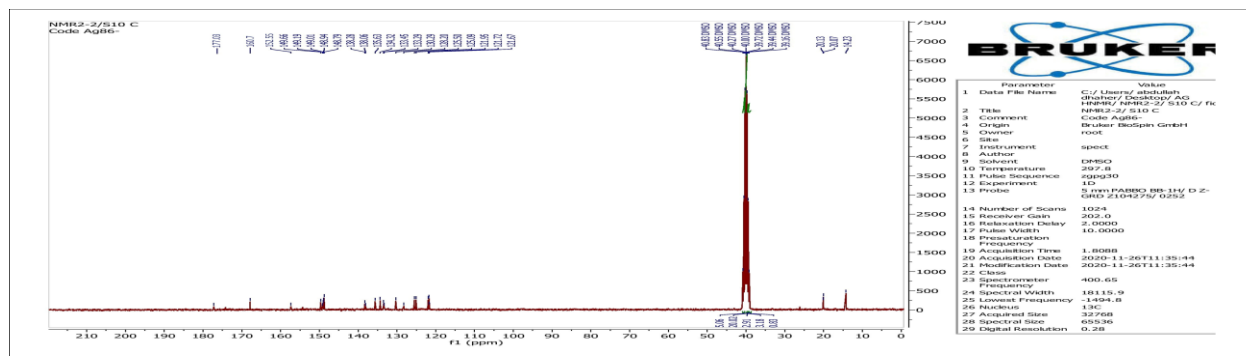


Figure 8:  $^{13}\text{C}$ NMR spectrum of (E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl) ethylidene)hydrazine-1-carbonothioyl) benza mide ligand (MNEC-H)

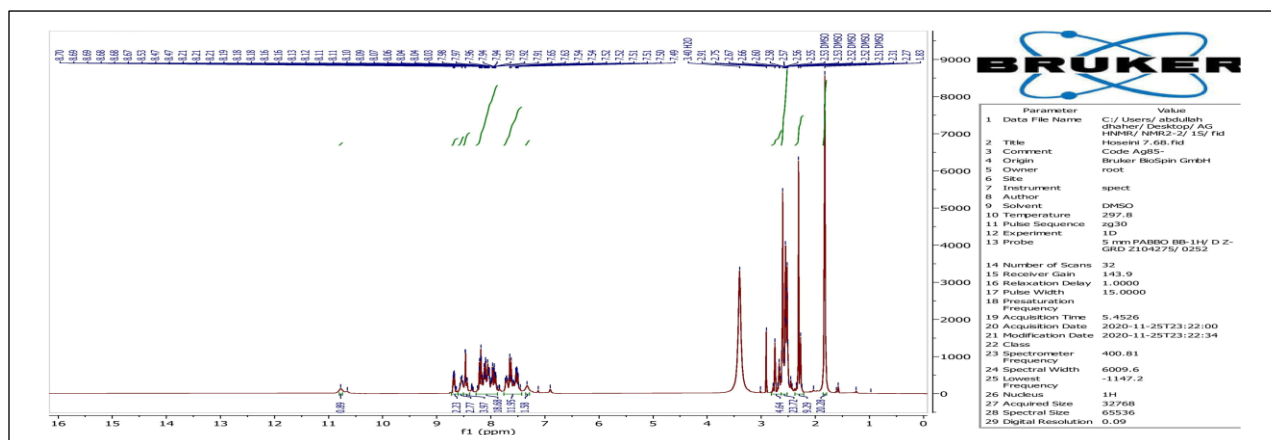


Figure 9 :  $^1\text{H}$ NMR Spectrum of Compound [(MNEC-H)ZnCl<sub>2</sub>]

### 3.3-Electronic absorption spectra

The solutions of thiosemicarbazone ligand MNEC-H and its complexes Cu(II), Ni(II), Zn(II), Co(II) ions in DMSO were prepared and the electronic absorption spectra were recorded in the range 200–1200 nm at room temperature and the electronic bands are listed in Table 2, The absorption bands for the ligand MNEC-H was observed in the region 245 nm ( $14792 \text{ M}^{-1} \text{ cm}^{-1}$ ) were assigned to transitions  $\pi-\pi^*$  (phenyl ring) and 265 nm ( $12491 \text{ M}^{-1} \text{ cm}^{-1}$ ) were assigned to transitions  $n-\pi^*$  (corresponding to C=N, C=O and C=S) less intensity than the previous bands as transitions are not allowed [36], The electronic spectra of (1:1) and (1:2) [M:L] mole ratios of Cu(II) ,Ni(II), Zn(II), Co(II), complexes [(MNEC-H)CuCl]Cl,[(MNECH)CoCl]Cl, [(MNEC-H)NiCl]Cl, [(MNEC-H)ZnCl<sub>2</sub>], [(MNEC-H)<sub>2</sub>Cu], [(DEHC-H)<sub>2</sub>Co]Cl<sub>2</sub>, [(DEHC-H)<sub>2</sub>Ni] and [(DEHC -H)<sub>2</sub>Zn]. with ligand DEHC-H show a shift towards longer wavelength for  $\pi-\pi^*$  and  $n-$

$\pi^*$  transitions as compared to their corresponding free ligand. This is due to the electropositive charge of metals ion which withdraws electrons towards it, The electronic spectra of Cu(II) (1:1) (1:2) complexes  $[(MNEC-H)CuCl]Cl$ ,  $[(MNEC-H)_2Cu]$  appears complex (1:1) one LMCT bands observed at 410 nm ( $876 M^{-1} cm^{-1}$ ) and d-d transition at it exhibits characteristic bands at and 670 nm ( $227 M^{-1} cm^{-1}$ ) spectral evidence confirms the square planar structure[27-28], Appears complex Cu(II) (1:2) one LMCT band observed at 480 nm ( $10.38 M^{-1} cm^{-1}$ ) and three d-d transition at It exhibits characteristic bands at 550 nm ( $477 M^{-1} cm^{-1}$ ) and 670 nm ( $258 M^{-1} cm^{-1}$ ) which are due to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$  transitions respectively . suggesting an octahedral geometry around the Cu (II) ion[25,29], Electronic spectrum of Ni (II) (1:1) complex  $[(MNEC-H) NiCl]Cl$  show LMCT band observed at 410 nm ( $1580 M^{-1} cm^{-1}$ ) and d-d transition at It exhibits characteristic bands at 590 nm ( $15879 M^{-1} cm^{-1}$ ) , spectral evidence confirms the square planar structure and electronic spectrum of Ni(II)(1:2) complex  $[(MNEC-H)_2 Ni]$  shows three bands at 450 nm ( $749 M^{-1} cm^{-1}$ ), 555 nm ( $390 M^{-1} cm^{-1}$ ), 565 nm ( $148 M^{-1} cm^{-1}$ ) assignable to be  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  transitions, suggesting an octahedral geometry around the nickel (II) ion [25,30]. As the following Figure 10, Zn(II) (1:1) (1:2) complexes (MNEC-H)  $ZnCl_2$  and (MNEC-H) $_2Zn$  does not exhibit any d-d electronic transition due to its completely filled  $d^{10}$  electronic configuration, however often exhibit charge transfer spectra. The Zn(II) complex shows an absorption band at 405nm ( $569 M^{-1} cm^{-1}$ ) and 395 nm ( $698 M^{-1} cm^{-1}$ ) attributed to the L  $\rightarrow$  M charge transfer transition, which is compatible with this complex having a square pyramid geometry [31], as the following Figure 11, Electronic spectrum of Co(II) (1:1) complex  $[(MNEC-H)CoCl]Cl$  exhibits LMCT bands observed at 415 nm ( $296 M^{-1} cm^{-1}$ ) and d-d transition at It exhibits characteristic bands at 635 nm ( $0279 M^{-1} cm^{-1}$ ), spectral evidence confirms the square planar structure and electronic spectrum of Co(II) (1:2) complex  $[(MNEC-H)_2Co]Cl_2$  shows three bands at 465 nm ( $722 M^{-1} cm^{-1}$ ), 505 nm ( $695 M^{-1} cm^{-1}$ ), 630 nm ( $556 M^{-1} cm^{-1}$ ) assignable to be  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  transitions, suggesting an octahedral geometry around the cobalt (II) ion [29].

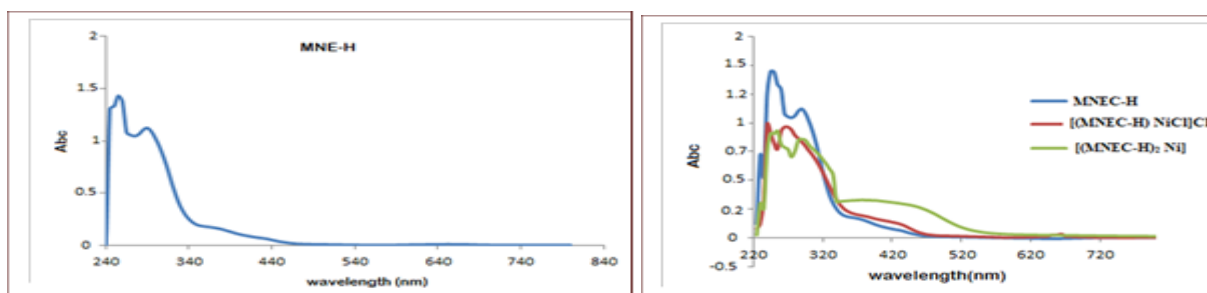
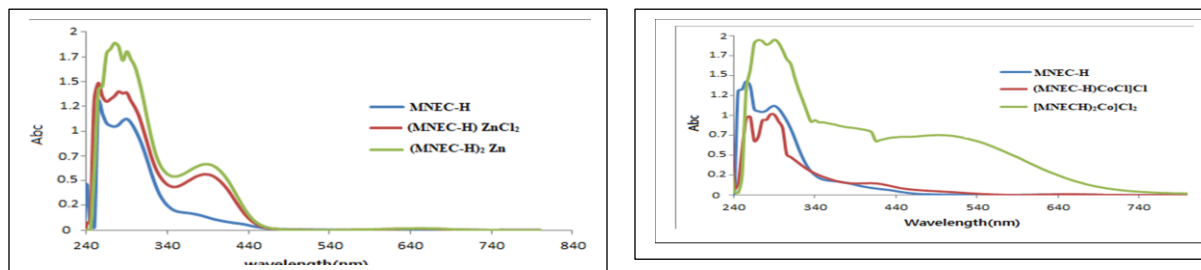


Figure 10: UV-visible spectra for ligand MNEC-H and complexes Ni ( $[(MNEC-H) NiCl]Cl$ ,  $[(MNEC-H)_2 Ni]$ )



**Figure 11: UV-vis for complexes Zn ([MNEC-H) ZnCl<sub>2</sub>], [(MNEC-H)<sub>2</sub> Zn] Co ([MNEC-H)CoCl]Cl,[MNECH)<sub>2</sub>Co]Cl<sub>2</sub>).**

**Table 2: UV-visible data for compounds**

Compound symbol	$\lambda_{max} (\text{nm}) (\text{M}^{-1}\text{cm}^{-1})$			
	$\pi-\pi^*$	$n-\pi^*$	LMCT	d-d transition
MNEC-H	245(14792)	265(12491)	----	----
[(MNEC-H)CuCl]Cl	255(19710)	285(18170)	480(148)	670(11580)
[(MNEC-H) <sub>2</sub> Cu]	250(18860)	285(16610)	470(151)	550(1287) 650(877)
[(MNEC-H)NiCl]Cl	240(19880)	270(19783)	410(158)	590(15879)
[(MNEC-H) <sub>2</sub> Ni]	255(18591)	280(15110)	415(855)	450(749) ,555(390) 565(148)
[(MNEC-H)ZnCl <sub>2</sub> ]	275(18887)	290(17125)	405(569)	----
[(MNEC-H) <sub>2</sub> Zn]	260(15098)	280(14544)	395(698)	----
[(MNEC-H)CoCl]Cl	255(11205)	285(13003)	415(296)	820(765)
[(MNECH) <sub>2</sub> Co]Cl <sub>2</sub>	265(19885)	285(19703)	400(881)	465(722) 505(695) 630(556)

The magnetic sensitivity of the prepared metal complexes was calculated at room temperature 298<sup>o</sup>K, where most of the complexes showed paramagnetic properties, the paramagnetic complexes consist of Para magnetic centers (the metal atom) and diamagnetic groups, its obtained magnetic sensitivity values are corrected relying on Pascal constants [32] to calculate the correction factor (D) to reduce the error rate resulting from the diamagnetic effects , Table 3. shows the magnetic data which includes mass magnetic susceptibility  $\chi_{mass}$ , molar magnetic susceptibility  $\chi_M$  and magnetic moments  $\mu_{eff}$  measurements. the magnetic moment values were calculated according to the following equations:

$$\mu_{eff} = 2.82 \times (X_A \times T)^{1/2}$$

$$X_A = X_M - D$$

$$X_M = X_g \times M.Wt$$

$$X_g = CI (R - R_0) / 10^9 \times m$$

T = Absolute temperature, X<sub>A</sub> atomic susceptibility, X<sub>M</sub> molarity susceptibility, X<sub>g</sub> grammatical susceptibility, D diamagnetic correction factor,  $\mu_{eff}$  magnetic moment, M.wt molecular weight, B.M Bohr Magnetron is a unit of magnetic moment. R Weight of matter in the presence of the magnetic field and R<sub>0</sub> Weight of matter in the Absent of the magnetic field ,

$m =$  Weigh the tube with the material - Weigh the tube Empty .

It was found through the magnetic moment value is 1.936 B.M of the complexes in the table below that the copper (II) (1:1) complex [(MNEC-H)CuCl]Cl possess only one electron  $d^9$ , then they are paramagnetic materials and took the geometrical square planer shape and hybridization  $sp^2d$  [33], either copper (II) (1:2) complex [(MNEC-H)<sub>2</sub>Cu] possess only one electron  $d^9$ , it was found through the magnetic moment value is 1.76 B.M then they are paramagnetic materials and took the geometrical octahedral shape and hybridization  $sp^3d^2$  [34]. The observed magnetic moments of Ni(II) (1:1) complex [(MNEC-H)NiCl]Cl is zero confirming the diamagnetic properties of the square planar complexes and hybridization  $dsp^2$ , either nickel (II) (1:2) complex [(MNEC-H)Ni] possess two electron  $d^8$ , it was found through the magnetic moment value is 3.933 B.M [35] then they are paramagnetic materials and took the geometrical octahedral shape and hybridization  $sp^3d^2$  [36]. The observed values of magnetic moment for cobalt(II) (1:1) complex [(MNEC-H)CoCl]Cl are generally diagnostic of the coordination geometry about the metal ion. Low-spin square-planar cobalt (II) complexes are 2.734 B.M arising from one unpaired electron plus to possess  $d^7$  and hybridization  $sp^2d$  [37], orally cobalt (II) (1:2) complex [(MNECH)<sub>2</sub>Co]Cl<sub>2</sub>. It was found through the magnetic moment value is 3.704 B.M in the table below that the cobalt complexes  $Co^{+2}$  possess three electrons  $d^7$ , then they are paramagnetic materials and took the high-spin geometrical octahedral shape and hybridization  $sp^3d^2$  [38]. Table 3 shows values of magnetic moment of prepared complexes .

**Table 3: The magnetic moment data of the prepared complexes**

Comp. sym.	$\chi_g (10^{-4})$	$\chi_M (10^{-4})$	$D (10^{-6})$	$\chi_A (10^{-3})$	$\mu_{eff}$	No of unpaired electron	Hybrid.
[(MNECH)CuCl]Cl	0.027	13.306	-245.91	1.575	1.936	1e	$Sp^2d$
[(MNECH) <sub>2</sub> Cu]	0.0069	61.852	-418.72	6.603	1.76	1e	$Sp^3d^2$
[(MNECH)NiCl]Cl	0.027	13.175	-246.91	1.563	1.928	2e	$Sp^2d$
[(MNECH) <sub>2</sub> Ni]	0.069	62.55	-419.72	6.674	3.988	2e	$Sp^3d^2$
[(MNECH)CoCl]Cl	0.055	26.79	-213.16	3.138	2.734	1e	$Sp^2d$
[(MNECH) <sub>2</sub> Co]Cl <sub>2</sub>	0.096	53.45	-419.66	5.759	3.704	3e	$Sp^3d^2$

### 3.5- Measurement of Molar conductivity

The conductivity of the complexes [(MNEC-H)CuCl]Cl, [(MNECH)CoCl]Cl, [(MNEC-H)NiCl]Cl, [(MNEC-H)ZnCl<sub>2</sub>], [(MNEC-H)<sub>2</sub>Cu], [(DEHC-H)<sub>2</sub>Co]Cl<sub>2</sub>, [(DEHC -H)<sub>2</sub>Ni] and [(DEHC -H)<sub>2</sub>Zn]. for (Cu(II), Ni(II), Co(II), Zn(II) for every mole ratios (1:1) and (1:2) with the prepared ligand [MNECH] was studied using DMSO solvent In order to know the behavior of

the complexes and the extent of their conductivity, their conductivity was measured with the same studied concentrations of complexes ( $10^{-3}$ - $10^{-6}$  mol.L<sup>-1</sup>) and at the temperature of 25°C, the equations below were used and the graphical relationship between the square root ( $C^{1/2}$ ) M of the concentration and the molar conductance  $\Lambda_m$  (ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>) was drawn[39].

$$K_{\text{complex}} = K_{\text{solution}} - K_{\text{solvent}}$$

K= Qualitative conduction at unit ohm<sup>-1</sup>.cm<sup>-1</sup>

$$\Lambda = 1000 K/C$$

$\Lambda$ = molar conductivity at unit ohm<sup>-1</sup>.cm<sup>2</sup>/mol

C= molar concentration

$$\Lambda_m = \Lambda_o - S (C)^{1/2}$$

It was found that the molar conductivity of metals complexes (1:1) Cu(II), Ni(II), Zn(II), Co(II) whose symbols are (complexes [(MNEC-H)CuCl]Cl, [(MNECH)CoCl]Cl,[(MNEC-H)NiCl]Cl, [(MNEC-H)ZnCl<sub>2</sub>],) respectively, increases in the dilute solution they have a curve shape ,this indicates that the prepared complexes possess good electrolyte behavior in DMSO, they are of (M-L) (1:1) therefore do possess an counter ion outside the coordination sphere. Also the molar conductivity values range at a concentration of ( $1 \times 10^{-3}$  M) of (60 – 85 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>). The results obtained from this study are consistent with previous studies [40-42].But the complexes (1:2) Cu(II), Ni(II), Zn(II) whose symbols are ([ (MNEC-H)<sub>2</sub>Cu], [(DEHC -H)<sub>2</sub>Ni] and [(DEHC-H)<sub>2</sub>Zn]) respectively the molar conductivity values range at a concentration of ( $1 \times 10^{-3}$  M) of (14 – 7 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>), Therefore do not possess an counter ion outside the coordination sphere, This indicates to those complexes Non ionic [43-44]. See Table 4.

**Table 4: The molar conductivity of compounds prepared with concentration  $1 \times 10^{-4}$**

Symbol comp.	$\Lambda$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	Molecular formula	Electrolyte type	Geometric shape
MNEC-H	----	[C <sub>16</sub> H <sub>15</sub> N <sub>5</sub> O <sub>3</sub> S]	Neutral	----
[(MNEC-H)CuCl]Cl	75.2	[Cu(C <sub>16</sub> H <sub>15</sub> N <sub>5</sub> O <sub>3</sub> S)Cl]Cl	Ionic	Square planer
[(MNEC-H) <sub>2</sub> Cu]	13	[Cu(C <sub>16</sub> H <sub>15</sub> N <sub>5</sub> O <sub>3</sub> S) <sub>2</sub> ]	Non ionic	Octa
[(MNEC-H)NiCl]Cl	72.6	[Ni(C <sub>16</sub> H <sub>15</sub> N <sub>5</sub> O <sub>3</sub> S)Cl]Cl	Ionic	Square planer
[(MNEC-H) <sub>2</sub> Ni]	12	[Ni(C <sub>16</sub> H <sub>15</sub> N <sub>5</sub> O <sub>3</sub> S) <sub>2</sub> ]	Non ionic	Octa
[(MNEC-H)ZnCl <sub>2</sub> ]	8	[Zn(C <sub>16</sub> H <sub>15</sub> N <sub>5</sub> O <sub>3</sub> S)Cl <sub>2</sub> ]	Neutral	square pyramid
[(MNEC-H) <sub>2</sub> Zn]	7	[Zn(C <sub>16</sub> H <sub>15</sub> N <sub>5</sub> O <sub>3</sub> S) <sub>2</sub> ]	Neutral	Octa
[(MNEC-H)CoCl]Cl	104	[Co(C <sub>15</sub> H <sub>16</sub> N <sub>4</sub> O <sub>3</sub> S)Cl]Cl	Ionic	Square planer
[(MNEC-H) <sub>2</sub> Co]Cl <sub>2</sub>	85.2	[Co(C <sub>15</sub> H <sub>16</sub> N <sub>4</sub> O <sub>3</sub> S) <sub>2</sub> ]Cl <sub>2</sub>	Ionic	Octa



### 3.6- Electrochemical studies

The cyclic voltammetry technique was used in the interpretation of the electrochemical study of the prepared complexes, where a study was conducted scanning of Cu(II), Co(II) and Ni(II) complexes of DEHC-H ligand in the ratio (1:1) (M:L) [(MNEC-H)CuCl]Cl, [(MNEC-H)CoCl]Cl [(MNEC-H)NiCl]Cl were studied. And at a ratio of (1:2) (M:L) ], [(MNEC-H)<sub>2</sub>Cu], [(DEHC-H)<sub>2</sub>Co]Cl<sub>2</sub>, [(DEHC-H)<sub>2</sub>Ni] in the DMSO solvent in the range (+0.2v to -0.2) at room temperature using [Bu<sub>4</sub>N][PF<sub>6</sub>] at a concentration of (0.1 M) and at a scan rate of 100 mv. Sec<sup>-1</sup>. The same cell was used in all measurements and used (E<sub>1/2</sub> = 0.505 V, ΔE<sub>p</sub> = 130 mV) ferrocene / ferrocenium (Fc / Fc<sup>+</sup>) as a reference. The cyclic voltammetric measurements of the prepared thiosemicarba- zone ligand (MNEC-H) do not show any oxidation or reduction peak in the range that studied[46], as the following Figure 12, The cyclic voltammetry for the prepared copper (II) complexes [(MNEC-H)CuCl]Cl, [(MNEC-H)<sub>2</sub>Cu], are similar as following Figures 21 and 22 are showing the cyclic voltammetry for the [(MNEC-H)CuCl]Cl, [(MNEC-H)<sub>2</sub>Cu] complexes. From the cyclic voltammetric measurements of all the prepared copper(II) complexes, a quasi-reversible single process was observed, with single electron oxidation E<sub>pa</sub> = (-0.275, -0.298) volts relative to (Fc/Fc<sup>+</sup>) A significant value of the separation between the two bundles are observed at ΔE<sub>p</sub> = (327-551mV) as shown in Table 5. The voltage difference between the two beams is noted to be much more than it is in the standard reversible process, which indicates that the nature of the process is quasi-reversible. This may be due to the structural geometry rearrangement when moving from Cu(II) to Cu(III) oxidative states. In addition, the ratio between I<sub>pc</sub> and I<sub>pa</sub> is less than one, which also supports the semi-reversible nature of the Cu(II)/Cu(III) bundle [46-49]. The peak current increases with the increase of the square root of the scanning speed, and this confirms the electrode operations and also controls the propagation.

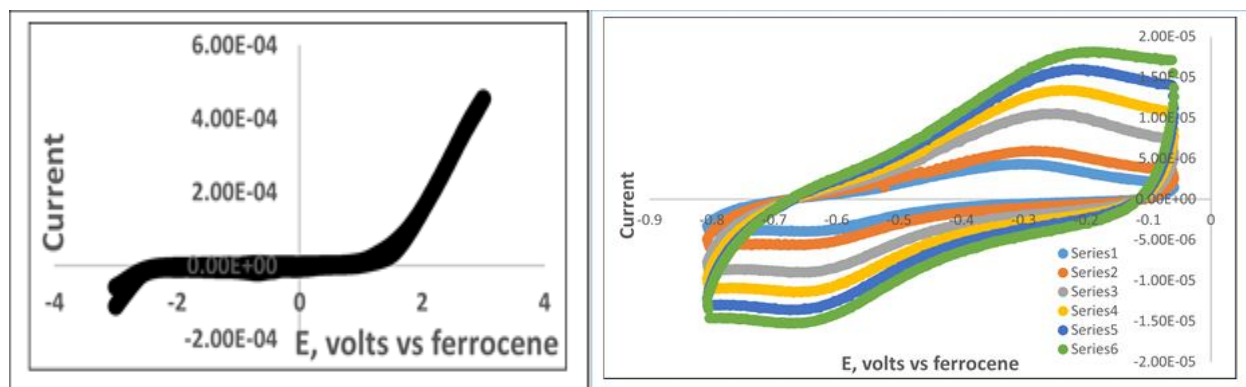


Figure 12: cyclic voltammetry for ligand (DEHC-H) and [(DEHC-H)CuCl]Cl in DMSO solvent by rate scanning 100 mv/sec.

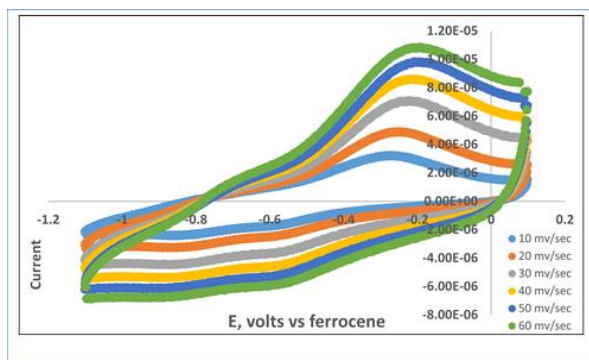


Figure 13: cyclic voltammetry for ligand (DEHC-H) and [(DEHC-H)CuCl]Cl in DMSO solvent by rate scanning 100 mv/sec.

Table 5: Electrochemical process for the quasi-reversible processes of the copper(II) complexes (DEHC-H CuCl, (DEHC-H)<sub>2</sub>CuAC) in the DMSO solvent and the supporting electrolyte [Bu<sub>4</sub>N][PF<sub>4</sub>] at a concentration of 0.1M, 25°C 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>
L <sup>4</sup> CuAC	-0.275	-0.826	551	-0.551	2.406	3.235	0.744
L <sup>4</sup> CuCl	-0.298	-0.625	327	-0.465	3.920	4.317	0.908

As for the cyclic voltammetry of the cobalt (II) and nickel(II) complexes [MNEC-H CoCl]Cl, [MNEC-H)<sub>2</sub>Co]Cl<sub>2</sub>) and [MNEC-H NiCl], [MNEC-H)<sub>2</sub>NiCl] showed one irreversible oxidative band [(+0.4623, +0.4535) volts versus (Fc/Fc<sup>+</sup>) for cobalt complexes and [+0.4459, +0.4587] volts versus (Fc/Fc<sup>+</sup>) for nickel complexes [50-51] as in Figures 14 - 15. See Table 6.

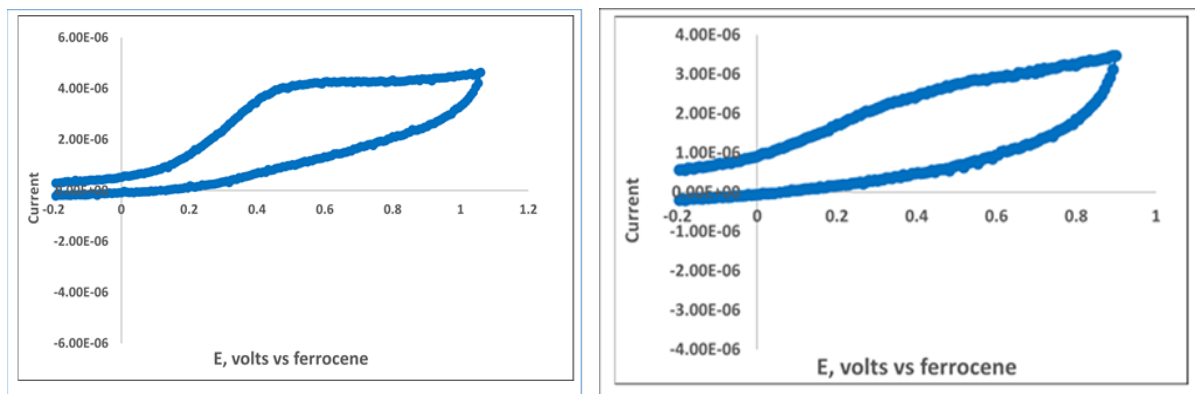


Figure 14: Cyclic voltammogram for [MNEC-H CoCl]Cl and (MNEC-H)<sub>2</sub>Co]Cl<sub>2</sub> compound exhibiting the irreversible manner in acetonitrile solution at the scan rate 102 mv/sec.

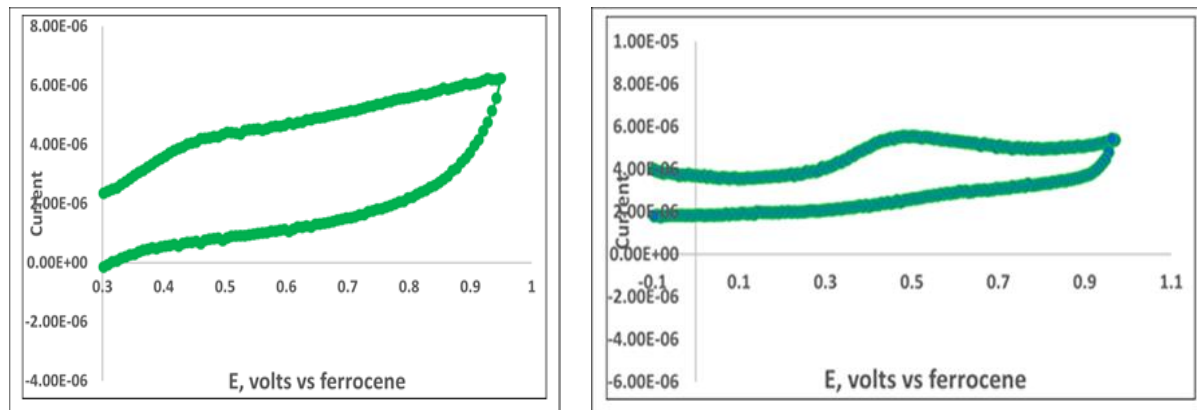


Figure 15: Cyclic voltammogram for [MNEC-H NiCl]Cl and [(MNEC-H)<sub>2</sub>Ni] compound exhibiting the irreversible manner in acetonitrile solution at the scan rate 102 mv/sec.

Table 6: Electrochemical parameter for the irreversible oxidation process exhibited by Ni(II) and Co(II) chloride and acetate complexes in acetonitrile solution, supporting electrolyte [Bu<sub>4</sub>N][PF<sub>6</sub>] (0.1 M), t=25° C measured at 10 mv/sec.

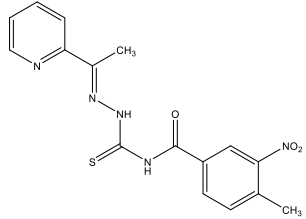
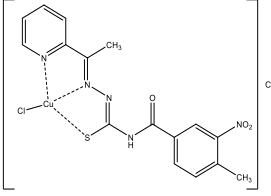
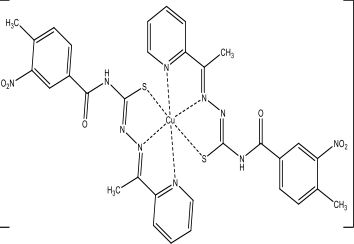
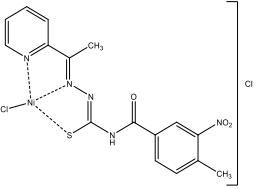
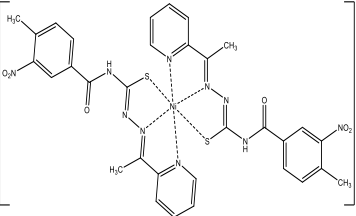
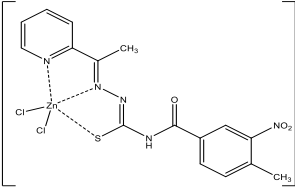
complex	$E_p/V$ vs Fc/Fc <sup>+</sup> irreversible Oxidative Peak
L <sup>4</sup> CoAC	+0.4535
L <sup>4</sup> CoCl	+0.4623
L <sup>4</sup> NiAC	+0.4459
L <sup>4</sup> NiCl	+0.4587

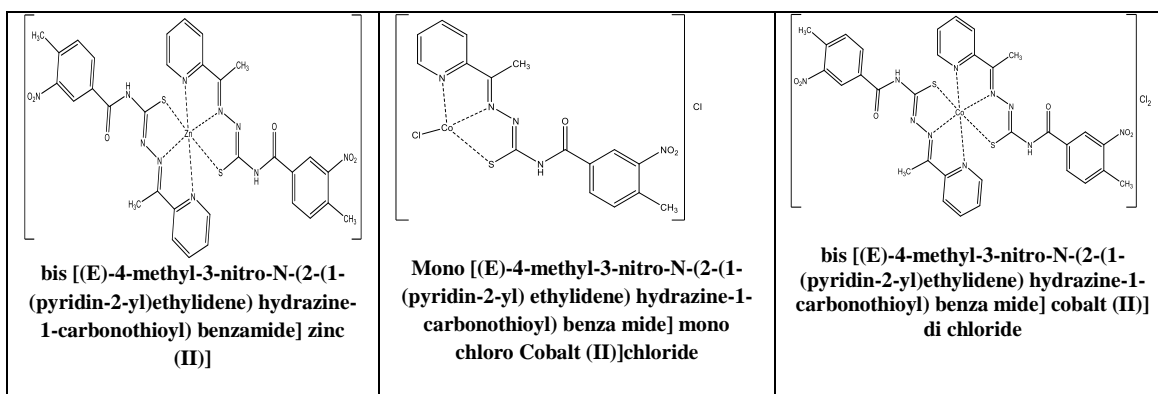
#### **4. Conclusion**

In this study, New series complexes of Cu(II), Ni(II), Zn (II) and Co(II) ions were derived from the novel thiosemicarbazone compound, (E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl) benzamide (MNEC-H) ligand can be synthesized to obtain four coordinated heteroleptic for chloride complexes [(MNEC-H)CuCl]Cl, [(MNEC-H)CoCl]Cl, [(MNEC-H)NiCl]Cl, [(MNEC-H)ZnCl<sub>2</sub>] in addition to six coordinated homoleptic for acetate complexes [(MNEC-H)<sub>2</sub>Cu], [(MNEC-H)<sub>2</sub>Co]Cl<sub>2</sub>, [(MNEC-H)<sub>2</sub>Ni], [(MNEC-H)<sub>2</sub>Zn] have been synthesized and characterized by The different available and possible techniques and measurements were employed to characterize the free ligand and its complexes like elemental analysis (CHNS), Fourier-transform infrared (FT-IR), <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, mass spectroscopy, Ultra-violet visible (UV-vis), magnetic moments measurements, conductance investigation. 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 free ligand, (E)-4-methyl-3-nitro-N-(2-(1-(pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl) benzamide (MNEC-H) as thiosemicarbazone derivative is including verious sites to chelate with the element ions synthesizing stabilized compounds and the used techniques and measurements explored and confirmed its coordination modus and the coordinated sites. The chloride complexes were confirmed as tetrahedral four coordinated complexes with [M(MNEC-H)Cl]Cl structural form as well as the metal ion bonded with N,N and S atoms of C=N in pyridyl and C=N, C=S groups founding in the free ligand (MNEC-H) and one chloro group take part in the coordination sphere and another one chloro group outside the coordination sphere except the complex zinc(II) [(MNEC-H)ZnCl<sub>2</sub>] two chloro group take part in the coordination sphere. While the acetate compounds adopt octahedral six coordinated geometry with [(MNEC-H)<sub>2</sub>Cu]structure .Two moles of free ligand MNEC-H coordinated with the element ion via N,N and S atoms in C=N, C=N and C=S groups to form the octahedral form. The most striking result to emerge from the obtained data is that when the reaction is achieved between the free ligand MNEC-H and the element chloride salts in mole ratios 1:1(L:M), take form [M(MNEC-H)Cl]Cl. Whilst the product of reaction between the free ligand MNEC-H and acetate salts in mole ratios 2:1(L:M),adopt the formula [(MNEC-H)<sub>2</sub>M]. So the structure of chloride complexes was formed take form [M(MNEC-H)Cl]Cl and this is due to the presence of two chloride groups which are considered with its small size as great sticking and bad leaving groups. Therefore, there is no chance to the free ligand to replace instead of chloro group. As contrast, in the related with the acetate compounds, it is easy to two moles of the free ligand to coordinate with the metal ion despite the existence of acetate ions because these ions are deemed with the big size as good leaving group. The electrochemical investigation was accomplished via CV probe which exhibit a

unique quasireversible process in the cathodic potential for the Cu(II) thiosemicarbazone chloride and acetate compounds. It is attributing to Cu(II) to Cu(III) reduction/oxidation system. Whilst one irreversible systems were characterized in Co(II) and Ni(II) chloride and acetate complexes that are corresponding to Co(II)/Co(III) and Ni(II)/Ni(III) reduction/oxidation processes. These findings will doubtless pointed that the free ligand MNEC-H support and stabilizing Cu(II) in their derivatives whereas the prepared Co and Ni complexes are founded not stabilizing Co(II) and Ni(II) ions in DMSO solution. Another surprising result is the lower potential value which noticed in chloride compounds than acetate derivatives and this is relating to the presence of chloro species that enhancing the electropositivity of element ion through their high electron withdrawing characteristic .

**Table: Suggested Chemical Structure and Name of Synthesized thiosemicarbazone complexes**

Chemical structure of Thiosemicarbazone	Chemical structure of Thiosemicarbazone	
 <p data-bbox="240 1234 578 1314"><b>(E)-4-methyl-3-nitro-N-(2-(1-pyridin-2-yl)ethylidene)hydrazine-1-carbonothioylbenzamide</b></p>	 <p data-bbox="618 1207 972 1314"><b>Mono [(E)-4-methyl-3-nitro-N-(2-(1-pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl]benzamide mono chloro Copper(II)chloride</b></p>	 <p data-bbox="1003 1255 1365 1325"><b>bis [(E)-4-methyl-3-nitro-N-(2-(1-pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl]benzamide cupper (II)</b></p>
 <p data-bbox="240 1564 578 1671"><b>Mono [(E)-4-methyl-3-nitro-N-(2-(1-pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl]benzamide mono chloro nickel (II)chloride</b></p>	 <p data-bbox="618 1564 972 1646"><b>bis [(E)-4-methyl-3-nitro-N-(2-(1-pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl]benzamide nickel (II)</b></p>	 <p data-bbox="1008 1556 1365 1654"><b>Mono [(E)-4-methyl-3-nitro-N-(2-(1-pyridin-2-yl)ethylidene)hydrazine-1-carbonothioyl]benzamide di chloro zinc(II)</b></p>



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