

Synthesis and Spectroscopic Study of Cobalt(II), Nickel(II), Copper(II) and Zinc(II) complexes Derived from Bi dentate 2-Pyrazoline-Based Ligand

Mahmoud Najim Al-Jibouri* and Taghreed M Musa

Department of Chemistry, College of Science, Al-Mustansiriya University, Baghdad, Iraq

*Corresponding author: Mahmoud Najim Al-Jibouri, Department of Chemistry, College of Science, Al-Mustansiriya University, Baghdad, Iraq, Tel: +964-7713460946; E-mail: mahmoud_inor71@uomustansiriyah.edu, Taghreedmohya@yahoo.com

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Abstract

The present work describes the synthesis, characterization, and spectroscopic studying of cobalt(II), nickel(II), copper(II), and zinc(II) complexes with new bi dentate ligand namely [3-(2-pyridyl)-5-(4-hydroxyphenyl)-2-pyrazoline] which has been prepared by ring closure of (E)-3-(4-hydroxyphenyl)-1-(pyridin-2-yl)prop-2-en-1-one with hydrazine hydrate in (2% w/v) of sodium hydroxide. The new 2-pyrazoline based ligand was identified by melting point, solubility in common organic solvents, mass spectra, NMR and FT-IR spectra. The optimization conditions like acidity, time of reaction, and the molar ratio (M:L) were estimated in order to get the pure colored solid complexes of cobalt, nickel, copper, and zinc(II) by the direct reactions of their metal chlorides in aqueous methanol with the methanolic solution of the ligand. The new metal complexes were characterized by the (C.H.N) elemental analyses, FTIR, UV-Visible spectra, and the molar conductivity in DMSO, and the magnetic susceptibility measurements via Faraday's method were carried out to reveal the octahedral geometry around the metal ions.

Keywords: 2-pyrazoline complexes; Spectroscopic study of pyrazole complexes; Synthesis of transition metal complexes with 2-pyrazoline ligands

Introduction

The features of the chemistry of 2-pyrazolines as pharmacologically attractive scaffolds [1-2] were described in a number of reviews in which the main approaches to the synthesis of mentioned heterocyclic derivatives and their biological activity were screened in wide spectrum [3]. Furthermore, the pyrazole hybrids as biologically active compounds is poorly discussed in the context of pharmacophore hybrid approach [4]. The coordination chemistry of pyrazole ligands have attractive interests by the scientists and many authors due to their applications in the fields of green analytical chemistry and pharmacological industry

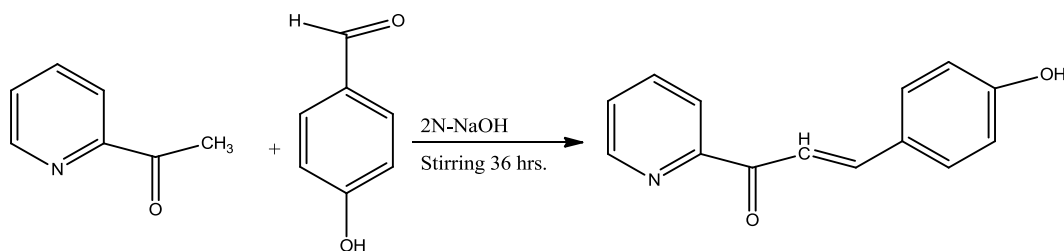
[5,6]. As well as, the anticancer drugs from palladium(II), and platinum(II) chelates with poly dentate ligands of pyrazole have extensively spread out in bio-inorganic chemistry [7,8]. However, these development in the metal wide scope of pyrazole complexes interested us to investigate new bi dentate ligand derived from the acetyl pyridine and 4-hydroxy benzaldehyde then it's complexes with some transition elements of the 3d- block have synthesized, and spectrally studied.

Experimental

Materials and methods

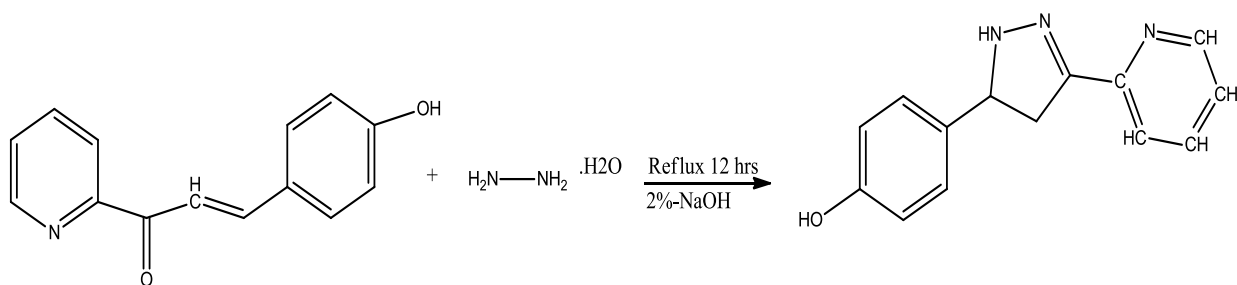
All the chemicals used for synthetic purposes were of Analar grade. Solvents like methanol, nitric acid, chloroform, dimethyl sulfoxide and ethanol were purchased from Sigma Aldrich Company and used as received. Commercial methanol was purified by distillation and used. The metal salts used for the synthesis of complexes were chlorides of cobalt(II), Ni(II) and Cu(II) and Zn(II).

Synthesis of (E)-3-(4-hydroxyphenyl)-1-(pyridin-2-yl) prop-2-en-1-one: The alfa-beta carbonyl derivative (A) was prepared according to the method described in literature [9], (SCHEME 1).



SCHEME 1. Synthesis of chalcone (A).

Synthesis of 3-(2-pyridyl)-5-(4-hydroxyphenyl)-2-pyrazoline: A mixture of (0.01 mole, 0.251 gm) of chalcone in 25 ml absolute ethanol was added to to (0.0125 mole, 10 ml) of hydrated hydrazine then stirring with addition of 5 m of (2% w/v-NaOH). The reaction mixture was refluxed on water bath for 24 hours ((SCHEME 2). After completion the reaction, the mixture was poured in ice-water with neutralization to pH=7.0 with addition 1-2 ml of 0.001 N HC. The pale-yellow precipitate was filtered off, and dried in desiccator overnight, re-crystallized from hot ethanol to afforded 0.135 gm, 65% yield of yellow crystals of the free 2-pyrazoline ligand. The physical properties, and the elemental analyses were shown in TABLE 1.



SCHEME 2. Synthesis of 3-(2-pyridyl)-5-(4-hydroxyphenyl)-2-pyrazoline (L).

Synthesis of metal complexes: A solution of (1 mmole, 0.170 gm) of copper(II) chloride dihydrate in (10 ml) distilled water was added to hot solution of the ligand L (2 mmoles, 0.480 gm) in (25 ml) absolute ethanol and heated the mixture on water bath at 7°C. The green precipitate separated out after one hour of reaction was filtered off, washed several times with hot distilled water and ethanol. The crystallization of the Cu(II)-L complex from (DMF: H₂O) yielded pure pale green crystals of the complex, TABLE 1. As well as, the rest metal complexes of cobalt(II), nickel(II) and zinc(II) were prepared by the above procedure by the using of their hydrated chlorides after adjusting the pH of the mixture to 7.5 and the periods of completion the reactions reached to (2-3) hours on water bath.

TABLE 1. Physical properties and elemental analysis of the prepared ligand L and its metal complexes.

Compounds	Molecular weight (g/mol) formula	Colour	M.P. (°C)	%C Calc. (Found)	%H calc. (Found)	%N calc. (Found)	%M calc. (Found)
A	225.18 C ₁₄ H ₁₁ NO ₂	Dark yellow	122-124	74.65 (74.00)	4.92 (4.11)	6.22 (5.88)	--
L	239.22 C ₁₄ H ₁₃ N ₃ O	Yellow	180-182	70.38 (69.22)	5.48 (4.77)	17.56 (16.99)	---
[CoL ₂ (H ₂ O) ₂] Cl ₂	644 C ₂₈ H ₃₀ Cl ₂ CoN ₆ O ₄	Green	244-246	54.38 (53.88)	5.00 (4.84)	70.38	10.11 (9.66)
[NiL ₂ (H ₂ O) ₂] Cl ₂	645.33 C ₂₈ H ₃₀ Cl ₂ NiN ₆ O ₄	Olive	266 ^d	52.55 (51.66)	4.98 (3.82)	12.99 (13.22)	9.12 (8.97)
[CuL ₂ (H ₂ O) ₂] Cl ₂	654.22 C ₂₈ H ₃₀ Cl ₂ CuN ₆ O ₄	Pale green	288 ^d	51.38 (50.22)	4.08 (4.00)	12.38 (12.99)	10.99 (9.22)
[ZnL ₂ Cl ₂]	615 C ₂₈ H ₂₆ Cl ₂ N ₆ O ₂ Zn	Off white	277-279	50.77 (49.98)	13.29 (12.94)	13.67 (14.00)	10.70 (9.71)

Physical measurements

The elemental percentage analyses of the free ligand were carried out using Carl-Erba CHN analyzer. The metal percentage analyses were conducted using FAAS on Shimadzu 670AA flame atomic spectrometer at Al-Mustansiriyah university laboratories via standard addition method [10]. The UV-visible spectra were recorded using 0.001 M solutions of ligands and complexes in methanol and DMF. The IR spectra of the compounds were recorded by their thin KBr discs. The mass spectra of the chalcone and 2-pyrazoline ligand were done with accelerating voltage, 10 kV MS spectra at chemistry department, college of science, Al-Mustansiriyah University. The NMR spectra were obtained using DMSO-d₆ as solvent and TMS as internal standard on Bruker 300MHz NMR spectrometer at Al-Bait university-Amman (Jordan). The magnetic susceptibility was determined at room temperature on Sherwood Magnetic susceptibility instrument which was calibrated with Hg[Co(NCS)₄] at AL-Yarmook university(Jordan). The thermal analyses TG/DTG of the metal complexes were carried out at helium inert gas with Tonosi-Thermo with a heating rate of 10 C/min. at Ibn-Haithum college for pure science-Baghdad-University.

Results and Discussion

The chalcone derivative was (A) has prepared via Claisen-Schmidt condensation between 2-acetylpyridine and 4-hydroxy benzaldehyde at room temperature. The successive reaction of the chalcone (A) with hydrazine hydrate gave hydrazine derivative which followed ring closure up on attacking of -NH- on HC=C- to result the 2-pyrazoline-based ligand. The new

ligand was identified with the help of mass spectra, FTIR, and NMR spectroscopy methods. The solid complexes of cobalt, nickel, copper, and zinc(II) were isolated from their solutions reactions with the methanolic solution of (L) ligand after adjusting the conditions involving the time of reaction, PH, and the molar ratios of (M:L) via Job-method [11]. All the complexes are insoluble in common organic solvents like methanol, ethanol, chloroform, and sparingly soluble in acetonitrile, whereas it's solubility in DMF and DMSO was greatly, therefore the measurements of molar conductivity and electronic spectra were done in DMSO. The compositions of the prepared compounds were supported by comparison of their observed (carbon, hydrogen, and nitrogen) elemental analysis with the values calculated via Cambridge-Chem. office, TABLE 1.

Mass spectra

The FIG. 1 shows the mass spectra of the chalcone (A) where the absorption at 225 may be assigned to the expected molecular ion of the prepared chalcone with $C_{14}H_{11}NO_2$ formula. As well as, the FIG. 2 displays the apparent peak with 80% relative intensity at $m/e=239$ that is suggested to the ring closure of chalcone (A) with hydrated hydrazine to afford the 2-pyrazoline-based ligand with proposed formula $C_{14}H_{13}N_3O$ formula (TABLE 2).

TABLE 2. IR spectra of the ligand (L) and its metal complexes.

Compounds	$\nu_{OH, -NH}$	$\nu_{C=O}$	$\nu_{C=N-}$	ν_{C-N}	ν_{M-N}	ν_{M-Cl}
A	3600 (br.)	1678 (s)	630-1590 (sh.)	1280 (s)	-	-
L	3500 (m)	-	1577	1300-1270 (s)	-	-
$[CoL_2(H_2O)_2] Cl_2$	3280 (m)	-	1550	1310-1240 (m)	510 (w)	360 (w)
$[NiL_2(H_2O)_2] Cl_2$	3400 (br.)	-	1610-1532 (m)	1266 (m)	570 (w)	280-320 (w)
$[CuL_2(H_2O)_2] Cl_2$	3380 (br.)	-	1600 (s)	1290 (m)	570 (w)	376 (m)
$[ZnL_2Cl_2]$	3590 (br.)	-	1615 (s)	1276 (s)	422 (w)	259 (w)

Br: Broad; M: Medium; S: Strong; Sh: Shoulder

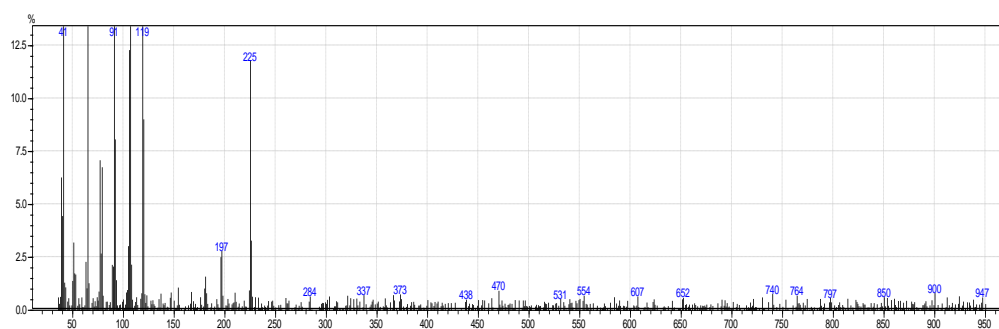


FIG 1. Mass spectra of Chalcone (E)-3-(4-hydroxyphenyl)-1-(pyridin-2-yl) prop-2-en-1-one.

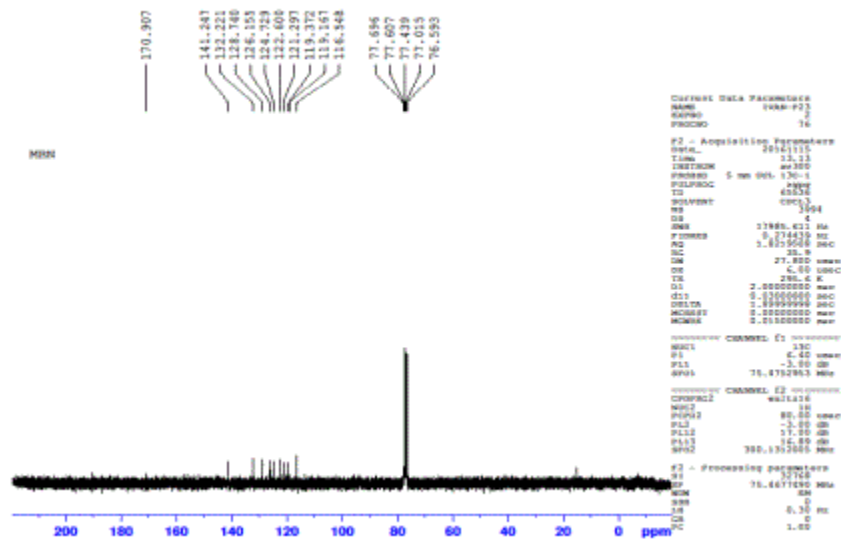


FIG. 4. ^{13}C NMR spectra of ligand (L) in $\text{d}_6\text{-DMSO}$ solvent.

FTIR spectra

The IR spectra fully confirmed the proposed structures of the prepared compounds. The FT-IR spectra of the chalcone (E)-3-(4-hydroxyphenyl)-1-(pyridin-2-yl) prop-2-en-1-one, exhibited strong absorptions at 1685, and 1612 cm^{-1} which are resulted from asymmetric vibrations of -C=O and -CH=CH- of the alpha-beta-carbonyl compounds [14]. The absence of the absorptions carbonyl moiety in the FT-IR spectra of the free ligand, FIG. S.1, confirmed the formation of ring closure to afford 2-pyrazoline ligand (L). As well as, the observation of new bands around 3433-3340, and 1627-1454 cm^{-1} assigned to vibration modes of -NH , -OH , and -C=N- , -C-N- of the pyrazoline ring. However, the FT-IR spectra of all metal complexes at CsI discs displayed remarkable changes in the positions and intensities of the imine- C=N- , and -NH- groups which confirmed the participation of two nitrogen atoms of pyridine and 2-pyrazoline rings in coordination with the metal ions [15,16]. The appearance of strong absorptions in the regions 1610-1612 cm^{-1} , 1580-1577, and 13200-1280 cm^{-1} may be assigned to -C=N- and -C-N- moieties of pyrazoline and pyridine rings respectively, then revealed the formation of five-member ring with ions of cobalt(II), nickel(II), copper(II), and zinc(II) (FIG. 5).

The broad bands around 3500-3200 cm^{-1} besides the bending of coordinated water molecules in the regions 1560-1550 cm^{-1} , and 845-822 cm^{-1} supported the -OH coordinated by water in the inner sphere of metal complexes [17]. Furthermore-IR spectra of the zinc(II) complex showed weak to medium bands around 250-375 cm^{-1} supporting Zn-Cl bonds (TABLE 3). The lower frequency regions of IR spectra of all complexes recorded weak bands around 422-570 cm^{-1} that are attributed to M-N bonds [17,18]. The data obtained from FT-IR spectra investigated the bi dentate behavior of the ligand through two nitrogen atoms of pyrazoline and pyridine rings, thereby gives strong proof for the metal complexes formation and kinetic stability of the five-member ring chelate with the selected bivalent metals [18].

TABLE 3. UV-visible absorptions, molar conductivity and magnetic moments of the prepared complexes.

Compound	λ max (nm)	ν cm^{-1}	Λ $\text{oh}^1\text{mcm}^2\text{mol}^{-1}$	μ B.M.
L	250	50000	-	-
	310	32258		
[CoL ₂ (H ₂ O) ₂] Cl ₂	950	10527	78	4.60
	600	16666		
	345	28985		
[NiL ₂ (H ₂ O) ₂] Cl ₂	750	13333	68	2.88
	480	20832		
	322	31055		
[CuL ₂ (H ₂ O) ₂] Cl ₂	830	12048	65	1.80
	370	27027		
[ZnL ₂ Cl ₂]	336	29761	12	0.0
	275	36363		
Λ: Molar conductance in DSO solutions of 0.001M concentration.				

Electronic spectra and magnetic properties

The UV-Visible spectra of the free ligand in methanol (0.001 M) recorded high intensity peaks around 250, and 310 nm which are resulted from $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively [10,19]. The green solution of cobalt (II) in DMSO showed three spin-allowed transitions around 950, 600, and 345 nm that are assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ respectively [20], thereby confirmed the octahedral environment around cobalt(II) ion. By the same way, the complexes solution of nickel (II) in DMSO displayed two weak absorptions in the regions 750-480 nm and another intense peak at 375 nm which are ascribed from ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and MLCT respectively.

The agreement of the splitting energies for cobalt (II), and nickel (II) complexes in the range 667-160 KJ/mole indicates the high-spin octahedral geometry complexes around cobalt (II), and nickel (II) ions (FIG. 6). Furthermore, the green solution of copper (II) complex in DMSO exhibited a broad peak at 835 nm that is due to the resolute transitions of ${}^2B_{1g} \rightarrow {}^2B_{2g}$, and ${}^2B_{1g} \rightarrow {}^2E_g$ thereby supports the distorted octahedral environment around copper (II) ion [21].

The pale-yellow color of zinc (II) complex in DMSO may be resulted from LMCT in the region 275-336 nm. The magnetic moments of cobalt (II), nickel (II), and copper (II) complexes obtained from Faraday's method at 295 K were found to be 4.65, 2.88, and 1.80 BM respectively. These values are in accordance with the presence of three, two, and one unpaired electrons in the d-shell of the metal ions respectively [22,23]. The increasing in the magnetic susceptibility of cobalt (II) complex may be caused from the orbital contribution of electron motion in the t_{2g} level.

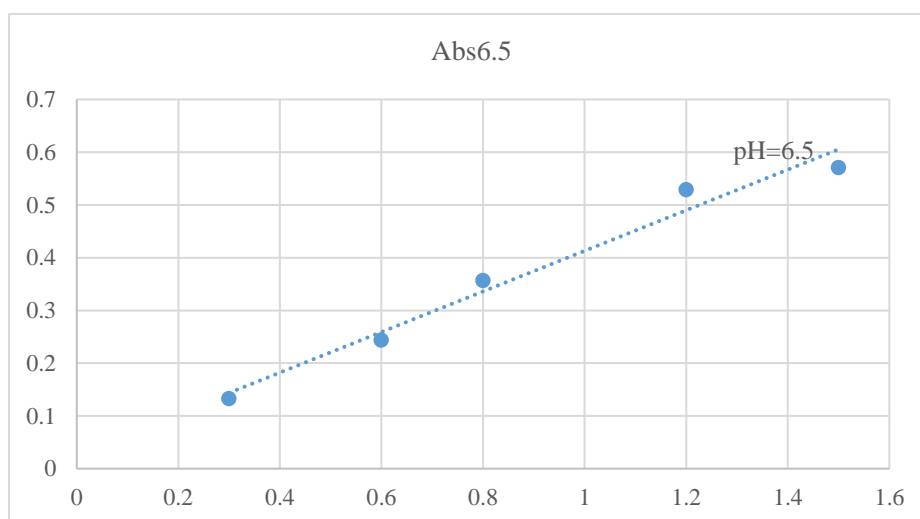
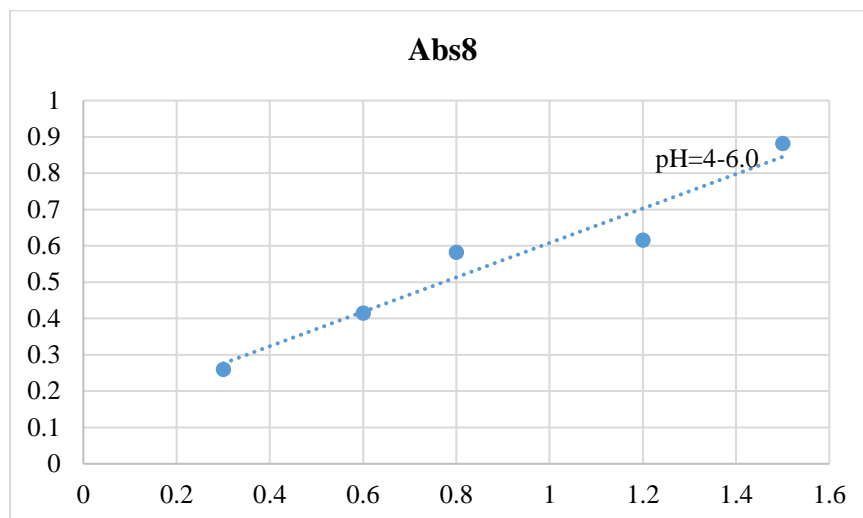


FIG 5. Effect of Ph on formation of Cu(II)-L complex at 835 nm.

Effect of pH on the formation of metal complexes

The UV-Vis spectra of M(II)-ligand mixed solution with a concentration range of (2×10^{-3} - 10^{-4}) M were studied. The concentration of 2×10^{-4} M was obeyed the Lambert-Beer's law and showed a clear intense color. A straight line, with correlation factor ($r=0.95$), was obtained when the absorbance plotted against the molar concentration, as well as the investigation of 2:1 molar ratio of the ligand to metal ion in methanolic solution after adjusting the acidity of mixture and the absorption of d-d regarding copper(II)-L complex at 835 nm.

Thermal analysis

The thermo gravimetric analysis of the cobalt (II) and copper(II) complexes with new pyrazoline ligand were recorded in helium gas, and are presented and showed in FIG. 4-7. The TG curve of cobalt(II) complex show weight losses in two exothermic decomposition at 12.2182% in the temperature ranges 210-240 and 350-430°C respectively with endothermic

processes of thermal decomposition thereby agree well with the thermo grams of DSC which confirms the stability of cobalt(II) complex [24].

As well as, the TG curves of copper(II) complex showed endothermic pattern with two stages in the temperature ranges 180-220°C, and 250-450°C respectively, assigning to cleavage of two water molecules in the first step, and the decomposition of organic moiety of ligand with departure of chloride ions, then confirms the proposed structures of the complexes. The stable phases of TG-DSC for the two complexes of cobalt(II), and copper(II) were Co_3N_2 , and CuO respectively, then there are in accordance with the literature surveys of TG analyses of pyrazoline metal chelates [25,26].

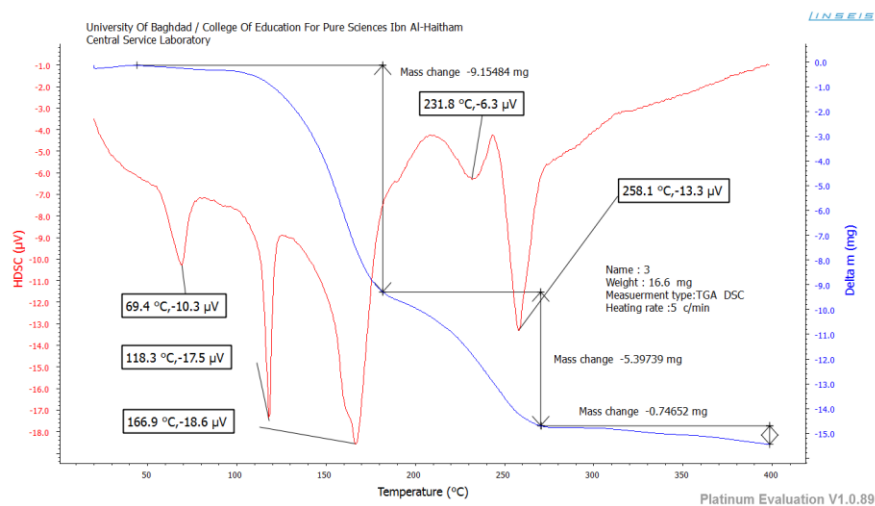


FIG. 6. TG-DSC diagram of Cobalt(II)-L complex in He gas.

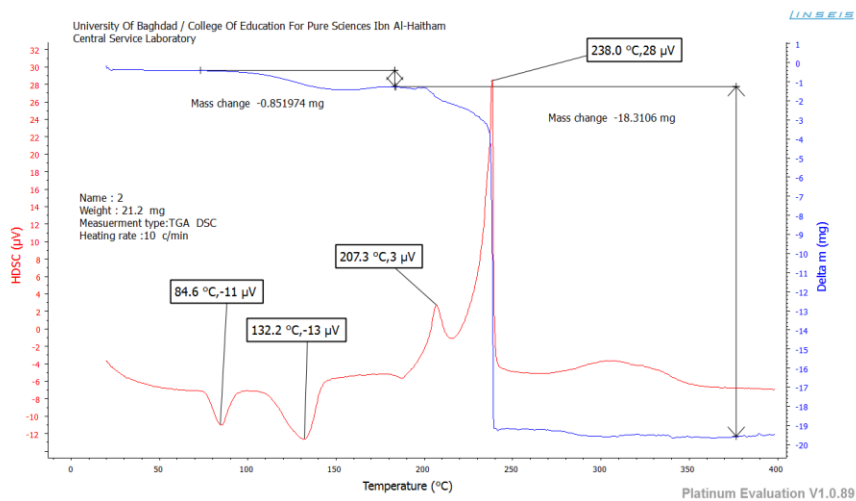
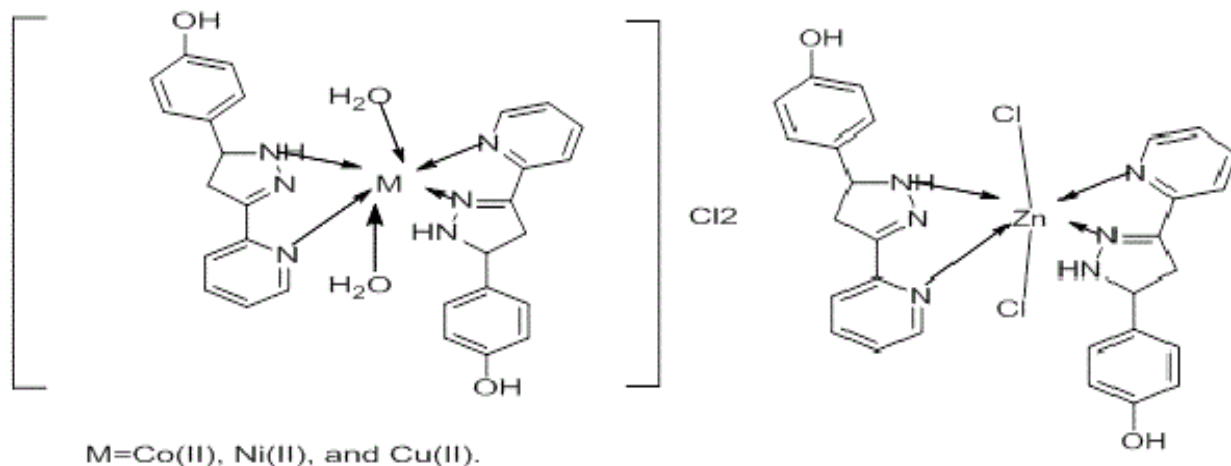


FIG. 7. TG-DTG diagram of copper(II)-L complex in He gas.

Conclusion

According to the results obtained from elemental analyses, NMR, FTIR, Mass spectra and magnetic moments, the new derivative of 2-pyrazoline behaved as bi dentate ligand toward the cobalt (II), nickel (II), cooper (II), and zinc (II) ions. These all complexes were isolated in the solid state after optimization, the conditions of time, acidity, and the molar ratio. The active sites of the ligand in bonding with the metal ions are the two nitrogen atoms of N_2^- of pyrazoline ring and N^1 of pyridyl moiety

which suffered red shift in their FTIR spectra. The SCHEME 3, shows the octahedral symmetry of the prepared complexes with the general formula, $[M(L)2(H_2O)_2] Cl_2$, (SCHEME 3).



SCHEME 3. Octahedral geometrical structures of the prepared metal complexes.

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