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Review Article

Review on Preparation, Coordination and Clinical Chemistry of 2-Pyrazoline Derivatives: Synthesis and Characterization of 5-(thiophen-2-yl)-3-(pyridin-3-yl)-4,5-Dihydro-1*H*-Pyrazole-1-Carbothioamide and their Co(II), Ni(II), Cu(II) and Zn(II) Complexes

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ABSTRACT

The *N*-substituted 2-pyrazoline derivative has received significant encouragement from researchers for their effective roles in wide range of biological activities and has been used as catalysts and colorimetric reagents in the determination of trace heavy metals. This review article focuses on the pyrazolines routes, such as the preparation of pyrazole derivatives via chalcones. It also demonstrates that 2-pyrazoline complexes were biologically active and have had a range of clinical applications. The recent review collects the significances of 2-pyrazoline ligands and main methods of preparation and their role in the field of coordination chemistry. The observed data from update literature investigates the well-known method of Micheal addition of hydrazine or thiosemicarbazide derivatives to the ά-β-unsaturated carbonyl compounds. Furthermore, the chelation ability for most prepared 2-pyrazoline ligands have confirmed the active sites of immine moiety of pyrazole ring beside the sulfur atom forming five-membered ring with the studied d-metals. Likewise, the recent work involves the synthesis of new ligand of 2-pyrazoline from condensation chalcone with 4-thiosemicarbazide in alkaline medium. The new prepared ligand5-(4-thiophen-2-yl)-3-(pyridin-3-yl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide and its metal complexes with cobalt(II), nickel(II), copper(II), and zinc(II) were fully characterized with the elemental micro-analyses (C.H.N.S), determination of metal content, FT-IR, and UV-Visible spectra. Furthermore, the magnetic susceptibility of solid metal complexes and molar conductivity measurements of their solutions in DMSO solvent have confirmed their chemical structures. The observed data from analytical methods revealed the octahedral geometry in 2:1 mole ratio (L:M) except the tetrahedral structure in [ZnLC]Cl formula. The diamagnetic complex of nickel(II) was approved as square planner geometry with high value of molar conductance.

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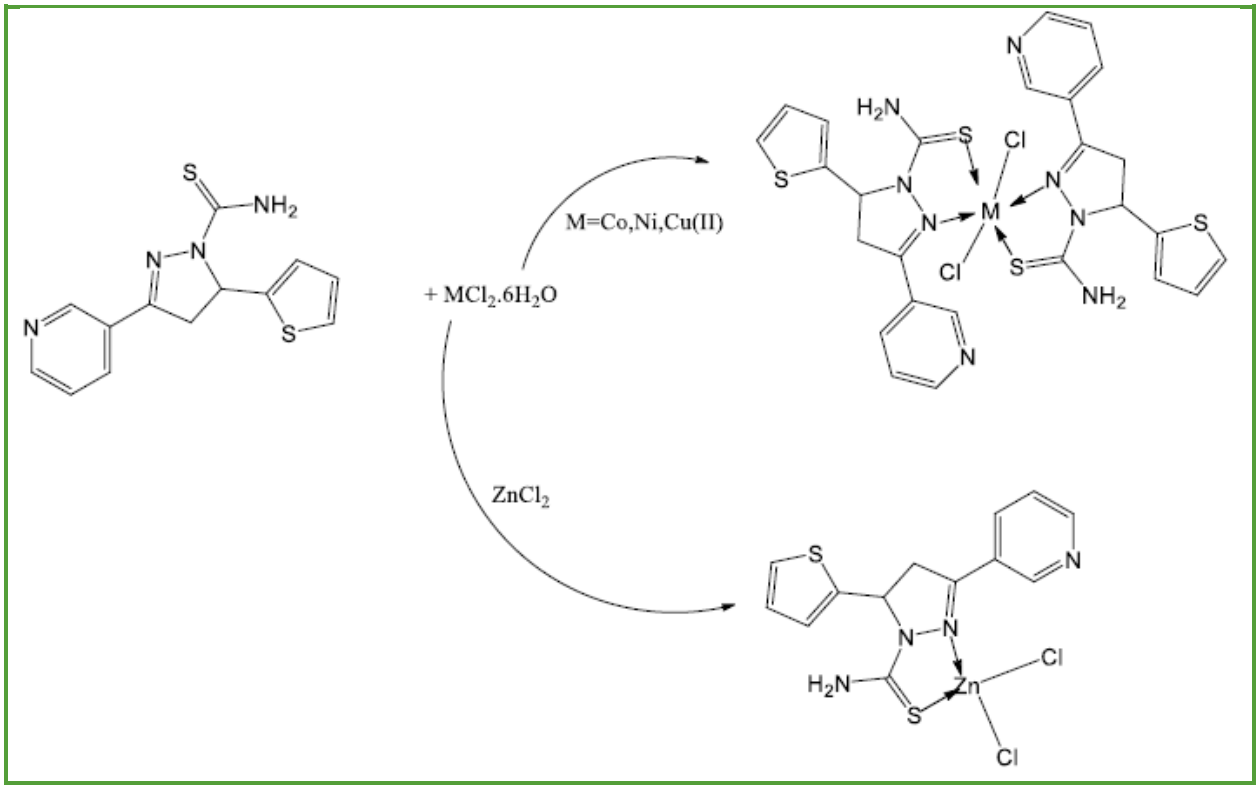
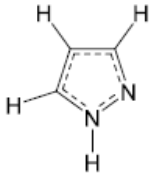
Graphical Abstract



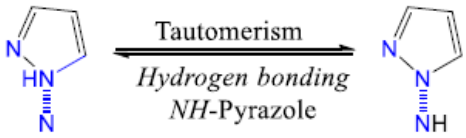
Introduction

The five membered ring of pyrazole is already has a π-excessive system involving two adjacent nitrogen atoms, as displayed in Scheme 1. The discovery of ring closure reaction by Fischer and *Knovenagel* in the late 19th century like of acrolein with phenylhydrazine1 to provide a 2-pyrazoline type compound have provided ideal example for its synthesis [1, 2].

The pyrazole in its solutions can act both as weak bases and moderately weak acids due to ability of –C=N- group to accept proton and their ability of –N-H to lose the proton. Likewise, hydrogen bonding interactions and tautomeric properties of these compounds are strictly related to the nature of their heteroatoms as well as by the electronic effect of the substituent groups on the pyrazole core [3], as depicted in Scheme 2.



Scheme 1. Structure of pyrazole



Scheme 2. Pyrazole tautomerism

The presence of functional groups like immine and thiocarbamoyl moieties in the structures of 2-pyrazoline derivatives has given strong activity to their applications in biological systems [4, 5].

Metal complexes derived from pyrazole have attracted considerable interest due to their wide spectrum in framework in coordination chemistry especially their uses as catalysts and pharmaceutical industry [5, 6]. The coordination bonds between transition metal ions and heterocyclic ligands containing nitrogen atom have proved to be useful for the construction of solid-state architectures and inorganic crystal engineering. Some metal ions are biologically essential, such as cobalt, nickel and copper. The chelating ability of copper (II) and its positive reduction potential allow participation in biological transports [7]. Cobalt is known to be a central element of metabolically important biomolecules, as mentioned in cobalmine, and therefore its bio speciation in biological fluids constitutes a theme worthy of chemical and biological perusal. The utilities of the pyrazoline are of increasing, although its synthesis is more challenging. Thermal stability of pyrazoline derivative has assisted the researchers to carry out great applications in wide range of biological and clinical activities and less toxicity, for pharmaceutical applications [5, 6].

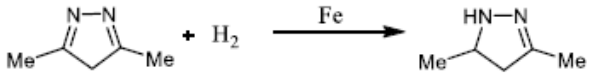
As such, eighteen novels 1-*N*- substituted-3,5-diphenyl-2-pyrazoline derivatives, a series of twenty 1-(4-sulfamylphenyl)-3-trifuoromethyl-5-indolyl pyrazolines, some 2-naphthyl pyrazolines and exclusive fluorine substituted pyrazoline derivatives were designed, synthesized and screened for cyclooxygenase (COX-1, COX-2) inhibitory, anti-inflammatory, analgesic and antimicrobial activities, some which possessed acceptable activity [7, 8]. The substituted 2-pyrazolines have showed antimalarial properties, in addition their active role as compounds target the malaria parasite by inhibiting the hem detoxification process [9, 10].

Methods of synthesis of pyrazolines

The pyrazolines preparation is explored using a variety of approaches, mostly one-pot and two-pot techniques. A one-pot method uses a direct reaction of aromatic aldehyde, ketone, and hydrazine64, whereas a two-pot method uses chalcones followed by a cyclization reaction with hydrazine to create pyrazoline, the one-pot synthesis process has piqued the interest of chemists and researchers because to its several advantages, including the minimum intermediate separation, reduced chemical waste, time, and solvent savings during intermediate purification. However, a one-pot reaction had several downsides, such as unwanted compounds that increased as reaction conditions changed. The two-pot synthetic process has several advantages, involving high purity of product. Long reaction times, high temperatures, and time-consuming two-step procedures are some of the downsides of the two-pot technique [8, 11].

Synthesis of 2-subsituted pyrazoline by reduction of pyrazole

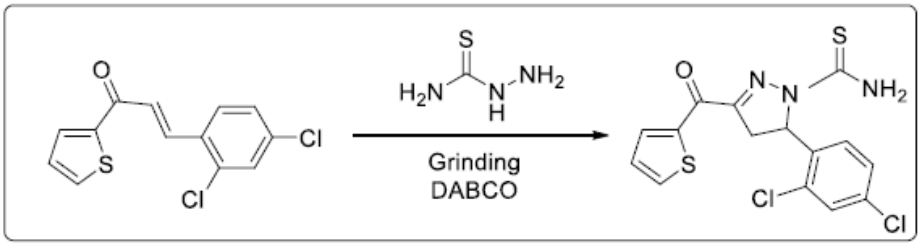
The well-known route for preparation of 2-pyrazoline is the reduction of 3,5-dimethylpyrazole by hydrogen gas in presence of iron catalyst, as depicted in Scheme 3 [12, 13].



Scheme 3. Reduction method to isolate 3,5-dimethyl-2- pyrazoline

Synthesis of pyrazoline by ring closure of chalcones with thiosemicarbazide

The ring closure of *a-β* unsaturated carbonyls with excess of thiosemicarbazide in presence of DABCO catalyst have introduced ideal and green chemistry method for almost the researchers to isolate high yield of *N*-thiocarbamoyl-2-pyrazoline derivative, as shown in Scheme 4 [17].



Scheme 4. The ring closure of thiophene chalcones with thiosemicarbazide

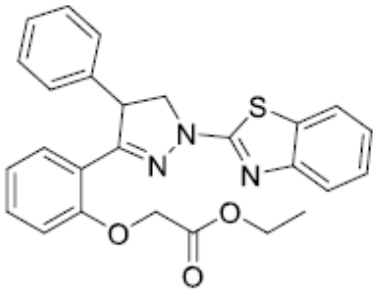
Furthermore, the condensation -1-(4-chlorophenyal)-3-(2-thienyl)prop-2-en-1-one with excess thiosemicarbazide in potassium hydroxide catalyst have afforded modified procedure to get high yield of 2-pyrazoline derivatives [18].

Synthesis pyrazole derivative by Micheal addition

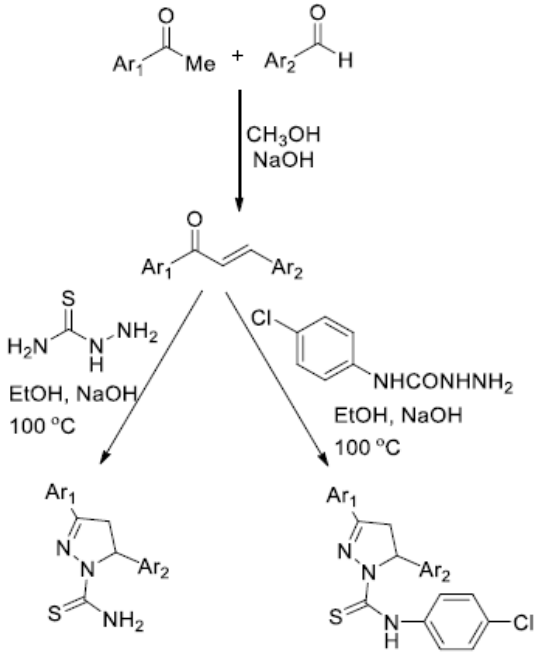
The fluorescence properties of poly dentate ligands of 2-pyrazoline, Scheme 5 have been assigned where the ethyl 2-(2-(1-(benzo[*d*]thiazol-2-yl)-4-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)phenoxy)acetate was prepared from Micheal addition followed ring closure of corresponded chalcone with 2-hydrazino-benzothiazole in alkaline medium. The increasing the intensity emission the derivative was enhanced up on chelation with aluminum(III) ion [19].

Preparation of pyrazoles from chalcones

Due to their well-established pharmacological properties, the synthesis of chalcones (1,3-diarylprop-2-en-1-ones) and 2-pyrazoline derivatives has been an interesting topic of research [20]. The *Claisen*-Schmidt condensation was used to make a series of chalcones using methyl aryl ketones and substituted aldehydes in the presence of sodium hydroxide and methanol. The heat refluxing chosen chalcones and thiosemicarbazide in alkaline media, 3,5-disubstituted-4,5-dihydro-1*H*-pyrazole-1-carbothioamides were produced.



Scheme 5. Fluorescent dye of -pyrazoline derivative

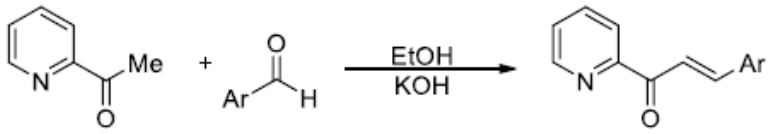


Scheme 6. Synthesis pyrazole derivative by chalcone

Similarly, chosen chalcones were refluxed with *N*-(4-chlorophenyl) semicarbazide in alkaline media to produce *N*-,5-trisubstituted-

4,5-dihydro-1*H*-pyrazole-1-carboxamides. The measurements of elemental micro-analyses, GC-MS and NMR spectra have been confirmed the structures of the synthesized compounds, which were in agreement with the hypothesized structures, as depicted in Scheme 6.

The well-known *Claisen-Scmidt* condensation of aromatic aldehydes with 2-acetylpyridine at room temperature have employed by many researchers to get high yields of chalcones derivatives which are already considered the precursors of 2-pyrazolines, as shown in Scheme 7 [18, 19].



Scheme 7. Pyrazole synthesis by Claisen Schmidt condensation

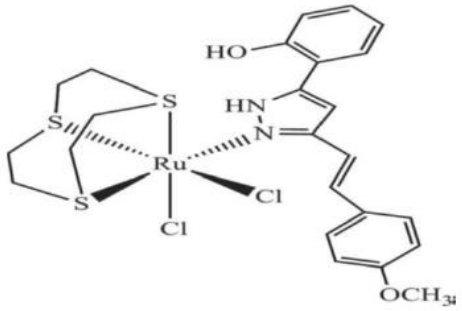


Figure 1. Ruthenium(II) complex with trithiacyclononanone-pyrazole ligands

Synthesis of 2-pyrazoline via Mannich bases reactions with thiosemicarbazide

The preparation of anticancer 2-pyrazoline derivatives from condensation of Mannich bases with excess of thiosemicarbazides [20, 21]. The spectroscopic techniques of NMR, HPLC-MS and FT-IR have carried out to give strong evidences for the structres of 2-pyrazolines in this manner [21].

The in vitro antiamoebic activities of the pyrazoline compounds have confirmed their micro dilution method against Hemi IMSS strain of Endameba histolytic and compared with the standard drug, metronidazole. It was concluded that 3-chloro and 3-bromo substituents on the phenyl ring at position 3 of the pyrazoline ring enhanced the ant amoebic activity. Due to their well-established pharmacological properties, the synthesis of chalcones (1,3-diarylprop-2-en-1-ones) and 2-pyrazoline derivatives has been a hot topic of research.

The heating under reflux of suitable chalcones with the excess of thiosemicarbazide in alkaline media have resulted in formation of 3,5-disubstituted-4,5-dihydro-1*H*-pyrazole-1-carbothioamides. Similarly, chosen chalcones were refluxed with *N*-(4-chlorophenyl)semicarbazide in alkaline media to produce *N*-3,5-trisubstituted-4,5-dihydro-1*H*-pyrazole-1-carboxamides.

Clinical application of pyrazolines

Sakai *et al.* [21] have been prepared platinum(II) complexes of pyrazoline ligands and studied the anticancer activity against some

cancer line cells of dichloro-bis(pyrazole)platinum(II), $PtCl_2(pzH)_2$ and dichloro-bis(pyrazoledicarboxylic-acid)platinum(II) dipotassium salt, $PtCl_2(3\text{-}CO_2H,5\text{-}CO_2KpzH)_2$ in human colorectal cell lines (DLD-1, HCT15 (AGS)).

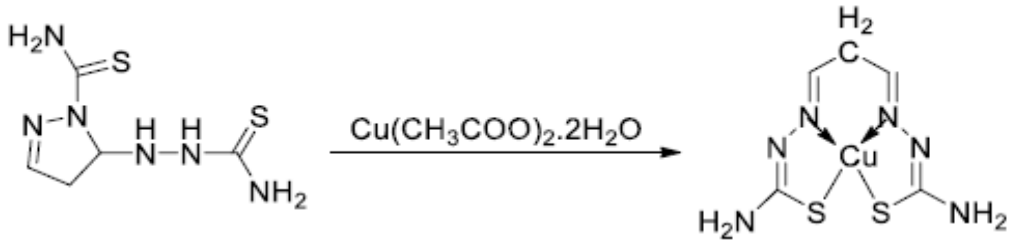
The dichloro-bis(pyrazole)platinum(II), $PtCl_2(pzH)_2$ was active against the four cell lines indicated above, but $PtCl_2(3\text{-}CO_2H,5\text{-}CO_2KpzH)_2$ was unsuccessful. Furtehrmore, pyrazoles complexes shows a biological activity as antitumor, antioxidant, antimicrobial, antitubercular, antimalarial, anti- amoebic, DPPH radical scavenging, anti-diabetic [21], antiviral, and amine oxidase. Also, thiazoles are known to have anticonvulsant, anti-mycobacterial, antimicrobial, anti-inflammatory, anticancer, ant diabetic, anti-HIV,anti-Alzheimer, antihypertensive, antifungal, and antioxidant activities and also their metal ion complexes with cobalt(II), nickel(II), and copper(II) have special importance in the biochemical systems. The substituted pyrazoline with other heterocyclic rings like pyrimidine have been also exhibited wide spectrum of antimicrobial activity like 3-(4-pyridyl)- 2-*H*-Naphtho-1,2-C-pyrazoles [21, 22].

Pyrazole complexes

Pyrazines, thiadiazole, and bis-2-pyrazolines are arguably the most important polydentate N,S, and O-heterocycles used in the isolation of coordination compounds, especially with d-block components**.** The complexes of ruthenium(II) with mixed ligands of 5-(2-hydroxyphenyl)-3-(4-methoxystyryl)pyrazole ligand and trithiacyclonoanone, as demonstrated in Figure 1. The cytoxocity of these prepared complexes have assessed against some cell lines and showed great activity [22, 23].

The first divalent copper chelate of a tridentate thiosemicarbazido-pyrazoline has been recently prepared and it is antimicrobial assessment studied by researchers [20, 22]. The reaction of excess thiosemicarbazide with acetyl acetone in acidic medium produced cyclic pyrazoline ligand with two substitutions at C-3 and C-5 of the ring whereas the open ring was confirmed up on chelation with copper acetate at optimized P_H =(7.5-8.0) and these results were concluded on the basis of single crystal X-ray diffraction, as depicted in Scheme 8.

Mahmoud N.Al-jibouri *et al.* [23] have studied the preparation and spectroscopic properties of chromium(III), manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) complexes with 2-[5-(2-hydroxy phenyl) 1,3,4-oxadiazol-2yl]-5-methyl-2, 4 dihydro-3*H*-pyrazol-3-one]. The results data observed from FT-IR and NMR spectra approved the bi dentate behavior of the ligand through nitrogen of pyrazoline ring and carbonyl of oxadiazole ring, respectively.



Scheme 8. Open ring of pyrazoline up on chelation with Cu(II) acetate

Experimental

Materials and Methods

The starting materials; 2-acetylpyridine and thiophene-2-carboxaldehyde were supplied from Merck Chemical Company with 99% purity and used without purification. All the chemicals that used in this work were commercially available and used without further purification. Likewise, the solvents and thiosemicarbazide were supplied from Sigma-Aldrich Company and used without purification. The hydrated metal chlorides of $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, and $NiCl_2.6H_2O$ and were supplied from Merck, Chemistry Department, College of Science, Mustansiriyah University.

Physical measurements

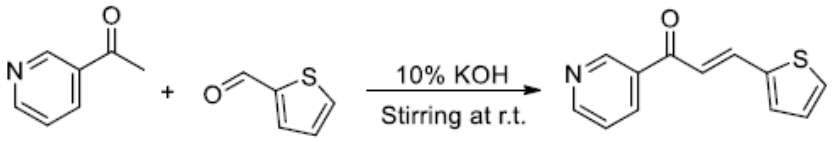
The decomposition points of prepared chalcones and their corresponding ligands were measured by Stuart- SMP30. The vibrational frequencies of the solid prepared ligands and metal complexes were measured in the region (4000-400) cm^{-1} on (8400 S-FT-IR SHIMADZU) spectrometer at Mustansiriyah University, College of Science, Iraq. The molecular weights of the chalcones, A, B and their ligands as well as metal complexes were determined by mass spectra technique with GC-DIMS QP2010 ultra and orbitrap LTQ XL- Thermo Fisher scientific mass spectrometer at University of Tehran , Iran.

Furthermore, ^{13}C-NMR and ^{1}H-NMR spectra of the prepared chalcones and their 2-pyrazoline ligands were measured on 500 MHz Bruker NMR spectrometer at Tahran University, Faculty of Chemistry, Iran.

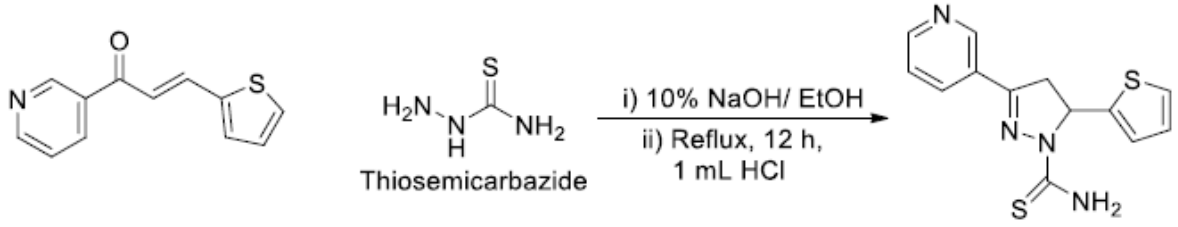
Synthesis of (E)-3-(thiophen-2-yl)-1-(pyridin-3-yl)prop-2-en-1-one

The modified procedure of *Claisen-Schmidt* was used to prepare the precursors chalcones , A and B, as explained as follow.

A solution of 3.99 g (10 mmol) of 3-acetylpyridine in 15 mL methanol was added gradually to (3.45 g, 10 mmol) of thiophene-2-carboxaldehyde in 10% KOH solution was stirred at room temperature for 12 hours. The pale yellow precipitate was formed, collected by filtration and the re-crystallization from chloroform afforded deep-yellow crystals of the novel chalcone, as shown in Scheme 9.



Scheme 9. Synthesis of chalcone



Scheme 10. Synthesis of (L) ligand

Synthesis of 5-(thiophen-2-yl)-3-(pyridin-3-yl)-4,5-dihydro-1H-pyrazole-1-carbothioamide, L

The ligand was prepared according to the modified procedure established in literature. A solution of (2.54 g, 10 mmol) of (*E*)-3-(thiophen-2yl)-1-(pyridin-3-yl)prop-2-en-1-one and 4-thiosemicarbazide (1.33 g, 22 mmol) in 50 mL hot ethanol was stirred in water bath for 45 minutes then added (0.62 g) of sodium hydroxide was added and heated under reflux the mixture for 18 hours. The completion of reaction was followed by TLC in (chloroform: ethyl acetate) solvents as eluent. The white off crude was collected after standing in room temperature for two hours the filtered, dried in vacuum desiccators over anhydrous $CaCl_2$.was complete. The re-crystallization from hot methanol afforded yellow precipitated, as illustrated in Scheme 10.

Synthesis of metal complexes

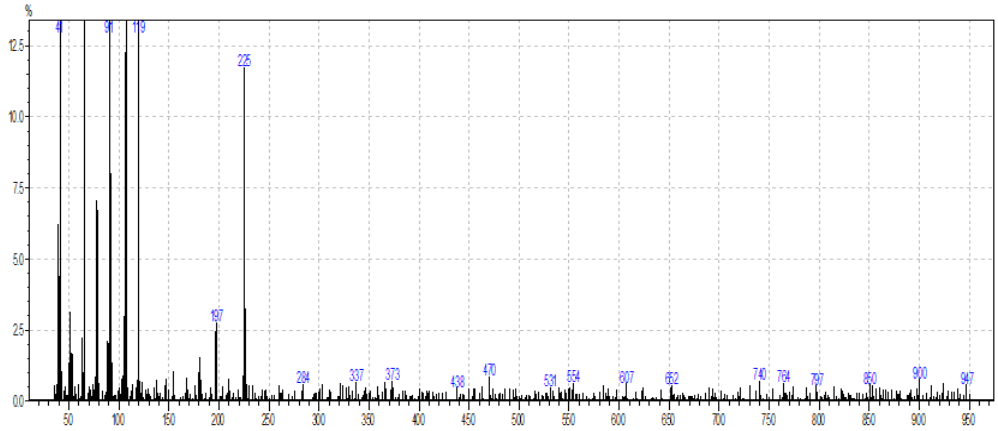
Metal(II) chloride [$CoCl_2.6H_2O$ (1.71 g, 2 mmol), $NiCl_2.6H_2O$ (0.09 g), $CuCl_2.2H_2O$ (0.273 g, 2 mmol), and $ZnCl_2$ (0.09 g,)] in ethanol (5 mL) was added with stirring to a methanolic solution of L (0.288 g, 1 mmol) and refluxed on a water bath for 3-4 hours. The separated colored solids of complex were filtered, washed with hot ethanol, and dried in vacuo.

Results and discussion

Physical properties and characterization

The chalcone formed up on condensation of (*E*)-1-(pyridin-3-yl)-3-(thiophen-2-yl)prop-2-en-1-one was confirmed its structure by the distinct mass spectrum at *m*/e=*215* which is consistent with its chemical formula as well as the molecular ion of MS spectrum for the new 2-pyrazoline ligand at 340 reveals the proper chemical formula of (L) with other peaks due to the cleavage of $-CH_3$ and thioamide groups, Figures 2A and B. The physical properties of the prepared complexes are presented in Tables 1 and 2. All the elemental analyses observed are in good agreement of their calculated values [17, 20]. The MS spectra of chalcone, A and MS spectrum of the 2-pyrazoline ligand were demonstrated in Figures 2A and B, respectively.

The molecular ions at 215, 225 for the intermediate chalcone investigates the suggested chemical structure and confirms the condensation of 3-acetylpyridine with the thiophene-2-carboxaldehyde in 10% KOH catalyst as well as the appearance of high intense peak at 289 for the MS spectrum of the 2-pyrazoline ligand is consistent with the molecular weight of the 2-pyrazoline derivative, L.



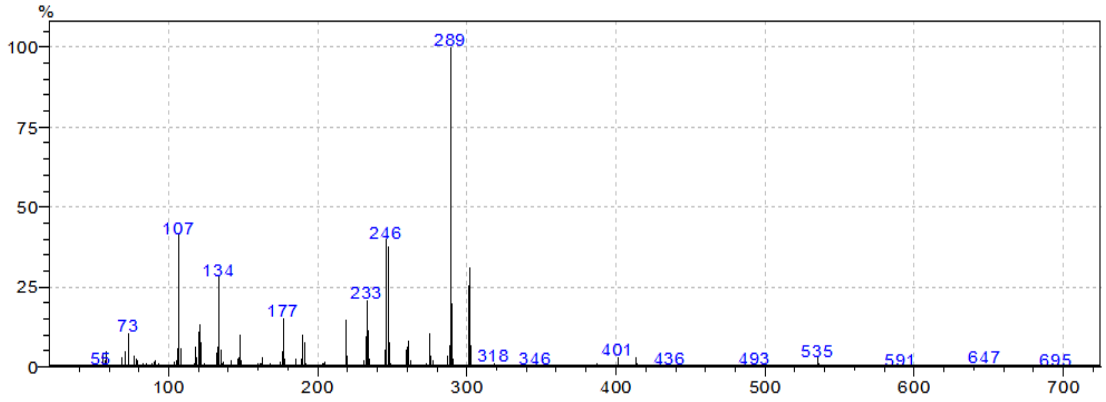


Figure 2. a) MS spectrum of chalcone, A; b) MS spectrum of ligand, L

Table 1. Symbols, molecular formulas and IUPAC-names of the prepared complexes

Symbol	Molecular formula	Name
A	$C_{12}H_9NOS$	(E)-1-(pyridin-3-yl)-3-(thiophen-2-yl)prop-2-en-1-one
L	$C_{13}H_{12}N4S_2$	3-(pyridin-3-yl)-5-(thiophen-2-yl)-4,5-dihydro-1H-pyrazole-1-carbothioamide
C1	$[Co(C_{13}H_{12}N4S_2)_2Cl_2]Cl$	[di chloro-bis-(3-(pyridin-3-yl)-5-(thiophen-2-yl)-4,5-dihydro-1H-pyrazole-1-carbothioamidediaquacobalt (III)] chloride
C2	$[Ni(C_{13}H_{12}N4S_2)_2]Cl_2.H_2O$	Bis-(3-(pyridin-3-yl)-5-(thiophen-2-yl)-4,5-dihydro-1H-pyrazole-1-carbothioamidenickel (II)]chloride mono hydrate
C3	$[Cu(C_{13}H_{12}N4S_2)_2Cl_2].2H_2O$	Dichloro-bis(3-(pyridin-3-yl)-5-(thiophen-2-yl)-4,5 dihydro-1H-pyrazole-1-carbothioamidediaquacopper (II)] di hydrate
C4	$[Zn(C_{13}H_{12}N4S_2)Cl_2]$	Dichloro-(3-(pyridin-3-yl)-5-(thiophen-2-yl)-4,5-dihydro-1H-pyrazole-1-carbothioamidezinc (II)]

Table 2. Physical properties and elemental analysis of the prepared metal complexes

Chemical Formula	Δ S.Cm²/mole	% Yield	M.P c⁰	Exact Mass	%Found %(Calculated) C	H	N	S	M
A	-	88	175-172	215.90	65.90 (66.95)	4.03 (4.21)	5.77 (6.52)	14.22 (14.89)	-
$C_{12}H_9NOS$									
L	-	72	160-163	288.40	53.99 (54.15)	4.00 (4.20)	19.15 (19.43)	21.95 (22.23)	-
$C_{13}H_{12}N4S_2$									
C1	50	83	286 Dec	704.90	65.80 (66.11)	5.01 (5.33)	13.22 (13.07)	5.72 (6.13)	6.15 (6.88)
C2	135	75	275 Dec	711.90	52.77 (53.53)	4.20 (4.79)	14.09 (13.83)	7.95 (8.44)	6.43 (7.09)
C3	42	90	278 Dec	746,55	52.45 (52.78)	4.67 (4.90)	13.09 (13.15)	6.12 (7.70)	7.43 (8.09)
C4	15	65	290 Dec	425.09	50.44 (51.22)	5.99 (6.99_	19.03 (18.11)	10.88 (11.32)	(13.66) 12.88

NMR spectra

The ^{1}H-NMR of ligand, L in DMSO-d_6 solvent displayed multiple and triplet peaks in the shielded region 3.81-3.91 ppm assigning to the adjacent CH^{x}-CH^{y} protons and germinal ^{x}H–C-H^{z} protons then it confirms the ring closure of chalcone with thiosemicarbazide reactants. The peak at 8.83 ppm as singlet is attributed to protons directed attached to NH_2-C=S functional group. Furthermore, the triplet and quartet peak at 3.80-3.92 ppm confirms the nuclear spin of ethoxy group –CH_2-CH_3 attached to C4 of aromatic ring [13, 15]. Likewise, the resonated protons of thiophene ring was showed at around 7.2-7,70 ppm region, Figure 3.

The ^{13}C-NMR spectrum of L exhibited de shielded peaks at low field frequencies 9205-199.6, 156.85-152.03 ppm concerning the nuclear spin of N1–C=S of thioamide, -C=N- (2-pyrazoline) and HC=C-N atoms, respectively [10, 23].The other peaks at 113-122.9, 123.1-128.7 and 132.9-148.32 ppm are assigned to CH=CH-C-S and Ar-CH=CH- carbon atoms of aromatic thiophene ring. However, the shielded chemical shifts located at around 14.41, 43.32, and 52.58 ppm revealed the CH_2-CH- in pyrazoline ring and also confirmed the presence of adjacent –CH-CH_2- moiety of 2-pyrazoline ring [18, 23].

FT-IR spectra

The IR spectrum of chalcone, A showed strong bands at around 1685, 1500-1480 cm^{-1} due to the stretching frequencies of H-CH=CH- conjugated with carbonyl group formed up on *Claisen-Schmidt* reaction [6, 14]. As well as the IR spectrum of the pyrazoline ligand shows disappearance of –C=O vibration due to the condensation with amino group of 4-lthiosemicarbazide starting material. The distinct absorptions at around 3387, 1588, and 1275-1089 cm^{-1} are strong evidence for the formation of pyrazoline ring and assigned to –C=N-, -NH-, and thioamide HN-C=S moieties, respectively, Figure 4 [15].

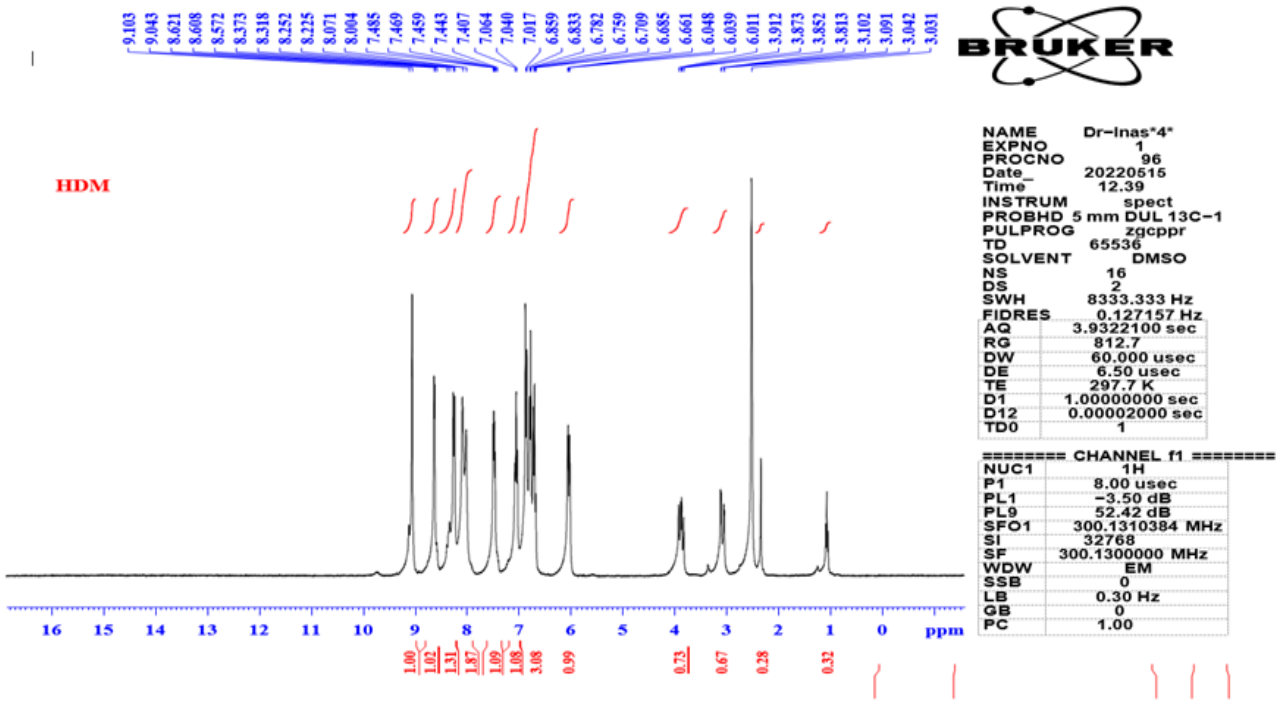


Figure 3. ^{1}H-NMR spectrum of L in DMSO-d_6

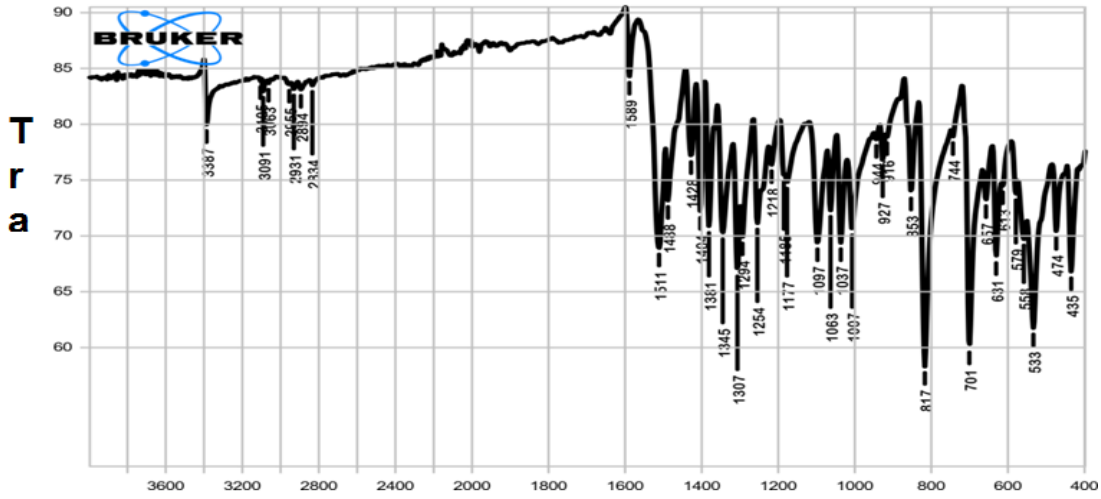


Figure 4. FT-IR spectrum of ligand

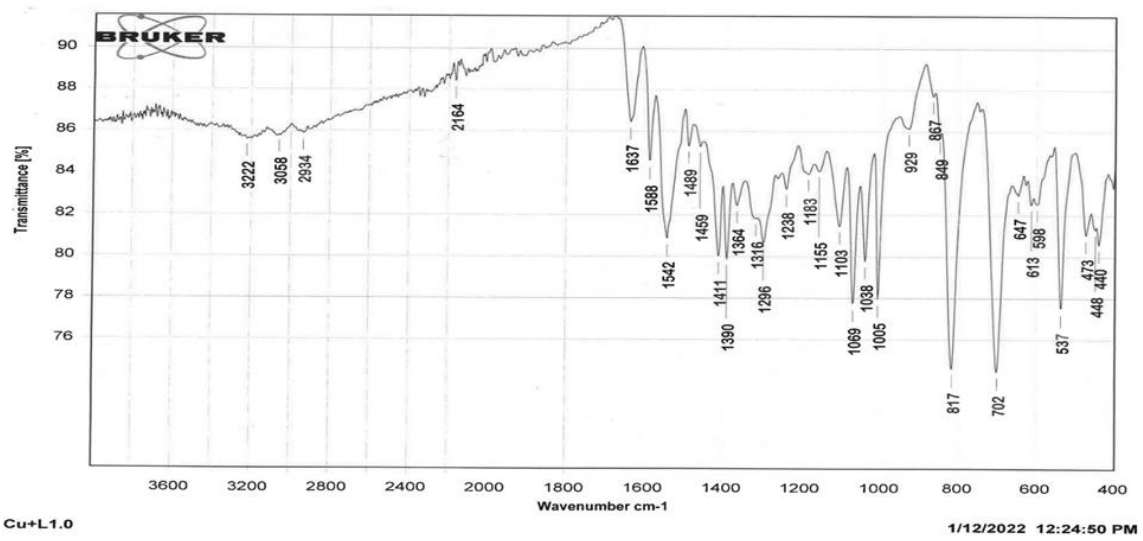


Figure 5. FT-IR spectrum of C3 complex at CsI disc

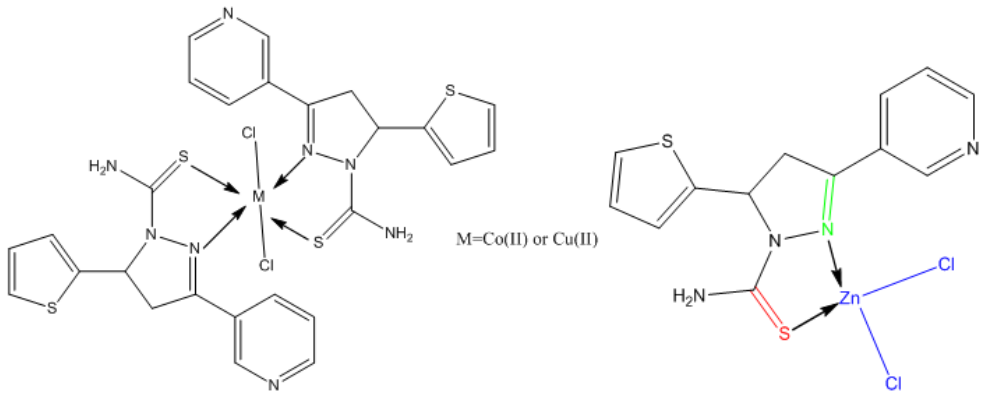


Figure 6. Octahedral and tetrahedral structures of the prepared complexes

Furthermore, the IR spectra of C1-C4 complexes exhibited lower frequencies in the vibrations of –C=N- of pyrazoline and pyridine-3-yl groups due to the participation of such functional groups in binding with the metal ions. Besides, the shift in the frequencies of thioamide to a region 1050-1010 cm^{-1} is consistent with the donation lone pairs from sulfur atom to the empty orbitals of metal ions. The weak bands at around 375-422 and 460-594 cm^{-1} in all IR spectra of complexes revealed the coordination bonds (M-S) and (M-N), respectively, Figure 5 [22, 23].

Conclusion

According to the recent review on the coordination chemistry of 2-pyrazoline ligands, the most favorable route for ring closure of thiosemicarbazide with chalcones is the Micheal mechanism due to the stability of hydrazine formation in the rate determining step and the main functional groups that have been contributing in the chelation are the nitrogen atoms of pyrazoline ring and terminal of pyridine and pyrrole rings. It is also observed from update literature that the %yield of ring closure of 2-pyrazoline rings have increased with the presence of thioamide –C=S groups attached directly to N1- of the derivatives. Furthermore, the experimental section of this article concluded the formation of new ligand,L in good yield with spectroscopic evidences from NMR, MS and FT-IR spectra. Moreover, the octahedral geometry of cobalt(II) and copper(II) complexes were confirmed on their basis of UV-Visible spectra, molar conductance measurements, and magnetic susceptibility. The diamagnetic properties of cobalt complex revealed the strong field of the tri dentate ligand and oxidation cobalt(II) to cobalt(III), Figure 6. Likewise, the diamagnetic properties of nickel(II) complex with low-spin state is consistent with its square-planner geometry.

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Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the article and agreed to be responsible for all the aspects of this work.

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