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RESEARCH ARTICLE

Synthesis and Characterization of a Cu(II) complex using a New Schiff base-Azo Reagent (HTYPIM)

Muntadhar Adnan Rahman[1*], Muneer A. Al-Da'amy[2]

[1] *Chemistry Department, College of Education for Pure Science, University of Kerbala, Kerbala, Iraq*

[2] *Chemistry Department, College of Science, University of Kerbala, Kerbala, Iraq*

***Corresponding author:** Muntadhar Adnan Rahman, montather.a@s.uokerbala.edu.iq

ABSTRACT

In this study a new organic Schiff base-azo ligand was prepared using two steps the condensation and diazotization reaction, this ligand used for reacting with the copper (II) ion to form a copper complex and determination small amounts of it, the prepared ligand and complex were characterized by UV-Vis, FT-IR, 1HNMR spectra, also measured Molar electrical conductivity for complex. Ion copper (II) was determined by a rapid, sensitive, simple and cheap spectrophotometric method, the copper compound has a molar absorbance of (3.193×105) L.mol-1.cm-1, a Sandel sensitivity of (1.989×10-4) µg.cm-2, and a maximum absorbance of (420) nm, with a limit of detection of (0.0083) µg.mL-1 and a limit of quantitation of (0.027) µg.mL-1, the metal concentration obeys Beer's law within the range (0.04-2) µg.mL-1 with a correlation coefficient value of 0.9994 indicating the degree of linearity of the standard calibration for copper. In the complex, the molar ratio of the metal to the ligand was [1:2], the results indicate that the complex has a high stability constant of)1.8645×108 (mol.L-1, and these results showed that this method was more sensitive, more precise and accurate through the calculation of (Re, Erel, R.S.D) %.

Keywords: Schiff bsae; Azo methene; Cu (II); 2-Aminothiazole

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1. Introduction

Copper (Cu), a transition element located in group 11 of the periodic table with atomic number 29, is a fundamental pillar upon which human civilization and modern scientific advancements have been built, distinguished by its reddish-orange hue and exceptional ductility and malleability, copper's discovery marked a historical turning point that paved the way for the (Bronze Age) in the context of contemporary science, copper transcends its traditional role as an industrial metal to become a focal point of research in inorganic and medicinal chemistry, owing to its superior ability to form coordination complexes with unique properties [1,2], geologically, copper is classified as an element of moderate abundance in the Earth's crust, with an average concentration ranging between 60 and 68 parts per million (ppm) [3], although it can exist in nature in its free elemental state (Native Copper), its primary industrial sources are concentrated in mineral ores, these are predominantly categorized into sulphide Ores, such as Chalcopyrite ($CuFeS_2$) and Chalcocite (Cu_2S), which represent the most significant global sources, and Oxide Ores, such as Malachite and Azurite, found in superficial layers [4], these ores require precise metallurgical extraction techniques to produce high purity copper suitable for delicate applications [5,6], Copper applications are diverse, covering a wide spectrum of strategic sectors, Industrially the majority of global copper production is consumed by the electrical and electronic industries, as copper serves as the standard benchmark for electrical conductivity after silver, making it the backbone of power transmission grids and motors [7], furthermore, it plays a pivotal role in the renewable energy sector, where electric vehicles and wind turbines require significantly higher quantities of copper compared to traditional technologies, granting it critical future importance in the Green Economy [8], On the chemical and biological front, copper and its alloys (such as brass and bronze) are utilized not only for their mechanical properties and corrosion resistance but also for their (Contact Killing) phenomenon, Copper surfaces have a self-ability to eliminate bacteria and viruses, which has encouraged their use in healthcare facilities to reduce hospital-acquired infections[9], at the molecular level, copper possesses a rich coordination chemistry attributed to its electronic configuration $^{[Ar]18}3d^{10}4s^{1}$, the divalent oxidation state Cu(II) emerges as the most stable and prevalent form, the Copper (II) ion exhibits a strong tendency to form geometrically distorted complexes typically elongated octahedral or square planar due to the Jahn-Teller effect, which endows these compounds with dynamic stability and distinct spectral characteristics [10,11], modern research relies heavily on reacting copper with various Organic Ligands, most notably Schiff Bases, these ligands function as polydentate chelating agents (often containing donor atoms such as N and O) to form stable rings around the metal center, thereby enhancing the complex's stability via the "Chelate Effect" [12], this field has further evolved to include the synthesis of Mixed-Ligand Complexes, a strategy aimed at fine-tuning the physical properties of the complex, such as increasing its lipophilicity, this modification facilitates permeability through cell membranes, opening new horizons for utilizing these complexes as antioxidants, antimicrobial agents, and promising therapeutic candidates for cancer treatment [13, 14].

Aims of the Study are synthesis of a new Schiff base-azo reagent via reflux and conventional diazotization methods, followed by its characterization using (FT-IR, UV-Vis, ^{1}H-NMR) spectroscopy to investigate its chelating behavior and coordination sites as well as the measurement of its melting point, the research aims to utilize this reagent for the spectrophotometric determination of trace heavy transition metals, specifically conducting a method validation for Cu(II) ion, this involves optimizing reaction conditions such as (effect of pH, reagent concentration, temperature, effect of Time, and effect of the order of addition), and concentration Range Obeying Beer's Law, as well as determination of the Metal-to-Ligand ratio (stoichiometry) of the complexes using the Mole Ratio and Continuous Variation (Job's) methods and stability constants, Additionally to calculating the stability constants and determining the thermodynamic Functions ($\Delta G°$, $\Delta H°$, $\Delta S°$) of the solid complexes At various temperatures, Furthermore the study encompasses the synthesis of solid metal complexes and their characterization through analytical spectra which was used in the characterization of the ligand, and conducting measurements for it including (molar conductivity, magnetic Sensitivity, melting point, solubility), and then the geometrical structure of the copper complex is proposed.

2. Methodology

2.1. Materials:

All solvents and chemical Reagents used in this study have high purity and are supplied by C.D.H, Thomas baker, Himedia and Merck (Sigma Aldrich) companies without any additional purification processes (ethanol absolute, glacial acetic acid, P-aminophenol, Salicylaldehyde, sodium nitrite, hydrochloric acid, sodium hydroxide, 2-Aminothiazole, and Copper(II) chloride dihydrate).

2.2. Instrumentation

All techniques that were used in the characteristic study of the new synthesized ligand and its complexes were aUv-Vis spectrophotometer, (Jenway 7315, England), FT-IR spectrophotometer, (Shimadzu IRPrestige

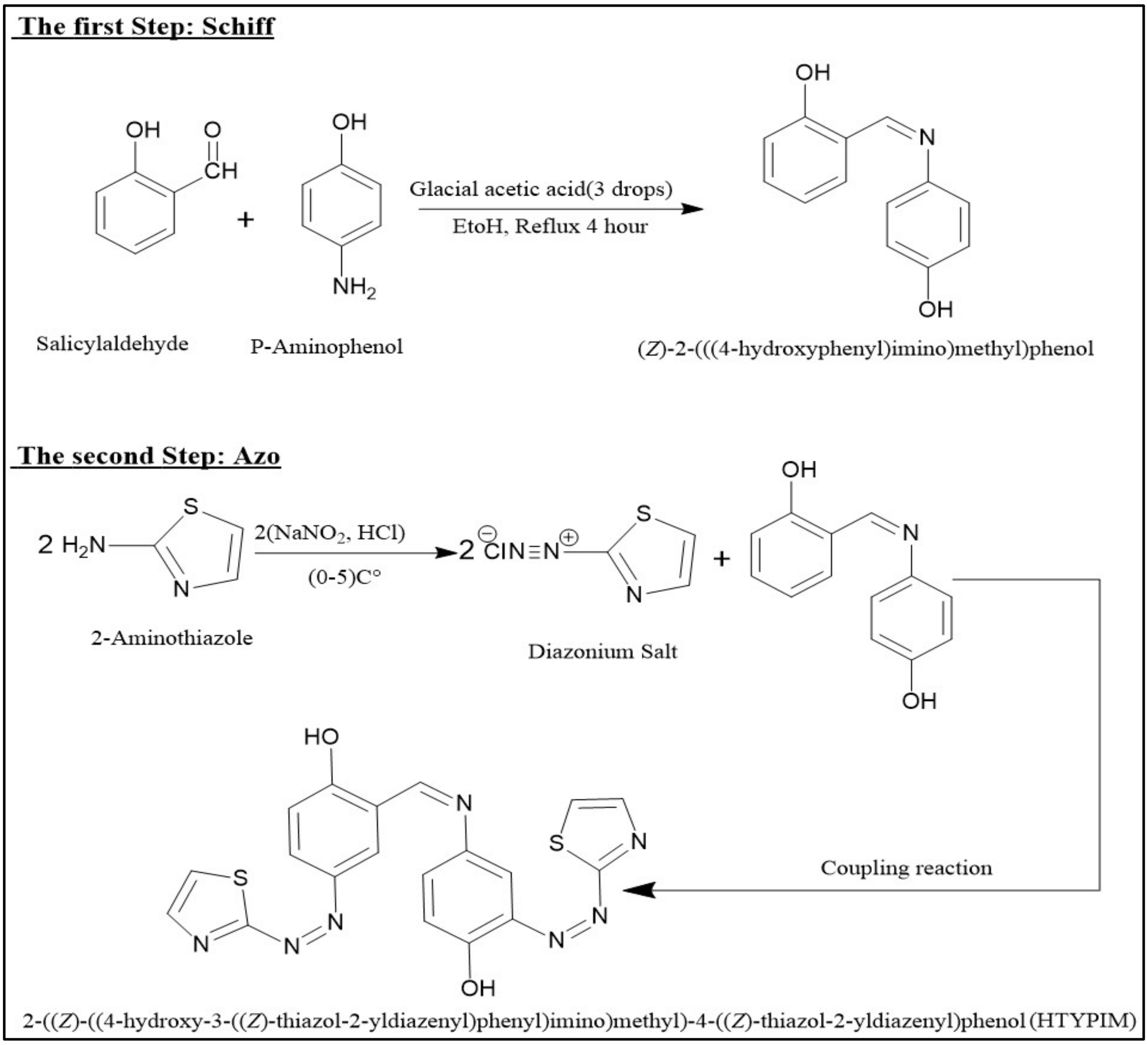
21, Japan), PH-meter, (inolab WTW 530, Germany), Digital Conductivity meter, (inolab WTW 7310, Germany), Melting point instrument SMP 30, (Stuart, England), Balance BL 2105 (Sartorius, Germany), ^{1}H-NMR Spectrophotometer, (Bruker 400 MHZ, Germany).

2.3. Experiments:

2.3.1. Synthesis of the Ligand

In the first step(Schiff), a(0.02 mol, 2.18 g)of p-aminophenol was dissolved in (5) mL of absolute ethanol was mixed with a(0.02 mol, 2.44 g) of salicylaldehyde was dissolved in (5) mL of absolute ethanol, the reaction mixture was placed in a reflux flask, and three drops of glacial acetic acid were added as a catalyst, the mixture was refluxed for (3-4) hours at (70-80) °C, The progress of the reaction was monitored using Thin Layer Chromatography (TLC), Upon completion of the reflux, the reaction mixture was cooled to room temperature and placed in an ice bath for 30 minutes, A yellow crystalline precipitate was observed was filtered off and allowed to air-dry, it was subsequently recrystallized from absolute ethanol and washed with hexane to remove unreacted starting materials, finally the product was dried in an oven at (45) °C for 30 minutes, the solid was ground, weighed, and stored in an amber bottle, the yield was (95.08%)[15].

In the second step (Azo), a(0.02 mol, 2.00 g) of 2-aminothiazole was dissolved in a mixture consisting of (10 mL of HCl [2 M] and 20 mL of distilled water), The solution was placed in an ice bath at (0–5) °C for 10 minutes. Subsequently, (0.022 mol, 1.51 g) of sodium nitrite dissolved in (7.5) mL of distilled water was added dropwise, gradually, with continuous stirring and cooling for 30 minutes to complete the formation of the diazonium salt, Subsequently, (0.001 mol, 0.06 g) of urea was added to the mixture to eliminate excess nitrous acid and left for 10 minutes, the diazonium salt solution was then gradually added to the pre-prepared Schiff base solution, which had been left for 30 minutes. The Schiff base solution was prepared by dissolving (0.01 mol, 2.13 g) of the base in a mixture of 10 mL of absolute ethanol and (0.025 mol, 1 g) of sodium hydroxide dissolved in 10 mL of distilled water, under continuous stirring and cooling at (0–5) °C. The reaction mixture turned dark brown at pH = 9.5 and was left for 15 minutes to complete the formation of the Schiff–azo ligand, the pH was then adjusted to 7.15 by adding diluted hydrochloric acid, A reddish-brown precipitate was formed, the mixture was left for 15 minutes to allow precipitation, followed by filtration and repeated washing with cold distilled water. The product was air-dried, recrystallized from absolute ethanol, and dried in an oven at 45 °C for 30 minutes. Finally, the solid was ground, weighed, and stored in a dark container, the yield was (75.27%), the melting point was measured to be approximately (121–123C°), As illustrated in the (scheme1)[16].



Scheme 1. The steps to synthesis of ligand

2.3.2. Preparation of Standard Solutions:

A ligand solution with a concentration of (1×10^{-4}M) was prepared by dissolving (0.0043 g) of the ligand in absolute ethanol and was placed in a (100) mL volumetric flask, the copper (II) ion solution was prepared at a concentration of (1×10^{-4}M) by dissolving (0.0017g) of copper(II) chloride dihydrate in deionized water and was placed in a (100) mL volumetric flask, the buffer solution was prepared at a concentration of (0.01 M) by dissolving (0.77 g) of ammonium acetate in deionized water and was placed in a (1000) mL volumetric flask, from this solution several (100mL) volumetric flasks were prepared covering the pH range (4–11) by adding drops of diluted ammonium hydroxide or diluted acetic acid.

3. Results and Discussion:

3.1. Study of ultraviolet –visible spectra for ligand and copper(II) complex

Ligand and Cu(II) complex solutions were prepared at a concentration of (1×10^{-5}M) and placed in two 10 mL volumetric flasks and using absolute ethanol as the Blank solution, a spectroscopic survey of the ligand and the Cu^{2+} complex was conducted in the ultraviolet-visible region of the spectrum and within the range (200-700) nm, in the electronic spectrum of the ligand showed three bands at (λ = 233) nm, (λ = 272) nm and (λ = 350) nm, while in the Cu(II) complex spectrum showed three absorption bands at (λ = 221) nm,

(λ = 252) nm identified for charge transition (C.T.) and (λ_{max} = 420) nm due to (d-d) transition, as show in (Figure 1, 2) [17].

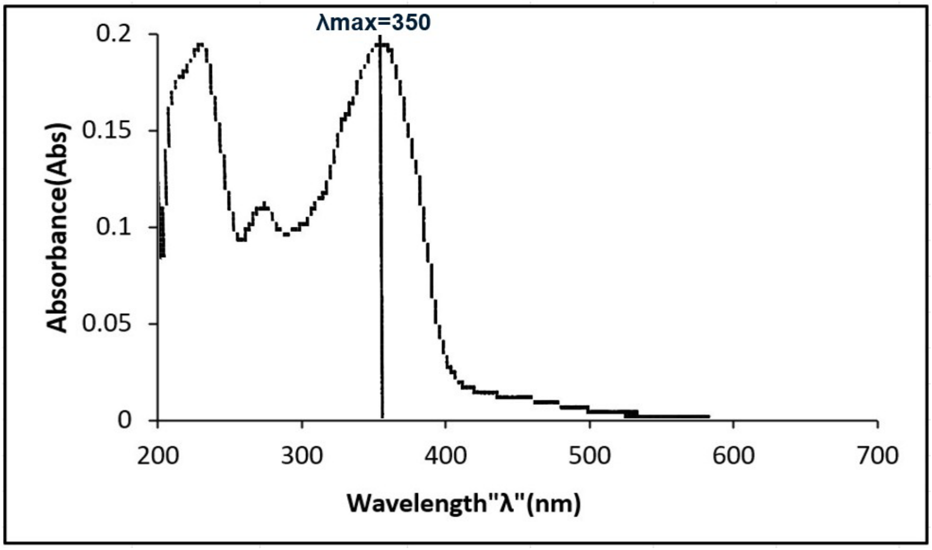


Figure 1. Ultraviolet-visible spectrum of Ligand

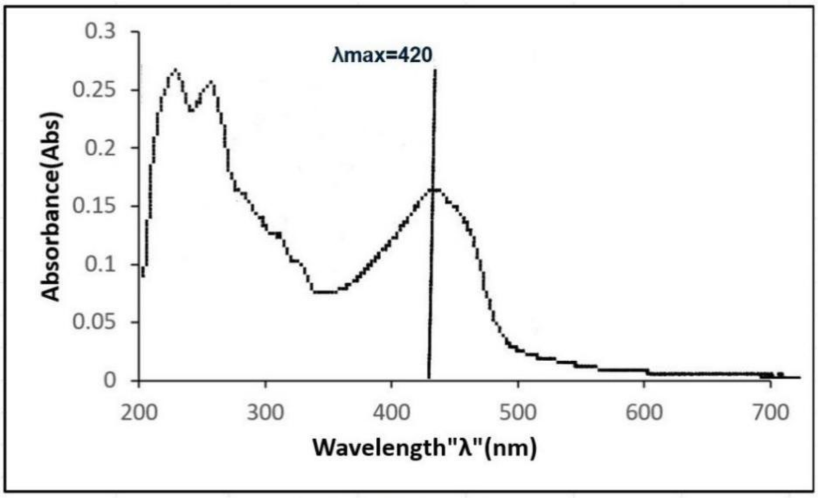


Figure 2. Ultraviolet-visible spectrum of Cu (II) complex

3.2. Study FT-IR spectra for ligand and copper complex

The FT-IR spectrum of the prepared new ligand and Cu (II) complex respectively shows a broad band belonging to (νO-H) at (3410, 3356) cm^{-1} due to hydrogen bonding, a band at (1618, 1616) cm^{-1} belonging to (νC=N), a band at (1508, 1502) cm^{-1} belonging to (νN=N),a band at (1280,1261) cm^{-1} belonging to (νC-O), a band at (559) cm^{-1} belonging to (νM-O), a band at (474) cm^{-1} belonging to (νM-N), The band values reveal a shift toward lower frequency and the appearance of new bands, absent in the ligand spectrum, indicating the occurrence of coordination, as show in (Figure 3) and (Figure 4) [18].

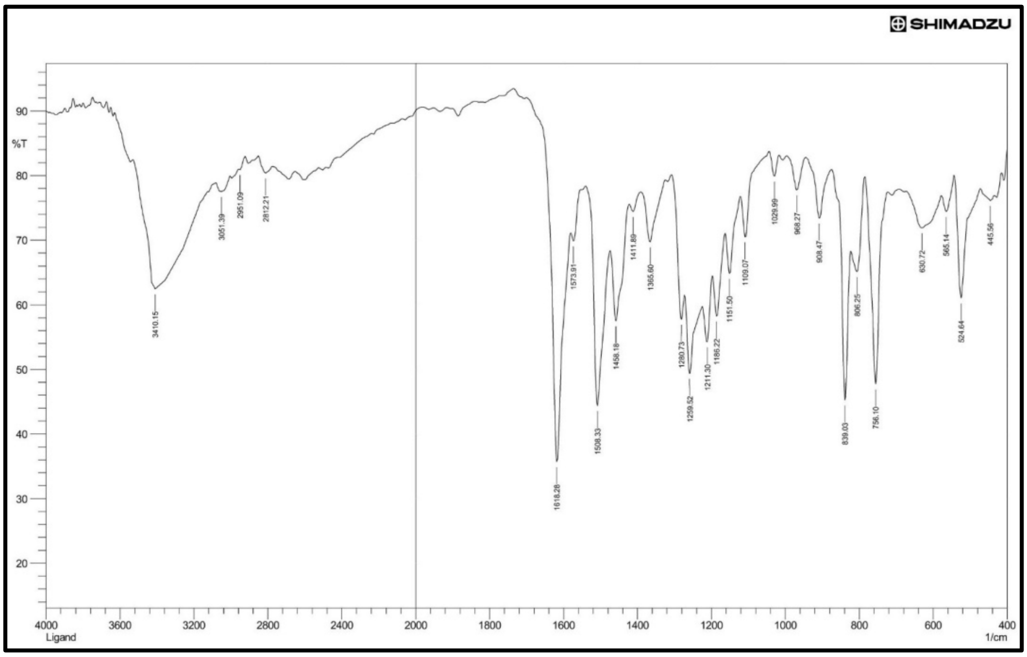


Figure 3. FT-IR spectrum of ligand

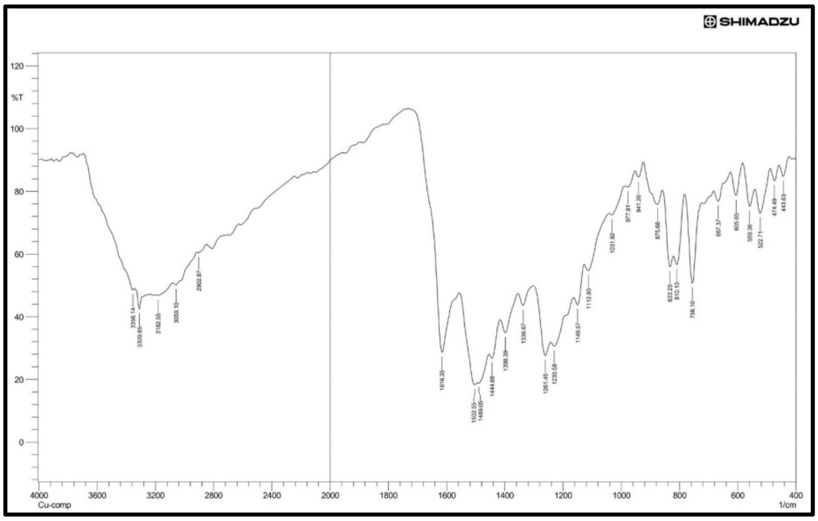
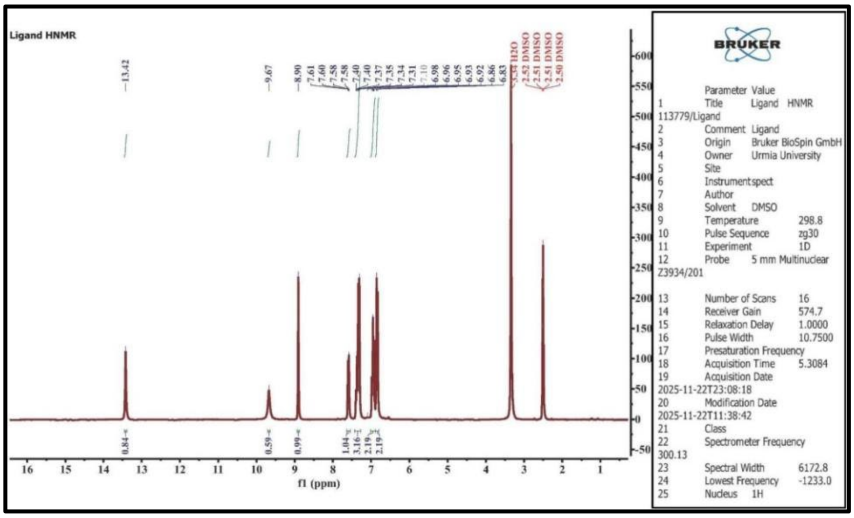


Figure 4. FT-IR spectrum of Cu (II) complex

3.3. HNMR spectrum for ligand and copper complex

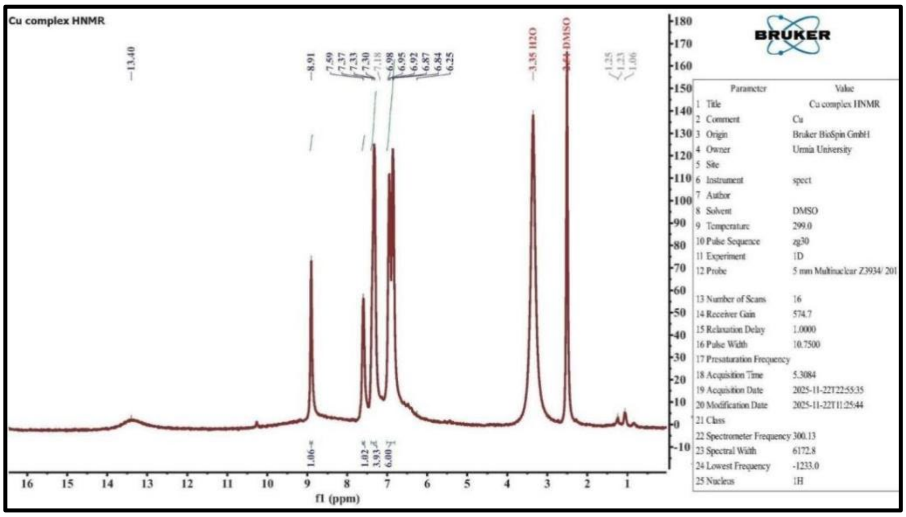
From the signals appearing in the spectrum 1HNMR for ligand and Cu(II) complex respectively, the singlet signal at (δ = 13.42,13.40 ppm, 1H) refers to the proton of the Phenolic (OH) group adjacent to the azomethine group (-CH=N-), Another singlet signal was observed, corresponding to the proton of the second phenolic OH group adjacent to the azo (-N=N-) at (9.67 ppm, 1H) the absence of the signal in the copper complex is likely due to the fact that the acidic protons (OH) within the complex are often affected by rapid exchange with the solvent or by strong exposure, which causes them to merge into the baseline, the signal may have shifted to overlap with the aromatic region, while the singlet signal of the azomethine proton (CH=N) appears at (8.90, 8.91 ppm, 1H) this signal is highly characteristic of Schiff bases and its presence provides strong evidence for the formation of the bond and the chemical shift of the signal confirms the occurrence of coordination, whereas multiple signals appeared within the range of (6.83–7.61 ppm) and (6.25-7.59 ppm), corresponding to the protons of the aromatic rings (benzene and thiazole), with a total of

(10H), the signal at (3.34,3.35ppm) indicates the presence of moisture H_2O and the signal at (2.50-2.52 ppm) and (2.51 ppm) indicates the solvent DMSO-d^6, as illustrated in (Figure 5, 6) [19].



	Parameter	Value
1	Title	Ligand HNMR 113779/Ligand
2	Comment	Ligand
3	Origin	Bruker BioSpin GmbH
4	Owner	Urmia University
5	Site	
6	Instrument	spect
7	Author	
8	Solvent	DMSO
9	Temperature	298.8
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	5 mm Multinuclear Z3934/201
13	Number of Scans	16
14	Receiver Gain	574.7
15	Relaxation Delay	1.0000
16	Pulse Width	10.7500
17	Presaturation Frequency	
18	Acquisition Time	5.3084
19	Acquisition Date	2025-11-22T23:08:18
20	Modification Date	2025-11-22T11:38:42
21	Class	
22	Spectrometer Frequency	300.13
23	Spectral Width	6172.8
24	Lowest Frequency	-1233.0
25	Nucleus	1H

Figure 5. 1HNMR spectrum for ligand



	Parameter	Value
1	Title	Cu complex HNMR
2	Comment	Cu
3	Origin	Bruker BioSpin GmbH
4	Owner	Urmia University
5	Site	
6	Instrument	spect
7	Author	
8	Solvent	DMSO
9	Temperature	299.0
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	5 mm Multinuclear Z3934/ 201
13	Number of Scans	16
14	Receiver Gain	574.7
15	Relaxation Delay	1.0000
16	Pulse Width	10.7500
17	Presaturation Frequency	
18	Acquisition Time	5.3084
19	Acquisition Date	2025-11-22T22:55:35
20	Modification Date	2025-11-22T11:25:44
21	Class	
22	Spectrometer Frequency	300.13
23	Spectral Width	6172.8
24	Lowest Frequency	-1233.0
25	Nucleus	1H

Figure 6. 1HNMR spectrum for Cu (II) complex

3.4. Study the optimum condition for the copper(II) complex

3.4.1. pH effect

A wide range of buffer solutions were chosen, ranging from pH (4-11) by measuring the absorption at the maximum wavelength of the copper(II) complex and at the concentration ($1x10^{-5}$M), in (Figure 7) it was shown that the absorption increased at pH = 9 [20].

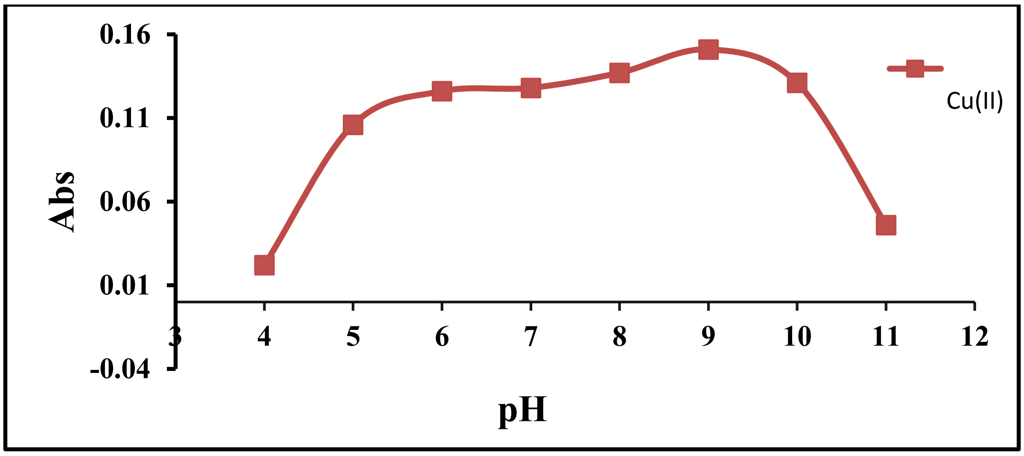


Figure 7. Effect of pH value in Cu(II) complex

3.4.2. Effect of ligand concentration

A set of volumetric flasks (10 mL capacity) was prepared, each containing (1) mL of copper ion solution at a concentration of (1×10^{-4}M) was added then different volumes of the ligand solution with a concentration (0.5×10^{-4}-5×10^{-4}M), and the volume was completed with the buffer solution at pH=9 to obtain a wide range of concentrations ($0.5\times10\text{-}5^{-5}\times10^{-5}$M), then The absorbance of all solutions was measured at (λ_{max}= 420nm) against the reagent and ethanol as blank solution, where it was found that the best concentration of the ligand It is (4×10^{-5}M), as illustrated in (Figure 8) [21].

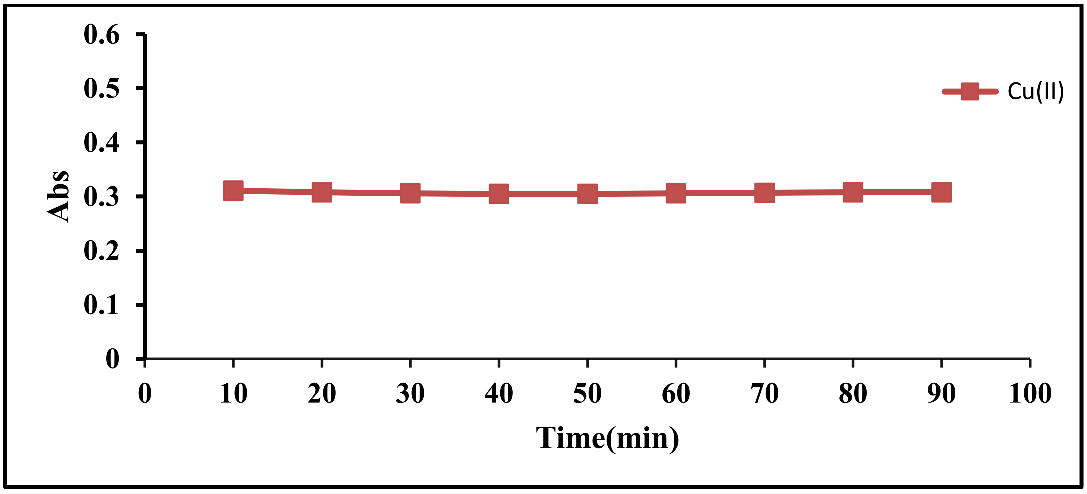


Figure 8. Effect of ligand concentration on Cu (II) complex

3.4.3. Time's impact on stability of copper (II) complex

A set of volumetric flasks (10 mL capacity) was prepared, each containing (1 mL) of copper ion solution at a concentration of (1×10^{-4}M), Subsequently (1 mL) of the optimal ligand concentration (4×10^{-4}M) was added to each flask, and the volume was completed with the optimal buffer solution at pH 9, The absorbance of all solutions was measured at (λ_{max} = 420 nm) against the reagent and ethanol as blank solution, at different time intervals ranging from (10-90) min, It is observed from the (figure 9) that the absorbance remains constant, which demonstrates that the prepared copper complex exhibits high stability and persistence [22].

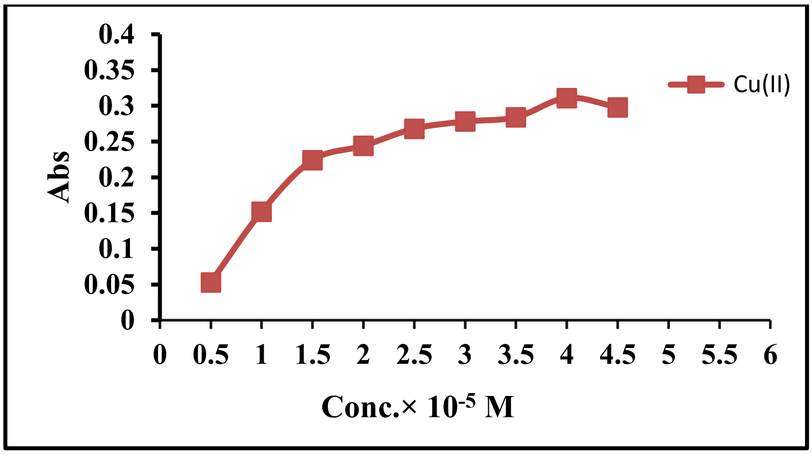


Figure 9. Time's impact on stability of Cu (II) complex

3.4.4. Effect of temperature in stability of copper(II) complex

A set of volumetric flasks (10 mL capacity) was prepared, each containing (1 mL) of copper ion solution at a concentration of (1×10^{-4}M), Subsequently (1 mL) of the optimal ligand concentration (4×10^{-4}M) was added to each flask, and the volume was completed with the optimal buffer solution at pH=9, The solutions were placed in a water bath with a temperature range of (10–70) °C, The absorbance of all solutions was measured at (λ_{max} = 420nm) against the reagent and ethanol as blank solution, The absorbance values of the complex reach their peak and give the best color intensity at the temperature between (10-25) °C and then the absorbance of the complex decreases with increasing temperature, This is due to dissociation of the complex at high temperatures, as shown in (Figure 10) [23].

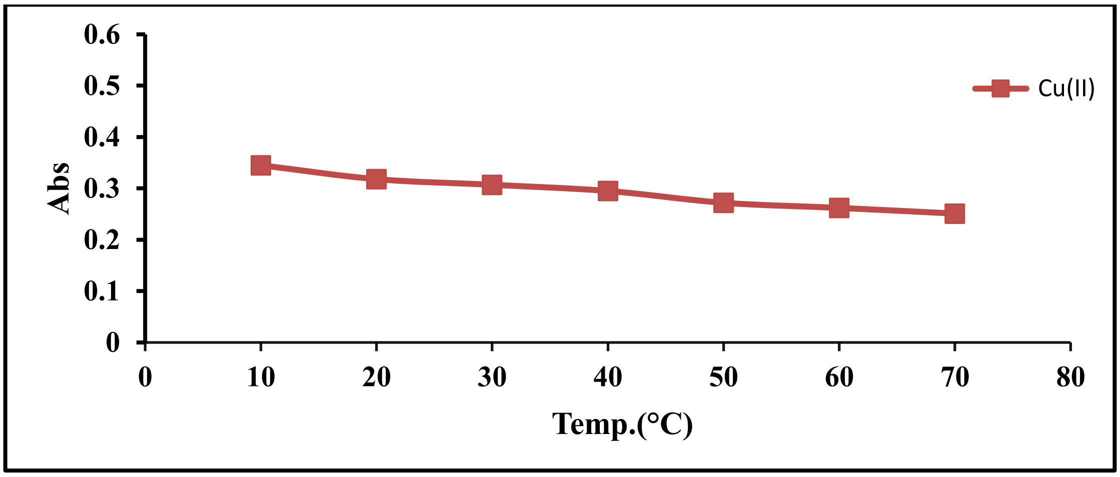


Figure 10. Effect of temperature in stability of Cu(II) complex

3.4.5. Study effect of order of addition for copper(II) complex

The complex solution was prepared in the same manner as in the above studies, but with a different order of addition, The purpose of this study is to determine the best addition order to form the copper complex under optimal conditions, The first case as shown in the (Table 1) was chosen as the best addition because it gives the highest absorption [24].

Table 1. Effect of the Cu (II) complex composition's order of addition

Sequence of addition number	Sequence of addition	Abs. of Cu(II) complex
1	M+R+pH	0.311
2	R+M+pH	0.298

3	M+pH+R	0.385
4	pH+M+R	0.281

Where M = Cu (II), R = Reagent, pH = Buffer solution.

3.5. Study of explanation of the calibration curve for copper(II) complex

A set of volumetric flasks (10 mL capacity) was prepared, each containing 1 mL of the copper(II) solution at different concentrations ranging from $(1\times10^{-7}$-$1\times10^{-4} M)$ This corresponds to (0.0063–6.354) µg.mL^{-1} of copper ion, *Subsequently, 1 mL of the optimal concentration of reagent* $(4\times10^{-4} M)$ *was added to each flask, and the volume was completed with the optimal buffer solution for the copper complex at pH = 9, the absorbance of all solutions was then measured at* λ_{max}*= 420 nm against the reagent and ethanol as blank solution,* the concentrations that obey the Beer-Lambert law were determined for the copper complex by drawing a calibration curve, many concentrations were excluded due to their deviation from the Beer- Lambert law and the appearance of absorption peaks outside the measurement limits, Therefore the concentrations that obey the Beer-Lambert law are (0.04-2) µg.mL^{-1}, as shown in (Figure 11), and (Table 2) shows some characteristics of the calibration curve for the copper which was extracted using this equations [25]:

$$A = \varepsilon bc \qquad \text{Eqn. 1}$$

$$S = \frac{At.wt}{\varepsilon} \qquad \text{Eqn. 2}$$

$$L.O.D = \frac{3\times S.D.}{SLOP} \qquad \text{Eqn. 3}$$

$$L.O.Q = \frac{10\times S.D}{SLOP} \qquad \text{Eqn. 4}$$

Where ε = Molar absorptivity, A= Absorbance, b= Path length cell (1cm), C= Molar concentration, S = Sandell's sensitivity, At.wt = Atomic weight, L.O.D = limit of detection, L.O.Q = limit of quantification

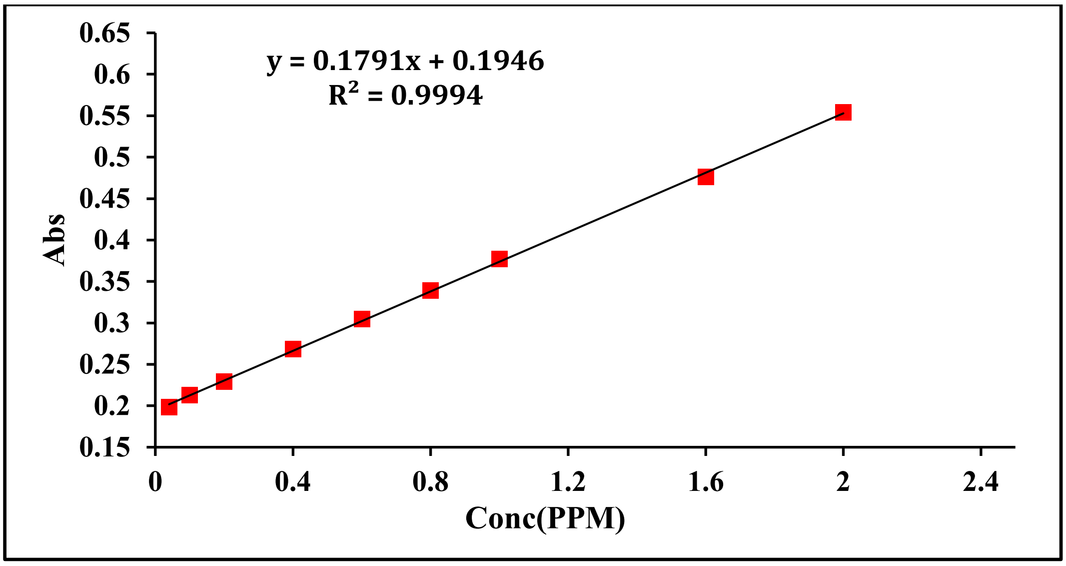


Figure 11. Calibration curve for Cu(II) complex

Table 2. Some properties of the calibration curve for Cu(II) complex

Conc. obey the Beer-Lambert law (µg/mL)	Straight-line equation	slope	ε (L/mol.cm)	S (µg.cm^{-2})	R^2	L.O.D (µg/mL)	L.O.Q (µg/mL)
(0.04 – 2)	y=0.1791x+ 0.1946	0.1791	3.193×10^{5}	1.989×10^{-4}	0.9994	0.0083	0.027

3.6. Study the stoichiometry composition of copper(II) complex

Two methods were used to appoint the ratio of metal to ligand, the molar ratio method and the continuous variation method:

In molar ratio method, a set of 10 mL volumetric bottles, several solutions were prepared containing a fixed concentration of copper(II) solution with a variable concentration of ligand solution (0.5-4) mL, and complete the volume with the best pH=9 value, and then the absorbance was measured at the maximum wavelength, the results of the study showed that the ratio is [1:2] (metal:ligand), In continuous variation method, different volumes of the metal ion solution (0.5-4) mL were mixed with different volumes of the ligand (4-0.5) mL solution, and the results gave that the ratio between (metal: ligand) is [1:2] also, as shown in (Figure 12, 13) [26].

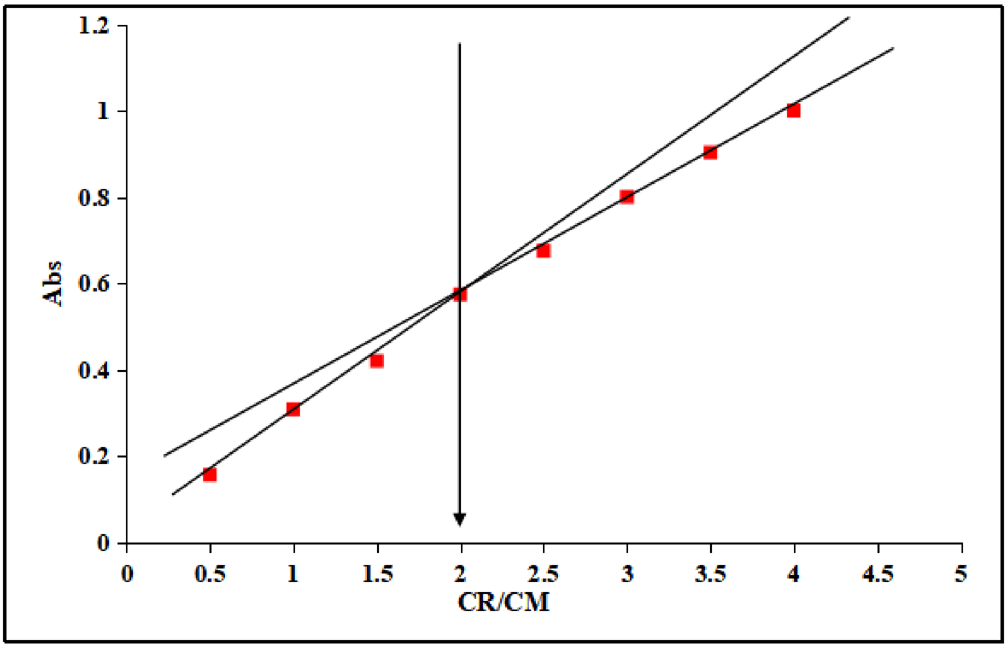


Figure 12. Stoichiometry composition of molar ratio method of Cu(II) complex

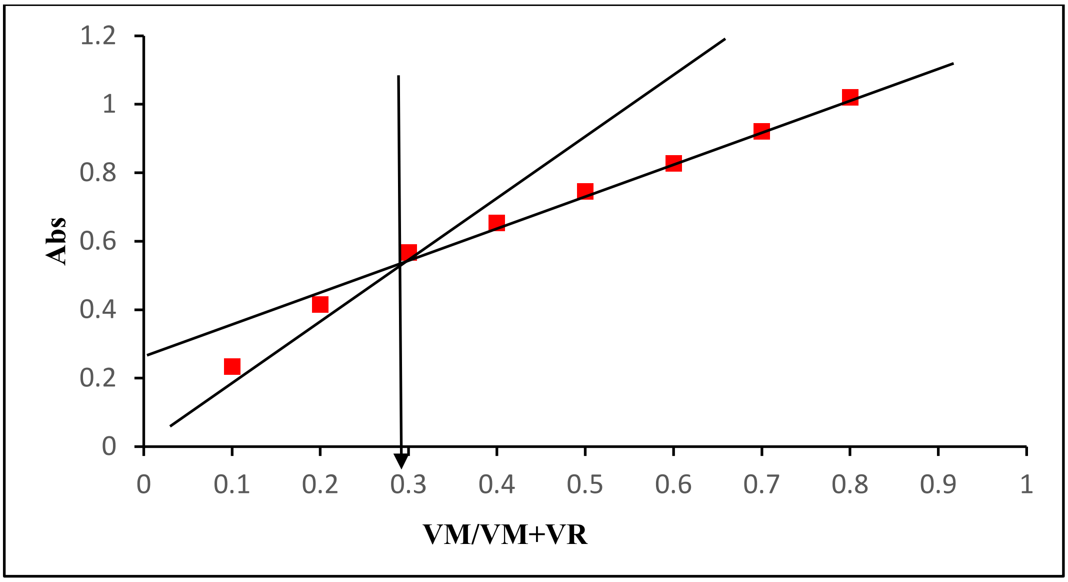


Figure 13. Stoichiometry composition of continuous variation method of Cu(II) complex

3.6.1. Calculation of the stabilization constant for complex

The stability of the copper(II) complex with the ligand was studied by calculating the degree of dissociation and the stability constant based on the absorption values obtained As shown in the (Table 3), From the results, it is clear that the complex have a high degree of stability, which enhances the possibility of using the detector in the spectral estimation of these elements, Which was extracted using the following equations [27]:

$$M^{+2}+2L \leftrightharpoons ML_2 \qquad \text{Eqn. 5}$$

$$\alpha c \quad 2\alpha c \qquad (1-\alpha)c \qquad \text{Eqn. 6}$$

$$K_{st}=\frac{(1-\alpha)c}{(\alpha c)(2\alpha c)^2} \qquad \text{Eqn. 7}$$

$$K_{st}=\frac{(1-\alpha)}{4(\alpha^3\, c^2\,)} \qquad \text{Eqn. 8}$$

$$K_{inst}=\frac{1}{kst.} \qquad \text{Eqn. 9}$$

$$\alpha=\frac{Am-AS}{Am} \qquad \text{Eqn. 10}$$

Where M= Metal ion, L= Ligand, α= Degree of Dissociation, C= Molar concentration of the complex, Kst. = Stability constant, kinst.= Instability constant, Am= The absorption of the complex is at its maximum value, As= Absorption of the complex at the equivalence point.

Table 3. Shows the absorption values (Am) and (As) of the copper complex, as well as the values of (α), (Kst.) and (Kinst.)

The controlling metal ion	**As Value**	**Am Value**	**α**	**Kst mol.L^{-1}**	**Kinst L.mol^{-1}**	**Log Kst**
Cu (II)	0.575	1.001	0.4255	1.8645×10^{8}	5.3633×10^{-9}	8.2705

3.6.2. Studying the effect of thermodynamic functions (ΔG^0, ΔH^0, ΔS^0) on the formation of the copper(II) complex

This study aims to know the effect of temperature on the thermodynamic functions of the copper(II) complex, which were calculated as shown in the (Table 4) and (Figure 14), it is clear from the results in (Figure 14) for the copper(II) complex that a negative enthalpy value (ΔH^0) indicates that the reaction is exothermic, and this is due to the strong bonding between the metal ion and the ligand to form the complex, and that negative (ΔG^0) values indicate the Spontaneity interaction of the reaction, As it is known, a positive value of entropy(ΔS^0) is a measure of randomness, so a negative value of entropy indicates a decrease in randomness and was extracted using this equations [28]:

$$\Delta G^\circ = -2.303\, R\, T\, logKst$$

$$\text{Slope} = \frac{-\Delta H^\circ}{2.303R}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Where ΔG^0= The change in Gibbs free energy, R= gases constant(8.314 J.mol^{-1}.k^{-1}), ΔH^0= The change in enthalpy, ΔS^0= The change in entropy, T= temperature in kelven.

Table 4. Temperature's effect on thermodynamic performance for Cu(II) complex

Metal ion complex	T(K)	1/T×10^3 (k^{-1})	Log K$_{st}$	-ΔG° (KJ/mole)	-ΔH° (KJ/mole)	ΔS° (KJ/mole.k)
Cu(II)	288	3.47	8.3230	45.8961	0.00343	0.1593
	298	3.35	8.2699	47.1868		0.1583
	308	3.24	8.2185	48.4671		0.1573

318	3.14	8.1693	49.7411		0.1564
328	3.04	8.1222	51.0095		0.1555
338	2.95	8.0741	52.2534		0.1546

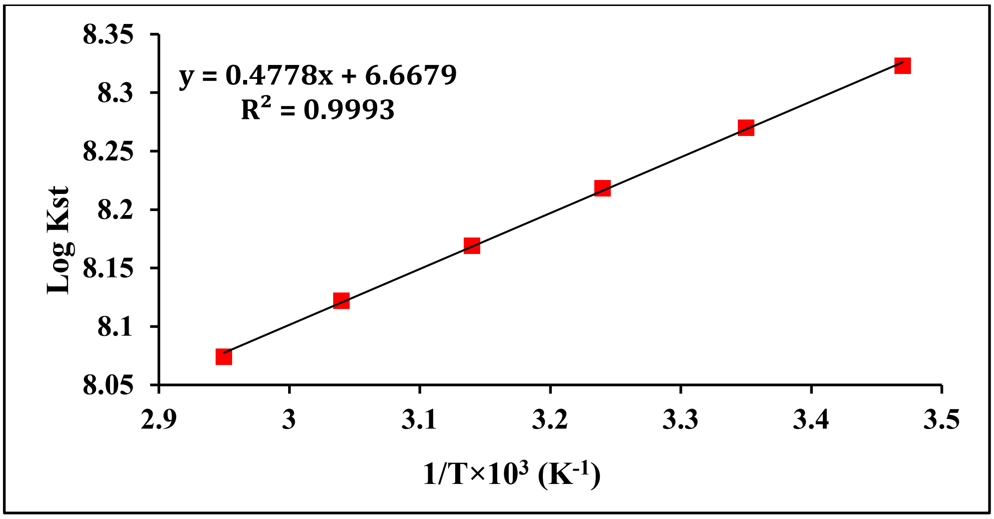


Figure 14. The relationship between (Log Kst) and (1/T) for the Cu(II) complex

3.7. Statistical processing of results

3.7.1. Precision

done Calculation the values of the standard deviation (S.D) and the relative standard deviation (RSD%) for the copper(II) complex under ideal conditions to ensure the accuracy of the analytical method by using the following equations, and they are displayed in (Table 5) [29]:

$$X' = \sqrt{\frac{\sum xi}{N}} \qquad \text{Eqn. 13}$$

$$S.D = \sqrt{\frac{\sum (xi - x')^2}{N-1}} \qquad \text{Eqn. 14}$$

$$RSD\% = \frac{S.D}{X} \times 100\% \qquad \text{Eqn. 15}$$

Where: xi = Reading for every absorption, x' = mean, N = Number of readings

Table 5. Values for standard deviation and relative standard deviation

Metal ion complex	Conc. of ion(ppm)	S.D	R.S.D%
Cu (II)	0.04	0.0005	0.2520
	0.6	0.0013	0.4245
	2	0.0016	0.2492

3.7.2. Accuracy

The accuracy of the analytical method for the copper(II) complex was determined by calculating the absolute error (d), relative error (Er%), and recovery percentage (Re%) for the copper(II) complex using the absorbance readings of the calibration curve under ideal conditions. The method proved to be sensitive and accurate and they are displayed in (Table 6) [30]:

$$d = Experimental\ value - True\ value \qquad \text{Eqn. 16}$$

$$E_{rel}\,\% = \frac{d}{\mu} \times 100\% \qquad \text{Eqn. 17}$$

$$Re\% = 100 \pm E_{rel}\% \qquad \text{Eqn. 18}$$

Table 6. Relative error (d), absolute error (Erel%), and recovery percentage (Re%) values

Complex of metal ion	Analytical value(ppm)	d	Erel%	Re%
Cu (II)	0.04	-0.0004	-0.20	99.80
	0.6	0.0018	0.58	100.58
	2	-0.0026	-0.46	99.54

3.8. Preparation of solid copper(II) complex

The complex was prepared in a molar ratio (metal: ligand) (1:2) by adding (0.002 mol, 0.87 g) of ligand dissolved in 20 mL of absolute ethanol to (0.001 mol, 0.17 g of copper chloride ($CuCl_2$.2H2O) dissolved in 10mL of the best buffer solution (pH= 9), with the best conditions for the complex fixed, was heated to a temperature of (70-80)C° for an (1-2) hour, then left aside to precipitate. It was observed that a precipitate with a brownish-green color formed and it was recrystallized with absolute ethanol, and the yield percentage was (58.83%), the melting point was measured to be approximately (218-220)C° [31].

3.9.- Molar electrical conductivity of the copper(II) complex

The molar electrical conductivity of a solution of solid copper complex at a concentration of (1×10^{-3}M) was measured in pure (DMSO) solvent and at laboratory temperature, It was shown from the conductivity result in Table 7 that the copper complex it is an electrolyte with neutral charge, it contains one chloride ion inside the coordination sphere and another outside it to balance the charge, in a [1:1] ratio [32].

Table 7. Conductivity values for the Cu(II) complex in (DMSO)

Molecular formula	Molar electrical conductivity ($Ohm^{-1}.mole^{-1}.cm^2$)
$[Cu(C_{19}H_{13}O_2N_7S_2)_2(H_2O)Cl]Cl$	64

3.10. The solubility of solid copper(II) complex

The solubility of the ligand and copper complex was studied in a number of solvents and the results are shown in the Table 8 [33].

Table 8. Solubility of ligand and copper(II) complex in different solvents

Solvent	Ligand	Complex of Cu (II)
Water	-	-
Methanol	÷	÷
Ethanol	+	÷
Acetone	+	+
DMSO	+	+
DMF	+	+
Chloroform	÷	÷

Where: (+) = Complete dissolution, (-) = Undissolved, (÷) = Partial dissolution

3.11. The Magnetic susceptibility of copper(II) complex

The magnetic susceptibility of the prepared solid copper(II) complex was measured at laboratory temperature (17C°) using the Faraday method to obtain the gram susceptibility values (X_g), based on

Pascal's constants, the effective magnetic moment (μeff) was calculated and compared with the theoretical magnetic moment according to the following equations [34]:

Theoretical magnetic moment equation:

$$\mu_S = \sqrt{n(n+2)}$$

Equations of the practical effective magnetic moment:

$$X_M = X_g \times \text{M.wt}$$

$$X_A = X_M - D$$

$$D = (-\text{M.wtcomp.}/2) \times 10\text{-}6$$

$$\mu_{eff} = 2.828\sqrt{X_A.T} \quad (B.M)$$

Where: n= number of unpaired electrons of the central atom, T= absolute temperature X_M= molar susceptibility X_A= atomic susceptibility, X_g= Gravimetric susceptibility D= Magnetic correction factor, B.M.= Bohr Magneton, μ_{eff}= Effective magnetic moment $\text{M.wt}_{\text{Comp.}}$= Molecular weight of the complex

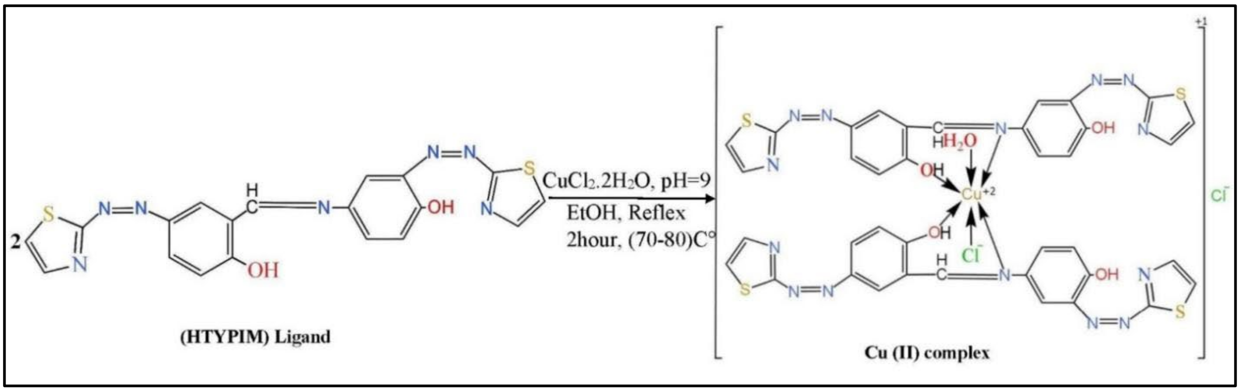
Magnetic susceptibility results revealed that the copper(II) complex exhibit paramagnetic characteristics and possess octahedral geometry, as illustrated in Table Table 9.

Table 9. Presents the magnetic susceptibility measurement of the Cu(II) complex

Metal complex	Cu (II)complex
Xg	0.027×10^{-4}
X_M	0.002811888
D	-0.00052072
X_A	0.003332608
μ_{eff}	2.7799
T(K)	17+273=290

3.12. The proposed geometrical structure of copper(II) complex

Based on the literature concerning the available coordination sites of the ligand and its binding mode with the metal ion, and in light of the obtained results, it can be concluded that the ligand behaves as a bidentate, it coordinates with the metal ion at a ligand-to-metal molar ratio [L:M] of [1:2] for the copper complex, accordingly the proposed geometric structure of the copper(II) complex is octahedral with (sp^3d^2) hybridization, as illustrated in Scheme 2 below [35]:



Scheme 2. The proposed geometric structure of Cu (II) complex

Conclusions

A new organic Schiff-Azo ligand was prepared from simple, available and cheap materials in two steps, the first step includes preparation of a Schiff base from the condensation reaction of salicylaldehyde with p-aminophenol, and the second step includes diazotization reaction of a Schiff base with 2-aminothiazole for the synthesis of the ligand, the prepared ligand and complex were characterized by Ultraviolet-Visible, FT-IR, ^{1}HNMR spectra, It was used as a ligand to determine small amounts of Copper (II) ion by the reaction of the ligand with the copper ion to form a highly stable colored complex at pH=9 and the metal to ligand ratio was [1:2], this method proved, through the results obtained, It exhibits high sensitivity and selectivity for copper ion determination, based on the measurements the geometry of the copper complex is octahedral.

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