

Spectrophotometric Determination of Cu(II) in Analytical Sample Using a New Chromogenic Reagent (HPEDN)

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Abstract: A sensitive, accurate and rapid spectrophotometric method that can be used for the determination of Cu(II) in analytical samples using a new chromogenic reagent azo-Schiff base 1-((4-(1-(2-hydroxyphenylimino)ethyl)-phenyl)diazanyl) naphthalene-2-ol (HPEDN) was studied. The synthesized new (azo-Schiff base) ligand was complexed with copper(II) and characterized using UV/Vis spectroscopy, IR spectra, ¹H-NMR, ¹³C-NMR spectra, Molar electrical conductivity, and measuring of their melting points. The obtained complex showed a brown color with maximum absorption at $\lambda_{max} = 500$ nm at pH = 9. Beer's law was obeyed in the concentration range of 1.7 to 5.4 $\mu\text{g/mL}$. The molar absorption and Sandell's sensitivity values of the Cu(II) complex were found to be $0.5038 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0039 \mu\text{g cm}^{-2}$, respectively. The structure of the prepared complex was investigated by using the continuous variation, mole ratio method and slope analysis method. The obtained results showed that the complex has (1:2) (M:L) molar ratio and these results showed that this method was more sensitive, more precise and accurate through the calculation of (Re, Erel, R.S.D)%. The most important interferences were Co^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Pd^{2+} , Fe^{3+} , thus suitable masking agents were used. This method was applied for the determination of Cu(II) in alloy. The obtained results were compared with flame atomic absorption spectrometry method and showed that results of both methods were in good agreement.

Keywords: azo-Schiff base compounds; 2-amino phenol Schiff base; precise and accuracy

■ INTRODUCTION

Copper is a reddish-colored metal and a heavy metal that changes color and properties when it is combined with other elements forming different compounds [1-2]. Copper is a soft material that can be reacted chemically [3] or physically with external source [4]. In addition to that, its advantages include a slow rate of reaction with diluted acids [5-6]. Copper is a fundamental supplementary element to plants and other living species [7].

Copper has electrical conductivity, thermal conductivity, is oxidative and can undergo hydrolysis [8] and has the ability to be used in the manufacturing of alloys [9-10], including biscuit alloy with zinc. Copper compounds are also used in analytical chemistry, such as the Vlnk solution which is used in the detection of sugars [11]. Copper can enter the composition of the skin and

hair, for example in the form of Batali that is responsible for coloring hair and skin. In addition, copper can enter the formation of joints and nerves, which is responsible for the sense of taste. Copper is also involved in the synthesis of many enzymes, thus maintaining the activity and health of the heart.

Many techniques can be used to determine copper percentage in its compounds. Some of these are atomic absorption spectrometry [12-14], inductive coupled plasma-emission spectrometry [15], potentiometry [16], derivative potentiometric stripping analysis [17], flow injection catalytic photometric method [18-19], and inductive coupled plasma-mass spectrometry [19]. Several studies were published for spectral estimation of Cu(II).

Rao [20] was able to estimate copper(II) spectrophotometrically by using an organic detector (4-

HBTS), where the yellow colored complex that was formed showed a maximum absorption peak at 370 nm, in pH = 6.5, with absorption coefficient of $(2.85 \times 10^4) \text{ L mol}^{-1} \text{ cm}^{-1}$, sandal sensitivity of $0.00032 \mu\text{g cm}^{-1}$, and value of % R.S.D equal to (0.025). A colorimetric method was used for the determination of Cu(II) by using chromogenic reagent (CDSAII) in a neutral medium at 588 nm with concentration range of $6\text{--}0.25 \mu\text{g mL}^{-1}$ and D.L = $0.15 \mu\text{g mL}^{-1}$ [21].

The aim of this work is to prepare a new reagent to be used in a new method, that is more sensitive, easy and have low cost for the extraction and determination of copper(II) ion from industrial samples, and to study all the conditions that affects the determination process, such as the pH of reaction solution, the time needed to complete the reaction of the complex formation, and the optimum concentration of reagent that will result in complete complexation reaction with copper ions.

EXPERIMENTAL SECTION

Materials

All solvents and chemical Reagents used in this study have high purity and are supplied by B.D.H, Fluka and Merck companies without any additional purification

processes. The materials used were ethanol absolute, glacial acetic acid, *p*-aminoacetophenone, 2-naphthol, sodium nitrite, hydrochloric acid, sodium hydroxide, and *o*-aminophenol.

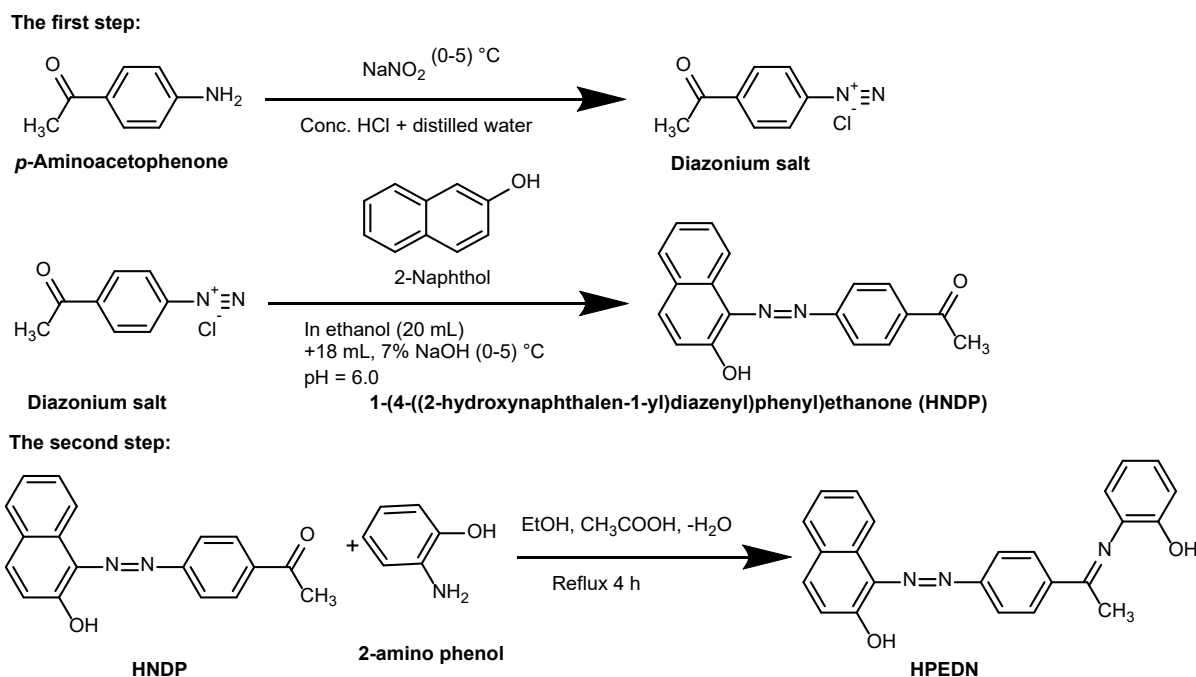
Instrumentation

All techniques that were used in the characteristic study of the new synthesized ligand and its complexes were a-UV-6100 PC Double beam Spectrophotometer (EMCLAB, Germany), FT-IR Spectrophotometer 8400S (Shimadzu, Japan), pH-meter (InoLab, WTW, 135i, Germany), Conductivity meter (Digital, InoLab, Germany), Melting point instrument (SMP 30, Stuart, England), Balance BL 2105 (Sartorius, Germany), Mova 400 MHz, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectrophotometer.

Procedure

Synthesis of the new ligand (HPDN)

The ligand 1-((4-(1-(2-hydroxyphenylimino)ethyl)phenyl)diazenyl)naphthalene-2-ol (HPDN) was synthesized in two steps (Scheme 1). The first step was to prepare the azo derivative by reacting *p*-aminoacetophenone with 2-naphthol in controlled conditions and the addition of azo which was conducted



Scheme 1. Pathway of synthesis of 1-((4-(1-(2-hydroxyphenylimino)ethyl)phenyl)diazenyl)naphthalene-2-ol (HPEDN) ligand (step one and two)

in a snowy environment due to the exothermic process of the reaction. The obtained precipitate showed a dark red color with a yield of 75.37% and melting point of 145–147 °C.

The second step includes the reaction of the Azo derivative 1-(4-((2-hydroxynaphthalen-1-yl)diazenyl)phenyl)ethanone (HNPD) with 2-aminophenol, by refluxing of the mixture for 4 h which was later cooled to room temperature, dried and recrystallized with absolute ethyl alcohol. The resultant precipitate yield was 72.51% of reddish brown crystals and the melting point was 178–180 °C.

Preparation of buffer solution

The buffer solution was prepared by dissolving 0.7708 g, 0.01 mole of ammonium acetate in 1000 mL of distilled water. Different pH values were obtained by adding certain amounts of concentrated ammonia solution or concentrated acetic acid in order to prepare solutions with pH range between 4 and 12.

Synthesis of the divalent copper(II) complex

The metal complexes were prepared by the molar ratio (1:2) (M:L) by dissolving (1 mmol) of the metal chloride salt in 10 mL of buffer solution in optimal acidic function. Chlorides were selected as good leaving groups and to prevent interference with negative ions and for ease of use in the buffer solution with optimum acid function and 2 mmol of ligand was dissolved in 20 mL of ethanol absolute. The metal ligand mixture solution was then

heated at (50–60 °C) for 1 h, and the precipitate was washed and recrystallized with ethanol absolute and later dried in air. Table 1 shows the physical properties of the ligand and its complexes.

RESULTS AND DISCUSSION

UV-Visible Spectrophotometry

The absorption spectra of the (HPEDN) ligand solution in ethanol was recorded at wavelengths from 200–800 nm. The maximum absorption peak of the ligand was at 326 nm. The maximum absorption of the Cu²⁺ complex was at 500 nm after the application of optimal conditions. This observation confirms the formation of stable complexes as shown in Fig. 1 and Table 2.

When comparing absorption spectra of the ligand with that of the complex, a clear difference can be observed in the value of the maximum absorption peak which indicates a red shift and the formation of a complex with higher absorption in comparison with the ligand [22].

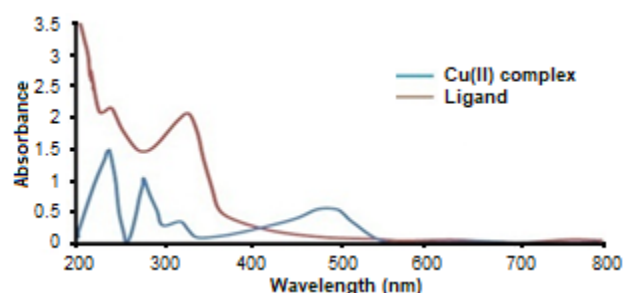


Fig 1. Electronic spectra for HPEDN ligand and its Cu(II) complex

Table 1. Physical properties of the azo-Schiff base ligand and its complexes

No.	Molecular formula	Color	m.p (°C)	Yield (%)	Am/Ohm ⁻¹ mol ⁻¹ cm ²			Reaction time
					DMF	Ethanol	DMSO	
1	C ₂₄ H ₁₉ N ₃ O ₂	Reddish brown	178–180	72.51	-	-	-	4 h
2	[Cu(C ₂₄ H ₁₉ N ₃ O ₂) ₂ Cl ₂]	Brown	196–198	63.11	16.5	11.3	10.3	1 h

Table 2. The electronic transitions for HPEDN ligand and complex

Molecular formula of ligand	λ (nm)	Wave number (cm ⁻¹)	Transition type
C ₂₄ H ₁₉ N ₃ O ₂	326	30674	n→π*
	237	42194	π→π*
[Cu(C ₂₄ H ₁₉ N ₃ O ₂) ₂ Cl ₂]	500	20000	CT
	314	31840	n→π*
	285	35087	π→π*
	226	44247	π→π*

Study of the Optimal Conditions for the Formation of the Complex

Effect of pH solution on the formation of the complex

A series of copper ions solutions with ligand (HPEDN) were prepared at pH ranges of 4–12, and were each measured for their absorbance at the maximum wavelength of the copper complex. The results showed that the best pH was 9, which gave the highest absorbance for the metal complex. It was also observed that the absorption values were varied with variation of pH values of the solution. This may be due to the change in chemical nature of the ligand or the competition between hydroxyl ions in the ligand with metal ions. It was also found that absorption values of the complex decreased with increasing value of pH, and this can be attributed to the deposition of ions of the element and the formation of an unstable complex [23], as shown in Fig. 2.

Effect of the concentration of ligand on the complex formation

To investigate the effect of the concentration of ligand on the complex formation, a series of solutions containing different concentrations of ligand (HPEDN) ranging from 0.5×10^{-4} – 4×10^{-4} M were mixed with constant concentration (1×10^{-4} M) of copper(II) ion solution. The pH of solution was adjusted to 9, and then the absorbance was measured against water and ethanol as a blank solution. The obtained results showed that the optimal concentration of ligand was 1.5×10^{-4} M, which gave the highest absorption of the complex. Higher

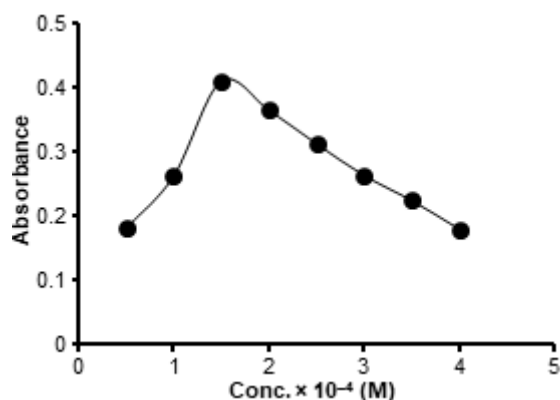


Fig 3. Effect of ligand concentration

concentrations of ligand, caused a decrease in absorption intensity this may be due to the formation of new species in the solution that are absorbed at different wavelengths and possibility to the condensation of the ions or the solubility of the reagent with the solvent completely. As shown in Fig. 3.

Effect of time on the formation of the Cu(II) complex

Fig. 4 shows that the formed complex gave high absorbance after 15 min of reaction time and remained constant for 48 h at optimal conditions. The results of this study showed that the prepared ligand can be used to estimate the concentration of copper by forming a stable complex, similar to other reagents that have been used to estimate the concentration of other ions spectrally [24].

The effect of additive sequencing of ligand, metal ion and buffer solution on the absorption intensity of the

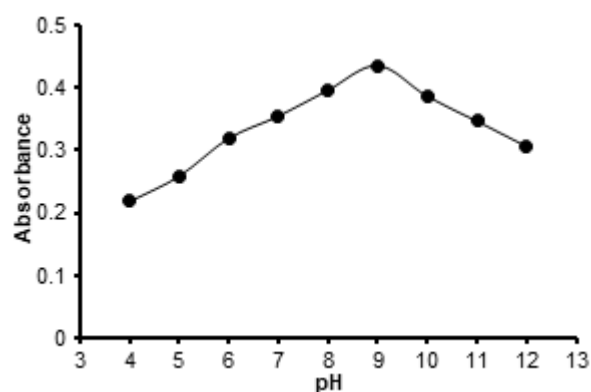


Fig 2. Effect of pH values of solution on complex formation

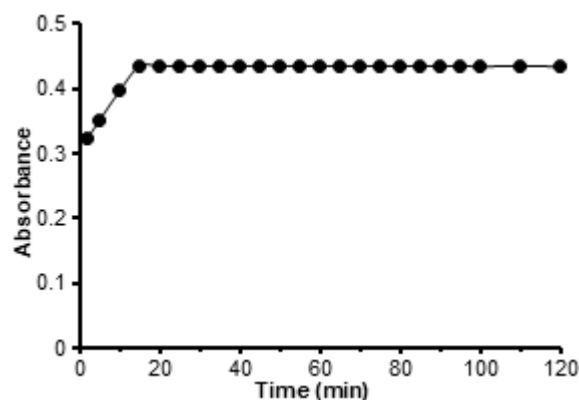


Fig 4. Effect of time on the stability of the copper(II) complex

formed complex was investigated in this part. The obtained results showed first and second sequential succession which exhibited low absorption values. This is due to positive and negative completion of ions of the acid and base in the metal bonding, that leads to low absorption values. Therefore, the third sequencing was used to determine the absorption values and to prepare the complex as shown in Table 3.

Effect of temperature

The effect of temperature on the stability of the synthesized complex was investigated in temperatures ranging between 5 and 50 °C. The obtained results showed that the copper complex absorbance remained almost constant at 15–30 °C. After that, the absorption decreased. This result may be due to the decomposing of the complex at temperatures above 30 °C, so it is preferable to study copper complex within this range of temperature. The results are shown in Fig. 5.

Mole Ratio Method

The possible compositions for the preparation of the complex were determined using the molar ratio method. The method was conducted by taking different volumes of ligand and a constant volume of the metal ion at the same concentration. The results showed that the complex

has the mole ratio of (1:2) (Metal:Ligand) as shown in Fig. 6.

The Continuous Variation Method (Job Method)

In this method, different volumes of both the ligand and the metal were selected with the same concentration at the optimal acid function and the absorbance of each solution was measured at the maximum wavelength of the copper complex. When drawing the absorbance values against $\frac{V_m}{V_m+V_l}$, V_m represents the volume of metal and V_l is the volume of ligand. The ratio was found to be (1:2), one mole of metal to 2 moles of the ligand as shown in Fig. 7.

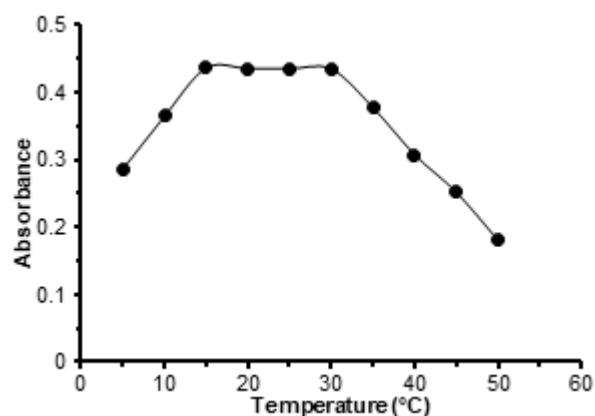


Fig 5. Effect of temperature on the stability of the complex

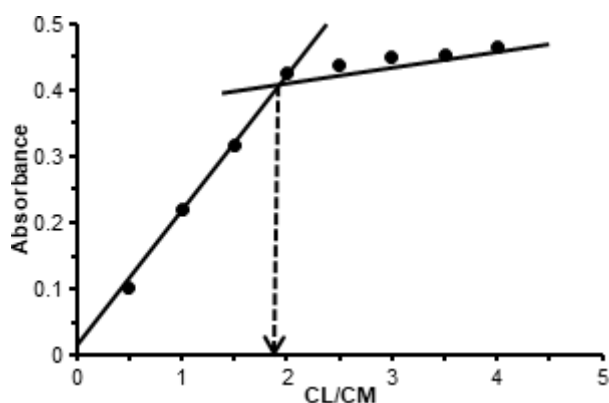


Fig 6. Molar ratio method of copper(II) complex

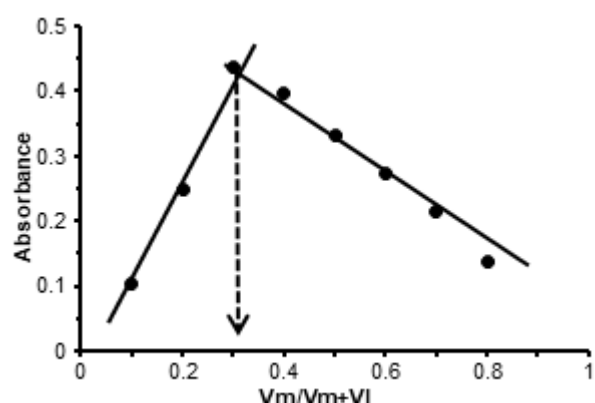
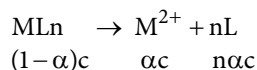


Fig 7. Continuous variation method of copper(II) complex

Table 3. Effect of Sequence of addition on the formation of Cu^{2+} complex with HPEDN ligand at pH = 9

The sequence of addition number	Sequence of addition	Absorbance
1	Metal + buffer solution to adjusting pH + ligand	0.3166
2	Ligand + Metal + buffer solution to adjusting pH	0.3325
3	Metal + Ligand + buffer solution to adjusting pH	0.4357

The values of the stability constant of the complex were calculated according to the following equations and the value of stability and instability constants are shown in Table 4.



$$K_{inst} = \frac{(ac)(nac)^n}{c(1-a)} \quad (1)$$

$$K_{st} = \frac{1}{K_{inst}} \quad (2)$$

The results of the stability constants showed that the copper complex is more stable. The reason is that the

higher the atomic number, the higher the nuclear charge, causing it to have more ability to attract ligands compared to other ions in the same period of the periodic table, which leads to more electric field absorbed by the positive ions of the ligand, which increases the stability of the complex [26].

Effect of Interference and Masking Reagent on the Absorption of the Copper(II) Complex

The effect of interference on the absorption of the copper complex with ligand was studied by selecting several positive and negative ions as shown in Table 5.

Table 4. Absorption values (A_s) and (A_m) as well as values of each (α) and (K_{st}) and (K_{inst}) of the copper complexes

Metal complex	A_s	A_m	α	K_{inst}	K_{st}	Log K_{st}
CuL	0.3922	0.4536	0.1353	1.145×10^{-10}	8.728×10^9	9.956

Table 5. Effect of addition of positive and negative ions on the absorption values of the divalent copper complex

Foreign ions	$1 \times 10^{-4}M$		d	E%	% Re
	Absorbance after addition of ions				
Cation					
Without Cation		0.4374	-----	-----	-----
Ni ⁺²		0.4266	-0.012	-2.46	97.54
Co ⁺²		0.4305	0.00069	-1.57	98.43
Cd ⁺²		0.3992	0.0382	-8.73	91.26
Pd ⁺²		0.4564	0.019	4.34	104.34
Mn ⁺²		0.4428	0.0054	1.23	101.34
Fe ⁺²		0.3197	-0.1207	-27.5	72.41
Zn ⁺²		0.2872	-0.1512	-34.3	65.66
Anion					
Without anion		0.4374	-----	-----	-----
CO ₃ ⁻²		0.3958	-0.041	-9.51	90.48
SO ₄ ⁻²		0.4283	-0.009	-2.08	97.91
C ₂ O ₄ ⁻²		0.4207	-0.016	-3.81	96.18
CH ₃ COO ⁻²		0.3984	-0.039	-8.91	91.08
NO ₂ ⁻¹		0.4092	-0.028	-5.95	94.04
SCN ⁻¹		0.4163	-0.021	-0.99	99.00
Cl ⁻¹		0.3995	-0.072	-3.49	96.50
Masking agent					
Without masking agent		0.4374	-----	-----	-----
Ascorbic acid		0.2793	-0.158	-36.14	63.85
Potassium Thiocyanate		0.4368	-0.0006	-0.137	99.862
EDTA		0.1806	-0.2568	-58.71	41.28
Thiourea		0.3512	-0.0862	-24.81	75.187
Potassium chloride		0.4084	-0.029	-6.63	93.36
Tartaric acid		0.2347	-0.2027	-46.34	53.65
Salicylic acid		0.3095	-0.1279	-29.24	70.75

The positive ions were found to decrease or increase the absorbance. This is due to the competition of these ions with the copper ion on the bonding with the reagent to form the complex, where part of the reagent is taken to be a new complex. The low absorbance values after the addition of the negative ions were due to their use as a masking reagent, where KSCN was used as a masking reagent to eliminate the effect of the interference by returning the absorption values to the original calculated output without interference [29].

FTIR Spectra of the Ligand and the Complex

Fig. 8 shows the IR FTIR spectra of the ligand and its complex, in which the ligand appeared as a narrow, weak-intensity band at 3416 cm^{-1} due to the stretching vibrations of the hydroxide group in the ligand. When compared with the complex at 3454 cm^{-1} , there was a change in the intensity, and location of the peak due to the bonding

of the carboxyl group, after they lost their proton [30].

The ligand spectrum showed a medium-intensity absorption at 1666 cm^{-1} attributed to $\nu(\text{C}=\text{N})$ and this site suffered less displacement when aligned with copper as well as a change in intensity and shape in the complex spectra.

The ligand spectra have shown to have a strong absorption at 1413 cm^{-1} , which is attributed to the vibration band of $\nu(\text{N}=\text{N})$, that had undergone a shift toward a lower wavelength when it was associated with the metal. The consistency of copper and the ligand was observed by the nitrogen atom of the azo group.

The low frequency region is limited to 593 cm^{-1} absorption bands for the metal-oxygen bonds and 473 cm^{-1} due to metal-nitrogen bonds. This result is due to the formation of a homogeneous bond between the deposited atoms with the central copper ion [31]. All these bands are summarized in Table 6.

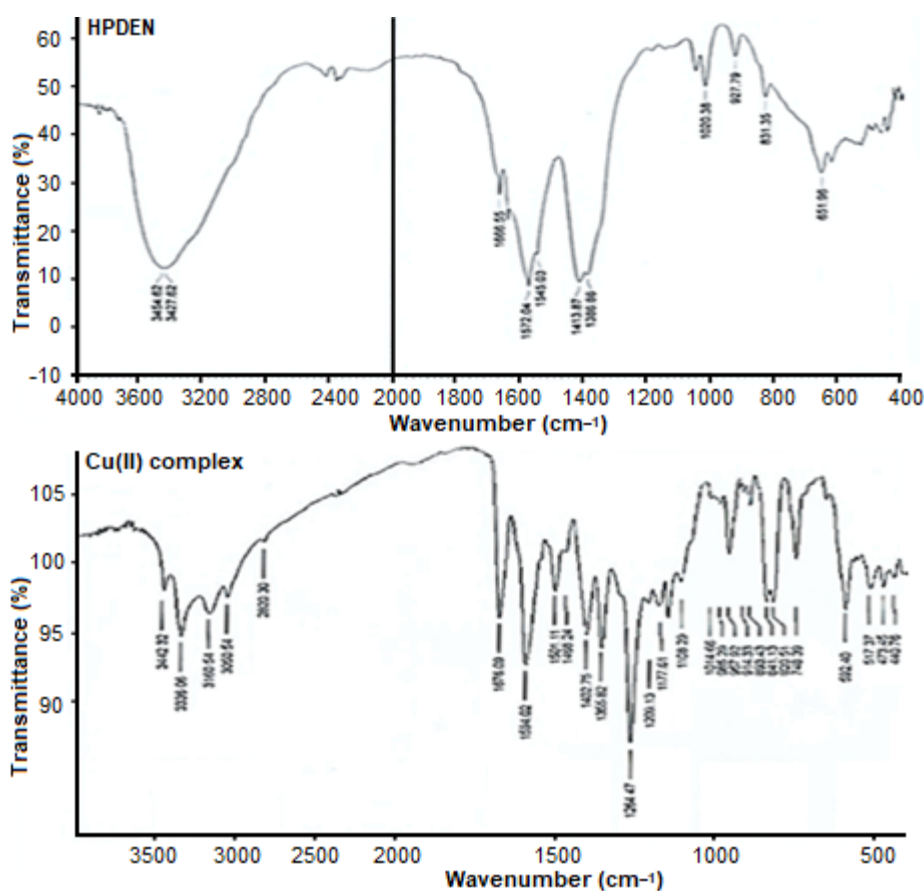


Fig 8. FT-IR spectrum of the ligand (HPDEN) and its complex with Cu(II)

Table 6. Typical FT-IR absorption frequencies for reagent and complexes

Compound	OHv	N=Cv	N=Nv	M-Nv	M-Ov
Ligand HPEDN	3454(s.)	1666(m.)	1413(s.)	-	-
Cu(II) complex	3442(w.)	1676(w.)	1468(w.)	473(w.)	593(w.)

w.: weak s.: strong m.: medium comp.: complex

¹H-NMR and ¹³C-NMR Spectra of Ligand (HPEDN)

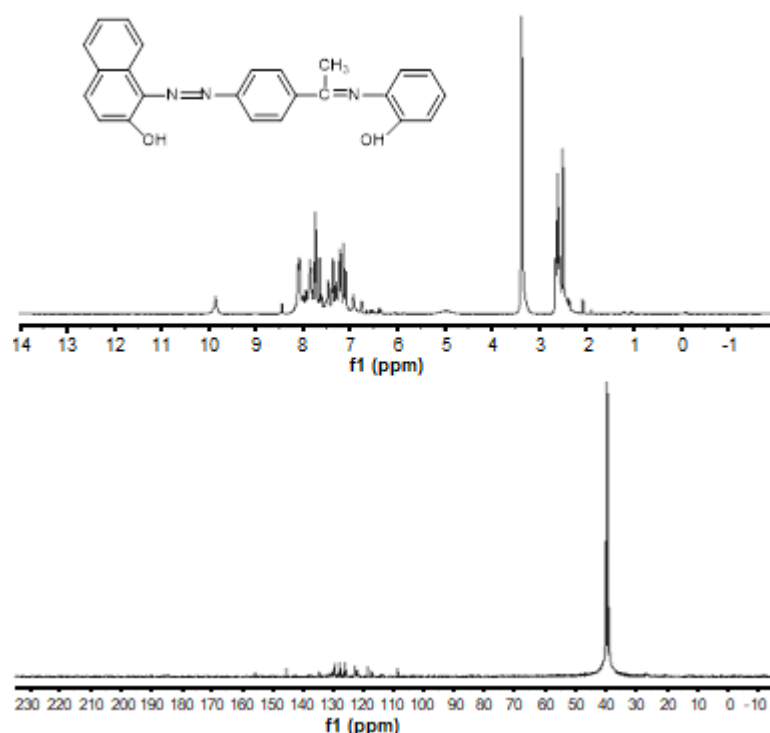
The ¹H-NMR Spectra of the ligand shows the chemical displacements of aromatic and elliptical protons. The single band at 9.8491 ppm belong to the proton of the hydroxyl group (OH), the three single bands at 2.5895, 2.6189 and 2.6471 ppm are attributed to the protons of the methyl group (CH₃), the multiple bands at 6.7574 to 8.4526 ppm belong to the nine protons of the aromatic rings, while the band at (2.500 ppm) relates to (DMSO d⁶) [32]. Proton NMR spectra of the ligand are shown in Fig. 9. ¹³C-NMR spectra of the ligand, shows the appearance of a single band at 39.520 ppm which belongs to the carbon of the methyl group (CH₃), the single band at 155.3790 ppm belongs to the carbon of azomethine (-C=N-), and the multiple bands at 108.6402 to 145.3493 ppm belong to the 22 carbons of the aromatic rings [32].

The Suggested Structures of the Copper(II) Complex

From the results of the electrical conductivity, molar ratios and continuous variation methods and also all the spectral methods applied for the study of the copper(II) complex [33-34], we concluded that the complex structure consists of 2 moles of ligand and one mole of metal and the complex was uncharged, therefore the shape of the complex must be octahedral with the hybridization of d²sp³ as shown in Fig. 10.

Construction of the Calibration Curve

In order to construct a calibration curve, a series of different concentrations of the metal ion were prepared ranging from 1.7–8.4 μg mL⁻¹ with constant concentration of the ligand (1.5 × 10⁻⁴ M) using absolute ethanol as the

**Fig 9.** ¹H-NMR and ¹³C-NMR spectra of ligand (HPEDN)

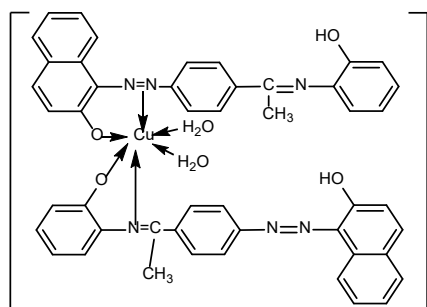


Fig 10. The suggested structures of copper(II) complex

solvent, where the results showed that the calibration curve follows the Lambert Beer's law for a range of concentrations 1.7–5.4 $\mu\text{g mL}^{-1}$. The Sandell's Sensitivity was equal to 0.0039, while the limit of detection (LOD) and limit of quantification (LOQ) was equal to 0.2217 and 0.7385, respectively. This shows that the method is highly sensitive and can be used to determine metals with low concentrations with agreeable accuracy and precision under the optimal conditions of the reaction [25]. These results were calculated by Eq. 3, 4 and 5 as shown in Table 7 and Fig. 11.

$$\text{LOD} = \frac{3\text{SD}}{\text{Slop}} \quad (3)$$

$$\text{LOQ} = \frac{10\text{SD}}{\text{Slop}} \quad (4)$$

$$\text{SD} = \sqrt{\frac{\sum (X_i - \bar{X})^2}{n-1}} \quad (5)$$

where x_i is the absorbance, \bar{x} is the mean of the absorbance, and n is the number of the measurement.

Precision

The precision of the analytical method was determined by calculating the amount of standard deviation (SD) for five measurements of absorbance, and the relative standard deviation (% RSD) by dividing the SD with the mean of the absorbance (\bar{x}) of the complex in optimal conditions as shown in Table 8. The sensitivity of this method was calculated using the detection limit (DL) and the limit of appreciation. This method is therefore

used to estimate metal ions [27]. These values were calculated by using Eq. 3, 4, 5 and 6. The result showed that this method is able to be used to determine Cu(II) concentrations with high precision compared with other spectrophotometric methods.

$$\text{RSD}\% = \text{SD}/\bar{x} \quad (6)$$

Accuracy

Accuracy means the closeness of the practical value from the theoretical value to determine if the results of an analytical method are accurate. The accuracy of the analytical method in this research was calculated by using the percentage relative error and the pre-processing ratio of the previously prepared complexes as shown in Table 9. The results show that the method that

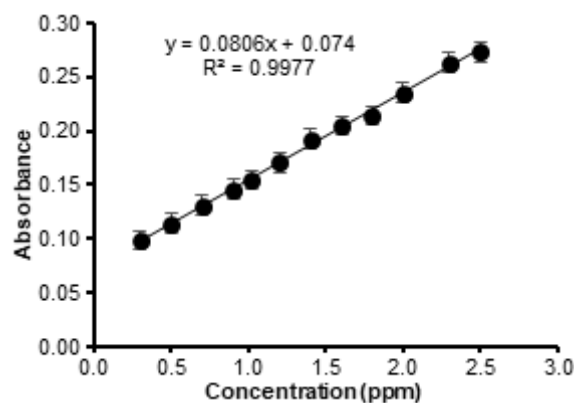


Fig 11. Calibration curve of the copper complex

Table 7. Construction of calibration curve of metal complexes

λ max (nm)	500
Beer's Law limit ($\mu\text{g mL}^{-1}$)	1.7–5.4
Molar Absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)	0.5038×10^4
Sandell's Sensitivity ($\mu\text{g cm}^{-2}$)	0.0039
Limit of Detection ($\mu\text{g mL}^{-1}$)	0.2217
Limit of Quantification ($\mu\text{g mL}^{-1}$)	0.7385
Regression Equation	$y = 0.2519x + 0.0043$
Slope	0.2520
Correlation coefficient (R)	0.9994

Table 8. Values of standard deviation, percentage standard deviation

No.	1	2	3	4	5	Average \bar{x}	Sum $(x_i - \bar{x})^2$	SD	% RSD
Complex of Cu(II)	0.4378	0.4377	0.4377	0.4376	0.4376	0.4377	3×10^{-7}	0.00086	0.1964

Table 9. The relative percentage error and the pre-processing ratio of the complex

Complex ion	Analytical value (mol L ⁻¹)	d	% E _{real}	% Re
Cu(II)	0.971 × 10 ⁻⁴	-0.029 × 10 ⁻⁴	-2.9	97.1

Table 10. The percentages of copper determination by ligand in a copper alloy using an atomic absorption method

Sample	Content %	By Spectrophotometric method %	% E _{rel}	% Re	By Flame atomic absorption %	% E _{rel}	% Re
Alloy copper	70	69.4	0.6	100.6	68.8	1.2	101.2

was used to measure the metal concentration using ligand (HPDN) was highly accurate [28].

$$\%E_{\text{real}} = \frac{d}{\mu} \times 100 \quad (7)$$

where μ = analytical value, d = analytical value - theoretical value

Applications

The prepared ligand was used as a reagent to determine copper in an alloy that contains 70% copper and 30% zinc, using the UV-Vis method, and the results were compared to the flame atomic absorption method as shown in Table 10.

From Table 10 we can observe the compatibility between the UV-Vis method and the atomic absorption method, so we can conclude that the UV-Vis method can be widely used in the determination of copper in different models with precision, selectivity and high sensitivity.

CONCLUSION

The current study showed the success of the preparation of a reagent and the possibility of its use in determining micro amounts of copper in different models with high accuracy and sensitivity by forming a color complex. The optimal conditions to obtain the copper(II) complex were: pH = 9, temperature = 0–50 °C, the ratio of ligand to metal(1:2), SD = 0.00086, % RSD = 0.1964, DL ($\mu\text{g mL}^{-1}$) = 0.2217. According to this study, we can suggest that the shape of the complex must be an octahedral shape with the hybridization of d^2sp^3 .

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