

## تحضير وتشخيص كاشف مولد للون واستخدامه في تعيين القياسات الطيفية لايون النحاس الثنائي

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الكلمات المفتاحية: ليكند مولد للون، القياسات الطيفية، قواعد شف، النحاس الثنائي، بار-ا-بس (٤-كلوروفنيلايامين) فنلين.

### الخلاصة:

تمت دراسة طريقة التقدير الطيفي لتقدير التراكيز المايكروية لايون النحاس الثنائي بواسطة تحضير بار-ا-بس [ ٤-كلوروفنيل (ايامين) فنلين ] كليكند. استندت الطريقة على اساس تكوين معقد ١:٣ بين ايون النحاس الثنائي والليكند وتم دراسة الظروف المثالية لتقدير النحاس واثبتت مطاوعتها لقانون لامبرت بيير بحدود (٢٥-١) مايكروغم لكل مل. تمت دراسة الظروف المثالية لتقدير النحاس مثل تأثير الدالة الحامضية وتأثير تركيز الليكند وتكافؤية المعقد. اظهر المعقد الناتج اعلى قمه امتصاص عند الطول الموجي (٤٧٠) نانوميتر، كذلك ثابت معدل تكوين المعقد و قيمة الامتصاصية المولية  $l.mol^{-1}.cm^{-1}$  ( $7.7 \times 10^3$ ), ( $4.8 \times 10^7$ ) على التوالي. اظهرت الطريقة ان قيمة كل من حدود الكشف والكمية هي  $\mu g ml^{-1}$  ( $3.38 \times 10^{-2}$ ), ( $1.12 \times 10^{-2}$ ) على التوالي. اثبتت الطريقة دقتها وبساطتها وامكانية استخدامها لتعيين ايون النحاس الثنائي.

# Synthesis and Characterization Chromogenic Reagent and Its Spectrophotometric Determination of Cu (II)

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**Key word:** chromogenic reagent, spectrophotometric determination, Schiff base, copper (II), P-bis (4-chloro phenyl-imine) phenylenes

## Abstract

A simple, Sensitive spectrophotometric method was proposed for the micro determination of Cu(II) using the synthesized P-bis (4-chloro phenyl-imine) phenylenes (p-b(cpi)p). The method was based on the formation of (1:3) complex between the Cu(II) and the ligand. The optimum conditions for the determination were established, The Beer's law was applicable in the range (1-25)  $\mu\text{g/ml}$ . The complex has maximum absorption at 470 nm and molar absorption coefficient and stability constant of the complex was found to be ( $7.7 \times 10^3$ )  $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  ( $4.8 \times 10^7$ ) respectively. The limits of detection and quantitation for the developed method are ( $1.12 \times 10^{-2}$ ) and ( $3.38 \times 10^{-2}$ )  $\mu\text{g ml}^{-1}$  respectively. The method was simple, sensitive, accurate and was successfully applied for the determination of copper (II).

## Introduction

The separation and determination of heavy metal ions in the environmental and biochemical research have been one of the most important topics of analytical chemistry.

As compared with the other techniques, spectrophotometry is very simple, rapid and less expensive for determination of elements in a variety of samples. Developing highly functional chelating agents such as Schiff bases has been a great concern of many analytical chemists. Many investigations have been centered on the structure and bonding in Schiff bases but few have been directly concerned with analytical application [1-6]. Copper is essential for life but is highly toxic above certain algae, fungi and bacteria viruses [7, 8]. The concentration of copper plays a very important role which decides its vitality and toxicity for many biological systems. [9, 10] It has been reported that the toxic copper species are  $\text{Cu}(\text{OH})^+$ ,  $\text{Cu}_2(\text{OH})_2^{2+}$  and  $\text{CuCO}_3$ . Therefore, Copper ions present in various aqueous systems are considered to be the most toxic of dissolved copper species. [11,12] The excess concentration of copper in water systems is harmful to human beings, affects the self-purification of bulk water [13] and disturbs the microbiological treatment of waste water. [14] Thus, the determination of trace amounts of Cu(II) is becoming increasingly important because of the increased interest in environmental pollution. [15]

In addition, the accumulation of copper in the human liver is a characteristic of Wilson's disease, which produces neurological and psychiatric defects. There are conventional methods for copper (II) determination [17-19]. However, the colorimetric methods are often preferred due to the fact that they involve less expensive instruments and show rapid results. This work has

been aimed to develop a highly sensitive and efficient spectrophotometric method for copper (II) determination, based on the formation of colored complex which were formed by the reaction of copper ion with P-bis(4-chloro phenyl imines) phenylens.

## Experimental Section

Synthesis of p-bis(4-chloro phenyl imine) phenylens was achieved according to scheme (1) by refluxing 1mole of phenylene diamine with two moles of p-chloro benzyldehyde in absolute ethanol for 3 hr. The product was washed, recrystallized and dried at 55 °C for 2hr under reduced pressure to a yellow crystal. The product was characterized by  $^1\text{H-NMR}$ , IR spectroscopy. The  $^1\text{H-NMR}$  spectrum of the ligand, shows the following characteristic chemical shift, for protons of three aromatic rings appear at the range  $\delta$  (7.3-7.8), furthermore, the signal at  $\delta$  (10.3) due to (C-H) proton.

The FT-IR spectrum Fig (1) for the ligand using a KBr pellet method had absorption peaks assigned to the stretching vibration of an imine bond ( $-\text{N}=\text{C}-$ ) around ( $1616\text{ cm}^{-1}$ ) of schiff base and disappearance of the absorption bands assigned to ( $-\text{NH}_2$ ) stretching at ( $3406 - 3201\text{ cm}^{-1}$ ) and ( $\text{C}=\text{O}$ ) stretching at ( $1693\text{ cm}^{-1}$ ) in phenylene diamine and p- chloro benzyldehyde respectively. Also, the FT-IR spectrum showed the suggested bands for olefinic (C-H) at ( $2877\text{ cm}^{-1}$ ), (C-Cl) at ( $1091\text{ cm}^{-1}$ ) and bands (C-H) (C=C) Aromatic at ( $3082\text{ cm}^{-1}$ ) ( $1589, 1492\text{ cm}^{-1}$ ) respectively. The melting point of the ligand was about  $180^\circ\text{C}$ .

Analytical reagent grade chemicals and distilled, deionized water used throughout. The standard stock solution ( $5.8 \times 10^{-5}\text{M}$ ) of copper was prepared by dissolving 0.001 gm. of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Merck) in distilled water in a 100ml volumetric flask. Working solution was prepared by appropriate dilution of the stock solution with water.

A 4% solution of the ligand was prepared by dissolving 0.04gm of the ligand in 100ml acetone. An acetic acid-Sodium acetate buffer solution ( $\text{pH}=6.0$ ) was used.

All absorbance measurement was made with a UV-Visible spectrophotometer double Beam.CECIL, CE7200, England (190-1100nm) using 1cm quartz cell. All pH measurement were made with a pH-meter (Philips-PW, 418, England) IR Affinity (Fourier transform infrared spectrophotometer (SHIMADZU) and the  $^1\text{H-NMR}$  spectra were recorded a BRUKER-400MHz operating at 300 MHz with tetra methyl silan as internal standard in  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  as solvent, measurement were made at chemistry department, AL-Baath University-Syria

## General Procedure

An aliquot of copper solution containing 1-25 $\mu\text{g}$  of Cu (II) were placed in a conical flask fitted with a ground glass stopper. The pH was adjusted to 6 with 1ml buffer acetate. 1.5ml of 0.04% ligand solution was added, and then adjusted the volume to about 5ml with (1:1) acetone, deionized water. It was waited 100min. And the absorbance at the required wavelength 470nm in 1cm quartz cell against the reagent blank was measured.

## Result and Discussion

### 1- Effect of pH on the absorbance of the complex

Figure (2) shows the effect of pH on the intensity of the color reaction. The complex solution showed maximum absorbance in a medium of  $\text{pH}=6$ . Hence further analytical investigations were carried out in buffer media of  $\text{pH}=6$ .

The absorption spectra of solution containing metal complex against the reagent blank, and ligand solution against corresponding buffer solution blank is shown in figure 3,4 respectively.

The metal complex has maximum absorbance at 470 nm. Further neither the metal ion nor the

reagent has appreciable absorbance at specified wavelength. Hence further investigation was carried out at 470 nm.

## 2- Effect of reagent concentration

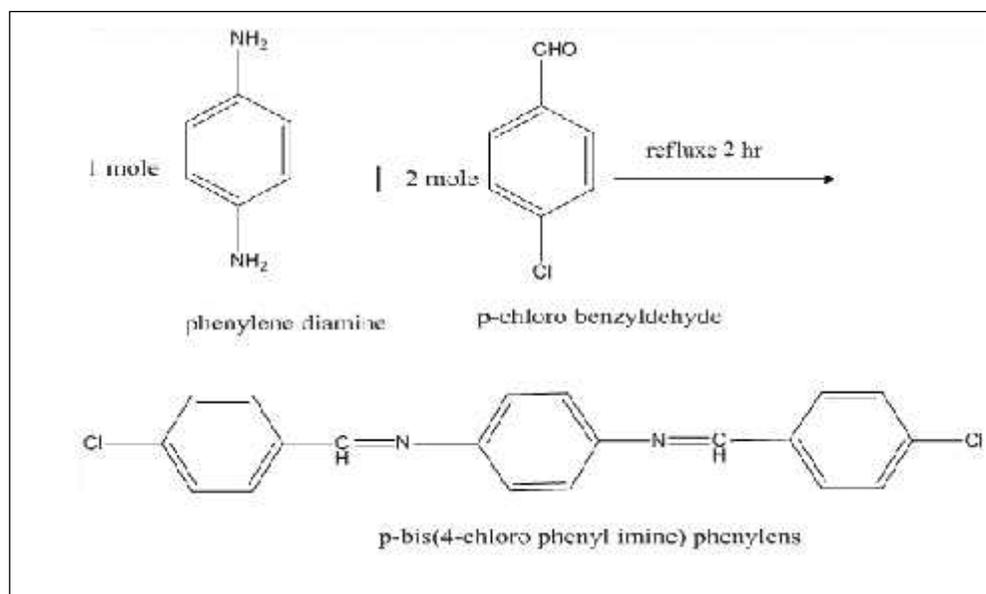
A series of solution containing different amounts of reagent, fixed amount of copper (II) were taken in appropriate buffer media. The absorbance of solutions was recorded at 470 nm using respective reagent solution as blank. The studies reveal that, a reagent was sufficient for the metal complex color reaction. However the addition of excess of the reagent solution does not alter the intensity of the color reaction.

## 3- Analytical determination of metal ion

The absorbance of the series of solution containing different concentration of the metal ion is determined. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Cu(II) can be determined in the range of (1-25) $\mu$ g/ml. The pertaining calibration graph is shown in the Fig.5. The regression equation is  $A=0.007C-0.004$  (A is absorbance and C is the concentration Cu (II) in  $\mu$ g/ml) with a correlation coefficient 0.9991.

## 4- Stoichiometry of the Cu (II) complex

The Stoichiometry of the complex determined by mole ratio method was found to be 1:3 (Metal: Ligand) .The corresponding data is shown in Figure 6. The stability constant was found to be  $(4.8 \times 10^7)$ .



**Scheme (1) preparation of p-bis (4-chloro phenyl imine) phenylens**

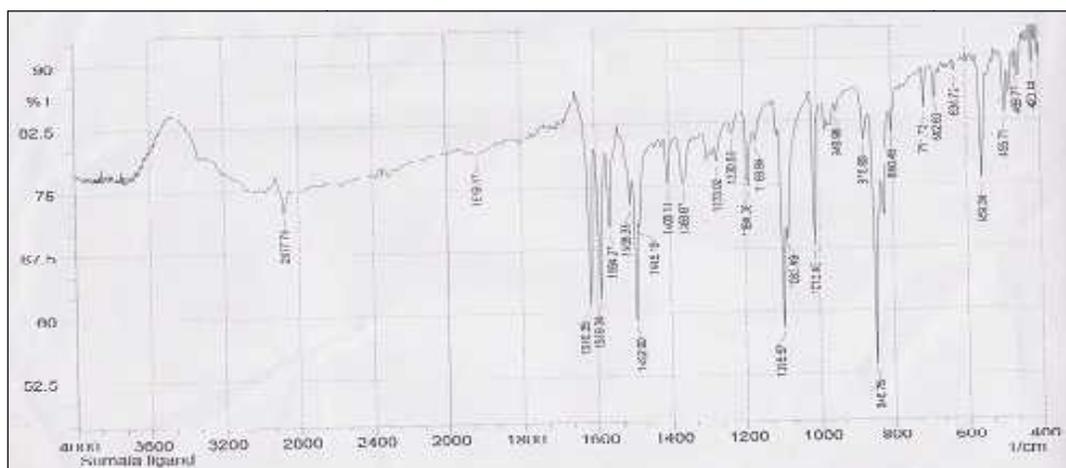
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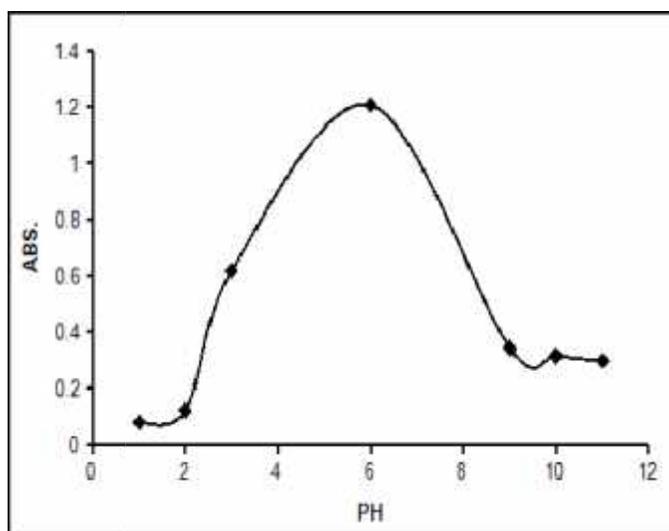
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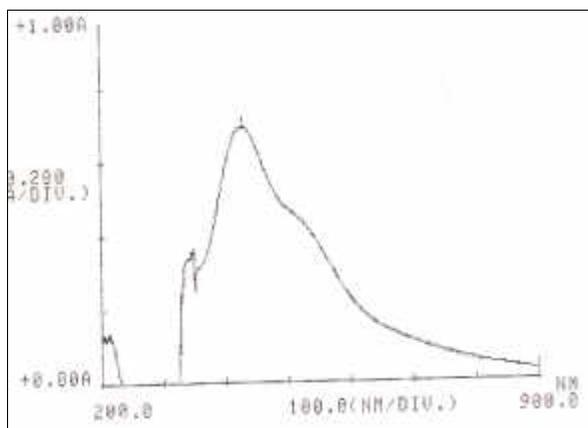
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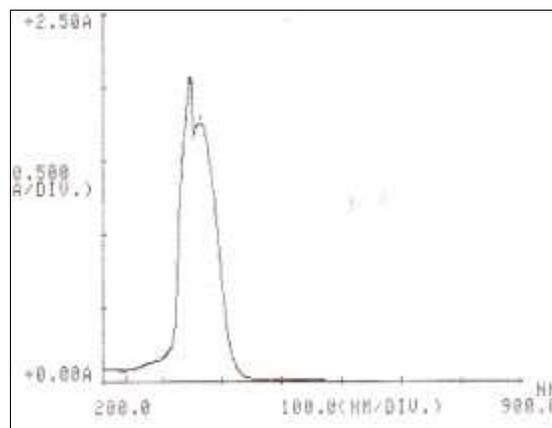
**Fig.(<sup>1</sup>)** : IR spectra of P-bis (4-chloro phenyl-imine) phenylenes



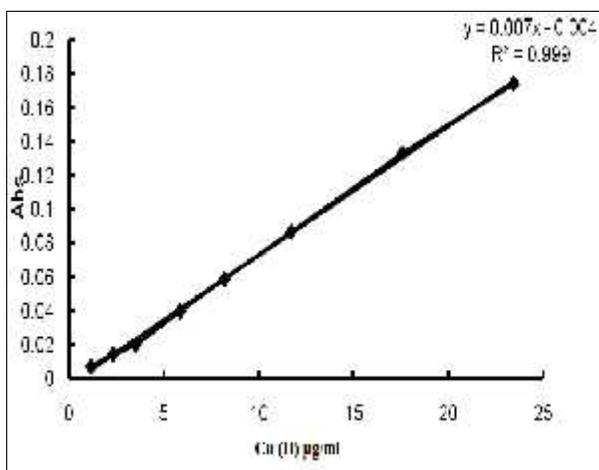
**Fig.(<sup>2</sup>)** : Effect of pH on absorbance. Of [Cu (II)] =  $1.173 \times 10^{-4}$ , [p-b(cpi)p] =  $3.4 \times 10^{-4}$  M;  $\lambda_{\max} = 470$  nm; pH=6



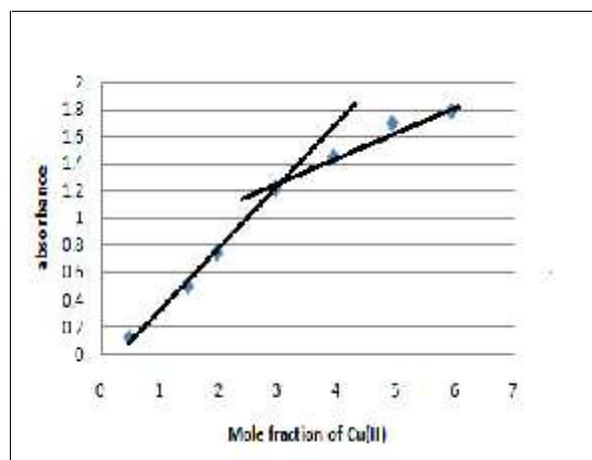
**Fig.(3):**Absorption spectra of [Cu(II)]- [p-b(cpi)p] complex against reagent blank



**Fig.(4):**Absorption spectra for P-bis (4-chloro phenyl-imine) phenylenes



**Fig.(5):** Analytical determination of [Cu(II)] [(p-b(cpi)p)];  $\lambda_{max} = 470 \text{ nm}$ ; pH = 6.



**Fig.(6):**mole ratio Method [Cu (II)] =  $1.173 \times 10^{-3}$  , [p-b(cpi)p]=  $3.4 \times 10^{-4} \text{ M}$ ;  $\lambda_{max} = 470 \text{ nm}$ ; pH=6