

New spectrophotometric determination of copper (II) using an organic reagent derived from imidazole and 4-aminoantipyrine and applied onto different samples

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Abstract

Ligand 2-[(4-antipyrinyl)azo]imidazole were prepared and then react with metal salt in ethanol :water as solvent in 1:1 ratio (metal : ligand) . The complex which have the general formula $[CuLCl_2 \cdot H_2O]$. ligand its metal complex are characterized using metal analysis by Infrared spectra, Electronic spectra, 1H NMR spectral studies, Molar conductance , and Magnetic moment measurements, the measurements indicated that the ligand coordinate with the metal (II)ion in neutral tridentate manner. All the studies reveal coordination sixe for the metal in the complex. Octahedral structures are suggested for metal complex. Determining the trace amounts of Copper (II) was proposed in this paper. The methods was based upon the reaction of Copper (II) with 2-[(4- antipyriyl) azo] imidazole (4- APAA) as organic reagent in order to complex formation. The absorbance of complex, which is directly proportional to Copper (II) concentration at 578 nm. Various parameters that affect the signal response have been optimized in order to get the better sensitivity have been investigated. Absorbance was recorded at pH 8-9, with reagent concentration of 1×10^{-5} mol/l .The observed to be stable at various at temperatures (5-60) °C and for a longer period of time 1440 min. The calibration graph was linear in the range of 1×10^{-5} – 1×10^{-4} mol/l. The practically detection limit was 1×10^{-6} mol/l.

Key word: Copper ion, Organic reagent, Determination

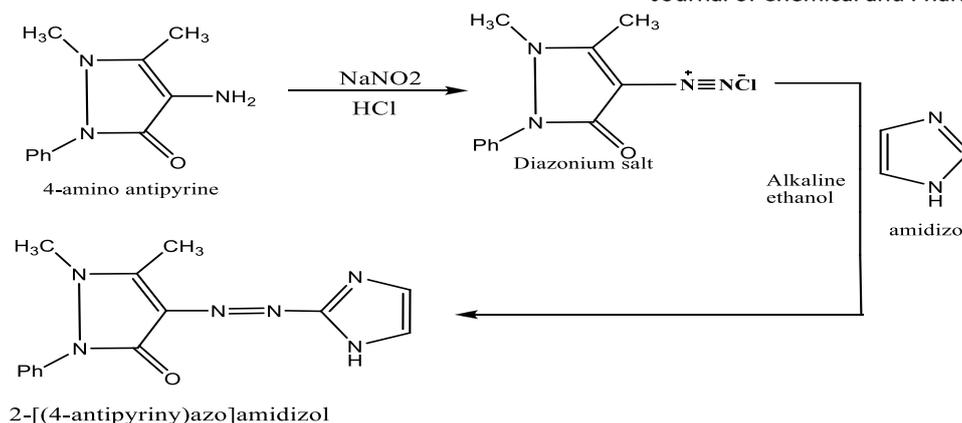
INTRODUCTION

Copper (Cu, At. mass 63.54) occurs in its compounds in II oxidation state, and less often in the copper (I). The properties of copper (I) are similar to those of Ag(I) ,Au(I) and Tl(I). Copper (II) forms ammine, cyanide ,tartrate, and EDTA complexes(Z.Marczenko and M.Balcerzak, 2000).A variety of techniques requiring expensive instrumentation have been applied for the determination of copper (Jana Skrikova and et al ,2011) The voltammetry method used in determination copper at gold microelectrode(Jianmei Zhuang, 2011)and used kinetic spectrophotometric to determine of trace copper (II)ion by their catalytic effect on the reduction of brilliant creasy blue by ascorbic acid (Halil Ibrahim Ulusoy, 2011).A simple spectrophotometric method for the determination of copper in some real, environmental, biological, food and soil samples using salicylic aldehyde benzoyl hydrazine(M.Jamaluddin Ahmed and TasnimaZannat , 2012).Azo compound are very important molecules and have attracted much attention in both academic and applied research(Nishihara H.Multi, 2004). The formation of azo dyes usually involves the reaction between diazole species with coupling components.This class of organic compounds receive attention due totheir use as models for biological systems, Such as inhibition of DNA ,RNA ,and protein synthesis(BadeaM.olar R and et al , 2004)and can also be used as analytical reagents(H.C.Mandalia and V.K.Jain, 2012) Several azo dyes containing imidazole are reported for dyeing of textiles as well as used their as chelating agents for a large number of metal ions, as they form a stable five-member ring after complication with the metal ion(Abbas.S.Abd,Muslem, 2014).Aim of the study is determine the copper (II) by new spectrophotometric method with analytical reagent derived from imidazole and 4-aminoantipyrine and application in different sample.

MATERIALSAND METHODS

All the chemicals were supplied by BHD and Fluke and used without further purification.The electro thermal melting point modern 9300 was used to measure the melting point of the ligand and its complexes. Elemental analyses were carried out by means of micro analytical unit of 1180 C. H. N elemental analyzer. Electronic spectra (in ethanol) were recorded on Shimadzu spectrophotometer double beam model 1700 Uv-Vis spectrophotometer FTIR spectra were recorded in KBr medium on FTIR Shimadzu spectrophotometer made 8400 in wave number $4000-400$ cm^{-1} . The 1H NMR spectra were obtained in DMSO solution using (Broker, Ultra Shield 3000 MKZ, Switzerland). Magnetic susceptibility measurements were carried out on a balance magnetic MSB-MKI using faraday method. The diamagnetic corrections were made by Pascal's constants.

Preparation of the azo ligand HL:2-[(4-antipyrinyl)azo]imidazole: A(2.03gm,0.01mol) from4- aminoantipyrine was dissolved in 4ml of con.HCl and 40ml of water, it is then cooled in ice bath. Then 20ml of (0.7gm, 0.01mol) Sodium nitrite solution was added to the above solution with constant stirring. Cooled solution(30ml)10% NaOH solution of (0.68gm,0.01mol) imidazole was added drop wise to the resulting solution with stirring and the mixture was left for 2hr at 0C°.Red precipitate was filtered and recrystallized from hot ethanol and then dried in over at50 C° for 12hours.



Scheme.1.Preparation of ligand HL(4-APAA)

Preparation of metal complex: The metal complex were prepared by the mixing ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) salt dissolved in water with the 50ml of ethanol solution of azo compound in (1:1) (metal :ligand) ratio. The resulting mixture was stirred for 30min. The precipitated complex were filtered, washed and recrystallized with ethanol several times and dried over anhydrous CaCl_2 in desiccators.

RESULTS AND DISCUSSION

1. Microanalysis: The elemental analysis data the complex as shown in Table 1 exhibit the formation 1:1 [M:L] ratio. It was found that the theoretical values are in a good agreement with the found data. The purity of the azo ligand were tested by TLC technique and C, H and N elemental analyses.

Table.1. Physical data and analysis of the ligand and its complex

Comp.	Color	yield	m.p °C	Formula	Found(called) %				Ohm ⁻¹ cm.mol ⁻¹
					C	H	N	M	
Ligand	Red	75	299	$\text{C}_{14}\text{H}_{14}\text{N}_6\text{O}$	59.21 (59.57)	4.33 (4.96)	29.11 (29.78)	-----	-----
$[\text{CuL}]\text{Cl}_2$	Violet	78	250	$[\text{Cu}(\text{C}_{14}\text{H}_{14}\text{N}_6\text{O})\text{Cl}_2 \cdot 2\text{H}_2\text{O}]$	38.66 (38.98)	3.68 (3.99)	19.33 (19.86)	14.61 (14.74)	0.35

2. IR spectra: In order to clarify the mode of bonding and the effect of the metal ion on the ligand, the IR spectra of the free ligand and the metal complex are studied and assigned based on careful comparison of their spectra with that of the free ligand. Relevant IR bands for the ligand and metal complex are presented in Table 2. The bands in the region 3416 cm^{-1} due to stretching mode of NH in the spectra of the ligand undergo some change in the spectra of the complex. The spectrum of ligand show two band at $1410, 1492 \text{ cm}^{-1}$ due to (N=N) group. This band appearing at 1400 cm^{-1} with different shape and reduced in intensity of the spectra of complex. Band shifted and reduced intensity due to complex formation (Abbas Alisalih Al-hamdani, and Shayma .A. Shaker, 2011). Strong band in 1653 cm^{-1} region in the ligand were observed due to $\nu(\text{C}=\text{O})$ of the Kato group in a pyrazolen ring (Layla Ali Mohammed and et al 2013, K. M. Govindaraju D. Gopi L. Kavitha Inhibiting, 2009).

In the complex, this band are shifted to lower frequency at 1608 cm^{-1} , indicating the coordination of carbonyl oxygen to the metal ion which is further supported by the formation of new bands in the regions $(445-520) \text{ cm}^{-1}$ which are attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ bands respectively [Ali ,A. M., 2004, Muna A. Hadi and et al, 2014]. The spectrum of free ligand show absorption band at 1580 cm^{-1} due to $\nu(\text{C}=\text{N})$ of the N_3 imidazole nitrogen. In the complex, this band are shifted to lower frequency at (1550 cm^{-1}) . These differences suggest the linkage of metal ion with nitrogen imidazole ring (K. Nakmoto, 1978). The complex show a broad band at $(3444) \text{ cm}^{-1}$ that suggests that water is coordinated to the central metal ion (B. Anupama and C. Gyana Kumara, 2011). Also the complex show an intense peak at $(806) \text{ cm}^{-1}$ may be attributed to rocking and wagging modes of coordinated water (Layla. A. Mohammed and et al, 2013).

Table.2. Characteristic IR absorption bands of the ligand and its complex in cm^{-1}

Ligand/complex	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{H}_2\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
Ligand	3416	1653	1585	1492, 1410	---	---	---
$[\text{CuL}(\text{H}_2\text{O})\text{Cl}_2]$	3420	1608	1550	1402	3444, 806	520	445

6.1. Optimum condition of determination process:

A. Effect the pH: The pH of medium was varied in the range 5–12 in order to determine the ideal pH for complexity, the best pH of determination was when the pH = 8–9 and results are shown in Figure 4A, after that preparation the suitable buffer from sodium phosphate and HNO_3 to adjust the pH value. Therefore, the pH 8–9 was chosen for further work.

B. Effect the reagent concentration: The reagent concentration was varied in the range 1×10^{-6} – 5×10^{-4} mol/l in order to maximize the absorbance. Figure 4B shows the effect of reagent concentration on the complexity. The maximum absorbance was obtained with 1×10^{-5} mol/l of reagent. Therefore, the 1×10^{-5} mol/l reagent was chosen for further work.

C. Effect the volume reagent on the determination of metal ion: Prepare the complex by mixing 2 ml of metal ion with different volume of 1×10^{-5} mol/l reagent Figure 4C shows the effect of reagent volume on the determination, the ideal volume for metal ion 2 ml and 2 ml of reagent, the volume ratio was 1 : 1.

D. Effect of the time on complex formation: Conducted a study to determine Stability complex during the time found that the complex was stable during 1440 minutes as a Figure 4D.

E. Effect temperature: Copper ion determination in different temperatures of (5–60) $^\circ\text{C}$ and Figure 4E shown the results, from results found that a stable complex of 0–60 $^\circ\text{C}$ and it begins to dissociation the complex thermal degrees up the 60 $^\circ\text{C}$.

F. Study effect stoichiometric of complex formation: Equivalent been studied using a complex method of mole ratio from results found that was 1:1 (reagent:ion) ratio as Figure 4F.

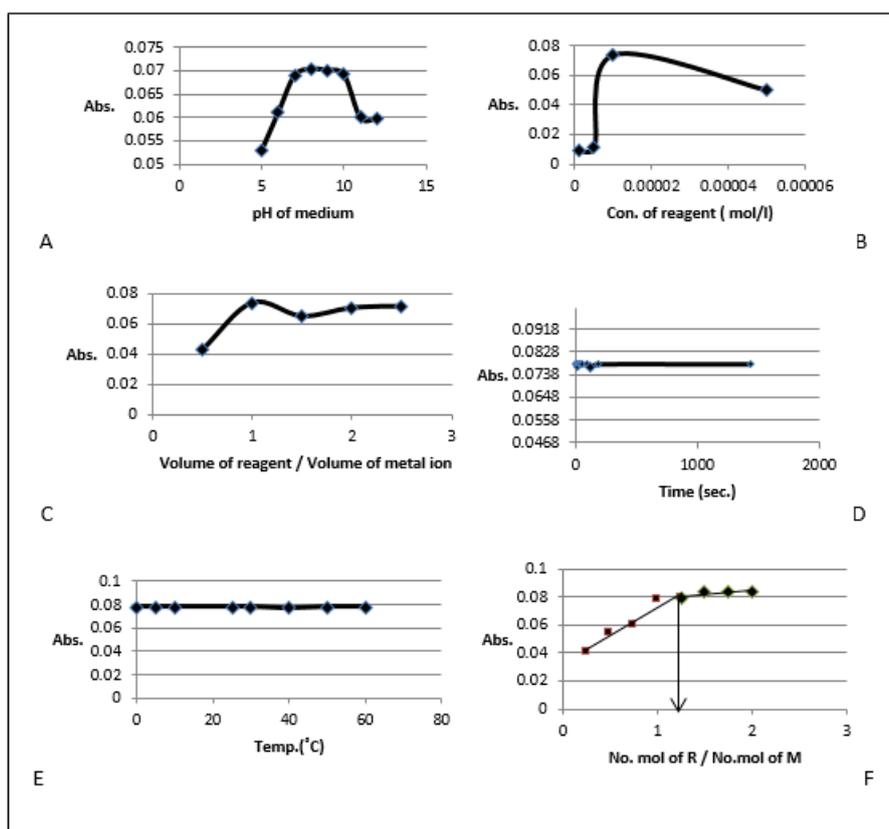


Figure.4. A)Effect of pH on absorbance,B)Effect of con. reagent on absorbance, C)Effect of volume reagent,D) Effect of time on absorbance, E)Effect of temperature on absorbance, F) mole ratio method

6.2. Calibration graph in spectrophotometric method: A series of Cu(II) solutions of the range 1×10^{-6} – 1×10^{-3} mol/l were prepared from stock solutions and under the optimum conditions, the results are shown in Figure 5. The calibration graph was linear in the range of 1×10^{-5} – 1×10^{-4} mol/l. The practically detection limit was 1×10^{-6} mol/l.

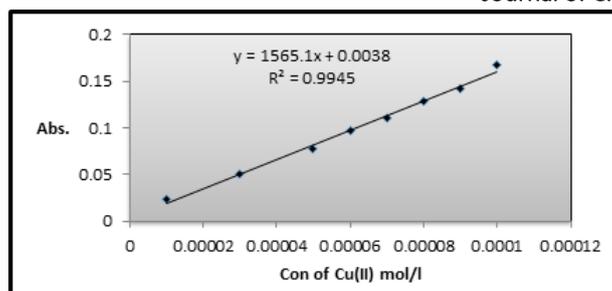


Figure.5. Calibration curve of copper ion

6.3. Interference: We tested the effect of other metal ion interferences on the absorbance of copper complex. The deviations in absorbance due to interference of other ions are reported in Table 3. The greatest absorbance for the copper complex was 0.078, when the exchange was ideal 5×10^{-5} mol/l copper ion in complex. We also tested the effect of action and anions on the absorbance found that absorbance was not deviated due to their presence (K^+ , Na^+ , Co^{2+} , Ni^{2+} , F^- , I^- , $C_2O_4^{2-}$, NO_3^- and CH_3COO^-).

Table.3. Interference of the foreign cations

No.	Metal ion	Con. mol/l	Abs.	Interference	Treatment with masking agent
1	Cd^{2+}	5×10^{-5}	0.067	-0.011	One drop of I^- (0.1 mol/l)
		5×10^{-4}	0.063	-0.015	Two drops of I^- (0.1 mol/l)
2	Hg^{2+}	5×10^{-5}	0.053	-0.025	Two drops of I^- (0.1 mol/l)
		5×10^{-4}	0.043	-0.035	Three drops of I^- (0.1 mol/l)
3	Fe^{3+}	5×10^{-5}	0.061	-0.017	Two drops of I^- (0.1 mol/l)
		5×10^{-4}	0.059	-0.019	Two drops of I^- (0.1 mol/l)
4	Pb^{2+}	5×10^{-5}	0.061	-0.017	One drop of I^- (0.1 mol/l)
		5×10^{-4}	0.041	-0.037	Two drops of I^- (0.1 mol/l)
5	Mn^{2+}	5×10^{-5}	0.065	-0.013	One drop of $C_2O_4^{2-}$ (0.1 mol/l)
		5×10^{-4}	0.060	-0.018	Two drops of $C_2O_4^{2-}$ (0.1 mol/l)

6.4. Application of the method: The proposed method was successfully applied to the determination of Cu(II) in pharmaceutical preparation syrups and milk. The results which are shown in Table 4 indicate that a good recovery was obtained.

Table.4. Analytical applications

Sample	Cu(II) Con. mol/l	Recovery (%) of Cu(II)*
Milk Diallak	0.001	99.99%
Drug Fermera	0.001	97.00%
Vitaqlupin syrup	0.001	97.00%

*Average of three determination.

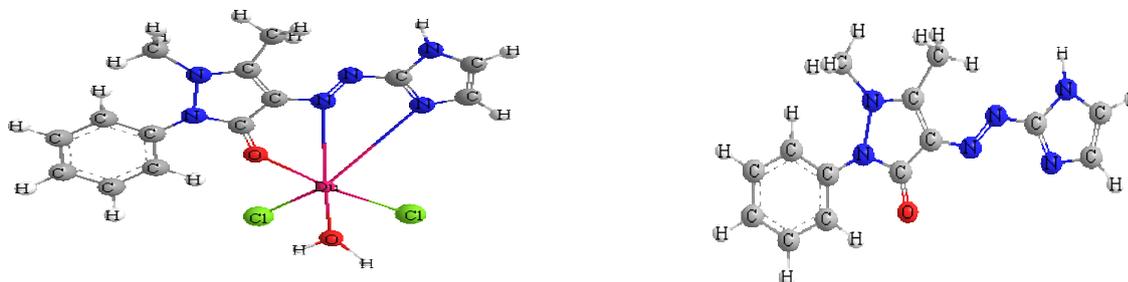


Figure.6. The 3d-geometrical structure for the ligand and complexes

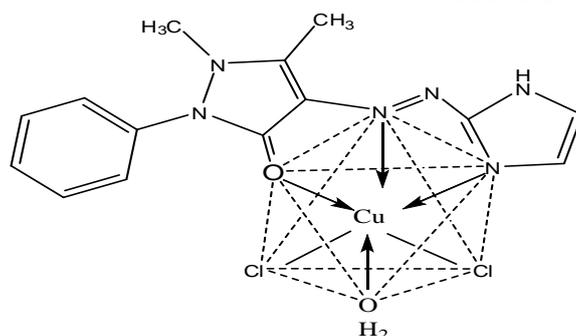


Figure.7.The proposed structural formula of the metal chelate complex

CONCLUSION

This paper report in clouding flowing:

1. The ligand behaves as natural tridentate manner, by coordination with Cu(II) metal ion.
2. The complex an stable and no ionic.
3. The proposed geometry of the complex are octahedral. According to these results the structural formulas of these complex may be proposed in figure 5.
4. The copper complex of new reagent shown maximum absorbance at 578 nm. The ideal parameter for determination of copper ion by new reagent such as the optimum absorbance was recorded at pH 8-9, with reagent concentration of 1×10^{-5} mol/l .The observed to be stable at various at temperatures (5-60) °C and for a longer period of time 1440 min.

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