Preparation and Spectrophotometric Study of Reagent 2-[2⁻-(6-chloro benzothiazolyl) azo]-Resorcinol as an Analytical Reagent for Determination of Nickel (II) and Copper (II) Ions

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Abstract: The present paper describes the preparation of new organic reagent 2-[2⁻-(6-chloro benzothiazolyl) azo]-resorcinol (6-CIBTAR = LH$_2$) and used for the spectrophotometric determination of traces microgram amount of nickel (II) and copper (II) was found to form Ni(II)-CIBTAR at pH 7.5 giving a green coloured complex with maximum absorption at wavelength 636 nm and copper (II) was found to from Cu(II)-CIBTAR at pH 6.5 giving green bluish coloured complex with maximum absorption at wavelength 648 nm. The molar absorptivity ($\in$) of the complexes are 0.3695×10^4 L·mol^{-1}·cm^{-1} and 0.3933×15^4 L·mol^{-1}·cm^{-1} for Ni(II) and Cu(II) respectively. Calibration curves for the determination of nickel(II) and copper (II) conformed to beers law over the concentration rang of (1-20) µg·mL^{-1}. The DL (detection limit), RSD (relative standard deviations), RE (relative errors) and recovery for Ni(II) and Cu(II) complexes were found to be D.L = 0.45, 0.61; R.S.D% = 1.81, 2.04; E$_{rei}$% = 1.3, 0.86 and Re% = 98.7, 99.14 respectively. The analytical data show the metal to reagent ratio (mole ratio method; M:L) in Ni(II) and Cu(II) complexes are 1:2.

Key words: 2-[2⁻-(6-Chloro benzothiazolyl) azo]-Resorcinol, nickel (II), copper(II) spectrophotometry.

1. Introduction

The thiazolyl azo compounds and its derivatives are used in different applications such as synthesis of drugs [1, 2] and used largely as an analytical reagent [3, 4] specially in the spectra determination because of high sensitivity and selectivity [5]. Many benzothiazolyl azo compounds have been synthesized and proposed as highly sensitive chromogenic reagents for the determination of several metal ions and give colored chelating complexes especially with some transition metal ions [6, 8].

Nickel and Copper metals appear together in many real samples. Several techniques such as X-ray, fluorescence [9], atomic fluorescence spectrometry [10], paleography [11], high performance liquid chromatography [12], electrothermal [13] and derivative spectrophotometry [14] have been applied for simultaneous determination of these ions in different samples. The analytical methods are those based on UV-visible spectrophotometry techniques due to both experimental rapidity and simplification.

This paper reports the preparation of new reagent 2-[2⁻-(6-chloro benzothiazolyl) azo]-resorcinol (6-CIBTAR=LH$_2$) and used for spectrophotometric determination of traces micrograms quantities of nickel(II) and copper (II). The method is based on the formation of complexes of Ni(II) and Cu(II) ions with

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reagent (6-CIBTAR).

2. Experimental

2.1 Apparatus and Materials

Absorption spectra in absolute ethanol were recorded using shimadzu, UV-visible 1650 spectrophotometer double beam using 1 cm quartz cells, while absorbed measurements were obtained with RSP-721 UV-visible spectrometer. Functional groups of reagent and its complexes were identified with a FT-IR spectrometer shimadzu 8000, in range (4000-400) cm^{-1} using KBr disc. Elemental analyses were obtained by using micro analytical unit, a C.H.N.O.S. Euro EA 300 elemental analyzer. pH measurements were carried out using a microprocessor 211 pH meter (pH $\pm$ 0.001). The metal content of the complexes was measured using atomic absorption technique by shimadzu AA-160. Electric molar conductivity measurements were carried out room temperature at concentration of 10^{-3} mol in DMF by using digital conductivity meter 214 HANNA. Electro thermal melting point 9300 was used to measure the melting point of reagent and its complexes. All chemical and solvents are of highest purity and used as supplied by manufactures except of 2-amino-6-chloro benzothiazole was prepared as described in the literature [15]. The buffer solution ammonium acetate was prepared as described earlier [16]. All solutions were prepared using deionized water.

2.2 Preparation of the Reagent

The azo reagent is prepared by coupling reaction of diazonium salt solution of 2-amino-6-chloro benzothiazole with appropriate amount of resorcinol as coupling compound in alkaline solution, as seen in Fig. 1. 2-Amino-6-chloro benzothiazole (1.38 gm; 0.01 mol) was dissolved in 5 mL of concentrated hydrochloric acid then 40 mL of cold distilled water was added. This solution was (0.75 gm; 0.01 mol) of sodium nitrate in 20 mL of disilled water was added drop wise at 0-5 °C, and left stirring to stand 50 min. The resulting diazonium chloride solution was added drop wise with cooling to a solution of resorcinol (1.1 gm, 0.01 mol) dissolved in 100 mL alkaline ethanol. The mixture was allowed to stand overnight and neutralized with dilute hydrochloric acid at pH = 6.0. The solid product was filtered off, washed with cold distilled water and recrystallized twice from hot ethanol and then dried in oven at 60 °C for several hours.

2.3 Preparation of Metal Complexes

The Ni(II)-complex and Cu(II)-complex were prepared by dissolving (3.06 gm, 0.01 mol) of reagent in 50 mL hot ethanol and added dropwise with stirring
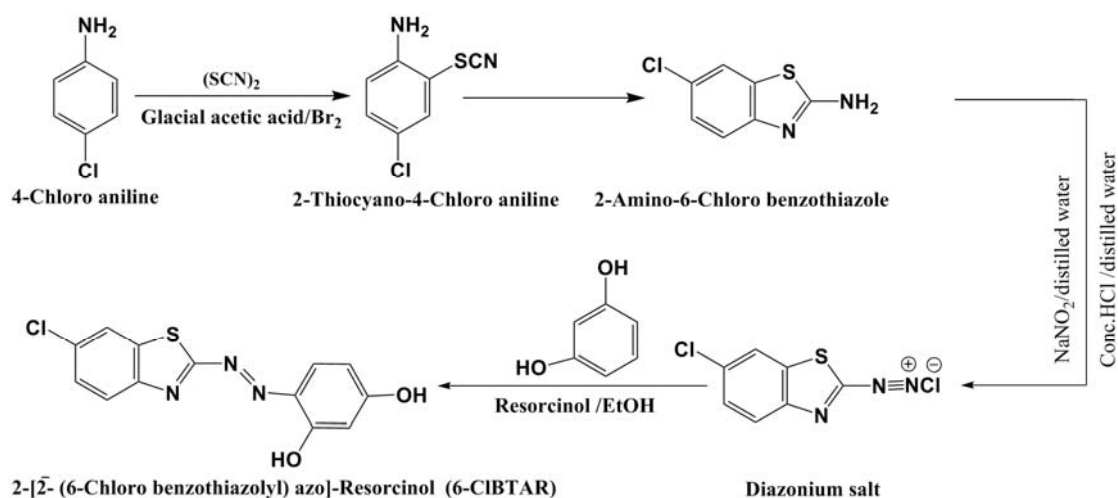

Fig. 1 Preparation of the reagent (6-CIBTAR).

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to an aqueous solution of Ni(II) and Cu(II) chlorides (0.005 mol) in 20 mL of suitable buffer solution (mole ratio method; M:L=1:2) The mixture was stirred at room temperature for 50 min, and left overnight. The complexes were filtrated and the precipitates were washed with hot ethanol and distilled water and dried in oven at 60 °C for Several hours.

2.4 Standard Ni(II) Solution

This solution was prepared by dissolving (0.4050 gm) of $NiCl_2 \cdot 6H_2O$ in 100 mL deionized water working standard Ni(II) solutions (1,000 ppm) were prepared by simple dilution of the appropriate volume of the standard Ni(II) solution (1,000 ppm) with distilled water.

2.5 Standard Cu(II) Solution

A stock solution of Cu(II) (1,000 ppm) was prepared by dissolving (0.2680 gm) of $CuCl_2 \cdot 2H_2O$ in 100 mL deionized water, working solutions were prepared freshly by appropriate dilution of the stock solution.

2.6 Standard Reagent Solution

A solution of 1×10^{-3} M was prepared by dissolving (0.075 gm) of reagent (6-CIBTAR) in 250 mL of ethanol.

2.7 General Procedure

1 mL of solution containing less than 100 μ g·mL^{-1} of copper and Nickel were transferred to 10 mL calibrated flash and adjust the pH to 6.5 and 7.5 with ammonium acetate buffer, add 3 and 5 mL from 1×10^{-4} M ethanolic (6-CIBTAR) solution and diluted to

the mark with deionized water. The absorbance of the resultant solution was measured after 10 min at 636 nm and 648 nm at 25 °C against a reagent blank prepared in a similar way but without analyte.

3. Results and Discussion

3.1 Some Physical Properties of the Reagent and its Complexes

The reagent is orange crystals melting at 138 °C, which is in soluble in water but soluble in most organic solvents such as ethanol, methanol, acetone, ether, benzene, carbon tetra chloride, chloroform and DMF. Red and yellow color solution obtained when his reagent dissolved in strongly acidic solution and alkaline solution media respectively. The reaction of the reagent (6-CIBTAR) with the Ni(II) and Cu(II) ions gives different color crystals. These complexes are stable in air and insoluble in water but soluble in most organic solvents.

Some physical and analytical data of reagent (6-CIBTAR) and its complexes (Ni(II) & Cu(II)) which are recorded in Table 1.

3.2 Infrared Spectra

IR spectra data of the reagent (6-CIBTAR) and their complexes are summarized in Table 2. These are complicated due to the extensive overlap of a number of bands arising from υ(O-H), υ(C=N) and υ(N=N) groups in addition f other bands originated from phenyl and thiazole rings appeared in the region 4000-400 cm^{-1}. The shifts in the position of these bands compared with those absorption bands due to the free reagent suggest the probable modes of bonding

Table 1 Analytical and physical data of the reagent (6-CIBTAR) and its complexes.

Comound	Color	m.p °C	Yield%	Molecular formula (Mol.Wt)	Found (Cac.)%				
					C	H	N	S	M
6-CIBTAR=LH$_2$	Orange	138	82	C$_{13}$H$_8$N$_3$O$_2$SCl(305.74)	51.07 (51.29)	2.64 (2.78)	13.74 (13.98)	10.62 (10.49)	-
[Ni(LH)$_2$]·H$_2$O	Green	167	58	C$_{26}$H$_{16}$N$_6$O$_5$S$_2$Cl$_2$Ni (686.16)	45.28 (45.51)	2.26 (2.35)	11.94 (12.25)	9.58 (9.34)	8.83 (8.55)
[Cu(LH)$_2$]·H$_2$O	Green bluish	189	76	C$_{26}$H$_{16}$N$_6$O$_5$S$_2$Cl$_2$Cu (691.02)	44.97 (45.19)	2.24 (2.33)	11.95 (12.16)	9.42 (9.28)	9.39 (9.20)

Table 2 The optimal pH values, optimal concentration, wavelength (λ_{max}), geometry and hybridization of complexes in aqueous ethanolic solution 50% V/V.

Reagent	Metal Ions	Optimal pH	Optimal Conc x 10^{-5} M	λ_{max} nm	Absorption bands (cm^{-1})	Geometry	Hybridization
λ_{max} = 432 nm Conc = 1.75 × 10^{-5} M ϵ= 2.611 × 10^4 L·mol^{-1} cm^{-1}	Ni(II)	7.5	1.25	636	15723	Octahedral	sp^{3}d^2 highspin
	Cu(II)	6.5	2.00	648	15432	Octahedral distorted	sp^{3}d^2

in the complexes. Some of these main shifts and conclusion are given bellow.
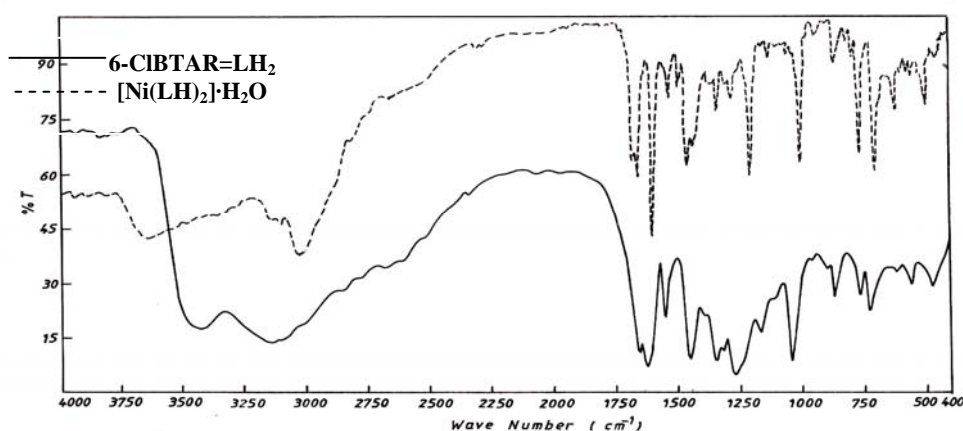
The spectrum of azo reagent showed abroad weak band around (3430-3465) cm^{-1} due to υ(O-H). This suggest a strong intermolecular hydrogen bonding [17, 18]. In the spectra of Ni(II)-complex and Cu(II)-complex, the broad weak absorption bond around 3580 cm^{-1} and 3535 cm^{-1} due to meta hydroxyl group υ(O-H) respectively [19].

The weak bands observed at 3125 cm^{-1} and 2985 cm^{-1} in the spectrum of reagent which are due to υ(C-H) aromatic and aliphatic respectively, these bands are stable in position in both reagent and metal complexes [20]. The band observed at 1625 cm^{-1} in reagent spectrum is considered to be υ (C-N) of thiazole ring [21], this band is shifted to a lower frequencies at 1600 cm^{-1} and 1595 cm^{-1} in the complexes spectra of Ni(II) and Cu(II) respectively with alittle change in shape. These differences suggest a linkage of metal ions with nitrogen atom of thiazole ring [22].

The spectrum of free reagent shows two absoption bands at 1530 cm^{-1} and 1485 cm^{-1} due to azo group υ(N=N). The position of these bands in the spectra of

the prepared complexes are shifted to a lower frequencies at (1505, 1470) cm^{-1} and (1435, 1425) cm^{-1} with decreased in intensity. This shift could be attributed to the metal-azo back bounding [23, 24]. Another bands appeared at 1275cm^{-1} and 855 cm^{-1} in the free reagent spectrum, due to υ(C-S) of the hetero cyclic thiazole ring [25]. The unchanged of these bands in Ni(II)-complex and Cu(II)-complex means that the sulpher atom of the heter cyclic ring does not participate in coordination [22, 26]. The IR spectrum of the free reagent shows a medium band at 715 cm^{-1} assignable to the υ(C-Cl) of benzothiazole ring. This band remains in the same region in free reagent and in solid complexes spectra [27].

Some other new bands appear in the region of (540-465) cm^{-1} in the complexes spectra, which are not present in the spectrum of the free reagent may attributed to the υ(M-O) and υ(M-N) [28, 29]. Thus the above IR spectra data leads to suggest that the reagent behaves as a tridentate chelating agent coordinating through the position of phenolic oxygen (ortho OH), nitrogen of azo group and thiazole ring nitrogen. Fig. 2 shows the spectra of reagent (6-CIBTAR) and Ni(II)-complex.

Fig. 2   FT-IR spectra of the reagent (6-CIBTAR = LH$_2$) and [Ni(LH)$_2$]·H$_2$O.

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3.3 Absorption Spectra

The absorption spectra of reagent (6-CIBTAR) and their complexes in absolute ethanol medium are shown in Fig. 3. The wavelength for the maximum absorption (λ_{max}) is located at 432 nm but these colored complexes have a maximum for absorption (λ_{max}) at 636 nm for Ni(II)-complex and 648 nm for Cu(II)-complex. The wavelength difference ($\Delta\lambda_{max}$) is (204-216) nm. The reagent reacts immediately with Ni(II) and Cu(II) ions forming an green and green bluish complexes in aqueous ethanolic solution at pH = 7.5 and 6.5 respectively. The absorbance reached its maximum with 15 min, and remained stable for at least 24 h at room temperature.

3.4 Effect of pH

The effect of pH on the absorbance of metal complexes solutions which determined the optimal pH in each case are shown in Fig. 4. The final pH of each aqueous solution was measured at 636 nm for Ni(II)-complex and 648 nm for Cu(II)-complex after stable the wavelength for the maximum absorption(λ_{max}) with optimal concentration for the complexes solution. The optimal pH, optimal concentration and wavelength (λ_{max}) with molar absorptivity ($\in$) for Ni(II) and Cu(II) complexes are shown in Table 2.
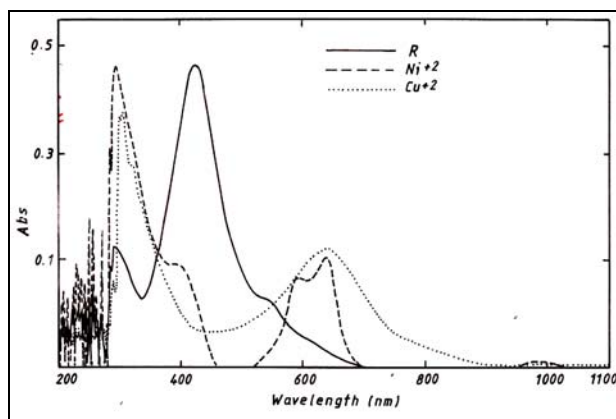

Fig. 3 Absorption spectra of reagent (R = 6-CIBTAR) and its complexes, Conc. = 1.75×10^{-5} M for reagent; Ni^{+2} Cnoc. = 1.25×10^{-5} M; pH = 7.5; and Cu^{+2} Conc. = 2.0×10^{-5} M; pH = 6.5, in aqueous ethanolic solution 50%(V/V).

3.5 Effect of Reagent Concentration

For up to 40 µg·ml^{-1} of Ni(II) and Cu(II), about (3-5) mL of 1.75×10^{-5} mol/L of reagent (6-CIBTAR) solution has been found to be sufficient for a complete reaction and develop the color to its full intensity, and give a minimum blank value and was considered to be optimum for the concentration range 1.25×10^{-5} mol/L and 2.0×10^{-5} mol/L of Ni(II) and Cu(II) ions respectively.

3.6 Effect of Time

After mixing the components, the absorbance reaches its maximum within 15 min, at room temperature and remains stable for 5 h in aqueous solution. The chelates complexes of Ni(II) and Cu(II) are stable at least 24 h, when it was used the ethanolic solution medium. The results are shown in Fig. 5.

3.7 Effect of Temperature

The effect of temperature on the absorbance of the Ni(II)-complex and Cu(II)-complex were studied.
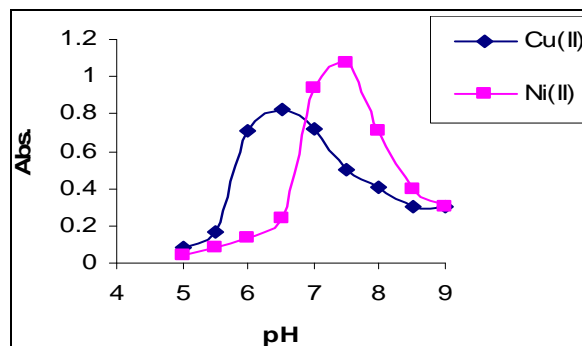

Fig. 4 Effect of pH an absorbance of 6-CIBTAR-metal chelats. Reagent Conc. = 1.75×10^{-5} M; Ni(II) Conc. = 1.25×10^{-5} M; Cu(II) Conc = 2.0×10^{-5} M.
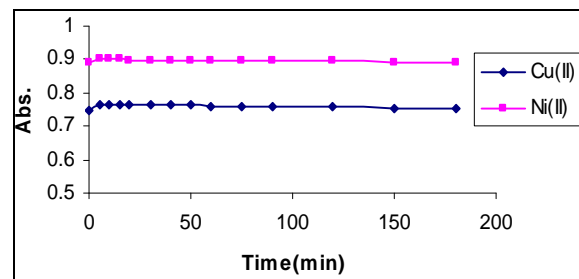

Fig. 5 Effect of time on the absorbance of Ni(II)-complex and Cu(II)-complex.

The study was performed at temperature between 10 °C and 70 °C. The maximum absorption was obtained when the temperature was varied between 20 °C and 30 °C at higher temperature than 35 °C. The absorbance gradually decreased with increasing temperature until it reaches 70 °C, which may be attributed to dissociation of the chelates complexes. The results are shown in Fig. 6.

3.8 Conductivity Measurements

The chelat complexes of Ni(II) and Cu(II) ions with the reagent 6-CIBTAR give a molar conductions value 14.03 S·cm^2·mol^{-1} and 11.67 S·cm^2·mol^{-1} respectively in DMF (10^{-3} M) at room temperature. The values of conductivity indicate the complexes of Ni(II) and Cu(II) ions are a non-electrolytes nature, where suggest that no anions present outside the coordination spheres [30].

3.9 Composition and Stability Constant of Complexes

The composition of the chelat complexes were determined by mole ratio method. This methods showed that the molar ratio of Ni(II) and Cu(II) ions to reagent 6-CIBTAR are 1:2 (M:L). The stability constant (β) are found to be 6.5×10^{10} L·mol^{-2} and 3.4×10^{10} L^2·mol^{-2} for Ni(II) and Cu(II) complexes respectively. The structural formula of prepared complexes can be suggested and showed in Figs. 7 and 8.

From the previous mentioned chemical analysis data, we can suggest the following geometrical structure for the prepared chelate complexes as shown in Fig. 9.
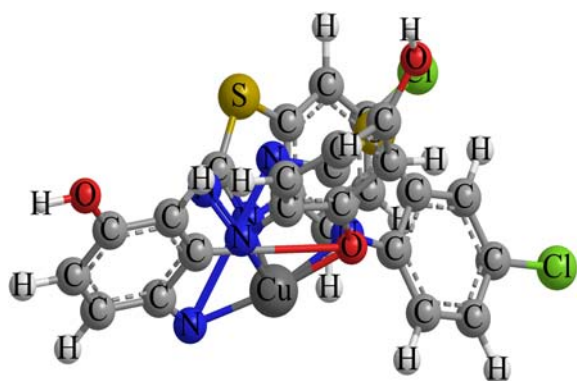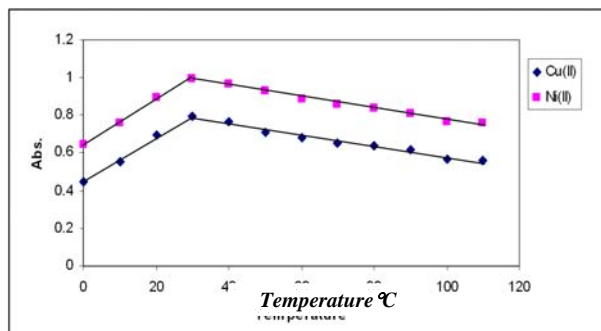

Fig. 6   **Effect of temperature on the absorbance of Ni(II)-complex and Cu(II)-complex.**
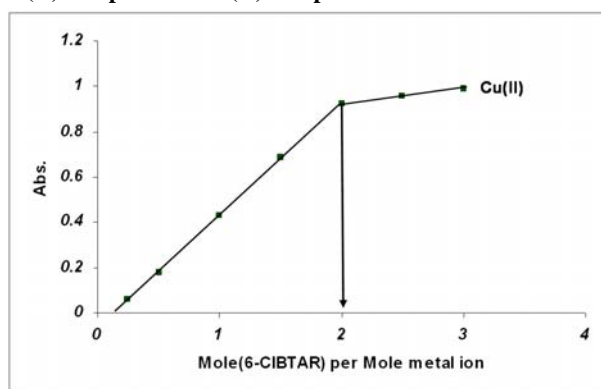
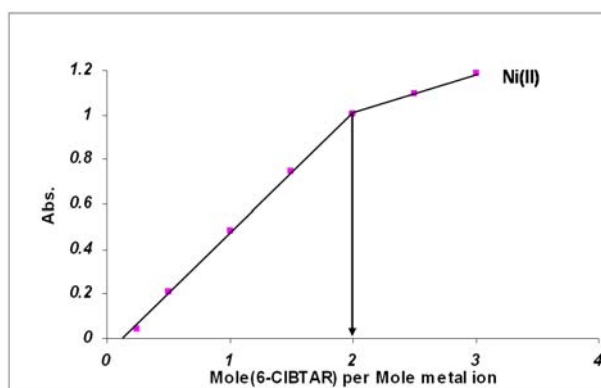**Fig. 7**   **Mole ratio method for Cu(II)-complex at pH = 6.5.**

Fig. 8   **Mole ratio method for Ni(II)-complex at pH = 7.5.**

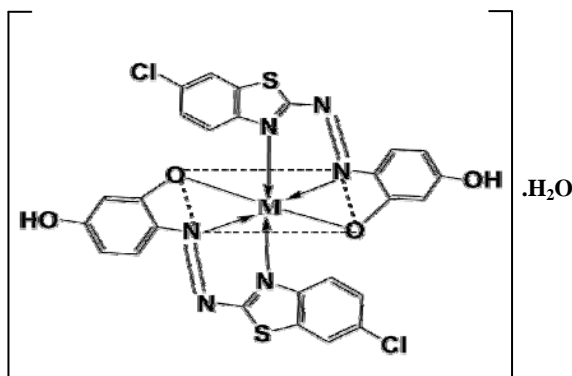**Fig. 9**   **The proposed structural formula of Ni(II) and Cu(II)-complex.**

Table 3   The Sandell's sensitivity, accuracy and precision of the method.

Complex	Sandell's sensitivity($\mu g \cdot cm^{-2}$) $\times 10^{-3}$	R.S.D%	Re%	D.L	$E_{rel\%}$	Sensitivity ($L \cdot mol^{-1} \cdot cm^{-1}$) $\times 10^4$
[Ni (LH)$_2$]·H$_2$O	16.039	1.81	98.7	0.45	1.31	0.3659
[Cu(LH)$_2$]·H$_2$O	16.157	2.04	99.14	0.61	0.86	0.3933

3.10 Calibration Curve and Sensitivity

The calibration curve show that beers law is obeyed in the concentration range of 1-20 ppm of Ni(II)-complex and Cu(II)-complex. The sandell's sensitivity, correlation coefficient(r), relative error (Re%), percentage relative standard deviation (R.S.D%) and detection limited (D.L) for complexes were show in Table 3. These results indicating that this method is high accuracy and precision.

4. Conclusions

In this paper, the preparation and identification of new tridentate heterocyclic azo reagent derived from benzothiazolyl azo and its complexes with Ni(II) and Cu(II) metal ions were investigated. The preparation of reagent (6-CIBTAR) is very simple and the proposed method is more simple, speed and sensitive to determination of nickel and copper. All complexes show octahedral stereo chemistry. The Ni(II)-complex and Cu(II)-complex under optimum conditions are stable to more than 24 h.

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