

SYNTHESIS, SPECTRAL, DYEING PERFORMANCE AND BIOLOGICAL ACTIVITY STUDIES OF AZO DYES COMPLEXES WITH SOME METAL IONS

AMER J. JARAD & ZANIAB SALMAN KADHIM

Department of Chemistry, College of Education for Pure Science, Ibn-Al-Haitham
University of Baghdad, Adhamiyah-Anter Square, Baghdad, Iraq

ABSTRACT

Some azo compounds were prepared by coupling the diazonium salts of amines with 2,4-dimethylphenol. The structure of azo compounds were determined on the basis of elemental analyses, $^1\text{H-NMR}$, FT-IR and UV-Vis spectroscopic techniques. Complexes of nickel(II) and copper(II) have been synthesized and characterized. The composition of complexes has been established by using flame atomic absorption, (C.H.N) Analysis, FT-IR and UV-Vis spectroscopic methods as well as conductivity magnetic susceptibility measurements. The nature of the complexes formed were studied following the mole ratio and continuous variation methods, Beer's law obeyed over a concentration range (1×10^{-4} - 3×10^{-4} M). High molar absorptivity of the complex solutions were observed. Analytical data revealed that all the complexes exhibited 1:2 metal-ligand ratios. On the basis of physicochemical data tetrahedral geometries were assigned for the complexes. Biological activity of the ligand and complexes were screened. In addition, the dyeing performance of the prepared ligands and their complexes were applied on cotton fabric. The dyes were tested for light and detergent fastness.

KEYWORDS: Metal Complexes, Synthesis Dyes, Biological Activity

INTRODUCTION

Azo dyes are characterized by the presence of one or more azo group ($-\text{N}=\text{N}-$) in molecular structure^(1,2). These compounds represent the single largest chemical class industrial colorants⁽³⁾. Azo compounds are the oldest and largest class of industrial synthesized organic dyes due to their versatile application in various field, such as dyeing textile fiber, biomedical studies, advanced application in organic synthesis and high technology areas such as laser, liquid crystalline displays, electro-optical device and ink-jet printers^(4,6). The coordination complexes of transition metals with azo ligands are of current attraction due to the interesting physical, chemical, photophysical and photochemical, catalytic and different material properties⁽⁷⁻⁹⁾. Recently, azo metal chelates have also found great attention due to their important electronic and geometrical structures in connection with their application for molecular memory storage⁽¹⁰⁾. In this work, a ligands of azo functional group derived from 3- and 4-aminobenzoic acid as diazo component and 2,4-dimethylphenol as coupling agent, were prepared. The complex of this ligand with some metal ions has been prepared and characterized physicochemically.

EXPERIMENTAL

Instrumentation

UV- Vis spectra were recorded on a Shimadzu UV- 160A Ultra Violet-Visible Spectrophotometer. IR- spectra were taken on a Shimadzu, FT-IR- 8400S Fourier Transform Infrared Spectrophotometer in the $4000- 400 \text{ cm}^{-1}$ spectral region with samples prepared as KBr discs. Atomic absorption was obtained using a Shimadzu A.A-160A Atomic

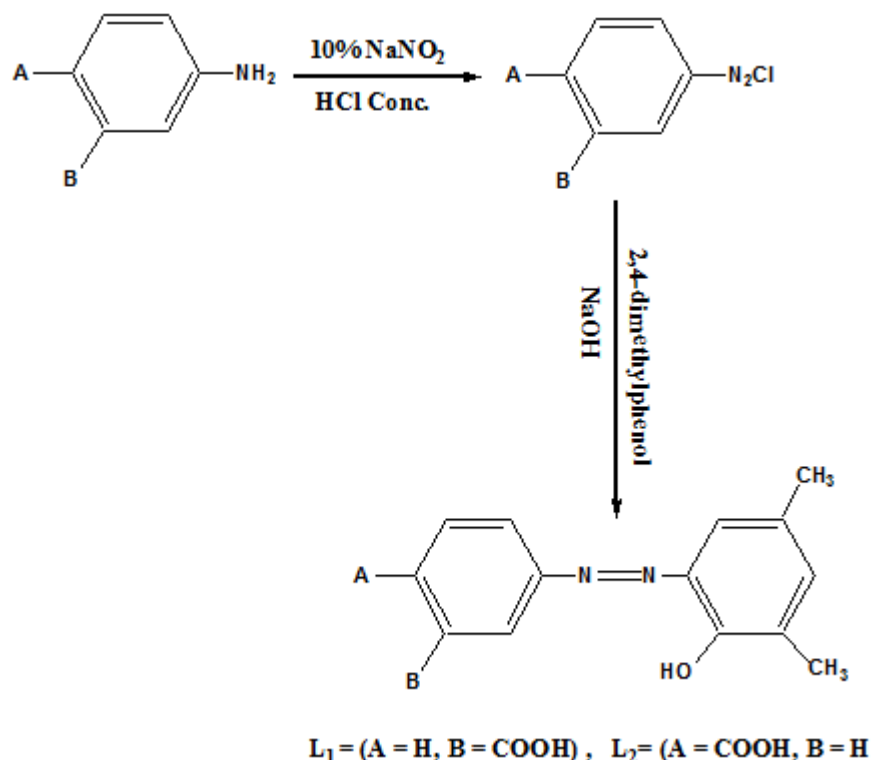
Absorption/Flame Emission Spectrophotometer. The $^1\text{H-NMR}$ spectra were recorded on a Bruker-300 MHz Ultra Shield spectrometer at the University of Al- al- Bayt using DMSO as the solvent and TMS as the reference. Microelemental analysis (C, H, N) were performed at the Al- al- Bayt University, Jordan, using Euro vector EA 3000A Elemental Analyser. Conductivities were measured for 10^{-3} M solutions of complexes in ethanol at 25°C using Philips PW- Digital Conductimeter. Magnetic properties were performed by using Auto Magnetic Susceptibility Balance Sherwood Scientific instrument at 25°C . In addition, melting points were obtained using Stuart Melting Point Apparatus.

MATERIALS AND REAGENTS

The following chemicals were used as received from suppliers: nickel chloride hexahydrate 99.9% and copper chloride dihydrate 99.8%(Merck), 3-aminobenzoic acid, 4-aminobenzoic acid and 2,4-dimethylphenol (B.D.H).

Preparation of the Ligands⁽¹¹⁾

A solution was prepared, of amines (0.342 g, 1mmole) in (10ml) of EtOH containing (2ml) conc. HCl which was diluted with 10 ml H_2O , and diazotized at 5°C with 10% solution of NaNO_2 . The diazotized solution was added drop wise with stirring to a cooled ethanolic solution of (0.305 g, 1mmole) of 2,4-dimethylphenol. Then 25 ml of 1M sodium hydroxide solution was added to the dark colored mixture and precipitation of the azo ligand was observed. This precipitate was filtered, washed several times with (1:1) ethanol: water, mixture then left to dry. The reaction is shown in scheme 1, while Table 1 describes the physical properties and elemental analysis.



Scheme 1: Synthesis of the Azo Ligands

Buffer Solution

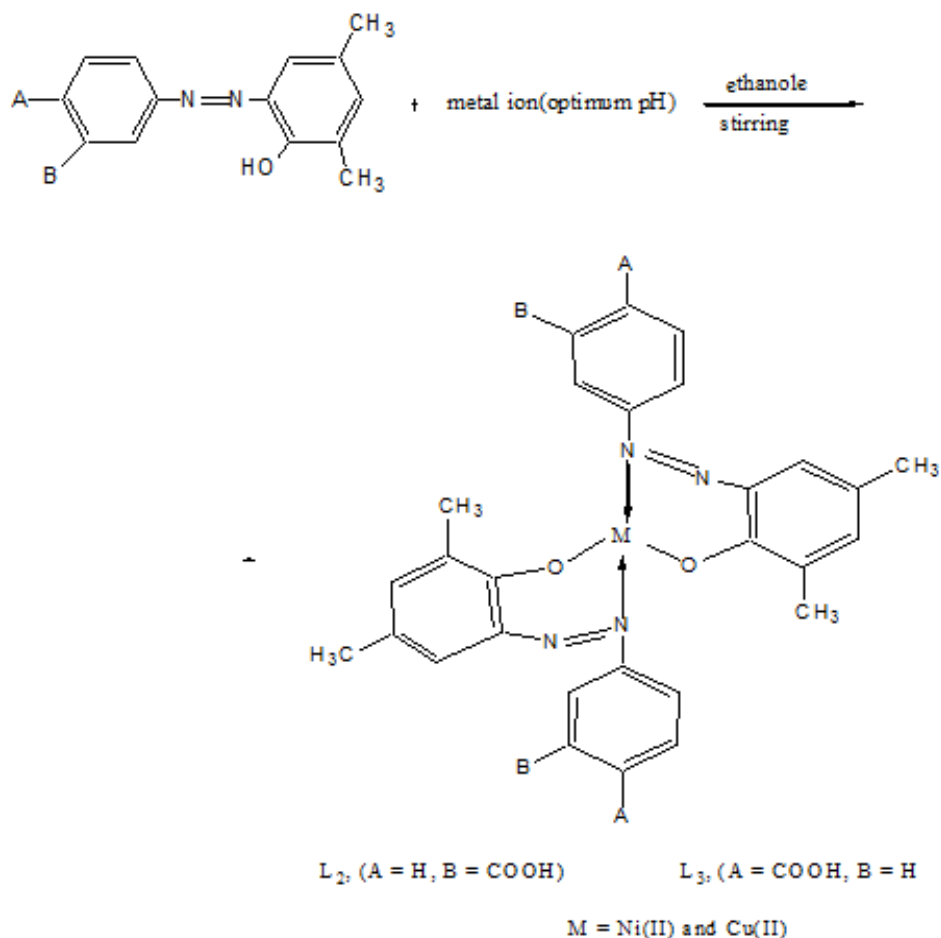
0.01M, 0.771 gm) of ammonium acetate was dissolved in one liter of doubly deionized water. For adjusted pH range (4-9) was used acetic acid or ammonia solution.

Standard Solution

A series of standard solutions of metal chlorides of [Ni(II) and Cu(II)] were prepared in different concentration (10^{-5} - 10^{-3} M) at pH range (4-9). At the same time a series of ethanolic solutions of ligand within the range of concentrations (10^{-5} - 10^{-3} M) was also prepared.

Preparation of Metal Complexes (General Procedure)

An ethanolic solution of the ligand (0.270g, 2mmole) was added gradually with stirring to the 0.118g NiCl₂.6H₂O and CuCl₂.2H₂O, respectively dissolved in the buffer solution with the required pH. The mixture was cooled until dark colour precipitate was formed, filtered, and washed several times with 1:1 water: ethanol mixture, then with acetone.



Scheme 2: The Expected Structure of the Metal (II) Complexes of (L₁ and L₂)

Study of Biological Activity

The antibacterial activity for these compounds was evaluated by using method similar with the traditional disc diffusion method^(12,13), sterile 5 mm filter paper discs (Whatman,no.1) were soaked in this compound (Disc loaded with the DMSO as a solvent and as a control) and allowed until complete evaporation to be used. Then discs were placed onto the surface of the Muller Hinton agar plates at different areas on the surface of each plate, after a 24 hr culture of the pathogenic strains (E.Coli, S.aureus and B.cereus) were spreading over the surface of Muller Hinton agar plates with a

sterile cotton swab. The plates were incubated at 37C° for 24 hr. Results were indicated by recording the diameter (mm) for a zone of inhibition around each disc on the plate.

Dyeing Method

The dyeing properties of the prepared ligand and their complexes were tested on "Hilla- Fine Textile State Company" using the Azoic Dyes Method. Dyes were applied on cotton fabric as (1% shade). The dyeing of the fabric was done at (15- 20C°) for (1 hr), and at pH (10).

RESULTS AND DISCUSSIONS

For the preparation of the ligands (L₁ and L₂) a coupling of 3,5-dimethylphenol with the appropriate diazotized in alkaline solution was carried out. The solubility of the ligands was investigated and was found to be soluble in organic solvents and was stable toward air and moisture. Synthesized ligands were characterized by ¹H-NMR, FT-IR, Elem. Anal. (C,H,N) and UV-Vis spectroscopic technique. An aqueous-ethanolic solutions were always performed to study the interaction of the metal ions Ni(II) and Cu(II) with the prepared ligands. The Colors of these mixed solutions over the molar concentration and acidity range performed were varied from brown to red.

¹HNMR Spectrum

The ¹HNMR spectrum of the ligand (L₂) in DMSO (Figure 1) shows multiplet signals at δ=6.886-8.105 ppm refers to aromatic protons⁽¹⁴⁾. On the other hand, the signal at δ=6.747 ppm due to proton of phenol⁽¹⁵⁾. Whereas, the signal at δ=13.11 ppm is assigned to proton of carboxylic group⁽¹⁶⁾. The signal at δ=2.236 ppm due to δ(CH₃) of phenol and the signal at δ=2.50 ppm referred to DMSO-d₆⁽¹⁷⁾.

Calibration Curve

Several molar concentration (10⁻⁵–10⁻³ M) of mixed aqueous-ethanolic of ligands and metal ions, only the concentration in the range (1-3×10⁻⁴M) obeyed Beer's law and appeared perspicuous intense color. Best fit straight lines were obtained with correlation factor R>0.9980 as shown in Figure 2.

Optimum Conditions

To investigate the interaction between the prepared ligands and metal ions under study for the preparation of the complexes, the spectra of blending solutions for the ligand and metal ions to reach to optimum pH and concentration, as well as fixed wave length (λ_{max}) were studies first. Then mole ratio metal to ligand (M:L) was appointed to prepare the complexes. Optimum concentration was chosen for complex solution based on which solution gives the highest absorbance at constant (λ_{max}) at different pH, and results are described in Table 2.

The empirical results proved that the absorbance of all prepared complexes are maximum and constant in a buffer solution of ammonium acetate in the pH range (4-9). It was found that all prepared complexes had optimum pH as is shown in Figure 3.

Stoichiometry of Complexes

The composition of complexes formed in solutions has been established by mole ratio and job methods. In both cases the results reveal a 1:2 metal to ligand (L) ratio. A selected plot is presented in Figure 4. Table 2 summarizes the results obtained, as well as conditions for the preparation of the complexes.

Physical Properties

The solid complexes have been prepared by direct reaction of alcoholic solution of the ligands (L_1 and L_2) with the aqueous solution of the metal ions at the optimum pH and in a M:L ratio of 1:2. The result of C.H.N analysis and the metal content of these complexes were in good agreements with the calculated values. The molar conductance of 10^{-3} M in ethanolic solutions of these complexes indicated their non- electrolytic nature;⁽¹⁸⁾ data are presented in Table 2. The magnetic susceptibility for all prepared complexes (Table 2) have been found to be paramagnetic (high spin) which has been reported for most tetrahedral geometry⁽¹⁹⁾.

Determination of Stability Constant and Gibbs Free Energy

The successive stability constant (K) of the (1:2) metal: Ligand complex can be calculated from the relationship.

$$K = \frac{1 - \alpha}{4\alpha^3 C^2} ; \quad \alpha = \frac{A_m - A_s}{A_m}$$

Where c = the concentration of the complex solution in mole/ L α = degree of dissociation, A_s = the absorption of solution containing a stoichiometric amount of ligand and metal ion and A_m = the absorption of solution containing the same amount of metal and excess of ligand. The high values of (K) refers to high stability of prepared complexes⁽²⁰⁾. The thermodynamic parameters of Gibbs free energy (ΔG) were also studied. The ΔG data have been calculated from the equation⁽²¹⁾.

$$\Delta G = -R T \ln k$$

Where; R = gas constant = $8.3 \text{ J.mol}^{-1}.\text{K}$, T = absolute temperature (Kelvin). All results were recorded in Table 3. The negative value of (ΔG) indicates that the reaction between (L_1 and L_2) and metal ions understudy are spontaneous.

Electronic Spectra

The UV-Vis spectra of the prepared ligands and their complexes dissolved in ethanol (10^{-3} M) have been measured and the data obtained are included in Table 2. The UV- Vis spectra of an ethanolic solution of the ligands 10^{-3} M displayed mainly three peaks, the first and second peaks were observed within the ranges (250-252 nm) and (332-338 nm) were assigned to the moderate energy $\pi - \pi^*$ transition. The third peak was observed in the range (392- 402 nm) was referred to the $n - \pi^*$ transition^(22,23). The spectra of Ni(II) complexes appeared absorption peaks in the ranges (252-4056 nm) were related to ligand field, then other peak in the $[\text{Ni}(L_1)_2]$ spectrum at 397 nm was assigned to charge transfer. The peaks at 683 and 732 nm due to electronic transition type^(24,25) ${}^3T_{1(F)} \rightarrow {}^3T_{1(P)}$. The spectra of Cu(II) complexes showed peaks at the ranges (238-342 nm) due to ligand field. Other two peaks at 464 and 485 nm found to be caused by charge transfer. The peaks at 978 and 980 nm due (d-d) electronic transition type⁽²⁶⁾ ${}^2T_2 \rightarrow {}^2E$. Figure 5 shows spectra of the ligands and their Cu(II) complexes.

Fourier Transforms Infrared Spectra

The FT-IR spectra of the free ligands (L_1 and L_2) and the prepared complexes have been compared, and the data was tabulated in Table 4. The IR spectra of the ligands exhibited broad bands at 3452 and 3460 cm^{-1} , which were assigned to the stretching vibration of $\nu(\text{OH})$ phenol and carboxyl group⁽²⁷⁾. The band of (OH) phenol group was absent in the spectra of all prepared complexes, which indicated deprotonation and involvement of the enol oxygen in chelation⁽²⁸⁾.

The IR spectra of the ligands appeared bands at 1685 and 1689 cm^{-1} which were assigned to the stretching modes of $\nu(\text{C}=\text{O})$. Since no significant change in these bands was noticed, the possibility that coordination occurs via the donating atoms in these groups were excluded^(29,30). Band characteristic of the azo bridge vibration at 1489 and 1492 cm^{-1} shifted to lower and higher frequency with change in shape in spectra of complexes, which is an indication of the engagement of this group in the coordination with the metal ion⁽³¹⁾. The bands in IR spectra of the ligands at the ranges (1350-1631 cm^{-1}) due to bending frequency of (δCH_3) and stretching vibration of $\nu(\text{C}=\text{C})$ ^(32,33). The appearance of new bands in the region of 443-489 cm^{-1} are tentatively assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ (Metal-Ligand) stretching bands^(34,35). according to the results obtained, a tetrahedral structure has been tentatively suggested to these complexes.

Biological Efficiency and Dyeing Properties

All the prepared compounds have been examined with Gram-negative and Gram-positive bacteria. Table 5 shows the deactivation capacity against the bacteria specimen. The dyeing performance of the prepared ligands and their complexes was assessed on cotton fabric. The dyes were tested for light and detergent fastness. Thus all dyes showed very good dyeing properties and depth on the fabric. Some of the dyeing was showed on Figure 6.

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APPENDICES

Table 1: Physical properties of the Ligands and its Complexes

Compounds	Color	M.P °C	Yield %	Analysis Calc (Found)			
				M%	C%	H%	N%
Ligand (L ₁)	Orange	192	85	-	66.66 (66.18)	5.18 (4.84)	10.37 (9.74)
[Ni(L ₁) ₂]	Brown	182	78	9.73 (8.92)	60.40 (59.98)	4.36 (3.87)	9.39 (8.92)
[Cu(L ₁) ₂]	Reddish brown	223	75	10.63 (9.86)	59.80 (59.17)	4.31 (3.88)	9.30 (8.73)
Ligand (L ₂)	Yellowish orange	264	81	-	66.66 (65.79)	5.18 (4.93)	10.37 (9.82)
[Ni(L ₂) ₂]	Yellow	280	72	9.73 (8.72)	60.40 (59.69)	4.36 (3.75)	9.39 (8.85)
[Cu(L ₂) ₂]	Deep brown	272	73	10.63 (9.69)	59.80 (58.76)	4.31 (4.03)	9.30 (8.57)

Table 2: Conditions for the Preparation of the Complexes and UV-Vis, Magnetic Susceptibility and Conductance Measurements Data

Compounds	Optimum pH	Optimum Molar Conc. x 10 ⁻⁴	M:L Ratio	(λ _{max}) nm	ABS	ε _{max} (L.mol ⁻¹ .cm ⁻¹)	Λ _m (S.cm ² .mol ⁻¹) In Absolute ethanol	μ _{eff} (B.M)
Ligand(L ₁)	-	-	-	252 332 392	1.030 1.950 0.930	1030 1950 930	-	-
[Ni(L ₁) ₂]	8	2.5	1:2	252 336 397 732	0.480 0.930 0.410 0.090	480 930 410 90	1.26	3.80
[Cu(L ₁) ₂]	7	2.5	1:2	338 464 980	1.710 0.480 0.070	1710 480 70	5.71	2.01
Ligand(L ₂)	-	-	-	250 338 402	0.630 1.520 0.710	630 1520 710	-	-
[Ni(L ₂) ₂]	6.5	2.5	1:2	340 405 978	1.320 0.667 0.027	1320 667 27	9.49	3.45
[Cu(L ₂) ₂]	6	2	1:2	238 342 485 978	0.660 0.740 0.380 0.080	660 740 380 80	5.70	1.97

Table 3: Stability Constant and Gibbs Free Energy of the Prepared Complexes

Complexes	A _s	A _m	α	k	Lin k	ΔG kJ.mol ⁻¹
[Ni(L ₁) ₂]	0.140	0.240	0.416	34.35×10 ⁶	17.352	-42.990
[Cu(L ₁) ₂]	0.080	0.210	0.619	6.45×10 ⁶	15.679	-38.845
[Ni(L ₂) ₂]	0.105	0.164	0.359	58.27×10 ⁶	17.880	-44.298
[Cu(L ₂) ₂]	0.057	0.132	0.568	36.00×10 ⁶	17.399	-43.107

Table 4: The Main Frequencies of the Ligands and their Complexes (cm⁻¹)

Compounds	$\nu(\text{NH}_2)$ + $\nu(\text{OH})$	$\nu(\text{C=O})$ + $\nu(\text{C=C})$	$\nu(\text{N=N})$	δCH_3 as,s	$\nu(\text{M-N})$ + $\nu(\text{M-O})$
Ligand(L1)	- 3471 br.	1689 sh. 1631 s. 1585 s.	1492 sh.	1423 sh. 1350 sho.	443 w. 420 w.
[Ni(L1)2]	- 3363 br.	1685 sho. 1600 s. 1558 s.	1489 sh.	1388 s.	509 w. 443 w.
[Cu(L1)2]	- 3363 br.	1688 s. 1624 s. 1600 sho.	1481 sh.	1419 sho. 1381 sh.	-
Ligand(L2)	- 3452 br.	1685 sh. 1631 sho. 1600 s.	1489 s.	1423 sh. 1388 s.	518 w. 474 w.
[Ni(L2)2]	- 3407 br.	1683 sh. 1627 s. 1591 s.	1479 s.	1421 s. 1380 sho.	540 w. 443 w.
[Cu(L2)2]	- 3407 br.	1683 sh. 1629 sho. 1600 s.	1496 s.	1423 s. 1388 s.	443 w. 420 w.

As = asymmetry, s = symmetry, br = broad, sh = sharp, s = strong, w = weak, sho =shoulder

Table 5: Diameters (mm) of Deactivation of Bacteria for the Ligands and its Complexes

Compounds	Bacillus Cereus	Staphylococcus Aureus	Esherichia Coli
Ligand(L1)	-	-	-
[Ni(L1)2]	-	-	-
[Cu(L1)2]	-	-	-
Ligand(L2)	-	-	-
[Ni(L2)2]	-	+	++
[Cu(L2)2]	-	-	-

(-) = No inhibition, (+) =Inhibition diameter (6-8) mm, (++) =Inhibition diameter (8-10) mm.

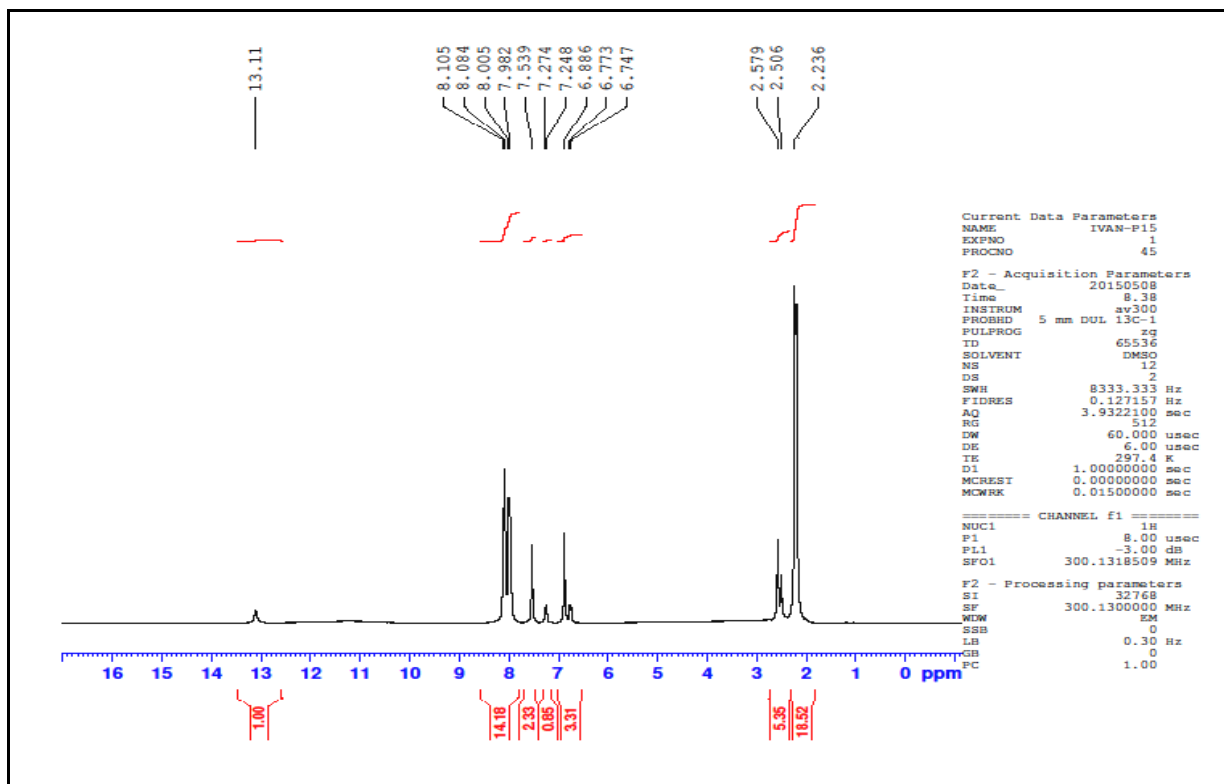


Figure 1: ¹H NMR Spectrum of the Ligand (L₂)

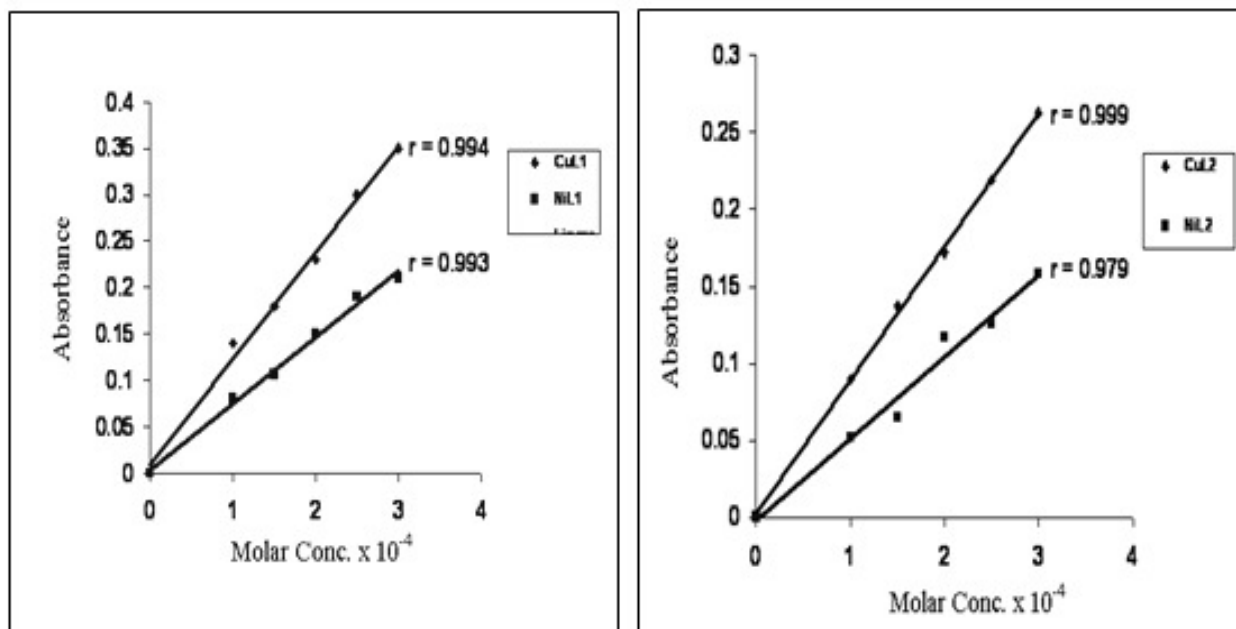


Figure 2: Linear Correlation between Molar Concentration and Absorbance

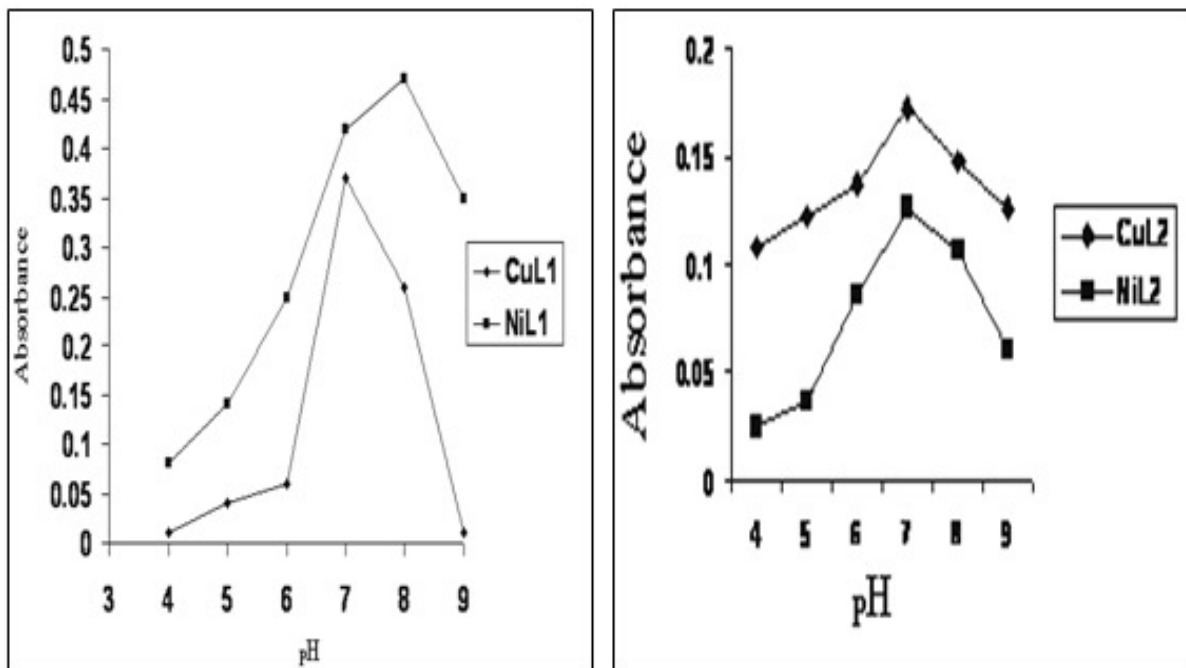


Figure 3: Effect of pH on Absorbance (λ_{max}) for Complex

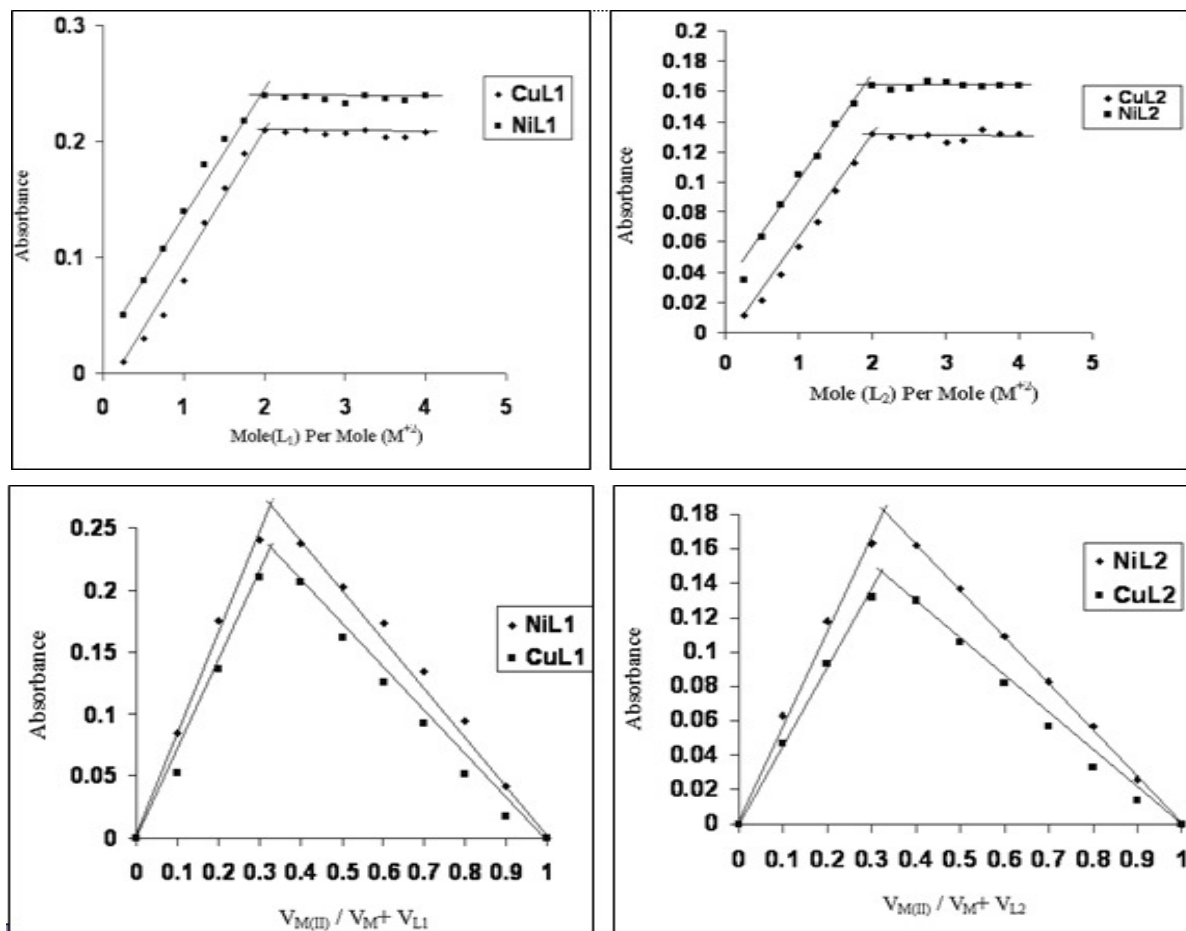


Figure 4: Mole Ratio and Job Methods for Complexes' Solutions

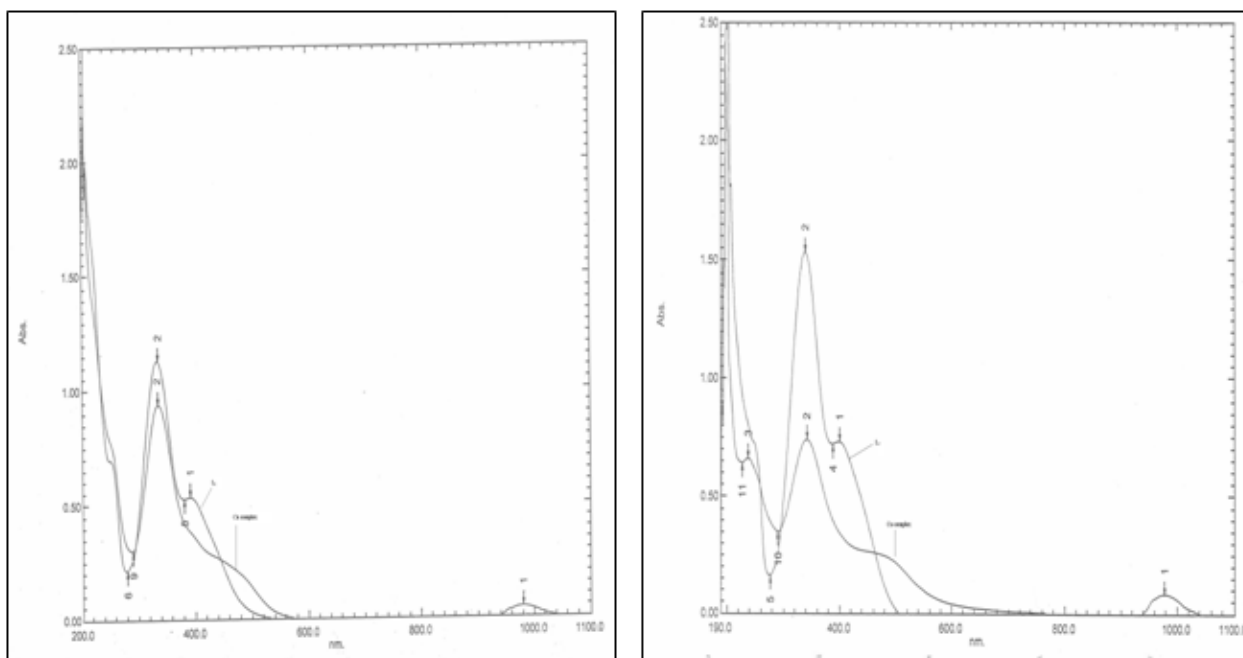


Figure 5: UV-Vis Spectra of the Ligand and their Cu Complexes

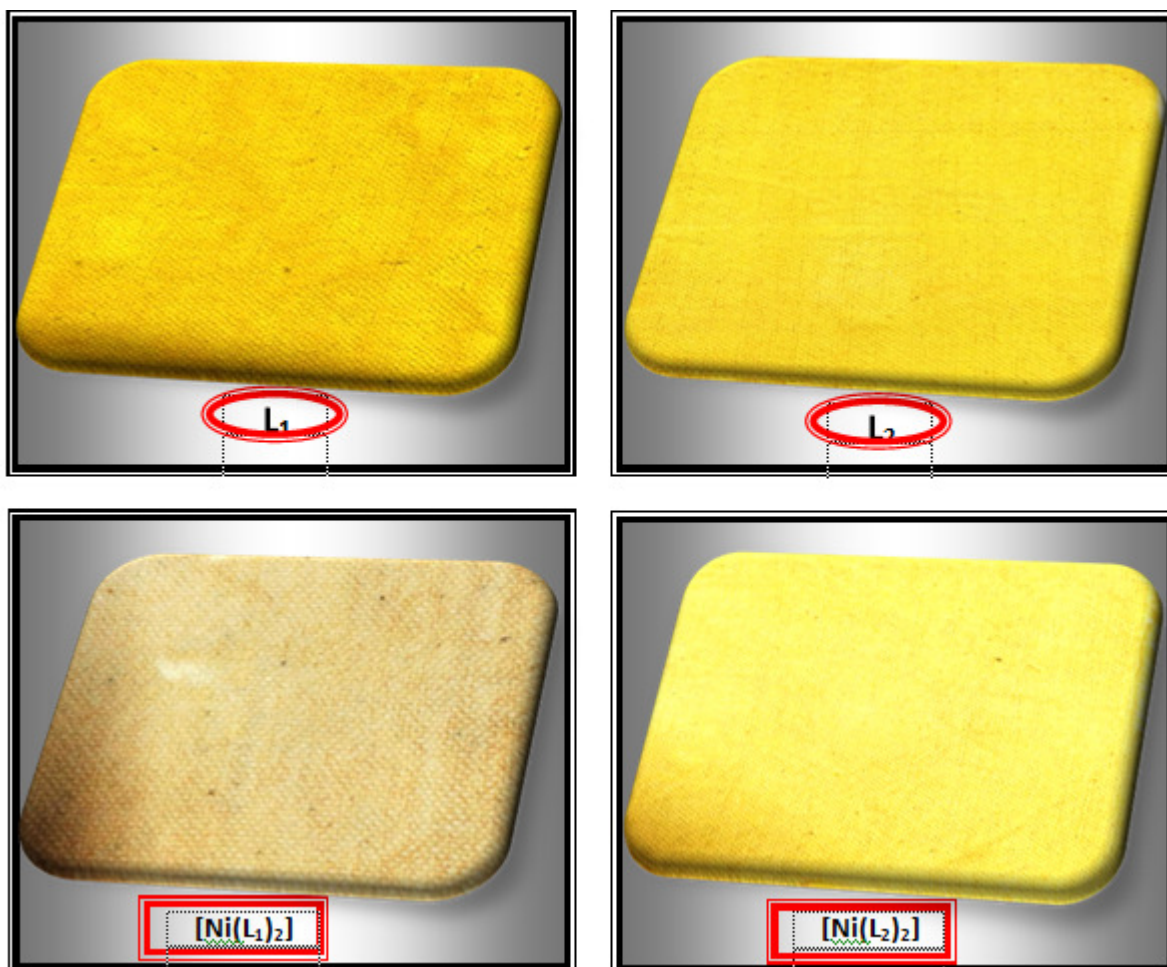


Figure 6: Samples the Textiles Dyeing of the Ligand and their Complexes

