

# Synthesis, Spectral of Azo Dyes Complexes with Ni (II) and Cu (II) and Their Industrial and Bacteriological Application

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**Abstract:** Azo dye ligand was produced by coupling the diazonium salt of 4-aminoantipyrine with 2, 4-dimethylphenol. The structure of azo compound was someone by elemental analyses, <sup>1</sup>H-NMR, FT-IR and UV-Vis spectroscopic mechanics. Metal complexes of nickel (II) and copper (II) have been performed and depicted. The formation of complexes has been identified by using flame atomic absorption, (C.H.N) Analysis, FT-IR and UV-Vis spectral process as well as, conductivity and magnetic properties quantifications. The nature of the complexes formed were studied succeed the mole ratio and continuous variation methods, Beer's law followed over a concentration scope ( $1 \times 10^{-4}$  -  $3 \times 10^{-4}$  M). High molar absorptivity of the complex solutions were observed. Analytical data showed that all the complexes offered 1: 2 metal-ligand ratios. On the origin of physicochemical data tetrahedral structures were described for the complexes. Biological activity of the ligand and complexes were assayed. In addition, the dyeing carried out of the produced compounds was practical on cotton fabric. The dyes were examed for light and detergent fastness

**Keywords:** complexes, azo dyes, biological activity, antipyrine azo

## 1. Introduction

Azo dyes are a variety of chemical geometry that is running receiving attention academic research<sup>(1, 2)</sup>. Azo dyes which have been containing one or more azo groups (-N=N-) in molecular structure<sup>(3)</sup>. Azo dyes are preceding and largest grade of industrial performed organic dyes due to their more applying in types field, such as dyeing textile fiber, biomedical studies, advanced application in organic performed and high technology areas such as laser, liquid crystalline displays, electro-optical devise and ink-jet printers<sup>(4, 5)</sup>. Azo structures are roomy employment in analytical chemistry for the spectrophotometric appreciation of several elements. Recently, many literatures growth a sensible course for in recognition of metal ions azo ligands as complexometric revealing by polarographic and voltammetric mechanisms<sup>(6, 7)</sup>. Complexes of azo compounds have been extensively studies for their medical and biological applications<sup>(8-10)</sup>. In this work, a ligand of azo functional group derived from 4-aminoantipyrine as diazo component and 2, 4-dimethylphenol as coupling agent, were prepared. The complexes of this ligand with several metal ions have been prepared and depicted physicochemically.

## 2. Experimental

### Instrumentation

FT-IR- spectra in the extent 4000-400  $\text{cm}^{-1}$  spectral regions with samples produced as KBr discs were carried out on a Shimadzu, FT-IR- 8400S Fourier Transform Infrared Spectrophotometer. Atomic absorption was obtained using a Shimadzu A.A-160A Atomic Absorption/Flame Emission Spectrophotometer. UVV is spectra were listed on a Shimadzu UV- 160A Ultra Violet-Visible

Spectrophotometer. Elemental analysis (C, H, N) were executed at the Al- al- Bayt University, Jordan, using Euro vector EA 3000A Elemental Analyser. The <sup>1</sup>H-NMR spectrum was inscribed 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. Conductivity were gauging for  $10^{-3}$  M solutions of complexes in ethanol at 25°C using

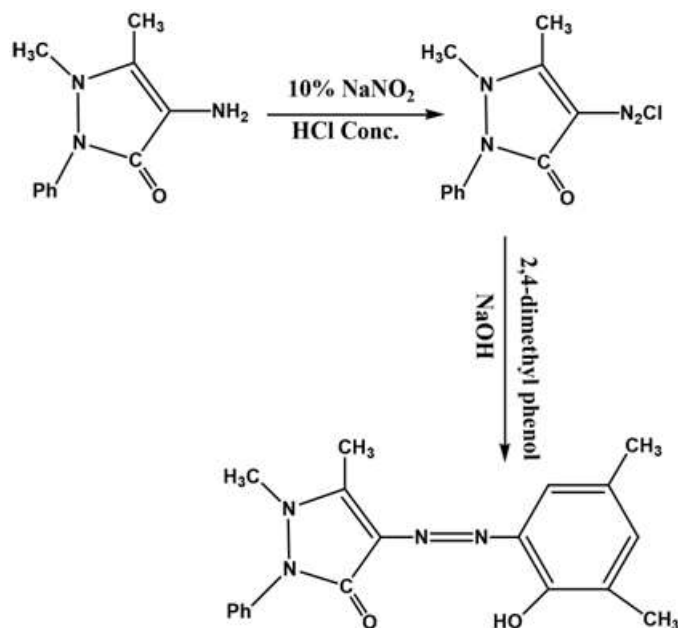
Philips PW- Digital Conductimeter. Magnetic properties were completed by using Auto Magnetic Susceptibility Balance Sherwood Scientific instrument at 25°C. In addition, melting points were realized using Stuart Melting Point Apparatus.

### Materials and Reagents

The obeyed chemicals were used as obtained from suppliers: NiCl<sub>2</sub>.6H<sub>2</sub>O 99.9% and CuCl<sub>2</sub>.2H<sub>2</sub>O 99.8% (Merck), 4-aminoantipyrine and 2, 4-dimethylphenol (B.D.H).

### Preparation of the ligands<sup>(11)</sup>

A solution was prepared, of 4-aminoantipyrine (0.503 g, 1mmole) in (10ml) of ethanol containing (2ml) conc. HCl which was diluted with 10 ml H<sub>2</sub>O, and diazotized at 5°C with 10% solution of NaNO<sub>2</sub>. The diazotized solution was appended gradually with stirring to a cooled ethanolic solution of (0.305 g, 1mmole) of 2, 4dimethylphenol. Then 25 ml of 1M NaOH solution was appended to the deep colored blend and precipitation of the azo ligand was observed. This precipitate was filtered, washed more once with (1: 1) ethanol: water, blend then left to dry. The reaction is exhibit in scheme 1, while Table 1 recorded the physical estates and elemental analysis.



Scheme 1: Synthesis of the azo ligand (L).

#### Buffer Solution

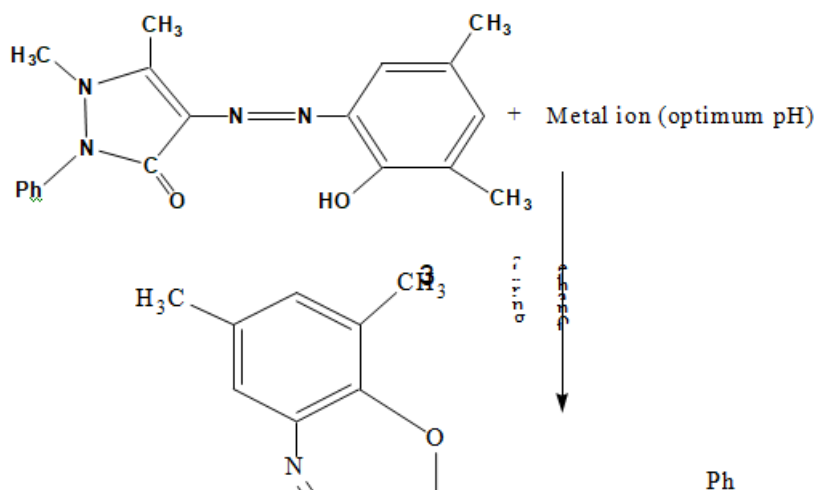
(0.01M, 0.771 gm) of ammonium acetate was dissolved in one liter of doubly deionized water. For only pH average (4-9) was utilization acetic acid or ammonia solution.

#### Standard Solution

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

#### Preparation of Metal Complexes (general procedure)

(0.336g, 2mmole) of the ligand dissolved in ethanol and appended progressively with stirring to the 0.118g and 0.085g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  successively dissolved in the desired pH solution. The blend was cooled until deep color precipitate was done, filtered, and washed more once with 1: 1 water: ethanol mixture, then with acetone. The preparation was shown in scheme 2.



Scheme 2: The expected geometry of the metal (II) complexes of ligand (L)

#### Study of Biological Activity

The antibacterial activity for the ligand and their complexes were determined by using appreciation similar with the traditional disc diffusion way<sup>(12,13)</sup>, 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 permitted complete evaporation to be used. Then discs were placed onto the surface of the Muller Hinton agar plates at differing 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  $37\text{C}^\circ$  for 24 hr. Results were assigned by carried out the diameter (mm) for a zone of inhibition around each disc on the plate.

#### Dyeing Method

The dyeing properties of these compounds were examined on "Hilla- Fine Textile State Company" using the Azoic Dyes Method. Dyes were application on cotton fabric as (1%

shade). The dyeing of the fabric was formed at (15- 20C<sup>o</sup>) for (1 hr), and at pH (10).

### 3. Results and Discussion

For the readying of the ligand (L) a linkup of 2, 4-dimethylphenol with the appropriate diazotized in alkaline solution was carried out. The solubility of the ligand was examined and was found to be soluble in organic solvents and was stable toward air and moisture. Performed ligand was identified by <sup>1</sup>H-NMR, FT-IR, (C, H, N) analysis and UV-Vis spectral mechanisms. An aqueous-ethanolic solutions were always performed to study the interaction of the metal ions Ni (II) and Cu (II) with the prepared ligand. The Colors of these mixed solutions over the molar concentration and acidity varying performed were varied from brown to violet.

#### <sup>1</sup>H-NMR Spectrum

The <sup>1</sup>H-NMR spectrum of the ligand (L) in DMSO (Figure 1) display various signals at  $\delta=6.484-7.559$  ppm refers to aromatic protons<sup>(14)</sup>. The signal at  $\delta=5.931$  ppm lead to proton of phenol<sup>(15)</sup>. Finding, the signals at  $\delta=2.095$  ppm and  $\delta=3.364$  ppm describe to  $\delta$  (N-CH<sub>3</sub>) and  $\delta$  (CH<sub>3</sub>) of pyrazole respectively<sup>(16)</sup>, the signal at  $\delta=2.198$  ppm due to  $\delta$  (CH<sub>3</sub>) of phenol and the signal at  $\delta=2.50$  ppm assigned to DMSO-d<sub>6</sub><sup>(17)</sup>.

#### Calibration Curve

Varied molar concentration (10<sup>-5</sup>-10<sup>-3</sup> M) of mixed aqueous-ethanolic of ligand and metal ions, only the concentration in the reach (1-3×10<sup>-4</sup>M) followed Beer's law and appeared obvious intense color. Best fit straight lines were happened with correlation factor R>0.9980 as shown in Figure 2.

#### Optimum Conditions

To search out the interaction between the prepared ligand and metal ions under education for the preparation of the complexes, the spectra of combining solutions for the ligand and metal ions to attain to optimum pH and concentration, as well as frim wave length ( $\lambda_{max}$ ) were studies first .Then mole ratio metal to ligand (M: L) was defined to prepare the complexes. Perfect concentration was chosen for complex solution based on which solution gives the highest absorbance at constant ( $\lambda_{max}$ ) at different pH, and results are described in Table 2.

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

#### Stoichiometry of Complexes

The typesetting of complexes shaped in solutions has been appointed by mole ratio and job methods. In both situations the results spread a 1: 2 (metal: ligand) ratio. A picked plot is shown in Figure 4. Table 2 synthesizes the results gated, as well as specification for the making complexes.

#### Physical properties

The solid complexes have been produced by immediate interaction of the ligand melted in ethanol with the metal

ions melted in perfect pH and in a (Metal: Ligand) ratio of 1: 2. The outcome of elemental analysis and the metal import of these complexes were in real identical with the calculated values. The molar conductance of the complexes (10<sup>-3</sup> M) melted in ethanol display their non- electrolytic nature<sup>(18)</sup> data are included in Table 2. The magnetic properties for all produced complexes (Table 2) indicated a paramagnetic (high spin) which has been recorded for octahedral structure<sup>(19)</sup>.

#### 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.

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

Where  $c$  = the concentration of the complex solution in mole/ L  $\alpha$  = degree of dissociation,  $A_s$  = the absorption of solution including a stoichiometric deal of ligand and metal ion and  $A_m$ = the absorption of solution including the same deal of metal and surplus of ligand. The high values of (K) refers to high stability of prepared complexes<sup>(20)</sup>. The thermodynamic parameters of Gibbs free energy ( $\Delta G$ ) were also studied. The  $\Delta G$  data have been calculated from the equation<sup>(21)</sup>.

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

Where; R = gas constant = 8.3 J.mol<sup>-1</sup>.K, T = absolute temperature (Kelvin). All results were included in Table 3. The negative value of ( $\Delta G$ ) indicates that the reaction between (L) and metal ions understudy are spontaneous.

#### Electronic spectra

The UV-Vis spectra of the produced compounds melted in ethanol (10<sup>-3</sup> M) have been gauging and the data received are recorded in Table 2. The UV- Vis spectrum of an ethanolic solution of the ligand 10<sup>-3</sup> M (Figure 5) displayed generally three peaks, the first and second peaks at 246 and 382 nm were described to the moderate energy  $\pi-\pi^*$  transition. The third peak was realized at 432 nm was gestured to the  $n-\pi^*$  transition<sup>(22)</sup>. The spectrum of Ni (II) complex (Figure 6) raised absorption peaks at 248 and 368 nm due to ligand felid, then other three peaks at 476, 752 and 980 nm which were related to electronic transition type  $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ ,  $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$  and  $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$  successively<sup>(23)</sup>. The spectrum of Cu (II) complex (Figure 7) recorded peaks at 251, 380 and 490 nm described to ligand felid and charge transfer continually. Other peak at 980 nm due to  $^2E_g \rightarrow ^2T_{2g}$  (d-d) electronic transition<sup>(24)</sup>.

#### Fourier transforms infrared spectra

The FT-IR spectra of the produced compounds have been collated, and the data was scheduled in Table 4. The broad band in the FT-IR spectrum of the ligand (figure 8) at 3414 cm<sup>-1</sup>, which was related to the stretching vibration of  $\nu$  (OH) phenol, the disappearance of this band in the spectra of all produced complexes (Figure 9) indicated the deprotonation of phenol group to coordination with metal ion<sup>(25, 26)</sup>. The spectrum presented band at 1643 cm<sup>-1</sup> which was attributed to the stretching of  $\nu$  (C=O), on complexation (Figure 10) this band has been removed to lower frequency implying the

coordination with metal ion<sup>(27, 28)</sup>. Band differentiating of the azo group at 1527 cm<sup>-1</sup> displaced to lower wave number with alter in shape in spectra of all produced complexes<sup>(29, 30)</sup>. The band in IR spectrum of the ligand at the scopes (13691585 cm<sup>-1</sup>) refer to bending frequency of ( $\delta$ CH<sub>3</sub>) and stretching vibration of  $\nu$  (C=C)<sup>(31)</sup>. Stretching frequency bands for metal-nitrogen and metal-oxygen further<sup>(32, 33)</sup> confirmed by the presence of the bands around 432-543 cm<sup>-1</sup>. Pursuant to the results proected, an octahedral geometry has been offered for the produced complexes.

#### Biological Efficiency and Dyeing Properties

All the ready ligand and its complexes have been examined with Gramnegative and Gram-positive bacteria. Table 5 suggests the deactivation spread converse the bacteria specimen. The dyeing performance of the prepared compounds was defined on cotton fabric. The dyes were essay for light and detergent fastness. Thus all dyes appeared very excellent dyeing holding and depth on the fabric. The dyeing was referred on Figure 11.

#### 4. Conclusion

In this work, the metal ions complexes have been readied with the ligand. The willing compounds are described by melting point, flame atomic absorption, FT-IR and UV-Vis spectral, as well as magnetic sensitively and conductivity quantifications. Exploration of antimicrobial activities was lifted out opposite the experimented organism. The dye and their produced complexes were applied on cotton fabric.

According the result data an octahedral structure suggested for prepared complexes.

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**Table 1:** Physical properties of the ligand and its complexes

Compounds	Color	M.P°C	Yield %	Analysis Calc (Found)			
				M%	C%	H%	N%
Ligand (L)	Rose	192	77	-	67.85 (66.94)	5.95 (4.88)	16.66 (15.75)
[Ni(L) <sub>2</sub> ]	Reddish brown	182	83	7.96 (6.93)	62.63 (62.17)	5.22 (4.97)	15.38 (14.88)
[Cu(L) <sub>2</sub> ]	Violet	223	85	8.71 (8.07)	62.12 (61.94)	5.17 (4.84)	15.25 (14.79)

**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 <sup>-4</sup>	M: L Ratio	(λmax) nm	ABS	εmax (L.mol <sup>-1</sup> .cm <sup>-1</sup> )	Λ <sub>m</sub> (S.cm <sup>2</sup> .mol <sup>-1</sup> ) In Absolute ethanol	μ <sub>eff</sub> (B.M)
Ligand (L)	-	-	-	246 382 432	1.008 1.100 0.573	1008 1100 573	-	-
[Ni (L) <sub>2</sub> ]	7	2	1: 2	248 368 476 752 980	0.837 0.670 0.870 0.010 0.060	837 670 870 10 60	13.53	2.74
[Cu (L) <sub>2</sub> ]	7	2.5	1: 2	251 380 490 980	1.207 1.180 1.210 0.060	1207 1180 1210 60	14.15	1.81

**Table 3:** Stability constant and Gibbs free energy of the prepared complexes

Complexes	A <sub>s</sub>	A <sub>m</sub>	α	k	Lin k	ΔG kJ.mol <sup>-1</sup>
[Ni (L) <sub>2</sub> ]	0.120	0.370	0.670	0.68×10 <sup>6</sup>	13.429	-33.271
[Cu (L) <sub>2</sub> ]	0.270	0.590	0.540	1.18×10 <sup>6</sup>	13.981	-34.638

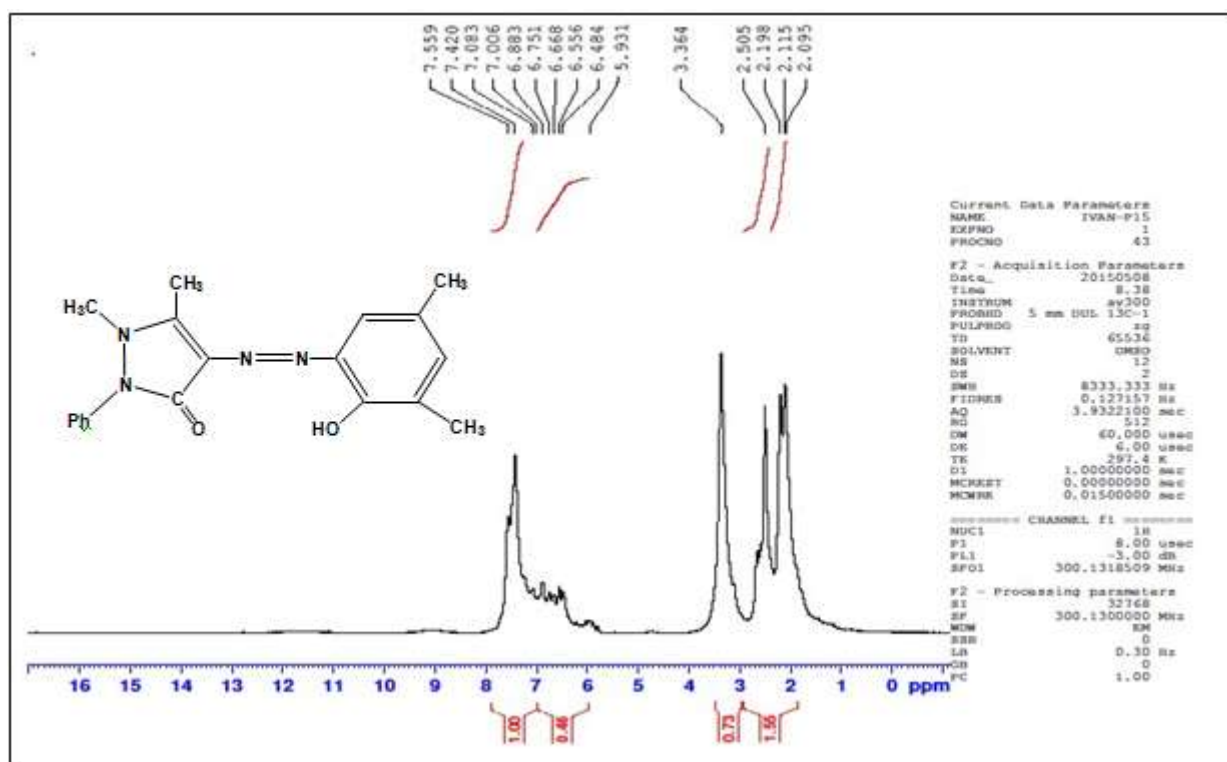
**Table 4:** The main frequencies of the ligand and their complexes (cm<sup>-1</sup>)

Compounds	ν(OH)	ν(C=O) + ν(C=C)	ν (N=N)	δCH <sub>3</sub> as,s	ν(M-N) + ν(M-O)
Ligand(L)		1643 s.	1527 s.	1477 s.	-
	3414 br.	1585 sho.		1454 sho. 1419 s. 1369 sho.	
[Ni(L) <sub>2</sub> ]	- -	1612 sh. 1585 sho.	1523sh.	1477 s. 1455 sho. 1423 sh. 1390 sho.	462 w. 432 w.
[Cu(L) <sub>2</sub> ]	- -	1606 sh. 1577sh.	1519 sh.	1477 s. 1455 sho. 1435 s. 1354 sho.	543 w. 447 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 ligand and its complexes

Compounds	Bacillus cereus	Staphylococcus aureus	Esherichia coli
Ligand (L)	-	-	-
[Ni (L) <sub>2</sub> ]	-	12	-
[Cu (L) <sub>2</sub> ]	6	8	10



**Figure 1:** <sup>1</sup>H NMR spectrum of the ligand (L)

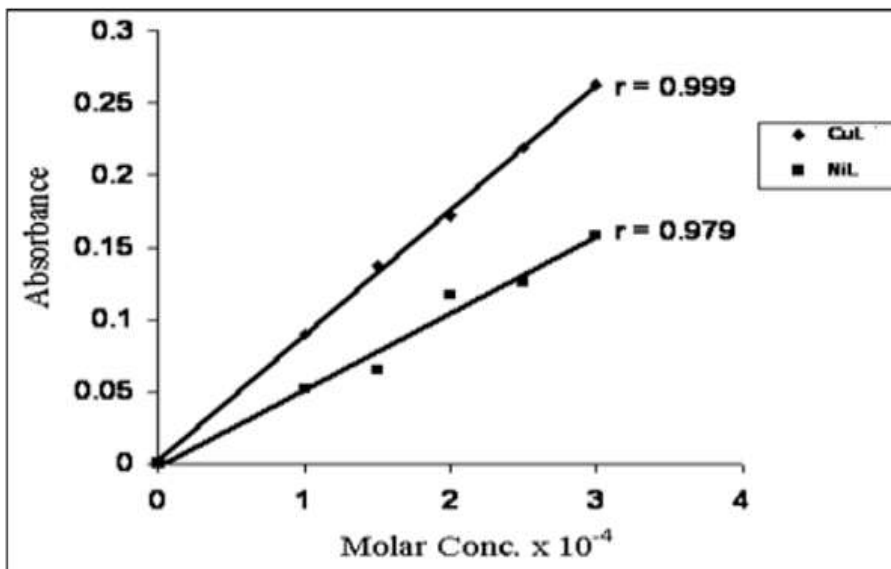


Figure 2: Linear correlation between molar concentration and absorbance

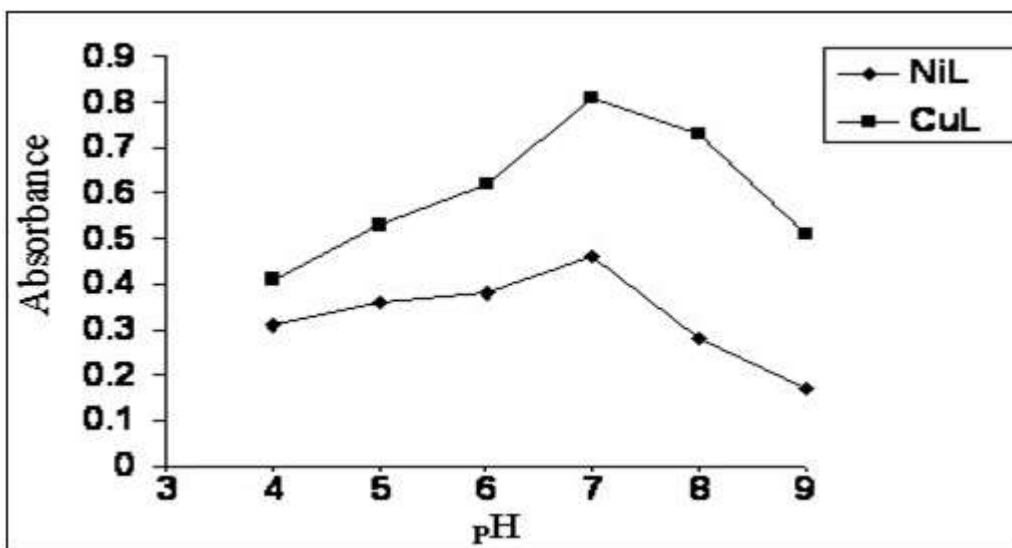


Figure 3: Effect of pH on absorbance ( $\lambda_{max}$ ) for complexes

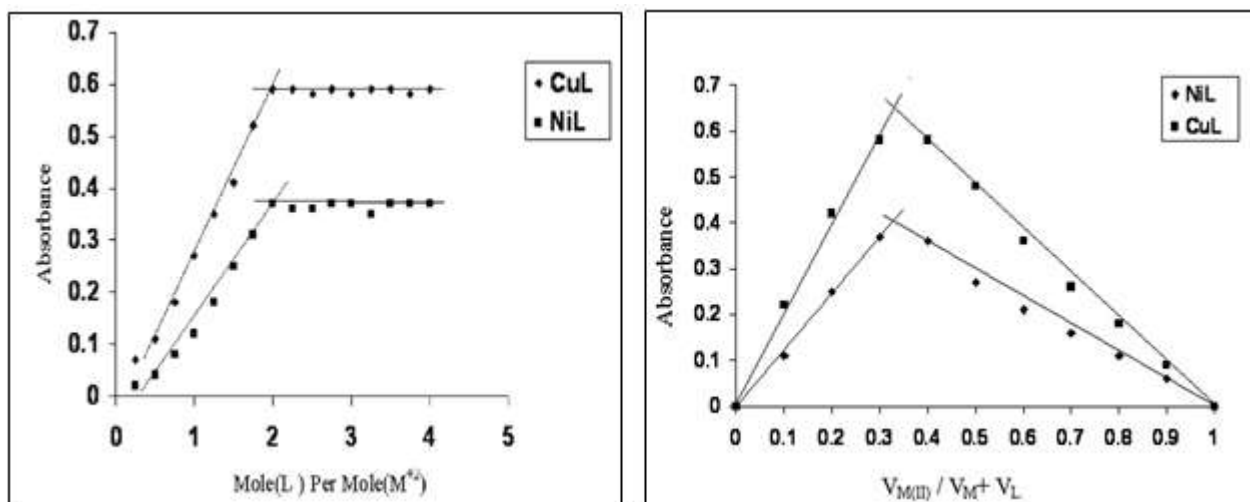


Figure 4: Mole ratio and Job methods for complexes solutions

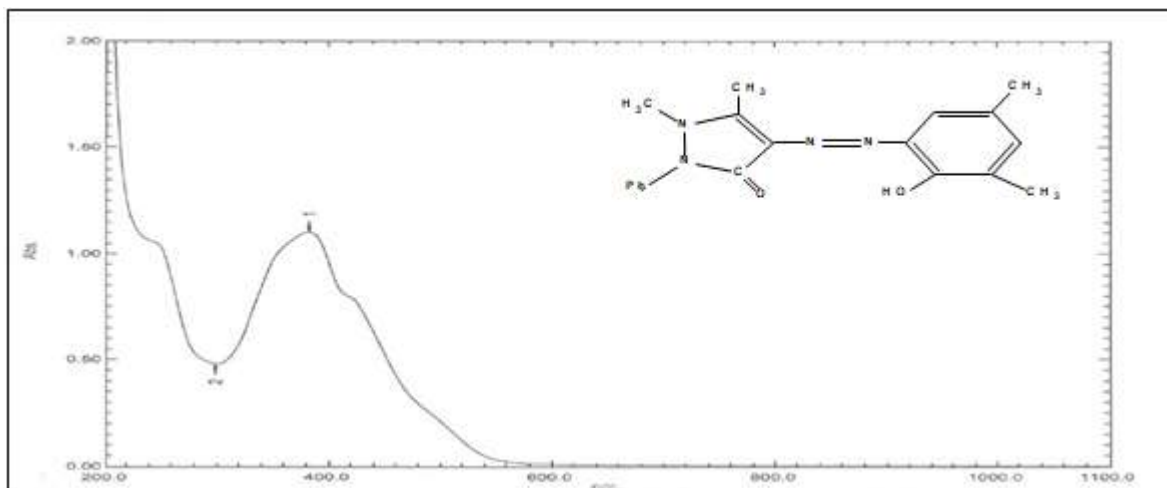


Figure 5: UV-V is spectrum of the ligand

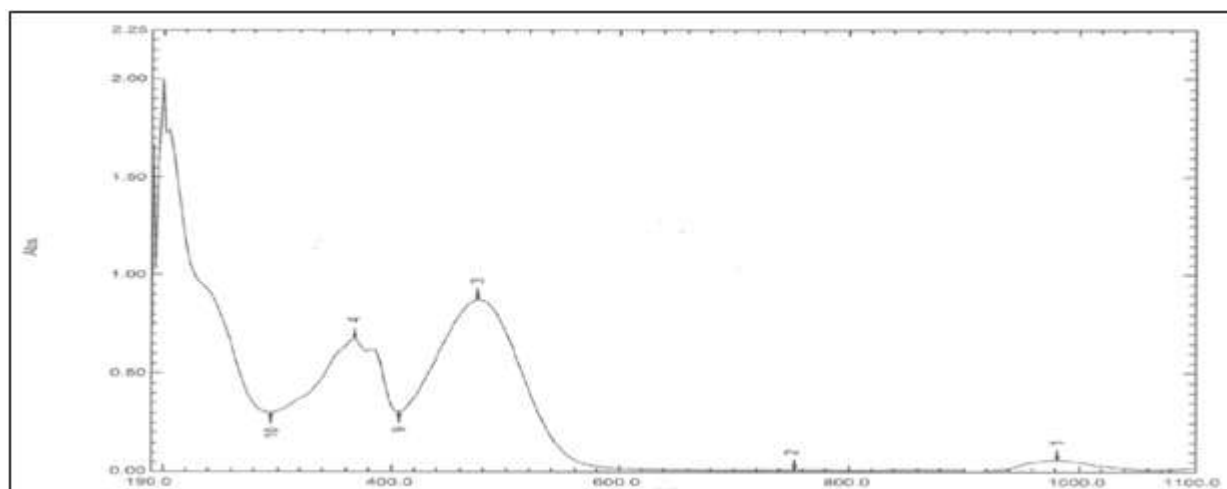


Figure 6: UV-V is spectrum of the [Ni(L<sub>2</sub>)] complex

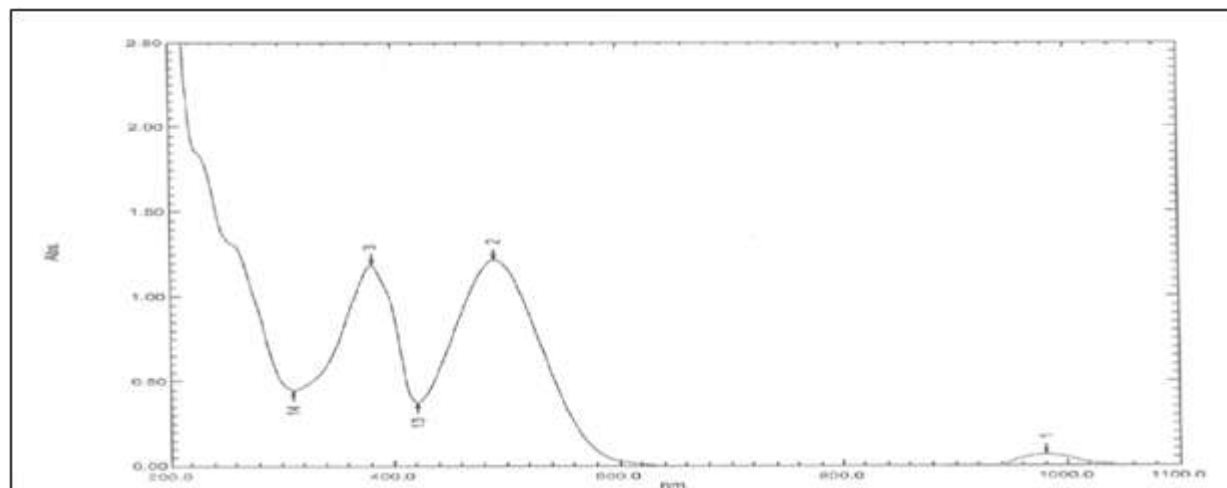


Figure 7: UV-V is spectrum of the [Cu(L<sub>2</sub>)] complex



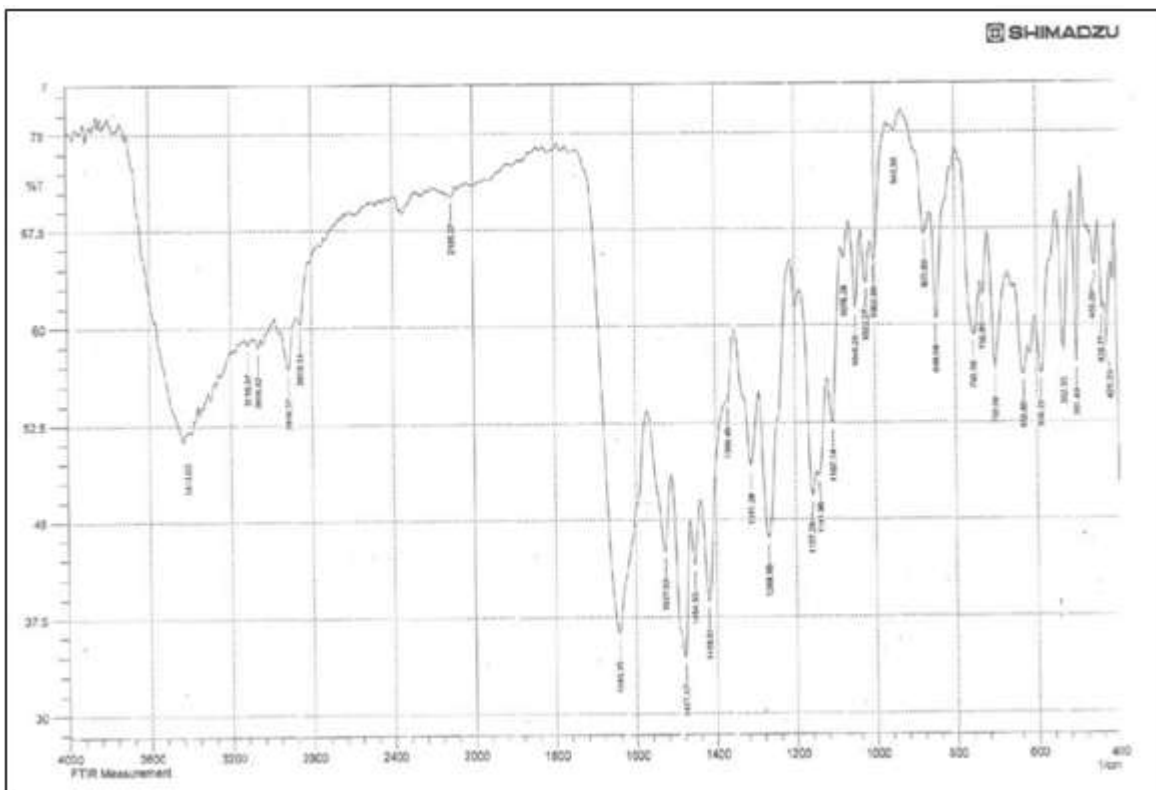


Figure 8: FT-IR Spectrum of the ligand.

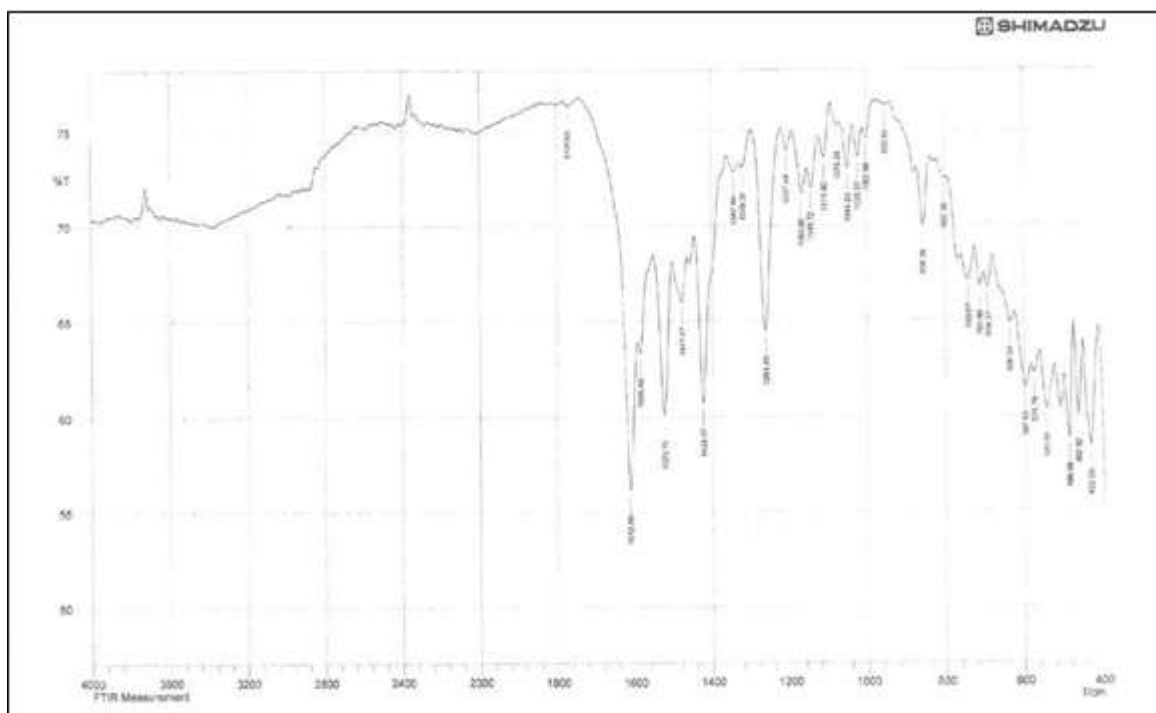


Figure 9: FT-IR Spectrum of the [Ni (L2)] complex

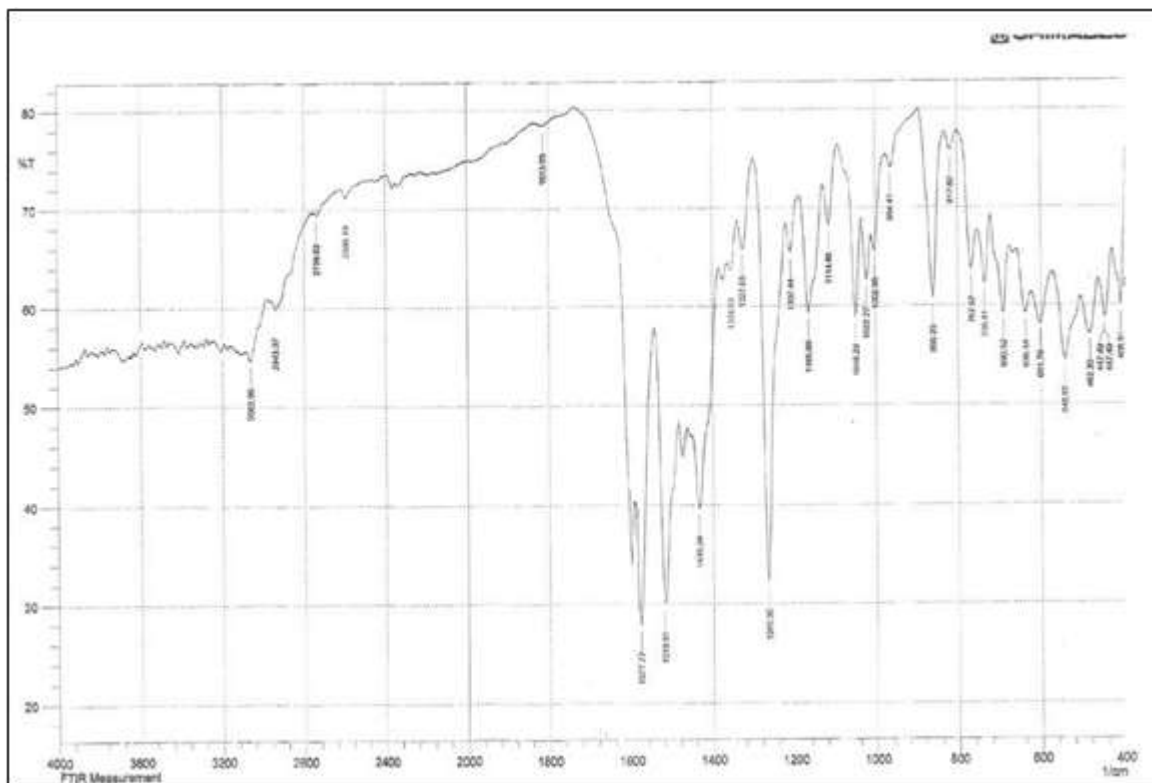
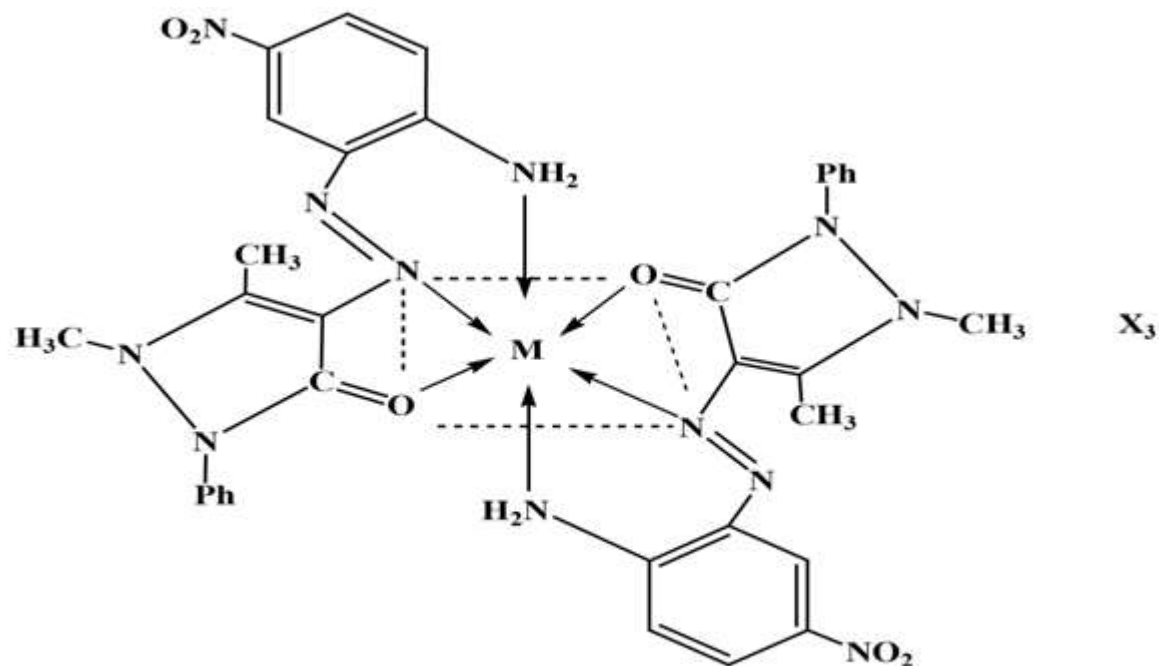


Figure 10: FT-IR Spectrum of the [Cu(L2)] complex



Figure



**M = Y(III) when  $x = \text{NO}_3$ , La(III) when  $x = \text{Cl}$**

**fig (11):-** Samples the textiles dyeing of the ligand and their complexes.