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Synthesis and characterization of azo dyes ligands complexes with Ni (II) and Cu (II) and studies their industrial and bacterial application.

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ABSTRACT

1-[4-(4-Acetyl-2-hydroxy-phenylazo)-phenyl]-ethanone (L_1) and 1-[3-Hydroxy-4(4-nitro-phenylazo)-phenyl]-ethanone (L_2) were readied by combination the diazonium salts of amines with 3-hydroxyacetophenone. (C.H.N) analyses, infrared spectra, UV–vis electronic absorption spectra, ^{1}H and ^{13}CNMR spectral mechanisms are use to identified of the ligands. Complexes of Ni^{+2} and Cu^{+2} were performed as well depicted. The formation of complexes has been identified by using atomic absorption of flame, elemental analysis, infrared spectra and UV-Vis spectral process as well conductivity and magnetic quantifications. Nature of compounds produced have been studied obeyed the mole ratio and continuous contrast methods, Beer's law followed during a concentration scope (1×10^{-4} - 3×10^{-4} M). height molar absorbtivity of compound solutions have been noticed. Analytical data showed that all the complexes offered 1:2 metal-ligand ratios. At the radix for physicochemical datum a tetrahedral geometry have been described at compounds. Biological activity at these complexes has been assayed. Other than, dyeing carried out of the produced compounds was practical at cotton fabric. Dyes have been examined of light and the stability of detergent.

Keywords: transition metals, azo dyes, biological activity, dyeing, acetophenone

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INTRODUCTION

Azo compounds establishes of the largest places of industrially preparation organic molecules that contain azo group (-N=N-) as part of their molecular geometries [1,2] Azo dyes have been used in different scoped and have several application of dye stuff industry and pharmaceutical [3,4].Various azo dyes have been practical as chromogentic reagents for the fixing of more metal ions [5]. Metal complexes of azo compounds who containing nitrogen atom in the aromatic rings have been applied in biological activities as antitumor, antibacterial and antifiungal [6]. This metal chalets because of electronic interesting and structural features at connection for their effecting to store molecular memory, nonlinear visual elements and printing system [7]. At that work, a ligands from azo functional group obtained from 4-aminoacetophenone and 4-nitroaniline like a component of diazo and 3-hydroxyacetophenone like agent coupling, have been produced. Complexes at $Ni^{(II)}$ and $Cu^{(II)}$ for these ligands were produced also identified physcio-chemically.

EXPERIMENTAL

Materials and Instrumentation

Atomic absorption has been recorded by employing a Shimadzu A.A-160A Atomic Absorption/Flame Emission Spectrophotometer. ^{13}C and ^{1}H-NMR spectrum have been noted at a Brucker-300 MHz Ultra Shield spectrometer on Al- al- Bayt University utilizing dimethylsulfoxide like the solvent also trimethylsaline like the reference. (C, H, N) analyses have been done in Al- al- Bayt University, Jordan, employing Euro vector EA 3000A Elemental Analyser. Conductivity for the compunds resolved at ethanol (10^{-3} M) was recorded at 25°C utilizing Philips PW- Digital Conductimeter. Magnetic properties have been completed through utilizing Auto Magnetic Susceptibility Balance Sherwood Scientific instrument at 25C°. UV- Vis spectrum have been registered at a Shimadzu UV- 160A Ultra Violet-Visible Spectrophotometer. IR- spectrum have been taken at a Shimadzu, FT-IR- 8400S Fourier Transform Infrared Spectrophotometer at the 4000- 400 cm^{-1} spectrum areas for models produced like KBr discs. Other than, melting points have been performed utilizing Stuart Melting Point Apparatus.

Obeying chemicals have been utilized like collected of purveyors: $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ (Merck), 4-aminoacetophenone, 4-nitroaniline and 3-hydroxyacetophenone (fluka).

Preparation of ligand

A solution was produced[8] of amines (0.337 gm and 0.345 gm, 1mmole) in mixture (10ml ethanol, 2ml conc. HCl), and diazotized at 5°C with 10% solution of $NaNO_2$. Diazotized solution has been added collyrium wise for stirring into a cooled ethanolic solution at (0.340 gm, 1mmole) for 3-hydroxyacetophenone. Then 25 ml at 1M NaOH solution has been followed into dusky colored mix and precipitation for azo ligand has been noticed. This deposit have been filtrated, washed number ounces for (1:1) C_2H_5OH: H_2O, mixture subsequently left into dry. The reaction is appear at scheme 1, whilst (Table 1) depicts the physical estates and elemental analysis.

Buffer solution

(0.01M, 0.771 gm) for ammonium acetate has been dissolved at one liter for doubly deionized water. For only pH rate (5-9) was the use of CH_3COOH or NH_3 solution.

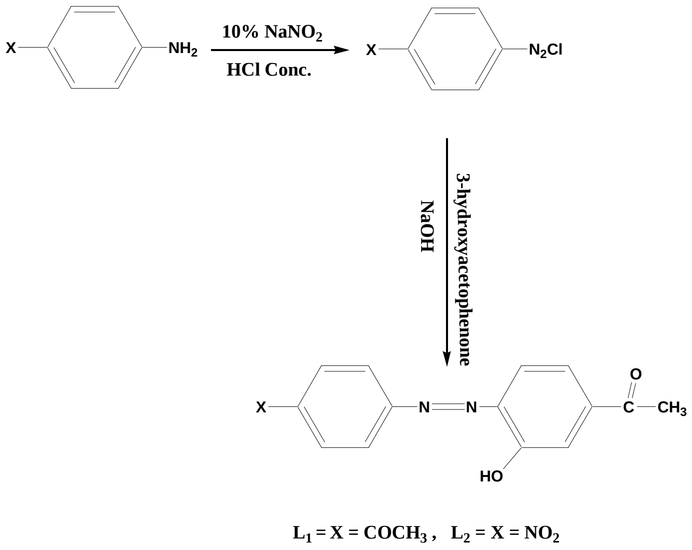
Standard solution

A bulk of standard solutions of the $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ were made in varying concentration (10^{-5}-10^{-3} M) at pH rat (5-9). At the same time a bulk of ethanolic solutions of ligands within the extent of concentrations (10^{-5}-10^{-3} M) was also produced.

Preparation of metal complexes

Ethanolic solution of the ligands (0.282gm and 0.285gm, 2mmole) was added drop wise with stirring to the 0.118gm and 0.085gm of NiCl2.6H2O and $CuCl_2.2H_2O$ dissolved in the pH solution with the needed pH.

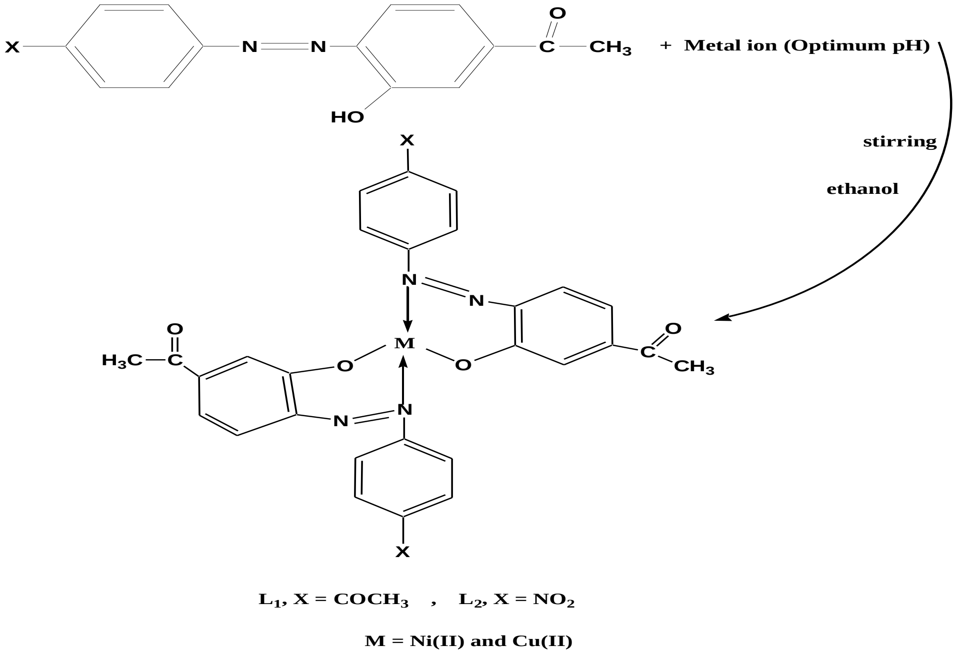
The mixture was cooled until dark color precipitate was formed, filtered, and washed number ounces with 1:1 H_2O: C_2H_5OH mixture. The preparation technique is shown in scheme-2.



Scheme 1: Synthesis of the azo ligands

Discuss the biological impact outcome of prepared compounds

Ligands and newly manufactured metal compounds have been tested in vitro of their antibacterial efficiency versus bacteria: *Staphylococcus aureus* and *E-coli* using the paper disc technique. The produced compounds in dimethylsulfoxide solution were applied in vitro by paper disc technique. All materials used were sterilized in a hot air oven and colony of each of the tested micro organisms were subcultured and incubated about (8 hours) before introducing into agar plates. The discs (7 mm diameter) were soaked with different test samples (concentration 1000ug/ml) drained and then placed on the agar plate using sterilized forcept. The plates were incubated at 37°C for (48 hours), at the end of the incubation period; the zones of inhibition of the different bacteria were carried out [9].



Scheme 2: The expected geometry of the metal (II) complexes of (L_1 and L_2)

Dyeing method

The dyeing techniques of the produced compounds were examined and used to cotton fabric like (1% shade). Dyeing to the fabric has been obtained in (15- 20C°) of (1 hr), and in pH (10).

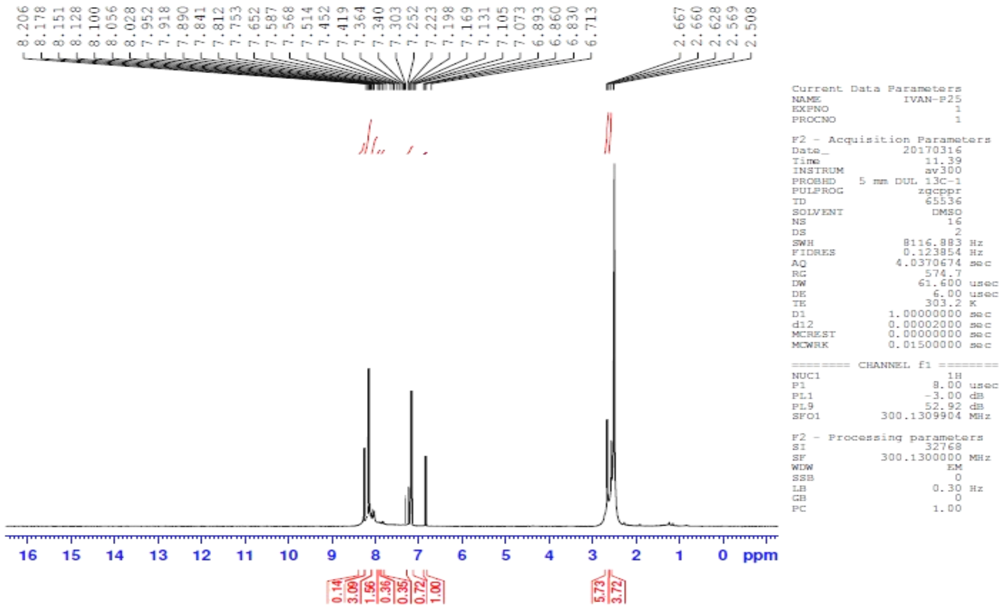
RESULTS AND DISCUSSION

For the production of the ligands (L_1 and L_2) a joined of 3-hydroxyacetophenone with the suitable diazotized in alkaline solution was performance. Synthesized ligands were identified by ^{1}H and ^{13}CNMR, FT-IR, (C,H,N) analysis and UV-Vis spectroscope technicality. Aqueous-ethanol solutions were constantly obtained into study of the interaction of metal salts with the produced ligands.

NMR spectrum

^{1}HNMR spectrum of ligand (L_1) at dimethylsulfoxide (Fig. 1) displays various signals in δ=7.073-8.206 ppm assigned into aromatic protons [10], the gesture in δ=6.713 ppm due into proton phenol [11]. The resonance at δ=2.628 ppm assigned to δ(CH_3) groups as well the signal in δ=2.50 ppm indicated into DMSO-d_6 [12]. ^{13}CNMR of (L_1) (Fig. 2) display symbol at δ=26.393 ppm due to carbon of (CH_3) in acetyl groups. The resonance at δ=196.070 ppm assigned to carbonyl groups. The various signals at (δ=160.000, 138.526, 133.649, 130.630, 129.440, 122.935, 120.445, 118.783 and 115.119 ppm attributed to carbon atoms of aromatic rings. The symbol at δ= 154.115 ppm due to carbon of (-OH) group as well signal in δ=39.536 ppm led into DMSO-d_6 [13]**.**

^{1}HNMR spectrum of ligand (L_2) shows various symbols at δ=7.028-8.258 ppm described into aromatic protons [14]. Symbol in δ=6.833 ppm due into proton phenol [15]. The symbol at δ=2.624 ppm due to δ(CH_3) of acetyl group as well symbol in δ=2.5 ppm due into DMSO-d_6 [16]. ^{13}CNMR of (L_2) display various signals at (δ=160.166, 155.061, 138.594, 134.219, 130.339, 128.777, 124.918, 119.517 and 115.124) ppm described to carbon atoms of aromatic rings. The symbol at δ=148.398 ppm described to carbon of (-OH) group. Signal in δ=28.763 ppm due into carbon for (CH_3) in acetyl group. Resonance in δ=196.104 ppm appointed into carbonyl group. The gesture at δ=39.520 ppm assigned to DMSO-d_6 [17].



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MCWRK           0.01500000 sec

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Figure 1: ^{1}HNMR spectra to the ligand (L_1)

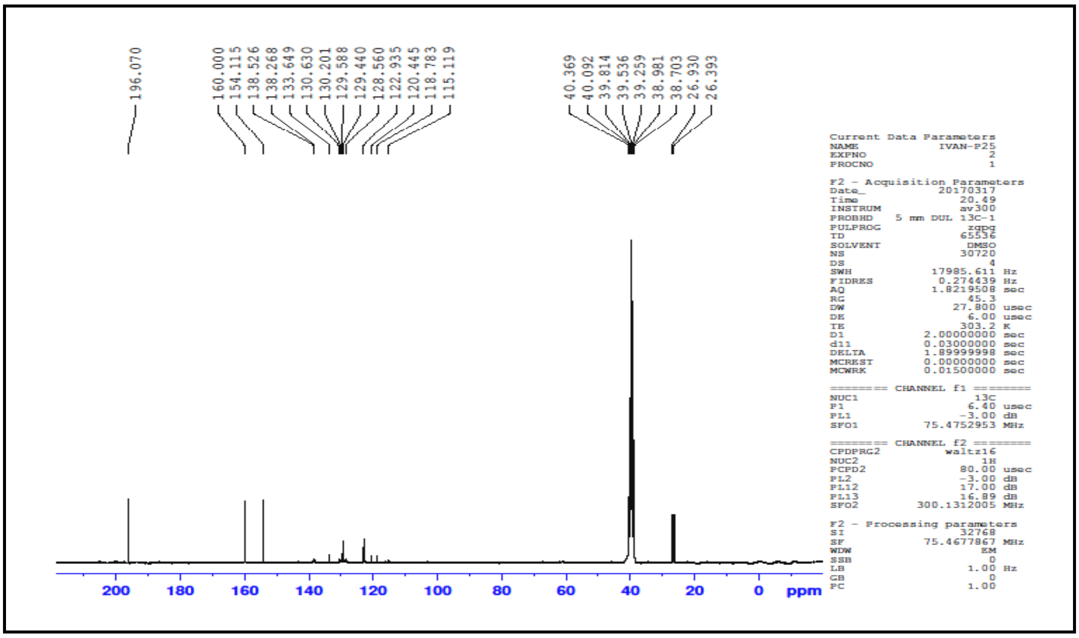

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Figure 2: ^{13}CNMR spectra to the ligand (L_1).

Calibration curve

Mixed aqueous-ethanol ligand and metal ions have been varied molar concentration (10^{-5}–10^{-3} M), only reach (1-3×10^{-4}M) concentration followed Beer’s law as well showed obvious intensive color. The best straight lines fit have been happened for correlation factor R>0.9980 like described at Fig. 3.

Model conditions

For search out interaction between produced ligand and metal ions beneath education at the preparation of compounds, the spectrum from combining solutions at ligand and metal ions into attain for optimum pH and concentration, as well firm wave length (λ_{max}) were the first studies .As well as mole ratio metal to ligand (M:L) has been defined into prepare compounds. Perfect concentration was option of compound solution based on that solution gives highest absorbance in fixed (λ_{max}) with various pH, and outcomes are described at Table 2. Trial outcomes proof such the absorbance for all prepared compounds are extreme and steady at a buffer solution from NH_4OOCCH_3 at the pH extent (5-9).All prepared compounds were found to have a perfect pH like is shown at Fig. 4.

Metal to ligand ratio

The Mole ratio and job techniques have been used to appoint the complexes in solutions. At both situations outcomes spread 1:2 (metal to ligand) ratio. Picked plot is shown at Fig. 5. Table 2 synopsizes outcomes gated, and specification into making compounds.

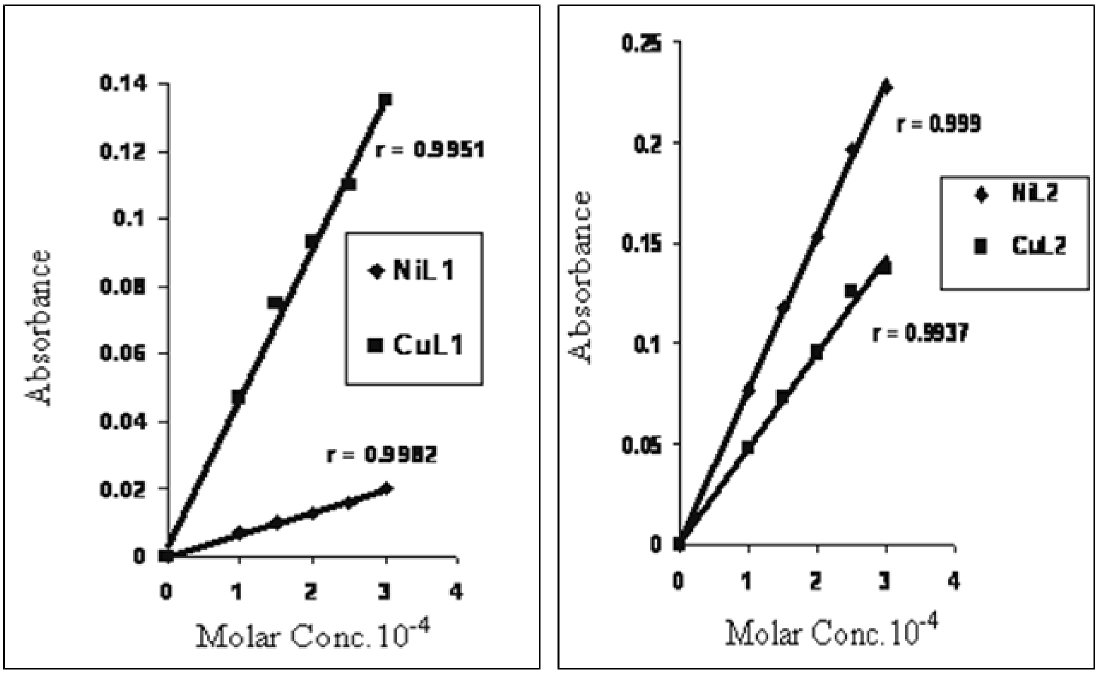


Figure 3: Linear relationship between molar condensation and absorption.

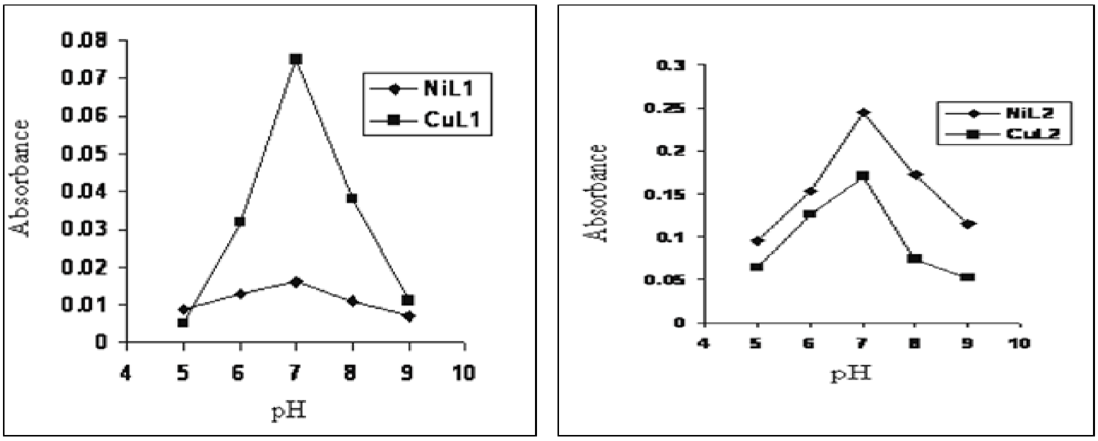
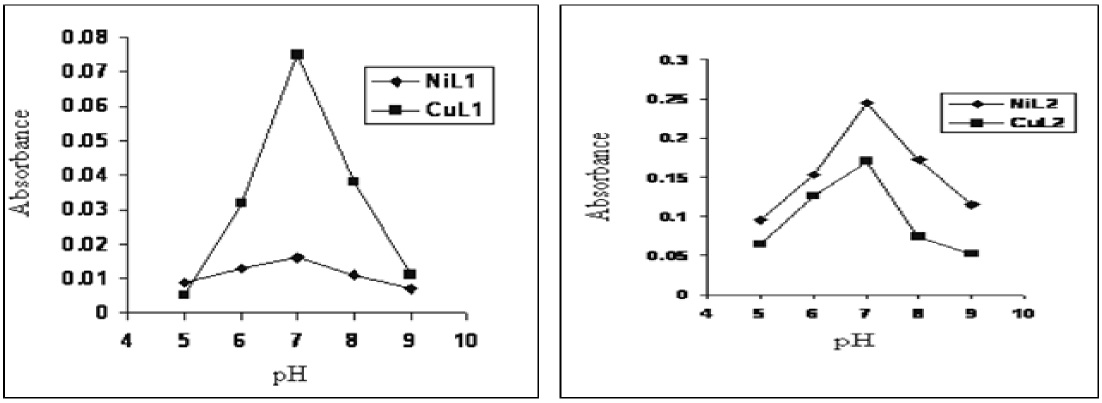


Figure 4: Effect of pH at absorption (λ_{max}) to the compounds.



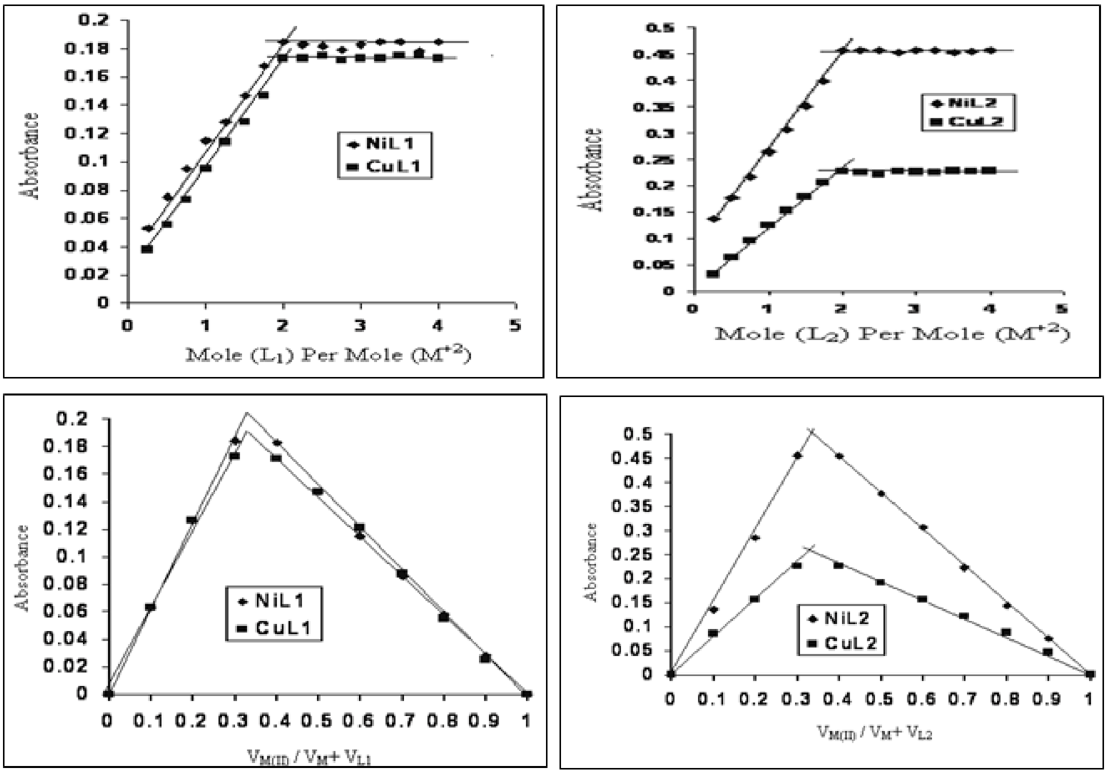


Figure 5: Mole ratio and Job manners to the compounds solutions.

Physical estates

Interaction of the ligand melted in ethanol with the metal ions melted in perfect pH and in a (Metal: Ligand) ratio of (1:2) have been produced to solid complexes. The outcome of elemental analysis and the metal import from compounds were in real identical as well calculated values. Conductivity from compounds melted at ethanol (10^{-3} M) display non- electrolytic type [18] data are included at (Table 1). Magnetic estates (Table 2) to the produced compounds have been happened to a paramagnetic that was accounted for tetrahedral structure [19].

Table 1: Physical properties to the compounds

Compounds	Color	M.P°C	Yield%	Analysis Calc (Found)			
				M%	C%	H%	N%
Ligand(L_1)	Brown	161	82	-	68.08 (67.95)	4.96 (4.78)	9.93 (8.75)
$[Ni(L_1)_2]$	Reddish brown	>300	86	9.35 (8.94)	61.93 (60.88)	4.19 (3.97)	9.03 (8.88)
$[Cu(L_1)_2]$	Orange	166	81	10.22 (9.12)	61.34 (60.98)	4.15 (3.84)	8.94 (7.93)
Ligand(L_2)	Deep brown	170	88	-	58.94 (57.86)	3.85 (3.27)	14.73 (13.74)
$[Ni(L_2)_2]$	Reddish brown	>300	80	9.26 (8.92)	53.67 (52.98)	3.19 (3.18)	13.41 (12.92)
$[Cu(L_2)_2]$	Brown	178	83	10.12 (9.96)	53.16 (52.55)	3.16 (3.12)	13.29 (12.78)

Determination of stability constant and gibbs free energy

The sequent stability constant (K) to the (1:2) metal to ligand compound can be computed according to the equations.

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

Where c = condensation to the compound solution at mole/ L α = degree for dissociation, As = Absorption in solution containing same amount of ligand and metal ion and Am= the absorption of solution containing the selfsame quantities for metal and surplus for ligand. High values for (K) refers to high constancy for produced complexes [20]. Thermodynamic parameters of Gibbs free energy (∆G) were also studied. The ∆G data have been reckoned from the equation [21].

$$\Delta G = -R\ T\ \mathrm{Ln}\ k$$

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

Table 2: Conditions of the preparation to the compounds and UV- visible, magnetic susceptibility as well as conductance mensurations datum

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)	-	-	-	234 274 326	0.825 1.190 1.106	825 1190 1106	-	-
[Ni(L_1)$_2$]	7	2	1:2	282 316 473 888 982	0.840 0.977 0.342 0.002 0.013	840 342 2 13	1.99	3.86
[Cu(L_1)$_2$]	7	1.5	1:2	304 481 980	1.908 0.466 0.046	1908 466 46	1.03	2.04
Ligand(L_2)	-	-	-	274 326 386	2.011 1.935 1.223	2011 1935 1223	-	-
[Ni(L_2)$_2$]	7	2	1:2	2773 18 380 462 888 982	1.325 1.815 0.705 0.472 0.009 0.033	1325 1815 705 472 9 33	5.86	3.91
[Cu(L_2)$_2$]	7	2.5	1:2	282 332 484 980	2.027 2.229 0.844 0.064	2027 2229 844 64	3.38	2.14

Table 3: The main frequencies to the ligands and compounds (cm^{-1})

Compounds	)OHυ(	υ(C=O) + υ(C=C)	υ (N=N)	$CH_{3\ as,s}\delta$	) M-N(υ + M-O)(υ
Ligand(L_1)	3437 br.	1685 s. 1597 s. 1500 sh.	1448 sh.	1361 sh.	-
[Ni(L_1)$_2$]	-	1681 s.	1415 s.	1415 s.	563 w.

		1597 s. 1504 s.		1396 sho. 1357 sh.	470 w.
[Cu(L₁)₂]	-	1681 s. 1597sh. 1500 s.	1419 sh.	1419 sh. 1393 sho. 1361 sh.	540 w. 501 w.
Ligand(L₂)	3402 br.	1685 sh. 1604 s.	1546 sh.	1496 sho. 1431 sh. 1346 sh.	-
[NiL₂)₂]	-	1685 sh. 1608 s.	1519 sh.	1496 sho. 1431 sh. 1408 sho. 1346 sh.	486 w. 420 w.
[Cu(L₂)₂]	-	1678 sh. 1604 sh.	1519 sh.	1489 sho. 1419 sh. 1386 sho. 1342 sh.	489 w. 459 w.

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

Effect of time

The reaction was complete in (5 min) at 25°C and continues stable for about (70 min), this shows that the ligands strong coordination with metal salts. The results are shown in Fig. 6.

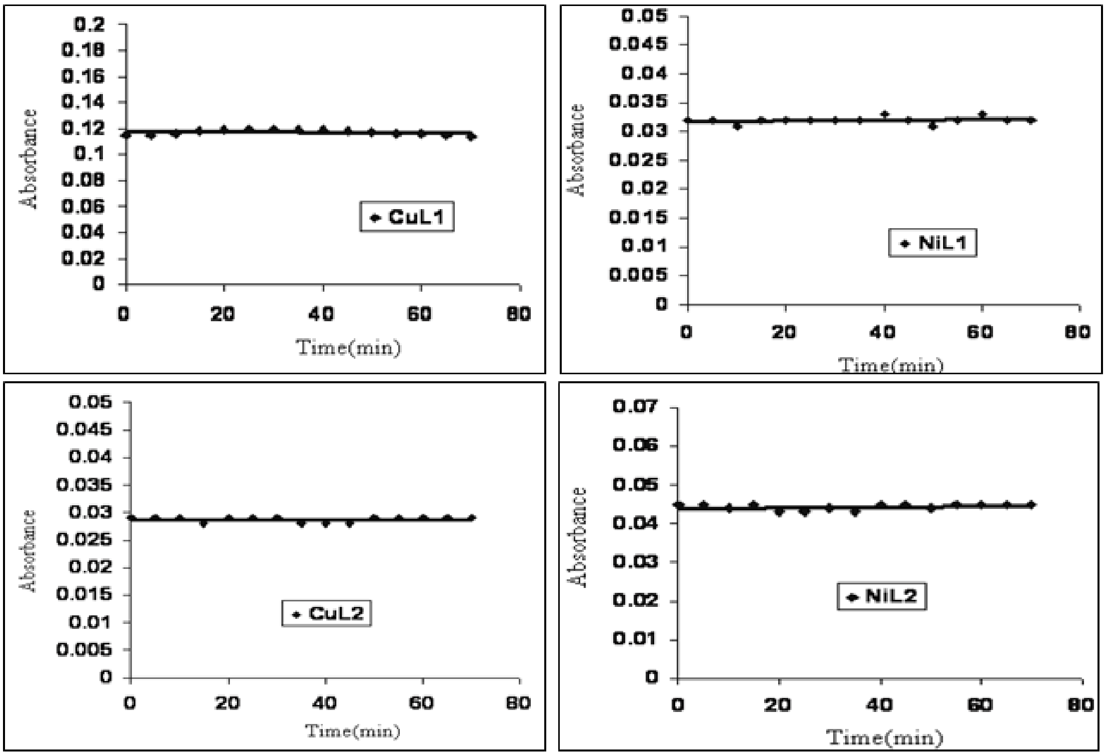


Figure 8: Effect of time on the produced compounds.

Electronic spectra

UV-Vis spectrum to the readied compounds melted at ethanol (10^{-3} M) were gauged as well the datum formed are listed at Table 2. UV- Vis spectra to the ligands shows peaks at the range (234-326 nm) were appointed into mild energy (π- π^*) transition and peak at 386 nm in the spectrum of ligand (L_2) due to (n-

π^*) transition [22,23]. The Ni(II) complexes spectra voiced absorption peaks in the range (277-380 nm) were concerning into ligand felid, thereafter else peaks at 473 and 462 nm described to charge transfer. The peaks at 888 and 982 nm else into electronic transition type $^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ and $^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ consecutively [24,25]. The Cu(II) complexes spectra showed peaks at the ranges (282-332 nm) appointed into ligand felid. Else two peaks in 481 and 484 nm found into be caused through charge transfer. The peak at 980 nm due to (d-d) electronic transition type [26,27] $^2T_2 \rightarrow {}^2E$. Shows spectra of the ligands and their Ni(II) and Cu(II) compounds.

FT-IR spectra

FT-IR spectra to the produced compounds have been collated, and the data was scheduled in Table 3. The broad band in the FT-IR spectra of the ligands at 3437 and 3433 cm^{-1}, that were described into the stretching vibration from υ(OH) phenol, the disappearance of this band at the spectra with all produced compounds pointed out the deprotonation for phenol group to coordination with metal ion [28,29]. The spectra presented band in 1685 cm^{-1} because of υ(C=O) vibration, since no significant change in this band was noticed, the possibility of coordination occur through donating atom in this group has been excluded [30, 31]. Bands differentiating of the azo groups at 1448 and 1546 cm^{-1} displaced into lower wave number for change during shape at spectra for all produced compounds [32, 33]. The bands at the range (1346-1500 cm^{-1}) due to bending frequency of (δCH_3) and stretching vibration of υ(C=C) [34, 35]. Stretching frequency bands to metal-nitrogen as well as metal-oxygen more [36, 37] assured by the existence to the bands around 420-563 cm^{-1}. Pursuant to the results protected, a tetrahedral geometry has been offered for the produced complexes.

Biological efficiency and dyeing methods

All the ready ligands and its complexes have been examined with Gram-negative and Gram-positive bacteria. Table 4 suggests the suppression spread converse bacteria sample. Dyeing performance of the ready compounds was defined at cotton fabric. Dyes have been essay of light and stability of detergent. So whole dyes shows much excellent dyeing holding as well as depth on the fabric. The dyeing was referred on Fig. 6.

Figure 6: Samples the textiles dyeing of the ligand and their complexes.

Table 4: Diameters (mm) at suppression for bacteria to the ligands and compounds

Compounds	*Staphylococcus aureus*	*Esherichia coli*
Ligand(L_1)	20	5
[Ni(L_1)$_2$]	15	8
[Cu(L_1)$_2$]	8	-
Ligand(L_2)	20	-
[Ni(L_2)$_2$]	10	5
[Cu(L_2)$_2$]	30	-

CONCLUSION

In this work, the metal ions complexes have been readied with the ligands. The willing compounds are described by melting point, atomic absorption of flame, IR and UV-visible spectral, as well conductivity quantifications. Exploration of antimicrobial activities was lifted out opposite the experimented organism. The dye and produced compounds have been applied at cotton fabric. According result data a tetrahedral structure suggested for readied complexes.

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