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Synthesis, Characterization And Microbial Efficiency Of Azo Dye Ligand Complexes With Some Metal Ions.

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ABSTRACT

4-[(2-hydroxy-4,6-dimethylphenyl)diazenyl]-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one has been readied by combination the diazonium salt of 4-aminoantipyrine with 3,5-dimethylphenol. Spectral studies (FTIR, UV-Vis, ¹H and ¹³CNMR) and microelemental analysis (C.H.N) are use to identified of the ligand. Complexes of some transition metals were performed as well depicted. The formation of complexes were characterized by using atomic absorption of flame, elemental analysis, infrared and UV-Vis spectral process as well conductivity and magnetic quantifications. Nature of compounds produced have been studied followed the mole ratio and continuous contrast methods, Beer's law followed during a concentration scope (1×10^{-4} - 3×10^{-4} M/L). height molar absorbtivity of compound solutions have been noticed. Analytical data showed that all the complexes outo 1:2 metal-ligand ratio. At the radix for physicochemical datum an octahedral structure have been described at compounds, other than the biological studies of all produced compounds was evaluation against different kindes of antimicrobial strains.

Keywords: complexes, azo dyes, microbial properties, antipyrine derivatives.

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INTRODUCTION

Azo dyes and their complexes have been varied important application in distrial and scientific resereach, its have a broad applications as redox, acidbase reagent and other uses(1). Because of azo dyes containing (O,N) donor atoms in their structure, it has been reacted with many metal ions and showed biological properties(2). Nitrogen atom in antipyrine derivatives display very important role in many biological process ,such as antibacterial, antifungal, antituberculosis, anticancer, cycotoxic, antioxadant, antitumor, anti-HIV analgesic and anti-inflammatory activity(3-5). The coordination property of antipyrine azo dye has modified felixible ligand and their complexes have been varied applications in different sides, such as pharmaceutical and medicinal uses(6). Many heterocyclic compounds of azo dyes are used in analytical chemistry for determination of metal ions(7). At that work, synthesis, identification and chelating of some metal complexes containing antipyrine azo dye as a ligand, other than the biological studies of all produced compounds was evaluation against different kindes of antimicrobial strains.

EXPERIMENTAL

Instrumentation

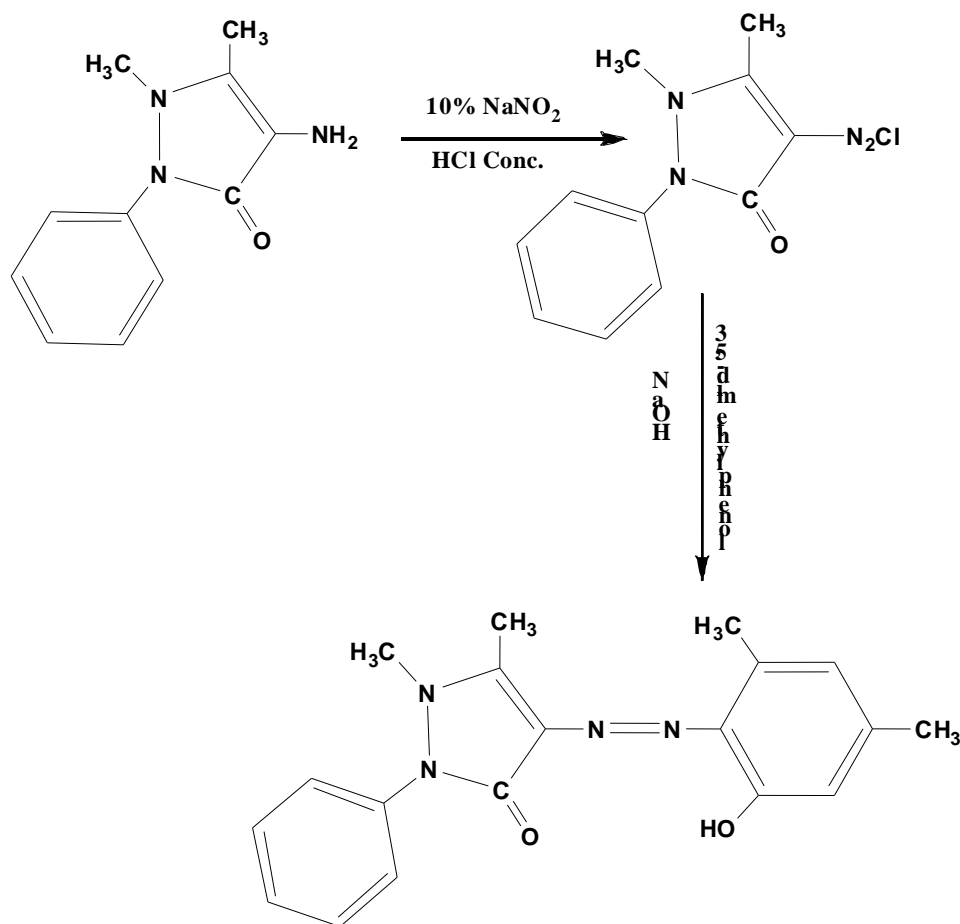
Atomic absorption has been recorded by employing a Shimadzu A.A-160A Atomic Absorption/Flame Emission Spectrophotometer. ^{13}C and ^1H -NMR spectrum have been noted at a Bruker-300 MHz Ultra Shield spectrometer on Al- al- Bayt University utilizing dimethylsulfoxide like the solvent also trimethylsaline like the reference. Microelemental analysis (C.H.N.S.O) have been done in Dimashq University, Syria, employing Euro vector EA 3000, single V.3.Osingle. Conductivity for the compunds resolved at dimethylsulphoxide (10^{-3} M/L) 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 25°C. UV- Vis spectrum have been registered at a Shimadzu UV- 160A Ultra Violet-Visible Spectrophotometer. IR- spectrum have been taken at a Shimadzu, FTIR- 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.

Materials and reagents

Obeying chemicals have been utilized like collected of purveyors: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 (Merck), 4-aminoantipyrine, 3,5-dimethylphenol (fluka).

Preparation of the ligand

A solution was produced (8), of 4-aminoantipyrine (0.503 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 (0.305 gm, 1mmole) for 3,5-dimethylphenol. 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) $\text{C}_2\text{H}_5\text{OH}$: H_2O , mixture subsequently left into dry. The reaction is appear at scheme 1.



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

Buffer solution

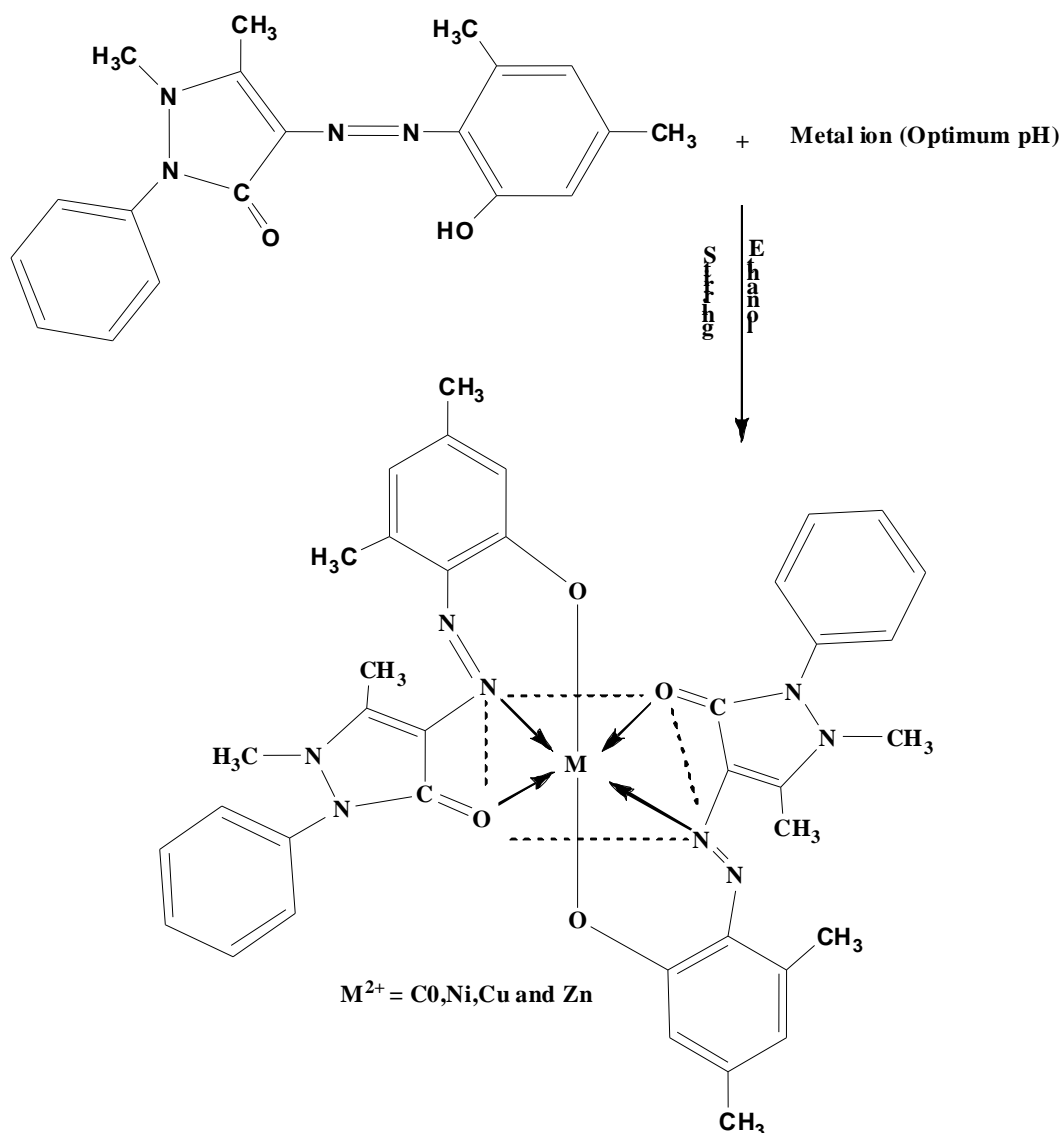
(0.01M, 0.771 gm) for ammonium acetate was dissolved at one liter for doubly deionized water. For only pH rate (5-9) was the use of CH_3COOH or NH_3 solution.

Standard solution

A bulk of standard solutions of the metal salts were made in varying concentration (10^{-5} - 10^{-3} M/L) at pH average (5-9). At the same time a bulk of ethanolic solutions of ligand within the extent of concentrations (10^{-5} - 10^{-3} M/L) was also produced.

Preparation of metal chelats

EtOH solution of the ligand (0.336 gm, 2mmole) was added drop wise with stirring to the 0.118, 0.118, 0.085 and 0.064 gm of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 dissolved in the pH solution with the needed pH. The mixture was cooled until dark color precipitate was contained, filtered, and washed number ounces with 1:1 H_2O : $\text{C}_2\text{H}_5\text{OH}$ mixture. The preparation technique is shown in scheme-2, other than the physical esatates and (C.H.N.S.O) analysis are listed in Table 1.



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

Microbial properties

Azo ligand and newly metal chelates were screened in vitro for their antibacterial and antifungal activity against: *Staphylococcus aureus*, *Escherichia Coli*, *Candida albicans* and *Candida tropicalis*. The zone of inhibition of the ligand and their metal chelates against the growth of bacteria and fungi were tested utilizing the agar diffusion technique(9). The organism tested were the agar media were inoculated with test organisms and a solution of the tested compound (100µg/ml) was placed separately in cups (10mm diameter) in the agar medium. The plates were incubated for 24 h at 37°C and the well was filled with the test solution using micropipette. During this period, the test solution was diffused and affected the growth of the inoculated microorganisms. Activity was determined by measuring the diameter of the zone showing complete inhibition(nm). Growth of inhibition was compared with the control (dimethylsulphoxide), the microbial activity results revealed that these compounds shown a good activity.

RESULTS AND DISCUSSION

Production of the azo ligands (L) a joined of 3,5-dimethylphenol with the suitable diazotized in alkaline solution was performance. Synthesized ligand was identified by spectral studies (1H , $^{13}CNMR$, FT-IR,

UV-Vis) and microelemental analysis (C.H.N.S.O). Aqueous-ethanol solutions were constantly obtained into study of the interaction of metal salts with the produced ligand.

NMR spectra

¹HNMR spectrum of the ligand (L) at dimethylsulfoxide (Fig. 1) display various signals at (δ=6.688-7.618) ppm refers to aromatic protons(10). The signal obtained at (δ=6.571) ppm lead to proton of phenol(11). Finding, the signals at (δ=3.413) ppm and (δ=2.619) ppm describe to δ(N-CH₃) and δ(CH₃) of pyrazole respectively(12). Signal at (δ=2.320) ppm was assigned to δ(CH₃) of phenol and the signals at (δ=4.506) ppm and (δ=2.50) ppm due to water(D₂O) and DMSO-d₆(13). ¹³CNMR spectrum of the ligand display resonance at (δ=19.514) ppm and (δ=34.662) ppm due to carbon of (CH₃) in phenol ring. The resonance at (δ=10.444) ppm and (δ=38.016) ppm due to carbon of (CH₃) in pyrazole group. The various signals at (δ=156.295, 140.259, 139.618, 133.117, 129.676, 129.406, 128.501, 126.674, 122.805, 115.894 and 94.185) ppm attributed to carbon atoms of aromatic rings. Signals at (δ=157.127) ppm and (δ=151.140) ppm due to carbon of (C=O) and (C-OH) groups and the indicative in (δ=39.500) ppm due into DMSO-d₆(14,15), see Fig. 2.

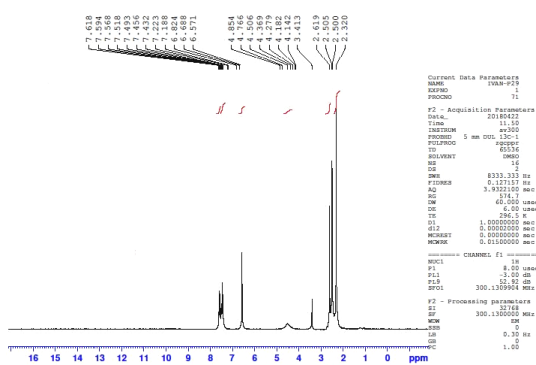


Fig 1: ¹HNMR spectrum to the azo ligand (L).

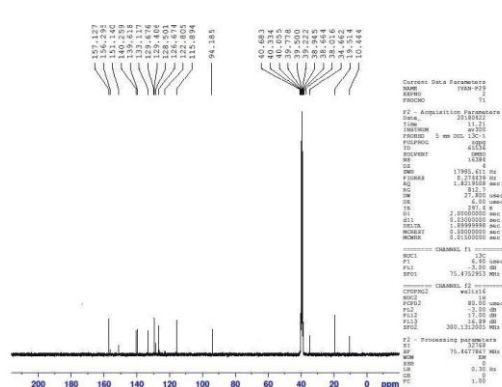


Fig 2: ¹³CNMR spectrum to the azo ligand (L).

Calibration curve

Mixed aqueous-ethanol ligand and metal ions have been varied molar concentration (10⁻⁵-10⁻³ M/L), only reach (1-3×10⁻⁴ M/L) concentration followed Beer’s law as well showed obvious intensive color. The best straight lines fit have been taken for correlation factor R>0.9980 like assigned 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_{vmax}) 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 NH₄OOCCH₃ at the pH extent (5-9).All prepared compounds were found to have a perfect pH like is shown at Fig. 4.

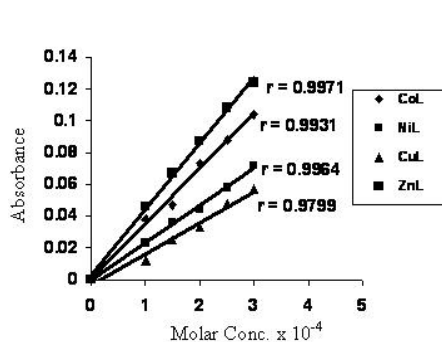


Fig 3: Linear relationship between molar condensation and absorption.

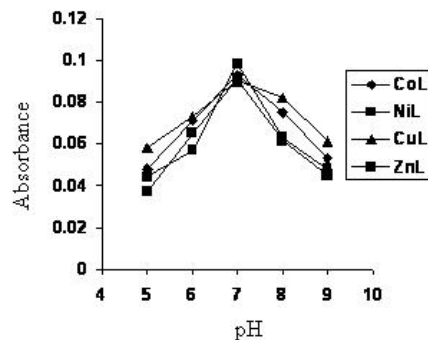


Fig 4: Effect of pH at absorption (λ_{max}) to the compounds.

Metal to ligand ratio

Mole ratio and job techniques have been tested 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 synthesizes outcomes gated, and specification into making compounds.

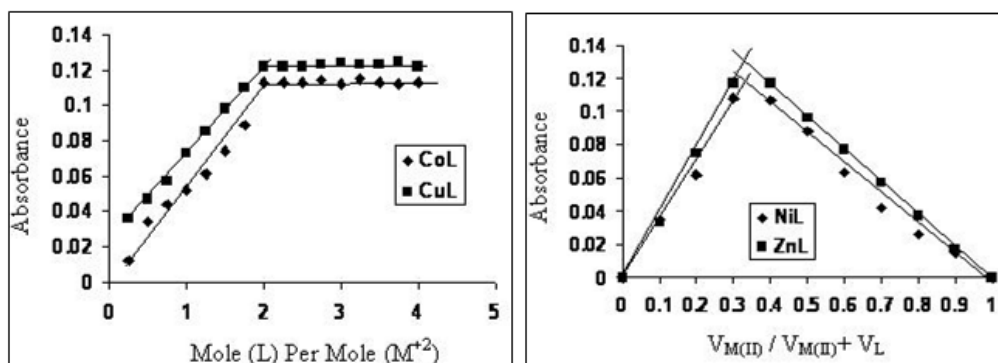


Fig 5: Mole ratio and Job manners to the compounds solutions.

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 dimethylsulphoxide (10^{-3} M/L) display non-electrolytic type(16) data are included at Table 2.

Table 1: Physical properties to the azo ligand and metal chelates

Compounds	Color	M.P ^o C	Yield %	Analysis Calc (Found)				
				M%	C%	H%	N%	O%
Ligand(L)	Yellowish orange	217	80	-	67.85 (66.88)	5.95 (4.66)	16.66 (15.92)	9.52 (8.77)
[Co(L) ₂]	Reddish brown	252	84	8.09 (7.94)	62.55 (61.85)	5.21 (4.97)	15.36 (14.88)	8.77 (7.83)
[Ni(L) ₂]	Brown	242	87	7.96 (7.12)	62.63 (61.98)	5.21 (4.84)	15.38 (14.79)	8.79 (8.04)
[Cu(L) ₂]	Deep brown	227	85	8.71 (7.92)	62.12 (61.83)	5.17 (4.96)	15.25 (14.92)	8.71 (8.11)
[Zn(L) ₂]	Orange	244	83	8.84 (8.06)	62.04 (61.68)	5.17 (4.92)	15.23 (14.78)	8.70 (7.98)

Table 2: Conditions of the produced 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 DMSO	μ _{eff} (B.M)
Ligand(L)	-	-	-	242 356 414	1.8941 .8531. 177	1894 1853 1177	-	-
[Co(L) ₂]	7	2.5	1:2	244 350 460 732 868 978	1.760 2.119 0.288 0.005 0.008 0.090	1760 2119 288 5 8 90	19.20	4.51
[Ni(L) ₂]	7	2.5	1:2	246 354 458 724 894 982	1.482 1.775 0.247 0.019 0.003 0.025	1482 1775 247 19 3 25	15.00	2.93
[Cu(L) ₂]	7	2.5	1:2	246 352 481 980	1.242 1.570 0.178 0.018	1242 1570 178 18	16.81	1.71
[Zn(L) ₂]	7	2.5	1:2	246 354 450	1.531 1.914 0.368	1531 1914 368	18.30	Dia

Determination of stability constant and gibbs free energy

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

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

Where c = condensation to the compound solution at mole/ L α = degree for dissociation, A_s = Absorption in solution containing same amount of ligand and metal ion and A_m = 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⁽¹⁷⁾. Thermodynamic parameters of Gibbs free energy (ΔG) were also studied. The ΔG data have been reckoned from the equation⁽¹⁸⁾.

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

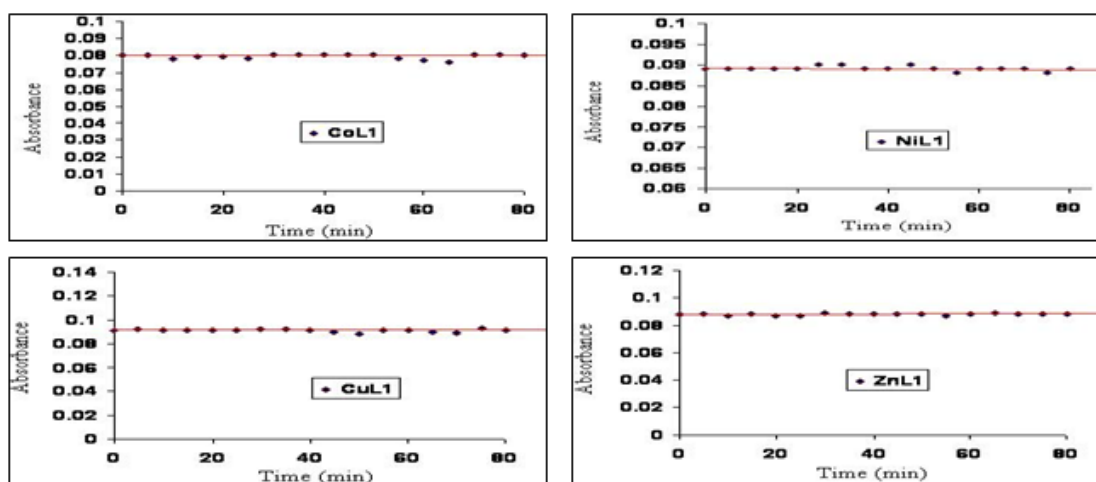
Where; R = gas constant = 8.314 J.mol⁻¹.K, T = absolute temperature (Kelvin). Negative value of (ΔG) due to the reaction between azo dye ligand (L) and metal ions understudy are spontaneous, see Table 3.

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

Complexes	A_s	A_m	A	k	Lin k	$\Delta G \text{ kJ.mol}^{-1}$
[Co(L) ₂]	0.052	0.113	0.539	12.13×10^6	16.311	-40.411
[Ni(L) ₂]	0.047	0.108	0.564	9.90×10^6	16.108	-39.908
[Cu(L) ₂]	0.073	0.122	0.401	39.93×10^6	17.502	-43.362
[Zn(L) ₂]	0.066	0.117	0.435	28.25×10^6	17.156	-42.505

Effect of time

Time effect have been studied for color complex solution under perfect condition (pH, concentration and wavelength), the reaction was complete in (5 min) at 25°C and continues stable for about (80 min), this shows that the ligands strong coordination with metal salts. The results are shown in Fig. 6.


Fig 6: Effect of time on the produced compounds.

Electronic spectra

UV-Vis spectra to the produced compounds melted at ethanol (10^{-3} M/L) were gauged as well the datum formed are listed at Table 2. UV-Vis spectrum to the azo ligand (Fig. 7) shows peaks at 242 and 356 nm were appointed into mild energy ($\pi-\pi^*$) transition and peak at 414 nm due to ($n-\pi^*$) transition (19, 20). Co(II) spectrum appears three peaks at 244, 350 and 460 nm attributed to ligand field and charge transfer, peaks at 732, 868 and 978 nm described to electronic transition type ${}^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$, ${}^4T_{1g(F)} \rightarrow {}^4A_{2g}$ and ${}^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$ respectively, also the value of the magnetic moment at 4.51 B.M may be taken as additional evidence for octahedral geometry (21). Ni(II) complex exhibited three absorption peaks at 246, 354 and 458 nm which were assigned to ligand field and charge transfer. Other peaks at 724, 894 and 982 nm were assigned to electronic transition type ${}^3A_{2g} \rightarrow {}^3T_{1g(P)}$, ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$ and ${}^3A_{2g} \rightarrow {}^3T_{2g(F)}$ respectively. Magnetic moment of this complex was found at 2.93 B.M which was very close to the octahedral environment (22). Cu(II) complex (Fig. 8) shows peaks at 246, 352 and 481 nm due to ligand field and charge transfer, while peak at 980 nm described to electronic transition type ${}^2E_g \rightarrow {}^2T_{2g}$, the magnetic moment of this complex was found at 1.71 B.M which was very close to the octahedral environment (23). Spectrum of Zn(II) complex show the charge transfer, and the magnetic susceptibility shows that the complex has diamagnetic moments, because d-d transition are not possible hence electronic spectra did not give any fruitful information, in fact this result is a good agreement with previous work of octahedral geometry(24).

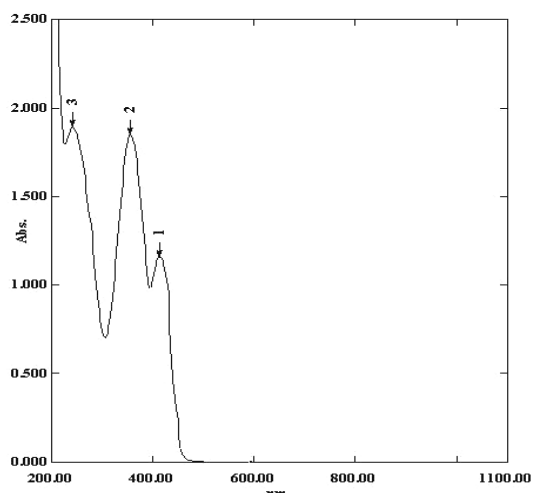
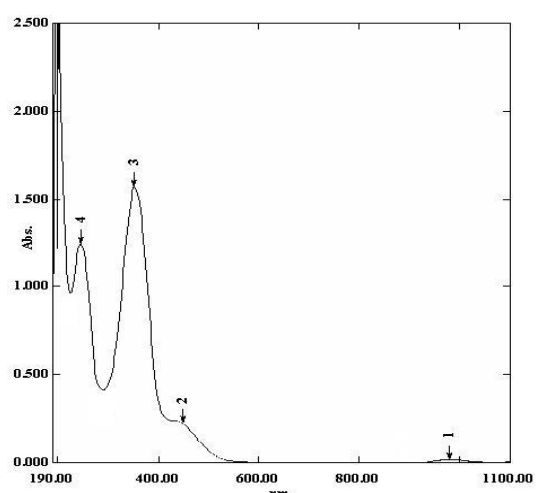


Fig 7: UV- Visible spectrum of the azo ligand (L).


 Fig 8: UV- Visible spectrum of the azo [Cu(L)₂] complex.

FT-IR spectra

FTIR spectra to the azo ligand and their metal chelates have been collated, and the data was scheduled in Table 4. The broad band in the spectrum of the ligand (Fig. 9) at 3410 cm⁻¹, that was described into the stretching vibration from $\nu(\text{OH})$ phenol, the disappearance of this band at the spectra with all produced compounds (Fig. 10) pointed out the deprotonation for phenol group to coordination with metal ion(25). Spectrum presented band in 1666 cm⁻¹ because of $\nu(\text{C}=\text{O})$ vibration, on complexation (Figure 10) this band has been removed to lower frequency implying the coordination with metal ion(26). Band differentiating of the azo group at 1585 cm⁻¹ displaced into lower wave number for change during shape at spectra for all produced compounds(27). The bands at the rate (1319-1496 cm⁻¹) due to bending frequency of (δCH_3)(28). Stretching frequency bands to metal-nitrogen on other than metal-oxygen more (29,30) assured by the existence to the bands at rate 432-489 cm⁻¹. Pursuant to the results protected, an octahedral geometry has been offered for the produced metal chelates.

Table 4: The main frequencies to the ligand and compounds (cm⁻¹)

Compounds	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{N}=\text{N})$	CH_3 as, s, δ	$\nu(\text{M}-\text{N})$ ($\nu(\text{M}-\text{O})$) ν_+
Ligand(L)	3410 br.	1666 sh.	1585 sh.	1496 sh. 1442 s. 1415 sho. 1369 sh. 1319 sh.	-
[Co(L) ₂]	-	1627 s.	1581 s.	1492 sh. 1458 sh. 1396 sh. 1311 sh.	459 w. 439 w.
[Ni(L) ₂]	-	1627 s.	1577 sho.	1492 sh. 1458 sh. 1419 sho. 1396 sh. 1311 sh.	474 w. 435 w.
[Cu(L) ₂]	-	1627 sh.	1581 s.	1492 s. 1458 sh. 1400 sh. 1373 sho. 1311 sh.	489 w. 459 w.
[Zn(L) ₂]	-	1627 sh.	1577 s.	1492 s. 1458 sh.	459 w. 432 w.

				1400 sh.	
				1311 sh.	

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

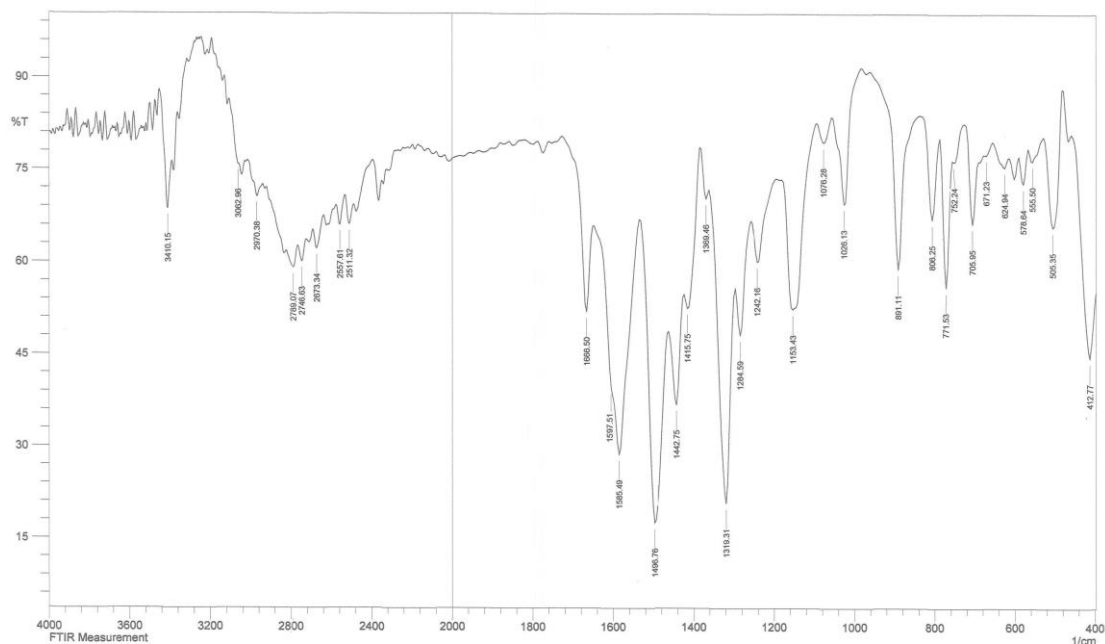


Fig 9: FTIR spectrum to the azo ligand (L).

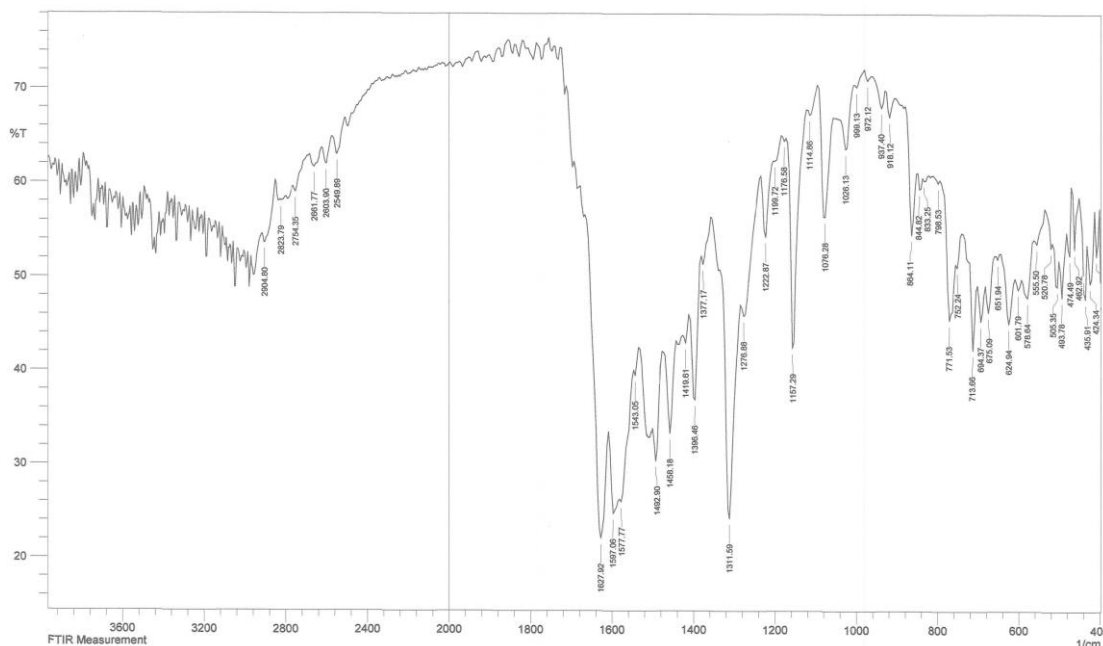


Fig 10: FTIR spectrum to the [Ni(L)₂] complex.

Microbial efficiency

All the ready ligands and its metal chelates have been examined with antibacterial and antifungal activity against: *Staphylococcus aureus*, *Esherichia Coli*, *Candida albicans* and *Candida tropicalis*, Table 5 suggests the suppression spread converse microbial sample.

Table 5: Diameters (mm) at suppression for microbial activity to the azo ligand and compounds

Compounds	Staphylococcus aureus	Esherichia coli	Candida albicans	Candida tropicalis
Ligand (L)	17	12	10	-
[Co(L) ₂]	15	15	-	-
[Ni(L) ₂]	14	13	16	-
[Cu(L) ₂]	11	11	8	-
[Zn(L) ₂]	15	11	11	-

CONCLUSION

In this work, the metal chelates complexes have been readied with the ligand. 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. According result data an octahedral structure suggested for readied complexes.

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