

Synthesis, Spectral Studies and Microbial Evaluation of Azo Dye Ligand Complexes with Some Transition Metals

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Abstract

1-(4-amino-3-(benzo[d]thiazol-2-ylidiazonyl)phenyl)ethanone has been synthesized by reaction of the diazonium salt of 2-aminobenzothiazole with 4-aminoacetophenone. Spectroscopic studies (FTIR, UV-Vis, ¹H and ¹³CNMR) and microelemental analysis (C.H.N.S.O) are used to identify the azo ligand. Metal chelates of some transition metals were performed as well depicted. Complexes were identified using atomic absorption of flame, elemental analysis, infrared and UV-Vis spectral processes 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} mol/L). Height molar absorptivity of compound solutions have been noticed. Analytical data showed that all the complexes follow a 1:2 metal-ligand ratio. At the radius of physicochemical datum an octahedral structure has been described at compounds. Other than the biological studies of all produced compounds was evaluation against different kinds of antimicrobial strains.

Keywords: metal chelates, azo dyes, microbial studies, thiazolyl derivatives.

1-INTRODUCTION

Heterocyclic azo dyes compounds and their derivatives have been used for dyeing industry, electrochromism, nonlinear optical elements and printing system [1]. Thiazolyl azo and their derivatives are assigned as heterocyclic compounds and very importance uses in different fields [2,3], it has been made to determination for many metal ions [4]. Because of the coordination chemistry of azo dyes and their derivatives, it has been used as complexing agents, dyeing materials, antidepressants, antitubercular agents and model for biological systems [5]. Metal chelates of azo dye ligands are higher important type for dyeing the wool, nylon and silks lead to higher fastness for washing and light [6]. Recently metal chelates containing azo dyes have attracted increasing attention into increasing electronic and structural features in connection with their application for molecular memory storage [7]. At that work, synthesis, identification and chelating of some metal complexes containing thiazolyl azo dye as a ligand, as well biological studies of all produced compounds was evaluation against different kinds of antimicrobial strains.

2-EXPERIMENTAL

2-1-Instrumentation

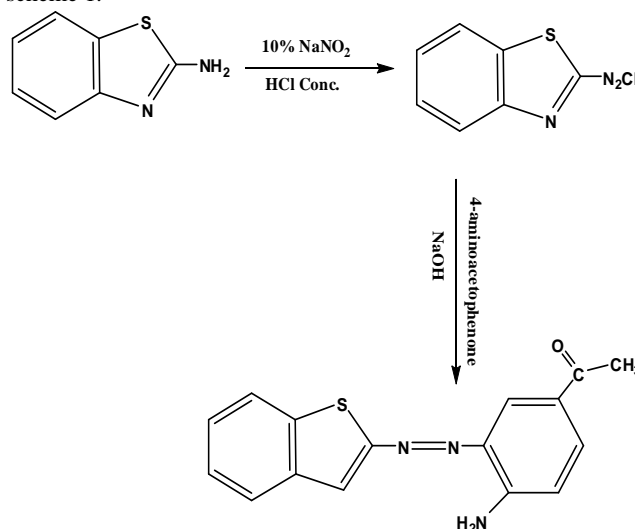
Magnetic properties have been completed through utilizing Auto Magnetic Susceptibility Balance Sherwood Scientific instrument at 25°C. Atomic absorption has been recorded by employing a Shimadzu A.A-160A Atomic Absorption/Flame Emission Spectrophotometer. ¹³C and ¹H-NMR spectrum have been noted at a 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.3.0 single. Conductivity for the compounds resolved at dimethylsulphoxide (10^{-3} mol/L) was recorded at 25°C utilizing Philips PW-Digital Conductimeter. 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.

2-2-Materials and reagents

Following chemicals have been utilized like collected of purveyors: CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O and ZnCl₂ (Merck), 2-aminobenzothiazole, 4-aminoacetophenone (B.D.H).

2-3-Preparation of the ligand

2-aminobenzothiazole [8] (0.335 gm, 1mmole) melted in mixture (10ml ethanol, 2ml conc. HCl), and diazotized at 5°C with 10% solution of NaNO₂. Diazotized solution has been added collyrium wise for stirring into a cooled ethanolic solution at (0.337 gm, 1mmole) for 4-aminoacetophenone. Then 25 ml at (1M, NaOH) solution has been followed into dusky colored mix and precipitation for azo ligand has been noticed. This deposit has been filtrated, washed number ounces for (1:1) C₂H₅OH: H₂O, mixture subsequently left into dry. The reaction is appear at scheme 1.



Scheme 1: Synthesis of azo ligand (L).

2-4-Buffer solution

(0.01 mol/L, 0.771 gm) for ammonium acetate was melted at one liter for doubly deionized water. For only pH scope (5-9) was the use of CH₃COOH or NH₃ solution.

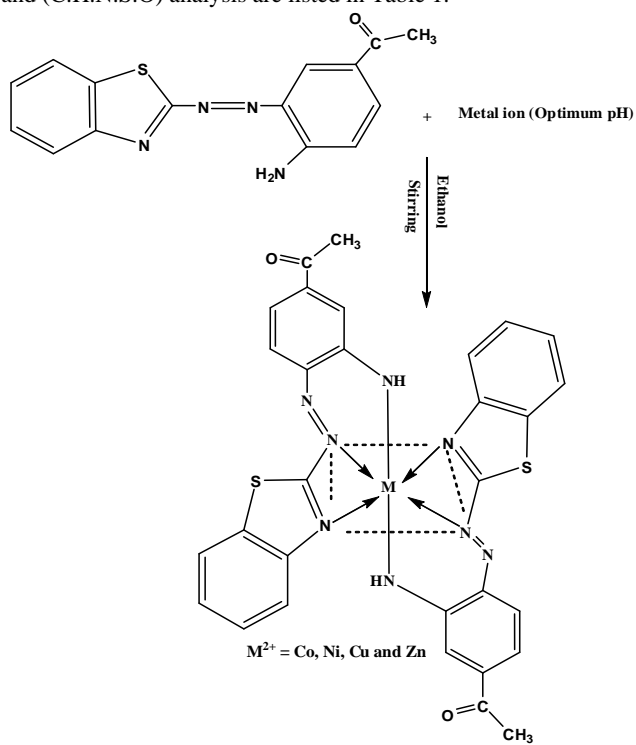
2-5-Standard solution

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

2-6-Preparation of metal chelates

EtOH solution of the ligand (0.296 gm, 2mmole) was added drop wise with stirring to the 0.118, 0.118, 0.085 and 0.064 gm of CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O and ZnCl₂ 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 H₂O: C₂H₅OH 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: Suggested structure of the metal (II) complexes of azo ligand (L).

2-7-Microbial evaluation

Qualitative screening for antimicrobial activities was performed preliminarily using the disc diffusion assay, in vitro microbial activities were measured from the diameter of clear inhibition zones caused by samples against the same bacteria and fungi

under the same experimental condition. To verify the stability of new complexes in dimethylsulphoxide (DMSO) solution a long term. Microbial activity of the ligand and its metal chelates were tested on microorganisms. Bioactive were appreciated by measuring the growth inhibition zone against test organisms and minimal inhibition concentration [9]. It was found that the synthesized new metal complexes exhibited promising antibacterial and antifungal activity against: *Staphylococcus aureus*, *Esherichia Coli*, *Candida albicans* and *Candida tropicalis*.

3-RESULTS AND DISCUSSION

Production of the azo ligand (L) a joined of 4-aminoacetophenone with the suitable diazotized in alkaline solution was performance. Produced ligand was identified by spectral studies (¹H, ¹³CNMR, 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.

3-1-NMR spectra

The ¹HNMR spectrum of the ligand at dimethylsulfoxide (Fig. 1) display many signals at (δ=7.048-7.897) ppm assigned to aromatic protons [10]. Signals obtained at (δ=7.926) ppm and (δ=2.672) ppm due to δ(NH₂) and δ(CH₃) of acetyl group sequences [11], the signal observed at (δ=2.50) ppm lead to DMSO-d₆. ¹³CNMR spectrum of the azo ligand (Fig. 2) shows resonance at (δ=196.370) ppm and (δ=152.921) ppm were described to carbon of (C=O) of acetyl and amino groups sequences. Various signals at (δ=155.030, δ=131.896, δ=131.743, δ=131.680, δ=129.543, δ=124.984, δ=121.719, δ=120.936, δ=119.533, δ=118.578 and δ=99.966) ppm lead to carbon atoms of aromatic rings. Resonance at (δ=13.550) ppm and (δ=36.115) ppm due to carbon of (CH₃) in pyrazole group. The resonance at (δ=26.381) ppm and (δ=39.783) ppm due to carbon of (CH₃) in acetyl group and DMSO-d₆ [12,13].

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%	S%
Ligand(L)	Brown	179	83	-	60.81 (59.93)	4.05 (3.88)	18.91 (17.96)	5.40 (4.91)	10.81 (10.32)
[Co(L) ₂]	Yellowish orange	260 Dec	80	9.09 (8.91)	55.46 (55.12)	3.38 (2.97)	17.25 (16.77)	4.93 (3.89)	9.86 (8.94)
[Ni(L) ₂]	Yellow	300 >	81	8.95 (7.88)	55.55 (54.91)	3.39 (2.87)	17.28 (16.92)	4.93 (4.36)	9.87 (8.86)
[Cu(L) ₂]	Deep green	295 Dec	84	9.78 (8.92)	55.04 (54.11)	3.36 (3.05)	17.12 (16.85)	4.89 (4.62)	9.78 (8.94)
[Zn(L) ₂]	Reddish brown	178	83	9.92 (8.86)	54.96 (54.11)	3.35 (2.92)	17.09 (16.78)	4.88 (4.22)	9.77 (8.85)

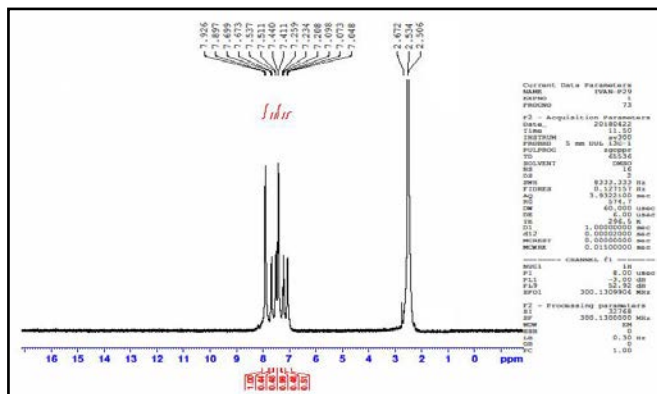


Fig. 1: ¹HNMR spectrum to the azo ligand (L).

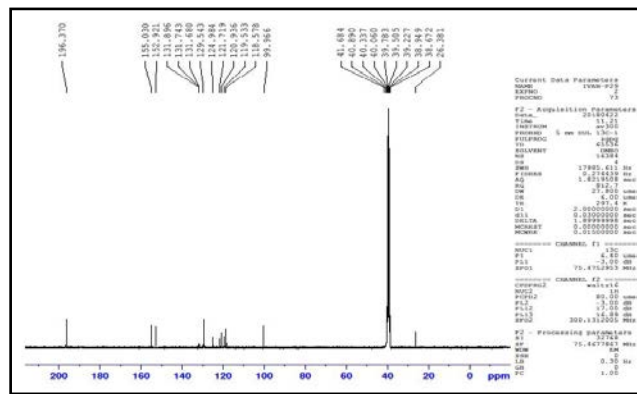


Fig. 2: ¹³CNMR spectrum to the azo ligand (L).

3-2-Calibration curve

Mixed aqueous-ethanol ligand and metal ions have been varied molar concentration (10^{-5} – 10^{-3} mol/L), only reach ($1-3 \times 10^{-4}$ mol/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.

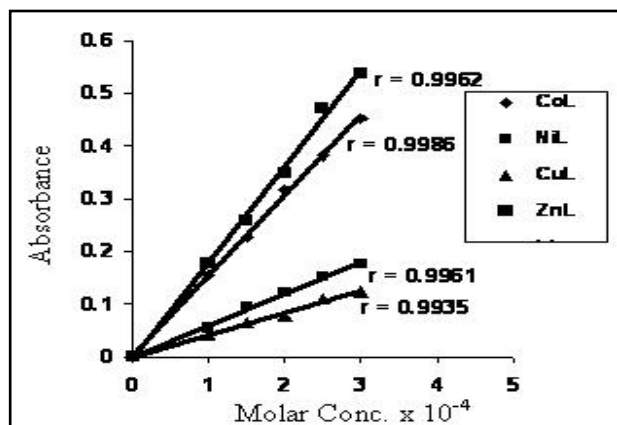


Fig. 3: Linear relationship between molar concentration and absorption.

3-3-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.

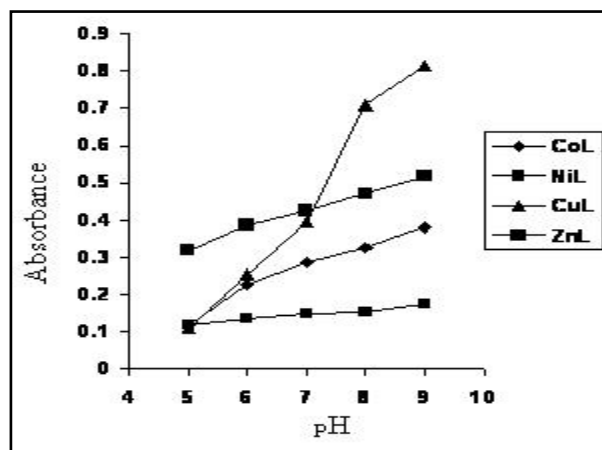


Fig. 4: Effect of pH at absorption (λ_{max}) to the compounds.

3-4-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 synopsis outcomes gated, and specification into making compounds.

3-5- 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 ligand and metal chelates melted at dimethylsulphoxide (10^{-3} mol/L) display non-electrolytic type [14], data are recorded at Table 2.

Table 2: Conditions of the produced compounds and UV- Visible, magnetic susceptibility as well as conductance mensurations datum.

Compounds	Optimum pH	Optimum Molar Conc. $\times 10^{-4}$	M:L Ratio	(λ_{max}) nm	ABS	ϵ_{max} ($L.mol^{-1}.cm^{-1}$)	$\Lambda_m(S.cm^2.mol^{-1})$ In DMSO	μ_{eff} (B.M)
Ligand(L)	-	-	-	218 270 396	1.950 1.066 2.039	1950 1066 2039	-	-
[Co(L) ₂]	9	2.5	1:2	217 271 418 458 754 864 978	0.914 0.587 0.961 0.618 0.006 0.009 0.096	914 587 961 618 6 9 96	16.77	4.72
[Ni(L) ₂]	9	2.5	1:2	220 272 400 466 732 886 972	1.829 1.118 2.276 0.500 0.004 0.006 0.062	1829 1118 2276 500 4 6 62	13.70	3.01
[Cu(L) ₂]	9	2.5	1:2	220 272 404 470 886	1.877 1.138 1.817 0.725 0.075	1877 1138 1817 725 75	18.32	1.72
[Zn(L) ₂]	9	2.5	1:2	218 274 398 472	0.843 0.489 0.799 0.247	843 489 799 247	17.70	Dia

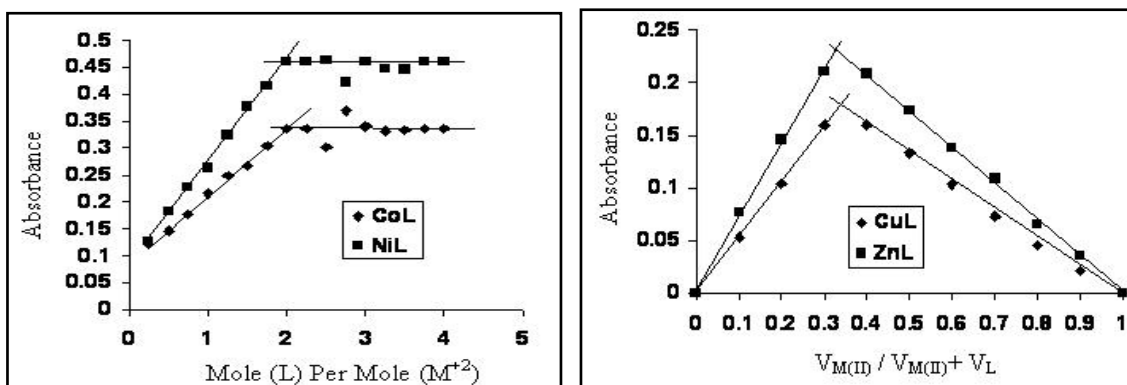


Fig. 5: Mole ratio and Job manners to the compounds solutions.

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

Complexes	A _s	A _m	α	k	Ln k	ΔG kJ.mol ⁻¹
[Co(L) ₂]	0.216	0.337	0.359	58.27×10 ⁶	17.880	- 44.298
[Ni(L) ₂]	0.263	0.460	0.428	30.10×10 ⁶	17.220	- 42.663
[Cu(L) ₂]	0.095	0.162	0.413	34.53×10 ⁶	17.357	- 43.003
[Zn(L) ₂]	0.115	0.211	0.454	23.74×10 ⁶	16.982	- 42.074

3-6-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 [15]. Thermodynamic parameters of Gibbs free energy (ΔG) were also studied. The ΔG data have been reckoned from the equation [16].

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

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.

3-7-Time effect

Time effect have been studied for color complex solution under exactly condition (pH, concentration and wavelength), the reaction was complete in (5 min) at 25°C and continues stable for about (90 min), this shows that the ligand strong coordination with metal salts. The results are shown in Fig. 6.

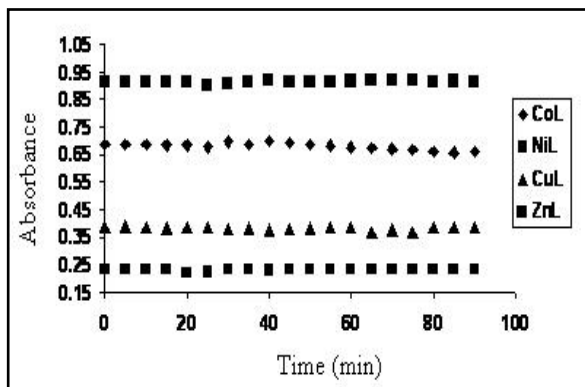


Fig.6: Effect of time on the produced compounds.

3-8- Electronic spectra

UV-Vis spectra for the ligand and their metal chelates melted at ethanol (10⁻³ mol/L) were gauged as well the datum formed are listed at Table 2. UV-Vis spectrum to the azo ligand (Fig. 7) display peaks at 218, 270 and 396 nm were appointed into mild energy (π-π*) transition [17]. Co(II) spectrum shows peaks at 217, 271, 418 and 458 nm attributed to ligand field and charge transfer, other peaks at 754, 864 and 978 nm due to electronic transition type ⁴T_{1g(F)}→⁴T_{1g(P)}, ⁴T_{1g(F)}→⁴A_{2g} and ⁴T_{1g(F)}→⁴T_{2g(F)} respectively, also the value of the magnetic moment at 4.72 B.M may be taken as additional evidence for octahedral geometry [18]. Ni(II) complex (Fig. 8) exhibited fourth absorption peaks at 220, 272, 400 and 466 nm which were described to ligand field and charge transfer. Peaks at 732, 886 and 972 nm were assigned to electronic transition type ³A_{2g}→³T_{1g(P)}, ³A_{2g}→³T_{1g(F)} and ³A_{2g}→³T_{2g(F)} respectively. Magnetic moment of this complex was found at 3.01 B.M which was very close to the octahedral environment [19]. Cu(II) complex appears peaks at 220, 272, 404 and 470 nm lead to ligand field and charge transfer, other than peak at 886 nm described to electronic transition type ²E_g→²T_{2g}, the magnetic moment of this complex was found at 1.72 B.M which was very close to the octahedral environment [20]. Zn(II) complex display 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 [21].

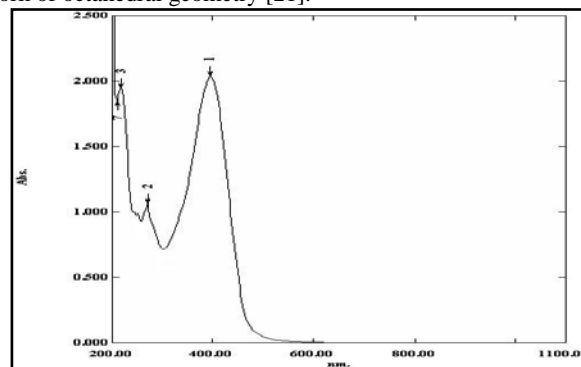


Fig. 7: UV- Visible spectrum of the azo ligand (L).

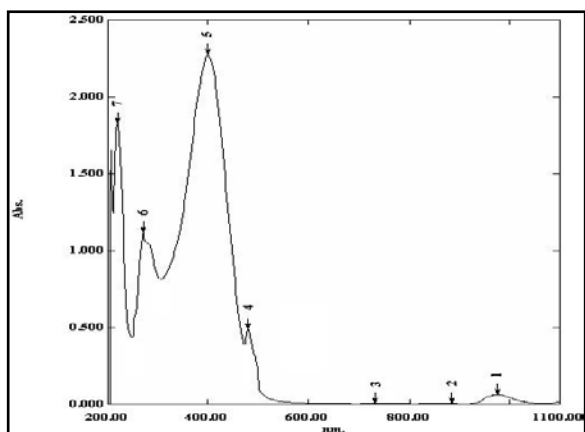


Fig. 8: UV- Visible spectrum of the azo [Ni(L)₂] complex.

3-9- FTIR spectra

FTIR spectra to the azo ligand and their metal chelates have been collated, and the data was scheduled in Table 4. Spectrum of the

ligand (Fig. 9) exhibited bands at 3483 cm⁻¹ and 3414 cm⁻¹ which were assigned to stretching vibration of ν(NH₂), at the spectra of all produced compounds (Fig. 10) pointed out the deprotonation for amino group to coordination with metal ion [22]. Band at 1678 cm⁻¹ due to carbonyl ν(C=O) of acetyl group, no significant change in this band was noticed, the possibility that coordination occur via the donating atom in this group was excluded [23]. Strong band at 1654 cm⁻¹ described to ν(C=N) of thiazole ring, at the spectra of metal chelates this band has been removed to lower frequency implying the coordination with metal ion [24]. Band of the azo group at 1531 cm⁻¹ displaced into lower wave number for change during shape at spectra for all produced compounds [25]. Bands at 1589 cm⁻¹ and 1570 cm⁻¹ attributed to ν(C=C), and the bands at (1442, 1423, 1396 and 1342) cm⁻¹ lead to bending vibration of δ(CH₃) group [26]. Stretching frequency bands to metal-nitrogen more [27,28] assured by the existence to the bands at rate 432-484 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	ν(NH ₂) ν(NH)+	ν(C=O) +ν(C=N)	ν(C=C) +ν(N=N)	δCH ₃ as,s	ν(M-N)
Ligand(L)	3483 sh. 3414 sh.-	1678 sho. 1654 s.	1589 sh. 1570 sho. 1531 s.	1442 sh. 1423 sh. 1396 sh. 1342 sh.	-
[Co(L) ₂]	-3421 br.	1678 sh. 1635 sho.	1597 sh. 1570 sho. 1508 sh.	1446 sh. 1415 sh. 1346 s.	484 w. 455 w.
[Ni(L) ₂]	-3421 br.	1678 sh. 1639 s.	1597 sh. 1586 sho. 1512 sh.	1446 sh. 1419 sh. 1357 sh.	459 w. 432 w.
[Cu(L) ₂]	-3425 br.	1678 s. 1635 sho.	1597 sh. 1572 sho. 1519 sh.	1450 sh. 1423 sh. 1392 sh. 1357 s.	470 w. 451 w.
[Zn(L) ₂]	-3479 br.	1678 sh. 1620 sho.	1600 sh. 1558 sho. 1508 sh.	1454 sh. 1427 sh. 1396 sh. 1357 sh.	482 w. 451 w.

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

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

Compounds	Staphylococcus aureus	Esherichia coli	Candida albicans	Candida tropicalis
Ligand (L)	13	11	-	-
[Co(L) ₂]	14	14	-	-
[Ni(L) ₂]	11	14	15	10
[Cu(L) ₂]	21	21	-	-
[Zn(L) ₂]	13	12	-	-

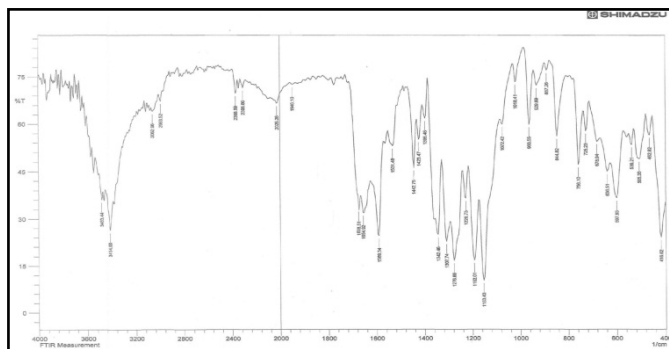


Fig. 9: FTIR spectrum to the azo ligand (L).

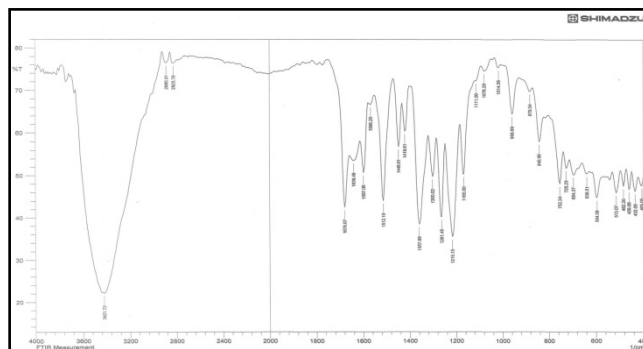


Fig. 10: FTIR spectrum to the [Ni(L)₂] complex.

3-10-Microbial evaluation

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

4-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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