



## Synthesis and Characterization of 6- (4- Acetylphenyl azo) - 3 - Aminobenzoic Acid Complexes for Some Transition Metals

Abaas Obaid Hussein<sup>1\*</sup>, Rana Abdulilah Abbas<sup>2</sup>, Zainab A.Al-Mousway<sup>3</sup>, Nibras Abdul-Ameer Aboud<sup>2</sup>

<sup>1</sup>. Ministry of Education, Babylon Education, Iraq.

<sup>2</sup>. Department of Chemical Industrial, Institute of Technology/ Baghdad, Middle Technical University, Iraq.

<sup>3</sup>. University of Baghdad, College of Agricultural, Division of Basic Science, Iraq.

\*Corresponding Author: Abaas Obaid Hussein

### Abstract

Azo dye 6-(4-acetylphenyl azo)-3-aminobenzoic acid was produced by grouping the diazonium salt from 4-aminoacetophenone for 3-aminobenzoic acid. Geometry of azo - ligand was resolved on origin of elemental analysis, spectroscopic studies such as <sup>1</sup>H and <sup>13</sup>CNMR, FTIR and UV-Vis. Handling produced azo ligand for transition metal chelates at aquatic ethanol for a 1:2 metal: ligand ratio, as well in perfect pH. The metal chelates have been described by utilizing atomic absorption flame, elemental analysis, FTIR and UV-Vis, as well conductivity and magnetic susceptibility mechanism. Nature for produced compounds have been studied obeyed mole ratio as well, methods of continuous variation, Beer's law yielded up a condensation rate ( $1 \times 10^{-4}$  -  $3 \times 10^{-4}$ M). High molar were absorbtivity were observed for complex solutions. On origin data a tetrahedral geometry were assigned for the produced complexes. Biological activity of the produced compounds was assayed.

**Keywords:** Metal chelate, Azo dyes, Complexes, Biological activity.

### Introduction

Azo dyes are very important in the industrial application and more stabile group of prepared organic dyes with a tremendous number of industrial applications [1]. Azo compounds have been involved biological reaction according to inhibition of DNA, RNA and protein synthesis [2]. The azo dyes are largely active towards the many metal ions. Because these compounds contain more than one active group, they have great importance in the chemical analysis, which is able chelate with transition metals distinguished by their color and ability to dissolve in different solvents [3].

Metal chelate with azo ligand lead to the interesting physical, chemical, catalytic and varied material properties [4]. In this work, we produced azo ligand derivative of 4-aminoacetophenone like a diazo - component as well 3-aminobenzoic acid like linked factor.

This ligand compounds have been produced for transition metals as well as confirmed using different spectral studies.

### Experimental

#### Instrumentation

Magnetic properties were completed by using Auto Magnetic Susceptibility Balance Sherwood Scientific instrument at 25°C. Elemental analysis was recorded in the Al-al- Bayt University, Jordan, employing Euro vector EA 3000A Elemental Analyser. NMR spectrum were registered at the Bruker-300 MHz Ultra Shield spectrometer at the University from Al- al- Bayt utilizing DMSO such as the solvent as well TMS like the reference.

UV- Vis spectra were taken on a Shimadzu UV- 160A Ultra Violet-Visible Spectrophotometer. FTIR- spectrum have

been registered at a Shimadzu, FT-IR-8400S Fourier Transform Infrared Spectrophotometer at 4000- 400  $\text{cm}^{-1}$  spectral regions for samples produced like KBr discs. Atomic absorption has been obtained utilizing a Shimadzu A.A-160A Atomic Absorption / Flame Emission Spectrophotometer. Conductivity has been measured at  $10^{-3}$  M solutions for compounds at ethyl alcohol in  $25^{\circ}\text{C}$  employing Philips PW- Digital Conductimeter. Other, melting points have been formed utilizing Stuart Melting Point and Apparatus.

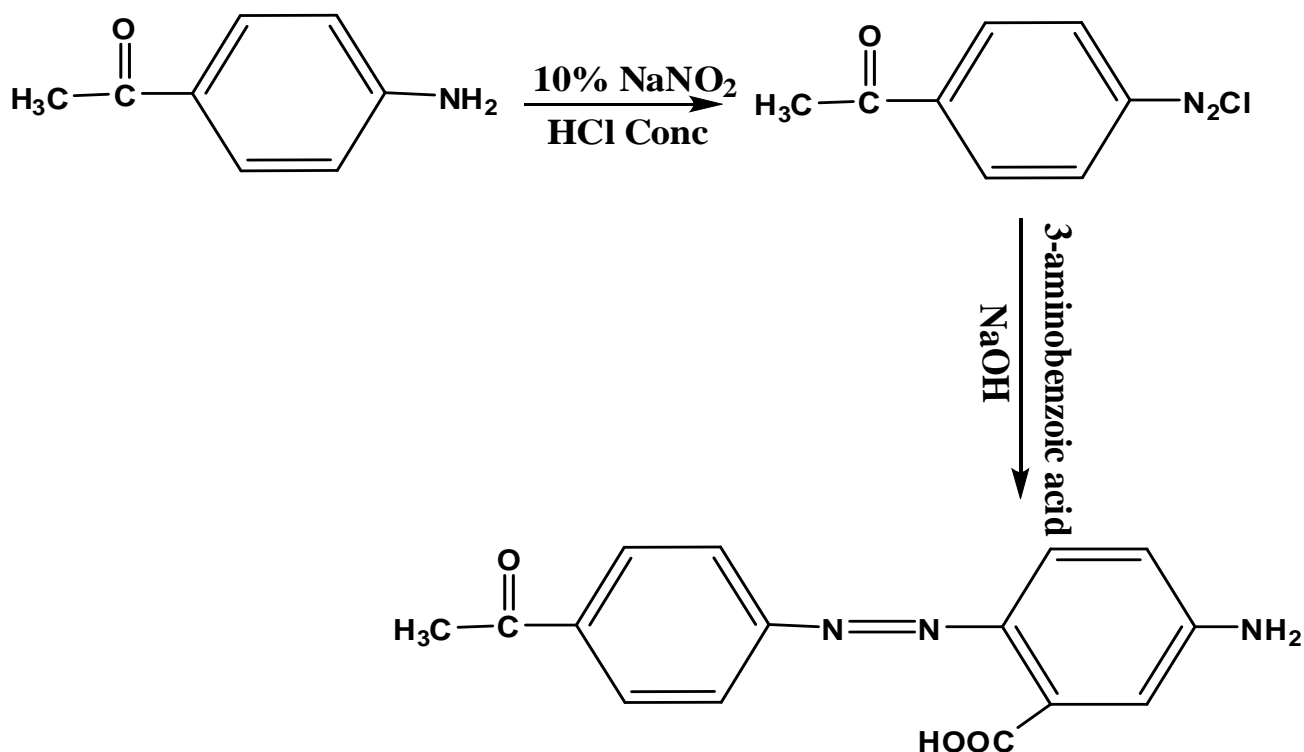
### Materials and Reagents

Obeying chemicals have been utilized such as collected of providers:  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{ZnCl}_2$  (B.D.H),

4-aminoacetophenone as well as 3-aminobenzoic acid (Merck).

### Prepare the ligand

(0.337gm, 1mmole) of 4-aminoacetophenone [5] was melted in a mixture of (10ml) of ethanol including (2ml) conc. HCl and (10ml) water, and diazotized at  $5^{\circ}\text{C}$  with 10% solution of  $\text{NaNO}_2$ . The diazotized solution has been added gradually for stirring into a cooling ethanol solution at (0.342gm, 1mmole) of 3-aminobenzoic acid. After that 25 ml at 1M of Noah solution has been appended into mix the dark color and precipitation at azo ligand has been noticed. This precipitate was filtered, washed several times with ethanol, then leave into dry. The interaction appears at Scheme 1.



Scheme 1: Synthesis of an azo ligand

### Buffer Solution

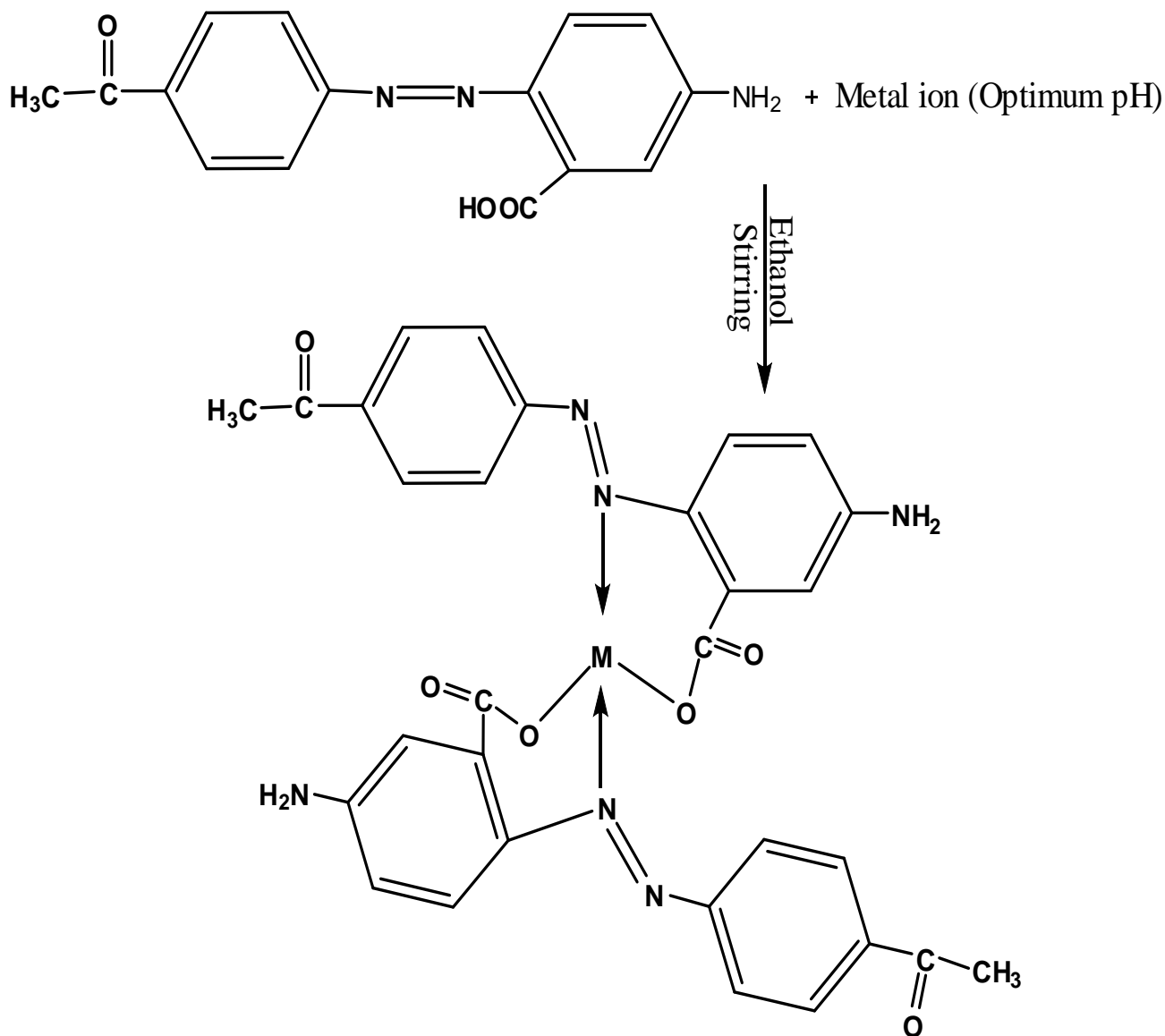
(0.01M, 0.771 gm) for ammonium acetate has been melted at one liter at doubly deionized water. To adjust the pH rate (4-9) has been employed  $\text{CH}_3\text{COOH}$  or  $\text{NH}_3$  solution.

### Standard Solution

A series from standard solutions for metal chloride of  $[\text{Co}^{+2}, \text{Ni}^{+2}, \text{Cu}^{+2}$  and  $\text{Zn}^{+2}]$  have been produced at the ( $10^{-5}$ - $10^{-3}$  M) variant concentration in pH range (4-9). In the same time a series for ethanolic solutions for ligand were also produced in the same concentration.

### Preparation of Metal Complexes

(0.283g, 2mmole) of the ligand dissolved in ethanol was appended progressively for stirring into 0.118g, 0.118g, 0.085g and 0.068g (1mmole) from  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{ZnCl}_2$  continuously resolved at buffer solution for exactly pH. The mixture was cooled even dark color deposit was formed, filtered, as well as washed number of times for ethanol, there after leave into dry.



Scheme 2: Suggested geometry to the metal (II) complexes

### Study of Biological Activity

The ligand and their metal chelates have been tested *in vitro* for antibacterial activity versus bacteria: *Staphylococcus aureus*, *E. coli*, *Pseudomonas* as well as *Bacillus*. Inhibition zone from the produced compounds versus the growth from bacteria have been given at (Table 1) were examined employing the agar deployment mechanism [6].

The organism were tested the agar media were vaccinated for checkup organisms and a solution from examined compound (100µg/ml) has been put severally at cups (10mm diameter) at agar medium. Plates have been incubated at 24 h in 37°C and the well has been stuffed for exam solution employing micropipette. Through that interval, the test solution has been circulated and influenced the growth to the vaccinated microorganisms. Efficiency was specified through

standardizing the diameter at zone performance perfect inhibition (nm).

Outgrowth from inhibition has been likening for the control (DMSO), the antibacterial efficiency outcomes detected the ligand and their metal chelates shown weakened into good efficacy while the base from Tweed's chelation theory. At metal compounds, in chelation the polarity for metal ion will be concluded into a greater range consequent into interfere for ligand orbital as well as partial participation to the over the complete chelate ring [7].

### Results and Discussion

To prepare for ligand (L) a linkup from 3-aminobenzoic acid for convenient diazotized at alkaline solution was performed. Performed ligand was characterized by  $^1\text{H}$  and  $^{13}\text{C}$ NMR, FTIR, elemental analysis and UV-Vis spectra.

## NMR Spectrum

$^1\text{H}$ NMR spectral to the ligand (L) at dimethylsulfoxide (Fig.1) offers various symbols in  $\delta=7.129-8.630$  ppm assigned into aromatic protons [8]. Signal in  $\delta=13.282$  ppm result into proton for carboxyl group [9]. Other than, signals at  $\delta=3.836$ , 2.661 and 2.50 ppm were appeared into proton about ( $\text{NH}_2$ ), ( $\text{CH}_3$ ) groups as well DMSO-d6 gradually [10].

The  $^{13}\text{C}$ NMR spectral to the azo ligand (Fig. 2) offer resonance in  $\delta=197.359$  ppm assigned to carbonyl group. The gesture at  $\delta=166.924$  ppm described into carbon of carboxyl group. Signals at  $\delta=131.997$ , 130.484, 130.090, 129.897, 129.671, 126.846 and 115.951 ppm described into carbon atoms from aromatic rings. Signals in  $\delta=26.509$  as well 39.542 ppm due into carbon of ( $\text{CH}_3$ ) in acetyl group and DMSO-d6 [11].

## Physical Estates

Metal chelates were produced through immediate reaction from ethyl alcohol solution for ligand (L) for aqueous solution from metal (II) ions in ideal pH as well at a M: L ratio from 1:2. Datum elemental analysis and metal contain for compounds were at good agreements for calculated values, datum registered at Table 2.

Molar Connectivity for ( $10^{-3}$  M) at ethyl alcohol solution for compounds described non-electrolytic type [12], datum are recorded in Table 3. Magnetic estates (Table 3) from produced complexes were occurred into a paramagnetic that has been show caused with tetrahedral structure [13].

## Calibration Curve

Deferent molar condensation ( $10^{-5}$ – $10^{-3}$  M) from a mixed ethyl alcohol solution into ligand as well as metal (II) ions, only rate ( $1-3 \times 10^{-4}$  M) condensation followed Beer's law as well showed apparent intensive color. The best straight lines for the correlation factor occurred  $R > 0.9980$  accordingly shown at Fig. 3.

## Perfect Conditions

To inquire into interaction between produced ligand as well metal(II) ions beneath learning for preparation to the compounds, spectral from combining solutions to the ligand and metal(II) ions into attain at best pH as well

condensation, as well as firm wave length ( $\lambda_{\text{max}}$ ) were studies at foremost.

Thereafter mole ratio metal (II) ions into ligand (M: L) has been defined for equip of the compounds. Ideal condensation has been selection to composite solution on the basis that solution give higher absorption in steady ( $\lambda_{\text{max}}$ ) in various pH, as well as outcomes are described at Table 2. Probation outcomes guide that absorption all of the produced compounds are extreme as well as steady at a buffer solution from  $\text{NH}_4\text{OOCCH}_3$  at pH range (4-9). It has been found which all produced compounds had perfect pH as shown at Fig. 4.

## Stoichiometry of Complexes

A mole ratio and job method writing of complexes done in solutions has been permanent. In two positions outcomes disclose 1:2 metals into ligand ratio. Choice chart is exemplified at Fig.5. Tables 3 identify the results gained, other, conditions into preparation for compounds.

## Electronic Spectra

The UV-Vis spectral from produced azo ligand as well as metal (II) chelates melted at  $\text{C}_2\text{H}_5\text{OH}$  ( $10^{-3}$  M) have been recorded as well datum assigned at Table 3. UV- Vis spectral from ligand (L) (Fig.6) show peaks in 238 and 374 nm due into ( $\pi$ -  $\pi^*$ ) electronic transition [14]. The spectral from  $\text{Co}^{2+}$  complex (Fig.7) display peaks at (240 and 381) nm consequent to ligand felid, else three peaks at (781, 890 and 978) nm related to electronic transition type  $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$ ,  $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{F})$  and  $4\text{A}_2 \rightarrow ^4\text{T}_2(\text{F})$  continually [15].

The spectral from  $\text{Ni}^{2+}$  complex displays peaks in (263 and 388) nm lead to ligand felid. Two peaks at 874 and 980 nm described to electronic transition  $^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_1(\text{P})$  and  $^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_2(\text{F})$  gradually [16]. The spectrum of  $\text{Cu}^{2+}$  appears peaks in (277 and 393) nm assigned into ligand felid, else peak at 980 nm due into  $^2\text{T}_2 \rightarrow ^2\text{E}$  electronic transition [17].

The electronic spectral from  $\text{Zn}^{2+}$  complex do offer the transfer of charge, due to d-d transition are not probable subsequently, electronic spectroscopic did not give each fruitful information, actually this outcome is a good deal for previous work to the tetrahedral geometry [18].

**Table 1: Diameters (mm) of suppression to the bacteria with the ligand and its complexes**

Compounds	<i>Staph. aureus</i>	<i>E-coli</i>	<i>Bacillus</i>	<i>Pseudomonas</i>
Ligand(L)	15	18	20	15
[Co(L) <sub>2</sub> ]	20	17	15	18
[Ni(L) <sub>2</sub> ]	10	20	18	15
[Cu(L) <sub>2</sub> ]	15	18	20	17
[Zn(L) <sub>2</sub> ]	12	15	20	15

**Table 2: Physical properties for ligand and its compounds**

Compounds	Color	M.P°C	Yield%	Analysis Calc (Found)			
				M%	C%	H%	N%
Ligand(L)	Reddish brown	185	77	-	63.60 (62.88)	4.59 (3.94)	14.84 (13.88)
[Co(L) <sub>2</sub> ]	Deep brown	217	73	9.47 (8.93)	57.78 (56.92)	3.85 (3.04)	13.48 (12.82)
[Ni(L) <sub>2</sub> ]	Orange	230	76	9.32 (8.98)	57.87 (56.89)	3.85 (2.94)	13.50 (12.93)
[Cu(L) <sub>2</sub> ]	brown	215	80	10.19 (9.84)	57.32 (56.87)	3.82 (2.98)	13.37 (12.74)
[Zn(L) <sub>2</sub> ]	Yellow	220	75	10.33 (9.94)	57.23 (56.85)	3.81 (3.11)	13.35 (12.88)

**Table 3: Conditions to the preparation in the compounds, UV-Vis, conductance and magnetic properties menstruation datum**

Compounds	Optimum pH	Optimum Molar Conc. x 10 <sup>-4</sup>	M:L Ratio	(λ <sub>max</sub> ) nm	ABS	ε <sub>max</sub> (L.mol <sup>-1</sup> .cm <sup>-1</sup> )	Δ <sub>m</sub> (S.cm <sup>2</sup> .mol <sup>-1</sup> ) At Absolute ethyl alcohol	μ <sub>eff</sub> (B.M)
Ligand(L)	-	-	-	238 374	1.002 1.975	1002 1975	-	-
[Co(L) <sub>2</sub> ]	7	2	1:2	240 381 781 890 978	0.794 1.260 0.035 0.041 0.043	794 1260 35 41 43	9.66	4.15
[Ni(L) <sub>2</sub> ]	7	2.5	1:2	263 388 874 980	0.667 1.218 0.006 0.042	667 1218 6 42	7.87	3.84
[Cu(L) <sub>2</sub> ]	7	2.5	1:2	277 393 980	0.512 0.937 0.034	512 937 34	6.83	2.18
[Zn(L) <sub>2</sub> ]	7	2.5	1:2	268 391	0.634 2.037	634 2037	9.28	Dia

**Table 4: Major frequencies of ligand as well their compounds (cm<sup>-1</sup>)**

Compounds	ν(OH) + ν(NH <sub>2</sub> )	ν(C=O)	ν(COO) asy +sy	ν (N=N)	ν(M-N) + ν(M-O)
Ligand(L)	3471 br. 3429 br. 3414 br.	1670 s.	1597 sh. 1527 sh.	1496 sho.	
[Co(L) <sub>2</sub> ]	- 3428 sh. 3414 sh.	1672 sh.	1580 s. 1558 s.	1450 s.	532 w. 443 w.
[Ni(L) <sub>2</sub> ]	- 3429 s. 3412 sh.	1671 sh.	1558 s. 1543 sh..	1435 s.	524 w. 478 w.
[Cu(L) <sub>2</sub> ]	- 3433 sh. 3410 sh.	1670 sh.	1572 s. 1554 s.	1467 sh.	543 w. 459 w.
[Zn(L) <sub>2</sub> ]	- 3430 s. 3410 s.	1670 s.	1563 s. 1557 sh.	1442 sh.	540 w. 441 w.

Br=broad, sh=sharp, s=strong, sho=shoulder, w=weak

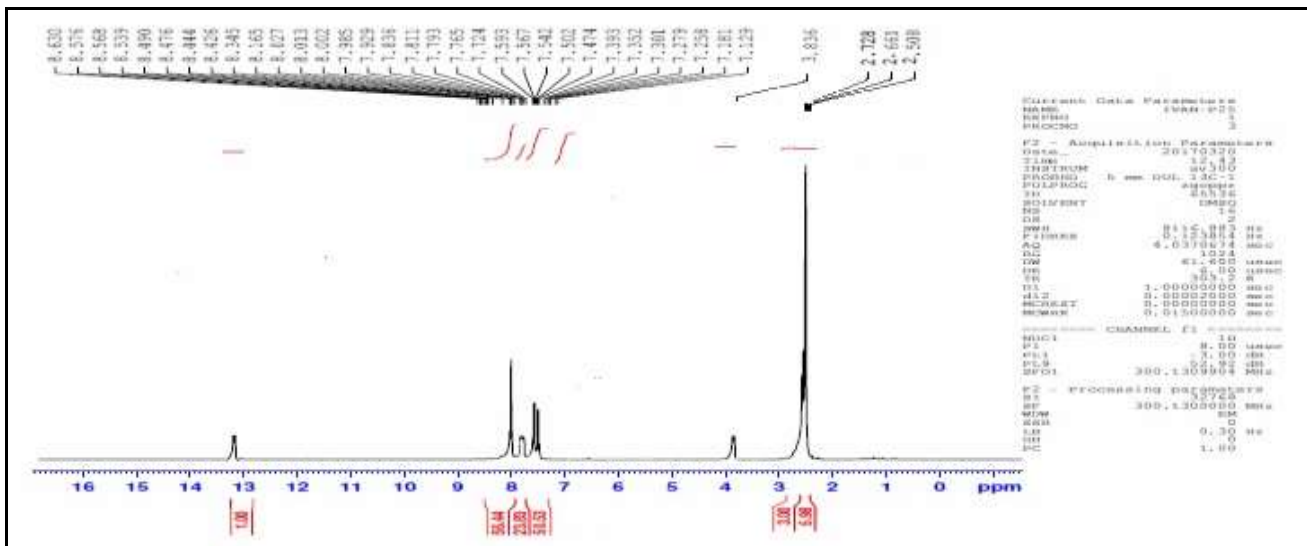


Fig.1: <sup>1</sup>H NMR spectral for ligand (L)

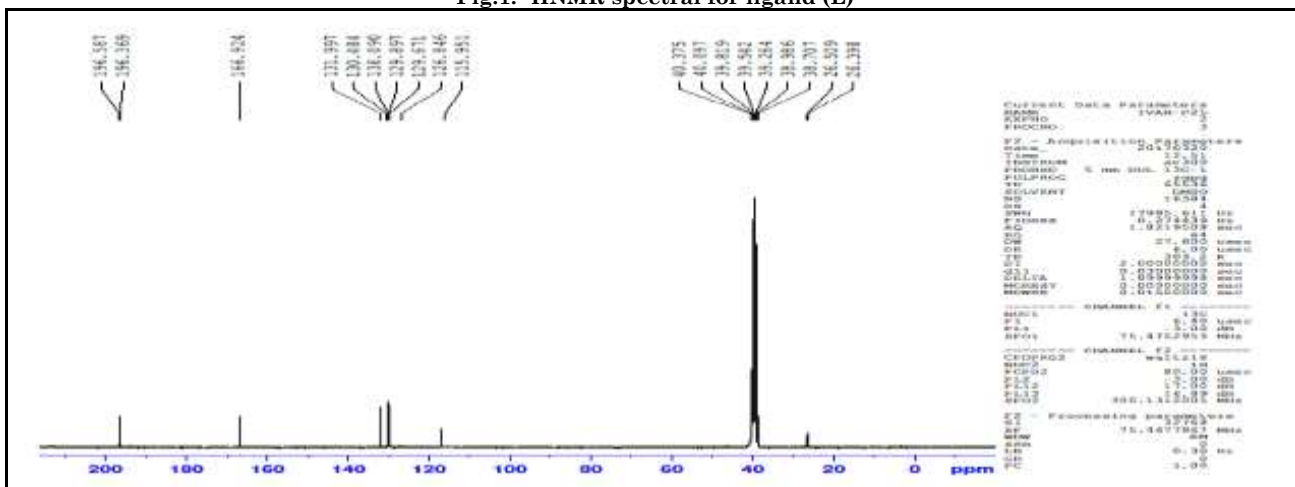


Fig. 2:- <sup>13</sup>C NMR spectral for ligand (L)

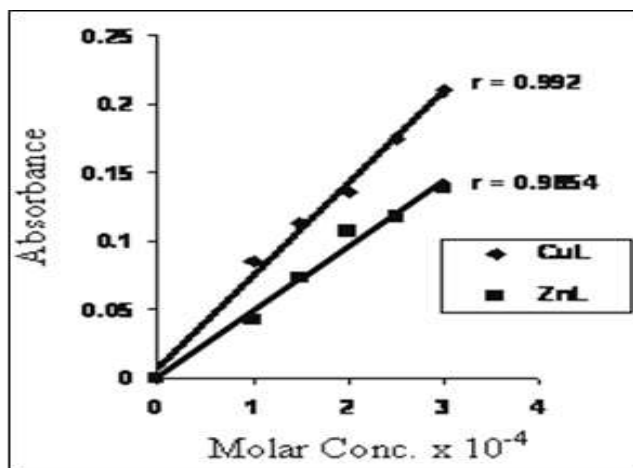
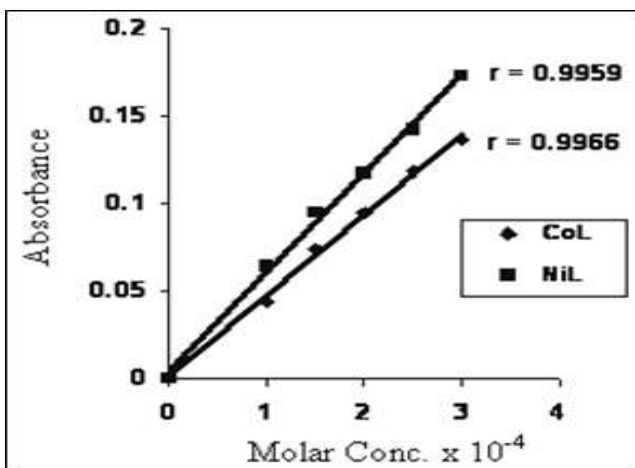


Fig.3: Linear relationship amidst molar condensation as well absorbance

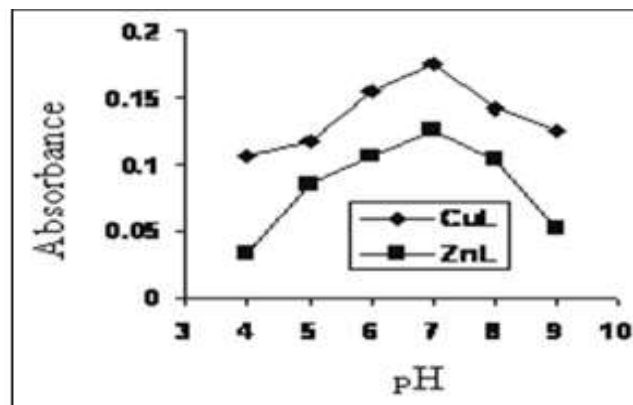
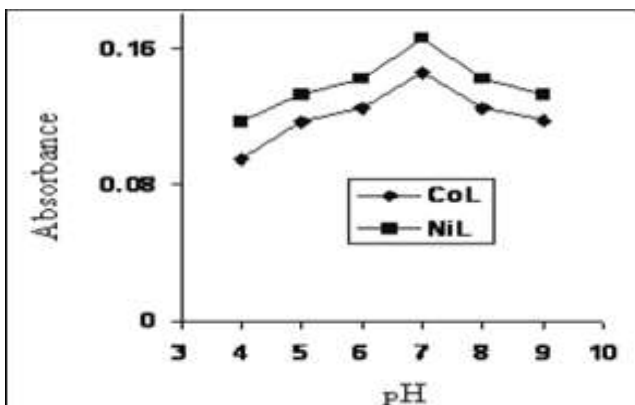


Fig. 4: Effect for pH at absorption ( $\lambda_{max}$ ) to the compounds

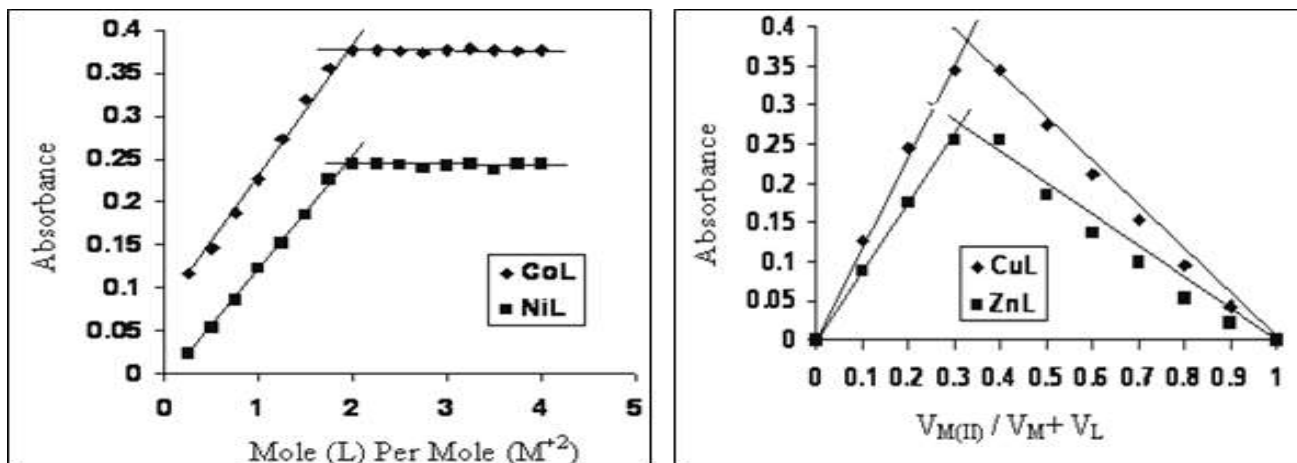


Fig. 5: Mole ratio as well Job methods for compounds solutions

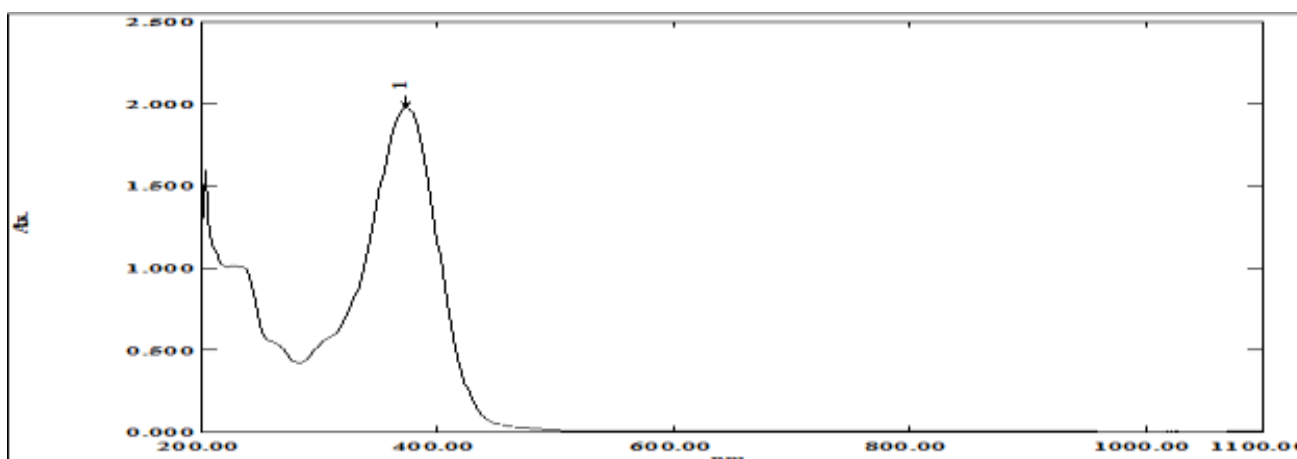


Fig. 6: UV-Vis spectral for ligand (L)

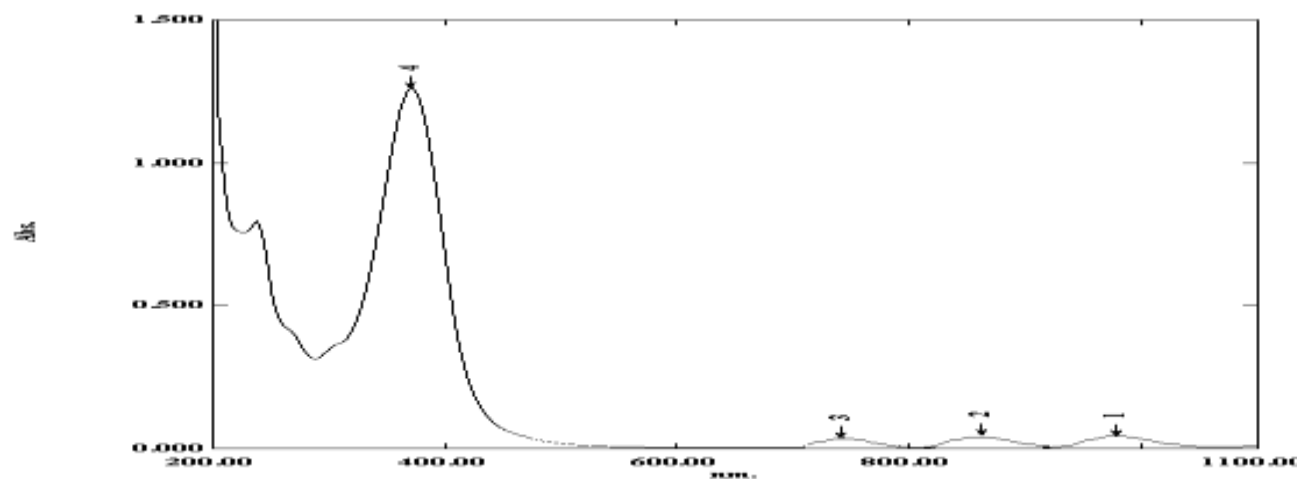


Fig. 7: UV-Vis spectral for [Co (L)<sub>2</sub>] complex

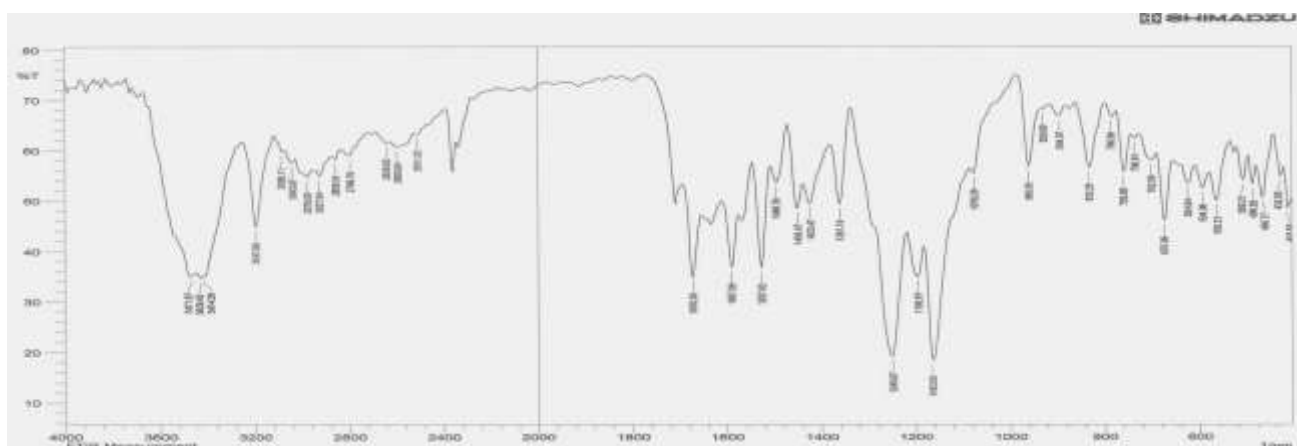


Fig.8: FT-IR spectral for ligand (L)

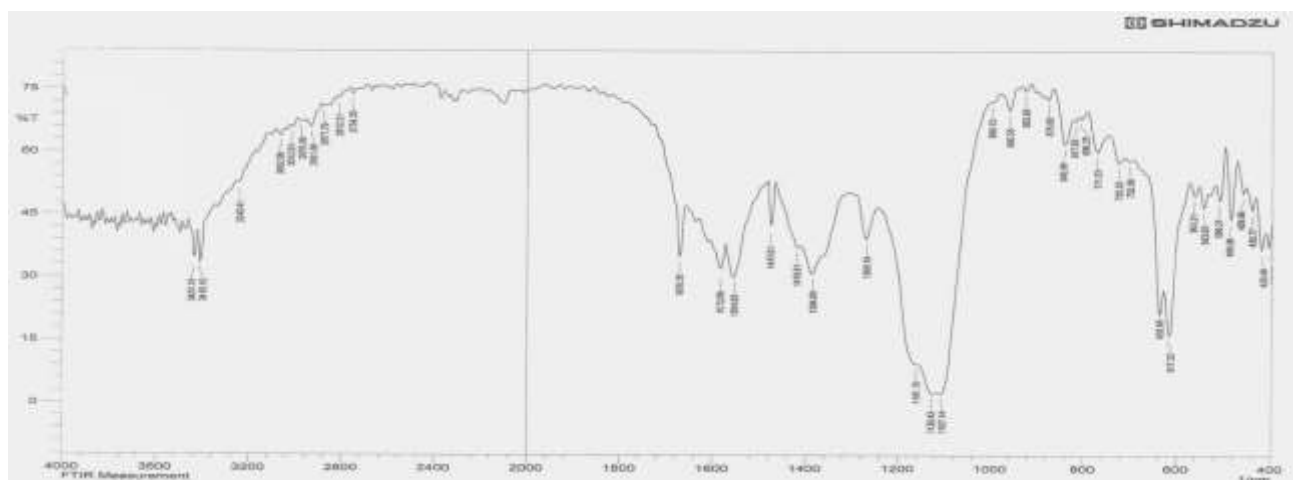


Fig.9: FT-IR spectral for [Cu (L)<sub>2</sub>] compound

### Fourier Transforms Infrared Spectra

Band in  $3471\text{ cm}^{-1}$  to the ligand (L) spectrum (Fig.8) described into stretching vibration from  $\nu(\text{OH})$  carboxyl group, that band was absent in the spectra (Fig.9) on all metal chelates, that showed to coordinate for metal(II) ion [19]. Bands in ( $3429$  and  $3414$ )  $\text{cm}^{-1}$  shows consequent into the stretching mode for  $\nu(\text{NH}_2)$ , no change at these bands was observed, lead to possibility coordination with metal chelates [20].

The spectral presented band in  $1670\text{ cm}^{-1}$  due into  $\nu(\text{C}=\text{O})$  vibration, no change in this band was noticed in the spectra of metal chelates [21]. A change at the density and at position into reduce wave number has been noticed in metal chelates spectra for band to the ligand (L) spectral in  $1597\text{ cm}^{-1}$ , that shows consequent into  $\nu_{\text{as}}(\text{COO})$  asymmetric vibration. Band at  $1527\text{ cm}^{-1}$  at the spectrum into the ligand (L), related into  $\nu_{\text{s}}(\text{COO})$  symmetric vibration, afforded a large change

into higher wave number in metal chelates spectra [22]. Azo bridge in  $1496\text{ cm}^{-1}$  shifted into lower frequency for change at form to spectra for metal chelates, indication the connection from that group at coordination for metal ion [23]. Stretching frequency bands of metal-nitrogen as well as metal-oxygen moreover surfed by the existence for bands around ( $441$ - $543$ )  $\text{cm}^{-1}$ . Pursuant into the outcomes donated, a tetrahedral structure was offered for the produced metal chelates [34].

### Conclusion

In this work, the transition chelates were readied for ligand (L). The interesting compounds have been assigned through fusion point, atomic flame absorption, FTIR as well UV-Vis spectroscopic, as well as conductivity and magnetic susceptibility quantifications. Exploration for antimicrobial efficiencies has been elevated out obverse the experimented organism. According the result datum a tetrahedral structure suggested with produced metal (II) chelates.

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