ISSN: 0975 -8542

Journal of Global Pharma Technology

Available Online at: www.jgpt.co.in

RESEARCH ARTICLE

Synthesis, Characterization and Spectroscopic Studies of a6, 6'-((1E, 1'E)-(1, 2-phenylene bis (azanylylidene)) bis (methanylylidene)) bis (3-(phenyldiazenyl) phenol) and their Complexes

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Abstract

A new ligand 6, 6'-((1E, 1'E)-(1, 2-phenylenebis (azanylylidene)) bis (methanylylidene)) bis(3-(phenyldiazenyl)phenol) (L_2) was prepared and characterized by UV-visible, FT-IR, ^{1}H-NMR and Mass spectra. Two complexes with Cu (II) and Co (II) ions were prepared. The preparation has demeanor after limitation the optimum conditions through (UV-Vis) spectrophotometric study of these complex solutions have been studied such as determination wavelength (λmax), volume reagent, effect of time, effect of temperature and effect of pH .Also study determination of dissociation degree and stability constant under wavelength (λmax) and optimum pH values. The structures of complexes are Evidenced approbate to job method which were gained from the spectroscopic studies of the complex solutions and characterized by molar conductance measurements, infrared spectra and mass spectra at room temperature. The infrared spectra of the chelating complexes have been studied, this may suggest that coordination between the metal ions and the prepared ligand takes place. The analytical data show that the metal to ligand ratio [M: L] in two complexes is (1:1) (metal: ligand) stoichiometry. depending on these results, the ligand acts as a bidentate ligand coordination through –C=N and –OH groups, the proposed geometrical structures of the complexes of Cu(II) and Co(II) ions are octahedral.

Keywords: *Azo-azomethine, Metal complexes, Synthesis, Spectral Studies.*

Introduction

Azo and azomethine dyes are organic dyes that contain the characteristic –N=N– and –CH=N– chromophores[1]. Azoschiff bases compounds derived from the reaction between the schiff bases and azo represented in important series of widely studies organic ligands [2]. Azo-Schiff bases, having imine groups(C=N), are formed by the condensation reaction of (NH_2) primary amines with (CHO) aldehydes or (CO) ketones[3–5] and having azo groups (–N=N–), are formed by acoupling reaction between a diazonium salt and a coupling agent[6] .

A large number of (N, N')-doner ligands in azo imine family have been prepared in the last few years [7, 8]. The spectral properties of azo dyes depend on the nature of both the azo and the coupling components. For example, azometine compounds which have some interesting structural properties and uses can be prepared by coupling of azo and methine groups [9, 10].

Azo-azomethine dyes are relatively robust and chemically stable and their spectral properties depend on the combination of electron-donating and withdrawing moieties in the molecules [11]. Furthermore, considerable attentions have been paid to the study of azo-azomethine dyes containing hydroxyl groups in recent years due to their metabolites are toxic, carcinogenic, and mutagenic[12,13].Azo-azomethine ligands contain both azo and azomethine groups. Azo groups possess excellent donor properties and play an important role in coordination chemistry [23, 24].

These compounds have received special attention in coordination chemistry due to their mixed hard–soft donor character and versatile coordination behavior[25].Azo-azomethines are known to be interesting because of the existence of both hard nitrogen and/or oxygen donor atoms in the backbones of these compounds, some of which have

interesting physical and chemical properties[26]. Azo-Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions such as cobalt(II), nickel(II) and copper(II). The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species [27]. Azo-azomethine complexes contain both azo and azomethine groups.

Azo group is characterized by a lone pair of orbital containing two electrons on nitrogen atom, if linked to an aromatic ring carrying an additional donor sites is well suitable for chelation and its complexes contain both azoand azomethine groups [28].These compounds have a great ability to coordinate with many metal ions and form stable complexes. The coordination compounds of azo–azomethine ligands are also widely used in medicine, for corrosion prevention, metal recovery as well as to treat nuclear wastes [29].

Materials and Methods

Apparatus

The UV-Vis spectrophotometer model T 60, PG Instruments Ltd, (Germany). The FT-infrared measurements were recorded by using FT-IR affinity Spectrophotometer (Shimadzu) Japan; Mass spectra are recorded of compounds using Agilent Technology (HP) / MS Model 5973 Network Mass Selective Detector in the University of Tehran, Iran. The ^{1}H- NMR with using DMSO as solventin Tehran, Iran.

Reagent and Materials

All analytical grade reagents were used withoutfurther purification as received from different company.deionized water was used for diluting the standard, reagents and samples. Acetic acid (glacial) (99.5%), Copper (II) chloride dihydrate(99.0%), Cobalt chloride(II) hexahydrate (97.0%), Aniline (99.0%), Na OH (99.0%) , HCl (37%),$NaNO_2$;(99%) were purchased from BDH and O-phenylenediamine (99.5%) and Salicylaldehyde (99.0%) from sigma Aldrich. The stock solution of Cu (II) was prepared by accurately weighing 0.2675gm of $CuCl_2.2H_2O$into a 50 ml beaker, added minimum amount of deionized water and swirled to dissolve. The content was transferred quantitatively to a 100 ml volumetric flask, and then diluted to the mark with deionized water. The stock solution of Co (II) was prepared by accurately weighing 0.4038gm of $CoCl_2.6H_2O$ into a 50 ml beaker, added minimum amount of deionized water and swirled to dissolve. The content was transferred quantitatively to a 100 mL volumetric flask, and then diluted to the mark with deionized water. To prepare 100µg ml^{-1}, 10ml of the standard for each metalions of stock solutions were pipetted and added in to 100 ml volumetric flask finally diluted to the mark with deionized water and the solution was mixed thoroughly.

A stock solution of *A*6,6'-((1E,1'E)-(1,2-phenylenebis (azanylylidene)) bis (methanylylidene)) bis(3-(phenyl diazenyl) phenol) (L_2) reagent solution at concentration of $1x10^{-3}$ M was prepared by dissolving 0.0131gm into a 10 ml beaker, added minimum amount of DMSO and swirled to dissolve. The content was transferred quantitatively to a 25 ml volumetric flask, and then diluted to the mark with DMSO.

Synthesis of Azo Dye

2-hydroxyl-4-(phenyldiazenyl) benzal dehyde reagent was prepared by dissolving (1.863gm, 1.808ml,0.02mole) of aniline in mixture containing30ml distilled water and 5ml of concentrated hydrochloric acid and cooled to (0-5)^{o}C. The solution was diazotized at (0-5)^{o}C with (1.38gm, 0.02mole) sodium nitrate was dissolved in 20ml distilled water was added drop wise to amine solution and stirring continuously at (0-5)^{o}C and left to stand 30 min. This diazonium solution was added to salicylaldehyde (2.442gm, 2.13ml, 0.02mole) was dissolved in 25ml ethanol and 30 ml of 6% sodium hydroxide.

The mixture was stirred continuously for 2h. At (0-5) ^{oC} in ice-bath and allowed to stand in the refrigerator overnight and acidified with dilute hydrochloric acid to pH=6. The precipitate was filtered and washed with distilled water and ethanol solution to remove the excess of unreacted substances and recrystallized from ethanol and dried in oven at 50^{o}C for two hours [30]. The purity was confirmed by TLC technique.

Yield 85.06%, mp59-60˚C.The chemical structure of 2-hydroxyl-4-(phenyldiazenyl) benzaldehydeis shown in Figure (1).

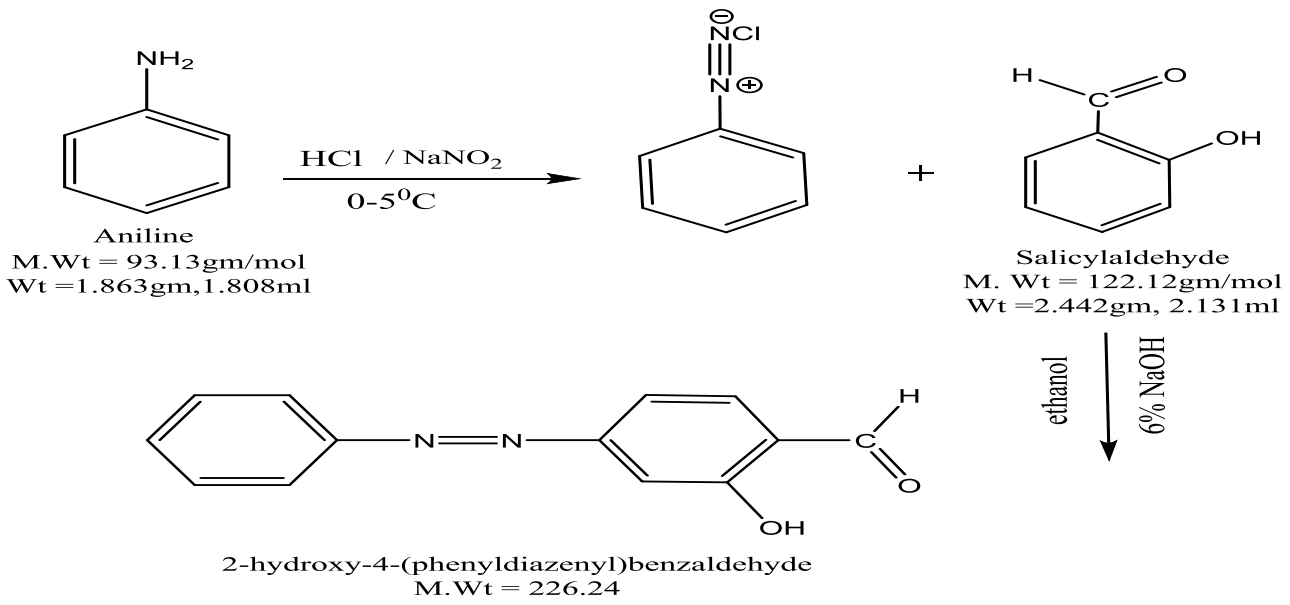
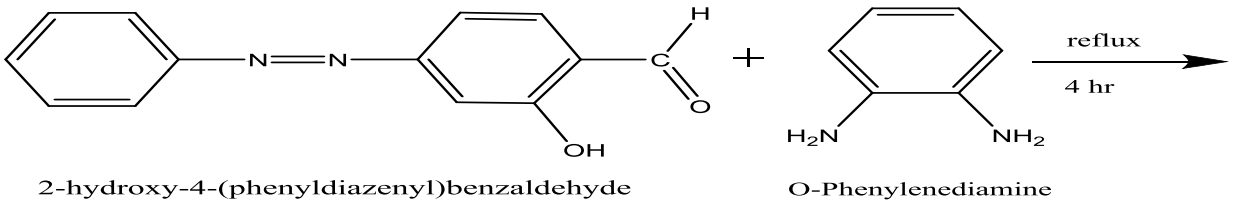
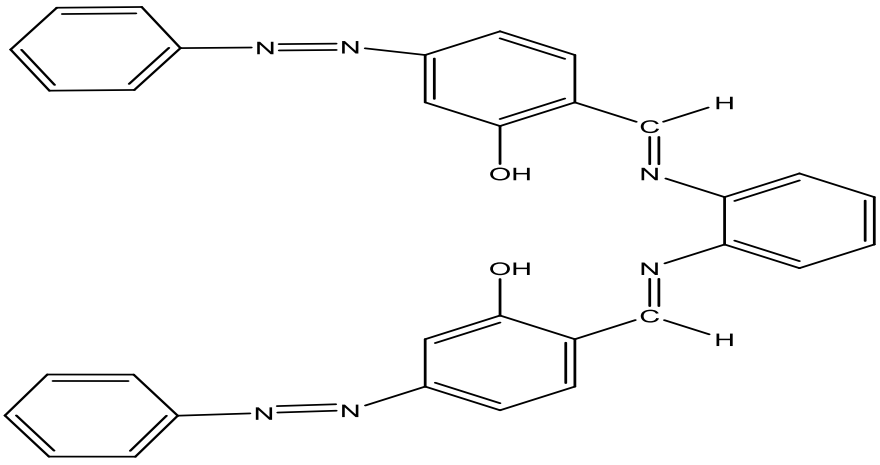


Figure 1

Synthesis of Azo-azomethine

The azo-azomethine ligand was synthesized by condensation reaction of O-phenylenediamine with azo dye compound **2-**hydroxyl-4-(phenyldiazenyl) benzaldehyde by dissolving (2.262gm,0.01mol) of (AZ_1) in (20ml) absolute methanol then mixed with a solution (0.541gm, 0.005mol) of (O-phenylenediamine) dissolved in (10ml) of the same solvent with the addition of four drops of glacial acetic acid as a catalyst followed by reflux for (4) hours. The reaction was followed using TLC[31].The brown precipitate was formed, It was filtered ,dried and recrystallized in absolute ethanol. Yield 80.00%, mp210-212˚C. The chemical structure of 6, 6'-((1E, 1'E)-(1, 2-phenylenebis (azanylylidene)) bis (methanylylidene)) bis (3-(phenyldiazenyl) phenol) is shown in Figure (2).





6,6'-((1*E*,1'*E*)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(3-(phenyldiazenyl)phenol)

Figure 2

Primary Testing of Complex Formation between Metal ions and Reagent

In a number of test tube added (1 ml) of metal solution (100 µg.ml^{-1}) then added (2ml) of reagent solution (1×10^{-3}M) drop wise with mixing and the change of color is observed divided the solution in two halve add few drops of 0.05 M of Na OH for one halve and 0.05M of HCl for another the show in Table (1).

Table1: Primary test for reaction between metal and reagent in 0.05M NaOH but no there are changing in the color in present 0.05M HCl

No.	Ions	Ion solution color	Ion solution color after adding the reagent	The result
1	Cu^{2+}	Light blue	Reddish orange	Cu^{2+} and $Co^{+2}$with L_2
2	Co^{2+}	Light purple	Yellow orange	
3	Cr^{3+}	Light green	No color change	
4	Ni^{2+}	Light green	No color change	
5	Cd^{2+}	Colorless	No color change	

Study of Spectroscopic Measurement for Reagent

UV-Vis spectra were obtained for (1×10^{-3}M) of an DMSO solution for reagent using (1cm) quartz cell in the wavelength (200-600) nm for ligand and (360-800) nm for complexes.

General Procedure for Spectrophotometric Determination of Cu and Co with L_2 reagent

After determining the metal ions that react to reagent in Table (1), can be determination λ max, volumetric flask of capacity (10ml) has been taken and (1ml) of the ion concentration of solution (100µgml^{-1}) was added, (2ml) of reagent (1×10^{-3}M) added and complete the volume to the mark with deionized water , the blank solution was prepared in the same way except for the addition of the ion under study .

Optimization of the Experimental Conditions

Effect of Reagent Volume

Reagent $L_2$of various volumes (0.5-4ml) of concentration (1×10^{-3}M) were taken in 10ml volumetric flask, 1.0 ml of (100 µgm^{-1}) Cu(II) solution added and the mixture solution was well shaken then the volume was completed to the mark with deionized water. The absorbance of metal-chelate was recorded at λmax of copper complex against reagent blank prepared in a same way without Cu (II). The same experiment was repeated for the reagent with cobalt ion.

Effect of Reaction Time

The effect of time was studied in order to signify the stability of the complexes optimum volume of reagent concentration (1×10^{-3}M) was taken in 10ml volumetric flask , 1.0 ml of (100 µgm^{-1}) Cu(II) solution added and the mixture solution was well shaken then the volume was completed to the mark with deionized water. The absorbance of metal-chelates was recorded at λmax of copper complex at (0-50) min against reagent blank prepared in a same way without Cu (II). The same experiment was repeated for the reagent with cobalt ion.

Effect of PH

The influence of pH value on the absorbance of complexes was studied at different pH by using HCl and Na OH (0.05M) solutions at (pH 2-12), two volumetric flask (10ml) were taken put in the first (1ml) of copper solution (100 µgml^{-1}), in the second (1ml) of cobalt solution (100 µgml^{-1}) was put and to two solutions were added optimum volume of reagent solution L_2(1×10^{-3}M) after adjusting the pH then complete the volume to the mark.

After appropriate time the absorbance was measured at appropriate λmax of complexes against a reagent blank prepared in a similar way without ions. The same experiment was repeated for the other reagents with selected metal ions.

Effect for Temperature

The effect temperature was studied by using two volumetric flask (10ml) were taken put in the first (1ml) of copper solution (100µgml^{-1}), in the second volumetric flask (1ml) of cobalt solution (100µgml^{-1})was put and to two solutions were added optimum volume of reagent solution L_2 (1×10^{-3}M) after adjusting the pH then complete the volume to the mark and put it in a water bath at different temperatures at (20-70)^{o}C after appropriate optimum time.

The absorbance was measured at appropriate λmax of complexes against a reagent blank prepared in a similar way without ions.

Determination of Dissociation Degree and Stability Constant

The stability constants are obtained by measuring the absorbance of solution mixture of ligand and metal ion at fixed wavelength (λmax) and optimum pH values. The conditional or apparent stability constant of (Metal: Ligand) product were evaluated as follows:

In order to measure Am and As value used to calculate the dissociation degree and stability constant.

This was done by taking equivalent volumes from the reagent and metal ion solutions (1×10^{-4}M) and after optimum condition of each complex the absorbance was measured at appropriate λmax against a reagent blank prepared in a similar way without ions, and we obtain (*As*) which represent the complex in partial dissociation. The experiment return by excess the volume of reagent then the absorbance was measured at appropriate λ max of complexes against a reagent blank prepared in a similar way without ions to obtain (*Am*) which represent the UN dissociation complex [32]. The interaction between the metal ions and the reagents proceeds according to the equations:

$$\alpha = \frac{A_m - A_s}{A_m}$$

$$\begin{array}{ccccc} ABn & \rightleftharpoons & A & + & nB \\ C & & 0 & & 0 \\ C(1-\alpha) & & \alpha C & & n\alpha C \end{array}$$

$$K_{inst} = \frac{(AC)(N\,\alpha C)^{n}}{C(1-\alpha)}$$

Where

C = concentration of the ligand which is equal the concentration of the metal.

α = degree of dissociation

As = the absorption of solution containing a stoichiometric amount of ligand and metal ion

Am = the absorbance of solution containing the same amount of metal and excess of ligand.

n = no. of mole

The stability constant is equal to

$$K_{st} = \frac{1}{K_{inst}}$$

Determination of the Stoichiometry of the Complex

The stoichiometries of the complexes were investigated by Continuous variation method (Job's method) in order to find M: L ratio, the absorption of metal ion and ligand solution mixture was obtained at optimum pH.

Continuous Variation Method (JOB Method)

In this method, variable volumes of solutions containing same molar concentration (1×10^{-4}M) of ligand and metal ions were mixed together. The total volume was kept constant at 2ml. The absorbance of each solution was measured at λmax and the relation between the mole fraction of the volume Vm / (Vm + VL) on the X-axis (where Vm and VL represent the volume of the metal and ligand solutions respectively) was plotted against the absorbance on the Y-axis.

Synthesis of Azo–Azomethine Complexes

The Azo-Azomethine complexes were synthesized by dissolving the ligand (0.262 gm, 0.0005 mole)in 20 ml hot ethanol and added drop wise with a stoichiometric amount of 1:1 [M:L] molar ratio (0.0005 mole) for Co (II), Cu(II) chloride salt dissolved in 20ml hot pH solution from (0.05M HCl and 0.05M Na OH) at optimal pH for each metal ions. The reaction mixture was heated to 30-45 °C for 50 min, until solid complexes were precipitated then left over night. The solid product thus formed was filtered off, washed distilled water until the solution become colorless and washed with 10 ml hot ethanol to remove any traces of the unreacted

materials and left to dry. The recrystallized using absolute ethanol [33].

Table 2: Some physical and chemical properties for the prepared ligand and their complexes

Chemical formula	M.Wt	pH	Color	λ max	m.p°C	Yeild%
$C_{32}H_{24}N_6O_2$ (L_2)	524	6	Brown	238	210-212	80.00
CoL_2Cl_2	655	7	Dark brown	600	282-282	82.57
CuL_2Cl_2	659	6	Black	647	261-263	80.50

Results and Discussion

UV-Vis Spectrum

The UV-Vis spectra for the synthesized reagent Azo-azomethine 6,6'- ((1E,1'E)- (1,2-phenylenebis (azanylylidene)) bis (methanylylidene)) bis (3- (phenyldiazenyl) phenol)(L_2) in Figure (3), show two distinct absorption peak, the first at wave length 238 nm due to π-π* in aromatic ring[34]and the second peak at 470 nm due to interior intra molecular charge transfer n-π*[35]which is belong to the –N=N- and C= N groups. The highest absorption intensity belong to the (n → π*) transitions was observed in DMSO[35].In the complexes the absorption maximum λmax of Co(L_2)Cl_2 show at 600 nm, while λmax of Cu(L_2)Cl_2 show at 647 nm (Figures 4 and 5) and these packages are attributable to the d-d transitions of type M→L between the metal and ligand which confirms formation the complexes[36].In the complexes, (π→π*) transitions were shifted to longer wavelengths as a consequence of coordination when binding with a metal, confirming the imine nitrogen was coordinated to the metal atom[31]. Its shift to longer wavelengths can be related to the donation of the lone pairs of the nitrogen atom of imine group to the metal ion [31].In the metal complexes; new bands at higher wave lengths support the formation of strong (M–O) and (M–N) bonds [37].

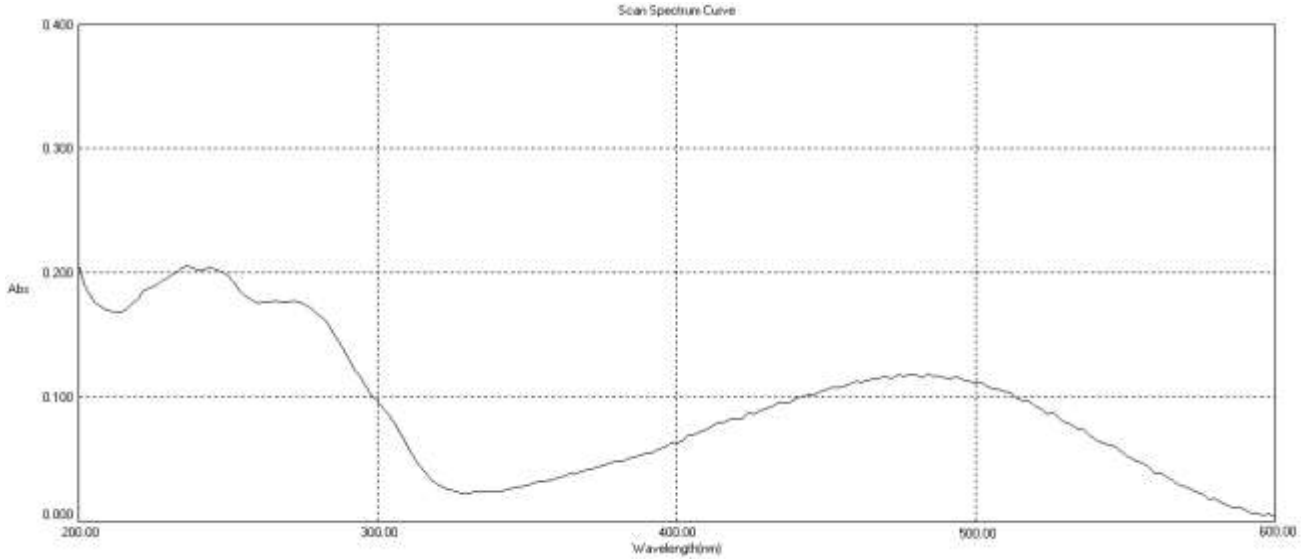


Figure3: UV-VIS spectrum for Azo-Azomethine (L_2)

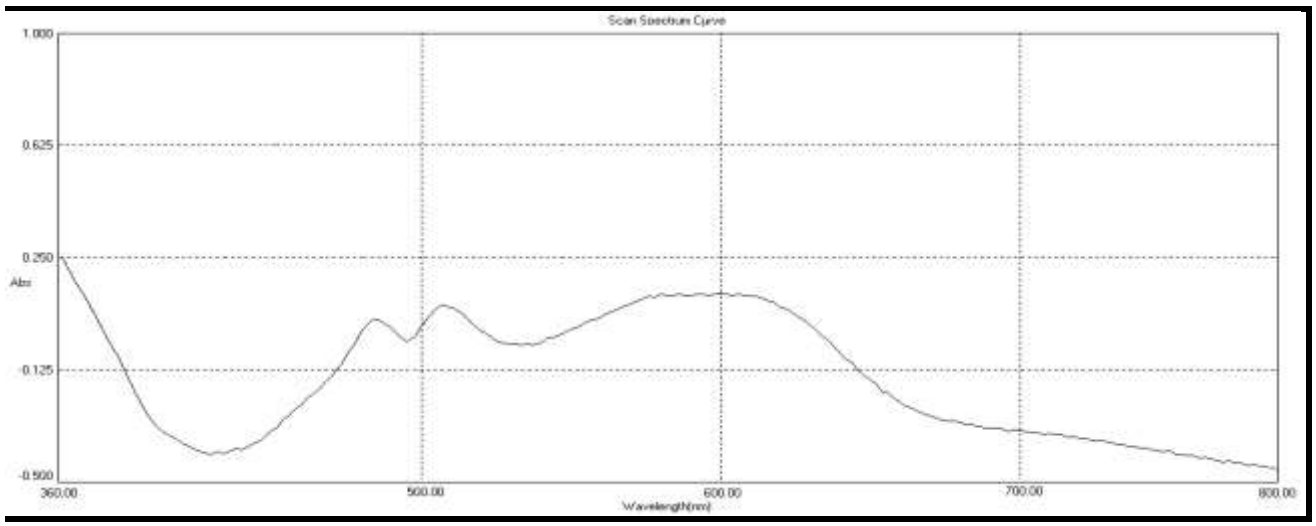


Figure 4: UV-Visible spectrum of [Co (L_2) Cl2]

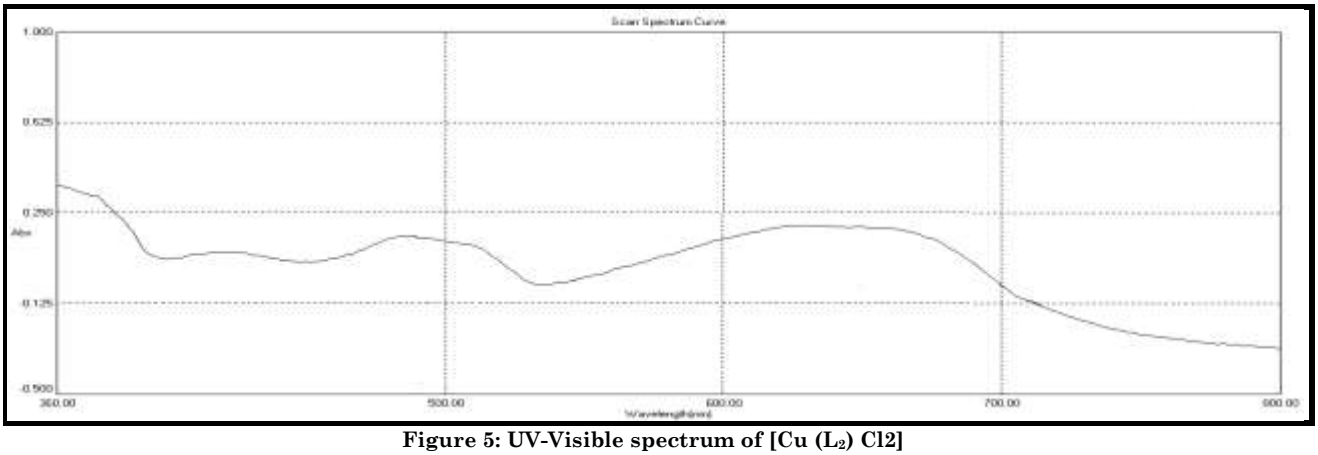


Figure 5: UV-Visible spectrum of [Cu (L_2) Cl2]

Optimization of the experimental Condition

Effect of Reagent Volume

The effect of reagent volume was studied by using different volume (0.5-4.0) ml of the reagent (1×10-3M) with 1ml of 100µgml-1 of metal and recorded the absorbance at λ max. Highes absorbance at the 1.5ml of the reagent with Cu (II), 2ml of the reagent with Co (II). It is optimized volumes for the formation of the complexes with metal ions. The results are in Figure (6).

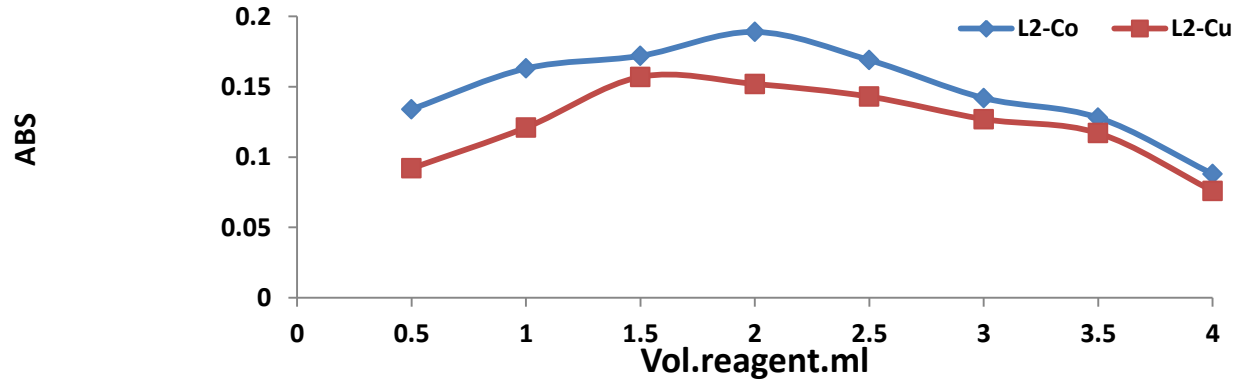


Figure 6: Effect of reagent volume at λmax=600nmfor L2-Co and λmax=647nmfor L2-Cu complexes

Effect of Reaction Time

The effect of time to get the complex is an important factor to obtain knowledge of the time period maintains the complex on stability especially employed in the field of analytical chemistry. The study was obtained at time (0-50) min. When the components were mixed at room temperature, maximum absorbance of the complexes were reached from (10-15) min from the moment start mixing and this useful in the field of spectral determination of metal ion, the reaction remains stable for 24 h. This show the ligands strong coordination with metal ions [33].The results are in Figure (7).

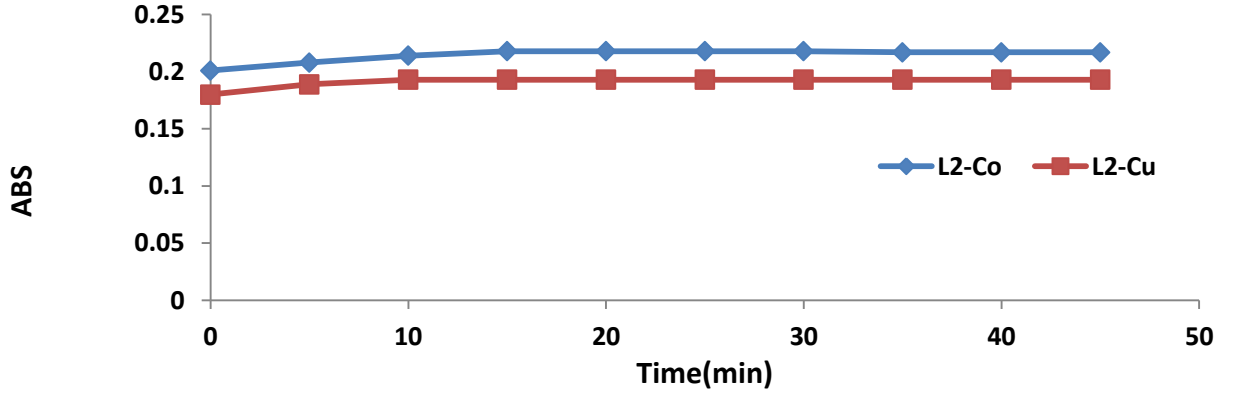


Figure 7: Effect of reaction time at λ max=600 nm for L2-Co and λ max = 647nm for L2-Cu complexes

Effect of Temperature

The effect of temperature on the absorbance of complex was examined. The study was performed at temperature between (20-60) °C. Figure (8) demonstrated that the maximum absorbance obtained at temperature range (30-45) °C. Which was viewed as an appropriate temperature of complex formation [38].At temperatures higher than 50°C the absorbance decreases due to dissociation of complex gradually [39].

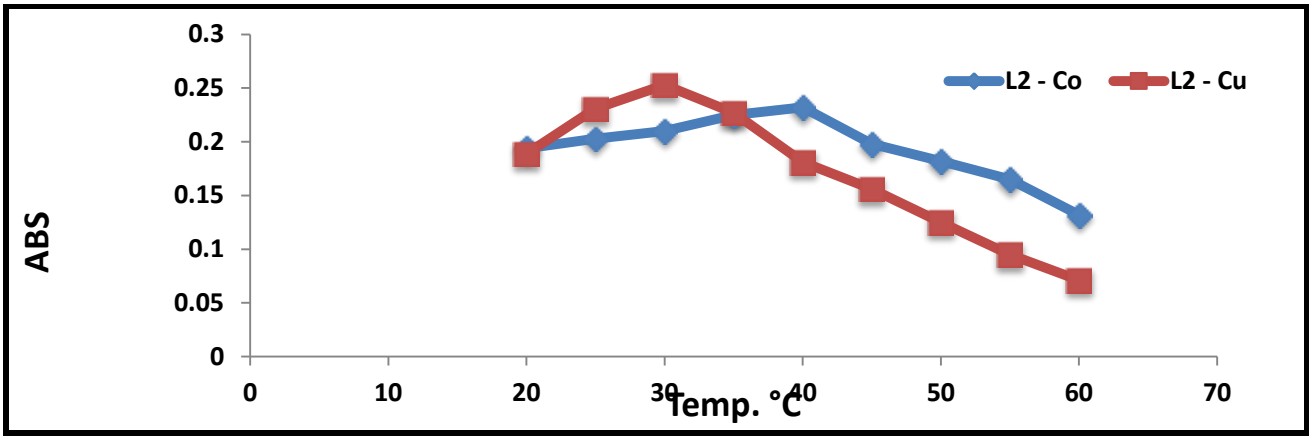


Figure8: Effect of temperature at λ max = 600nm for L2 – Co and λ max = 647nm for L2 – Cu complexes

Effect of PH

Figure (9) show that the absorbance of copper (II) and cobalt (II), complexes measured at λ max change with solution pH. The absorbance of each complex measured at λ max starts low on the acidic side, reaches a maximum at the optimum pH value and then decreases again as pH is increased. The optimum pH values obtained from the plots give pH =6 for Cu (II) [40] and pH=7 for Co (II) [41]. The absorbance gradually decreased may be due to forming another chromophoric formala of reagent at higher pH [42]. The simplest explanation for these observations is probably that the ligand is highly protonated at low pH, making the nonbonding electron-pairs unavailable and therefore diminishing the tendency to form complexes with the metal cations. On the other hand, when the pH is the optimum value, hydrolysis of copper (II) and cobalt (II) ions become more significant and reduce the concentration of the complex [43].

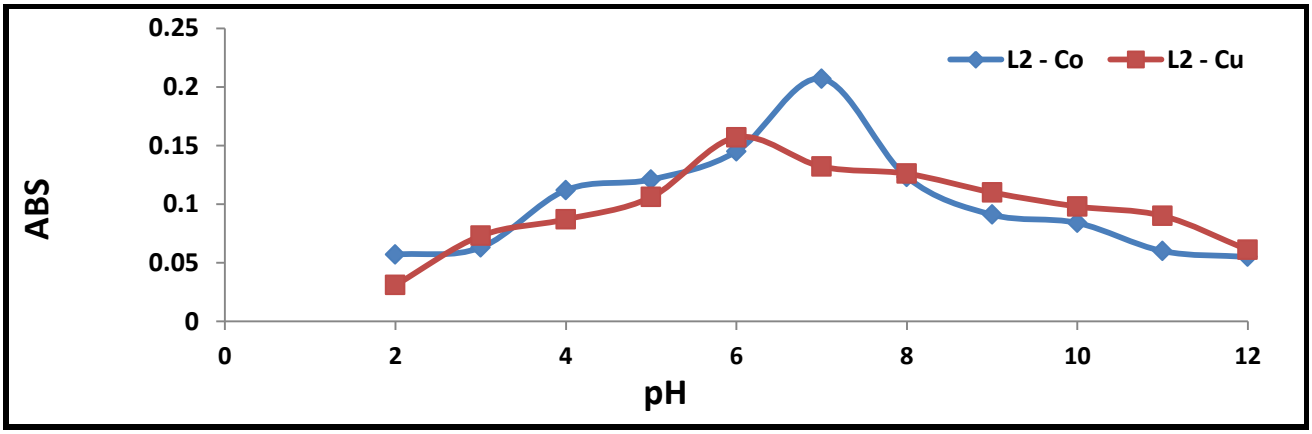


Figure 9: Effect of pH at λmax = 600 nm for L_2-Co and λmax = 647 nm for L_2-Cu complexes

Determination of the Stoichiometry of the Complex

The continuous variation method (Job's method) was used for the determination the stoichiometry of the complexes and their stability of ligands complexes. A series of solutions were prepared, with constant molar concentration of metal and ligand. The absorbance recorded at λ max. The results are showed that the M: L ratio for all complexes are 1:1(metal: ligand) stoichiometry, the results are tabulated in Table (3) and Figures (10), (11).

Table 3: Absorbance Values at (λmax) of Complexes by continuous variation method (Job's method)

Seq.	V_L 1× 10^{-3} M	V_M 1× 10^{-3} M	V_M/V_M+V_L	$A_{L2\text{-}Co}$	$A_{L2\text{-}Cu}$
1	1.8	0.2	0.10	0.054	0.053
2	1.6	0.4	0.20	0.065	0.087
3	1.4	0.6	0.30	0.114	0.126
4	1.2	0.8	0.40	0.173	0.158
5	1	1	0.50	0.213	0.185
6	1.2	0.8	0.60	0.175	0.147
7	1.4	0.6	0.70	0.136	0.120
8	1.6	0.4	0.80	0.091	0.082
9	1.8	0.2	0.90	0.069	0.045

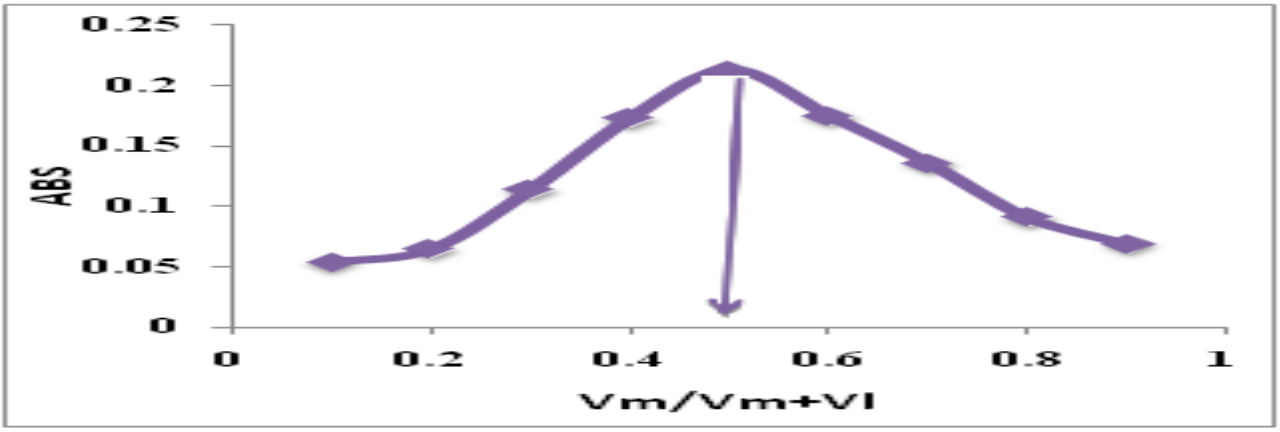


Figure 10: Job's method for the L2-Co at λmax = 600nm

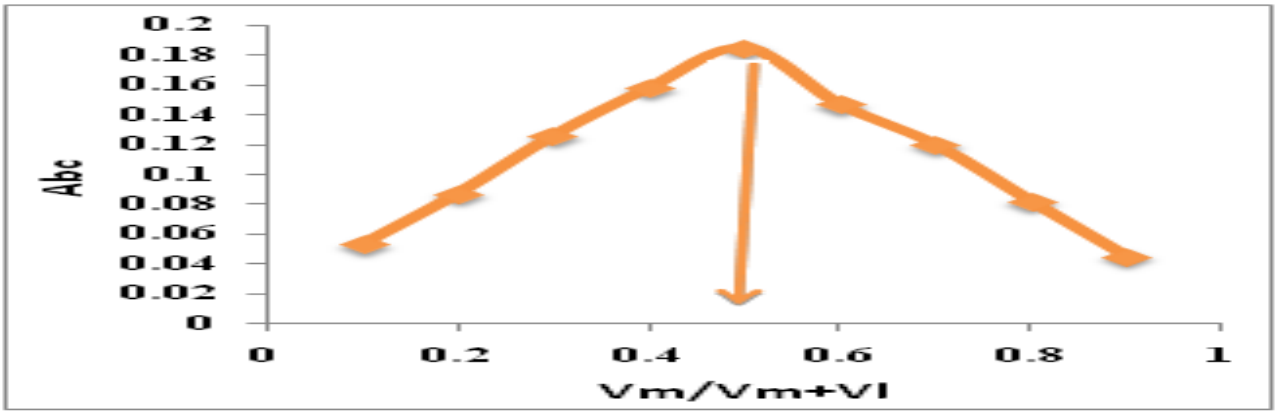


Figure 11: Job's method for the L_2-Cu at λmax = 647nm

Calculation of the Metal Complexes Stability Constant (Kst)

Stability constant of complexes were obtained spectrophotometrically by measuring the absorbance of solutions of reagent and metal ion at fixed wavelength λ max, and fixed pH. The degree of formation of the complexes (K_{st}) were obtained from the relationship of K_{st} = (1-α /$α^2$C) for 1:1 (M: L) metal complex and α=Am-As/Am, where Am and as are the absorbance of equivalent amount of L: M and excess amount of ligand with constant volume of metal formed complex respectively [32]. The calculated K_{st} values for the complexes are given in Table (4). The values of stability constant indicated high stability complexes [41].

Table 4: Stability Constant Values (K_{st}) at (λmax) and pH of Complexes

Complexes	λmax nm	pH	As	Am	α	K_{st}
$Co(L_2)Cl_2$	600	7	0.182	0.232	0.216	0.167 × 10^6
$Cu(L_2)Cl_2$	647	6	0.176	0.210	0.162	0.320 × 10^6

FT-IR Spectrum

The IR spectrum were obtained for Azo-Azomethine ligand prepared as KBr but the complexes as CsI disk by using a Shimaduz FT–IR spectrophotometer, The results show in table (5) and figures (12),(13),(14).

The spectra show absorption band in 3294cm^{-1}belong to OH [44]. The absorption band at 1630 cm^{-1}belong to stretching vibration of

C=N of imine [31,35]. Also a strong bandin the range at 1481Cm^{-1} due to the stretching vibration of the (N=N) [27]. The C=C appear stretching vibration at 1543 Cm^{-1}[45]. But stretching vibration for the C-H aromatic appears weak band at 3093 cm^{-1}[45, 46]. Complexes spectrum identify appearance of new bands were not present in the spectrum of ligand due to stretching vibration (M-N), (M-O) and (M-Cl), where appeared band (M-O) [47, 48].

In addition, the vibration band of the azochromogen group both in the ligand and the complexes were observed at (1481) cm^{-1}. Although the azochromogen group has a donor character and can from coordination compounds, the constant value of its vibration both in the ligand and the complexes shows that there is no coordination between the azochromogen group and the metal ions [48]. All the vibrational data proposes that the metal ions are bonded to the azo-azomethine ligand through the phenolic oxygen and the imino nitrogen atoms [46].

Table 5: FT-IR spectra of the azo-azomethine and complexes

Comp.	C=N azom.	N=N	C=C	OH	C-H arom.	C-H aliph.	M-O	M-N	M-Cl
L_2	1630 s.	1481s.	1543m.	3294 br.	3093 w.	-	-	-	-
$[Co(L_2)Cl_2]$	1626 s.	1481s.	1535	3281 br.	3078 w.	-	547m.	462m.	378 m.
$[Cu(L_2)Cl_2]$	1612 s.	1481v.s.	1533m.	3276 br.	3062 w.	-	476m.	416m.	331 s.

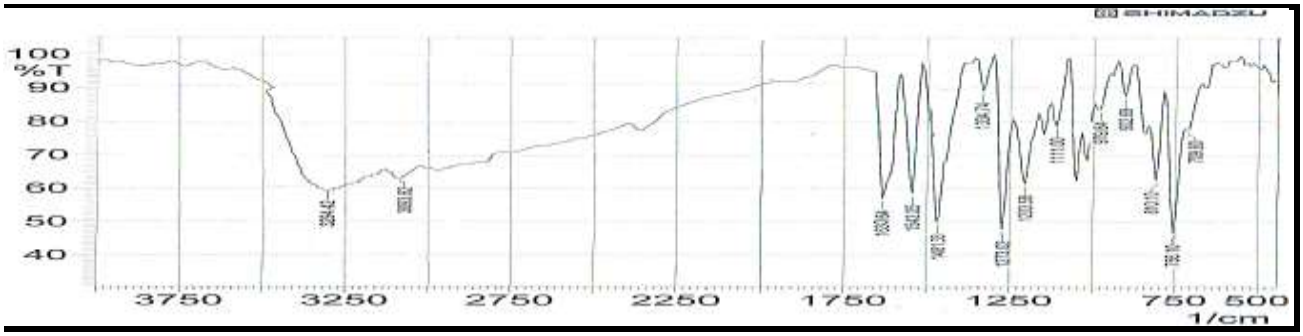


Figure 12: IR spectrum of L_2 by KBr

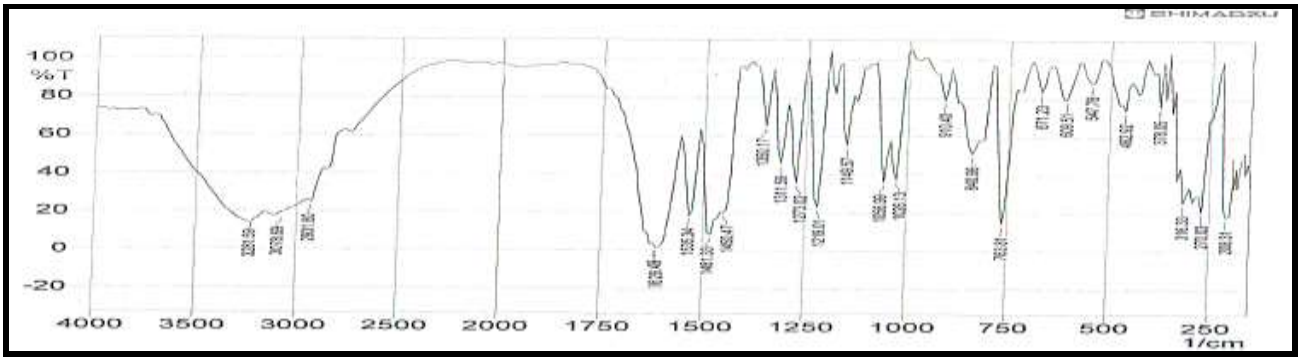


Figure 13: IR spectrum of [Co $(L_2)_2Cl_2$] by CsI

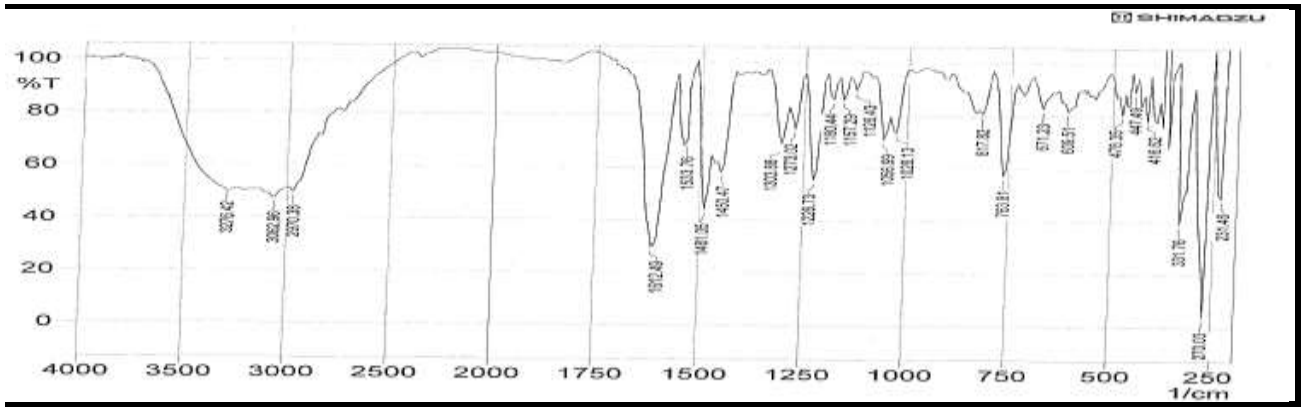


Figure 14: IR spectrum of [CuL_2 Cl_2] by CsI

^{1}H-NMR Spectrum

The ^{1}H-NMR spectrum of L_2 was recorded in DMSOas solvent in Figure (15). The chemical

shift δ ppm at 7.54-7.62(s, 10H, aromatic rings), 7.91-7.97(s, 10H, aromatic rings) [49], δ at 8.11 (s, 2CH=N) [49] and 10.13 (s, 2H, OH) [44, 49].

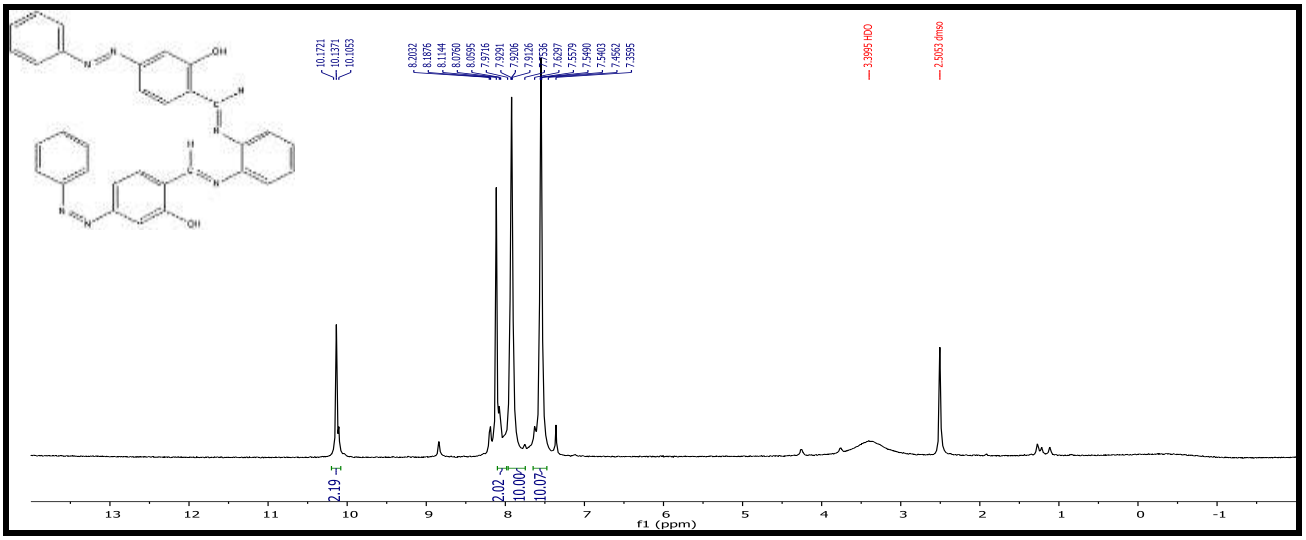


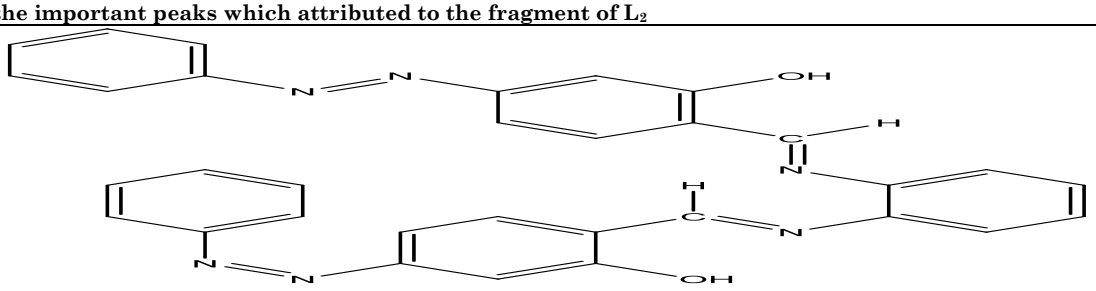
Figure 15: ^{1}H-NMR of L_2

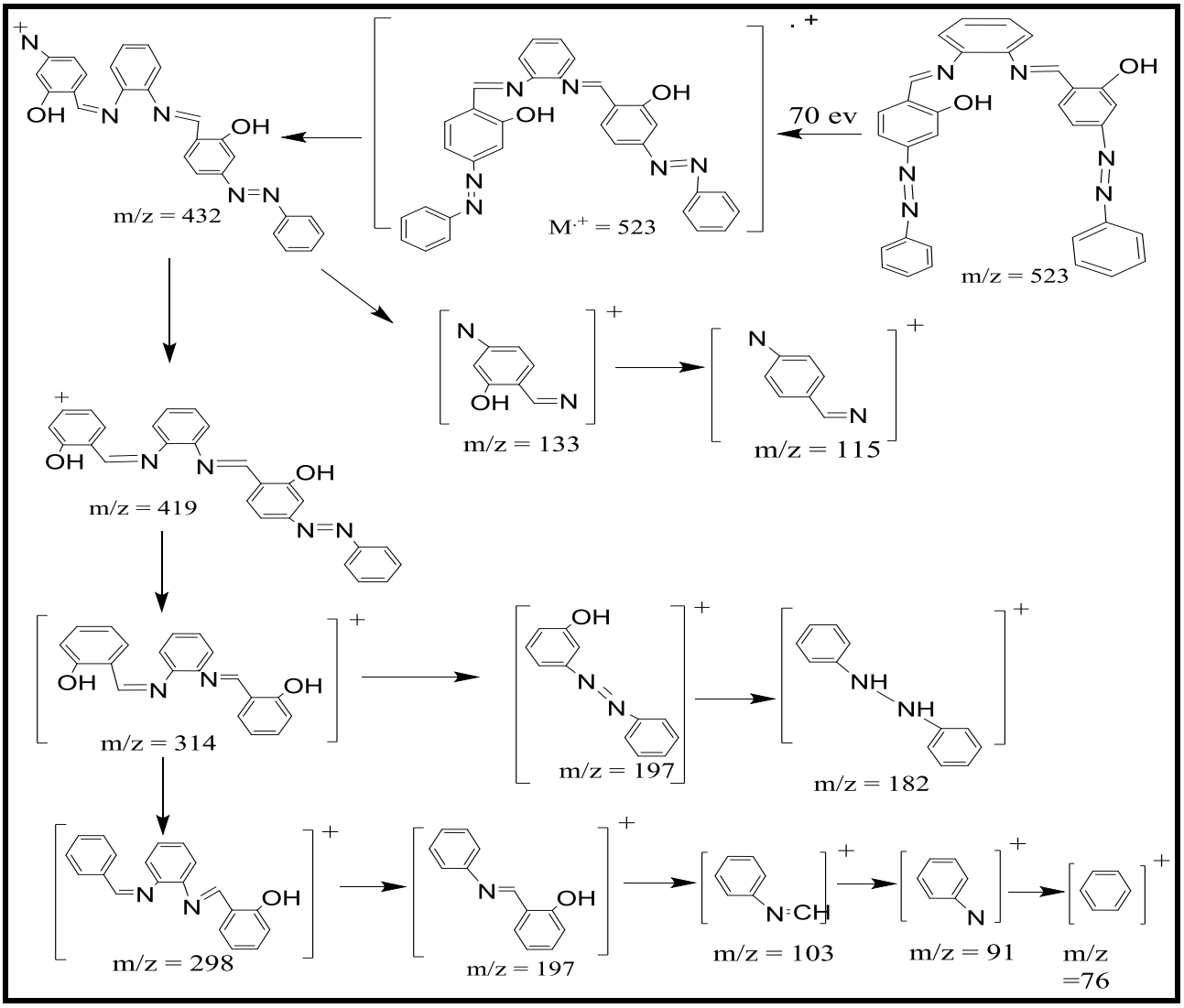
Mass Spectra of L_2 and Complexes

Characterize mass spectra of the ligand appearance of molecular ion peak ($M^{\cdot+}$) at 523 m/z and the spectrum showed a series of peaks (Figure 16) at m/z = 432, 419, 314, 298, 197, 182, 133, 103, 91 and 76 corresponding to$[C_{26}H_{19}N_5O_2]^+$,$[C_{26}H_{19}N_4O_2]^+$,$[C_{20}H_{14}N_2O_2]^+$,$[C_{20}H_{14}N_2O_1]^+$, $[C_{12}H_9N_2O_1]^+$, $[C_{12}H_{10}N_2]^+$, $[C_7H_5N_2O_1]^+$, $[C_7H_5N_1]^+$,$[C_6H_5N_1]^+$ and $[C_6H_4]^+$ respectively. list in Table (6). The mechanics of break- up are embedded in the Scheme (1).

The mass spectra of the complex $[CuL_2Cl_2]^{\cdot+}$ (Figure 17) shows of molecular ion ($M^{\cdot+}$) at 659 m/z and appearance other peaks at 588 m/z back to exit of the two chlorine atoms $[CuL_2]^{\cdot+}$ and 523 m/z due to L_2 $[C_{32}H_{24}N_6O_2]^{\cdot+}$. While the mass spectra of the complex $[CoL_2Cl_2]$ (Figure 18) shows of molecular ion ($M^{\cdot+}$) at 656 m/z and appearance other peaks at 621m/z , 587 m/zback to exit of the chlorine atoms $[CoL_2Cl]^{\cdot+}$, $[CoL_2]^{\cdot+}$ and 523 m/z due to L_2 $[C_{32}H_{24}N_6O_2]^{\cdot+}$.

Table 6: Includes the important peaks which attributed to the fragment of L_2

m/z	
523	$[C_{32}H_{24}N_6O_2]^+$
432	$[C_{26}H_{19}N_5O_2]^+$
419	$[C_{26}H_{19}N_4O_2]^+$
314	$[C_{20}H_{14}N_2O_2]^+$
298	$[C_{20}H_{13}N_2O_2]^+$
197	$[C_{12}H_9N_2O_1]^+$
182	$[C_8H_8N_2O_1]^+$
133	$[C_7H_5N_2O_1]^+$
103	$[C_7H_5N_1]^+$
91	$[C_6H_5N_1]^+$
76	$[C_6H_4]^+$



Scheme 1: Mass spectra for the ligand L_2

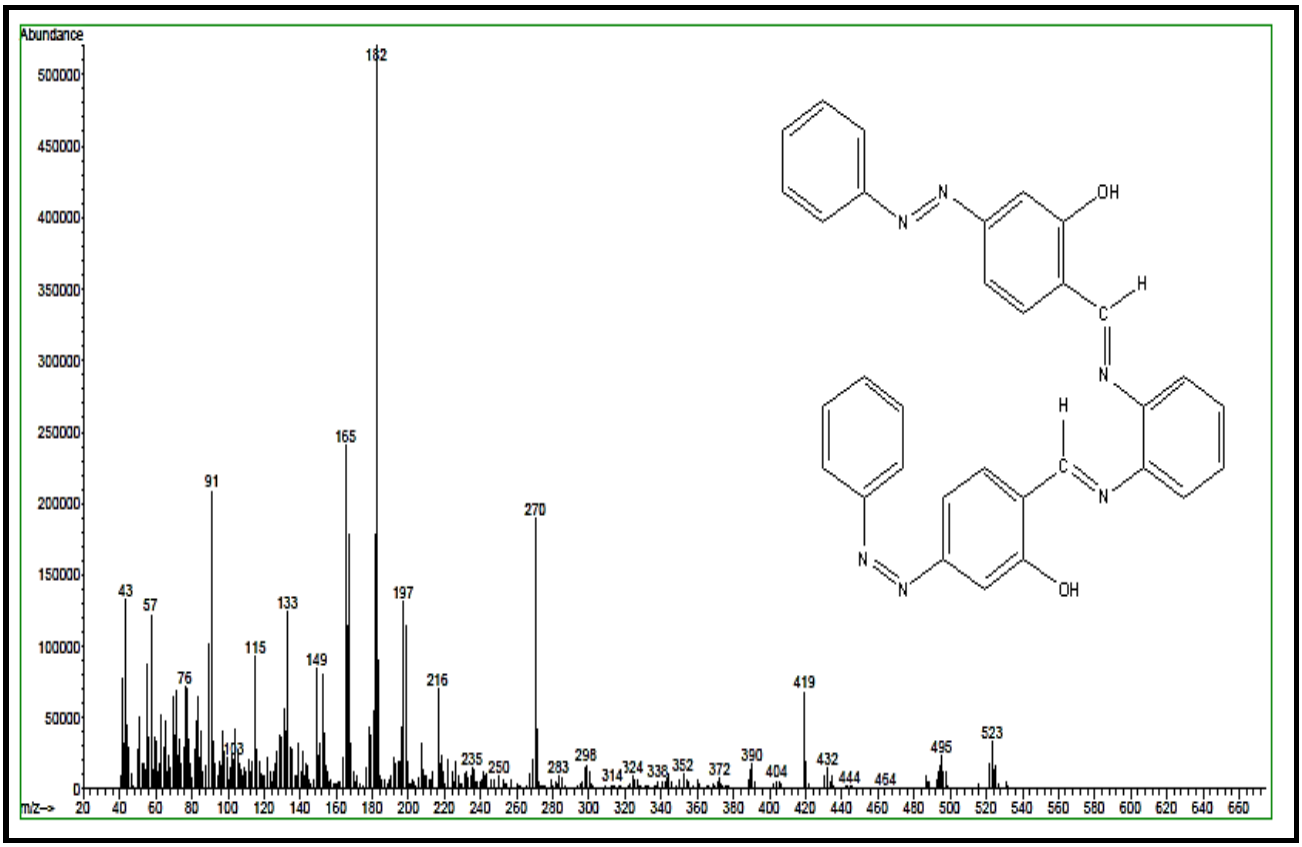


Figure 16: Mass spectrum of the L_2

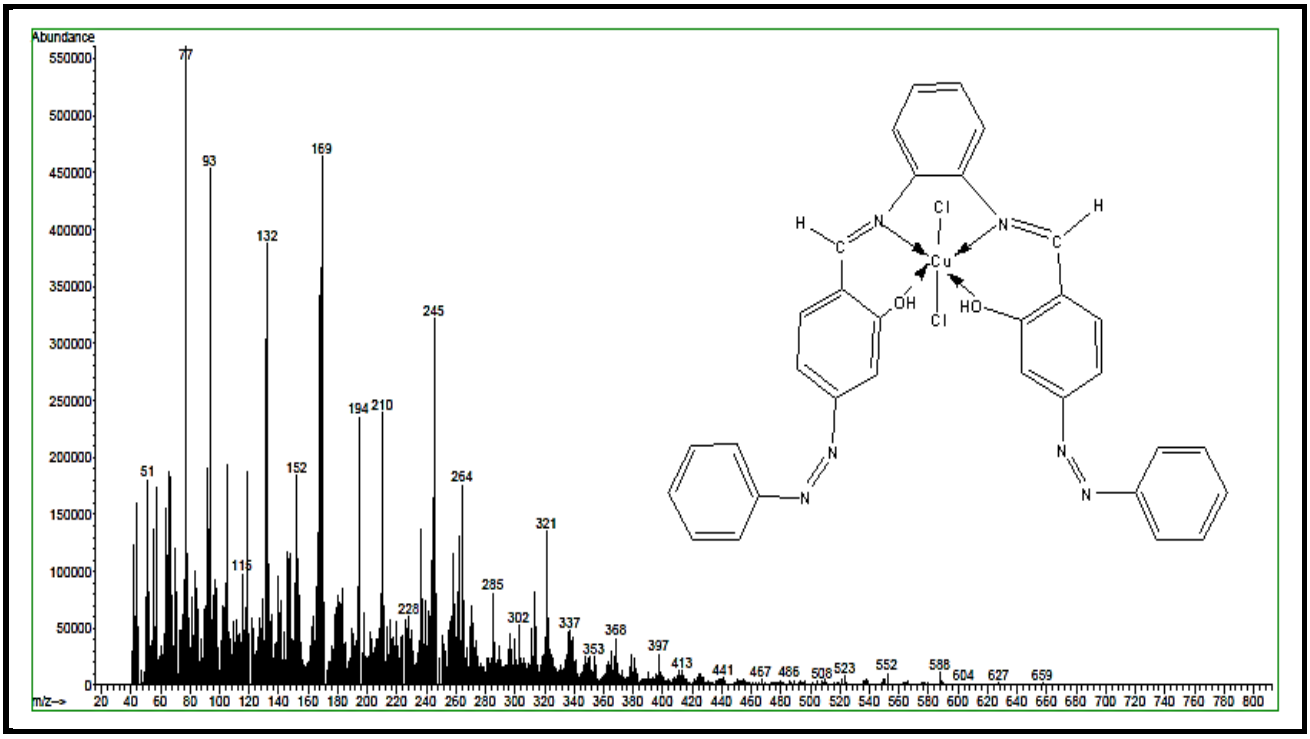


Figure 16: Mass spectrum of the complex [CuL_2Cl_2]

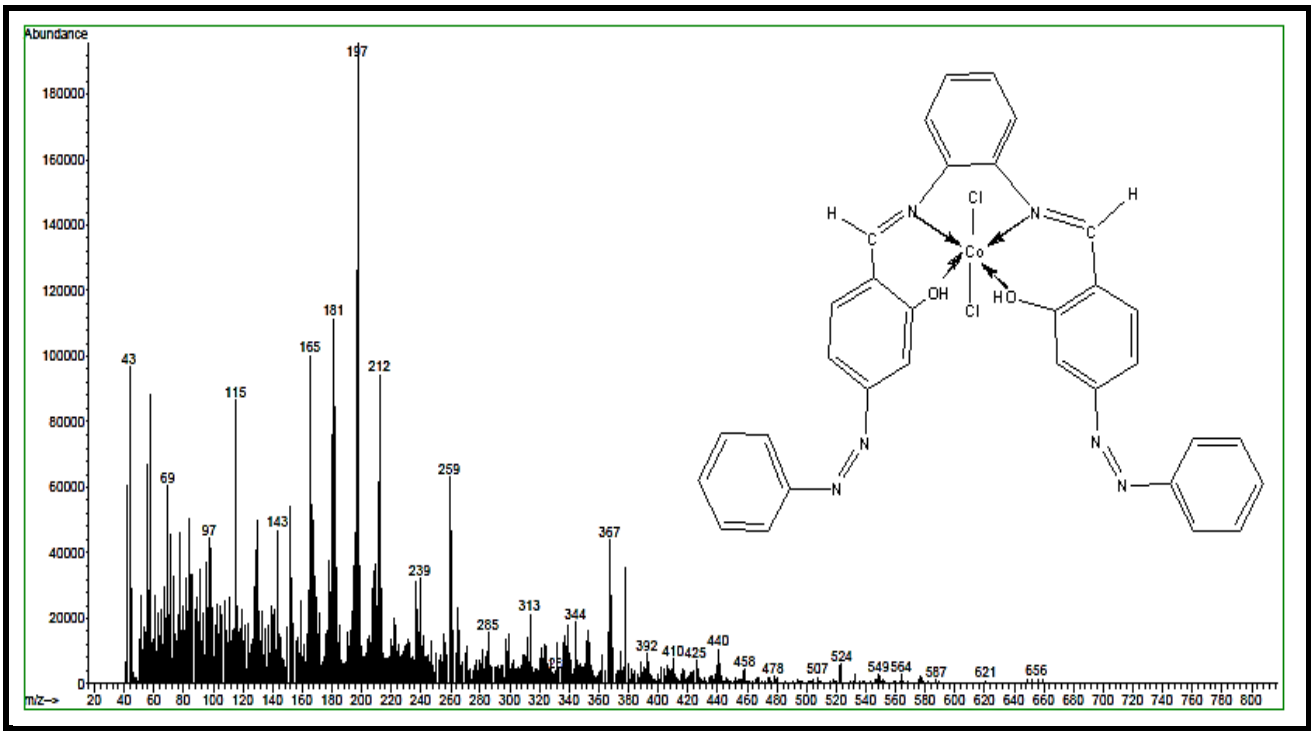


Figure 17: Mass spectrum of the complex [CoL_2Cl_2]

Molar Electrical Conductivity

The electrical conductivity is regarded as one of the important and simple means for knowing the ionic formula of the compounds which are complex in their solutions and the degree of electrical conductivity is suited ejectively with the number of ions which are released by the complex in the solution. It takes low values, when the complex does not have any ionic feature[50]. The water is not favored to be used as a solvent in the process of measuring the molar electrical conductivity for coordinative complexes because of some complexes sometimes hydrolysis or difficult dissolved in water, But the organic solvents are often used, such as methyl cyanide, nitromethane, dimethyl form amide , dimethyl sulfoxide and other, where the solvent inactive for the complexes have a dielectric constant and low viscosity[51].Definition molar conductivity 1 cm^3 of solution that contains 1 mole of the solute and the molar conductivity can be counted by the following relations.

$$\mathbf{L\ complex = A\ solution - A\ solvent}$$

$$\mathbf{K = L\ complex \times K\ cell}$$

$$\mathbf{\wedge m = 1000\ K/C}$$

K cell = cell constant (cm^{-1}), **L** complex = complex conductivity (S)
A solution = solution conductivity (S), **A** solvent = solvent conductivity
K = specific conductance ($s.cm^{-1}$), **C** = molar concentration (mole. Cm^{-3})
∧m = molar conductivity (s.cm2. mole-1)

Table 7: The values of molar conductivity ∧m = complexes ligand L_2solvent DMSO concentration of 10^{-3} M at a temperature of 298 Kin

No.	Complexes	∧m($s.cm^2$. $mole^{-1}$) in DMSO	Electrolyte Type
1	$[CuL_2Cl_2]$	17	Non-Electrolyte
2	$[CoL_2Cl_2]$	16	Non-Electrolyte

It was measured molar conductivity for solid complexes solutions of ions Cu(II) and Co(II) ions with L_2 ligand concentration of 10^{-3} M dissolved in dimethylsulfoxide (DMSO) each separately at a laboratory temperature, has been used distilled water as a reference . The results are included in Table (7) was found from the conductivity values of the complexes behave neutral compounds (non-electrolytic) the the lack of any adjective –ionic, because of the lack of chloride ions out of the coordination sphere as counter ions of the center ion, to make sure there is no chloride outside the coordination sphere by adding aqueous solution of silver nitrate $AgNO_3$ to complex solution (complex dissolved in DMSO) where noted not appearance or turbidity the solution, this refers to the absence of chloride ion outside the coordination sphere while if the chloride out of the coordination sphere white precipitate it will form, and turbidity increasing the number chloride atoms outside of the coordination sphere as counter ions. The obtained results were appropriate with the molecular formula and stereochemistry proposed of the prepared complexes.

Conclusion

The ligand 6, 6'-((1E, 1'E)-(1, 2-phenylenebis (azanylylidene)) bis (methanylylidene)) bis (3-(phenyldiazenyl) phenol) (L_2) was successfully synthesized. The ligand was bonded to two transition metal to from the corresponded complexes. It may be concluded that the ligand coordinate through Nitrogen atoms and hydroxyl groups. The ligand acts as a bidentate ligand coordination through –C=N and –OH groups. The FT- IR, Mass spectral and Molar electrical conductivity observations suggest the octahedral geometry for two prepared complexes.

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