Synthesis ,Coordination ,Chemical Analysis, Biological Activity of Ligands (Imidazole, Oxazole, thaizole) Derivatives with Zn

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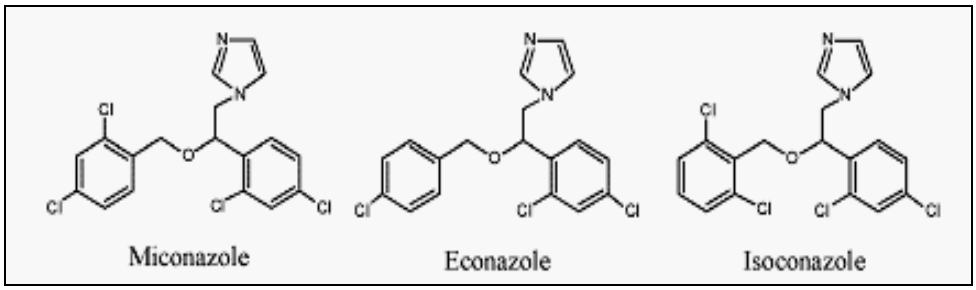
ABSTRACT :*The aim of our work is preparation of new three ligands represented by benzo- (thiazole , imidazole , oxazole) – derivatives with three complexes with zinc ion (II) ., all reactions involved cyclization reaction of di amine compounds or ortho hydroxy aniline or ortho thiol aniline by condensation reaction.*
Our ligands with complexes were investigated by(((I.R ,UV–Vis ,H.NMR) and (molar conductance , melting points , biological studying , Chromatography Analysis ,
and other physical studying)). The three ligands showed good indicators and their complexes through many studies for determination of optimal conditions of complexation with mole ratio (M:L) (1 : 1) and the ligand (L_1), ligand (L_2) and ligand (L_3) gave octahedral shape through coordination of six – atoms donor.
Keywords : import , atom, chromatoghragh .

I.INTRODUCTION

Imidazole ring was first reported in year 1858 via the German-British chemist Heinrich Debus, although various imidazole substituted had been discovered as early as the 1840[1-3].The substituted imidazole derivatives are valuable in treatment of many systemic fungal infections[4-8] Imidazoles belong to the class of azole anti bacterial or fungals, which act (ketoconazole, miconazole, and clotrimazole), etc…



Scheme (1): imidazole ring in drugs

Imidazole ring is an organic compound with the structure (C_3H_4N). This aromatic heterocyclic is a "1, 3-diazole" and is classified as an alkaloid. Imidazole refers to the parent compound, where as thiazole or imidazoles are a classes of heterocyclic with similar ring structure, but varying substituents. This ring system is present in important biological building blocks, like histidine[9-14] .Imidazole ,thiazole, oxazole have been used extensively as a corrosion inhibitors on transition metals, like copper. Preventing copper corrosion is important, especially in aqueous systems, where the conductivity of the copper decreases due to corrosion. Imidazoles , thiazole, and oxazole can also be used as organic structure[15-21] directing agents to synthesize zeollites.
Coordination ligands can often bind in more than one arrangement, putting varying degrees of strain into the ring formed. (Five , six or seven)- membered rings are often favored with saturated C and N based ligands[9,13,22] according to number of coordinated atoms in ligands.

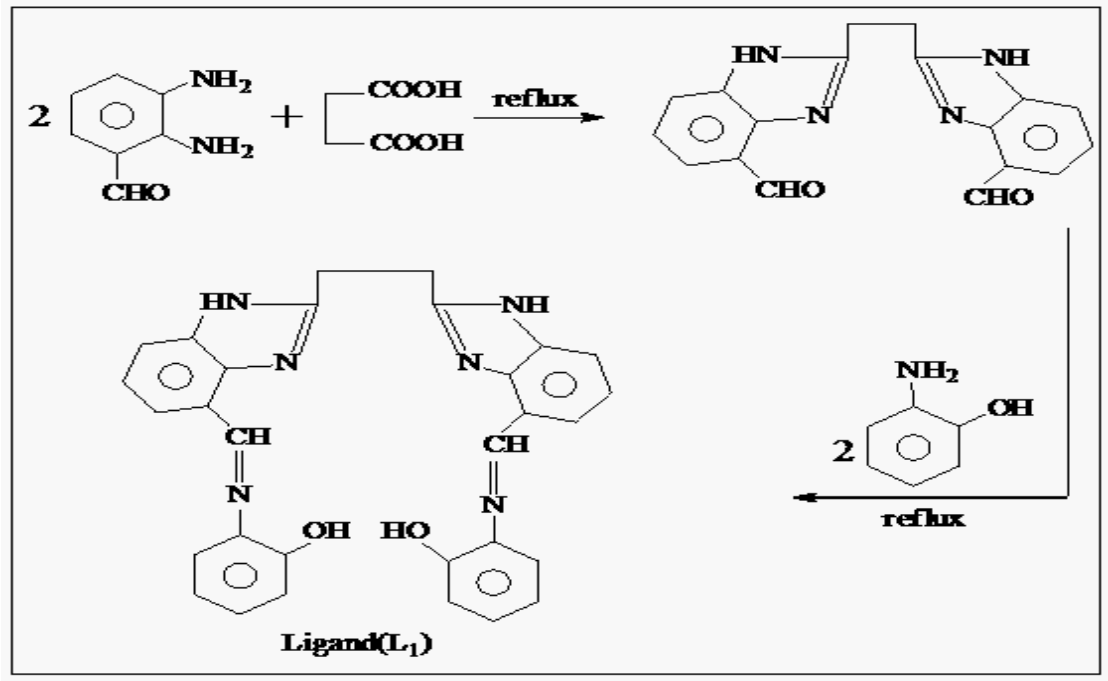
II. EXPERIMENTAL

All measurements such as: Melting points were determined in open capillary tube and were uncorrected . The I.R- spectra were recorder in KBr–disc , Shimadzu (8300) . Chromatography Analysis(Chromatogram Curves)

.UV –Vis –spectra photometer .Molar conductance (DMSO–solvent) , (H.NMR) – SPECTRA in Canada ., TLC - plate .,Biological Activity.

STEP .1 : Preparation of First Coordination ligand (L_1) :

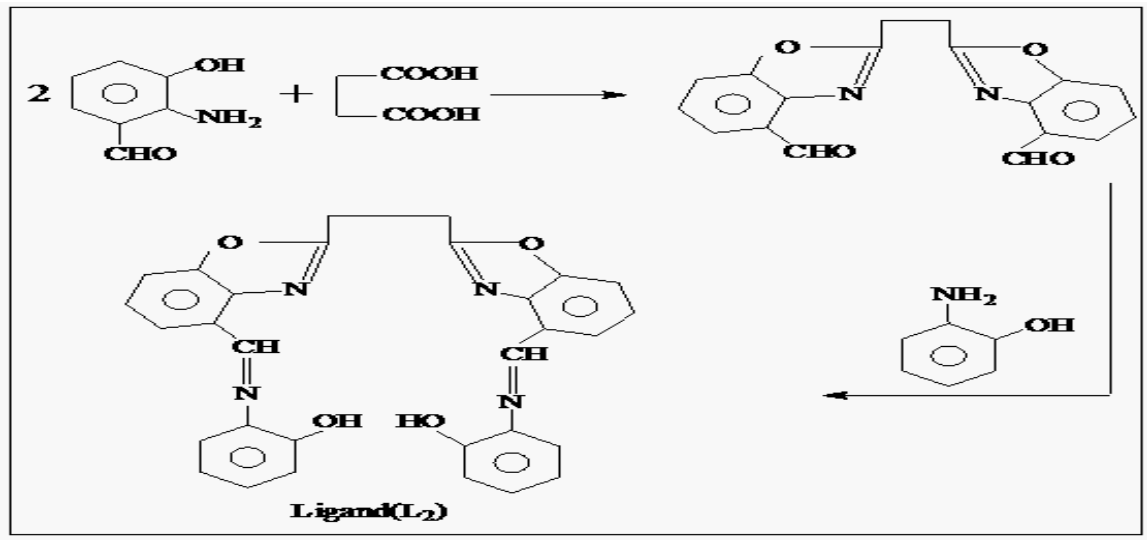
A mixture (0.2mole) of 3-formal -1,2-phenylene diamine was dissolved in (10ml) of concentrated hydrochloric acid with (0.1 mole) of succinic acid in present of ethanolic solution, after (5 hrs) , the precipitate was filtered and dried , which (0.1mole) refluxed with (0.2mole) of (o-amino phenol) .,according procedures[14-16] ,the precipitate were filtered and dried to yield (76 %) from ligand (L_1) which acts benzo imdazole ligand.



Scheme (2): Preparation of First Ligand

STEP .2 : Preparation of Second Coordination ligand (L_2) :

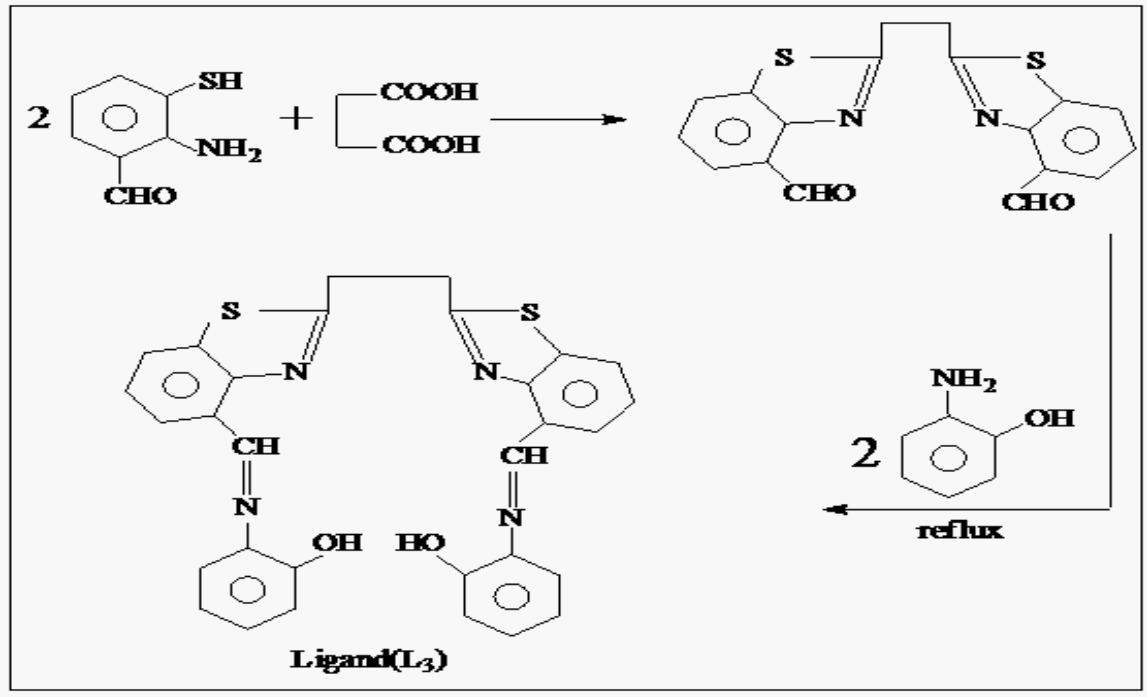
A mixture (0.2mole) of 3-formal -2-amino phenol was dissolved in (10ml) of concentrated hydrochloric acid with (0.1 mole) of succinic acid in present of ethanolic solution, after (5 hrs) , the precipitate was filtered and dried , which (0.1mole) refluxed with (0.2mole) of (o-amino phenol) .,according procedures[14-16] , the precipitate were filtered and dried to yield (72 %) from ligand (L_2) which acts benzo oxazole ligand.



Scheme (3): Preparation of Second Ligand

STEP .3 : Preparation of Second Coordination ligand (L_3) :

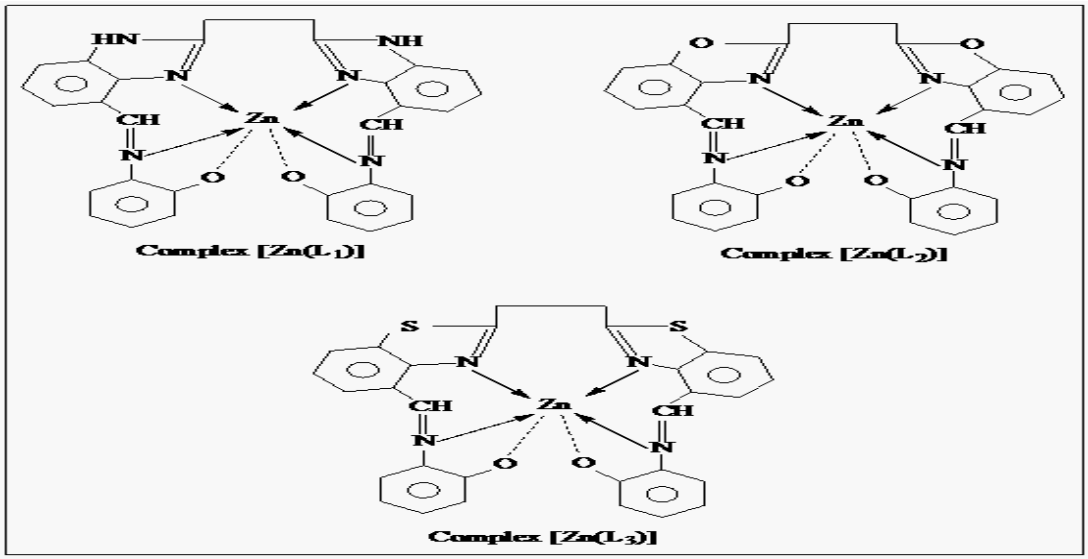
A mixture (0.2mole) of 3-formal –mercapto aniline was dissolved in (10ml) of concentrated hydrochloric acid with (0.1 mole) of succinic acid in present of ethanol , after (5 hrs), the precipitate was filtered and dried , which (0.1mole) refluxed with (0.2mole) of (o-amino phenol) .,according procedures[14-16] ,the precipitate were filtered and dried to yield (78 %) from ligand (L_3) which acts benzo thiazole ligand.



Scheme (4): Preparation of Third Ligand

STEP .4 : Synthesis of Two Complexes with Ion (Zn^{2+}) :

According to procedures[21] ,the hot ethanolic solution of ligands [(L_1) or (L_2) or (L_3)] respectively was added to solution of ion salt of chloride ($ZnCl_2$) in mole ratio (metal**:** ligand) (1**:**1) respectively after stirring (2 hrs) ,precipitates formed , dried and re crystallized to give (74% ,80 , 76 %) respectively from complexes of three ligands respectively .



Scheme (5): Preparation of Complexes

III. RESULTS AND DISCUSSION

Hexa dentate ligands from benzo(imidazol , thiazole, oxazole) - Anil compounds are specific and inorganic ligands in coordination chemistry. The anil is basic and exhibits pi-acceptor properties in most of ligands .All ligands and complexes were investigated and characterization by many methods :

Determination of Condition of complexes Complexation with Zn :

To optimal conditions of complexes with ion Zn(II) were tested in this work like calibration curves of optimal concentration of Zn^{2+}= (0.40 $X10^{-4}$m) , while concentration of ligands **[** 0.60 $X10^{-3}$M of ligand (L_1) **.,** 1 $X10^{-3}$M of ligand (L_2) , 0.75 $X10^{-3}$M of ligand (L_3)**]** ., while optimal (PH=8) for the three complexes of ligand (L_1) and ligand (L_2) with ligand (L_3) in base medium for removing proton of hydroxyl group from ligands , and chemical identification UV-Visible . Other studies of these complexes in table (1) and figs (1-4) .

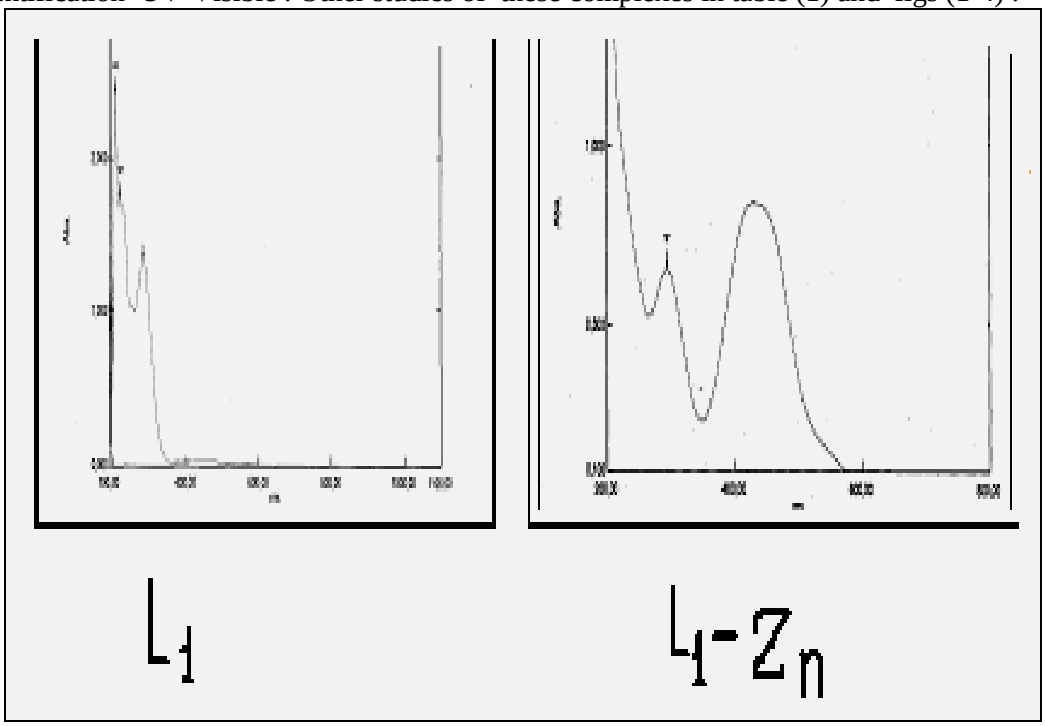


Fig (1): UV-Vis Spectrum of Ligand (L_1) and Complex

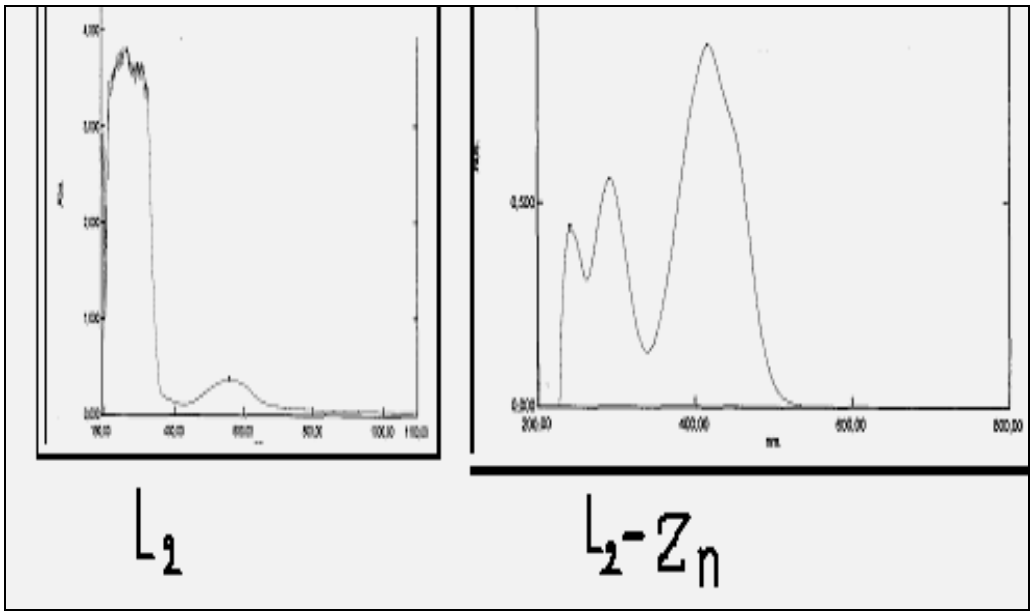


Fig (2): UV-Vis Spectrum of complex [Zn (L_2)] and Complex

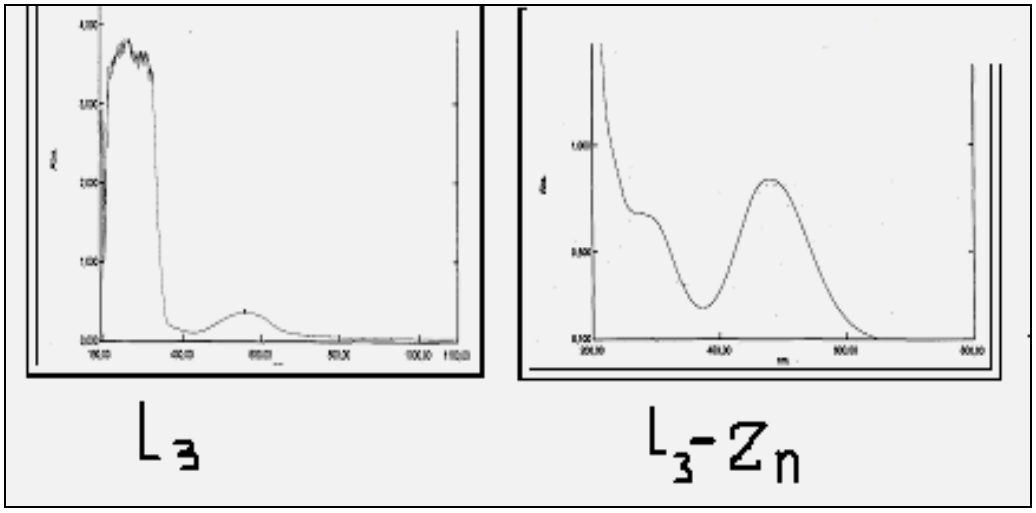
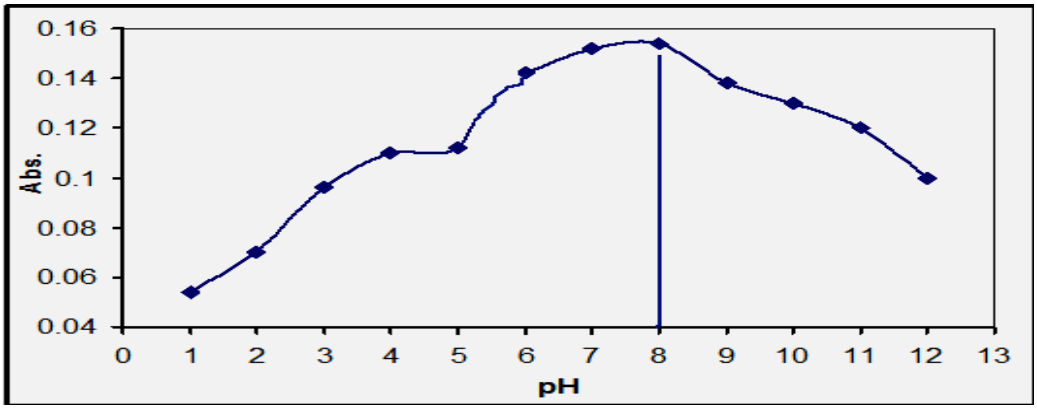


Fig (3): UV-Vis Spectrum of Ligand (L_3) and Complex



Fig(4): Optimal pH of Three complex [Zn (L)]

Mole Ratio of Complexes:

The complexation with ligands- zinc by job method and mole ratio method through series solutions were tested which having a constant concentration ($1X10^{-3}M$) of Zn salt ($ZnCl_2$) and ligand ., the (M**:**L) ratio was determined from relationship between the absorption and mole ratio (M **:**L) which appeared ratio (1**:**1) for all complexes. From our results ((mole ratio ,calibration curve , stoichiometry ,chemical spectra) indicate that the Zn- complexes with the three ligands were stoichiometry (metal **:** ligand) (1**:**1).

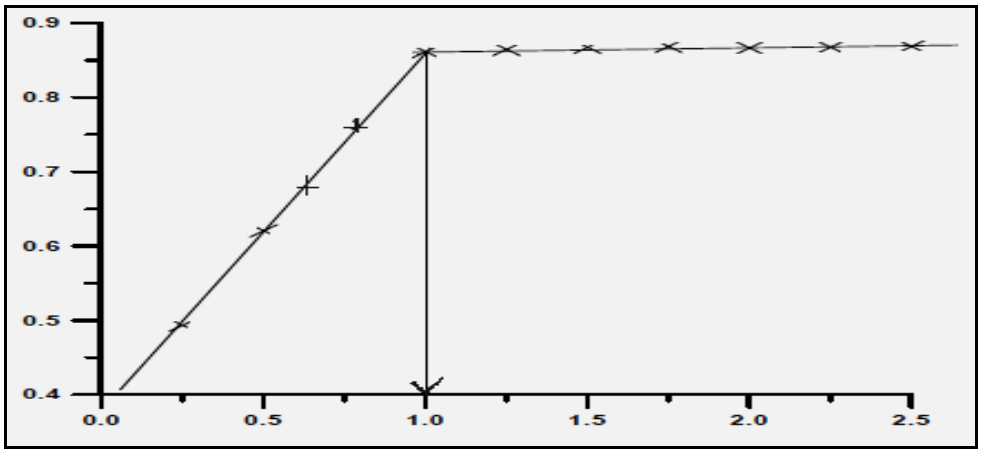


Fig (5) : Mole ratio of Three Complex [Zn(L)]

The conductivity of Complexes:

Table (1) indicated to all results of physical measurements like melting point ,conductivity measurements which were (0.92 **,** 1.14 , 1.32) $ohm^{-1}.mole^{-1}.cm^2$ of ($1x10^{-3}$M) solution in (DMSO) which indicates that the (Zn - Complexes) are non-electrolytic in nature ., and other properties like melting points ,UV- Visible are shown in table (1):

Table(1): physical Measurements and UV-Visible of ligands with Complexes

Ligands & Complexes	M.P $(C)^0$	λ_{max}	Conductance $\Omega^{-1}.Cm^2.mole^-$
Ligand (L_1)	190	344	/
Ligand (L_2)	210	356	/
Ligand (L_3)	198	378	/
Complex [Zn(L_1)]	226	538	1.32
Complex [Zn(L_2)]	248	554	1.14
Complex [Zn(L_3)]	236	550	0.92

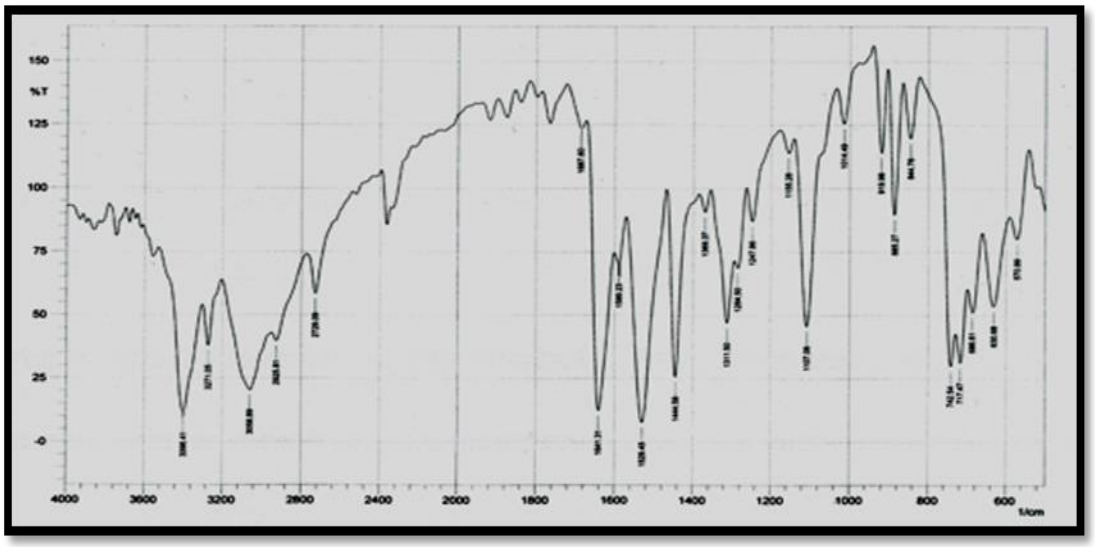
Spectral Investigation:

I.R – spectra : From results of infra red spectra , which appeared absorption band in amine group (NH) at (3299) cm^{-1} in ligand (L_1) in free ligand and bands of ligands [(L_1), (L_2) , (L_3)] at (3394, 3323 , 3380) cm^{-1} due to hydroxyl groups[21] of phenol in ligand (L_1 , L_2 , L_3) respectively which disappeared in spectra of their complexes indicating the coordination through phenolic oxygen moiety and at bond (M–O) are (546-575) cm^{-1} .The I.R–spectra of (Anil group CH=N)[14-16] respectively in ligands exhibit bands at (1602 , ,1620 , 1676)cm^{-1}respectively ,which have been shifted towards other bands at (1615,1605 , 1641) cm^{-1} respectively in complexes to coordination[21] with ion (Zn^{2+}) .

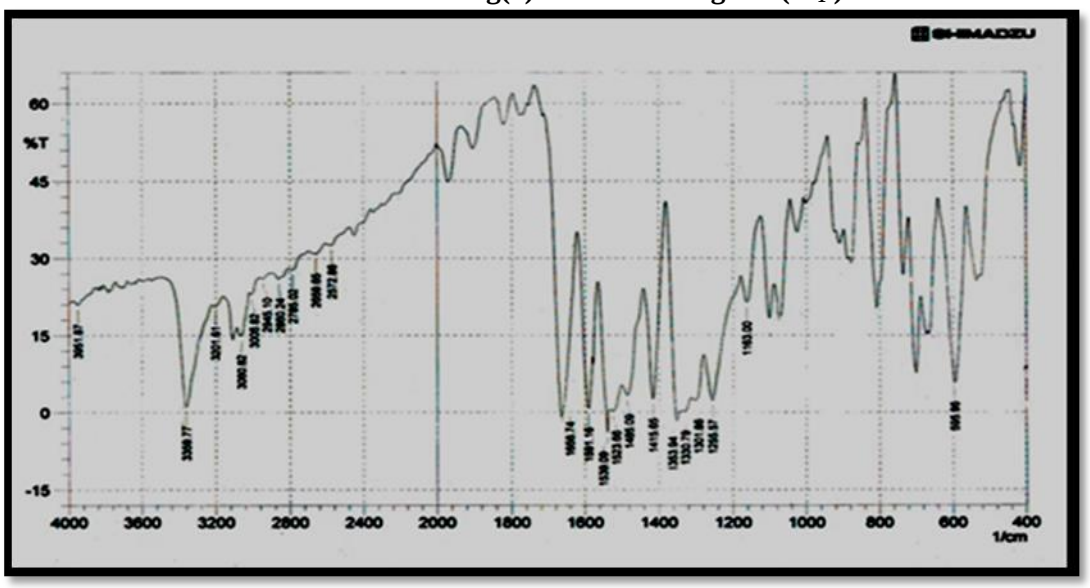
While the coordination via nitrogen of anil group (CH=N) and oxygen of hydroxyl group of phenol in complexes , Table (2) and figs (6-11) .

Table (2) :FT.IR data (cm^{-1}) of ligands with complexes .

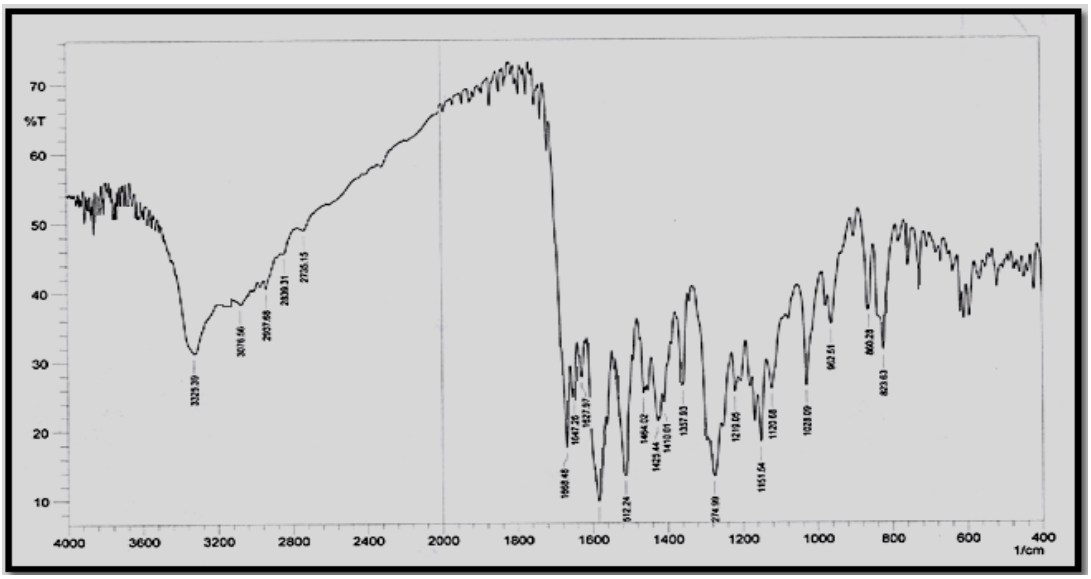
Ligands & Complexes	(CH=N) Anil group	(C=N) Endo Cycle	Other Groups	(-OH) Phenol	(M-N)	(M-O)
(L_1) Ligand	1602	1640	(NH):3299	3394	/	/
(L_2) Ligand	1620	1655	/	3323	/	/
(L_3) Ligand	1676	1637	(C-S): 731	3380	/	/
[Zn(L_1)] Complex	1615	1650	(NH):3290	/	420	575
[Zn(L_2)] Complex	1605	1647	/	/	460	546
[Zn(L_3)] Complex	1641	1615	(C-S): 729	/	483	567



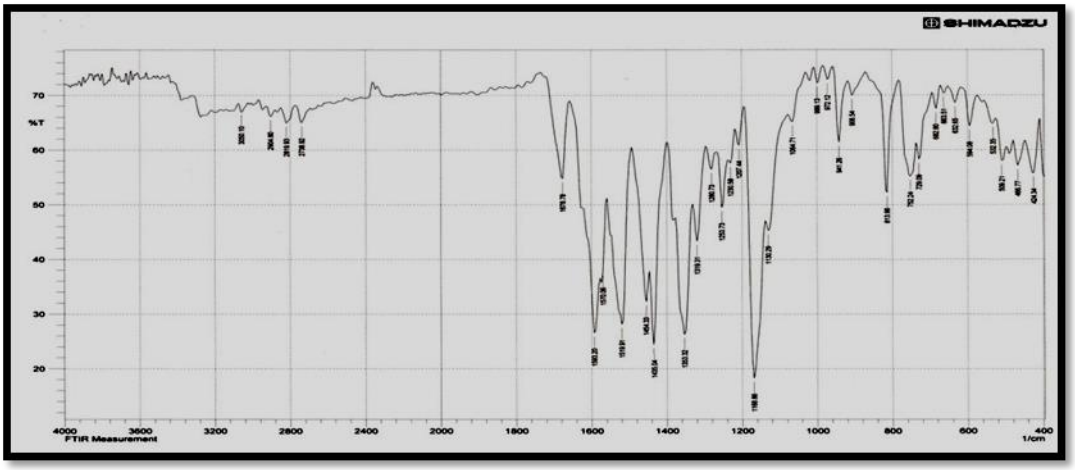
Fig(6): FT.IR of Ligand (L_1)



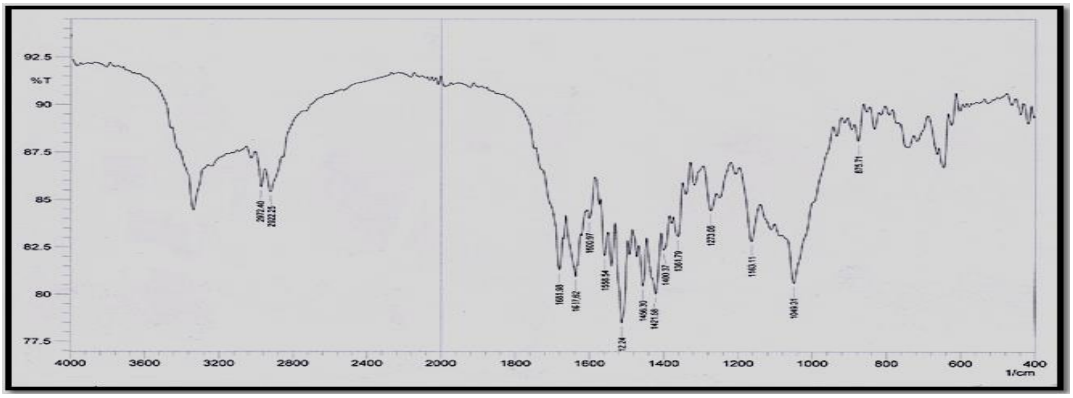
Fig(7): FT.IR of Complex [Zn (L_1)]



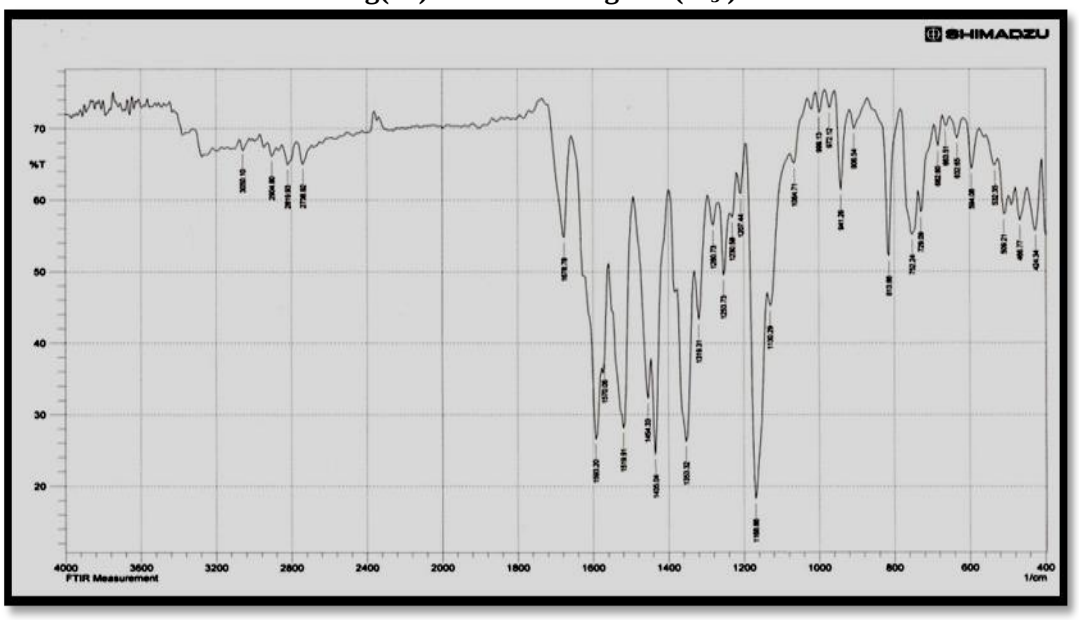
Fig(8): FT.IR of Ligand (L_2)



Fig(9): FT.IR of Complex [Zn (L_2)]



Fig(10): FT.IR of Ligand (L_3)



Fig(11): FT.IR of Complex [Zn (L_3)]

Studying of H.NMR- spectra :spectra of ligands showed signals at δ (11.10 , 11.04 , 11.15) for hydroxyl group of phenol in free ligands ., which disappeared in their complexes as a result of coordination with (Zn^{2+})., and other peaks are listed in table (3) and figures **(**12-17**)** .

Table (3) : H.NMR data (δ ppm) of Ligands with Complexes .

Ligands & Complexes	(OH) phenol	(CH=N) Anil group	Other groups ((only functional groups))
Ligand (L_1)	11.10	8.09	(-Ph-): proton of phenyl ring : (6.95– 7.99) ., (NH): 8.00 Proton of amine
Ligand (L_2)	11.04	8.11	(-Ph-) proton of phenyl ring : (6.70 – 7.65) .
Ligand (L_3)	11.15	8.55	(-Ph-) proton of phenyl ring :(6.76 – 7.95) .
Complex [Zn(L_1)]	/	8. 94	(-Ph-) proton of phenyl ring (6.78 – 7.96) **.,** (NH): 8.43 Proton of amine
Complex [Zn(L_2)]	/	8.70	(-Ph-): proton of phenyl ring : (6.98– 7.95) .,
Complex [Zn(L_3)]	/	8.84	(-Ph-): proton of phenyl ring : (6.55– 7.47 .,

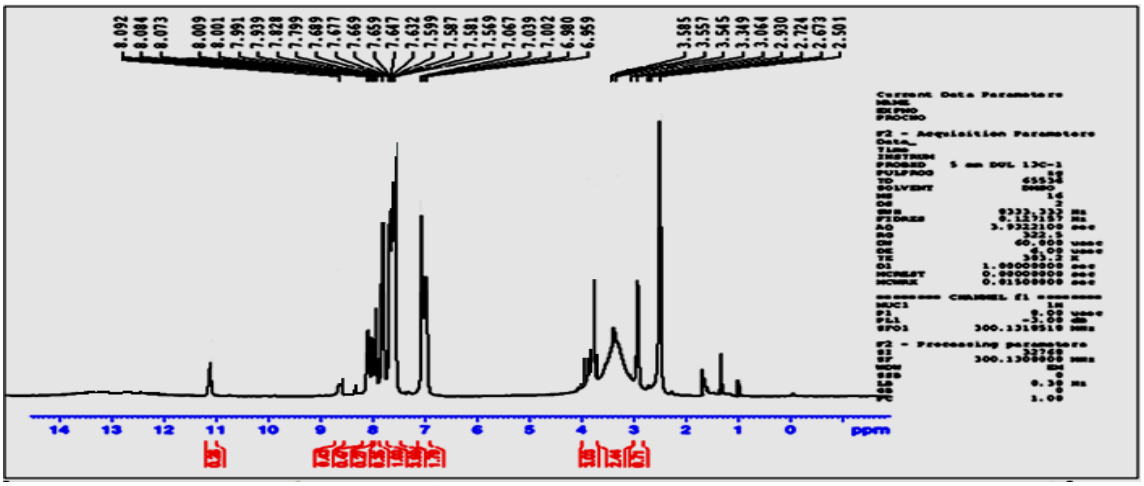


Fig (12): H.NMR of Ligand (L_1)

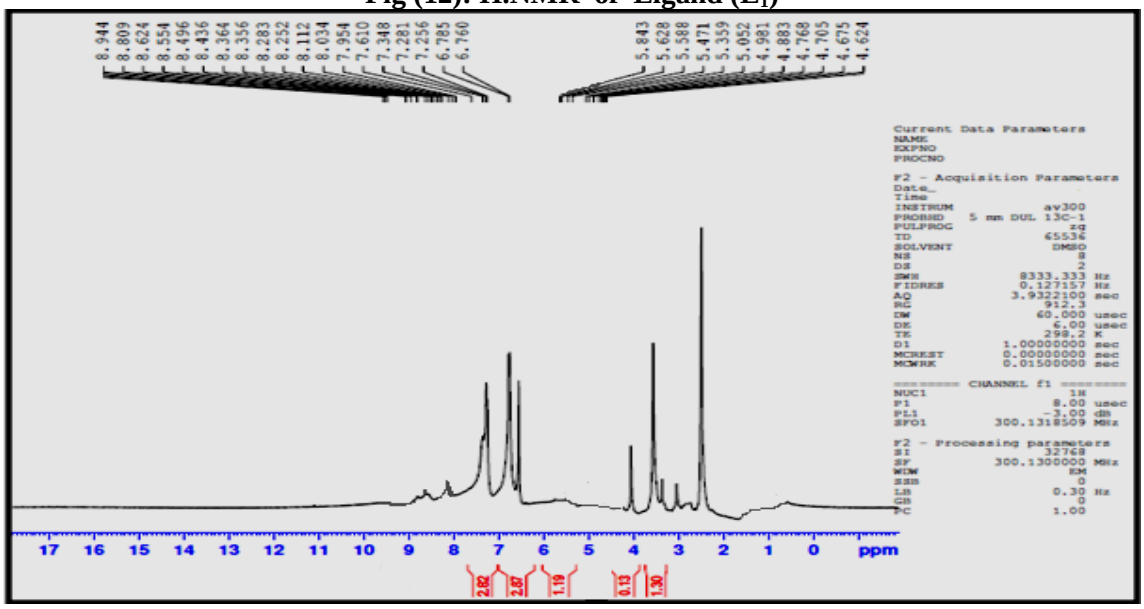


Fig (13): H.NMR of Complex [Zn (L_1)]

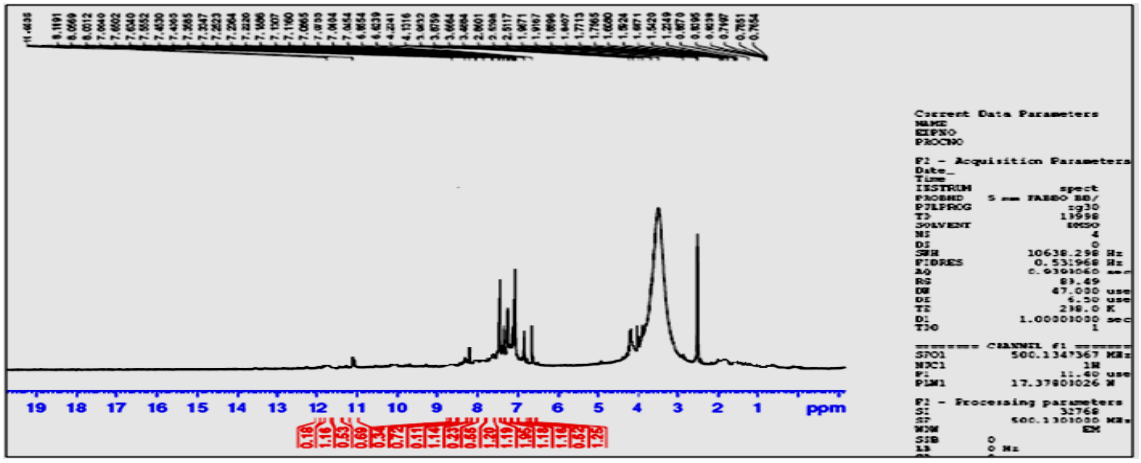


Fig (14): H.NMR of Ligand (L_2)

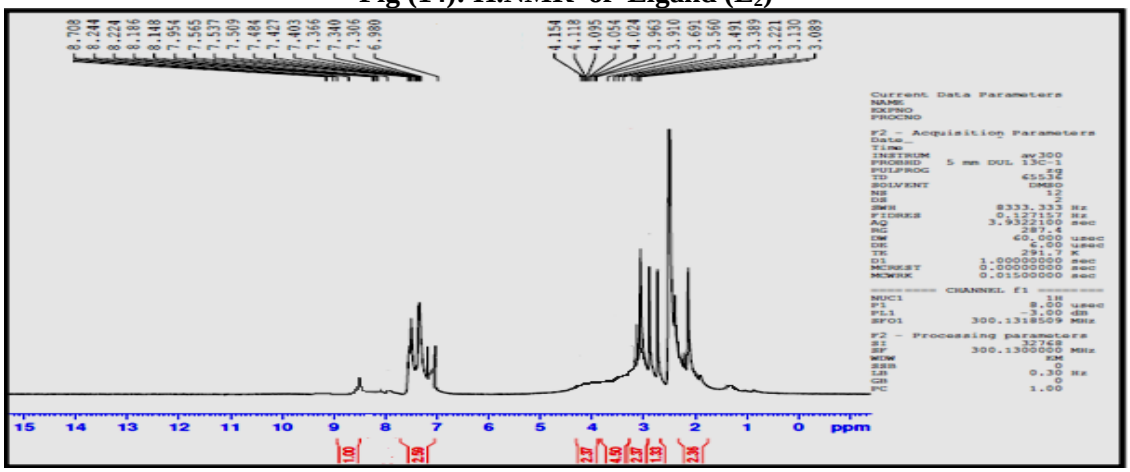


Fig (15): H.NMR of Complex [Zn (L_2)]

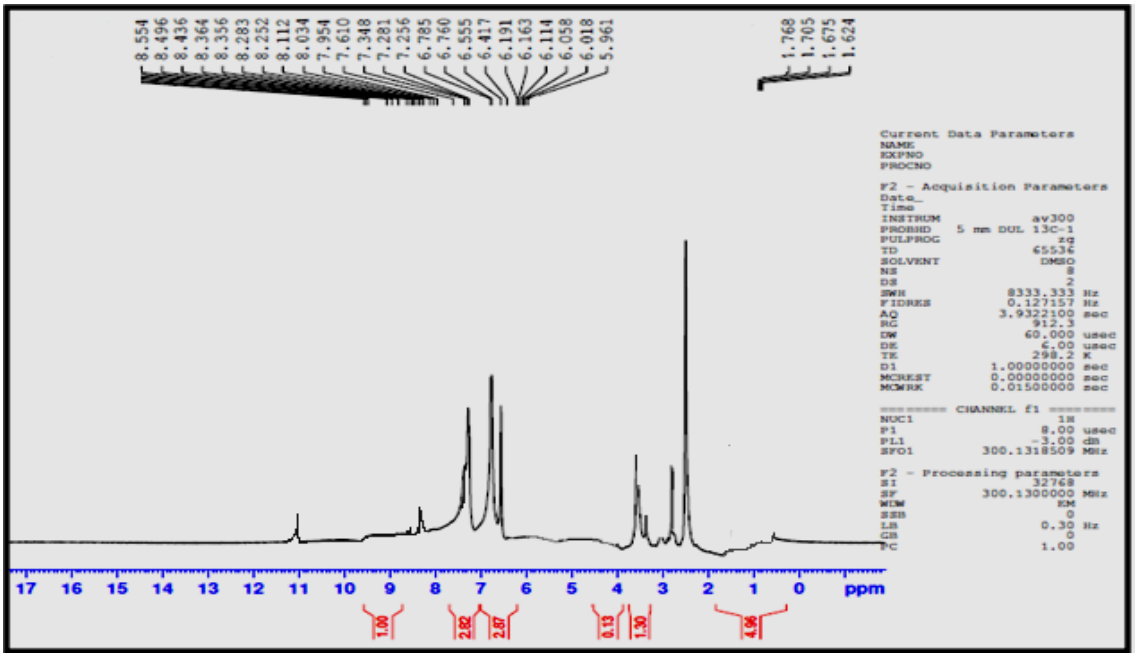


Fig (16): H.NMR of Ligand (L_3)

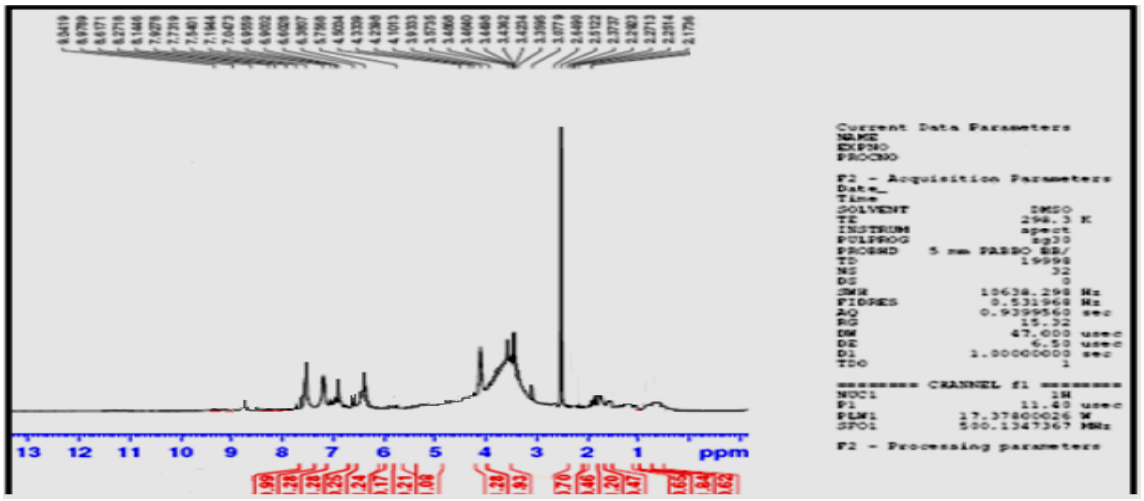
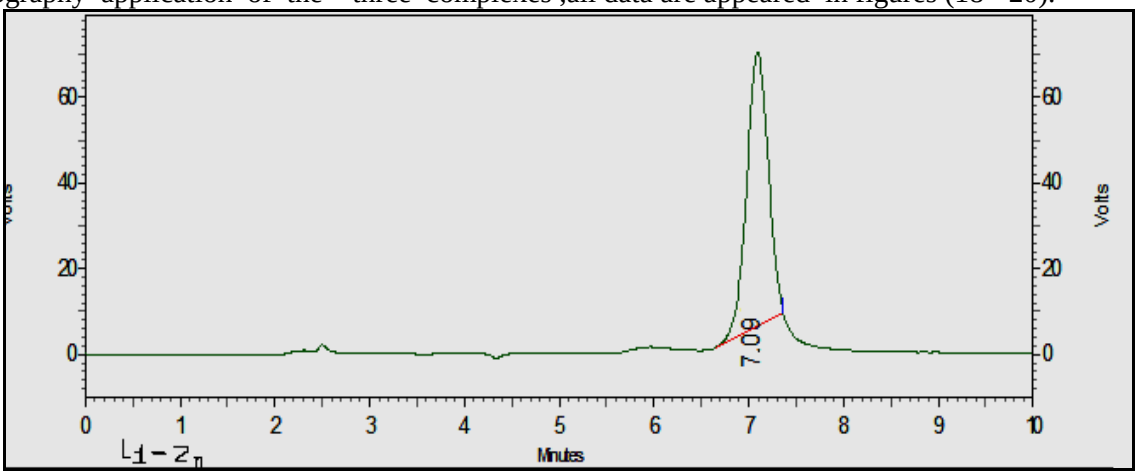


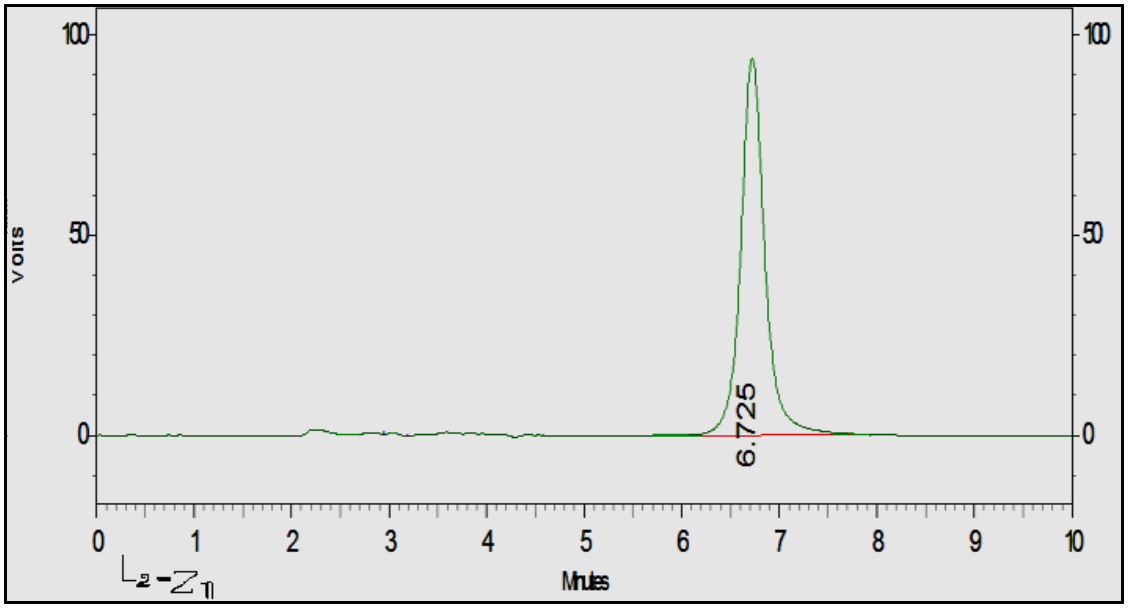
Fig (17): H.NMR of Complex [Zn (L_3)]

Studying of Chromatographic Application :

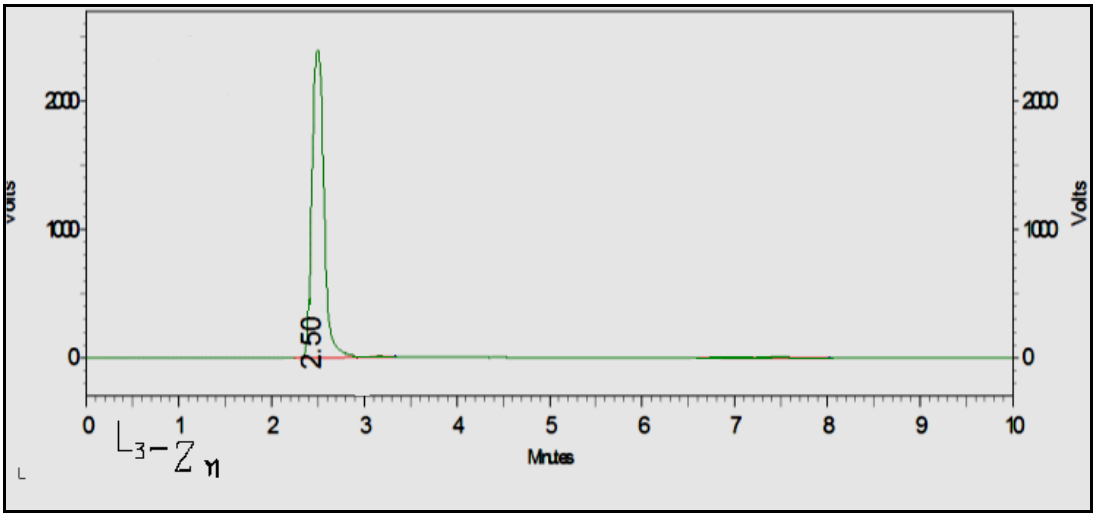
In this work and according to procedure of studying[21] we screened our formatted compounds in the chromatography application of the three complexes ,all data are appeared in figures (18 - 20).



Fig(18): Chromatogram of Complex [Zn (L_1)]



Fig(19): Chromatogram of Complex [Zn (L_2)]



Fig(20): Chromatogram of Complex [Zn (L_3)]

The effect of anil group with (imdazole , oxazole , thiazole)-benzo derivatives gave a wide applications in analytical and inorganic chemistry field like in chromatography ,from the results ,we found all complexes separated according to molecular weight and interaction between them in column through separation in chromatography column according to their polarity .

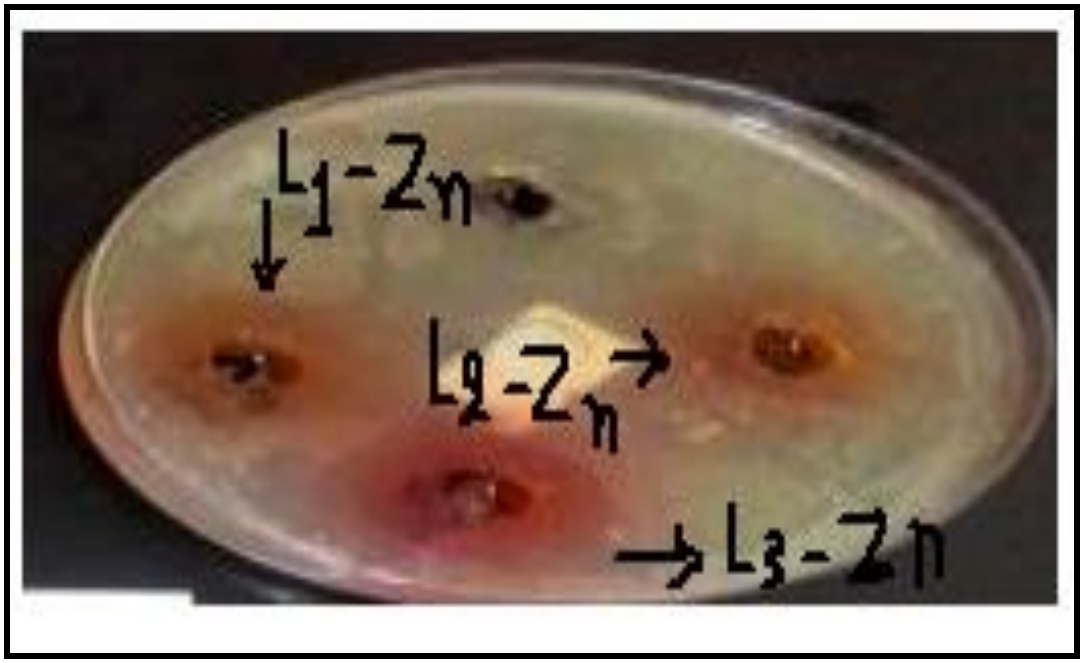
Biological Tests[16, 27] :

The test of the sensitivity of the bacterial isolates were positive for gram, which involved in this work on two classes of bacteria to measure the biological activity according to studies[16, 27] of certain compounds which bacteria positive for the dye gram (bacteria-*Staphylococcus aureu*) and negative gram (bacteria- *E-Coli*), and Table (4) shows the diameter of inhibition zone for vehicles chemical measured in (mm) towards the species bacterial.

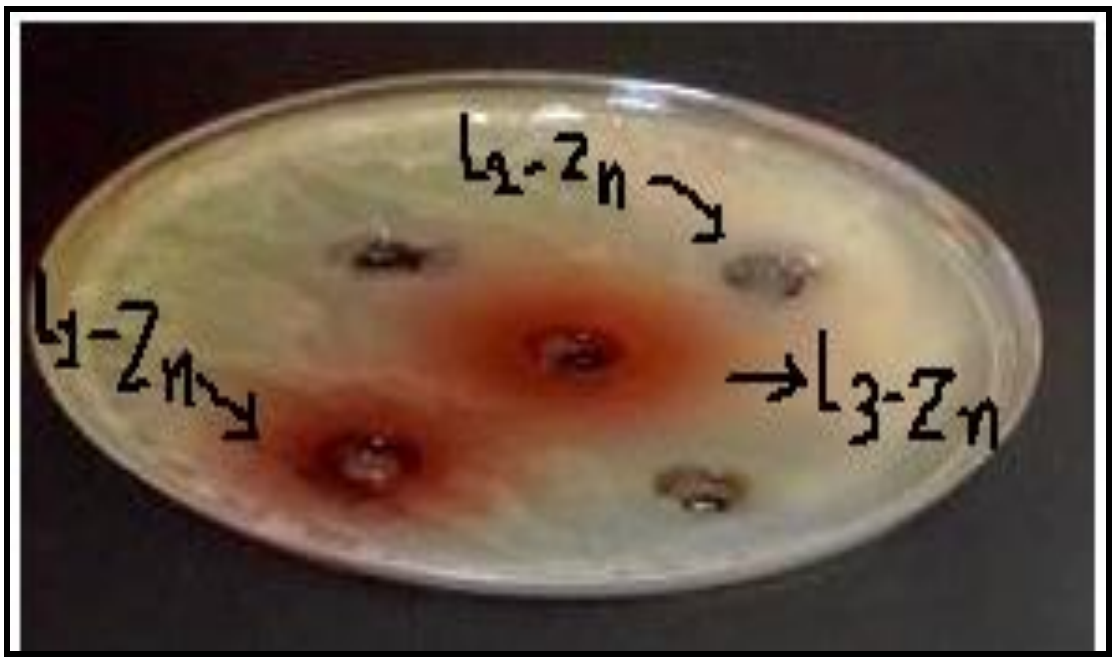
Table 4: Biological Activity (Inhibition Zone in (mm)) of Complexes in Concentration (0.001 M).

Complexes	(G +) *Staphylococcus. Aureus*	(G -) *E- Coli*
Complex [Zn(L_1)]	12	10
Complex [Zn(L_2)]	10	8
Complex [Zn(L_3)]	14	10

The results showed the Biological Activity for complex with (L_3) is more than other complexes with (L_2 , L_1) because the complex with (L_3) involved sulfur as thiazole in structure which gave high effectiveness on the two types of bacteria, and the following pictures appear results:



Pict.(1):Inhibition of Complexes on *Staphylococcus Aureu*



Pict.(2):Inhibition of Complexes on E-Coli

Conclusion : The compounds which involved thiazole ring in their structures have higher biological activity than other compounds from ligands and complexes .

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