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Spectral Studying and Chemical Properties of (Imine and Formazan)-Ligands with Some Complexes With Zinc(Zn^{2+})

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Abstract
Formazan compounds are readily synthesized via the reaction of azo group with anile compound to produce high quantitative yields and high purity. In the last few years, formazan derivatives have been proved to have interesting biological activities., for this reason , series of imine and formazan compounds were synthesized as a ligands , studying optimal conditions for its complexes with zinc ion . Synthesized ligands with two complexes were identified by spectral techniques like ((FT.IR–spectra **,** ^{1}H.NMR-spectra **,** UV.Vis –spectra)) , and physical studies such as ((molar conductance **.,** polarity effect of series from solvents **.,**melting point)). The results indicate that the ligands behave as tridentate donor ligands forming chelates with (1:2) (Zn**:** ligand).
Keywords: formazan , imine, complex , ligand, tridentate , Zn.

1.Introduction

Various studies have been reported the applicability of imine compounds but not on formazan .Formazan compounds have great applicability in pharmaceutics

Due to their specific chemical reactivity. They resemble essential metabolism and they fit biological receptors and block their normal working. These compounds are useful in the field of coordination chemistry for complexation of transition metals and in preparation of new reagents in analytical chemistry [1-4] . Formazan compounds includes two parts in their structure (azo group -N=N - linked with imine group -CH=N-)) in same compound [4-7]. Azomethines are the compounds, which contain (–C=N-)group. These compounds are also known as imines or anils but most commonly, they are known as Schiff bases[8-11] .Azo ligands are very widely distributed in complexes chemistry and in many applications .Metal complexes of anils ligands have been studied extensively in recent years due to the sensitivity of these ligands towards most of metals[12-14] . It is well known from the literature that Schiff base ligands containing hydrazin groups have pharmaceutical activity as antimicrobial , antifungal , anticancer , and many applications as an effective corrosion inhibitor , applications in polymers & and in other fields[13-16] .

2.Experimental

Melting points were recorded on Gallenkamp melting point apparatus and were uncorrected . FT-IR spectra were recorded by using (FT-IR 8300 Shimadzu) in the range (400-4000) cm-1 as KBr discs .UV-Vis spectra for the compounds were measured in the region (200-900) nm for 10^{-3}M solution in DMSO by using

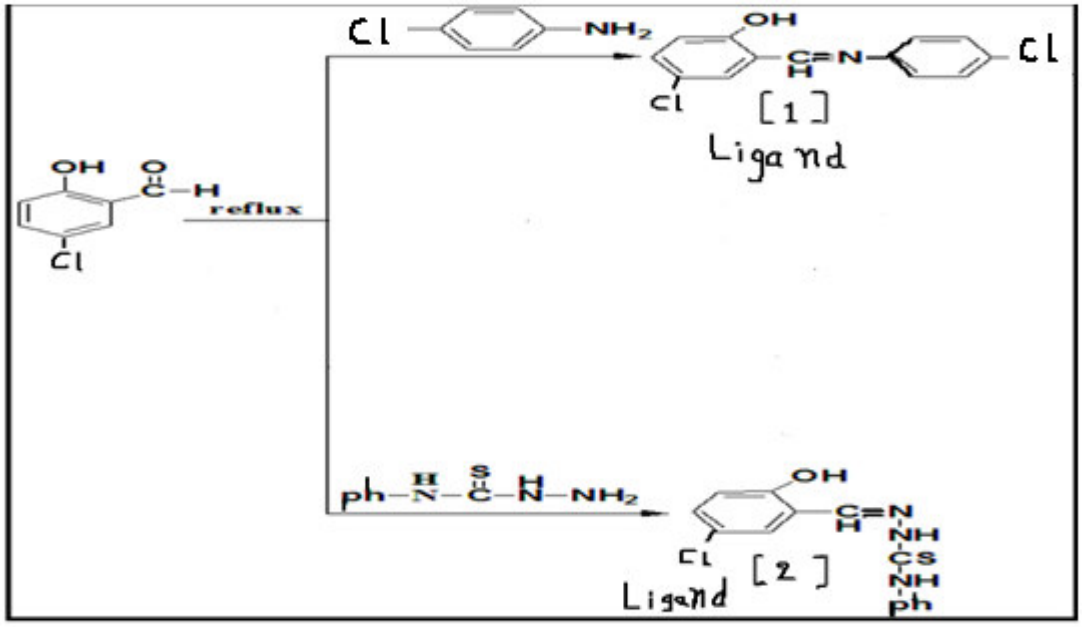
VARIAN 100 conc uv-vis, ^{1}H.NMR–spectra in DMSO–solvent were carried out in Canada , , and physical properties such as : Molar conductance in DMSO–solvent.

3. Preparation of Imine Ligand ((Ligand 1))

(0.01mole) Of 4-chloro- 2-formal phenol was refluxed with 4-chloro aniline (0.01mole) for (2hrs) in presence of drops from glacial acetic acid in absolute ethanol as a solvent according to studies[4,5] , to yiled precipitate of Ligand (1) which filtered and dried then re crystallized to yield imine ligand.

4. Preparation of Imine Ligand ((Ligand 2))

(0.01mole) Of 4-chloro- 2-formal phenol was refluxed with phenyl thiosemicarbazide (0.01mole) for (3hrs) in presence of drops from glacial acetic acid in absolute ethanol as a solvent according to studies[4,5] , to yiled precipitate of Ligand (2) which filtered and dried then re crystallized to yield imine ligand.

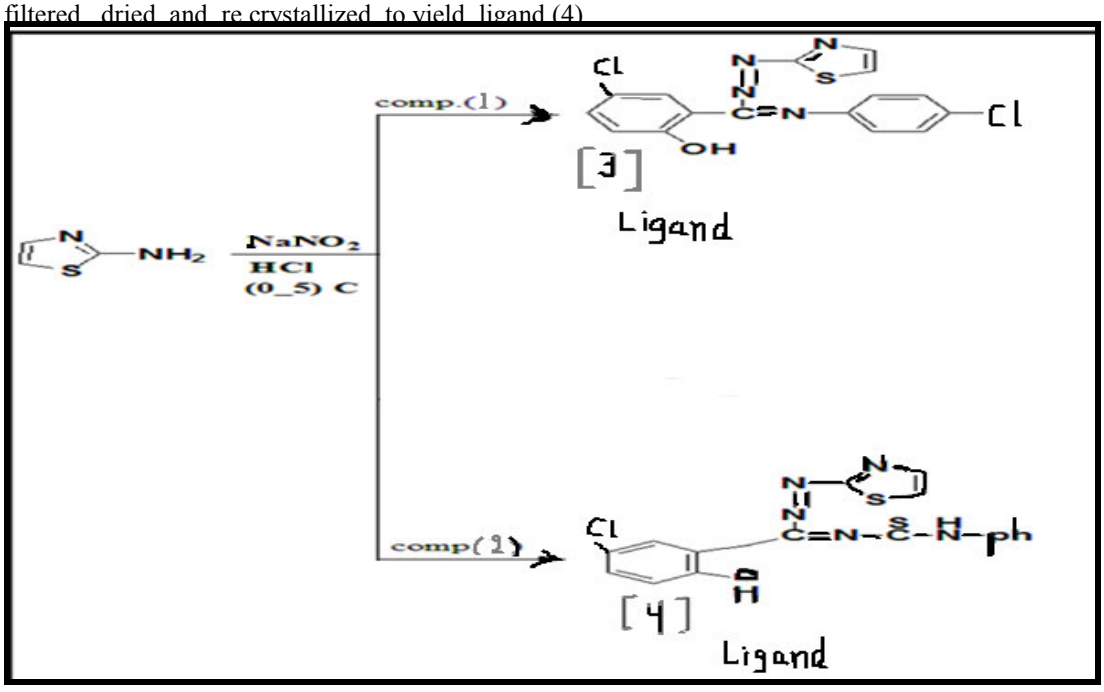


5. Preparation of Formazan Ligand ((Ligand 3))

According to studies[4-6],(0.0lmole)of 2-Amino thiazole dissolved in 4 ml of hydrochloric acid with cold solution of sodium nitrite in ice medium (0- 5)C ,then added compound (1) to the mixture ,after 72 hrs filtered , dried and re crystallized to yield ligand (3) .

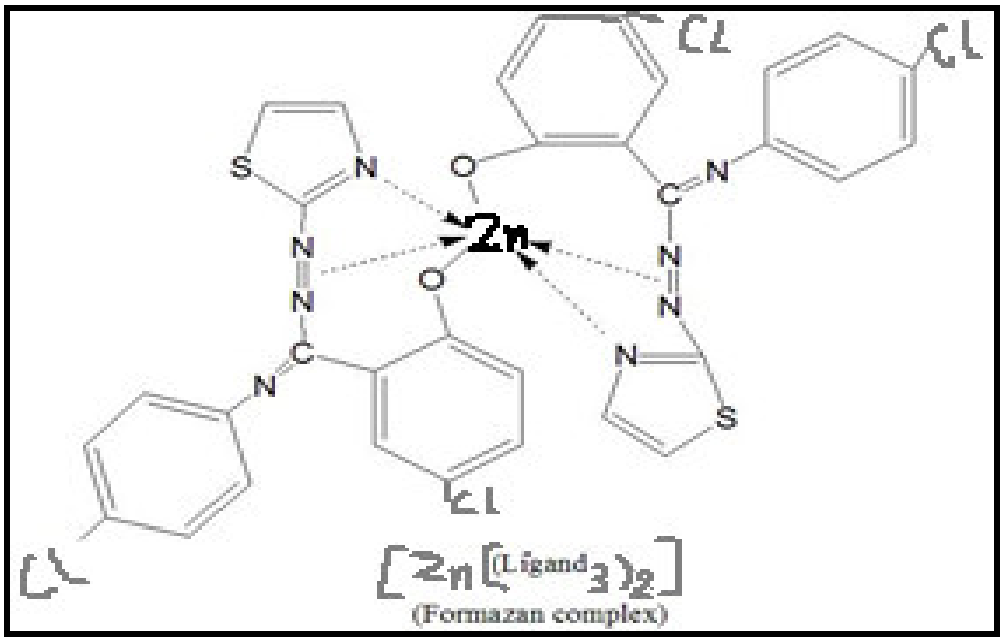
6. Preparation of Formazan Ligand ((Ligand 4))

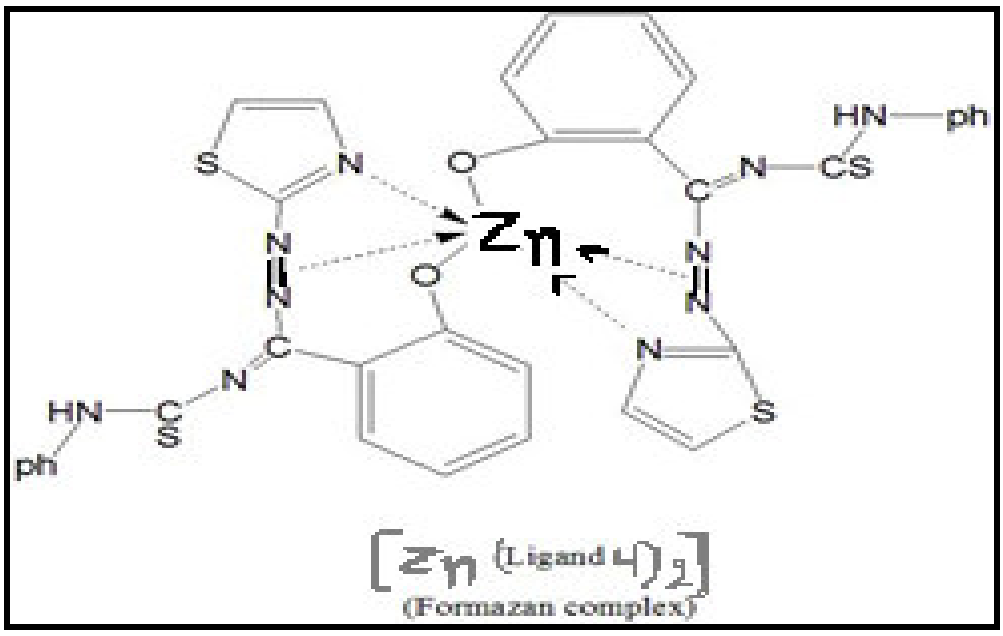
According to studies[3-6],(0.0lmole)of 2-Amino thiazole dissolved in 4 ml of hydrochloric acid with cold solution of sodium nitrite in ice medium (0- 5)C ,then added compound (2) to the mixture ,after 72 hrs filtered , dried and re crystallized to yield ligand (4)



7. Complexation of Two Ligands with (Zn^{2+})

According to procedure[3] ,The complexation of Ligands were prepared through mixed of the hot solution of ligands (two types of formazan ligands 3 and 4) respectively were mixed with of zinc chloride ($ZnCl_2$) according to optimal conditions which were studied in this paper with mole ratio (metal: ligand) (1:2) for two complexes ., after mixing and stirring for (1hrs) ,the precipitates were precipitated ,dried and re crystallized to give two complexes from formazan respectively .





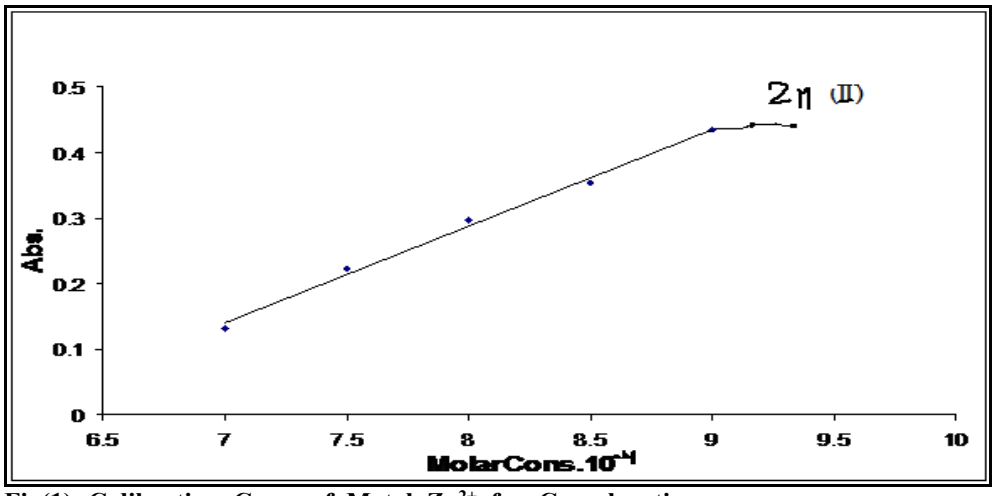
7. Results and Discussion

Formazan compounds are readily synthesized via the reaction of azo group with anile compound to produce high quantitative yields and high purity**.** Fomazan compounds bearing ((--N=C-N=N--)) donor atoms have also been introduced to coordination chemistry. Detailed study on the preparation and structures of such compounds seems important in coordination chemistry.

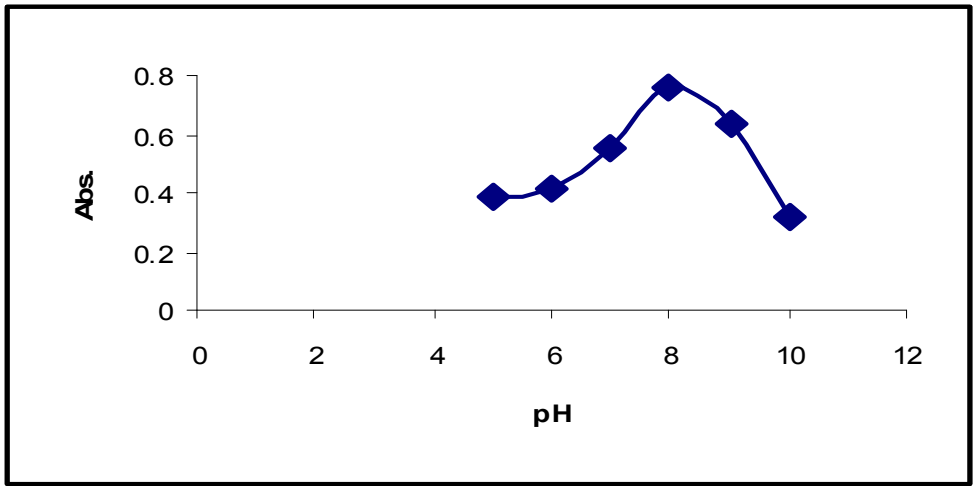
In this work , four ligands were synthesized from (two imine ligands and two formazan ligand) with (Zn^{2+}), Identification by many techniques and studying of optimal conditions of complexation :

8. Studying of Optimal Conditions for Complexation

For complexation process , optimal conditions were studied like (calibration curves for ligands and Zn ion ., the optimal concentration of (Zn^{2+} =0.90 x10^{-4}M), while concentration of ligands [0.10x10^{-3}M of formazan ligand3 , 0.50x10^{-3}M of formazan ligand4] ., studying of optimal pH of complexes were [pH=8 for two complexes] .,while the stochiometry of complexes in mole ratio procedure[3] gave (M:L) ratio (1:2) for two complexes., and other chemical and physical measurements of complexes in figures (1 , 2).



Fig(1): Calibration Curve of Metal Zn^{2+} for Complexation



Fig(2):Determination of Optimal PH of Complexes

9. Stochiometry and Optimal wave Length for Complexes:

Some physical properties were measured like melting point and spectral studying UV-Visible . All results ((mole ratio ,calibration curve , stoichiometry ,chemical spectra) indicate that the Zn- complexes with all ligands were stoichiometry (metal **:** ligand) (1:2) ., Table (1)., Figures (3 , 4 ,5 ,6)

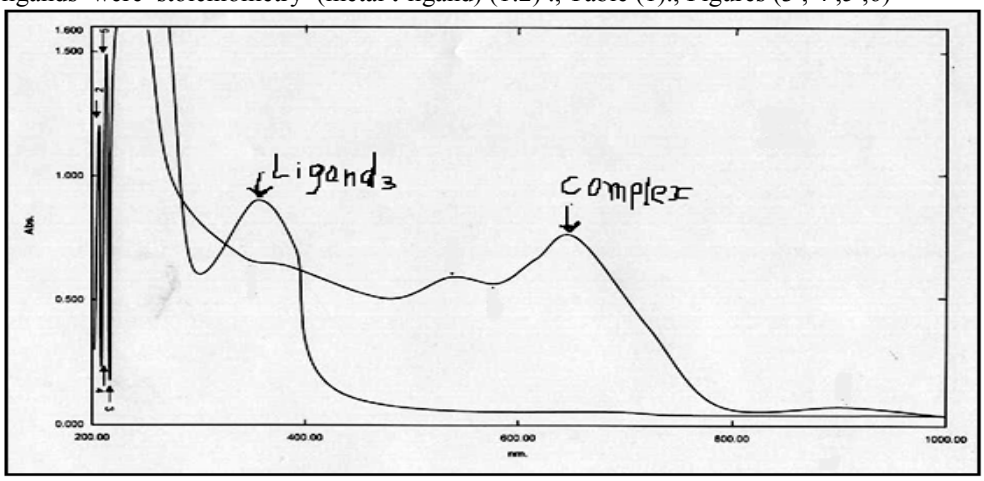


Fig (3) : UV-Visible of Ligand 3 and its complex

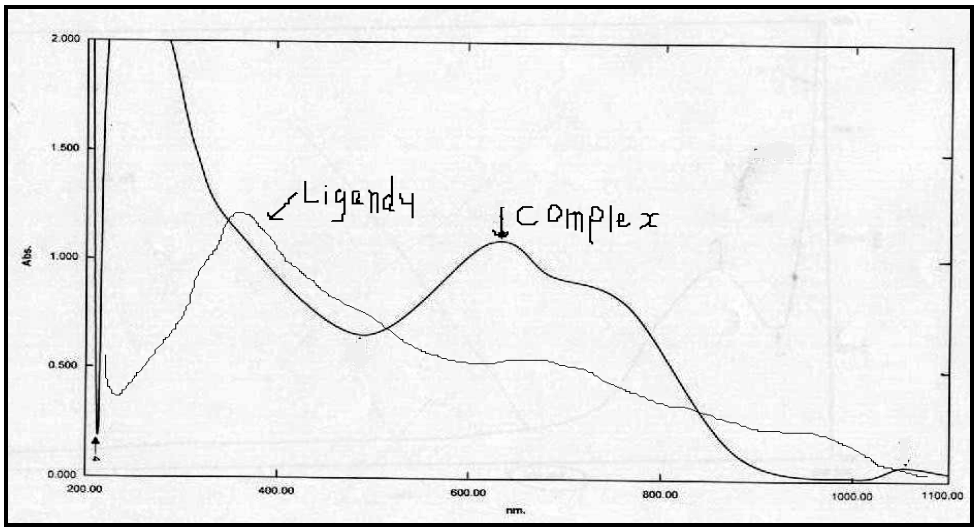


Fig (4) : UV-Visible of Ligand 4 and its complex

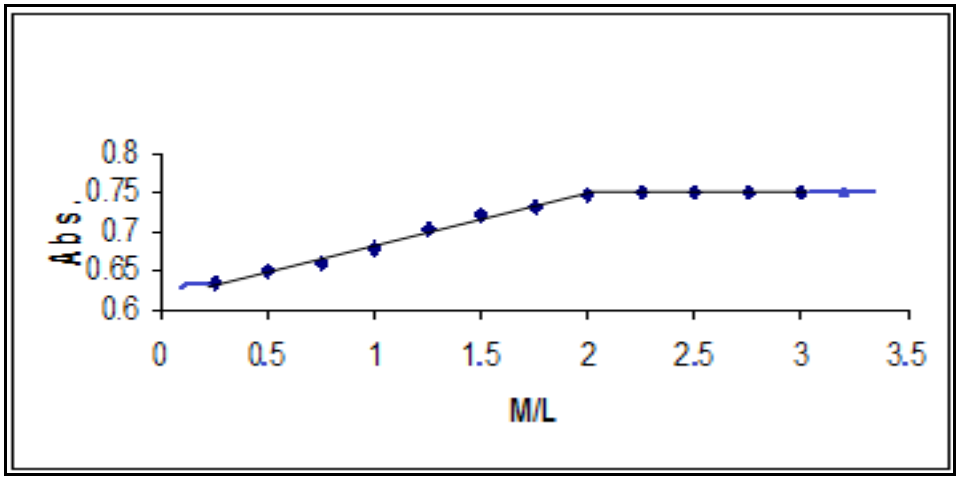


Fig (5) : Mole ratio of Complex [Zn(Ligand 3)$_2$]

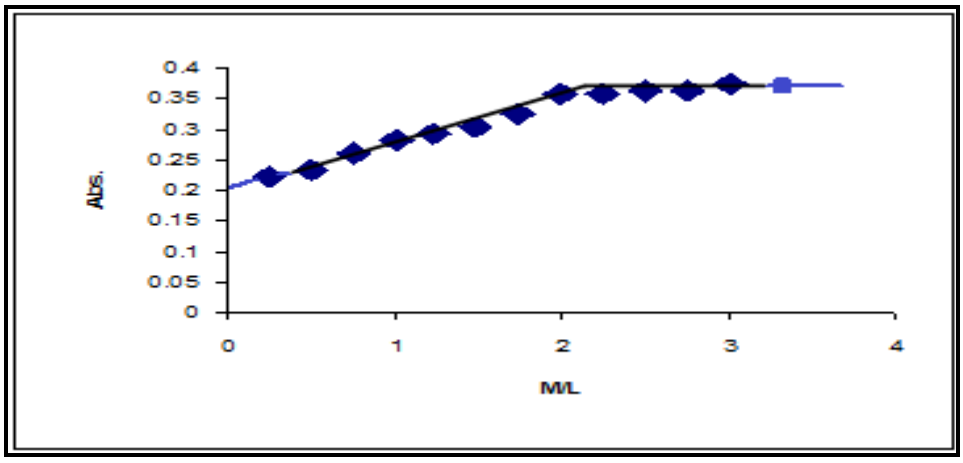


Fig (6) : Mole ratio of Complex [Zn(Ligand 4)$_2$]

10. The Conductivity of Complexes

From results of conductivity measurements for ligands and their complexes which were (1.26 -1.42) ohm^{-1}.mole^{-1}.cm^2 with concentration (1x10^{-3}M) solution which indicates that the (Zn - Complexes) are non-electrolytic in nature , Table(1).

Table (1) : Spectral and chemical data for Ligands with Complexes.

Ligands and Complexes	M.P (C°)	λ_{max}	$\Omega_{ohm^{-1}.Cm^2.mole^{-1}}$ Conductance
Ligand1 (Imine Ligand)	176	365	-------
Ligand2 (Imine Ligand)	168	380	-------
Ligand3 (Formazan Ligand)	184	384	-------
Ligand4 (Formazan Ligand)	178	370	-------
[Zn(L3)$_2$] Complex	>300	630	1.42
[Zn(L4)$_2$] Complex	>300	600	1.26

FT.IR- spectra :shown absorption bands in all ligands at (3480-3315)cm^{-1} due to hydroxyl[3] group (OH) of phenol ring in free ligands which disappeared in spectra of their complexes as a result of coordination with ion and other frequency appeared represented in bands [(470-488) cm^{-1} and (525-575)cm^{-1}] due to [(M-N) and (M-O)] respectively in complexes as a result of coordination with zinc ion (II) .,other bands at (1453-1486) cm^{-1} due to azo group[3-6] (-N=N-) in two ligands(3 and 4) which shifted towards lower frequency at (1420-1432) cm^{-1} respectively in their complexes .,other data of bands in table (2) and figures (7-10).

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

Ligands & Complexes	(-N=N-) Azo	(OH)	(M-N)	(M-O)	Other Data
Ligand1 (Imine Ligand)	-----	3315	-----	-----	(CH=N) :1618
Ligand2 (Imine Ligand)	-----	3365	-----	-----	(CH=N) :1620 ,NH:3235
Ligand3 (Formazan Ligand)	1453	3422	-----	-----	**,**(C=N):1628
Ligand4 (Formazan Ligand)	1486	3480	-----	----	(NH)**:**3212**,**(C=N):1626
[Zn(L3)$_2$] Complex	1420	----	470	525	(C=N):1625
[Zn(L4)$_2$] Complex	1432	----	488	575	(NH) :3208**,**(C=N):1624

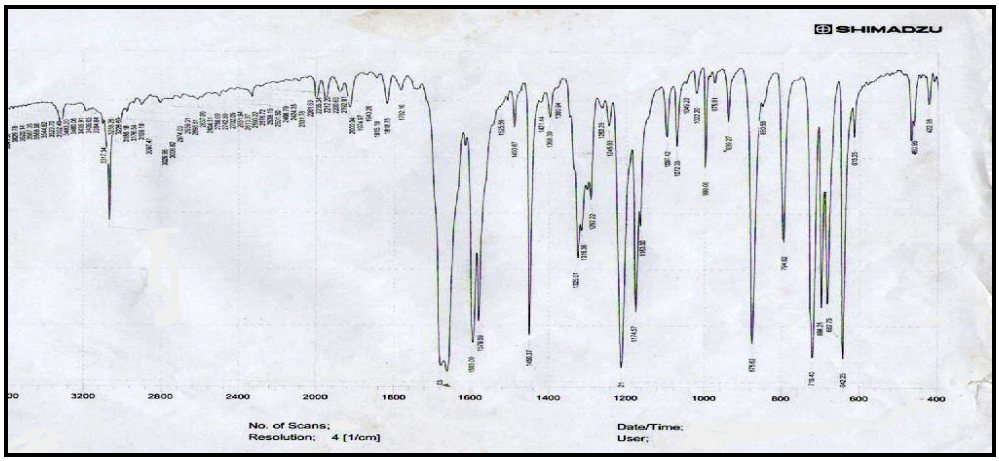


Fig (7): FT.IR of Ligand3 – Formazan

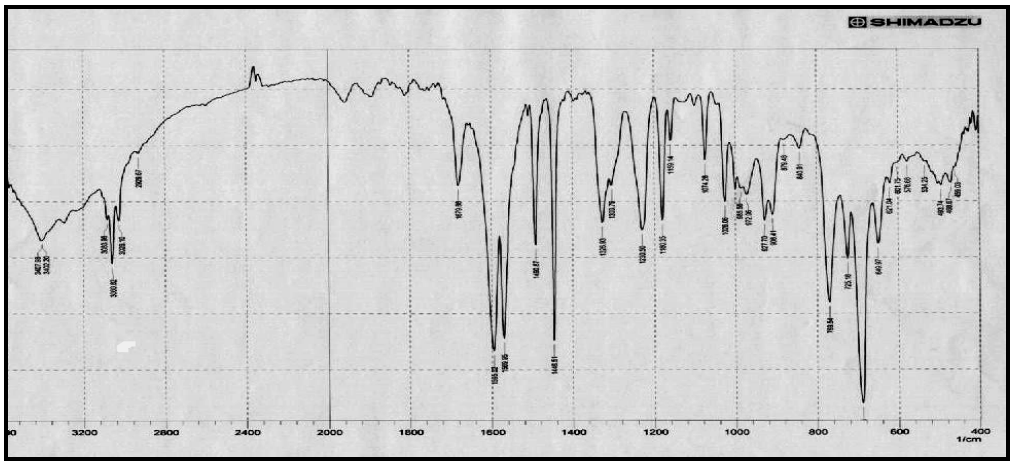


Fig (8): FT.IR of Ligand4 - Formazan

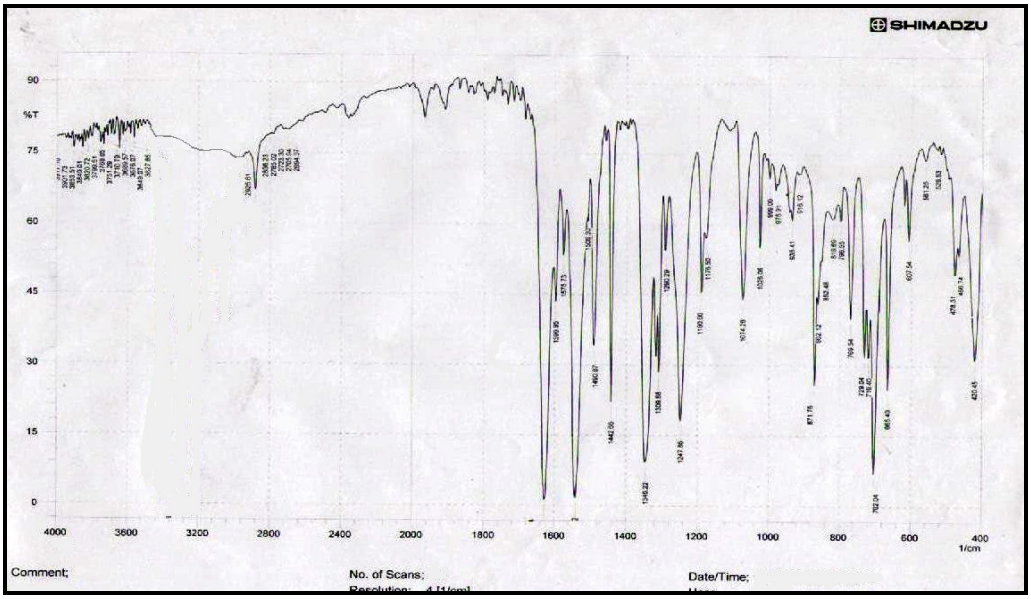


Fig (9): FT.IR of Complex of Ligand3- Zn

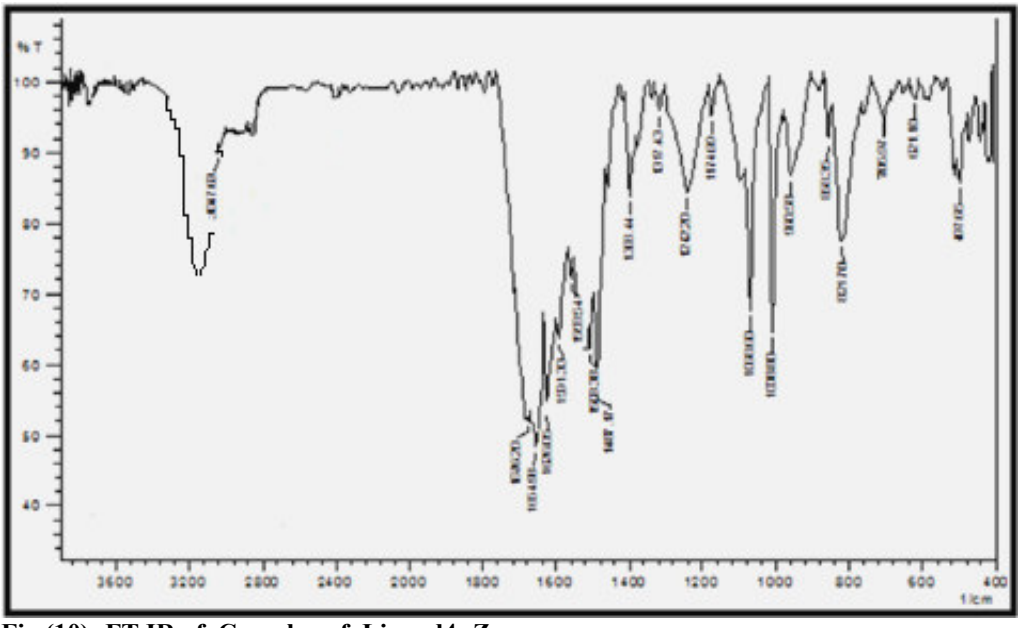


Fig (10): FT.IR of Complex of Ligand4- Zn

H.NMR- spectra :spectra of ligands showed peaks at δ (11.40-11.91) for hydroxyl[5] group (OH) in free ligands ., which disappeared in their complexes as a result of coordination[3] with (Zn^{2+})., and other signals are shown in table (3) and some of figures **(**10 **,** 11 ,12**)** .

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

Ligands & Complexes	(OH) phenol	Other groups ((only functional groups))
Ligand1 (Imine Ligand)	11.05	8.28(CH=N) :proton of imine group., (6.90-7.76)aromatic protons.
Ligand2 (Imine Ligand)	11.16	8.51(CH=N) :proton of imine group. (6.82-7.87)aromatic protons.
Ligand3 (Formazan Ligand)	11.00	(6.89-7.98)aromatic protons.
Ligand4 (Formazan Ligand)	11.22	5.82 (NH) **,** (6.94-7.69)aromatic protons.
[Zn(L3)$_2$] Complex	-----	(7.04-7.79)aromatic protons.
[Zn(L4)$_2$] Complex	-----	5.79 (NH) , (6.95-7.97)aromatic protons.

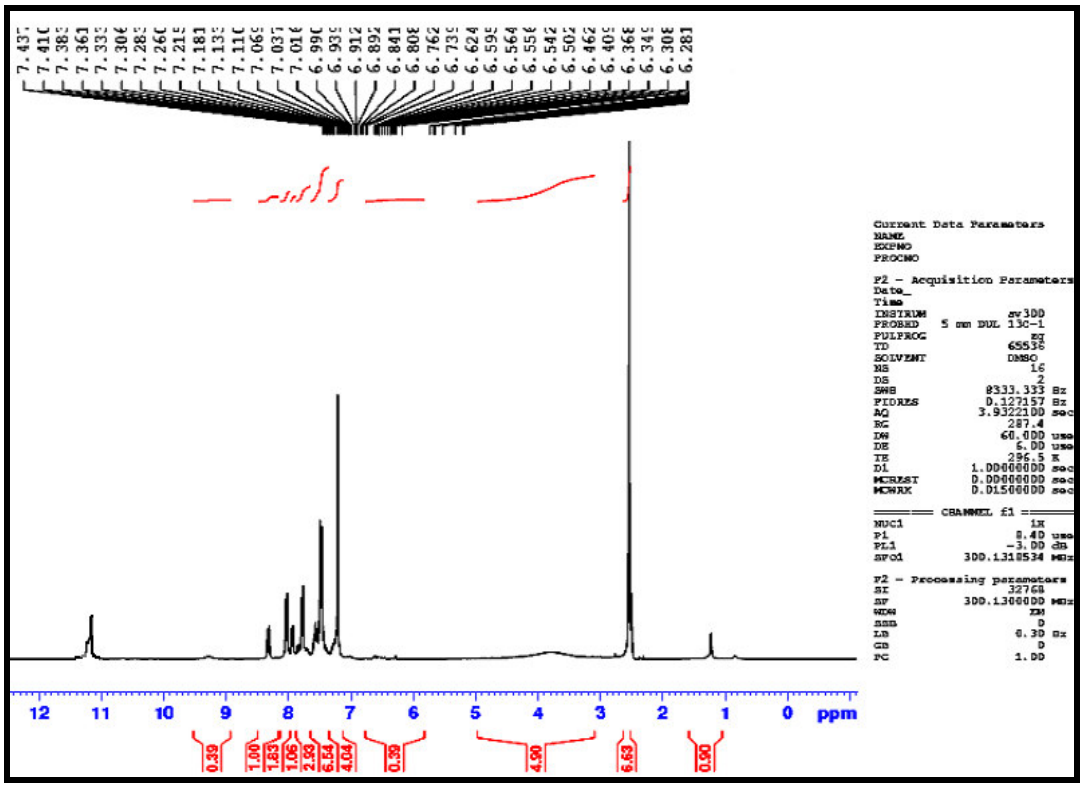


Fig (11): H.NMR of Ligand3 - Formazan

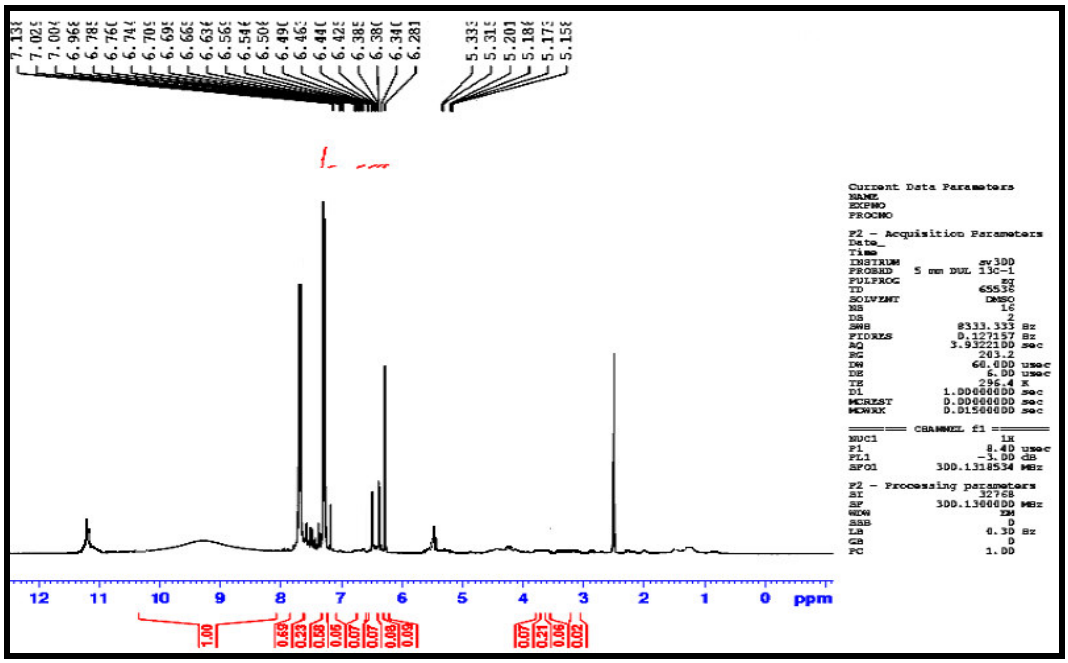


Fig (12): H.NMR of Ligand4 - Formazn

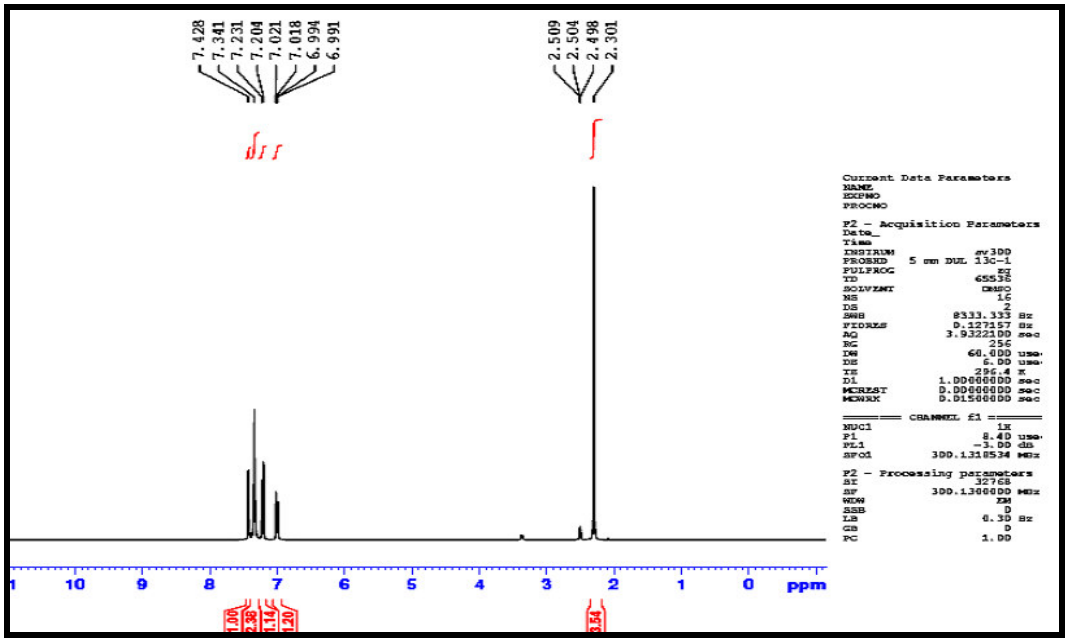


Fig (13): H.NMR of Complex [Zn (Ligand3)$_2$]

11.Complexation of Ligands with Zn :

All spectral and Chemical studies like (stochiometry method , mole ratio and other studies) indicate that the ligands (Ligand3 and Ligand4) are tri dentate ,the coordination through nitrogen of azo group (-N=N-) and oxygen of hydroxyl group[3] with nitrogen atom of thiazole ring to give octahedral geometry (Six-coordination[3] complexes) in formula: (ML_2) .

12.Effect of Series solvents in Ligands:

From results of solubility of the four ligands , we found that the ligands was solving in some solvents but in soluble in other due to nature of solvents

(according to polarity of groups in ligands), the results are listed in table (4).

Table (4) : Effect of Series solvents in Ligands.

Ligands	Solvents					
	Ethanol	CCl_4	$CHCl_3$	Benzene	1,4-Dioxan	Hexane
Ligand1	+	-	-	-	-	+
Ligand2	+	-	-	-	-	+
Ligand3	+	-	-	-	-	-
Ligand4	+	-	-	-	-	-

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