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Chemo - Spectral and Biological Studying of New Ligands.

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ABSTRACT

Two ligands were synthesized in the present work by using condensation reaction between carbonyl compounds with amine compounds to give anil compounds which included azo - azomethine groups in same ligands, the prepared ligands have more than one position for donation , which including six – dentate in same ligand and hexa – donation with their complexes., all steps of reaction included azotation reaction , condensation reaction. The synthesized ligands and their complexes with mercury ion Hg (II) were investigated by (I.R ,UV–Vis, H.NMR) ,molar conductance for complexes and melting points, and other physical studying. The results of two ligands appeared evidences and their complexes with mercury ion Hg (II) through many studies for determination of optimal conditions of complexation with mole ratio (M:L) (1 : 1) and the ligand (L_1) and ligand (L_2) showed octahedral shape through six – atoms.

Keywords: octa, ratio, dentate.

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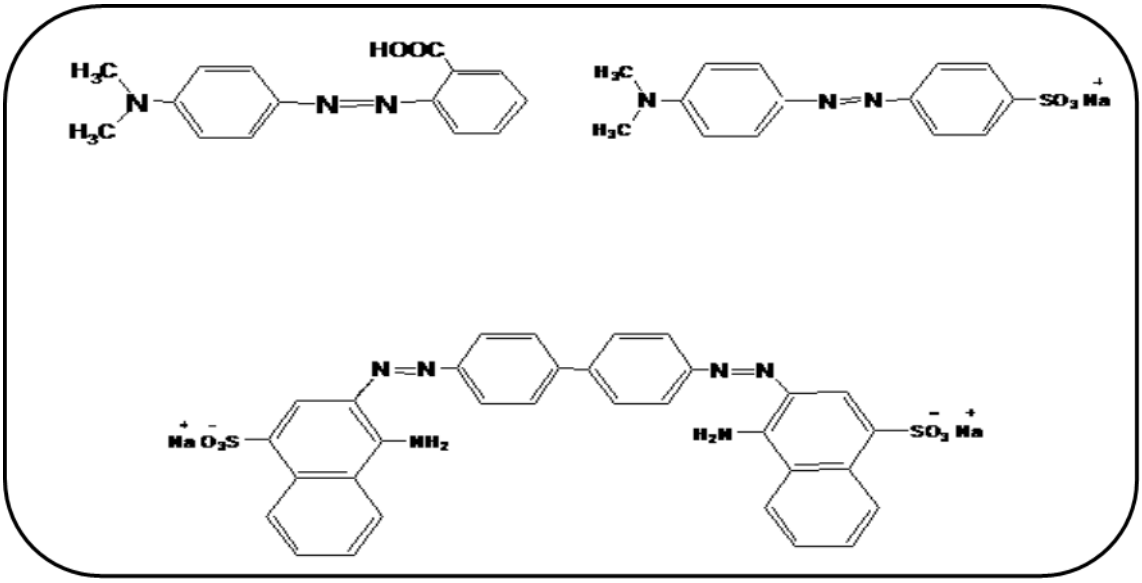
INTRODUCTION

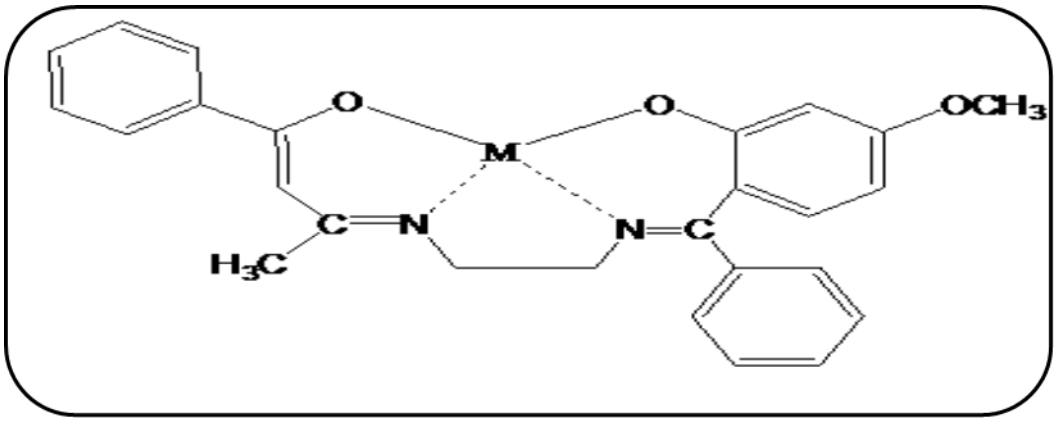
Azo compounds are one of the largest classes of organic compounds. Aliphatic azo compound such as azo bis isobutylonitrile can be as radical initiators in polymerization reactions of alkenes to formation plastics[1-4]. The best example of azo dyes :



Azo compounds are important in the preparation of medical and pharmaceutical drugs , detergents and industrial field such as dyes which used as commercial colorants in industrial factories[5-7] .Azo dyes have many advantages other commercial dyes including their wide color range, good color fastness and they can be prepared cheaply because the starting materials are readily available and inexpensive compounds[8-11].

Azomethine compounds were prepared by refluxing between primary amines compounds with carbonyl groups in compounds (aldehyde or ketones) in absolute ethanol with presence of acid like glacial acetic acid or hydrochloric acid[12-16].

Azomethine compounds have been coordinated as chelating ligands in coordination chemistry with many ions as complexes are great interest for several years[17-22].



Azomethine are important intermediates for the preparation of several bioactive molecules and drugs ,they are reported to show a variety of interesting microbial activity such as antibacterial, antifungal[16, 23].

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EXPERIMENTAL

All analysis and instruments such as:

Melting points were determined in open capillary tube and were uncorrected.,The I.R- spectra were recorder in KBr–disc ,Shimadzu (8300) .,UV –Vis –spectra photometer ., Molar conductance(DMSO–solvent) .,(H.NMR)– Spectra in Canada., optimal conditions.

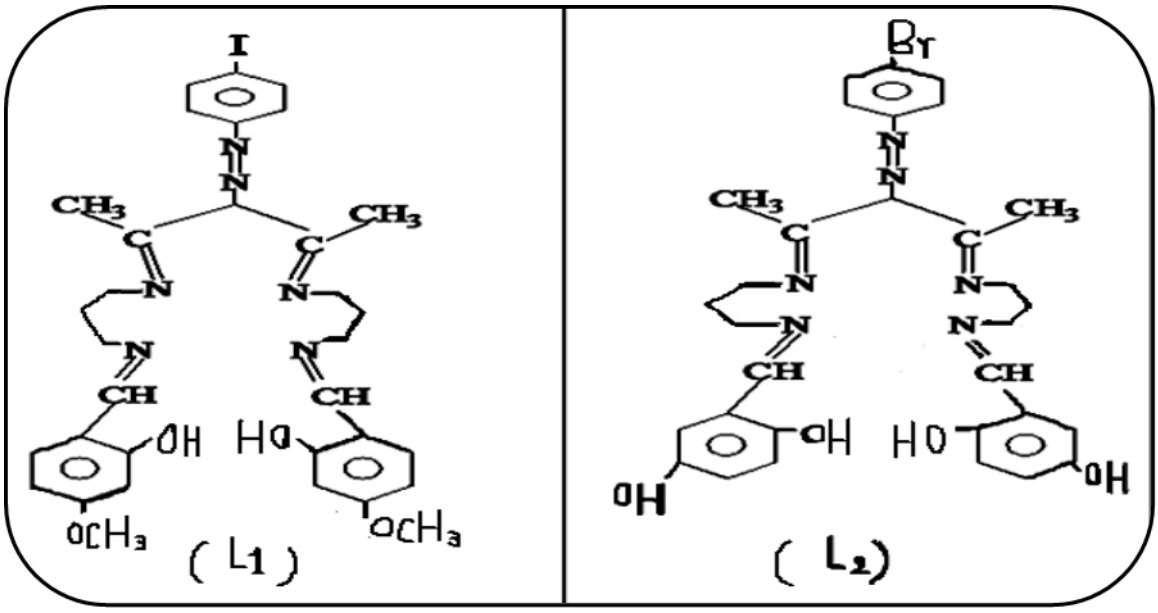
Methodology Part :

Preparation of ligand (L_1) :

The first ligand prepared by dissolving (0.01mole) of p-iodo aniline in (4 ml) of concentrated hydrochloric acid with (0.6gm) of sodium nitrite solution in (0-5) C then addition of acetyl acetone (0.01mole), after (24 hrs) , the precipitate was filtered , washed and dried , which (0.01mole) refluxed with (0.02mole) of (propylene di amine) ., according procedures[15,16] ,the precipitate were filtered and dried , which (0.01mole) reacted with (0.02mole) of (1-hydroxy- 5-methoxy-benzaldehyde) to produce (84 %) of ligand (L_1).

Preparation of ligand (L_2) :

The second ligand prepared by dissolving (0.01mole) of p-bromo aniline in (4 ml) of concentrated hydrochloric acid with (0.6gm) of sodium nitrite solution in (0-5) C then addition of acetyl acetone (0.01mole), after (24 hrs) , the precipitate was filtered , washed and dried , which (0.01mole) refluxed with (0.02mole) of (propylene di amine) ., according procedures[16, 22],the precipitate were filtered and dried , which (0.01mole) reacted with (0.02mole) of (1, 4-di hydroxy-benzaldehyde) to produce (78 %) of ligand (L_2).



Preparation of Two Complexes with Ion (Hg^{2+}) :

According to previously procedure[23] ,the hot ethanolic solution of ligands [(L_1) or (L_2)] was added to solution of ion salt of chloride ($HgCl_2$) in mole ratio (metal**:** ligand) (1**:**1) after stirring (1 hrs) respectively from each complexes ,precipitates formed , dried and re crystallized to produce (74% ,78 %) respectively from complexes of two ligands in our study .

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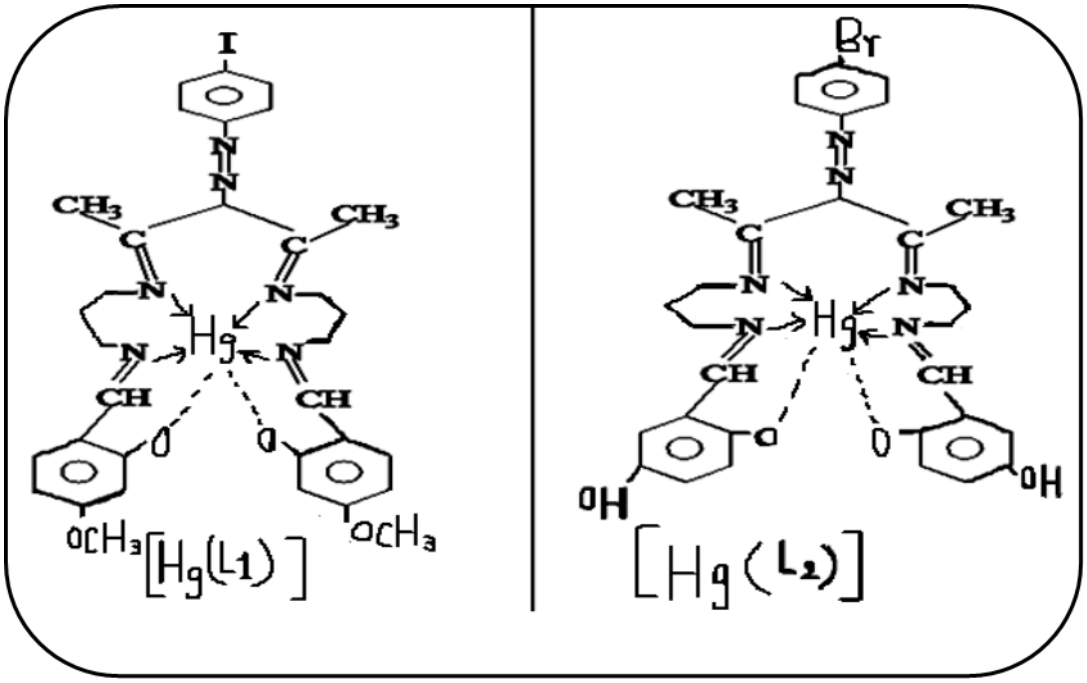

RESULTS AND DISCUSSION

Hexa donation ligands represented in this work by azo – azomethine ligands are important in coordination field. The azomethine group exhibits pi-acceptor properties in ligands .The prepared ligands and their complexes were identified and by many techniques and methods :

Selection of Optimal Conditions of Complexes :

The selection of optimal conditions of complexes with ion Hg(II) were tested in our paper which act: calibration curves of the best concentration of Hg^{2+}= (0.90 $X10^{-4}$m) ,but the best concentration of ligands **[** 0.60 $X10^{-3}$M of ligand (L_1) **.,** 0.65 $X10^{-3}$ M of ligand (L_2)**]** ., while optimal (PH=8.5) for the two complexes of ligand (L_1) and ligand (L_2) in basic medium, and the identification by UV-Visible and other studies with conditions of complexes in Table (1) and figures (1-5) .

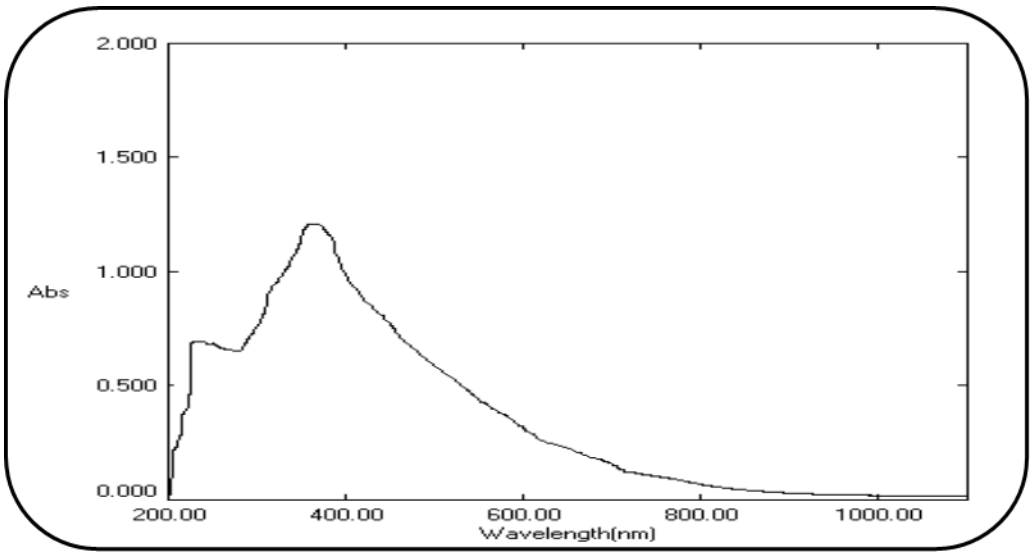

Fig (1): UV-Vis Spectrum of Ligand (L_1)

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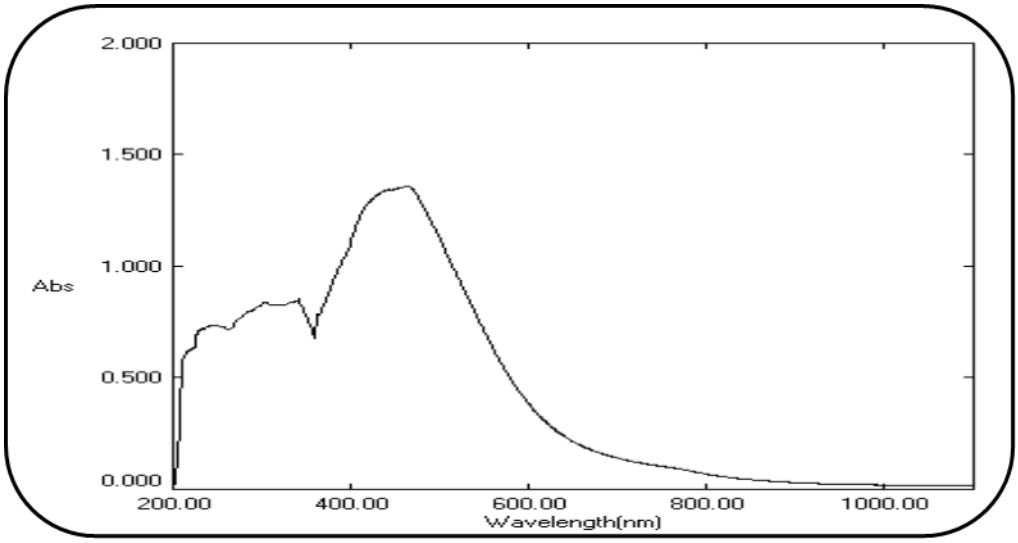

Fig (2): UV-Vis Spectrum of complex [Hg (L_1)]

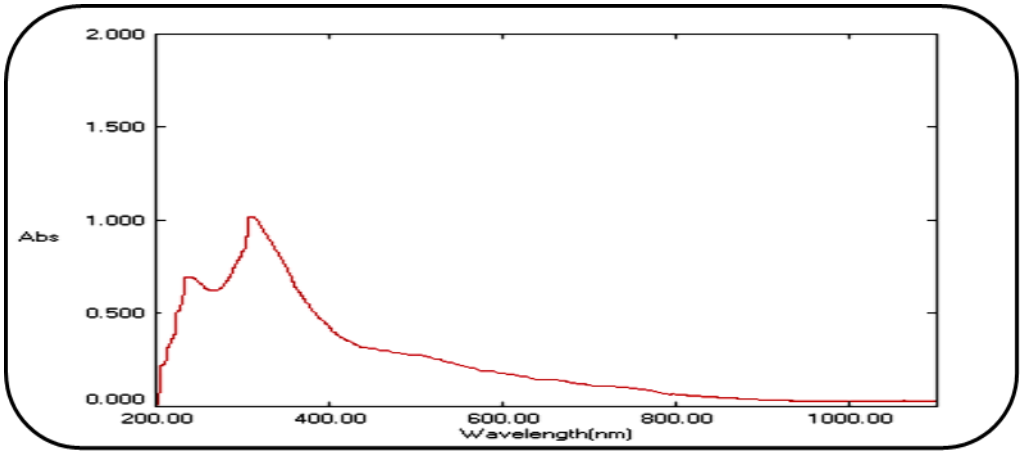

Fig (3): UV-Vis Spectrum of Ligand (L_2)

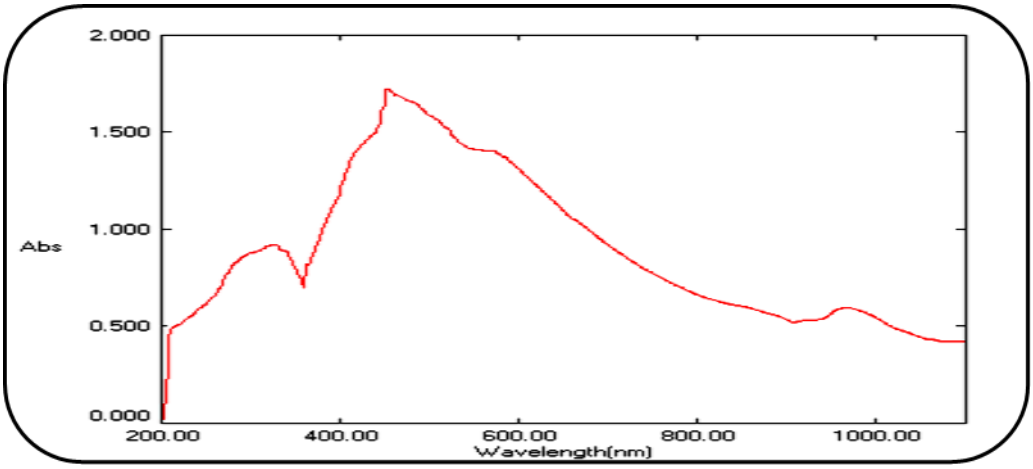

Fig (4): UV-Vis Spectrum of complex [Hg (L_2)]

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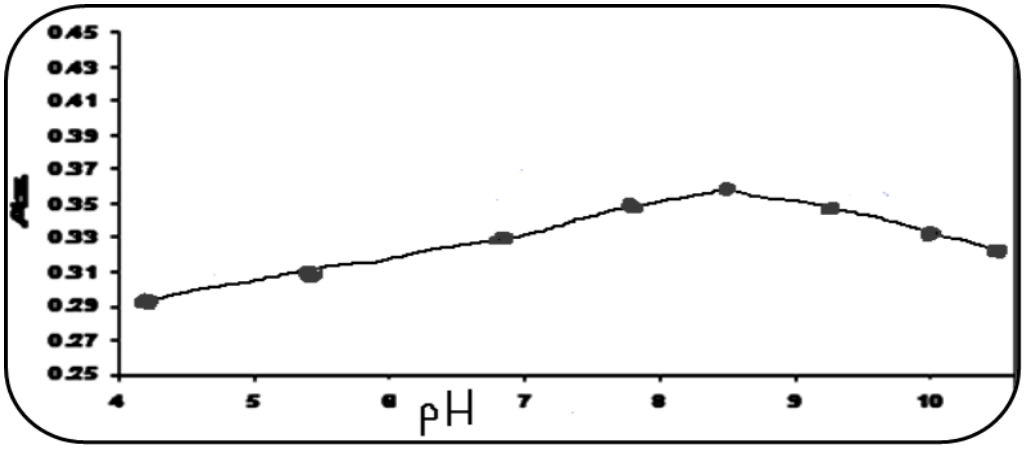

Fig(5): Optimal pH of Two complexes Hg

Mole Ratio of Complexes:

Formation of complexes by job method and mole ratio method through series solutions were prepared having a constant concentration ($1X10^{-3}M$) of Hg salt ($HgCl_2$) and ligand ., the (M:L) ratio was determined from relationship between the absorption and mole ratio (M :L) found to be (1:1) for all complexes. All results ((mole ratio ,calibration curve , stoichiometry ,chemical spectra) indicate that the Hg-complexes with the two ligands were stoichiometry (metal : ligand) (1:1) by two methods (mole ratio and Job Method):

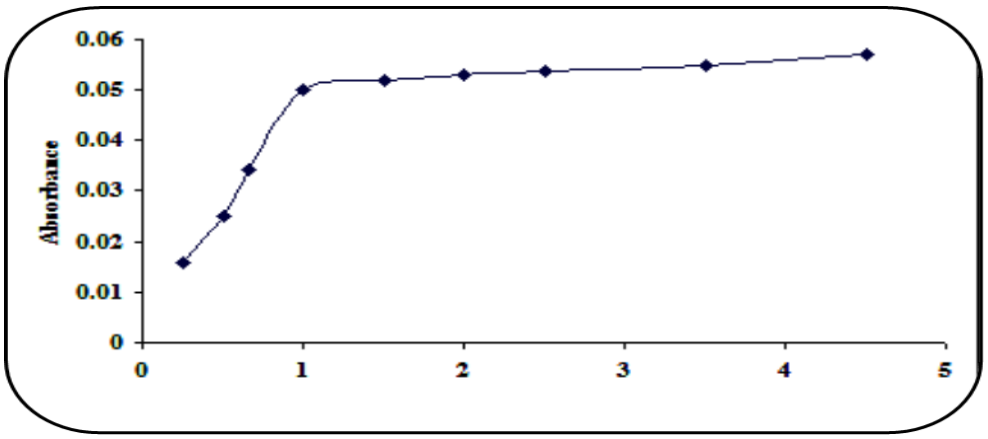

Fig (6) : Mole ratio method of Complexes of Hg

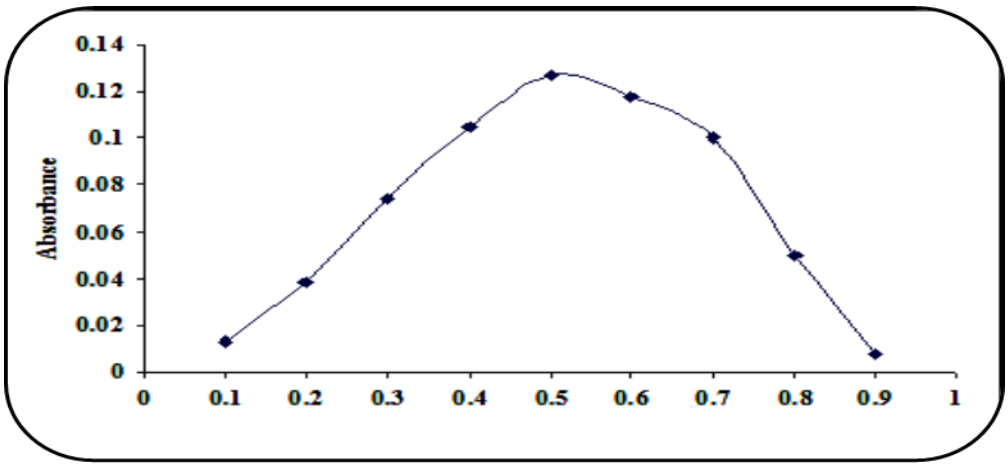

Fig (7) : Job method of two Complexes of Hg

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The conductivity

Table (1) showed all results of some physical properties were measured such as melting point ,conductivity measurements which were (1.06 , 1.23) $ohm^{-1}.mole^{-1}.cm^2$ of ($1x10^{-3}M$) solution in (DMSO) which indicates that the (Hg - Complexes) are non-electrolytic in nature ., and other property such as melting points , UV- Visible are listed in table (1):

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

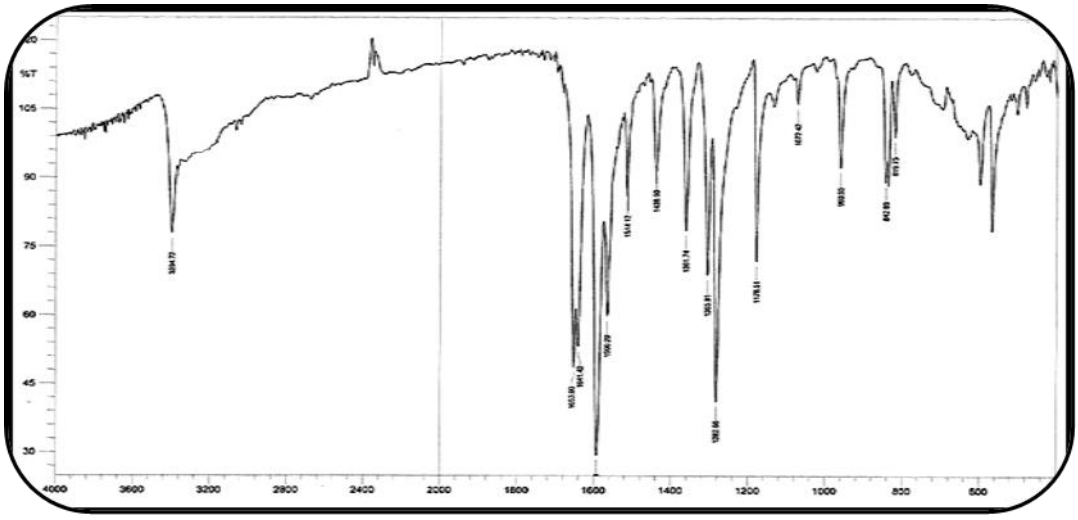
Ligands & Complexes	M.P (C)^0	λ_{max}	Conductance $\Omega^{-1}.Cm^2.mole^-$
Ligand (L_1)	198	394	/
Ligand (L_2)	180	366	/
Complex [Hg(L_1)]	236	440	1.23
Complex [Hg(L_2)]	210	416	1.06

I.R- Investigation :

The spectra showed absorption bands in first and second ligands [(L_1), (L_2)] at (3384 , 3394) cm^{-1} due to hydroxyl groups[15] of phenol in two ligands (L_1 and L_2) respectively in free ligands which disappeared in figures of their complexes with Hg ion as a result of coordination through phenolic oxygen atom (two oxygen atoms) in bond (M–O) are (545 , 591) cm^{-1} . The spectra of (azomethine group CH=N)[15,16] respectively in two ligands exhibit bands at (1625 , 1643)cm^{-1} respectively ,which have been shifted to hiegher positions at (1640 ,1649) cm^{-1} respectively in complexes of (Hg) to coordination with ion (Hg^{2+}) .The coordination bonding from nitrogen of azomethine group (CH=N) and two oxygen atoms of hydroxyl group of phenol in complexes , table (2) and figs (8-11) .

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

Ligands & Complexes	(N=N) Azo group	(-C=N)	(-OH) Phenol	(M-N)	(M-O)
(L_1)	1438 , 1514	1625	3394	/	/
(L_2)	1450 , 1500	1643	3384	/	/
[Hg(L_1)]	1444 , 1510	1640	/	461	545
[Hg(L_2)]	1413 , 1515	1649	/ 3423	480	591



Fig(8): FT.IR of Ligand (L_1)

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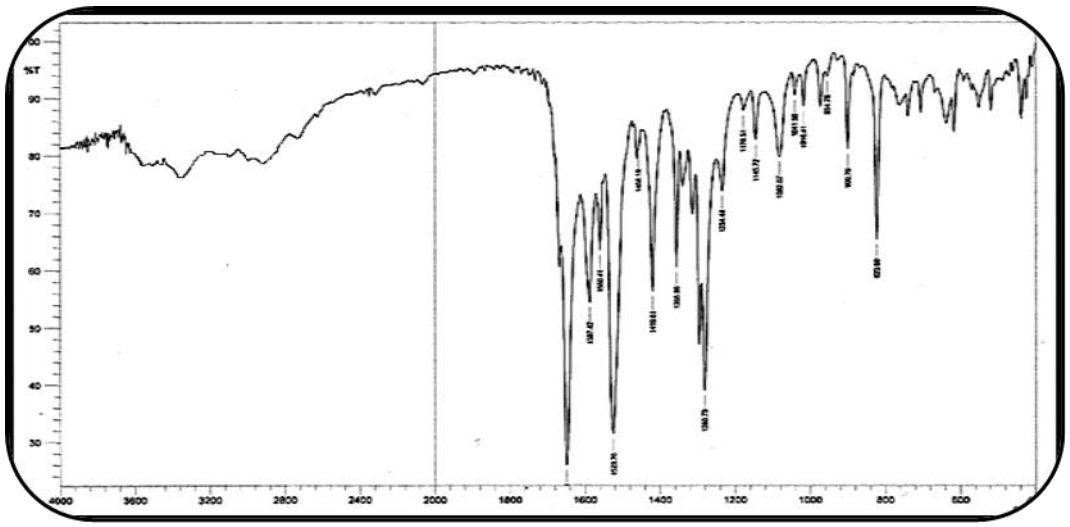
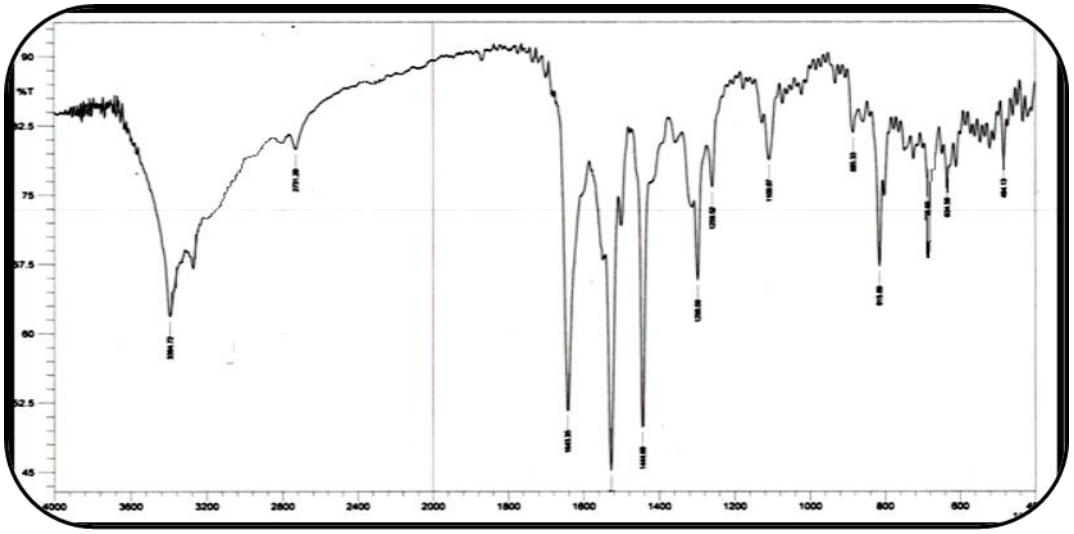
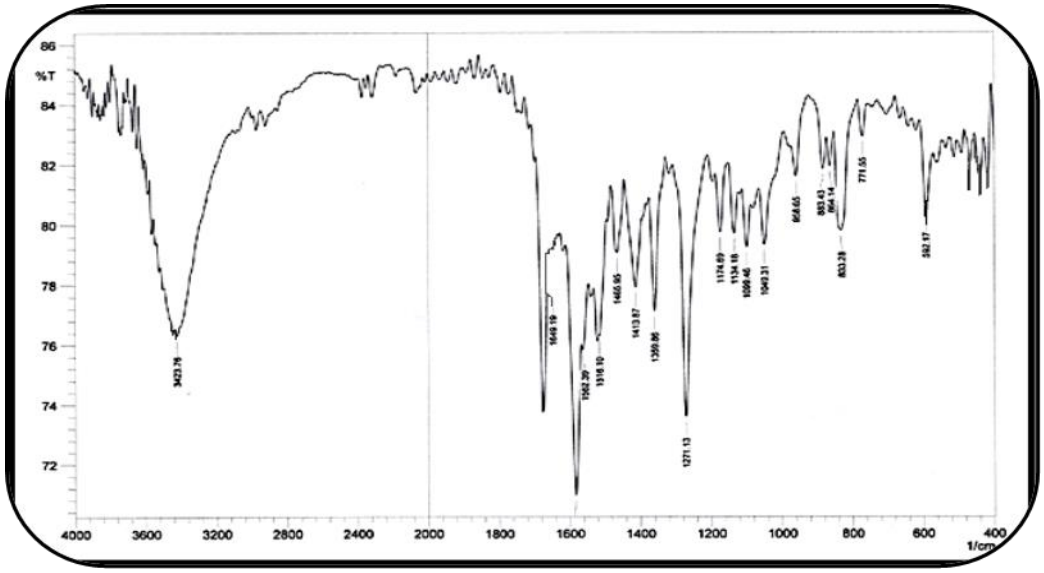


Fig(9): FT.IR of Complex [Hg (L_1)]



Fig(10): FT.IR of Ligand (L_2)



Fig(11): FT.IR of Complex [Hg (L_2)]

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H.NMR- Investigation :

Spectra of two ligands gave peaks at δ (10.40 , 10.95) for hydroxyl group of phenol (OH) in free ligands ., which disappeared in complexes with mercury ion as a result of coordination with (Hg^{2+})., and other peaks are listed in table (3) and figures **(**12 - 15**)** .

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

Ligands & Complexes	(OH) phenol	(CH=N) Imine group	Other groups ((only functional groups))
Ligand (L_1)	10.40	8.5	(-Ph-) proton of phenyl ring :(6.95– 7.99) , (N-CH_2-CH_2-CH_2-N) :(2.67-3.78), (-OCH_3): 3.82 ,(CH_3): 0.98 .
Ligand(L_2)	10.95	8.62	(-Ph-) proton of phenyl ring :(6.95– 7.93) , (N-CH_2-CH_2-CH_2-N) :(2.67-3.58),(CH_3): 1.0 .
Complex [Hg(L_1)]	/	8.11	(-Ph-) proton of phenyl ring :(6.62– 7.69) , (N-CH_2-CH_2-CH_2-N) :(2.65-3.67), (-OCH_3): 3.94 ,(CH_3): 0.93 .
Complex [Hg(L_2)]	10.10	8.10	(-Ph-) proton of phenyl ring :(6.89 7.42) , (N-CH_2-CH_2-CH_2-N) :(3.40-4.10), ,(CH_3): 1.02 .

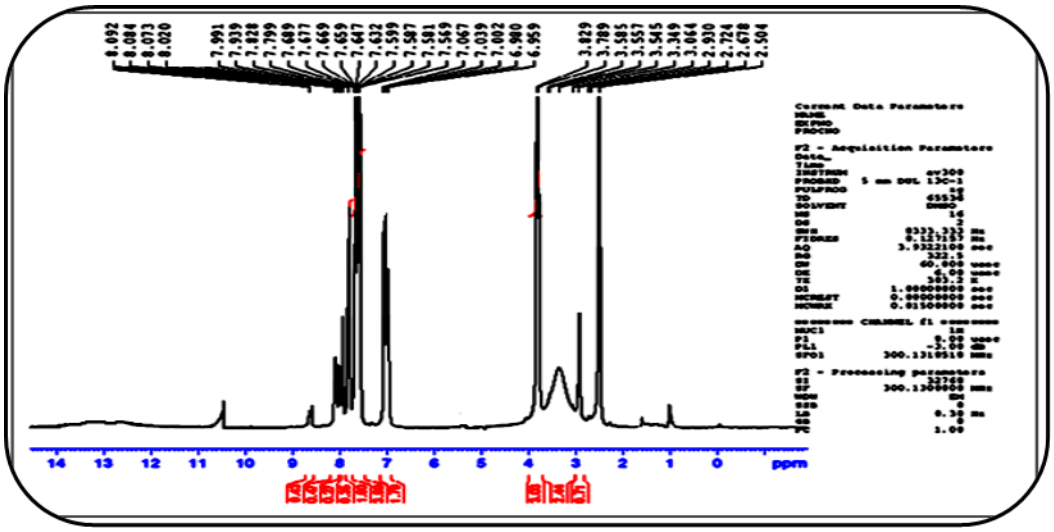

Fig (12): H.NMR of Ligand (L_1)

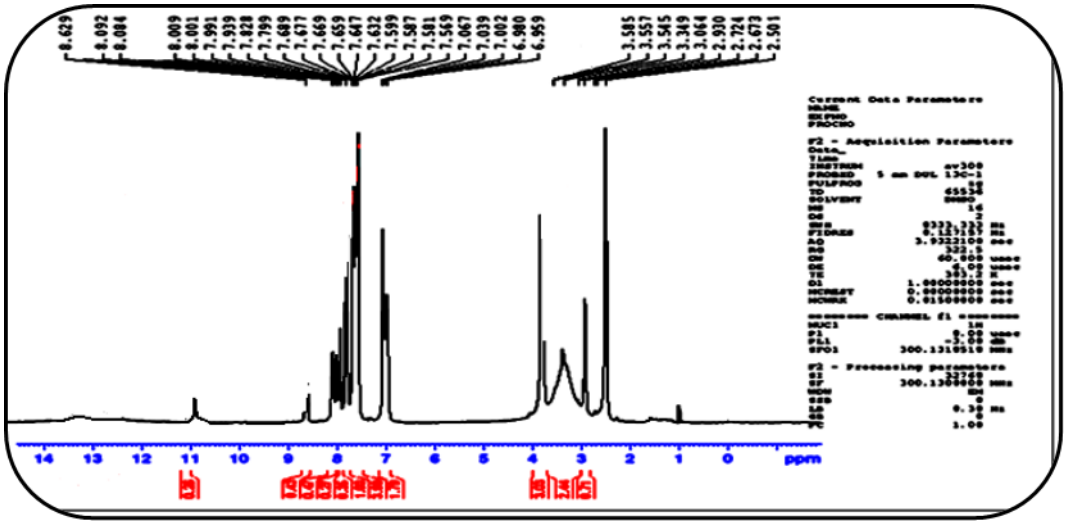

Fig (13): H.NMR of Ligand (L_2)

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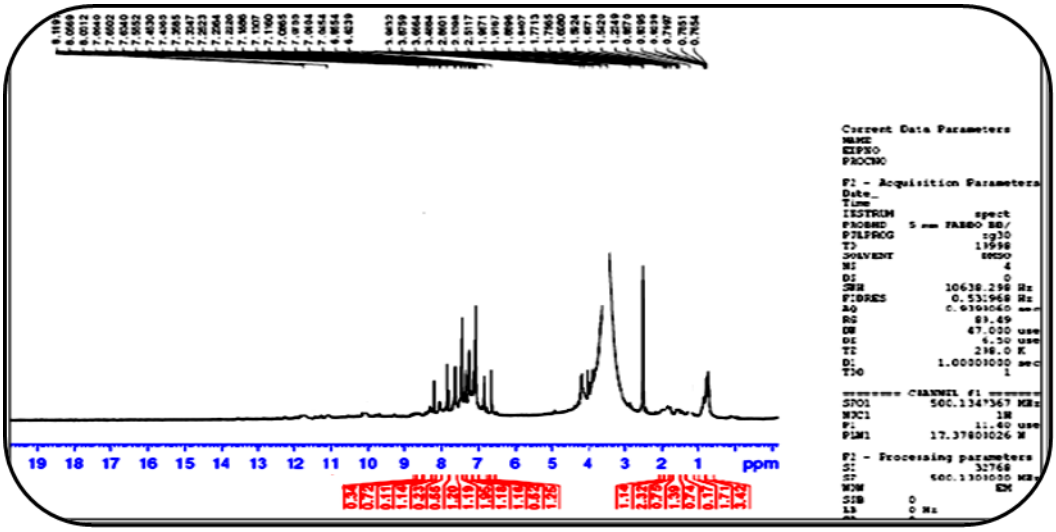

Fig (13): H.NMR of Complex [Hg (L_1)]

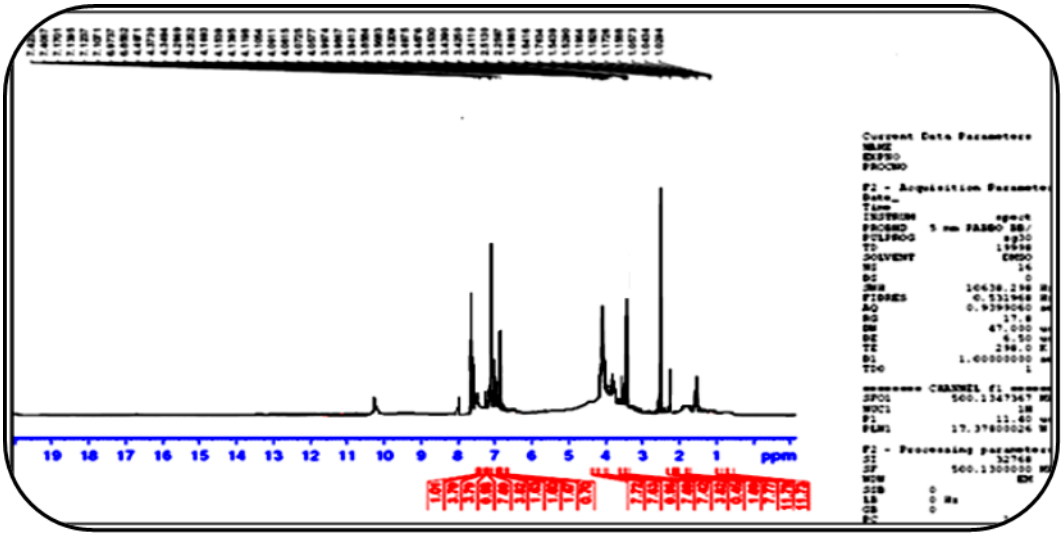

Fig (15): H.NMR of Complex [Hg (L_2)]

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