

Synthesis, Characterization and (Chemical, Spectral, Antimicrobial) Studies of New Inorganic Ligands

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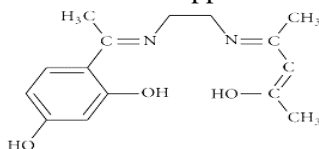
ABSTRACT

New three inorganic ligands were synthesized in this work, which was bearing anil group and azo group in their structure, our paper involved, synthesis of three ligands by diazotation reaction and condensation reaction of anil compounds to yield three new ligands (L₁, L₂, L₃) and investigation with several chemical and spectral studies. All inorganic ligands were identified by using (TLC) and techniques (Uv.Visible, FT.IR, ¹H.NMR, Chromatography Analysis, thermal Analysis), then studying (biological activity studying, chromatography behavior, studying of physical characterization and other analytical studies like solubility in various solvents).

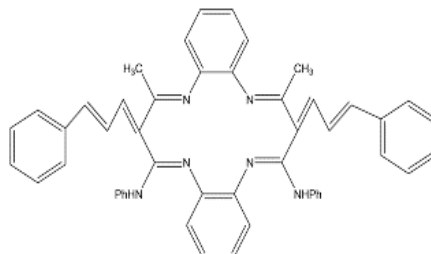
KEY WORDS: Biological Activity, Azo, Imine, Ligands.

1. INTRODUCTION

Most scientific researchers have studied many chemical and biological implementation in a matter of medical characteristics of the anil compounds (Lippard, 1994; Kumar, 2009; Krygowski, 1997; Upadhyay, 2008) and their complexes in coordination chemistry to guarantee the best application.

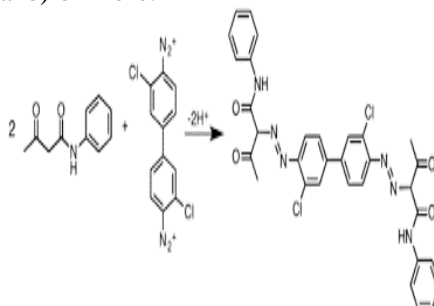


Anil compounds are very interesting compounds due to their important applications in many pharmaceutical, medical and in reagents chemistry, condensation products of primary amines with carbonyl of aldehydes- represent valuable intermediates in organic synthesis and, at the same time, compounds with several applications in many fields (Radecka, 2007; Boghaei, 2008; Prashanthi, 2008; Mohamed, 2005; Parashar, 1989; Maihub, 2007; El-Ajaily, 2010).

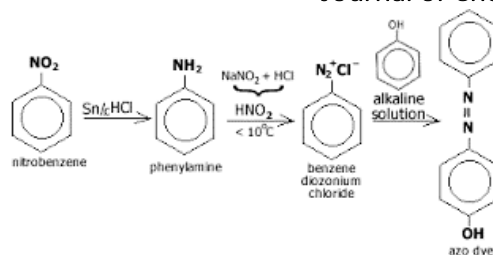


Anil form an important class of the most widely used organic molecules and have a wide variety of applications in many fields including analytical, biological, and inorganic chemistry. Imine compounds have gained importance in medicinal and pharmaceutical fields (El-Ajaily, 2013; Singh, 2009; Jesmin, 2010) due to a broad spectrum of biological activities like anti-inflammatory, analgesic, antimicrobial, anticonvulsant, anticancer, antioxidant.

The azo compound class accounts for 60-70% of all dyes. Most azo dyes contain only one azo group, but some contain two (*dis azo*), three (*tris azo*) or more.



Azo dyes compounds give bright, high intensity colours, much more so than the next most common dye class (anthraquinones). The general composition to form an azo dye need two organic compounds- a coupling component and a diazo component. These compounds can be altered significantly, a wide range of possible dyes are available, especially as the starting compounds are readily available and cheap (Mounika, 2010; Gordon, 1983; Fatemeh, 2016).

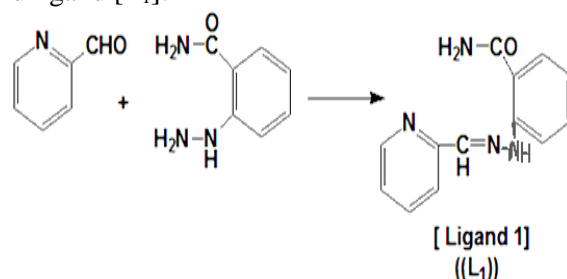


2. MATERIALS AND METHODS

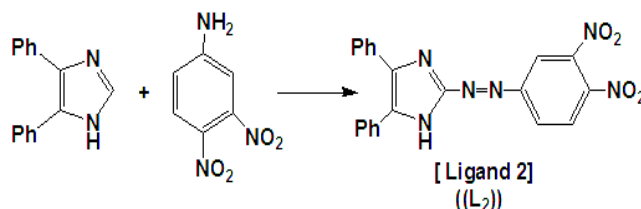
Melting points were recorded on Gallenkamp melting point apparatus and were uncorrected. FT-IR spectra were recorded by using (FT-IR 8300 Shimadzu) in the range (400-4000) cm^{-1} as KBr discs.

^1H .NMR-spectra in DMSO- d_6 solvent were carried out for three ligands, UV- Visible spectra, and chromatographic Analysis, thermal analysis, physical and analytical studies with biological studying.

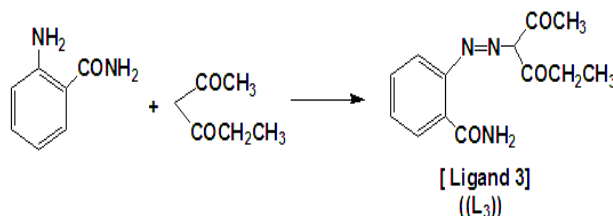
A-Synthesis of Ligand [L₁]: Equimolar quantities of 2-formyl pyridine (0.01mole) and o-hydrazo benzamide with quantity of ethanol was taken in 100ml of round bottomed flask fitted with condenser according to studying (Naghani, 2015). The mixture was heated in reflux for 3hrs. When the solutions are mixed then added 1-2 drops of glacial acetic acid, the reaction mixture was set aside for cooling. The solid deposit was collected by filtration. The product was recrystallized from ethanol to yield ligand [L₁].



B-Synthesis of Ligand [L₂]: According to studies (Shibata, 1976; Hawraa, 2014) 3,4- dinitro aniline dissolved in (3ml) of concentrated hydrochloric acid, after that, solution of sodium nitrite was added, then, reaction of ethanolic solution of 4,5-diphenyl imidazole with mixture solution, after (48 hrs) gave precipitation which filtered and dried then re-crystallized to yield ligand [L₂].



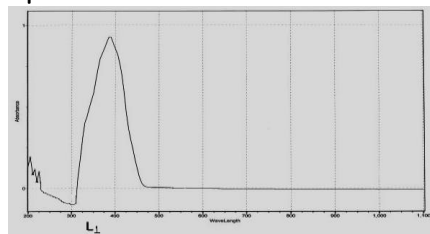
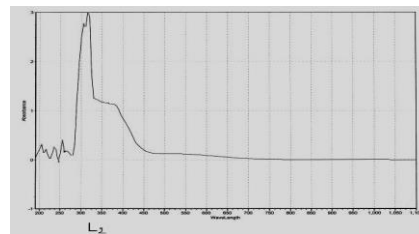
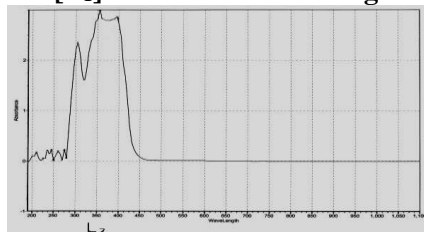
C-Synthesis of Ligand [L₃]: Ortho amino benzamide (0.01mole) dissolved in (3ml) of concentrated hydrochloric acid according to studies (Shibata, 1976; Naghani, 2015), after that, solution of sodium nitrite was added, then, reaction of ethanolic solution of hexan-2,4-dione with mixture solution, after (48 hrs) gave precipitation which filtered and dried then re-crystallized to yield ligand [L₃].



3. RESULT AND DISCUSSION

In the present work of our work, we synthesized Monomers [1- 10] and will identified them by spectral methods like (UV-Visible, FT-IR, H.NMR) and studying of various analytical measurements with bio chemical behavior like (Thermal measurements, Solubility in series solvents, chromatography behavior, biological activity):

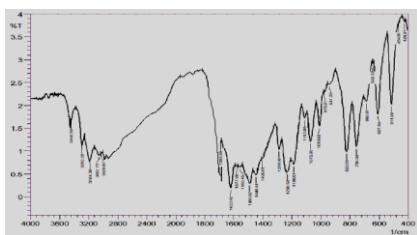
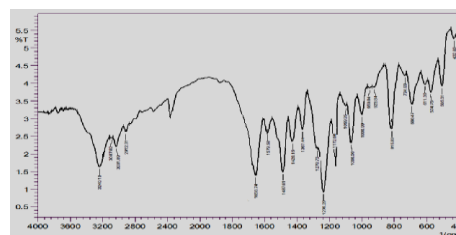
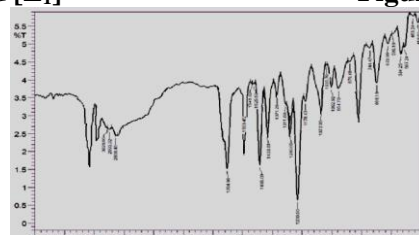
A-The UV-Visible –spectrum: All the new ligands have screened in UV-Visible spectrophotometer to give three curves from spectra which act optimal wave length for ligands.

Figure.1. UV-Visible of Ligand [L₁]Figure.2. UV-Visible of Ligand [L₂]Figure.3. UV-Visible of Ligand [L₃]

B-The FT.IR-spectrum: Showed a vibration frequency at $(1622)\text{cm}^{-1}$ in ligand [L₁] returns to imine group (CH=N), with other band at $(1689)\text{cm}^{-1}$ to (CO-NH) carbonyl of amide, but band (N=N) Azo: $(1443, 1410)$ in ligand [L₂], and ligand [L₃] gave many bands at (NH₂): $3350, 3364$, (CO-NH)carbonyl of amide: 1686 , (N=N) Azo: $1472, 1453$, (CO) ketone: 1707 .

Table.1. FT.IR- data (cm^{-1}) of ligands

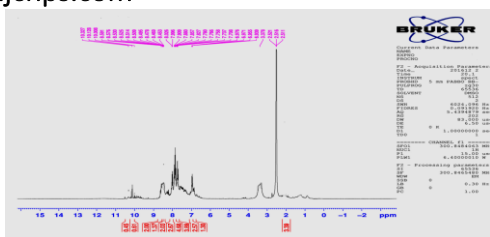
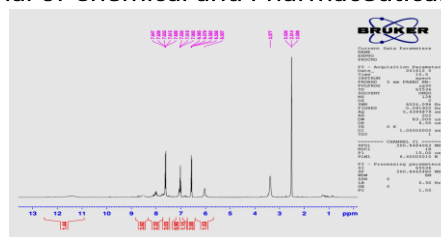
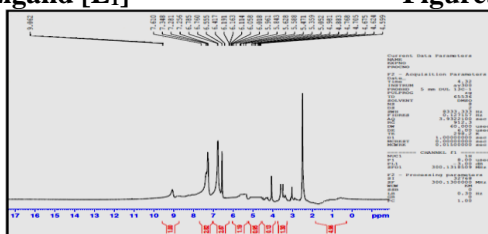
Ligands	I.R _(KBr) (Only Important Groups)
[L ₁]	(C=N) imine group :1622, (NH ₂) amine : 3320, 3300, (CO-NH) carbonyl of amide : 1689
[L ₂]	(C=N) endo cycle :1640, (NH) amine : 3210, (N=N) Azo: 1443, 1410 .
[L ₃]	(NH ₂): 3350, 3364, (CO-NH)carbonyl of amide :1686, (N=N) Azo: 1472, 1453, (CO)ketone: 1707

Figure.4. FT.IR of Ligand [L₁]Figure.5. FT.IR of Ligand [L₂]Figure.6. FT.IR of Ligand [L₃]

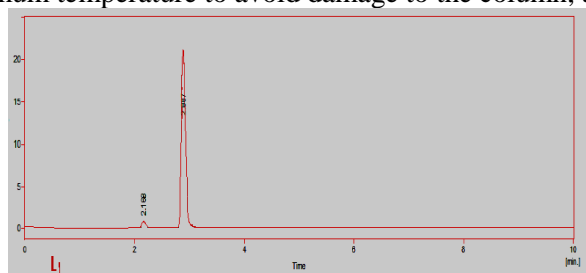
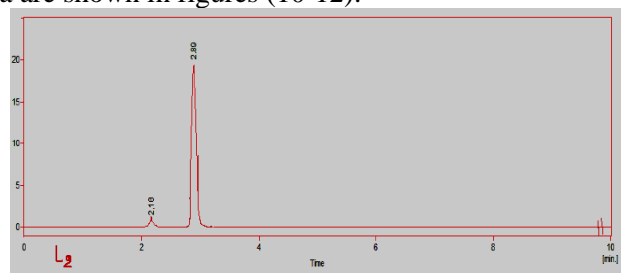
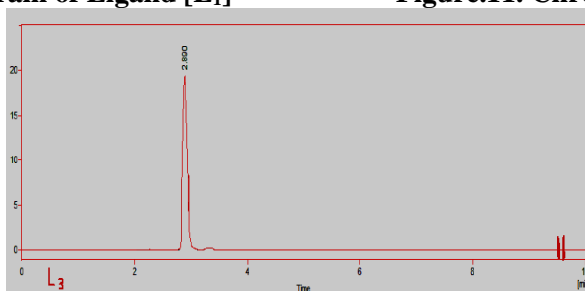
C-The ¹H.NMR- Spectra: showed signals at 5 protons of (NH):3.37, proton of (NH-CO)amide: 10.32, (CH=N) proton of imine group: 8.59, (Ph-)protons of phenyl groups and pyridine ring: (6.99-7.99) for ligand [L₁]. (NH) Proton of amine group in imidazole: 3.37, (Ph-) protons of phenyl groups: (6.58-7.64) for ligand [L₂]. Protons of di ketone (CO-CH₃) and (CO-CH₂CH₃): (3.0 – 4.98), (NH-CO) amide: 9.06, (Ph-)protons of phenyl group: (6.55-7.61) for ligand [L₃].

Table.2. H.NMR- data (δ - ppm) of Ligands

Ligands	H.NMR (Important Peaks)
[L ₁]	protons of (NH):3.37, proton of (NH-CO)amide: 10.32, (CH=N) proton of imine group: 8.59, (Ph-)protons of phenyl groups and pyridine ring: (6.99-7.99).
[L ₂]	(NH) proton of amine group in imidazole: 3.37, (Ph-)protons of phenyl groups: (6.58-7.64).
[L ₃]	protons of di ketone (CO-CH ₃) and (CO-CH ₂ CH ₃): (3.0 – 4.98), (NH-CO) amide: 9.06, (Ph-)protons of phenyl group: (6.55-7.61).

Figure.7. H.NMR of Ligand [L₁]Figure.8. H.NMR of Ligand [L₂]Figure.9. H.NMR of Ligand [L₃]

D-Studying of Ligands in Chromatography Technique: Analysis of ligands Through Chromatography Technique (Nagham, 2016). Preparation of diluted concentrations (concentration of 1ppm for vehicles) from ligands [L₁, L₂, L₃] after dissolved with ethanol, with shaking continuous, injected models by using a syringe (Hamilton) with a capacity of 10ml individually and then injected the mixture, and then install the measurement conditions through the use of nitrogen a gas flow of 25ml/min bus speeds and injection temperature was 25⁰C degrees higher than the temperature separation column and then use a flame ionization detector is 50⁰C higher than the temperatures of the column either column of (90-160) temperature programmed gradual increase of maxi- C^o, taking into consideration the mum temperature to avoid damage to the column, all data are shown in figures (10-12).

Figure.10. Chromatogram of Ligand [L₁]Figure.11. Chromatogram of Ligand [L₂]Figure.12. Chromatogram of Ligand [L₃]

In the past studies, many papers and several methods developed and reported in the past work for ligands analysis. The trend is to develop multi-ligands analysis methods which are simple and easy to separation. The use of hetero cycles in ligands like pyridine covered a wide area application in biochemistry, pharmaceutical and analytical field like chromatography.

The chromatogram curves gave evidence that all ligands separated according to molecular weight and interaction between active groups in the ligands in separation column of chromatography technique.

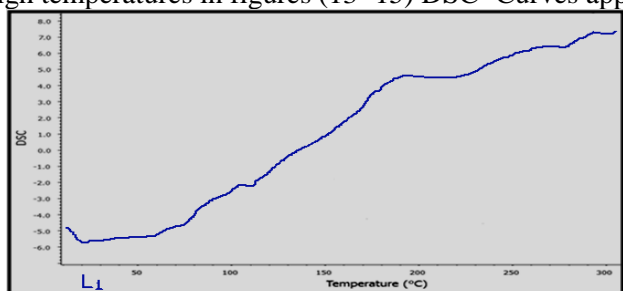
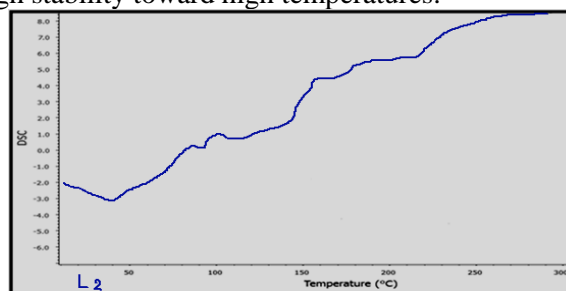
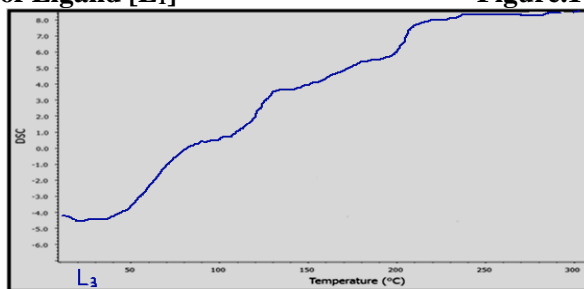
E- Effect of Using Types of Solvents: The salvation of ligands were screened in many types of solvents according to polarity type of solvents, the results are summarized in Table (3).

Table.3. Interaction of Compounds in Different Solvents.

Ligands	Solvents					
	DMF	CH ₃ OH	CH ₂ Cl ₂	Ether	CCl ₄	DMSO
[L ₁]	+	+	-	-	-	+
[L ₂]	+	+	-	-	-	+
[L ₃]	+	+	-	-	-	+

The interaction of synthesized compounds depend on solubility and activity of functional group and terminal groups (polarity of group) in solvents which cause interaction represented in $(\text{NO}_2\text{- group, CO-NH-group})$ or any other active groups.

F-DSC – Thermal Analysis (Naghham, 2016): DSC – measurements of all ligands carried out for stability of ligands in high temperatures in figures (13- 15) DSC- Curves appear high stability toward high temperatures:

Figure.13. DSC of Ligand [L₁]Figure.14. DSC of Ligand [L₂]Figure.15. DSC of Ligand [L₃]

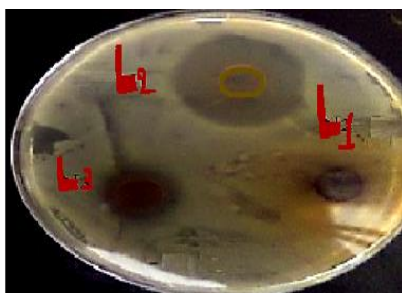
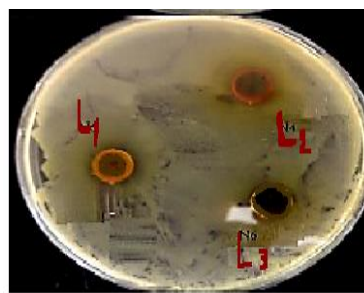
G-Antibacterial Studying for Ligands: The biological activities of synthesized compounds have been studied for their antibacterial by agar via biological methods (Naghham, 2016). The antibacterial activities were done at three concentration (5, 8, 12) mg/ml concentrations in DMSO solvent, but concentration (12 mg/ml) gave higher activity than other concentrations with two types of bacteria (Gram – Positive) like: (*Bacillus subtilis*, *Streptococcus pyogenes*). These bacterial strains were incubated for 24 hr at 37°C.

All ligands [L₁, L₂, L₃] were tested according to their action against bacteria are described table (4) and figures (16,17). The presence of heterocyclic ring like pyridine and imidazole are reported to possess antibacterial effect may enhance or increase the antimicrobial activity of the hetero cycles derivatives.

The antibacterial results are summarized in table (4), which appeared that the results of antibacterial studies it was found to be potentially activity against all type of bacteria, which gave evidence from the results that the biological activity of all ligands have high biological activity which inhibit the growth of bacteria due to hetero cycle nuclei in some ligands which shown to inhibit cellular protein and RNA synthesis, they included some groups with sulfur atoms and hence inhibit the bacterial growth.

Table.4. Antibacterial Activity (Gram –Positive) of Compounds (Inhibition Zone in (mm) and in Concentration (12 mg.ml⁻¹)

Ligands	<i>Streptococcus pyogenes</i>	<i>Bacillus subtilis</i>
[L ₁]	18	12
[L ₂]	20	16
[L ₃]	14	14

Figure.16. Inhibition zone of compounds against *Streptococcus pyogenes*Figure.17. Inhibition zone of compounds against *Bacillus subtilis*

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