

Synthesis, Structural and Biological Efficiency Studies of New Azo Ligands and Their complexes with Zn(II), Cd(II) and Hg(II) Metal ion

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Abstract

The formation of Zn(II), Cd(II) and Hg(II) complexes was studied with two new heterocyclic azo ligands 2-[4-(1-sulfonaphthalene)azo]-L-Histidine (L_1) and 2-[7-(1-hydroxy-3-sulfonaphthalene)azo]-L-Histidine (L_2) derived from coupling reaction of diazonium salt of naphthionic acid and 7-amino-1-naphthol-5-sulfonic acid with L-Histidine in an alkaline ethanolic solution. The structural features of all new compounds have been characterized from their elemental analyses, metal content, magnetic moment measurement, molar conductance & FT-IR, UV-Vis. and ^1H NMR spectral studies. Furthermore, the composition of complexes have been studied following the mole ratio method after fixing the optimum condition (pH and concentration). Beer's law was obeyed over a concentration range (6×10^{-5} - 8×10^{-5} M). All data showed that the complexes with (1:2) (M:L) metal to ligand, may be formulated as $[\text{M}(\text{L})_2\text{Cl}_2]$ and octahedral geometry, in which the ligands (L_1 and L_2) act as N,N-bidentate chelating agents, coordinated through the azo nitrogen near naphthyl moiety and heterocyclic nitrogen in L-Histidine. The stability constant (β) and Gibbs free energy (ΔG) of the complexes have also been studied. Biological efficiency of ligands and their complexes were tested against *Escherichia coli* and *Staphylococcus aureus*.

Keywords: L-Histidine, Azo ligands, structural studies, biological efficiency.

Theoretical

Scientists found that some naphthalen derivatives have been embodied as new range of active antimicrobials effective against a wide range of human pathogens [1] and thus considered medicinally important part of antibiotic drugs such as nafcillin, naftifine, tolnaftate, etc. which play vital role in the control of microbial infection [2]. The synthesis and development of biologically active compounds have received much attention in the literature [3], and prompting the medicinal chemist have always tried to prepare drug of maximum therapeutic application and minimum toxicity [4]. On the other hand the literature survey on synthetic naphthyl azo heterocyclic compounds containing active azo imine moiety ($-N=N-C=N-$), showed that they act as N,N-donor atoms and π -acidic ligand [5] with higher electron negativity of C and N [6]. Moreover they have been studied extensively in which the heterocyclic atoms at formally involved in the coordination to a positively charged metal centre might confirm the reactions of nucleophiles with the ligand and thus formed a stable five or six-membered ring assigned to the presence of π^* -molecular azo centered [7], therefore activities of metal complexes differ from those of either the free ligands or metal ions [8]. This type of compounds has been used in a number of biological reactions such as inhibition of RNA, DNA and protein preparation, nitrogen establishing, antifungus and anticancer agent [9]. Furthermore azo compounds play an important role in many applications that involve textile dyestuff industry [10] additives [11], cosmetic [12], organic synthesis [13], analytical [14], and non-linear optics [15] as well as photoelectronics [16] especially in optical information storage [15]. All these applications based on high intensity absorption bands in the UV-Vis region which include at least a conjugated chromophore azo ($-N=N-$) moiety in combination with one or more aromatic heterocyclic ring [16]. In spite of having good thermal stability as well as more light stable, weather fastness and impedance to solvents and water [17].

However this type of compounds is less reported, here in this paper the preparation, characterization and antibacterial efficiency of two new ligands, 2-[4-(1-sulfonaphthalene)azo]-L-Histidine (L_1) and 2-[7-(1-hydroxy-3-sulfonaphthalene)azo]-L-Histidine (L_2) and their metal chelate complexes with [Zn(II), Cd(II) and Hg(II)] ions are investigated

Experimental

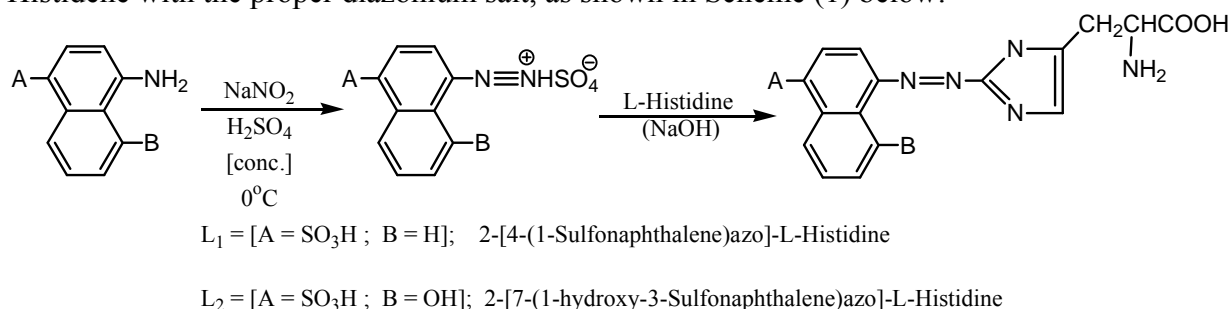
Materials and Instruments

All reagents and solvents are of highest purity and used as obtained from the manufactures.

Microelemental analysis (C.H.N.S) was gained on a (Euroveetor EA 3000A Elemental Analyser) in Al-al-Bayt University- Jordan. UV-Vis. Spectra were performed in ethanol on a (Shimadzu UV-160A) ultra violet-visible spectrophotometer. IR-spectra were recorded on a (Shimadzu FTIR-8400s Fourier Transform Infrared) spectrophotometer ($200-4000$) cm^{-1} using CsI discs. The 1H NMR spectra were gained on a (Jeol Ex270 MHz, Bruker-400MHz) University of Al-Al-Bayt-Jordan using DMSO as a solvent and (TMS) as a references. Conductivities were determined for ($10^{-4}M$) of complexes in ethanol and DMSO at $25^\circ C$ using (HANNA instruments / Conductivity Tester). pH measurement were performed using (HANNA instruments pH Tester / Pocket pH Tester). Melting points have been gained by using (Stuart Melting Point Apparatus).

Synthesis of Naphthyl Azo Ligands (L_1 and L_2)

The ligands (L_1 and L_2) were prepared as in literature [18] by coupling reaction of L-Histidine with the proper diazonium salt, as shown in Scheme (1) below:

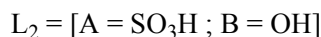
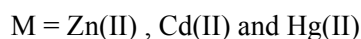
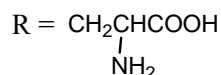
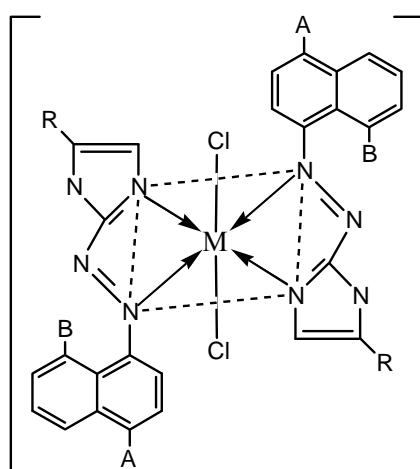


A concentrated sulphuric acid (5 ml) was added to precooled aqueous solution of (0.1 mole, 6.9 gm) sodium nitrite till brown fumes were evolved. Then the resulting solution was added dropwise at (0°C) to (0.01 mole; 2.23 gm and 2.40 gm) of ethanolic solution of the proper amine (naphthionic acid and 7-amino-1-naphthol-5-sulfonic acid respectively).

The diazonium sulphate solution was added dropwise with stirring to (0.01 mole, 1.55 gm) an alkaline solution of L-Histidine cooled below (0°C). The resulting mixture was stirred for (2 hr.) in an ice bath. The product is left in the refrigerator for (24 hr). And then the colored products were filtered, washed several times with (1:1) EtOH: H_2O , and dried in vacuum desiccator. (M.P. = 260 and 272°C for L_1 and L_2 respectively).

Synthesis of Complexes

The complexes were prepared by adding gradually with stirring hot ethanolic solution of (2mmole) of ligands to stoichiometric amount of (1:2) (M:L) mole ratio (1mmole) of metal chlorides of [Zn(II), Cd(II) and Hg(II)] were dissolved in the buffer solution at optimum pH. The resultant mixture was heated at (60°C) with stirring for (2 hr), then left to cool to room temperature. The colored precipitates were filtered, washed and dried in vacuum desiccator. The expected stereochemical structure of the complex is shown in Scheme (2).



Buffer Solution

(0.01M, 0.771 gm) of ammonium acetate was dissolved in one liter of doubly deionized water. For adjusted pH range (4-10) was used acetic acid or ammonia solution.

Standard Solution

A series of standard solutions of metal chlorides of [Zn(II), Cd(II) and Hg(II)] were prepared in different concentration (10^{-6} - 10^{-3} M) at pH range (4-10). At the same time a series of ethanolic solutions of ligands (L_1 and L_2) within the range of concentrations (10^{-6} - 10^{-3} M) were also prepared.

Study of Biological Efficiency

The agar-well diffusion method [19] was used to screen the antibacterial activity. The in vitro antibacterial activity of the synthesized ligands (L_1 and L_2) and their prepared complexes in ethanol (10^{-4} M) were tested against Gram-positive bacteria: *Staphylococcus aureus* and Gram-negative bacteria: *Escherichia coli* using nutrient agar medium. Then (0.1 ml) of test solution was added carefully in spot on the surface of inoculated solid media. The petridishes were incubated at (37°C) for (24 hr). The inhibition zone formed by the compounds against the particular test bacterial strain were measured in diameters to evaluate the antibacterial activities of the prepared compounds.

Results and Discussion

A well established synthetic route to azo compounds is based on general procedure for the diazo-coupling reaction [18, 19]. Azo compounds are prepared by diazotization of heterocyclic or aromatic primary amines and followed by coupling the diazonium salt to a nucleophile, like aromatic heterocyclic or substituted aromatic ring [20]. which at least azo moiety linked to sp^2 -hybridized carbon atoms [21], according to it, has been prepared the ligands (L_1 and L_2) as in Scheme (1). The elemental analysis data of the prepared (L_1 and L_2) and their complexes with [Zn(II), Cd(II) and Hg(II)] are in good convention with the calculated result from expected formula of each synthesized compounds Table(1). which indicates that diazo-coupling reaction between the diazotized aminonaphthalene and L-Histidine occurred in a (1:1) molar ratio.

The ligands and their complexes are stable at room temperature, non hygroscopic and slightly soluble in water but soluble in most organic solvents. All the prepared complexes recorded high melting points ($> 360^\circ\text{C}$).

Calibration Curve

It was constructed as in the general procedure [22]. Several molar concentration (10^{-6} - 10^{-3} M) of mixed aqueous-ethanolic of ligands and metal ions, only the concentration in the range ($6-8 \times 10^{-5}$ M) obeyed Beer's law and appeared perspicuous intense color. Best fit straight lines were obtained with correlation factor $R > 0.9991$ as shown in Figure.(1).

Optimum Conditions

To investigate the interaction between the prepared ligands and metal ions under study for the preparation of the complexes, the spectra of blending solutions for the ligands and metal ions to reach to optimum pH and concentration, as well as fixed wave length (λ_{max}) were studied first. Then mole ratio metal to ligand (M:L) was appointed to prepare the complexes. Optimum concentration was chosen for complex solution based on which solution gives the highest absorbance at constant (λ_{max}) at different pH. And results are described in Table (2).

The empirical results proved that the absorbance of all prepared complexes are maximum and constant in a buffer solution of ammonium acetate in the pH range (4-10). It was found that all prepared complexes had optimum performance at (pH = 7) as is shown in Figure (2).

Absorption Spectra

The reaction of the prepared ligands (L_1 and L_2) with metal ions under study at optimum conditions in solution were studied. The absorption spectra showed an absorption maximum (λ_{max}) for ethanolic solution for (L_1 and L_2) at (387 and 375 nm) respectively, whereas the ethanolic-aqueous solution for their complexes are located at wave length range (429-518) for (L_1) and (546-570 nm) for (L_2). Hence a great red shift in the visible region was observed in the complexes solutions spectra when compared with the spectra of ethanolic solution of the free ligands which confirm the complex formation. Figure (3) shows a comparison between the spectra of L_1 and $[Zn(II)-L_1]$ mixed solution.

Stoichiometry of Complexes

The composition of the prepared complexes performed in solution by mole ratio method at exact pH and concentration at certain wavelength of maximum absorption (λ_{max}). The ratio was (1:2) metal ion to ligands at pH (7) Figure (4 and 5). The condition for the preparation of complexes are presented in Table [2]. All obtained results are in agreement with the values recorded for some naphthyl azo imidazole complexes [22].

Determination of Stability Constant and Gibbs Free Energy

The successive stability constant (β) of the (1:2) metal:ligand complex can be calculated from the relationship [23]:

$$\beta = \frac{1 - \alpha}{4\alpha^3 C^2} ; \quad \alpha = \frac{A_m - A_s}{A_m}$$

Where: A_m and A_s = the absorbance of the fully and partially formed chelating complex respectively at optimum pH and concentration at (λ_{max}) of solution

C = the molar concentration of the complex solution

α = degree of dissociation

The values of (β) and $\log \beta$ for prepared complexes are give in Table (2). The high values of (β) refers to high stability of prepared complexes, which they follows the sequence,; $[Hg(II) > Zn(II) > Cd(II)]$ for (L_1) complexes while for (L_2) complexes have been noticed the sequence $[Cd(II) > Zn(II) > Hg(II)]$, that basis on the differences between stereochemical structures of the two ligands (L_1 and L_2) [24].

The thermodynamic parameters of Gibbs free energy (ΔG) were also studied. The ΔG data have been calculated from the equation [24]:

$$\Delta G = -R T \ln k$$

Where; R = gas constant = $8.3 \text{ J.mol}^{-1} \cdot \text{K}$

T = absolute temperature (Kelvin)

All results were recorded in Table (2). The negative value of (ΔG) indicates that the reaction between (L_1 and L_2) and metal ions understudy are spontaneous.

Molar Conductance

All prepared complexes showed low molar conductance value in the solution (10^{-4} M) ethanol and DMF at room temperature. The results indicate that they have non-ionic character Table (1) and well within the expected. which proposes a formula $[ML_2Cl_2]$ where $M(II) = (Zn, Cd \text{ and } Hg)$. So the two chloride ions coordinated with metal ion [25].

Magnetic Susceptibility

The magnetic susceptibility for all prepared complexes have been found to be diamagnetic (d^{10}) ($t_2g^6 e_g^4$), and the electronic spectra don't show any (d-d) band [26].

Spectroscopic Characterization

FTIR Spectra and Mode of Binding

The FTIR-spectra of the ligands (L_1 and L_2) and their prepared complexes were recorded in (CsI) over the range ($200-4000 \text{ cm}^{-1}$). The main vibrational bands have been assigned on the basis of the listed assignments of the FTIR spectra bands in the literature m [27, 28]. which are given in Table (3), while Figure (6-9) showed the spectra of (L_1 and L_2), [$Zn(II)-L_1$] and [$Cd(II)-L_2$]. As mentioned, the (L_1 and L_2) have different chelating sites. Thus a detailed translated of the spectra of (L_1 and L_2) and the effect of binding mode of metal ions under study on the vibration frequencies of the free ligands are discussed.

The spectra of (L_1 and L_2) are showed a medium and broad band at (3423 and 3467) cm^{-1} respectively due to stretching vibration modes of $\nu(N-H)$ of the imidazole moiety [29]. The position of this band remained at nearly in the same region in the spectra of all prepared complexes, which may be explained its non involvement in the coordination of the two ligands to the metal ions [30]. The spectrum of (L_1) has showed a sharp band at (1631) cm^{-1} , while (L_2) spectrum showed triplet band at (1647 , 1623 and 1593 cm^{-1}), can be attributed to stretching vibration of $\nu(C=N)$ of (N-3) imidazole nitrogen which is in agreement with the observation of previous authors [31], on coordination with metal ions, this band was observed with a little change in the shape and locale, these differences support of the π -acidic character of ($-N=N-C=N-$) azoimine moiety, while metal ions showed π -back donation and suggested the binding of metal ion with nitrogen atom for imidazole moiety [32]. The characteristic band in the spectra of free ligands (L_1 and L_2) at (1508 and 1492) cm^{-1} respectively attributed to stretching vibration $\nu(N=N)$, within shifts to lower wave number ($\Delta\nu = 74-91$) cm^{-1} in the spectra of the (L_1 -complexes) and ($\Delta\nu = 17-88$) cm^{-1} in the spectra of (L_2 -complexes), due to complex formation and presence ($d M^{II} \rightarrow \pi^*$) (azo of ligands) back bonding [25]. At the far FTIR spectra for all prepared complexes showed new weak bands that are not present in the spectra of the ligands. These bands are located at ($418-429$) cm^{-1} which attributed to the $\nu(M-N)$ of an azo group and imidazole moiety [33]. As sell as another weak new band was appeared in the region ($210-227$) cm^{-1} which assignable to the $\nu(M-Cl)$ [28]. Thus the IR results lead to the proposal that the (L_1 and L_2) act as neutral N,N-bidentate chelate agent, coordinating through the nitrogen atom of azo group nearest to a naphthyl ring and N-3 atom of imidazole moiety to give five membered chelat ring. Based on the above, the proposed structure of the prepared complexes can be illustrated an octahedral as in Scheme (2).

Electronic Spectra

The UV-Vis. Spectra of (L_1 and L_2) and their prepared complexes were established in ethanol (10^{-4} M) at room temperature in the region ($200-1100$) nm. All results are listed in Table (4), Figure (10-13). The value of molar extinction coefficient (ϵ) of the two new ligands and their complexes in the range ($1040-15490 \text{ L.mol}^{-1}.\text{cm}^{-1}$), which leads to denote high sensitivity. The spectra of free (L_1 and L_2) have been appeared three bands, the first and the second bands were noticed at the ranges (205 and 242) nm and (248 and 289) nm

respectively. These two bands were attributed to ($\pi \rightarrow \pi^*$) transition of intra ligand charge transfer for imidazole and naphthalene moieties [34]. while the third band (λ_{\max}) was noticed at (387 and 375) nm, which owing to ($\pi \rightarrow \pi^*$) transition of intermolecular charge transfer from imidazole to naphthalene ring through the azo moiety [LMCT] [$d\pi(M^{II}) \rightarrow \pi^*(L)$] transition [35,36]. On the other hand the (UV-Vis.) spectra for [Zn(II), Cd(II) and Hg(II)] complexes in ethanol solution have been showed high intense charge transfer [MLCT] transition as in Table (4).

The ^1H NMR Spectrum

The HNMR spectra of the (L_1 and L_2) and the diamagnetic [Hg(II)- L_1] complex were registered in DMSO solution with TMS as an internal standard. In the HNMR spectra for free azo ligands (L_1 and L_2) have noticed the main signals as in Figure (14 and 15), a signal of one proton at ($\delta = 10.88$ ppm) that approved the presence of carboxyl moiety in L-Histidine. As well as a singlet signal at ($\delta = 8.42$ ppm) attributed to (NH) proton of the imidazole moiety and don't shift significantly in spectra of [Hg(II)- L_1] complex compared with the ligand which indicate that the (NH) of imidazole moiety don't involve in the coordination. At the same time the multiplet signals at ($\delta = 6.96-7.10$ ppm, 7H) and ($\delta = 6.94-7.19$ ppm, 6H) for (L_1 and L_2) respectively, referrer to aromatic protons of naphthyl and imidazole moieties. Slightly chemical shift was observed in the spectrum of [Hg(II)- L_1] due to complex formation. Furthermore the doublet and triplet signals at high field in the spectra of free ligand (L_1 and L_2) due to aliphatic protons for (CH_2) ($\delta = 3.48-3.40$ ppm) and (CH) ($\delta = 3.8-3.46$ ppm), were noticed changes on coordination with metal ion [35].

Biological Efficiency

All the prepared complexes and (L_1 and L_2) have been examined with Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* bacteria for the presence of antibacterial constituents, by using disc diffusion method [9]. The data are recorded in Table (5). The results explained that all prepared complexes have more toxicity than free ligands. So we owed to the Tweedy's chelation theory [36]. Accordingly the coordination compounds reduce the polarity of metal ions due to the partial positive charge within doner moiety and in spite of the electron delocalization ($d\pi \rightarrow \pi^*$) [MLCT] which leads to increase the lipophilic properties of chelating complexes, so performing it's force during the lipid layers for the cell membrane. Otherwise the presence of the (C=N) and (N=N) group with active centers of cell component gives in the interference with normal cell process.

Conclusion

The N,N-bidentat (L_1 and L_2) were found to be linked with [Zn(II), Cd(II) Hg(II)] through the azo nitrogen nearest to naphthyl moiety and the imidazole nitrogen. And so, tentative structure of the prepared complexes could be clarified as in Scheme (2). The characteristic of the ligands and their complexes have been studied by different physico-chemical techniques FTIR, HNMR and UV-Vis. Spectroscopies and elemental analysis gave satisfactory results corresponding to mole ratio of (1:2) metal to ligand after definition optimum pH and concentration at the (λ_{\max}). The (L_1 and L_2) and their prepared complexes have showed antibacterial efficiency.

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Table (1): Synthetic physical and analytical data of ligands and their complexes

Compound [M.wt. (gm/mole)]	Color	Yield%	Elemental analysis Found (Calcd.)						Λ $\text{ohm}^{-1}.\text{cm}^2.\text{mol}^{-1}$	
			C%	H%	N%	S%	M%	Cl%	Ethanol	DMSO
L ₁ [389]	Reddish brown	88	49.37 (49.35)	3.80 (3.76)	17.95 (17.99)	8.20 (8.22)	-	-	-	-
[Zn(L ₁) ₂ Cl ₂] [914]	Red	74	42.00 (42.01)	3.20 (3.28)	18.56 (18.59)	7.01 (7.00)	6.78 (6.82)	7.47 (7.76)	8.43	7.81
[Cd(L ₁) ₂ Cl ₂] [961]	Pink	81	39.96 (39.95)	3.16 (3.12)	17.59 (17.68)	6.61 (6.65)	11.65 (11.60)	7.35 (7.38)	7.58	5.11
[Hg(L ₁) ₂ Cl ₂] [1049]	Reddish purple	72	36.66 (36.60)	2.81 (2.85)	16.27 (16.20)	6.20 (6.10)	19.11 (19.06)	6.61 (6.76)	9.38	8.16
L ₂ [405]	Orange	85	47.49 (47.40)	3.81 (3.70)	17.30 (17.28)	7.78 (7.90)	-	-	-	-
[Zn(L ₂) ₂ Cl ₂] [946]	Reddish purple	69	40.55 (40.59)	3.20 (3.17)	14.77 (14.79)	5.01 (6.76)	7.02 (6.87)	7.48 (7.50)	7.32	7.35
[Cd(L ₂) ₂ Cl ₂] [993]	Purple	73	38.47 (38.65)	3.18 (3.01)	14.20 (14.09)	3.16 (3.22)	11.28 (11.31)	7.09 (7.15)	4.89	6.93
[Hg(L ₂) ₂ Cl ₂] [1081]	Violet	67	35.64 (35.52)	2.60 (2.77)	13.01 (12.95)	5.78 (5.92)	18.49 (18.50)	6.58 (6.62)	6.28	8.55

Table (2): Metal:Ligand ratio , Stability constant and Gibbs free energy data

Ligand	Metal ion	Optimum pH	Optimum molar conc. $\times 10^{-5}$	λ_{max} (nm)	M:L	$\log\beta$	ΔG° J.mol^{-1}
L ₁	Zn(II)	7.0	7.0	518	1:2	8.328	-43.450
	Cd(II)	7.0	7.0	484	1:2	8.069	-42.099
	Hg(II)	7.0	7.0	429	1:2	8.743	-45.615
L ₂	Zn(II)	7.0	6.5	570	1:2	8.428	-43.972
	Cd(II)	7.0	7.5	546	1:2	9.019	-47.055
	Hg(II)	7.0	6.5	550	1:2	7.980	-41.635

Table (3): The main IR absorption bands of the ligands and their metal complexes in cm^{-1} units

Compound	$\nu(\text{N-H})$	$\nu(\text{C-H})$ Ar.	$\nu(\text{C=N})$	$\nu(\text{N=N})$	$\nu(\text{O=S=O})$	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$
L_1	3423 br.m	3060 v.w.	1631m.	1508 w.	1357 w.	-	-
$[\text{Zn}(L_1)_2\text{Cl}_2]$	3483	3060 v.w.	1655.3m.	1434 w.	1366 w.	345 w.	227w.
$[\text{Cd}(L_1)_2\text{Cl}_2]$	3481.2	3070.4v.w.	1656.7m.	1417 w.	1384.7 w.	329 w.	235 w.
$[\text{Hg}(L_1)_2\text{Cl}_2]$	3482	3066.6v.w.	1653m.	1421 w.	1367 w.	341 w.	225 w.
L_2	3467 m.br.	3051 v.w.	1647 1623 1593 } t.m.	1492 w.	1338 w.	-	-
$[\text{Zn}(L_2)_2\text{Cl}_2]$	3470 m.br.	3060 v.w.	1612 1556 1527 } t.m.	1475 1444 } d.m.	1350 w.	418.6 w.	217 w.
$[\text{Cd}(L_2)_2\text{Cl}_2]$	3477 m.br.	3055 v.w.	1622 1595 } d.m. 1568 sh.m.	1438 1404 } d.m.	1346 w.	420 w.	212 w.
$[\text{Hg}(L_2)_2\text{Cl}_2]$	3475 m.br.	3060.8 v.w.	1612 1598 1569 } t.m.	1471 1436 } d.m.	1346.2 w.	418 w.	210.2 w.

w = weak, m = medium, v = very, b = broad, t = triplet

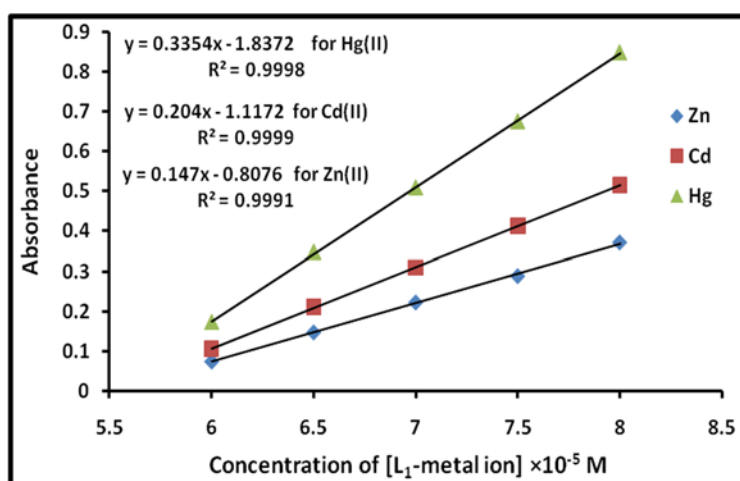
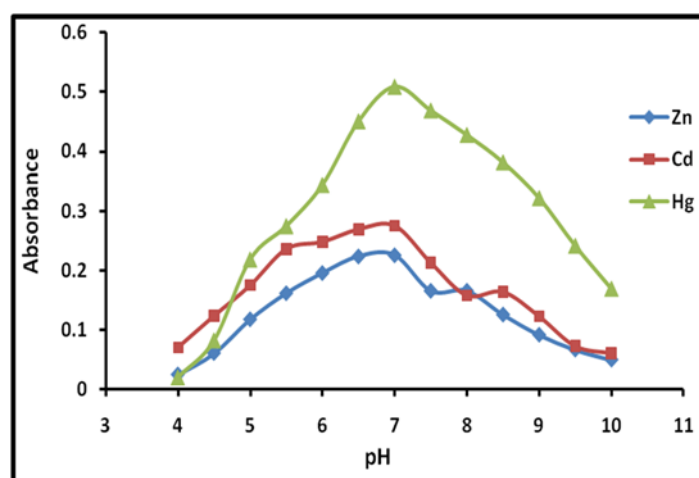
Table (4): Electronic spectral data of the ligands and their complexes

Compound	λ_{max} (nm)	Absorption band (cm^{-1})	Transition	$\epsilon \times 10^4$ $\text{L.mol}^{-1}.\text{cm}^{-1}$
L_1	387	25839	$\pi \rightarrow \pi^*$	1.549
	248	40322		0.650
	205	48780		0.380
$[\text{Zn}(L_1)_2\text{Cl}_2]$	518	19305	C.T.	0.221
$[\text{Cd}(L_1)_2\text{Cl}_2]$	484	20661	C.T.	0.311
$[\text{Hg}(L_1)_2\text{Cl}_2]$	429	23310	C.T.	0.513
L_2	375	2666	$\pi \rightarrow \pi^*$	1.422
	289	34602		0.244
	242	41322		0.577
$[\text{Zn}(L_2)_2\text{Cl}_2]$	570	17543	C.T.	0.156
$[\text{Cd}(L_2)_2\text{Cl}_2]$	515,546	19417,18315	C.T.	0.398,0.465
$[\text{Hg}(L_2)_2\text{Cl}_2]$	550	18181	C.T.	0.104

Table (5): Antibacterial efficiency for the ligands and their complexes

Compound	<i>E. coli</i> gram (-)	<i>Staphylococcus aureus</i> gram (+)
L ₁	++	+
[Zn(L ₁) ₂ Cl ₂]	+++	++
[Cd(L ₁) ₂ Cl ₂]	++	++
[Hg(L ₁) ₂ Cl ₂]	+++	+++
L ₂	++	+
[Zn(L ₂) ₂ Cl ₂]	++	+++
[Cd(L ₂) ₂ Cl ₂]	++	++
[Hg(L ₂) ₂ Cl ₂]	+++	+++

(+) = 6-8 mm, (++) = 8-10 mm, (+++) > 10 mm

**Fig. (1): Calibration curve for [L₁-metal ion]****Fig. (2): Effect of pH on the absorption intensity of L₁-complexes solution**

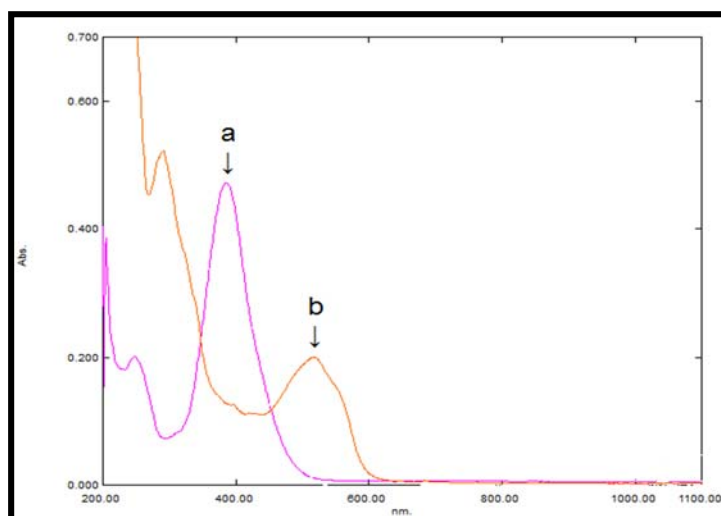


Fig. (3): UV-Vis spectra of : a-free Ligand (L_1) solution, b- (L_1-Zn^{II}) mixed solution

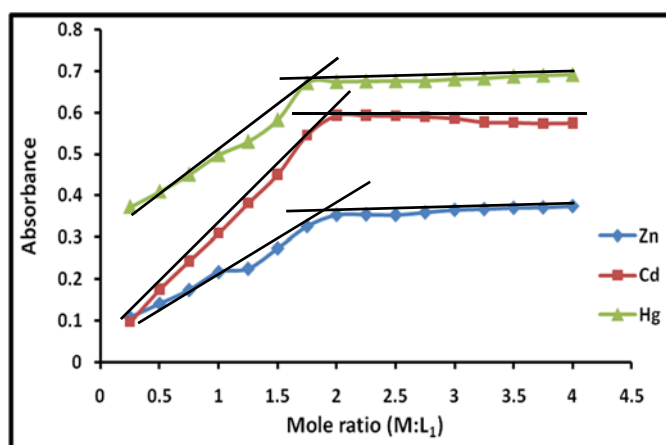


Fig. (4): Mole ratio for [L_1 -complexes solutions]

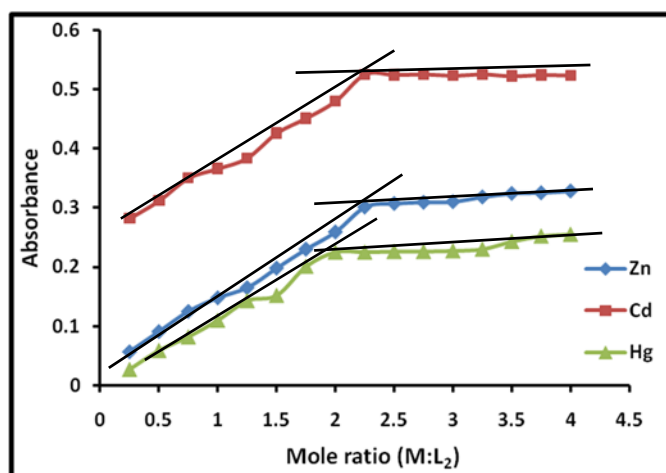
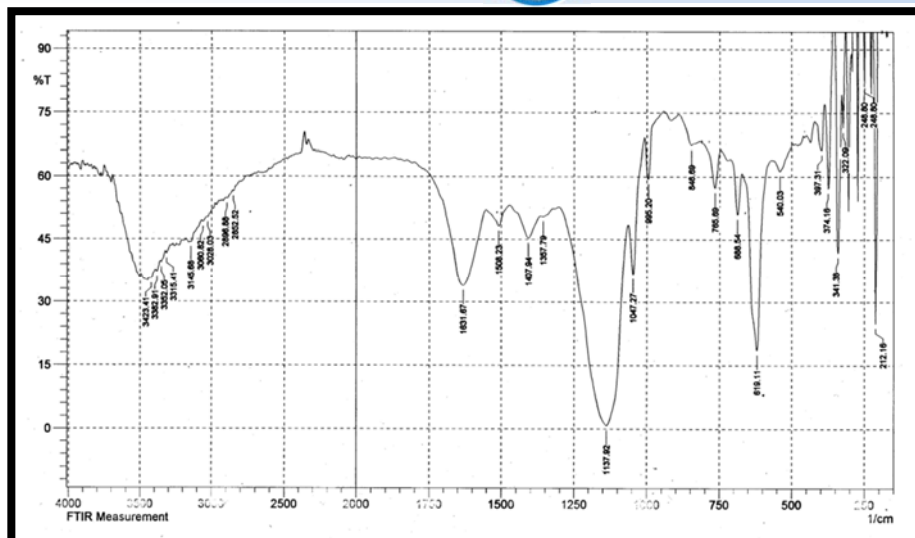
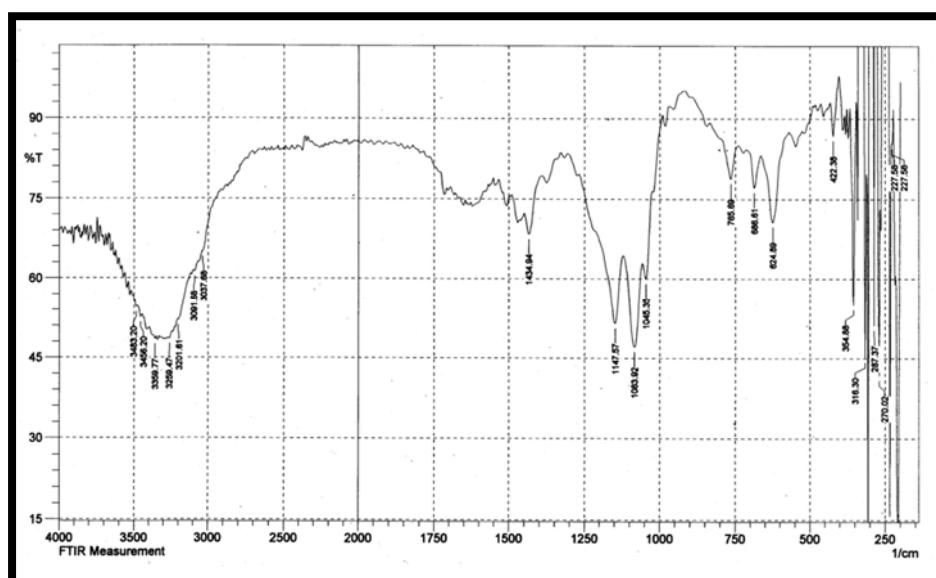


Fig. (5): Mole ratio for [L_2 -complexes solutions]

Fig. (6): FT-IR spectrum of the ligand L_1 Fig.(7): FT-IR spectrum of the complex $[Zn(L_1)_2Cl_2]$

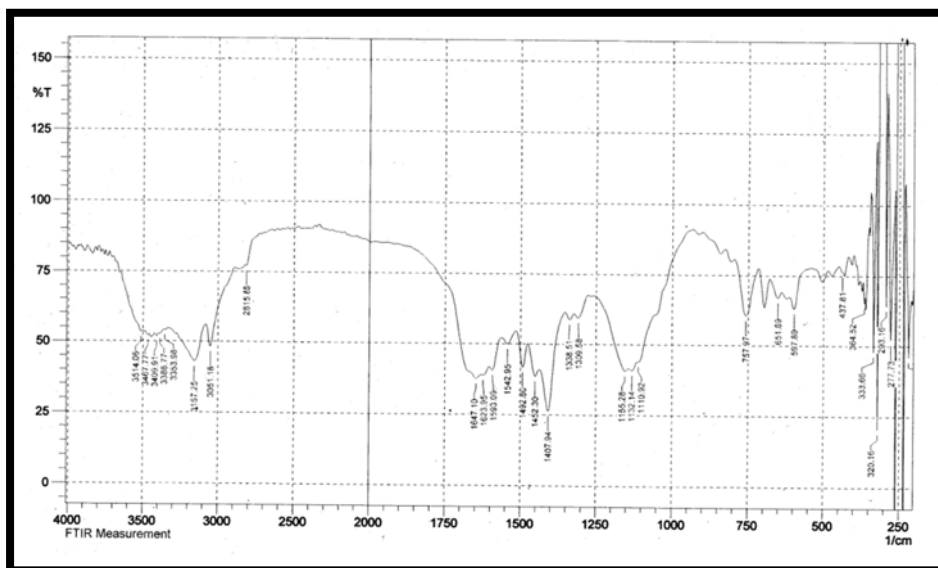


Fig.(8): FT-IR spectrum of the ligand L₂

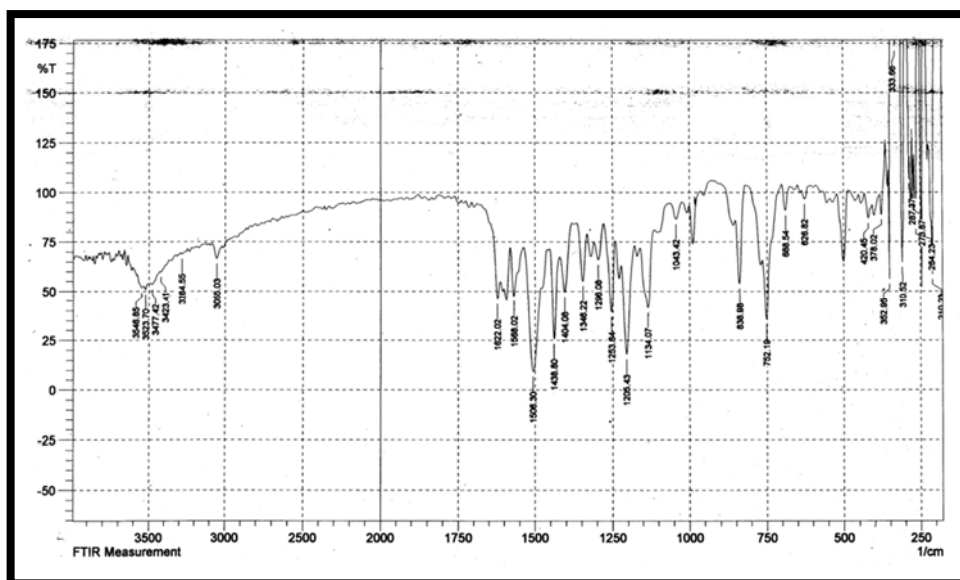
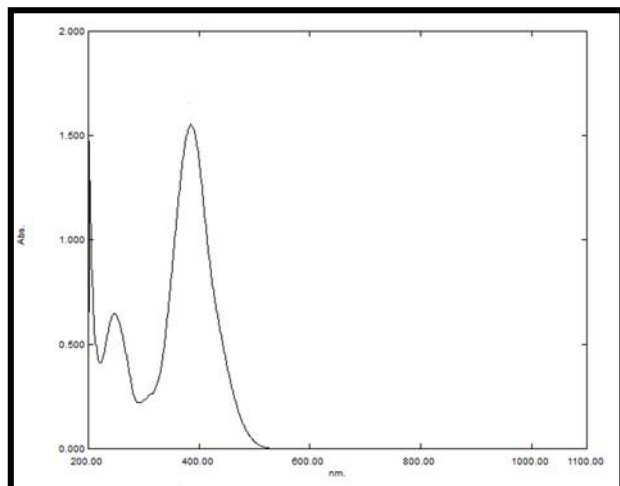
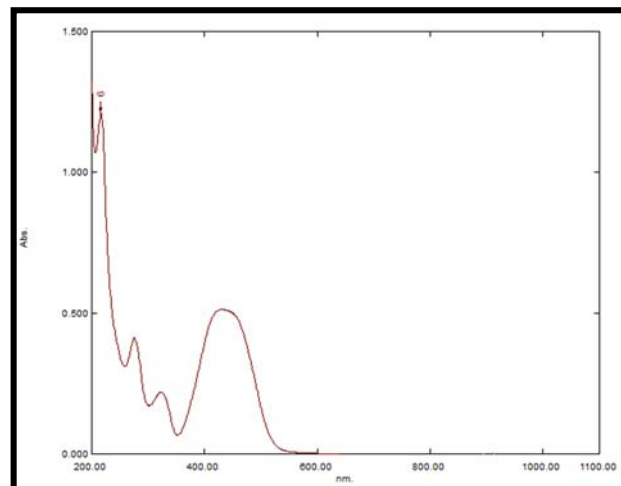
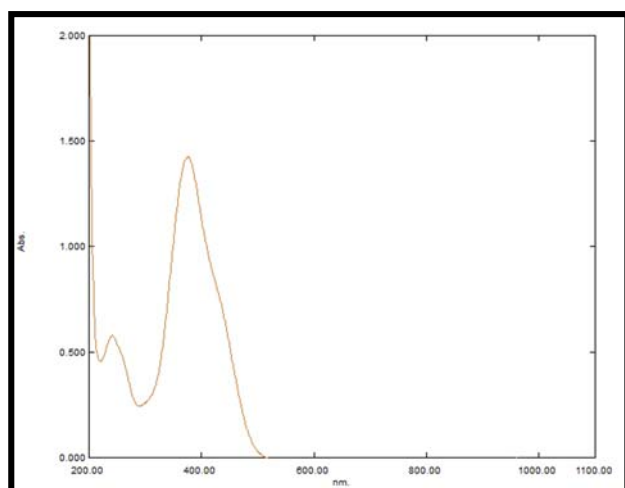
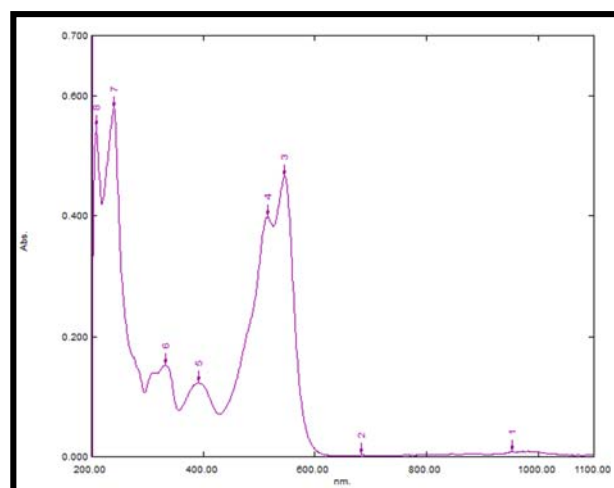


Fig. (9): FT-IR spectrum of the complex [Cd(L₂)₂Cl₂]

Fig. (10): UV-Vis. Spectrum of L₁Fig. (11): UV-Vis. Spectrum of [Hg(L₁)₂Cl₂]Fig. (12): UV-Vis. Spectrum of L₂Fig. (13): UV-Vis. Spectrum of [Hg(L₂)₂Cl₂]

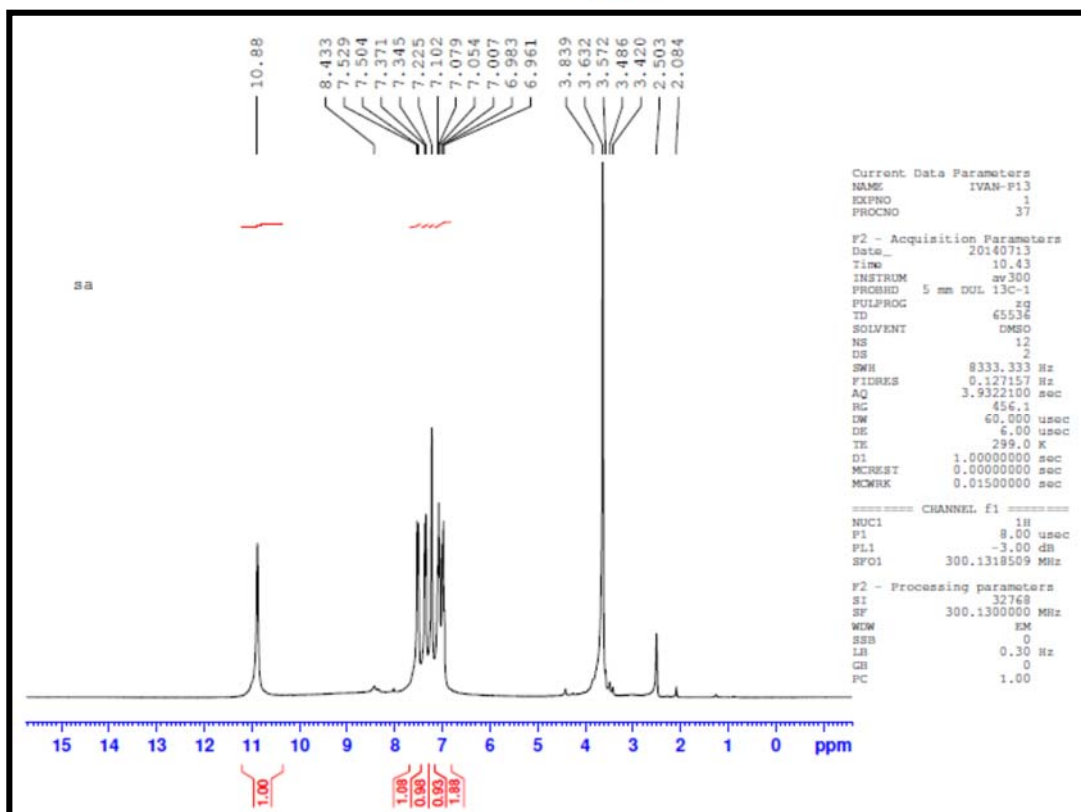


Fig. (14): ¹H NMR spectrum of the ligand L₁

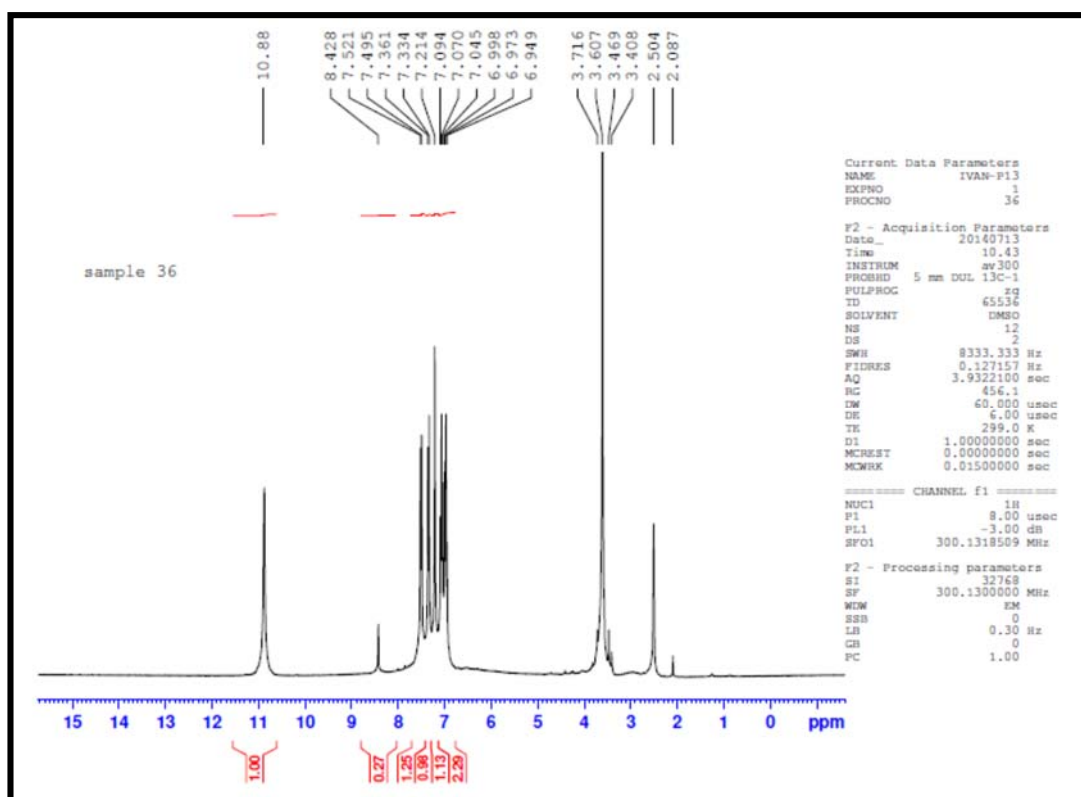


Fig. (15): ¹H NMR spectrum of the ligand L₂

تحضير، دراسة تركيبية والفعالية البيولوجية لليكاندات أزو جديدة ومعقداتها مع الأيونات الفلزية [Zn(II), Cd(II) and Hg(II)]

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استلم في: 24/أيار/2015 ، قبل في: 23/حزيران 2015

الخلاصة

تم تحضير معقدات لـ [Zn(II), Cd(II) and Hg(II)] مع ليكاندي الأزو الجديدة غير المتجانسة الحلقة (L_1 and L_2) والمشتقة من التفاعل الأزواجي لملاح الدايزونيوم لحامض النفثونك و 7-امينو-1-نفثول-5-حامض سلفونيك مع الهستدين في المحلول الكحولي القلوي. الصيغة التركيبية لجميع المركبات المحضرة شخّصت من خلال التحليل الدقيق للعناصر وقياس الحساسية المغناطيسية والتوصيلية المولارية والدراسات الطيفية للأشعة تحت الحمراء والأشعة فوق البنفسجية-المرئية و HNMR. فضلا عن دراسة النسبة المولية لمعرفة نسبة الفلز: الليكاند لتحضير المعقدات باستعمال طريقة النسبة المولية بعد تثبيت الظروف المثلى من تركيز و pH عند الطول الموجي الاعظم (λ_{max}). باستعمال مدى التراكيز ($10 \times 8 - 6 \times 10^{-5}$) التي هي تطيع قانون لامبرت-بير. جميع النتائج اثبتت ان النسبة المولية هي كنسبة (L:M) (1:2) فلز:ليكاند والتي لها الصيغة $[M(L)_2Cl_2]$ ذات شكل هندسي ثماني السطوح. اذ ان الليكاندين (L_1 و L_2) تسلك كليكاندات مخلبية ثنائية السن (N,N-) ترتبط مع الفلز عن طريق نتروجين مجموعة الأزو القريبة من حلقة النفثالين و نتروجين الحلقة غير المتجانسة في الهستدين. كذلك اجريت دراسة ثابت الاستقرارية والطاقة الحرة لكبس للمعقدات فضلا عن دراسة الفعالية البيولوجية باستعمال *Escherichia coli* و *Staphylococcus aureus*.

كلمات مفتاحية: الهستدين، ليكاندات الأزو، الدراسات التركيبية، الفعالية البيولوجية