Synthesis, Spectroscopic and Dyeing Performance Studies of Some New Heterocyclic Azo Dyes and Their Complexes with Selected Metal Ions

T. J.Al-Hasani and A. J.Jarad
Department of Chemistry, College of Science,University of Baghdad

Abstract

Coupling reaction of m-and p- amino acetophenone and p-amino benzoic acid with (L-Histidine) gave the new bidentate azo ligands (L_1, L_2 and L_3). The prepared ligands were identified by FT-IR, UV-Vis, ^{1}HNMR and GC- mass spectroscopic technique. Treatment of the prepared ligands with the following metal ions (Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II}) in aqueous ethanol with a 1:2 M:L ratio and at optimum pH, yielded a series of neutral complexes of the general formula $[M(L)_2 Cl_2]$. The prepared complexes were characterized by using flame atomic absorption, FT-IR, UV-Vis and ^{1}HNMR spectroscopic methods as well as magnetic susceptibility and conductivity measurements. Chloride ion content was also evaluated by (Mohr method). The nature of the complexes formed was studied following the mole ratio and continuous variation methods, Beer's law obeyed over a concentration range (1×10^{-4}- 3×10^{-4}M). High molar absorbtivity of the complex solutions was observed. The stability constant of the complexes have also been studied.

In addition the dyeing performance of the prepared ligands and some of their complexes was applied on cotton fabric. The dyes were tested for light and detergent fastness. Biological activity of the ligands and complexes against three selected types of bacteria was also examined. Some of the complexes exhibit good bacterial activities.

Introduction

A great deal of interest has been simulated to the preparation and studies of organic reagents in the previous years [1-3]. Many of these organic reagents have attracted much attention as they are sensitive, chromogenic reagents in addition to being interesting complexing agents[4,5]. The presence of substitution groups containing one or more donor atom such as – OH, - CO_2H, - SO_3H, - NH_2 and – N= N-, provided coordination sites with the metal ion, forming stable colored complexes[6,7].

Azo compounds with (- N= N-) group, are among the most profoundly explored classes of organic reagent both from the theoretical and practical view point[8]. The presence of an azo linkage in aromatic compounds makes them highly important in dyestuff industry[9-11], pharmacy and dosimetry[12,13], and more recently[14], in the field of non- linear optics. All these applications depend critically on the presence of intense absorption bands in the visible or near- UV region.

In recent years [15-18] much studies have been devoted to heterocyclic azo dyestuffs and their related compounds, in which the heterocyclic atom is at least formally involved in coordination with metal atom.

By far many important groups of heterocyclic azo derivatives have been synthesized and their applications have also been extensively studied [19-23].

In this respect an attempt has been made to synthesize and characterize three new azo bidentate ligands (L_1, L_2 and L_3), derived from m - and p- amino acetophenone and p- amino benzoic acid as diazo component, and (L- Histidine) as coupling agent. The complexes of these ligands with some metal ions has also been studied and characterized physicochemically. The dyeing performance of the ligands and complexes was assessed. The biological activities of all the ligands and complexes have also been studied.

Experimental

Instrumentation:

UV- Vis spectra were recorded on a (Shimadzu UV- 160A) Ultra Violet-Visible Spectrophotometer. IR- spectra were taken on a (Shimadzu, FTI R- 8400s Fourier Transform Infrared) Spectrophotometer (4000- 400)cm^{-1} with samples prepared as KBr discs. The ^{1}HNMR spectra were obtained on a (Jeol Ex270 MHZ, Brucker- 400 MHZ) University of London and on (Brucker- 300 MHz Ultra Shield) University of Al- al- Bayt- Jordan using DMSO as a solvent and (TMS) as a reference. Microelemental analysis (C, H, N) were performed in Al- al- Bayt University- Jordan using (Euro vector EA 3000A Elemental Analyser). Conductivities were measured for 10^{-3}M of complexes in ethanol at 25°C using (Philips PW- Digital Conductimeter). Magnetic susceptibilities were performed by using (Brucker Magnet B. M. 6) instrument at 25°C. Melting Points were obtained using (Stuart Melting Point Apparatus).

Materials and Reagents

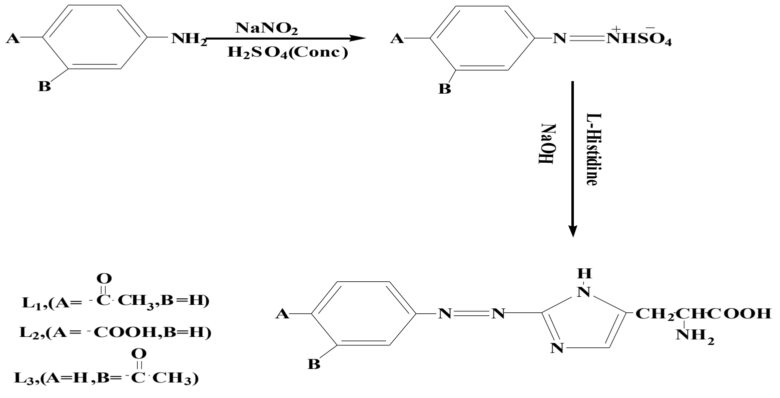
The following chemicals were used as received from suppliers; cadmium chloride mono hydrate 98%, mercuric chloride 98% (Fluka); cobaltous chloride hexahydrate 98.8%, nickel chloride hexahydrate 99.9%, copper chloride 98%, zinc chloride 99%, p- amino acetophenone 99% (Merck); m- amino acetophenone 99%, p- amino benzoic acid 98.8%, L-Histidine 99% (B. D. H).

The pH of the medium (4-9) was adjusted with ammonium acetate –ammonia – glacial acetic acid buffer solution .

Solutions were made of L_1, L_2 and L_3 ($1X10^{-5}$-$1X10^{-3}$M) in absolute ethanol and same concentration range of metals salts in buffer solutions.

Preparation of the Ligands (L_1, L_2 and L_3)

0.002 mole of the appropriate amine (m- and p- amino acetophenone and p- amino benzoic acid), was dissolved in a mixture of 2 ml sulphuric acid, 10 ml ethanol and 10 ml distilled water, and diazotized at 5°C with sodium nitrite solution. The diazo solution was added dropwise with stirring to a cooled ethanolic solution of 0.387g 0.002 mole of L-Histidine. 25 ml of 1 M sodium hydroxide solution was added to the dark colored mixture. The precipitate was filtered off and washed several times with (1: 1) ethanol: water, mixture then left to dry. The reaction is shown in scheme (1), while (Table- 1) describes color, melting point, % yield and weight of amine used.



Scheme (1): Preparation of Ligands (L_1 , L_2 and L_3)

Preparation of Metal Complexes (general procedure).

An ethanolic solution of the ligand (2m mole) was added gradually with stirring to (1m mole) of the metal salt dissolved in the buffer solution of the required pH. The mixture was cooled until dark color precipitate was formed, filtered and washed several times with (1: 1) water: ethanol then with acetone. (Table-2) consists of the weight of metal salt and ligand required, the pH of the solution and some of the physical properties of the prepared complexes.

Dyeing Method

The dyeing properties of the prepared ligand and their complexes were tested on "Hilla- Fine Textile State Company" using the "Azoic Dyes Method"[12] . Dyes were applied on cotton fabric as (1% shade). The dyeing of the fabric was done at (15- 20^{o}C) for 1 hr and at pH =10.

Study of Biological Activity

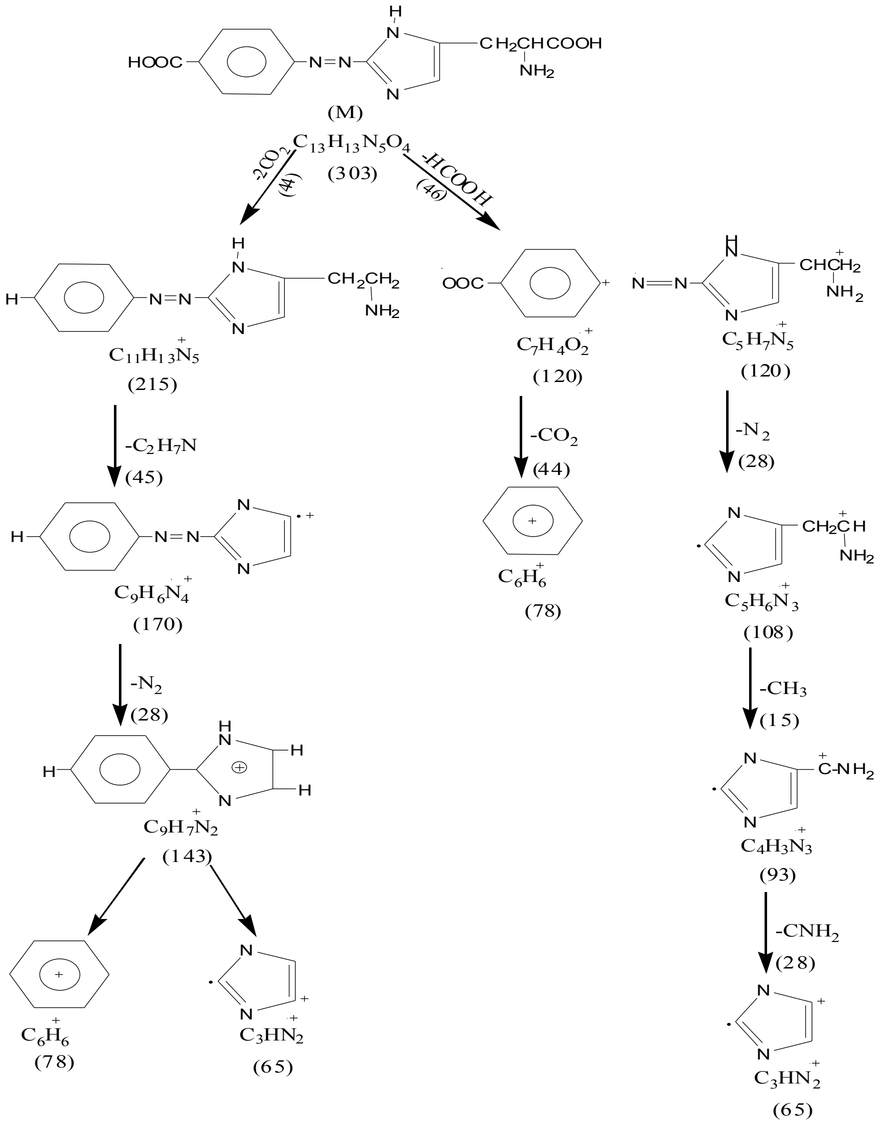
Three selected types of bacteria were used including, Escherichia Coli (E. Coli) as Gram Negative Bacteria, Staphylococcus Aurous (Staph. Aurous) as Gram Positive Bacteria and Pseudomonas Aeruginosa (Ps. Aeruginosa) in Nutrient Agar medium, using (DMSO) as a solvent and as a control, the concentration of the compounds in this solvent was 10^{-3}M, by using disc sensitivity test. This method involves the exposure of the zone of inhibition toward the diffusion of micro- organism on agar plate. The plates were incubated for 24hr. at 37^{o}C.

Results and Discussion

The ligands (L_1, L_2 and L_3) were prepared by coupling L- Histidine with the appropriate diazotate in alkaline solution. They are sparingly soluble in water but soluble in organic solvents, stable toward air and moisture.

The synthesized ligands were characterized by FT IR, UV- Vis spectra; L_1 was subjected to (^{1}HNMR) while L_2 and L_3 were characterized by GC-mass.

The mass spectrum of ligand L_2 and of ligand L_3 (Fig- 1) shows peaks centered at m/z 303 and 301 corresponds with (M^+), $C_{13}H_{13}N_5O_4$ and $C_{14}H_{15}N_5O_3$ respectively. The general pattern for the fragmentation reveals more than one way for the cleavage, either by losing the azo group as nitrogen molecule or by the cleavage of benzoic acid- azo bond, the main fragments are summarized in (Table- 3), while scheme (2) shows the fragmentation pattern of ligand L_2.



Scheme (2): Fragmentation Pattern of Ligand L_2

The (^{1}HNMR) spectrum of ligand (L_1) in (DMSO) (Fig- 2) shows signal for (NH) of imidazole at (δ= 8.87 ppm). The multiplet signals at (δ= 8.13-7.79 ppm) refer to aromatic proton while the (CH) of imidazole shows signal at (δ= 6.78 ppm). On the other hand, the aliphatic (CH) and (CH_2) appear as doublet and triplet signals respectively in the range (δ= 3.37- 2.43 ppm). Whereas, the signal at (δ= 1.23 ppm) is assigned to NH_2 and the signal peak at (δ= 2.5 ppm) referred to (DMSO)- d_6.

The three ligands (L_1 , L_2 and L_3) were also characterized by UV- Vis spectroscopic technique. The spectra of an ethanolic solution of the ligands (10^{-3} M) display mainly three peaks, the first and second peaks were observed within the ranges (223- 245 nm) and (278- 310 nm) respectively. These two peaks were assigned to the moderate energy π- π^* transition of the aromatic rings. The third peak (λ_{max}) was observed in the range (383- 405 nm) which referred to the π- π^* transition of intermolecular charge- transfer taken place from benzene to imidazole ring through the azo group (-N=N) [24].

Interaction of the metal ions (Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II}) with the three prepared ligands has been studied in solution; aqueous- ethanolic solutions were always performed over wide molar concentration and acidity range. The colors of these mixed solutions were varied from yellow or yellowish- brown to orange or red.

The interaction of the metal ion with the ligand manifests itself in the absorption spectra by the appearance of a peak in the range (431- 442 nm). A great bathochromic shift in the visible region was detected in the complex solutions spectra with respect to that of the free ligand. The high shift in the (λ_{max}) gave a good indication for complex formation. (Fig-3) showed a comparison between the spectra of the ligand and (Cd^{II}- L_1) mixed solution.

From the wide studied range of molar concentration (10^{-5}-10^{-3}M) of the mixed solutions, only the concentration of (10^{-4} M) obeyed Lambert- Beer's law and showed intense color. A calibration curve was plotted on absorbance against molar concentration in the range (1×10^{-4}- 3×10^{-4} M). Best fit straight lines were obtained with correlation factor R> 0.998.

The optimum concentration which chosen for complex solution gave rise to a constant (λ_{max}) at different pH.

The influence of pH was also studied at pH range 4 to 9 and the absorbance- pH curves for each metal ion measured at certain (λ_{max}) were plotted. (Fig- 4) showed a selective pH- absorbance curves. The plateau of the curves represented the completion of the reaction and consequently represented the optimum pH.

The composition of the complexes formed in solution was established by mole ratio and job methods. In both cases the results reveal (1:2) metal to ligand ratio. Chosen plots were represented in (Fig- 5). (Table- 4) summarizes the results obtained as conditions for the preparation of the complexes.

The apparent stability constant (K) of the (1:2) metal: ligand complex was evaluated spectroscopically by using the following equations:

$$K = \frac{1-\alpha}{4\alpha^{3}c^{2}} \quad \textbf{and} \quad \alpha = \frac{A_m - A_s}{A_m}$$

Where c = the concentration of the complex solution in mole/ L
α = degree of dissociation,As= the absorption of solution containing a stoichiometric amount of ligand and metal ion and Am= the absorption of solution containing the same amount of metal and excess of ligand.
The As and Am were measured at (λ_{max}) of solution. The values of (As, Am, α, K and log K) were tabulated in (Table- 5). The high values of K may reflect the high stability of the prepared complexes [25].

The solid complexes were prepared by direct reaction of alcoholic solution of the ligands with the aqueous solution of the metal ions at the optimum pH and in a (M: L) ratio of (1: 2).

The (C. H. N) and chloride analysis with metal contents of these complexes were in good agreements with the calculated values (Table-6). High melting points (> 360 °C) were recorded for these complexes.

The molar conductance of the complexes as (10^{-3} M) in DMF and in methanol, lies in the ranges (3.37- 17.53) and (2.12- 14.37) $S.cm^2.mol^{-1}$ respectively, indicating their non-electrolytic nature[26], therefore, the two (Cl) ions was considered to be coordinated with the metal ion. The physical and analytical data of the prepared complexes were given in (Table-7).

The effective magnetic moments of Co(II) complexes lie in the range (3.45- 3.70) B.M. This value refers to a paramagnetic (high spin) planar structure for these complexes. In the case of Ni (II) complexes, the magnetic moments lie in the range (2.33- 3.08) B. M which has been reported for most octahedral nickel (II) complexes[27]. The magnetic moments of Cu (II) complexes lie in the range of (1.62-1.86) B.M. indicating the presence of an unpaired electron and the complex is not a dimer.

The UV- Vis spectra of the prepared complexes dissolved in methanol (10^{-3} M) have been measured and the data obtained were included in (Table- 7).Again the large bathochromic shift of the (λ_{max}) assigned to (π- π^*) transition of the ligand suggesting the involvement of the ligand in the bond formation with the metal ion.

In order to study the binding mode of the new ligands (L_1, L_2 and L_3) with the metal ions, a comparison was made for the FT IR spectra of the free ligands and those of the prepared complexes and the data was tabulated in (Table- 8). The IR spectra of the three ligands exhibited three bands in the ranges (3460- 3406) cm^{-1}, (3330- 3070) cm^{-1} and (3260- 3070) cm^{-1} which were assigned to the stretching modes of υ(OH), υ(- NH) of the primary amine , and υ(-NH) of the imidazole ring respectively[28,29]. Since no significant changes in these bands were noticed, the possibility that coordination occurs via the donating atoms in these groups were excluded. Strong band in the ligands spectra was observed in the range (1639- 1631) cm^{-1} ascribed to the υ(C= N) for the imidazole ring [30]. Significant change was observed in this band on coordination with metal ion, it is either disappeared or appeared as a weak shoulder. This change may confirm the involvement of the imidazole nitrogen in bonding. The strong characteristic band in the free ligand spectra at (1413- 1409) cm^{-1} which was assigned to the (-N= N-) stretching [31,32] suffered a great change in the intensity and in position, splitting to lower frequency was also observed on complexation with metal ion. This may suggest the participation of the azo nitrogen in this complexation.

Two new stretching bands were noticed around (480- 418) cm^{-1} which were assignable to the υ(M- N) of the azo group and the imidazole ring[33,34] Another weak new band was also appeared around 410 cm^{-1} which attributed to the υ(M-Cl) mode.

The (^{1}HNMR) spectra in DMSO (Fig-6),for one of the prepared complexes have been measured for reason of comparison. The signal belongs to the (NH) of the imidazole was shifted to higher region (lower frequency) (δ= 8.38) with respect to that of the ligand (δ= 8.87). Change was observed in the shape and position of the multiplet signals belong to the protons of the benzene ring (δ= 8.16- 7.46). These signals were observed in the ligand spectra at (δ=8.13 -7.79). The (CH) signal of the imidazole ring was shifted to lower region (δ=7.13), this was recorder at (δ=6.78) for the free ligand. On the other hand, the triplet(δ= 3.56,2.95 and 2.34) and the doublet (δ= 2.21 and 2.14) refer to aliphatic (CH) and (CH_2) and the singlet(δ= 2.33) belongs to (CH_3) protons of the acetyl group, were also undergo shift to higher region, while the (NH_2) proton signal(δ= 1.23) stays nearly at same position as that of the free ligand.

On the basis of these evidences, it is concluded that the ligands (L_1, L_2 and L_3) behave as neutral bidentate molecules coordinating through the azo and the imidazole nitrogen. Therefore, the suggested structure of the prepared complexes can be illustrated as in (Fig-7).

The dyeing performance of the prepared ligand and some of their complexes was assessed on cotton fabric. The dyes were tested for light and detergent fastness. Thus all dyes showed very good dyeing properties, they provided colors as orange, brown, red and finally pink with good brightness and depth on the fabric. Some of the dyeing were shown on (Fig-8).

Finally, the biological activities of the ligand and their complexes have also been tested against selected type of bacteria.The results show that the Hg-complexes and Ni-L_1 complex show a relatively strong activating capacity. Whereas, all the parents ligands possessed no activity towards the same specimen of bacteria.

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Table (1): Physical Properties of the Ligands

Ligand	Name	Wt. of Amine (g)	Color	m. p°c	Yield%
L_1	2-(p-Acetophenone azo)-α-amino- 1H- imidazole- 4-propionic acid	0.337	Deep Brown	140-142	81.85
L_2	2-(p-Benzoicacid azo)-α-amino-1H- imidazole- 4- propionic acid	0.342	Yellowish Orange	210-212	75.32
L_3	2-(m-Acetophenone azo)-α-amino- 1H- imidazole- 4-propionic acid	0.337	Orange Brown	192-194	83.74

Table (2): Reaction Conditions and Some Physical Properties of the Complexes

Complexes	Wt. of Ligand (g)	Wt. of Metal Ion (g)	pH	color	Yield %
$[Co(L_1)_2Cl_2]$	0.301	0.118	6.5	Reddish Brown	72
$[Ni(L_1)_2Cl_2]$	0.301	0.118	6.5	Brown	80
$[Cu(L_1)_2Cl_2]$	0.301	0.085	7	Deep Violet	82
$[Zn(L_1)_2Cl_2]$	0.301	0.068	6.5	Reddish Brown	77
$[Cd(L_1)_2Cl_2]$	0.301	0.100	7	Orange	73
$[Hg(L_1)_2Cl_2]$	0.301	0.135	6	Reddish Orange	65
$[Co(L_2)_2Cl_2]$	0.303	0.118	6	Brown	76
$[Ni(L_2)_2Cl_2]$	0.303	0.118	7	Reddish Brown	74
$[Cu(L_2)_2Cl_2]$	0.303	0.085	7	Yellowish Green	71
$[Zn(L_2)_2Cl_2]$	0.303	0.068	6.5	Yellow	84
$[Cd(L_2)_2Cl_2]$	0.303	0.100	6	Reddish Orange	79
$[Hg(L_2)_2Cl_2]$	0.303	0.135	7	Orange	70
$[Co(L_3)_2Cl_2]$	0.301	0.118	6.5	Brown	88
$[Ni(L_3)_2Cl_2]$	0.301	0.118	6.5	Dark Green	85
$[Cu(L_3)_2Cl_2]$	0.301	0.085	7	Dark Brown	89
$[Zn(L_3)_2Cl_2]$	0.301	0.068	6	Reddish Orange	86
$[Cd(L_3)_2Cl_2]$	0.301	0.100	6	Reddish Orange	78
$[Hg(L_3)_2Cl_2]$	0.301	0.135	6	Reddish Brown	89

Table (3): Mass Spectral Data of the Ligands L_2 and L_3

L_2		
Fragment	m/z	Relative abundance
Parent Ion	303	7
$C_{11}H_{13}N_5^{+}$	215	2
$C_9H_6N_4^{\cdot+}$	170	5
$C_9H_7N_2^{+}$	143	4
$C_5H_7N_5^{\cdot+}$	137	67
$C_7H_4O_2^{\cdot+}$	120	88
$C_5H_6N_3^{\cdot+}$	108	4
$C_4H_3N_3^{\cdot+}$	93	69
$C_5H_6^{+}$	78	13
$C_3HN_2^{\cdot+}$	65	65
L_3		
Parent Ion	301	9
$C_5H_5N_3^{\cdot+}$	135	96
$C_8H_7O^{+}$	120	92
$C_5H_4N_3^{\cdot+}$	106	4
$C_5H_2N_3^{\cdot+}$	92	100
$C_6H_6^{+}$	78	17
$C_3HN_2^{\cdot+}$	65	85

Table (4): Conditions for the Preparation of the Complexes

Ligand	Co(II) Complexes			Ni(II) Complexes			Cu(II) Complexes		
	Optimum pH	Optimum molar Conc. $\times10^{-4}$	M:L Ratio	Optimum pH	Optimum molar Conc. $\times10^{-4}$	M:L Ratio	Optimum pH	Optimum molar Conc.$\times10^{-4}$	M:L Ratio
L_1	6.5	2	1:2	6.5	2.5	1:2	7	1.5	1:2
L_2	6	2	1:2	7	2	1:2	7	2.5	1:2
L_3	6.5	2	1:2	6.5	2	1:2	7	2	1:2
Ligand	Zn(II) Complexes			Cd (II) Complexes			Hg (II) Complexes		
	Optimum pH	Optimum molar Conc. $\times10^{-4}$	M:L Ratio	Optimum pH	Optimum molar Conc. $\times10^{-4}$	M:L Ratio	Optimum pH	Optimum molar Conc.$\times10^{-4}$	M:L Ratio
L_1	6.5	2	1:2	7	3	1:2	6	2.5	1:2
L_2	6.5	2.5	1:2	6	2.5	1:2	7	2.5	1:2
L_3	6	2	1:2	6	2.5	1:2	6	3	1:2

Table (5): Stability Constants of the Prepared Complexes

L_1					
Complex	A_S	A_M	α	K	Log K
Co(II)	0.112	0.173	0.352	1.080×10^8	8.033
Ni(II)	0.200	0.421	0.524	1.322×10^7	7.121
Cu(II)	0.180	0.242	0.256	7.440×10^8	8.871
Zn(II)	0.248	0.512	0.515	2.309×10^7	7.363
Cd(II)	0.148	0.280	0.471	1.430×10^7	7.155
Hg(II)	0.355	0.638	0.443	2.652×10^7	7.423
L_2					
Complex	A_S	A_M	α	K	Log K
Co(II)	0.195	0.302	0.354	9.228×10^6	6.965
Ni(II)	0.360	0.552	0.347	1.088×10^7	7.036
Cu(II)	0.161	0.221	0.271	1.822×10^7	7.260
Zn(II)	0.162	0.291	0.443	2.652×10^7	7.423
Cd(II)	0.394	0.798	0.506	1.543×10^7	7.188
Hg(II)	0.215	0.422	0.490	1.758×10^7	7.245
L_3					
Complex	A_S	A_M	α	K	Log K
Co(II)	0.056	0.121	0.537	1.929×10^7	7.285
Ni(II)	0.086	0.173	0.503	2.485×10^7	7.395
Cu(II)	0.118	0.205	0.424	4.800×10^7	7.681
Zn(II)	0.154	0.243	0.366	9.057×10^7	7.956
Cd(II)	0.727	1.281	0.432	2.989×10^7	7.475
Hg(II)	0.329	0.543	0.394	2.750×10^7	7.440

Table (6): Elemental Analysis Data for the prepared Complexes

Ligand	Co (II) Complexes					Ni (II) Complexes				
	C%	H%	N%	M%	Cl%	C%	H%	N%	M%	Cl%
L_1	-	-	-	8.05 (7.80)	9.70 (9.37)	-	-	-	8.02 (7.50)	9.70 (8.15)
L_2	-	-	-	8.01 (7.90)	9.65 (9.20)	-	-	-	7.97 (7.50)	9.64 (8.51)
L_3	-	-	-	8.05 (7.70)	9.70 (8.50)	-	-	-	8.02 (7.86)	9.70 (9.22)
Ligand	Cu (II) Complexes					Zn (II) Complexes				
	C%	H%	N%	M%	Cl%	C%	H%	N%	M%	Cl%
L_1	-	-	-	8.68 (8.23)	9.63 (9.35)	-	-	-	8.81 (8.43)	9.62 (9.22)
L_2	-	-	-	8.64 (8.34)	9.59 (9.20)	42.10 (43.08)	3.50 (3.19)	18.89 (18.60)	8.76 (8.49)	9.57 (9.15)
L_3	48.95 (48.95)	4.10 (4.11)	19.00 (19.33)	8.68 (8.31)	9.63 (8.50)	-	-	-	8.81 (8.62)	9.62 (9.28)
Ligand	Cd (II) Complexes					Hg (II) Complexes				
	C%	H%	N%	M%	Cl%	C%	H%	N%	M%	Cl%
L_1	-	-	-	14.27 (14.30)	9.04 (8.73)	-	-	-	22.90 (21.98)	8.13 (7.80)
L_2	-	-	-	14.20 (14.11)	9.00 (8.57)	-	-	-	22.82 (22.63)	8.10 (7.80)
L_3	-	-	-	14.27 (14.22)	9.04 (8.75)	-	-	-	22.90 (22.10)	8.13 (7.90)

Table (7): UV- Vis, Magnetic Susceptibility and Conductance Measurements Data

Compounds	$\lambda_{(max)}$ (nm)	$\epsilon_{max} \times 10^3$ L. Mol.$^{-1}$ Cm^{-1}	μ_{eff} (B.M)	Λ_m (S.cm^2. mol^{-1})	
				In DMF	In Methanol
[Co $(L_1)_2$ Cl_2]	455	0.243	3.61	15.32	13.62
[Ni $(L_1)_2$ Cl_2]	459	0.644	2.33	11.10	8.57
[Cu $(L_1)_2$ Cl_2]	476	0.155	1.62	12.49	6.63
[Zn $(L_1)_2$ Cl_2]	461	0.282	-	9.53	6.52
[Cd $(L_1)_2$ Cl_2]	475	0.415	-	3.37	2.54
[Hg $(L_1)_2$ Cl_2]	475	1.255	-	4.09	2.30
[Co $(L_2)_2$ Cl_2]	458	0.512	3.45	5.27	3.43
[Ni $(L_2)_2$ Cl_2]	463	0.624	2.42	6.12	4.83
[Cu $(L_2)_2$ Cl_2]	471	0.248	1.86	20.3	13.36

[Zn $(L_2)_2$ Cl_2]	456	0.102	-	8.51	5.74
[Cd $(L_2)_2$ Cl_2]	467	0.382	-	4.87	2.12
[Hg $(L_2)_2$ Cl_2]	444	0.279	-	4.85	2.80
[Co $(L_3)_2$ Cl_2]	519	0.216	3.70	15.84	12.77
[Ni $(L_3)_2$ Cl_2]	512	0.212	3.08	16.52	14.37
[Cu $(L_3)_2$ Cl_2]	532	0.970	1.61	10.74	8.77
[Zn $(L_3)_2$ Cl_2]	587	0.553	-	10.48	8.84
[Cd $(L_3)_2$ Cl_2]	522	1.254	-	3.84	2.84
[Hg $(L_3)_2$ Cl_2]	527	0.377	-	3.54	2.54

Table (8) :The Main Frequencies of the Ligands and Their Complexes(cm^{-1})

Comp.	υ (O-H)	υ(N-H) Prim + υ(N-H) Imid		υ(C=O) + υ(C=N)	δ(N-H) prim	δ(N-H) Imid	υ(N=N)		υ(M-Nazo) + υ(M-N_{Imid})
L_1	3460 br.	3231 3175	br.d.	1631 s.	1587 v.s	1500 w.	1409 v.s.		-
$[Co(L_1)_2Cl_2]$	3458 br.	-		-	1595 s.	1519 w.	1421 m.		480 w.
$[Ni(L_1)_2Cl_2]$	3444 v.s.	-		1640 w.sh.	1595 v.s.	1519 w.	1420 m.		466 w.
$[Cu(L_1)_2Cl_2]$	3460 br.s.	3261 3160	Sh.d.	1637 w.sh.	1598 s.	1500 w.	1429 s. 1375 sh.	d.	468 w.
$[Zn(L_1)_2Cl_2]$	3460 br.	3250 3165	Sh.d.	1635 w.sh.	1593 s.	1519 v.w.	1439 1385	s.d.	468 w.
$[Cd(L_1)_2Cl_2]$	3450 br.	3240 3100	br.d.	1640 w.sh.	1589 v.s.	1518 v.w.	1411 s.		480 w. 435 w.
$[Hg(L_1)_2Cl_2]$	3477 w.br.	3240 3100	v.w.d.	1643 v.w. sh.	1595 v.s.	1519 m.	1426 1377	s.d.	470 w. 445 w.
L_2	3406 m.	3070	br.	1639 s.	1595 s.	1504 v.s.	1413 s.		-
$[Co(L_2)_2Cl_2]$	3406 m.	3100	br.	1645 m.	1600 m.	1504 s.	1408 s. 1400 sh.	d.	433 w.
$[Ni(L_2)_2Cl_2]$	3406 br.	3100	br.	1629 .sh.	1600 s.	1506 m.	1406 1399	s.d.	435 w.
$[Cu(L_2)_2Cl_2]$	3406 br.	3249 3120	br.d	1642 sh.	1602 s.	1502 m.	1402 v.s. 1368 sh.	d.	433 w.
$[Zn(L_2)_2Cl_2]$	3404 m.	3160sh. 3072br.	d.	1636 sh.	1598 v.s.	1508 s.	1429 v.s. 1380 sh.	d.	460 w. 430 w.
$[Cd(L_2)_2Cl_2]$	3404 m.	3160sh. 3068br.	d.	1637 m.	1595 v.s.	1508 m.	1400 v.s.		470 w. 450 w.
$[Hg(L_2)_2Cl_2]$	3406 v.w.	32189 3070	br.d	1632 v.w. sh.	1596 s.	1508 w.	1429 1396	s.d.	480 w. 418 w.
L_3	3444 s.	3330 3260	s.d.	1633 s.	1595 v.s.	1514 m.	1407 v.s.		-
$[Co(L_3)_2Cl_2]$	3355 br.	3330 br.		1637 w.sh.	1590w.	1514 m.	1460 1427	m.d.	460 w. 418 w.
$[Ni(L_3)_2Cl_2]$	3365 br.	3330 br.		1640 sh.	1590 m.	1512 m.	1440 w. 1421 m.	d.	470 w. 420 w.
$[Cu(L_3)_2Cl_2]$	3380 br.	-		1640 sh.	1593 m.	1506 m.	1429 1418	m.d.	470 w. 418 w.
$[Zn(L_3)_2Cl_2]$	3508 w. br.	3263 3160	br.d	1638 sh.	1598 s.	1508 m.	1429 1398	m.d.	480 w. 430 w.
$[Cd(L_3)_2Cl_2]$	3461 s.br.	3344 3160 3080	Sh.T	1639 v.w.sh.	1593 s.	1506 w.	1434 1396	m.d.	468 w. 420 w.
$[Hg(L_3)_2Cl_2]$	3458 s.br.	3260 3100	s.d.	1638 v.w.sh.	1596 s.	1508 w.	1429 1396	m.d.	470 w. 440 w.

Prim = primaryamine , Imid= Imidazole, v.s.=verystrong, m= medium, w=weak, br=broad, d=doublet, sh= shoulder.

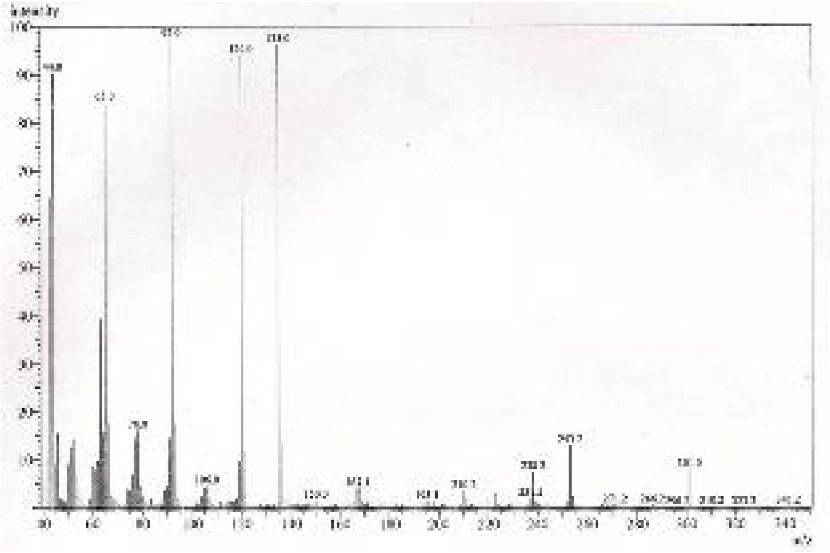


Fig.(1) Mass Spectrum of Ligand L_3

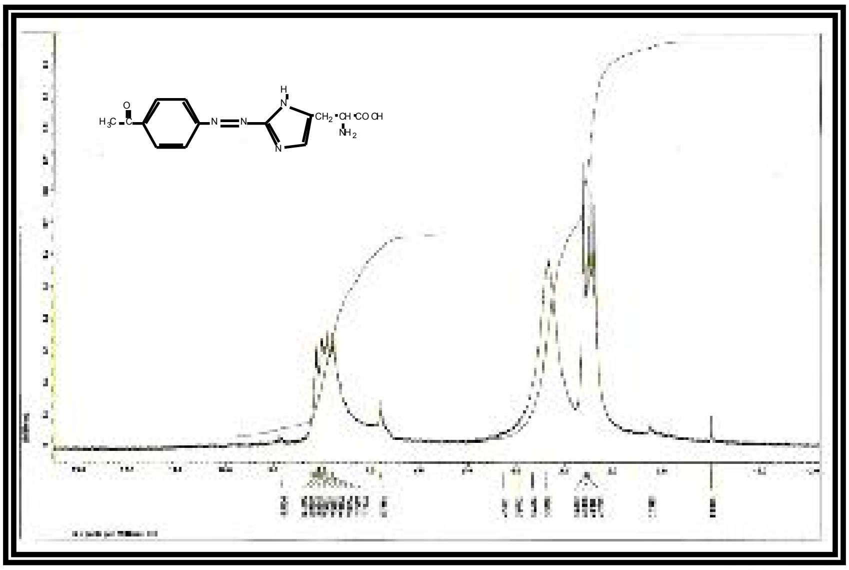


Fig. (2) ^{1}HNMR Spectrum of the Ligand L_1

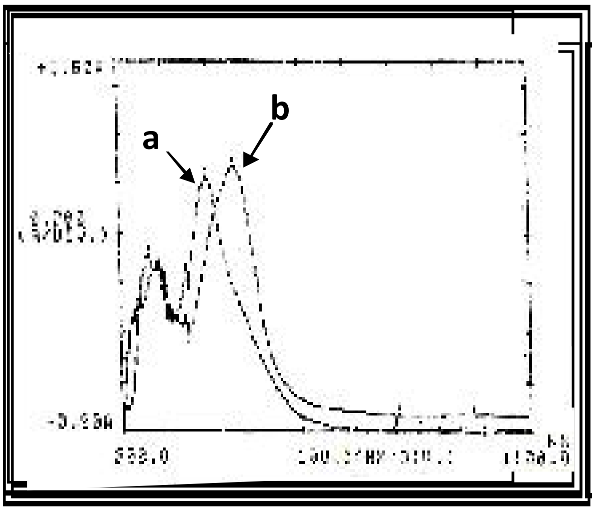


Fig. (3): UV- Vis Spectra of a-Free Ligand at Solution b-Cd^{II}-L_1 Mixed Solution

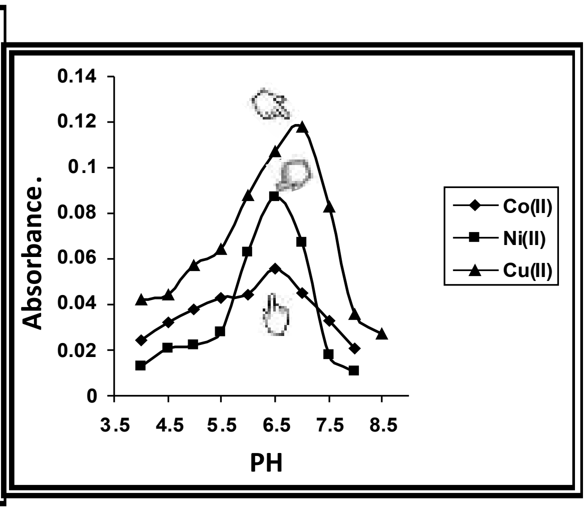


Fig. (4): Effect of pH on Absorbance (λ_{max}) for L_3 - Complexes Solutions

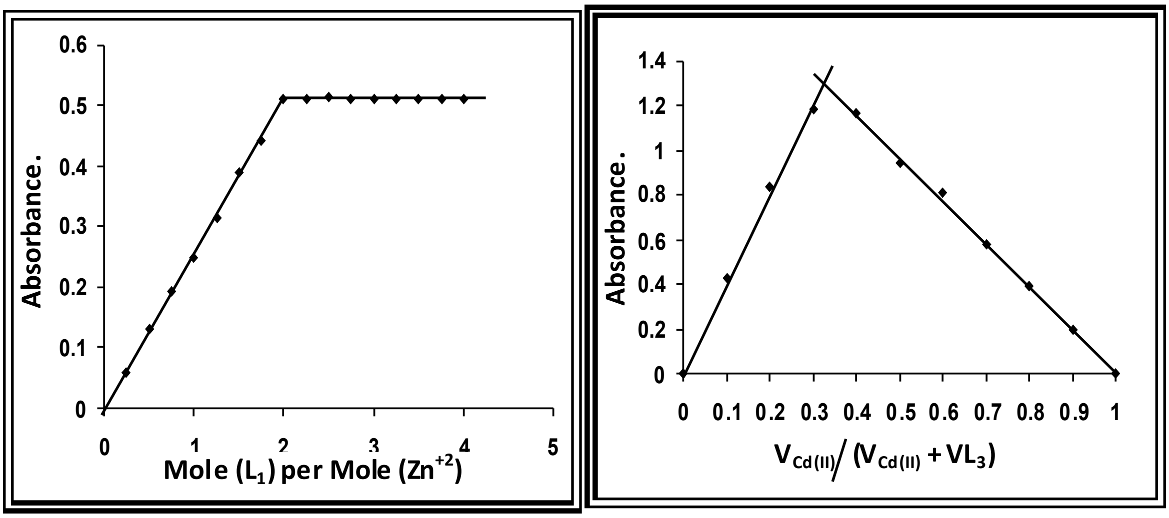


Fig. (5): Mole ratio and Job Methods for Complexes Solutions

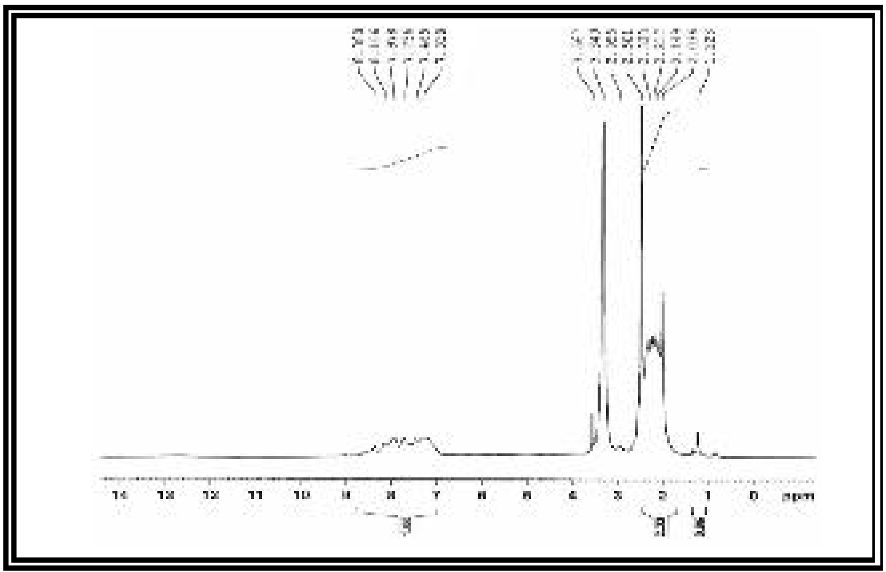
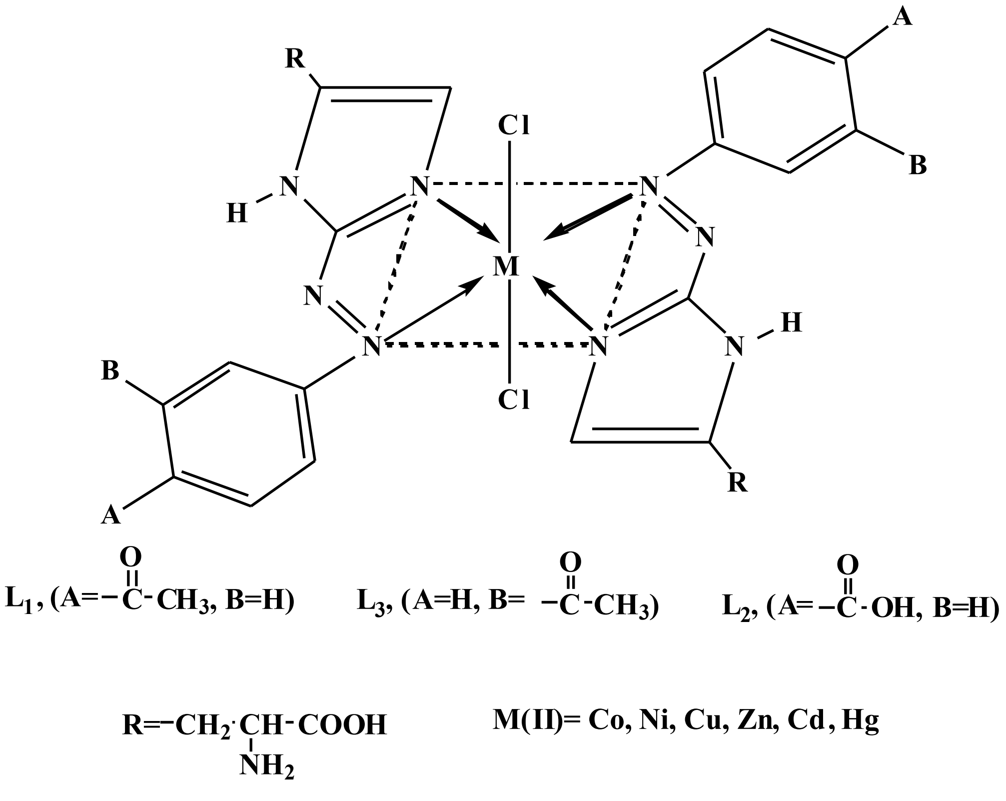


Fig. (6) : ^{1}HNMR Spectrum of the Complex $[Cd(L_1)_2Cl_2]$



L_1, (A= $-\overset{O}{\overset{\|}{C}}-CH_3$, B=H) L_3, (A=H, B= $-\overset{O}{\overset{\|}{C}}-CH_3$) L_2, (A= $-\overset{O}{\overset{\|}{C}}-OH$, B=H)

R= $-CH_2-\underset{NH_2}{\underset{|}{CH}}-COOH$ M(II)= Co, Ni, Cu, Zn, Cd, Hg

Fig. (7) :The Suggested Structure of the Prepared Complexes

Fig. (8): Dyeing of Cotton by Some Ligands and its Complexes

تحضير ودراسة طيفية لمعقدات بعض الأيونات الفلزية المنتخبة مع صبغات ازو غير متجانسة الحلقة جديدة ومتابعة ادائها كصبغات

ثناء جعفر الحسني، عامر جبار جراد
قسم الكيمياء، كلية العلوم، جامعة بغداد

الخلاصة

حضرت ليكاندات (L_3,L_2,L_1) جديدة من تفاعل ازدواج بارا– امينو حامض البنزويك وبارا –وميتا – امينو اسيتوفينون مع (الهستدين). شخصت الليكاندات المحضرة بوساطة أطياف الأشعة تحت الحمراء وفوق البنفسجية– المرئية، والرنين النووي المغناطيسي للبروتون، وطيف الكتلة – كروموتوغرافيا الغاز. تمت مفاعلة هذه الليكاندات مع بعض الايونات الفلزية المنتخبة ($Hg^{II},Cd^{II},Zn^{II},Cu^{II},Ni^{II},Co^{II}$) في وسط ايثانول – ماء وبنسبة فلز: ليكاند (2:1) وفي الدالة الحامضية المثلى، وخضعت محاليل هذه المعقدات لقانون لامبرت –بير ضمن مدى التراكيز (1×10^{-4} - 3×10^{-4} M) وتم الحصول على سلسلة من المعقدات ذي الصيغة العامة $[M(L)_2Cl_2]$.

شخصت هذه المعقدات باستخدام تقنية الامتصاص الذري اللهبي، أطياف الأشعة تحت الحمراء والأشعة فوق البنفسجية – المرئية وطيف الرنين النووي المغناطيسي للبروتون فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية .كما قدر محتوى الكلور باستخدام طريقة مور. درست تراكيب المعقدات باستخدام طريقتي النسب المولية والمتغيرات المستمرة ،كما حسبت استقرارية المعقدات المحضرة .

لقد تمت الإفادة من الليكاندات والمعقدات قيد الدراسة حول إمكانية استخدامها كأصباغ لصباغة الأنسجة القطنية نظرا لما تتميز به هذه المركبات من ألوان زاهية .وقد تبين أن ألوانها ثابتة وذا مقاومة عالية للغسل والمنظفات ولضوء الشمس، كذلك درست الفاعلية البايولوجية ووجد أن لهذه المعقدات قابلية متباينة على قتل الأنواع المنتخبة من البكتريا.