Synthesis and Spectral Studies of Zn^{II},Cd^{II} and Hg^{II} Complexes with 5-(2-Benzoic acid azo)-8-hydroxy quinoline Ligand

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Abstract:

Coupling reaction of 2-amino benzoic acid with 8-hydroxy quinoline gave bidentate azo ligand. The prepared ligand has been identified by Microelemental Analysis,^{1}HNMR,FT-IR and UV-Vis spectroscopic techniques. Treatment of the prepared ligand with the following metal ions (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 $[M(L)_2]$. The prepared complexes have been characterized by using flame atomic absorption, (C.H.N) Analysis, FT-IR and UV-Vis spectroscopic methods as well as conductivity measurements. The nature of the complexes formed were 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 have been observed. The stability constant of the complexes has also been studied.

Key words:Azo-dyes, synthesis, azo complexes

Introduction:

Acid dyes have found wide application in dyeing wool, polyamide fibers and blends of both these fibers but they have to meet very high requirements as regards their application and fastness[1]. The development of new structures of azo dyes has been a subject of interest and many novel structure of these dyes, useful in the commercial application to polyester, polyamide or poly acrylic as well as their blends with other fibers[2-6]. Azo dyes were known to be largely non-biodegradable in aerobic conditions and to be reduced to more hazardous intermediates in anaerobic conditions[7]. It is well known that O,O-dihydroxo azo dyes and their metal complexes were principally chromium and cobalt complexes for obtaining dyeing protein and polyamide fibers with excellent light and wash fastness [8]. Azo dyes with the heterocyclic diazo component from colored complexes with many metal ions in solution[9,10]. In recent years we have been interested of azo dyes in coordination chemistry[11]. In this work, we synthesized azo dye derived from 2-amino benzoic acid as diazo component and 8-hydroxy quinoline as coupling agent. The complexes of this ligand with some metal ions have also been studied and characterized physciochemically.

Materials and Methods:

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. Atomic absorption were

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obtain by using a(Shimadzu A.A-160A) Atomic Absorption/Flame Emission Spectrophotometer. The ^{1}HNMR spectra were obtained on a (Brucker- 300 MHz Ultra Shield) University of Al- al- Bayt using DMSO as a solvent and (TMS) as a reference. Microelemental analysis (C. H. N) was 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^{o}C using (Philips PW- Digital Conductimeter). In addition, melting points were obtained by using (Stuart Melting Point Apparatus).

Materials and Reagents

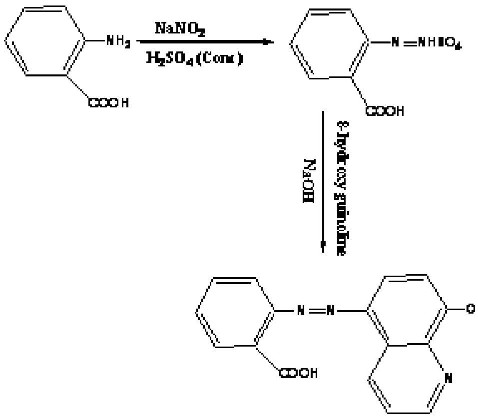
The following chemicals were used as received from suppliers; zinc chloride 98.8%, cadmium chloride monohydrate 99.9%, mercury chloride 98% (Merck) 2- amino benzoic acid 98.8%, 8-hydroxy quinoline 99% (B. D. H).

The pH of the medium (4-8) were adjusted with ammonium acetate –ammonia – glacial acetic acid buffer solution .

Solutions were made of the ligand (1×10^{-5}-1×10^{-3} M) in absolute ethanol and same concentration range of metals salts in buffer solutions.

Preparation of the Ligand[12]

(0.34g, 1mmole) of 2- amino benzoic acid has been dissolved in a mixture of (2 ml) sulphuric acid, (10 ml) ethanol and (10 ml) distilled water, and diazotized at 5^{o}C with sodium nitrite solution. The diazo solution was added dropwise with stirring to a cooled ethanolic solution of (0.36g, 1mmole) of 8-hydroxy quinoline. (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 the physical properties and elemental analysis.



Scheme (1): Preparation of the Ligand.

Table (1):- Physical Properties and Elemental Analysis of the Complexes.

Compounds	Color	M.P°C	Yield%	Analysis Calc.(Found)			
				M%(Metal)	C%	H%	N%
Ligand	Reddish Violet	193	81	-	65.53 (65.02)	3. 75 (3.21)	14.33 (13.93)
$[Zn(L)_2]$	Brown	>360	74	10.01 (9.64)	59.16 (58.88)	3.08 (2.97)	12.94 (12.27)
$[Cd(L)_2]$	Red	>360	87	16.14 (15.22)	55.14 (55.11)	2.87 (2.43)	12.06 (11.85)
$[Hg(L)_2]$	Orange	>360	77	25. 60 (24. 81)	48.91 (48.72)	2.54 (2.07)	10.70 (10.30)

Preparation of Metal Complexes (general procedure)

An ethanolic solution of the ligand (0.293g,2mmole) has been added gradually with stirring to the 0.068g,0.10g and 0.135g (1mmole) of $ZnCl_2$,$CdCl_2.H_2O$ and $HgCl_2$ respectively dissolved in the buffer solution of the required pH. The mixture has been cooled until dark color precipitate was formed, filtered and washed several times with (1: 1) water: ethanol then with acetone

Results and Discussion:

The ligand has been prepared by coupling 8-hydroxy quinoline with the appropriate diazotate in alkaline solution. The ligand sparingly soluble in water but soluble in organic solvents,stable toward air and moisture.

The synthesized ligand has been characterized by ^{1}HNMR, FT.IR and UV-Vis spectroscopic technique.

The ^{1}HNMR spectrum of the ligand in DMSO (Fig-1) shows multiplet signals at (δ=6.915-8.097 ppm) refers to aromatic protons [13].On the other hand, the signal at (δ=6.630 ppm) due to proton of phenol. Whereas, the signal at (δ=12.432 ppm) is assigned to proton of carboxylic group and the signal peak at(δ=2.495ppm referred to DMSO-d6[14] .

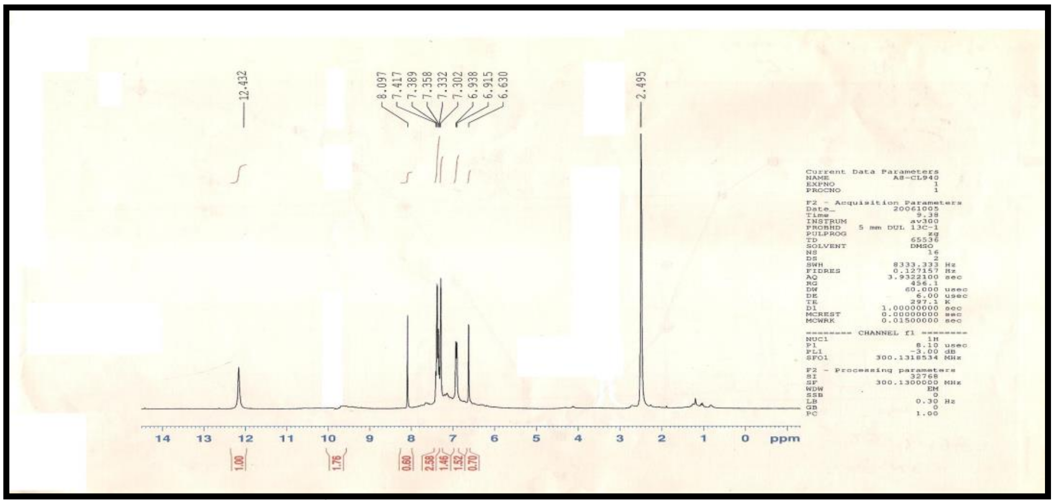


Fig.(1): ^{1}HNMR Spectrum of the Ligand.

The UV- Vis spectrum of an ethanolic solution of the ligand (10^{-3} M) displayed mainly three peaks, the first and second peaks were observed at (224 nm) and (263 nm) were assigned to the moderate energy π- π^{*} transition of the aromatic rings. The third peak (λ_{max}) was observed at the (444 nm) was referred to the π- π^{*} transition of intermolecular charge-transfer taken place from benzene through the azo group(-N=N) [15].

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

The interaction of the metal ion with the ligand manifest itself in the absorption spectra by the appearance of a peak in the range (532- 589 nm). A great bathochromic shift in the visible region has been 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-2) showed a comparison between the spectra of the ligand and Zn^{II} mixed solution.

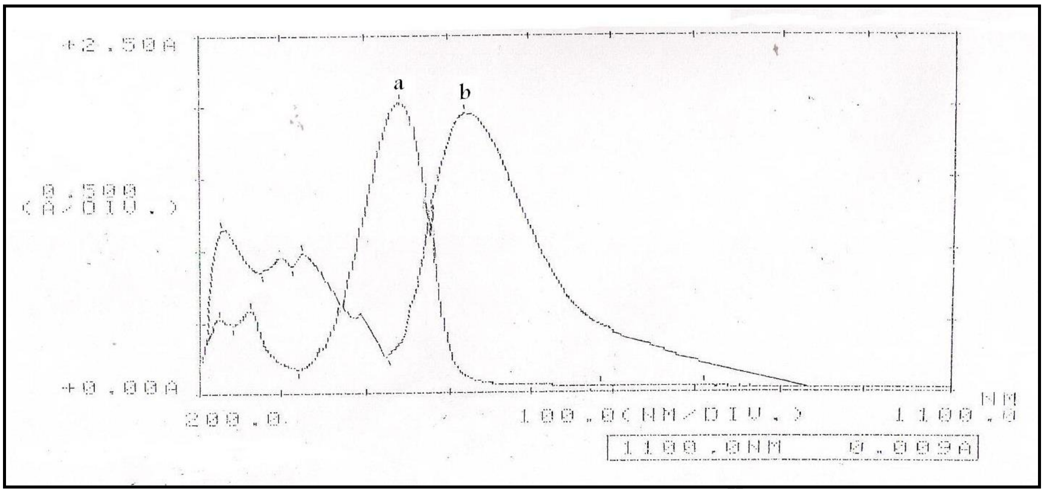


Fig.(2): UV-Vis spectra of a- free Ligand Solution b- Zn^{II}- L Mixed Solution.

From the wide studied range of molar concentration (10^{-5}-10^{-3} M) of the mixed solutions, only 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 (Fig-3) with correlation factor R> 0.998.

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

The influence of pH was also studied at pH range (4-8) 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 represent the completion of the reaction and consequently represent the optimum pH.

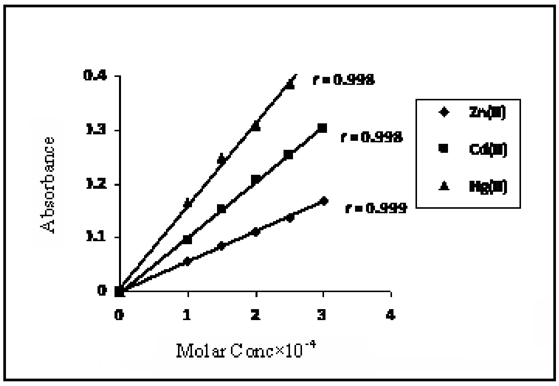


Fig.(3): Linear Relation Between Molar Concentration and Absorbance.

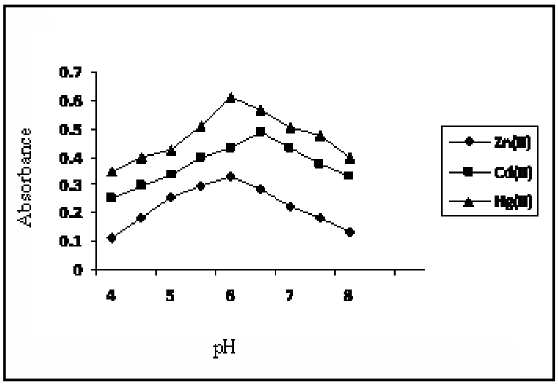


Fig.(4): Effect of pH on Absorbance (λ_{max}) for Complexes.

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

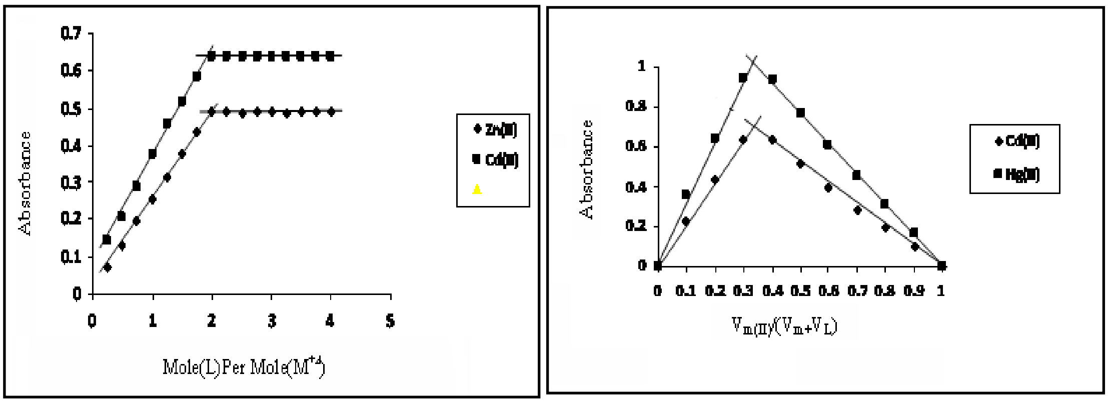


Fig.(5): Mole Ratio and Job Methods for Complexes Solutions.

Table (2):- Conditions for the Preparation of the Complexes and UV-Vis and Conductance Measurements Data.

Compounds	**Optimum pH**	**Optimum Molar Conc. x 10^{-4}**	**M:L Ratio**	**(λ_{max}) nm**	**ABS**	**ϵ_{max} (L.mol^{-1}.cm^{-1})**	**Λ_m(S.cm^2.mol^{-1}) In Absolute ethanol**
Ligand	-	-	-	444	2.027	2027	-
$[Zn(L)_2]$	6	2	1:2	532	0.296	296	12.36
$[Cd(L)_2]$	6.5	2.5	1:2	595	0.216	216	15.81
$[Hg(L)_2]$	6	2	1:2	589	0.740	740	10. 75

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

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

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-3). The high values of K may reflect the high stability of the prepared complexes [16].

Table (3):- Stability Constant of the Prepared Complexes.

Complexes	**A_s**	**A_m**	**α**	**k**	**Log k**
$[Zn(L)_2]$	0.255	0.488	0.477	3.07×10^5	5.487
$[Cd(L)_2]$	0.378	0.637	0.406	7.89×10^7	7.897
$[Hg(L)_2]$	0.416	0.944	0.560	1.57×10^7	7.195

The solid complexes have been prepared by direct reaction of alcoholic solution of the ligand 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 metal contents of these complexes were in a good agreements with the calculated values .

The molar conductance of the complexes as (10^{-3} M) in ethanol indicating their non-electrolytic nature[17], the data have been recorded in (Table-2). The UV- Vis spectra of the prepared complexes dissolved in ethanol (10^{-3} M) have been measured and the data obtained were included in (Table- 2). 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 ligand with the metal ions, a comparison have been made for the FT. IR spectra of the free ligand and the prepared complexes and the data has been tabulated in (Table-4).

Table (4): - The Main Frequencies of the Ligand and Their Complexes (cm^{-1}) .

Compounds	ν(OH)carboxyl + ν(OH)phenol	ν(C=O)	ν $_{as}$(COO)	ν $_{s}$(COO)	ν(-N=N-) + ν (-C=N-N=C)	ν (M-O)	ν (M-N)
Ligand	3414 br. 3387 br.	1620 s.	1589 sh.	1497 sh.	1454 sh. 1411 sh. 1373 sh.	-	-
[Zn(L)$_2$]	3363 br.	1678 sh.	1573sho.	1543sh.	1485sh. 1392sh.	497w.	447w.
[Cd(L)$_2$]	3370br.	1670s.	1562sh.	1552s.	1490sh. 1380sho.	550w.	430w.
[Hg(L)$_2$]	3380br.	1680sh.	1570s.	1547sh.	1488s. 1387sh.	530w.	420w.

br = broad, s= strong, , sh = sharp, sho = shoulder, w = weak , as= asymmetric, s= symmetric

The IR spectrum of the ligand (Fig-6) exhibited broad band at (3414 cm^{-1}) has been assigned to the stretching vibration of υ(OH) of carboxyl group[18], disappearance of this band in the spectra of all complexes indicated the deprotonation of carboxyl prior to and indicated the coordination with the metal ion. The band at (3387 cm^{-1}) in the spectrum of the ligand refered to υ(OH) of phenol[19]. Strong band in the ligand spectrum has been observed at (1620 cm^{-1}) ascribed to the υ(C=O) for the carboxyl group[20]. Signifificant change in the position to higher frequency has been also observed on complexation with metal ion. The strong band in the free ligand spectrum at (1589 cm^{-1}) due to υ(COO) asymmetric vibration, significant change in the intensity and in position to lower frequency was observed on complexation with metal ion (Fig-7). The band at (1496 cm^{-1}) in the spectrum of the ligand was assigned to the υ(COO) symmetric, suffered a great change to higher frequency on complexation with metal ion[21]. Bands characteristic of the azo bridge vibration at (1454 cm^{-1}) and (1411 cm^{-1}), on complexes shiften with change in shape was observed indication the engagement of this group in the coordination with the metal ion[22,23]. The absence of new band around (550-497) and (447-420 cm^{-1}) due to metal nitrogen and oxygen respectively[24,25].

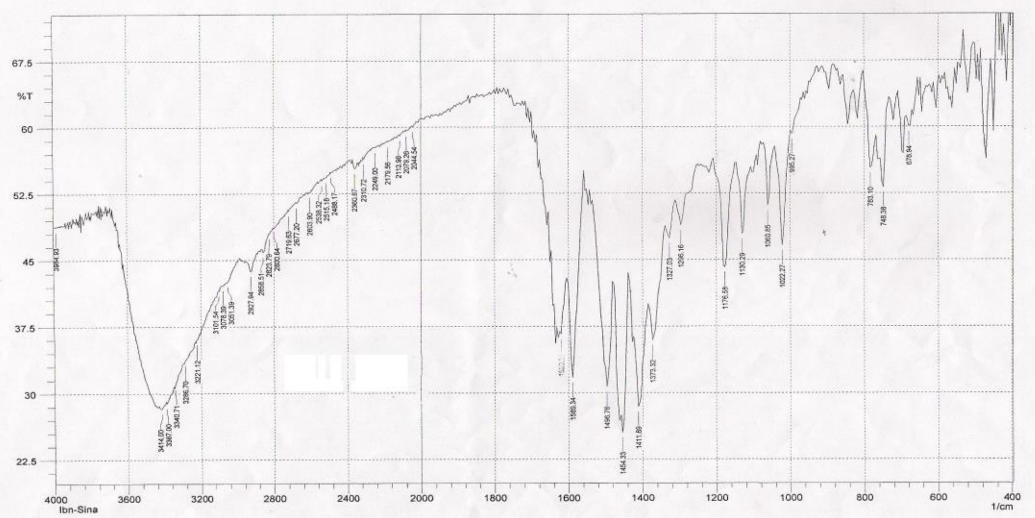


Fig.(6): FT.IR Spectrum of the Ligand.

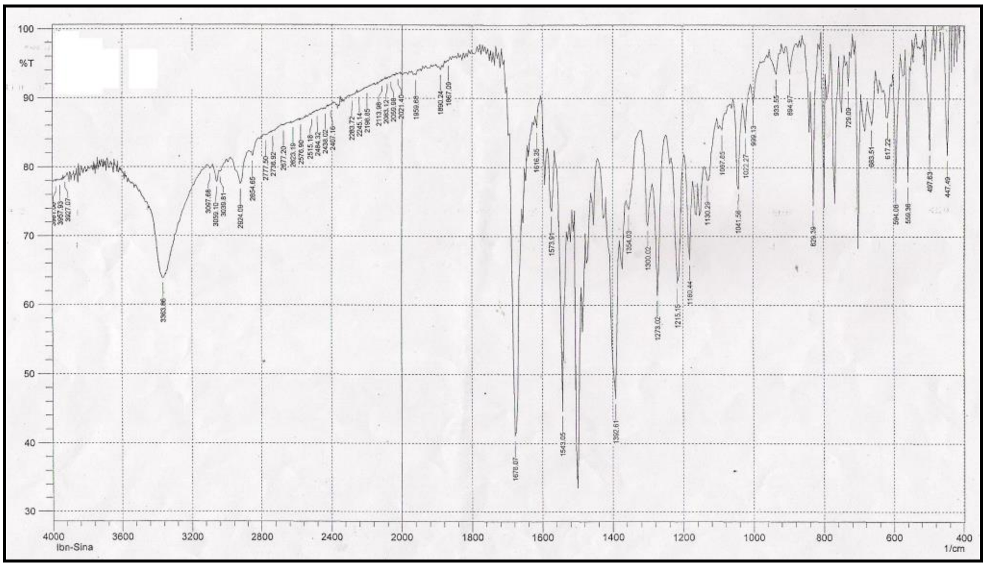
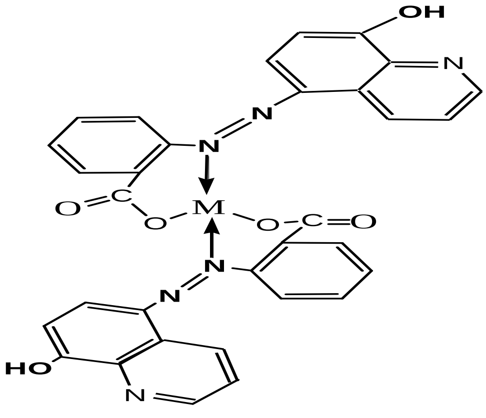


Fig.(7): FT.IR Spectrum of the $[Zn(L)_2]$ Complex.

According to the results obtained an tetrahedral structure has been suggested to these complexes.



M^{+2}=Zn,Cd,Hg

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تحضير و دراسة طيفية لمعقدات الزنك (II) والكادميوم (II) والزئبق (II) مع ليكاند 5-(2-بنزويك اسد آزو)-8-هيدروكسي كوينوين

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الخلاصة:

حضرت الليكاند 5-(2- بنزويك اسد ازو)- 8-هيدروكسي كوينولين من تفاعل ازدواج 2- امينو حامض البنزويك مع (8-هيدروكسي كوينولين). شخص الليكاند المحضر بوساطة أطياف الرنين النووي المغناطيسي ^{1}HNMR والأشعة تحت الحمراء وفوق البنفسجية- المرئية والتحليل الدقيق للعناصر(C.H.N) . تمت مفاعلة الليكاند مع بعض ألايونات ألفلزية المنتخبه (ZnII,CdII andHgII) 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 ذات الصيغة العامة $[M(L)_2]$. شخصت هذه المعقدات باستخدام تقنية الامتصاص الذري اللهبي، أطياف الأشعة تحت الحمراء والأشعة فوق البنفسجية – المرئية والتحليل الدقيق للعناصر(C.H.N) فضلا عن قياسات التوصيلية الكهربائية .درست تراكيب المعقدات باستخدام طريقتي النسب المولية والمتغيرات المستمرة ،كما تم حساب استقرارية المعقدات المحضرة .