Synthesis,Characterization,Thermal and Kinetic Photo Chemical Decomposition Study of New Azo Dye 7-[2-(BenzImidazolyl)Azo]-8-Hydroxy Quinoline and its Znic (II) Complex

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ABSTRACT

This research includes preparation and spectral identification of a new azo ligand7-[2-(Benzimidazolyl) azo]-8-Hydroxy quinoline (BIAHQ) by using UV-Vis, IR, 1H-NMR and mass spectra.The preparation of Zn(II)-complex of this ligand and identification by UV-Vis, IR radation spectrum,which characterized by elemental analysis.The analytical data shows that the metal to ligand ratio [M:L] of Zn(II)complex is 1:2.Decomposition kinetics was studied photochemical complex through irradiation solution complex single wavelength light λ=365 nm ,at temperature of 25 ˚C for 60 minutes and ethanol solvent was found to be the reaction from first order. Also,the calculated rate concetant photolysis kd mediated follow spectral changes during the process of irradiation . In order to reach the optimal conditions for the dissolution of the complex, it has been studied the impact of several factors on photochemical reaction of disintegration of the complex which include : Study the effects of the change in the intensity of light. More over disintegration of the complex has been studied in temperature range 15-30˚C, and studied the effects of the acidic function within range 3-9.The effects of several alcoholic solvents were studied on the rate of disintegration and these solvents are methanol, ethanol, isopropanol and1-butanol.Free ligand and Zn(II)complex were submitted to thermal analysis(TGA and DSC) activation thermodynamic data are calculated.

1- INTRODUCTION

The imidazole derivatives characterized ligands azo dyes of hetrocyclic compounds as highly effective against most of the periodic table as chemistry complexes.These ligands from a wide fied of in practice.It is well known that this type of compound has different atoms such as of oxygen and nitrogen for the link with the different elements and that small traces of these elements lead to inhibit of vitality activities (1-3).Using to azo imidazole in different fields that has used in medicine, science and technology,which givis results of great importance in life(4,5). The use of azo compounds depends on the chemical composition and method of application where generally used in the processes of dyeing wool(6), silk(7), cotton(8), rubber(9),print(10), plastic(11) .In the fact that some drugs including discouraging the growth of germs(12,13).The important uses of these compounds are analytical reagents(14-16)for solvent extraction to determine some metal ions.The azo imidazole compounds have important role in spectral determination field to identify the trance amount of elements especially transition metal ions because of its sensitivity(17)and selectivity(18,19

this class of azo dyes is a(-acidic) azo imine (-N=N-C=N-)for this reason a number of these dyes are synthizad and their abilities as chelating ligands(20,21).In this work,the authors report the preparation and spectral identification of new ligand which contiain mono azo group, and chelate complex with Zn(II)metal ion, and study kinetic under effect UV Radation .The thermal decomposition of this ligand and Zn(II) complex is studied , defferent activation thermodynamic data is calculated .

2-EXPERIMENTAL

2.1-Materials and Measurements

All chemicals and solvents were of highest purity from commercial suppliers such as BDH,Fluk, Merck and Aldrich.All chemicals are used without additional purification .Elemental analysis (C.H.N) was performed on a Euro EA 1106 elemental analyzer (Babylon University Iraq). FT-IR spectra of the ligand as well as the complexes were recorded as KBr discs in the range (400-4000)cm-1 on a FT-IR Teast scan shimaduz model 8400S.Electronic spectra were recorded on a UV-vis. Shimaduz model 1650 pc of the ligand and its complexes in absolute ethanol at 25oC using 1cm quartz cell.TGA and DSC analysis (England-model pL-TG) (Tarbbiat Modars Universty Iran). (1H-NMR) for the prepared ligand was carried out using NMR-unter Bruker 250Mhz Spectromete with DMSO as solvent(Tarbbiat Modars Universty Iran).Mass Spectrum was obtained of ligand using Agilent Technologies 5975 Cat 70e and MSD energy using a direct insertion probe (Acq method low energy)at temperature 90-110 oC(Tarbbiat Modars Universty Iran). pH measurements were carried out using aphilips pw 9421 pH meter(pH±0.001).Device for measuring low pressure mercury lamp Lambda USA, A LLE-

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* This work is a part of M.Sc.Thesis.

1. Melting point apparatus melting point \ SMP,Stuart.

2.2-Synthesis of The Azo Dye Ligand:

The hetrocyclic azo dye ligand(BIAHQ) has been Synthesized by the diazotization coupling reaction by using shibat method(22)with some modification (Scheme1).2-Amino benzimidazole (1.33 gm,0.01 mole) was dissolved in mixture 30 ml distilled water and 5 ml of concenterated hydrochloric acid and 20 ml ethanol.The filtered solution was diazotized at 0-5 oC with (0.75 gm,0.01mol) sodium nitrite in 25 ml distilled water drop wise,and stirred for 20 min at 0-5oC.The resulting diazonium chloride solution was added drop wise with cooling and stirring continuously at 0-5 oC.to alkalin solution of 8-hydroxy quinoline(1.45 gm 0.01 mol), dissolved in mixture of 150 ml absolute ethanol and 30 ml of % 8 sodium hydroxid solution in the mixture was stirred continuosly for 1 hour at 0-5 oC in ice –bath and allowed to stand over night.The mixture was acidified with dilute hydrochloric acid until pH=6.0.The sprecipitate was filtered and washed several times with cold distilled water as well as with 10 ml absolute ethanol to remove the excess of unreacted substance. The isolated dark red crystals was rescrstallized from hot ethanol and dried in oven at 60oC for several hours and stored in a desiccator over anhydrous calcium chloride. The   yield was 83% and melting point found to be 238.2oC. The structure of ligand was confirmed by IR,1H-NMR,Mass spectrum and C.H.N analysis.
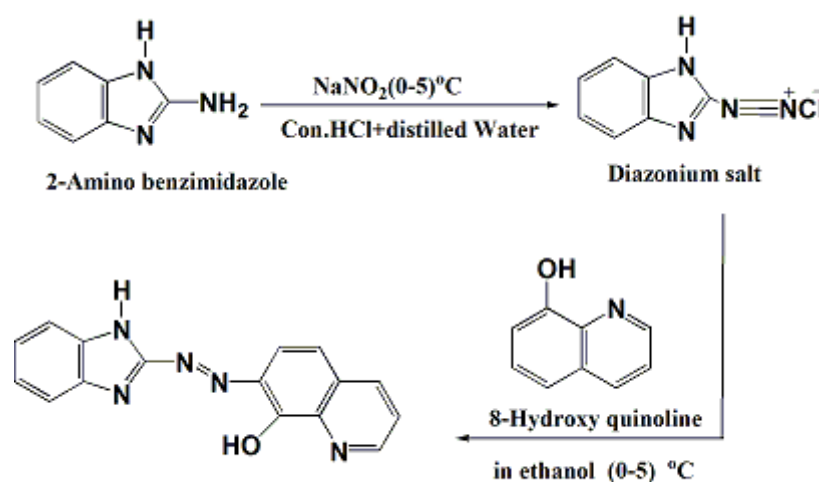
Scheme (1):-Synthesis of azo dye ligand 7-[2-(Benzimidazolyl)azo] 8-Hydroxy Quinoline (BIAHQ)

2.3-Preparation of Zn(II)-Complex

It was prepared by adding(0.289g, 0.001 mol) of ligand dissolved in 50 ml of absolute ethanol gradually with stirring a stoichiometric amount of[1:2] M:L molar rati for (0.068 g,0.0005 mol) of zinc chloride (II), dissolved in 20 ml buffer solution ammonium acetate at pH=7.5 the reaction mixture heated for 50-60 ^{o}C at 30-40 min,until solid complex were precipitated then left over night, the solid product thus formed was filtered off,washed distilled with water until the the solution become color less and washed with 5 ml ethanol to remove traces of the unreactted materials and returned Crystallized.

3-RESULTS AND DISCUSSION
3.1-Metal: Ligand Ratio:

For the purpose of finding possible structure formula of prepared complex was studied by molar ratio method at(λ_{max})the solution of prepared complex increase the intensity of the color as approach of point intersection ratio (M:L) and color continous concetantat passing this point wich indicates that the complex formed in constant solution[23-26].A 1:2 [M:L] molar ratio suggested the formation of complex [Zn (BIAHQ)$_2$].H$_2$O

Table (1):- Some physical properties and elemental analysis for ligand (BIAHQ) and its Zn(II) complexe

Compound	m.p (^{o}C)	Colour	m.f (m.wt)	Found(Calc.)(%)		
				C	H	N
L=BIAHQ	238	Dark red	$C_{16}H_{11}N_5O$ (289.266)	66.51 (66.45)	3.71 (3.83)	24.31 (24.21)
$[Zn(L)_2].H_2O$	258	Purple	$C_{32}H_{22}N_{10}O_3Zn$ (659.96)	58.71 (58.23)	3.30 (3.35)	21.28 (21.22)

3.2-Infrared Spectra

The infrared spectroscopic data of azo dye ligand and its Zn(II)-complex have been studied.The comparison between spectra of ligand with the coordination Zn(II)-complex have revelaed certain characteristic differences of some of these main shifts along with conclusion are give below.

1-The spectrum of free ligand shows abroad a weak absorption band around at 3380cm^{-1} due to υ(OH).This suggests strong inter molecular hydrogen bonding[27,28]the spectrum of Zn(II)–complex show abroad a weak band around at 3317cm^{-1} which attributed to the coordination of water molecculer[29] .

2-Two weak bands had been observed at 3047cm^{-1} and 2661 cm^{-1} in the spectrum of the free ligand due to υ(C-H) aromatic and aliphaetic respectively[30].These bands are stable in position as well as in intensity for both ligand and Zn (II)–complex.

3-The free ligand shows a medium band at 1573cm^{-1} due to υ(C-O) of 8-hydroxy quinoline[29].This band shifting at 1563 cm^{-1} ,producing another evidence about involvement of 8-hydroxy quinoline in coordination with metal ion Zn(II) via oxygen atom of OH group[27-29].

4-The υ(C=N) of benzimidazole 8-hydroxy quinolin in ligand shows two absorption bands at 1580 cm^{-1}and at 1504cm^{-1} recpetively.In the spectra of Zn (II)–complex these bands shift to lower frequences at 1515cm^{-1}and 1604cm^{-1} with a little change in the shape.These differences suggest a linkage of Zn(II) ion with nitroge of hetero cyclic benzimidazole ring[27,28].

5-The spectrum of ligand shows two absorption bands at 1473 cm^{-1} and 1411cm^{-1} due toazo group υ (N=N).The position of these bands in the spectrum of Zn (II) –complex is shifted to a lower frequencies at 1465 cm^{-1}and 1419 cm^{-1}with decreased in intensity.this may indicates that it has been effected on coordination with Zn ion[30].

6- New weak bands at 601cm^{-1}and 501 cm^{-1} in the spectrum of the Zn(II)–complex may be attribted to υ (M-O) and (M-N) respectively[31-33]. Infara red spectra data leads to suggest that the ligand be haves as a atridentate chelating ligand coordination thorugh the phenolic oxygen, nitrogen atom of azo group which is the nearest 8-hydroxy quinoline ring and N3 of benzimidazole ring to give two five membered chelate ring.Some representative spectra are given in Fig 1 and 2 .
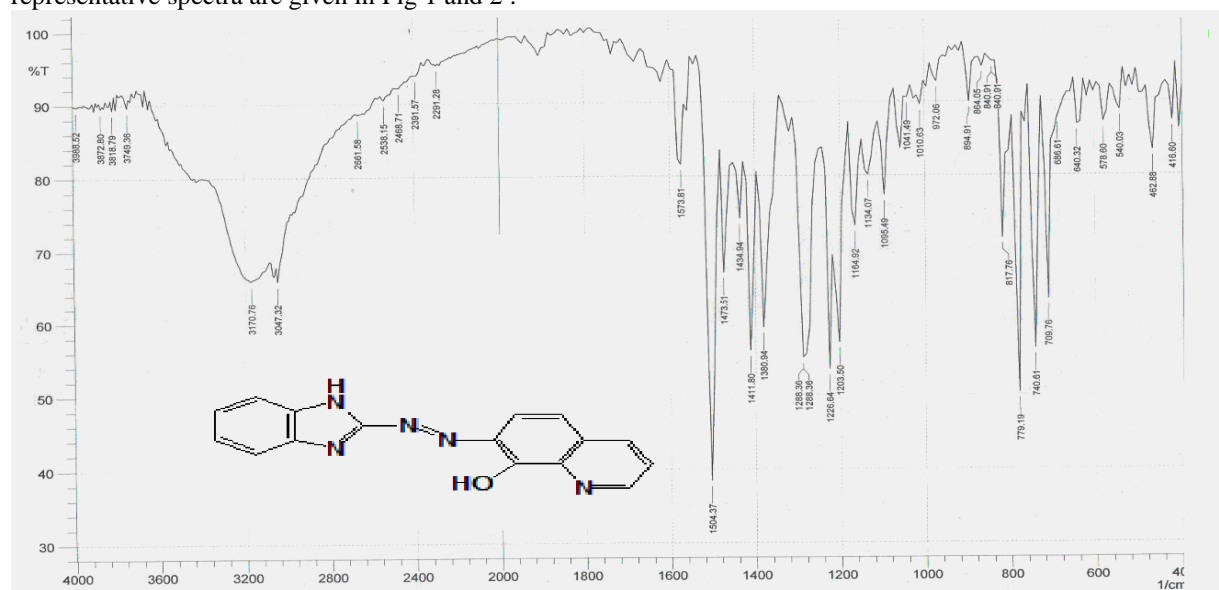

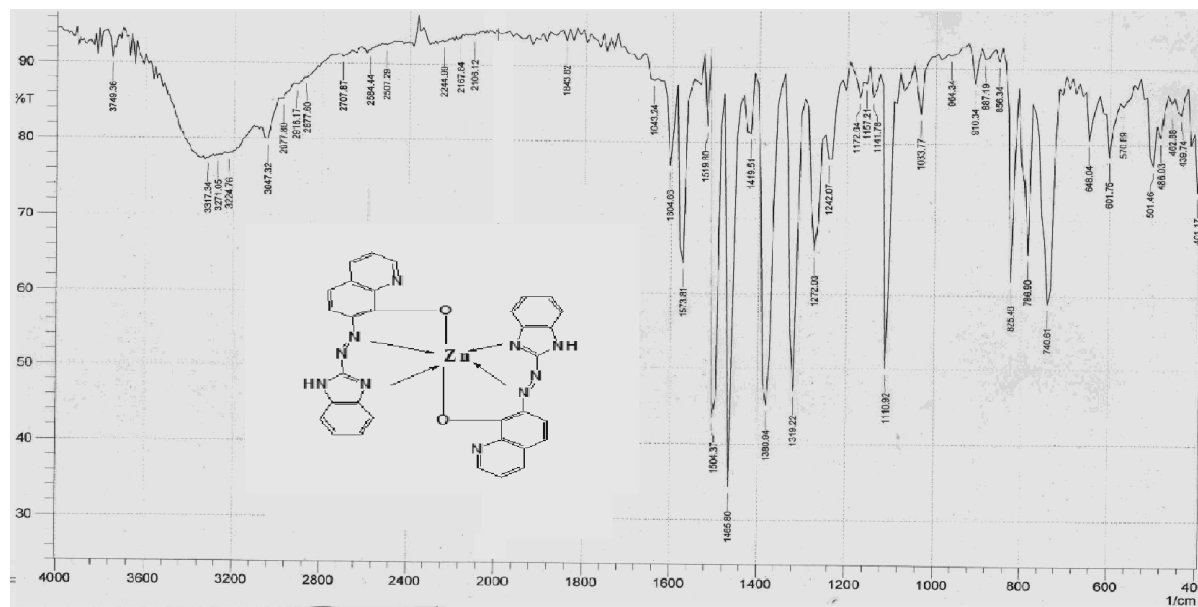**Fig.(1):-Infrared spectrum of ligand (BIAHQ)**

Fig. (2):- Infrared spectrum of Zn(II) -Complex

**Table (2):-Selected IR absorbtion bands of the ligand (BIAHQ) and its Zn(II)-complex in cm^{-1} unit (KBr disc)**

| Compoud υ (M—O) υ (M—N) imidazole N)quinol	υ (O-H)	υ(N.H)	υ(C-O)	υ(C=N) imidazole	υ (N=N) hydroxyl	υ(C=C)	υ(C–N=N–C)	υ(C-N) υ(C-
L=BIAHQ — —	3380	3170 w.br	1573 m.br	1620 m. m.	1473 m.	1380 s.	1288 s.br. 1319 s.	1226 s. 779 s.
[ZnL₂] H₂O 601 501 1220 s.	3317	3271 w.	1563 w.br w.	1604 m. w. s.	1465 s. 1515 s.	1390 1419 w.	1319 V.s.	1272 m. s.

w=weak; s=strong;m=medium; Vs=very strong; br=broad

3.3-Electronic Spectra

The electronic Spectra of azo dye ligand and itsZn(II)-complex were studied in absolute ethanol as a solvent(10^{-3}M).The free ligand spectrum gives three absorption bands were detected first band located at 517 nm (19342 cm^{-1}) for n→π*transition of the azo group(-N=N-),this band showed a red shift on coordination with a metal ion. The second band observed at 310 nm (32258cm^{-1}) due to π→π* transition to the (C=C) group in hetrocyclic benzimidazole and hydroxyl quinoline rings[32] while the third band at 241 nm (41494cm^{-1}) for n→σ*transition to the (C=N) group in the ligand structure[33].The electronic Spectrum of Zn(II)–complex does not show any d-d transition bands[34].

The absorption band at 555 nm (18018cm^{-1}) is assigned to a charge transfer (M→L,CT) transition to complex.The magnatic susceptibility show that this complex is diamagnetic moment for d^{10} ion,(μ_{eff} =0.00) B.M,octahedral geometry and hybridization SP^3d^2 ($t2g^6$ eg^4). Fig.3 and 4 shows the spectra of ligand and [Zn(L)2].H2O .
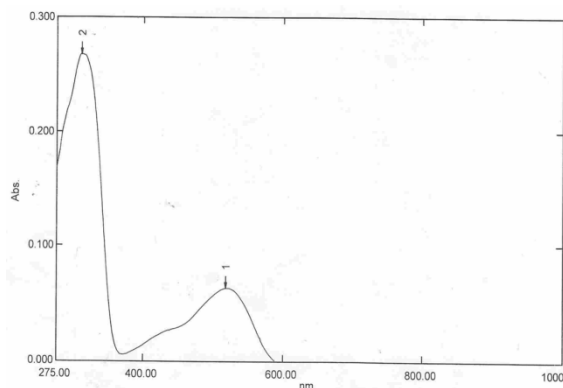
Fig(3):- UV- vis spectrum of ligand (BIAHQ)
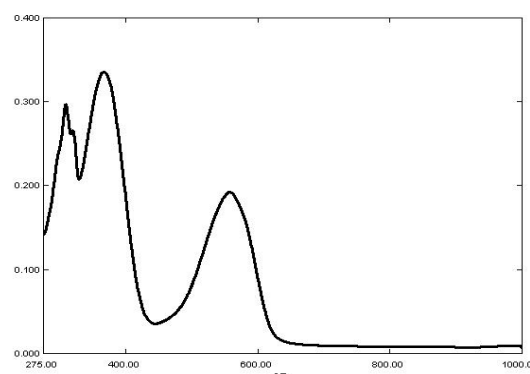
Fig(4):- UV- vis spectrum of Zn(II)–Complex

3.4-Mass Spectrum of Azo Dye Ligand

The mass fragmentation of the free azo dye ligand is shown in Fig.5 the base peak at m/z=289.2 is corresponding to the original molecular weight of the ligand 289.26with relative abundance 13.63% under investigation.the molecular ion of ligand with high stability shows the clear peak at 260.2 with relative abundance 100% is this emphasis on the health of the molecular structure of the prepared ligand.This ligand takes the route to the mass fragmentation.
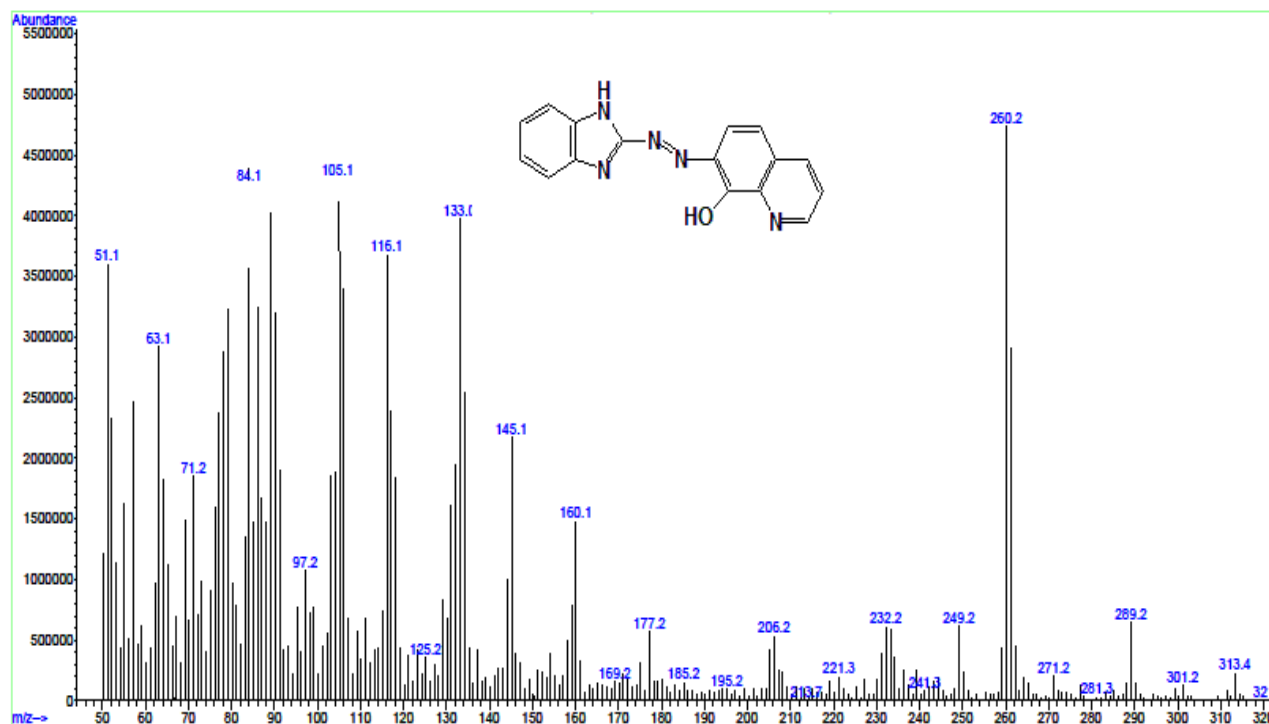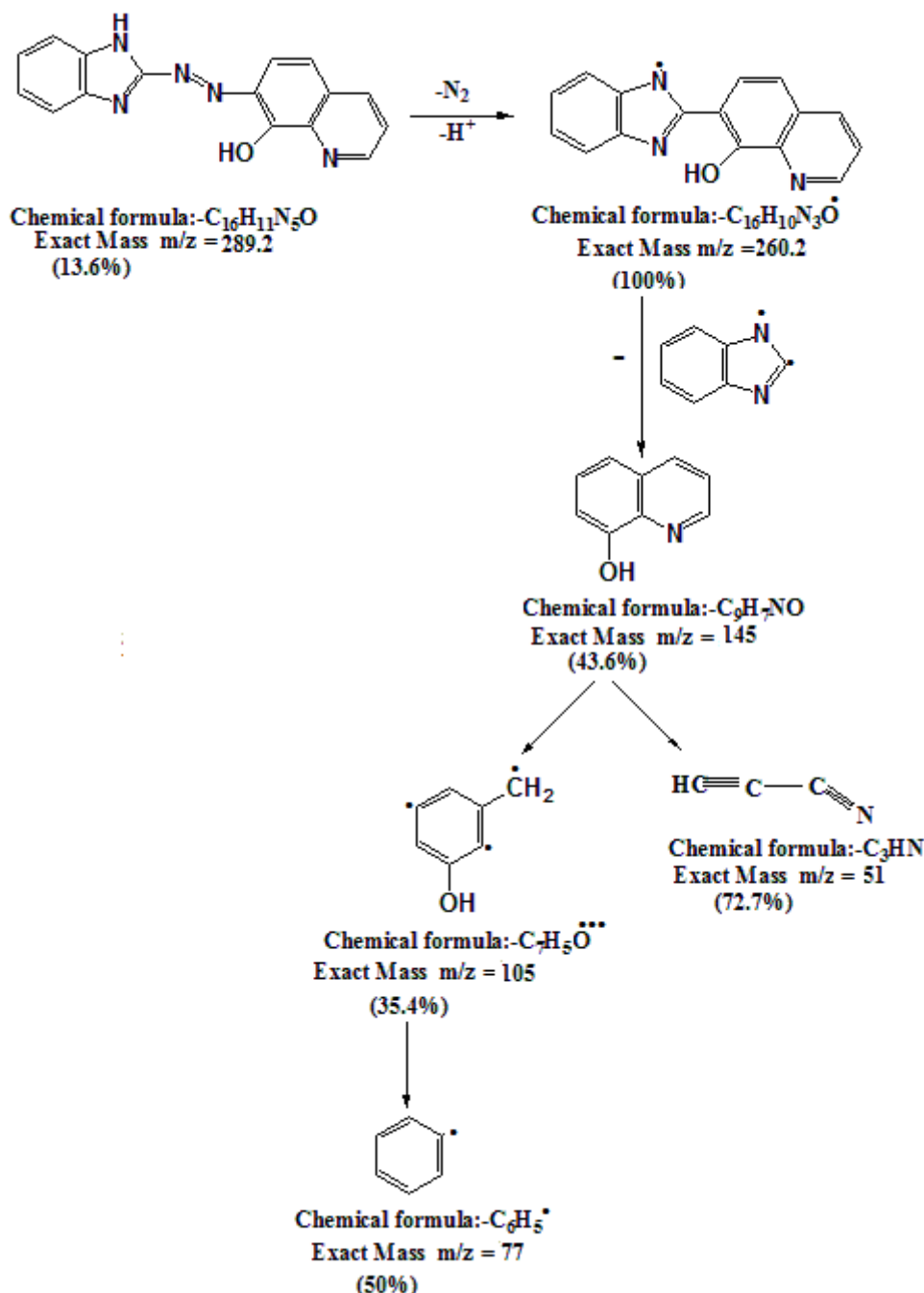

Fig.(5):- Mass spectrum of ligand (BIAHQ)

Scheme (2):- Mass fragmentation pathways for ligand (BIAHQ)

^{1}H-NMR Specrum of Azo Dye Ligand[35,36] 3.5-

The proton nuclar magnetic resonance specrum for the ligand was carried out using DMSO as asolvent and the following peaks were detected Fig.6.

1-single peak at δ = 2. 5 ppm for benzimidazole of group NH

2-single peak at δ=3.5ppm forH3,H5 and H6 proton of hydroxyl quinoline ring .

3-Dblat peak at δ=3.5-3.7 ppm for H8 proton of hydroxyl quinoline ring.

4-single peak at δ=3.80 ppm forH2 proton of hydroxyl quinoline ring .

5-single peak at δ=6.90-6.93 ppm for H4 and H7 proton of benzimidazole ring   .

6-single peak at δ=7.23-7.64 ppm for H5 and H6 proton of benzimidazole ring.

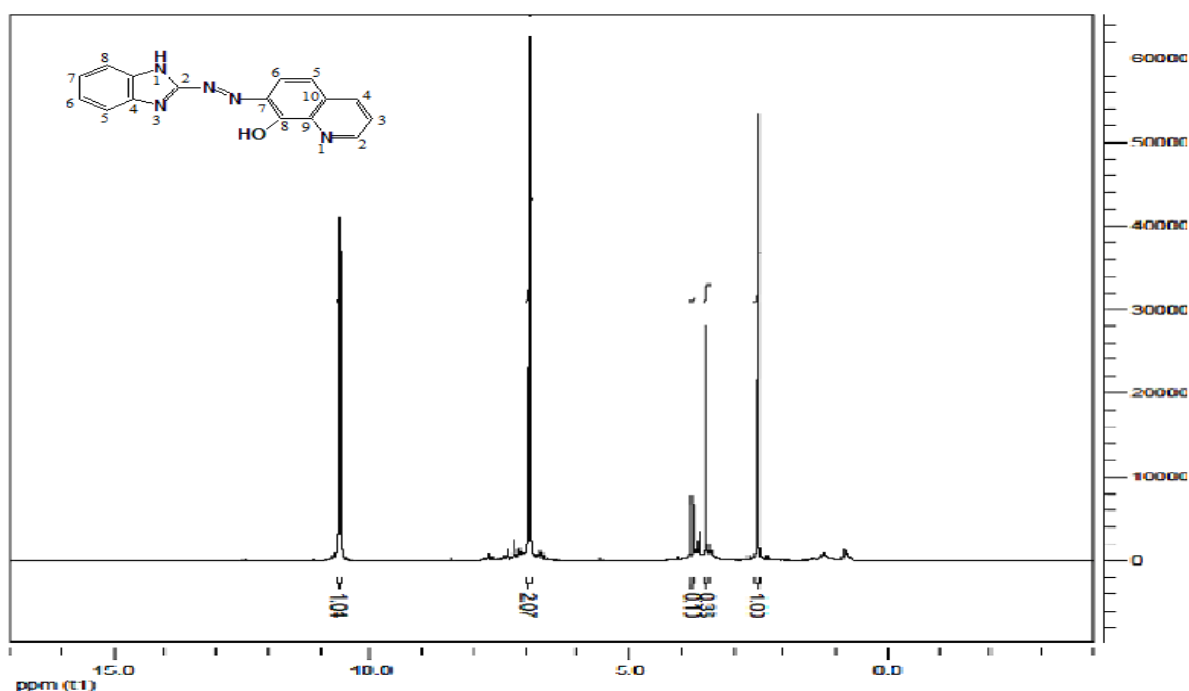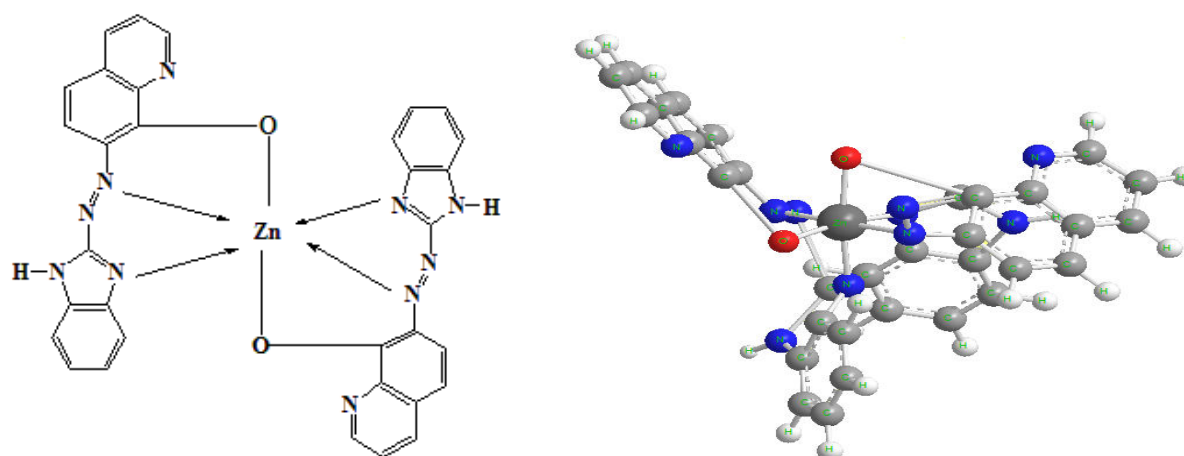7-single peak at δ=10.104 ppm for OH group of hydroxyl quinoline ring .

Fig.(6):- ^{1}H-NMR spectrum of   ligand (BIAHQ)

A ccording to their results and discussed through different techniques suggest below the proposed the structural formula of Zn(II)-complex prepared and shown in Fig.(7).

Fig(7):-The proposed chemical formula of Zn(II)-Complex,[Zn(L)$_2$].H$_2$O

3.6-The study of the effects of some factors on the decomposition of [Zn(L)2].H2O complex .
3.6.1- The effect of irradiation time and the concentration of the complex : [Zn(L)2].H2O :
   This study showes the effects of irradiation time on the concentration of the complex during the periods of time confined to extent of between 0-60 min and the absorbance was measured at that time,noting that the absorption spectrum complex when all wavelengths was below with an increase of the irradiation time,the results are shown in Fig.8; which shows the absorption spectrum.
   A ppointed as rate constant to the decomposition of the complex (k_d) mediated reaction rate equation of the first order [37]. $\ln (A_t - A_\infty) = \ln (A_0 - A_\infty) - kdt$.
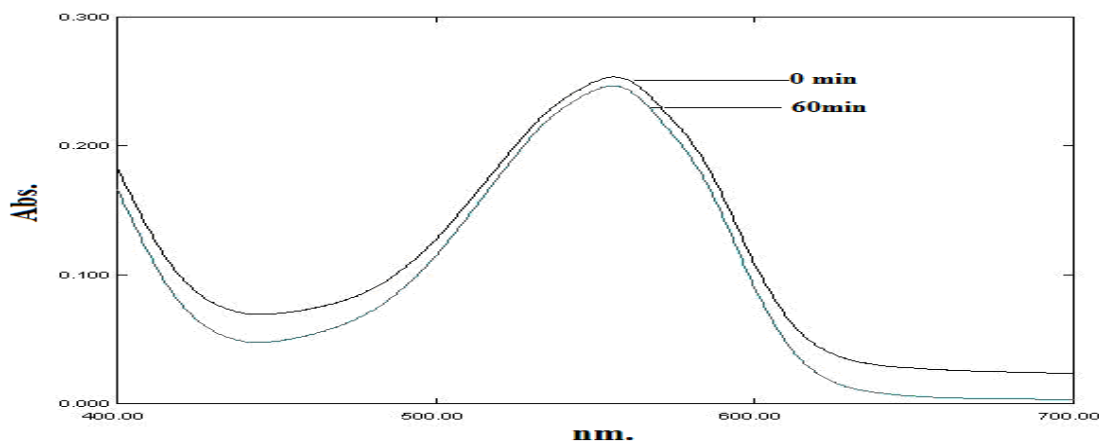
Fig. (8):-Absorption spectrum UV-vis to[Zn(L)2].H2O conc.=1x 10^{-4}M as a function of irradiation time
at 298 K , pH = 7.5 , I_o = 5×10^5 mw.cm^2

3.6.2- Effect of Light Intensity

   The study includes a follow-up impact of the change in the intensity of light falling on the disintegration of the complex [Zn(L)2].H2O by changing the distance between the radiation source and the irradiated sample,which was limited to distances between 5-12.5cm ,where you can study the effect of light intensity according to the inverse square law,which defines the relationship between the radiation from a point source and distance. It states that the intensity per unit area varies in inverse proportion to the square of the distance [38]. In general, its found that whenever lees the distance between the lamp and sample increases the rate of the disintegration of the complex, Fig.9; shows the effect of irradiation on the change in distance dissociation rate constant for the complex.
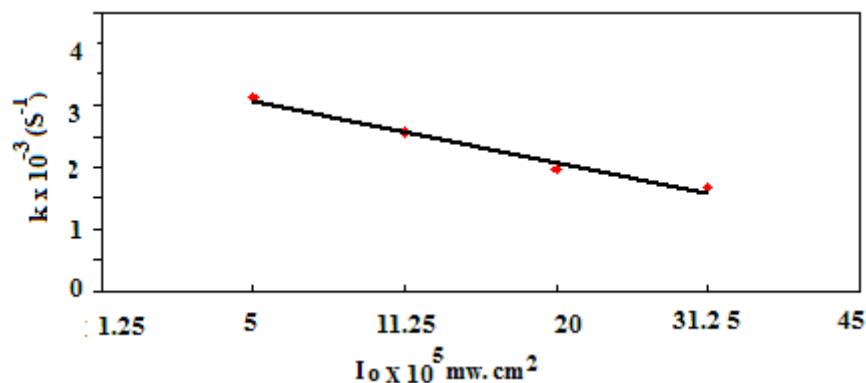

Fig. (9):- Effect of light intensity on the rate constant for the decomposition complex
conc.= 1x 10^{-4} M at 298 K and   pH = 7.5

3.6.3-Effect of Temperature.

   Experiments were performed on the complex within the range of thermal limited between 293-303K. It was found that it increasing temperature leads to incrise in the rate of decomposition of the complex.The increase in temperature leads to an increase in the rate of generation of free radicals, which affects the "direct" on the rate of interaction [39]. Arrhenius equation is used to describe the relationship between temperature and the decomposition rate constant through drawing this relationship for interaction photolysis of complex was calculated activating energy and the results are shows in the Fig.10; ln k = ln A-Ea \ RT. k: rate constant of reaction (sec^{-1}), A: frequency factor, R: gas constant 8.314 J / mol. K. T: temperature unit Kelvin. Arrhenius equation for the dissolution of the complex when draws a relationship between the inverted temperature (1/T) and ln k produces a straight line to be slope equal to ($-E_a$ / R) and it is calculated activation energy of complex,found that the activation energy Ea =0.120.70KJ/mole of the complex.

$$y = -14.518x + 44.978$$
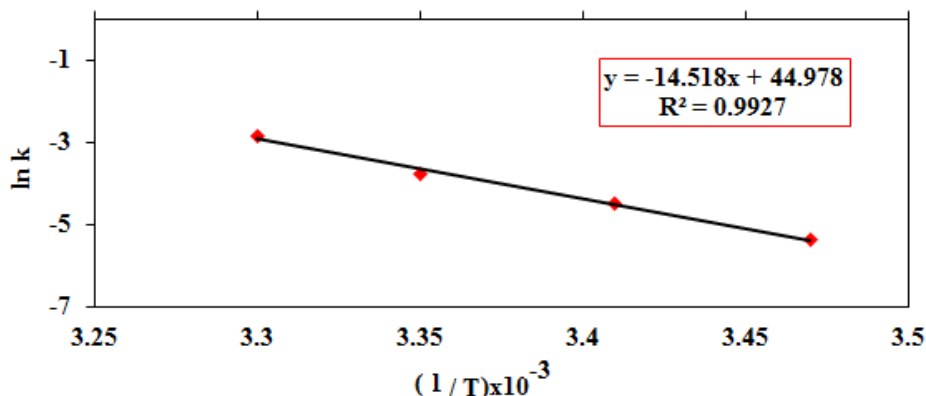$$R^2 = 0.9927$$

Fig.(10):- Arrhenius equation for the decomposition complex conc. =1x 10^{-4}M as a function of irradiation time at pH = 7.5 , I_o = 5x10^5 mw.cm^2

3.6.4-Effect of pH Medium

This study includs the effect of different values of pH function limited between 3-9 on the dissolution of the complex, is found that the maximum rate of disintegration of the complex when the value of pH = 9.This is because which in the middle baseband increases susceptibility molecular absorption of light energy, will disintegrate certain atoms or free radicals product "varieties" negative increase speed optical interaction as shown Fig.11; shows the effect of the change in pH value on the diecomposition of the rate constant for the complex[40].
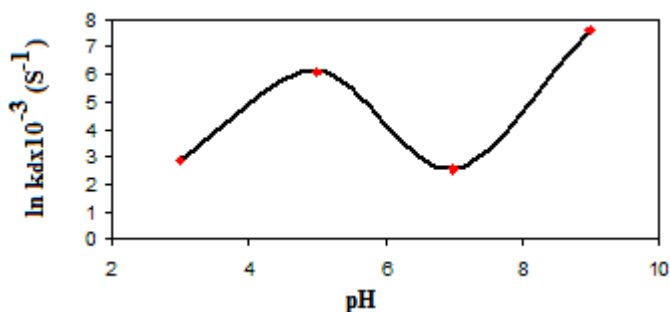
Fig.(11):- Effect of the acidic function on the rate constant for the decomposition complex conc.= 1x 10^{-4}M at 298 K , I_o = 5x10^5 mw.cm^2

3.6.5-Effect of the solvent

The study includs four follow-up effects of polar solvents on the disintegration of the complex and the solvent is methanol, ethanol ,1- butanol and isopropanol. By the results that have been get it was found that the rate of decomposition of the complex increase with increasing polarity of the solvent [41] .Fig.12; shows the relationship between the constant rate of the optical decomposition of the complex in various solvents with the values of those polar solvents .
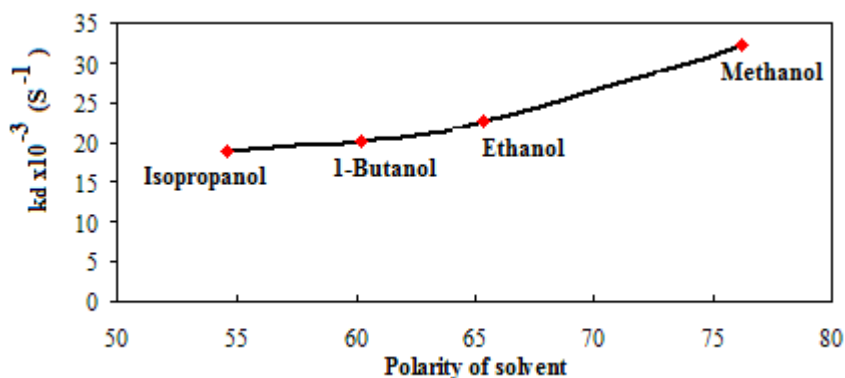
Fig. (12):-Effect of the solvent polarity on the rate constant for the decomposition complex conc.=1x 10^{-4}M at 298 K , pH = 7.5 , Io = 5x10^5 mw.cm^2

3.7-Thermoanylatical Study:

The thermogravimetric (TGA) and the differential scanning calorimetric (DSC) curves for the ligand and their complex are presented in Fig.13 and 14 thermal analytical results (TGA,DSC) of BIAHQ and its metal complex are given in Table (3).

The TGA curve reveal the ligand of the formula $C_{16}H_{11}N_5O$ decompose in 2 steps in the temperature rang 100-536°C.In the first step,which is rapid, ligand loses benzimidazole group by breakage of (C-N) bound around (100-186) ^{o}C with an estimated mass loss 41.04 % (calcd. mass loss40.55%).In this step of decomposition,the DSC curve shows endothermic peak at180^{o}C,effected and intermediate then decomposes exothermally in temperature rang 186-536°C(second step), liberating the gases with an estimated mass 2.21%(calcd.mass loss 2.07%).The (TGA) curve complexof the formula $[ZnC_{32}H_{20}N_{10}O_2].H_2O$ shows that decompose in 2 steps in the temperature reang 100-650°C,the first step involves loss one molecue of H2O around (100-126)^{o}C with an estimated mass loss 2.55% (calcd. mass loss2.72%) ,the second step involves loss one molecue of ligand around 126-650°C with an estimated mass loss 56.25 %(calcd. mass loss 55.99%) the residue left in the crucible consist of corresponding ZnO and for this step of decomposition the DSC curve shows exothermic peak at 330°C. DSC curves a melting process for ligand at 420°C followed by decomposition represented by exothermic process at 510 ^{o}C while a melting process for its complex at 480 ^{o}C and presented exothermic peak at 330 ^{o}C product from crystallization the complex, decomposition represented by exothermic process at 680 ^{o}C.
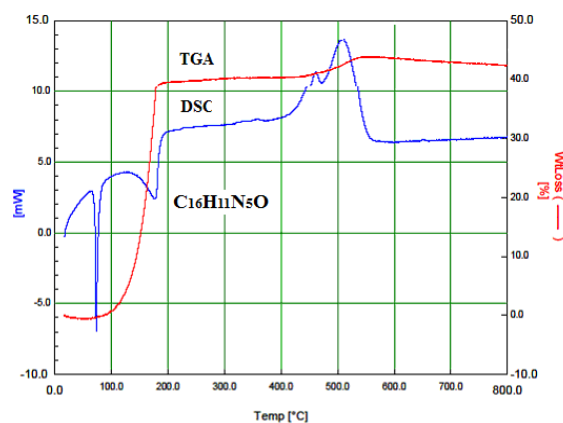

Fig.(13):-Thermal analysis (TGA and DSC)
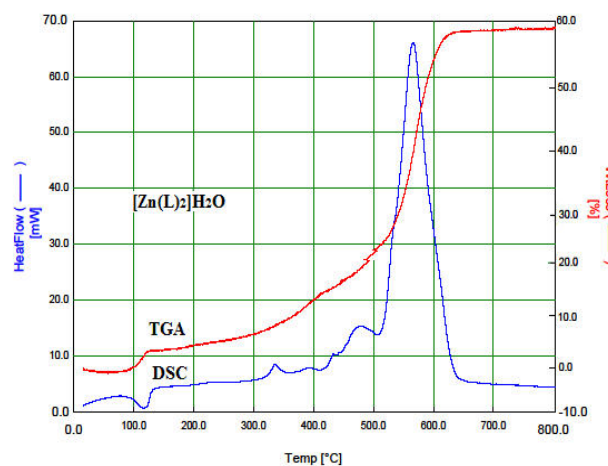
of ligand (BIAHQ)

Fig.(14):-Thermal analysis (TGA and DSC)

of Zn(II)-Complex.

Table (3):- Thermal analytical results (TGA,DSC) of ligand (BIAHQ) and its Zn(II)-Complex

Complex	TGA range (^{o}C)	Mass loss%	Assignment	DSC Peaks(^{o}C)
L=BIAHQ	100-186	41.04(40.45)	Loss benzimidazol group	180(+)
	186-536	2.21(2.07)	LiberationCH$_4$,N$_2$O gases	510(-)
$[Zn(L)_2].H_2O$	100-126	2.65(2.72)	Loss H$_2$O molecule	330 (-),420(+)
	126-650	56.25(55..99)	Loss of one ligand molecule and formation of ZnO	680(-)

3.8-Kinetic Analysis

The first stage of dehydration of the ligand and their complex was studied in detailed manner.The kinetic parameters such as activation energy (ΔE^*),enthalpy(ΔH^*), entropy(ΔS^*), and free energy change of the decomposition (ΔG^*) were evaluated graphically by employing the Coast-Redefern relation[42] : as the equations(1-4).

$$\log\left[\frac{\log\{W_f/W_f-W)\}}{T^2}\right]$$

$$=\log\left[\frac{AR}{\Theta E^*}\left(1-\frac{2RT}{E^*}\right)\right]-\frac{E^*}{2.302\,RT} \qquad (1)$$

where Wf is the mass loss at the completion of the reaction, W is the mass loss up to temperature T,R is the gas constant,E the agtivation energy in KJmol^{-1},Θ is the heating rate and (1-(2RT∕E*))≈1.

Aplot of the left-hand side of Eq.(1) agnaist $1/T$ gives a slope from which E*was calculated A(Arrhenius constant) was determined from the intercept. The entropy of activation (ΔS*),enthalpy of activation (ΔH*) and the free energy change of activation (ΔG*) were calculated using the following equations:

$\Delta S^* = 2.303[\log(Ah/kT)]R$ (2)

$\Delta H^* = E^* - RT$ (3)

$\Delta G^* = H^* - TS^*$ (4)

Where k and h are Boltizman and Blanck constant,respectivel.The caculated values of E^*, A ΔS*,ΔH*,and ΔG^* for the decomposition steps are given in the Table (4).

Table (4):-Thermodynamic data of the thermal decomposition of ligand (BIAHQ) and its Zn(II)-complex

Complex	Decomposition range(^{o}C)	E* (KJ mol^{-1})	A(S^{-1})	ΔS* (JK^{-1}mol$^-$)	ΔH* (KJ mol^{-1})	ΔG* (KJ mol^{-1})
L=BIAHQ	100-186	20.34	1.29x10^{16}	73.85	19.71	13.35
	186-536	20.70	3.6x10^7	101.6	17.79	-17.77
[Zn(L)$_2$]. H$_2$O	100-126	15.55	2.5X10^4	140.45	15.31	11.65
	126-650	14.72	1.8x10^3	187.31	10.36	-87.49

CONCLUSIONS

In this work we report the preparation and indentification, heterocyclic azo ligand derived from imidazole and its complexe with Zn(II) metal ion.The ligand characterized solid metal complex is stable in air and moisture, and high melting point gives further proof of the stability of metal complex [Zn(L$_2$)].H$_2$O prepared when the concentration was concetante, the rate of reaction of the photolysis of the complex was directly proportional to the intensity of the light used, as can control through the intensity of the lightl distance between irradiated sample and the radiation source.The reaction of rate photolysis of the complex when increased temperature of solution, and increase the rate reaction photolysis of the Zn(II)-complex at increasing the base of the mediume increase the concentration of negative species that directly affect the rate of reaction. photolysis achieved highest rate of reaction photolysis for the complex when methanol is used as solvent "complex in solution, but lower the reaction of rate photolysis which recorded at the use isopropanol as a solvent", It was found that the reaction rate is directly proportional "with the polarity of the solven.By(TGA and DCS) study found the thermal stability of the Zn(II)-complex than the ligand.

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