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Synthesis And Spectroscopic Study of Groups IIb And IIIb Metal ions Complexes with New Azo Ligand 2-[(6-Nitro -$\bar{2}$- benzo thiazolyl) azo]-hydroquinon (6 – NO_2 BTAHQ)

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Abstract

The new ligand 2-[(6-nitro -$\bar{2}$ benzo thiazolyl) azo]-hydroquinon (6-NO_2BTAHQ=LH_2) was prepared by coupling reaction between (6-nitro-2-benzothiazolyldiazonium) chloride with quinol in alkaline alcoholic solution.Six new chelate complexes of Zn(II), Cd(II), Hg(II), Ga(III), In(III) and Tl(III) have been synthesized. These complexes were prepared after fixing the optimum conditions of pH and molar concentration by studying Uv-vis. Spectra of the solutions that mixing the metal ions with the ligand solution in a wide ranges pH = 4.5-9.0 and molar concentration that obeyed Lambert-Beer's law. The structures of the prepared complexes have been characterized by using the molar ratio method for the metal: ligand, which is (1:2), the ligand and its complexes were investgatal by using element analysis, molar conductance measurement, stability constant (β), Uv-vis., infrared spectra and mass spectrum of the ligand. Atomic absorption, flame emission spectrophotometer was used to determined the precents of metal ions in the prepared complexes.

الخلاصة

يتضمن هذا البحث تحضير الليكاند الجديد 2-[(6-نايترو -$\bar{2}$- بنزوثيازوليل) ازو] - هايدروكوينون (6-NO_2BTAHQ=LH_2) وذلك من مفاعلة كلوريد(6-نايترو -$\bar{2}$- بنزوثيازوليل الديازونيوم) مع الكوينول في الوسط القاعدي، كما يتناول البحث تحضير معقدات جديدة للزنك (II)و الكادميوم (II)و الزئبق (II)و الكاليوم (III) و الانديوم (III) والثاليوم (III) مع الليكاند المذكور. قد حضرت هذه المعقدات بعد تثبيت الظروف الفضلى من دالة حامضية وتركيز مولاري من خلال دراسة أطياف الأشعة فوق البنفسجية – المرئية لمحاليل مزج الايونات الفلزية مع محاول الليكاند انفة الذكر ولمدى واسع من الدالة الحامضية (pH= 4.5-9.0) والتراكيز المولارية الخاضعة لقانون لامبرت-بير.عينت صيغ المعقدات المحضرة باستخدام طريقة النسبة المولية وقد بينت النتائج ان نسبة (الليكاند: الفلز) هي (1:2) لجميع المعقدات.تم تشخيص الليكاند ومعقداته بوساطة التحليل الدقيق للعناصر والموصلية المولارية وثابت الاستقرارية واطياف الاشعة فوق البنفسجية – المرئية والاشعة تحت الحمراء وطيف الكتلة لليكاند.كما استخدم مطياف الامتصاص الذري اللهبي لغرض تعيين النسب المئوية للايونات الفلزية في المعقدات المحضرة.

Introduction

Heterocyclic thiazolyl azo compounds are distinguished as being well coordinative ligands with the metal ions because they contain N & S donor atoms, and other substitution groups participating in coordination process .Moreover bridged azo group is also present which has a great importance in adding colour characteristics into these compounds and complexes which it formulates(1-3). This characteristics is manipulated widely in the spectral studies (4,5). These compounds have various applications in different biological and industrial fields (6,7).

Physical and chemical behavior of azo dyes differs relatively according to the difference in heterocyclic which is related to it, although they all participate in the presence of N atom in ortho position in relation to bridge azo group which differs in its basicidity and solubility in water and the colour of the complexes produce with metal ions (8,9). The group in ortho position which is considered more important than meta position (10). The hydroxyl group participates in the coordination with metal ions by making chealtic coordination with metal ions by making chealte complexes which are dusting wished by its colour and its ability to soluble in different solvents(2,3,10). Complexes solutions of these compounds are widely studied as presented in the literature review and they are widely used in identifying trace concentrations of metals by using Uv-vis. Spectra (6,7,11).

Azo compound produce colored solutions when they react with metal ions(6-9).Many researchers were distinguished by preparing these organic compounds , studying their characteristics, activity and studying their complexes solutions which makes them more important in different fields (10,13).

The studies present of thiazolyl azo compounds which contain ortho hydroxyl group in the homocyclic such as TAR, TAN, BTAR and organic derivatives whose heterocyclic contain S and N atom which cannot coordination via S atom present in heterocyclic inside chealitic cyclic.(14,15) The reason is related to partially positive charge on the S atom inside thiazol cyclic which is produced from the participation of ion pair of this atom to equate partial electronic deficiency for C atom in the (2) position for thiazol cyclic which falls under the great impact of heterocyclic N atom.(16) The molecular orbital calculations showed that that the S atom carries big positive and that metal ion does not prefere to link with S atom because of steric distortion of the formed chealitic cyclic (17).

In this work, new thiazolylazo ligand (6-NO_2BTAHQ) and their complexes were synthesized and characterized.

Experimental

1- Measurements and Materials

Mass spectrum of ligand was obtained using G.C-Mass Shimdzu QP1000A Gas-Mass Spectrophotometer. Elemental analysis were carried out using Perkin-Elmer 2400 elementary analyzer , and FTIR spectra were recorded with FTIR-8000 shimadzu,spectrophotometer were used for spectral measurement, in the 4000-200 cm^{-1} rang using CsI disc. Absorbance curves were obtained with a model Uv-vis 1650 Shimadzue spectrophotometer with cm^{-1} cells using EtOH as solvent.

Metal contain were measured using atomic absorption/flame emission spectrophotometer (Shimadzu – AA-160). Electrical conductivity was measured by conductivity Bridge model 31A. pH meter, WTWpH 521 was also used . Stuart melting point apparatus was used to measure the melting point of ligand and its complexes. All chemicals used were Fluka , Merck and BDH, expect of 2-amino-6-nitro benzothiazole was prepared as described in the literature(18) . Organic solvents including methanol, ethanol, acetone, chloroform and DMF were used purified by the usual methods(19).

2- Preperation and characterization of ligand (6-NO_2BTAHQ)

Ligand was prepared by dissolving a cooled (0-5 C°) solution of 2-amino-6-nitrobenzothiazole (1.95 g 0.01 mol) in 40 ml of distilled water and 5 ml of concentrated hydrochloric acid was treated with sodium nitrate solution (0.75 g , 0.01 mol) , in 30 ml^3 of distilled water dropwise until iodo-starch paper change to blue. This diazonium solution was added dropwise into 500 ml beaker containing (1.1 g,0.01 mol) of quinol dissolved in 150 ml alkaline ethanol. The mixture was stirred for additional 2 hrs. , in ice-bath and allowed to stand over night and acidified with dilute hydrochloric acid to pH=6.0. Redistilled water was added to the mixture, and the precipitated dye was filtrated, dried and recrystallized twice from hot ethanol. The yield was 62% of Reddish-brown crystals melting at 179 °C.The structural formula of this ligand as shown in fig.(1).

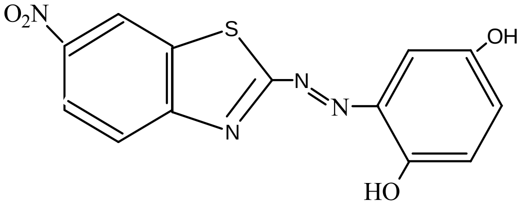


Fig.(1) : - structural of the ligand (6-NO_2 BTAHQ=LH_2)

3- Synthesis of complexes

A hot solution of the ligand (1.58 g, 0.005 mol) in ethanol (50 ml) was added dropwise with vigorous stirring to a solution(0.0025 mole) of metal chloride , M= Zn(II), Cd(II), Hg(II), Ga(III), In(III), and Tl(III) dissolved in 30 ml buffer solution at optimal pH for each metal ions. The reaction mixture was heated to 50-60^0C for 30 min. that left over night.Complexes were precipitated, filtrated, washed with redistilled water , ethanol and dried in a desiccator over anhydrous calcium chloride ($CaCl_2$).

The physical properties of Ligand and its complexes are given in Table (1). on the basis of elemental analysis data, the general molecular formula of their complexes was assigned to be : $[M(LH)_2]$, when M=Zn(II), Cd(II)and Hg(II), and [$M(LH)_2]Cl.H_2O$ whn n=Ga(III), In (III), and Tl(III) .

Table (1):- physical properties and analytical data of ligand and its complexes.

No	Metal complexes	pH	Color	M.P.°C	Yield %	Molecular Formula (M.Wt)	Found (Calc.) %			
							C	H	N	M
1.	**LH_2**	6.0	Brown reddish	179	62	$C_{13}H_8O_4SN_4$ (316.28)	49.05 (49.37)	2.34 (2.55)	17.48 (17.71)	———
2.	**$[Zn(LH)_2]$**	7.0	Purple bluish	204	78	$C_{26}H_{14}S_2O_8N_8Zn$ (695.93)	44.78 (44.87)	1.94 (2.02)	15.97 (16.10)	9.54 (9.39)
3.	**$[Cd(LH)_2]$**	7.5	Purple	196	71	$C_{26}H_{14}S_2O_8N_8Cd$ (742.96)	41.89 (42.03)	1.92 (1.89)	15.14 (15.08)	15.28 (15.13)
4.	**$[Hg(LH)_2]$**	8.5	Purple reddish	221d.	67	$C_{26}H_{14}S_2O_8N_8Hg$ (831.14)	37.46 (37.57)	1.57 (1.69)	13.63 (13.48)	———
5.	**$[Ga(LH)_2]Cl.H_2O$**	6.5	Violet purple	187	73	$C_{26}H_{14}S_2O_8N_8ClGn$ (753.74)	41.16 (41.43)	1.98 (2.14)	14.64 (14.87)	9.47 (9.25)
6.	**$[In(LH)_2]Cl.H_2O$**	6.0	Violet reddish	215	76	$C_{26}H_{14}S_2O_8N_8ClIn$ (798.84)	39.31 (39.09)	2.15 (2.02)	13.74 (14.03)	14.18 (14.37)
7.	**$[Tl(LH)_2]Cl.H_2O$**	8.0	Dark purple	237d.	69	$C_{26}H_{14}S_2O_8N_8ClTl$ (888.39)	35.36 (35.15)	1.94 (1.82)	12.34 (12.61)	23.27 (23.03)

LH_2=6-NO_2BTAHQ; d= complex melt with decomposition.

4 - Standard metal solutions

A stock solution of 1000 p.p.m.Zn (II), Cd(II), Hg(II), Ga(III), In(III), and Tl(III) were prepared by dissolving the appropriate weight of $ZnCl_2$, $CdCl_2$, $HgCl_2$, $GaCl_3$, $InCl_3$ and $TlCl_3$ (purity 99.98% , Merck and BDH Analar) in buffer solution.

A series of standard Zn (II), Cd(II), Hg(II), Ga(III), In(III), and Tl(III) solutions were prepared by several dilutions of the above stock solution.

5- Buffer solution:

.01 M ammonium acetate 0.771 gm. was dissolved in 1 liter of doubly distilled deionized water (DDDW), 0.2 M acetic acid and 0.2M ammonium solution were used for pH adjustment.

6- Standard ligand solution

An absolute ethanolic solution (10^{-3} M) of the ligand was prepared as stock solution .This solution was stable for several months if stored in amber bottle.

Results and discussion

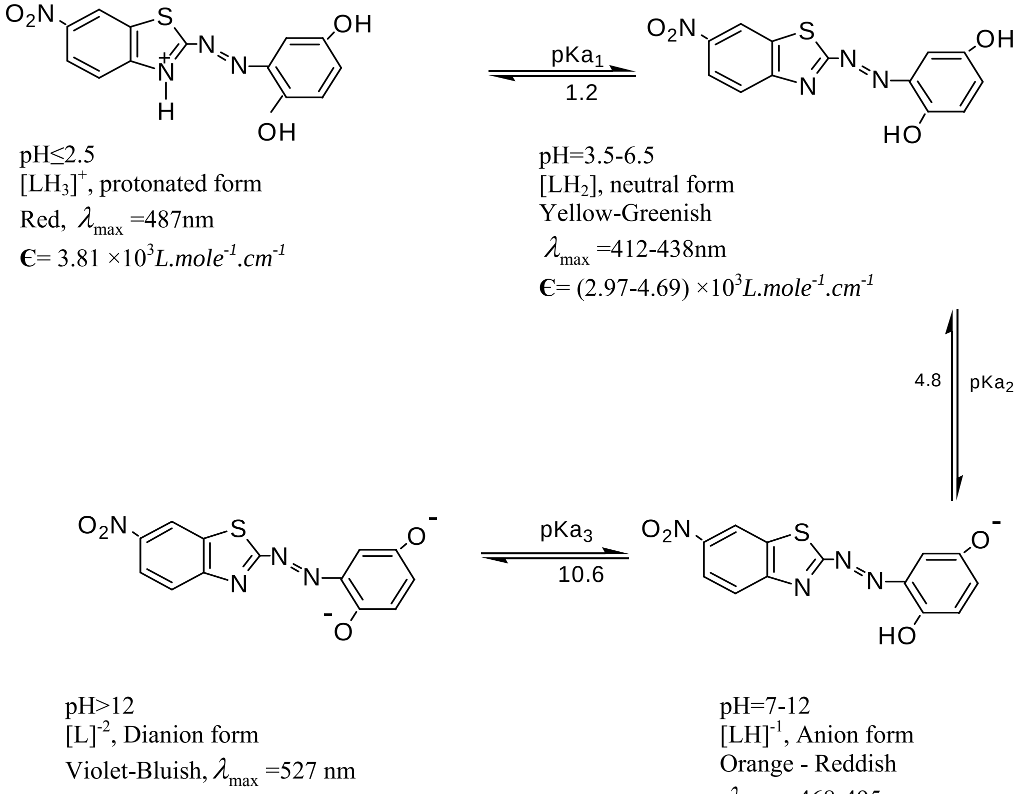
1- Color reactions with metal ions

Complex of The chelation of the ligand with Zn (II), Cd (II), Hg (II), Ga (III), In (III), and Tl (III) ions with the chelate ligand were easily prepared by adding a few drops of solution of the ligand in absolute ethanol (yellow-Greenish) to a solution of the metal ions. UV-vis. Spectra of the prepared complexes in aqueous ethanolic solution 50 % (V/V) showed a bathochromic shift ranging between (88- 127) nm depends on the type of metal ions.

Generally solutions containing metal ions and ligand showed a purple or violet-purple colour under suitable

2- Dissociation behavior

The azo dye ligand and its complexes were insoluble in water but soluble in some organic solvents including methanol, ethanol, benzene, chloroform , DMF, and acetone.The ligand showed acid-base indicator properties and was red in strongly acidic solution, yellow-greenish in neutral solution, orange–reddish in alkaline solution, but violet-bluish in strongly alkaline solution. Four species of the ligand, $[LH_3]^+$, $[LH_2]$, $[LH]^-$ and $[L]^{-2}$ (20,21). The dissociation of 6-NO_2BTAHQ may formulate as follows:



pH≤2.5
$[LH_3]^+$, protonated form
Red, λ_{max} =487nm
ϵ= 3.81 ×10^3 $L.mole^{-1}.cm^{-1}$

pH=3.5-6.5
$[LH_2]$, neutral form
Yellow-Greenish
λ_{max} =412-438nm
ϵ= (2.97-4.69) ×10^3 $L.mole^{-1}.cm^{-1}$

pH>12
$[L]^{-2}$, Dianion form
Violet-Bluish, λ_{max} =527 nm
ϵ= 5.07 ×10^3 $L.mole^{-1}.cm^{-1}$

pH=7-12
$[LH]^{-1}$, Anion form
Orange - Reddish
λ_{max} = 468-495 nm
ϵ= (4.02-5.63) ×10^3 $L.mole^{-1}.cm^{-1}$

3- Mass spectrum of Ligand (6-NO_2BTAHQ)

Mass spectrum data support the proposed structure. The Ligand was run using the direct insertion. The base peak had a measured mass of 316 corresponding to a molecular formula of $C_{13}H_8O_4SN_4$, the calculated formula weight is (316). This formula is the Ligand molecular formula. A fragment peak at (M/Z = 195) corresponding to the 2-amino-6- nitro- benzothiazole compound (22). Another fragment at (M/Z=180 and 110) due to 6-nitro benzothiazole and quinol respectively.The successive fragmentation peaks are shown in Fig. (2).

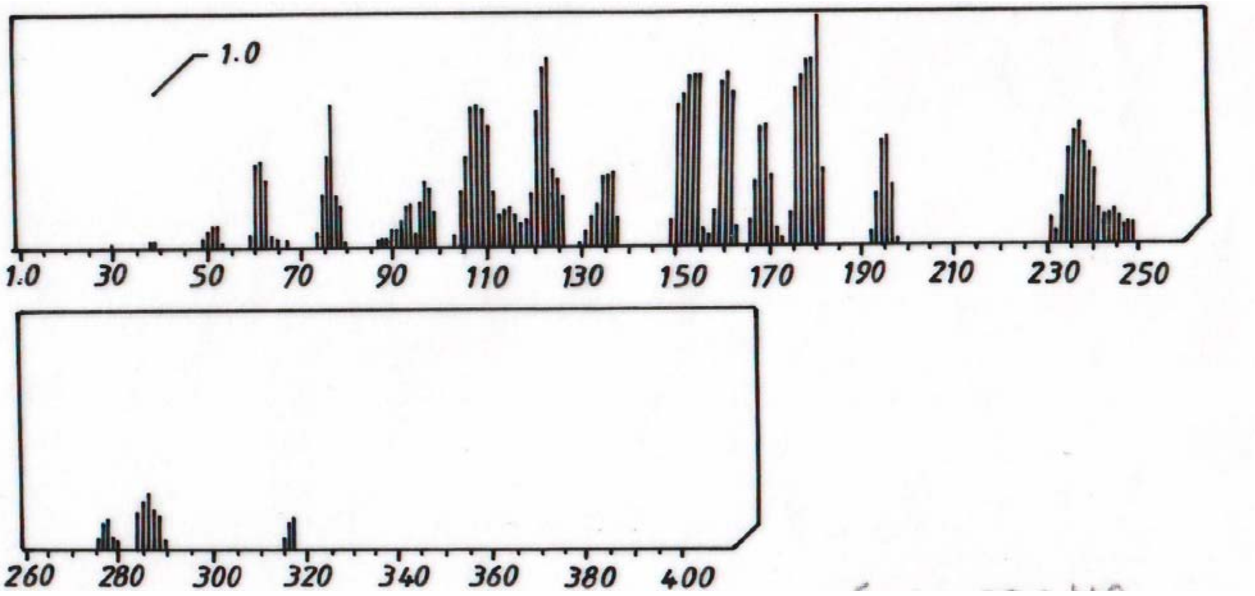
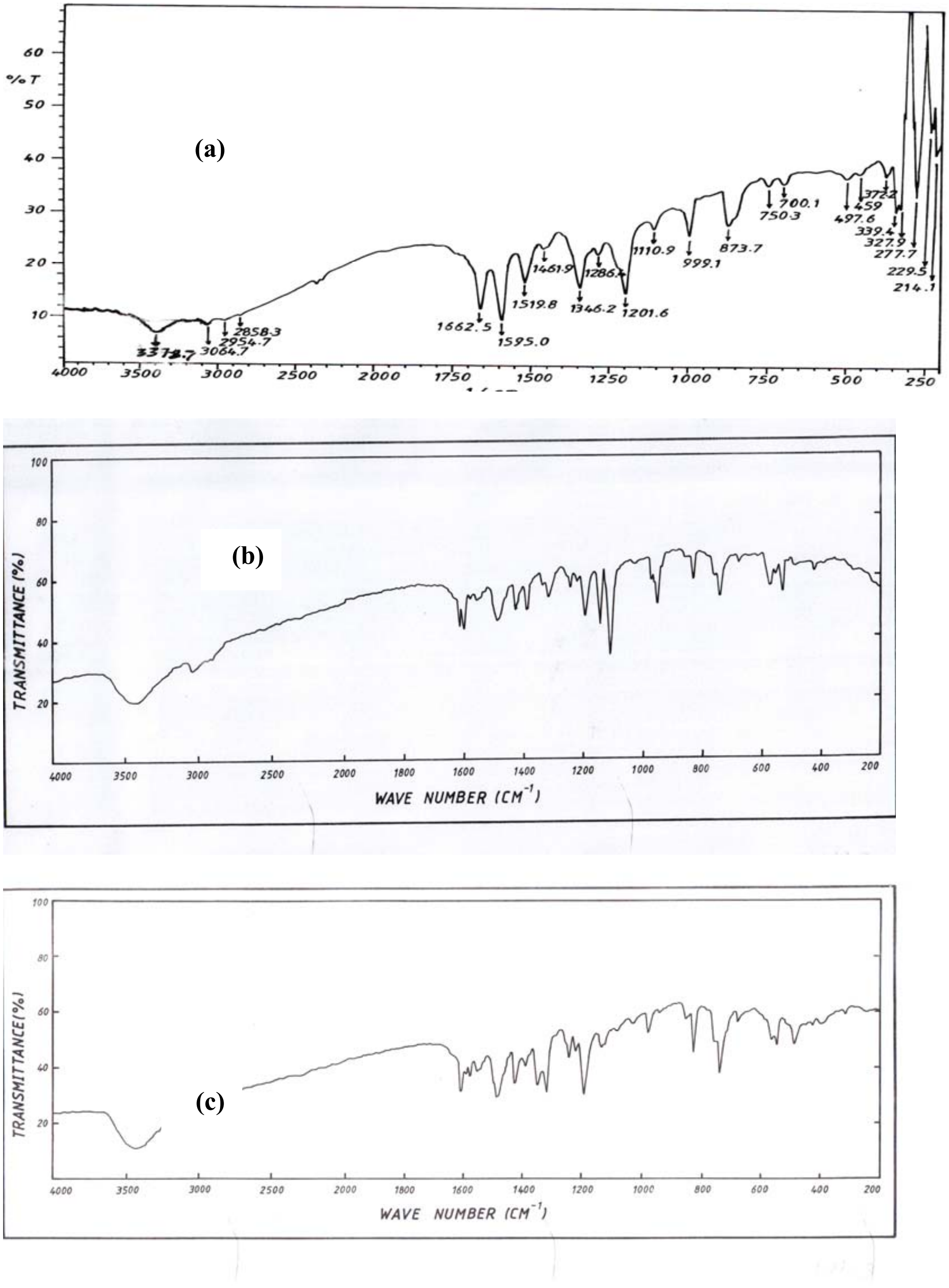


Fig.(2):- The mass spectrum of Ligand (6-NO_2BTAHQ)

4-Infrared spectra

The I.R.spectrum of the ligand (6-NO_2BTAHQ) showed a characteristic broad band at 3379cm^{-1} dueto the υ(O-H)$^{(23,24)}$. The band at 3065 was dueto υ(C-H) aromatic. The band at 1663cm^{-1} is dueto υ(C=N) of thiazole ring $^{(25)}$. The bands at 1520cm^{-1} and 1462 cm^{-1} due to υ(N=N)$^{(26,27)}$.Another band appeared at 1286cm^{-1}and 874 cm^{-1} in spectrum of free ligand of the υ(C-S)of thiazole ring . The shift in the positions of complexes bands compared with those absorption band of the free ligand suggest the modes of bonding in the complexes. In spectra of Ga(III), In(III) and Tl(III) showed bands at (3425-3465) cm^{-1} indicates the presence of water molecule in these complexes$^{(23)}$. Some of these main shifts along with the conclusions are summarized in table (2). Representative example for their spectra is given in fig.(3)



Fig(3):FTIR spectra of ;(a)the ligand (6-NO_2BTAHQ),(b)[Cd(LH)$_2$]and (c)[Ga(LH)$_2$]Cl.H_2O

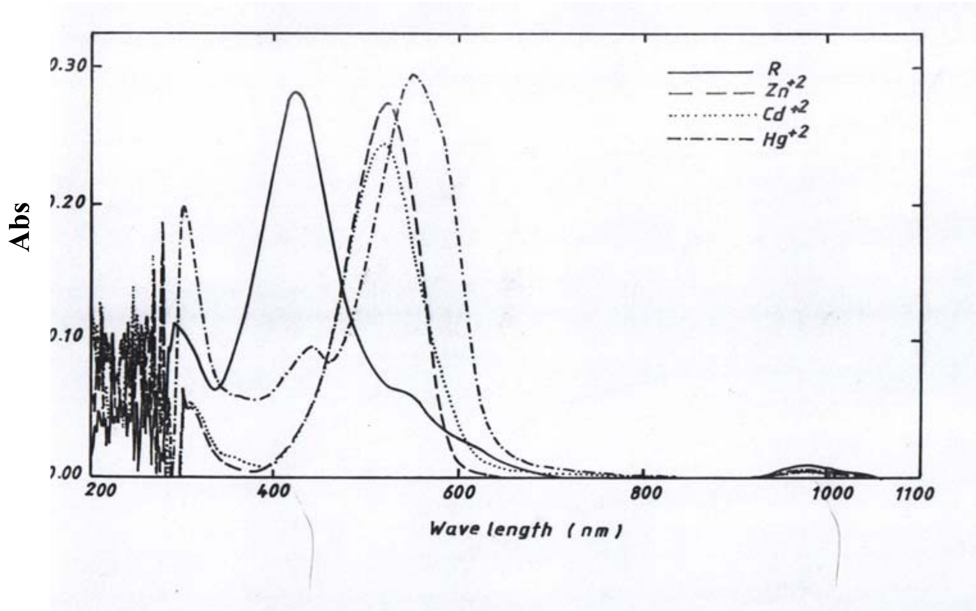
Table2: Important IR frequencies for the Ligand and its complexes (CsI disc; cm^{-1})

Compound	v (O-H)	v(C=N)	v(N=N)	v(C-S)	v(M-O)	v(M-N)
LH_2	3379 wbr.	1663 m. 1595 s.	1520 m. 1462 w.	874 m. 1286 W.	———	———
$[Zn(LH)_2]$	3540 wbr.	1615 s. 1580 s.	1415 m.	1265 W. 835msh.	485w.	390W.
$[Cd(LH)_2]$	3475 wbr.	1595 s. 1565msh.	1445m.	1275 m. 840 W	480W.	385W.
$[Hg(LH)_2]$	3500	1610 s. 1575W.	1435msh.	1280 W 835 m.	440W.	360W.
$[Ga(LH)_2]Cl.H_2O$	3465 wbr.	1620 m. 1585Lv.	1465 m. 1435 m.	1270 m. 845 m.	430W.	325W.
$[In(LH)_2]Cl.H_2O$	3450 wbr.	1625msh. 1590 m.	1475 m. 1395W.	1275 W. 850 m.	425W.	340W.
$[Tl(LH)_2]Cl.H_2O$	3425 wbr.	1615 m. 1585vs.	1440 s. 1410W.	1280 W. 850 m.	430W.	325W.

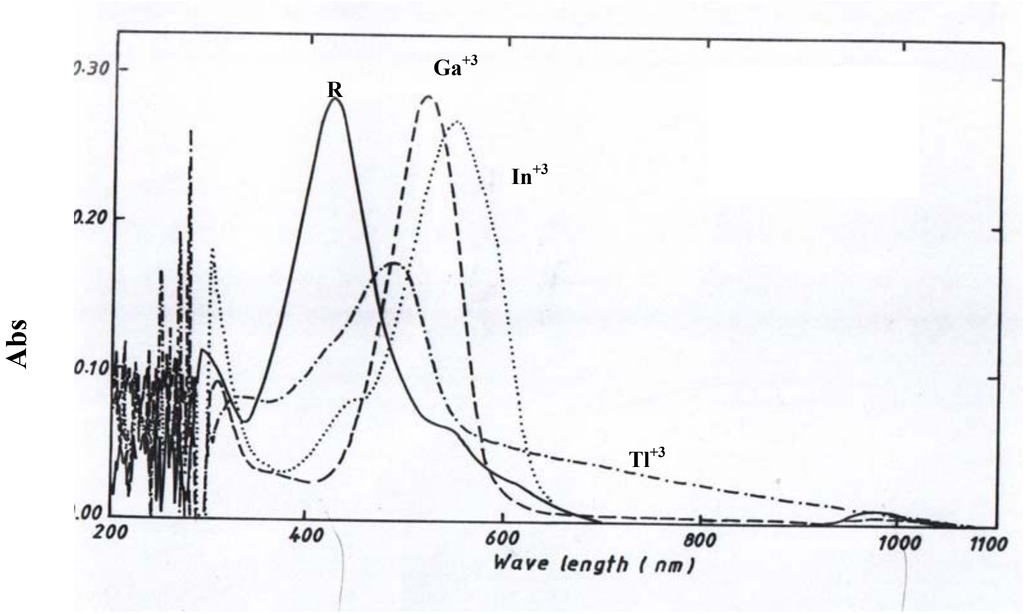
LH_2=Ligand (6-NO_2BTAHQ) ; W=weak; m=medium; s=strong; sh=shoulder; and br=broad.

5- Absorption spectra

The absorption spectra of the azo dye ligand and its complexes with Zn(II), Cd(II), Hg(II), Ga(III), In(III), and Tl(III)ions were recorded within wave length range (511-550)nm. It was found that the absorption maxima (λ_{max})of the free Ligand is 423nm. The spectra of ligand and its complexes in aqueous 50 %(v/v) ethanolic solution were studied. The absorption spectra of the free ligand and its complexes are shown in Figs.(4 and 5).



Fig(4):- The absprption spectra of free ligand (R) and its complexes in a suitable pH (1.75×10^{-4}M) in aqueous ethanolic solution 50%(V/V); R=6-NO_2 BTAHQ



Fig(5):- The absprption spectra of free ligand (R) and its complexes in a suitable pH (1.5×10^{-4}M) in aqueous ethanolic solution 50(V/V); R=6-NO_2 BTAHQ

3.6-Effect of pH :

Suitable pH values for complex formations were found to be in the range of (4.5-9.0). For evaluation of the optimal pH values for determination of Zn(II), Cd(II), Hg(II), Ga(III), In(III), and Tl(III) the effects of pH on the absorbance were studied results are shown in Figs.(6 and 7).The absorption spectra did not change over the whole range. The optimal pH and wave length (λ_{max})with molar absorptivity (€)of Zn(II), Cd(II), Hg(II), Ga(III), In(III) complexes are shown in table (3).

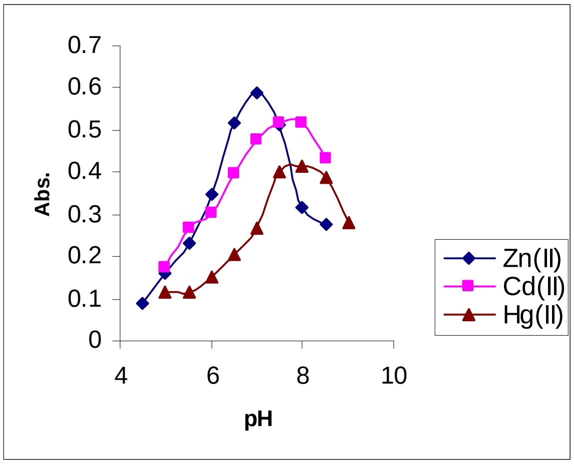


Fig6: The effect of PH on the absorbance of 6-NO_2 BTAHQ- metal chelats. Ligand conc. =1.75×10^{-4} M,metal ions conc. = 1.75×10^{-4}M, ʋs. ligand blank 1-cm cells .

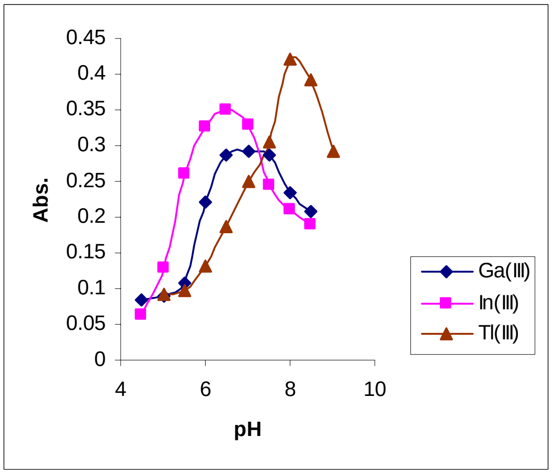


Fig7:- The effect of PH on the absorbance of 6-NO_2BTHQ-metal chelats. Ligand conc. = 2.0×10^{-4}M, metal ions conc.=1.5×10^{-4}M, ʋs.ligand blank 1-cm cells

Table(3): The optimal pH values and wave length (λ_{max})with molar absorptivity (€)of metal ions in aqueous 50%(v/v) ethanol solution.

Ligand	Metal ions	Optimal pH	Molar absorptivity $€\times10^3$ L.mol^{-1}.cm^{-1}	Wave length λ_{max} nm
6-NO$_2$BTAHQ **λ_{max} =423 nm** **€=5.64 x 10^3 L.mol^{-1}.cm^{-1}**	Zn(II)	7.0	2.87	536
	Cd(II)	7.5	2.56	518
	Hg(II)	8.5	2.99	550
	Ga(III)	6.5	2.91	523
	In(III)	6.0	2.73	546
	Tl(III)	8.0	1.71	511

7- Conductivity measurement

The conductivity measurement of Zn(II),Cd(II) and Hg(II) complexes showed values ranging between (5.38-8.16)S.mole^{-1}.cm^2, Ttable (4), in methanol at room temperature, these values indicating nonionic structure of these complexes[(28)]. But the lower conductivity values for the Ga(III), In(III) and Tl(III) complexes were found ranged between (39.81-45.09) S.mole^{-1}.cm^2, in the same solvent indicating that the complexes are (1:1) electrolyte [(29)].

8- Calculation of the metal complexes stability constant(β)

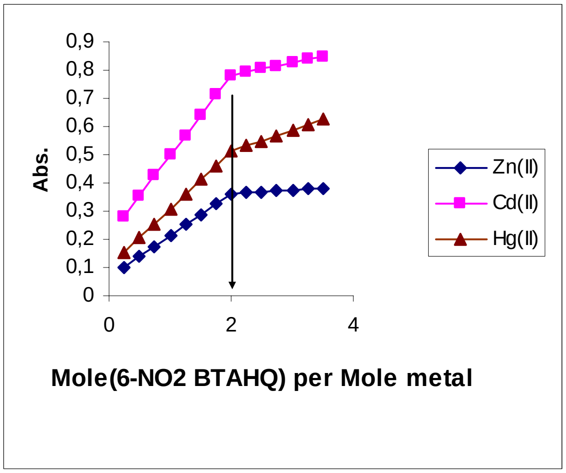
Chelate stability constants of metal complexes were obtained spectrophotometrically by measuring the absorbance of solutions of ligand and metal mixture at fixed wave length (λ_{max})and pH values. The degree of formation of the complex is obtained from the relation ship [(27,30)], $\beta=(1-\alpha)/(4\alpha^3c^2)$ and $\alpha=(Am-As)/Am$ where A$_m$, A$_s$ are the absorbance of the partially and fully formed complex respectively at optimum concentration. The calculated (β) and (log β) values for prepared complexes are given in Table (4). The stability follows the sequence. In(III) > Zn(II)> Cd(II) > Tl(III) > Hg (II) >Ga(III). The high stability of (6-NO$_2$BTAHQ) to word In (III) is remarkable over the other ions . This implies a considerably higher affinity toward this ion .

Table(4) :-Conductivity and stability constant(β) values

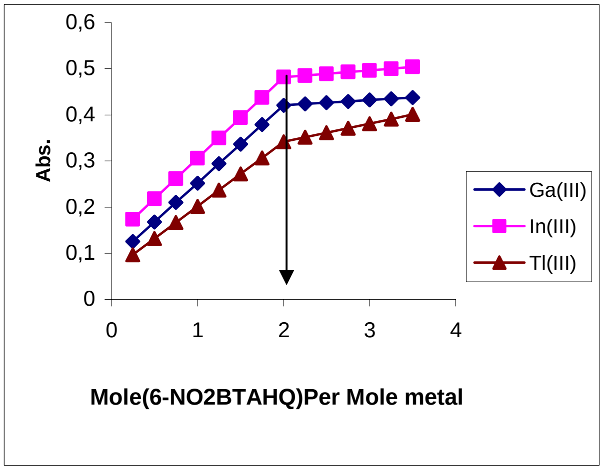
Ligand	Metal ions	Conductivity S.mole^{-1}.cm^2	β mol^{-1}.L	logβ
6-NO$_2$BTAHQ	Zn(II)	5.38	2.346 x 10^{10}	10.370
	Cd(II)	5.48	6.707 x 10^9	9.826
	Hg(II)	8.16	1.217 x 10^9	9.085
	Ga(III)	42.67	1.287 x 10^7	7.109
	In(III)	39.81	1.306 x 10^{11}	11.116
	Tl(III)	45.09	3.043 x 10^9	9.483

3.9- Nature of complexes:

The empirical formula of the colored complexes was determined by spectrophotometric methods (mole-ratio) at the optimal pH and wave length (λ_{max}). The results indicate the formation of (1:2)(M:L) for complexes as shown in Figs.(8 and 9).The stability of complexes are increases with the increasing of the volume of chelating ring[(31,17)], the metal ions may be banded with the ligand molecule through the positions of oxygen ortho OH group of quinol, nitrogen of azo group and thiazole ring nitrogen, so ligand will be tridentate with Zn(II), Cd(II), Hg(II), Ga(III), In(III), and Tl(III) complexes.



Fig(8):-Mole ratio (M:L) of 6- NO_2BTAHQ-metal chelats .



Fig(9):-Mole ratio (M:L) of 6-NO_2BTAHQ –metal chelats .

According to these results the structural formula of prepared complexes in this work may be proposed in fig.(10) .

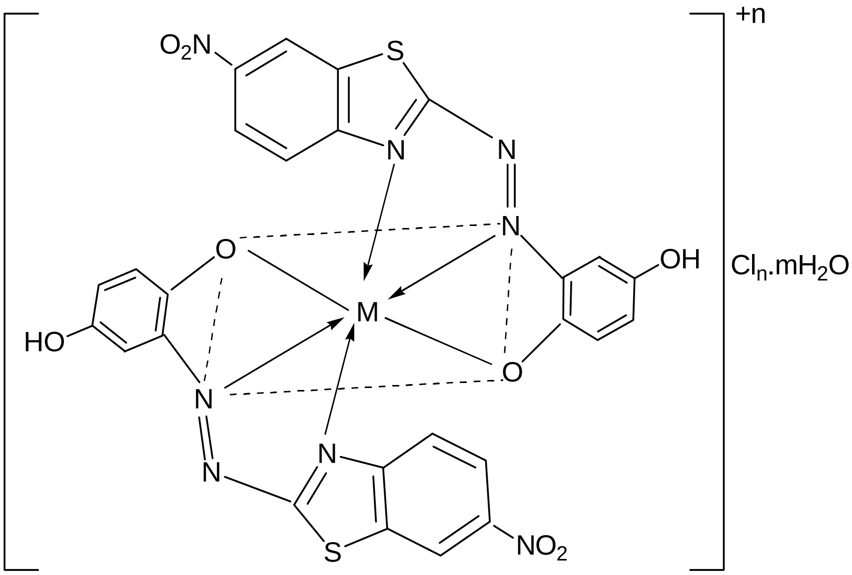


Fig: (10) :- The proposed structural formula of complexes.M=Zn(II), Cd(II), Hg(II), n=0, m=0.Ga(III), In(III), Tl(III), n=1, m=1.

Conclusion:-

The preparation of chelating complexes after the fixation of the ideal circumstances like concentration , pH and mole ratio are simple . The general complexes were prepared in basic medium . The prepared complexes are not influenced by moisture and air and they have high melting points which refers to its high stability . The suggested structural forms for the complexes present clearly that ligand (6-NO_2BTAHQ) follow tridantate ligand when they coordinationating with metal ions to make tow linked five rings which increase the stability constants of the formed complexes .

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