Synthesis, Spectroscopic studies and Theoretical Treatment of Zn(II),Cd(II) and Hg(II) complexes of 1,3-Bis (4,5-diphenyl imidazole azo) benzene (BABI)

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Abstract

A new chelate complexes of Zn(II),Cd(II) and Hg(II), have been prepared by reacting these ions with the ligand 1,3-Bis (4,5-diphenyl imidazole azo) benzene (BABI),The preparation of the complexes have been conducted after fixing the optimum conditions such as pH and concentration .UV- visible spectra of these complexes solution have been studied for a range of pH and concentration which obey Lampert-Beers Law .The structure of complexes are deduced according to mole ratio method which were obtained from the spectroscopic studies of the complexes solution .The ratios of metal: ligand obtained are (1:1) for these complexes . (UV-Vis) absorption spectra of ethanolic solution of complexes showed bathchromic shift , as compared with that of free ligand .The infrared spectra of the chelating complexes have been studied , Depending on these results the coordination between our ligand and the metal ions take place.

The conductivity measurements , elemental analysis ,the percentage of metal ions was determined .Depending on these results ,we may conclude that the ligand was tetradentate . Also the proposed geometrical structure of the complexes of Zn(II),Cd(II) and Hg(II) ions are octahedral. .Semi-empirical methods (ZINDO/1, PM3 and ZINDO/S) were carried out by using hyper chem.program to evaluate heat of formation $\Delta H^{\circ}f$, binding energy ΔE_b, dipole moment, for all complexes , also the vibration frequencies, and electronic transitions was calculated for prepared ligand(BABI)..

***Keywords*: Synthesis, spectroscopic studies, Bis (imidazole azo) ligand, and Elemental analysis. theoretical treatment.**

Introduction

The discovery of diazo compounds occurred around the year 1858, which parallels the beginning of what is considered the starting point of modern organic chemistry[1].Azo dyes contain one or more azo groups (- N =N -) which are linked to SP^2 hybridized carbon atoms, based on the number of such groups [2].

Aromatic azo compounds are widely used in the chemical industry as dyes and pigments[3], food additives, indicators[4], and therapeutic agents[5]. In addition, azo compounds have shown promise in electronics[6] and drug delivery[7],

Biological importance of azo compounds is well known for their use as antineoplastics, antidiabetics, antiseptics, anti-inflammatory, and other useful chemotherapeutic agents [8-11].

Azo compounds are also of interest for a more accurate diagnosis of Alzheimer's disease because their physiological activity can be used as a diagnostic probe for the visualization of amyloid plaques in the brains of mentally deteriorating patients[12].Basically sulfur &Nitrogen nucleus containing heterocyclic families are very interesting due to their versatile pharmacological activities, such as anti-tumour, diuretics, fungicides, bactericides, antihelmintic, antiallergic, antiulcer and local analgesic[13-15]. Azo dyes compounds are also have a plenty of applications in industry and photodynamic therapy as well as photosensitive species in photographic or electro photographic systems and are dominant organic photoconductive materials[16].

Azo linkage was used to protect drug from undesirable reaction, such as prontosil was found to protect against, and cure streptococcal infections in mice. Interestingly prontosil was inactive on bacterial cultures. Prontosil is totally in active in vitro but possesses excellent activity *in vivo*[17] .

In this study, the synthesis and characterization of new bis (imidazole- azo) ligand derived from m-phenylenediamine and 4,5-diphenyl imidazole as coupling component and its Zn(II) ,Cd(II) ,Hg(II) complexes are described.

Experimental

Materials and physical measurements

All chemicals used were of highest purity (BDH or Fluka) and used with out further purification .

Elemental analysis was carried out by means of (Euroverctor, EA300A,Italy) C.H.N element analyzer .Absorption spectra were recorded by Shimadzu UV-Vis 1700 spectrophotometer, for solution of the complexes in aqueous ethanol at room temperature. Using 1cm quartz cell. IR spectra were recorded with FT-IR-8000 Shimadzu, in the range of (4000-400) cm^{-1} using KBr disc. Electrical conductivity measured by digital conductivity meter Alpha – 800 with the prepared complexes concentration of 10^{-3}M in ethanol at room temperature. pH measurements were carried out using (pH– meter), 720 , WTW 82362.

Synthesis of the ligand[18]

m-phenylenediamine (1.08g / 0.01mol) was dissolved in a mixture of 5mL of water and 10mL of concentrated hydrochloric acid. While 20mL concentrated hydrochloric acid was diluted with about 60g of crushed ice and cooled with a cooling mixture. To this a cold solution of sodium nitrite (2.5g/10 mL water) was added. Immediately meta-phenylenediamine hydrochloride solution was added and stirred for about 1hr till a dark red colored solution was obtained. The coupling agent 4,5-diphenyl imidazole dissolved in NaOH (0.02mol) was cooled and added to the tetrazo solution slowly with continuous stirring and maintaining the temperature (0-5) ^{o} C. The dye was washed with cold water and

collected by vacuum filtration.Then ligand recrystallized by Water-Ethanol(1:1). shown in fig.1

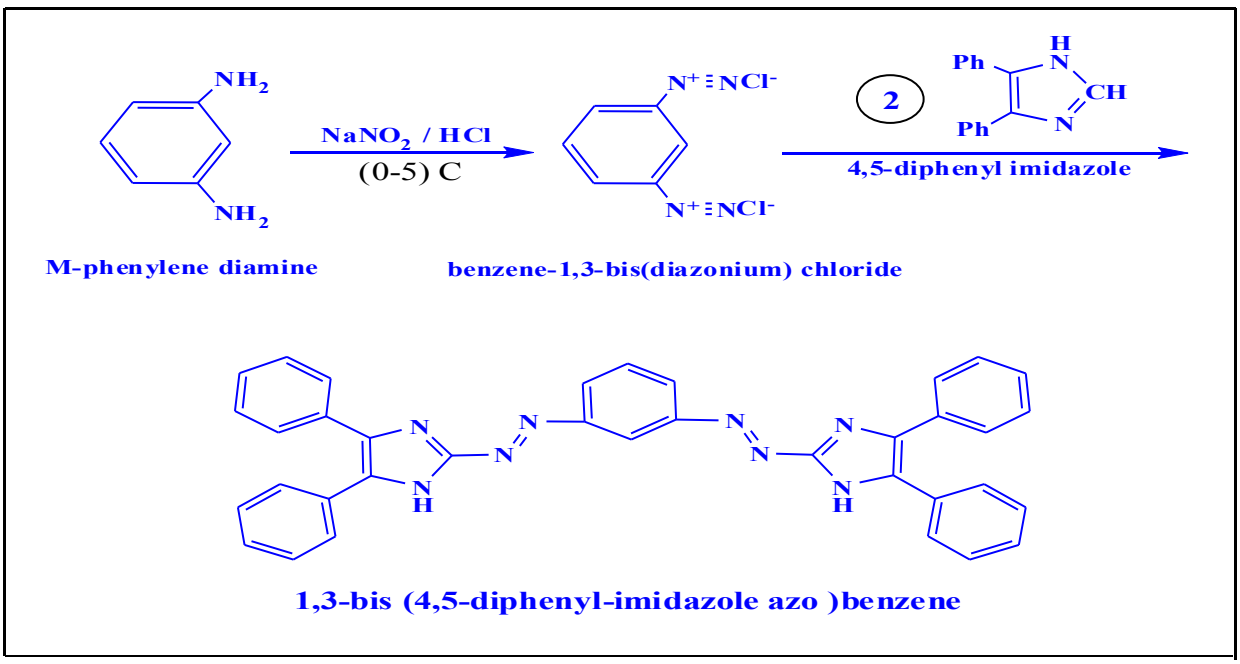


Figure 1: **General route for the synthesis of azo ligand**

Synthesis of complexes

The chelate complexes have been synthesized at pH values dissolved (0.057gm, 0.01 mol) of ligand (BABI) in 10 mL ethanol and then (0.01 mol) of metal chloride, M= Zn(II),Cd(II),Hg(II) dissolved in 10 mL distilled water is added drop wise with vigorous stirring to the ligand solution. The reaction mixture was left over night then the complexes are filtered off washed with distilled water. Table.1 collects some physical properties and analytical data for these complexes.

Table 1: Some Physical properties and analytical data of the ligand(BABI) and Zn(II),Cd(II),Hg(II) complexes.

= co po io

No.	Compound	Color	m. p °C	Found (Calc.)%			
				C	H	N	M
1	$C_{36}H_{26}N_8$	Red	160	75.77 (75.6)	4.59 (4.4)	19.64 (19.9)	—
2	[Zn $(C_{36}H_{26}N_8)Cl_2$]	Orange	190 d	67.98 (67.7)	4.12 (4.0)	17.62 (17.7)	10.28 (10.3)
3	[Cd $(C_{36}H_{26}N_8)Cl_2$]	Reddish brown	210 d	63.30 (63.1)	3.84 (3.7)	16.40 (16.7)	16.46 (16.4)
4	[Hg $C_{36}H_{26}N_8)Cl_2$]	Red	225 d	56.06 (55.8)	3.40 (3.2)	14.53 (14.6)	26.01 (25.8)

d de m sit n

temp.

Results and discussion

Effect of pH

Suitable pH values for metal complexes solution was found to be in the range of (5 – 10). to evaluate the optimal pH values of metal complexes solution .The effect of pH on the absorbance were studied, and the results are shown in Fig.2

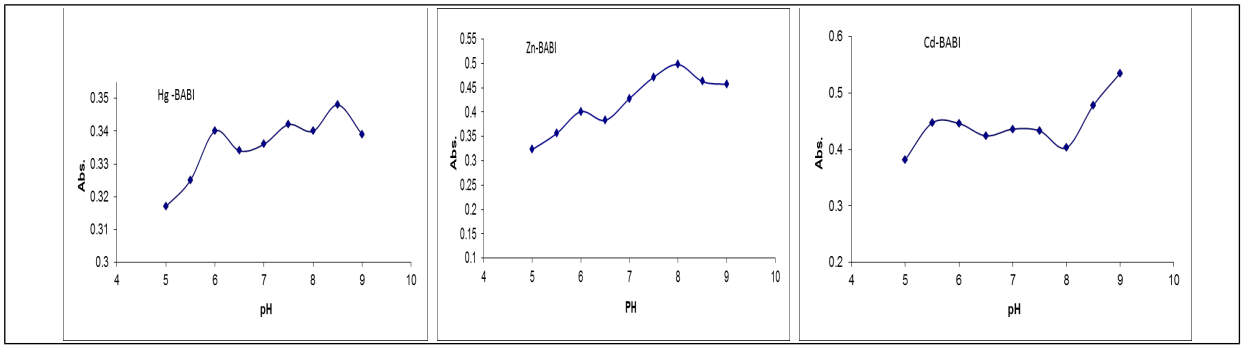


Figure 2: The effect of pH on the pH of Zn(II) ,Cd(II) ,Hg(II) complexes

Metal: ligand ratios

The metal : ligand ratio(M:L) of complexes was determined by the mole- ratio method at (λ_{max}) ,fixed pH and concentration . The results are in agreement with the values reported for some imidazolyazo complexes[19,20].which indicate that the ligand (BABI) was to form chelate complexes with Zn(II),Cd(II),Hg(II) ions, as shown in Fig.3.

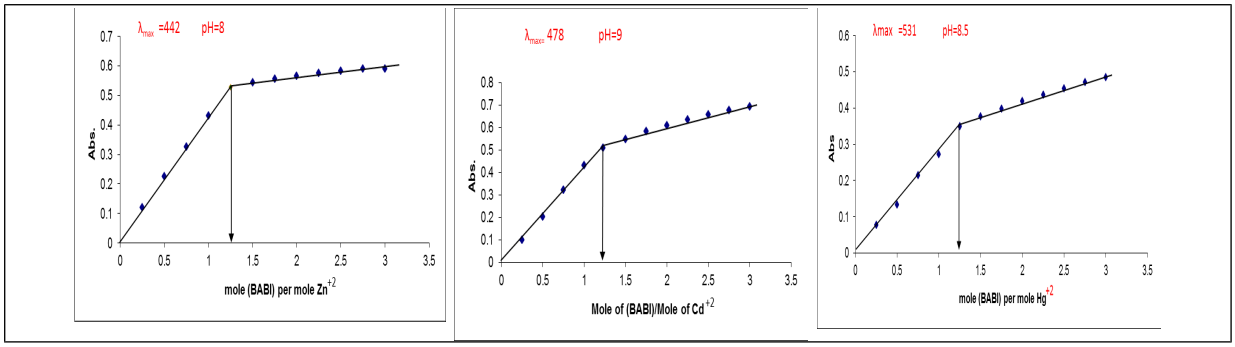


Figure 3: The mole ratio (M: L) of Zn(II) ,Cd(II) ,Hg(II) with (BABI) at optimal conc. = 9 x 10^{-5} M

Absorption spectra

The absorption spectra of ligand (BABI) and its complexes were studied and shown in figures (4-5). The wavelength for the maximum absorption (λ_{max}) of the ligand was found at 421nm. The spectra of metal complexes were recorded within wavelength range (442– 531) nm. The absorption maxima (λ_{max}) of the each complexes also shown in Table.2. .Two absorption bands were appear at the free ligand (BABI) spectrum. The band at 313 nm referring to the $\pi \rightarrow \pi^*$ transitions of imidazole ring while the band at 421nm is due to $n \rightarrow \pi^*$ the charge transfer characters[21].Since the UV-Visible spectra of d^{10}ion do not furnish a lot of information so some shifting and change in the shape of the bands were compared with those of the ligand[22]

The spectrum of the complex shows relative change in the bands position compared to that of the free ligand ,as showed in figures(**5-7**).

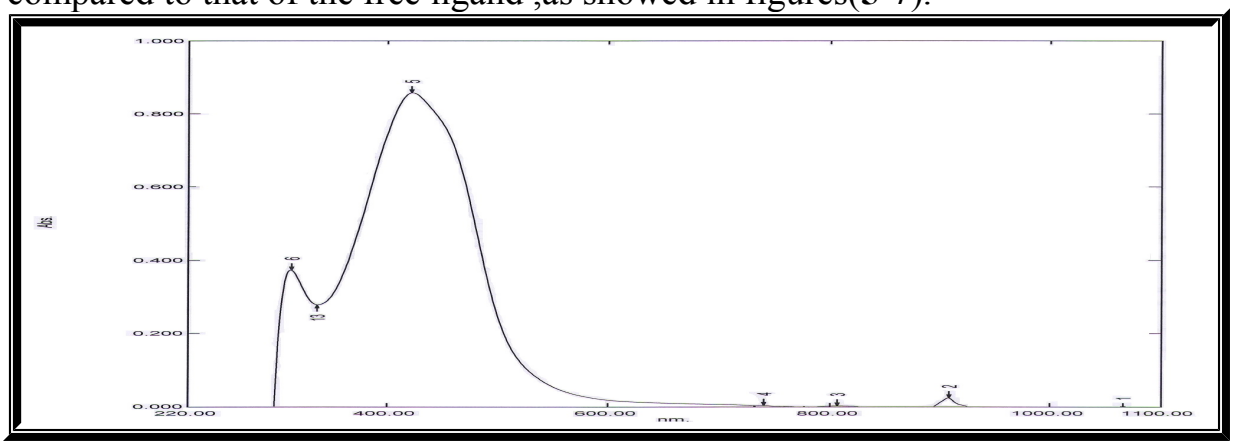


Figure 4: Absorbance spectrum of ligand (BABI)

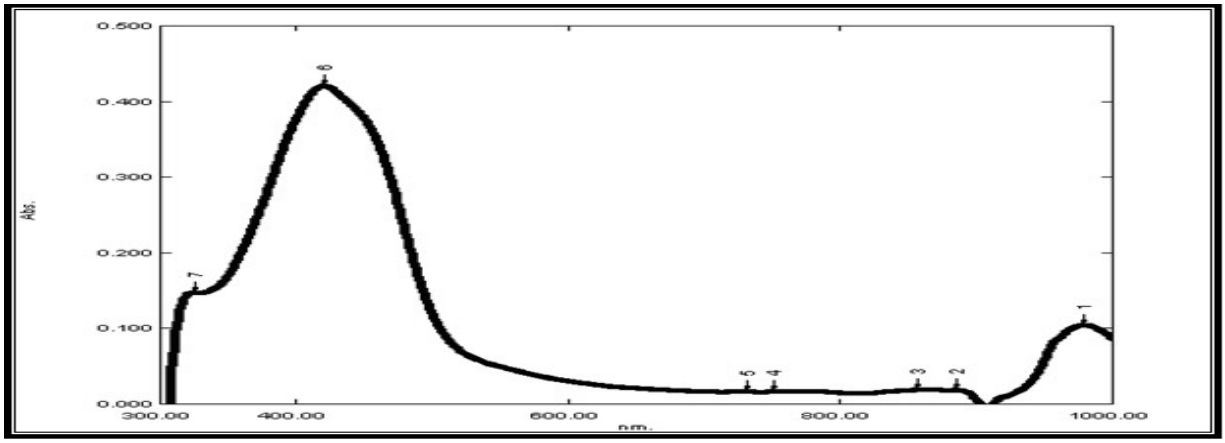


Figure 5: Absorbance spectrum of ligand (BABI) with Zn(II) In Conc.9x 10^{-5} M

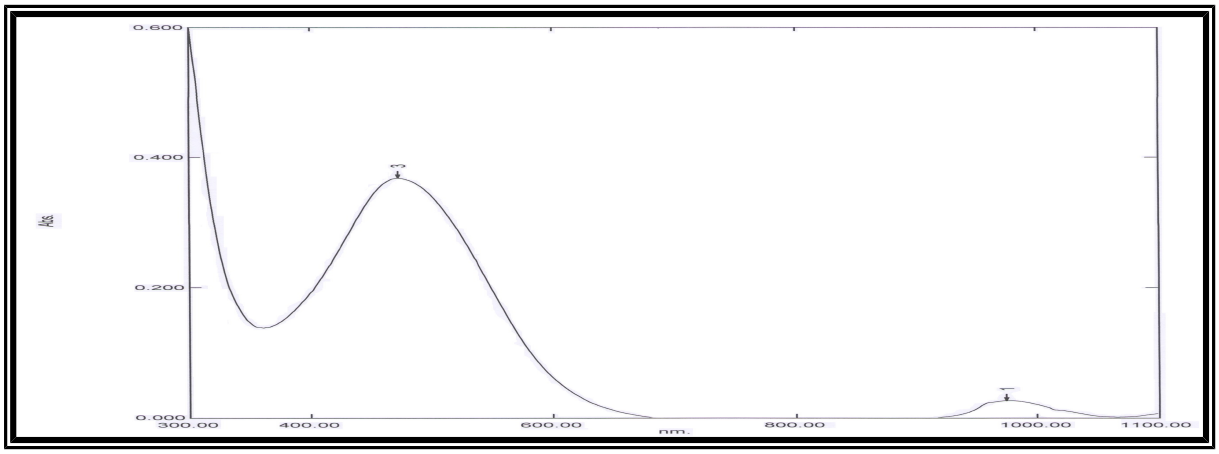


Figure 6: Absorbance spectrum of ligand (BABI) with Cd(II) In Conc.9x 10^{-5} M

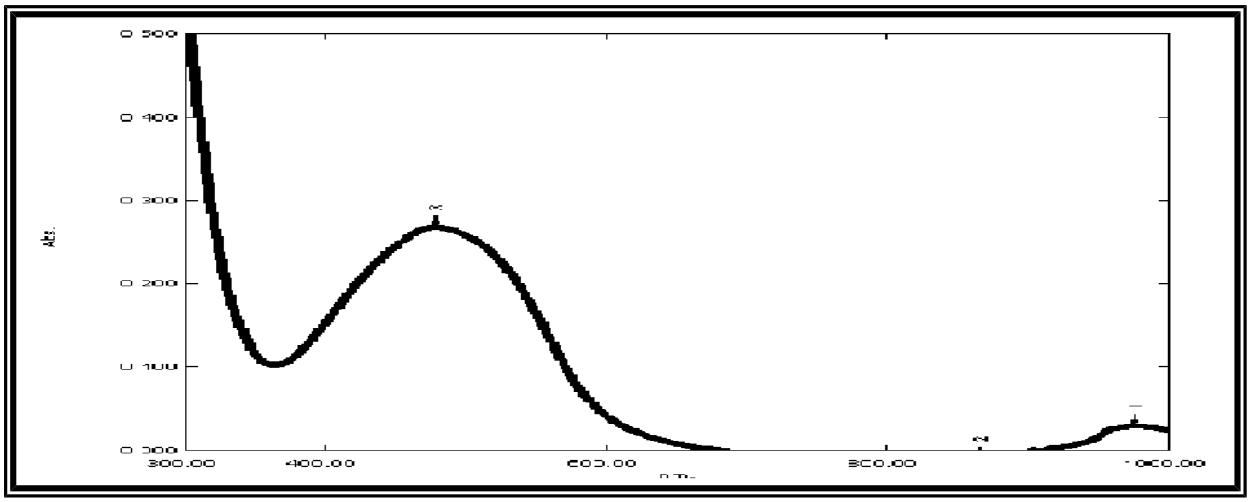


Figure 7: Absorbance spectrum of ligand (BABI) with Hg(II) In Conc.9x 10^{-5} M

Table 2: The optimal pH values, optimal molar concentration and wavelength (λ_{max}) metal ions

Metal	Optimal	Optimal molar	Optimal wave	$\Delta\lambda_{max*}$

Ions	pH	conc.	length (λ_{max}) nm	Nm
Zn(II)	8	9×10^{-5}	442	+21
Cd(II)	9	9×10^{-5}	478	+57
Hg(II)	8.5	9×10^{-5}	531	+110

*$\Delta\lambda_{max} = \lambda_{max}$ Complex - λ_{max} ligand

Infrared spectra

The infrared spectra of the free ligand (BABI) and its complexes with Zn(II),Cd(II),Hg(II) ions are given in Table.3. These spectra are complicated owing to the extensive overlap of number of bands arising from υ(N─H), υ(C═N), υ(N═N) and other bands due to the phenyl and imidiazole rings[23] which appeared in the region below 1680 cm^{-1}. The comparison between the IR spectral data of the free ligand with that of its complexes are discussed as follow:-

1- The spectrum of azo ligand (BABI) show absorption band around 3390cm^{-1}due to the υ(N─H)groups. This suggests that the band due to(N─H)group in imidiazole ring [24]. The same band in Zn(II),Cd(II),Hg(II) ions complexes indicates that this band didn't share in complexation.
2- The spectrum of ligand shows absorption band at 1602 cm^{-1} due to υ(C═N) of imidiazole ring[25].This band is observed with a little change in shape and shifted to higher frequencies υ(1600-1627) cm^{-1} in complexes . These differences may suggest the linkage of metal ions with nitrogen of hetrocyclic imidiazole ring.
3- The azo group (N═N) appears at (1442) cm^{-1} in the free ligand spectrum. This band has been shifted to a higher frequencies (1444-1467) cm^{-1} in complexes spectra; this means that some linkage of metal ion with nitrogen atom of azo group which is the farthest of imidiazole ring takes place[26].
4- Finally a new weak bands appears at (464-551) cm^{-1} in the complexes spectra which may suggest the linkage of metal ions with nitrogen atom[27]. The IR spectra indicate that imidiazole azo ligand (BABI) behaves as a tetradentate chelating agent coordinated through nitrogen of azo group and the nitrogen atom of imidiazole ring. Figs.(8- 11) shows the spectra of ligand (BABI), and it's complexes spectra .

Table 3: Characteristic IR absorption bands of the ligand (BABI) and it complexes in cm^{-1} units.

Compound	υ(N─H)	υ(C═N)	υ(N═N)	υ(M─N)
$C_{36}H_{26}N_8$	3390	1602	1442	─

[Zn ($C_{36}H_{26}N_8$)Cl_2]	3397	1627	1456	551
[Cd ($C_{36}H_{26}N_8$)Cl_2]	3394	1612	1444	511
[Hg ($C_{36}H_{26}N_8$)Cl_2]	3398	1600	1467	464

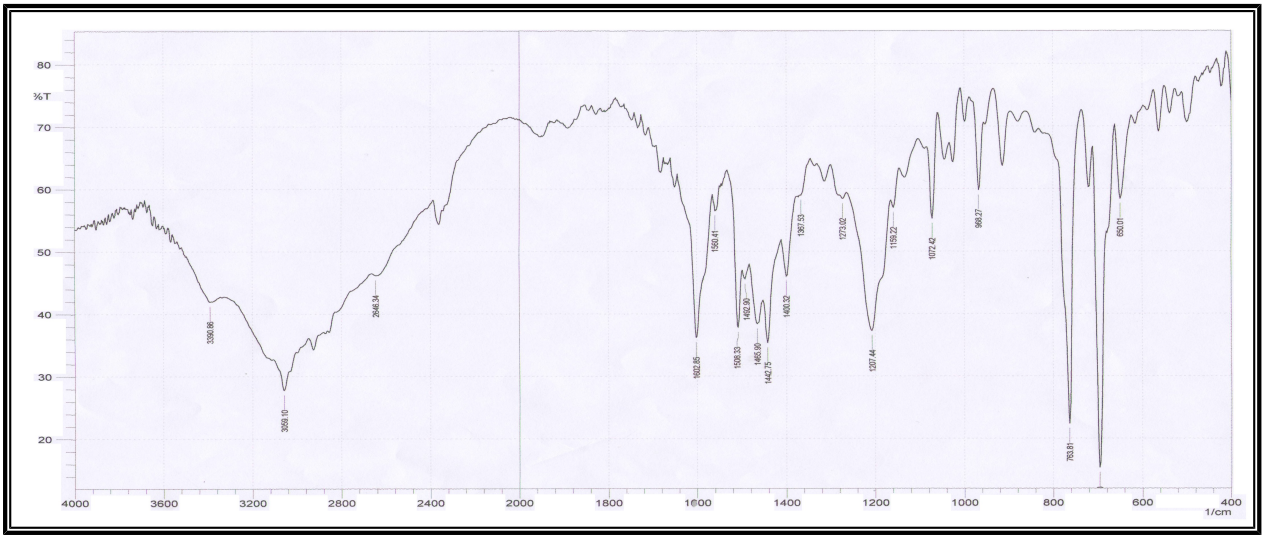


Figure 8: FT-IR spectrum of (BABI)

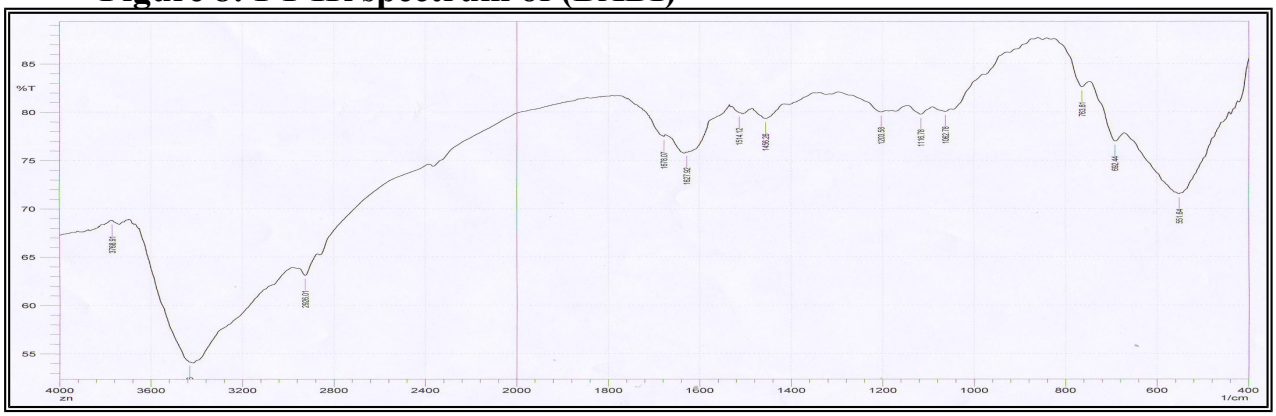


Figure 9: FT-IR spectrum of ion complex of Zn (II) with (BABI)

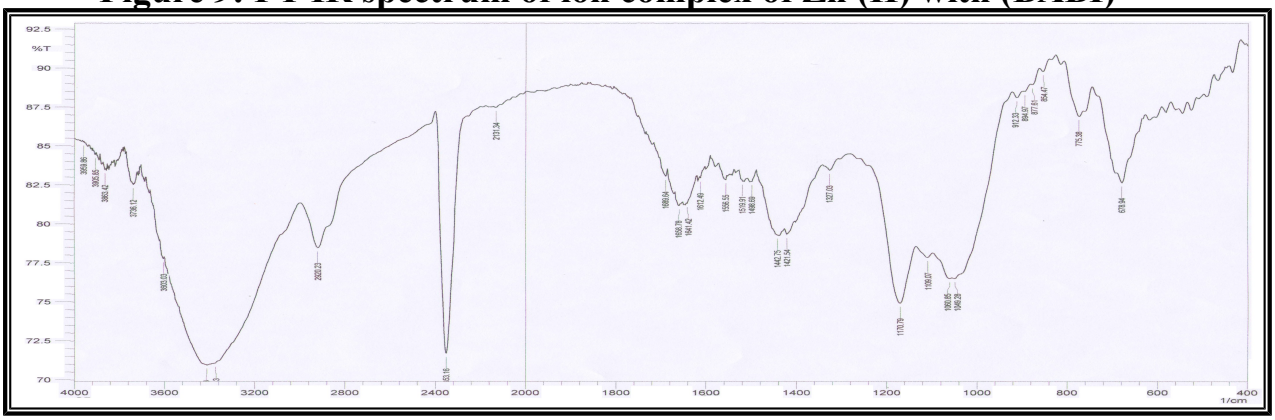


Figure 10: FT-IR spectrum of ion complex of Cd (II) with (BABI)

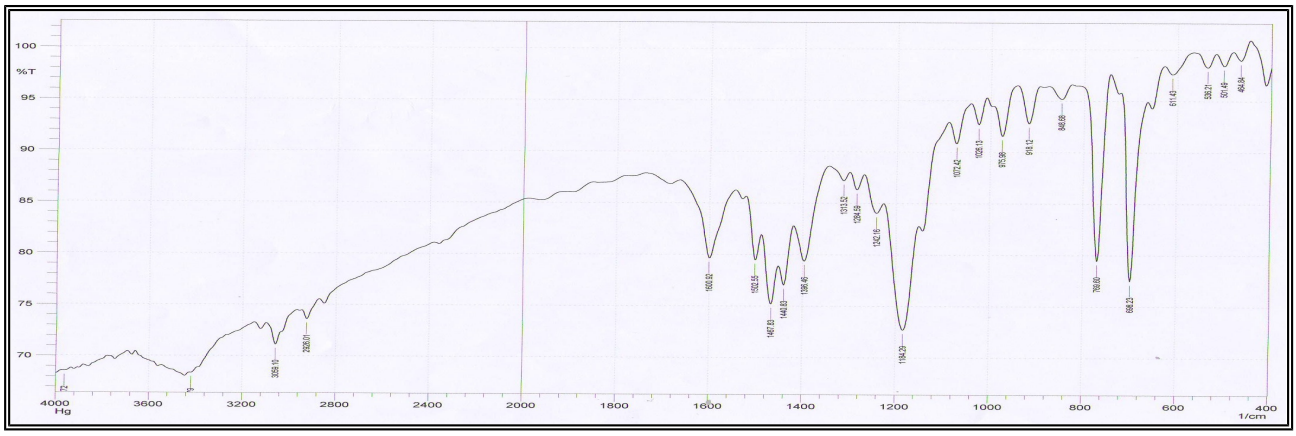


Figure 11: FT-IR spectrum of ion complex of Hg (II) with (BABI)

Conductivity measurements

All complexes show the conductivity measurement values ranging between (8.7 – 17.9) $S.cm^2. mol^{-1}$ in ethanol solution at room temperature ,these values indicating nonionic structure of these complexes. The conductivity values are listed in Table 4.

Table 4: Conductivity measurements of complexes in ethanol

Magnetic susceptibility:

The magnetic susceptibility of Zinc (II), Cadmium (II) and Mercury (II) complexes show that have diamagnetic moment, and the electronic spectra of this complexes do not show any (d-d)transition band .

According to the results , the elemental

Complex	Conductivity $S.cm^2.mol^{-1}$
$[Zn(C_{36}H_{26}N_8)Cl_2]$	17.9 17.9
$[Cd(C_{36}H_{26}N_8)Cl_2]$	14.4 14.4
$[Hg(C_{36}H_{26}N_8)Cl_2]$	8.7 8.7

analysis(C.H.N) and the percentage of metal ions by using atomic absorption technique , the coordination number of metal ions is found to be six with bonding through the (N) of bis azo group and the two (N) atoms of imidazole. The structural formula of prepared complexes is most probably octahydral as shown in fig .12

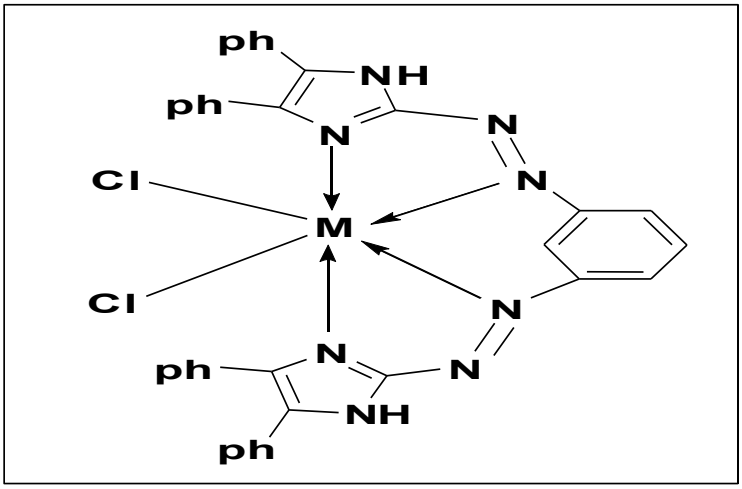


Figure 12: The proposed structural formula of Zn(II),Cd(II) and Hg(II) with the ligand (BABI)

Theoretical Study:

The program Hyper Chem-8 was used for the semi-empirical and molecular mechanical calculation at optimized energies, the result of ZINDO/1 method of calculation in gas phase for heat of formation ($\Delta H^{\circ}f$), binding energy (ΔE_b) and dipole moment (μ) for free ligand and its complexes of Zn(II),Cd(II) and Hg(II), table**(5)**. PM3 was used for evaluating the wave number for the ligand and compared with the experimental frequencies to predict the deviation, table (**6**). ZINDO/S method was used to calculate electronic transitions for the ligands and compared with experimental transition to explain the transitions.

Table (5): Conformation energetic (in K.J.mol^{-1}) and dipole moment (in Debye) for ligand(BABI) and its metal complexes.

	ZINDO/1			**AMBER**
Comp.	$\Delta H^{\circ}f$	ΔE_b	μ	$\Delta H^{\circ}f = \Delta E_b$
L	-68979.73	-104170.06	8.215	----------
ZnL	-75180.69	-110744.03	13.48	----------
CdL	-72701.55	-108246.27	7.811	
HgL	---------	----------	13.47	1201.57

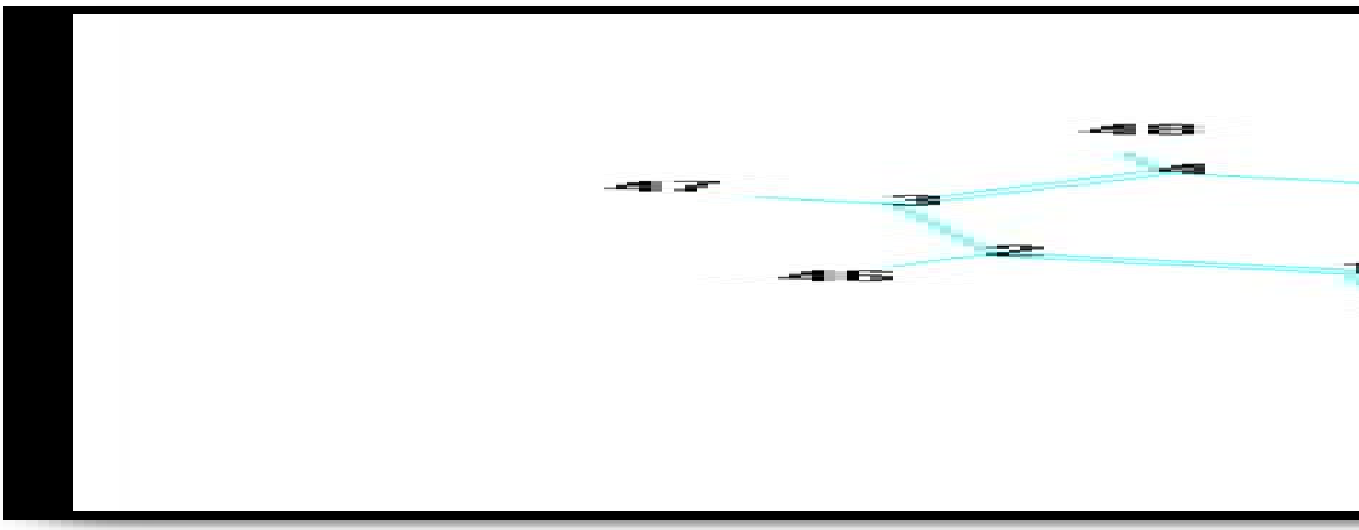
The table above explained that the heat of formation of complexes is smaller than it for ligand, and the binding energy also smaller than it for ligand thus, we expected that the complexes are to be thermodynamically more stable than ligand.

Table (6): Comparison of experimental and theoretical vibrational frequencies for BABI ligand.

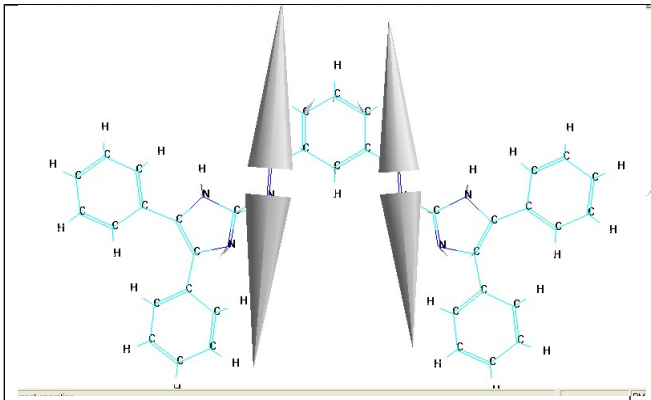
Symb.	*υ(N-H)*	*υ(C=N)*	*υ(N=N)*
L	3390* 3402** (0.35)***	1602* 1629** (1.65)***	1442* 1400** (-2.91)***

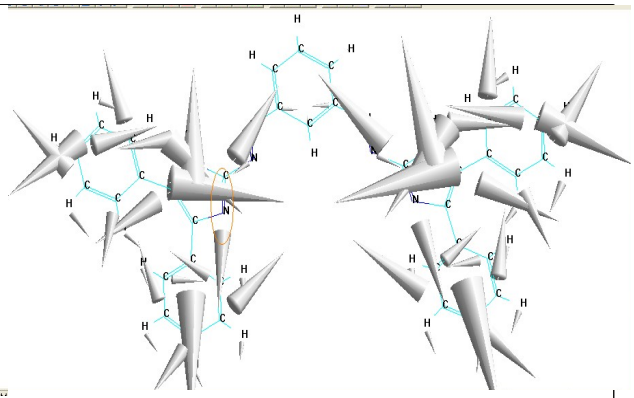
Where:*Experimental frquency,theoretical frequency,***Error% due to main different measurements and theoretical treatment of vibrational spectra.**

The theoretical UV-spectrum of ligand was calculated using ZINDO/S method and showed some deviations from the experimental values .These deviations are generally acceptable in theoretical calculations[27-28]. The serial number of atoms was plotted in the structure of ligand in order to determine the type orbitals than type of transition figure (14).The theoretical UV-spectrum of ligand BABI showed two absorption peaks at 314.9 and 431.5 nm. The quantum data indicate that these peaks are generated mainly from π→π* transition (N15→C16 or N29 →C28) and n→π* transition (N26→ N27 or N29→ N28).The experimental spectrum also showed two peaks at 313.00 and 421.00 nm

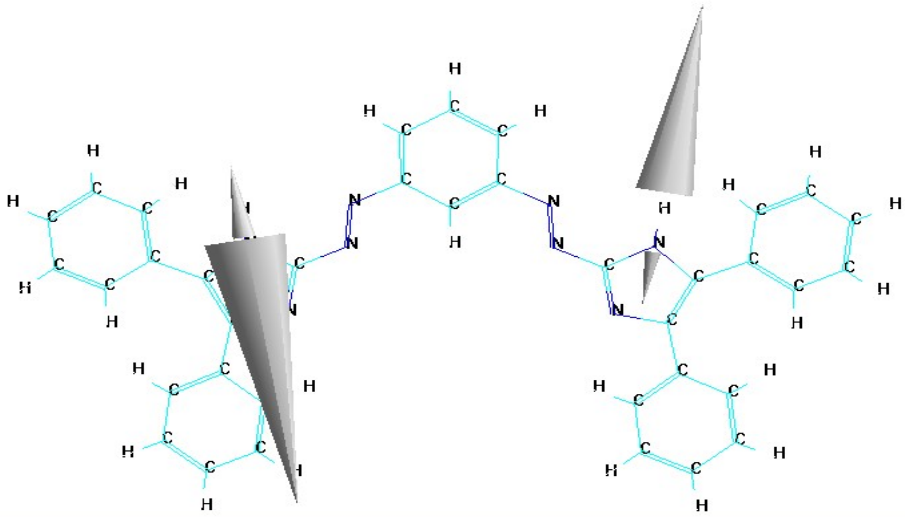


Figure(14):Serial number of atoms view of (BABI).ligand





υ (N=N)1400	υ (C=N) (1629)



υ(N─H):3402

Figure(15):Calculated vibrational frequencies of the ligand (BABI).

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تحضير ودراسة طيفية ومعالجة نظرية لمعقدات أيونات الخارصين(II) والكاديوم (II) والزئبق (II) مع الليكاند 1,3- بس (5,4- ثنائي فنيل اميدازول آزو) بنزين

الخلاصــة

تم تحضير ودراسة طيفية لمعقدات ايونات الخارصين(II) والكاديوم (II)والزئبق (II) مع الليكانـد 1,3 بس (5,4- ثنائي فنيل اميدازول آزو) بنزين. وقد تم التحضير بعد تثبيت الظروف الفضلى من تركيز ودالة حامضية من خلال دراسة أطياف الأشعة فوق البنفسجية – المرئية لمزج محاليـل الايونـات الفلزيـة الثنائية مع محلول الليكاند ولمدى واسع من الدالة الحامضية والتراكيز الخاضعة لقانون لامبرت – بيير .
وقد تم التعرف على تركيب المعقدات المحضرة عن طريق إيجاد النسبة المولية لعلاقة (الفلز : الليكانـد) بوساطة دراسـة أطيـاف (UV-Vis.) لمحاليـل خلـط الايونـات الفلــزية المدروسـة مـع الليكانـد ، وبينـت الدراســـة إنهـــا (1 : 1)(L:M) لهذه المعقدات. شخص الليكاند والمعقدات الصلبة المحضرة بالوسائل التحليلية والطيفية المتاحة فقد تم تشخيصها بوساطة ألاطياف الالكترونية ، كما تم دراسـة أطيـاف الأشـعة تحت الحمـــراء (F.T.IR) للمعقدات المدروسة. وقد بينت دراسـة التوصـيلية المولاريـة انعـدام الصـفة الأيونية للمعقدات المذكورة كما تم إجراء التحليل الـدقيق للعناصـر وحسـاب نسـبة الايونـات الفلزيـة لهـذه المعقدات ، وبالاعتماد على النتائج المستحصلة استطعنا الاستنتاج بان المعقدات الكيليتية المحضرة تتخـذ الشكل الهندسي الثماني السـطوح. أجريـت دراسـة تكـون المعقـدات نظريـاً فـي الطـور الغـازي باسـتخدام برنامج (Hyperchem-8) باستخدام الطرق شبه التجريبية PM3,ZINDO/S , ZINDO/1 لحساب حـرارة التكـوين وطاقـة الـترابط والعـزم ثنـائي القطـب عنـد درجـة حـرارة 298 كلفـن لليكانـد ومعقداته المحضرة. كذلك تم حساب الترددات الاهتزازية والانتقالات الالكترونية لليكاند المحضر.