Synthesis and Spectral Studies of some Zn(II),Cd(II) and Hg(II) complexes with the Ligand 2-{4- Bromo phenyl azo } -4,5-diphenyl imidazole *(p-BrPAI)*

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الخلاصــة

تـم تحضـير ودراسـات طيفيـة لعدد مـن معقدات ايونـات الخارصـين (II)و الكـادميوم (II) والزئبـق(II) مـع الليكاند ٢{٤- برومو فنيل ازو} -٤،٥- ثنائي فنيل اميدازول وقد تم التحضير بعد تثبيت الظروف الفضلى من تركيز ودالة حامضية من خلال دراسة أطياف الأشعة فوق البنفسجية – المرئيـة لمحاليل مـزج هذه الايونـات مـع محاليل الليكاند ولمدى واسع من الدالـة الحامضية والتراكيز الخاضـعة لقانون لامبرت – بيير .وقد تم التعرف على التراكيب للمعقدات المحضرة عن طريق إيجاد النسبة المولية لعلاقة (الفلز : الليكاند) بوساطة دراسة أطياف (UV-Vis.) لمحاليل خلط الايونـات الفلــزية المدروســـة مع الليــكاند ، وبينت الدراســـة إنهـــا (L:M)(2 : 1) لكـل المعقـدات. شـخص الليكانـد والمعقـدات الصـلبة المحضـرة بالوسـائل التحليليـة والطيفيـة المتاحـة فقد تـم تشخيصـها بوسـاطة ألاطيـاف الالكترونيـة ، كمـا تـم دراسـة أطيـاف الأشـعة تحـت الحمـــراء (IR) للمعقدات المدروسة. وقد بينت دراسة التوصيلية المولارية انعدام الصفة الأيونية للمعقدات المـذكورة كمـا تـم إجـراء التحليـل الـدقيق للعناصـر وحسـاب نسـبة الايونـات الفلزيـة لـبعض هذه المعقدات ً ، وبالاعتماد على النتائج المستحصلة استطعنا الاستنتاج بان المعقدات الكيليتية اتخذت الشكل الهندسـي الثمـاني السطوح.

Abstract

A new chelate complexes of Zn(II),Cd(II) and Hg(II) have been prepared by reacting these ions with the ligand 2-{4- Bromo phenyl azo }-4,5-diphenyl imidazole (p-BrPAI) ,The preparation of the complexes have been conducted after fixing the optimum conditions such as pH and concentration .UV- visible spectra of these complex solutions have been studied for a range of pH and concentration which obey Lampert-Beers Law .The structures of complexes are deduced according to mole ratio method which were obtained from the spectroscopic studies of the complex solutions .The ratios of metal: ligand obtained are (1:2) for all 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 takes place.

The conductivity measurements , elemental analysis ,the percentage of some metal ions were determined .Depending on these results ,we may conclude that the ligand was bidentate . Also the proposed geometrical structures of the complexes of Zn(II), Cd(II) and Hg (II) ions are octahedral.

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Keywords: Synthesis, Spectral studies, imidazole azo ligand, and Elemental analysis.

Introduction

The azo compound class account for 60-70% of all dyes, they all contain an azo group, -N=N-, which links two sp2 hybridized carbon atoms. Often, these carbons are part of aromatic systems, but this is not always the case. Most azo dyes contain only one azo group, but some contain two (diazo), three (trisazo) or more. Azo actually refers to chemical compounds that bear the function group R-N=N-R', in which N is Nitrogen; R and R' can be either aryl or alkyl. A series of studies regarding many azo compounds were reported by many workers [1,2,3], using IR, and Raman spectroscopy, CHN analysis and H^1-NMR. Some azo dyes were published as antimicrobial agents[4], , for example; prontosil salicyl azo, sulfopyriden. Azo dyes constitute the largest group of colorants used in industry; however, the environmental fate of these pollutants is not well understood. Azo dyes do not occur in nature and are produced only through chemical synthesis[5]. The general formula for making an azo dye requires two organic compounds a coupling component and a diazo component. Since these can be altered considerably, an enormous range of possible dyes are available, especially as the starting molecules are readily available and cheap. Furthermore, the simplicity of the reactions mean that the process can be scaled up or down very easily. Energy requirements for the reaction are low, since most of this reaction at or below room temperature. The environmental impact is reduced by the fact that all reactions are carried out in water, which is easy and cheap to obtain, clean and dispose of. All these factors make azo dyes very cheap to produce[6].

Azo dyes are much more stable than most of the natural food dyes. They are stable in the whole pH range of foods, are heat stable and do not fade when exposed to light or oxygen. This makes azo dyes applicable in nearly all foods. The only disadvantage is that azo dyes are not soluble in oil or fat. Only when azo dyes are coupled to a fat soluble molecule, or when they are dispersed as very fine particles, oils can be coloured [7]. In this work we describe the preparation and characterization of new imidazole azo ligand and some of their transition metal complexes.

Experimental

Materials and physical measurements

All chemicals used were of highest purity (BDH or Fluka) and used with out further purification except of 2-{4- Bromo phenyl azo }-4,5-diphenyl imidazole, this was prepared as described in the literature[8].

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. ,the metal percentages were determined by atomic absorption technique by Shimadzu -AA-160. The magnetic susceptibilities of the complexes were measured on powered samples using the faraday method, for this purpose Balance Magnetic susceptibility model – M.S.B.

Synthesis of complexes

The chelat complexes have been synthesized at optimal pH values dissolved (0.0818gm, 0.02 mol) of ligand (p-BrPAI) in 10 ml ethanol and then (0.01 mol) of metal chloride, MCl_2= Zn (II), Cd (II) or 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 those complexes.

Table 1: some Physical properties and analytical data of the ligand (p-BrPAI) and its complexes.

No.	Compound	Color	m.p C°	Analysis% Found (Calc.)			
				C	H	N	M
1	$C_{21}H_{15}N_4Br$	Orange	209	62.11 (62.53)	3.52 (3.72)	13.36 (13.89)	—
2	[Zn(p-BrPAI)$_2$Cl$_2$]	Red	178d*	53.03 (53.53)	3.23 (3.18)	11.51 (11.89)	6.61 (6.94)
3	[Cd(p-BrPAI)$_2$Cl$_2$]	Brown	221	50.73 (50.99)	3.18 (3.03)	11.51 (11.33)	11.40 (11.37)
4	[Hg(p-BrPAI)$_2$Cl$_2$]	Red	156d	46.51 (46.79)	2.89 (2.78)	10.22 (10.39)	12.29 (12.17)

d = decomposition temp.

Results and discussion

Effect of pH

Suitable pH values for metal complex solutions were found to be in the range of (5 – 10). to evaluate the optimal pH values of metal complex solutions .the effect of pH on the absorbance were studied, and the results are shown in Figs. 1-3.

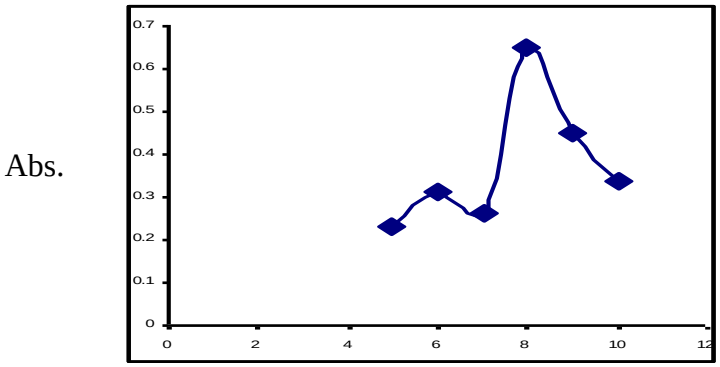


Figure 1: The effect of pH on the pH of Zn- p-BrPAI complex

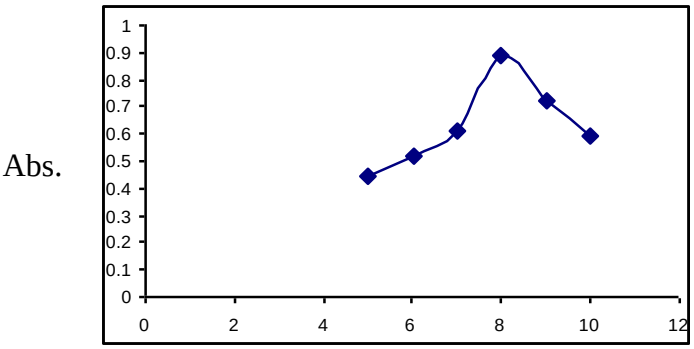


Figure 2: The effect of pH on the pH of Cd- p-BrPAI complex

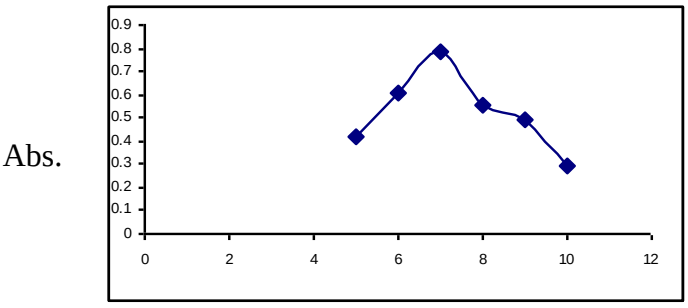


Figure 3: The effect of pH on the pH of Hg –p-BrPAI complex

Metal: ligand ratios

The metal : ligand ratio(M:L)of complexes were 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[8,9].which indicate that the ligand (p-BrPAI) was to form chelate complexes with the metal ions of Zn(II),Cd(II) and Hg(II) as shown in Figs. 4- 6.

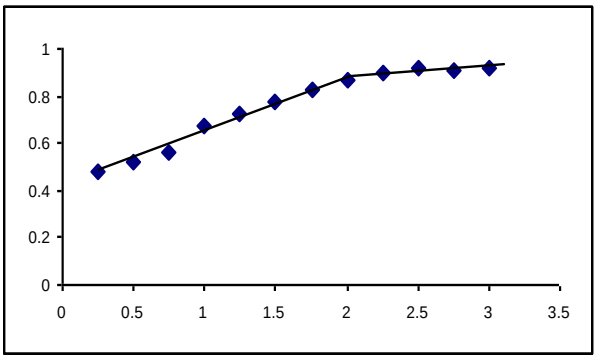


Figure 4: The mole ratio (M:L)Of Zn(II) with (p-BrPAI) at optimal conc. = 9 x 10^{-5} M

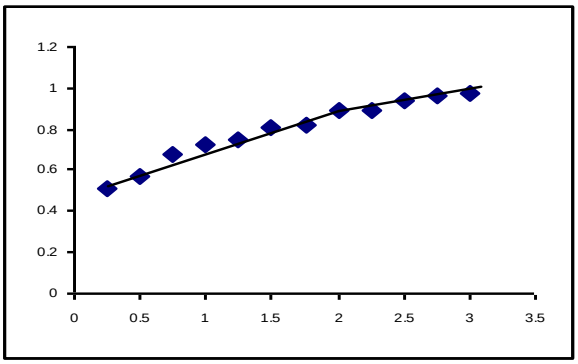


Figure 5: The mole ratio (M:L)Of Cd(II) with (p-BrPAI) at optimal conc. = 9 x 10^{-5} M

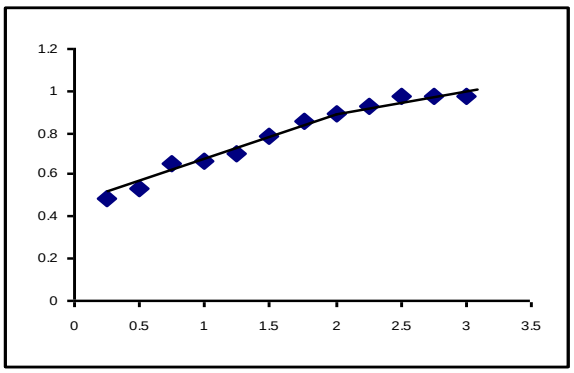


Figure 6: The mole ratio (M:L)of Hg (II) with (p-BrPAI) at optimal conc. = 9 x 10^{-5} M

Absorption spectra

The absorption spectra of ligand (p-BrPAI) and its complexes were studied and shown in figures7- 10. The (λ_{max}) of the ligand was found at 424nm. The spectra of metal complexes were recorded within wavelength range (430 – 496) nm. The absorption maxima (λ_{max}) of each complex also shown in Table.2. .Two absorption bands were appear at the free ligand (p-BrPAI) spectrum. The band at 293 nm referring to the $\pi \rightarrow \pi^*$ transitions of imidazole ring while the band at 424 nm is due to the charge transfer characters[3,10].

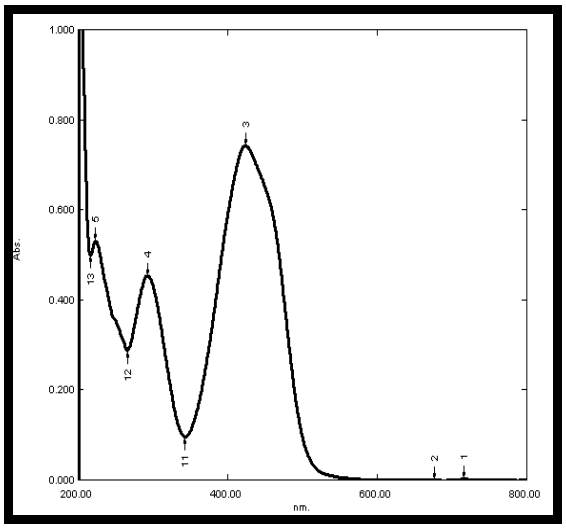


Figure 7: Absorbance spectrum of ligand (p-BrPAI)

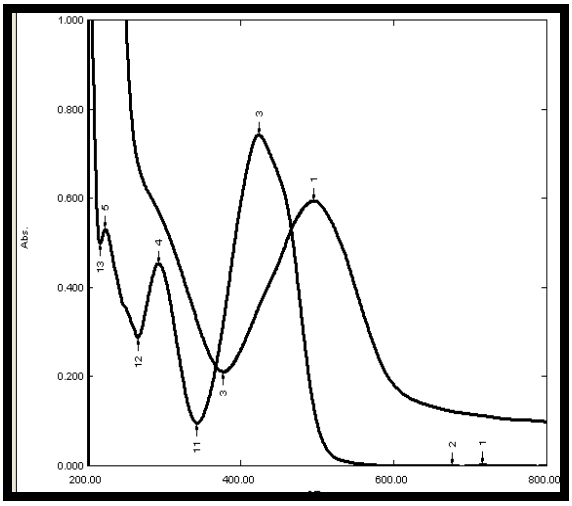


Figure 8: Absorbance spectrum of ligand (p-BrPAI) with Zn(II) In Conc.9x 10^{-5} M

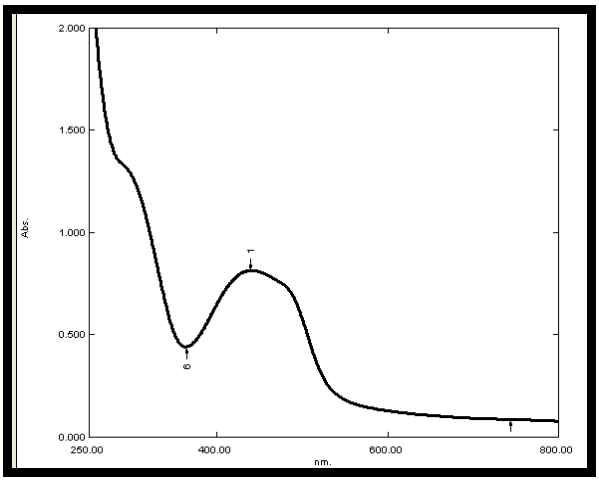


Figure 9: Absorbance spectra of ligand (p-BrPAI) with Cd(II) In Conc. 9x 10^{-5} M

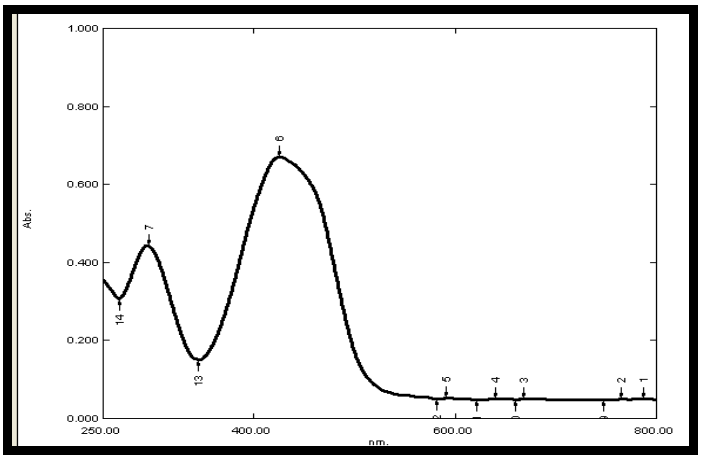


Figure 10: Absorbance spectra of ligand (pBrPAI) with Hg(II) In Conc. 9x 10^{-5} M

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

Metal Ions	Optimal pH	Optimal molar conc. 9X 10^{-5} M	Optimal wave length (λ_{max})nm	$\Delta\lambda_{max}$* nm
Zn(II)	8	9	496	+72
Cd(II)	8	9	439	+15
Hg(II)	7	9	430	+6

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

Infrared spectra

The infrared spectra of the free ligand (p-BrPAI) and its complexes with Zn(II) , Cd ((II) and Hg (II) 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[8] 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 (p-BrPAI) show absorption band around 3400 cm^{-1}due to the υ(N─H)groups. This suggests that the band due to(N─H)group in imidiazole ring [11,12]. The same band in each of Zn (II), Cd (II) and Hg(II) complexes indicates that this band didn't share in complexation[8].

2- The spectrum of ligand shows absorption band at 1585 cm^{-1} due to υ(C═N) of imidiazole ring[9, 12].This band is observed with a little change in shape and shifted to higher frequencies υ (1577 – 1620) cm^{-1} in complexes. These differences may suggest the linkage of metal ions with nitrogen of hetrocyclic imidiazole ring[13].

3- The azo group (N═N) appears at 1452 cm^{-1} in the free ligand spectrum. This band has been shifted to a lower frequencies (1440-1448) cm^{-1} in complexes spectra; this means that some linkage of metal ions with nitrogen atom of azo group which is the farthest of imidiazole ring takes place[13].

4- Finally a new weak bands appears at (411-420) cm^{-1}in the complexes spectra which may suggest the linkage of metal ions with nitrogen atom[9,12]. The IR spectra indicate that imidiazole azo ligand (pBrPAI) behaves as a bidentate chelating agent coordinated through nitrogen of azo group and the nitrogen atom of imidiazole ring. Figs. 11- 14 shows the spectra of ligand (p-BrPAI), and it's complexes spectra .

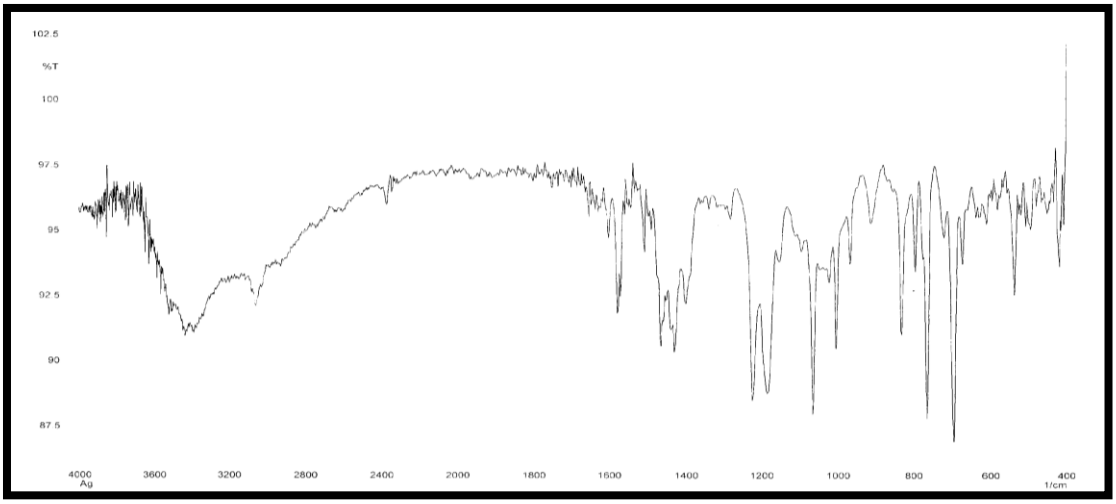


Figure 11: FT-IR spectrum of (p-BrPAI)

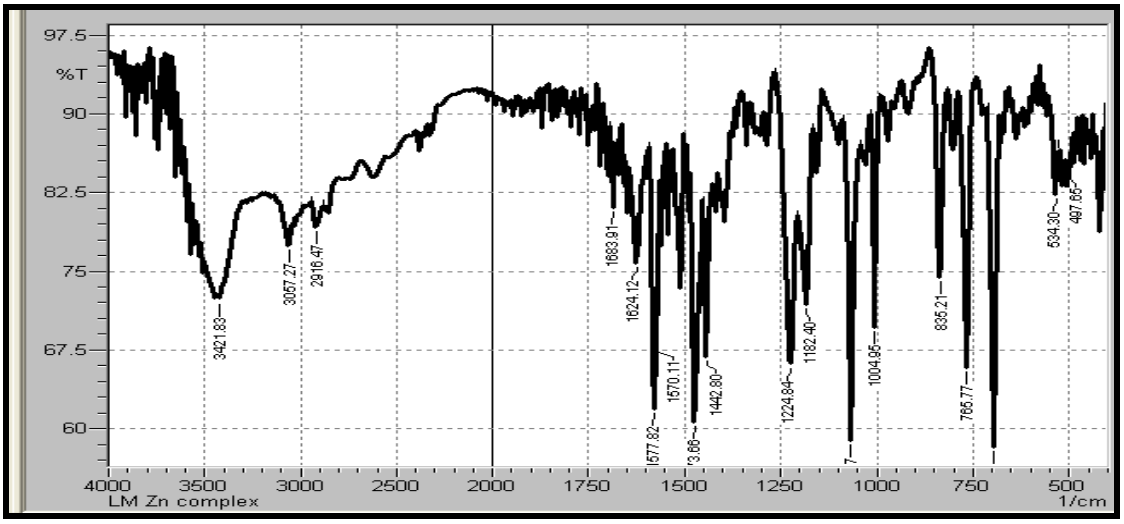


Figure 12: FT-IR spectrum of ion complex of Zn (II) with (p-BrPAI))

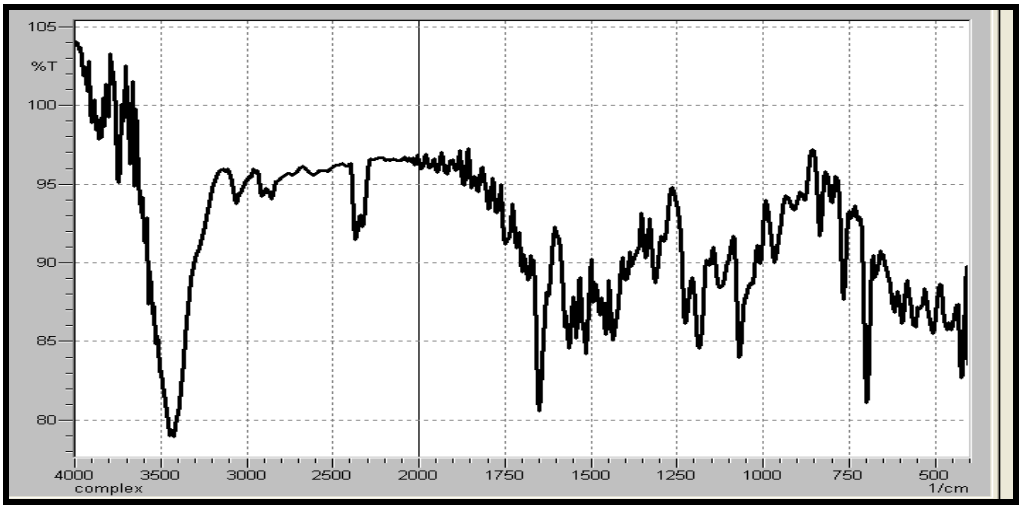


Figure 13: FT-IR spectrum of ion complex of Cd (II) with (p-BrPAI))

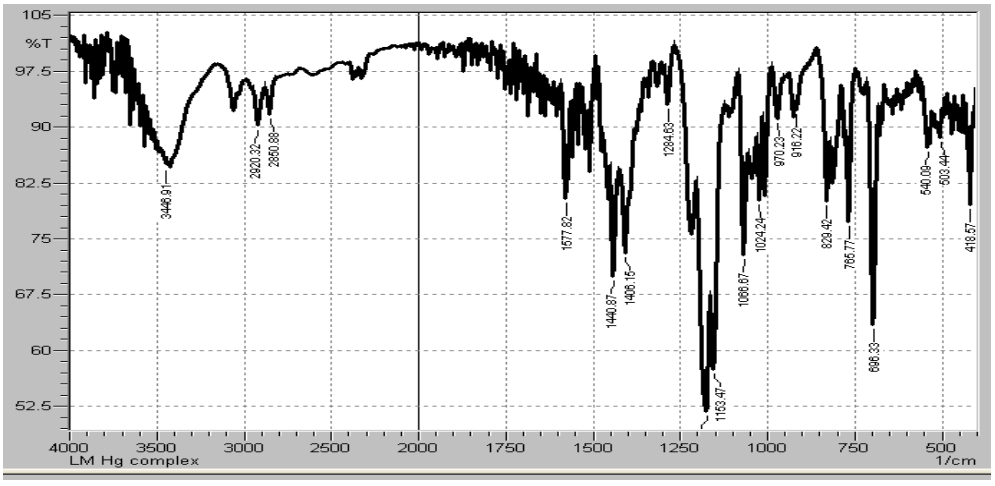


Figure 14: FT-IR spectrum of ion complex of Hg (II) with (p-BrPAI)

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

Compound	υ(N─H)	υ(C═N)	υ(N═N)	υ(M─N)
$C_{21}H_{15}N_4Br$	3400	1585	1452	─
$[Zn\ (C_{21}H_{15}N_4Br)_2Cl_2]$	3421.	1577	1442	420
$[Cd(C_{21}H_{15}N_4Br)_2Cl_2]$	3400	1620	1448	411
$[Hg(C_{21}H_{15}N_4Br)_2Cl_2]$.	3446	1577	1440	418

Conductivity measurements

All complexes show the conductivity measurement values ranging between (5.54– 11.32) S.cm2. mol-1 in ethanol solution ,these values indicating nonionic structure of these complexes(8). The conductivity values are listed in Table 4.

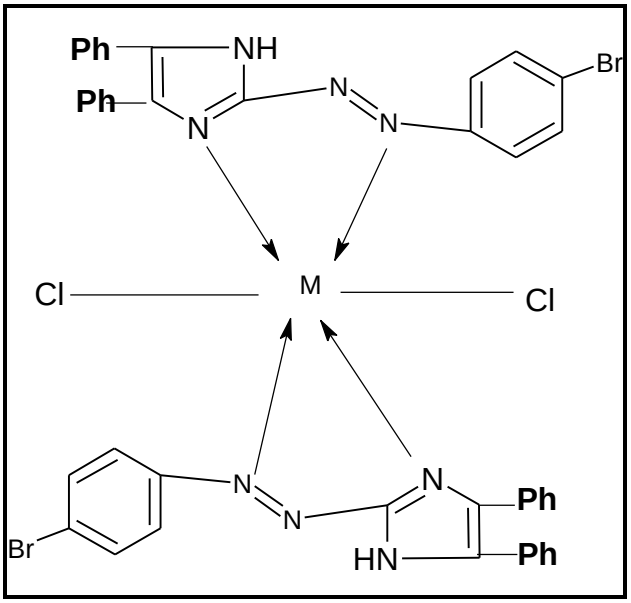
Table 4: Conductivity measurements of complexes in EtOH

Complex	Conductivity $S.cm^2.mol^{-1}$
$[Zn\ (C_{21}H_{15}N_4Br)_2Cl_2]$	11.32
$[Cd(C_{21}H_{15}N_4Br)_2Cl_2]$	7.02
$[Hg(C_{21}H_{15}N_4Br)_2Cl_2]$.	5.54

Magnetic susceptibility:

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

According to the results , the elemental analysis(C H N) and the percentage of metal ions by using atomic absorption technique , the coordination number of all metal ions is found to be six with bonding through the N of azo group and the N atom. Of imidazole The structural formula of prepared complexes is most probably octahydral shown in fig.15.



M= Zn (II), Cd (II) and Hg (II)

Figure 19: The proposed structural formula of Zn (II), Cd (II) and Hg (II)with the ligand (p-BrPAI)

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