

Synthesis and Characterization studies of Some New Transition Metal Complexes with Tridentate Azo Ligand Type (ONO)

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الخلاصة

تم تحضير الليكاند 2- [(4-انتيبيريل)ازو] - 3,5 ثنائي هيدروكسي تولوين كما تم تحضير معقدات هذه الليكاند مع ايونات الخارصين(II) و الكادميوم (II) والزنابق (II) ، وقد تم التحضير بعد تثبيت الظروف الفضلى والتركيز من خلال دراسة اطياف الاشعة فوق البنفسجية - المرئية لمحاليل مزج هذه الايونات مع محاليل الليكاند ولمدى واسع من التراكيز الخاضعة لقانون لامبرت - بير. وقد تم التعرف على التراكيب المحضرة للمعقدات عن طريق ايجاد النسبة المولية لعلاقة (الفلز : الليكاند) بوساطة دراسة اطياف (-UV Vis). محاليل خلط الايونات الفلزية مع الليكاند ، وبينت الدراسة انها (1 : 2) لكل المعقدات. شخص الليكاند والمعقدات الصلبة المحضرة بالوسائل التحليلية والطيفية المتاحة فقد تم تشخيصها بوساطة اطياف الاشعة فوق البنفسجية - المرئية ، كما تم دراسة اطياف الاشعة تحت الحمراء (IR) للمعقدات. وقد بينت دراسة التوصيلية المولارية انعدام الصفة الايونية للمعقدات المذكورة كما تم اجراء التحليل الدقيق للعناصر وحساب نسبة الايونات الفلزية لبعض هذه المعقدات ، وبالاعتماد على النتائج المستحصلة استطعنا الاستنتاج بان المعقدات الكيليتية اتخذت الشكل الهندسي الثماني السطوح في كل من معقدات الخارصين(II) و الكادميوم (II) والزنابق (II) .

Abstract

Three New chelate complexes have prepared by reacting the ligand 2-[(4-Antipyril)azo]-3,5di hydroxyl toluene (4-AAPDHT) with the metal ions Zn(II),Cd(II) and Hg(II). The preparation has demeanor after limitation the optimum stipulations and concentration through (UV-Vis)spectrophotometric study of these complex solutions have been studied for an extent of pH and concentrations which conform Lambert-Beers Law. The structures of complexes are Evidenced approbate to mole ratio method which were gained from the spectroscopic studies of the complex solutions .The proportion of metal:ligand obtained are (1:2) for all complexes ions. (UV-Vis) absorption spectra of ethanol solution of complexes exhibited bathochromic shift, as compared with that of free ligand. The infrared spectra of the chelating complexes have been studied ,this may suggest that coordination between the metal ions and the prepared ligand takes place. The elemental analysis, metal contents and the conductivity measurements of complexes It has been identified, depending on these results, the

proposed geometrical structures of the complexes of Zn(II), Cd(II) and Hg(II) ions are octahedral.

Keywords: *Synthesis , characterization and Tridentate Azo Ligand*

Introduction

A great deal of work has been reported on the synthesis, spectral determination, physical properties and elemental analysis of different types of azo dyes and their complexes with transition and non – transition elements, the transition metal complexes synthesis containing azo dyes ligands are an important area of study in inorganic chemistry and industrial chemistry [1]. For many years a great interest of azo dyes as chelating ligands and their metal complexes in coordination chemistry because of the widely studied azo dyes metal complexes in industrial and spectral analytical applications [2]. The most significant class of synthetic dyes are azo colorants representing (60-80%) of all organic colorants they are used vastly in substrates such as plastic, waxes, textile fibers, mineral oils, papers, food stuffs and cosmetics [3]. Many other industrial applications, such as the manufacturing of dyes, cosmetics, rubber and medicines, release wastes into streams with concentrations as high as 10 g /L [4,5]. Because of their menace to the environment, diverse methods have been sophisticated to equipping a swift and ticklish means to reveal these compounds [6-9]. "The general formula" for making an azo dye necessitates two organic compounds a conjugation component and a diazo component. Since these can be altered highly, a massive range of possible dyes are available (obtainable), especially as the starting molecules are readily available and scrumpy. Moreover, the simplicity of the reactions mean that the process can be scaled up or down very readily, which is constantly a key factor in the cost of chemicals [7]. As other dye classes become less fertile from either an environmental or economic causes, azo dyes become ever more attractive options [10]. Azo dyes are more probative than most of the natural food dyes they are stable in the whole pH range of foods, are warm up stable and do not vanish when bared to oxygen or light [8]. This makes azo dyes usable in almost all foods. The only deficiency 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 downy particles, oils can be colored [11]. 4-Aminoantipyrine (4-AAP is a significant derivative of the 5-pyrazolone denomination and is used for the disclosure and determination of number of compounds. However, literature on the use of (4-AAP) is very scanty as an electrophilic coupling reagent in analytical chemistry [12].

Experimental

Materials and physical measurements

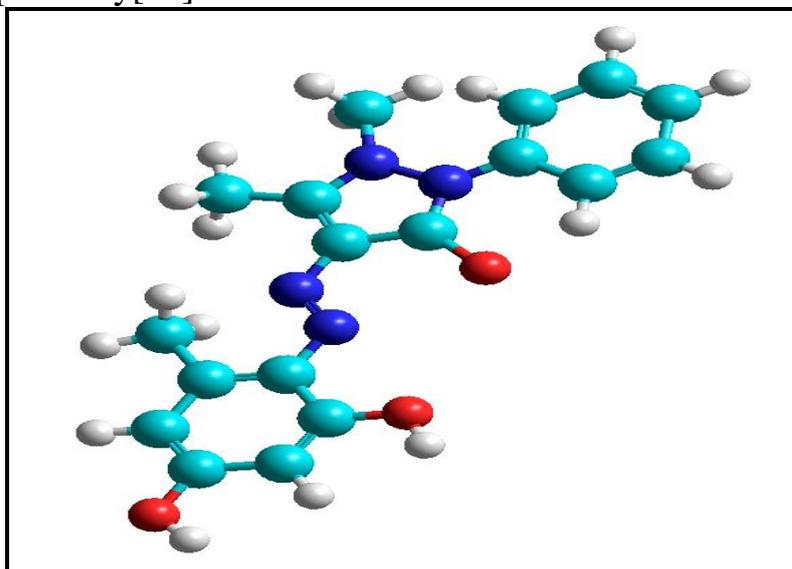
All chemicals used were of highest purity (B.D.H or Fluka) and used with out further purification.

Elemental analysis was carried out by means of micro analytical unit of (Eurovector, EA300A, Italy) C.H.N element analyzer. Absorption spectra were

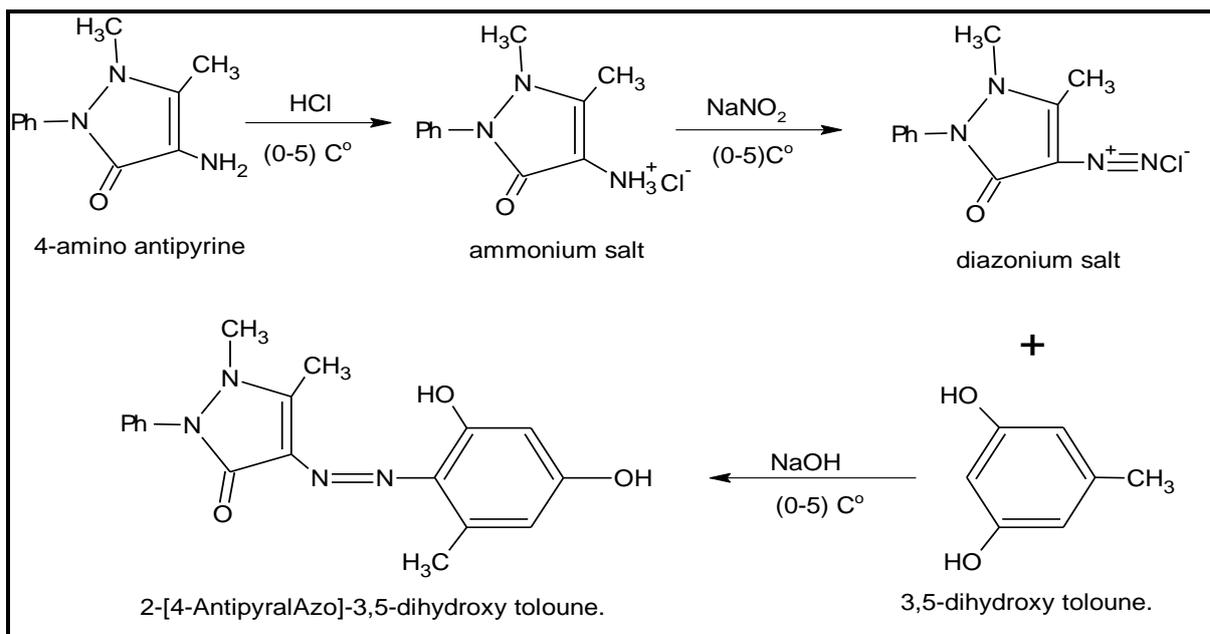
recorded using Shimadzu UV-Vis 1700 spectrophotometer, for solution of the complexes in aqueous ethanol at room temperature. Using 1cm quartz cell. IR spectra were recorded with FT-IR-8000 Shimadzu, in the range of (4000-400) cm^{-1} using KBr disc. Electrical conductivity measured by digital conductivity meter Alpha – 800 with solute concentration of (10⁻³M) in ethanol at room temperature. pH measurements were carried out using (pH– meter), 720 , WTW 82362. Metal content of the complexes were measured by using atomic absorption technique by Shimadzu -AA-160.

Synthesis and characterization of azo ligand (4-AAPDHT)

The ligand prepared by dissolving (2.03 gm, 0.01 mol) of 4-amino antipyrine in 30 ml of distilled water and 5ml of concentrated hydrochloric acid, then the filtrated solution was cooled below 0-5 °C, to this mixture a solution of (0.75gm, 0.01 mol) of sodium nitrite in 20 ml of distilled water was added drop wise with maintaining the temperature at 0-5 °C [12]. Afterward, the diazonium solution was added drop wise to a 500 ml beaker containing (1.24, gm 0.01 mol) of 3,5–di hydroxyl toluene dissolved in 150 ml of alkaline ethanol with keeping temperature at 0-5 °C. The mixture was allowed to stand over night and acidified with dilute hydrochloric acid to pH=6. The crude dyes were collected by filtration and recrystallized twice from ethanol and then dried in the oven at 50 °C for two hrs to give yield of 79%. The melting point of the ligand was (264°C) and the structural formula and the preparation of ligand is illustrated in figure(1) and Schema(1) respectively[12].



Figure(1):- Structure of the ligand 2-[(4-Antipyril)azo]-3,5di hydroxyl Toluene (4-AAPDHT)



Schema(1):Preparation of the ligand 2-[(4-Antipyril)azo]-3,5-di hydroxyl toluene (4-AAPDHT)

Synthesis of complexes

The chelate complexes have been synthesized at optimal pH values dissolved (0.676gm, 0.002 mol) of ligand (4-AAPDHT) in 10 ml ethanol and then (0.01 mol) of metal chloride, $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and $\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 10 ml of buffer solution of ammonium acetate for each them (at optimal pH) is added drop wise with vigorous stirring for one hour to the ligand solution. The reaction mixture was left over night then the complexes are filtered off washed with distilled water, then with ethanol and dried in desiccators over anhydrous CaCl_2 . Some physical properties and analytical data for the ligand and its complexes are shown in Table (1).

Thin layer chromatography (TLC)

The solution of ligand (4-AAPDHT) and its complexes in ethanol as solvent appeared in one spot, this is confidence that all these compounds are pure and have one isomer. Table (1) shows the R_f for complexes and ligand.

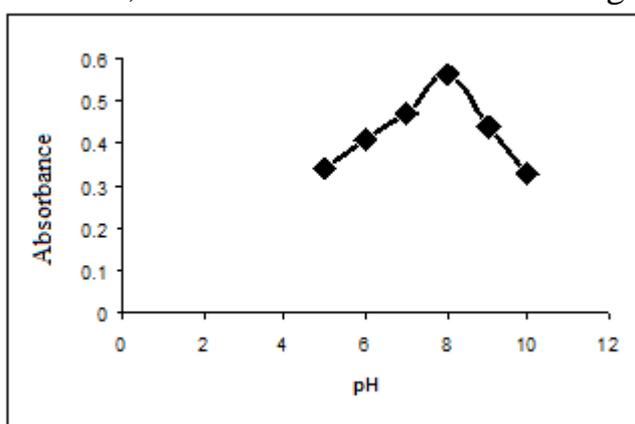
Table(1):- Physical properties and analytical data of the ligand (4AAPDHT) and its complexes.

Compound	Color	m.pc°	Found (Calc.)%				R _f
			C	H	N	M	
C ₁₈ H ₁₈ N ₄ O ₃	Brawn	264	65.97 (66.05)	5.41 (5.50)	17.05 (17.12)	—	0.45
[Zn(C ₁₈ H ₁₇ N ₄ O ₃) ₂]	green	240	60.11 (60.31)	4.52 (4.73)	15.39 (15.61)	8.81 T (8.99) P	0.34
[Cd(C ₁₈ H ₁₇ N ₄ O ₃) ₂]	Pale yellow	231	56.51 (56.67)	4.28 (4.45)	14.41 (14.65)	14.241 T (14.103) P	0.31
[Hg (C ₁₈ H ₁₇ N ₄ O ₃) ₂]	Light yellow	220	56.20 (56.64)	4.31 (4.44)	14.28 (14.65)	22.864 T (23.007) P	0.29

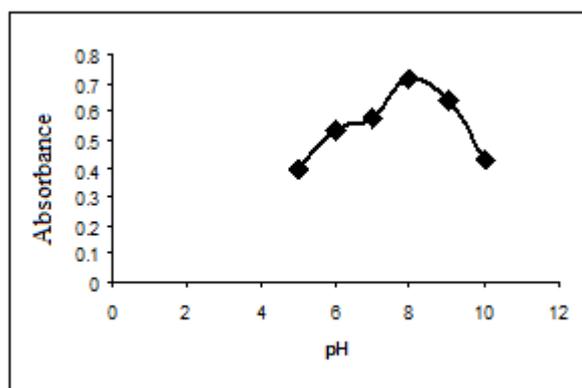
Results and discussion

Effect of pH

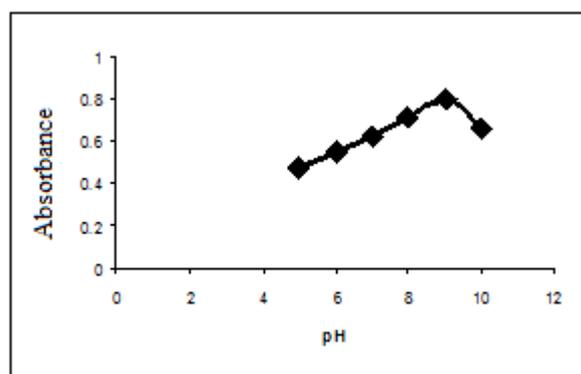
Suitable pH values for metal complex solutions were found to be in the range of (5–10). To evaluate the optimal pH values of metal complex solutions by using buffer solution of ammonium acetate. The preparation of the complexes have been conducted after fixing the optimum conditions of concentration which obey Lambert-Beers Law these concentration were (5 - 9) x 10⁻⁴M. The effect of pH on the absorbance were studied, and the results are shown in Figures.(2, 3 and 4).



Figure(2):-The effect of pH on the absorbance of metal ion Zn(II) with the ligand (4-AAPDHT)) at optimal conc. = 9 x 10⁻⁴ M



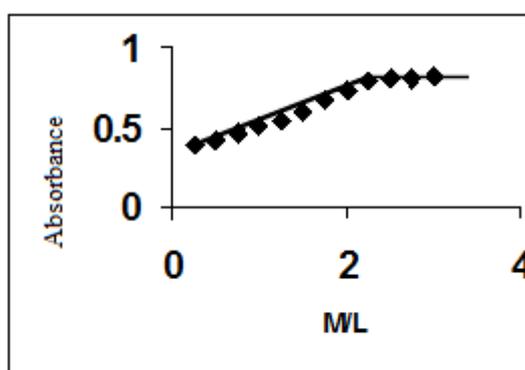
Figure(3):-The effect of pH on the absorbance of metal ion Cd(II) with the ligand (4-AAPDHT)at optimal conc. = 9×10^{-4} M



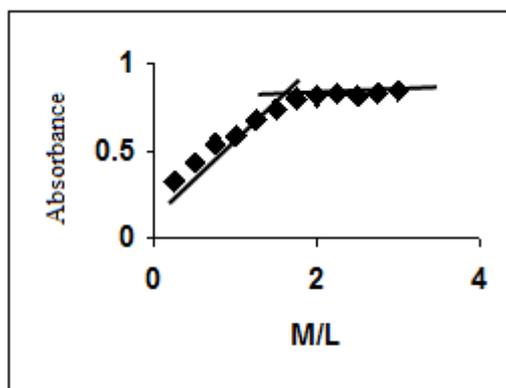
Figure(4):-The effect of pH on the absorbance of metal ion Hg(II) with the ligand (4-AAPDHT)at optimal conc. = 9×10^{-4} M

Metal: ligand ratios

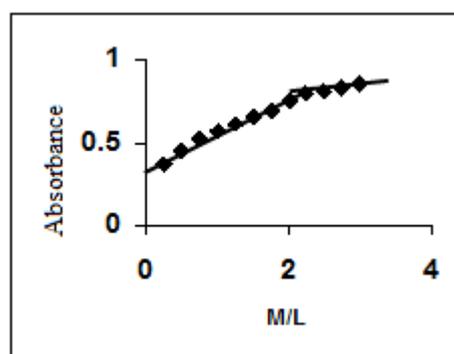
The metal : ligand ratio (M:L)of complexes were determined by used the molar ratio method at the wavelength of maximum absorption (λ_{max}) and fixed pH and concentration .The ligand (4-AAPDHT) was found to form chelates with all metal ions mention as shown in Figs.(5, 6 and 7). The results are in agreement with the values reported for some antipyril azo complexes[13,14].



Figure(5):- The molar ratio (M:L) of metal ion Zn(II) with the ligand(4-AAPDHT)) at optimal conc. = 9×10^{-4} M



Figure(6):- The molar ratio (M:L) of metal ion Cd(II) with the ligand (4-AAPDHT) at optimal conc. = 9×10^{-4} M



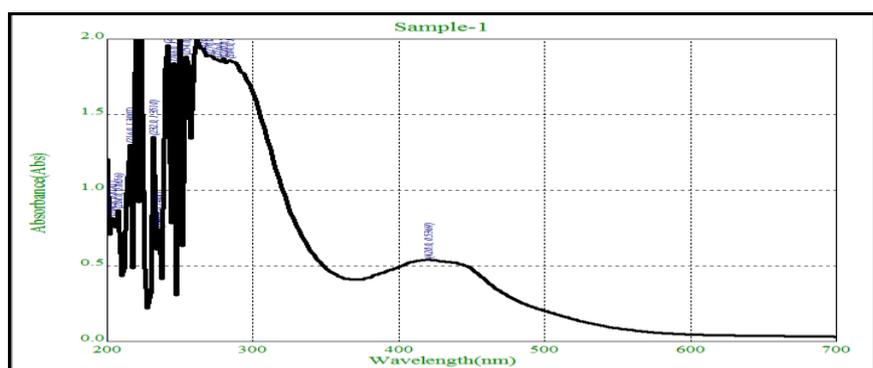
Figure(7):- The molar ratio (M:L) of metal ion Hg(II) with the ligand(4-AAPDHT) at optimal conc. = 9×10^{-4} M

Electronic spectra

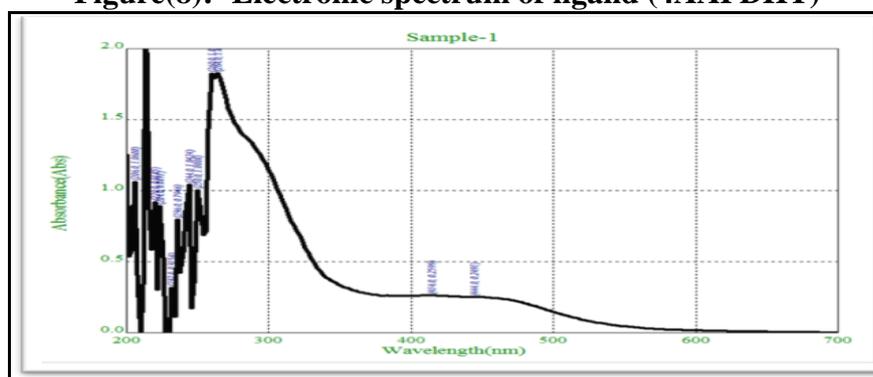
The electronic spectra of ligand (4-AAPDHT) and its complexes were studied and shown in figures (8,9,10 and 11). The wavelength for the maximum absorption (λ_{max}) of the ligand was found at 420nm. The spectra of metal complexes were recorded within wavelength range (440–462) nm. The absorption maxima (λ_{max}) of each complex also shown in Table.(2). Two absorption bands were appear at the free ligand (4-AAPDHT) spectrum. The bands at 391 nm referring to the $\pi \rightarrow \pi^*$ transitions of antipyrine ring while the band at 425 nm is due to the charge transfer characters[13].

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

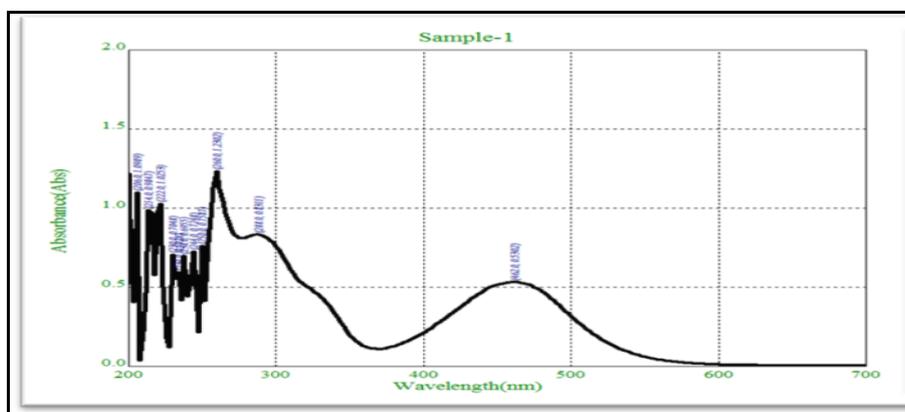
Metal Ions	Optimal pH	Optimal molar conc. X 10^{-4} M	Optimal wave length (λ_{max})nm
Zn(II)	8	9	444
Cd(II)	8	9	462
Hg(II)	9	9	440



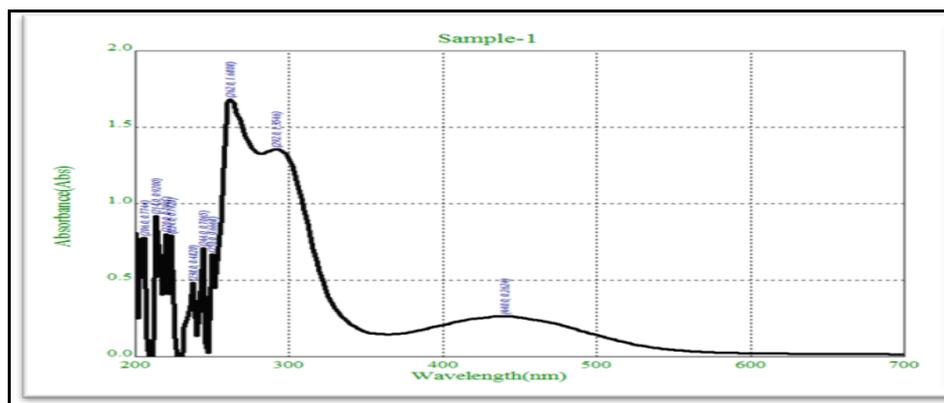
Figure(8):- Electronic spectrum of ligand (4AAPDHT)



**Figure(9):- Electronic spectra of ligand (4AAPDHT) with ion complex of Zn(II)
Conc. 9×10^{-4} M at $\lambda_{\text{max}} = 444$**



**Figure(10):- Electronic spectra of ligand (4AAPDHT) with ion complex of Cd(II)
Conc. 9×10^{-4} M at $\lambda_{\text{max}} = 462$**



**Figure(11):- Electronic spectra of ligand (4AAPDHT) with ion complex of Hg(II)
Conc. 9×10^{-4} M at $\lambda_{\text{max}} = 440$**

Infrared spectra

The infrared spectra of the free ligand (4AAPDHT) 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 $\nu(\text{O-H})$, $\nu(\text{C=N})$, $\nu(\text{C=O})$, $\nu(\text{N=N})$ and other bands due to the Antipyrine ring which appeared in the region below 1700 cm^{-1} . The comparison between the IR spectral data of the free ligand with that of its complexes are discussed as follow:-

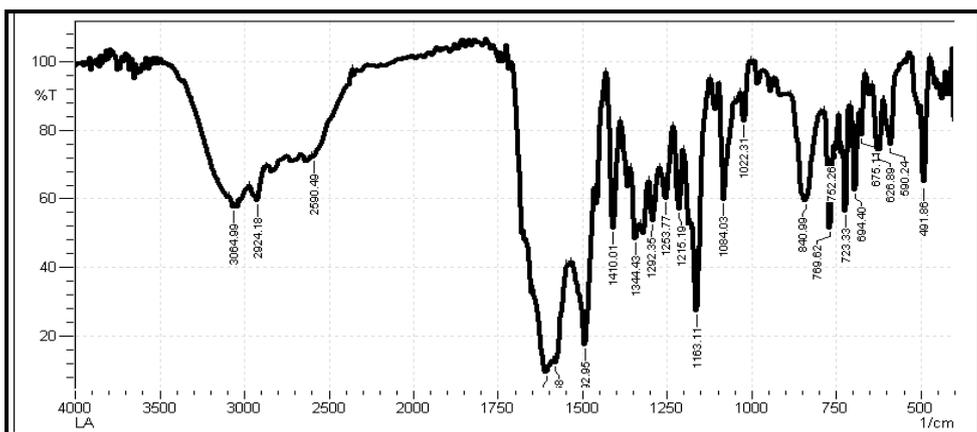
1-The spectrum of azo ligand (4AAPDHT) show absorption band around 1610 cm^{-1} due to the $\nu(\text{C=O})$ group in antipyrine ring[13], this band is observed with a little change in shape and shifted to different frequencies ($1600\text{--}1620 \text{ cm}^{-1}$ in each of Zn (II), Cd (II) and Hg(II) complexes indicates that this band sharing in Complexation.. These differences may suggest the linkage of metal ions with oxygen of carbonyl group of heterocyclic Antipyrine ring.

2-The spectrum of ligand shows absorption band at 1568 cm^{-1} attributed to $\nu(\text{C=N})$ of Antipyrine and phenyl rings[13-15], this band is changed in shape and shifted to lower frequency in all complexes in the range ($1570\text{--}1600 \text{ cm}^{-1}$ these differences may suggest the linkage of metal ions with nitrogen of heterocyclic Antipyrine ring[13].

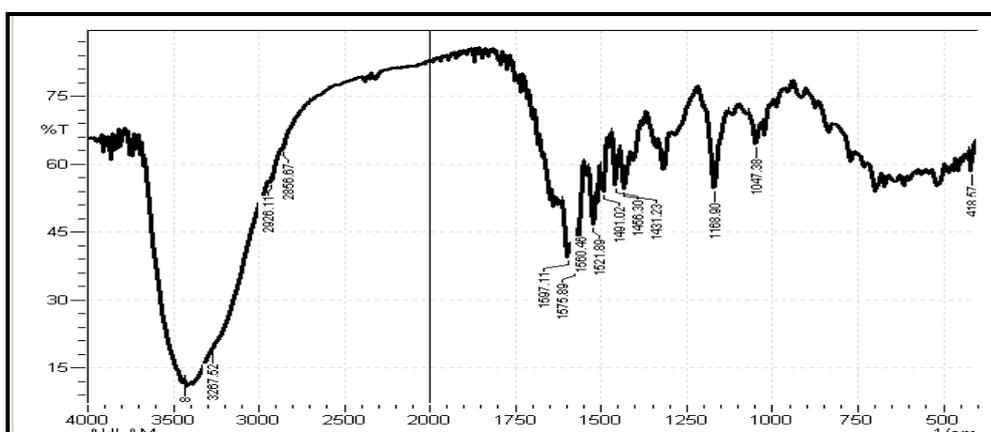
The azo group (N=N) appears at 1492 cm^{-1} in the free ligand spectrum, this band is observed with change in shape and has been shifted to different frequencies at range ($1521\text{--}1558 \text{ cm}^{-1}$ in complexes spectra; this means that some linkage of metal ions with nitrogen atom of azo group takes place[20,21].

Finally a new weak bands observation in the spectra of all metal complexes in the lower frequency at the region ($450\text{--}467 \text{ cm}^{-1}$ and ($418\text{--}422 \text{ cm}^{-1}$ characteristic to M-N and M-O stretching vibration respectively [13,16]. The IR spectra indicate that the azo ligand (4AAPDHT) behaves as a tridentate chelating agent coordinated through nitrogen atom of azo group and the oxygen atom of carbonyl group of heterocyclic antipyrine ring and the oxygen atom of hydroxide group of phenyl ring.

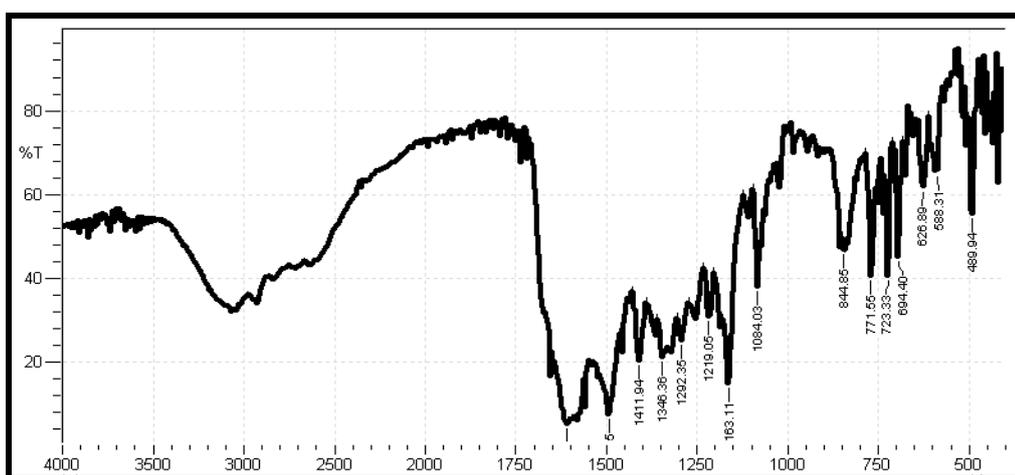
Figures. (12, 13, 14 and 15) shows the spectra of ligand (4AAPDHT), and its metal complexes spectra .



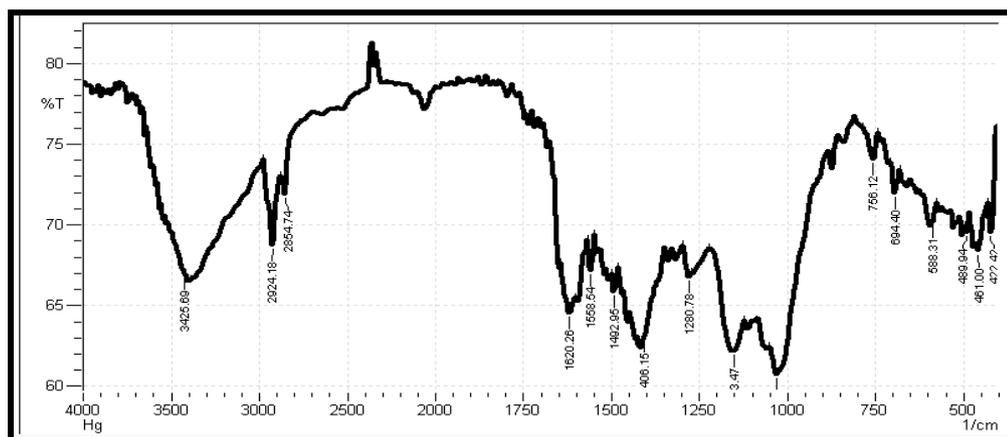
Figure(12):- IR spectrum of the ligand (4AAPDHT)



Figure(13):- IR spectrum of ion complex of Zn(II) with the ligand (4AAPDHT)



Figure(14):- IR spectrum of ion complex of Cd(II) with the ligand (4AAPDHT)



Figure(15):- IR spectrum of ion complex of Hg(II) with the ligand (4AAPDHT)

Table(3):- Characteristic IR absorption bands of the ligand (4AAP-2-N) and its complexes in cm^{-1} units.

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
$\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_3$	1680	1600	1568	1492	—	—
$[\text{Zn}(\text{C}_{18}\text{H}_{17}\text{N}_4\text{O}_3)_2]$	1649	1623	1575	1521	450	418
$[\text{Cd}(\text{C}_{18}\text{H}_{17}\text{N}_4\text{O}_3)_2]$	1660	1612	1570	1520	467	420
$[\text{Hg}(\text{C}_{18}\text{H}_{17}\text{N}_4\text{O}_3)_2]$	1656	1620	1600	1558	461	422

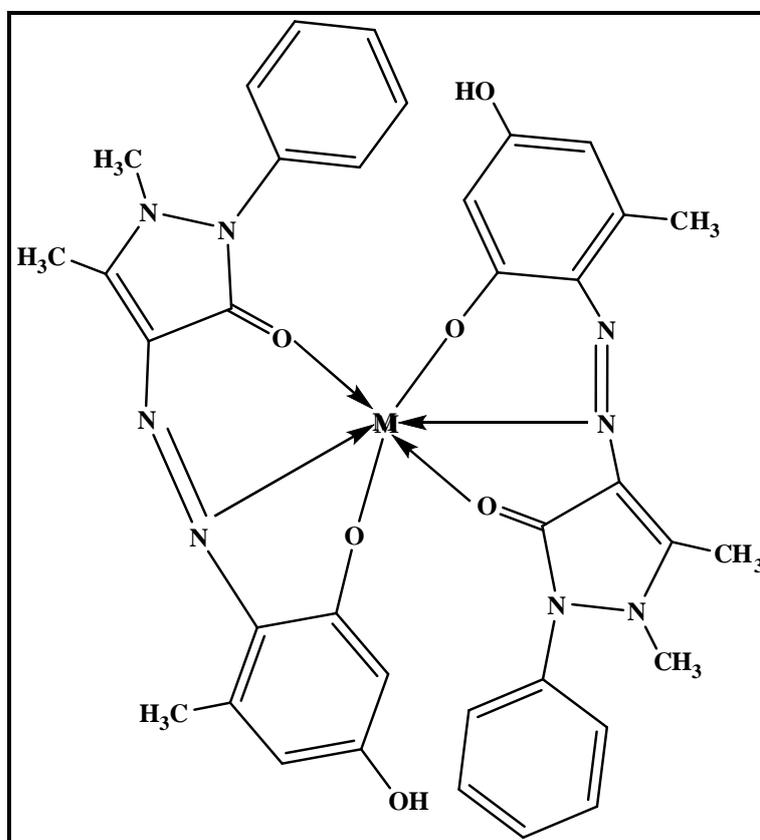
Conductivity measurements

All complexes show the conductivity measurement values ranging between $(9.67 - 11.74) \text{ S.Cm}^2. \text{ mol}^{-1}$ in DMSO as solvent at $(1 \times 10^{-3} \text{ M})$ concentration and room temperature, these values indicating that all prepared complexes were non-electrolytes, these data can help to achieve the suggested structures of complexes supported by the results obtained from elemental microanalyses, atomic absorption, FT-IR and UV-visible [6]. The conductivity values are listed in table 4.

Table(4):- Conductivity measurements of complexes

Complex	Conductivity S.Cm ² .mol ⁻¹
[Zn(C ₁₈ H ₁₇ N ₄ O ₃) ₂]	9.67
[Cd(C ₁₈ H ₁₇ N ₄ O ₃) ₂]	10.32
[Hg (C ₁₈ H ₁₇ N ₄ O ₃) ₂]	11.74

According to the results the coordination number of all metal ions is found to be six with two molecules from ligand (4AAPDHT) acted as a tridentate ligand through the bonding mono dentate with each of the N atom of azo group and the O atom of carbonyl group of heterocyclic antipyrine ring and the O atom of phenoxide of phenyl ring. The structural formula of prepared complexes is most probably octahedral shown in fig.16.



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

Figure(16):- The proposed structural formula of Zn (II), Cd(II) and Hg (II) with the ligand (4AAPDHT)

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