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Preparation and spectral Characterization of Some Transition Metal Complexes With New Azo Ligand 2-[(4-Quinaldine)Azo] – imidazole (Q_dAIm)

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Abstract

New heterocyclic azo imidazole dye ligand 2-[(4-Quinaldine)Azo]–imidazole (Q_dAIm), was prepared by reacting a dizonium salt solution of 4– amino quinaldine with imidazole in alkaline aqueous solution. Six complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) were prepared and characterized by elemental analysis, spectroscopic by infrared, electronic spectra, magnetic susceptibility and molar conductance measurements. The atomic absorption/flame emission – spectrophotometer was used to specify the precents of metal ion in the prepared complexes. The stability constant of prepared complexes have been determined by spectrophotometric method. The stability of complexes follows the sequence; Cd(II) > Cu(II) > Co(II) > Hg(II) > Zn(II) > Ni(II).

The isolated complexes are found to have the general formula $[ML_2Cl_2].xH_2O$, M=Co(II), Cu(II), Hg(II), X=1, M= Ni(II), Zn(II), Cd(II), (X=0). The analytical data show that the metal to ligand ratio in all complexes are (1:2).

التحضير والتشخيص الطيفي لمعقدات بعض العناصر الانتقالية مع ليكاند الآزو الجديدة
2-[(4-كوينالدين) آزو)]- إميدازول (Q_dAIm)

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الخلاصـــــة

تضمن البحث تحضير صبغة آزو إميدازول غير متجانسة الحلقة جديدة وهي 2-[(4- كوينالدين) آزو]-إميدازول (Q_dAIm) وذلك بمفاعلة محلول ملح الديازونيوم للمركب 4- أمينوكوينالدين مع محلول الاميدازول في محيط قاعدي. وحضرت ستة معقدات جديدة لكل من الكوبلت(II) والنيكل(II) والنحاس (II) والخارصين(II) والكادميوم(II) والزئبق (II) مع اليكاند المحضرة في هذا البحث. وقد شخصت الليكاند ومعقداتها بواسطة التحليل الدقيق للعناصر وطيفياً باستخدام الأشعة تحت الحمراء والأطياف الالكترونية ودراسة الخواص المغناطيسية والتوصيلية المولارية ومطياف الامتصاص الذري اللهبي لغرض تعيين النسب المئوية للايونات الفلزية في المعقدات المحضرة. تم تعيين ثوابت الاستقرارية للمعقدات المحضرة بالطريقة الطيفية وقد اتخذت الترتيب التالي الكادميوم (II) > النحاس (II) > الكوبلت(II) >الزئبق (II) >الخارصين (II) >النيكل (II) واستناداً الى معطيات النتائج التحليلية المذكورة أعلاه فقد تم اقتراح الصيغ التركيبية للمعقدات الصلبة وكانت $[ML_2Cl_2].H_2O$ لكل من الكوبلت (II) والنحاس (II) والزئبق (II) أما معقدات النيكل (II) والخارصين(II) والكادميوم (II) فقد اتخذت الصيغة $[ML_2Cl_2]$. وقد بينت النتائج التحليلية أن نسبة (الفلز: الليكاند) هي (2:1) لجميع المعقدات.

1- Introduction

The chemical study of the imidazole shows that it is mixture of the pyridine and pyrole characteristics formulates many polarizational salts and as basic it is stronger than the pyridine[1,2]. Imidazole is a ubiquitous ligand in chemical and biological systems[3-5]. This class of azo dyes being a π - acidic azo imine system ─N=N─C=N─ for this reason a number of these dyes were synthized and their abilities as chelating ligand[6-8]. One of the most important used as analytical reagents[9,10], in addition to used it's as reagents for solvent extraction to determination of some metal ions[11,12].

The coupling of diazonium salt occurs in position 2 of imidazole molecule in alkaline solution to give crimson dyes[13]. The azo imidazole reagents does not have the same interest in research and investigation because of the rarity in the preparation of this kind of reagents although the imidazole was known before 150 years[14,16].

This paper report the preparation and identification of new heterocyclic azo dye derived from imidazole and some of it's transition metal complexes .

2- Experimental

2.1- Physical measurements and materials

Elemental analysis C.H.N were carried out by perkin Elmer 2400 Elemental analyzer. Absorbance curves were obtained with a model UV–1650 shimadzu spectrophotometer with 1 cm quartz cells and absolute ethanol as solvent.IR spectra were recorded with FTIR-8000 shimadzu spectrophotometer, in the (4000- 200)cm^{-1} range using CsI disc ,but in the (4000-400) cm^{-1} range using KBr disc of ligand (Q_dAIm) . The magnetic susceptibility for the prepared complexes were obtained at room temperature using Farady Method, for this purpose Balance Magnetic MSB-MKI was employed. Electric molar conductivity measurements were carried out at room temperature at concentration of (10^{-3} M) in DMF using conductivity bridge model 31A. Metal amount have determined using atomic absorption / flam emission spectrophotometer shimadzu- AA-160. pH measurements were carried out using a Philips pw 9421 pH meter (pH $\mp$0.001). Electro thermal, malting point, 9300 was used to measured the melting point of ligand and it's complexes. All chemical and solvents were highest purity obtained from Fluk, Merck and BDH.

2.2- preparation and characterization of the ligand (Q_dAIm)

The azo ligand was prepared by dissolving (1.58 gm , 0.01 mol) of 4- amino quinaldine in 70 cm^3 of distilled water and 10 cm^3 of concentrated hydrochloric acid and diazotized below 5C^o with $NaNO_2$ (0.7 gm , 0.01 mol) dissolved in 25 cm^3 distilled water. The resulting diazonium chloride solution was mixed with imidazole (0.68 gm , 0.01 mol) dissolved in 300 cm^3 alkaline ethanol and

cooled to 0-5 C^o. The mixture was stirred for additional 5 hrs , in ice-bath and allowed to stand over night and acidified with dilute hydrochloric acid to pH = 6.0. The precipitated was filtered, washed with cooled distilled water dried, and recrystallized from hot ethanol and then dried in the oven at 60 C^o for several hours the yield was 61% of brown needle crystals. The structural of this ligand as shown in fig. 1.

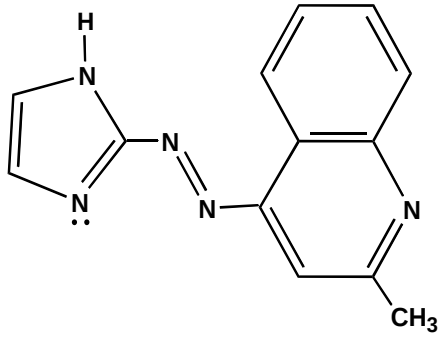


Fig. (1) :- Structure of the ligand (Q_dAIm)

2.3:- preparation of complexes:

The complexes were prepared by dissolved (0.02 mol) from ligand in hot ethanol (150 cm^3) then added drop wise with vigorous stirring to a stoichmetric amount of(1:2) metal : ligand ratio for Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) chloride salt(0.01 mol) dissolved in 20 cm^3 buffer solution (ammonium acetate) at optimal pH for each metal ions. The mixture was heated to 50 C^o for 35 min. Then the complexes were precipitation,filtered off washed with 10 cm^3 ethanol to remove the remaining un reacted substances and dried in a desiccator over anhydrous$CaCl_2$. The analytical and physical data of the ligand and it's complexes are listed in table 1.

Table (1):- Physical properties and analytical data of the ligand (L) and it's complexes.

No.	Compound	pH	Color	M.P C^o	Yield %	Molecular formula (Mol.wt)	Found(Calc.%)			
							C	H	N	M
1	L	6.0	Brown	164	61	$C_{13}H_{11}N_5$ (237.26)	65.81 (65.74)	4.67 (4.78)	29.52 (29.37)	___
2	$[CoL_2Cl_2].H_2O$	7.0	Purple reddish	207d.	76	$C_{26}H_{24}N_{10}OCl_2Co$ (622.38)	50.18 (50.26)	3.89 (4.02)	22.50 (22.34)	9.47 (9.65)
3	$[NiL_2Cl_2]$	7.5	Green	198	68	$C_{26}H_{22}N_{10}Cl_2Ni$ (604.12)	51.69 (51.78)	3.67 (3.56)	23.18 (23.01)	9.71 (9.96)
4	$[CuL_2Cl_2].H_2O$	6.5	Dark green	209	72	$C_{26}H_{24}N_{10}OCl_2Cu$ (626. 99)	49.81 (49.68)	3.86 (3.75)	22.34 (22.53)	10.13 (10.31)

5	**$[ZnL_2Cl_2]$**	7.0	Rose Reddish	237	79	$C_{26}H_{22}N_{10}Cl_2Zn$ (610. 81)	51.13 (51.24)	3.63 (3.72)	22.93 (22.78)	10.07 (10.53)
6	**$[CdL_2Cl_2]$**	8.0	Purple	261d.	63	$C_{26}H_{22}N_{10}Cl_2Cd$ (657. 84)	47. 47 (47.34)	3.37 (3.46)	21.29 (21.42)	17.09 (16.93)
7	**$[HgL_2Cl_2].H_2O$**	8.5	Dark purple	217	71	$C_{26}H_{24}N_{10}OCl_2Hg$ (764. 04)	40.87 (40.74)	3.17 (3.09)	18.33 (18.16)	ـــ

L= (Q_dAIm);d= Complex melt with decomposition

3- Results and discussion

3.1:- Absorption spectra

The complexes of the ligand (Q_dAIm) with the metal ions under studies are not soluble in water but soluble in a aqueous organic solvents. The absorption spectra in aqueous ethanolic solution 50% (v/v) were studied for the prepared complexes showed abthochromic shift ranging between(107-262)nm depending on the metal ion. The absorption spectra of the Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) chelat complexes are shown in figs. 2 and 3.

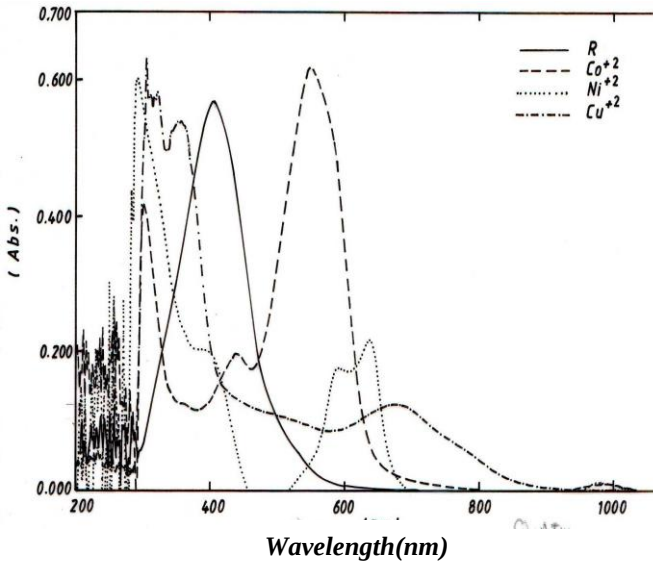


Fig. (2) :- Absorption spectra of QdAIm- metal chelats (1.75 x10^{-4} M) in aqueous ethanolic solution 50% (v/v) ; R= QdAIm

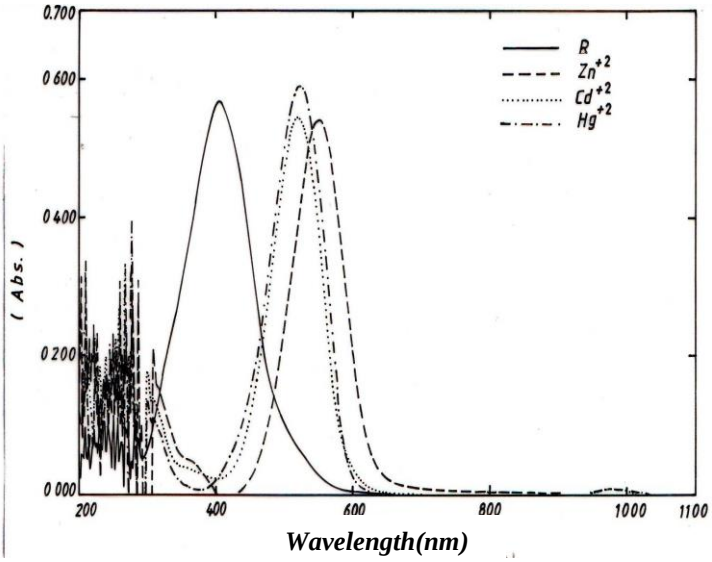


Fig. (3):- Absorption spectra of QdAIm- metal chelats (1.75 x10^{-4} M) in aqueous ethanolic solution 50% (v/v) ; R= QdAIm

.2:- Effect of pH

For evaluation of the pH values for the determination of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), the effects of pH on the absorbance were studied with the result shown in figs 4 and 5. The absorption spectra for complexes did not change over the whole rang. The optimal pH, optimal concentration and wave length (λ_{max}) with molar absorpitivity (ϵ) of ion complexes are shown in table 2.

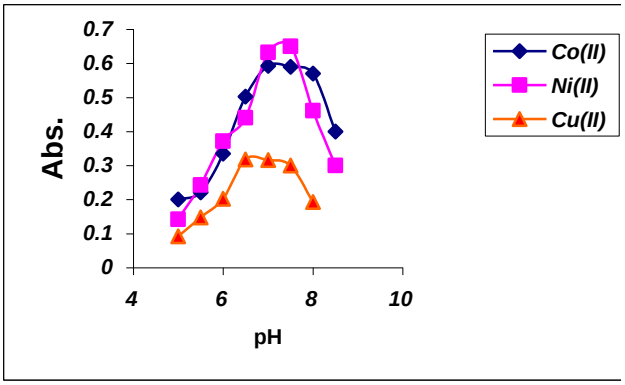


Fig. (4) :- Effect of pH on Absorbance of QdAIm- metal chelats, ligand Conc.=1.75 x10^{-4} M , metal ions = 1.5 x 10^{-4}M

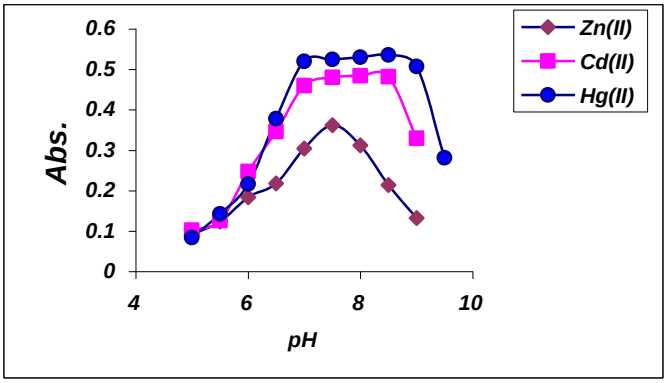


Fig . (5):- Effect of pH on Absorbance of QdAIm- metal chelats, ligand Conc.=1.75 x10^{-4} M , metal ions = 1.25 x 10^{-4}M

Table (2):- The optimal pH values, optimal concentration and wavelength(λ_{max}) with molar absorpitivity (ϵ)of metal ions in aqueous ethanol solution 50% (V/V).

Ligand	Metal ions	Optimal pH	Optimal molar conc. × 10^{-4} M	Molar absorpitivity ϵ × 10^{3} L.mol^{-1}.cm^{-1}	Optimal wave length (λ_{max}) nm
Q_dAIm (λ_{max})= 412nm	Co(II)	6.5-7.5	1.75	2.87	550
	Ni(II)	7.0-7.5	1.75	1.57	636
	Cu(II)	6.5-7.0	1.75	1.26	674
	Zn(II)	7.0-8.0	1.25	5.47	544
	Cd(II)	7.5-8.5	1.25	5.63	519
	Hg(II)	8.0-9.0	1.25	5.94	521

3.3 - Infrared Spectra

The IR spectra of the free ligand (Q_dAIm) and it's complexes are listed in table 3. The comparison between spectra of the ligand with those of there coordination complexes have revealed certain characteristic differences.

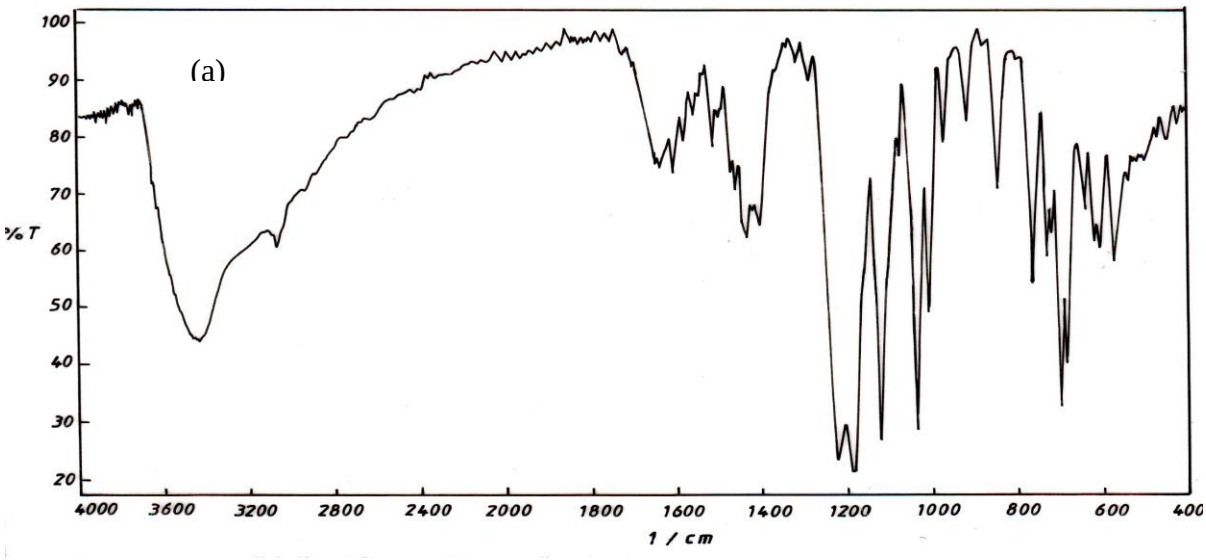
The medium and broad band at 3395 cm^{-1} in the spectrum of the ligand may be attributed to the υ (N-H) group in imidazole ring .The unchanged of this band in all metal complexes means that the (N-H)group dose not participate in coordination[17,18]. In the spectra of Co(II), Cu(II) and Hg(II) complexes the broad band at (3370-3375) cm^{-1} indicates the presence of water molecule in this

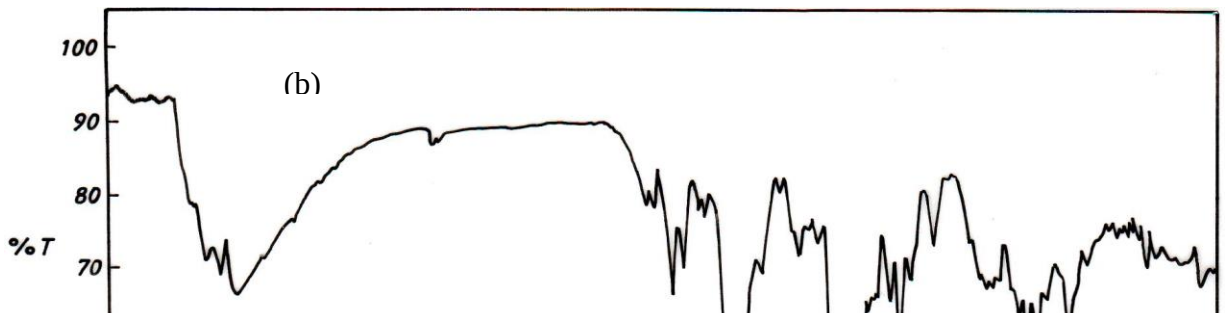
complexes[19,20]. The spectrum of ligand shows two weak band at 3065 cm^{-1} and 2985 cm^{-1} due to υ(C-H) aromatic and aliphatic respectively. These bands are stable in position and intensity in both ligand and it's metal complexes[18,19].

The υ(C=N) of imidazole ring appear at 1658 cm^{-1} in the spectrum of ligand. This band shifts to lower frequency at(1580-1595) cm^{-1} in the prepared complexes spectra. These differences suggest the linkage of metal ion with nitrogen of imidazole ring[17,21,22].

The υ(N=N) stretching vibration appears at 1512 cm^{-1} and 1435 cm^{-1} in the spectrum of free ligand. This band appearing at (1475 - 1495) cm^{-1} and (1410 – 1435) cm^{-1} in the prepared complexes spectra. Both bands shifted and reduced in intensity due to complexes formation[23,24].

In the far IR spectra of all complexes, there are new weak bands in the region of (260-575) cm^{-1} occurring in the spectra of complexes. These bands did not present in the spectrum of ligand. The bands observed at (565-575) cm^{-1} due to υ (M-N) and (260-290) cm^{-1} due to υ (M-Cl)[18,25,26]. The infrared spectra of the ligand(Q_dAIm) and some metal complexes are shown in fig. 6.





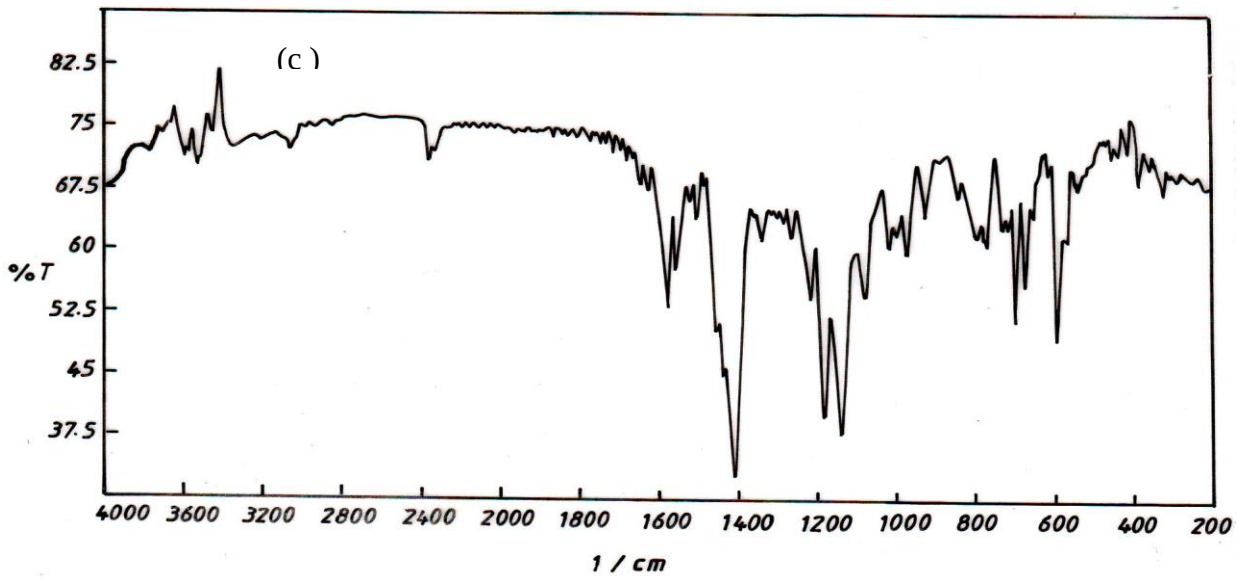


Fig. (6):- FT-IR spectra of the (a) Ligand(Q_dAIm);(b)[CuL_2Cl_2].H_2O and (c)[CdL_2Cl_2].

Table(3):-Important IR frequencies for the ligand(KBr ,disc) and it's complexes in cm^{-1} units(CsI disc).

Compound	υ (O-H)	υ (N-H)	υ (C=N)	υ (N=N)	υ (M-N)	υ (M-Cl)
L	____	3340 m.br.	1615 m.	1512m. 1435m.	____	____
$[CoL_2Cl_2].H_2O$	3370 w.br	3340 m.br.	1595 m.sh	1485 m.sh 1420m.	565 w.	270 w.
$[NiL_2Cl_2]$	____	3345 m.br.	1590 m.sh	1470 m. 1415m.	570 w.	275 w.
$[CuL_2Cl_2].H_2O$	3375 w.br	3340 m.br.	1580 m.sh	1495 m. 1435s.	575 w.	265 w.
$[ZnL_2\ Cl_2]$	____	3340 m.br.	1595 m.sh	1485 m. 1425m.	575 w.	280 w.
$[CdL_2Cl_2]$	____	3345 m.br	1590 m.sh	1475 s. 1405m.	565 w.	260 w.
$[HgL_2\ Cl_2].H_2O$	3370 w.br	3340 w.br	1580 m.sh	1480 s. 1410m.	570 w.	290 w.

L=Ligand(Q_dAIm), m = medium, w= weak, sh= shoulder, br = broad, s= strong.

Based on the results presented above lead to suggest that the ligand behaves as a bidentate chelating agent, and the coordination with metal ion by nitrogen of azo group and nitrogen atom of the imidazole ring[27,28].

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

Stability constants are obtained spectrophotometrically by measuring the absorbance of solutions complexes of fixed pH values and wave length ((λ_{max}). The formation of the complex is obtained from the relationship[29]:-

$\beta = (1-\alpha)/(4\alpha^3 C^2)$ and $\alpha = (Am - As)/Am.$

where A_m and As are the absorbance of fully and partially formed complex respectively at optimum concentration. The stability of complexes follows the sequence Cd(II) > Cu (II) > Co (II) > Hg (II) > Zn (II) >Ni (II)[30]. The high stability of Q_dAIm-Cd(II) chelate is remarkable over the other ions. This implies aconiderably higher affinity to ward these ions. The calculated β and $\log\beta$ values for the prepared complexes are given in table 4 .

3.5- Magnetic susceptibility and Electronic spectra measurements

The spectra data and the magnetic of each complexes are listed in table 4 . The value of magnetic moment for Co(II) complex found to be 5.49 B.M which is with in the range of octahedral cobalt(II) complexes[31]. The electronic spectra of this complex shown three absorption bands at 11415 cm^{-1}, 18182 cm^{-1} and 22727 cm^{-1} these are assigned to $^4T_1g(F) \longrightarrow {}^4T_2g(F)$ (υ_1), $^4T_1g(F) \longrightarrow {}^4A_2g(F)$ (υ_2), and $^4T_1g(F) \longrightarrow {}^4T_1g(P)$ (υ_3) transitions, respectively, which are characteristic of octahedral stereochemistry[32]. The value of magnetic moment for Ni(II) complex found to be 3.07 B.M, and d-d transition of this complex show three bands at 10235 cm^{-1}, 15723 cm^{-1} and 16978 cm^{-1}, corresponding to $^3A_2g \longrightarrow {}^3T_2g(F)$ (υ_1), $^3A_2g \longrightarrow {}^3T_1g(F)$ (υ_2), $^3A_2g \longrightarrow {}^3T_1g(P)$ (υ_3) transitions with an octahydral high spin structure [18,21,33] . The magnetic moment for Cu(II) complex found to be 1.78 BM due to presence of one unpaired electron in this compound. The electronic spectra show a broad absorption band at 14837 cm^{-1} which may assigned to $^2E_g \longrightarrow {}^2T_2g$ transition. It is reasonable to assign distorted octahedral structure[18,21,34].

Zinc, cadmium and mercury complexes are diamagnetic moments and the electronic spectra of these complexes do not show any d-d transition bands. There were three absorption bands appear at the free ligand (Q_dAIm) spectrum, those are appearing at the position, 40816 cm^{-1}, 33670 cm^{-1} and 24272 cm^{-1}, the bands 40816 cm^{-1} and 33670 cm^{-1} referring to the $\pi \rightarrow \pi^*$ transitions while the band at 24272 cm^{-1} is due to the charge transfer characters[35].

3.6- Conductivity measurement

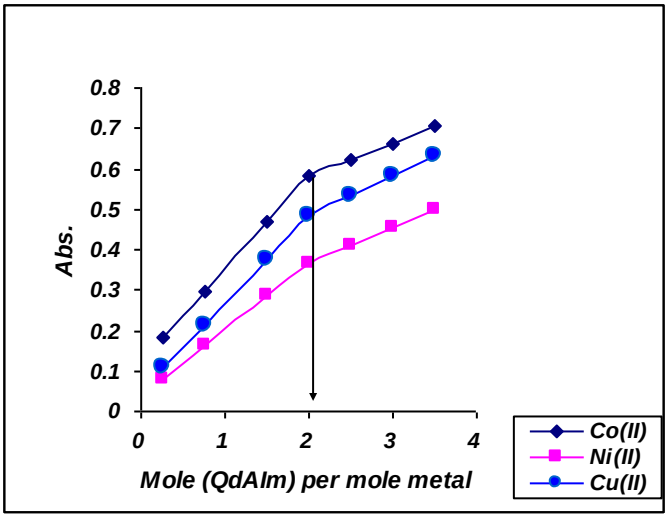
The data obtained from the measurement of electrical conductivity are shown in table (4). All the prepared complexes showed values ranging between (4.93-8.13) $S.mol^{-1}.cm^2$ in DMF at room temperature indicating non ionic structure of these compounds[18,21,36].

Table(4):- Electronic spectra, measurement, Magnetic moment data of complexes and Stability constant value (β)

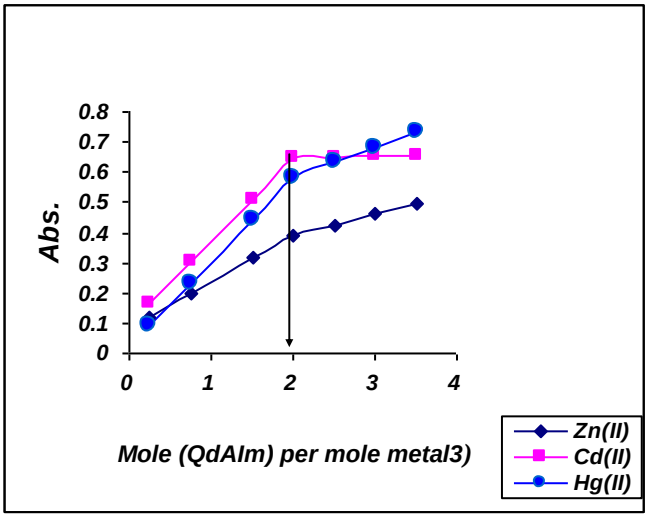
Complexes	Absorption Bands (cm^{-1})	Transition	Conductivity $S.mol^{-1}.cm^2$	μ eff (B.M)	β $mol^{-1}.L.$	Log β
$[CoL_2Cl_2].H_2O$	11415	$^4T_1g(F) \xrightarrow{\upsilon_1} {}^4T_2g\ (F)$	6.31	5.49	$1.604x10^9$	9.205
	18182	$^4T_1g(F) \xrightarrow{\upsilon_2} {}^4A_2g\ (F)$				
	22727	$^4T_1g(F) \xrightarrow{\upsilon_3} {}^4T_1g\ (P)$				
$[NiL_2Cl_2]$	10235	$^3A_2g \xrightarrow{\upsilon_1} {}^3T_2g\ (F)$	4.93	3.07	$4.286x10^8$	8.632
	15723	$^3A_2g \xrightarrow{\upsilon_2} {}^3T_1g\ (F)$				
	16978	$^3A_2g \xrightarrow{\upsilon_3} {}^3T_1g\ (P)$				
$[CuL_2Cl_2].H_2O$	14837	$^2Eg \rightarrow {}^2T_2g$	7.32	1.78	$1.747x10^9$	9.242
$[ZnL_2Cl_2]$	____	____	5.85	dia	$1.414x10^9$	9.150
$[CdL_2Cl_2]$	____	____	6.34	dia	$6.048x10^{11}$	11.782
$[HgL_2Cl_2].H_2O$	____	____	8.13	dia	$1.496x10^9$	9.170

3.7- Composition of the Complexes

The empirical formula of complexes were determined by the spectro Photometric method (mole ratio) at the optimal pH , molar concentration and wave lengths of maximum absorption in aqueous 50% (v/v) ethanol solution. The curves indicated the formation a(1:2) metal : ligand were obtained as shown in figs . 7 and 8 .

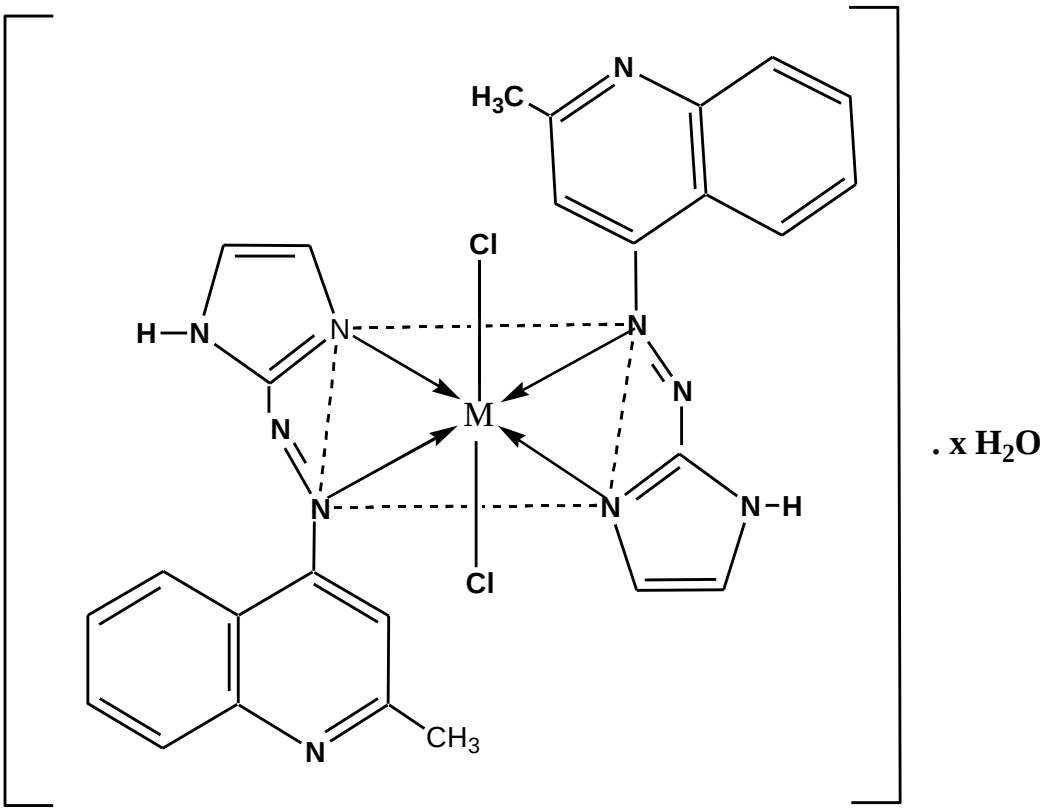


Fig(7): - mole ratio (M:L) of QdAIm – metal chelates.



Fig(8): - mole ratio (M:L) of QdAIm – metal chelates.

According to these results the following structural formula of synthesis chelat complexes in this work may be proposed in Fig (9).



Fig(9):- The suggested structural formula of complexes .
M=Co(II),Cu(II), and Hg(II),X=1
M=Ni(II),Zn(II), and Cd(II),X=0

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