Synthesis and Spectral Studies of Co(II),Ni(II),Zn(II) and Cd(II) Complexes with Ligand 2-[4- Carboxy methyl phenyl azo] -4,5-diphenyl imidazole (4CMeI)

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Abstract :

A new chelate complexes of Co(II),Ni(II),Zn(II) and Cd(II) were prepared by reacting these ions with the ligand 2-[4- Carboxy methyl phenyl azo]-4,5-diphenyl imidazole (4CMeI) The preparation were conducted after fixing the optimum conditions such as (pH) and concentration .UV- visible spectra of these complex solutions were studied for a range of (pH) and concentration which obey lampert-Beers Law.The structures of complexes were deduced according to mole ratio method which were obtained from the spectroscopic studies of the complex solutions .The ratios of metal: ligand obtained were (1:2) for all complexes..(UV-Vis) absorption spectra and The infrared spectra of the chelating complexes were studied ,this may indicate that coordination between the metal ions and our ligand takes place.The conductivity measurements , elemental analysis ,the percentage of some metal ions and the measurements of magnetic susceptibility of the complexes were determined ,Depending on these results , in addition to, We may conclude that the ligand was bidentate Also the proposed geometrical structures of the complexes of Co(II), Ni(II), Zn(II) and Cd (II) ions are octahedral.

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

Introduction:

Many organic reagents have attracted much attention as they are sensitive , chromogenic reagents in addition to being interesting complexing agents [1]. Azo colorants are the most important class of synthetic dyes representing (60-80%) of all organic colorants used widely in substrates such as textile fibers , leather, plastic , papers , hair , mineral oils , waxes ,food stuffs and cosmetics [2]. Aryl azo heterocyclic and their chemistry of transition and non-transition metals have been explored for more than two decades [3].Aromatic azo compound are used as acid – base indicators such as methyl red ,methyl orange [4]. Many studies are concentrated on metal complexes based on imidazole azo ligands[5]. Because of the π-acidic azo imine group (─ N═N─C═N─) a number of these ligands were prepared as chelating agents [6-8]. This paper describes the preparation and characterization of new chelate complexes of Co(II),Ni(II),Zn(II) and Cd(II) with the ligand 2-[4- Carboxy methyl phenyl azo]-4,5-diphenyl imidazole (4CMeI).

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Materials and Methods:

Materials and physical measurements

All chemicals used were of highest purity (BDH or Fluka) and used with out further purification except of 2-[4-Carboxy methyl phenyl azo]-4,5-diphenyl imidazole, this was prepared as described in the literature[9].

Elemental analysis was carried out by means of micro analytical unit of (Euroverctor, 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. 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. Auto.Electrical conductivity measured by Digital conductivitymeter Alpha – 800 with solute 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 using atomic absorption technique by Shimadzu -AA-160.

Synthesis of azo ligand (4CMeI)

The ligand was prepared by dissolving (0.01 mol) of 4-aminoacetophenone in 10 ml of distilled water and 2ml of concentrated hydrochloric acid, then the solution was cooled below 5 °C. To this mixture a solution of (0.01 mol) of sodium nitrate in 10 ml of distilled water was added drop wise at 0-5 °C and the mixture was stirred for 15 min. This diazonium solution was added drop wise to a 500 ml beaker containing (0.01 mol) of 4,5-diphenyl imidazole[9].

Dissolved in 150 ml of alkaline ethanol. The mixture was allowed to stand over night The crude dyes were collected by filtration and recystallized from1:1 Ethanol and water and then dried by the air. The structural formula of the ligand is shown in figure.1.

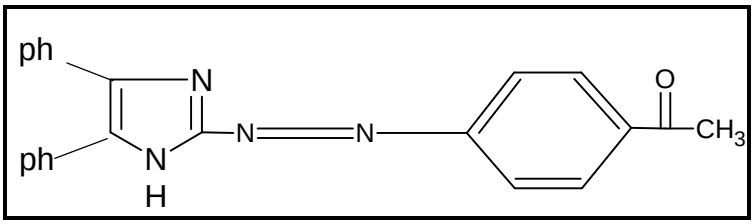


Fig.(1):- Structure of the ligand1 2-[4- Carboxy methyl phenyl azo]-4,5-diphenyl imidazole(4CMeI)

Synthesis of complexes

The chelat complexes were synthesized at optimum pH values as shown in Table(2) dissolved (0.732gm, 0.02 mol) of ligand (4CMeI) in 10 ml ethanol and then (0.01 mol) of metal chloride, M= Co(II), Ni(II), Zn((II) or Cd(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, then with ethanol and dried in desiccators over anhydrous $CaCl_2$. Table.1 contains the physical properties and analytical data for the complexes.

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

No.	Compound	Color	m.p C°	Found (Calc.)%			
				C	H	N	M
1	$C_{23}H_{18}N_4O$	Orange	229-230	75.40 (75.12)	4.91 (5.01)	15.30 (14.93)	—
2	$[Co(C_{23}H_{18}N_4O)_2Cl_2]$	Brawn	121d	64.11 (64.06)	4.18 (3.91)	13.00 (12.89)	6.84 (6.37)
3	$[Ni(C_{23}H_{18}N_4O)_2Cl_2]$	Dark Red	110d	64.13 (63.89)	4.18 (4.11)	13.01 (12.86)	6.81 (6.57)
4	$[Zn(C_{23}H_{18}N_4O)_2Cl_2]$.	Dark Brawn	136d	63.63 (63.41)	4.15 (3.98)	12.91 (12.51)	7.53 (7.32)
5	$[Cd(C_{23}H_{18}N_4O)_2Cl_2]$	Red	131d	60.36 (60.11)	3.93 (3.56)	12.24 (11.90)	12.29 (12.17)

d=decomposition.

Results and Discussion:

Effects of pH

Suitable pH values for metal complex solutions were found to be in the range of (5 – 10). To evaluate the optimum pH values of metal complex solutions .The effects of pH on the absorbance were studied, and the results are shown in Figs. 2, 3, 4 and 5.

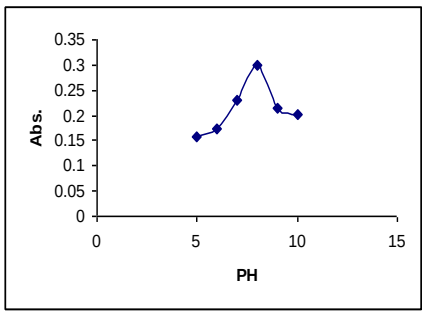


Fig.(2):-The effect of pH on the absorbance of metal complexe Co(II) with the ligand(4CMeI)at optimum conc. = 9 x 10^{-5} M

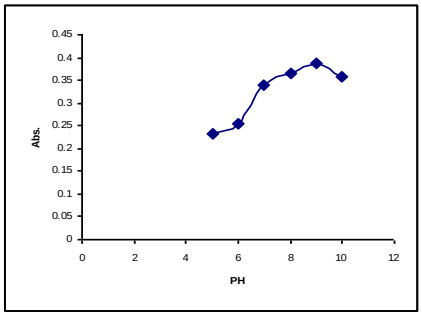


Fig.(3):-The effect of pH on the absorbance of metal complexe Ni(II) with the ligand(4CMeI)at optimum conc. = 9 x 10^{-5} M

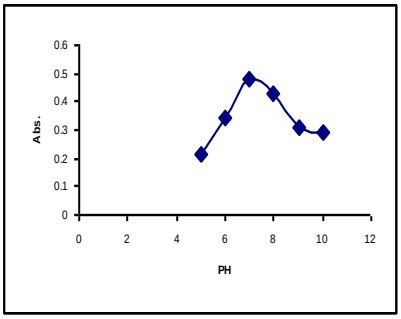


Fig.(4):-The effect of pH on the absorbance of metal complexe Zn (II) with the ligand(4CMeI)at optimum conc. = 9 x 10^{-5} M

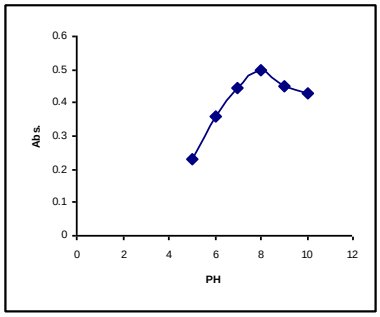


Fig.(5):-The effect of pH on the absorbance of metal complexe Cd (II) with the ligand(4CMeI)at optimum conc. = 9 x 10^{-5} M

Metal: ligand ratios

The metal : ligand ratio (M:L)of complexes were determined by the molar ratio method at the wavelength of maximum absorption (λ_{max}) and fixed pH and concentration .The ligand (4CMeI) was found to form chelates with all metal ions mentioned as shown in Figs. 6, 7, 8 and 9. The results are in agreement with the values reported for some imidazolyazo complexes[10,11].

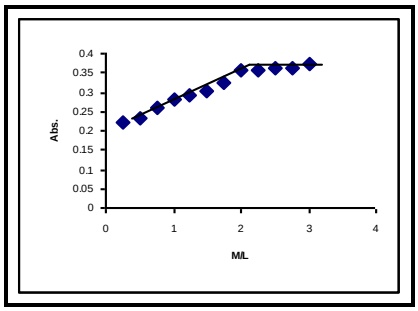


Fig.(6):- Molar ratio (M:L)
Of metal ion Co(II) with the ligand(4CMeI)
at optimal conc. = 9 x 10^{-5} M

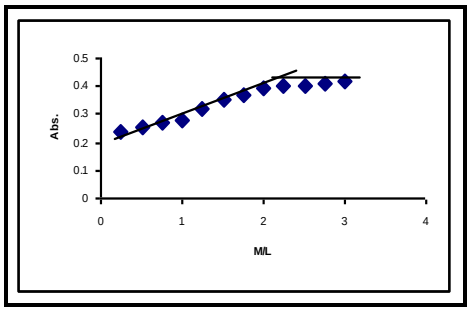
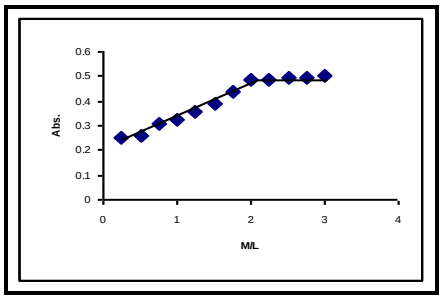


Fig.(7):- Molar ratio (M:L)
Of metal ion Ni(II) with the ligand(4CMeI)
at optimal conc. = 9 x 10^{-5} M



Figu.(8):- Molar ratio (M:L)
Of metal ion Zn (II) with the ligand(4CMeI)
at optimal conc. = 9 x 10^{-5} M

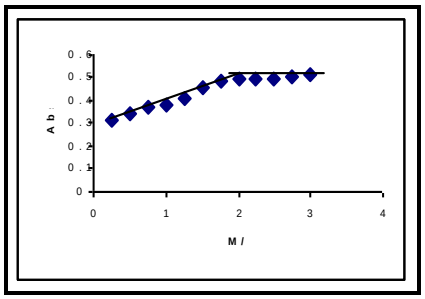


Fig.(9):- Molar ratio (M:L)
Of metal ionCd (II) with the ligand(4CMeI)
at optimal conc. = 9 x 10^{-5} M

Absorption spectra

The absorption spectra of ligand (4CMeI) and its complexes were studied and shown in figures 10,11,12 ,13and 14. The wavelength for the maximum absorption (λ_{max}) of the ligand was found at 456.5nm. The spectra of metal complexes were recorded within wavelength range (491.5 – 508.5) nm. The absorption maxima (λ_{max}) of each complex also shown in Table.2. .Two absorption bands were appeared at the free ligand (4CMeI) spectrum. The bands at 285 nm referring to the $\pi \rightarrow \pi^*$ transitions of imidazole ring while the band at 465.5 nm (23923cm^{-1}) is due to the charge transfer characters[4].

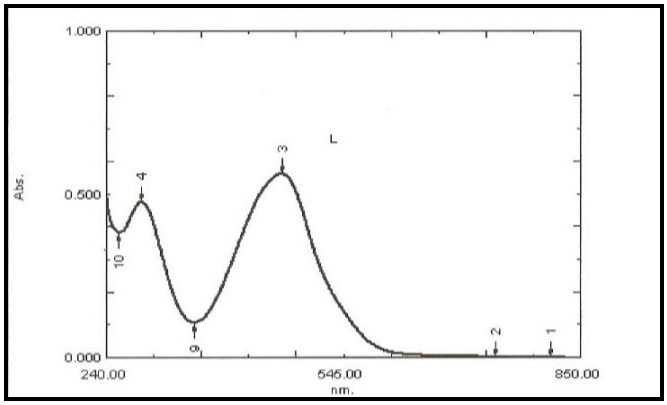


Fig.(10):- Absorbance spectrum of ligand (4CMeI)

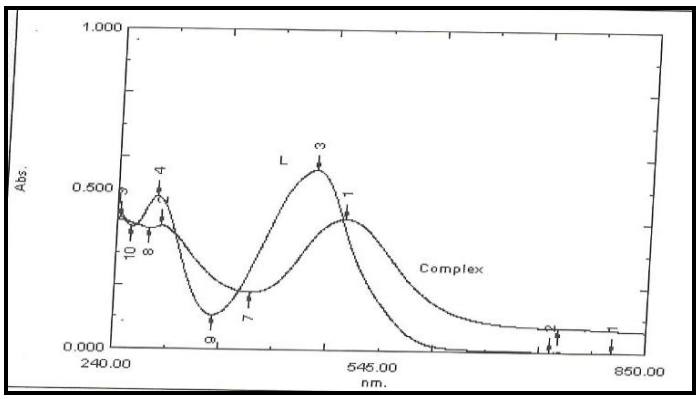


Fig.(11):- Absorbance spectrum of ligand (4CMeI) with ion complex of Co(II) Conc.9x 10^{-5} M

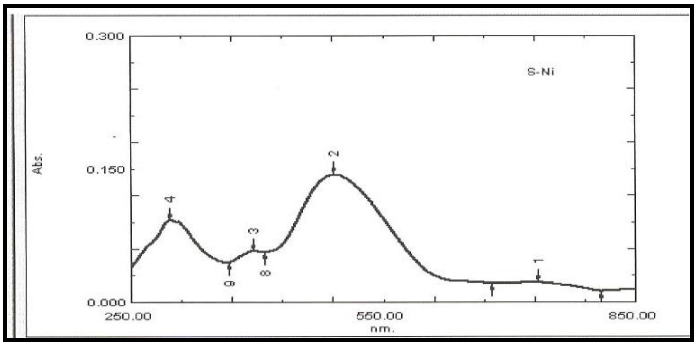


Fig.(12):- Absorbance spectrum of ligand (4CMeI) with ion complex of Ni(II) Conc. 9x 10^{-5} M

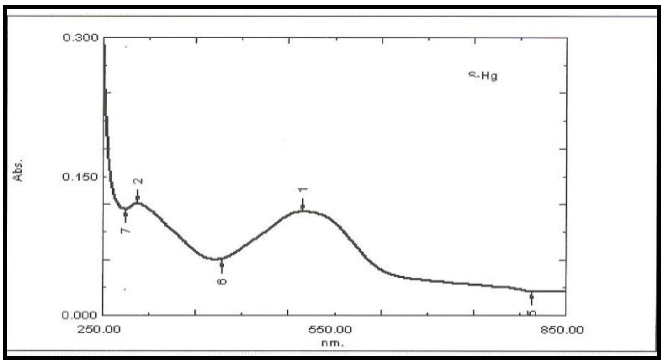


Fig.(13):- Absorbance spectrum of ligand (4CMeI) with ion complex of Zn(II) Conc. 9x 10^{-5} M

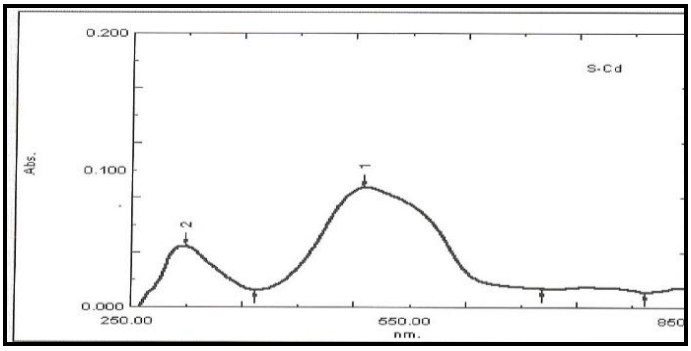


Fig.(14):- Absorbance spectrum of ligand (4CMeI) with ion complex of Cd(II) Conc.9x 10^{-5} M

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

Ligand	Metal Ions	Optimaum pH	Optimaum molar conc. X 10^{-5} M	Optimaum wave length (λ_{max})nm	$\Delta\lambda^{a}_{max}$ nm
4CMeI λ_{max}=465.5 nm	Co(II)	8	9	501	35.5
	Ni(II)	9	9	491.5	26
	Zn(II)	7	9	508.5	43
	Cd(II)	8	9	500	34.5

$\Delta\lambda^{a}_{max} = \lambda_{max}$ **Complex -** λ_{max} **ligand**

Infrared spectra

The infrared spectra of the free ligand (4CMeI) and its complexes with Co (II),Ni (II) , Zn ((II) and Cd (II) are given in Table.3. A number of bands arising from υ(N─H), υ(C═N), υ(N═N) and other bands due to the phenyl and imidiazole rings which appeared in the region below 1680 cm^{-1}. The comparison between the IR spectral data of the free ligand with those of its complexes is discussed as follow:-

The spectrum of azo ligand (4CMeI) shows an absorption band around 3420 cm^{-1}due to the υ(N─H)groups this suggests that the band due to(N─H)group in imidiazole ring [12,13]. An absorption band around 1680 cm^{-1}due to the υ(C═0)groups in phenyl ring [9]in the spectrum of the ligand and the same bands in each of Co (II),Ni(II),Zn(II) and Cd (II) complexes [14] Indicates that these bands didn't share in the complexation .

The spectrum of ligand shows an absorption band at 1540 cm^{-1} due to υ(C═N) of imidiazole ring[6, 14].This band is observed with a little change in shape and shifted to higher frequencies (1550 – 1600) cm^{-1} in complexes. These differences may suggest the linkage of metal ions with nitrogen of heterocyclic imidiazole ring[15].

The azo group (N═N) appears at 1430 cm^{-1} in the free ligand spectrum. This band has been shifted to a higher frequencies (1435-1450) 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[15,16].

The bands at 750 $cm^{-1}$and 720 cm^{-1} has also been appeared in the ligand spectrum which is due to υ(ph─imid)

of imidiazole ring [7,17].The fixed postion of this band in all chelate complexes means that the phenyl groubs of imidiazole ring does not share in coordination .

Finally a new weak bands appears at (401-418) cm^{-1}in the complexes spectra which may suggest the linkage of metal ions with nitrogen atom [6,13]. The IR spectra indicates that imidiazole azo ligand (4CMeI) behaves as a bidentate chelating agent coordinated through nitrogen of azo group and the nitrogen atom of imidiazole ring. Figs.15, 16, 17 , 18 and 19 shows the spectrum of ligand (4CMeI), and it's complexes spectrum .

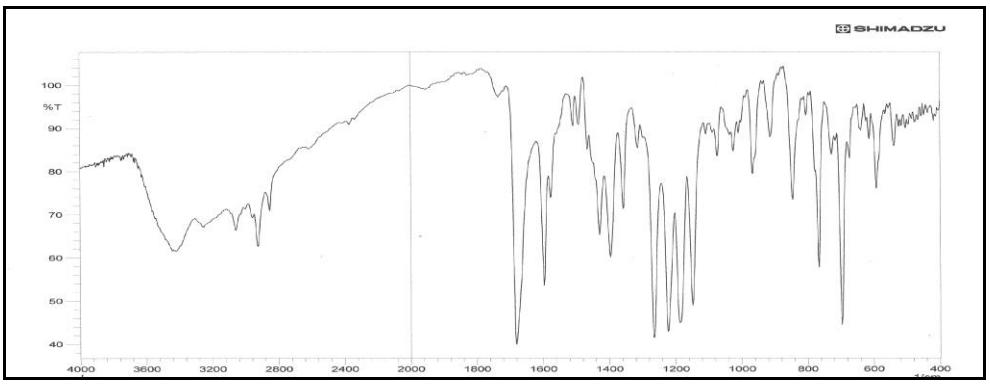


Fig.(15):- IR spectrum of the ligand (4CMeI)

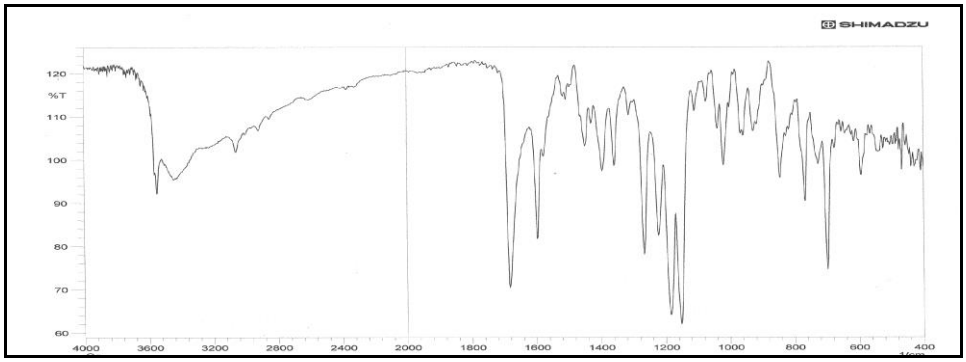


Fig.(16):- IR spectrum of Co(II) complex .

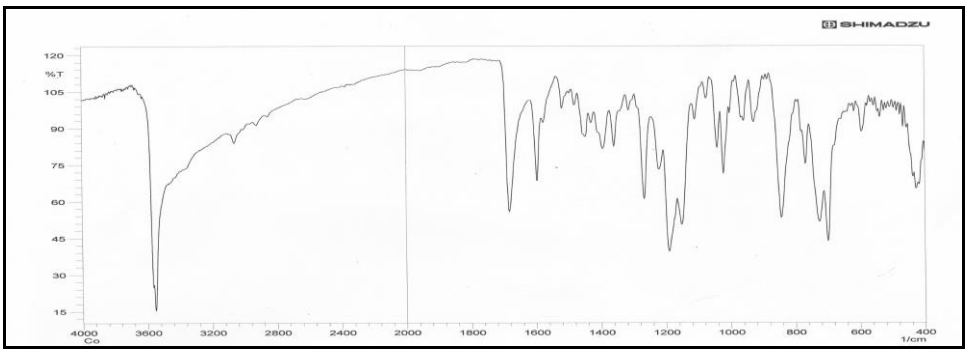


Fig.(17):- IR spectrum of Ni(II) complex.

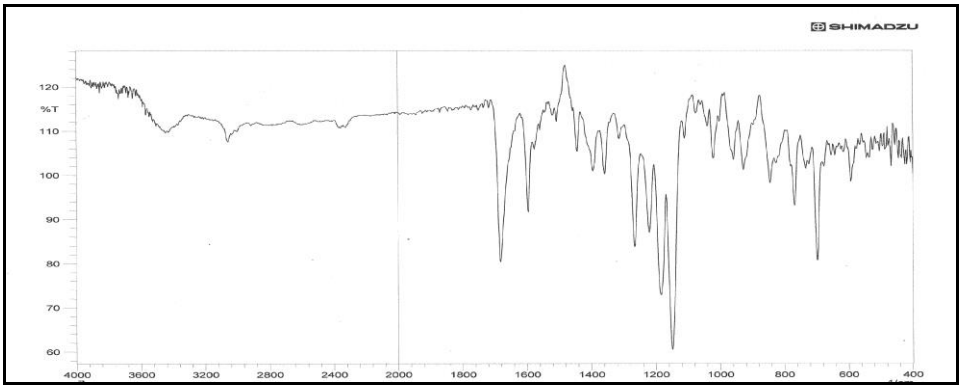


Fig.(18):- IR spectrum of Zn (II) complex .

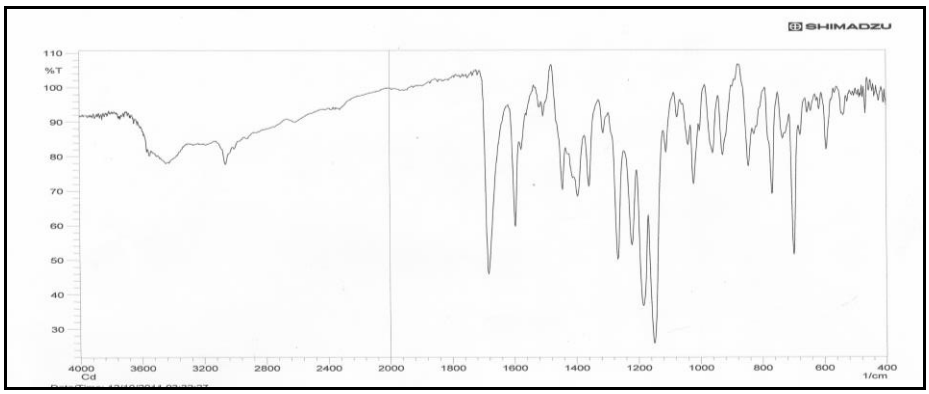


Fig.(19):- IR spectrum of Cd (II) complex .

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

No.	Compound	υ(N─H)	υ(C═0)	υ(C═N)	υ(N═N)	υ(ph─imid)	υ(M─N)
1	$C_{23}H_{18}N_4O$	3420	1680	1540 .	1430 .	750 720	─
2	$[Co(C_{23}H_{18}N_4O)_2 Cl_2]$	3420.	1680	1550	1435 .	750 720	410
3	$[Ni(C_{23}H_{18}N_4O)_2 Cl_2]$	3420	1680	1600 .	1440	750 720	401
4	$[Zn(C_{23}H_{18}N_4O)_2Cl_2]$.	3420	1680	1580 .	1450 .	750 720	410
5	$[Cd(C_{23}H_{18}N_4O)_2 Cl_2]$	3420	1680	1580 .	1450	750 720	418

Magnetic susceptibility and electronic spectra measurements

The magnetic momentum and electronic spectra studies were used to confirm the geometry of the complexes .These data are listed in Table.4.

Cobalt (II) complex

The value of magnetic moment of Co (II) was found to be 4.43 B.M which can be a normal value for octahedral [6,7]. The magnetic momentum of the Co (II) complex has been found to be paramagnetic and the

high spin behavior of this complex indicates that Co (II) is not oxidized to Co (III) during complexation..

Nickel (II) complex

The value of magnetic moment of Ni (II) was found to be 2.98 B.M which can be a normal value for octahedral Ni (II) complex[11,14] .

Zinc (II) and Cadmium (II) complexes

The magnetic susceptibity show that all complexes have diamagnetic moment, and the electronic spectra of these complexes do not show any d-d transition band [7].

Conductivity measurements

All complexes show the conductivity measurement values ranging between (5.54 – 11.32) $S.cm^2.mol^{-1}$,these values indicating nonionic structure of these complexes[12].The conductivity values are listed in table 4.

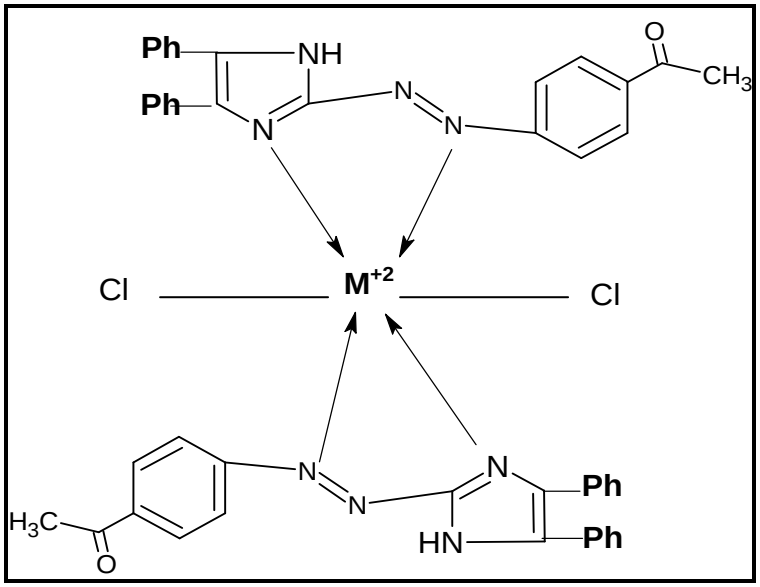
Calculation of the metal complexes stability constant (β)

Stability constant of prepared complexes are obtained spectrophotometrically by measuring the absorbance of ligand solutions and metal ion mixture at fixed wavelength ($\lambda_{max)}$, and pH. The degree of formation of the complexes (β) are obtained from the relationship[16] of $\beta = (1- \alpha)/ 4 \alpha^3 C^2$ and $\alpha = (A_m - A_s)/ A_m$, where α=degree of dissociation , A_s and A_m are the absorbance of the partially and fully formed complex respectively. The calculated β and log β values are listed in Table.4.The values of stability constant indicated high stability complexes .

Table(4):- Electronic Spectrum, Conductivity measurements, Magnetic moment and stability constant values (β) of complexes

Complex	Conductivity $S.cm^2.mol^{-1}$	μ_{eff} B.M	$B L^2. mol^{-2}$	Logβ
$[Co(C_{23}H_{18}N_4O)_2Cl_2]$	11.32	4.43	4×10^{11}	11.60
$[Ni(C_{23}H_{18}N_4O)_2 Cl_2]$	10.85	2.98	23.75×10^{10}	11.37
$[Zn(C_{23}H_{18}N_4O)_2Cl_2]$	7.02	dia	11.14×10^9	10.04
$[Cd(C_{23}H_{18}N_4O)_2Cl_2]$	5.54	dia	21.06×10^{10}	11.32

According to the results the coordination number of all metal ions is found to be six with bonding through N of azo group and N of imidazole The structural formula of the prepared complexes is most probably octahydral as in fig.20.



M= Co (II), Ni(II), Zn (II) and Cd (II)

Fig.(20):- The proposed structural formula of Co (II), Ni (II), Zn (II) and Cd (II)

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تخليق ودراسة طيفية لمعقدات Co(II),Ni(II),Zn(II) and Cd(II) مع الليكاند 2- [4- كاربوكسي مثيل فنـــيل ازو]-5.4 – ثنائي فنيل اميدازول (4CMeI)

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الخلاصـــة :

تم تحضير المعقدات الجديدة لايونات الكوبلت (II)، النيكل (II) ،الخارصين(II) والكادميوم(II) مع الليكاند 2[4- كاربوكسي مثيل فنيل ازو] -5,4- ثنائي فنيل اميدازول وقد تم التحضير بعد تثبيت الظروف الفضلى من تركيز ودالة حامضية من خلال دراسة اطياف الاشعة فوق البنفسجية – المرئية لمحاليل مزج هذه الايونات مع محاليل الليكاند ولمدى واسع من الدالة الحامضية والتراكيز الخاضعة لقانون لامبرت – بير . تم التعرف على التراكيب للمعقدات المحضرة عن طريق ايجاد النسبة المولية (الفلز : الليكاند) بوساطة دراسة اطياف (UV-Vis.) لمحاليل خلط الايونات الفلزية موضوع الدراسة 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 و اطياف الاشعة تحت الحمراء (IR). وقد بينت دراسة التوصيلية المولارية انعدام الصفة الايونية للمعقدات المذكورة كما تم اجراء التحليل الدقيق للعناصر وحساب نسبة الايونات الفلزية لبعض هذه المعقداتً ، وبالاعتماد على النتائج المستحصلة فضلا عن قياسات الحساسية المغناطيسية استطعنا الاستنتاج بان المعقدات الكيليتية اتخذت الشكل الهندسي الثماني السطوح.