Preparation and Characterization of New Azo Ligand and Some of Its Chelate Complexes

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Abstract

New arylazo imidazole ligand (HMAI) was prepared by coupling 4-acetylphenyldiazonium chloride with 4,5-Bis-(*p*-.Methoxy phenyl) imidazole in alkaline acetone medium. The obtained azo compound was characterized by micro elemental Analysis, FT-IR, UV-Vis ^{1}H-NMR, and mass spectroscopy. The reaction of this azo ligand with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) chloride salts produced eight heteroleptic complexes. These metal-azo chelate compounds were characterized using flame atomic absorption, elemental Analysis, FT-IR and UV-Vis spectroscopic methods as well as magnetic susceptibility and conductivity measurements. From the obtained data the octahedral structure was suggested for Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) metal ion complexes with general formula $[ML_2Cl_2].H_2O$ and tetrahedral geometry for Zn(II), Cd(II) and Hg(II) metal ion complexes with general formula $[MLCl_2].H_2O$.

Keywords: Preparation, Azo dye ligand, heteroleptic complexes, characterization.

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1. Introduction

1,3-diaza-2,4-cyclopentadiene commonly named as imidazole. This a planar, five member ring molecule was first named as glyoxaline [1]. Imidazole compounds and their derivatives have a lot of applications. They play an important role in many areas such as medicinal chemistry [2], material sciences for nonlinear optical application [3], also some imidazole derivatives are used as a catalyst in industrial uses [4], and others have been used as corrosion inhibitors for a certain transition metals [5]. Among the various ligands, azo imidazoles have significant importance because they are potentially capable of forming stable complexes with metal ions [6-8]. These molecule bears the azoimine (–N=N–C=N–) functional group, and it is an efficient π– acid system for stabilization of low oxidation state metal ions [9,10]. On the other hand, azoimdazole dyes behaves as a bidentate imidazole-N, azo-N chelate, with 3d-transition metal ions [11,12], while some of these molecules binds with non-transition (Group 12 elements) either as a monodentate (imidazole-N) or a bidentate chelate ligands [13,14].

The present work deals with the preparation and characterization of metal chelate complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions with new azo ligand, (E)-1-(4-((4,5-bis(4-methoxyphenyl)-1H-imidazole-2-yl) diazenyl) phenyl) ethan-1-one derived from 4,5-Bis(*p*-methoxy phenyl) imidazole and 4-aminoacetophenone

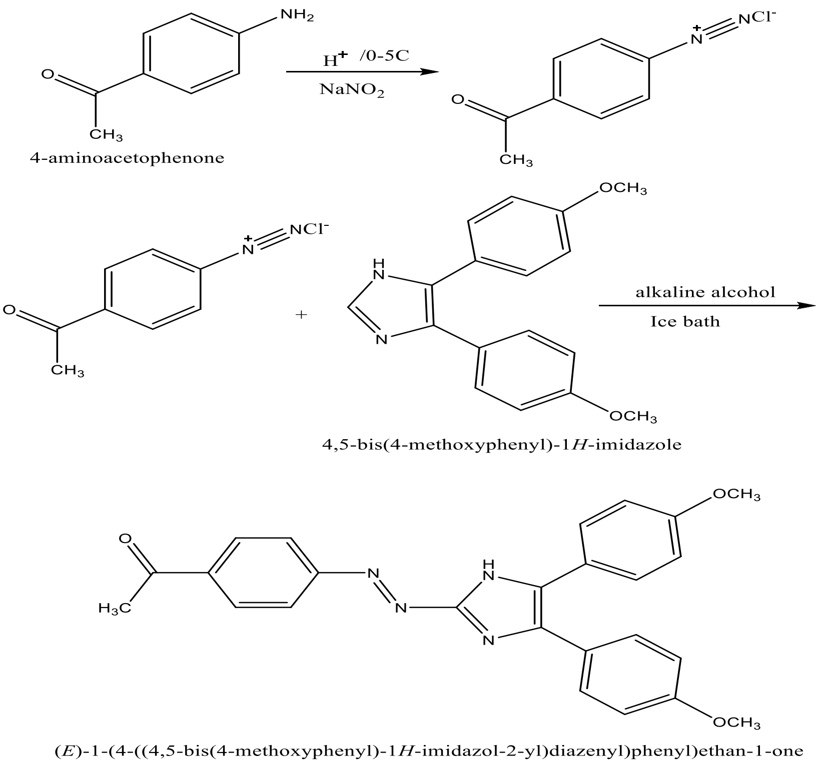
2. Experimental

2.1. Reagents and physical measurements

All the reagents and solvents were needed for the present work were commercially available, analytical grade and used as received except of 4,5-Bis(*p*-methoxy phenyl)- imidazole which was prepared as described before [15]. Melting points were determined in an open glass capillary tube using a Stuart melting point SMP10 and are uncorrected. The mass spectrum analysis of ligand was done on a Shimadzu Agilent (HP) 5973 mass spectrometer. ^{1}HNMR spectrum was conducted using a Varian Gmph instrument (300 MHz) in DMSO-d_6 as a solvent consisting TMS as the internal reference compound. Microanalytical data (Carbon, Hydrogen and Nitrogen) was carried out on Euroverctor, EA300A elemental analyzer. FT-IR spectra studies were carried out using KBr discs on FTIR Testscan Shimadzu 8400 Spectrophotometer in the range of 4000 – 400 cm^{-1}**.** Electronic spectra were recorded in ethanol on Shimadzu model 1700 UV–Vis Spectrophotometer. The metal content of the complexes was measured using atomic absorption technique by (Phoenix-986 AA). Magnetic susceptibilities were measured as powder samples using Faraday method, Balance Magnetic (Sherwood Scientific) was employed for this purpose. Molar conductance measurements were determine in DMF by using a (470 WTW) conductivity meter.

2.2. Preparation of the ligand (HMAI)

This heterocyclic azo ligand was prepared as described before [15] (Scheme.1). A solution of 4-aminoacetophenone (1.35 g, 10 mmol) in 100 mL water and 5 mL concentrated HCl (37%) was stirred until a clear solution was obtained. This solution was cooled to 0–5 ℃ and while maintaining the temperature below 5 ℃ a solution of sodium nitrite (0.75 g, 11 mmol) in 10 mL water was then added drop by drop. The resulting mixture was stirred for 30 min in an ice bath and excess nitrite was destroyed by addition of urea [16]. The resulting diazonium chloride solution was mixed with coupling component 4,5-Bis-(*p*-.Methoxy phenyl) imidazole (2.80 g, 10 mmol) dissolved in 150 mL alkaline acetone cooled below 5 ℃. After leaving in the refrigerator for 24 hour, the mixture was acidified with (0.1 M) hydrochloric acid until (pH = 6). The red crude precipitate was filtered and washed several times with distilled water, air dried and twice recrystallized from hot ethanol, and then dried in oven at 80 ^{O}C. Some analytical and physical data for this azo dye were tabulated in Table (1) .



Scheme.1: Syntheses of the (HMAI = L) ligand

2.3. Preparation of the metal complexes

The methanolic solution of respective salts [$MnCl_2.4H_2O$, $FeCl_2.4H_2O$, $CoCl_2$.- $6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$], was slowly mixed with hot stirring methanolic solution of (HMAI) ligand in (2:1) (L:M) molar ratio. After stirring for 30 min, colored precipitates formed at room temperature, the rustling solids were filtered off, washed with 5 mL hot (50%) ethanol to remove any traces of the unreacted starting materials air dried and recrystallized from ethanol and heated in the oven at 90 ^{O}C. While non-transition metal salts [$ZnCl_2$, $CdCl_2.2H_2O$, $HgCl_2.2H_2O$] were mixed with azo ligand in a similar procedure to prepared chelate complexes except the molar ratio (1:1) which afforded colored complexes..

3. Results and Discussion

3.1. Identification of ligand and its metal complexes

The azo ligand was red powder, but all complexes are fine powder, vary in color depended of metal ions, stable, non-hygroscopic solids and are soluble in most organic solvents such as methanol, ethanol, dimethylformamide, dimethyl sulfoxied, chloroform, acetone, and pyridine giving stable solutions at room temperature. The analytical data of (HMAI = L) ligand and its chelate complexes are presented in Table (1). This data are in good agreement with the calculated values which suggest that the metal and the ligand are coordinated in the ratio 2:1 or 1:1 (M:L). Based on the analytical data, [$Mn(L)_2Cl_2$]. H_2O, [$Fe(L)_2Cl_2$]. H_2O, [$Co(L)_2Cl_2$]. H_2O, [$Ni(L)_2Cl_2$]. H_2O[$Cu(L)_2Cl_2$]. H_2O, [Zn(L) Cl_2]. H_2O, [Cd(L) Cl_2]. H_2O and [Hg(L) Cl_2]. H_2O. are the empirical formulae suggested for the complexes. The molar conductance at room temperature was determined using (10^{-3}M) solutions of the complexes in the solvent DMF. These values support the non-electrolytic nature of all the complexes. The conductance values along with the magnetic moments are also shown in Table (3).

Table (1): Some physical and analytical data of the ligand and its complexes

Compound	Formula	m.p. °C	Yield %	Color	Found (Caled) %)			
					C	H	N	M
L= (HMAI)	$C_{25}H_{22}N_4O_3$	208-210	67	Red	70.63 (70.42)	5.06 (5.16)	13.35 (13.15)	…… …….
$[Mn(L)_2Cl_2].H_2O$	$C_{50}H_{46}N_8O_7Cl_2Mn$	220 Dec.	65	Deep red	60.46 (60.25)	4.51 (4.61)	11.37 (11.24)	5.77 (5.51)
$[Fe(L)_2Cl_2]$. H_2O	$C_{50}H_{46}N_8O_7Cl_2Fe$	175-177	71	Deep red	60.53 (60.19)	4.52 (4.61)	11.45 (11.23)	5.83 (5.60)
$[Co(L)_2Cl_2]$. H_2O	$C_{50}H_{46}N_8O_7Cl_2Co$	270 Dec.	73	Deep violet	60.41 (60.00)	4.52 (4.60)	11.09 (11.20)	6.12 (5.89)
$[Ni(L)_2Cl_2]$. H_2O	$C_{50}H_{46}N_8O_7Cl_2Ni$	250 Dec.	74	Purple	60.35 (60.02)	4.55 (4.60)	11.29 (11.20)	5.64 (5.87)
$[Cu(L)_2Cl_2]$. H_2O	$C_{50}H_{46}N_8O_7Cl_2Cu$	190-188	72	Deep violet	59.51 (59.73)	4.49 (4.57)	11.04 (11.15)	6.53 (6.32)
$[Zn(L)Cl_2],H_2O$	$C_{25}H_{24}N_4O_4Cl_2Zn$	158-160	70	Deep red	51.47 (51.69)	4.04 (4.13)	9.42 (9.65)	11.52 (11.26)
$[Cd(L)Cl_2]$ H_2O	$C_{25}H_{24}N_4O_4Cl_2Cd$	210-212	73	Deep red	47.45 (47.82)	3.76 (3.82)	8.44 (8.92)	……. ……
$[Hg(L)Cl_2]$ H_2O	$C_{25}H_{24}N_4O_4Cl_2Hg$	138-140	70	Deep red	42.32 (41.92)	3.27 (3.35)	8.61 (7.82)	…… ……

3.2. Mass spectrum of azo ligand (HMAI)

The mass spectrum of the azo dye ligand (HMAI) was displayed a well defined molecular ion peak at m/z 426.48 which is equivalent to it corresponding molecular mass. A fragment at (Z/e =398.46.) corresponding to the azo molecule after losing nitrogen gas (azo-group) [17]. Another fragment at (Z/e=280.33, 140.18 and 120.15) due to 4,5-Bis-(*p*-.Methoxy phenyl) imidazole, 4-

phenyl imidazole and acetophenone respectively. The successive fragmentation peaks are shown in Fig(1).

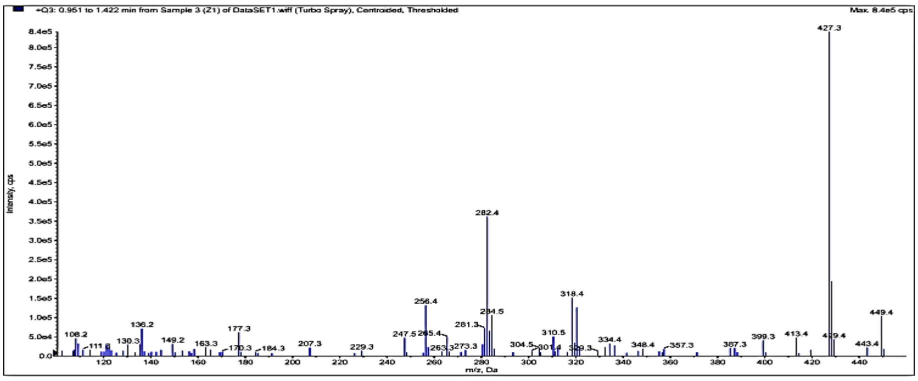


Fig.1 :The mass spectrum of azo ligand (HMAI)

3.3. ^{1}HNMR Spectrum of (HMAI) ligand

The ^{1}HNMR spectrum of (HMAI) was recorded in (DMSO-d$_6$) solvent Fig.2 exhibited, a singlet signal at 2.62 ppm attributed to protons of acetyl group while the two singlet signals at 3.29 and 3.78 ppm were related two methoxy group which appear to be nonequivalent in magnetic field , the weak signal at 13.47 ppm caused by imidazole (-NH-) proton while the multiplate at the range (6.93 – 8.17) ppm due to protons of phenyl rings.

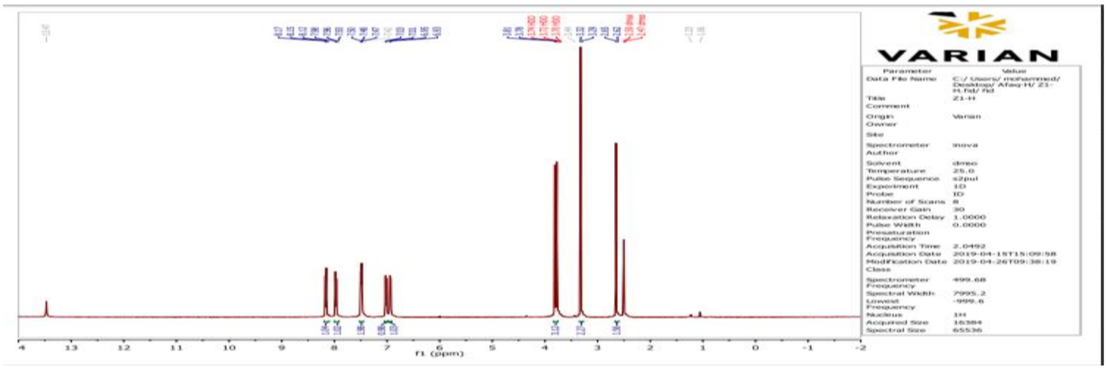


Fig.2 : The ^{1}HNMR spectrum of (HMAI) ligand

3.4. Infrared spectra

The IR spectra of azo ligand and its metal complexes were recorded as KBr pellets in the region 4000-400 cm^{-1} and the data furnished the binding modes and the functional group of ligand connected to metal ions are displayed in Table (2). In the IR spectrum of the ligand (HMAI), the absorption band due to (N–H) stretching vibrations in imidazole ring was observed at 3277 cm^{-1} [18]. This (N–H) stretching band disappeared in all the complexes spectra due to covered by lattice water stretching vibrations. The existence of sharp band at 1678 cm^{-1} indicating carbonyl functional group of the azo ligand, which appeared almost at the same region in all the complexes excepting slight shift in its position indicating their non participation in complexation [19]. Also the spectrum of (HMAI) ligand exhibited medium band at 1612 cm^{-1} due to (C=N) stretching vibration of imidazole. This band was shifted to lower frequency in complexes and observed at 1604-1608 cm^{-1}, suggesting the involvement of azomethine group in complexation with the metal ions [20]. The stretching frequency due to azo group (–N=N–) was observed at 1475 cm^{-1} in the ligand. The azo group is shifted to lower frequency and appeared at 1460-1471 cm^{-1} indicating the participation of one of the azo nitrogen atom in coordination with metal ion [21]. All the metal complexes exhibited a band in the region 3383-3496 cm^{-1} due to the existence of lattice water molecules [22]. The formation of complexes between the azo ligand and metal ions through coordination bond was furthermore established by the existence of low intensity of non ligand bands in the range of 455 - 482 cm^{-1} in all the complexes are due to ν (M–N) stretching frequencies respectively [23]. Thus the above IR spectral data lead to suggest that the ligand behaves as a neutral bidentate chelating agent, and the coordination sites are, the nitrogen atom of azo group nearest to a phenyl ring, and N3 atom of the imidazole ring, to give five-membered chelate ring. Figs.(3) and (4), shows the spectra of azo ligand and $[NiI(L)_2 Cl_2]. H_2O$ complex.

Table (2): Characteristic IR frequencies (in cm^{-1}) of the azo ligand and its metal chelate complexes

Compound	ν (O─H) H_2O	ν (N─H)	ν (C=O)	ν (C═N)Im	ν (N═N)	ν (M─N)
L= (HMAI)	………..	3277 m.	1678 s	1612 m	1475 w	…….
$[Mn(L)_2Cl_2].H_2O$	3415 m.br	………	1676 s	1604 m	1462 w	474 w
$[Fe(L)_2Cl_2]. H_2O$	3388 m.br	………	1672 s	1608 m	1471 w	468 w
$[Co(L)_2Cl_2]. H_2O$	3383 m.br	………	1674 s	1604 m	1463 w	474 w
$[Ni(L)_2Cl_2]. H_2O$	3385 m.br	………	1680 s	1608 m	1463 w	455w
$[Cu(L)_2Cl_2]. H_2O$	3415 m.br.	………	1676 s	1606 m	1465 w	464 w
$[Zn(L)Cl_2],H_2O$	3414 m.br	………	1678 s	1604 m	1460 w	470 w
$[Cd(L)Cl_2] H_2O$	3414 m.br	………	1674 s	1604 m	1463 w	482 w
$[Hg(L)Cl_2] H_2O$	3496 m.br	………	1678 s	1606 m	1463 w	462 w

S= strong, m = medium, w = weak , br = broad

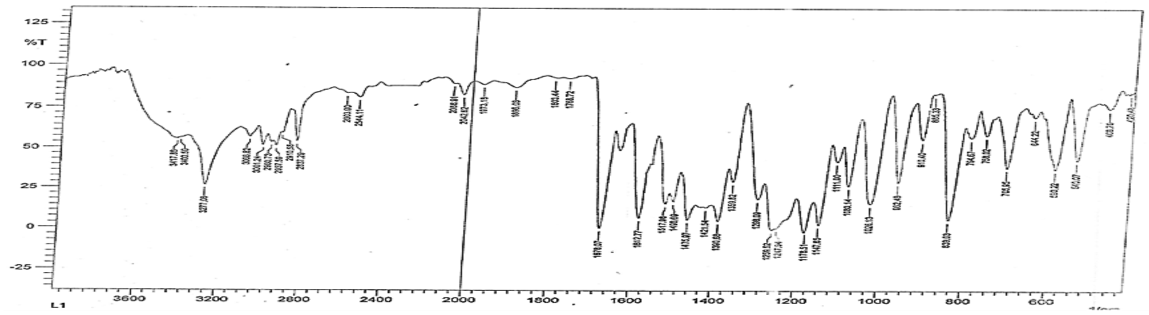


Fig. 3: IR Spectrum of azo ligand (HMAI)

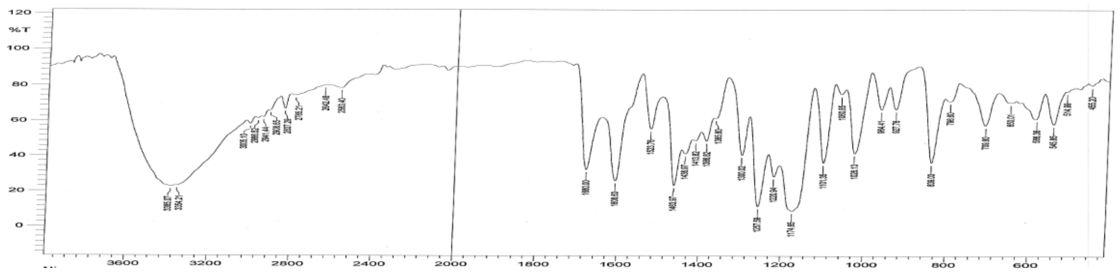


Fig. (4): IR Spectrum of [Ni $(L)_2$ Cl_2]. H_2O complex

3.5. Absorption spectra

The electronic absorption spectra of all the compounds were recorded using ethanol solution in the range 200-1100 nm at room temperature Table (3). The spectral data of free ligand (HMAI) exhibited two recognizable absorption bands. The band which appeared at (230 nm) can be ascribed to the ($\pi \rightarrow \pi^*$) transition of the phenyl rings while, the other band appeared at (476 nm) can be assigned to ($n \rightarrow \pi^*$) electronic transition due to the azo group [24]. Further, it is recognized that the absorptions bands were shifted to longer wavelength in all the metal complexes, which may be assigned to $d(M^{2+}) \rightarrow \pi^*$ (ligand) charge transfer transitions suggesting metallization with the azo dye ligand [25].

3.6. Magnetic moment and conductivity measurements

The magnetic susceptibility and molar conductance values are listed in Table (3). The magnetic moment values are found to be 5.42, 5.37, 5.19, 3.11 and 1.78 (B.M) for Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes, respectively, suggesting an octahedral geometry [26,27]. While Zn(II), Cd(II) and Hg(II) complexes was diamagnetic and according to its empirical formula, an tetrahedral geometry was proposed for these complexes. Molar conductance data of the complexes were measured in DMF and the complexes were found to be nonelectrolytic in nature [28].

4. Conclusions

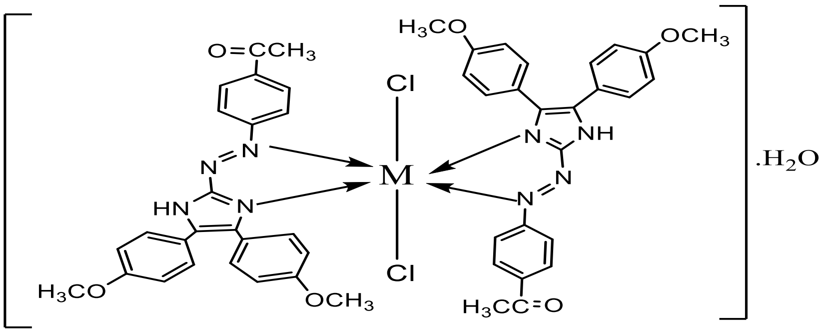
This work described the preparation and spectroscopic characterization of a series of manganese, iron, cobalt, nickel, copper, zinc, cadmium and mercury complexes with new arylazo imidazole ligand. These complexes with azo dye were characterized by using different physiochemical techniques. The IR spectra revealed that (HMAI) behaves as neutral bidentate ligand coordinated to the metal ions through imidazole-N, azo-N donor atoms. The spectral and magnetic studies of the prepared metal complexes of azoligand reveals that Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) metal complexes are having octahedral geometry and the (metal : ligand) ratio is 1:2. But Zn(II), Cd(II) and Hg(II) metal complexes are having tetrahedral geometry with 1:1 (metal : ligand) ratio. The ligand can be good analytical reagent for some metal ions.

According to the above data the structural formula of metal complexes may be proposed in Figs. (5) and (6).

Table (3) : Electronic spectra, conductivity and magnetic moment of complexes

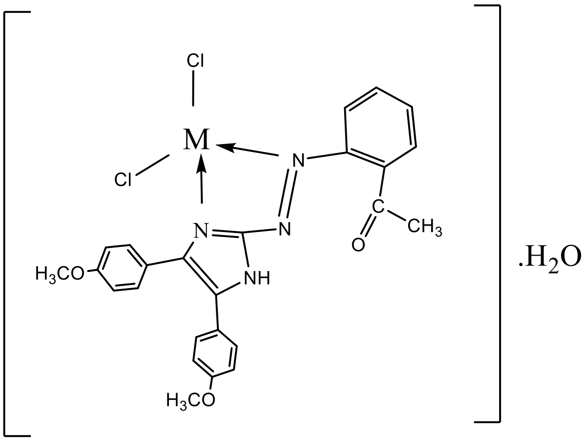
Compound	Absorption bands (n.m)	Transition	Conductivity S. $cm^2 .mol^{-1}$	μeff (B.M)
L= (HMAI)	230 476	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	……….	……….
$[Mn(L)_2Cl_2].H_2O$	281 354 538	$\pi \rightarrow \pi^*$ ILCT MLCT	9.13	5.42
$[Fe(L)_2Cl_2]. H_2O$	240 355 574	$\pi \rightarrow \pi^*$ ILCT MLCT	8.42	5.37
$[Co(L)_2Cl_2]. H_2O$	282 357 603	$\pi \rightarrow \pi^*$ ILCT MLCT	9.47	5.19
$[Ni(L)_2Cl_2]. H_2O$	288 355 541	$\pi \rightarrow \pi^*$ ILCT MLCT	8.23	3.11
$[Cu(L)_2Cl_2]. H_2O$	283 353	$\pi \rightarrow \pi^*$ ILCT		1.78

	582	MLCT	8.72	
[Zn(L)Cl_2],H_2O	206 357 563	π→ π* ILCT MLCT	11.17	Dia
[Cd(L)Cl_2] H_2O	236 295 484	π→ π* ILCT MLCT	13.15	Dia
[Hg(L)Cl_2] H_2O	284 356 521	π→ π* ILCT MLCT	14.22	Dia



M=Mn(II),Fe(II),Co(II),Ni(II)andCu(II)

Fig. (5): structural formula of transition metal complexes



M= Zn(II),Cd(II)andHg(II)

Fig. (6): structural formula of non- transition metal complexes

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