

PREPARATION, CHARACTERIZATION AND BIOLOGICAL STUDY OF NEW HETEROCYCLIC AZO LIGAND AND SOME OF ITS CHELATE COMPLEXES

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ABSTRACT

Coupling reaction of 4-amino antipyrine with 4,5-bis(4-methoxyphenyl) imidazole gave a new azo ligand **2**-[(4-Aminoantipyrin)azo]-4,5-bis(4-Methoxyphyl)-H-imidazole (AAMPI). The prepared ligand was identified by Microelemental Analysis, Mass spectrum, C^{13} NMR, HNMR, FT-IR and UV-Vis spectroscopic techniques. The structure and nature of this organic ligand and its metal complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) in aqueous ethanol with a 1:2 M:L ratio, yielded a series of neutral complexes of the general formula $[M(L)_2]Cl_2.H_2O$. The prepared complexes were characterized using molar conductance measurements, flame atomic absorption, magnetic susceptibility, IR, (C.H.N), and UV-Vis. Depending on these results, we may conclude that the ligand was tridentate. Also the proposed geometrical structure of structure of the complexes ions are octahedral

Key words: Azo ligand, Metal complexes, coupling reaction, biological activity.

INTRODUCTION

Azo dyes are known for extended application in different field⁽¹⁾ and have been attracting attend of synthetic and theoretical chemists. Also textile dyes⁽²⁾, due contain azo group $-N=N-$ and being conjugated bonds gave color and absorption in the visible region. Azo compound derived from heterocyclic amines containing nitrogen in the aromatic rings and their metal complexes, Particularly fused with imidazole or pyrazole as the heterocyclic, have been drawing the interest of many studies due to their biological activities⁽³⁻⁵⁾. The imidazole ring is found in very significant endogenous biomolecules example biotin, the autacoid histamine and the essential amino acid histidine⁽⁶⁾. Additionally, the imidazole derivatives is highly importance in medicinal chemistry research, a lot of imidazole-containing compounds show biologicalactivities like of antifungal, antibacterial⁽⁷⁾, anti-inflammatory and anthelmintic⁽⁸⁾, antitubercular⁽⁹⁾, antibloodpressures⁽¹⁰⁾, antiallergic⁽¹¹⁾, antiasthma⁽¹²⁾ and anticancer⁽¹³⁾. Antipyrine is well known for its pharmaceutical as well as medical application like antibacterial, antifungal⁽¹⁴⁾, antituberculosis⁽¹⁵⁾, anticancer, cytotoxic⁽¹⁶⁾, antitumor⁽¹⁷⁾, antioxidant⁽¹⁸⁾. Depending on these results, we report the preparation and characterization of new heterocyclic azo dye ligand 2[(Aminoantipyren)azo]-4,5-bis(4-Methoxyphenyl)-Himidazole(AAMPI) and its metal complexes for Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions.

2.Experimental

2.1.Materials and physical measurements

All chemicals were highest purity obtained from BDH and Fluka. Elemental analysis (C.H.N) were obtained using EA300 C.H.N elemental analyzer.Masssperaagilent technologies 5973C at 70° and MSD energy.The¹HNMR and ¹³CNMR spectrophotometer in DMSO-D6 were recorded on Bruker 500 MHZ spectrophotometer using TMS as an internal reference. The IR spectra of azo ligand and its complexes were recorded in KBR in the rang (4000-400) cm^{-1} on FT-IR test scan shimaduz model 8400S. While the UV-Vis spectra in the range of (200-1100)nm in absolut ethanol on shimaduz model 1650PC. Magnetic susceptibilities measurments of the complexes were carried out on abalance magnetic MSB-MKI using faraday method, the diamagnetic corrections were made by Pascal's constants. Molar conductance measurements were recorded in ethanol by using 3IA conductivity bridge at room temperature. The metal contents of the complexes was measured by using atomic absorption techingue by shimaadzu AA-160. Melting points were specified on SMP10 melting point.

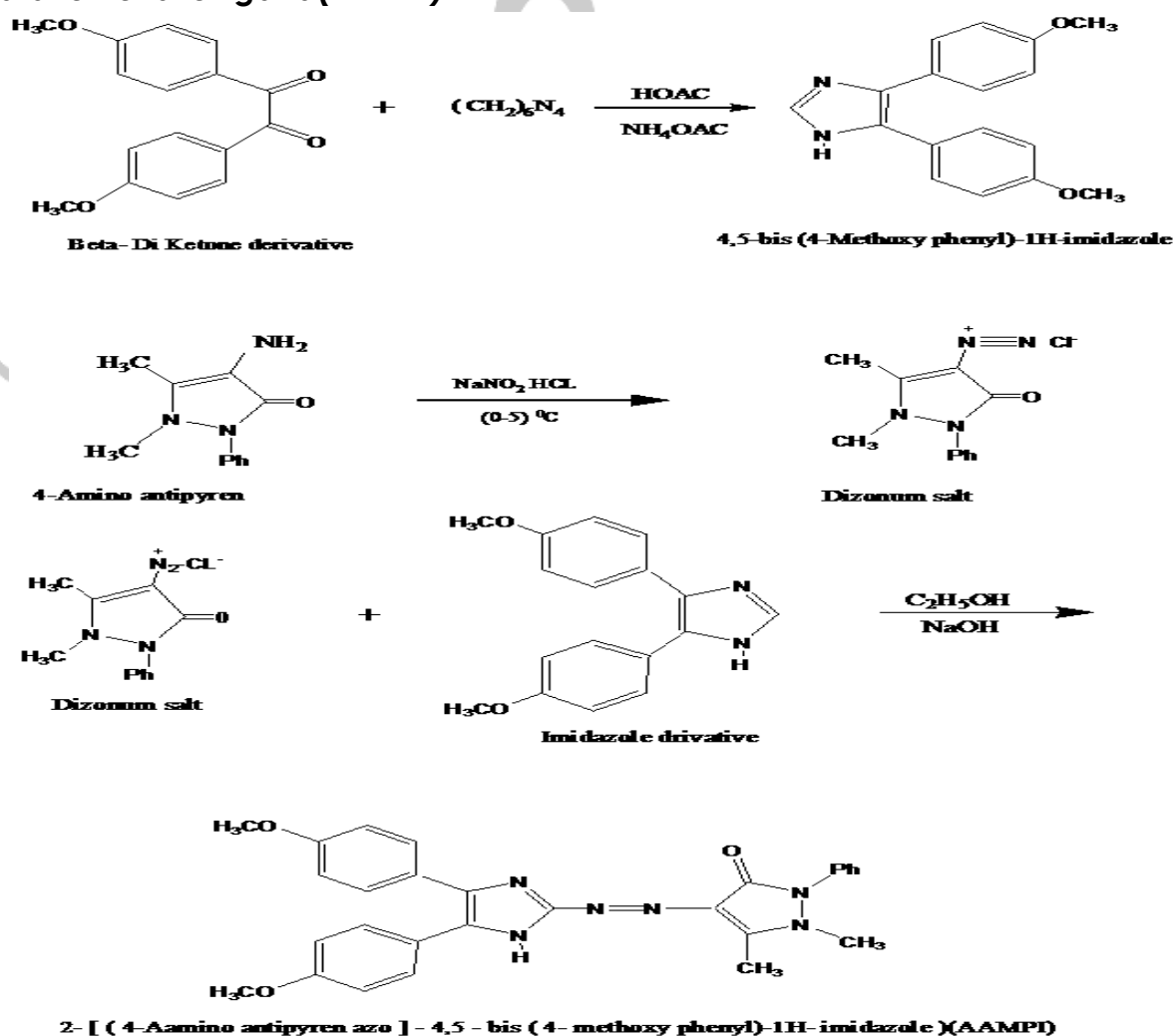
2.2.Preparation of derivative imidazole

Theimidazole derivative obtained from the interaction of derivative benzyl and hexa methylene tetra amine in the presence of glacial acetic acid⁽¹⁹⁾. In a round flask (250) ml add (50) ml of glacial acetic acid to a mixture of (2.90gm, 0.01mol)of derivative

benzyl, (0.256 gm, 0.005mol) of hexamethylene tetra amine and (6.0gm,0.23mol) of ammonium acetate. Heated reflux the solution for 90 min, by using reflected condenser, dilution the solution after cooling beaker (1)liter by adding (400) ml of distal water. Precipitate the imidazole derivative by adding solution of ammonium hydroxide, by filtration collected the white precipitate and then washing four times distal water, re-crystallization from hot ethanol to obtain white crystalline then drying at room temperature. The yield (79%) and m.p. (72-74°C).

In atypical preparation⁽²⁰⁾, 30 ml of distilled water containing 3 ml from hydrochloric acid was added to (2.4g, 0.01mol) 4-aminoantipyren. It is then cooled in ice bath, then a solution of (0.7g, 0.01mol) ammonium nitrite in 10 ml of water was added dropwise. The formed diazonium chloride was coupled with an alkaline solution of (2.80g, 0.01mol) 4,5-bis(4-Methoxy phenyl) imidazole, in 100 ml of ethanol. The orange solution produced, the mixture was left in the refrigerator overnight. The precipitate was filtered off, washed several times in water and air dried. in fig.1.

2.3.Preparation of azo ligand(AAMPI)



Scheme.1: preparation of azo ligand (AAMP)

Preparation of chelate complexes

The metal complexes were prepared⁽²¹⁾ by dissolved (0.988g, 0.002mol) from ligand in ethanol (50 ml) and add dropwise with stirring to (0.001 mol) molar ratio of 1:2 (metal ligand), chlorides salts of Co(II), Cu(II), Ni(II), Zn(II), Cd(II) and Hg(II), dissolving in water. The product precipitated were filtered, washed in hot ethanol-water 1:1 to remove any traces of the unreacted starting material.

3. Results and Discussion

3.1. Characterization of Azo Dye Ligand (AAMPI) and its Metal Complexes

Table 1. Elemental analysis and physical properties for ligand (AAMPI) and its metal complexes

Cheimiecal formul (M.W)(g/mol)	m.p	Color	Yield %	C Found % (cal.)	H Found % (cal.)	N Found % (cal.)	M Found % (cal.)
$(C_{28}H_{26}N_6O_3) = L$	115-117	orange	72	67.82 (67.80)	5.20 (5.19)	16.82 16.80	-----
$] (L)Co_2O_2H_2Cl[$	200-198		86	58.98 (59.16)	4.64 (4.75)	14.66 (14.79)	4.97 (5.18)
$L_2]Cl_2.H_2O)Ni]$	195-193		80	58.92 (59.17)	4.62 (4.75)	14.64 (14.79)	4.94 (5.16)
$L_2]Cl_2.H_2O)Cu]$	142-140		81	58.71 (58.92)	4.64 (4.73)	14.59 (14.73)	5.32 (5.57)
$L_2]Cl_2.H_2O)Zn]$	240-238		78	58.55 (58.82)	4.61 (4.72)	14.57 (14.70)	5.72 (5.72)
$] L)Cd_2O_2H_2Cl[$	138-136		69	56.36 (56.50)	4.41 (4.54)	13.93 (14.12)	9.33 (9.45)
$] L)Hg_2O_2H_2Cl[$	152-150		83	52.45 (52.60)	4.12 (4.22)	12.97 (13.15)	15.65 (15.70)

The azo ligand (AAMPI) was orange crystal but the metal complexes were found to be different colour. The azo ligand and its metal complexes were soluble in most organic solvent example methanol, ethanol, DMF, DMSO and acetone, but insoluble in water. And were stable at room temperature. The analytical and physical properties of azo dye ligand and

its metal complexes are explained in Table 1.

3.2. Mass spectra of new azo ligand

The mass spectrum of the azo dye ligand (AAMPI) in (Fig.1) showed a molecular ion peak $M^{+}_{atm}/z=494$ attributed to the molecular weight of ligand (494) and the peak at $m/z=280$ due to molecular derivative imidazole molecular weight (280).

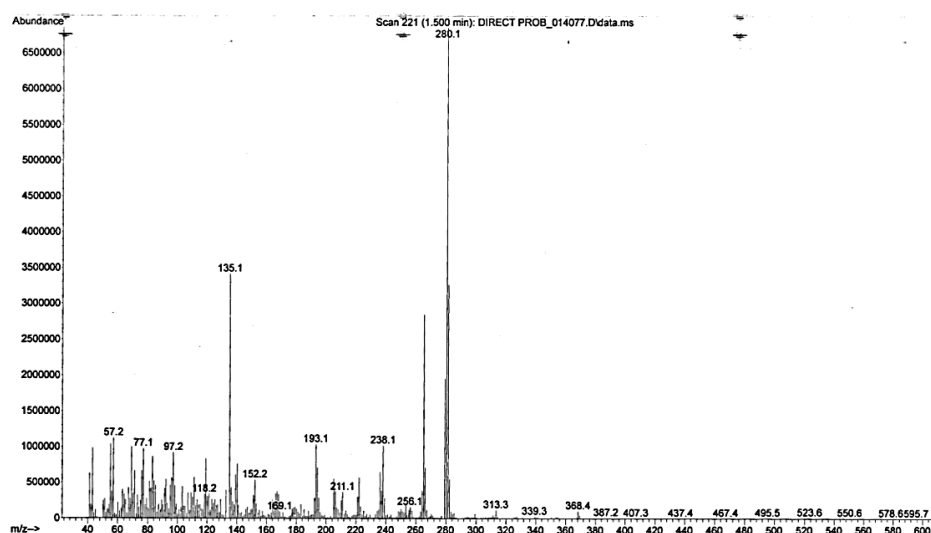


Fig 1. Mass spectra of azo ligand (AAMPI)

3.3. ^1H NMR spectra

The ^1H NMR spectra of new azo ligand (AAMPI) Fig(2), was measured in TMS as an internal reference with $\text{DMSO}-d_6$ as a solvent. The spectrum of ligand showed a signal at $\delta=2.486$ ppm due to the methyl group ($\text{H}_3\text{C}-\text{C}=\text{C}-$) of pyrazole molecule⁽²²⁾,

a signal at $\delta=2.73$ ppm due to methoxy group⁽²³⁾ in derivative imidazole. A signal at $\delta=3.376$ ppm to methyl group ($\text{H}_3\text{C}-\text{N}<$) of antipyrine ring, while a signal at $\delta=10.64$ ppm due to NH group in imidazole molecule. The signal at $\delta=2.51$ ppm solvent proton.

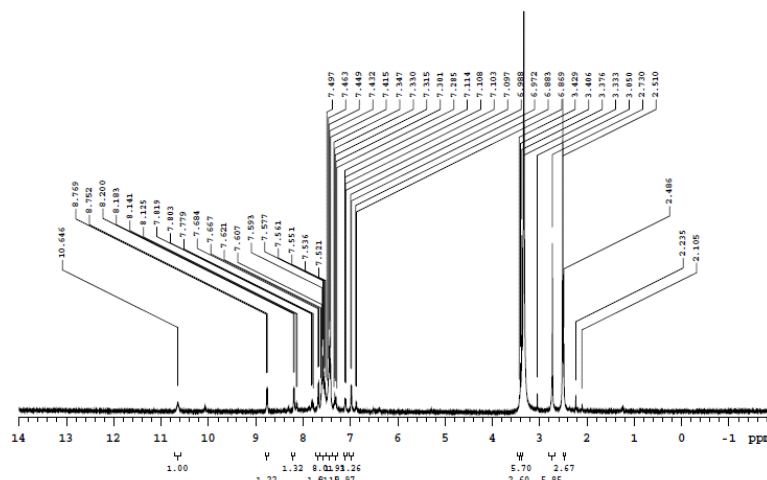


Fig2. ¹H NMR Spectra of azoligand(AAMPI)

3.4.¹³CNMR spectra

The ^{13}C NMR of the azo ligand show several signals, Fig(3) the signal observed at 158 ppm is assigned to carbonyl group ($\text{C}=\text{O}$) of antipyrine. Also, the spectrum showed peak at 34 ppm attributed to methyl group ($\text{N}-\text{CH}_3$) of antipyrine ring, while the signal at 155 ppm assigned to ($\text{C}3$) of pyrazole ring. As for the signals at

(135, 127, 129, 130) refer to (C1, C2, C3, C4) respectively, to phenyl of antipyrine ring. For the imidazole derivative, the signal observed at 56 ppm to two methoxy group, a signal at 126 ppm to (C4.C5) of imidazole rang, while a signal at 153 ppm to (C2). And the signals at (134, 128, 114, 156) to (C1, C2, C3, C4) respectively, of imidazole phenyl ring.

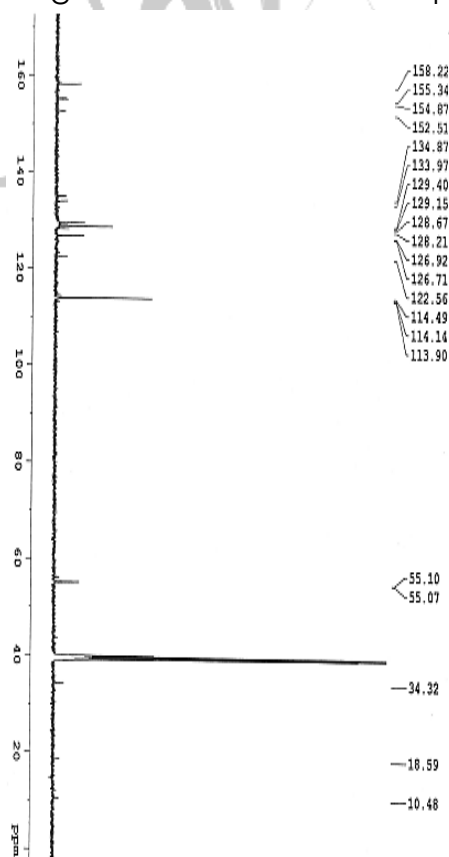


Fig 3. ¹³NMR Spectra of azoligand(AAMPI)

3.5.FT-IR Spectra

Infrared spectral data (KBr disk) of ligand (AAMPI) and its metal complexes are summarized in table (2). The IR Spectrum of 4-amineoantipyrin shows strong stretch at 3431 and 3327 cm^{-1}

Which correspond to H_2N group and $\text{C}=\text{O}$ group. The IR Spectrum of 4-amineoantipyrin shows strong stretch at 3431 and 3327 cm^{-1} which correspond to H_2N group and $\text{C}=\text{O}$ group. The IR Spectrum of 4-amineoantipyrin shows strong stretch at 3431 and 3327 cm^{-1} which correspond to H_2N group and $\text{C}=\text{O}$ group.

avoided at 3364 cm^{-1} for H_2N group. The IR Spectrum of 4-amineoantipyrin shows strong stretch at 3431 and 3327 cm^{-1} which correspond to H_2N group and $\text{C}=\text{O}$ group. The IR Spectrum of 4-amineoantipyrin shows strong stretch at 3431 and 3327 cm^{-1} which correspond to H_2N group and $\text{C}=\text{O}$ group.

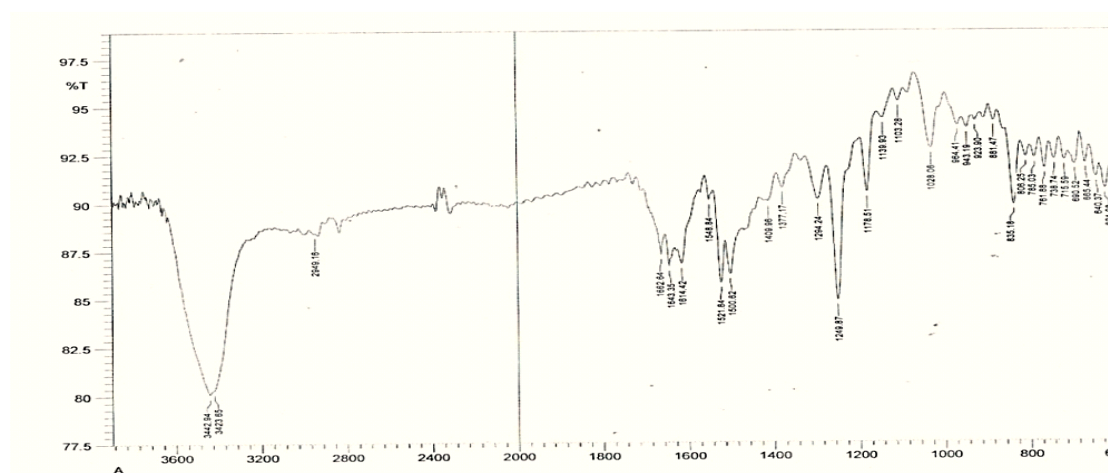


Fig 4.FT-IR of azo ligand (AAMPI)

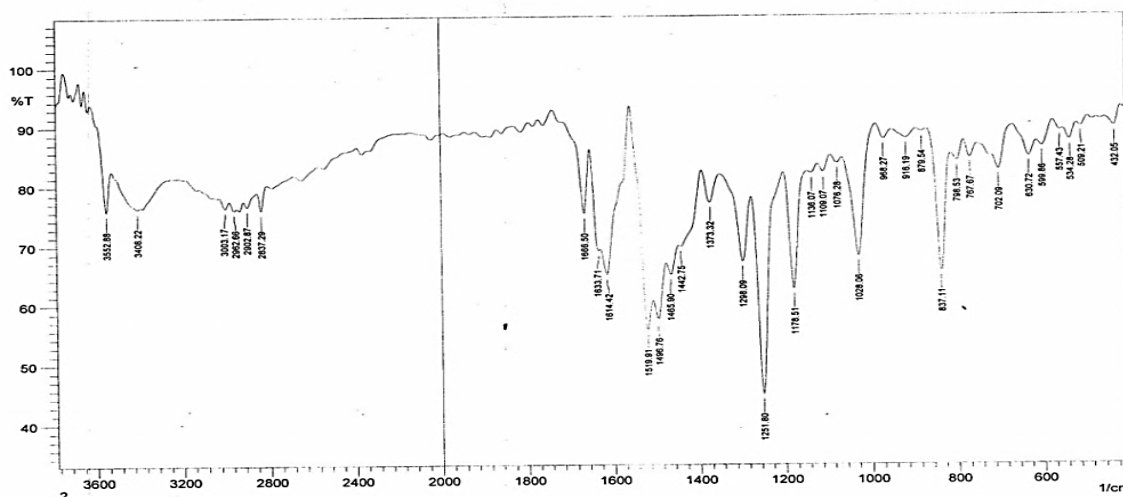


Table 2.Characteristic IR absorption bands of the ligand (AAMPI) and its complexes in cm⁻¹ units

$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{N=N})$	$\nu(\text{C=N})$	$\nu(\text{C=O})$	$\nu(\text{C-H})_{\text{al}}$	$\nu(\text{C-H})_{\text{ar}}$	$\nu(\text{N-H})$	Compounds
---	---	1500 m	1521s	1662 s	2949 w	3010	3442 m	AAMPI
459w	534w	1465w	1519m	1614m	2962w	3003w	3408w	[Co(AAMPI) ₂]Cl ₂ .H ₂ O
424w	505w	1463w	1517s	1620s	2937w	3003w	3414m	[Ni(AAMPI) ₂]Cl ₂ .H ₂ O
470w	532w	1462w	1500s	1616	2901w	3005w	3425w	[Cu(AAMPI) ₂]Cl ₂ .H ₂ O
439w	528w	1462w	1516m	1651m	2839w	2931w	3448w	[Zn(AAMPI) ₂]Cl ₂ .H ₂ O
443w	532w	1415w	1516m	1647m	2935w	3171w	3429m	[Cd(AAMPI) ₂]Cl ₂ .H ₂ O
460w	532w	1462w	1519m	1612m	2835w	2935w	3410w	[Hg(AAMPI) ₂]Cl ₂ .H ₂ O

S= strong, m= medium, W= weak

3.6. Electronic Spectral Studies

Electronic spectra of the metal complexes were recorded in the UV-Vis region (200-1100)nm in ethanol solution. The spectral data and the magnetic moment of prepared complexes are showed in Table 3. UV-Vis spectral studies of the metal complexes exhibit transition at lower than 500 nm corresponding to intramolecular $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ charge transition (). Intense absorption bands ($\epsilon \sim 10^4$) appear in the range (458-493)nm (ligand) charge transfer transition. The electronic spectra of the azo ligand Fig 6. Show intense bands ($\epsilon \sim 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ at 245, 312 and 440 nm. They may be ascribed to azo ligand centred $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition,

respectively, are complexes Fig 7. Shift these transition to longer wavelength by 24-53nm along with a weak broad transition $\epsilon \sim 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$ centred at 500 nm. The red shifting of ligand transition in the metal complexes of bonding interaction between metal and ligand. As well, weak transition at 500 nm maybe refer to $d(\text{metal}) \rightarrow (d\text{ligand})^* \pi$ ligand π azo group and participate in metal \rightarrow ligand charge transfer transition, () in complexes Fig exhibit ligand transitions at longer wavelength (53-24) nm compared to the free ligand data.

Table 3. Spectral data, conductivities, magnetic moment and proposed structure of metal complexes.

Complex	Assignment	(Absorption band (nm))	($\epsilon \text{ (S.cm}^2.\text{mol}^{-1})$)	(M.B. μ_{eff} ())	Proposed Structure
AAMPI	$n \rightarrow \pi^*$	440, 312, 245	-----	---	---
$\text{Co(AAMPI)}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$.C. T	464	70.12	4.90	Oh
$\text{Ni(AAMPI)}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$.C. T	463	86.32	3.06	Oh
$\text{Cu(AAMPI)}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$.C. T	473	75.60	1.77	Oh
$\text{Zn(AAMPI)}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$.C. T	459	71.2	Dia	Oh
$\text{Cd(AAMPI)}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$.C. T	458	79.6	Dia	Oh
$\text{OHg(AAMPI)}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	C. T.	493	80.4	Dia	Oh

3.7. Molar conductivity

Molar conductance data in Table 3. of the metal complexes were measured in DMSO as a solvent at room temperature. The high values of molar conductivity for the

complexes refer that it is of the nature electrolyte (1:1) due of the being of chlorine ion (Cl^-) outside the coordination sphere. As shown in Table 3.

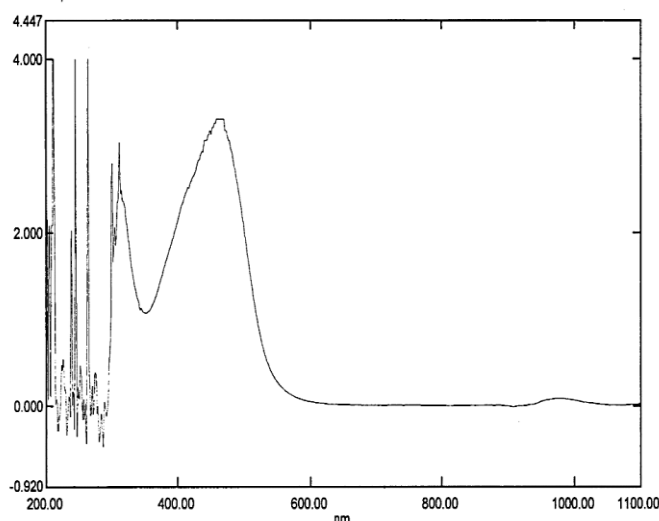


Fig 6. UV-Vis spectra of azoligand(AAMPI)

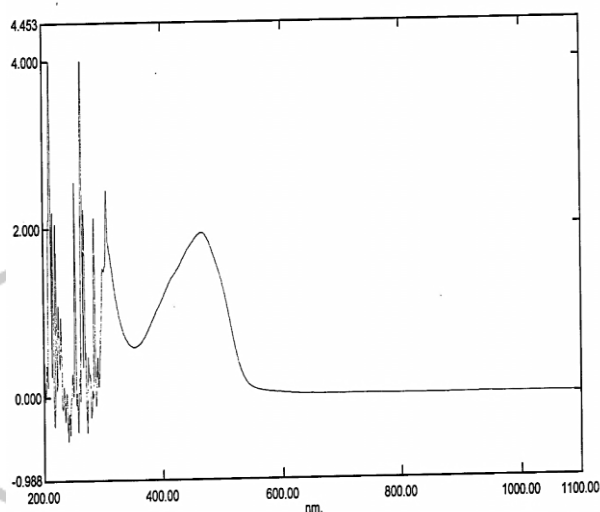


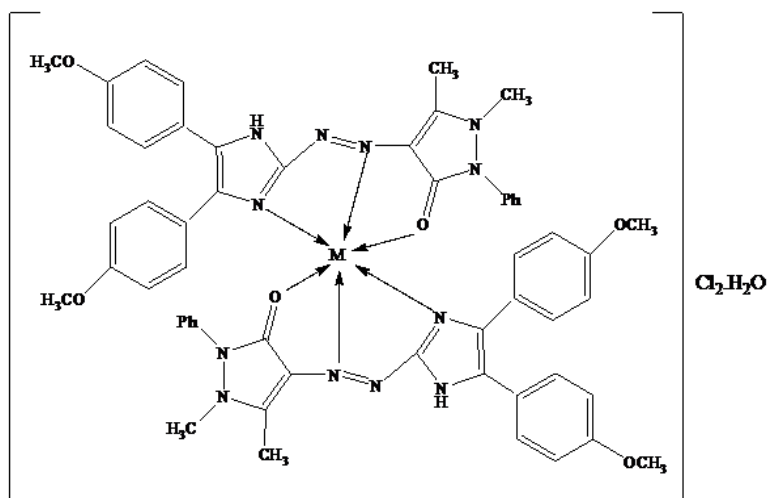
Fig 7. UV-Vis spectra of Co(II) complexes

3.8.Magnetic measurements

The magnetic moment values for metal complexes in Fig 3. have been used as criterion to define the type of coordination for the metal ion. Because the intrinsic orbital angular momentum in the round state. In the metal complexes the magnetic moment (4.90 B.M.) suggests an octahedral geometry for the Co(II) complexes in the high spin state⁽¹⁾. Magnetic moment value (3.06 B.M.) for a high- spin Ni(II) complexes^(3.09)⁽¹⁾ depends

on the magnitude of the orbital contribution. For Cu(II) complexes, the magnetic moment value (1.77 B.M.) expected for one unpaired electron which offers the potential of an octahedral geometry⁽¹⁾. While the magnetic moment value of Zn(II), Cd(II) and Hg(II) metal complexes are diamagnetic consistent with the (d^{10}) configuration⁽¹⁾.

Depending to these results the structure of these chelate complexes may be proposed in Fig 8. Shown below:-



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

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