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Synthesis, identification, structural, studies and biological activity of some transition metal complexes with novel heterocyclic azo-schiff base ligand derived from benzimidazole

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ABSTRACT

The novel azo-Schiff base ligand 2- ((E) – (1H- benzo [d] imidazol-2-yl)diazenyl)-5-(E-4-(dimethyl amino) benzyliden amino) phenol, (BIADMebP) has been synthesized from condensation of 2-[(2-benzimidazolyl) azo] -5-amino phenol with N,N-dimethyl benzaldehyde. The azo-schiff base ligand reacted with some divalent transition metal ions such us Co(II),Ni(II), Cu(II), Zn(II), pd(II) and pt(IV) forming six chelates complexes. The prepared azo-schiff and its metal complexes where checked by different spectral technique in terms, C.H.N elemental analyses, metal content, magnetic moment measurements, molar conductance, FT-IR, UV-vis, ^{1}H-NMR and mass spectra studies. The data show that the complexes have the composition of l:2[M:L] chelates type and octahedral geometry with Co(II), Ni(II),Cu(II),Zn(II) and Pt (IV) ions and l:l[M:L] cheats type and square planer geometry with Pd(II)ion. All complexes that non electrolytes and no conductive species excepted the Pt(IV)-complex is 1:2 electrolyte nature. The pathogenic activities of the synthesized ligand (BIADMebP) and its complexes were tested invitro against the sensitive organisms Escherichia coli, staphylococcus as antibacterial and candida albicans, Aspergillus Niger as antifungal. The activity data show that the metal complexes higher anti bacterial and antifungus activity than the free ligand. The result are discussed.

Key words: Synthesis, azo-schiff base, metal complexes, spectral studies, Biological activity.

INTRODUCTION

Azoschiff bases compounds derived from the reaction between the schiff base and azo compounds. Schiff bases derived from the reaction of aromatic aldehydes and aliphatic or aromatic amines represented in important series of widely studies organic ligands[1]. Schiff bases and azo schiff bases important intermediates for the synthesis of some application such as biological activity[2-4], clinical[5,6], analytical[7,8], Anticancer[9,10] and catalystical[11,12]. Azo schiff base compounds are highly important well known and widely used substances in textile, paper and coloring agents for foods and cosmetics industries[13,14]. Azo schiff base and their complexes with transition metal ions are also of importance due to their complexing, catalystical, biological properties[15,16]. and corrosion inhabitation in acid media[17,18].This class of azo compounds posses active $(\pi - acidic)$ azo imine (- N = N-CH=N-) function, for this reason a number of these azoimidazoles were prepared and their abilities as chelating ligands was investigated[19-21].In this paper we report the preparation, identification, structural studies and biological activity of the novel tridantateazo schiff base ligand, 2- ((E) –(1H-benzo[d] imidazole-2-yl) diazenyl) -5- ((E)-4- (dimethy amino) benzyliden amino) phenol (BIADMebP) and its metal complexes with Co(II), Ni (II), Cu(II), Zn(II), Pd(II) and Pt(IV) ions.

EXPERIMENTAL SECTION

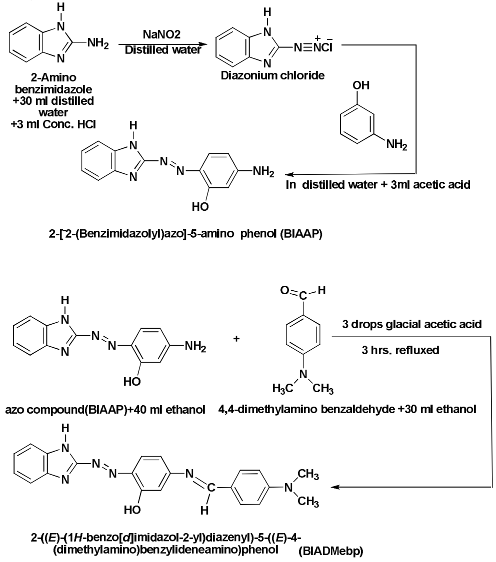
All the chemicals used were of analar grade, procured for Aldrich, BDH, Sigma and Merck. Solvents used were of analytical grade. The solvents were purified by distillation and double distilled water were used through the experiment. IR spectra were recorded as KBr discs using a shimadazu 8400 FT-IR Spectrophotometer in the rang (4000-400). Electronic spectra were measured in the rang (200-1100) nm using 10^{-3} M solution absolute ethanol at room temperature using a UV-Vis. T80-PG spectrophotometer. ^{1}H- NMR spectra were recorded with a model Bruker AMX400 MHZ spectrometer operating at 400 MHZ using DMSO as a solvent and TMS as an internal standard. Mass speetra were recorded on a shimadzu Agilent Technologies 5975C at 70 and MSD energy using a direct insertion probe (Acq method low energy) at temperature 90-110^{o}C. Elemental analysis (C.H.N) were carried out using a C.H.N EA-99 mth instrument. The metal contents of complexes was measured using atomic absorption technique by shimadzu AA-6300.Magnetic susceptibility measurements of the metal complexes in powder from were carried out on Balance Magnetic (MSB- MKI) apparatus by using farady method at room temperature and diamagnetic correction for the complexes were calculated using pascal's constant. Molar conductivity measurements were made with DMSO solution (10^{-3} M) at room temperature using a 31 A digital conductivity meter. The PH measurement were carried out using a Philips PW 9421 PH meter ($\pm$0.001). Melting points was determined by open capillary tube method and are uncorrected by using a Electro thermal melting point 9300.

Synthesis of the azo dye compound (BIAAP)

The azo dye compound 2-[ˉ2-(benzimidazolyl)azo]-5-amino phenol (BIAAP) has been synthesized by the diazotization coupling reaction by flowing methods proposed shibat *etal al* [22]. and AL-adilee *et* al[23]. with some modification (schem-1) 2-Amino benzimidazole (1.33 gm, 0.01mol) was dissolved in mixture a solution from 3ml HCl(37%) and 30 ml distilled water. An aqueous solution 20 ml of $NaNO_2$ (0.75 gm, 0-0.1mol, dissolved in 20ml distilled water) was added in drops while maintaining the temperature between 0-5°C to the mixture with continuous stirring. After that the diazonium chloride was added drop wise respectively with constant stirring to cold aqueous solution of 3-amino phenol (1.2gm,0.01mol) and then solution of 2ml acetic acid was added to the dark red colored mixture. The mixture was stirred for 1 hour at 0-5°C. The precipitate was filtered and washed with distilled water and 5ml ethanol solution to remove the excess of unreacted substances and recrystallized from ethanol and dried in oven at 60°C for several hours. The purity was confirmed by the elemental analysis (C.H.N) and TLC techniques. The yield was 82% of dark red crystals and m.p=140°C. The structure of azo compound (BIAAP) is convert by 'H-NMR. mass spectrum , IR and UV-vis. spectra.

Synthesis of novel azo-Schiff base ligand (BIADMebp)

The novel azo-schiff base ligand (BIADMebP),(scheme 1) was synthesized by condensation of 4,4-dimethyl amino benzaldehyde (1.5 gm, 0.01 m ole) with azo dye compound 2-[ˉ2-(benzimidazolyl)azo]-5-amin phenol (BIAAP) (1.21gm,0.01 mole) in 70 ml ethanol in the presences 4 drops of glacial acetic acid as a catalyst. The mixture refluxed for three hours, then the obtained product was concentrated in vacuum to remove ethanol. A readdish orange color precipitate were obtained, Which were filtered and washed with distilled water and twice recrystallized from hot ethanol, then dried in oven at 70°C for several hours. The yield 78% of reddish orange crystals and m.p=185°C.The purity was confirmed by the elemental analysis and TLC techniques. The structure of azo schiff base ligand (BIADMebp) is convert by 'H-NMR, mass spectrum, IR and UV-visb. spectra.



Scheme(1):- Synthesis of novel azo-schiff base ligand(BIADMebp)

Synthesis of azo Schiff base chelate complexes

The reaction of azo Schiff base by dissolving the ligand (BIADMebp) in 50ml ethanol(0.769gm;0.002mole) with 0.001 mole of metal salts (0.237, 0.238,0.171,0.136 and 0.409 gm) of $CoCl_2.6H_2O$,$NiCl_2.6H_2O$, $CuCl_2.2H_2O$,$ZnCl_2$ and $H_2[ptCl_6]$ respectively in a molar ratios 1:2 [metal: Ligand] excepted pd(II)-complex was added in a molar ratios 1:1[metal: Ligand], the metal chlorid$PdCl_2$ (0.177gm; 0.001mole) and (0.384gm, 0.001 mole of ligand BIADMebP). This metals chlorides dissolved in 50 ml buffer solution except the $PdCl_2$was dissolved in methanol were refluxing with stirring for 30 mint, colored precipitate formed at room temperature, than the resulting solids were filtered and washed several times with distilled water until the filtrate become colorless. The chelate complexes were dried in air and recrystallized from ethanol and dried in the oven at 70°C for several hours.

Antibacterial activity studies

The in vitro antibacterial activity of the azo Schiff base ligand (BIADMebP) and its metal complexes were test against the bacteria *Escherichia Coil, staphylococcus, Candida albicans* and *Aspergillus niger.* Stock solutions were prepared by dissolving the ligand and its metal complexes in DMF solvent (10^{-3}M). The nutrient agar medium was poured into petridish. One ml of the tested microorganism was spread over the solid nutrient agar plates with help of a spreader. An amount of 0.1 ml of test solutions was added carefully in spots on the surface of the inoculated solid media. After evaporating the solvent, the petridishes were placed at low temperature for two hours to allow the diffusion of the chemical materials and then incubated at 37°C for 24 hours. The diameter of the inhibition Zones measured in millimeters[19,20,24].

RESULTS AND DISCUSSION

The azo Schiff base ligand (BIADMebp) was reddish orange semi-crystal, but the chelates complexes of this ligand vary in color depended of metal ions. The ligand and its metal complexes were stable in air and insoluble in water but soluble in common organic solvents such as methanol, ethanol, DMF, DMSO and chloroform giving stable solutions at room temperature.

The suggested molecular formula are also supported by subsequent spectral and mole ratio, magnetic moment and conductivity measurements. The analytical data indicates which are correspond to empirical formula that azo Schiff base ligand (BIADMebP) is behaving as a tridentate in the metal complexes. The physical properties and analytical data of ligand and its metal complexes are given in table 1, which in a satisfactory agreement with calculated values.

Table(1): Physical properties and analytical data for ligand (BIADMebp)and its metal complexes

Compound	Color	m.p°C	Yield %	Molecular formula (Mol.wt)	Found (cacl.)%			
					C	H	N	M
LH=Ligand	Raddish orange	185	78	$C_{22}H_{20}N_6O$ (384.44)	(68.73) 68.88	(5.24) 5.26	(21.86) 21.46	-
$[Co(L)_2].H_2O$	Brown	221	64	$C_{44}H_{40}N_{12}O_3Co$ (843.81)	(62.63) 63.35	(4.77) 5.45	(19.91) 19.69	(6.98) 6.57
$[Ni(L)_2].H_2O$	Dark Brown	203	69	$C_{44}H_{40}N_{12}O_3Ni$ (843.51)	(62.65) 62.76	(4.78) 5.01	(19.92) 19.71	(9.91) 7.17
$[Cu(L)_2].H_2O$	Green	172	82	$C_{44}H_{40}N_{12}O_3Cu$ (848.43)	(62.28) 62.45	(4.75) 4.64	(19.81) 19.37	(7.48) 7.69
$[Zn(L)_2].H_2O$	Reddish Brown	153	73	$C_{44}H_{40}N_{12}O_3Zn$ (850.27)	(62.15) 61.92	(4.74) 4.62	(19.76) 19.96	(7.69) 7.93
$[Pd(L)Cl].H_2O$	Brown	300	79	$C_{22}H_{21}N_6O_2ClPd$ (543.32)	(48.63) 48.41	(3.80) 3.63	(15.46) 15.18	(19.58) 19.86
$[Pt(L)_2]Cl_2$	purple	198	87	$C_{44}H_{38}N_{12}O_2Cl_2pt$ (1032.83)	(51.16) 51.54	(3.70) 3.84	(16.27) 15.97	(18.87) 18.56

LH=BIADMebp

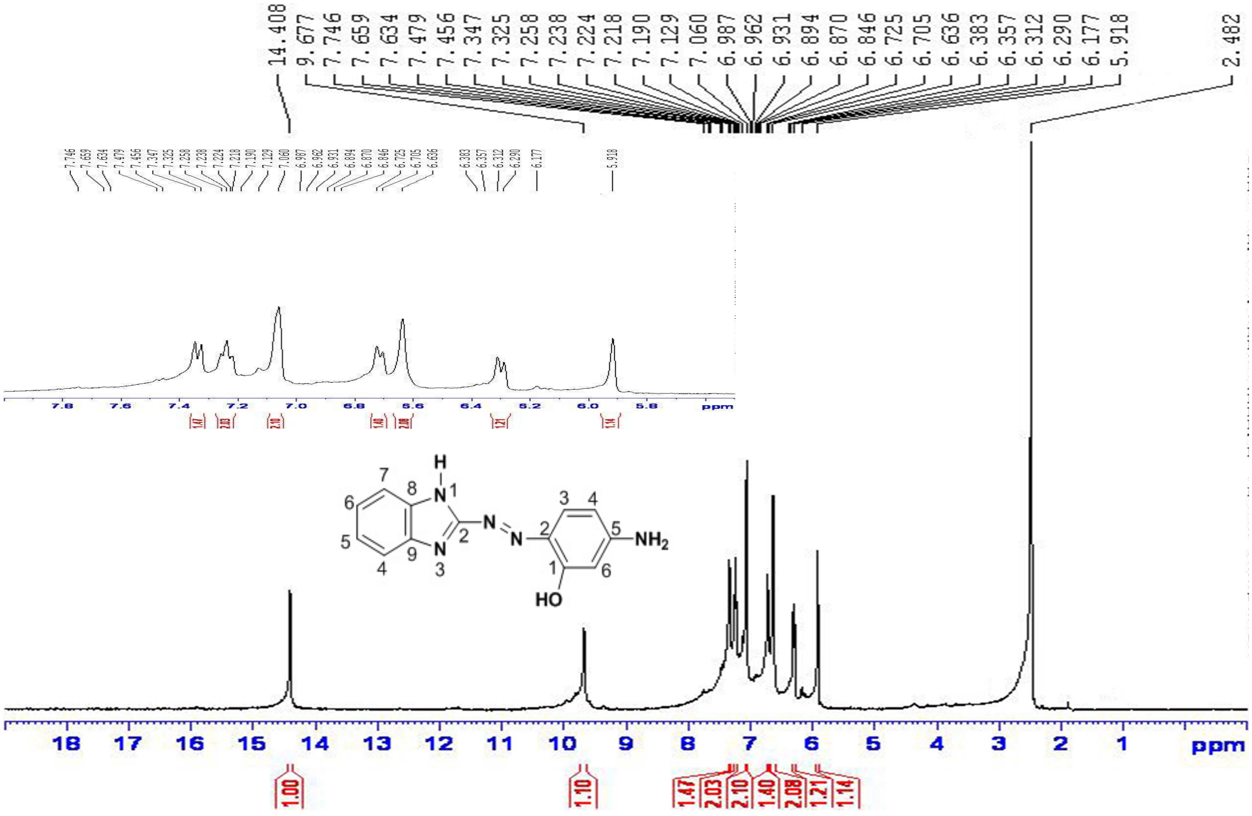
^{1}H-NMR spectral studies

The data of ^{1}H-NMR spectra of azo dye compound (BIAAP),azo Schiff base ligand and Ni(II)–complex are shown in table 2, figures 1,2 and 3 respectively, was measured in d^6-DMSO solvent with TMS as an internal reference. The ^{1}H-NMR spectrum of the azo dye compound showed a singlet signals at 14.5ppm and 9.6 ppm assigned to the protons OH and NH_2 groups respectively, this compound gives the following signals: signal peak at 5.9 ppm attributed to protons of NH benzimidazole. The doublet peaks at (6.2-6.3) ppm attributed to the presence of protons 3H and 5H of phenol ring and doublet peaks at 6.17 ppm due to proton 4H in phenol ring, while the protons 5H and 6H in benzimidazole molecule appearance at (7.1-7.4) ppm a triplet peaks at (6.6-6.7)ppm due to of3H,6Hof benzimidazole ring protons. The ^{1}H-NMR spectrum of azo Schiff base ligand the signals of NH_2 group not appearance because of formation of Schiff base and gives doublet peak at 7.66-7.68ppm a Which is assigned to the presence of azomethine and remaining in the same region in spectrum ofNi(II)-complex indicating non involvement in coordination of the azoschiff base. Doublet peaks at (6.75-6.77) ppm due to NH group of benzimidazole, while the doublet peaks at (3.01-3.07) ppm attributed to $N(CH_3)_2$ group in azo-schiff ligand. The protons of phenol, phenyl and phenyl in benzimidazole rings no appearance is clear but interference. The singal peak of OH group no appeared in the spectrum of Ni(II)-complex because of involvement in complexation[25,26]. The signals at 2.48ppm (signal) and 1.02-1.05ppm (triplet) due to the existence of methyl group in ligand $-N(CH_3)_2$ and methyl solvent respectively. The single peak at 5.9 ppm in spectrum og Ni(II)-complex due to proton of NH group in benzimidazole moleculs. This complex gives peaks at 6.2-6.3 ppm (doublet) due to protons of 5H and 6H in benzimidazole molecules but the quartet peaks at 6.6 – 6.7 ppm attributed to protons 4H and 7H in benzimidazole. The peaks of phenol and phenyl rings in spectrum of Ni(II)-complex is interference and appearance at 7.22-7.35 ppm (multiple) and 7.65-7.67 ppm(doublet).

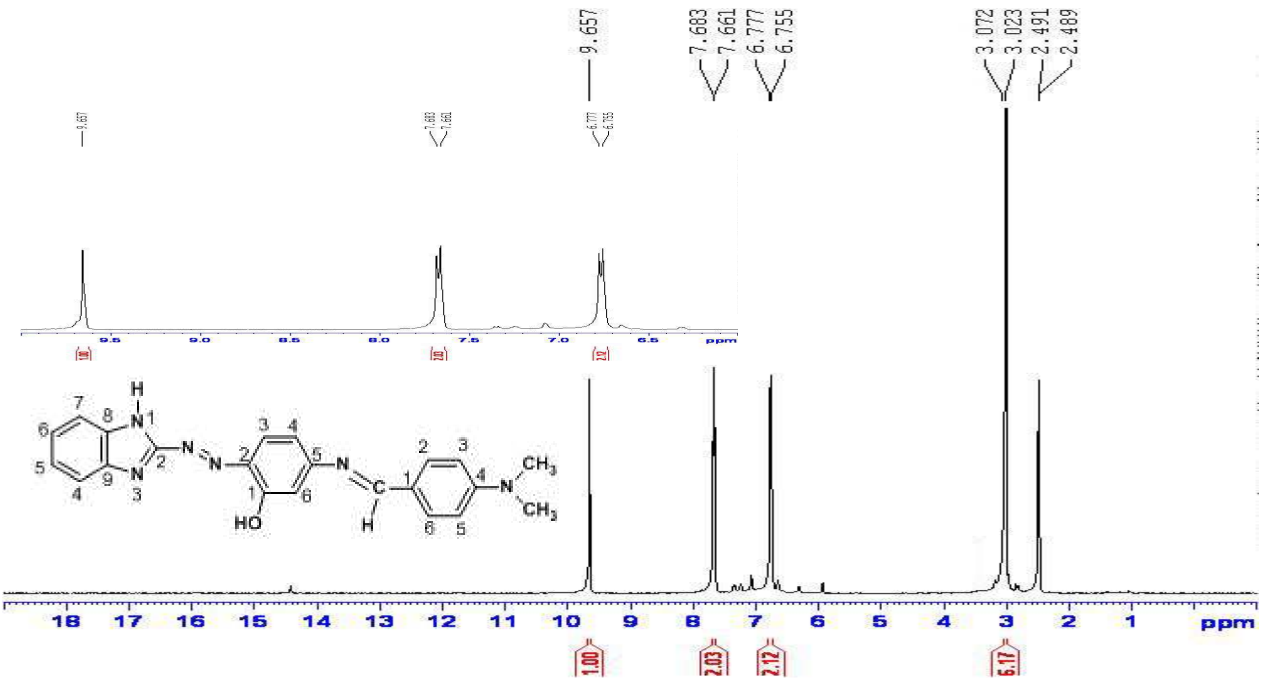
Table(2):-^{1}H-NMR spectra of azo dye compound (BIAAp),azo Schiff base ligand (BIADMebp) and Ni(II)-complex.

Chemical shifts s(ppm)						
Compound	OH	NH benzimidazole	NH_2 phenolic	CH=N	C-H Aromatic	C-H benzimidazole
BIAAP (azo dye)	14.5(s)	5.9(s)	9.6(s)	-	6.2-6.3(d) 3H,6H 6.17(d) 4H	6.6-6.7(t) 5H,6H 7.1-7.4(m) 4H,7H (d)
LH=ligand (azo Schiff base)	9.6(s)	6.75-6.77(d)	$-N(CH_3)_2$ 3.02 3.07(d)	7.66-7.68 (d)	a	a
Ni(II)-complex	-	5.9(s)	$-N(CH_3)_2$ 2.48(s)	7.06(s)	7.22-7.35(m) 7.65-7.67(d) (b)	6.2-6.3(d) 5H,6H 6.6-6.7(q) 4H,7H

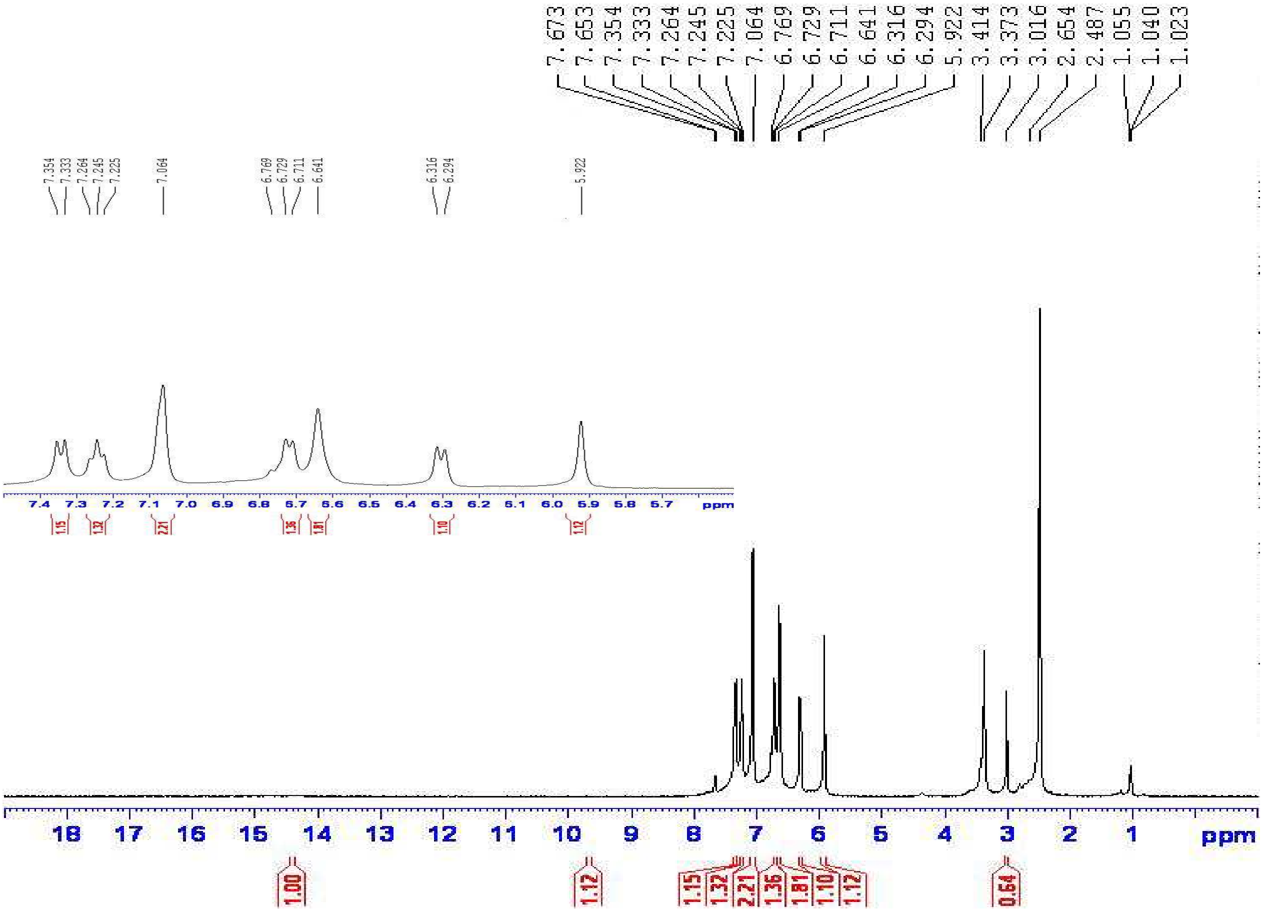
LH=BIADMebp, s=signal , d=doublet ,t=triplet, m=multiplet, q=quartet, a=the peaks of protons phenol, phenyl and benzimidazole ring interference with each other and appearance at 6.6-7.6 ppm b=peaks of phenol and phenyl rings ,



Figure(1):-^{1}H-NMR spectrum of azo dye compound (BIAAP)



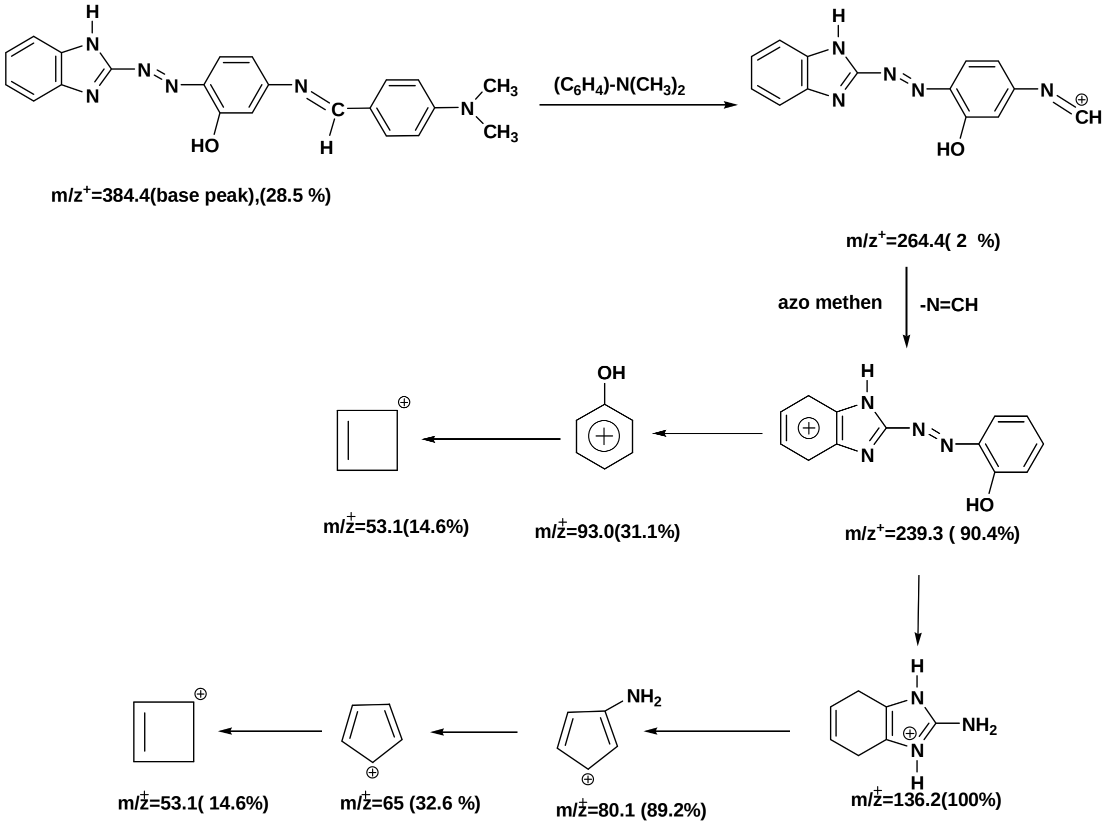
Figure(2):-^{1}H-NMR spectrum of azoshiff base ligand (BIAMebP)



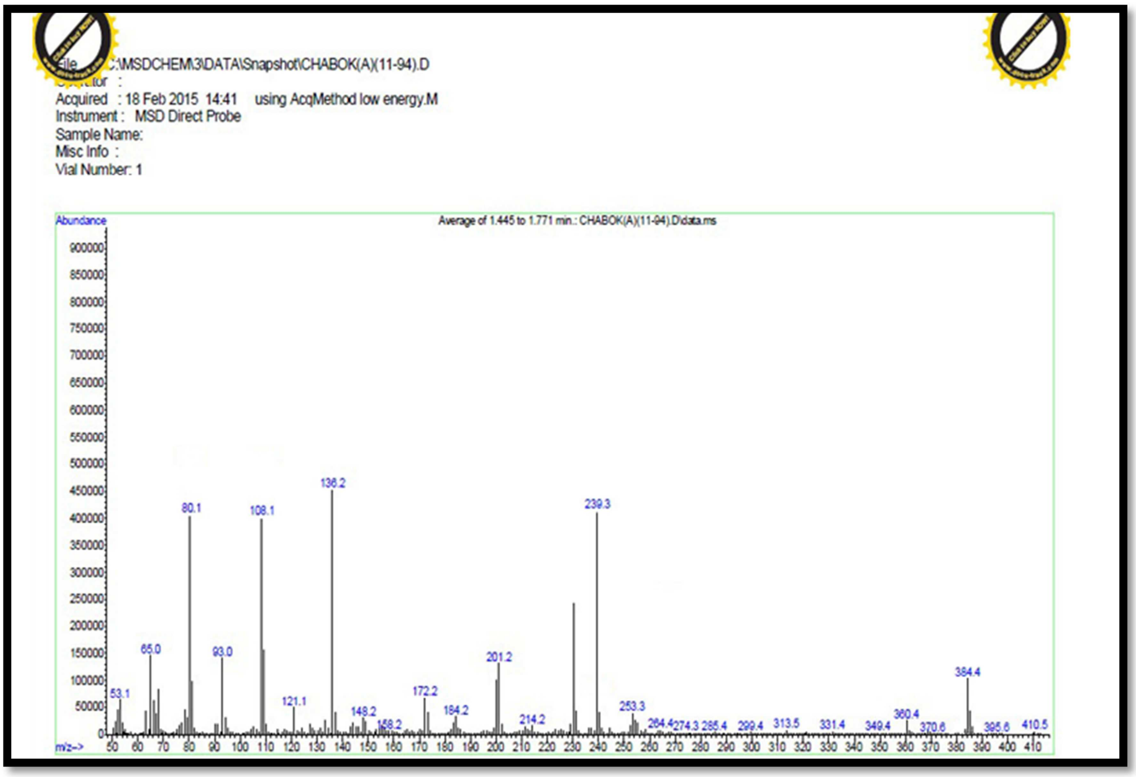
Figure(3):-^{1}H-NMR spectrum of Ni(II)-complex

Mass spectra of novel azoschiff base ligand and its pd (II)-complex

The mass spectral fragmentations of the azo schiff base ligand (BIADMebP) and its pd(II)-complex is shown in schemes 2 and 3 and figures 4 and 5. The mass spectrum of the novel azo Schiff base ligand, displays a base peak at $m/^{+}z$=384.4 is attributed to the original molecular weight[17]. The peak at m/z^{+}=264.4 due to loss of $C_8H_{10}N^{+}$ion, while a peak at m/z^{+}=239.3 lead to the loss of azomethine (-N=CH) group. The peak at m/z^{+}=93.0 is corresponding to $C_6H_6O^{+}$ion. The loss of two carbon, one hydrogen and oxygen atoms gives a peak at $m/^{+}z$=53.1 is attributed to appearance of $C_4H_5^{+}$.The same spectrum shows apeak at m/z^{+}=136.2 due to the molecular of 2-amino benzimidazole ($C_7H_{10}N_3^{+}$).A peak at m/z^{+} =80.1 analogues to $C_5H_6N^{+}$ion.while the peak at m/z^{+}=65 leads to the loss of the amino group(-NH_2).The mass spectrum of Pd(II)-complex displays abse peak at m/z^{+}=544.13 which corresponds to the exact molecular weight of the Pd(II)-chelate [Pd(L)Cl].H_2O, the spectrum exhibited a peak at m/z^{+}=268.3 due to loss $[C_8H_{12}O_2NPdCl]^{+}$ion. The peak at m/z^{+}=168.2 attributed to loss of (N=N), N_2H and OH groups. The peaks appeared at m/z^{+}=85.1 and 53.1 attributed to $C_5H_{11}N$ and $C_4H_5^{+}$ions respectively. The same spectrum of [pd(L)Cl].H_2O complex shows a peak at m/z^{+}=148 due to $C_7H_8N_4$ion and m/z=68.2 is attributed to molecule of imidazole ($C_3H_4N_2$) [27,28].



Scheme(2):- Mass spectral fragmentation of the novel azo-schiff base ligand(BIADMePI)



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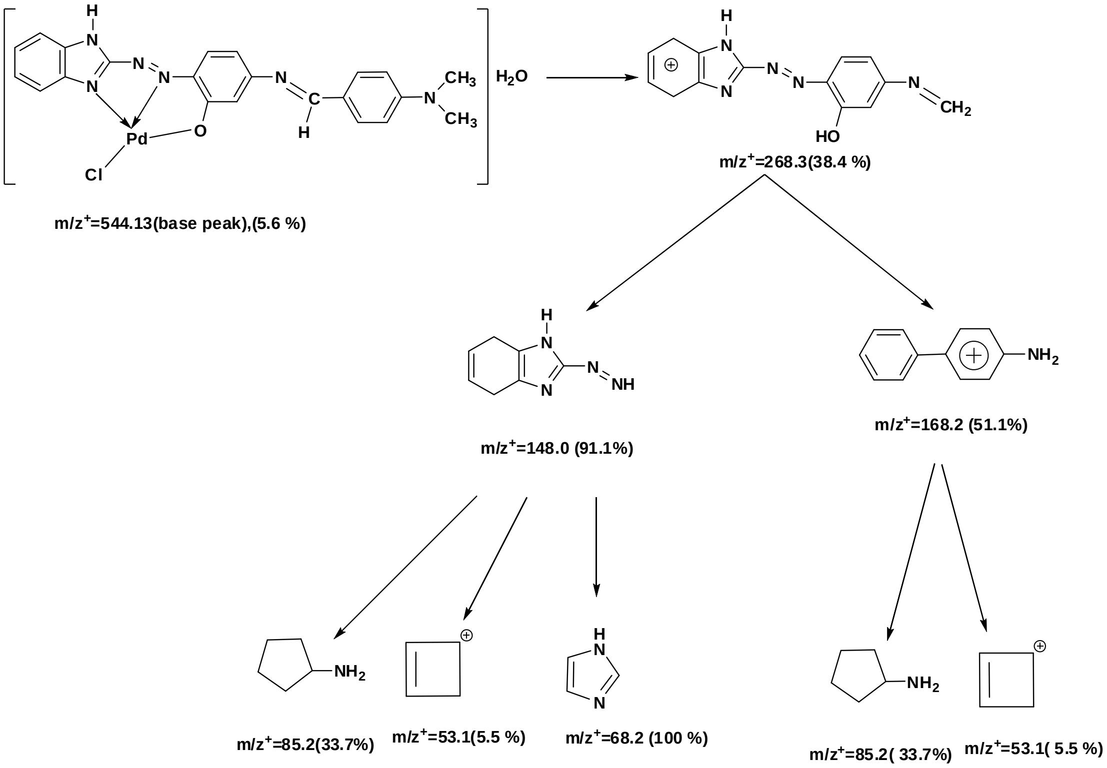
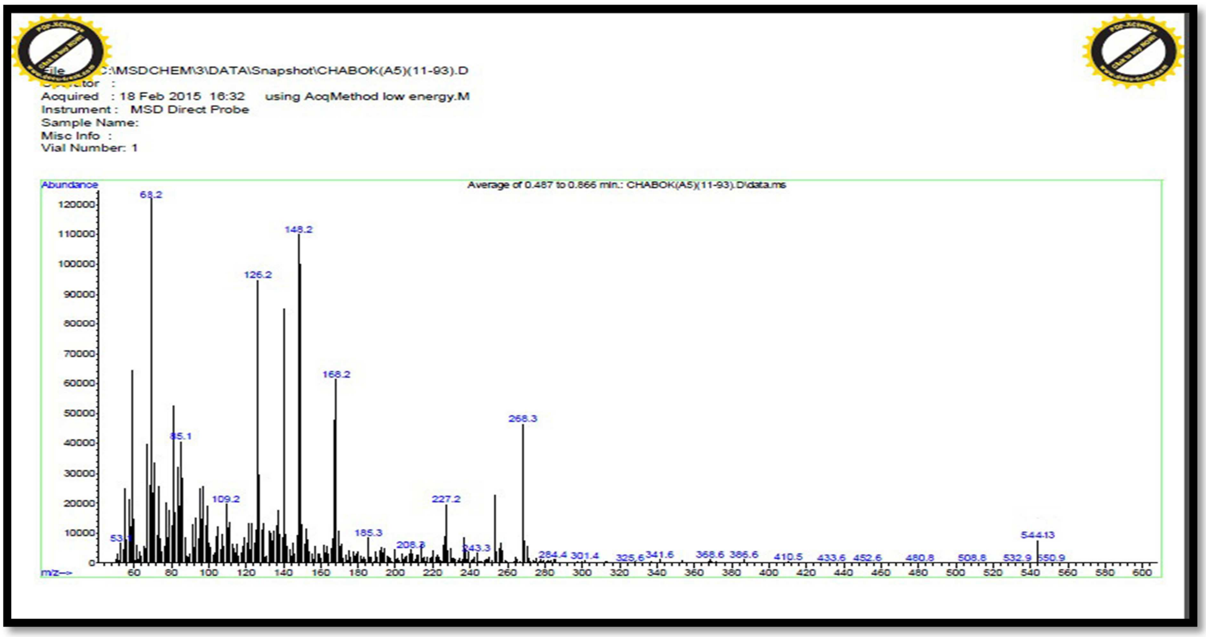
Figure(4):-Mass spectrum of the novel azo schiff base ligand (BIAMebP)



Scheme(3):- Mass spectral fragmentation of Pd(II)-complex, [Pd(L)Cl].H_2O



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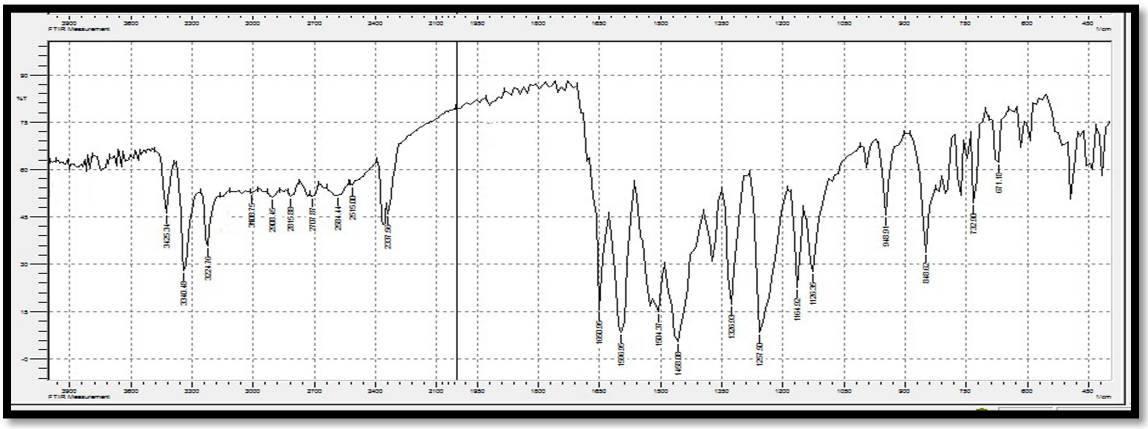
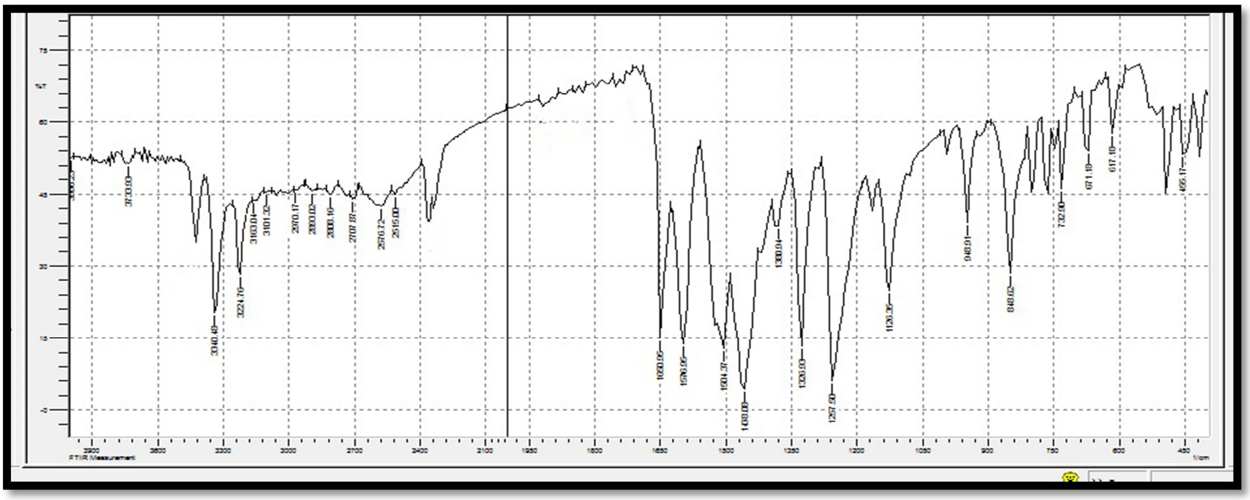
Figure(5):-Mass spectrum of Pd(II)-complex, [Pd(L)Cl].H_2O

IR Spectra of azo schiff base ligand and its chelats complexes

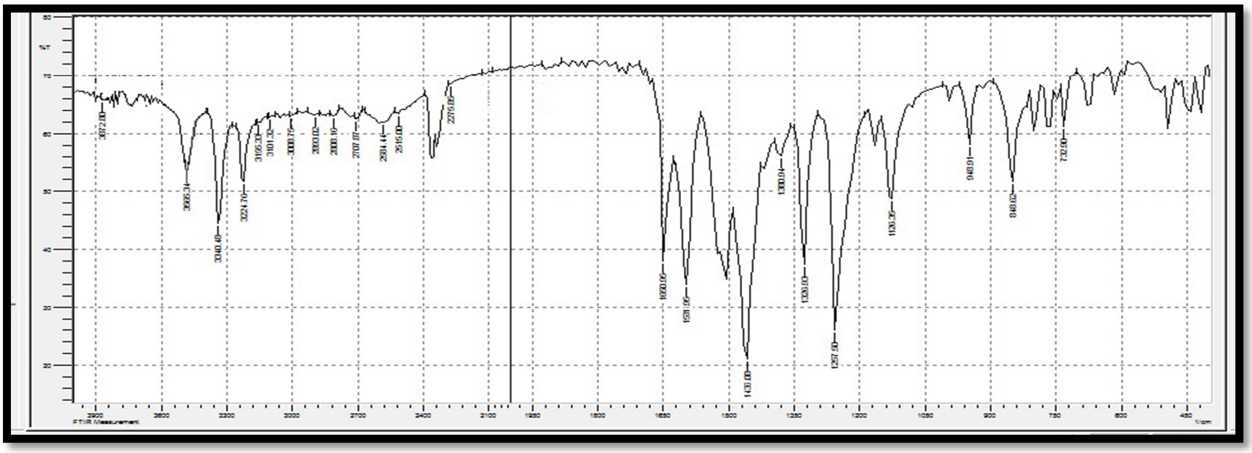
The infrared spectral data are shown in table 3 and IR spectra of the free ligand, Ni(II)-complex, Cu(II)-complex and Pt(IV)-complex are given in figures 6,7,8 and 9.The IR spectrum of the azo schiff base ligand (BIADMebP) showed a sharp and medium band at 3425 cm^{-1}, which can be attributed to $\upsilon(OH)$phenolic group, this band was shifted and changing to lower frequency in chelates complexes, indicating the metal ion coordination with phenolic oxygen[16,23,26]. The sharp and medium band at 3340cm^{-1} in free ligand which can be assigned to the stretching vibration of this band remained in the same frequency in spectra of the metal complexes which may be non coordination with metal ions in complexes[23,25,30]. The IR spectrum of azo schiff base ligand shows characteristic bands at 3224 cm^{-1},3108cm^{-1} and 2908cm^{-1} due to the $\upsilon(-CH_3), \upsilon(C-H)$ or manicuring due to the stretching vibration of the azomethine $\upsilon(-HC=N)$group of the azo schiff base ligand. This band did not show any frequency shift in infrared spectra of the chelates complexes[19,31]. The spectrum of the free ligand shows a band at 1597 cm^{-1} attributed to $\upsilon(C=N)$ of the N3benzimidazolering,the changing in shape and shifted to lower frequencies of this band in the prepared complexes spectra comparing to the free ligand (BIADMebP)(1589-1576) cm^{-1} confirmed the involvement of this group in chelation through the N3atom of benzimidazole molecule[19,23,25,31].Also the azo schiff base ligand spectrum displays the azo group $\upsilon(-N=N-)$ at 1458cm^{-1}, this band is changing to lower frequency (1465-1436)cm^{-1} suggests its participation in bonding with the metal ions to formation the complex[33,34]. New bands at (617-528) and (435-416) cm^{-1} which are not present in the azo schiff base ligand are attributed to $\upsilon(M-O)$ and$\upsilon(M-N)$respectively [18,35]. Thus the above infrared spectral data lead to suggest the azo schiff base ligand (BIADMebp) behaves as a tridentate chelating agent, and the coordination sites are the nitrogen atom (N3) of the heterocyclic benzimidazole ring, phenolic oxygen and nitrogen atom (N_3) of azo group nearest to phenol ring.



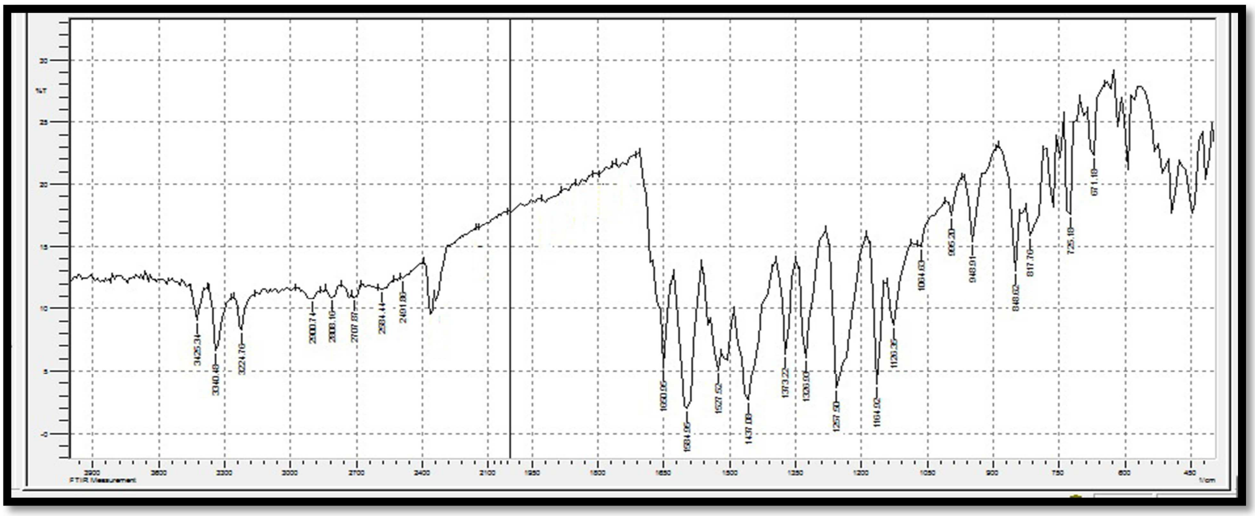
Figure(6):- IR spectrum of the azo schiff base ligand (BIAMebP)



Figure(7):- IR spectrum of the [Co (L)$_2$].H$_2$O chelate complex



Figure(8):- IR spectrum of the [Zn (L)$_2$].H$_2$O chelate complex



Figure(9):- IR spectrum of the [Pt (L)$_2$]Cl$_2$ chelate complex

Table(3): Infrared spectral dat (cm^{-1},KBr dise) of the azo schiff base ligand (BIADMebp) and its metal complexes

compounds	$\upsilon(OH)$ Phenolic H_2O	$\upsilon(NH)$ Ben Im.	$\upsilon(-CH_3)$	$\upsilon(C = N)$ schiff	$\upsilon(C = N)$ Ben.Im	$(N = N)$	υ(pheny ring	$(M - O)$	$\upsilon(M - N)$
LH=ligand	3425m. $\upsilon(OH)$	3340s.	3225m.	1651 s.sr	1597 s.br.	1458 M.	849m. 733m.	-	-
$[Co(L)_2].H_2O$	3734w.br. υ (H_2O)	3340s.	3225m.	1651 m.sr.	1576 s.sr.	1438 m.br	849m. 732m.	528 m.	455 w.
$[Ni(L)_2].H_2O$	3625w.br υ (H_2O)	3340m.	3224m.	1651 s.	1586 s.br.	1442 m.br.	848s. 733m.	617 w.	416 w.
$[Cu(L)_2].H_2O$	3734w.br υ (H_2O)	3341w.br.	3225m.	1650 m.sh.	1589 m.br	1465 m.br	849m. 734w.	617 w.	435 w.
$[Zn(L)_2].H_2O$	3565m.br. υ (H_2O)	3340m.sr.	3225m.	1651 m.sr.	1581 s.	1436 s.	848m. 732w.	538 w.	418 w.
$[pd(L)cl].H_2O$	3733w.br υ (H_2O)	3410m.	3217w.	1651 w.sh.	1589 m.br.	1447 m.br.	871w. 786w.	543 w.	427 w.
$[pt(L)_2]Cl_2$	-	3425w.	3225m.	1651 m.sr.	1584 s.br.	1437 m.br.	849m. 725m.	532 w.	423 w.

Ligand (LH)= BIADMebp,W=weak, s=strong, m=medium; br=broad ;Sh.=sholder ;sr=sharp; ben.Im =benzimidazole

Electronic spectral studies

The electronic spectral results of the azo schiff base ligand (BIADMebP) and its metal complexes are listed in table(4) and figures 10,11,12 and 13. The electronic spectra were recorded in absolute ethanol solvent in the UV-vis. region (200-1100)nm. The electronic spectrum of the azo Schiff base ligand show two bands at 241nm (41494cm^{-1}) and 339nm (29498 cm^{-1})attributed to $\pi \longrightarrow \pi^*$ (phenyrings) and $n \longrightarrow \pi^*$ (HC=N and –N=N-) transitions respectively[18,36].The electronic spectrum of Co(II)-complex gave three at 1020 nm (9804 cm^{-1}), 445nm(22472 cm^{-1}) and 345 nm (28985 cm^{-1}), Which may be assigned to ${}^4T_{1g}\rightarrow{}^4T_{2g(F)}\upsilon_1$, ${}^4T_{1g}\rightarrow{}^4T_{1g(F)}\upsilon_2$ and${}^4T_{1g}\rightarrow{}^4T_{1g(p)}$,$(\upsilon_3)$ transitions, respectively.For Ni(II)-complex also three bands at976nm (10246 cm^{-1}) 439nm (22779 cm^{1})and 227nm (44053 cm^{-1})correspond to ${}^3A_{2g}\rightarrow{}^3T_{2g(v1)}$,${}^3A_{2g}\rightarrow{}^3T_{1g(F)(\upsilon_2)}$and,${}^3A_{2g}\rightarrow{}^3T_{1g(p)(\upsilon_3)}$transitions respectively[37].The electronic spectrum of Cu (II)-complex one band at 628 nm (15923 cm^{-1}) due to${}^2E_g\rightarrow{}^2T_{2g}$transition. The Pd(II)complex gave only one band due to ${}^1A_{1g}\rightarrow{}^1B_{1g}$ transition at 442nm (22624cm^{-1})[38].The electronic spectrum of pt(IV)-complex has found three bounds were observed at 532nm (18797 cm^{-1}), 468nm(21367 cm^{-1}) and 338nm(29586 cm^{-1}), due to ${}^1A_{1g}\rightarrow{}^1T_{1g}(F)(\upsilon_1)$,${}^1A_{1g}\rightarrow{}^1T_{2g}(\upsilon_2)$ and ${}^1A_{1g}\rightarrow{}^1E_g(\upsilon_3)$. The spectrum of Zn(II)-complex gave band assigned to charge transfer (M→ L, CT) transitions with electrons (d^{10}), this band at 449nm (22272) cm^{-1} transition.

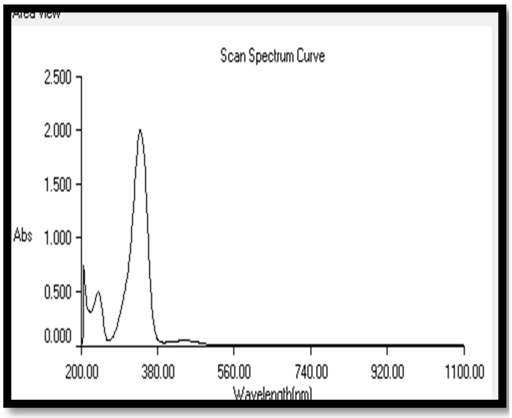
Table(4):- Electronic spectra, magnetic moment, molar conductance, geometry and hybridization

Compounds	λmax (nm)	Absorption bands (cm^{-1})	Transitions	μ_{eff}(B.M)	Molar conductance ($s.cm^2.mol^{-1}$)	Geometry	Hybridization
LH=Ligand	241	41494	$\pi \rightarrow \pi^*$	-	-	-	-
	339	29498	$n \rightarrow \pi^*$				
$[Co(L)_2].H_2O$	1020	9804	${}^4T_{1g}\rightarrow{}^4T_{2g(\upsilon_1)}$	4.59	12.56	Octahedral distorted (z-out)	Sp^3d^2 (high spin)
	445	22472	${}^4T_{1g}\rightarrow{}^4T_{1g(F)(\upsilon_2)}$				
	345	28985	${}^4T_{1g}\rightarrow{}^4T_{1g(p)(\upsilon_3)}$				
$[Ni(L)_2].H_2O$	976	10246	${}^3A_{2g}\rightarrow{}^3T_{2g(\upsilon_1)}$	3.61	17.43	Octahedral regular	Sp^3d^2 (high spin)
	439	22779	${}^3A_{2g}\rightarrow{}^3T_{1g(F)(\upsilon_2)}$				
	227	44053	${}^3A_{2g}\rightarrow{}^3T_{1g(p)(\upsilon_3)}$				
$[Cu(L)_2].H_2O$	628	15923	${}^2E_g\rightarrow{}^2T_{2g}$	1.77	11.97	Octahedral distorted (z-inor z-out)	Sp^3d^2
$[Zn(L)_2].H_2O$	449	22272	M→ L, CT	dia	10.22	Octahedral regular	Sp^3d^2
$[Pd(L)Cl].H_2O$	442	22624	${}^1A_{1g}\rightarrow{}^1B_{1g}$	dia	9.65	Square planer	dsp^2
$[Pt(L)_2]\ Cl_2$	532	18797	${}^1A_{1g}\rightarrow{}^1T_{1g}(F)(\upsilon_1)$	dia	78.03	Octahedral regular	d^2sp^3 (Low spin)
	468	21367	${}^1A_{1g}\rightarrow{}^1T_{2g}(\upsilon_2)$				
	338	29586	${}^1A_{1g}\rightarrow{}^1E_g(\upsilon_3)$				

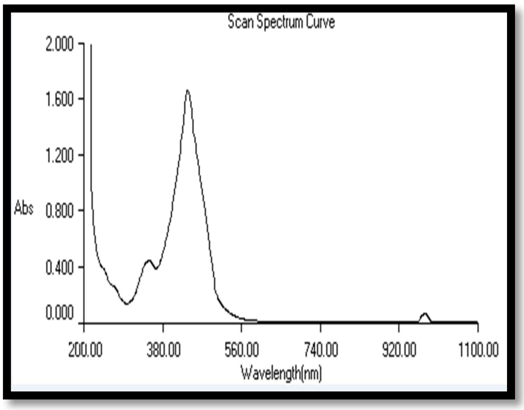
LH= BIADMebp

Magnetic moment measurements

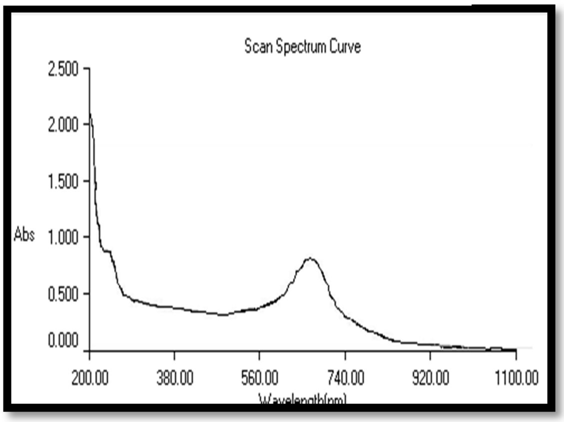
The magnetic moment value of Co(II)-complex has been found 4.59B.M, the larger variation in the magnetic moment for a high spin has a d^7 (t_2g^5 eg^2)configuration depend on the magnitude of the orbital contribution. The high value of magnetic moment because of presence three unpaired electrons which may be suggest an distorted octahedral geometry (z-out) and sp^3d^2hybrdization[19,36,39].For the Ni(II)-complex, the magnetic moment value is 3.61 B.M because of two unpaired electrons, a high spin (t_2g^6 eg^2) configuration which may be suggest a regular octahedral geometry and sp^3 d^2hybrdization[23,25].The magnetic moment value of Cu(II)-complex is 1.77 B.M due to presence one electron unpaired which may be suggests an distorted octahedral geometry (Z-in or z-out) and sp^3d^2 hybridization, (t_2g^6 eg^3) configuration. ,The magnetic moment value of Zn(II),pd(II) and pt(IV) metal complexes are diamagnetic consistent d^{10}configurat (t_2g^6 eg^4)for Zn(II)-complex and octahedral geometry with sp^3d^2hybrdization but Pd (II)-complex is a low spin, d^8 (t_2g^8 eg^0)configuration and square planer geometry with dsp^2 hybridization[28]., while pt(IV)-complex is a low spin, d^6(t_2g^6 eg^0)configuration which may be suggested a regular octahedral geometry with d^2sp^3hybrdization[38]. This results are given in table4.



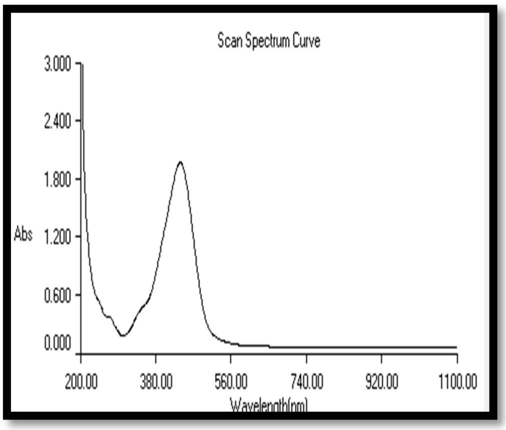
Figure(10):- The absorption spectrum of the azo schiff base ligand (BIAMebP)



Figure(11):- The absorption spectrum of $[Ni(L)_2].H_2O$ chelate complex



Figure(12):- The absorption spectrum of $[Cu(L)_2].H_2O$ chelate complex



Figure(13):- The absorption spectrum of $[Pd(L)Cl].H_2O$ chelate complex

Solvent effect

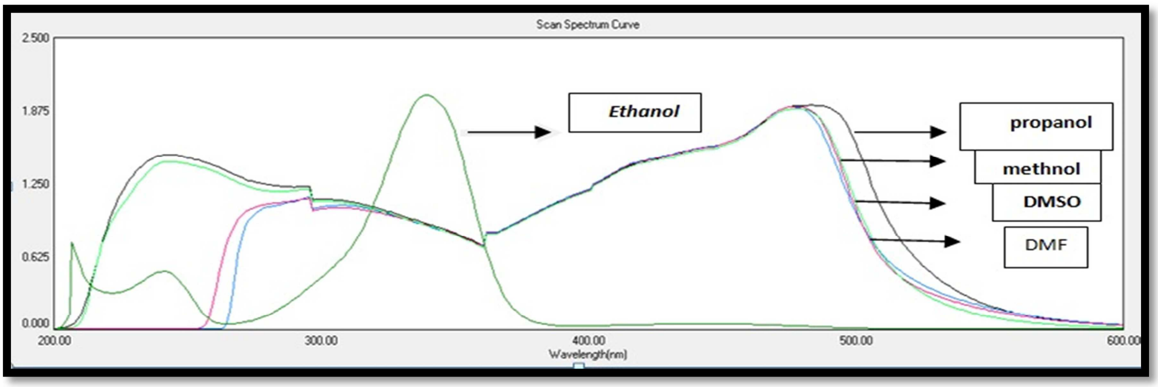
The absorption spectra of azo Schiff base ligand (BIADMebP) were recorded in various solvents at a concentration 10^{-3}M in room temperature, the results are summarized in table(5).

The visible absorption spectra of the azo Schiff base ligand was found to exhibit strong solvent dependency, which show variation with polarity of the solvents. Figure (14) shown the effect of polarity the solvent on the absorption space of the ligand (BIADMebp) in ethanol, methanol, 1-propanol, DMSO and DMF and in all proton accepting solvents significantly changed the absorption spectra to ward bathochromic shift[33].

Table(5): Absorbance maxima (λ_{max})of the azo Schiff base (BIADMebp) in different solvents

Solvents	$\lambda max_{(nm)}$
Ethanol	339_S, 241
Methanol	479_S,296,244
1-propanol	484_S,243
DMSO	477_S,307,296
DMF	476_S,308,296

s=strong



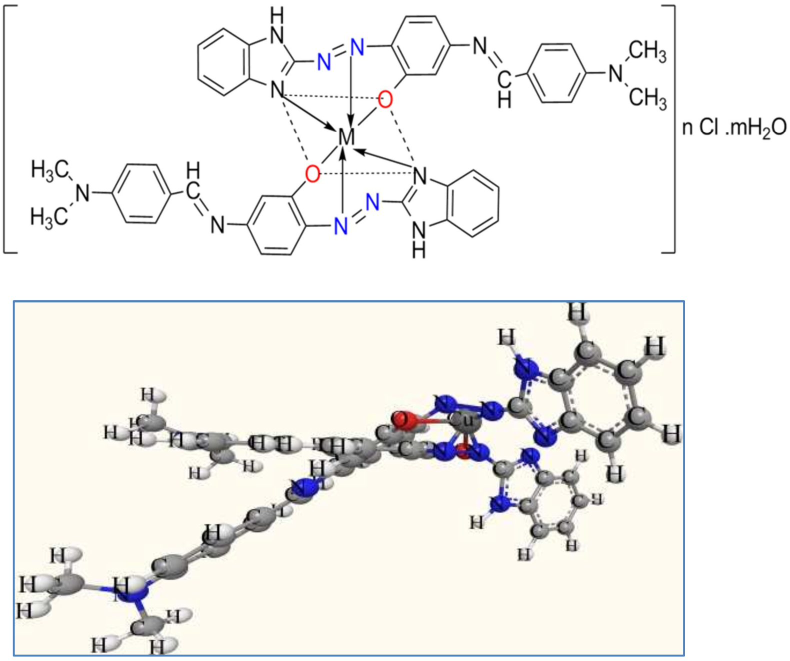
Figure(14):- Absorbance spectrum of the azoshiff base ligand (BIAMebP) in different solvents

Molar conductivity measurements

Molar conductance (Λ_m) measurements of the metal complexes table(4) carried out using DMSO as the solvent at the concentration of 10^{-3} M in room temperature. All chelate complexes prepared in this wok showed conductivity values ranged between (9.65-17.43) $s.mol^{-1}.cm^{2}$ that non-electrolyte and no conductive species exist because of the chloride ion is located inside the coordination sphere and is directly involved in coordination with metal ion center[23,38,40,41]. While the molar conductance of Pt(IV)-complex is 78.03 $s.mol^{-1}.cm^{2}$ indicating the electrolytic nature (1:2) electrolyte of this complex furthermore the chloride ions ($2Cl^{-}$)are located outside the coordination sphere[22,38,40].

Structural interpretation

According to there results and discussed through different techniques suggest below, the structures of the prepared metal complexes and shown in figures 15 and 16. Depend on the spectral and analytical data the novel azo schiff base ligand (BIADMebP) behaves as a tridentate chelating agent coordination through the nitrogen atom (N_3) of azo group nearest to phenol ring, phenolic oxygen and nitrogen (N3) atom of benzimidazole ring to give two-five membered chelate ring.



Where M=Co(II), Ni(II), Cu(II), Zn(II); n=0, m=1
M=Pt(IV), n=2, m=0
Figure (15): The proposed structural formula of Co(II),Ni(II),Cu(II),Zn(II) and Pt(IV) complexes

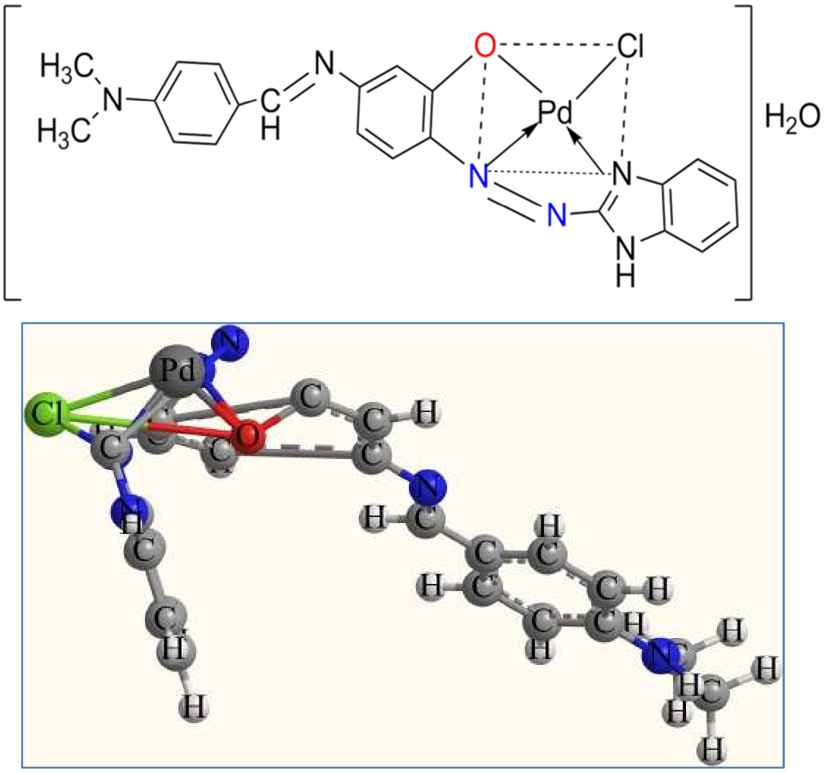


Figure (16):-The proposed structural formula of Pd(II)- complex

Antibacterial activates

The date of antibacterial activates of the prepare novel azo schiff base ligand (BIADMebP) and its metal complexes are given in table (6) and its statistical presentation is show in figure 17.The effect of the azo schiff base ligand and its chelate complexes have been tested for in vitro against the sensitive organisms *Escherichia Coli, staphylococcus aureus* as antibacterial and *candida albicans, Aspergillus Niger* as ant fungal. The ligand revealed that *Aspergillus Niger* as ant fungal. The ligand revealed that *Aspergillus Niger* was sensitive but insensitive to rest bacteria, all of tested of metal complexes show a remarkable antibacterial activity against tested bacteria. The chelate complex revealed that all bacteria was sensitive except the Ni(II)-complex avers activity to *Escherichia coli* while Cu(II) and Zn(II) complexes insensitive to words *candida albicans.* The metal complex Ni(II), pd(II) and Pt(IV)ions showed highly activity and sensitivity against all bacterial. The mechanism of action of antibacterial drug can be discussed[19]. as inhibition of cell wall, inhibition of cell membrane function inhibition of protein synthesis and inhibition of nucleic acid[42].

Table(6): Antibacterial activates data (zone of inhibition in mm) of azoschiff base ligand (BIADMebP) and its chelate complexes

Compound	*Anti-bacterial activity*		*Anti-fungal activity*	
	E.coli	*Staphylococcus*	*Candida albicans*	*Aspergillusniger*
LH=ligand	_	-	-	+
$[Co(L)_2].H_2O$	++	++	+	++
$[Ni(L)_2].H_2O$	-	+	+++	+++
$[Cu(L)_2]H_2O$	+++	++	-	+
$[Zn(L)_2].H_2O$	++	+	-	+
$[Pd(L)Cl].H_2O$	+	++	+	++
$[Pt(L)_2]Cl_2$	+	+	++	++

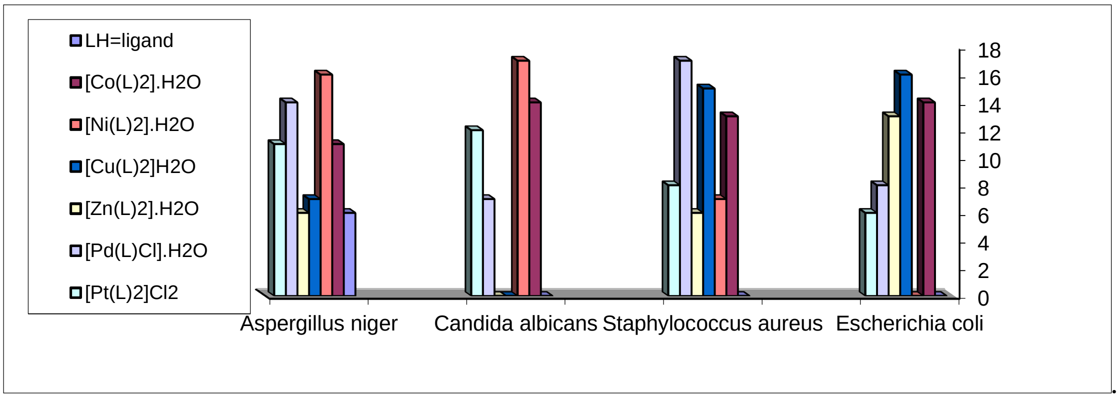


Figure (17) :Statistical representation for antibacterial activity of azo schiff base ligand (BIADMebp) and its chelate complexes

CONCLUSION

In this work we have the preparation and characterization of novel azo schiff base liganed (BIADMebp) and its chelate complexes with Co(II), Ni(II), Cu(II), Zn(II), pd(II) and pt(IV) ions. The ligand and its metal complexes were characterized by using several physical techniques such us elemental analysis molar conductivity, atomic absorption, IR, ^{1}H-NMR, UV-vis. and mass spectroscopes studies. Electronic spectral and magnetic susceptibility measurements support of all complexes are octahedral geometry but square planer geometry for pd(II)-complex. The azo schiff base ligand behaves as a tridentate agent coordination through the position of phenolic oxygen, nitrogen of azo group (N3)which is first of the benzimidazole molecule and nitrogen of benzimidazole to form two five membered metal rings. The chelate complexes are found to have higher biological activities as compared to the azo schiff base ligand. The molar conductance measurements of pt(IV)- complex is 1:2 electronic nature suggest the presence two chloride ions outside the coordination sphere.

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