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Synthesis and Spectral identifications of new azo – Schiff base ligand(4Cl-2DIBP) derived from (para-aminobenzylamine) with its some metallic complexes

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Abstract:

The New Heterocyclic ligand 4-chloro-2-(((4-((4,5-diphenyl-1H-imidazol-2-yl) diazenyl) benzyl)imino)methyl) phenol (4Cl-2DIBP) was prepared from the condensation of para-aminobenzylamine with 4,5-diphenyl imidazole, followed by the condensation of the resulting compound with 5- chloro-2- hydroxy benzaldehyde. Different analytical and characterization techniques including (Mass,^{1}HNMR, FT-IR and UV-Vis. spectroscopy and C.H.N elemental analysis) in the investigation of Newly prepared ligand. A series of Novel solid metal complexes of this ligand with Co (II), Ni (II), Cu (II), Zn ((II), Cd (II), and Hg (II) were prepared and all complexes were characterization by techniques above, excluding the Mass and the 1H-NMR spectroscopy of some prepared solid metal complexes and the use of flame atomic absorption spectroscopy to determine the percentages of metal ions in the prepared complexes also studied the magnetic susceptibility and molar conductivity of the metal complexes dissolved in DMSO at 1×10^{-3} M concentration laboratory temperature. The results of this studies showed that the coordination sites for the new Azo-Schiff base ligand with Co (II), Ni (II), Cu (II), Zn ((II) , Cd (II) and Hg(II) were to be through nitrogen of the imidazole ring, and the nitrogen of azo group,. The Electronic spectral and magnetic measurement data predict octahedral structure of the complexes. All complexes showed that Non-electrolytes properties.

Keywords: Azo – Schiff base ligand, 4,5-diphenyl imidazole , para-aminobenzylamine.

Introduction:

Azo - Schiff bases compounds are a new class of chemical compounds that are receiving increasing interest in scientific research (8) , compared to azo compounds and Schiff bases as they contain two active groups (-N=C-) and (-N=N-) (9), and azo - Schiff bases are considered of importance due to their electronic properties, structural flexibility and selectivity towards metal ions (10,11). Azo-schiff compounds can coordinate in many ways. They can be coordinated via azo-azomethine nitrogen (12), or by azo-nitrogen, and finally can coordinate via nitrogen atoms (azo-azomethine) (13). At the present time, Azo - Schiff bases compounds are showing remarkable applications in all areas of life (14), including industrial, biological and analytical fields, because they

contain the two groups mentioned above (15), as they have been used in the industrial field as antioxidants (16), and to prevent corrosion (17) As well as for the treatment of nuclear waste (18) and in the manufacture of plastics, leather, and textiles (19). Due to the emergence of cancer tumors that are highly resistant to the effectiveness of traditional chemotherapies, it has become interesting to discover different therapeutic approaches including the development of new active drugs against resistant cancers (20). Azo - Schiff bases complexes have proven their worth as antifungals, anticancer (21), antibacterial (22) and herbicides (23).

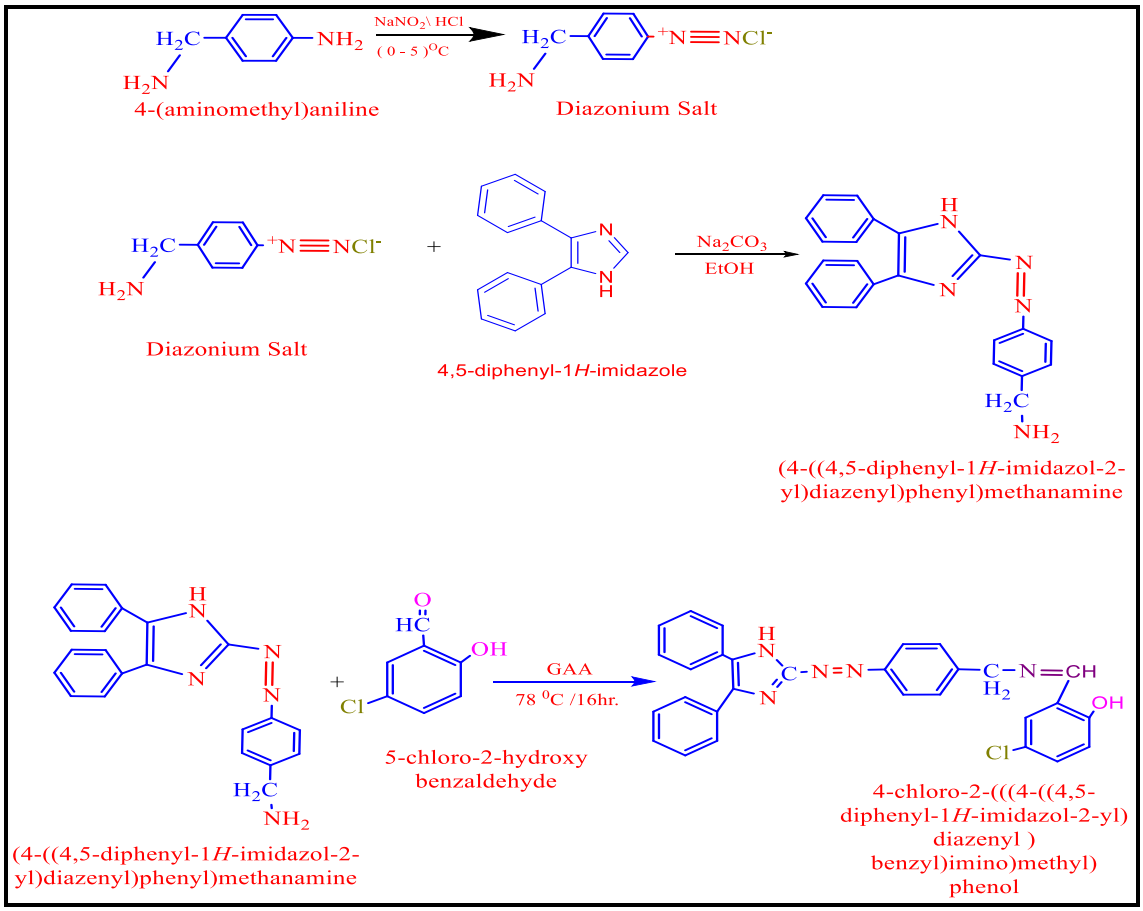
MATERIALS AND METHODS

All chemicals were obtained from Merck, BDH and Sigma - Aldrich and used without further purification. Melting point were determined using model 9300 of ligand and its complexes. ^{1}HNMR spectra were recorded as solution in DMSO d6 as solvent using (varian 500MHZ Spectrophotometer) and Mass Spectra were recorded on Shimadzu Agilent Technologies 5975C. The UV-Visible spectra were recorded on Shimadzu spectrophotometer double band model 1700. Magnetic susceptibility measurements were carried out on a balance magnetic MSB-MKI using faraday method. The diamagnetic corrections were made by Pascal's constants. IR spectra were recorded on Shimadzu FTIR 8400 spectrometer using KBr pellet in the wavelength range 4000-400 cm-1. C.H.N Elemental analyses were performed by means of EURO 2012EA 300 C.H.N Elemental analysis

Synthesis of the new Azo- Schiff base ligand(4Cl-2DIBP):

The new azo-Schiff base ligand(4Cl-2DIBP) was Synthesized by coupling reaction of diazonium salt with appropriate amount of (imidazole derivative) as coupling component in alkaline solution. A diazonium solution is prepared by dissolving (0.01 mol, 1.222gm) of Para aminobenzylamine in (30ml) distilled water with (8ml) of concentrated HCl acid with continuous shaking . To this mixture a solution of (0.01 mol, 0.7 gm) of sodium nitrate in 5ml of distilled water was added drop wise to the Diazonium solution with shaking and stirring to complete the process of Azotization at(0-5)^{0}C ,and left it to stand for (30min) .This diazonium solution was added drop by drop to (0.01 mol,2.202gm) of 4,5-di phenyl imidazole dissolved in(50ml)of absolute ethanol and (50ml) solution of (40% Na_2CO_3) at(0-5)^{0}C. A drop by a drop was observed to change the color to orange-red, indicating that the process of coupling between the two solutions and the formation of the azo compound then neutralized by adding drops of dilute HCl to the acidic function PH ~ 7.5. After that, The mixture was allowed to stand overnight and then the solution was filtered off, washed with distilled water, and recrystallized twice from hot ethanol and then dried in oven at 40^{0}C for 1 hours (28).

The second step included the preparation of the new Schiff base azo-ligand (4 Cl-2DIBP), as it dissolved (0.01 mol, 1.565 gm) of 5- chloro-2-hydroxy Benzaldehyde in (10 ml) of absolute ethanol alcohol, stirring for (2 min), then adding (2-3) drops of glacial acetic acid and then left for (5 min) at laboratory temperature, After that, a solution prepared by dissolving (0.01 mol, 4.759 gm) of azo dye is added in (10 ml) of absolute ethanol alcohol, and the solution was raised for (16 hr.) at a temperature (78^{o}C) where the azo - Schiff base ligand was obtained. the reaction was followed up by TLC technology using (0.5 ml methanol: 4.5 ml benzene), then the product was cooled, dried, collected and then recrystallized using hot absolute ethanol (29). The physical properties of it have been listed in Table 1. Scheme 1 shows the steps for preparing the new Azo - Schiff's base ligand (4 Cl-2DIBP).



Scheme-1: Synthesis of new azo-Schiff base ligand(4Cl-2DIBP)

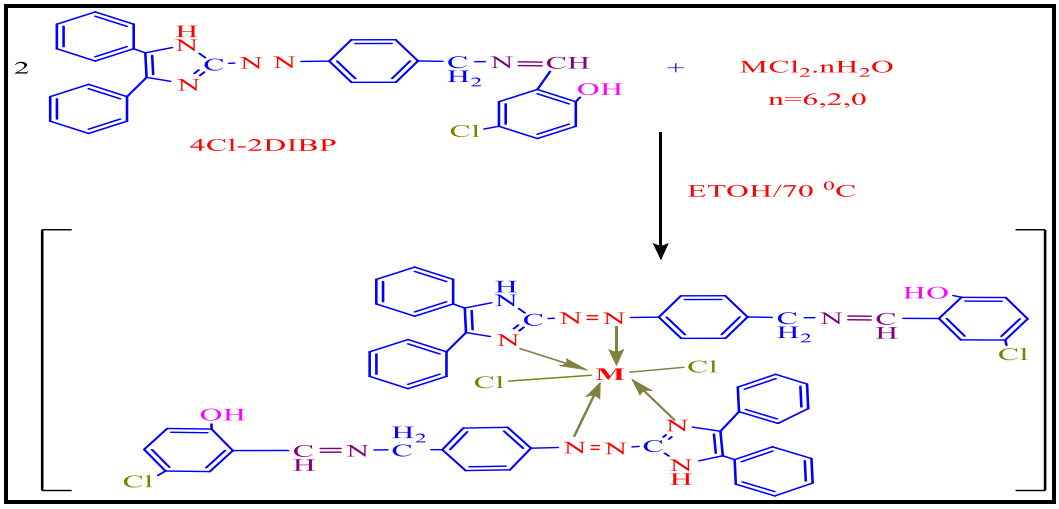
Synthesis of metal complexes:

The metal complexes were synthesized by mixing of (0.0002mol) in 10ml absolute ethanol solution of each of ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$,$CdCl_2$and Hg Cl_2) with 10ml absolute ethanol solution of (0.2g , 0.0004mol) of new azo-Schiff base ligand in (1:2) (metal: ligand) ratio. The resulting mixture was refluxed for 1h.The products of complexes were isolated after reduced of volume by evaporation .They were filtered off and dried under vacuum The physical properties of the complexes

under study are listed in Table 1.Scheme 2 illustrates the steps of preparing the metal complexes with the ligand (4Cl-DIBM).

Table (1) shows the physical properties of the new Azo Schiff base ligand and its complexes.

No	Chemical formula	Color	M.Wt g/Mole	M.P°C	Yield %	R_f
1	$C_{29}H_{22}N_5ClO$	Light Red	491.970	102-105	90	0.58
2	$[CO(C_{29}H_{22}N_5ClO)_2Cl_2]$	Dark Brawn	1113.779	213-215	87	0.52
3	$[[Ni(C_{29}H_{22}N_5ClO)_2Cl_2]$	Dark Brawn	1113.539	228-230 Dec	85	0.51
4	$[Cu(C_{29}H_{22}N_5ClO)_2Cl_2]$	Dark Brawn	1118.392	170-172 Dec	89	0.54
5	$[Zn(C_{29}H_{22}N_5ClO)_2Cl_2]$	Dark Brawn	1120.236	194-196	92	0.55
6	$[Cd(C_{29}H_{22}N_5ClO)_2Cl_2]$	Dark Red	1167.257	148-150	88	0.66
7	$[Hg(C_{29}H_{22}N_5ClO)_2Cl_2]$	Reddish Violet	1255.436	152-154 Dec	85	0.66



Scheme- 2: Synthesis of the metal complexes with the ligand (4Cl-2DIBP)

Results and discussion:

All our complexes are Freely soluble in DMF,DMSO,Methanol and Ethanol .Also They are stable in air .The ligand and its metal complexes were characterized by elemental analysis Table (2) ,molar conductivities, magnetic susceptibility, IR,UV-Vis,(Mass and ^{1}H,MNR spectrum for the ligand only) .The analytical data of the complexes are in agreement with the experimental data .The value reveal that the metal to ligand ratio

was(1:2) (M:L) and were presented in table.2.The magnetic susceptibility of the chelate complexes at room temperature were consistent with octahedral geometry, So as the around the central metal ions. All of chelate complexes prepared in this work showed lower conductivity values. This proves that complexes have non- electrolytic nature.

Table (2) shows the element Analysis the new azo Schiff base ligand(4Cl-2DIBP) and its complexes.

No	Formula	M.Wt	(Found) Calc. %			
			C%	H%	N%	M%
1	(4CI-2DIBP)= $C_{29}H_{22}N_5CLO$	491.97	70.799 (71.295)	4.507 (4.938)	14.235 (14.659)	-----
2	$[Co(4CI\text{-}2DIBP)_2Cl_2]$	1113.779	62.545 (62.981)	3.981 (4.429)	12.575 (12.981)	5.291 (5.442)
3	$[Ni(4CI\text{-}2DIBP)_2\ Cl_2]$	1113.539	62.559 (62.993)	3.982 (4.421)	12.578 (12.992)	5.270 (5.359)
4	$[Cu\ (4CI\text{-}2DIBP)_2Cl_2]$	1118.392	62.287 (62.747)	3.965 (4.462)	12.523 (12.926)	5. 681 (5.830)
5	$[Zn(4CI\text{-}2DIBP)_2Cl_2]$	1120.236	62.185 (62.525)	3.958 (4.349)	12.503 (12.958)	5.837 (5.870)
6	$[Cd(4CI\text{-}2DIBP)_2Cl_2]$	1167.257	59.680 (60.116)	3.799 (4.253)	11.999 (12.482)	9.630 (9.964)
7	$[Hg(4CI\text{-}2DIBP)_2Cl_2]$	1255.436	55.488 (55.892)	3.532 (3.949)	11.156 (11.592)	15.977 -----

Mass spectrum:

The mass spectra of the new azo Schiff base ligand(4Cl-2DIBP) was recorded at room temperature .The obtained peaks confirm the proposed formulae for the compound .The mass spectrum of Ligand show the molecular ion peak at m/z+ 491.2 compound ($C_{29}H_{22}ClN_5O$)confirm the proposed formulae for compound . This small abundance(1%) was due to the large molecular weight, high bombardment energy, and the large number of heterogeneous atoms in its chemical structure, which confirm the validity of the proposed formula for the compound. Figure 1 and Scheme 3 showed the mass spectrum of ligand and the proposed mass fractionation pathway for it (32,33).

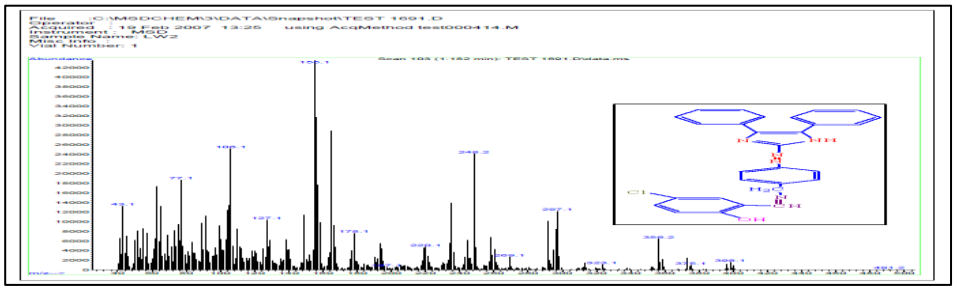
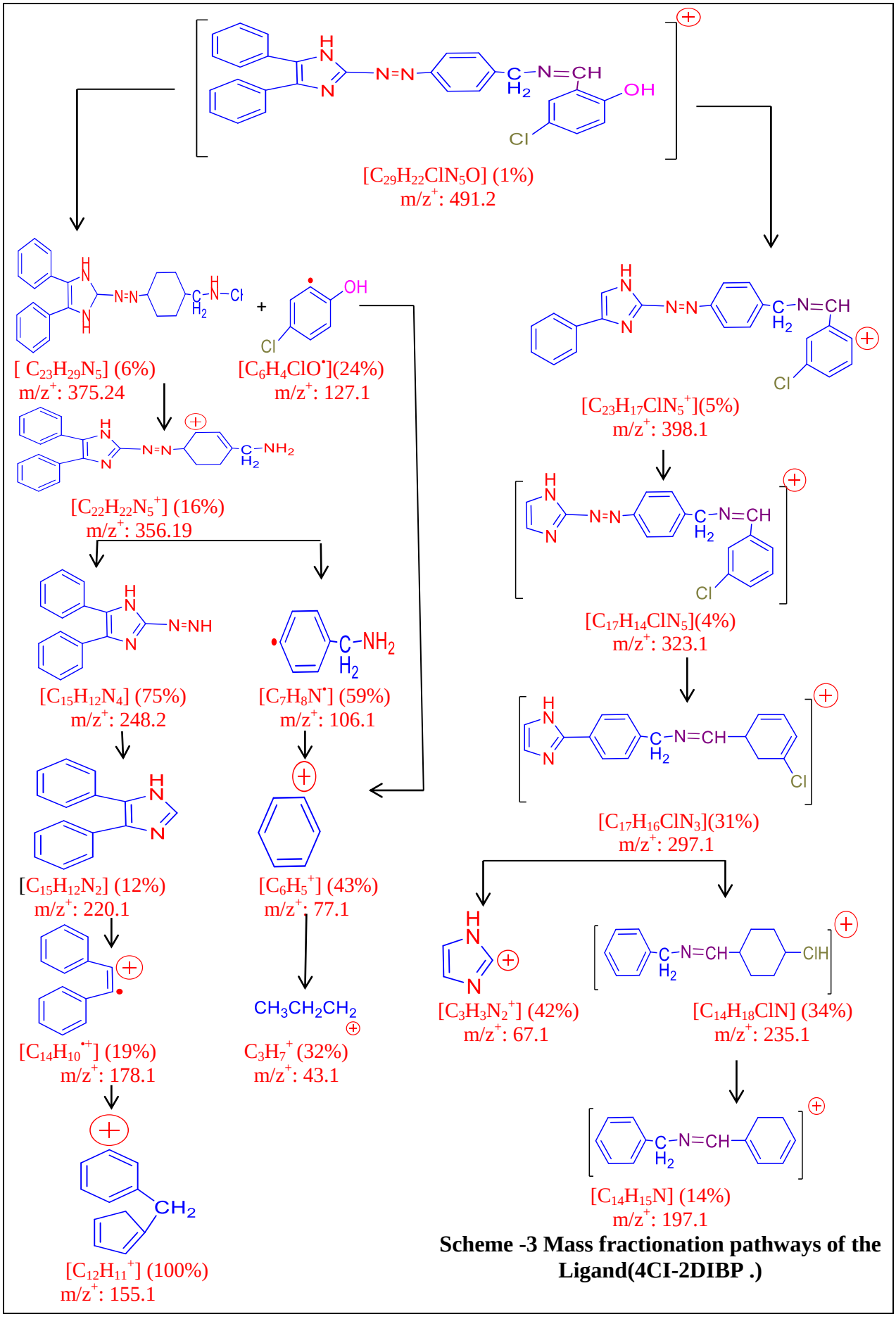


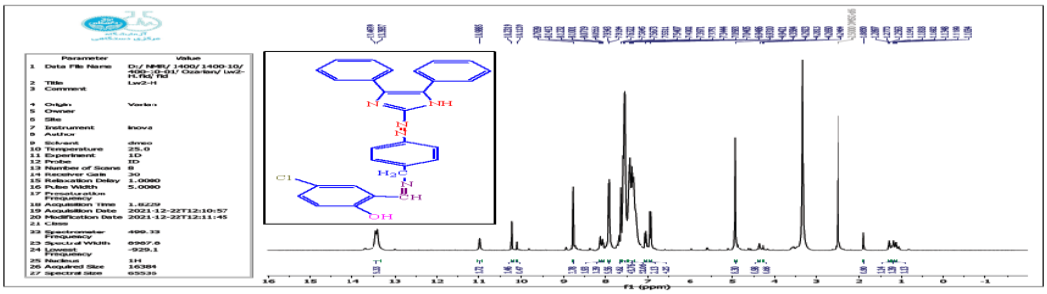
Fig1: Mass spectrum of the new azo Schiff base ligand .



Scheme -3 Mass fractionation pathways of the Ligand(4CI-2DIBP .)

^{1}H-NMR Spectra

The spectrum of newly synthesized ligand(4Cl-2DIBP) gave a satisfactory data and the molecular structure was assigned on the basic of ^{1}H - NMR chemical shift by using DMSO-d6 as a solvent with TMS as an internal reference. The 1H-NMR spectrum of the ligand showed clear signals involved singlet at δ (2.5) (ppm) belong to the protons of solvent (DMSO) and multiples signals at δ (6.95-8) ppm which were assigned to aromatic protons of phenyl ring of Imidazole and benzilidenimin. Singlet at δ (4.8) ppm belong to the proton of methyl(CH_2). Singlet at δ (11.1) ppm belong to the proton of hydroxyl(OH).Singlet at δ (8.7) ppm belong to the proton of (–CH=N), Singlet at δ (13.3) ppm belong to the proton of –C-NH imidazole ring (28) , as shown in Fig.(2).



Fig(2): ^{1}H-NMR spectrum of the ligand (4Cl-DIBM)

Infrared Spectra studies of the ligand and its complexes:

The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the Complexation(34,35), all data are listed in table (3).

Table (3) IR spectra frequencies for the new azo Schiff base ligand and its metal complexes in cm^{-1}

Compound Formula	υ(OH)	υ(CH) Aro	υ(CH) Alpha.	υ(C=N)Imda.	υ(C=N)Shiff	υ(N=N)	C-Cl	υ(M-N)
(4CI-2DIBP)= $C_{29}H_{22}N_5CLO$	3400	3055	2987	1633	1600	1369	696	-----
[Co(4CI-2DIBP) $_2Cl_2$]	3415	3057	2926	1643	1608	1388	696	588
[Ni (4CI-2DIBP)$_2Cl_2$]	3388	3055	2926	1631	1631	1390	696	586
[Cu (4CI-2DIBP)$_2Cl_2$]	3408	3051	2987	1630	1612	1390	698	538
[Zn (4CI-2DIBP)$_2Cl_2$]	3427	3055	2850	1641	1604	1396	698	507
[Cd(4CI-2DIBP)$_2Cl_2$]	3423	3057	2891	1641	1600	1409	698	445
[Hg(4CI-2DIBP)$_2Cl_2$]	3419	3057	2897	1635	1604	1398	698	509

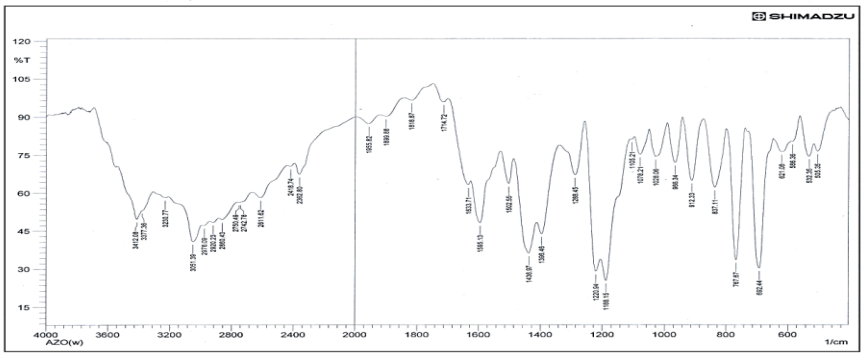


Fig (3): IR-spectra of the Azo compound

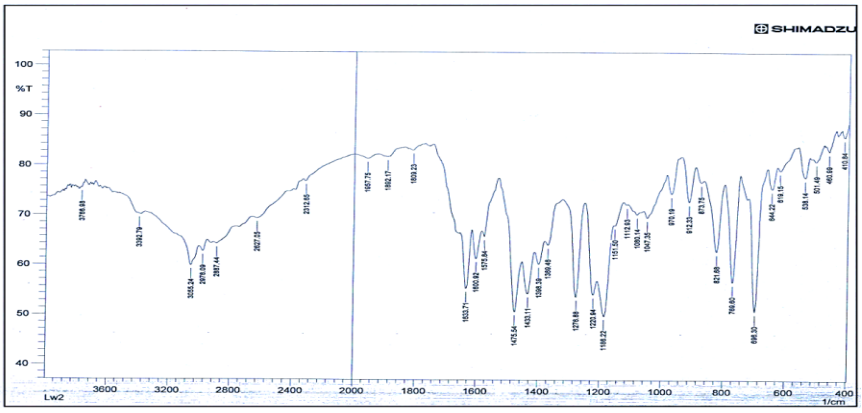


Fig (4): IR-spectra of the ligand (4Cl-2DIBP)

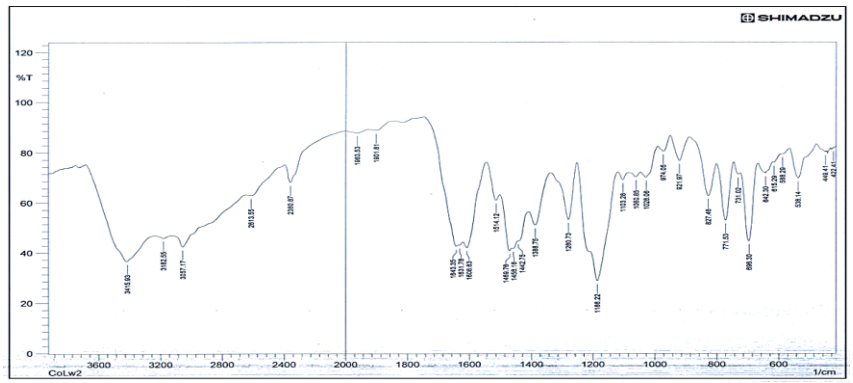


Fig (5): IR-spectra of Co (II) complex

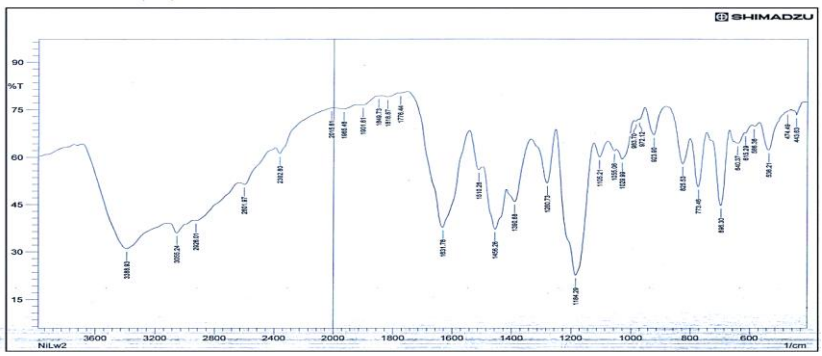


Fig (6): IR-spectra of Ni(II) complex

Magnetic susceptibility:

The results of the magnetic susceptibility measurements are listed in the table (4) where the magnetic moment value of the magnetic moment of Co(II) ,Ni (II) and Cu(II) Complexes reach (4.90,3.03, 1.78) B.M respectively , which indicates the presence of the paramagnetic characteristic (36). As for the complexes of Zn(II), Cd(II) and Hg(II) they have shown Di magnetic properties due to Electron cover saturation (nd) in the electrons(37).

Measurement of molar conductivity:

From the results obtained, it is clear that the molar electrical conductivity measurements for solutions of Chelate complexes of ions under study with the new ligand and with concentration of (1×10^{-3}) molar per complex at the laboratory temperature and using DMSO as solvent , were ranged from (8.21-17.36)S. $cm^2.mol^{-1}$and listed in table (4), We find the lack of ionic properties of all these complexes. These results are identical to what was stated in the literature for metallic complexes devoid of ionic properties (38).

Table (4) molar conductivity and Magnetic susceptibility values for the complexes

Compounds	μ_{eff} (B.M)	Conductivity $S.mol^{-1}.Cm^2$
$[Co(4CI\text{-}2DIBP)_2Cl_2]$	4.90	16.00
$[Ni(4CI\text{-}2DIBP)_2Cl_2]$	3.03	8.21
$[Cu(4CI\text{-}2DIBP)_2Cl_2]$	1.78	17.36
$[Zn(4CI\text{-}2DIBP)_2Cl_2]$	Dia	9.56
$[Cd(4CI\text{-}2DIBP)_2Cl_2]$	Dia	12.99
$[Hg(4CI\text{-}2DIBP)_2Cl_2]$	Dia	10.21

Electronic spectra:

The electronic absorption spectra are very useful in the estimation of effects equipped thru other approaches of structural exploration.

The spectrum of the new ligand (4CI-2DIBP) in solvent (DMSO) showed two absorption peaks, one at (294nm, 34013.60 cm^{-1}) due to the electron transition of the type ($\pi \rightarrow \pi^*$) while the second peak was attributed at (429 nm, 23310.02cm^{-1}) to the

electron transition (n → π*) due to the ligand having double bonds with atoms having unshared electron pairs . The spectrum of the ligand was compared with that of the cobalt (II) complex, which showed an absorption peak at (445 nm, 22471.91 cm^{-1}) has been attributed to the electron transition ν3 = $^4T_1g \rightarrow {}^4T_1g$ (P) This fact is consistent with the literature on the appearance of this band in octahedral cobalt(II) complexes (39).The UV-visible spectrum of nickel (II) complex solution recorded an absorption peak at (464 nm, 21551.72 cm^{-1}). to the electron transition v3=$^3A_2g(F) \rightarrow {}^3T_1g$ (P) and this is consistent with what was mentioned in the literature regarding octahedral nickel(II) complexes. While the UV-visible spectrum of copper (II) complex solution showed an absorption peak at (461 nm, 21691.97 cm^{-1}) due to the to the electron transition (($^2Eg \rightarrow {}^2T_2g$), and this is consistent with what was mentioned in the literature (40). As for electronic spectra of the zinc(II) , Cadmium (II) and mercury(II) complexes with new ligand (4Cl-2DIBP) , they does not possess type (d-d) electronic transmissions because of the fullness of the five (d) orbitals. As new peaks appeared in the metal ion complexes that were not visible in the ligand spectrum, this indicates the consistency of the metal ion with the new ligand due to the charge transfer (C.T)(41). the spectrum of the free ligand is red-shifted in complexes due to ligand to metal charge transfer (LMCT) transition , suggesting an octahedral geometry around metal(II) in the complexes as showed in Fig.(6) ,(7)and (8) .

Table (5) shows the electronic spectra of ligand 4CI-2DIBP and its metal complexes in ethanol solvent.

Compounds	λmax (nm)	ύ (cm^{-1})	Transitions	∈ ($\frac{M}{Cm}$)	Geometry	Hybridization
(4CI-2DIBP)= $C_{29}H_{22}N_5CLO$	294 429	34013.60 23310.02	π →π* n →π*	9420 10660	----------	----------
$[Co(4CI\text{-}2DIBP)_2Cl_2]$	445	22471.91	$\nu_3 = {}^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$	14360	Octahedral	Sp^3d^2
$[Ni\ (4CI\text{-}2DIBP)_2Cl_2]$	464	21551.72	$^3A_2g_{(F)} \rightarrow {}^3T_1g_{(P)} = \nu_3$	15340	Octahedral	Sp^3d^2
$[Cu(4CI\text{-}2DIBP)_2Cl_2]$	461	21691.97	$^2Eg \rightarrow {}^2T_2g$	19110	Octahedral	Sp^3d^2
$[Zn(4CI\text{-}2DIBP)_2Cl_2]$	283 432	35335.68 23148.14	IL.CT ML.CT	19160 7350	Octahedral	Sp^3d^2
$[Cd(4CI\text{-}2DIBP)_2Cl_2]$	432	23148.14	ML CT	18830	Octahedral	Sp^3d^2
$[Hg(4CI\text{-}2DIBP)_2Cl_2]$	440	22727.27	ML CT	19000	Octahedral	Sp^3d^2

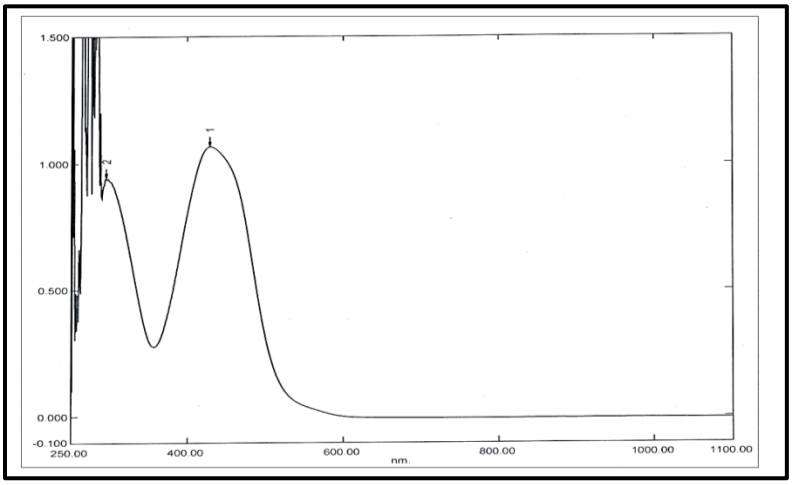


Fig (7): UV-Vis spectra of new Ligand

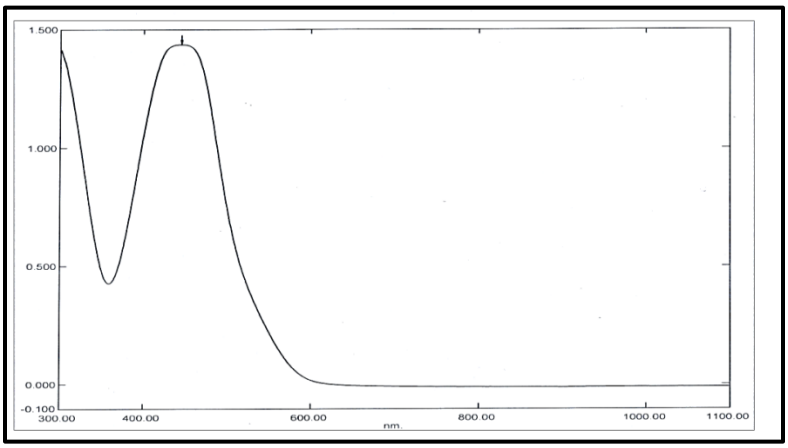


Fig (8): UV-Vis spectra of Co (II) complex

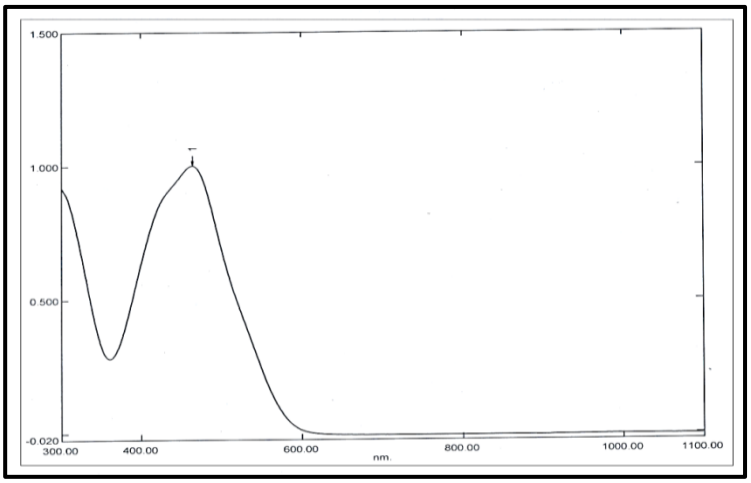


Fig (9): UV-Vis spectra of Ni (II) complex

Proposed Structural:

From the results reached it is possible to proposed the octahedral structure of all metal complexes with new Azo Schiff base ligand(4Cl-2DIBP). The Proposed Structural of metallic complexes can be illustrated in the Fig (9) .

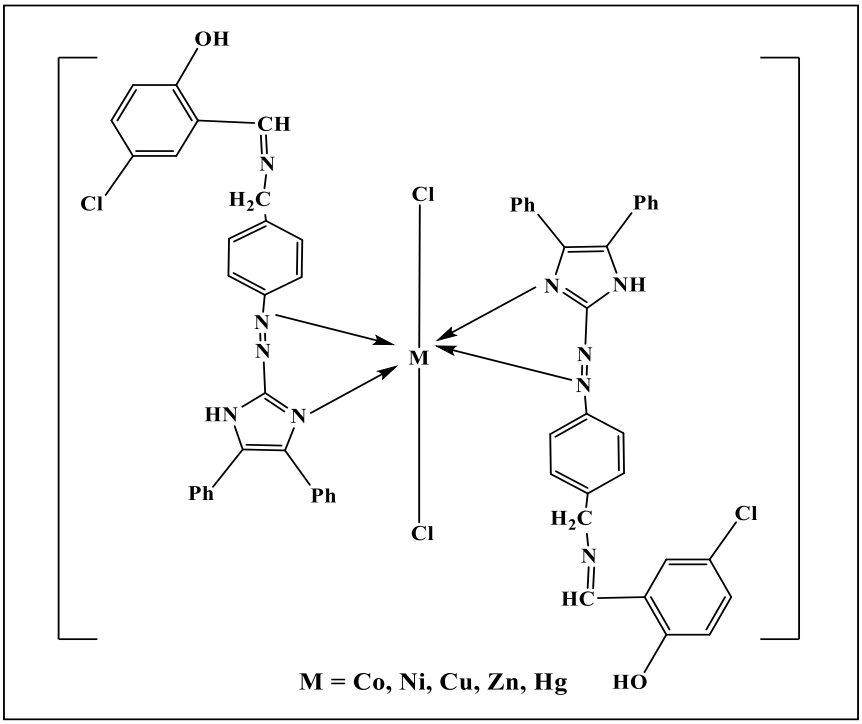


Fig.(9): Proposed Structural of the metallic complexes

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