

RESEARCH ARTICLE

Synthesis and Spectral Identification of New Azo-Schiff Base Ligand Derivative from Aminobenzylamine and its Novel Metal Complexes with Cu(II), Zn(II) and Hg(II)

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ABSTRACT

The research included the preparation of the New Azo Schiff Ligand derived from 4,5-diphenyl imidazole. The ligand was prepared from the amine reactor with the coupling component to prepare the azo amino benzylamine. After that the last compound and 4-hydroxy benzaldehyde which obtained the ligand mentioned some metallic complexes were prepared for the ions of Cu(II), Zn(II) and Hg(II). The new azo-schiff ligand complexes after purification were identification by using the available spectral and analytical methods such as Mass spectrum for the new ligand and (ultraviolet-visible, FTIR) spectroscopy, CHN analytics, Atomic absorption, and conductivity measurement.

According to these techniques the new azo-schiff ligand was pidentate and the proposed geometrical shape was octahedral for the three complexes.

Keywords: 4,5-diphenyl imidazole, Azo-schiff ligand, Metal complexes.

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INTRODUCTION

Schiff bases are a class of compounds containing the 'Azomethine' as a functional group that contains a carbon-nitrogen double bond ($>C=N-$), nitrogen being attached to an alkyl or aryl group, but not hydrogen.¹ These compounds were reported by a German Chemist Hugo Schiff in 1864 and therefore referred to his name.² The majority of the Schiff bases are represented by the general formula $R_1R_2C=NR_3$,³ while some of these have the general formula $R_1CH=NR_2$, in which carbon is attached with a hydrogen atom instead of an alkyl or aryl group.⁴ These are condensation products of ketones or aldehydes with primary amines.⁵ Usually, stable Schiff bases are those which are formed from the condensation reaction of aromatic amines and aromatic aldehydes.⁶

Schiff bases have been reported to possess a number of biological activities including antifungal,⁷ analgesic,⁸ anti-inflammatory,⁹ antibacterial,¹⁰ antioxidant,¹¹ antitumor,¹² cardiovascular,¹³ antitubercular¹⁴ and used as local painkillers.¹⁵ Their biological activities depend upon the type of substituent attached to the aromatic ring. In recent years, the attention of Schiff bases, as well as their metallic complexes, is increasing due to their remarkable catalytic and biological applications.¹⁶

Schiff bases also function as versatile ligands and can coordinate with a number of metal atoms or ions in various oxidation states and geometries. Schiff bases can form complexes with d-block elements and lanthanides.¹⁷ Schiff bases are capable of coordinating with metal ions via the imine nitrogen and other groups linked to the Schiff base.¹⁸ Schiff bases are called privileged ligands since they can be prepared simply by condensation between aldehydes and primary amines.¹⁹ Most of the Schiff bases have Nitrogen or Oxygen donor atoms, but sometimes sulfur or selenium can replace Oxygen atom.²⁰ Schiff bases may serve as monodentate, bidentate, tridentate or tetradentate ligands depending upon the number of donor atoms present in the molecule. They can make chelates (typically five or six-membered) on reaction with metal ion.²¹ Some of the Schiff bases in combinations with metal ions are used as insecticides, fungicides, and herbicides.²²

EXPERIMENTAL

In this work, the analytical and spectral measurements of the prepared ligand and the derived complexes of some selected metallic ions were used. The ultraviolet spectra of ligand and its chelating complexes were recorded using a device

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(Shimadzu 1700) within range (200–800 nm) dissolve in ethanol using quartz cell. The melting points of ligand and its solid canine complexes were measured using the device (Stuart melting points SMP 10). The molecular conductivity measurements were recorded for the complexes at $25 \pm 2^\circ\text{C}$ for solution (1×10^{-3}) of the sample in ethanol using a device (Digital conductivity meter Alpha -800). The infrared spectra of the azo compound and its metallic complexes are recorded in their solid state within the rang ($400\text{--}4000\text{cm}^{-1}$) in the solid potassium bromide with the apparatus completion (Shimadzu FTIR 8400 spectrophotometer). The mass spectrometer was also recorded by advice (MSD Direct Probe). Measurements of magnetic sensitivity of solid complexes and at laboratory temperature were performed using a device (Balance Magnetic Susceptibility Model-M.S.B Auto).

Synthesis of the New Azo Schiff Base Ligand

The new azo-schiff base ligand is prepared by coupling reaction of diazonium salt with appropriate amount of (amidazole derivative) as coupling component in alkaline solution. Adiazonium solution is prepared by dissolving (5.3 mL) of para aminobenzylamine in (100 mL) distilled water with (8 mL) of concentrated HCl acid with continuous shaking. To this mixture a solution of (3 gm) of sodium nitrate in 25 mL of distilled water was added drop wise to the Diazonium solution with shaking and stirring to complete the aromatic amine azotization process at ($0\text{--}5^\circ\text{C}$), and left to stand (30 minutes). This diazonium solution was added drop wise to (8.8 gm) of the amidazole derivative dissolved in (30 mL) of ethanol and (50 mL) of (2N) sodium hydroxide at ($0\text{--}5^\circ\text{C}$). 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 (the azo dye) was then neutralized by adding drops of dilute HCl to the acidic function $\text{pH} \sim 7.5$. 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°C for 1-hour.

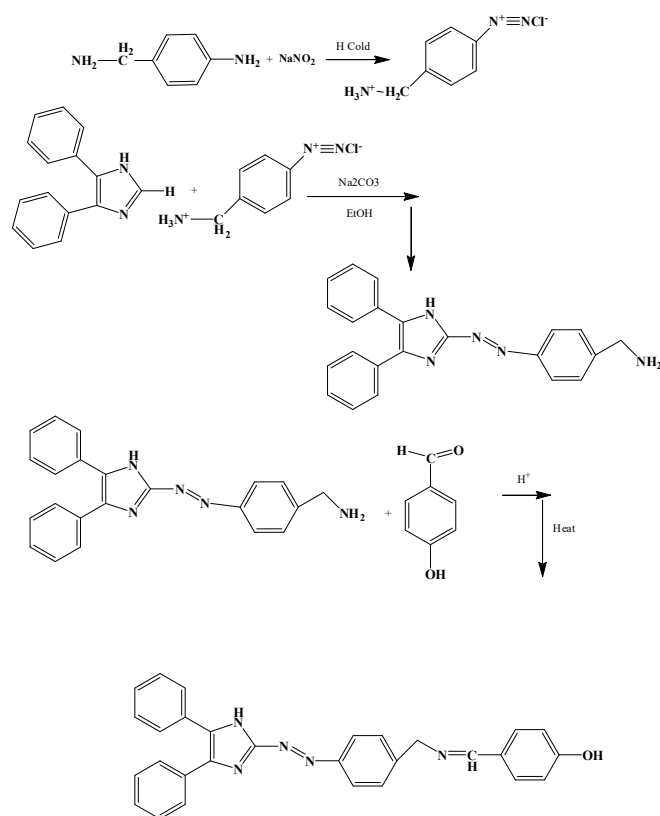
3.53 gm from pure azo dye dissolved in absolute alcohol (50 mL) and then mixed with (1.22 gm) (para-hydroxybenzaldehyde) dissolved in absolute alcohol. Three drops from glacial acetic acid were added and the mixture was refluxed with stirring for 6 hours. Azo-Schiff base ligand was isolated after the volume of the mixture was reduced to half by evaporation and precipitated product was recrystallized with hot absolute ethanol alcohol collected by filtered off and dried over anhydrous CaCl_2 and its melting point was recorded at ($129\text{--}131^\circ\text{C}$) while the product percentage reached 80% (Scheme 1).

Preparation of Metal Complexes

The metal complexes were prepared by mixing of 30 mL ethanol solution of each of ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 and $\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$) with 30 mL ethanol solution of (0.441 g) of new (azo-Schiff base) ligand in (1:2) (metal: ligand) ratio. The resulting mixture was refluxed for 1-hour. The products of complexes were isolated after reduced of volume by evaporation. They were filtered off, washed with ethanol and dried under vacuum. Melting points were recorded and measurement results were listed in Table 1.

RESULTS AND DISCUSSION

All our complexes are Freely soluble in DMF, DMSO, Methanol and Ethanol. Also They are stable in air. The metal complexes were characterized by elemental analysis Table 2, molar conductivities, magnetic susceptibility, IR, UV-vis, Mass and $^1\text{H-NMR}$ spectra. The analytical data of the complexes are in agreement with the experimental data. The value reveal that



4-((4-(E)-(4,5-diphenyl-1H-imidazol-2-yl)diazenyl)benzylimino)methyl)phenol

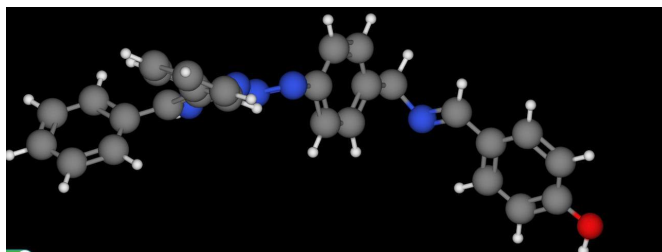
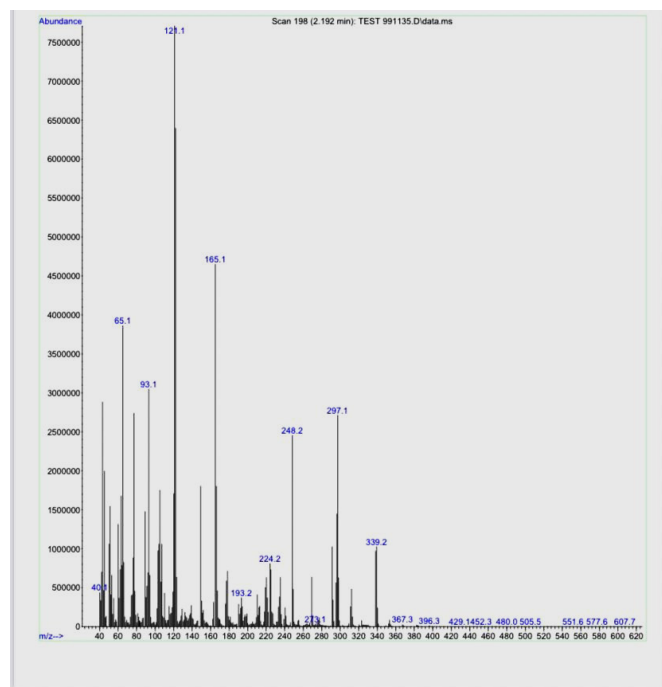
Scheme 1: Preparation of new (azo-Schiff base) ligand

Table 1: Physical properties of the new Azo schiff base ligand and its complexes.

No.	Compound	Colour	M.P.($^\circ\text{C}$)	Yield %	Rf (1:4) لون اثيري م : نيزن ب
1	$\text{L}_1 = \text{C}_{28}\text{H}_{21}\text{N}_5\text{O}$	Red	98–96	84	0.80
2	$[\text{Cu}(\text{L}_1)_2]\text{Cl}_2$	Perpile	170–171	80	0.82
3	$[\text{Zn}(\text{L}_1)_2]\text{Cl}_2$	Red	100–102	78	0.96
4	$[\text{Hg}(\text{L}_1)_2]\text{Cl}_2$	Red	115–117	76	0.60

Table 2: Element Analysis the new azo Schiff base ligand and its complexes.

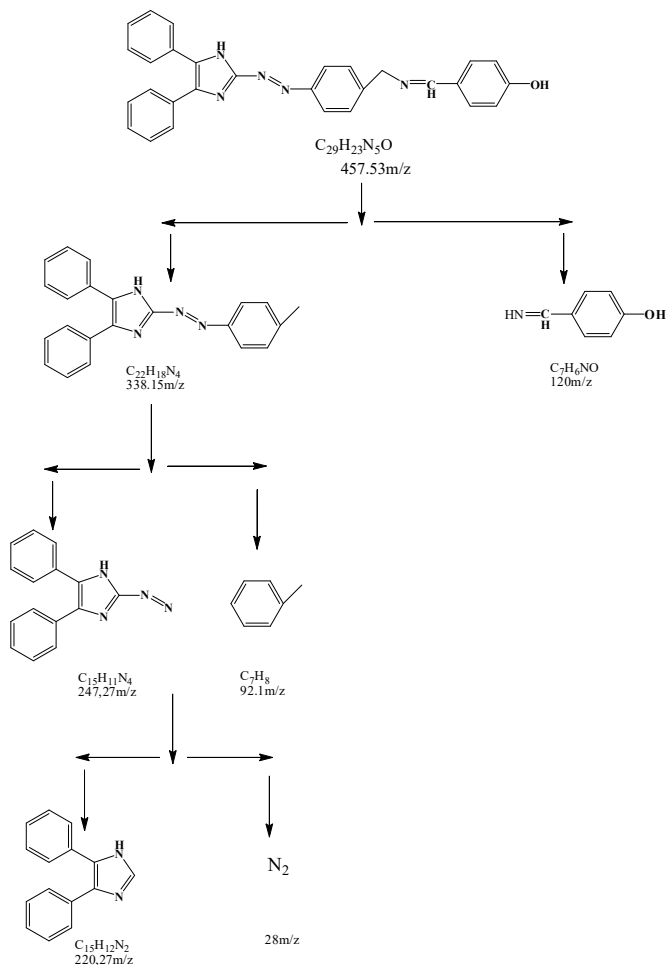
No	Formula	M.Wt	Found (Calc.)%			
			C%	H%	N%	M%
1	$L_1 = C_{29}H_{23}N_5O$	457.53	76.06)) 76.44	5.02)) 5.35	15.29 15.50	-----
2	$[Cu(L_1)_2].Cl_2$	1049.46	43.45)) 45.90	4.38)) 4.88	13.34)) 13.86	6.05)) 6.14
3	$[Zn(L_1)_2].Cl_2$	1051.36	43.37)) 43.66	4.37)) 4.78	13.31)) 13.56	6.22)) 6.79
4	$[Hg(L_1)_2].Cl_2$	1086.56	(38.43) 34.79	3.87)) 3.94	11.79 (11.87)	(16.90) 16.99


Figure 1: Structure of new Azo-Schiff base ligand

Figure 2: Mass spectrum of the new azo Schiff base.

the metal to ligand ratio was (1:2) (M:L) and were presented in Table 2. The magnetic susceptibility of the chelate complex of Cu(II) at room temperature was consistent with octahedral geometry, So as the Zn(II) and Hg(II) complexes suggest a an octahedral geometry around the central metal ions. All chelate complexes prepared in this work showed lower conductivity values. This proves that complexes have non-electrolytic nature.

Mass Spectrum

The mass spectra of the new azo Schiff base ligand was recorded at room temperature. The obtained peaks confirm the


Scheme 2: Segment fractionation of the new azo Schiff base Ligand

proposed formulae for the compound. The mass spectrum of Ligand show the molecular ion peak at m/z 457.53 compound ($C_{28}H_{21}N_5O$) confirms the proposed formulae for compound.

1H -NMR Spectra

The spectrum of newly synthesized ligand gave a satisfactory data and the molecular structure was assigned on the basic of 1H -NMR chemical shift by using DMSO as a solvent with tetra methyl saline 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 (7.3-7.9) ppm which were assigned to aromatic protons of phenyl ring of Imidazole and benzilidenimin.

Multiple signals at δ (8.2-8.6) ppm which belong to (CH) benzylidenimin groups. Singlet at δ (4.8) ppm belong to the proton of methyl (CH_2). Singlet at δ (10.5) ppm belong to the proton of ($-\text{C}-\text{NH}$), Singlet at δ (12.1) ppm belong to the proton of $-\text{C}-\text{NH}$ imidazole ring, as shown in Figure 3.

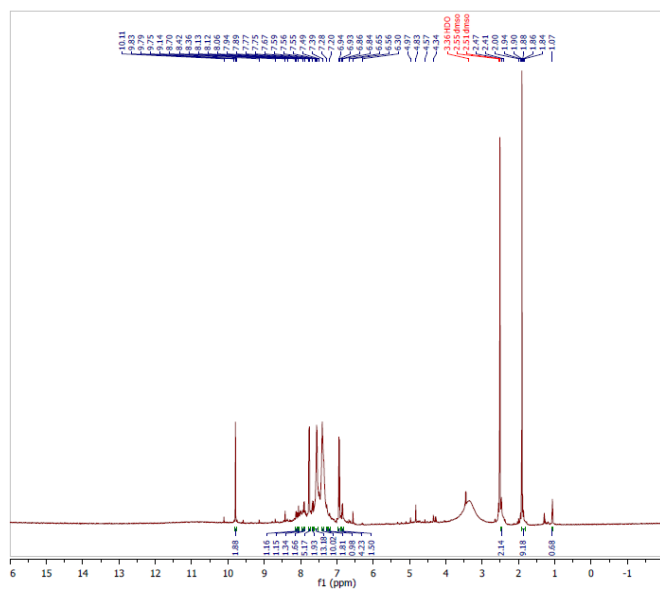


Figure 3: $^1\text{H-NMR}$ spectrum of the new azo Schiff base

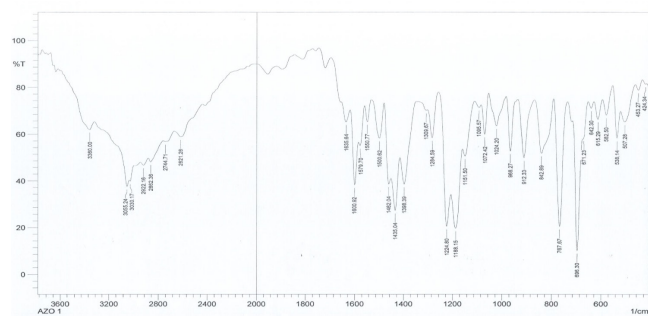


Figure 4: IR-spectra of the Azo compound

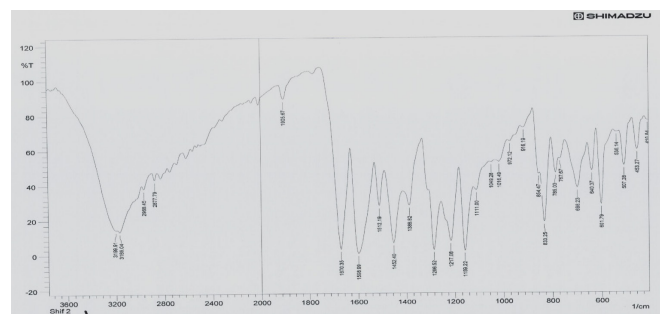


Figure 5: IR-spectra of the ligand

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, all data are listed in Table 3.

The ligand spectrum showed an absorption beam at the frequency (1670 cm^{-1}) that is due to $\nu(\text{C}=\text{N})\text{ cm}^{-1}$ bond of the imidazole ring,²³ while this package showed a clear difference in the frequency locations in addition to the difference in the intensity and shape of the beams in the spectra Complexes where they appeared at frequencies between ($1502\text{--}1558\text{ cm}^{-1}$), which means that the consistency process occurred through the imidazole nitrogen atom with the metal ion, and the ligand spectrum showed a sharp absorption beam at the frequency (1452 cm^{-1}) belonging to the azo group $\nu(\text{N}=\text{N})$ ²⁴ While the spectra of complexes showed a clear shift towards lower frequencies, they varied between ($1438\text{--}1444\text{ cm}^{-1}$), indicating The symmetry of the nitrogen atom also the ligand spectrum showed an absorption beam at the frequency

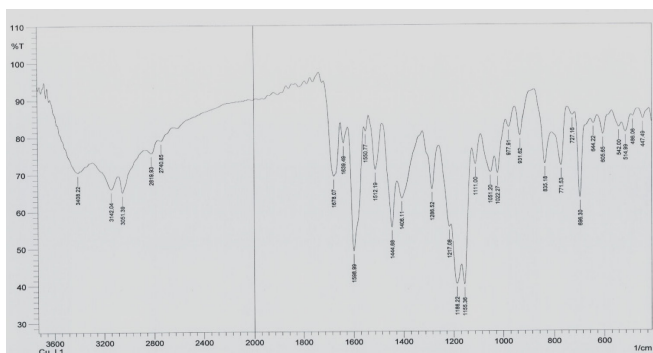


Figure 6: IR-spectra of Cu (II) complex

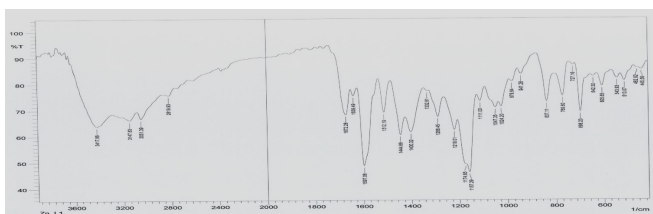


Figure 7: IR-spectra of Zn (II) complex

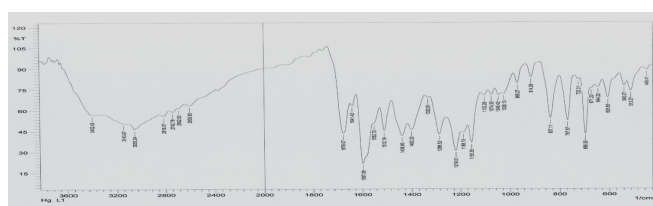


Figure 8: IR-spectra of Hg (II) complex

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

Compound formula	$\nu(\text{OH})$	$\nu(\text{CH})$ Aro	$\nu(\text{CH})$ Alpha.	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{M}-\text{N})$
$\text{L}_1 = \text{C}_{28}\text{H}_{21}\text{N}_5\text{O}$	3199	3169	2968	1512	1670	1452	----
$[\text{Cu}(\text{L}_1)_2]\text{Cl}_2$	3408	3051	2819	1512	1678,1639	1444	447
$[\text{Zn}(\text{L}_1)_2]\text{Cl}_2$	3417	3051	2891	1512	1672,1639	1444	445
$[\text{Hg}(\text{L}_1)_2]\text{Cl}_2$	3402	3143	2816	1512	1678,1641	1438	449

(3232) cm^{-1} belonging to the sphincter ν (N-H),²⁵ whereas in the complexes this bundle appeared at frequencies between (3140–3300) cm^{-1} . The frequency (3381) cm^{-1} returns to ν (O-H)²⁶ bond while appeared in the spectra of complexes at frequencies between (3199–3417) cm^{-1} . The ligand spectrum showed a beam at the (1678) cm^{-1} frequency that returns to ν (C=N)²⁷ for the azomethine group. Absorption beams appeared in the spectra of complexes at frequencies between (447–449) due to the association of ν (N-M)²⁸ harmonicity while the ligand spectrum was devoid of these packages, which indicates that the coordination process between ligand and metal ions occurred through the atom nitrogen atom of the azo group and the nitrogen of the imidazole ring. The ligand spectrum is a beam at the (2968) cm^{-1} frequency that returns to the ν (C-H) aliphatic. In the spectra of complexes, this beam appeared at frequencies between (2819–2891) cm^{-1} . Also, a beam appeared at the (3169) cm^{-1} frequency that goes back to (C-H)¹⁵ Aromatics and in the spectra of complexes appeared at the frequencies (3051–3143) cm^{-1} (Figures 4 to 8).

Magnetic Susceptibility

The results of the magnetic sensitivity measurements are listed in the Table 4 where the magnetic moment value of the magnetic moment of Cu(II) Complex reach (1.78B.M), which indicates the presence of the paramagnetic characteristic resulting from the presence of a single electron for the Cu(II) ion in its complexes.¹⁸ As for the complexes of both Zn(II), and Hg(II) they have shown Di magnetic properties due to the fullness of the plane (nd) in the electrons.¹⁹

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 ethanol as solvent, were ranged from (15.00–17.81S. $\text{cm}^2 \cdot \text{mol}^{-1}$) 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.²⁰

Table 4: Molar conductivity and magnetic susceptibility values for the complexes in ethanol solution.

Compounds	$\mu_{\text{eff}}(\text{B.M})$	$A_M(\text{S.cm}^2 \cdot \text{mol}^{-1})$
[Cu(C ₂₃ H ₁₉ N ₅ O) ₂]Cl ₂	1.78	17.81
[Zn(C ₂₃ H ₁₉ N ₅ O) ₂]Cl ₂	Dia	15.00
[Hg(C ₂₃ H ₁₉ N ₅ O) ₂]Cl ₂	Dia	14.81

Table 5: Electronic spectra of ligand and its metal complexes in ethanol solvent.

Compound	Assignment	Absorption band (nm) cm^{-1}	Proposed Structure
L=(C ₂₃ H ₁₉ N ₅ O)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	(280 nm)34482 (414nm)24154
[Cu(C ₂₃ H ₁₉ N ₅ O) ₂]Cl ₂	${}^2B_{1g} \rightarrow {}^2A_{1g}$	(906 nm)10245	oh
[Zn(C ₂₃ H ₁₉ N ₅ O) ₂]Cl ₂	M \rightarrow L,CT		oh
[Hg(C ₂₃ H ₁₉ N ₅ O) ₂]Cl ₂	M \rightarrow L,CT		oh

Electronic Spectra

The electronic absorption spectra are very useful in the estimation of effects equipped thru other approaches of structural exploration. The UV-vis spectra of new azo Schiff base ligand (L) (Figure 9), Table 5 showed two absorption peaks may be attributed to charge transfer(C.T) bands at the frequency (280 nm) (33112 cm^{-1}) and (414 nm) (22026 cm^{-1})²⁹ which were allotted to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. As for the octahedral copper (II) complex spectrum, it showed one absorption peak, at frequency (906 nm) (10245 cm^{-1})³⁰ and this indicate that the copper(II) complex took the octahedral shape deformed. As for electronic spectra of the zinc(II) complex, and mercury(II) complex with new azo Schiff base ligand (L), 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).³¹ 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 Figures 10 to 12.

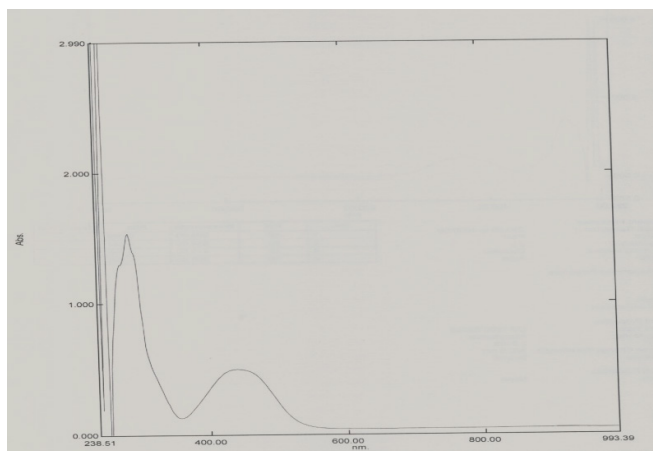


Figure 9: UV-vis spectra of new Ligand

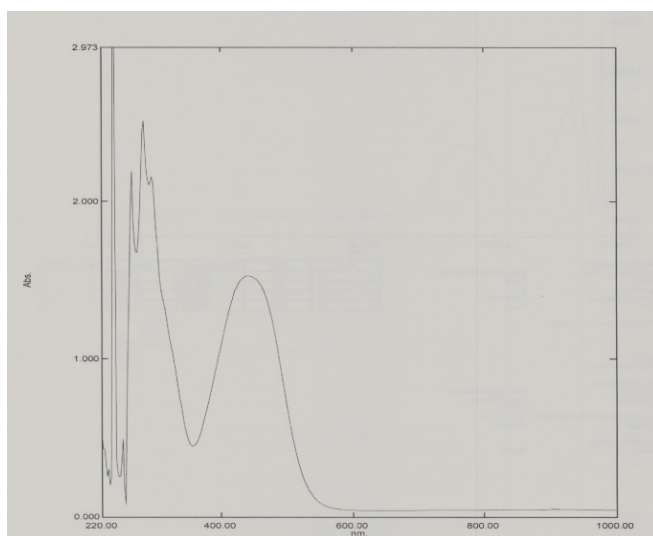


Figure 10: UV-Vis spectra of Cu (II) complex

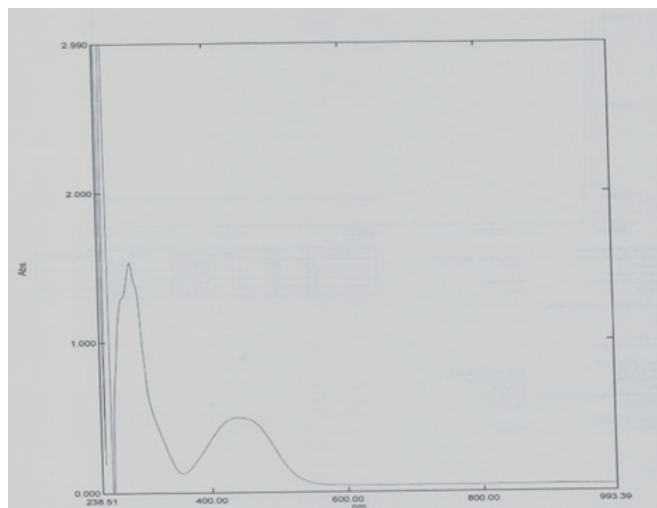


Figure 11: UV-Vis spectra of Zn (II) complex

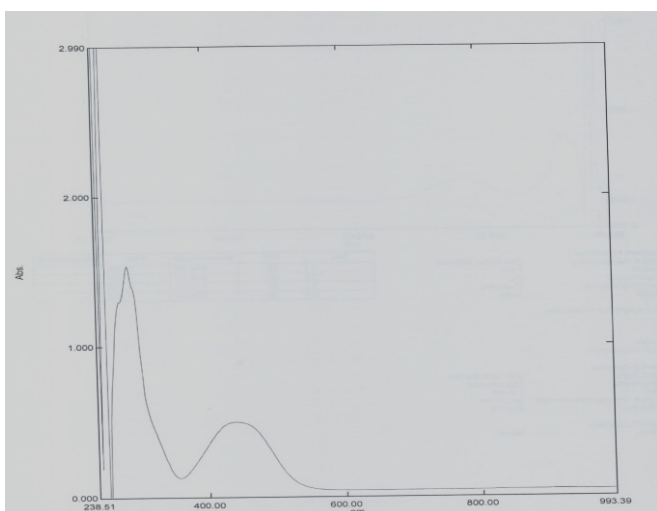


Figure 12: UV-Vis spectra of Hg(II) complex

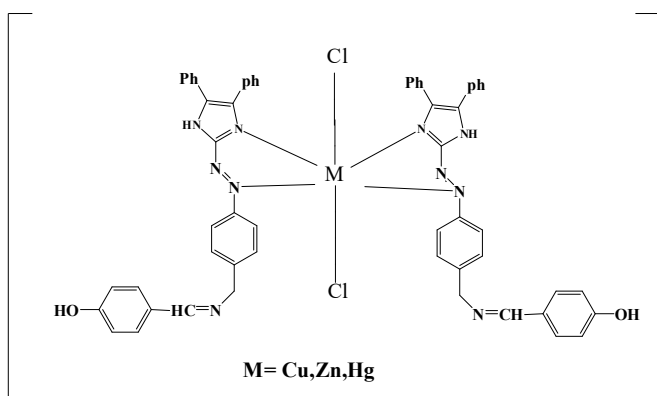


Figure 13: Proposed Structure of Cu(II), Zn(II) and Hg(II) complexes

Proposed Structure

From the results, it is possible to propose the octahedral structure of all metal complexes with new Azo Schiff base ligand (L). The proposed structural of metallic complexes can be illustrated in the Figure 13.

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