

New Metal Complexes with Azo-Schiff Base Ligand Synthesis, Characterisation and Biological Activity

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Abstract: Synthesis and characterization of a new azo-Schiff base ligand (1-(4-((E)-3-hydroxy-4-((E)-((4-nitrophenyl)imino)methyl)naphthalen-2-yl)diazenyl)phenyl)ethan-1-one) (HL), derived from ((E)-3-((4-acetylphenyl)diazenyl)-2-hydroxy-1-naphthaldehyde)) with 4-nitroaniline in a one to one molar ratio. Subsequently, the interaction of HL with various metal ions (CoII, NiII and CuII) in the ratio of one ligand to one metal, produced monomeric coordination connections. These compounds have been fully characterised using analytical methods and spectroscopic techniques, involve elemental microanalysis, ¹H and ¹³C-nuclear magnetic resonance, Fourier transform infrared spectroscopy, electronic and mass spectroscopy, as well as magnetic susceptibility and Conductivity measurements. The analytical data verified the formation of coordination compounds exhibiting four and six-coordinate geometries. The antibacterial evaluation for the ligand and its metal complexes against bacterial strains and fungus species showed a significant enhancement in the effectiveness of the antimicrobial ligand when forming complexes with metal ions. In addition, the study evaluated the antibacterial activity of synthesised compounds with a number of bacteria and fungi. The complex formation significantly enhanced the antibacterial efficacy of the ligand.

1 INTRODUCTION

Compounds that include both azomethine (--HC=N--) and azo (N=N) groups are called Azo-Schiff bases; the Schiff bases are formed by the condensation of ketones or aldehydes with primary amines, by Hugo Schiff in 1864 initially reported [1]. which are synthesised from the combining of the azo-dye compound (--N=N--) together with the Schiff base containing an azomethine linkage (--C=N--) [2]. Ligand of Schiff base produce stable complexes with different metals, so they have significant importance [3]. It has attracted significant interest from both synthetic and biological viewpoints [4]. Schiff bases can be used for multiple applications, such as preparation and purification of amino or carbonyl compounds and safeguarding these groups sensitive reactions or throughout complex [5]. In addition to biological roles, they serve as pigments and dyes [6], intermediary compounds, inhibiting corrosion [7] and polymeric stabilisers [8]. The reaction formation of the Schiff base is widespread due to the simplicity of its synthesis, high yield, and

simple separation [9]. The conjugation of two active parts within a single molecule will cause an increase of the physicochemical and biological properties of this group of chelators and their corresponding chelated complexes [10]. Derivatives of Azo-Schiff base-containing compounds remain constantly a focus of study because of their numerous uses, particularly in the pharmaceutical and chemical fields [11]. Previous research has shown that nitrogen atoms in the conjugated bridge (C=N) of compounds derived from Schiff bases have a considerable coordination capacity with transition metal ions [12]. Compounds derived from Azo-Schiff have been thoroughly examined for optical storage of data, nonlinear optics, and photoswitching, demonstrating photoresponsive behaviour [13]. They contain an extensive range of applications in both biological activity and synthesis of organic molecules. As an example, the plastic, leather, and fabric production. Metal ions coordinate with most of these Azo-Schiff bases to form stable complexes. These complexes are used in many fields, especially medicine, such as corrosion prevention, metal recovery, and nuclear

waste treatment [14]. In recent years, we have documented the production of azo chemicals and the complexes they create [15]-[17]. This study deals with the synthesis of a Schiff base containing heterocyclic and azo compounds. Examining the biological activities of the synthesised compounds and the coordination properties of HL when interacting with metal ions is another goal of this effort. The synthesis of the ligand is based on a two-step procedure, including the preparation of the azo moiety ((E)-3-((4-acetylphenyl)diazanyl)-2-hydroxy-1-naphthaldehyde) (L). The reaction of L with 4-nitroaniline generated the ligand of Schiff base (HL). Furthermore, the interaction of HL with the cobalt(II), nickel(II), and copper(II) ions resulted in the isolation of a number of paramagnetic coordination compounds. This study also investigated the antibacterial properties of these synthesised chemicals.

2 MATERIALS AND EXPERIMENTAL PROCEDURES

The ligand's nuclear magnetic resonance spectra, which include (^1H and ^{13}C) spectrum, Utilising dimethyl sulfoxide- d_6 as the solvent, the results have been obtained with a Bruker 400 MHz spectrometer. The measurement frequencies had been 400 MHz for ^1H and 100 MHz to obtain ^{13}C , using tetramethylsilane as the internal standard. Fourier transform infrared spectroscopy The spectrum has been obtained utilising KBr granules and collected by using the FTIR-600 infrared Fourier spectrometer throughout a spectrum range of 4000 to 200 cm^{-1} . Analyses utilising positive ion electrospray mass spectrometry were performed with a Sciex ESI mass spectrometer. We used a Stuart SMP4 electrothermal device to determine the melting points of compounds. The spectrum of UV-visible has been obtained within the wavelength range of 1000 to 200 nm utilising a Shimadzu UV-160A spectrophotometer. At room temperature, using dimethyl sulfoxide, the solutions were prepared at a concentration of $10^{-3} \text{ mol L}^{-1}$ and analysed in a one-centimetre quartz cuvette. The Eutech Instruments Cyber Can CON 510 digital conductivity meter was employed to determine the conductivity of the solution in DMSO with concentrations between 10^{-1} and 10^{-5} . At the Heraeus Vario EL and Shimadzu AA-7000 atomic absorption, elemental (C, H, N) and metal content were utilised for the analysis. Utilising a Metrohm 686 Titro

processor and a 665 Dosim unit, the quantification for chloride ions in compounds was conducted by potentiometric titration. Finally, using a magnetic balance from Johnson Matthey, the magnetic characteristics have been assessed at 30°C .

3 SYNTHESIS

3.1 Synthesis of Azo Schiff Ligand

A two-step procedure was employed for the synthesis of the azo Schiff ligand as follows;

3.1.1 Synthesis of Azo ((E)-3-((4-Acetylphenyl) Diazanyl)-2-Hydroxy-1-Naphthaldehyde) (L)

The synthesis of L performed according to the described procedure [17]-[20] as following; a round-bottomed flask (250 ml) containing 1.35g (10mmol) of 4-aminoacetophenone and 0.69g (10mmol) of sodium nitrite, 20ml of a 1:1 ethanol-water mixture had been added. At temperature range (0 to 5°C), the solution was cooled by using an ice bath. Subsequently, in a beaker containing 10 ml of cold distilled water, 3 ml of hydrochloric acid (36%) was placed, followed by the addition dropwise with stirring over one hour. Diazonium salt solution is the product of this process, then reacts with a coolant mix that has 0.8g (20mmol) of sodium hydroxide and 1.72g (10mmol) of 2-hydroxynaphthalene-1-carbaldehyde in 20 ml of ethanol. for two hours, the reaction mixture had been allowed to stir. Subsequent to the reaction, the precipitate was filtered at pH 4, washed with cold water until its pH became 6-7, and then allowed to dry. The precipitate was filtered and was orange-red in colour. The resulting product was washed with 5ml of cold ethanol then let too dry at room temperature. The yield: 2.293g (72.10%), having a melting point among $136\text{-}138^\circ\text{C}$. ^1H -nuclear magnetic (400 MHz, DMSO- d_6 , ppm), $H_{(a)}$ at δ 9.67 ppm. 8.54; 8.45 ppm (s, 1H), which equivalent to $H_{(b)}$ and $H_{(c)}$ protons, respectively. $H_{(g,g-)}$ at 8.33 (d, J = 9.1 Hz, 2H). $H_{(h,h-)}$ displays at 7.79 (d, J = 7.9 Hz, 2H). $H_{(d,f)}$ at 7.48, 7.39 (t, J = 7.5 Hz, 2H). at 7.01 (d, J = 9.2 Hz, 2H); 6.76 (d, J = 9.6 Hz, 1H) belongs to $H_{(j,k)}$. $H_{(i)}$ at 2.60 ppm. Finally, at 15.27 ppm belongs to the impact of tautomerism. The ^{13}C -nuclear magnetic resonance (100 MHz, DMSO- d_6 , ppm). Resonances at $\delta_c = 197.11$ and 193.27 ppm were assigned to: (ketonic C_a); (aldehydic C_b), respectively. The Signal of phenolic carbon (C_c) was detected at 177.23 ppm. Resonances assigned for N- (C_n), was observed at 164.44 ppm, when the other N-

(C_q) chemical shifts appeared at 147.06 ppm. The two signals displayed at 143.02; 138.89 were related to (C_w), (C_t), respectively. The peaks which related to (C_e), (C_x) and (C_k) showed with 134.54; 132.14; 130.62 ppm frequency respectively. The two groups of Carbon nucleuses of (C_{g,g-}); (C_{h,h-}), assigned at 129.75 and 124.71 ppm. Resonance of (C_u); (C_d) signals appears at 128.61; 122.71 ppm, respectively. The assignments of (C_f) and (C_j) resonance appeared at 117.70 and 119.20 ppm, respectively. The methyl group (C_m), appeared as a one peak at 27.15 ppm.

3.1.2 Synthesis of Azo-Schiff Base Ligand (1-(4-((E)-(3-Hydroxy-4-((E)-(4-Nitrophenyl)Imino)Methyl)Naphthalen-2-yl)Diazenyl) Phenyl) Ethan-1-One) (HL)

Initially, a mixture containing 4-nitroaniline 0.433g (3.14mmol) in 10ml of ethanol, were added three drops of glacial acetic acid, was mixed with (E)-3-((4-acetylphenyl)diazenyl)-2-hydroxy-1-naphthaldehyde 1.0g (3.14mmol), It was initially dissolved in a 20 ml solution of a one-to-one mixture of ethanol and benzene. For 6 h, the mixture was heated at ca. 75°C and subsequently filtered while still hot. The red produce has been filtrated and also washed with 5 ml of EtOH. The final result was dried in the air. yield of ligand (HL) was 0.801g (58.09%), having a melting point among 170-172°C (see Figure 1). ¹H-nuclear magnetic resonance (400 MHz, dimethyl sulfoxide-d₆,ppm), at δ 9.68 ppm (s, 1H attributed to H_(a). at 8.54; 8.45 ppm (s, 1H), which equivalent to H_(b) and H_(c), respectively. H_(g,g-) at 8.35 (d, J = 9.1 Hz, 2H). H_(l,l-) at 8.32 (d, J = 8.7 Hz, 2H) , 8.09 (d, J = 8.1 Hz, 2H) belongs to H_(h,h-). H_(m,m-) displays at 7.72 (d, J = 7.9 Hz, 2H). H_(d) appear at 7.48 (t, J = 7.5 Hz, 1H). H_(f) appear at 7.39 (t, J = 7.5 Hz, 1H). at 7.00 (d, J = 9.2 Hz, 2H); 6.77 (d, J = 9.6 Hz, 1H) belongs to H_(j,k). H_(i) showed at 2.60 ppm. The ¹³C-nuclear magnetic resonance (100 MHz, DMSO-d₆, ppm). Resonances at δc = 197.11 and 177.23 ppm assigned to (ketonic C_v); (iminic C_b), respectively. (C_p) was detected at 172.74 ppm. (C_n), was observed at 150.10 ppm, (C_q) appeared at 147.06 ppm. At 138.92 ppm was related to (C_r). (C_s) showed with 134.54 ppm, at 133.55; 128.94 ppm belongs to (C_{x,w}). (C_c) displayed at 127.46 ppm. (C_{g,g-}); (C_{m,m-}); (C_{l,l-}); (C_{h,h-}), assigned at 127.34, 126.20, 125.72 and 124.57 ppm. (C_j) appears at 122.82 ppm. (C_k) appeared at 122.31 ppm, (C_i) appeared at 121.63 ppm.(C_{f,d}) displayed at 121.25; 117.70 ppm. (C_u) detected at 109.62 ppm. The methyl group, (C_i) appeared as a one peak at 27.15 ppm.

3.2 Synthesis of Complexes

The synthesised complexes process was a similar process used to synthesise the Co(II) complex. The procedure is as follows: It has been placed 0.3g (0.68 mmol) from HL had been dissolv in 10 ml of mixed solution (5:5) (ethanol benzene), then 10 ml of ethanol solution KOH 0.038g (0.68mmol) has been added in a 100ml round-bottomed flask. We stirred the mix. Subsequently, the slow addition of a solution of Cobalt(II)chloride hexahydrate 0.16g (0.68mmol) in 5ml of EtOH was performed. For 2 hours, the reaction mix was subjected to reflux heating. Following the heat process, the substance underwent filtration, washed to remove any remaining unreacted material used a cold ethanol and allowed to air dry. 0.231g (61.48%) was the yield of the Co(II) complex, with a melting point above 300°C. The synthesis process has been described in Figure 2. See Table 1 for further information on yields, colors, quantity of metal salts utilised, and m.p. of the compounds resulting.

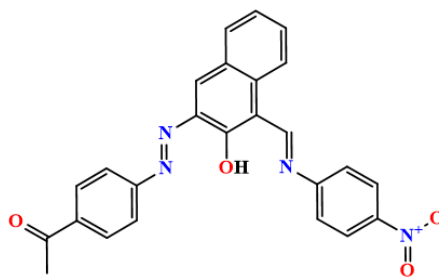


Figure 1: Chemical structure of Azo-Schiff ligand.

4 MICROBIOLOGICAL EVALUATION

The susceptibility of bacteria and fungi to the generated chemicals has been assessed utilising the Kirby-Bauer disk diffusion method. Organism colonies were suspended in an 85% sodium chloride solution to achieve a turbidity comparable to 0.5 McFarland standard. over the surface of Mueller Hinton agar in a Petri dish, this suspension was evenly spread. Wells on the agar were created with uniform spacing and concentration. In each well, 100 ml of the test sample diluted to 1 mg/ml DMSO was

Table 1: Yield, colors, metal salts quantites and m.p. of compounds.

compounds	Weight of metal salt(g)	Weight of complex(g)	Colour	m.p.°C	Yield (%)
[Co(L)H ₂ O]Cl	0.16	0.37	Brown	>300*	61.48
[Ni(L)H ₂ O]Cl	0.16	0.37	Green	>300*	52.83
[Cu(L)Cl(H ₂ O) ₂]	0.16	0.39	Dark Brown	>300*	63.32

Table 2: Microanalysis and physical characteristics of compounds.

compounds	Molecular Formula	M.Wt	Micro analysis found, (calculated)%				
			C	H	N	M	Cl
[Co(L)H ₂ O]Cl	C ₂₅ H ₁₉ ClCoN ₄ O ₅	549.83	(54.61) 54.15	(3.48) 3.11	(10.19) 10.00	(10.72) 10.24	(6.45) 6.23
[Ni(L)H ₂ O]Cl	C ₂₅ H ₁₉ ClNiN ₄ O ₅	549.59	(54.64) 54.15	(3.48) 3.29	(10.19) 10.08	(10.68) 10.19	(6.45) 6.12
[Cu(L)Cl(H ₂ O) ₂]	C ₂₅ H ₂₁ ClCuN ₄ O ₆	572.46	(52.45) 52.22	(3.70) 3.36	(9.79) 9.23	(11.10) 11.00	(6.19) 6.03

 Table 3: FT-IR data of the most prominent peaks (cm⁻¹).

Compounds	ν (C=O) ν (C=N)	ν (C=C)	ν N=N	ν C-O ν C-N	ν (H ₂ O) ν (M-OH ₂)	ν (M-O) phenoli	ν M-N	ν M-Cl
[Co(L)H ₂ O]Cl	1678 1618	1539 1504	1475	1382 1263	3452 752	661	474 420	-
[Ni(L)H ₂ O]Cl	1674 1618	1593 1539 1500	1454	1382 1263	3412 746	621	482 451	-
[Cu(L)Cl(H ₂ O) ₂]	1674 1618	1597 1541 1502	1465	1359 1265	3439 742	684	499 418	287

added. After incubating, zones of inhibition were evaluated for 24 hours at 37°C and compared to reference values [21]. Control experiments using DMSO solutions confirmed the absence of intrinsic anti-microbial activity. Any of the tested bacteria or fungus.

5 RESULTS AND DISCUSSION

The Azo-Schiff Base ligand (1-(4-((E)-(3-hydroxy-4-((E)-((4-nitrophenyl)imino)methyl)naphthalen-2-yl) diazenyl) phenyl) ethan-1-one)) (HL). 4-nitroaniline and ((E)-3-((4-acetylphenyl)diazenyl)-2-hydroxy-1-naphthaldehyde) reacting in EtOH at a one-to-one ratio. As a tridentate species the ligand functions, supplying the azo's nitrogen atom, hydroxyl and nitrogen imine as donor atoms. The interaction of the ligand with the chlorides of metal of cobalt(II), nickel(II), and copper(II), occurs in a mole ratio of one to one (Ligand to Metal) resulted in the isolation of four and six-coordinate monomeric

compound of the universal formula [M(L)H₂O]Cl with cobalt(II), nickel(II), [M(L)Cl(H₂O)₂] with copper(II) ion Figure 2. The isolated compounds exhibit stability in the air, exist as solids, and are soluble in DMSO and DMF. However, it is not soluble in other common organic solvents. Based on their physico-chemical data, complexes' coordination geometries and complexation behavior were assumed.

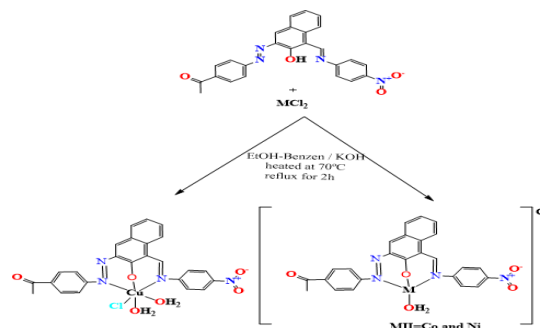


Figure 2: General route for the synthesis of HL complexes.

Results shown in Table 2 are well suited to the proposed formula. Conductance measurements of the compounds in dimethylsulfoxide solutions showed that the complexes are electrolytic and non-electrolytic. The entity of Azo-Schiff Base ligand was confirmed by C, H, N, M Table 2, Fourier transform infrared spectroscopy Table 3, Electron spectroscopy Table 4.

5.1 FT-IR and NMR Data

In Table 3 the main IR bands of the complexes with their duties have been listed. The peak is observable in the ligand spectrum at 3408 cm^{-1} due to $\nu(\text{OH})$ stretching vibration of the phenol hydroxyl group [22]. at 1624 and 1487 cm^{-1} . The noted bands correspond to stretching of the imine group $\nu(\text{C}=\text{N})$ and the stretching of the azo group $\nu(\text{N}=\text{N})$, respectively [23]. The complex spectrum had a noticeable extent between 1618 and 1614 cm^{-1} . which is related to $\nu(\text{C}=\text{N})$. Interaction between the metal ion and the $\nu(\text{C}=\text{N})$ imine group is explained by the bands that form upon complexation [22]. Band observed at 1487 cm^{-1} in HL, which belongs to the azo group $\nu(\text{N}=\text{N})$ [20], [22]. It was displaced and appeared at 1475 , 1454 and 1465 cm^{-1} in the five complexes in order. The occurrence might have been associated with the interaction of the nitrogen atom in complexation. In addition, the spectra of the metal complex exhibited novel bands in the region of (684 – 621) and (499 – 418) cm^{-1} that hadn't been apparent in the ligand spectra attributed to $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{N})$, and $\nu(\text{M}-\text{Cl})$, respectively [22], [23]. Finally, the complexes of cobalt(II), nickel(II), and copper(II) showed peaks at (3452), (3412) and (3439) cm^{-1} , respectively. were bound to aqua molecules. At 752 , 746 and 742 cm^{-1} , complex bands 1,2 and 3 can be found. These are linked to water-coordinated $\nu(\text{M}-\text{O})$ for 1,2 and 3 [24], [25]. The identification of peaks in the nuclear magnetic resonance spectra according to the numbering method illustrated in (Fig. 1). The spectrum ^1H -NMR of ligand with dimethyl sulfoxide- d_6 as a solvent, is seen in (Fig. 3). The chemical shift at $\delta 9.68\text{ ppm}$ (s, 1H), attributed to the phenolic proton $H_{(a)}$. The chemical shift that showed as a singlet signal at 8.54 ; 8.45 ppm (s, 1H), which equivalent to $H_{(b)}$ and $H_{(c)}$ protons, respectively. The spectrum shows doublet signal refers to $H_{(g,g-)}$ at 8.35 (d, $J = 9.1\text{ Hz}$, 2H). The signal reveals as doublet at 8.32 (d, $J = 8.7\text{ Hz}$, 2H) attributed to $H_{(l,l-)}$ when the frequency value 8.09 (d, $J = 8.1\text{ Hz}$, 2H) belongs to $H_{(h,h-)}$ proton. The doublet signal of attributed to

$H_{(m,m-)}$ displays at 7.72 (d, $J = 7.9\text{ Hz}$, 2H). The value of $H_{(d)}$ appear as a triplet signal at 7.48 (t, $J = 7.5\text{ Hz}$, 1H). The value of $H_{(f)}$ appear as a triplet signal at 7.39 (t, $J = 7.5\text{ Hz}$, 1H). when another doublets signals displayed at 7.00 (d, $J = 9.2\text{ Hz}$, 2H); 6.77 (d, $J = 9.6\text{ Hz}$, 1H) belongs to $H_{(j,k)}$ protons. The aliphatic region revealed a singlet peak along with a set of three singlet peak belongs to $H_{(i)}$ protons appeared at 2.60 ppm . The spectrum displayed peaks at 2.51 and 3.37 ppm , corresponding to the DMSO- d_6 solvent as well as the quantity of water molecules in the solvent, respectively. Figure 4 shows the ^{13}C nuclear magnetic resonance spectrum in DMSO- d_6 , which shows the correct number of carbon atoms in a molecule. Resonances at $\delta\text{c} = 197.11$ and 177.23 ppm were assigned to $:(\text{ketonic } C_v)$; (iminic C_b), respectively. The Signal of phenolic carbon (C_p) was detected at 172.74 ppm . Resonances assigned for N- (C_n), was observed at 150.10 ppm , when the other N- (C_q) chemical shifts appeared at 147.06 ppm . The signals displayed at 138.92 ppm was related to (C_r). The peak which related to (C_s), showed with 134.54 ppm frequency, when the other two peaks which revealed at 133.55 ; 128.94 ppm belongs to carbon nucleuses ($C_{x,w}$). The peak displayed at 127.46 ppm attributed to (C_c). The four couples set groups of Carbon nucleuses of ($C_{g,g-}$); ($C_{m,m-}$); ($C_{l,l-}$); ($C_{h,h-}$), assigned at 127.34 , 126.20 , 125.72 and 124.57 ppm . Resonance of (C_j) signals appears at 122.82 ppm . The assignment of (C_k) resonance appeared at 122.31 ppm , when the resonance of (C_i) appeared at 121.63 ppm . The two carbon atoms ($C_{f,d}$) displayed at 121.25 ; 117.70 ppm . The signal which related to (C_u) detected at 109.62 ppm . The methyl group, (C_i) appeared as a one peak at 27.15 ppm , when the solvent signals of the DMSO- d_6 resonances appeared at 40.17 ppm [26]–[29].

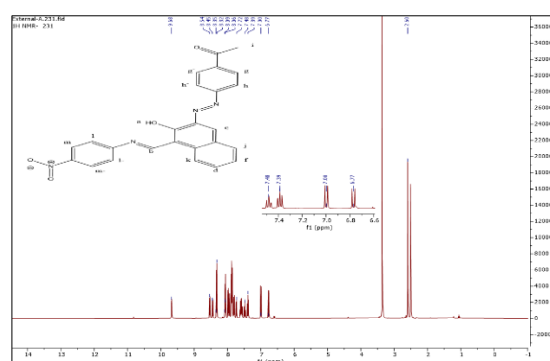


Figure 3: ^1H -NMR spectrum in DMSO- d_6 solutions of Azo-Schiff ligand.

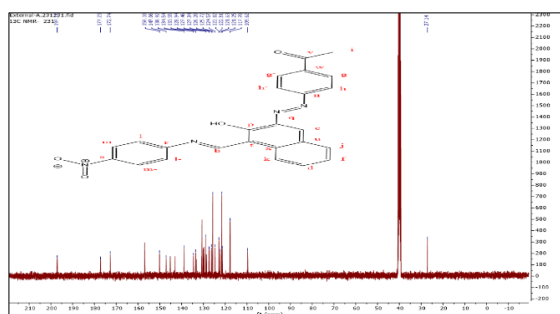


Figure 4: ^{13}C -NMR spectrum in DMSO- d_6 solutions of Azo-Schiff ligand.

5.2 Mass Spectrum

Mass spectrum HL was obtained by electron scattering positive mass spectroscopy, spectrum in Figure 5 showed the presence of a parent ion molecule (M-H^+) at $m/z=437.55\text{amu}$ (1%) determined for $\text{C}_{25}\text{H}_{18}\text{N}_4\text{O}_4$, which requires 438.13 amu. The fragmentation pattern ligand shown in Figure 6.

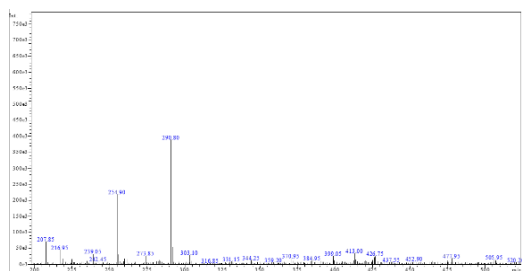


Figure 5: The electrospray (+) mass spectrum of ligand.

5.3 Electronic Spectra and Magnetic Moment

Magnetic moment and UV-visible is summarised in Table 4. Electron spectra of the complexes showed characteristic peaks in the range 257-298nm, indicating transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. Further, Charge transfer phenomena allow for the observed peaks in an array between 314-481nm [30], [31]. For the Co(II) complex, the spectrum exhibits bands at 676 nm of the d-d region that correspond with the transition $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{p})$. A four-coordinate complex suggested by these bands indicates a tetrahedral geometry around the ion of Co(II). The value of magnetic moment: 4.64 BM, agrees with a tetrahedral arrangement around the Co ion [30], [32]. The Ni(II) complex exhibits peaks at 400 nm and 522 nm, specified for $^1\text{A}_1\text{g} \rightarrow ^1\text{B}_1\text{g}$ and $^1\text{A}_1\text{g} \rightarrow ^1\text{A}_2\text{g}$, indicate the geometry of around the Ni atoms was square planar. Finally, the Cu(II) complex has a peak

at 498 nm, ascribed to the $^2\text{B}_{1\text{g}} \rightarrow ^2\text{A}_{2\text{g}}$ transition, which suggests a distorted octahedral geometry surrounding the ion Cu. The magnetic moment value for ion Cu(II): 1.83 BM is consistent with this structural interpretation [30], [32].

5.4 Biological Activity

By using *Tetracycline* as a reference medication. were utilised four bacterial strains to evaluate the antibacterial activity of the synthesised ligand along with their metal complexes: (*Escherichia coli* and *Proteus mirabilis* (G-)) and also (*Staphylococcus aureus* and *Bacillus cereus* (G+)). Control experiments separately using dimethyl sulfoxide showed the absence of any intrinsic antibacterial effects [33]-[35]. Table 5 shows the inhibiting area's diameters have been in comparison with those of the antibiotic syntriaxone. The main results were:

- 1) HL shows antibacterial activity against (*Escherichia coli* and *Proteus mirabilis* (G-)), (*Staphylococcus aureus* and *Bacillus cereus* (G+)).
- 2) The Co(II) complex exhibited greater potency against the tested strains.
- 3) The metal complexes of HL exhibited significant antibacterial activity comparable to *Tetracycline*, this might result in potential biological uses of the synthesised compounds.

Antifungal testing has been performed on the yeast (*Candida albicans*), utilising fluconazole as the reference medication. DMSO controls did not exhibit antifungal activity [36]-[39]. The observed antifungal activity The values for the tested substances have been shown in Table 6. The subsequent findings have been discerned:

- 1) Against *Candida albicans*. All substances exhibited antifungal activity.
- 2) Complexity substantially enhanced the antifungal activity of the free ligand, possibly as a result of the chelate process.
- 3) *Fluconazole* has shown greater effectiveness than complexes against *Candida albicans*.

Table 6: The Demonstrates of antifungal inhibition (mm) zones of ligand and the compounds.

Compounds	<i>Candida albicans</i>
DMSO	-
<i>Fluconazole</i>	9
HL	10
$[\text{Co}(\text{L})\text{H}_2\text{O}]\text{Cl}$	18
$[\text{Ni}(\text{L})\text{H}_2\text{O}]\text{Cl}$	15
$[\text{Cu}(\text{L})\text{Cl}(\text{H}_2\text{O})_2]$	17

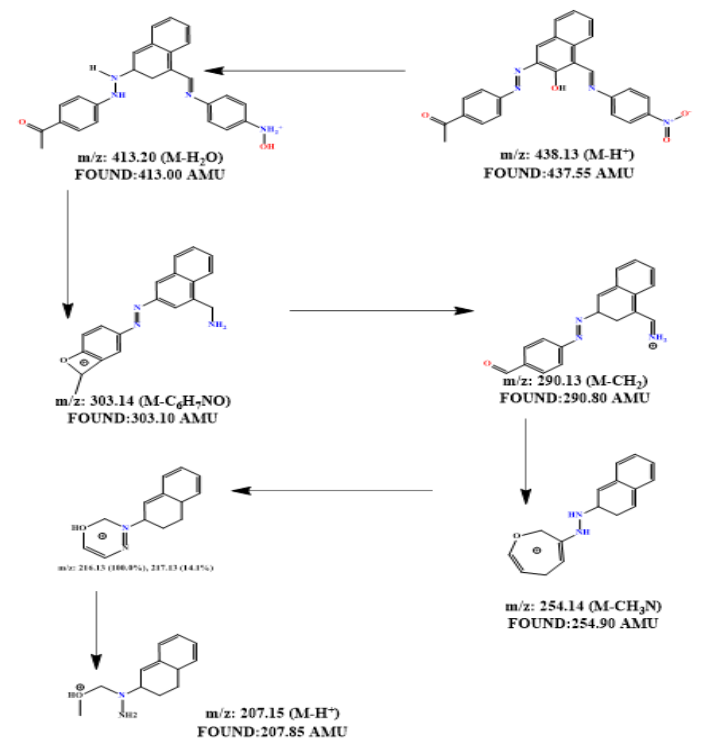


Figure 6: The fragmentation pattern ligand.

Table 4: Displays Uv-vis data for complexes in DMSO solutions.

Complex	λ_{nm}	Molar extinction coefficient ϵ_{max} ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	Assignment	Suggested Geometry
[Co(L)H ₂ O]Cl	279	1680	Intra-ligand $\pi \rightarrow \pi^*$,	Tetrahedral
	389	1780	$n \rightarrow \pi^*$	
	481	1190	C.T	
	676	1	C.T	
[Ni(L)H ₂ O]Cl	257	1820	$^4 A_2 (F) \rightarrow ^4 T_1 (p)$	Square planar
	314	241	Intra-ligand $\pi \rightarrow \pi^*$,	
	400	190	$n \rightarrow \pi^*$	
	522	105	C.T	
[Cu(L)Cl(H ₂ O) ₂]	298	1790	$^1 A_1 g \rightarrow ^1 B_1 g$	Distorted octahedral
	320	256	$^1 A_1 g \rightarrow ^1 A_2 g$	
	498	80	Intra-ligand $\pi \rightarrow \pi^*$,	
			$n \rightarrow \pi^*$	

Table 5: It shows the areas of antibacterial activity (mm) for HL and compounds.

Compounds	<i>Bacillus cereus</i> (G+)	<i>Staphylococcus aureus</i> (G+)	<i>Proteus mirabilis</i> (G-)	<i>Escherichiacoli</i> (G-)
DMSO	-	-	-	-
Tetracycline	30	27	14	14
HL	14	18	10	16
[Co(L)H ₂ O]Cl	21	16	12	22
[Ni(L)H ₂ O]Cl	16	21	17	17
[Cu(L)Cl(H ₂ O) ₂]	16	20	16	18

6 CONCLUSIONS

The Azo-Schiff ligand (HL) along with its metal complexes with cobalt(II), nickel(II), and copper(II) have been reported. The ligand HL was synthesised from reaction of the 4-nitroaniline with ((E)-3-((4-acetylphenyl)diazenyl)-2-hydroxy-1-naphthaldehyde) in a mole ratio one-to-one. The interaction of ligand with metal ions at a ratio (one-to-one) ligand-to-metal generated isolated compounds, they have been structurally characterised via several Physical and chemical techniques involve elemental microanalysis, ¹H and ¹³C-nuclear magnetic resonance, Fourier transform infrared spectroscopy, electronic and mass spectroscopy, as well as magnetic susceptibility, Conductivity measurements and Biological Activity. The ligand Prepared had yield (58.09%), having a melting point among 170-172°C, As for the complexes resulting from the reaction of the ligand with metal chlorides, the melting point was higher than 300°C for all complexes. The FTIR of ligand displayed characteristic peaks for phenolic, carbonyl, imine and azo groups. Complexation resulted in carbonyl peak shifts, indicating back-bonding, with additional bands related to the $\nu(\text{M-N})$, $\nu(\text{M-O})$ and $\nu(\text{M-OH}_2)$ observed in the complex spectra. Mass spectrum of ligand showed the presence of a parent ion molecule ($\text{M}+\text{H}^+$) at $m/z = 437.55\text{amu}$, measured for $\text{C}_{25}\text{H}_{18}\text{N}_4\text{O}_4$, which requires 438.13 amu. The UV/Vis indicates a tetrahedral geometry around the ion of Co(II), Square planar geometry around the Ni(II) complex and the Cu(II) complex which suggests a distorted octahedral structure. The value of magnetic moment is 4.64 and 1.83 BM for Co and Cu, respectively, this explanation agrees to the electron spectra of the complexes. At last, anti-bacterial and anti-fungal assays demonstrated enhanced bioactivity for the complexes produce a comparison to free ligand, emphasising the plus-side outcomes of complex formation.

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