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Synthesis, Characterisation and Biological Evaluation of Metal Complexes from Thiosemicarbazone

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ABSTRACT: The synthesis of a new azo-Schiff base ligand derived from a thiosemicarbazide molecule and its coordination compounds are mentioned in this work. The ligand, ((E)-2-((2-hydroxy-3-((E)-(3-nitrophenyl) diazenyl) naphthalen-1-yl) methylene) hydrazine-1-carbothioamide) (HL), was synthesised by the condensation reaction of ((E)-2-hydroxy-3-((3-nitrophenyl) diazenyl)-1-naphthaldehyde)) with a thiosemicarbazide in a 1:1 molar ratio. The isolation of monomeric coordination compounds was achieved by reacting the ligand (HL) with metal chlorides of Cr (III), Mn (II), Co (II), Ni (II), and Cu (II) in a 1:1 ligand: metal ratio. These compounds (ligand and coordination compounds) were fully characterised using spectroscopic analytical tools including elemental microanalysis, 1H and 13C-NMR, FT-IR, electronic and mass spectroscopy, magnetic behaviour, and molar conductance measurements. The characterisation results confirmed the entity of the ligand and its coordination compounds that adopt four and six coordinates. The antibacterial activity of the ligand and its coordination compounds towards phathagens (bacteri and fungus strains) showed the coordination compounds enhanced the activity, compared to the free ligand.

Keywords: Schiff base; complexes, ligand; 2-hydroxy-1-naphthaldehyde; Antimicrobial.

1. INTRODUCTION

A primary amine is typically condensed with a carbonyl molecule (ketone or aldehyde) to create Schiff bases that include azomethine (-C=N-). One of the most popular organic combinations is Schiff bases. They are widely used in numerous disciplines, such as analytical, biological, and inorganic chemistry [1,2]. A large class of physiologically active substances includes thiosemicarbazones and related metal complexes.[3].Mixed-ligand complexes of transition metals containing ligands with N, S donors are known to exhibit interesting stereochemical, electrochemical, and electronic properties[4,5]. Thiosemicarbazones have emerged as an important class of sulfur ligands particularly for transition metal ions. Schiff bases with an azo group are not only significant in biological systems but also used in the manufacturing of catalysts [6], pigments and dyes [7], intermediates, and polymer stabilizers [8], corrosion inhibitors [9]. Furthermore, they are employed in ion-selective electrodes for ion sensing [10-12]. In this work, we report the synthesis and structural characterization of a thiosemicarbazone ligand and its metal complexes. The synthesis process involves two steps: firstly, preparing the azo species ((E)-2-hydroxy-3-((2 nitrophenyl) diazenyl)-1-naphthaldehyde) (L) and subsequently reacting it with thiosemicarbazide to produce the target ligand HL. Recently, we reported the synthesis of azo and their complexes [13-15]. The reaction of this ligand with various metal ions (Cr^{III}, Mn^{II}, Co^{II}, Ni^{II}, and Cu^{II}) in a 1:1 ligand-to-metal ratio, results in the creation of paramagnetic complexes that are monomeric. In this study, the synthetic compounds' antibacterial and anti-fungal characteristics were also investigated.

2. Experimental

2.1 MATERIALS AND METHODS

The NMR spectra of the ligand, both proton (^{1}H) and carbon (^{13}C-NMR), were recorded on a Bruker 400 MHz spectrometer using DMSO-d_6 as the solvent. The frequencies for these measurements were 400 MHz for ^{1}H and 100 MHz for ^{13}C, with tetramethylsilane (TMS) being utilized as the internal standard. The FT-IR spectra were obtained using potassium bromide pellets and recorded with an FTIR-600 Fourier Transform Infrared Spectrometer across a spectral range of 4000 to 200 cm^{-1}. Positive-ion electrospray mass spectrometer analyses were performed on a Sciex ESI mass spectrometer. The melting points of substances were identified using a Stuart SMP40 electrothermal device. UV-visible spectra were collected in the spectral range of 1000 to 200 nm using a Shimadzu UV-160A spectrophotometer, with the solutions prepared in DMSO at a concentration of 10^{-3}mol L^{-1} and examined in a 1 cm quartz cuvette at room temperature. The conductivity of the solutions, with concentrations varying from 10^{-3} to 10^{-5} M in DMSO, was measured at 25 °C using a CyberScan CON 510 digital conductivity meter from Eutech Instruments. For elemental (C, H, N) and metal content analysis, a HeraeusVario EL and a Shimadzu AA-7000 atomic absorption spectrometer were employed. The quantification of chloride ions in the compounds was executed via potentiometric titration with a Metrohm 686 Titro Processor and a 665 Dosim unit. Lastly, the magnetic properties were determined at 30 °C by a magnetic balance from Johnson Matthey.

2.2 SYNTHESIS

There are two steps that involved in the synthesis of the azo Schiff ligand:

A- SYNTHESIS of ((E)-2-hydroxy-3-((3-nitrophenyl)diazenyl)-1-naphthaldehyde)) (L)

The preparation of L was based on a reported method [16,17] as follows;

In a charged 250ml round-bottom flask with *m*-nitroaniline (1.38g,10 mm) and sodium nitrite (0.69g, 10mm) was added 20ml of a mixture of ethanol-water (10-10). In an icy bath, the mixture was chilled to between 0 and 5°C. Subsequently, 3ml of hydrochloric acid (36%) was mixed for an hour, and 10 milliliters of water were added dropwise while stirring. This process yielded a diazonium salt solution, which was then reacted with a cooled mixture that contained 2-hydroxy-1-naphthaldehyde (1.72g, 10 mm) and Sodium hydroxide (0.4g, 10 mm) in 20 ml of EtOH. For two hours, the reaction mixture was left to agitate. Following the reaction, after being filtered at pH=4, the precipitate was repeatedly washed. with cold water. It was then left to dry until the pH was adjusted to 6-7. The final orange-red precipitate was filtered out, given a 5-milliliter cold ethanol wash, and allowed to air dry. Yield: 2.7g (84.11%), with a melting point of 159-161°C.

B- SYNTHESIS OF ((E)-2-((2-hydroxy-3-((E)-(3-nitrophenyl)diazenyl) naphthalen-1-yl) methylene) hydrazine-1-carbothioamide) (HL)

The synthesis of HL was conducted following a standard procedure outlined in reference [18]. Initially, a mixture containing thiosemicarbazide(0.14g, 1.56mm) in 10ml of hot methanol, with the addition of three drops of glacial acetic acid, was combined with of ((E)-2-hydroxy-3-((3-nitrophenyl)diazenyl)-1-naphthaldehyde))) (0.5g,1.56mmol), which was previously dissolved in a 20ml solution of benzene: ethanol mixture at a 1:1 ratio. After that, the reaction mixture was heated for six hours to a temperature of between 70 and 80°C. After the heating period, the solution was filtered while still hot. Subsequently, At room temperature, the mixture was allowed to cool and slowly evaporate. The resulting red precipitate, which formed upon cooling, was collected, separated from the solution, and then recrystallized from ethanol. The final product was air-dried. The yield of HL was 0.44g (71.68%), with a melting point of 197-199ºC, **Figure 1.** ^{1}H NMR ^{1}H NMR (400 MHz, DMSO-$_6$, ppm) δ 11.22(1H, s, O-*H*), 10.27*(1H, s, NH)*,9.750-9.005*(1H, s, -N=C$_2$-H)*,8.684-8.614 *(1H, s, C$_9$-H)*,8.538-8.521 *(2H,d,C$_{13}$,-H, J=7.5Hz)*,8.393-8.320*(1H, s, C$_{17}$-H)*, 8.2838-8.210*(3H, m, C$_{5,5}$-H)*,8.189-8.123*(3H, m, C$_{14}$-H)* ,8.072-8.005*(3H, m, C$_{15}$-H)*,7.899-7.836*(2H, d, C$_6$-H)*,7.710*(2H, d, C$_7$-H)*,5.047*(NH$_2$)*.The ^{13}C-NMR (100 MHz, DMSO-d_6, ppm) **Figure 2**.The spectrum indicated resonances at δ =173.33,164.91,149.28-149.09,145.95,142.25,133.02,131.57-131.38, 130.75-130.02, and 129.64ppm are allocated to (C_{17}), (C_{12}), (C_2), (C_{13}), (C_{11}),(C_{15}) (C_4),(C_{10}) and (C_{16}), respectively. Resonances recorded at 128.78-128.62, 127.19, 125.18, 124.76, 122.12, 121.40, 119.97, and 113.01ppm were assigned (C_9), (C_8), (C_6), (C_7), (C_{14}), (C_{18}), (C_5) and (C_3), respectively. Peak at δ_c =181.63ppm were related to(C=S). The spectrum revealed a peak at 40.59-39.33ppm which is associated with the solvent (DMSO-d_6), **Figure 3.**

2.3 SYNTHESIS OF COMPLXEXS

Complexes were synthesized using a method similar to that implemented for the synthesis of the Cr^{III} complex. The procedure is as follows:
In a 100ml round-bottomed flask, (0.2g, 0.507mmol) of HL was dissolved in 10ml of ethanol. To this solution, a 10ml ethanoic solution of KOH (0.056g, 1.01mmol) was added. The mixture was stirred, followed by the drop-wise addition of a solution of $CrCl_3.6H_2O$ (0.089g, 0.507mmol) in 5ml ethanol. The reaction mixture was then heated under reflux for 2 h. After heating, after filtering out the solid, the residue was cleaned with cold ethanol and allowed to air dry. The yield of the Cr^{III}-complex was 0.15g (57.69%) with a melting point exceeding m.p.244-246°C.This synthesis procedure is illustrated in **Scheme 1**. For additional details such as yields, colours, quantities of metal salts used, and melting points of the complexes, refer to **Table 1**

Table 1. Yields, colours, metal salts quantities and melting points of HL complexes.

Complexes	**Weight of metal salt (g)**	**Weight of complex(g)**	**Colour**	**m.p.ºC**	**Yield (%)**
[Cr(L) Cl_2.]	0.09	0.15	Greenish-brown	244-246	57.29
[Mn(L)Cl.H_2O]	0.10	0.17	Reddish-brown	285-287	66.81
[Co(L) Cl.H_2O]	0.12	0.18	Yellow	225-227	70.18
[Ni(L)] Cl	0.11	0.16	Dark Green	265-267	64.72
[Cu(L) Cl.H_2O]	0.09	0.15	Yellowish-brown	238-240	57.95

2.4 MICROBIOLOGICALTION

The antimicrobial efficacy of the synthesised compounds was performed using the Kirby-Bauer disc diffusion technique. The suspended microbial colonies were brought to a turbidity level equivalent to the 0.5 McFarland criterion using an 85% sodium chloride solution. In a Petri dish, the Mueller Hinton agar surface was equally covered with this suspension. On the agar, wells were made with consistent concentration and spacing. 100 µL of the sample, dissolved in 1 mg/mL DMSO, was added to each well. The inhibition zones were assessed and compared with standard drugs during the incubation period of 24 hours at 37 °C [19]. DMSO-based control trial solutions confirmed no inherent antimicrobial activity against any of the tested bacterial strains or fungal species. Four bacterial strains were used to assess the synthesized (HL) and its metal complexes' antibacterial activity: Staphylococcus aureus, Staphylococcus epidermidis (G+), Escherichia coli, and klebsiella species(G−) and type from the fungi species covered Candida albicaus.

3.RESULTS AND DISCUSSION

The synthesis of the azo Schiff base ligand, ((E)-2-((2-hydroxy-3-((E)-(3-nitrophenyl) diazenyl) naphthalen-1-yl) methylene) hydrazine-1-carbothioamide) (HL), was achieved by reacting (L) with thiosemicarbazide in a 1:1 molar ratio in ethanol (**Figure 1**). This multidentateazo Schiff ligand, potentially monobasic, was reacted with metal chlorides of Cr^{III}, Mn^{II}, Co^{II}, Ni^{II} and Cu^{II} in a 1:1 ligand-to-metal (L:M) molar ratio. This yielded monomeric paramagnetic coordination compounds with four and six-coordinate geometries, with general formulas [Cr(L)Cl_2], [M(L)Cl.H_2O] (where M=Mn^{II}, Co^{II} and Cu^{II}) and [Ni(L)] Cl, as shown in **Scheme 1**. The isolated monomeric complexes are air-stable solids, soluble in DMSO and DMF. The computed values and the microanalysis results, which included the compounds' metal and chloride contents, matched rather well. (**Table 2**). In DMSO solutions, molar conductance measurements revealed that the complexes are nonelectrolytes, except for the [Ni(L)]Cl complex, which demonstrated electrolytic behavior in a 1:1 ratio.

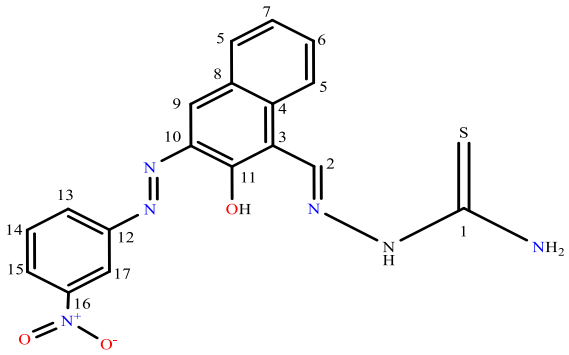
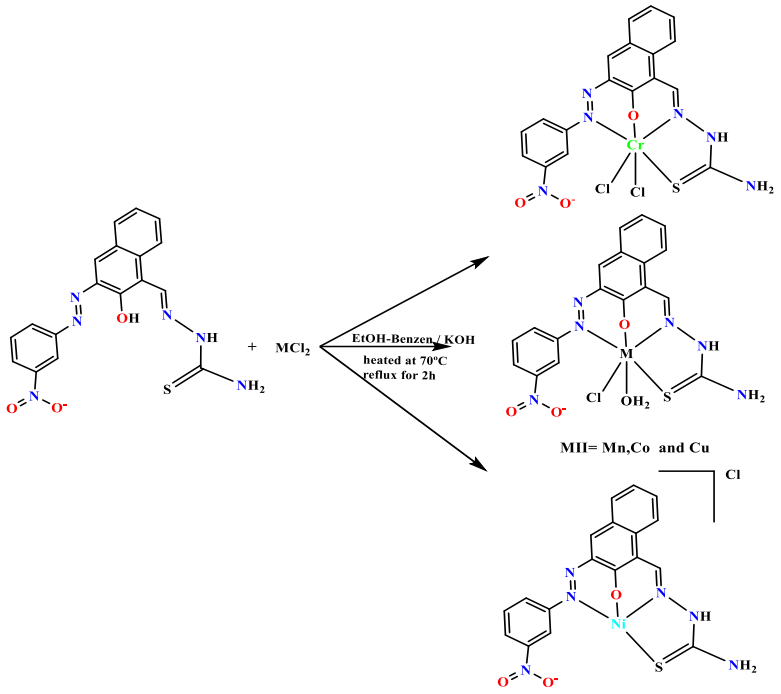


Figure 1. Chemical structure of HL.

Table 2. Microanalysis and physical characteristics of HL and its complexes.

Complex	Molecular formula	M.Wt	Micro analysis found, (calculated)%					
			C	H	N	M	S	Cl
[Cr(L)Cl_2.]	$C_{18}H_{13}Cl_2CrN_6O_3S$	516.30	(41.87) 41.19	(2.54) 2.22	(16.28) 16.04	(10.07) 9.87	(6.21) 6.00	13.73 13.73
[Mn(L) Cl..H_2O]	$C_{18}H_{15}ClMnN_6O_4S$	501.80	(43.08) 42.94	(3.01) 2.88	(16.75) 16.35	(10.95) 10.40	(6.39) 6.12	7.06 6.91
[Co(L) Cl..H_2O]	$C_{18}H_{15}ClCoN_6O_4S$	505.80	(42.74) 42.46	(2.99) 2.74	(16.62) 16.44	(11.65) 11.28	(6.34) 6.13	7.01 6.85
[Ni(L)] Cl.	$C_{18}H_{13}$ ClN_6NiO_3S	487.54	(44.34) 44.12	(2.69) 2.42	(17.24) 17.00	(12.04) 11.88	(6.58) 6.16	7.27 7.06
[Cu(L) Cl..H_2O]	$C_{18}H_{15}ClCuN_6O_4S$	510.41	(42.36) 42.18	(2.96) 2.81	(16.47) 16.28	(12.45) 12.45	(6.28) 6.10	6.95 6.43



Scheme 1: HL complexes' general synthesis route.

3.1 FT-IR and NMR data

The major bands infrared of compounds **Table 3** lists them along with their tasks. A peak could be seen in the HL spectrum at 3448 cm^{-1} because of the ν(OH) of the phenolic group [20]. The bands noticed at 1643 and 1452 cm^{-1} are due to ν(C=N) of the carbonyl group and the ν(N=N) azo group, respectively.[21]. The spectra of complexes showed a notable range at 1618-1612cm^{-1} that correlated to ν(C=N) imine. This band was observed in the spectrum of the ligand at 1643 cm^{-1}. The bands' formation upon complexation explains the metal ion's interaction with the nitrogen atom of the azomethine group ν(C=N) imine. [20]. The band observed at 1452cm^{-1} in HL which related to ν(N=N) azo group [9]. Was shifted and appeared at 1396,1448, 1450, 1450 and 1448cm^{-1}in 1,2,3,4 and 5, respectively. This could be related to how the nitrogen atom was implicated in the complexation. Furthermore, the spectra of the metal complexes revealed new bands around 599-545,462-420,362-314and 293-268 cm^{-1}, which were not seen in the spectrum of the ligand, assigned to ν(M-O),ν (M-N) ν(M-S) and ν(M-Cl) respectively [20,21]. Finally, peaks were detected at 3379, 3373 and 3394cm^{-1} in the complexes of $Mn^{(II)}$, $Co^{(II)}$and $Cu^{(II)}$, respectively. were correlated to aqua molecules. In complex 1,2,3,4 and 5, bands that were detected at 759, 757 and 757 cm^{-1} is related to ν(Mn-O), ν(Co-O) and ν(Cu-O) coordinated water [9]. The peak identifications in the NMR spectra follow the numbering scheme outlined in **Figure 1**.

The ^{1}H-NMR spectrum of the ligand dissolved in DMSO-d6 is illustrated in **Figure 2**. A singlet peak detected at δ_H11.22ppm corresponds to the hydroxyl proton (O-H) of the phenol group. The location of this peak in the downfield region might indicate the presence of intramolecular hydrogen bonding with nitrogen atoms within the molecule or intermolecular hydrogen bonding with the DMSO solvent. A singlet peak detected at δ_H10.27ppm is attributed to the hydrazonic group (N-H). Another distinct singlet peak at δ 9.750-9.005ppm corresponds to the hydrogen atom bonded to the nitrogen in the imine group (-N=C-*H*), validating the presence of an imine functional group and indicating the formation of the Schiff base. Peaks for aromatic protons are detected in the range of 8.684-7.710ppm. in the structure. The peak reported at 5.047ppm is assigned to NH_2. **Figure 3** presents the ^{13}C-NMR spectrum in DMSO-d_6, showing the correct count of carbon atoms in the molecule. The presence of a peak at 173.33 ppm is indicative of Schiff base formation, a conclusion further supported by the absence of a peak around 190 ppm, typically associated with the carbonyl aldehyde, confirming a condensation reaction has taken place. Additionally, the peak at 181.63ppm corresponds to the carbonyl (C=S) group within the semicarbazide component.

Table 3. FT-IR data of the most prominent prominent bands complexes (cm^{-1}).

Compounds	ν(N-H)$_{secoam}$	ν(N-H$_2$)$_{asy,}$	ν(C=N)	ν$_{ar}$(C=C) ν N=N	νa N-O νs N-O	ν (C=S)	ν(H$_2$O) ν(M-OH$_2$)	ν(M-O)	ν(M-N)	ν(M-S)	ν(M-Cl)
[Cr(L) Cl$_2$]	3448	3261 3165	1616	1570,1531 1396	1508 1350	1332 866	-	599	420	362	293 262
[Mn(L) Cl. H$_2$O]	3421	3263 3180	1618	1598,1552 1448	1502 1348	1317 865	3379 759	594	446 422	351	268
[Co(L) Cl.H$_2$O]	3429	3284 3178	1616	1558,1529 1450	1500 1348	1321 860	3373 757	568	439 420	349	285
[Ni(L)].Cl	3448	3261 3164	1612	1568,1531 1450	1502 1350	1332 862	-	599	439 420	333	-
[Cu(L) Cl.H$_2$O]	3413	3309 3274	1618	1556 1448	1529 1350	1350 837	3394 757	545	462 424	314	279

3.2 MASS SPECTRUM

The mass spectrum of HL was performed using an electrospray (+) mass spectroscopy, **Figure 4**. The spectrum indicated the parent ion molecule $(M-H)^+$ at m/z = 393.7 amu (2%) calculated for $C_{18}H_{13}N_6O_3S^-$ requires = 393.40 amu.

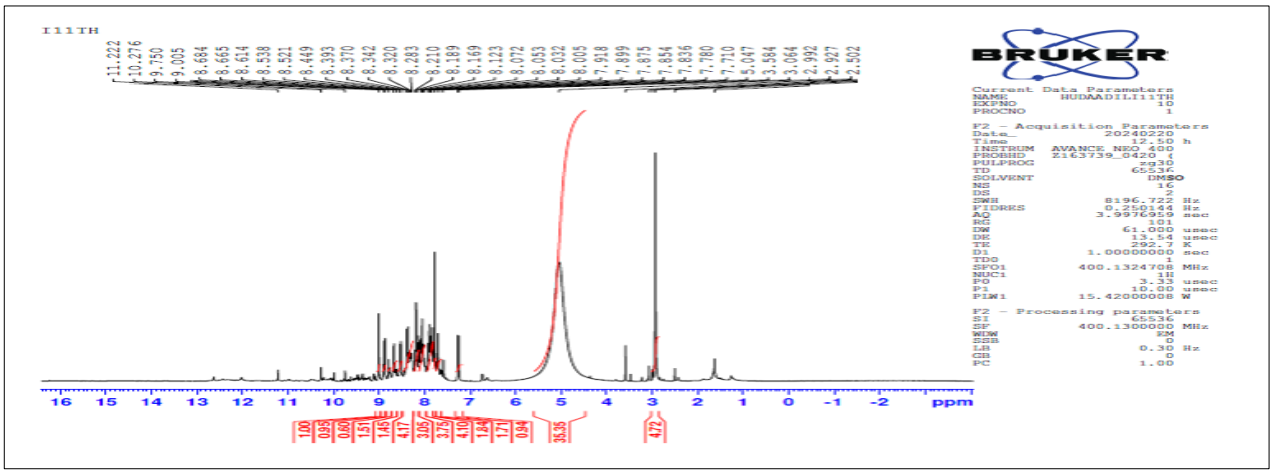


Figure 2. ^{1}H-NMR spectrum in DMSO-d$_6$ solution of HL.

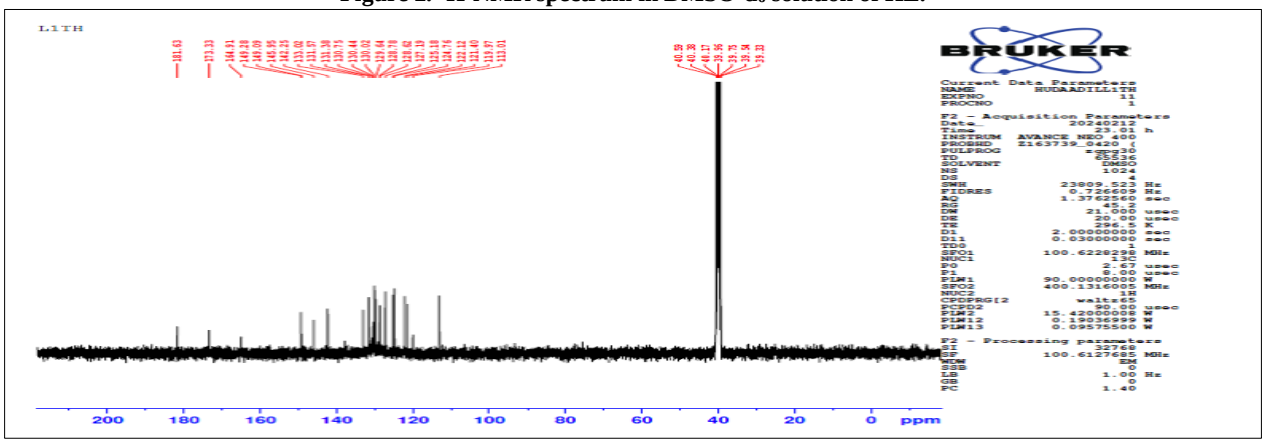


Figure 3. ^{13}C-NMR spectrum in DMSO-d$_6$ solution of HL.

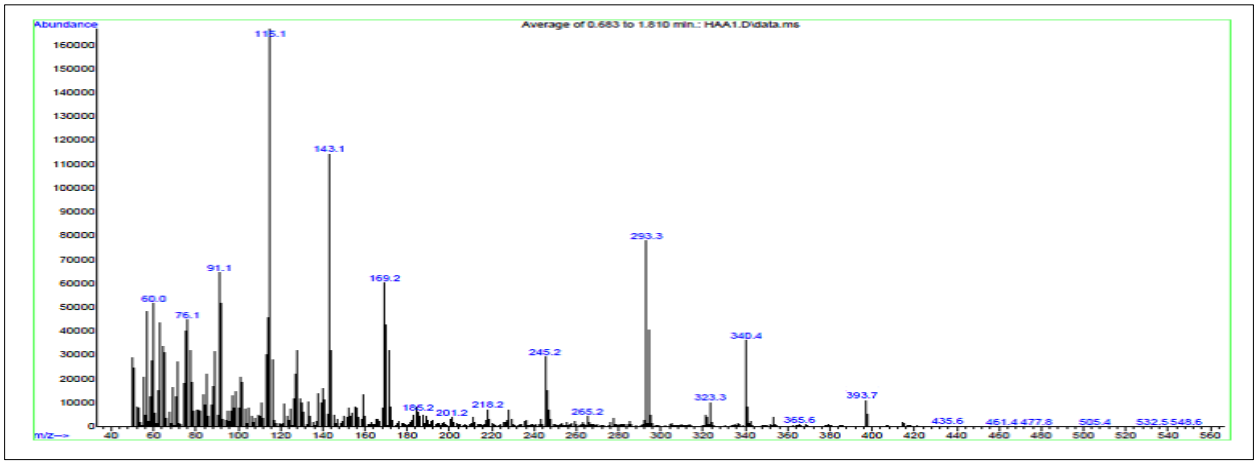
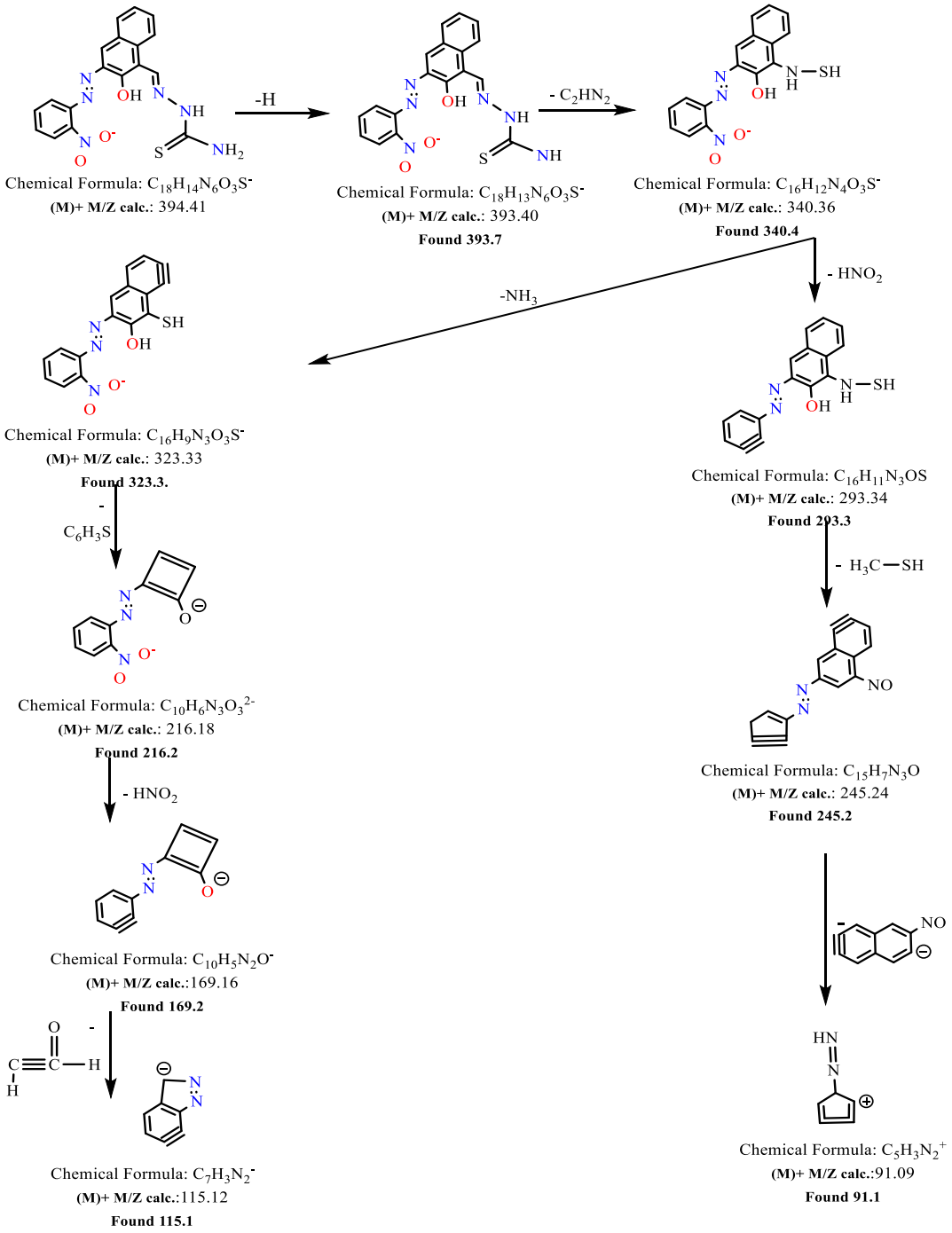


Figure 4. The electrospray (+) mass spectrum of HL.



Scheme 2: The fragmentation pattern and relative abundance of HL.

3.3 ELECTRONIC SPECTRA AND MAGNETIC SUSCEPTIBILITY

Table 4 summarizes information on magnetic moments and electronic spectra. The electronic spectra of the complexes exhibited characteristic peaks between 229-288nm, indicative of π→π* and n→π* transitions, respectively. Additional peaks observed in the range of 375-474nm were attributed to charge transfer (C.T) phenomena [22,23]. In the Cr^{III}-complex, the electronic spectrum shows a distinctive band at 500 nm corresponding to the $^4A_2g \rightarrow {}^2T_1g$, revealing a distorted octahedral structure around the Cr^{III} centre. This interpretation aligns with the magnetic moment value of 3.74 BM for the Cr^{III}-complex. The $[Mn(L)Cl.H_2O]$ complex shows a band at 990 nm in the d-d region, ascribed to the $^6A_{1g} \rightarrow {}^4T_{1g}{}^{(G)}$transition, indicative of a distorted octahedral geometry around the Mn ion. This finding is consistent with the magnetic moment measurement of 5.59 BM for the Mn^{II}-complex. For the $[Co(L)Cl.H_2O]$ complex, bands in the d-d

region at 480nm are observed, corresponding to the $^4T_{1g}{}^{(F)} \rightarrow {}^4T_{2g}{}^{(p)}$. This band suggest a six-coordinate complex with a distorted octahedral structure around the Co^{II} ion. The magnetic moment value μ_eff = 4.32 BM supports the octahedral configuration around the Co atom [23,24]. The Ni(II)-complex shows a peak at 481nm, assigned to the $^1A_1g \rightarrow {}^1A_2g$, indicative of Square planar geometry around the Ni atom. Lastly, the [Cu(L)Cl.H_2O] complex exhibits a peak at 907nm, attributed to the $^2B_1g \rightarrow {}^2A_2g$ transition, suggesting a distorted octahedral arrangement around the Cu ion. This structural interpretation is consistent with the value of the magnetic momentμ_eff = 1.83 BM for the Cu^{II}ion [23,24].

Table 4: displays the HL compounds' electronic spectra in DMSO solutions

Complex	λ_{nm}	Molar extinction coefficient ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)	Assignment	μ_eff	Suggested geometry
[Cr(L)Cl_2]	288 375 500	222 96 105	Intra-ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ C.T $^4A_2g \rightarrow {}^2T_1g$	3.74	Distorted octahedra
[Mn(L) Cl .H_2O]	255 474 990	1955 1438 11	Intra-ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ C.T $^6A_{1g} \rightarrow {}^4T_{1g}{}^{(G)}$	5.59	Distorted octahedral
[Co(L) Cl .H_2O]	274 437 480	261 113 125	Intra-ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ C.T $^4T_1g^{(F)} \rightarrow {}^4T_2g^{(p)}$	4.32	Distorted octahedral
[Ni(L)] Cl	287 481	192 93	Intra-ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ $^1A_{1g} \rightarrow {}^1A_{2g}$	Diamagnetic	Square planar
[Cu(L) Cl. H_2O]	229 437 471 907	721 514 482 8	Intra-ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ C.T C.T $^2B_1g \rightarrow {}^2A_2g$	1.83	Distorted octahedral

4. BIOLOGICAL ACTIVITY

1. Four bacterial strains were used to assess the synthesized (HL) and its metal complexes' antibacterial activity: *Staphylococcus aureus*, *Staphylococcus epidermidis (G+)*, *Escherichia coli, and klebsiella species(G−)*, using Norfloxacin (NOR10), Cefriaxone (CR30), Cefoxitin (FOX30), AMPicillin (AM10) and Tetracycline (TE30) as a standard drug. Separate control experiments with DMSO confirmed it had no inherent antimicrobial effects [25]. The inhibition zone diameters were compared to the antibiotic Norfloxacin (NOR10), Cefriaxone (CR30), Cefoxitin (FOX30), AMPicillin (AM10) and Tetracycline (TE30), as shown in **Table 5, Figure 5 to 8**.

. The key findings were:

1. The ligand exhibits antibacterial activity against *klebsiella species.*
2. Staphylococcus aureus and klebsiella species are two bacteria that the Cr^{III} -complex is active against.
3. Escherichia coli and Klebsiella species are among the microorganisms that the MnII and NiII-complexes show antibacterial action against.
4. The CuII-complexe exhibits antibacterial activity against *klebsiella species, Staphylococcusaureus and. Staphylococcus epidermidis*
5. The CuII-complexe exhibited greater potency against the tested strains.
6. The metal complexes of HL showed a good antibacterial activity that is well-matched with Norfloxacin (NOR10), Cefriaxone (CR30), Cefoxitin (FOX30), AMPicillin (AM10) and Tetracycline (TE30), which would lead to the potential biomedical applications of the prepared complexes.

Antifungal testing was performed against the yeast Candida albicans, using Clotrimazole (CC10), Fluconazole (FLC10), AMPhotericin (AP100) and Ketoconazole (KT10) as a standard drug. Again, DMSO controls showed no anti-fungal effects [26-30]. The obtained anti-fungal activity data against tested compounds are shown in **Table 6**, **Figure 9** The following conclusions have been pointed out;

2. All compounds displayed anti-fungal effects against *Candida albicaus*.

3. Complexation significantly improved antifungal activity over free HL, likely due to chelation.
4. CoII complex had the strongest inhibitory action against *Candida albicans.*
5. Clotrimazole (CC10), Fluconazole (FLC10), AMPhotericin(AP100) and Ketoconazole (KT10)exhibited greater from complexes potency against *Candida albicans*.

Table5. Demonstrates the zones of anti-bacterial activity (mm) for HL and compounds.

Compounds	*Escherichia coli (G−)*	*klebsiella species(G−)*	*Staphylococcus aureus (G+)*	*Staphylococcus epidermidis (G+)*
DMSO	-	-	-	-
Norfloxacin NOR10	30	29	30	22
Cefriaxone CR30	16	7	-	-
Cefoxitin FOX30	-	-	-	-
AMPicillin AM10	-	-	8	7
Tetracycline TE30	18	27	32	26
HL	-	10	-	-
[Cr(L)Cl 2.]	-	11	9	-
[Mn(L) Cl.H_2O]	14	12	-	-
[Co(L)Cl.H_2O]	-	11	10	10
[Ni(L)]Cl	13	11	-	-
[Cu(L) Cl.(H_2O]	14	9	10	-

Table 6. Demonstrates the zones of antifungal inhibition (mm) for HL and compounds.

Compounds	*Candida albicaus*
DMSO	-
Clotrimazole CC10	21
Fluconazole FLC10	22
AMPhotericin AP100	12
Ketoconazole KT10	19
HL	7
[Cr(L)Cl 2.]	10
[Mn(L) Cl.H_2O]	9
[Co(L) Cl.H_2O]	13
[Ni(L)]Cl	9
[Cu(L) Cl.H_2O]	9

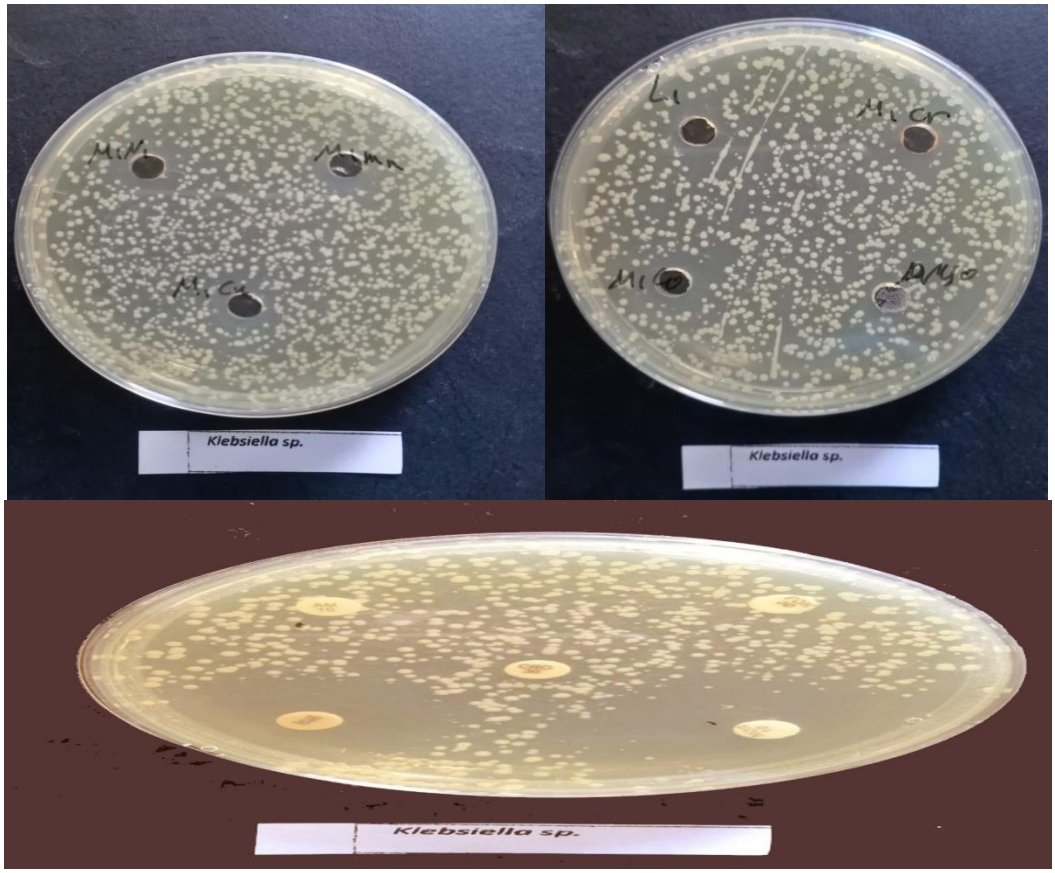


Figure 5: The biological evaluation of HL and their complexes against Kiebsiello sp

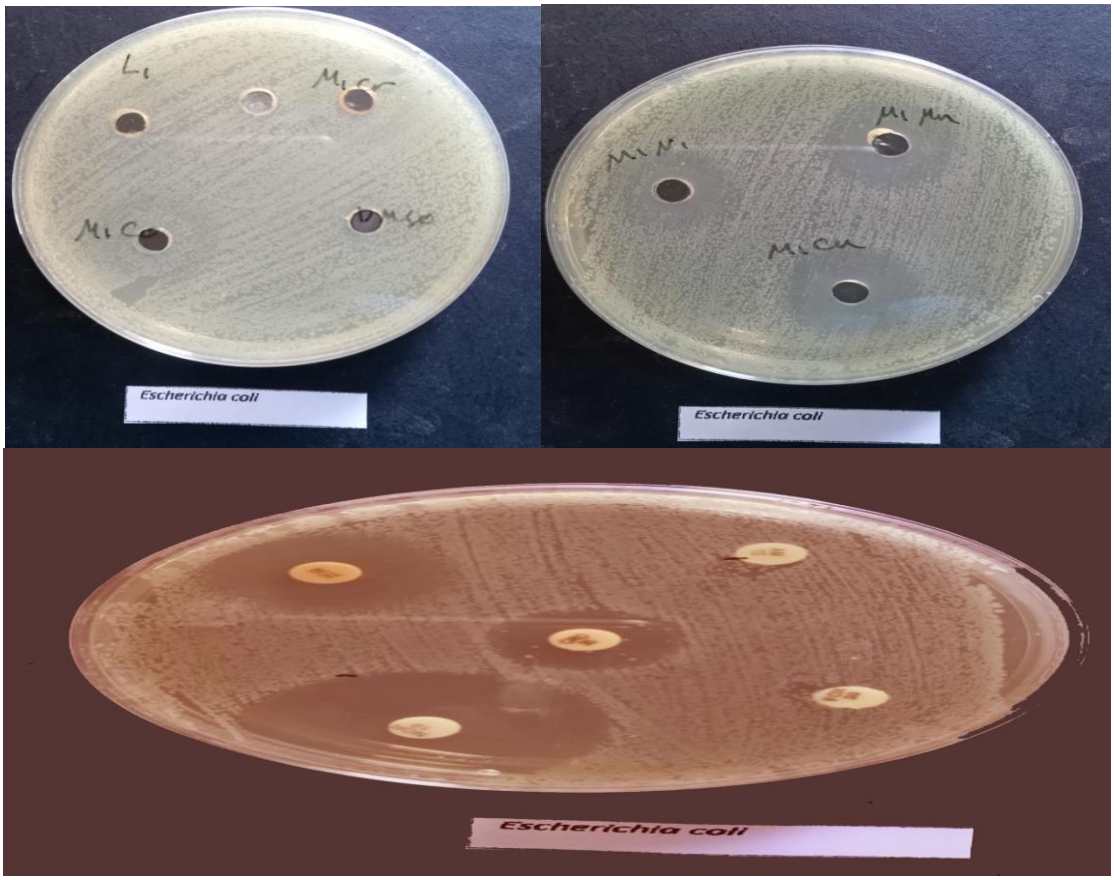


Figure 6: The biological evaluation of HL and their complexes against Escherichia cali.

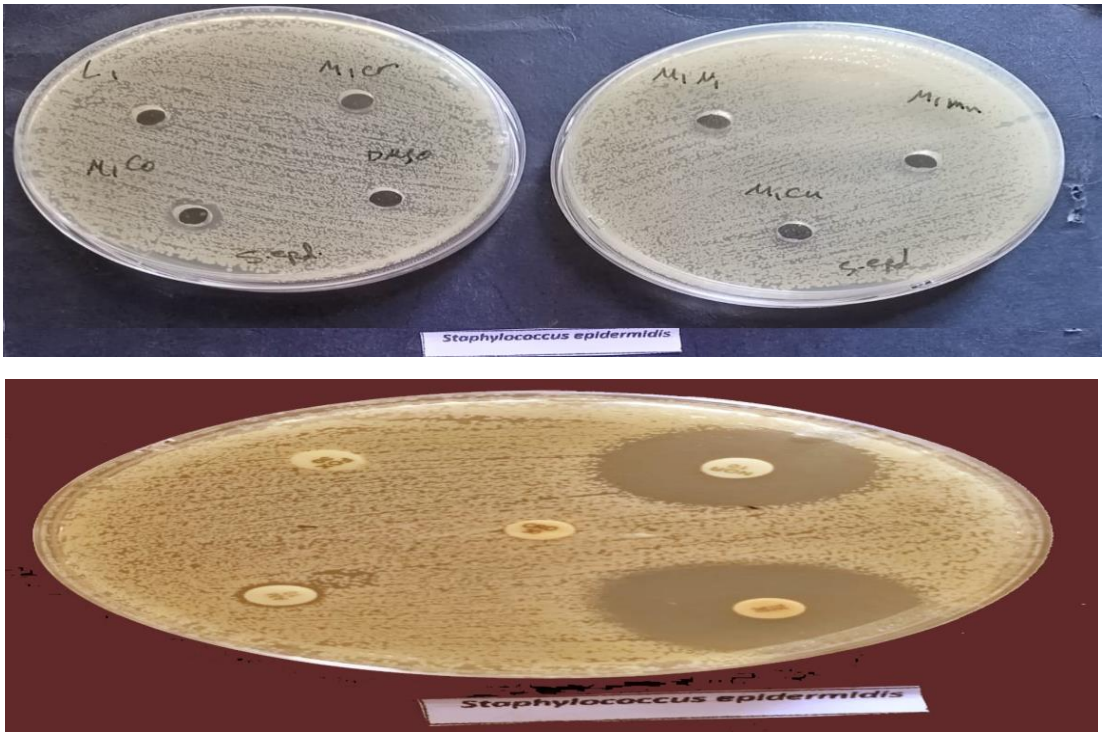


Figure 7: The biological evaluation of HL and their complexes against Staphylococcus epidermidis.

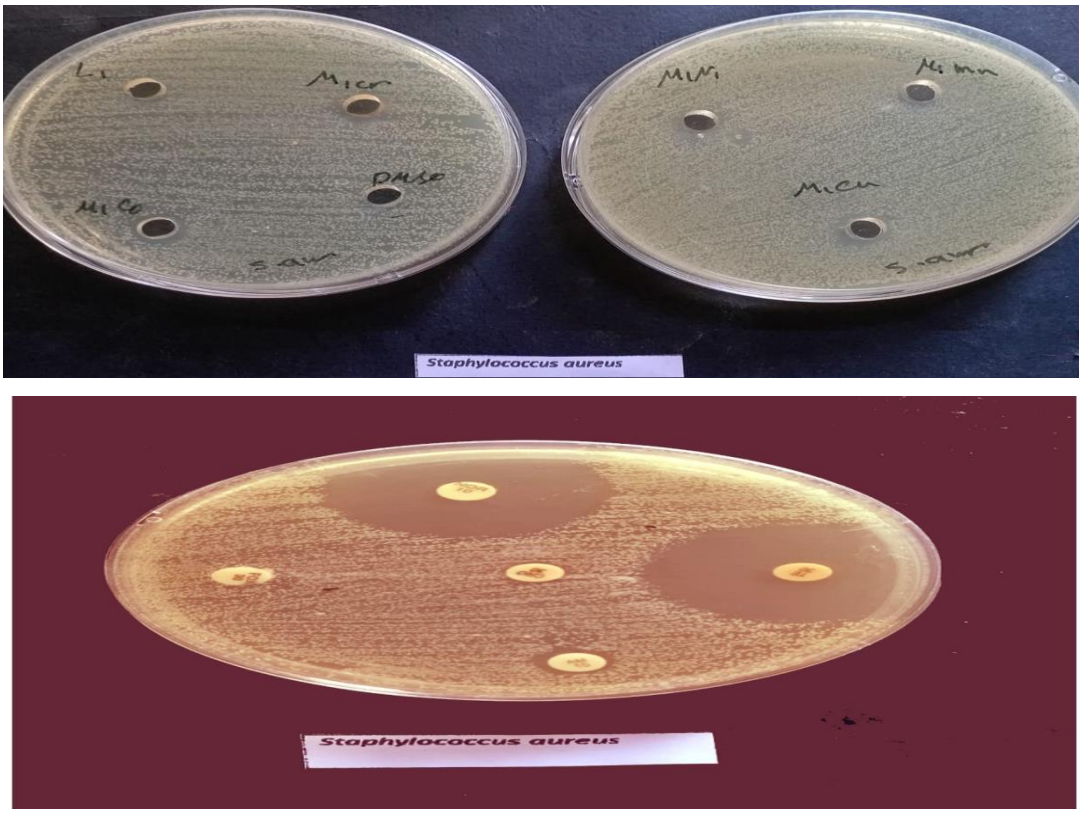


Figure 8: The biological evaluation of HL and their complexes against Staphylococcus aureus.

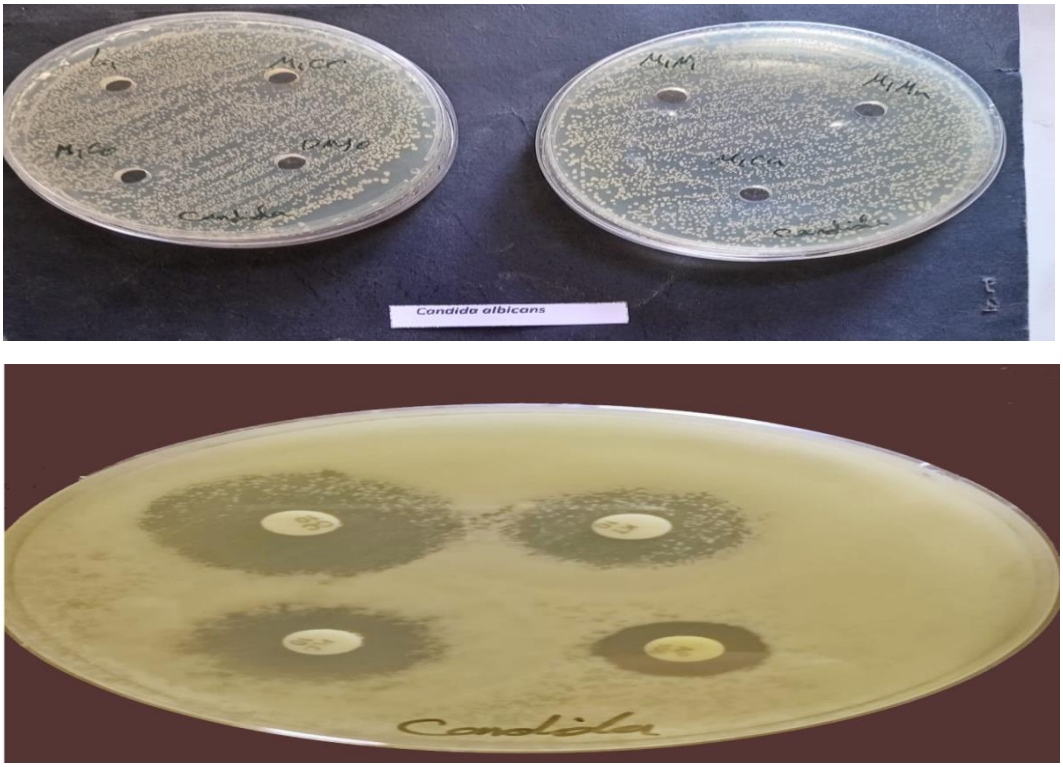


Figure 9: The anti-fungal evaluation of HL and its complexes against *Candida albicans.*

6. CONCLUSION

A azo-Schiff base ligand (HL) and the molecules that coordinate it with paramagnetic properties Cr^{III}, Mn^{II}, Co^{II}, Ni^{II}, and Cu^{II} have been reported. The ligand (((E)-2-((2-hydroxy-3-((E)-(3-nitrophenyl) diazenyl) naphthalen-1-yl) methylene) hydrazine-1-carbothioamide) (HL) was synthesized *via* condensation of (L) with thiosemicarbazide in a 1:1 mole ratio. The reaction of HL with the metal ions at a 1:1 ligand-to-metal ratio yielded monomeric complexes, which are structurally characterized using several physicochemical techniques. The analysis suggested coordination environments of four and six-coordinate geometries for the metal complexes. Finally, antibacterial and anti-fungal testing revealed enhanced bio activity of the metal complexes compared to the free HL ligand, highlighting the positive impacts of complexation.

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