

Synthesis, Structural Investigation and Biological Activity of a Heterocyclic Schiff-Base Ligand and Its Coordination Complexes

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ABSTRACT: This study reports the formation, characterisation and biological evaluation of a Schiff base ligand and its corresponding metal complexes. The Schiff base ligand (HL) was prepared through a condensation reaction involving isonicotinohydrazide and N'-((1R,2R,4R,5S, E)-2,4-bis(4-chlorophenyl)-3-azabicyclo[3.3.1]nonan-9-ylidene) isonicotinohydrazide (M) in EtOH solvent and (3-5) drops of conc. HCl. The interaction of HL with selected metal chlorides including Mn(+2), Co(+2), Ni(+2), Cu(+2) and Zn(+2) in a 2:1 (L:M) mole ratio resulted in the synthesis of complexes with the general formula [M(HL)Cl₂] (where: M = Mn(+2), Co(+2) and Ni(+2)) and [M'(HL)Cl₂] (where M' = Cu(+2) and Zn(+2)). The characterisation of the prepared compounds was carried out using a range of spectroscopic analyses, containing FT-IR and electronic spectroscopy, NMR (¹H and ¹³C), mass spectrometry, atomic absorption, as well as a range of analytical techniques to fully characterise the title compounds, including elemental microanalysis (C.H.N) for elemental composition determination, chloride percentage analysis, conductivity measurements to assess electrical conductivity in solution, magnetic moments to investigate the magnetic properties and melting point determination. These spectroscopic and analytical techniques were involved in validating the identity and structural properties of both the ligand and its corresponding coordination compounds. Besides the structural characterisation, the biological evaluation of the synthesised compounds toward both G⁺ and G⁻ bacterial strains was assessed. This investigation sheds light on the potential applications of these compounds in combating bacterial infections.

Keywords: Heterocyclic Schiff base Ligand; Metal complexes; Structural analyses; Biological evaluation.



1. INTRODUCTION

The Mannich approach is a prominent example of three-component reactions (MCRs) in synthetic organic chemistry, which represents a versatile tool in chemical synthesis. This reaction pathway has found applications including the fabrication of several natural product constituents, including the preparation of heterocyclic phenanthridine components [1-3], medicinal chemistry and the pharmaceutical field [4, 5]. The fabrication of a Mannich compound depends on a chemical process involving the amalgamation of a carbonyl compound (capable to form enol) with aldehyde (such as benzaldehyde) and ammonia, a primary or a secondary amine [6, 7]. Basically, in the formation of the Mannich compound, the amine undergoes a critical orientation and water molecule elimination, giving rise to the formation of an iminium ion. Subsequently, this iminium ion assists in a Mannich base formation through an aldol-like interaction with the electrophilic segment by the alpha carbon [8]. Looking for more sustainable and environmentally friendly chemical practices, researchers have explored several methodologies for the synthesis of Mannich bases. These strategies align with the principles of green chemistry and include the use of aqueous media, ionic liquids, solvent and catalyst-free conditions, ultrasonography, and biodegradable or reusable catalysts [9]. Mannich compounds have proven versatile beyond synthesis; they find utility as agents for capturing heavy metals from water streams and play a role in wastewater treatment [10]. Furthermore, Mannich compounds find versatile applications, ranging from environmental and agricultural sectors to analytical and polymer chemistry. They are also known for their potential as antibacterial and

anticancer agents [11]. Consequently, there is a substantial bulk of literature that discusses the synthesis of Mannich base ligands and their subsequent coordination with both transition and non-transition elements [12-14]. This study presents the formation and characterisation of a multidentate heterocyclic ligand (HL) and its coordination compounds [15, 16]. The anti-bacterial evaluation of the synthesised compounds was explored.

2. SYNTHESIS

2.1 Instruments and Measurements

A range of characterisation apparatuses were employed to identify the title compounds. A Stuart SMP10 thermoelectric apparatus was implemented to determine the melting points. FT-IR spectra were recorded with KBr and CsI discs on both a Shimadzu 8400s FT-IR and a Biotic 600 FT-IR. The ¹H and ¹³C NMR spectra of the ligand were acquired in DMSO-d₆ solutions using a Bruker-400 MHz spectrometer, with chemical shifts reported in ppm relative to TMS as an internal reference. Electrospray (ES) mass spectrum of the ligand was obtained with an LTQ-FT mass spectrometer from Thermo Fisher Scientific. U.V-Vis spectra, covering the range of 200-1100 nm, were recorded for 10⁻³ M solutions of the ligand and complexes at room temperature using a Shimadzu 1800 UV-Vis spectrophotometer. The chloride content in the coordination compounds was calculated with a 686-titro-665 Dosimat-Metrohm Swiss instrument, while the conductance of complexes in DMSO solutions was measured by a Eutech Instrument Co. 150 digital conductivity meter. Elemental analysis (C.H.N.) was carried out using an Eager 300 for EA1112. Magnetic moment measurements were conducted at 298K with a Sherwood Scientific Balance. Additionally, the biological evaluation of the synthesised compounds against (*Staphylococcus aureus*, *Escherichia coli*, *Salmonella* spp and *Streptococcus pneumoniae*) was performed at University of Baghdad, the College of Science.

2.2 Synthesis of (1R,2R,4R,5S)-2,4-bis(4-chlorophenyl-3-azabicyclo[3.3.1] nonan-9-one (M)

The isolation of M was achieved using a previously published method referenced in [12-14].

A reaction solution was prepared by stirring a mixture of 4-chlorobenzaldehyde (0.5g, 0.355mmol), ammonium acetate (0.136g, 0.177mmol) and cyclohexanone (0.18ml, 0.177mmol) [2:1:1] in ethanol (20ml) at a temperature range of 30-40 °C for 6 hours. Subsequently, the reaction was allowed to cool at RT, resulting in the formation of pale yellow solid. This solid was then separated by filtration, followed by washing with EtOH (5ml) and ether (5ml) and then allowed to dry in air. Yield: 1.32g (88%), m.p = 180-182 °C. FT-IR data (cm⁻¹), 3334 and 3294 ν(N-H), 3228 ν(C-H)arom., 2881 ν(C-H)aliph., 1712 ν(C=O), 1606 ν(C=C), 1575 δ(N-H).

2.3 Preparation of HL

A mixture of compound M (0.5 g, 0.00138 mmol) in 10 ml of EtOH containing 3 drops of concentrated HCl was combined with a solution of isonicotinohydrazide (0.19g, 0.00138 mmol) in 10 ml of EtOH, with continuous stirring. The reaction mixture was heated at reflux for a duration of 6 h. Following this, a white solid was generated. This was filtered off, washed with EtOH (5ml) and ether (5ml). Yield of the product was 0.78 g (92%), with a melting point of 166-168 °C. The necessary analytical data for the precursors and the ligand is provided in Table 1.

Table 1. Microanalysis percentage and additional data of the starting materials and HL.

Comp.	Empirical formula	M.wt g/mol	Yield (%)	m.p. °C	Colour	(Calc.) , %Found				
						C	H	N	O	Cl
M	C ₂₀ H ₁₉ Cl ₂ NO	360.278	88%	180-182	Pale yellow	(66.68) 66.14	(5.32) 5.72	(3.89) 4.15	(4.44) 4.72	(19.68) 20.24
A	C ₆ H ₇ N ₃ O	137.142	-	-	White	(52.55) 52.85	(5.15) 5.80	(30.64) 31.08	(11.67) 12.17	-
HL	C ₂₄ H ₂₄ Cl ₂ N ₄ O	479.405	92%	166-168	White	(65.14) 65.77	(5.05) 5.65	(11.69) 11.98	(3.34) 3.86	(14.79) 15.20

2.4 General procedure for complex formation

A mixture of metal chloride (0.0248g, 0.112mmol) in (10ml) of hot ethanol was added slowly to HL (0.1g, 0.21mmol) in 10ml of ethanol. The resulting mixture heated at reflux with stirring for 4 h, leading to the formation of a coloured solid. This was filtered off, washed with EtOH (5ml) and subsequently washed with diethyl ether (10ml). Table 2 includes the required elemental microanalyses of the precursors and the ligand, along with other details regarding melting points, colours and yields.

Table 2. Elemental microanalyses and other analytical data of coordination compounds.

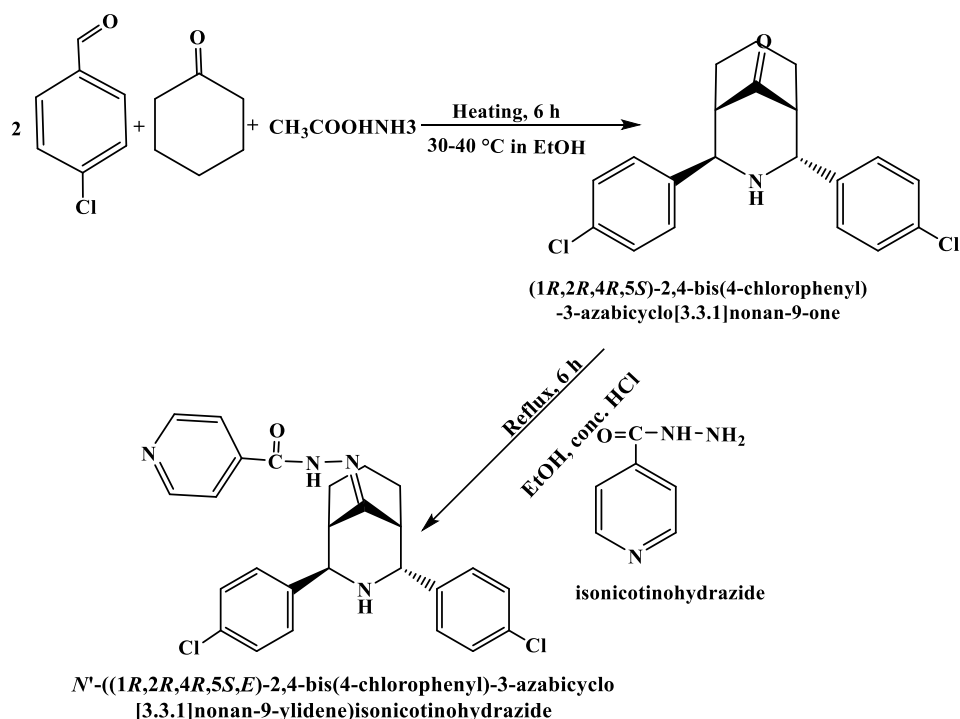
* = Decomposition temperature.

Comp.	M.wt	Yield	Colour	m.p. °C	Micro-analysis (calculated), found %					
					C	H	N	O	M	Cl
HL	479.40	92%	White	166-168	(65.14) 64.87	(5.05) 5.65	(11.69) 12.11	(3.34) 3.98	-	(14.79) 14.31
[Mn(HL)₂Cl₂]	1084.64	76%	Milky	299*	(57.58) 58.02	(4.46) 4.85	(10.33) 10.65	(2.95) 3.11	(5.07) 5.87	(19.61) 19.04
[Co(HL)₂Cl₂]	1088.64	88%	Pruple	298*	(57.37) 57.96	(4.44) 4.95	(10.29) 10.63	(2.94) 2.67	(5.41) 5.94	(19.54) 18.92
[Ni(HL)₂Cl₂]	1088.40	93%	Pale pruple	226-228	(57.38) 56.88	(4.45) 4.12	(10.30) 10.82	(2.94) 2.98	(5.39) 5.11	(19.54) 19.87
[Cu(HL)₂Cl₂]	1093.25	66%	Yellow greenish	202-204	(57.13) 58.07	(4.43) 4.77	(10.25) 10.90	(2.93) 2.21	(5.81) 5.43	(19.46) 19.14
[Zn(HL)₂Cl₂]	1095.09	78%	White	291*	(57.03) 57.93	(4.42) 4.09	(10.23) 10.72	(2.92) 2.46	(5.97) 6.13	(19.42) 19.88

3. PRODUCT CHARACTERISATION

3.1 Results and Discussion

A condensation reaction involving N'-((1R,2R,4R,5S, E)-2,4-bis (4-chloro phenyl)-3-azabicyclo [3.3.1] nonan-9-ylidene) isonicotinohydrazide and isonicotino hydrazide, as depicted in Scheme 1, was implemented to prepare the title ligand. This reaction was performed under reflux conditions in ethanol. The resulting free ligand exhibits solubility in DMF and DMSO with stirring, as well as in boiling ethanol and methanol. However, its solubility in other organic solvents is limited.

**Scheme 1. The synthetic pathway for HL.**

3.1.1 Characterisation the Ligand (H₂L)

The FT-IR spectrum of free ligand display bands due to $\nu(\text{N-H})$ amide at 3427 and 3305, $\nu(\text{C-H})$ arom. at 3112 $\nu(\text{C-H})$ alip. at 2956, $\nu(\text{C=O})$ amide at 1666, $\nu(\text{C=N})$ at 1633, $\nu(\text{C=C})$ arom. at 1602, $\delta(\text{N-H})$ at 1556 and $\nu(\text{C-N})$ at 1336 cm^{-1} , respectively. The ^1H NMR data (400 MHz, DMSO- d_6) is presented in Figure 1 and is stated as follows;

1.39 (4H, t, C_{9,9'}-H); 1.50 (2H, m, C₁₀-H); 2.64 (3H, t, C_{8,8'}-H); 4.13 (1H, s, N-H); 3.70 (2H, d, C_{7,7'}-H); 7.11 (4H, m, C_{2,2'}, C_{6,6'}); 7.40 (5H, dd, and 7.25, C_{3,3'}, C_{5,5'}); 7.47 (4H, m, Caromatic (1_{1,11'}, 1₂, 1_{2'})); 7.77 (1H, s, N-Hcyclic); 9.94 (N-Hamide). The ¹³C NMR (100 MHz, DMSO-d₆) is placed in Figure 2, and is reported as follows; 19.01 (C10); 29.48 (C9,9') 31.76 (C8,8'); 56.51 (C7,7'); 122.10 (C1); 127.76 (C_{2,2'}, C_{6,6'}); 129.39 (C_{3,3'}, C_{5,5'}); 134.43 (C_{4,4'}); 149.55 (C_{11,11'}); 150.79 (C_{12,12'}); 162.09 (C=N); 212.14 (C=O). The electro-spray MS (+) of the ligand, as shown in Figure 3, indicates the presence of the parent ion peak at the following mass ion: m/z 478.4(M)⁺ for C₂₆H₂₄Cl₂N₄O. Peaks detected at m/z = 384.4, 289, 279.9, 194.1, 184, 91.1 and 65.1 related to [M-(+H-N₂Cl₂)], [M-(+H-N₂Cl₂)+(C₅H₅N)], [M-(+H-N₂Cl₂)+(C₅H₅N)+(H₅-N₂)], [[M-(+H-N₂Cl₂)+(C₅H₅N)+(H₅-N₂)+(C₇H₂)], [[M-(+H-N₂Cl₂)+(C₅H₅N)+(H₅-N₂)+(C₇H₂)+(H₂)], [[M-(+H-N₂Cl₂)+(C₅H₅N)+(H₅-N₂)+(C₇H₂)+(H₂)+(C₇H₉) and [[M-(+H-N₂Cl₂)+(C₅H₅N)+(H₅-N₂)+(C₇H₂)+(H₂)+(C₇H₉)+(C₂H)], respectively.

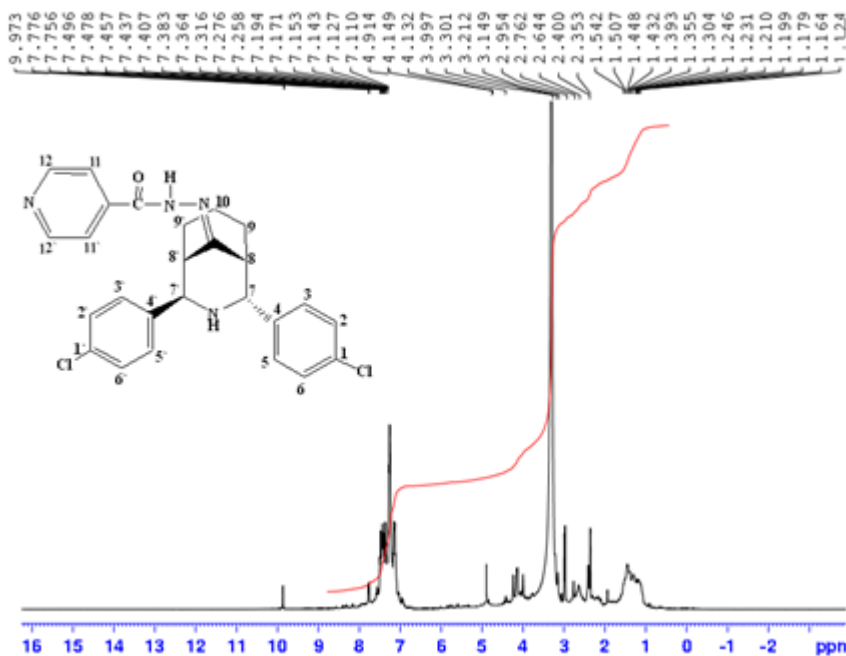


Figure 1. ¹H-NMR spectrum of the ligand in DMSO-d₆ solution.

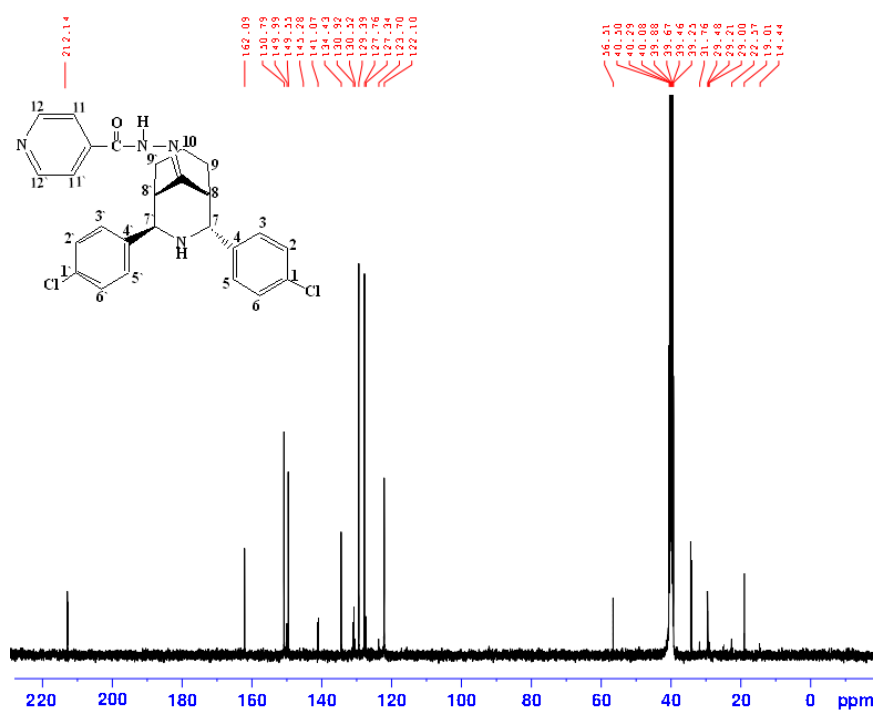


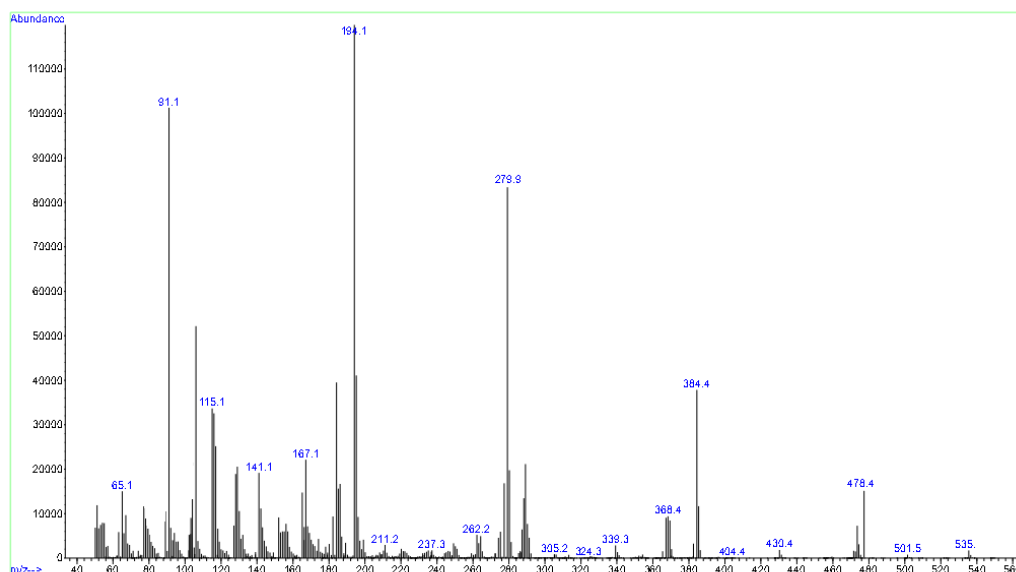
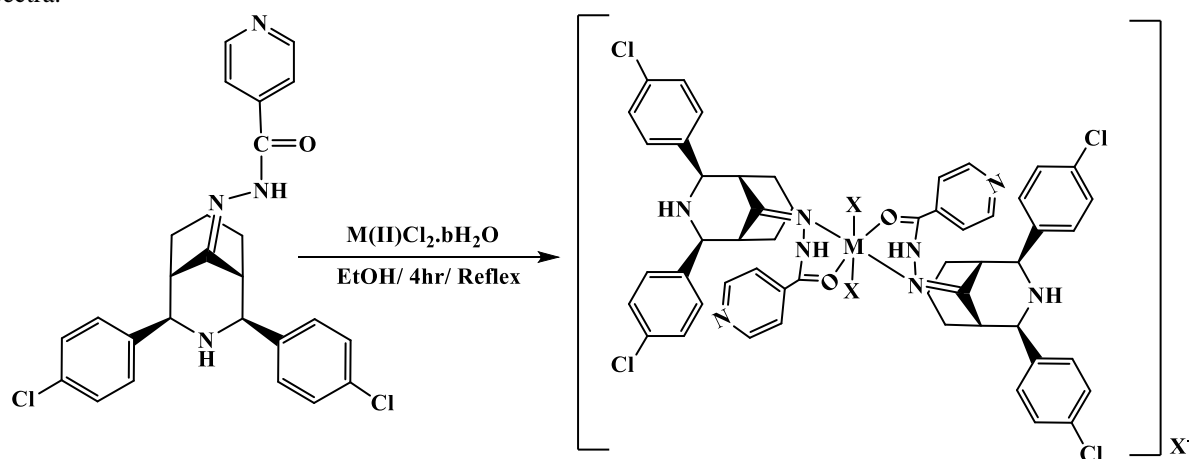
Figure 2. ^{13}C -NMR spectrum of the ligand in DMSO-d_6 solution.

Figure 3. ESI(+) mass spectrum of HL.

The coordination compounds were prepared, as shown in Scheme 2, by combining 2 moles of HL with 1 mole of each respective metal ion Mn^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} in EtOH medium at reflux. The results revealed that these complexes exhibited six-coordinated and four-coordinate donor atoms for (Mn (+2) Co (+2), and Ni (+2) and Cu (+2) and Zn (+2) ions, respectively. Characterisation of these synthesised compounds was conducted using elemental microanalyses (C.H.N.) as presented in Tables 1 and 2. Additionally, FTIR spectroscopy results are detailed in Table 3, and UV-Vis spectroscopy data can be found in Table 4. Further characterisation involved mass spectrometry, ^1H and ^{13}C NMR spectra.



$\text{M} = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}$

$\text{X} = \text{Cl}; \text{X}^- = 0$

$\text{M} = \text{Zn(II)}, \text{Cu(II)}$

$\text{X} = 0; \text{X}^- = 2 \text{ Cl}$

$\text{b} = \text{Number of water molecules}$

Scheme 2. The synthetic pathway for HL complexes.

3.1.2 Characterisation the Complexes

3.1.2.1 FT-IR data

Table 3 provides the infra-red data for the prepared compounds and their respective interpretations. In the spectrum of HL, several characteristic bands were observed including those attributed to $\nu(\text{N-H})$ [17], $\nu(\text{C=O})$ [18, 19] and (C=N) imine [20] at 3427, 3305, 1666 and 1633 cm^{-1} , respectively. Upon complex formation, the FTIR data revealed in the region of 1683-1652 cm^{-1} and 1604-1595 cm^{-1} , attributed to $\nu(\text{C=O})$ and $\nu(\text{C=N})$, respectively. These peaks suggested a decreased bond order in comparison to the free ligand, thus affirming the participation of the nitrogen atom in coordination with the metal centre [21, 22]. Additionally, the spectra of the complexes appeared bands in the range 543-514 and about 428-414 cm^{-1} were assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$, respectively. Furthermore, bands recorded at 316-310 and 291-289 in the FT-IR of $[\text{Mn}(\text{HL})_2\text{Cl}_2]$, $[\text{Co}(\text{HL})_2\text{Cl}_2]$ and $[\text{Ni}(\text{HL})_2\text{Cl}_2]$ were related to $\nu(\text{M-Cl})$ [23].

Table 3. FTIR data (cm^{-1}) of HL and its coordination compounds.

Comp.	$\nu(\text{N-H})$	$\nu(\text{C=O})$ amide	$\nu(\text{C=N})$ imine	$\delta(\text{N-H})$	$\nu(\text{C-N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$
HL	3427 3305	1666	1633	1556	1336	-	-	-
$[\text{Mn}(\text{HL})_2\text{Cl}_2]$	3272	1656	1604	1548	1326	518	414	310 291
$[\text{Co}(\text{HL})_2\text{Cl}_2]$	3257	1654	1602	1548	1330	543	428	316 289
$[\text{Ni}(\text{HL})_2\text{Cl}_2]$	3220	1652	1600	1548	1383	518	418	312 289
$[\text{Cu}(\text{HL})_2\text{Cl}_2]$	3240	1683	1591	1527	1332	540	420	-
$[\text{Zn}(\text{HL})_2\text{Cl}_2]$	3288	1654	1595	1544	1330	514	426	-

3.1.2.2 Electronic Spectra Measurements

The electronic absorption spectrum of HL indicates bands at 288 nm. This peak was ascribed to $\pi \rightarrow \pi^*$ transitions [24, 25]. The spectral data of complexes revealed a peak associated with the ligand field. The UV-Vis spectrum of Mn(+2) compound recorded bands at 387 and 481 nm related to C.T and ${}^6\text{A}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{G})$ transitions, respectively. These observations suggest a distorted octahedral arrangement around the Mn atom [26, 27]. Peaks recorded at 616 and 676 nm in the Co(II) complex spectrum were assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ respectively, suggesting a distorted octahedral geometry about the cobalt atom [7]. The spectrum of the Ni(+2) revealed bands at 322 nm, 683 nm and 758 nm attributed to the C.T and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ transition supporting a distorted octahedral geometry surrounding the nickel atom [5]. Conversely, the Cu(+2) compound exhibited a band in the visible area at 742 nm, assigned to the ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ transition, signifying a distorted square planar arrangement surrounding the copper atom [27, 28]. Lastly, the electronic data of the Zn(+2) complex revealed band at 54 nm related to the inner field of the ligands [29-31]. These observations align with the known d^{10} configuration of these metal ions. The collected electronic data are presented in Table 4.

Table 4. UV-VIS spectral data of coordination compounds in DMSO solutions.

Comp.	λ_{nm}	ϵ_{max} ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	$\tilde{\nu}$, cm^{-1}	Assignment	Suggested Geometry
HL	288	808	34722	$\pi \rightarrow \pi^*$	-
$[\text{Mn}(\text{HL})_2\text{Cl}_2]$	239 387 481	842 1037 34	41841 25839 20790	$\pi \rightarrow \pi^*$ C.T ${}^6\text{A}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{G})$	Distorted Octahedral
$[\text{Co}(\text{HL})_2\text{Cl}_2]$	284 616 676	1570 32 44	35211 16233 14792	$\pi \rightarrow \pi^*$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$	Distorted Octahedral

[Ni(HL)₂Cl₂]	294 322 683 758	933 673 72 79	34013 31055 14641 13192	$\pi \rightarrow \pi^*$ C.T $^3A_{2g} \rightarrow ^3T_{1g}^{(F)}$ $^3A_{2g} \rightarrow ^3T_{2g}^{(F)}$	Distorted Octahedral
[Cu(HL)₂Cl₂]	291 642	1569 711	34364 15576	$\pi \rightarrow \pi^*$ $^2B_{1g} \rightarrow ^2B_{2g}$	Distorted square planar
[Zn(HL)₂Cl₂]	254	2131	39370	$\pi \rightarrow \pi^*$	Distorted Tetrahedral

3.1.2.3 Biological activity

The synthesised compounds underwent screening toward four bacterial strains (*Staphylococcus aureus*, *Escherichia coli*, *Salmonella spp* and *Streptococcus pneumoniae*) using the disc diffusion approach, as indicated in Table 5. The results revealed prominent antimicrobial activity for the prepared compounds. This observed effect can be attributed to the chelation phenomenon, in which the ligand's donor atoms actively participate in counterbalancing the formal positive charge of the metal ion at the core of the complexes. This chelation process enhances the lipophilic characteristics of the metal chelate system, assisting in increased electron distribution throughout the entire chelate ring. Consequently, this improved lipophilicity makes it more feasible for the compounds to traverse cell membranes. Markedly, all the tested compounds exhibited antimicrobial activity against the tested bacterial strains [32, 34].

Table 5. The inhibition zone of the ligand and coordination compounds.

Compound	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>	<i>Salmonella spp.</i>	<i>Streptococcus pneumoniae</i>
HL	31	30	Zero	Zero
[Mn(HL) ₂ Cl ₂]	33	34	Zero	30
[Co(HL) ₂ Cl ₂]	27	Zero	Zero	Zero
[Ni(HL) ₂ Cl ₂]	22	30	28	30
[Cu(HL) ₂ Cl ₂]	21	35	29	34
[Zn(HL) ₂ Cl ₂]	36	38	31	37

4.CONCLUSION

This work covers the synthesis, characterisation and biological evaluation of the Schiff base (HL) and its coordination compounds. The ligand was synthesised by reacting and N'-((1R,2R, 4R,5S,E)-2,4-bis(4-chlorophenyl)-3-azabicyclo[3.3.1] nonan-9-ylidene)isonicotinohydrazide with isonicotinohydrazide using EtOH as a medium and a few drops of conc. HCl as a catalyst. Subsequently, the ligand was reacted with various metal chlorides yielding complexes. Structural confirmation of both the ligand and its coordination compounds was achieved through a series of spectroscopic and analytical techniques. These analyses revealed that Mn(+2), Co(+2) and Ni(+2) metal centres exhibit a distorted octahedral geometry, while the Cu(+2) complex adopts a square planar geometry. On the other hand, the Zn(+2) and complexes were found to adopt a tetrahedral arrangement around the metal centre. Furthermore, the synthesised compounds displayed remarkable antimicrobial activity when evaluated against four bacterial strains.

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