

COPPER(II) COMPLEXES OF NICOTINOYL AND ISONICOTINOYLHYDRAZONES: SYNTHESIS, SPECTRAL CHARACTERIZATION, AND ANTIBACTERIAL ACTIVITY

E. Lakshmi¹, K. Raja², P. Raveendra Reddy¹, K. Hussain Reddy¹
and A. Suseelamma^{3,✉}

¹Department of Chemistry, Sri Krishnadevaraya University, Anantapur-515001
(Andhra Pradesh), India

²Department of Chemistry, Rajeev Gandhi Memorial College of Engineering and Technology
(Autonomous), Nandyal-518501 (Andhra Pradesh), India

³Department of Chemistry, Hindu P.G. College for Women, Hyderabad-500018
(Telangana), India

✉Corresponding Author: suseela.3712@gmail.com

ABSTRACT

Based on physicochemical, mass, UV-visible IR, and ESR spectrum analyses, copper complexes of HANH, MBINH, and MAINH are characterized. The typical formula for the copper complexes of HANH is ML_2 (where L = HANH). The tridentate HANH ligand functions as a mono-negative ligand. The typical formula for copper complexes of MBINH & MAINH is $[ML_2]Cl_2$ (M=Cu, L=MBINH & MAINH), and these ligands behave as neutral tridentate ligands. The octahedral geometry for the complexes is represented by UV-VIS spectral data. ESR spectra are used to examine the copper complexes at liquid nitrogen temperature (LNT). Redox potentials of all complexes are shifted towards + or – values in the CV data when compared with the ligands. In the current work, the antibacterial activity of ligands and metal complexes is also studied.

Keywords: Copper(II) Complexes, Nicotinoylhydrazones and Isonicotinoylhydrazones, Cyclic Voltammetry, Antibacterial Activity.

RASĀYANJ. Chem., Vol. 16, No.3, 2023

INTRODUCTION

Copper complexes play a vital function in biological systems' metalloprotein active sites. We are aware of the potential uses for copper complexes in a variety of catalytic and electron transfer processes in living things. It is well known that copper complexes function as anticancer bodies.¹⁻⁵ These approaches are within the purview of medicinal chemistry⁷ and bioinorganic chemistry.⁶ Broadly speaking, heterocyclic base-Cu(II) complexes exhibit cytotoxicity and high DNA binding.⁸⁻¹³ Containing the Cu(II) metal ion, isonicotinoylhydrazones, and nicotinoylhydrazones containing ONO donor atoms exhibit a variety of binding characteristics. The anti-tubercular properties of Copper(II) complexes with different isonicotinoyl group ligands are shown.¹⁴ Due to stacking C-H interactions, the copper complexes of nicotinoyl and isonicotinoylhydrazones demonstrated enhanced DNA binding. Cleavage activity, cytotoxicity, and antibacterial activity were all displayed by the copper complexes.¹⁵⁻¹⁹ There have been very few investigations on nicotinoylhydrazone and isonicotinoylhydrazone copper complexes. As a result, research into a novel system of Cu(II) complexes of nicotinoylhydrazones and isonicotinoylhydrazones is deemed worthwhile. The synthesis of nicotinoylhydrazone, isonicotinoylhydrazone, and their metal complexes, as well as their analysis utilizing physicochemical and spectral techniques, has been done in light of the aforementioned information. Complexes of Cu(II) with antibacterial characteristics are reported.

EXPERIMENTAL

The following items were purchased from Sigma-Aldrich: agarose, nicotinic acid hydrazide, isonicotinic acid hydrazide, 2-hydroxy acetophenone, 2-methoxybenzaldehyde, and 2-Methoxy acetophenone. The

remaining compounds were of the AR grade. All of the solvents were distilled before being used to create the ligand. The VSM 7410 equipment measured the magnetic moment at 298 K. Molar conductivity measurements were made using an ELICO CM –62 conductivity meter at 298 K in DMF. Using a UV Lambda50 spectrometer (Perkin-Elmer), the UV-VIS spectra of copper complexes were measured in DMF as the solvent. On KBr discs, IR spectra of ligands and complexes between 4,000 and 500 cm^{-1} were recorded using a spectrometer (Perkin-Elmer spectrum100). By using electrochemical workstations (CH equipment), complexes were studied electrochemically. For CV measurement complexes (10-3), N_2 was pumped for 5 minutes before the complexes were produced in a degassed condition with 0.1 M Bu_4NPF_6 serving as the supporting electrolyte. Three electrodes were employed for the CV measurement: a reference electrode (Ag/AgCl), a working electrode (glassy carbon), and an auxiliary electrode (platinum wire).

Preparation of Ligands

Nicotinic acid and isonicotinic acid were used to react with various carbonyl compounds to create ligands. The RB-flask was filled with methanolic solutions of nicotinic acid hydrazide/isonicotinyldiazide (5 mmol) and carbonyl compound (5 mmol). You can get yellow or light yellow-colored crystalline products by adding a few drops of hydrochloric acid to the reaction mixture, heating it for 3-6 hours, and then cooling it to room temperature. The products are then washed with methanol, followed by hexane and vacuum dried. The ligands' structures are shown in Fig.-1 and 2 depicts the MBINH's ^1H -NMR spectrum.

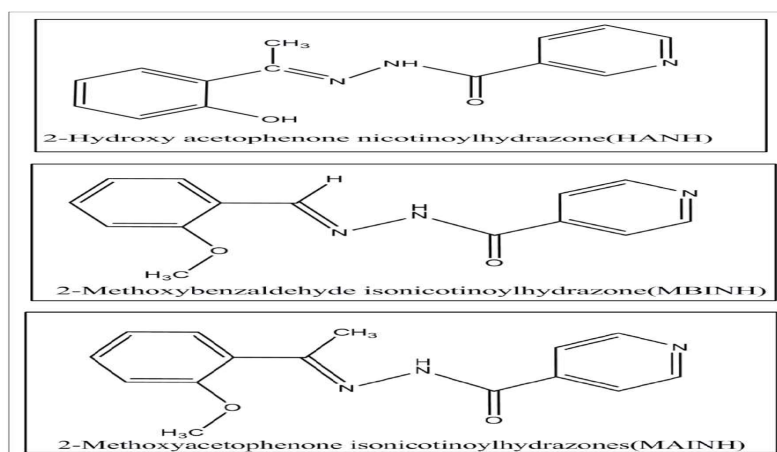


Fig.-1: Structure of the Ligands

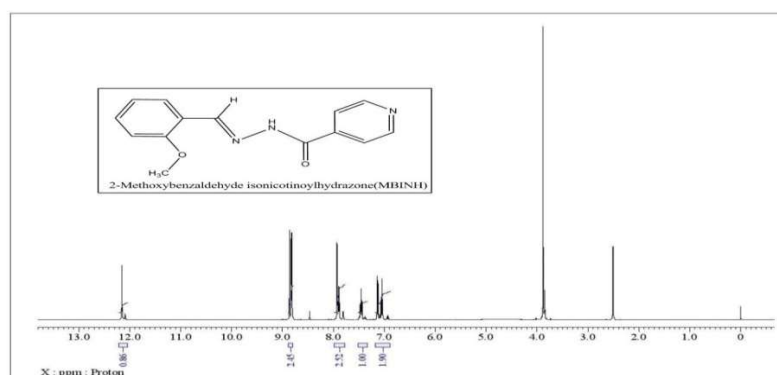


Fig.-2: ^1H -NMR Spectrum of MBINH

Characterization of Ligands

2-Hydroxyacetophenonenicotinoylhydrazide (HANH): Yield 73%, M.Pt. 238-239 $^{\circ}\text{C}$, ^1H -NMR spectra: δ (13.4) (s, 1H), δ (11.4-8.8) (m, 4H), δ (7.9-6.3) (m, 4H), δ (3.4) (s, 1H), δ (6.5) (s, 3H), assigned to phenolic-OH, nicotine ring H, and =CH-, phenyl H, imine H, methyl CH_3 protons respectively. In a HANH Mass spectrum molecular ion peak was observed at 255.

2-Methoxy benzaldehydeisonicotinoylhydrazone (MBINH)

Yield 69%, M.Pt. 249-251°C.; ¹H-NMR spectra: δ(12.2) (s, 1H), δ(8.8-7.9) (m, 4H), δ(7.4-7.2) (m, 4H), δ(3.8) (s, 1H), δ(2.50) (s, 3H), assigned to azomethine>CH=N, isonicotine ring H, phenyl H, imine H, methoxyH protons respectively. In a MBINH Mass spectrum molecular ion peak was observed at 255.

2-Methoxy acetophenoneisonicotinoylhydrazone (MAINH)

Yield 71%, M.Pt. 263-265°C, ¹H-NMR spectra: δ(8.8-7.4) (d, 4H), δ(7.1-6.5) (m, 4H), δ(3.8) (s, 1H), δ(2.9) (s, 3H), δ(2.8) (s, 3H), assigned to isonicotine ring H, phenyl H, imine H, methyl H, methoxyH protons respectively. In a MAINH Mass spectrum molecular ion peak observed at 269.

Synthesis of Complexes

Synthesis of Cu(HANH)₂ The ligand HANH (1.27 g, 5 mmol) was dissolved in 20 mL of methanol and then added to an RB flask along with CuCl₂·2H₂O (0.85 g, 5 mmol). After stirring for 1 hour, a precipitate developed, which was then collected through filtration, after being cleaned with methanol, the samples were vacuum-dried.

Synthesis of [Cu(MBINH)₂]Cl₂

After being dissolved in 20 mL of methanol and agitated for 1 hour, CuCl₂·2H₂O (0.85g, 5mmol) and the ligand MBINH (1.27g, 5mmol) precipitated. This precipitate was then collected through filtering, and after being cleaned with methanol, the samples were vacuum-dried.

Synthesis of [Cu(MAINH)₂]Cl₂

CuCl₂·2H₂O (0.85g, 5mmol) and the ligand MAINH (1.34g, 5mmol) were dissolved in 20 mL of methanol and agitated for up to one hour. Precipitate then formed and was collected by filtering before being cleaned with methanol and dried under vacuum.

Experiments In Antibacterial Activity

By using the paper disc technique, the anti-bacterial experiments for the compounds have been completed. Every testing tool, including paper discs, test tubes, conical flasks, Petri dishes, and forceps, was sterilized before use in order to prevent contamination.

Preparation of Sample Solution

All samples were dissolved in DMSO (Grade-AR) for the preparation of paper discs (Whatman No. 1), and paper discs were then dripped with various concentrations of the compounds (ranging from 100 g/ml to 25 g/ml).

Medium

The nutritional broth was made by dissolving glucose (15 g), peptone (12 g), and salt solution (50 ml) in 1000 ml of water. The pH was then adjusted to 7.2-7.4, and the nutrient broth was sterilized in an autoclave at 121 °C (at 15 lb pressure) for 15 minutes.

Bacteriological Testing

The paper disc technique is used to check for antibacterial activity.²⁰

Organisms Used

Two categories were established to separate the bacteria into gram-positive (*Staphylococcus aureus* and *Bacillus subtilis*) and gram-negative (*Pseudomonas aeruginosa* and *Escherichia coli*) strains. The previously described sterile nutritional agar was melted and put in marked containers after being cooled to 50°C. Separate swabs were used to inject agar slant culture suspensions of bacteria that were still in the process of developing. Standard Whatman No.1 filter papers were used to create sterile filter paper discs (6 mm in diameter), which were then dipped in the test solution (100 g/ml) and dried before being used to inoculate agar plates with the aforementioned bacterial strains. The test compound discs were incubated on plates for 24 hours at 35°C. After 24 hours, the growth inhibition zone in the Petri plates was evaluated. Around the paper disc was a zone that was clearly inhibiting development, indicating that the organism's growth was being constrained. The inhibitory zone surrounding the disc was measured in mm in the petri dish.

RESULTS AND DISCUSSION

All complexes, which are insoluble in organic solvents and exist in a solid crystalline form, were dissolved in DMSO and DMF. The suggested composition of the complexes is substantiated by analytical and physicochemical data. Table-1 presents the physical characteristics of the complexes. $\text{Cu}(\text{HANH})_2$ and $[\text{Cu}(\text{MBINH})_2]\text{Cl}_2$'s ESI mass spectra are displayed in Figs.-3 and 4, respectively. Peaks of two different molecular ions can be seen at 572 and 643 m/z, respectively. As a result, the complexes' postulated molecular formulas are congruent with the molecular weights determined from mass spectra.

Table-1: Physico-Chemical Properties of Metal Complexes

S. No.	Complex	Mol. Formula	M.P. °C	Mol. Wt, Found (Cal.)	μ_{eff}	ΔM^a
1	$\text{Cu}(\text{HANH})_2$	$\text{CuC}_{28}\text{H}_{26}\text{N}_6\text{O}_4$	>300	572 (573.5)	1.83	17.1
2	$[\text{Cu}(\text{MBINH})_2]\text{Cl}_2$	$\text{CuC}_{28}\text{H}_{26}\text{N}_6\text{O}_4\text{Cl}_2$	275	643 (642)	1.76	5.8
3	$[\text{Cu}(\text{MAINH})_2]\text{Cl}_2$	$\text{CuC}_{30}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}_2$	289	672 (671.5)	2.01	81.2

Conductivity Measurement

Measurements of conductivity were made in complexes' DMF solutions. $\text{Cu}(\text{HANH})_2$ 17.1 $\text{Ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$ molar conductance value indicates that the complex is non-electrolytic in nature. The $[\text{Cu}(\text{MBINH})_2]\text{Cl}_2$ and $[\text{Cu}(\text{MAINH})_2]\text{Cl}_2$ complexes are found to have molar conductance values of 85.2 and 81.2, respectively. The complexes' electrolytic nature is represented by the values.

Magnetic Susceptibility Measurements

Table-1 displays the magnetic susceptibility measurements for the copper complexes. The magnetic moment values (μ_{eff}) of the copper complexes range from 1.76 to 2.01 B.M, which is similar to the magnetic moments observed for a single unpaired electron and corresponds to spin-only values. The information shows that compounds behave monomerically and do not have axial Cu-Cu contacts.²¹

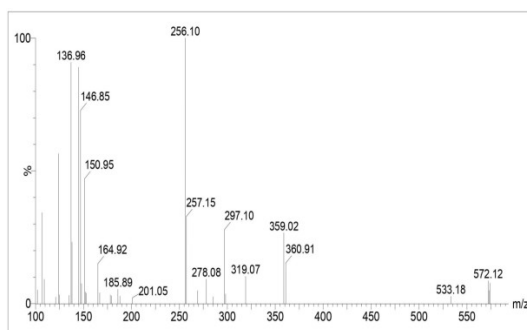


Fig.-3: Mass Spectrum of $\text{Cu}(\text{HANH})_2$

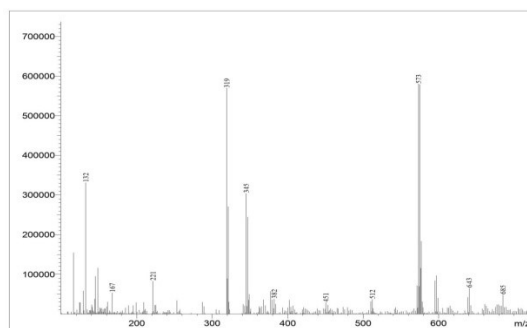


Fig.-4: Mass Spectrum of $[\text{Cu}(\text{MBINH})_2]\text{Cl}_2$

UV-VIS Spectra

Carried out UV-VIS spectra for the complexes in DMSO. Table-2 displays the peaks found in the spectrum complexes. The electronic spectra of the $[\text{Cu}(\text{MBINH})_2]\text{Cl}_2$ complex are shown in Fig.-5. The intraligand transition peak in the complexes is between 36764 and 35587 cm^{-1} . A second peak in the 31545 - 29854 cm^{-1} range corresponds to the azomethine group's $n\text{-}\pi^*$ transition. Medium intensity MLCT peak was seen at 25575 - 21653 cm^{-1} . Every complex has a broad, low-intensity peak between 15268 and 10526 cm^{-1} . It supports the octahedral shape and is attributed to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ electronic transition.²²

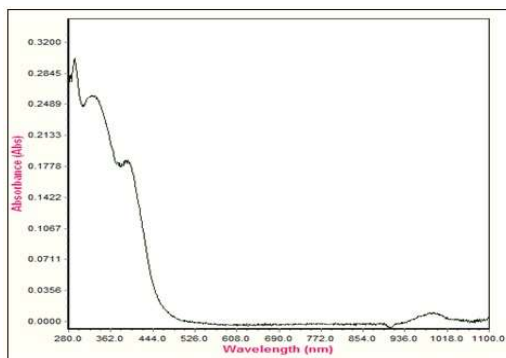


Fig.-5: Electronic Spectrum of Complex $[\text{Cu}(\text{MBINH})_2]\text{Cl}_2$

Table-2: Electronic Spectral Data of the Cu(II) Complexes

Complex	Bands(cm^{-1})	Assignments
$\text{Cu}(\text{HANH})_2$	36764	$\pi\text{-}\pi^*$
	29854	$n\text{-}\pi^*$
	24165	MLCT
	15268	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$
$[\text{Cu}(\text{MBINH})_2]\text{Cl}_2$	35872	$\pi\text{-}\pi^*$
	30462	$n\text{-}\pi^*$
	21653	MLCT
	12697	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$
$[\text{Cu}(\text{MAINH})_2]\text{Cl}_2$	35587	$\pi\text{-}\pi^*$
	31545	$n\text{-}\pi^*$
	25575	MLCT
	10526	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$

Infrared Spectra

Table-3 presents the prominent infrared (IR) spectral peaks for both the ligands and their corresponding Cu(II) complexes. By comparing the IR spectra of the ligand and the $\text{Cu}(\text{HANH})_2$ complex, the donor atoms of the ligand can be identified. The phenolic O-H group, which corresponds to a wide peak in the spectra of the HANH ligand at 3380 cm^{-1} , is discovered to be lacking in the copper complex. The C-O-M bond is formed as a result of the phenolic oxygen atom interacting with the copper ion, according to spectral shifts. In the ligand's spectra, a second prominent peak can be seen around 1642 cm^{-1} . It results from the stretching vibration of $\nu(\text{C}=\text{O})$. $\text{Cu}(\text{HANH})_2$ has a peak in its spectrum that shifts towards a lower wave number (1626 cm^{-1}), which indicates that the $>\text{C}=\text{O}$ group is engaged in coordination with the metal ion.²³ Due to the participation of azomethine nitrogen in interaction with the metal ion, the azomethine group is also detected in the equivalent copper complex with a shift to a lower frequency.²⁴

Table-3: IR Spectral Data of Ligands and Their Copper Complexes

HANH	$\text{Cu}(\text{HANH})_2$	MBINH	$[\text{Cu}(\text{MBINH})_2]\text{Cl}_2$	MAINH	$[\text{Cu}(\text{MAINH})_2]\text{Cl}_2$	Assignment
3380	-	-	-	-	-	O-H str
3038	3059	3089	3032	3246	3038	N-H str
-	-	2961	-	2884	-	Aliphatic $\text{sp}^3\text{C-H}$ str
1642	1626	1732	1656	1672	1642	C=O str

1604	1598	1610	1604	1612	1604	Azomethine C=N str
1572 1547	1565 1521	1561 1437	1563 1452	1578 1468	1572 1446	Aromatic (C=C) skeleton
1387	1384	1318	1374	1358	1387	Aromatic C-H bending
-	-	1221 1052	1216 1038	1291 1022	1257 1008	C-O-Me Asymstr C-O-Me Symstr
1154 1008	1162 1002	1154 1098	1151 1084	1159 1098	1154 1087	Aromatic C-H bending
860	859	845	851	853	860	C-H out of plane bending
734 662	731 664	772 692	776 664	756 671	771 662	C-C out of plane bending

[Cu(MBINH)₂]Cl₂ and [Cu(MAINH)₂]Cl₂

Due to the carbonyl stretching vibration, the peak is seen in the ligands MBINH and MAINH at 1732 cm⁻¹ and 1672 cm⁻¹, respectively. The carbonyl band of the corresponding copper complexes is seen at lower wave numbers 1643 cm⁻¹ and 1635 cm⁻¹, respectively. Because of the bonding with the copper ion, decreases in the >C=O group. In MBINH and MAINH, respectively, another peak is seen at 1612 cm⁻¹ and 1610 cm⁻¹. This peak is moved to a lower wave number in the corresponding copper complexes, indicating that azomethine nitrogen is involved in the coordination with copper ions.²³ Due to the presence of the C-O-Me group, the IR spectra of the MBINH and MAINH ligands, respectively, show two bands at 1221, 1291, and 1051, 1022 cm⁻¹. In the IR spectra of their equivalent copper complexes, these peaks shift towards lower wave numbers, indicating that the (C-O-Me) group is involved in bonding with the metal ion.

ESR Spectral Studies

The X-band and ESR spectra of a DMF solution containing copper(II) complexes were recorded at both ambient temperature and liquid nitrogen temperature (LNT). Figure-6 illustrates the typical ESR spectrum of Cu(HANH)₂. By utilizing TCNE free radicals as a reference, the g and g[⊥] values were calculated from the spectra and are presented in Table-4. The results indicate that g[⊥] > g_{||} > 2.0023, suggesting an octahedral geometry around the Cu(II) core. The measured g_{||} values for the copper complexes are below 2.3, consistent with Kivelson's findings, implying a covalent link between the copper and ligand.²⁵ Additionally, the fact that g_{||} & g[⊥] are greater than two suggests the presence of axial symmetry in the complexes. The observed pattern of the copper complexes, with g_{||} > g[⊥] > g_e(2.0023), indicates the existence of an unpaired electron in the dx²-y² orbital of the metal ion (copper).²⁶ The axial symmetry parameter, denoted as G, is defined as follows:²⁷

$$G = \frac{g_{||} - 2.0023}{g^{\perp} - 2.0023}$$

Table-4: ESR Data for Cu(II) Complexes

Complex	In Solid State				In Solution State				
	g	g [⊥]	g _{avg}	G	g	g [⊥]	g _{avg}	G	λ
Cu(HANH) ₂	2.106	2.054	2.0713	2.005	2.261	2.189	2.213	1.385	813
[Cu(MBINH) ₂]Cl ₂	2.128	2.069	2.088	1.884	2.038	2.051	2.046	0.733	146
[Cu(MAINH) ₂]Cl ₂	2.082	2.036	2.051	2.364	2.309	2.276	2.287	1.120	755

Based on the above spectral data we suggest the general structure of the metal complexes as shown in Fig.- 7.

Cyclic Voltammetry

Copper complexes are the subject of cyclic voltammetric investigations in DMF medium. As a supporting electrolyte, 0.1M TBFP (tetrabutylammoniumhexafluorophosphate) is utilized. The [Cu(MBINH)₂] Cl₂

complex cyclovoltammogram is shown in Fig.-8. Table-5 displays the electrochemical data of metal complexes. It was discovered that the values of the cathodic peak current function were not affected by the scan rate.

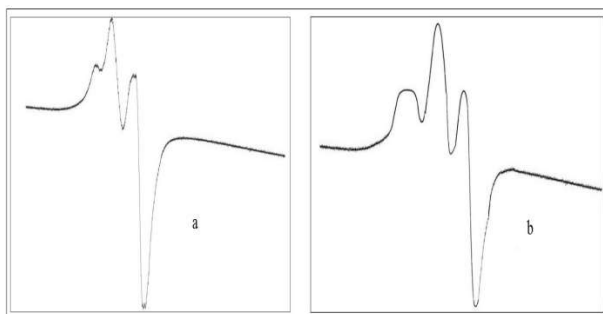


Fig.-6: (a) The X-Band Powder ESR Spectrum of Cu(HANH)₂ Recorded at LNT
(b) The X-Band Solution ESR Spectrum of Cu(HANH)₂ Recorded at LNT

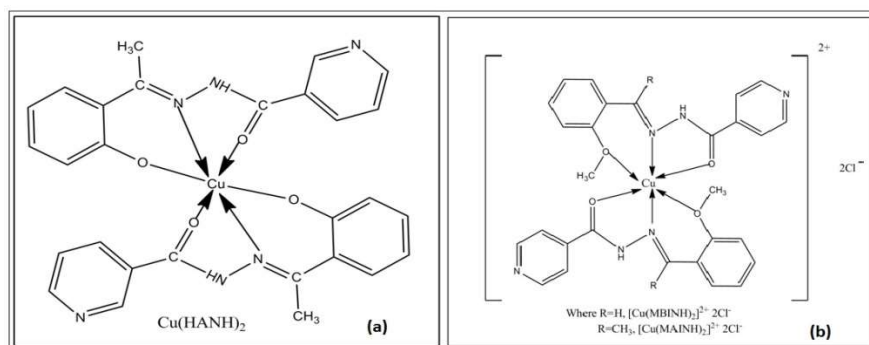


Fig.-7: (a) General Structure of Cu(HANH)₂ (b) General Structure of [Cu(MBINH)₂]Cl₂ & [Cu(MAINH)₂]Cl₂

The stable redox species are present in the solution, as shown by repeated scans at different scan speeds. For all copper complexes, the $E_{1/2}$ values are observed in the potential range of 0.339-0.569 V. All Cu(II) complexes are ultimately converted to Copper(I) species, according to this result. Different currents in the cathodic and anodic peaks imply that complexes are naturally quasi-reversible.²⁸ The quasi-reversible character of complexes is represented by a larger gap (E_p) between the cathodic and anodic peaks than the Nernst value of 59/n mV (where n is the number of electrons involved in the redox reaction).

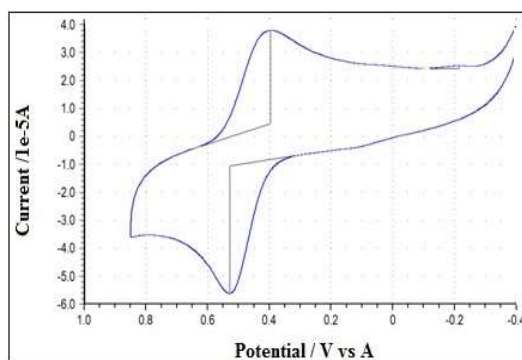


Fig.-8: Cyclic Voltammogram of [Cu(MBINH)₂]Cl₂

Table-5: Cyclic Voltammetric Data of Cu(II) Complexes

Complex	Redox couple	E_p V	E_a V	ΔE (mV)	$E_{1/2}$	$-i_c/i_a$	$\log K_c^a$	ΔG^{ob}
Cu(HANH) ₂	II/I	0.124	0.431	307	0.339	0.654	0.109	625
[Cu(MBINH) ₂]Cl ₂	II/I	0.392	0.531	139	0.461	0.648	0.241	1383
[Cu(MAINH) ₂]Cl ₂	II/I	0.314	0.511	197	0.569	0.629	0.171	981

^a $\log K_c = 0.434ZF/RT\Delta E_p$; ^b $\Delta G^\circ = -2.303RT \log K_c$

Antibacterial Activity

Using the disc diffusion technique, the antibacterial activity of three ligands and their copper complexes is assessed. Standard antibiotic use is s-ciprofloxacin. The produced compounds were evaluated against +ve (*S. aureus*, *B. cereus*) and -ve (*E. coli*, *S. typhi*). These findings suggest that copper complexes operate more effectively against microorganisms than do ligands. Table-6 shows how conventional medication, ligand, and their complexes affect the development of different microorganisms. Figure-9 displays antibacterial activity data for standard, ligands, and copper complexes. Copper complexes' antibacterial properties showed stronger effects on several bacterium strains. Generally speaking, the activity of metal complexes is superior to that of ligands. Due to the link of the partial positive charge shared by the metal ion and the ligand orbital during complexation, the polarity of the metal cation is reduced to a particular range. Chelation is increased when metal complexes interact with the organism. Resonance of π -electrons rises with chelation, which also makes complexes more lipophilic. Complexes can so quickly enter an organism and obstruct the enzyme sites of microorganisms. Metal complexes also prevent the cell's ability to respire, inhibit the manufacturing of proteins, and halt further organism growth. The chelation hypothesis proposed by Tweedy and the overtone notion led to an increase in the antimicrobial activity of metal complexes.^{29,30} The $[\text{Cu}(\text{MAINH})_2]\text{Cl}_2$ complex is discovered to have greater antibacterial activity when compared to the other two complexes. Figure-9 illustrates a graphical representation of the antibacterial activity exhibited by the ligands and their corresponding copper complexes.

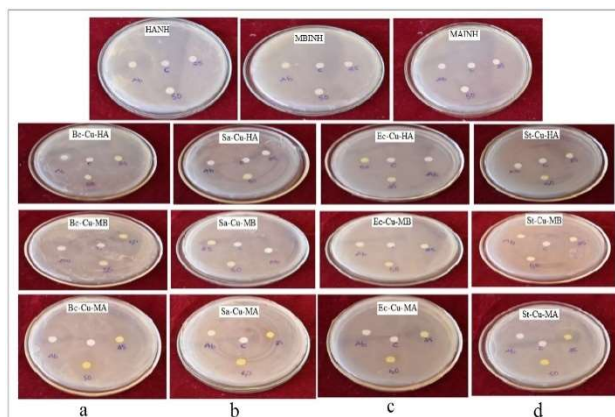
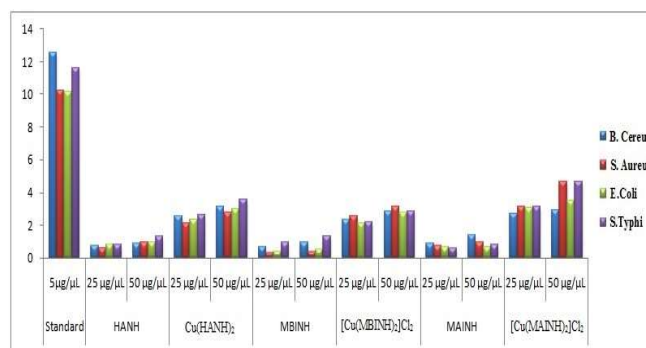


Fig.-8: Photographs Showing the Anti-Bacterial Activity of Metal Complexes (a) *B. Cereus* (b) *S. Aureus* (c) *E. Coli* (d) *S. Typhi* Bc-Bacillus Cereus, Sa-Staphylococcus Aureus, Ec-Escherichia coli, Sa-Salmonella Typhi, Cu-Copper, HA-HANH, MB-MBINH, MA-MAINH

Table-6: The Antibacterial Activity of Both the Ligands and Their Copper Complexes

Complex	Treatment	Bacterial growth inhibition zone (in mm)			
		<i>B. Cereus</i>	<i>S. Aureus</i>	<i>E. Coli</i>	<i>S. Typhi</i>
s-Ciprofloxacin	5 $\mu\text{g}/\mu\text{L}$	12.56	10.21	10.11	11.63
HANH	25 $\mu\text{g}/\mu\text{L}$	0.76	0.58	0.83	0.81
	50 $\mu\text{g}/\mu\text{L}$	0.88	0.91	0.94	1.28
$\text{Cu}(\text{HANH})_2$	25 $\mu\text{g}/\mu\text{L}$	2.52	2.10	2.33	2.61
	50 $\mu\text{g}/\mu\text{L}$	3.12	2.75	3.01	3.54
MBINH	25 $\mu\text{g}/\mu\text{L}$	0.68	0.28	0.36	0.92
	50 $\mu\text{g}/\mu\text{L}$	0.91	0.35	0.50	1.34
$[\text{Cu}(\text{MBINH})_2]\text{Cl}_2$	25 $\mu\text{g}/\mu\text{L}$	2.30	2.54	2.13	2.16
	50 $\mu\text{g}/\mu\text{L}$	2.84	3.15	2.73	2.81
MAINH	25 $\mu\text{g}/\mu\text{L}$	0.85	0.72	0.62	0.56
	50 $\mu\text{g}/\mu\text{L}$	1.39	0.93	0.64	0.79
$[\text{Cu}(\text{MAINH})_2]\text{Cl}_2$	25 $\mu\text{g}/\mu\text{L}$	2.68	3.10	3.02	3.10
	50 $\mu\text{g}/\mu\text{L}$	2.90	4.61	3.50	4.63



Standard: s-Ciprofloxacin

Fig.-9: Graphical Representation of the Antibacterial Activity of both the Ligands and Their Corresponding Copper Complexes

CONCLUSION

Physico-chemical, mass, UV-visible, IR, and ESR spectrum analyses are used to characterize the copper complexes of HANH, MBINH, and MAINH. According to the current findings, the Copper complex of HANH has the general formula ML_2 (where L equals HANH). The tridentate HANH ligand functions as a mono-negative ligand. The typical formula for copper complexes of MBINH & MAINH is $[ML]_2Cl_2$ ($M=Cu$, $L=MBINH$ & $MAINH$), and these ligands function as neutral tridentate ligands. The octahedral geometry of the complexes is shown by UV-visible spectrum data. ESR spectra are used to examine the copper complexes at both room temperature (RT) and liquid nitrogen temperature (LNT). The current work also studies the antibacterial activity of ligands and their metal complexes. When a complex forms, the ligand's biological activity usually increases. The $[Cu(MAINH)_2]Cl_2$ complex is discovered to exhibit greater antibacterial activity among the three complexes.

ACKNOWLEDGMENTS

The authors thank UGC and DST for providing equipment facilities under the SAP and FIST programs, respectively.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

E. Lakshmi <https://orcid.org/0009-0007-4718-6411>

K. Raja <https://orcid.org/0000-0003-3765-1467>

P. Raveendra Reddy <https://orcid.org/0009-0006-2775-8550>

K. Hussain Reddy <https://orcid.org/0000-0001-5543-7478>

A. Suseelamma <https://orcid.org/0009-0006-3177-7762>

Open Access: This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

REFERENCES

1. A. Chakraborty, P. Kumar, K. Ghosh, and P. Roy, *European Journal of Pharmacology*, **647**, 1(2010), <https://doi.org/10.1016/j.ejphar.2010.08.003>
2. F. Liang, C. Wu, H. Lin, T. Li, D. Gao, Z. Li, J. Wei, C. Zheng and M. Sun, *Bioorganic and Medicinal Chemistry Letters*, **13**, 2469 (2003), [https://doi.org/10.1016/S0960-894X\(03\)00489-X](https://doi.org/10.1016/S0960-894X(03)00489-X)

3. N. K. Singh, S. Shrestha, N. Shahi, R. K. Choudhary, A. A. Kumbhar, Y. R. Pokharel and P. N. Yadav, *RASĀYAN Journal of Chemistry*, **14**, 1600(2021), <http://doi.org/10.31788/RJC.2021.1436341>
4. R. Kothari and A. Agrawal, *RASĀYAN Journal of Chemistry*, **13**, 1672(2020), <http://dx.doi.org/10.31788/RJC.2020.1335717>
5. E. L. Hegg and J. N. Burstyn, *Coordination Chemistry Reviews*, **173**, 133(1998), [https://doi.org/10.1016/S0010-8545\(98\)00157-X](https://doi.org/10.1016/S0010-8545(98)00157-X)
6. A. Krishna, K. Hussain Reddy and D. Venkata Reddy, *Inorganic Chimica Acta*, **173**, 13(1990), [https://doi.org/10.1016/S0020-1693\(00\)91049-1](https://doi.org/10.1016/S0020-1693(00)91049-1)
7. R. H. Holm, P. Kennepohl, and E. I. Solomon, *Chemical Reviews*, **96**, 2239(1996), <https://doi.org/10.1021/cr9500390>
8. M. A. Ali, C. M. Haroon, M. Nazimuddin, S. M. M.-U. Majumder, M. T. H. Tarafder, and M. A. Khair, *Transition Metal Chemistry*, **17**, 133(1992)
9. P. HariBabu, K. HussainReddy, Y.K. Patil and M. Nethaji, *Indian Journal of Chemistry*, **52A**, 327(2013)
10. K. Hussain Reddy, M.R. Reddy and K.M. Raju, *Indian Journal of Chemistry*, **39A**, 1312(2000)
11. D. Kannan and M. N. Arumugham, *Elixir Applied Chemistry*, **74**, 27007(2014).
12. S. Dhar, D. Senapati, P. K. Das, P. Chattopadhyay, M. Nethaji, and A. R. Chakravarty, *Journal of American Chemical Society*, **125**, 12118 (2003), <https://doi.org/10.1021/ja036681q>
13. S. Dhar, P. A. N. Reddy, M. Nethaji, S. Mahadevan, M. K. Saha, and A. R. Chakravarty, *Inorganic Chemistry*, **41**, 3469 (2002), <https://doi.org/10.1021/ic0201396>
14. D. Shingnapurkar, P. Dandawate, C.E. Anson, A.K. Powell, Z. Afrasiabi, E. Sinn, S. Pandit, K.V. Swamy, S. Franzblau and S.Padhye, *Bioorganic and Medicinal Chemistry Letters*, **22**, 3172(2012), <https://doi.org/10.1016/j.bmcl.2012.03.047>
15. N. Mathew, M. Sithambaresan, M. R. P. Kurup, *SpectrochimicaActa A: Molecular and Biomolecular Spectroscopy*, **79**, 1154 (2011), <https://doi.org/10.1016/j.saa.2011.04.036>
16. L. Mitu, M. Ilis, N. Raman, M. Imran And S. Ravichandran, *European Journal of Chemistry*, **4**, 365 (2012), <https://doi.org/10.1155/2012/298175>
17. P. Ramadevi, R. Singh, A. Prajapati, G. Sarita, and D. Chakraborty, *International Journey of Inorganic Chemistry*, **1** (2014), <https://doi.org/10.1155/2014/630575>
18. M. LoredanaDianu, A. Krizal, N. StanicaAnd A. M. Magdalena, *Journal of Serbian Chemical Society*, **75**, 1515 (2010), <https://doi.org/10.2298/JSC091113121D>
19. S. S. Kolate, G. P. Waghulde and C. J. Patil, *RASĀYAN Journal of Chemistry*, **13**, 1008(2020), <http://dx.doi.org/10.31788/RJC.2020.132560>
20. B. Mounyr, M. Sadiki and S. K. Ibsouda, *Journal of Pharmaceutical Analysis*, **6**, 71(2016), <https://doi.org/10.1016/j.jpha.2015.11.005>
21. S. Mandal, R. Shukla P. K. Bharadwaj, *Polyhedron*, **11**, 1855(1992), [https://doi.org/10.1016/S0277-5387\(00\)83732-8](https://doi.org/10.1016/S0277-5387(00)83732-8)
22. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd. Edn, (Elsevier, Amsterdam) (1984).
23. V. L. Siji, M. R. S. Kumar, S. Sumaand M. R. P. Kurup, *SpectrochimicaActa Part A*, **76**, 22(2010), <https://doi.org/10.1016/j.saa.2010.02.035>
24. R. J. Kunnath, M. Sithambaresan, A. A. Aravindakshan, A. Natarajan and M. R. P. Kurup, *Polyhedron*, **113**, 73(2016), <https://doi.org/10.1016/j.poly.2016.04.003>
25. D. Kivelson and R. Neiman, *Journal of Chemical Physics*, **35**, 149(1961), <https://doi.org/10.1063/1.1731880>
26. K. K. Narang and P. V. Singh, *Transition Metal Chemistry*, **21**, 507(1996)
27. I. M. Procter, B. J. Hathaway, P. Nicholis, *Journal of Chemical Society A*, **(1968)**, 1678, <https://doi.org/10.1039/J19680001678>
28. A. Khumhar, S. B. Rendye, D. X. West, A. E. Libert, *Transition Metal Chemistry*, **16**, 276 (1991)
29. N. Dharmaraj, P. Viswanathamurthi and Natarajan, *Transition Metal Chemistry*, **26**, 105 (2001),
30. B. G. Tweedy, *Phytopathology*, **55**, 910 (1954), <http://dx.doi.org/10.4236/ojic.2015.54011>

[RJC-6764/2022]

