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Solvent Free Synthesis of some Metal Complexes of Novel Ligand Derived from 2-Amino-5, 6-Dimethyl Benzimidazole with 2-Bromo Isophthalaldehyde and Characterization, Biological Activity of Same

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Abstract: A solvent free and environmentally green synthesis using scientific microwave method of novel ligand derived from 2-amino-5,6-dimethyl benzimidazole with 2-bromo Isophthalaldehyde. Metal complexes were derived from nitrate of Mn(II) and chlorides Ag(I), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III) salts with novel ligand. At the end of the reaction all metal complexes show fine color. By TLC and melting point of each complex was confirming the formation of metal complex. Characterization of novel ligand carried out by elemental analysis, IR spectroscopy, ¹HNMR spectroscopy, LCMS and characterization of metal complexes carried out by IR spectroscopy, UV spectroscopy and TGA. The novel ligand and its all metal complexes show antibacterial activity against E-Coli, S.Aureus and S.Typhi.

Keywords: Solvent free, Green Synthesis, 2-amino-5,6-dimethyl benzimidazole, 2-bromo Isophthalaldehyde, Antibacterial activity.

I. INTRODUCTION

Solvent free, green and eco-friendly view of synthesis is increasing in chemistry. Now a day, use of scientific microwave for synthesis is becoming popular. This is the solvent free or less solvent synthesis. It helps to reduce pollution, gives better yield and reduces cost. Simple reaction conditions and important is time saving [1-3]. Synthesis using microwave irradiation technique is environmentally very safe and effective [4-5]. The compound containing Azomethine/Imine (C=N) group are known as Schiff base ligand [6]. The products of ketone or aldehyde with primary amine are generally known as Schiff base [7]. They are biologically very active compounds, having biological activities like antibacterial [8], antimicrobial [9], anticancer [10], plant growth inhibitors [11] and so on.

II. EXPERIMENTAL SECTION

All the chemicals used in this work were of analytical grade. 2-amino-5,6-dimethyl benzimidazole and 2-bromo Isophthalaldehyde form Sigma Aldrich and metal nitrates and chlorides from loba chem and MERCK. The novel ligand synthesized in scientific microwave oven. Metal complexes were synthesized by reacting novel ligand with metal salts in scientific microwave oven.

A. Material and Method

All the starting chemicals are of analytical grade. 2-amino-5,6-dimethyl benzimidazole and 2-bromo Isophthalaldehyde were purchased from Sigma Aldrich and metal salts from Loba chem and MERCK. The novel Schiff base ligand was synthesized by using scientific microwave oven. Syntheses of metal complexes were performed by reacting Schiff base ligand with metal salts in scientific microwave oven.

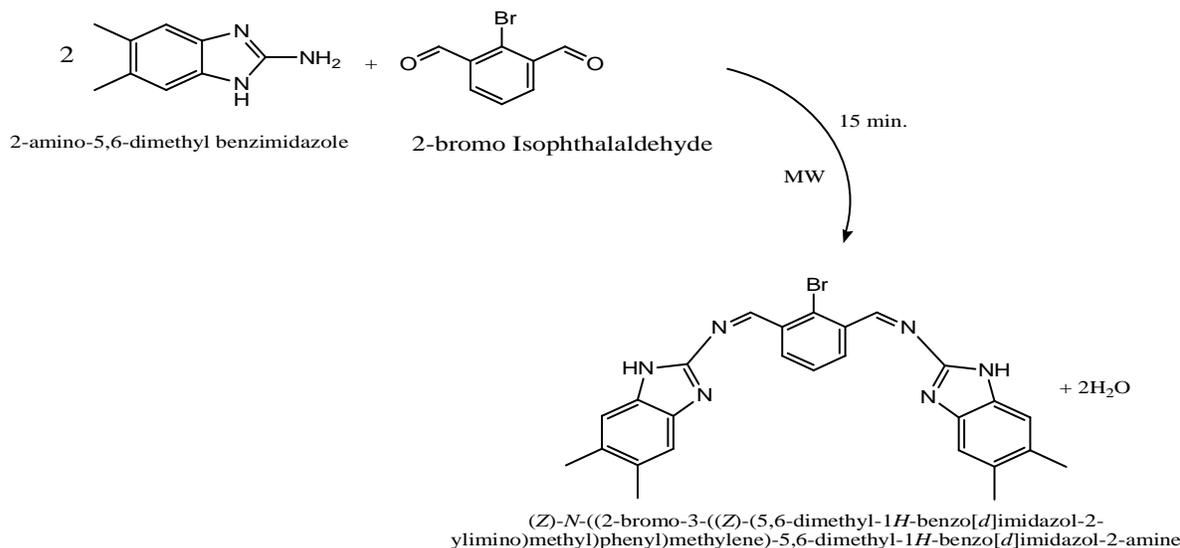
B. Techniques

Synthesis was performing in microwave extraction system in scientific microwave oven. Melting points were measured on digital melting point apparatus. The electronic absorption spectra were recorded in the wavelength range 200 to 400 nm using UV spectrophotometer. IR spectra were analyses on Shimadzu Dr 8031. The ¹HNMR spectra was analyse in DMSO D6 on Brakers 400 MHz instrument. The mass spectrum was recorded by LCMS spectrophotometer. The TGA were carried out in dynamic nitrogen atmosphere (30ml/min) with heating rate of 10⁰C/min using Shimadzu TGA 50H thermal analyser. TLC analysis performs on pre coated aluminium plates.

C. Preparation of Novel Ligand

The novel Schiff base ligand was prepared by the reaction between 2-amino-5,6-dimethyl benzimidazole (0.63 gm.) and 2-bromo Isophthalaldehyde (0.38 gm.) under solvent free condition in scientific microwave oven about 15 min. The irradiated product after cooling at room temperature washed with dry ether. The yield obtained was 0.84 gm. And melting point was 256^oC. The purity of the product confirm by TLC.

1) Reaction



D. Preparation of Metal Complexes

The metal complexes were synthesized under solvent free condition by irradiating metal nitrate or metal chloride with the required amount of the ligand. The reaction mixture was irradiated in microwave oven. The products were washed with dry ether, filter and dried at room temperature. The metal salts used were $MnCl_2$, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ and $AgNO_3$.

III. RESULT AND DISCUSSION

All metal complexes and novel ligand are colored, solid and stable at room temperature. They possess sharp melting point. The complexes are insoluble in common organic solvents but soluble in DMF and DMSO.

A. Physical Properties

Physical properties of the novel ligand and metal complexes summarized in Table I

Table I

Sr. No	Molecular formula	Color	Melting point (°C)	Time	Yield %
1	$C_{26}H_{23}N_6Br$	Yellow	256	15 min	83
2	$[(C_{26}H_{23}N_6Br)_2(H_2O)_4]Mn$	Dark Yellow	181	240 sec.	83
3	$[(C_{26}H_{23}N_6Br)_2(H_2O)_4]Fe$	Brown	188	60 sec.	85
4	$[(C_{26}H_{23}N_6Br)_2(H_2O)_4]Co$	Brown	174	120 sec.	96
5	$[(C_{26}H_{23}N_6Br)_2(H_2O)_4]Ni$	Light Green	208	60 sec.	100
6	$[(C_{26}H_{23}N_6Br)_2(H_2O)_4]Cu$	Green	148	60 sec.	100
7	$[(C_{26}H_{23}N_6Br)_2(H_2O)_4]Zn$	Dark Yellow	132	60 sec.	100
8	$[(C_{26}H_{23}N_6Br)_2(H_2O)_4]Cd$	Greenish	280	90 sec.	100
9	$[(C_{26}H_{23}N_6Br)_2(H_2O)_4]Ag$	Yellow	218	60 sec.	100

B. Mass Spectral Studies

The mass spectrum study of novel ligand showed a peak at m/z . 500(M+1) that corresponds to the molecular weight of the Schiff base ligand 499.

C. ^1H NMR Spectral Studies

Observed ^1H NMR peaks (ppm) of novel Schiff base ligand summarized in Table II.

Table-II

Compound	H-from four Methyl Groups in ppm	H-from Aromatic ring In ppm	H-from-NH of Imidazole In ppm
$\text{C}_{26}\text{H}_{23}\text{N}_6\text{Br}$	2.50 - 2.51	6.87 - 8.48	5.89

The ^1H NMR spectrum of novel ligand shows different peaks. The characteristic peak observed at 5.89 ppm is due to H-from NH-of Imidazole. The peaks observed at 6.87 – 8.48 ppm are due to H-from aromatic rings. The peaks observed at 2.50 - 2.51 ppm is due to H-from four Methyl Groups.

D. Infrared spectra analysis

Observed IR frequencies of novel ligand and its metal complexes summarized in Table III.

Table-III

Sr. No	Ligand/complex	C=N (cm^{-1})	C-H (cm^{-1})	N-H (cm^{-1})	C=C (cm^{-1})	M-N (cm^{-1})
1	$\text{C}_{26}\text{H}_{23}\text{N}_6\text{Br}$	1662.64	3280.92	3452.58	1471.69	---
2	$[(\text{C}_{26}\text{H}_{23}\text{N}_6\text{Br})_2(\text{H}_2\text{O})_4]\text{Ni}$	1730.15	3200.00	3420.00	1454.33	576.72
3	$[(\text{C}_{26}\text{H}_{23}\text{N}_6\text{Br})_2(\text{H}_2\text{O})_4]\text{Cu}$	1680.00	3190.00	3400.00	1575.84	513.07

The IR spectrum of novel ligand show characteristics band at 1662.64 cm^{-1} which indicates (C=N) stretching vibration of azomethine group [12-17]. The vibrational band at 3452.58 cm^{-1} assigned N-H stretching in the ligand. Band observed at 1471.69 cm^{-1} corresponds to C=C stretching. The band observed at 3280.92 cm^{-1} indicates aromatic C-H stretching in the ligand.

IR spectral study of Ni metal complex: The band appeared at 1730.15 cm^{-1} corresponds to azomethine (C=N) stretching, whereas same azomethine band is observed at 1662.64 cm^{-1} in spectrum of ligand. Which indicate coordination of ligand with metal ion [18]. The band appeared at 3200.00 cm^{-1} indicates the aromatic (C-H) stretching in complex, whereas same aromatic (C-H) stretching is observed at 3280.92 cm^{-1} in spectrum of ligand. The band observed at 3420.00 cm^{-1} assign to (N-H) stretching, whereas in spectrum of ligand it is observed at 3425.58 cm^{-1} . The vibration observed at 1454.33 cm^{-1} due to aromatic (C=C) stretching. The characteristics band appeared at 576.72 cm^{-1} assign to (M-N) vibration, which confirms coordination of azomethine and metal ion [19-20]. The weak bands observed at 825.53 cm^{-1} and 1035.77 cm^{-1} were due to OH wagging mode of vibration, indicating coordination of water molecule in metal complex [21-24]. Above bands which are appeared in spectrum of complex are not appeared in spectrum of ligand that confirm the formation of metal complex with stable metal ligand bonding.

IR spectral study of Cu metal complex: A stretching observed at 1680.00 cm^{-1} , which corresponds to azomethine (C=N) stretching vibrations, whereas same stretching is observed at 1662.64 cm^{-1} in spectrum of ligand. The band appeared at 3190.00 cm^{-1} assign to aromatic (C-H) stretching, whereas same stretching is observed at 3280.92 cm^{-1} in spectrum of ligand. The vibration observed at 1575.84 cm^{-1} due to aromatic (C=C) stretching. The coordination of metal to nitrogen was justified by stretching observed at 490 cm^{-1} [25]. The weak bands observed at 825.53 cm^{-1} and 1033.85 cm^{-1} were due to OH wagging mode of vibration, indicating coordination of water molecule in metal complex [21-24]. Above bands which are appeared in spectrum of complex are not appeared in spectrum of ligand that confirm the formation of metal complex with stable metal ligand bonding.

E. Electronic spectra

UV-Vis spectral data and probable geometry for the metal complexes summarized in Table IV

Table-IV

Sr. No.	Complex	UV-visible major bands. Absorption Maxima cm^{-1} (nm)	Assignment	Proposed geometry
1	$[(\text{C}_{26}\text{H}_{23}\text{N}_6\text{Br})_2(\text{H}_2\text{O})_4]\text{Ni}$	43898.15 (227.80)	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$	Octahedral
		44563.27 (224.40)	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$	
		47438.33 (210.80)	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$	
2	$[(\text{C}_{26}\text{H}_{23}\text{N}_6\text{Br})_2(\text{H}_2\text{O})_4]\text{Cu}$	40650.40 (216.00)	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$	Octahedral
		46296.29 (208.60)	${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$	
			${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	

UV-Vis spectrum of both metal complexes Ni(II), Cu(II) recorded in the wavelength region 200nm to 400nm in DMSO solution.

UV-Vis spectral data of Ni: Electronic spectrum of Ni(II) complex shows absorption maxima at 43898.15 (227.80), 44563.27 (224.40) and 47438.33 (210.80) assign to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions respectively indicating that complex possess octahedral geometry[26-27].

UV-Vis spectral data of Cu: Electronic spectrum of Cu(II) complex shows absorption maxima at 40650.40 (216.00) and 46296.29 (208.60) assign to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transitions indicating that complex possess octahedral geometry[28-29].

F. Thermo Gravimetric Analysis of Metal Complexes

Thermo gravimetric analytical data of metal complexes were summarized in Table V.

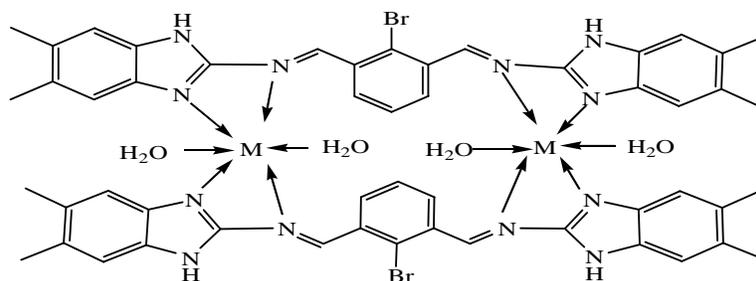
Table-V

$[(\text{C}_{26}\text{H}_{23}\text{N}_6\text{Br})_2(\text{H}_2\text{O})_4]\text{Ni}$		$[(\text{C}_{26}\text{H}_{23}\text{N}_6\text{Br})_2(\text{H}_2\text{O})_4]\text{Cu}$	
Weight loss %	Temperature $^{\circ}\text{C}$	Weight loss %	Temperature $^{\circ}\text{C}$
0	29.22	0	29.74
10	143.30	10	93.52
20	213.54	20	145.87
30	292.20	30	226.75
40	314.92	40	263.84
50	367.38	50	348.18
60	422.05	60	377.77
70	449.05	70	394.49
80	476.17	80	452.83
84.184% total wt. loss	500	84.832% total wt. loss	500

The TGA curve of Ni(II) was carried out in the temperature range from 29.22 $^{\circ}\text{C}$ to 500 $^{\circ}\text{C}$. The heating was carried out in the nitrogen atmosphere, with heating rate 10 $^{\circ}\text{C min}^{-1}$.

In the range of 29.94 $^{\circ}\text{C}$ to 143.30 $^{\circ}\text{C}$ water of crystallization lost with 10% weight loss is observed. Then loss up to organic moiety total weight loss of 84.184% at 500 $^{\circ}\text{C}$. Stable curve indicates formation of metal oxide of nickel.

The TGA curve of Cu(II) was carried out in the temperature range from 29.74 $^{\circ}\text{C}$ to 500 $^{\circ}\text{C}$. The heating was carried out in the nitrogen atmosphere, with heating rate 10 $^{\circ}\text{C min}^{-1}$. The thermogram of Cu(II) shows total weight loss of 69.51%. Firstly loss water of crystallization in the range of 29.74 $^{\circ}\text{C}$ to 93.52 $^{\circ}\text{C}$. Lastly loss of organic moiety with total weight loss at 500 $^{\circ}\text{C}$ was 84.832%. A stable curve shows the formation of metal oxide of copper.



Proposed structure of metal complex (M)=Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I).

G. Bioactivity Study

Antibacterial activity of novel Schiff base ligand and its metal complexes were summarized in Table VI.

Table-VI

Sr. No.	Compound	Minimum inhibition concentration (ug/ml)		
		E. Coli	S. Aureus	S. Typhi
1	C ₂₆ H ₂₃ N ₆ Br	250	125	250
2	[(C ₂₆ H ₂₃ N ₆ Br) ₂ (H ₂ O) ₄]Mn	62.5	500	250
3	[(C ₂₆ H ₂₃ N ₆ Br) ₂ (H ₂ O) ₄]Fe	500	500	100
4	[(C ₂₆ H ₂₃ N ₆ Br) ₂ (H ₂ O) ₄]Co	100	250	100
5	[(C ₂₆ H ₂₃ N ₆ Br) ₂ (H ₂ O) ₄]Ni	125	250	50
6	[(C ₂₆ H ₂₃ N ₆ Br) ₂ (H ₂ O) ₄]Cu	100	250	125
7	[(C ₂₆ H ₂₃ N ₆ Br) ₂ (H ₂ O) ₄]Zn	200	50	25
8	[(C ₂₆ H ₂₃ N ₆ Br) ₂ (H ₂ O) ₄]Cd	100	125	125
9	[(C ₂₆ H ₂₃ N ₆ Br) ₂ (H ₂ O) ₄]Ag	250	250	200

Antibacterial activity of synthesized novel ligand and its metal complexes were performing against Escherichia Coli, Staphylococcus Aureus and Salmonella Typhi. Which were grown overnight at 37⁰C temperature. The minimum inhibitory concentration (MIC) was evaluated against test bacteria. Concentration ranging is in between 0.4 ug/ml to 10 ug/ml.

Mn(II) shows better and Co(II), Cu(II), Cd(II) good antibacterial activity on E.coli as compared to rest of metal complexes and parent ligand. Zn(II) complex shows excellent antibacterial activity on S.Aureus as compared to rest of metal complexes and parent ligand. Zn(II) and Ni(II) shows excellent antibacterial activity on S.Typhi as compared to rest of metal complexes and parent ligand.

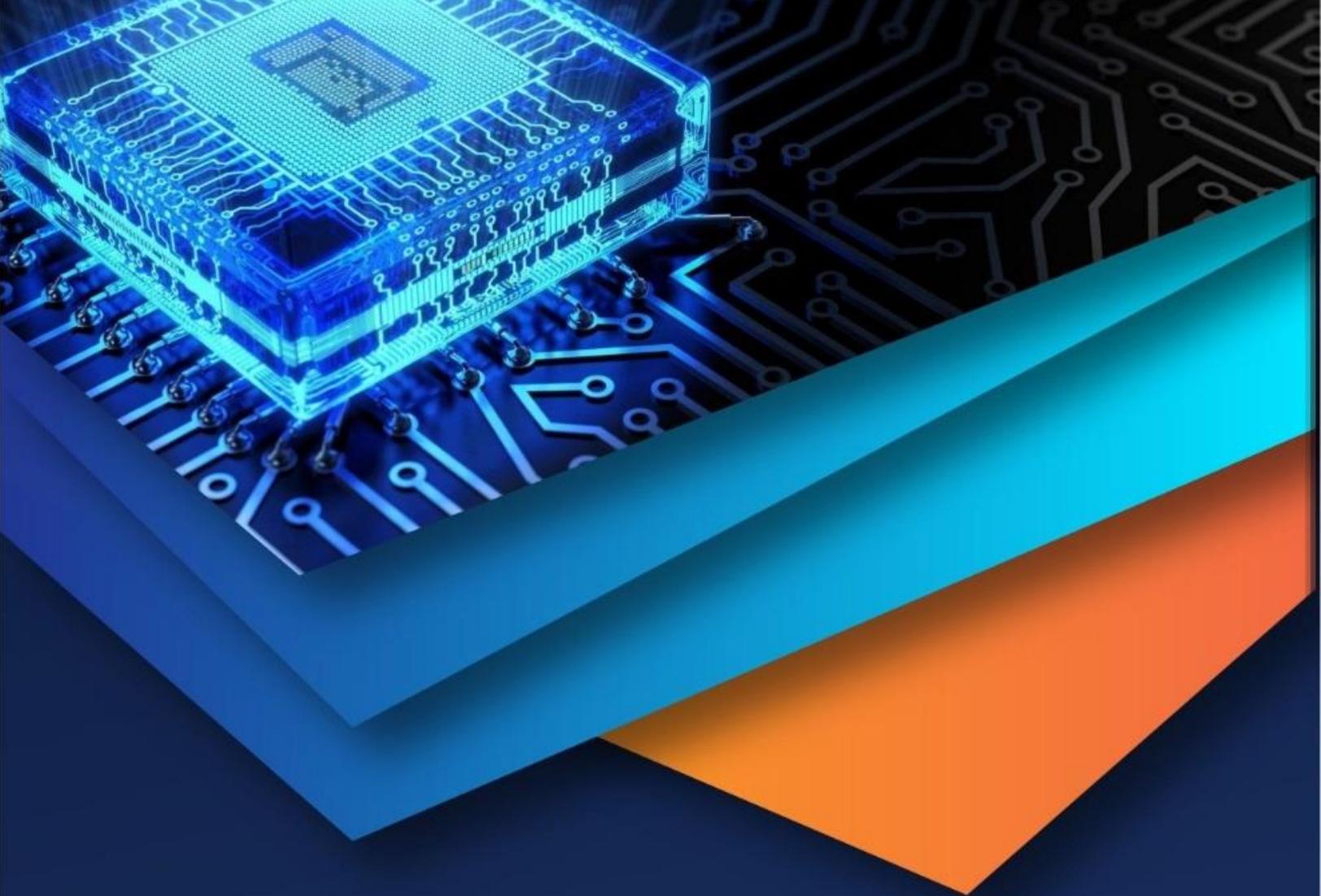
IV. CONCLUSION

The microwave method assures the principle of green chemistry. The novel ligand was synthesized from 2-amino-5,6-dimethyl benzimidazole and 2-bromo Isophthalaldehyde. It forms stable binuclear complexes with transition metal ions such as Mn(II), Fe(III), Ni(II), Cu(II), Co(II), Zn(II), Cd(II) and Ag(I). The novel ligand and its eight metal complexes show good antibacterial activity.

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