



SOLVENT FREE SYNTHESIS AND CHARACTERIZATION OF SOME BIOACTIVE METAL COMPLEXES OF SCHIFF BASE LIGAND DERIVED FROM 2-AMINO-5, 6-DIMETHYL BENZIMIDAZOLE AND 4, 4'-DIBROMO BENZIL

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ABSTRACT

A tetra dentate Schiff base ligand was synthesized by treating 2-Amino-5, 6-dimethyl benzimidazole with 4, 4'-dibromo benzil under solvent free condition in 2:1 molar proportion in a scientific microwave oven. Yield obtained was very high after purification of synthesized product. Some transition metal complex of this synthesized Schiff base ligand were prepared by using Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Ag(I) metal salts in microwave oven under solvent free condition. The metal complexes formed were confirmed by their distinguishing color and exact melting point. Schiff base ligand was further characterized by TLC, elemental analysis, IR spectroscopy, LCMS and ¹H NMR Spectroscopy. The metal complexes were identified by TLC and representatively characterized by IR spectroscopy, UV spectroscopy and DSC. Both Schiff base ligand and its synthesized metal complexes screened for bioactivity study against *Escherichia Coli*, *Staphylococcus Aureus* & *Salmonella Typhi* by MIC measurement. MIC study clearly indicates Fe (III) complex & Cu (II) complex displays highest activity against *Escherichia Coli*, Cu (II) complex & Ag (I) complex displays highest activity against *Staphylococcus Aureus* whereas Co (II) complex displays highest activity against *Salmonella Typhi* compared to novel ligand and rest of the metal complexes.

Keywords: Solvent free, 2-Amino-5, 6-dimethyl benzimidazole, 4,4'-dibromobenzil

1. INTRODUCTION

Schiff bases have attracted many researchers as these can be easily prepared by a condensation reaction between primary amine and an aldehyde / ketone. They have capacity to form coordinate bond with several metal ions to form stable structure [1, 2]. Schiff base ligands and their corresponding metal complexes show a very broad range of applications in medicinal sector and drug synthesis [3]. The azomethine group (>C=N-) of Schiff base forms stable complex with metal ions leading to chelation [4]. Chemically Schiff base is an imine molecule showing good pharmacophore characteristics in medicinal field [5]. The lone pair of electron in N atom of azomethine group show actual chelation with vacant d orbital of metal ions leading to medicinal applications [6, 7]. It is also observed that Schiff base having heterocyclic moiety shows noticeable chemotherapeutic and antioxidant properties [8, 9]. Current work basically focuses on solvent free microwave assisted synthesis of

Schiff base and its corresponding transition metal complexes. This method is of interest for many researchers due to its time saving, reduction in cost, no pollution factors [10, 11]. Along with that microwave assisted solvent free synthesis has several advantages including betterment in yield, lesser possibility of accident and being environmentally safe [12-14]. The Schiff bases and its corresponding metal complexes also show significant antimicrobial activities like herbicidal, antibacterial [15, 16], anticancer, antidiabetic [17], anti-inflammatory [18], antifungal [19, 20] and antitumor [21].

2. EXPERIMENTAL SECTION

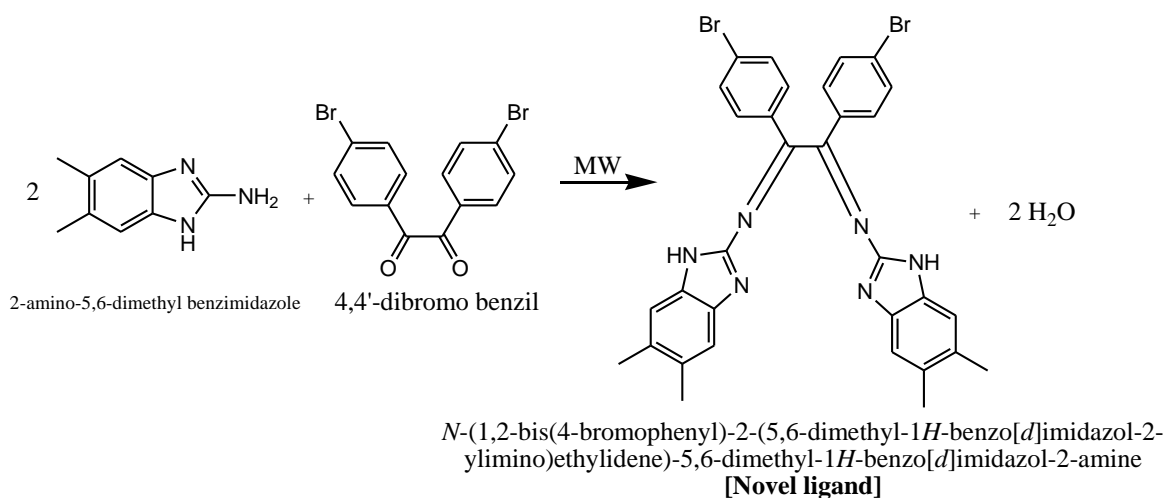
2.1. Material methods

Chemicals were purchased from Sigma Alderich, Merck, Loba Chem. 2-Amino-5, 6-dimethyl benzimidazole and 4, 4'-dibromo benzil were purchased from Sigma Alderich and metal nitrates from Merck, Loba Chem. All

chemicals were used as received. The parent ligand was synthesized by the condensation reaction between 2-Amino-5, 6-dimethyl benzimidazole and 4, 4'-dibromo benzil in 2:1 molar ratio under solvent free condition in a scientific micro oven. After preparation of parent ligand, metal complexes were synthesized by treating parent ligand with metal salt under solvent free condition in the same microwave oven.

2.2. Techniques

A scientific micro oven, 2450 MHz frequency and 800 W, was used to perform all syntheses. A digital melting point apparatus was used to record melting points. The IR spectrum was recorded on a Shimadzu Dr-8031 instrument. The electronic absorption spectra were recorded by using DMSO as a solvent in UV-VIS spectroscopy. The mass spectrum was recorded on LC-MS spectrophotometer. ¹HNMR spectrum was recorded in DMSO-d₆ on Bruker's 400 MHz instrument. The Differential Scanning calorimetry analyses [DSC] were carried out using Shimadzu TGA-50H thermal analyzer



2.4. Synthesis of metal complexes

The metal complexes were synthesized under solvent free condition by same microwave irradiation method. The metal salt was mixed with required amount of novel ligand, *N*-(1,2-bis(4-bromophenyl)-2-(5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-ylimino)ethylidene)-5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-amine, in a grinder to mix completely. Afterwards reactant mixture was irradiated for few seconds to minutes in the microwave at 750 W. The product obtained was washed and recrystallized with hot ethanol and dried at room temperature. The melting point of each metal complex was recorded. The metal salts used for the synthesis of metal complexes were MnCl₂, Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·

with a heating rate of 10°C min⁻¹ in a dynamic nitrogen atmosphere (30 ml/min). Precoated aluminium plates with silica gel were used to conduct TLC analysis and UV chamber was used to visualize TLC spots.

2.3. Synthesis of novel Schiff base ligand

The novel Schiff base ligand was synthesized by treating 2-Amino-5, 6-dimethyl benzimidazole [1.62 gm, 0.01mol] with 4, 4'-dibromo benzil [1.84 gm, 0.005mol] under solvent free condition. The reaction mixture was first thoroughly mixed in a grinder and then periodically irradiated about 40 minutes at 750 W in the microwave oven. The microwave irradiated product was then cooled at room temperature for some time and then washed with dry ether. Absolute ethanol was used for recrystallization to give dark yellow coloured crystals. The yield obtained was 2.9 gm [83 %] and melting point recorded was 208°C. The progress and purity of the product was examined by using TLC. Solvent mixture used for TLC was n-hexane + ethyl acetate (7:3).

6H₂O, Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, Cd(NO₃)₂·4H₂O and AgNO₃.

2.5. Antimicrobial Screening

All the synthesized compounds were evaluated for their antibacterial activity (MIC) *in vitro* against *Escherichia Coli*, *streptococcus Aureus* and *salmonella Typhi* by micro broth dilution method [41-43]. The standard stains were procured from Microbial Type Culture Collection (MTCC) Chandigarh and Microcare Laboratory & Tubercular Research Center, Surat, Gujrat. The assay was carried out in 96 well microtitre plates as per Rieckmann and co-workers micro assay protocol with few modifications [44, 45]. A stock solution of 5 mg/ml

of each test samples was prepared using DMSO solvent. Then dilutions were prepared with culture medium. 20 μ l of each diluted sample was added to test well to obtain final concentration (at fivefold dilution) in duplicate well ranging between 0.4 μ g/ml to 100 μ g/ml containing parasitized cell preparation. The culture plates were incubated at 37°C at about 36 to 40 hours. The slides were microscopically observed to record maturation of ring stage parasites into trophozoites and schizonts in presence of different concentrations of the test agents. The test concentration which inhibited the complete maturation was recorded as the minimum inhibitory concentration (MIC). The reference drug used was Streptomycin.

3. RESULT AND DISCUSSION

After completion of solvent free synthesis of novel Schiff base and its metal complexes by microwave assisted method, some important facts were seen. The reaction

time was much shorter and final yield obtained was high. Homogeneity of the reactant mixture was increased by constant rotation of reactant keeping tray during reaction. The reaction procedures were repeated twice for confirmation of results obtained. The overall procedures were finished from few seconds to minutes. The yield obtained in every synthesis was above 80%. Each synthesized metal complex showed exact color and melting point. Each metal complex was in solid state and stable at room temperature. All the synthesized metal complexes were found to be soluble in DMSO and DMF.

3.1. Elemental composition analysis and physical properties

Elemental analysis data of novel synthesized Schiff base ligand has been presented in table 1. Physical properties of the novel ligand and its metal complexes have been presented in table 2.

Table 1: The elemental analysis (CHNO) data for novel Schiff base ligand

Compound	Empirical Formula	Mole. Weight	% C Found (calculated)	% H Found (calculated)	% N Found (calculated)	% Br Found (calculated)
Novel ligand	C ₃₂ H ₂₆ N ₆ Br ₂	654	56.73 (58.72)	4.18 (3.98)	12.32 (12.84)	26.77 (24.46)

Table 2: The details of physical properties of the novel ligand and its metal complexes

Sr. No.	Molecular Formula	Colour	M.P. (°C)	Time	Yield (%)
1	C ₃₂ H ₂₆ N ₆ Br ₂	Dark yellow	208	40 minutes	83
2	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂] ₂ Fe	Brownish	221	70 seconds	82
3	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂] ₂ Mn	Greenish yellow	215	5 minutes	90
4	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂] ₂ Co	Olive green	278	2 minutes	95
5	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂] ₂ Ni	Light green	172	60 seconds	91
6	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂] ₂ Cu	Green	194	10 seconds	86
7	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂] ₂ Zn	Yellow	302	60 seconds	91
8	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂] ₂ Cd	Yellow	218	90 seconds	83
9	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂] ₂ Ag	Bright yellow	309	90 seconds	95

3.2. Infrared spectra analysis

3.2.1. Analysis of novel ligand

The IR spectra of novel ligand showed characteristic band at 1668.43 cm^{-1} due to azomethine, $\nu(\text{C}=\text{N})$ [22], stretching. In addition to that a band at 3400 cm^{-1} showed due to NH stretching of benzimidazole ring [22, 23]. The novel ligand spectrum revealed bands at 1473.62 cm^{-1} due to aromatic $\nu(\text{C}=\text{C})$ stretching [23, 24]. Appearances of these bands confirm formation of novel ligand.

3.2.2. Analysis of metal complex (L-Mn)

The IR spectrum of L-Mn complex revealed shift in frequency of azomethine, $\nu(\text{C}=\text{N})$, stretching from

1668.43 cm^{-1} to 1681.93 cm^{-1} as compared to novel ligand [25-27]. Also band due to imidazole NH stretching shifted from 3400 cm^{-1} to 3261.63 cm^{-1} and aromatic $\nu(\text{C}=\text{C})$ stretching shifted from 1473.62 cm^{-1} to 1483.26 cm^{-1} and another appeared at 1587.42 cm^{-1} . The most distinguishing bands of this metal complex are that of M-N and OH wagging $\nu(\text{H}_2\text{O})$. The M-N band appeared at 464.84 cm^{-1} . These bands confirmed formation of stable (L-Mn) metal complex [28-29]. The weaker bands observed at 833.25 cm^{-1} and 742.59 cm^{-1} are due to OH wagging mode of vibrations indicating presence of coordinated water (OH_2) molecules in metal complex

[30-33]. These last two characteristic bands are absent in the IR spectrum of novel ligand.

3.2.3. Analysis of metal complex (L-Co)

The IR spectrum of L-Co complex revealed shift in frequency of azomethine, $\nu(\text{C}=\text{N})$, stretching from 1668.43 cm^{-1} to 1691.97 cm^{-1} as compared to novel ligand [25-27]. Also band due to imidazole NH stretching shifted from 3400 cm^{-1} to 3439.08 cm^{-1} and aromatic $\nu(\text{C}=\text{C})$ stretching shifted from 1473.62 cm^{-1} to 1480

cm^{-1} and another appeared at 1587.42 cm^{-1} . The most distinguishing bands of this metal complex are that of M-N and OH wagging $\nu(\text{H}_2\text{O})$. The M-N band appeared at 480.28 cm^{-1} . These bands confirmed formation of stable (L-Mn) metal complex [28-29]. The weaker bands observed at 825.53 cm^{-1} and 761.88 cm^{-1} are due to OH wagging mode of vibrations indicating presence of coordinated water (OH_2) molecules in metal complex [30-33]. These last two characteristic bands are absent in the IR spectrum of novel ligand.

Table 3: Selected Infrared Frequencies (cm^{-1}) of novel ligand and its complexes

Ligand / Complex	$\nu(\text{C}=\text{N})$ Azomethine	$\nu(\text{NH})$ imidazole	$\nu(\text{C}=\text{C})$ Aromatic	$\nu(\text{M-N})$	$\nu(\text{H}_2\text{O})$ wagging
$\text{C}_{32}\text{H}_{26}\text{N}_6\text{Br}_2$	1668.43	3400	1473.62	-----	-----
$[(\text{C}_{32}\text{H}_{26}\text{N}_6\text{Br}_2)(\text{H}_2\text{O})_2]\text{Mn}$	1681.93	3261.63	1483.26, 1587.42	464.84	742.59, 833.25
$[(\text{C}_{32}\text{H}_{26}\text{N}_6\text{Br}_2)(\text{H}_2\text{O})_2]\text{Co}$	1691.97	3439.08	1480, 1587.42	480.28	761.88, 825.53

Table 4: Observed ^1H NMR Peaks (ppm) of novel ligand

Compound	H- from aromatic group (4,4'-dibromo benzyl moiety)	H- from aromatic group (benzimidazole moiety)	H-from imidazole	H-from 5,6 dimethyl group
$\text{C}_{32}\text{H}_{26}\text{N}_6\text{Br}_2$	8.83-7.18 ppm	6.87-6.85	5.91	2.51-2.19

3.3. ^1H NMR Spectral Studies

The peaks observed in ^1H NMR spectra of novel ligand clearly indicate following pattern. The multiple peaks observed at 8.83-7.18 ppm due to H-from aromatic rings (4, 4'-dibromo benzil moiety). The multiple peaks observed at 6.87-6.85 ppm due to H-from aromatic rings (benzimidazole moiety). The peak observed at 5.91 ppm (s, 2H) due to H from two imidazole NH group. The peaks observed at 2.51-2.19 ppm due to H-from methyl groups attached to aromatic rings.

3.4. Mass Spectral studies

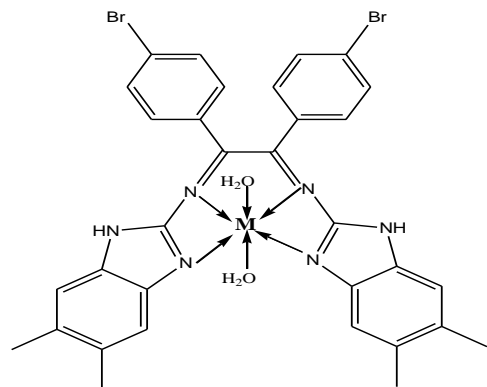
The mass spectrum study of novel ligand showed a peak at m/z 656 (M+2) which corresponds to molecular weight of the novel ligand *i.e.* 654.

3.5. Electronic spectra

The electronic spectrum of both the metal complexes (L-Mn, L-Co) recorded in the wavelength region 200 nm to 400 nm in DMSO solution. The electronic spectral data obtained for both the metal complexes is presented in Table 5.

Table 5: Electronic spectral data and probable geometries for the metal complexes

Sr.No.	Complex	UV Vis major bands Absorption maxima cm^{-1} (nm)	Assignment	Proposed Geometry
1	$[(\text{C}_{32}\text{H}_{26}\text{N}_6\text{Br}_2)(\text{H}_2\text{O})_2]\text{Mn}$	35236.08 (283.8)	$^6\text{A}_{1g} \rightarrow ^4\text{A}_{1g}(\text{G})$	Octahedral
		44208.67 (226.2)	$^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g}(\text{D})$	
		45913.68 (217.8)	$^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g}(\text{P})$ $^6\text{A}_{1g} \rightarrow ^4\text{E}_g(\text{D})$	
		47258.98 (211.6)	Charge transfer	
2	$[(\text{C}_{32}\text{H}_{26}\text{N}_6\text{Br}_2)(\text{H}_2\text{O})_2]\text{Co}$	35211.28 (284)	$^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$	Octahedral
		44642.86 (224)	$^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$	
		46948.36 (213)	$^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$	
		47125.35 (212.2)	Charge transfer	



Proposed structure of Metal complexes

[M = Mn(II) / Fe(III) / Co(II) / Ni(II) / Cu(II) / Zn(II) / Cd(II) / Ag(I)]

The electronic spectrum of the Mn (II) complex reveals major bands at 47258.98 cm^{-1} (211.6 nm), 45913.68 cm^{-1} (217.8nm), 44208.67 cm^{-1} (226.2 nm) and 35236.08 cm^{-1} (283.8 nm). The band at 47258.98 cm^{-1} is due to charge transfer supporting the coordination of the ligand to Mn (II). The last three correspond to ${}^6A_{1g} \rightarrow {}^4T_{1g}(P)$ & ${}^4E_g(D)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$, ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions respectively [34,35]. The electronic transition shown in spectrum also supports octahedral geometry of the complex [34]. The major bands also conforms $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

The electronic spectrum of the Co (II) complex reveals major bands at 47125.35 cm^{-1} (212.2 nm), 46948.36 cm^{-1} (213 nm), 44642.86 cm^{-1} (224 nm) and 35211.28 cm^{-1} (284nm). The band at 47125.35 cm^{-1} is due to charge transfer supporting the coordination of the ligand to Co (II).

Table 6: DSC analytical data of metal complexes

Complex	Onset temp. in °C	Peak temp. in °C	Endset temp. in °C	Transition enthalpy (ΔH) Joules/g	Sample mass (mg)
[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂] ₂ Mn	156.41	199.84	264.34	-33.64	1.8
	232.36	245.16	259.08	-9.76	
	264.87	288.33	317.66	-26.46	
[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂] ₂ Co	124.8	137.16	157.81	-21.7	2.59
	218.49	236.4	256.97	-238.63	

3.6.2. The DSC analysis of L-Co complex

The L-Co complex underwent decomposition in two stages as per thermogram. The peak data may be explained as follows. The first stage occurred in

The last three correspond to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions respectively [36, 37]. The electronic transition shown in spectrum also supports octahedral geometry of the complex [36]. The major bands also conforms $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

3.6. Differential Scanning Calorimetry (DSC) analyses of metal complexes

The DSC analyses of both the metal complexes (L-Mn, L-Co) were carried out up to temperature 360°C . The DSC curves obtained with the heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ under dynamic nitrogen atmosphere with flow rate of 80 ml / min. The thermal data obtained from the thermogram of both the complexes is presented in Table 6.

3.6.1. The DSC analysis of L-Mn complex

The L-Mn complex underwent decomposition in three stages as per thermogram. The peak data may be explained as follows. The first stage occurred in temperature range 156.41°C to 264.34°C with peak temperature at 199.84°C . This corresponds to dehydration process with loss of coordinated water molecules. The second stage occurred in temperature range 232.36°C to 259.08°C with peak temperature 245.16°C showing partial decomposition of ligand molecules. The third stage occurred in temperature range 264.87°C to 317.66°C with peak temperature 288.33°C showing decomposition of ligand and formation of MnO. These three areas of the exothermal peaks gave value of $\Delta H = -33.64\text{ Joules/g}$, $\Delta H = -9.76\text{ Joules/g}$ and $\Delta H = -26.46\text{ Joules/g}$ respectively [38-40].

temperature range 124.8°C to 157.81°C with peak temperature at 137.16°C . This corresponds to dehydration process with loss of coordinated water molecules. The second stage occurred in temperature

range 218.49°C to 256.97°C with peak temperature 236.4°C showing decomposition of ligand and formation of Co (III) oxide. These two areas of the exothermal peaks gave value of $\Delta H = -21.7$ Joules/g and $\Delta H = -238.63$ Joules/g respectively [38-40].

3.7. Bioactivity Study

The bioactivity was calculated in terms of % of inhibition *in vitro*. The Rieckmann and co-workers micro assay protocol was followed to conduct assay [44, 45]. The bioactivity of synthesized novel ligand and its corresponding metal complexes were screened against *Escherichia Coli*, *streptococcus Aureus* and *salmonellaTyphi* grown at 37°C overnight. The standard stains were obtained from MTCC Chandigarh.

The Micro Broth Dilution method was used for measuring minimum inhibition concentration at wavelength 475 nm using streptomycin as a reference drug [45]. The test samples were prepared by using DMSO solvent in the concentration range 4 µg/ml-100 µg/ml.

The MIC data summarized in Table 7 evidently shows Fe (III) complex and Cu (II) complex show excellent activity against *Escherichia Coli* as compared to novel ligand and rest of metal complex. The Cu (II) complex and Ag (I) complex display excellent activity against *streptococcus Aureus* compared to novel ligand and rest of the metal complexes. The Co (II) complex shows excellent activity against *Salmonella typhi* as compared to novel ligand and rest of the metal complexes.

Table 7: Antibacterial activity of ligand and their metal complexes

Sr.No.	Compounds	Minimal Inhibition Concentration (µg/ml)		
		<i>E. Coli</i>	<i>S. Aureus</i>	<i>S. Typhi</i>
1	C ₃₂ H ₂₆ N ₆ Br ₂	100	125	500
2	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂]Fe	62.5	500	250
3	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂]Mn	100	250	100
4	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂]Co	125	250	50
5	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂]Ni	125	250	100
6	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂]Cu	62.5	100	200
7	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂]Zn	100	125	250
8	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂]Cd	250	500	100
9	[(C ₃₂ H ₂₆ N ₆ Br ₂)(H ₂ O) ₂]Ag	100	100	62.5

4. CONCLUSION

In current work, we have synthesized a novel tetradentate Schiff base ligand, *N*-(1, 2-bis(4-bromophenyl)-2-(5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-ylimino)ethylidene)-5,6-dimethyl-1*H*-benzo[*d*]imidazole-2-amine, and its eight new metal complexes. The ligand and metal complexes formation and their structure are confirmed by several analytical and spectral techniques. The important features of this method are betterment in yield and lesser reaction time. This method is eco-friendly and cheaper.

5. ACKNOWLEDGEMENT

The authors are thankful to Shivaji Arts, Commerce and Science College Kannad, Aurangabad, Maharashtra, India, JES College Jalna, Dist.-Jalna Maharashtra, India and Dr. R.P. Pawar (Deogiri College, Aurangabad Maharashtra, India for their support.

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