

Microwave Assisted Synthesis, Characterization and Bioactivity Study of Binuclear Complexes of Schiff base derived from 2-Amino-5, 6-dimethyl benzimidazole and Terephthalaldehyde

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ABSTRACT

Microwave assisted solvent free synthesis of a bidentate novel Schiff base ligand was performed by treating 2-Amino-5, 6-dimethyl benzimidazole and Terephthalaldehyde in 2:1 molar proportion. Final yield obtained after purification was high. This novel ligand was further treated with some transition metal salts such as Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Ag(I) metal salts to give stable metal complex under solvent free condition in the same micro oven. Formation of both the novel ligand and its metal complexes was initially confirmed by their distinguishing color, exact melting points and TLC analysis. Novel Schiff base ligand was further characterized by elemental analysis, IR spectroscopy, LCMS and ¹H NMR Spectroscopy. The band observed in IR spectra and peaks observed in ¹H NMR supports predicted structure of ligand, also peaks observed in LCMS confirms ligand structure. The metal complexes were further representatively characterized by UV spectroscopy, IR spectroscopy and Differential Scanning Calorimetry (DSC). Both the novel ligand and its transition metal complexes were screened for antimicrobial activity against *Escherichia Coli*, *Staphylococcus Aureus* & *Salmonella Typhi* by MIC measurement.

Keywords: Microwave, solvent free, 2-Amino-5, 6-dimethyl benzimidazole, Terephthalaldehyde.

1. INTRODUCTION

Microwave assisted Schiff base synthesis is becoming widespread in researchers since last decade¹. Moreover solvent free approach explores ecofriendly and eco safety aspect of this method^{2,3}. Basically Schiff base has always got attention due to presence of versatile azomethine group (>C=N-) which is stable and has capacity to form coordination to metal ions^{4,5}. Schiff base is condensation product of a primary amine and an aldehyde / ketone. The azomethine group present in Schiff base is responsible for antimicrobial activity^{6,7}. It is also observed that Schiff base shows good pharmacophores' properties⁸. The heterocyclic moiety present in Schiff base also has anticancer properties^{9,10}. Many Schiff bases have remarkable ability of forming binuclear complexes¹¹⁻¹⁴. The present work focused on synthesis of binuclear Schiff base and their transition metal complexes. Terephthalaldehyde have two carbonyl groups resulting into formation of two azomethine groups when treated with primary amine which leads to binuclear structure^{15,16}. This microwave assisted synthesis method has several benefits like better yield, low accident probability and reduction in reaction time¹⁷⁻¹⁹.

2. EXPERIMENTAL SECTION

2.1 Material and methods

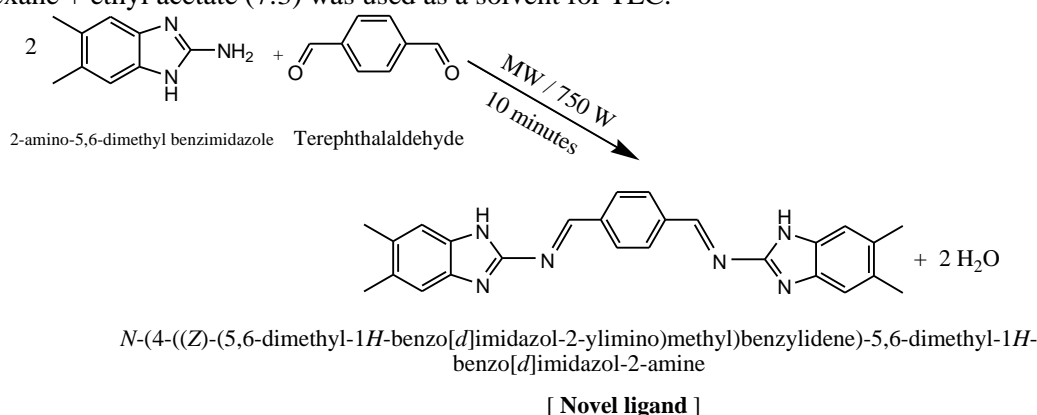
2-Amino-5, 6-dimethyl benzimidazole and Terephthalaldehyde were purchased from Sigma Alderich. Metal nitrates were purchased from Merck, Loba Chem. The chemicals were used in reaction as received without any treatment as these are of research and analytical grade. The microwave assisted synthesis of novel Schiff base ligand was carried out by treating 2-Amino-5, 6-dimethyl benzimidazole with Terephthalaldehyde in 2:1 molar ratio under solvent free condition. After successful synthesis of novel ligand, metal complexes were synthesized by same microwave method by treatment of novel ligand with metal salts under solvent free condition.

2.2 Techniques

All syntheses were completed in a scientific micro oven, 2450 MHz frequency and 800 W. All melting points were recorded on digital melting point apparatus. Shimadzu Dr-8031 instrument was used for recording IR spectra. UV-VIS spectroscopy was used to record electronic absorption spectra in DMSO solvent. LC-MS spectrophotometer used to record mass spectrum. Bruker's 400 MHz instrument used to record ¹HNMR spectra in DMSO-d₆. Shimadzu - 50H thermal analyzer used for Differential Scanning calorimetry analyses [DSC] in a dynamic nitrogen atmosphere (30 ml/min) with a heating rate of 10 °C min⁻¹. TLC analysis conducted on precoated aluminium plates with silica gel and TLC spots were visualized in UV chamber.

2.3 Synthesis of novel ligand

Synthesis of novel ligand was performed in microwave oven by condensation of 2-Amino-5, 6-dimethyl benzimidazole [2.14 gm, 0.014 mol] with Terephthalaldehyde [0.94 gm, 0.007 mol] under solvent free condition. Both the reactants were mixed together in a grinder and kept at room temperature for some time. Then this reactants mixture irradiated at 750 watt for about 10 minutes periodically in the microwave oven. The product obtained was cooled at room temperature and then washed with dry ether. Recrystallization of obtained washed product was carried out by absolute ethanol. Orange colored crystals were obtained. The final yield obtained was 3.08 gm [96 %] and melting point recorded was 92°C. The progress of the reaction and purity of the product was monitored by TLC. A mixture of n-hexane + ethyl acetate (7:3) was used as a solvent for TLC.



2.4 Syntheses of metal complexes

Syntheses of the metal complexes were carried out in same microwave under solvent free condition. The novel ligand, *N*-(4-((*Z*)-(5, 6-dimethyl-1*H*-benzo[*d*]imidazole-2-ylimino)methyl) benzylidene)-5, 6-dimethyl-1*H*-benzo[*d*]imidazole-2-amine, was mixed with metal salt in a grinder to mix thoroughly. After some time, the reactant mixture was exposed to microwave irradiation at 750 W from few seconds to minutes under solvent free condition. The final product obtained was then washed and recrystallized by using hot ethanol. Formation of metal complex was confirmed by recording melting point and TLC analysis. The metal salts used for metal complex synthesis were MnCl₂, Fe (NO₃)₃·9H₂O, Co (NO₃)₂·6H₂O, Ni (NO₃)₂·6H₂O, Cu (NO₃)₂·3H₂O, Zn (NO₃)₂·6H₂O, Cd (NO₃)₂·4H₂O and Ag NO₃.

3. RESULT AND DISCUSSION

Few important facts were observed after finishing microwave assisted solvent free synthesis of novel ligand and its metal complexes. There was remarkable reduction in

reaction time and betterment in yield. The reaction mixture was homogeneously exposed to irradiation by constant rotation of reactant tray. The products obtained were confirmed by repetition of procedure. Each procedure was finished in few seconds to minutes. The final yield obtained in each procedure was above 85 %. All the metal complexes show different color and melting point. All the metal complexes were found stable at room temperature and in solid state. These complexes found soluble in DMSO and DMF.

3.1 Elemental composition analysis and physical properties

Table 1: The elemental analysis (CHN) data for novel ligand

Compound	Empirical Formula	Mole. Weight	% C Found (calculated)	% H Found (calculated)	% N Found (calculated)
Novel ligand	C ₂₆ H ₂₄ N ₆	420.4	73.73 (74.22)	6.11 (5.71)	20.16 (20.07)

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

Sr. No.	Molecular Formula	Color	M.P. (°C)	Time	Yield (%)
1	C ₂₆ H ₂₄ N ₆	Orange	92	10 minutes	96
2	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Fe ₂	Brown	233	2 minutes	85
3	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Mn ₂	Reddish orange	321	4 minutes	85
4	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Co ₂	Dark brown	151	30 seconds	91
5	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Ni ₂	Reddish brown	199	60 seconds	95
6	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Cu ₂	Olive green	200	10 seconds	96
7	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Zn ₂	Light orange	202	60 seconds	91
8	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Cd ₂	Reddish brown	330	2 minute	86
9	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Ag ₂	Light orange	275	150 seconds	95

3.2 Infrared spectra analysis

3.2.1 Analysis of novel ligand spectra: The novel ligand's IR spectra show distinguishing band at 1707 cm⁻¹ due to azomethine, $\nu(\text{C}=\text{N})$, stretching^{15, 20}. A band observed at 3358.07 cm⁻¹ due to NH stretching of benzimidazole ring^{20, 21}. Also band observed at 1467.83 cm⁻¹ due to aromatic $\nu(\text{C}=\text{C})$ stretching^{21, 22}. These bands confirm formation of novel ligand.

3.2.2 Analysis of metal complex (L-Fe) spectra: The IR spectra of L-Fe complex clearly shows shift in azomethine, $\nu(\text{C}=\text{N})$, stretching frequency from 1707 cm⁻¹ to 1727.71 - 23-25. Band due to NH stretching shifted from 3358.07 cm⁻¹ to 3280 cm⁻¹ and band due to aromatic $\nu(\text{C}=\text{C})$ stretching shifted from 1467.83 cm⁻¹ to 1369.46 cm⁻¹. The characteristic bands of this metal complex are of due to M-N stretching and OH - wagging $\nu(\text{H}_2\text{O})$. The appearance of M-N band at 460.99 cm⁻¹ confirms formation of metal complex^{26, 27}. The weak band observed at 900.54 cm⁻¹ and 800 cm⁻¹ are due to OH wagging mode of vibrations indicating coordination of water molecules (H₂O) in metal complex²⁸⁻³¹.

3.3.3 Analysis of metal complex (L-Cu) spectra: The IR spectra of L-Cu complex clearly shows shift in azomethine, $\nu(\text{C}=\text{N})$, stretching frequency from 1707 cm^{-1} to $1695.43^{15, 23, 25}$. Band due to NH stretching shifted from 3358.07 cm^{-1} to 3441.01 cm^{-1} and band due to aromatic $\nu(\text{C}=\text{C})$ stretching shifted from 1467.83 cm^{-1} to 1502.55 cm^{-1} . The characteristic bands of this metal complex are of due to M-N stretching and OH - wagging $\nu(\text{H}_2\text{O})$. The appearance of M-N band at 482.2 cm^{-1} confirms formation of metal complex^{26, 27}. The weak band observed at 846.75 cm^{-1} and 771.53 cm^{-1} are due to OH wagging mode of vibrations indicating coordination of water molecules (H_2O) in metal complex²⁸⁻³¹.

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	$\nu(\text{M}-\text{N})$	$\nu(\text{H}_2\text{O})$ wagging
$\text{C}_{26}\text{H}_{24}\text{N}_6$	1707	3358.07	1467.83	-----	-----
$[(\text{C}_{26}\text{H}_{24}\text{N}_6)_2(\text{H}_2\text{O})_4]\text{Fe}_2$	1727.71	3280	1369.46	460.99	900.54, 800
$[(\text{C}_{26}\text{H}_{24}\text{N}_6)_2(\text{H}_2\text{O})_4]\text{Cu}_2$	1695.43	3441.01	1502.55	482.2	846.75, 771.53

3.3 ¹HNMR spectra analysis

The ¹HNMR spectra of novel ligand reveals following pattern. The singlet observed at 9.51-9.5 ppm is due to H-from CH of azomethine group (s, 2H). The multiple peaks observed at 8.26-8.08 ppm are due to H-from Terephthalaldehyde moiety. The multiple peaks observed around 7.38 ppm are due to H-from benzimidazole moiety. The singlet observed at 5.88 ppm due to H-from imidazole NH (s, 2H). The peak observed at 2.5 is due to H-from 5,6 dimethyl group attached to benzimidazole.

Table 4: Observed ¹HNMR Peaks (ppm) of novel ligand

Compound	H- from CH of azomethine group	H- from aromatic group (Terephthalaldehyde moiety)	H- from aromatic group (benzimidazole moiety)	H-from imidazole	H-from 5,6 dimethyl group
$\text{C}_{26}\text{H}_{24}\text{N}_6$	9.51-9.5	8.26-8.08	7.38	5.88	2.50

3.4 LC MS analysis

The LC MS study of novel ligand showed a peak at m/z 422.4 (M+2) which corresponds to molecular weight of the novel ligand i.e. 420.4.

3.5 Electronic Spectra

The electronic spectrums of both the metal complexes (L-Fe, L-Cu) were recorded in the wavelength region 200 nm – 400 nm in DMSO solution. The spectral data obtained for both the complexes is analyzed and presented in Table 5.

3.5.1 Electronic Spectra of Fe (III) complex:

The electronic spectra of Fe (III) complex shows major bands at 44169.61 cm⁻¹ (226.4 nm), 41288.19 cm⁻¹ (242.2 nm), 39401.1 cm⁻¹ (253.8 nm), and 35236.08 cm⁻¹ (283.8 nm). The band at 44169.61 cm⁻¹ is due to charge transfer associated to coordination of ligand to Fe (III). The last three correspond to ⁶A_{1g} → ⁴A_{1g}(G) & ⁴E_g(G), ⁶A_{1g} → ⁴T_{2g}(G) and ⁶A_{1g} → ⁴T_{1g}(G) transitions respectively^{32,33}. The electronic transition shown in spectrum supports octahedral geometry of the complex^{32,33}. The major bands confirm π → π* and n → π* transitions.

3.5.2 Electronic spectra of Cu (II) complex:

The electronic spectra of Cu (II) complex shows major bands at 46641.79 cm⁻¹ (214.4 nm), 46040.52 cm⁻¹ (217.2 nm), 44365.57 cm⁻¹ (225.4 nm), and 39032.01 cm⁻¹ (256.2 nm). The band at 46641.79 cm⁻¹ is due to charge transfer associated to coordination of ligand to Cu (II). The last three correspond to ²B_{1g} → ²A_{1g}, ²B_{1g} → ²B_{2g} and ²B_{1g} → ²E_g transitions respectively³⁴⁻³⁷. The electronic transition shown in spectrum supports octahedral geometry of the complex³⁴⁻³⁷. The major bands confirm π → π* and n → π* transitions.

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	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Fe ₂	35236.08 (283.8)	⁶ A _{1g} → ⁴ T _{1g} (G)	Octahedral
		39401.1 (253.8)	⁶ A _{1g} → ⁴ T _{2g} (G)	
		41288.19 (242.2)	⁶ A _{1g} → ⁴ A _{1g} (G) ⁶ A _{1g} → ⁴ E _g (G)	
		44169.61 (226.4)	Charge transfer	
2	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Cu ₂	39032.01 (256.2)	² B _{1g} → ² A _{1g}	Octahedral
		44365.57 (225.4)	² B _{1g} → ² B _{2g}	
		46040.52 (217.2)	² B _{1g} → ² E _g	
		46641.79 (214.4)	Charge transfer	

3.6 Differential Scanning Calorimetry (DSC) analyses of metal complexes

The DSC analyses of both the metal complexes (L-Fe, L-Cu) were conducted from room temperature to 360°C. The DSC curves obtained under dynamic nitrogen atmosphere with flow rate of 80 ml min⁻¹ and heating rate of 10 °C min⁻¹. The thermal data obtained from the thermogram of each metal complex is summarized in Table 6.

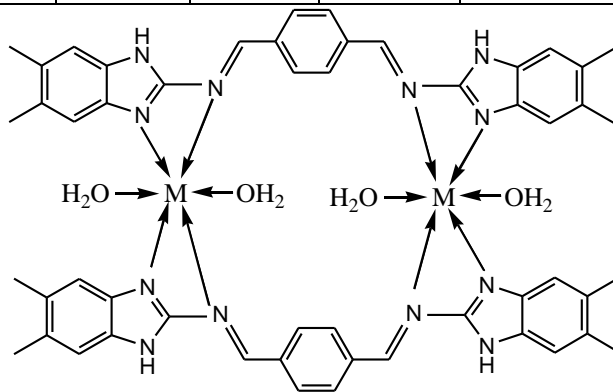
3.6.1 The DSC analysis of L-Fe complex: The L-Fe complex underwent decomposition in three stages as per the data obtained from thermogram. The peak data may

be explained as follows. The first stage occurred in temperature range of 100.01 °C to 145.04 °C with peak temperature 110.65°C. This corresponds to dehydration process with loss of coordinated water molecules. The second stage occurred in temperature range of 167.66 °C to 209.71 °C with peak temperature 193.39°C. These endothermic peak values correspond to partial decomposition of the ligand. The third stage occurred in temperature range of 266.05 °C to 299.53 °C with peak temperature 283.26°C, these endothermic peak values shows decomposition of ligand and formation of stable Fe₂O₃. These three peak areas gave value of $\Delta H = -17.1$ Joules/g, $\Delta H = 44.42$ Joules/g, $\Delta H = 227.18$ Joules/g respectively³⁸⁻³⁹.

3.6.1 The DSC analysis of L-Cu complex: The L-Cu complex underwent decomposition in three stages as per the data obtained from thermogram. The peak data may be explained as follows. The first stage occurred in temperature range of 97.9 °C to 155.87 °C with peak temperature 119.6°C. This corresponds to dehydration process with loss of coordinated water molecules. The second stage occurred in temperature range of 170.38 °C to 218.85 °C with peak temperature 195.22°C. These endothermic peak values correspond to partial decomposition of the ligand. The third stage occurred in temperature range of 264.11 °C to 301.95 °C with peak temperature 283.54°C, these endothermic peak values shows decomposition of ligand and formation of stable CuO. These three peak areas gave value of $\Delta H = -52.91$ Joules/g, $\Delta H = 53.02$ Joules/g, $\Delta H = 158.52$ Joules/g respectively³⁸⁻³⁹.

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 in mg
[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Fe ₂	100.01	110.65	145.04	-17.10	2.6
	167.66	193.39	209.71	44.42	
	266.05	283.26	299.53	227.18	
[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Cu ₂	97.9	119.6	155.87	-52.91	2.8
	170.38	195.22	218.85	53.02	
	264.11	283.54	301.95	158.52	



Proposed structure of Metal complexes
[M = Mn(II) / Fe(III) / Co(II) / Ni(II) / Cu(II) / Zn(II) / Cd(II) / Ag(I)]

3.7 Bioactivity analysis

The bioactivity of novel ligand and its metal complexes was calculated in terms of % of inhibition *in vitro*. The assay was conducted by adopting Rieckmann and co-workers micro assay protocol. The antimicrobial activity of synthesized novel ligand and its corresponding metal complexes were screened against *Escherichia Coli*, *streptococcus Aureus* and *salmonella Typhi* grown at 37 °C overnight. The minimal inhibition concentration (MIC) was measured by Micro Broth Dilution method at a wavelength 475 nm using streptomycin as a reference drug. The required test samples were prepared in the concentration range 4 µg/ml – 100 µg/ml by using DMSO Solvent.

The obtained MIC data is summarized in Table 7. It is clear from the data that Mn (II) complex show excellent activity against *Escherichia Coli* as compared to synthesized novel ligand and remaining metal complexes. The Fe (III) complex show excellent antimicrobial activity against *streptococcus Aureus* as compared to novel ligand and remaining metal complexes. The novel ligand and Co (II) complex show equally excellent activity as compared to rest of metal complexes. Among Mn (II) complex, Fe (III) complex and Co (II) complex of the ligand, Fe (III) complex shows highest activity.

Table 7: Antibacterial activity of ligand and their metal complexes

Sr. No.	Compounds	Minimal Inhibition Concentration (µg/ml)		
		E. Coli	S. Aureus	S. Typhi
1	C ₂₆ H ₂₄ N ₆	250	500	100
2	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Fe ₂	125	62.5	250
3	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Mn ₂	100	125	250
4	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Co ₂	250	125	100
5	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Ni ₂	250	100	250
6	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Cu ₂	250	125	250
7	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Zn ₂	250	125	500
8	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Cd ₂	250	125	125
9	[(C ₂₆ H ₂₄ N ₆) ₂ (H ₂ O) ₄]Ag ₂	500	100	500

4. CONCLUSION

In present work we have synthesized a novel bidentate ligand, *N*-(4-((*Z*)-(5, 6-dimethyl-1*H*-benzo[*d*]imidazole-2-ylimino) methyl) benzylidene)-5, 6-dimethyl-1*H*-benzo[*d*]imidazole-2-amine, and its eight news binuclear metal complexes. The structural confirmation of novel ligand and its binuclear metal complexes is done by several analytical and spectral techniques. The main advantages of this microwave assisted synthesis is less reaction time, better yield, ecofriendly and cheap.

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