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Ecofriendly Solvent Free Synthesis, Characterization and Bioactivity Study of Transition Metal Complexes of a New Schiff Base Derived From 2-Amino-5, 6-Dimethyl Benzimidazole and Acenaphthenequinone

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Abstract: An ecofriendly solvent free synthesis of a new Schiff base was carried out in a scientific microwave oven by reaction between 2-Amino-5, 6-dimethyl benzimidazole and Acenaphthenequinone. The transition metal complexes were prepared by reaction of this synthesized new Schiff base with salts of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Ag(I). The formation of new Schiff base was initially confirmed by melting point and thin layer chromatography. The confirmation of structure was done by different characterization techniques including elemental analysis, IR spectroscopy, ^{1}HNMR spectroscopy and LCMS. The synthesized metal complexes were recognized by thin layer chromatography, melting point and their differentiating color. The synthesized metal complexes were further characterized by EAS (UV) spectroscopy, IR spectroscopy and thermogravimetric analysis (TGA). The bioactivity study of this new Schiff base and its eight metal complexes were conducted by Micro Broth Dilution method. The new Schiff base and its eight metal complexes were tested against different bacteria including Escherichia coli, Staphylococcus aureus and Salmonella typhi. The bioactivity was measured and recorded as minimum inhibition concentration (MIC).

Keywords: Ecofriendly, Solvent free, 2-Amino-5, 6-dimethyl benzimidazole, Acenaphthenequinone, Microwave, MIC.

I. INTRODUCTION

Since last few decades, researchers are more concerned about ecofriendly methods of organic synthesis with or without use of any solvent in a scientific microwave oven [1, 2]. It is observed that microwave assisted synthesis cause reduction in pollution, low cost and better yield [3-5]. A Schiff base is simply formed by condensation reaction of a carbonyl group and primary amine [6, 7]. Schiff bases exhibit significant biological activities in medicinal domain such as analgesic, anti-tuberculosis, anticancer, antimicrobial, antispasmodic, anti-inflammatory, anthelmintic [8-12]. Many investigations proved that the metal complexes exhibit more potency than the parent drug [13]. In addition to that, many metal complexes are used as dyes, catalyst, intermediates and stabilizers [14]. Such vast applications of Schiff bases and their metal complexes encouraged us to perform present investigation.

II. EXPERIMENTAL SECTION

A. *Materials and Method*

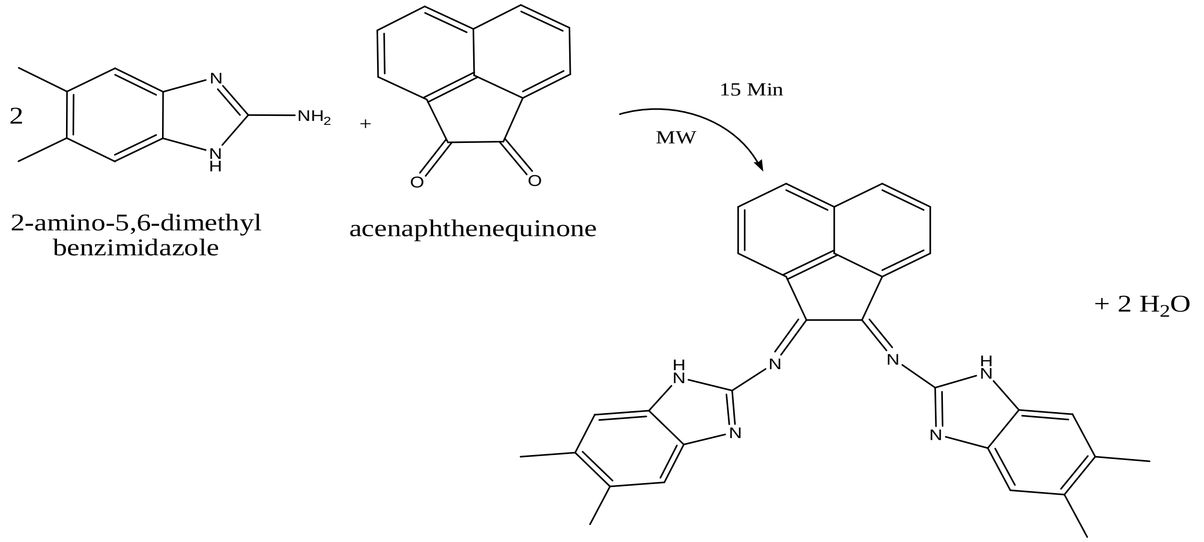
All chemicals were acquired from Sigma Alderich, S d fine Chem, Loba Chem, and Merck. 2-Amino-5, 6-dimethyl benzimidazole, Acenaphthenequinone were procured from Sigma Alderich and metal nitrates from Loba Chem, S d fine Chem and Merck. All chemicals were used as obtained. New Schiff base was synthesized by reaction of 2-Amino-5, 6-dimethyl benzimidazole and Acenaphthenequinone in the 2:1 molar ratio in a scientific microwave oven. After Schiff base preparation, metal complexes were produced by reacting Schiff base with metal salts in the same scientific microwave oven.

B. *Techniques*

Each and every synthesis was carried out in a scientific microwave oven. A digital melting point apparatus was used to record all the melting points. An UV spectrophotometer was used to record electronic spectra in DMSO solvent. Simadzu Dr 8031 instrument was used to record IR spectra. Brakers 400MHz instrument was used to record ^{1}HNMR spectrum. LCMS spectrophotometer was used to record mass spectrum. Simadzu TGA 50H thermal analyzer was used to conduct thermogravimetric analysis (TGA) with heating rate of 10 ℃ min^{-1} in a dynamic nitrogen atmosphere (30 ml min^{-1}). Precoated aluminium plates were used for TLC analyses.

C. Synthesis of New Schiff Base

The new Schiff base was synthesized by reacting 2-Amino-5, 6-dimethyl benzimidazole [1.62 gm, 0.01mol] with Acenaphthenequinone [0.92 gm, 0.005mol] in solvent free condition. The reaction mixture was first mixed thoroughly in a grinder and then irradiated for 15 minutes periodically at 750 W in a scientific microwave oven. The product obtained was then kept at room temperature and then washed with dry ether. The final product was then recrystallized using absolute ethanol to give faint pink crystals. The final yield obtained was 2.35 gm [92 %] and melting point recorded was 160°C. The progress of the reaction and pureness of the product was checked by using TLC. A solvent mixture of n-hexane + ethyl acetate (7:3) was used as developing solvent.



(*E*)-*N*-((*E*)-2-(5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-ylimino)
acenaphthylen-1(2*H*)-ylidene)-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-amine

Fig. 1 Synthesis of New Schiff Base

D. Synthesis of Transition Metal Complexes

The transition metal complexes were also synthesized by same microwave irradiation method in solvent free condition. The proportionate metal salt was mixed with required amount of new Schiff base, (E)-N-((E)-2-(5,6-dimethyl-1H-benzo[*d*]imidazol-2-ylimino)acenaphthylen-1(2H)-ylidene)-5,6-dimethyl-1H-benzo [*d*] imidazol-2-amine , in a grinder to mix properly. Then the mixture was irradiated in microwave oven for few minutes at 750 W. The end product obtained was washed, recrystallized with hot ethanol and then finally dried at room temperature. The melting point of each metal complex was noted. The metal salts used for these syntheses were $MnCl_2$, $Fe(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$, $Zn(NO_3)2.6H_2O$, $Cd(NO_3)_2.4H_2O$ and $AgNO_3$.

III. RESULT AND DISCUSSION

Some important facts were observed in these microwave assisted solvent free syntheses; these are safety in conducting reaction, high yield, less reaction time and no side product formed. The procedure was repeated twice for confirmation of result obtained. The synthesized transition metal complexes show distinguishing color and exact melting point. All the metal complexes found stable at room temperature and soluble in DMSO as well as in DMF.

A. Elemental (CHN) Analysis

The elemental (CHN) analysis data for new Schiff base is presented in Table I.

Table I

Compound	Empirical formula	Molecular Weight	C Found (Cal)	H Found (Cal)	N Found (Cal)
New Schiff Base	$C_{30}H_{24}N_6$	468	77.16 (76.92)	5.64 (5.13)	17.20 (17.95)

B. Physical Properties

The physical properties of new Schiff base and its corresponding metal complexes are presented in Table II.

Table II

Sr. No	Molecular Formula	Color	Melting Point (℃)	Time	Yield %
1	$C_{30}H_{24}N_6$	Faint Pink	160	15 Minutes	92
2	$[(C_{30}H_{24}N_6)(H_2O)_2]Mn$	Turbid Pink	129	5 Minutes	95
3	$[(C_{30}H_{24}N_6)(H_2O)_2]Fe$	Brown	280	2 Minutes	88
4	$[(C_{30}H_{24}N_6)(H_2O)_2]Co$	Brown	191	3 Minutes	90
5	$[(C_{30}H_{24}N_6)(H_2O)_2]Ni$	Grey	147	3 Minutes	95
6	$[(C_{30}H_{24}N_6)(H_2O)_2]Cu$	Brown	206	2 Minutes	90
7	$[(C_{30}H_{24}N_6)(H_2O)_2]Zn$	Pinkish	222	4 Minutes	95
8	$[(C_{30}H_{24}N_6)(H_2O)_2]Ag$	Pink	350	5 Minutes	95
9	$[(C_{30}H_{24}N_6)(H_2O)_2]Cd$	Light Pink	168	4 Minutes	90

C. Infrared Spectra Analysis

Table III

Sr. No	New Schiff base/Complex	Azomethine C=N (cm^{-1})	Aromatic C-H (cm^{-1})	Imidazole N-H (cm^{-1})	Aromatic C=C (cm^{-1})	M-N (cm^{-1})	OH wagging (cm^{-1})
1	$C_{30}H_{24}N_6$	1680	2900	3450	1500	----	-----
2	$[(C_{30}H_{24}N_6)(H_2O)_2]Cu$	1683.86	2968.45	3323.35	1492.90	410.84	827.46, 893.04
3	$[(C_{30}H_{24}N_6)(H_2O)_2]Ag$	1647.21	2872.01	3122.75	1485.19	460.99	829.39, 893.04

The IR spectrum of new Schiff base clearly exhibits a characteristic band at 1680 cm^{-1} due to azomethine (C=N) stretching. The spectrum also exhibits band at 3450 cm^{-1} due to imidazole N-H stretching [15]. The bands observed at 1500 cm^{-1} and 2900 cm^{-1} are due to aromatic C=C stretching and aromatic C-H stretching respectively [16].

Analysis of Schiff base-Cu complex: The IR spectrum of Schiff base-Cu complex clearly shows shifting of azomethine band from 1680 cm^{-1} to 1683.86 cm^{-1} and a band due to imidazole NH stretching is shifted from 3450 cm^{-1} to 3323.35 cm^{-1} [17]. Also the bands observed due to aromatic C=C stretching and aromatic C-H stretching shifted from 1500 cm^{-1} and 2900 cm^{-1} to 1492.90 cm^{-1} and 2968.45 cm^{-1} respectively. The distinguishing bands of this metal complex are that of M-N stretching and OH- wagging. A band appeared at 410.84 cm^{-1} is assigned to M-N stretching and two weaker bands observed at 827.46 cm^{-1}, 893.04 cm^{-1} are due to OH- wagging mode of vibrations representing coordination of water molecules (H_2O) in metal complex shown in Fig. 2 [18]. The bands due to M-N stretching and OH wagging are absent in IR spectrum of new Schiff base.

Analysis of Schiff base-Ag complex: The IR spectrum of Schiff base-Cu complex clearly shows shifting of azomethine band from 1680 cm^{-1} to 1647.21 cm^{-1} and band due to imidazole NH stretching is shifted from 3450 cm^{-1} to 3122.75 cm^{-1} [19]. Also the bands observed due to aromatic C=C stretching and aromatic C-H stretching shifted from 1500 cm^{-1} and 2900 cm^{-1} to 1485.19 cm^{-1} and 2872.01cm^{-1} respectively. The most distinguishing bands of this metal complex are that of M-N stretching and OH- wagging. A band appeared at 460.99 cm^{-1} is assigned to M-N stretching and two weaker bands observed at 829.39cm^{-1}, 893.04 cm^{-1} are due to OH- wagging mode of vibrations representing coordination of water molecules (H_2O) in metal complex shown in Fig. 2 [18, 20]. The bands due to M-N stretching and OH wagging are absent in IR spectrum of new Schiff base.

D. ^{1}HNMR Spectral Studies

Table IV

Compound	H-from Aromatic ring in ppm	H-from-NH of Imidazole in ppm	H-from four Methyl Groups in ppm
$C_{30}H_{24}N_6$	7.91-8.46	5.88	2.50-2.51

The ^{1}HNMR spectrum of new Schiff base exhibits different peaks as shown in Table IV. The peaks observed at 2.50-2.51 ppm are due to four methyl groups attached to aromatic ring of new Schiff base. A characteristic peak observed at 5.88 is due to H from NH of benzimidazole whereas different peaks observed at 7.91-8.46 are due to H-from aromatic rings.

E. Mass Spectral Studies

The new Schiff base exhibits a parent peak at m/z 470 which corresponds to molecular weight of the new Schiff base i.e. 468 (M^{+2}).

F. Electronic Spectra

Table V

Sr. No	Complex	UV-visible Major Bands. Absorption Maxima cm^{-1} (nm)	Assignment	Proposed Geometry
1	$[(C_{30}H_{24}N_6)(H_2O)_2]Cu$	41493.78 (241)	$^2B_{1g} \rightarrow {}^2A_{1g}$	Octahedral
		41806.02 (239.2)	$^2B_{1g} \rightarrow {}^2B_{2g}$	
		44052.86 (227)	$^2B_{1g} \rightarrow {}^2E_g$	
		48496.61 (206.2)	Charge transfer	
2	$[(C_{30}H_{24}N_6)(H_2O)_2]Ag$	40650.41 (246)	$^2E_g \rightarrow {}^2T_{2g}$	Octahedral
		42158.52 (237.2)	Charge transfer	

The Electronic absorption spectral (UV) data analysis Schiff base-Cu complex: The electronic spectrum of Schiff base-Cu complex display main bands at 48496.61 cm^{-1} (206.2 nm), 44052.86 cm^{-1} (227 nm), 41806.02 cm^{-1} (239.2nm), and 41493.78 cm^{-1} (241 nm). The band at 48496.61 cm^{-1} is due to charge transfer related to coordination of Schiff base to Cu (II). The last three correspond to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions respectively [21, 22]. The electronic transitions shown in spectrum clearly support octahedral geometry of the complex [21-23]. The chief bands confirm $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

The Electronic absorption spectral (UV) data analysis Schiff base-Ag complex: The electronic spectrum of Schiff base-Ag complex exhibit major bands at 42158.52 cm^{-1} (237.2 nm) and 40650.41 cm^{-1} (246 nm). The band at 42158.52 cm^{-1} is due to charge transfer related to coordination of Schiff base to Ag (I) and band at 40650.41 cm^{-1} corresponds to $^2E_g \rightarrow {}^2T_{2g}$ transition [21, 24]. The electronic transitions revealed in spectrum, electrostatic forces and covalent bonding forces clearly back octahedral geometry of the complex [21, 24-25]. The main bands confirm $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

G. Thermo Gravimetric Analysis of Metal Complexes

Table VI

$[(C_{30}H_{24}N_6)(H_2O)_2]Cu$		$[(C_{30}H_{24}N_6)(H_2O)_2]Ag$	
Weight Loss %	Temperature (℃)	Weight Loss %	Temperature (℃)
0	31.2	0	31.86
10	199.21	10	244.41
20	236.93	20	360.54
30	277.03	30	460.27
40	349.87	36.755 (Final Weight Loss)	500
50	384.13	-------	-------
60	407.39	-------	-------
70	422.71	-------	-------
80	443.31	-------	-------
85.278 (Final Weight Loss)	500	-------	-------

The TGA of both the metal complexes were conducted from room temperature to 500°C. The heating was carried out in a dynamic nitrogen atmosphere (30 ml min^{-1}) with heating rate of 10 ℃ min^{-1}. The thermal data obtained from thermogram is displayed in Table VI.

The thermal analysis of Schiff base-Cu complex: The thermogram of Schiff base-Cu complex exhibits total weight loss of 85.278%. Initially the water of crystallization lost in the temperature range of 30℃ to 199.21℃ and weight loss found was 10%. Then the loss of methyl group along with remaining aromatic moiety resulted in total weight loss of 85.278% up to 500℃. At 500℃, a stable curve is observed indicating formation of stable metal oxide (CuO) [26, 27].

The thermal analysis of Schiff base-Ag complex: The thermogram of Schiff base-Ag complex exhibits total weight loss of 36.755%. Initially the water of crystallization lost in the temperature range of 30℃ to 244.41℃ and weight loss found was 10%. Then the loss of methyl group along with remaining aromatic moiety resulted in total weight loss of 36.755% up to 500℃. At 500℃, a stable curve is observed indicating formation of stable metal oxide (Ag_2O). The lesser weight loss observed is might be due to formation of a polymeric adduct with Ag_2O at 500℃ [28, 29].

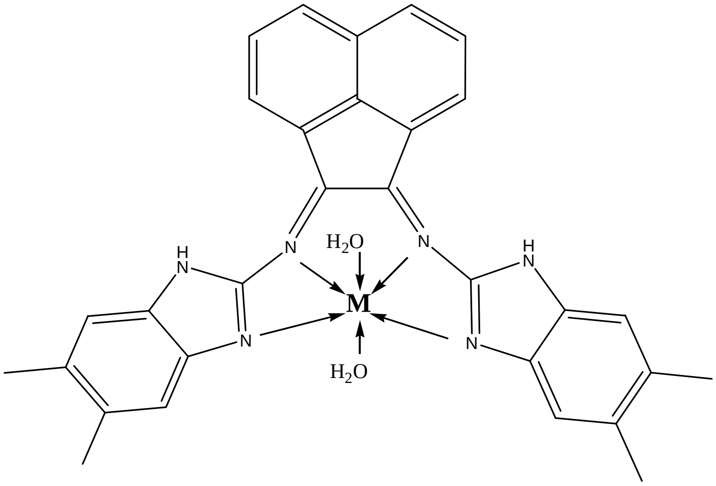


Fig. 2 Projected structure of metal complex (M)=Mn(II),Fe(III),Co(II),Ni(II),Cu(II),Zn(II), Ag(I),Cd(II).

H. Bioactivity Study

Table VII

Sr. No.	Compound	Minimum Inhibition Concentration (ug/ml)		
		E. Coli	S. Aureus	S. Typhi
1	$C_{30}H_{24}N_6$	500	250	500
2	$[(C_{30}H_{24}N_6)(H_2O)_2]Mn$	250	250	100
3	$[(C_{30}H_{24}N_6)(H_2O)_2]Fe$	250	250	50
4	$[(C_{30}H_{24}N_6)(H_2O)_2]Co$	62.5	100	200
5	$[(C_{30}H_{24}N_6)(H_2O)_2]Ni$	100	100	250
6	$[(C_{30}H_{24}N_6)(H_2O)_2]Cu$	500	250	500
7	$[(C_{30}H_{24}N_6)(H_2O)_2]Zn$	100	125	250
8	$[(C_{30}H_{24}N_6)(H_2O)_2]Ag$	62.5	500	250
9	$[(C_{30}H_{24}N_6)(H_2O)_2]Cd$	500	500	100

The bioactivity was calculated in terms of % of inhibition *in vitro*. The micro assay was conducted as per the micro assay protocol of Rieckmann and co-workers with fewer variations [30, 31]. The bioactivity of prepared new Schiff base and its transition metal complexes were screened against *Escherichia Coli*, *staphylococcus Aureus* and *salmonella Typhi* grown at 37 ℃ overnight. The minimum inhibition concentration was calculated by Micro Broth Dilution method at wavelength 475 nm with streptomycin as a reference drug. The test samples were set in the concentration range 4 μg/ml - 100 μg/ml using DMSO solvent.

The MIC data presented in Table VII clearly exhibit that Co (II) and Ag (I) complexes show better activity against *Escherichia Coli* compared to new Schiff base and rest of the metal complexes. The Co (II) and Ni (II) complexes show better activity against *staphylococcus Aureus* compared to new Schiff base and rest of the metal complexes. The Fe (III) complex displays better activity against *salmonella Typhi* as compared to new Schiff base and rest of the metal complexes.

IV. CONCLUSION

In the current work, ecofriendly solvent free syntheses of a new tetra dentate Schiff base, (E)-N-((E)-2-(5,6-dimethyl-1H-benzo[*d*]imidazol-2-ylimino)acenaphthylen-1(2H)-ylidene)-5,6-dimethyl-1H-benzo [*d*] imidazol-2-amine, and its transition metal complexes were performed using microwave irradiation method. All the prepared compounds were characterized by several analytical and spectral methods. The chief benefits of this method are lesser reaction time and higher yield.

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