Journal of Chemistry and Chemical Sciences, *Vol.11(4), 43-51, April, 2021* *ISSN 2229-760X (Print)*
(An International Research Journal), *www.chemistry-journal.org* *ISSN 2319-7625 (Online)*

Green and Efficient Synthesis, Characterization and Antimicrobial Activity of Transition Metal complexes of Novel Schiff base ligand derived from 2-hydrazino Benzothiazole and Benzil

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(Received on: March 29, 2021)

ABSTRACT

A green, efficient and environmentally green synthesis using scientific microwave method of novel Schiff base ligand derived from 2-hydrazino Benzothiazole and Benzil. Metal complexes with nitrate of Mn(II) and chlorides Ag(I), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III) salts. All metal complexes show fine color at the end of the reaction. TLC and melting point of each complex was confirming the formation of metal complex. Characterization of novel Schiff base ligand and its metal complexes carried out by elemental analysis, IR spectroscopy, ^{1}HNMR spectroscopy, LCMS, UV spectroscopy and TGA. The novel Schiff base ligand and its metal complexes show antibacterial activity against E-Coli, S.Aureus and S.Typhi.

Keywords: Green synthesis, 2-hydrazino Benzothiazole, Benzil.

1. INTRODUCTION

The azomethine group present in Schiff base ligand, which forms highly stable complex with transition metal ions. In the present work we focus on green and efficient synthesis of novel Schiff base ligand and their metal complexes. The main feature of microwave synthesis approach are shorter reaction time, larger the yield and simple

conditions for reaction. The few reports are on the synthesis of metal complexes by microwave assisted method[1-3].

The use of microwave assisted irradiation in synthesis of drugs and organic compounds have proved that it is effective, safe and eco-friendly with shorter reaction time[4-5]. Compound containing azomethine/imine (C=N) group are known as ligand[6]. The product of ketone and aldehyde with primary amine are generally known as Schiff base ligand[7]. They are biological very active compounds, having biological activities like antibacterial[8-11], antimicrobial[12], anticancer[13], plant growth inhibitors[14] and so on.

2. MATERIAL AND METHOD

All the chemicals used in this work were of analytical grade. 2-hydrazino Benzothiazole and Benzil form Sigma Aldrich and metal nitrates and chlorides from loba chem and MERCK. The novel Schiff base ligand synthesized in scientific microwave oven. Metal complexes were synthesized by reacting Schiff base ligand with metal salts in scientific microwave oven.

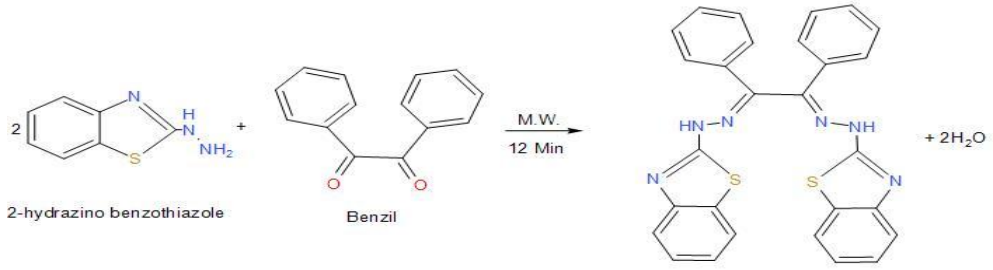
2.1 Techniques

Synthesis was performing in microwave extraction system in scientific oven. Melting points were measured on digital melting point apparatus. The electronic absorption spectra were recorded in the wavelength range 200 to 800 nm using UV spectrophotometer. IR spectra were analyses on Shimadzu Dr 8031. The ^{1}HNMR spectra was analyze 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 10^{0}C/min using Shimadzu TGA 50H thermal analyzer. TLC analysis performs on pre coated aluminum plates.

2.2 Preparation of novel Schiff base ligand

The novel Schiff base ligand was prepared by the reaction between 2-hydrazino Benzothiazole and Benzil under solvent free condition in scientific microwave oven about 12 min. The irradiated product after cooling at room temperature washed with dry ether. The yield obtained was 1 gm. And melting point was 212^{0}C. The purity of the product confirm by TLC using n-hexane and ethyl acetate as solvent.

Reaction-



2-[(E)-2-[(2E)-2-[2-(1,3-benzothiazol-2-yl)hydrazin-1-ylidene]-1,2-diphenylethylidene]hydrazin-1-yl]-1,3-benzothiazole

2.3 Preparation of metal complexes

The metal complexes were synthesized under solvent free condition by mixing metal nitrate or chloride with the required amount of the ligand in 1:1 metal ligand ratio. The reaction mixture was irradiated in microwave oven. The products were washed with ether, filter and dried at room temperature. The metal salts used 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 $AgNO_3$.

3. RESULT AND DISCUSSION

As a result of microwave assisted synthesis it was observed that the reaction was completed in a short time with higher yield compared to the conventional method. In microwave method homogeneity of reaction mixture was increased by the rotating of reaction platform Trey. The synthesis of title compound was in two steps. In first step 2-hydrazino Benzothiazole is irradiated with Benzil to get Schiff base ligand. In second step the metal salts were irradiate with Schiff base ligand to get metal complex.

All metal complexes 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

3.1 Physical properties

Physical properties of the novel Schiff base ligand and metal complexes summarized in Table 1

Table 1

Sr. No	Molecular formula	Color	Melting point (^{0}c)	Time	Yield
1	$C_{28}H_{20}N_6S_2$	Grey	212	12 min	1 gm
2	$[C_{28}H_{20}N_6S_2(H_2O)_2]Mn$	Light grey	241	120 sec.	140 mg
3	$[C_{28}H_{20}N_6S_2(H_2O)_2]Fe$	Dark blue	129	30 sec.	200 mg
4	$[C_{28}H_{20}N_6S_2(H_2O)_2]Co$	Purple	185	60 sec.	170 mg
5	$[C_{28}H_{20}N_6S_2(H_2O)_2]Ni$	Light purple	206	60 sec.	180 mg
6	$[C_{28}H_{20}N_6S_2(H_2O)_2]Cu$	Green	109	30 sec.	160 mg
7	$[C_{28}H_{20}N_6S_2(H_2O)_2]Zn$	Light brown	243	150 sec.	180 mg
8	$[C_{28}H_{20}N_6S_2(H_2O)_2]Cd$	Light grey	322	120 sec.	160 mg
9	$[C_{28}H_{20}N_6S_2(H_2O)_2]Ag$	Greenish brown	142	120 sec.	190 mg

3.2 Infrared spectra analysis

Infrared frequencies of novel Schiff base ligand and its metal complexes summarized in Table 2.

Table-2

Sr. No	Ligand/complex	C=N (cm^{-1})	C-H (cm^{-1})	N-H (cm^{-1})	C=C (cm^{-1})	M-N (cm^{-1})	M-S (cm^{-1})
1	$C_{28}H_{20}N_6S_2$	1670	2975	3350	1550	---	---
2	$[C_{28}H_{20}N_6S_2(H_2O)_2]Ni$	1643.35	3010	3286	1552	447	418
3	$[C_{28}H_{20}N_6S_2(H_2O)_2]Cd$	1768.72	2831	---	1554	490	416

The IR spectrum of novel Schiff base ligand show characteristics band at 1670cm^{-1} which indicates (C=N) stretching vibration of azomethine group[15-20]. The vibrational band at 3350 cm^{-1} assigned N-H stretching in the ligand. Band observed at 1550 cm^{-1} corresponds to C=C stretching. The band observed at 2975 cm^{-1} indicates aromatic C-H stretching in the ligand.

IR spectral study of Ni metal complex: The band appeared at 1643.35 cm^{-1} corresponds to azomethine (C=N) stretching, whereas same azomethine band is observed at 1670 cm^{-1} in spectrum of ligand. Which indicate coordination of ligand with metal ion[21]. The band appeared at 3010cm^{-1} indicates the aromatic (C-H) stretching in complex, whereas same aromatic (C-H) stretching is observed at 2975 cm^{-1} in spectrum of ligand. The band observed at 3286cm^{-1} assign to (N-H) stretching, whereas in spectrum of ligand it is observed at 3350 cm^{-1}. The vibration observed at 1552cm^{-1} due to aromatic (C=C) stretching. The characteristics band appeared at 447 cm^{-1} assign to (M-N) vibration, which confirms coordination of azomethine and metal ion. The band observed at 418 cm^{-1} indicates coordination of (M-S) in the complex[22-23]. The weak bands observed at 939.33 cm^{-1} and 825.33 cm^{-1} were due to OH wagging mode of vibration, indicating coordination of water molecule in metal complex[24-27]. 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 Cd metal complex: A stretching observed at 1768.72 cm^{-1}, which corresponds to azomethine (C=N) stretching vibrations, whereas same stretching is observed at 1670 cm^{-1} in spectrum of ligand. The band appeared at 2831 cm^{-1} assign to aromatic (C-H) stretching, whereas same stretching is observed at 2975 cm^{-1} in spectrum of ligand. The vibration observed at 1554 cm^{-1} due to aromatic (C=C) stretching. The coordination of metal to nitrogen was justified by stretching observed at 490 cm^{-1} [28] and coordination of metal to sulphur was observed at 416 cm^{-1} [29]. The weak bands observed at 929.69 cm^{-1} and 817.82 cm^{-1} were due to OH wagging mode of vibration, indicating coordination of water molecule in metal complex[24-27]. 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.

3.3 ^{1}HNMR spectral studies

Observed ^{1}HNMR peaks (ppm) of novel Schiff base ligand summarized in Table 3.

Table-3

Compound	H-from aromatic ring In ppm	H-from-NH of Hydrazine In ppm
Novel Schiff Base Ligand	6.87, 7.21, 7.39	5.91

The ^{1}HNMR spectrum of L_2 shows different peaks. The characteristic peak observed at 5.91 ppm is due to H-from NH-of hydrazine. The peaks observed at 6.87, 7.21 and 7.39 ppm are due to H-from aromatic rings.

3.4 Mass spectral studies

The mass spectrum study of novel Schiff base ligand showed a peak at m/z. 505(M+1) that corresponds to the molecular weight of the Schiff base ligand 504.

3.5 Electronic spectra

Electronic spectral data and probable geometry for the metal complexes summarized in Table 4

Table-4

Sr. No.	Complex	UV-visible major bands. Absorption Maxima cm^{-1}(nm)	Assignment	Proposed geometry
1	$[C_{28}H_{20}N_6S_2(H_2O)_2]Ni$	38314.17 (261.40)	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	Octahedral
		45662.10 (219.80)	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	
			$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	
2	$[C_{28}H_{20}N_6S_2(H_2O)_2]Cd$	38461.53 (260.40)	-------	Octahedral
		40650.40 (246.60)	-------	
		46296.29 (216.20)	Charge transfer	

Electronic spectrum of both metal complexes Ni(II), Cd(II) recorded in the wavelength region 200nm to 400nm in DMSO solution.

Electronic spectral data of L_2Ni: Electronic spectrum of Ni(II) complex shows absorption maxima at 38314.17 (261.40) and 45662.10 (219.80) assign to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively indicating that complex possess octahedral geometry[30-31].

Electronic spectral data of L_2Cd: Cd(II) has outer electronic configuration d^{10} So it did not show any d-d electronic transition. On the basis of bands observed in UV spectra, infrared spectra and TGA, suggested octahedral geometry for Cd(II) complex[32-33].

3.7 Thermal analysis of metal complexes

Thermo gravimetric analytical data of metal complexes were summarized in Table 5.

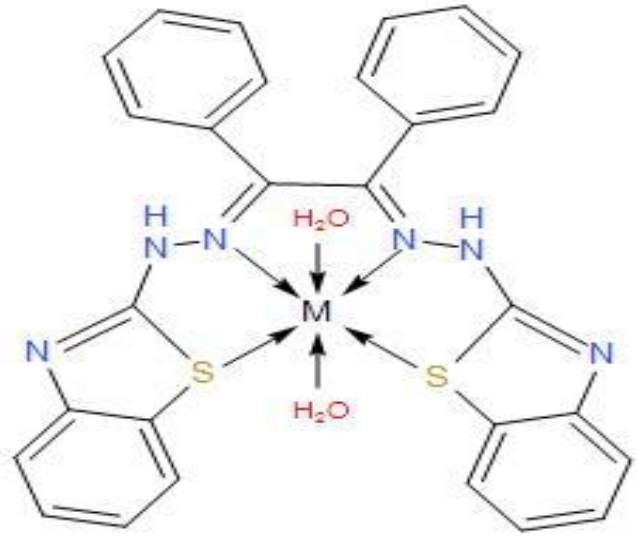
Table-5

$[C_{28}H_{20}N_6S_2(H_2O)_2]Ni$		$[C_{28}H_{20}N_6S_2(H_2O)_2]Cd$	
Weight loss %	Temperature ^0C	Weight loss %	Temperature ^0C
0	30.48	0	26.56
10	248.04	10	112.39
20	315.89	20	152.15
30	353.55	30	260.46
40	415.97	40	346.79
50	483.44	50	409.69
52.29% total wt. loss	500	60	496.66
		69.51% total wt. loss	600

The TGA curve of L_2Ni was carried out in the temperature range from room temperature to 500^0C. The heating was carried out in the nitrogen atmosphere, with heating rate $10^0C\ min^{-1}$.

The thermogram of L_2Ni complex shows total weight loss of 52.29% at 500^0C. In the range of 30.48^0C to 248.04^0C water of crystallization lost with 10% weight loss is observed. Then loss up to organic moiety total weight loss of 52.29% at 500^0C. Stable curve indicates formation of metal oxide of nickel.

The TGA curve of L_2Cd was carried out in the temperature range from room temperature to 600^0C. The heating was carried out in the nitrogen atmosphere, with heating rate $10^0C\ min^{-1}$. The thermogram of L_2Cd shows total weight loss of 69.51%. Firstly water of crystallization in the range of 26.56^0C to 112.39^0C. Lastly loss of organic moiety with total weight loss at 600^0C was 69.51%. A stable curve shows the formation of metal oxide of cadmium. Stable curve indicates formation of metal oxide of cadmium.



Proposed structure of metal complexes (M) = Ni(II), Cd(II)

3.8 Bioactivity study

Antibacterial activity of novel Schiff base ligand and its metal complexes were summarized in Table 6.

Table-6

Sr. No.	Compound	Minimum inhabitation concentration (ug/ml)		
		E. Coli	S. Aureus	S. Typhi
1	$C_{28}H_{20}N_6S_2$	250	125	250
2	$[C_{28}H_{20}N_6S_2(H_2O)_2]Mn$	100	50	250
3	$[C_{28}H_{20}N_6S_2(H_2O)_2]Fe$	250	250	100
4	$[C_{28}H_{20}N_6S_2(H_2O)_2]Co$	125	100	100
5	$[C_{28}H_{20}N_6S_2(H_2O)_2]Ni$	100	125	200
6	$[C_{28}H_{20}N_6S_2(H_2O)_2]Cu$	250	250	500
7	$[C_{28}H_{20}N_6S_2(H_2O)_2]Zn$	125	62.5	250
8	$[C_{28}H_{20}N_6S_2(H_2O)_2]Cd$	250	125	250
9	$[C_{28}H_{20}N_6S_2(H_2O)_2]Ag$	250	125	500

Antibacterial activity of synthesized novel Schiff base ligand and its metal complexes were performing against Escherichia Coli, Staphylococcus Aureus and Salmonella Typhi. Which were grown overnight at 37^0C temperature. The minimum inhibitory concentration (MIC) was evaluated against test bacteria. Concentration ranging is in between 0.4 ug/ml to10 ug/ml.

Mn(II) and Zn(II) complex shows excellent antibacterial activity on S.Aureus as compared to rest of metal complexes and parent ligand. Mn(II) and Ni(II) shoes good antibacterial activity on E.Coli as compared to rest of metal complexes and parent ligand. Fe(II) and Co(II) shows good antibacterial activity on S.Typhi as compared to rest of metal complexes and parent legend.

4. CONCLUSION

In the present research work, synthesis of novel Schiff base ligand and metal complexes were carried out by using scientific microwave oven. The main advantage of this method is better yield and decrease reaction time from hours to minutes. It is green and efficient method of synthesis. This method shows new and simple way of synthesis.

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