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Research Article

Green Synthesis, Characterization and Biological Activity Study of Transition Metal Complexes of Schiff Base Ligand (19Z)-N-(3-((Z)-(5,6-dimethyl-1H-benzo[d] imidazole -2 - ylimino) methyl) benzylidene) -5, 6 – dimethyl - 1H - benzo[d]imidazol-2-amine.

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Abstract

Novel Schiff base ligand was synthesized by using Scientific Microwave oven. The Schiff base (19Z)-N-(3-((Z)-(5,6-dimethyl-1H-benzo[d]imidazol-2-ylimino)methyl)benzylidene)-5,6-dimethyl-1Hbenzo[d] imidazol-2-amine was derived from 2-amino 5,6 Dimethyl benzimidazole and Isophthalaldehyde. The metal complexes were prepared by reaction of this novel ligand with transition metal salts in scientific micro oven under solvent free condition. The metal complexes were characterized by UV, IR and thermal analysis. The metal complexes exhibit coordination number 6 and exhibit octahedral geometry. The complexes are colored and stable in air. The antimicrobial activity of synthesized metal complexes show a good activity against the gram -positive bacteria Staphylococcus aureus and Gram-negative bacteria Escherichia coli, Salmonella Typhi. The antimicrobial results also indicate that the metal complexes are better antimicrobial agents as compared to the novel Schiff base.

INTRODUCTION

Schiff base metal complexes have been studied in the field of coordination Chemistry due their easy synthesis, availability of reactants, electronic properties and decent solubility in common solvents (Sharma *et al.*, 2010). The co-ordination chemistry of aza-oxa donor ligands is a motivating area of research. Such metal complexes due to a fine understanding of metal protein binding have been of great curiosity for many decades (Abdelaziz *et al.*, 2017). Microwave-assisted preparation belongs to ecofriendly synthesis due to shorter reaction time, higher yield etc. The use of microwave assisted preparation in organic, organometallic and co-ordination chemistry carry on to progress at a surprising speed (Gopalkrishnan *et al.*, 2007). Microwave-assisted preparation under solvent free or less solvent condition offer reduced pollution, low cost, better yield, ease in processing and handling [Sun et al. 2010].In microwave assisted organic synthesis, chances of accidents due to boiling, toxic and hazardous solvents are normally stopped (Ganguli *et al.*, 2015 and Maji, 2018). The usage of microwave irradiation for the preparation of medicines and organic compounds has proved harmless, economical and environmentally nontoxic

The projecting features of microwave irradiation technique are lesser reaction times, simple reaction settings and improvement in yield (Shinde *et al.,* 2014). Molecules comprising azomethine group (-HC=N-) are identified as Schiff bases (Mishra *et al.,* 2012). These are condensation products of aldehydes / ketones with primary amines and were first prepared by Hugo Schiff in 1864 (Guzen *et al.,* 2007). Schiff base metal complexes exhibit various biological activities such as anticancer (Yadav et al. 2015), plant growth inhibitors (Aras *et al.,* 2009) insecticidal (Prakash *et al.,* 2011), antidepressant (Kiruthikajol *et al.,* 2013), antibacterial [Masson *et al.,* 2013],anti-inflammatory [Kobayashi *et al.,* 2011], anti-tuberculosis (Kumar *et al.,* 2017), antimicrobial (Sriram *et al.,* 2006 and Prashanti *et al.,* 2010).

In the present paper, we have described synthesis, characterization and biological study of the metal complexes derived from novel ligand (19Z)-N-(3-((Z)-(5,6-dimethyl-1H-benzo[d]imidazol-2-ylimino)methyl)benzylidene)-5,6-dimethyl-1Hbenzo[d] imidazol-2-amine and metal salts of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ag(I) and Cd(II).

MATERIAL AND METHODS

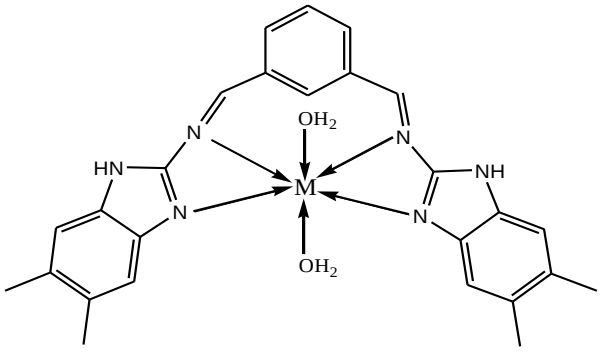
All chemicals were purchased from the sigma Aldrich including 2-amino 5, 6 Dimethyl benzimidazole, Isophthalaldehyde. Metal salts Mn(II)Chloride ,Fe(III)Nitrate, Co(II)Nitrate, Ni(II)Nitrate, Cu(II)Nitrate, Zinc (II) Nitrate, Cd(II)Nitrate, Ag(I)Nitrate were purchased from Loba Chem & Merck. All the chemicals were used as received. The Schiff base (19Z)-N-(3-((Z)-(5,6-dimethyl-1H-benzo[d]imidazol-2-ylimino)methyl)benzylidene)-5,6-dimethyl-1Hbenzo[d] imidazol-2-amine, synthesized by Pawar et al in scientific microwave oven.

Techniques:

Microwave syntheses were performed in a microwave extraction system in a scientific oven, 2450 MHz frequency, and 750W.Melting points were determined on digital melting point apparatus. The electronic absorption spectra were recorded in a DMSO solution in the wavelength range 200-800nm using a UV-VIS spectrophotometer. The IR spectra were recorded on a Shimadzu Dr-8031 instrument. The thermo gravimetric analyses (TGA) were carried out in dynamic nitrogen atmosphere (30ml/min) with a heating rate of 10 °C/min using Shimadzu TGA-50H thermal analyzers. TLC analyses were performed on pre-coated aluminum plates (silica gel) TLC spots were visualized with UV light.

Synthesis of metal complexes

The complexes were synthesized by mixing the appropriate metal chloride and/ or nitrate with the required amount of the ligand in a 1:1metal to ligand ratios. The reaction mixture was irradiated in a microwave oven at 750 W and the time required was in the range of 60 sec to 240 seconds. The final products were washed with hot ethanol, filtered and dried at room temperature.



M:Mn(II),Fe(III),CO(II),Ni(II),Cu(II),Zn(II),Cd(II),Ag(I)

RESULT AND DISCUSSION

As a result of microwave assisted synthesis, it was observed that the reaction time was shorter with higher yields. In the microwave method, homogeneity of reaction mixture was increased by the rotating of reaction platform tray. The confirmation of the results was also checked by repeating of the synthesis process. The microwave irradiation synthesis was completed within 10 second to 4 minutes and yield obtained 66-95%. All the metal complexes are colored, solid and stable towards air and moisture at room temperature. They possess sharp melting points. The complexes are

Physical properties:

The details of physical properties of the metal complexes are tabulated in Table 1.

Table 1: Physical properties of the metal complexes

Sr. No.	Molecular Formula	Colour	M.P.(°C)	Time (seconds)	Yield (%)
01	$[(C_{26}H_{24}N_6)_2(H_2O)_2]Mn$	Dark Yellow	164	240	80
02	$[(C_{26}H_{24}N_6)_2(H_2O)_2]Fe$	Brownish	174	60	66
03	$[(C_{26}H_{24}N_6)_2(H_2O)_2]Co$	Olive Green	210	90	90
04	$[(C_{26}H_{24}N_6)_2(H_2O)_2]Ni$	Light Green	250	60	95
05	$[(C_{26}H_{24}N_6)_2(H_2O)_2]Cu$	Green	202	10	85
06	$[(C_{26}H_{24}N_6)_2(H_2O)_2]Zn$	Yellow	198	90	88
07	$[(C_{26}H_{24}N_6)_2(H_2O)_2]Cd$	Light Green	159	80	89
08	$[(C_{26}H_{24}N_6)_2(H_2O)_2]Ag$	Bright Yellow	224	180	92

Infrared spectral analysis:

IR spectra of Schiff Base ligand show a broad band around 3452 cm^{-1} which can be attributed to NH stretching vibration of benzimidazole moiety.IR spectrum of the Schiff base ligand showed the most characteristic bands at 1670 cm^{-1}ν(C=N) due to azomethine stretching [Allen and Tidwell 2012]. The band 1670 cm^{-1} due to the azomethine group of the Schiff base was shifted to lower frequencies (1680 cm^{-1}) after complexation, indicating bonding of the azomethine nitrogen to the metal ions. This can be explained by the donation of electrons from nitrogen to the empty d-orbital of the metal atom. This shift confirms the participation of oxygen in the C–O–M bond [Nurul et al. 2014]. This band was observed in the complexes, indicating the presence of coordinated water molecules in the Ni (II) complex. In the low frequency region, the band of weak intensity observed in the spectra of the complex, (M-O) band found at 554 -574 $cm^{-1}$and (M–N) band at 457-480 cm^{-1}.

Table 2: Selected Infrared Frequencies (cm^{-1}) of ligand and its complexes

Ligand/Complexes	υ(C=N) Azomethine	υ(N-H)	υ(M-N)	υ(M-O)
$C_{26}H_{24}N_6$	1670	3452	-	-
$[(C_{26}H_{24}N_6)_2(H_2O)_2]Ni$	1680	3441	480	553
$[(C_{26}H_{24}N_6)_2(H_2O)_2]Cu$	1647	3415	457	574

Electronic spectra analysis:

The UV–visible spectra of the complexes were recorded in DMSO solutions in the wavelength range 200-800 nm at room temperature. The spectral data of the transition metal complex Ni(II) and Cu(II) complex are given in table 3.The electronic spectrum of the Ni (II)complex shows three absorption bands at 45454 cm^{-1}, 45662$cm^{-1}$and 47619cm^{-1},which may be assigned to $^3A_{2g}\rightarrow{}^3T_{2g}(F)(\nu_1)$, $^3A_{2g}\rightarrow{}^3T_{1g}$ $(F)(\nu_2)$ $^3A_{2g}\rightarrow{}^3T_{1g}$ (p) (ν_3) respectively. This complex shows octahedral geometry. Cu (II) complex indicates the three absorption bands at 42194 cm^{-1}, 43103 cm^{-1} and 44445cm^{-1} nm. These transitions may be assigned to $^2B_{1g}\rightarrow{}^2A_{1g}$ (ν_1), $^2B_{1g}\rightarrow{}^2B_{2g}$ (ν_2), $^2B_{1g}\rightarrow{}^2Eg$ (ν_3) respectively [Nagesh et al. 2015]. The electronic spectrum of Cu(II) complex shows transitions which are consistent with the characteristic octahedral geometry.

Table 3: Electronic spectral data and geometries for the metal complexes

Complexes	Frequencies nm/cm^{-1}	Assigning	Geometry
$[(C_{26}H_{24}N_6)_2(H_2O)_2]Ni$	220/45454	$^3A_{2g}\rightarrow{}^3T_{2g}(F)$ (ν_1)	Octahedral
	219/45662	$^3A_{2g}\rightarrow{}^3T_{1g}(F)$ (ν_2)	
	210/47619	$^3A_{2g}\rightarrow{}^3T_{1g}(p)$ (ν_3)	
$[(C_{26}H_{24}N_6)_2(H_2O)_2]Cu$	237/42194	$^2B_{1g}\rightarrow{}^2A_{1g}(\nu_1)$	Octahedral
	232/43103	$^2B_{1g}\rightarrow{}^2B_{2g}$ (ν_2)	
	225/44445	$^2B_{1g}\rightarrow{}^2Eg$ (ν_3)	

Thermal analysis of metal complexes:

The TGA curves of the metal complexes were studied where the heating rates were suitably controlled at 10℃ min^{-1}under nitrogen atmosphere and the weight loss was measured from 32℃ to500℃.The TG curve of Ni(II) complex indicates a total weight loss of 79.26%(calcd.82.06%)which is observed in two steps, first step a small weight loss of 5.16% (cal. 5.02%) in the range of 32- 204℃ loss of two water molecule [Eibindary and Eisonbaty 2000]. Second step involved a weight loss of 7.20% (cal.7.70%) in the range of 204-420℃ attributable to the loss of methyl group after that weight loss of 79.26% (Cal.82.06%) in the range of 420-525℃ with loss of organic moiety and formation of stable metal oxide (NiO).

The TGA curve of Cu(II) complex indicates a total weight loss of 85.61% (calcd.84.26%) which is observed in two steps; first step a small weight loss of 5.26% (calcd.5.32%) in the range of 30-220 ℃ loss of two water molecule [Chandralekha and Chandramohan 2014] and second step involved a weight loss of 7.19% (cal.6.70%) in the range of 220-410 ℃ attributable to the loss of methyl group after that weight loss of 85.61% (Calcd.84.26%) in the range of 410-535℃ with loss of organic moiety and formation of stable metal oxide (CuO).

Antibacterial Study:

Antibacterial activities of metal complexes were screened against bacteria such as Escherichia Coli, Staphylococcus Aureus, and Salmonella Typhi. They were grown overnight at 37℃ temperature [Isenberg 1998].The standard strains were obtained from MTCC Chandigarh. Determination of minimum inhibitory concentrations (MIC) was done by micro broth dilution method. It was evaluated against test bacteria for the concentration ranging between0.4µg/ml to 100µg/ml. Solutions of metal complexes was prepared in DMSO. The measured efficiency metal complexes were compared with antibiotics viz. Streptomycin. The metal complexes of Fe (III) and Mn (II) was observed with excellent activity, Co(II) and Cu(II) showed very good activity. Antibacterial activities are summarized in table no.4.

Table 4: Antibacterial Activity of Novel ligand and their Metal Complexes

Sr. No.	Compounds	Minimum Inhibitory Concentration (µg/ml)		
		Escherichia Coli	Staphylococcus Aureus	Salmonella Typhi
01	Mn (II)	500	125	500
02	Fe(III)	500	500	250
03	Co(II)	250	62.5	500
04	Ni(II)	500	100	125
05	Cu(II)	500	125	250
06	Zn(II)	250	125	250
07	Cd (II)	500	250	500
08	Ag (I)	100	125	250

CONCLUSION

In the present work, we have synthesized a new metal complexes of (19Z)-N-(3-((Z)-(5,6-dimethyl-1H-benzo[d]imidazol-2-ylimino)methyl)benzylidene)-5,6-dimethyl-1H-benzo[d]imidazol-2-amine Schiff base ligand by Microwave method. These synthesized compounds were characterized by spectral analyses. In the result of microwave–assisted synthesis; it has been observed that the reaction time decreased from hours to minutes with better yield. This method is simple, mild and eco-friendly from green chemistry approach.

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