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Microwave Assisted Synthesis, Characterization, and Antibacterial Activity of Novel Ni(II) Zn(II) Cd (II) Ag(II) Metal Complexes with Bidentate Schiff's base Ligand

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Abstract

Few new metal complexes of Ni(II), Zn((II), Cd(II), Ag(I), and Schiff's base (derived from 2-aminobenzimidazole and syringaldehyde) by using Scientific Microwave. The Schiff's base and its metal complexes are characterized by elemental analysis, electronic spectra, Infrared ^{1}H NMR , LC-MS and thermal analysis. The Schiff's base and metal complexes show an excellent antimicrobial activity against Gram positive bacteria such as Streptococcus Aureus Gram negative bacteria such as Escherichia Coli, and Salmonella Typhi

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Keywords: Microwave method, Schiff's base, Thermal analysis, Electronic Spectra

Introduction

Schiff's base ligands have been studied in the field of coordination chemistry due to their facile syntheses, easy availability, electronic properties and good solubility in common solvents and they easily form stable complexes with most transition metal ions [1-2]. Microwave assisted synthesis have an environmental friendly approach as well as an economical benefit and have great demand in coordination chemistry [3-6].Microwave irradiation is well known to promote the synthesis of a variety of organic and inorganic compounds, where chemical reactions are accelerated because of selective absorption of microwave by polar molecules [7].Schiff's bases and their metal complexes have been found to possess important biological and catalytic activity [8]. Due to their great flexibility and diverse structural aspects, a wide range of Schiff's bases have been synthesized conventionally and their complexation behavior was studied [9-10]. The field of bioinorganic chemistry has increased the interest in Schiff's base complexes [11-12], since it has been recognized that many of these complexes may serve as models for biologically important species and were investigated for antifungal,[13] antimicrobial,[14] anti- bacterial,[15] anti-inflammatory, anti-convulsant, anticancer activities [16]. Imidazole derivatives of Schiff's base have application in the field of medical science due to having their high chemotherapeutic properties [17].

Experimental Section

Material Methods:

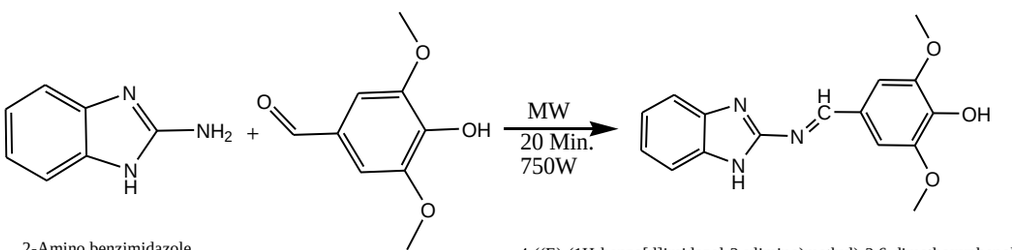
All chemicals were purchased from the Sigma Aldrich including 2-aminobenzimidazole, syringaldehyde , Metal salts were purchased from Loba chem. & Merck were used as received, Ni (II) Nitrate, Zn(II) Nitrate, Cd (II) Nitrate and Ag(I) Nitrate. The Schiff's base ligands were prepared by the condensation of the aldehyde and amine in the 1:1 molar ratio by microwave method.

Techniques

Microwave syntheses were performed in a microwave extraction system in a scientific oven, 2450 MHz frequency, 800W. 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 .^{1}HNMR spectra were recorded in DMSO-d6 on Bruker's 400MHz.The mass spectra were recorded by LC-MS Spectrophotometer. The thermo gravimetric analyses (TGA) were carried out in dynamic nitrogen atmosphere (30ml/min) with a heating rate of 10 ^{0}c/min. using Shimadzu TGA-50H thermal analyzers . TLC analyses were performed on pre-coated aluminium plates (silica gel) TLC spots were visualized with UV light.

Synthesis of Schiff's base ligand :

The Schiff's base was synthesized by the reaction of 2-amino benzimidazole (1.33gm, 0.01mmole) and syringaldehyde (1.82gm,0.01mmole). The reaction was carried out in a microwave for 20 minutes and 750W. The condensation product was washed with dry ether and then filtered. The final product was recrystallized from absolute ethanol to give yellowish crystals. (2.82gm, 90%) M.P.102 ^{0}C. The purity of the product was monitored by the use of TLC, using n-Hexane and ethylacetate (7:3).

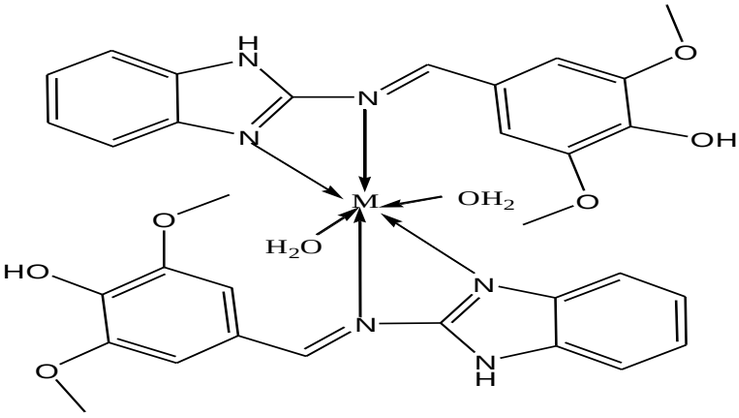


2-Amino benzimidazole Syringaldehyde 4-((E)-(1H-benzo[d]imidazol-2-ylimino)methyl)-2,6-dimethoxyphenol

*[Sinkar et al. [30] synthesized bidentate ligand has been shown in above reaction]

Synthesis of metal complexes :

The complexes were synthesized by mixing the appropriate metal nitrate with the required amount of the ligand in a 1:2 metal to ligand ratio. The reaction mixture was irradiated in a microwave oven at 750 W for 60 second. The final products were washed with hot ethanol, filtered and dried at room temperature. The metal salts used were $Ni(NO_3)_2.6H_2O$, $Zn(NO_3)_2.6H_2O$, $Cd(NO_3)_2.4H_2O$, $AgNO_3$.



Proposed structure of Metal complexes (M) = Ni (II), Zn (II), Cd(II), Ag(I)

Result and Discussion

As a result of microwave assisted synthesis, it was observed that the reaction was completed in a short time 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 done by the repeating of the synthesis process. The microwave irradiation technique was completed with 2-5 minutes and yield 90-97%. All the metal complexes were coloured, solid and stable towards air and moisture at room temperature. They possess sharp melting points. The complexes are insoluble in common organic solvents but soluble in DMF and DMSO.

Elemental analysis:

The elemental analysis of Schiff's base ligand (Found: C = 60.23); H = 5.26; N =14.31; O = 20.2%) Calcd: C = 64.65%; H = 5.05%; N =14.14%; O = 16.16 %) indicated that the ligand may have the molecular formula i.e.$C_{16}H_{15}N_3O_3$.

Physical properties

The details of physical properties of the ligand and its complexes are tabulated in **(table 1).**

Sr.No.	Formula of complex	Colour	M.P.(^{0}C)	Yield (%)

1	$C_{16}H_{15}N_3O_3$	Yellowish	102	90
2	Ni[$C_{16}H_{15}N_3O_3(H_2O)_2$]	Beige Green	180	95
3	Zn[$C_{16}H_{15}N_3O_3(H_2O)_2$]	Yellowish Brown	90	97
4	Cd[$C_{16}H_{15}N_3O_3(H_2O)_2$]	Yellow	112	93
5	Ag[$C_{16}H_{15}N_3O_3(H_2O)_2$]	Brown	98	94

Infrared spectral analysis:

IR spectra of novel ligand and metal complex reveal the binding mode of ligand to metal ions which is confirmed by a negative shift in the position of absorption peaks. IR spectra of free ligand show a broad band around 3284 cm^{-1} which can be attributed to NH stretching vibration of benzimidazole moiety [19]. IR spectrum of the Schiff's base ligand showed the band at 1608 cm^{-1} ν(C=N, azomethine), and 1124 cm^{-1} ν(C–O) [20]. The phenolic C–O stretching vibration that appeared at 1039 cm^{-1} in Schiff' base shifted towards higher frequencies (1124 cm^{-1}) in the complex [20].This shift confirms the participation of oxygen in the C–O–M bond. This band was observed in the complex, 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 in the region of 419 cm^{-1} is attributed to (M–O) and in the region 504 cm^{-1} to (M–N) [21].

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

Ligand/Complex	υ(C=N) Azomethine	υ(OH) Phenolic	υ(C-O) Phenolic	υ(M-N)	υ(M-O)
$C_{16}H_{15}N_3O_3$	1608	3284	1124	-	-
Ni[L_2]	1642	3311	1213	504	419

^{1}H-NMR Spectra

The H-NMR spectrum for Schiff's base showed a peak at 3.84 ppm (s, 3H, $–OCH_3$),a peak at 9.78 ppm (s, 1H, N=CH),10.29 ppm (s ,1H, -OH).The multiplet signals within the 7.21- 6.83 ppm range are assigned to the aromatic protons of both rings [22].

Mass Spectra

The mass spectrum of the Schiff's base showed the molecular ion peak at m/z 298 (M+1) that corresponds to the molecular weight of the Schiff base ligand i.e. 297 [23]. This ion peak can be attributed to parent ion. Hence the molecular formula $C_{16}H_{15}N_3O_3$. is suggested.

Electronic spectra

The UV–visible spectra of the complex were recorded in DMSO solutions in the wavelength range 200–800 nm at room temperature. Only charge transfer transition was observed in metal complexes therefore geometry of complex suggested is octahedral [24].

The electronic spectrum of the Ni(II) complex shows three bands at 29,411cm^{-1}, 32,786cm^{-1}, 41,667cm^{-1}, 340,305 and 240nm, $^3A_{2g}$ (F)$\rightarrow{}^3T_{2g}$, $^3A_{2g}$(F)$\rightarrow{}^3T_{1g}$ and $^3A_{2g}$(P)$\rightarrow{}^3T_{1g}$, respectively [23].This suggests octahedral geometry [25].

Complex	Frequency cm^{-1}	Assignment	Geometry
Ni [$C_{16}H_{15}N_3O_3(H_2O)_2$]	29,411cm^{-1}	$^3A_{2g} \rightarrow {}^3T_{2g}$ (F)	Octahedral
	32,786cm^{-1}	$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)	
	41,667cm^{-1}	$^3A_{2g} \rightarrow {}^3T_{1g}$ (P)	

Thermal analysis of metal complexes

The TGA curve of the metal complexes were studied where the heating rates were suitably controlled at 10^0C min^{-1} under nitrogen atmosphere and the weight loss was measured from 28^0 C to 500 ^{0}C [26]. Ni (II) complex indicated a total weight loss is 87.72% the first step in the range of 30-121^{0}C, weight loss was 5.20% (calcd.5.24%) loss of two water molecule and the second step, involved a weight loss 86.72% (calcd.86.34%) in the range of 121-458^{0}C loss of organic moiety and formation of stable residue of nickel oxide [27].

Antibactrial Study:

Antibacterial activity of synthesized Schiff's base and its metal complexes were screened against bacteria such as *Escherichia Coli, Streptococcus Aureus Salmonella Typhi* were grown overnight at 37 ^{0}C temperature[28]. Determination of minimum inhibitory concentrations (MIC) by Micro Broth Dilution Method was evaluated against test bacteria for the concentration ranging between 0.4µg/ml to 100µg/ml. DMSO and compared with antibiotics viz. Streptomycin.[29] The Schiff's base ligand and Zn (II) complex was observed excellent activity such as *Escherichia Coli and Streptococcus Aureus* and Ag (I) complex showed very excellent activity against bacteria such as *Streptococcus Aureus and Salmonella Typhi.*

Table 3: Antibacterial activity of ligand (L_1) and their metal complexes:

Sr.No.	Compounds	Minimal inhibition Concentration (µg/ml)		
		E.Coli	S.Aureus	S.Typhi
L1	Ligands	125	62.5	100
1	Ni(II)	500	250	100
2	Zn(II)	25	50	250
3	Cd (II)	125	250	250
4	Ag (I)	200	50	25

Conclusion

In the present work, we have synthesized novel metal complexes Ni (II) Zn(II), Cd (II), Ag(I) and a new Schiff's base ligand 4-((E)-(1H-benzo[d]imidazol-2ylimino)methyl)-2,6-dimethoxy phenol by Microwave method . All the complexes were six coordinated and exhibited octahedral geometry. 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 and availability of the products are more than 85% yield.

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