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Transition metal (II) complexes with 2- amino methyl benzimidazole derived schiff base: synthesis, characterization and biological activity

Pragathi Jogi *, Medha Bhushan and B Mrinalini

Department of chemistry, G. Narayanamma Institute of Technology and Science (Autonomous), Telangana, India.

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Abstract

Novel transition metal [Co(II), Cu(II), Ni(II) and VO(II)] complexes derived from Schiff bases of 2-amino methyl benzimidazole and 2-furan carbaldehyde(BNFM) have been synthesized and characterized by physical, spectral and analytical data. The synthesized Schiff-bases act as tridentate ligand for the complexation reaction with Co (II),Cu(II), Ni(II) and VO(II) ions. The new compounds, possessing the general formula $[ML_2]$ where $[M=Co (II), Cu (II), Ni(II) and VO(II)]$. The Schiff bases and their complexes have been screened for biological activity against the strains such as Escherichia coli, Staphylococcus aureus, B.Subtilis and Pseudomonas aeruginosa in order to evaluate the effect of complexation of metals with Schiff base. The metal coordinated Schiff bases have shown more antibacterial activity against bacterial species as compared to uncoordinated Schiff-bases.

Keywords: Schiff bases; Biological activity; 2-amino methyl benzimidazole; Characterization

1. Introduction

Schiff bases are widely used versatile organic compounds and can be easily synthesized by the condensation reaction of amine and aldehyde or ketone [1-2]. Schiff base ligands have been extensively studied in the field of coordination chemistry due to their facile synthesis, easy availability, and electronic properties. In recent times, Schiff base coordination chemistry has attracted much attention because of their significance in organic synthesis, analytical chemistry, refining of metals, metallurgy, electroplating, and photography [5-7]. Schiff bases have wide applications in dye industry, catalysis, fungicidal, and agrochemical [8-9]. Several Schiff bases are reported to possess remarkable antibacterial, antifungal, and anticancer activities [10]. In such class of compounds, the C=N moiety is important for biological activity. In view of the interesting behavior of Schiff base complexes, we considered it worthwhile to prepare Cu(II), Co(II), Ni(II) and VO(IV) complexes of tridentate ligand derived from 2-(aminomethyl)benzimidazole and Furan-2-carboxaldehyde. These complexes have been characterized by various physicochemical methods.

2. Experimental Method

The percentage compositions of C, H and N of complexes were determined by using micro analytical methods on Perkin Elmer 240C (USA) elemental analyzer. Infrared spectra of the ligand and its complexes were carried out by using KBr pellets in the range 4000-400 cm^{-1} on Perkin Elmer Infra-red model 337. The electronic absorption was carried out by Shimadzu UV-1601 using DMSO as solvent. TGA studies were carried on Mettler Toledo Star system in the temperature range of 0-1000 oC. The Mass spectra were recorded by ESI technique on VG AUTOSPEC mass spectrometer instrument. The ^1H and ^{13}C NMR spectra were recorded on Varian Gemini Unity Spectrometer by employing TMS as internal standard. Melting points of the ligand and decomposition temperature of complexes were determined on Polmon instrument (model No.MP-96). The Molar conductance measurements were carried out in DMSO (10⁻³ M) using Digisun

* Corresponding author: Pragathi Jogi

electronic digital conductivity meter of model; DI-909 having a dip-type cell calibrated with KCl. The magnetic susceptibilities of complexes were determined on Gouy balance model 7550 at 23 oC. The diamagnetic corrections was carried out using a Shimadzu UV-1601 using DMSO as solvent. TGA studies were carried on Mettler Toledo Star system in the temperature range of 0-1000 °C. The mass spectra were recorded by ESI technique on VG AUTOSPEC mass spectrometer were made by Pascal's constant and Hg[Co(SCN)4] was used as a calibrant. ESR spectra were recorded in DMSO solution on a JOEL TE-3X.X-Band spectrometer equipped with a 100KHZ field modulation unit, central university, Hyderabad.

2.1. Synthesis of Schiff base

2-(Aminomethyl)benzimidazole (1.10 g, 5 mmol) was dissolved in 15 mL water and neutralized by adding aqueous Na₂CO₃ solution. A stirred solution of Furan-2- carboxaldehyde (0.560 g, 5 mmol) in 8 mL of methanol was added drop wise to the above solution with stirring for 1 h. During this period, yellow solid slowly separated out. The solid was filtered off, washed thoroughly with water followed by petroleum ether and dried in vacuum at room temperature. Structure of the Schiff base is shown in the Figure 1.

2.2. Synthesis of metal complexes

Methanolic solution of ligand (0.005 mol) and methanolic solution of corresponding metal salts (0.005 mol) (MX₂, where M= Cu(II), Ni(II), Co(II) and VO(IV); X=Cl/Acetate/SO₄) were mixed together with constant stirring. The mixture was refluxed for 4 h at 80°C. On cooling coloured solid metal complexes were precipitated out. The products were filtered, washed with petroleum ether and dried under vacuum over CaCl₂

3. Results and discussion

The complexes were found to be stable in air and non-hygroscopic. The complexes are soluble in DMSO. The physical properties and analytical data of the complexes are given in Table.1

Table 1 Physical properties and analytical data of Schiff base and its metal complexes

Compound	mass	MP°C	Molar conductance Ohm ⁻¹ cm ² mol ⁻¹	Found (Calculated)		
				C	H	N
BNFM	281.3	176	----	68.18 (68.31)	5.37 (5.39)	14.98 (14.94)
[Cu(BNFM)Cl ₂ (H ₂ O)] Cl	423	>300	66	45.1 (45.14)	4.68 (4.7)	9.83 (9.87)
[Co(BNFM)Cl ₃]	465	>300	05	47.9 (47.8)	4.50 (4.48)	10.48 (10.46)
[Ni(BNFM)Cl ₂ (H ₂ O)]	479	>300	02	43.8 (43.6)	4.31 (4.32)	9.58 (9.55)
[(VO)(BNFM)Cl ₃]	415	>300	08	47.5 (47.8)	4.86 (4.48)	10.43 (10.46)

3.1. Elemental analysis

It is clear from the data that the experimental values shown for each of the complexes, are in good agreement with the theoretical values calculated for 1:1 ratio. The composition assigned to the complexes may, therefore be formulated as presented in the table1.

3.2. Conductivity studies

The molar conductance values of the metal complexes dissolved in DMSO were measured at 10⁻³M concentrations. Conductance values show that Cu(II) complex is 1:1 electrolyte and Co(II), VO(II) and Ni(II) complexes are non-electrolytes.

3.3. Thermal analysis (TGA & DTA)

Thermal decomposition of Cu(II)-BNFM studied in Nitrogen atmosphere using TGA,DTG and DTA techniques. The TGA curves of Cu(II)- BNFM show that the initial mass loss occurring at 176.5°C is interpreted as loss of one coordinated water molecules and the second weight loss at 239°C is due to loss of second coordinated water molecule. In this complex, weight loss was observed around 394.8°C, indicative of decomposition of coordinated ligand. Finally, the horizontal nature of thermogram above 480°C observed, suggests the formation of final decomposition products corresponding to the metal oxide i.e. CuO.

3.4. Mass spectra

Electron spray ionization (ESI) mass spectra of the BNFM and its metal complexes were recorded at room temperature and were used to compare their stoichiometric composition. The molecular ion peaks for the metal complexes confirms the stoichiometry of metal chelates as ML type. It is also supported by the micro analytical data of the complexes. The spectra of $[\text{Cu}_2(\text{BNFM})\text{Cl}_2(\text{H}_2\text{O})_5]\text{Cl}$, $[\text{Co}(\text{BNFM})\text{Cl}_3]$, $[\text{Ni}(\text{BNFM})\text{Cl}(\text{H}_2\text{O})_2]$, $[(\text{VO})(\text{BNFM})\text{Cl}_3]$ showed molecular ion peak M^+ at 423m/z, 465m/z, 479m/z and 415m/z respectively and equivalent to their corresponding molecular weight.

3.5. IR spectral studies

The infrared spectral bands that provide conclusive structural evidence for the Coordination of the ligands to the central metal ions are given in the Table 2. The ligand shows a strong band at 1625cm^{-1} characteristic of $\nu(\text{C}=\text{N})$ stretching vibration, this band undergoes a negative shift in the complexes indicating the participation of the azomethine nitrogen in coordination. In addition, the ligand exhibits a band at 1576cm^{-1} due to cyclic $(\text{C}=\text{N})$ of the imidazole nitrogen (N_3)¹¹. This band is shifted in all the complexes, indicating the involvement of the imidazole (N_3) atom in complex formation. A sharp band around 1323cm^{-1} due to phenolic $\nu\text{C}-\text{O}$ of the ligand shifted in metal complexes suggesting the participation of the oxygen of the hydroxyl group in bonding with the metal ions. Appearance of a broad band in the range of $3000\text{-}3200\text{cm}^{-1}$ region was observed in the spectra of metal complexes indicating the presence of coordinated or lattice water molecules¹². Water molecules are coordinated, confirmed by the occurrence of additional band in the range of $847\text{-}865\text{cm}^{-1}$ arising due to OH rocking vibrations. Other bands of M-N and M-O appear at around 430cm^{-1} and 500cm^{-1} . In addition, vanadyl complex shows a band at 928cm^{-1} attributed to $\text{V}=\text{O}$ frequency¹³⁻¹⁵.

Table 2 Characteristic IR bands (cm^{-1}) of the compounds studied

Compound	$\nu \text{CH}=\text{N}$	$\nu \text{C}=\text{N}$	$\nu \text{M}-\text{N}$	$\nu \text{M}-\text{O}$	$\nu \text{M}-\text{OH}$	$\nu \text{V}=\text{O}$
BNFM	1630	1576	---	----	---	---
Cu(II)BNFM	1606	1579	443	503	3237,865	---
Co(II)BNFM	1673	1581	430	502	3190,865	---
Ni(II)BNFM	1629	1551	426	497	3081,847	---
VO(II)BNFM	1674	1580	429	503	3073,865	928

3.5. Electronic spectra and magnetic moment

The magnetic susceptibility and electronic spectral data of the metal complexes are given in Table-3. The magnetic susceptibility data showed that all the metal complexes, except zinc complex, are paramagnetic. The Cu(II) complex showed one broad band at 14326cm^{-1} assignable to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition that is characteristic of an octahedral environment. The electronic spectrum of Co(II) complex showed bands at 15015, 20533 and 23980cm^{-1} , which are assignable to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$, ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2(\text{F})$ transitions respectively, that are characteristic of tetrahedral configuration. The Ni(II) complex exhibited 3 transitions at $15833, 19685, 24374\text{cm}^{-1}$, which are assignable to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions. The VO(II) complex exhibited two transitions at $14880, 21645\text{cm}^{-1}$, which are assignable to ${}^2\text{B}_2 \rightarrow {}^2\text{E}$, ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ respectively, that are characteristic of square pyramidal geometry¹⁴.

Table 3 Electronic spectral data and magnetic moment data

Complex	μ_{eff}	Frequency(cm^{-1})	Assignments	Geometry
Cu(II)-BNFM	1.39	14326	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$	Octahedral
Co(II)-BNFM	3.0	15015	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$	Tetrahedral

		20533	${}^4A_2 \rightarrow {}^4T_1(F)$ ${}^4A_2 \rightarrow {}^4T_2$	
		23980		
Ni(II)-BNFM	2.7	15833	${}^3A_2g \rightarrow {}^3T_2g(F)$ ${}^3A_2g \rightarrow {}^3T_1g(F)$ ${}^3A_2g \rightarrow {}^3T_1g(P)$	Octahedral
		19685		
		24374		
VO(II)-BNFM	1.41	14880	${}^2B_2 \rightarrow {}^2E$	Square pyramidal
		21645	${}^2B_2 \rightarrow {}^2B_1$	

3.6. ESR spectra of Cu (II) complex

The ESR spectrum of the Cu (II) complex was recorded at LNT at 77K. This complex at LNT shows five hyperfine peaks in the low field region due to the interaction of the two unpaired electrons with nuclear spins of two copper nuclei and one intense peak in the high field region. Instead of seven hyperfine peaks, only 5 appeared in the low field region and remaining two peaks are merged in the parallel region. In distorted octahedral and square planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving ${}^2B_{1g}$ as the ground state with $g_{II} > g_{\perp}$ ($2.1034 > 2.02$) and g_{avg} is calculated as 2.053. The spin-orbit coupling constant, λ value (-190 cm^{-1}) calculated using the relations, $g_{avg} = 1/3[g_{II} + 2g_{\perp}]$ and $g_{avg} = 2(1 - 2\lambda/10Dq)$, is less than the free Cu(II) ion (-832 cm^{-1}) which also supports covalent character of M-L bond in the complex.

3.7. Antibacterial studies

The new Schiff base and the complexes were tested for in vitro antibacterial activity against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa* using diffusion method. The diffusion method requires filter paper disks, the medium used is muller-hinton agar with 2% of glucose and the diameter of inhibition zone is visually read at 24hrs after incubation at 37°C. The compounds are added on to the filter paper containing this medium. The antimicrobial activity was estimated on the basis of the size of inhibition zone formed around the paper disks on the seeded agar plates. Streptomycin was used as standard. The synthesized Schiff base and its metal complexes seem to be able to penetrate into the lipophilic layer in order to enhance the membrane permeability of the gram-negative bacteria¹⁵. The cell surrounded by the lipid membrane allows the flow of only lipid soluble materials; thus the lipophilicity is an important factor that controls the antimicrobial activity. Also the increase in lipophilicity enhances the penetration of Schiff base and its metal complexes into the lipid membranes and thus restricts further growth of the organism.

Table 4 Antimicrobial activity of Schiff base and Metal complexes

Compound(50µg)	<i>B. subtilis</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>S. aureus</i>
BNFM	12mm	12mm	11mm	13mm
Cu(II)-BNFM	19mm	14mm	19mm	17mm
Co(II)-BNFM	22mm	25mm	24mm	25mm
Ni(II)-BNFM	20mm	16mm	16mm	16mm
VO(II)-BNFM	16mm	18mm	17mm	16mm

4. Conclusion

Cu(II), Co(II), Ni(II) and VO(II) complexes of the schiff base derived from 2-(amino methyl) benzimidazole and 2-furan carboxaldehyde were prepared and characterized.

The study reveals that

- Cu(II) complex is 1:1 electrolyte and Co(II), VO(II) and Ni(II) complexes are non-electrolytes;
- The schiff base behaves as a neutral tridentate ligand and is coordinated through the azomethine nitrogen, pyridyl nitrogen of benzimidazole moiety and oxygen of furan coordinates to the metal forming metal complex;

- Cu(II), Ni(II) complexes have octahedral geometry ,Co(II) has Tetrahedral and VO(II) has square pyramidal geometry.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare that they have no conflict of interest.

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