Original Research Article

Synthesis, spectral characterization and biological evaluation of metal complex of N-(thiophen-2-ylmethylene)benzo[d]thiazol-2-amine

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Abstract

Metal complexes derived from heterocyclic compounds containing nitrogen, sulphur and oxygen as ligand atoms are interest of simple structural models of more complicated biological systems. Schiff base ligand N-(thiophen-2-yl methylene)benzo[d]thiazol-2-amine (NTBT) have been prepared from the condensation of 2-thiophenecarboxyaldehyde and 2-aminobenzothiazole. Metal complex of Zinc (II) derived from N-(thiophen-2-ylmethylene)benzo[d]thiazol-2-amine have been characterized using different chemical techniques such elemental analysis, FT-IR, FT-NMR, and electronic spectra. Schiff base under investigation behaves as bidentate ligand. The UV-VIS spectra and magnetic moment data suggested tetrahedral geometry of Zn(II) complex. The obtained chemical analysis data showed the formation of 1:2 (metal: ligand) ratio and spectral studies revealed that binding sites of ligand with metal ions through the azomethine nitrogen. The Schiff base and metal complex show a good activity against the bacteria and fungi. Their antimicrobial results indicate that the metal complex are better antimicrobial agents as compared to the Schiff bases.
Key Words: 2-aminobenzothiazole, azomethine, antimicrobial, Schiff base, metal complexes.

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INTRODUCTION

2-Aminobanzthiazole is bicyclic ring with multiple application and also have been studied extensively and found to have diverse chemical reactivity and show broad spectrum of activity, like antimicrobial, antihelmentics, antitumor, anti-inflammatory activity[1-2]. To build up drug-like molecules the combination of different heterocyclic compounds is a well-known approach that allows achieving compounds with new pharmacological profile, toxicity lowering abilities or action strengthening[3]. Schiff base formation affords the opportunity of such combinations that possess wide range of biological applications[4]. Specifically, shows positive activity towards Parkinson's disease[5]. Schiff-bases have been widely used as ligands because of their high stability to the coordination compounds and their good solubility in common solvents such as ethanol, methanol, chloroform, dimethylformamide[6].The biological activity of these compounds are connected to their ability to form complexes with certain metal ions which may lead to locked geometry via coordination mechanism so that, only few substances are able to become attached to the frame work of this interaction[7]. Schiff base act as a useful chelating agent when a suitable functional groups like –OH, -SH, -COOH etc., are present sufficiently close to azo-methine group so as to form five or six member chelate ring upon reaction with metal ion[8,9]. By changing the nature and position of the donor atoms it's possible to control the size of the chelate ring formed and exploit the effect of substitution. These factors make Schiff bases good chelating agents and potential analytical reagents. As the biological activity is often

augmented when the ligand forms the complexes, the resulting complex may be of potential biological importance[10,11]. Benzothiazole derivatives show significant activities against various viruses such as human cytomegalovirus (HCMV), 1 herpes (HSV-1),2,3, HIV 4,5 influenza and many more[12,13]. A thorough literature search shows that a very little work is done on the Schiff base prepared from the condensation reaction of 2-aminobenzothiazole and 2-thiophenecarboxaldehyde i.e. N-(thiophen-2-ylmethylene) benzo [d] thiazol-2-amine. In the present paper we are reporting the synthesis, characterization and in-vitro antibacterial activity of the Schiff base ligand N-(thiophen-2-ylmethylene) benzo [d] thiazol-2-amine and its metal complexes with Zn (II).

EXPERIMENTAL

Chemicals: All the chemicals used were of analytical reagent (AR) grade and of highest purity available. These include 2-aminobenzothiazole, 2-thiophenecarboxaldehyde (Sigma Aldrich) and $ZnCl_2$ (Hi-media). Organic solvents used are methanol, ethanol, acetone, DMF DMSO and benzene.

Physical measurements: Elemental analysis was carried out on Perkin Elmer 240c model Elemental Analyzer from IIT Powai. The infrared spectra were recorded on Model RZX (Perkin Elmer) Spectrophotometer using KBr pellets from SAIF, Punjab University, Chandigarh.^{1}HNMR spectra of synthesized compounds were recorded on Bruker Advance II Spectrophoto- meter at 400 MHz frequency in Deuterated chloride ($CDCl_3$) as well as dimethylsulfoxide (DMSO) using tetramethylsilane (TMS) as internal standard (chemical shift δ in ppm). Electronic spectra were recorded on a UV-VIS-NIR-Spectrophotometer Model Synthesis Lambda 750 Perkin Elmer from SAIF, PU, Chandigarh. The magnetic susceptibility measurements were carried out on a Vibrating Sample Magnetometer (VSM) from IIT, Roorkee. The melting points of the ligand and the complexes were determined in open capillaries with electronic melting point apparatus and are uncorrected.

Synthesis of Schiff base ligand: The Schiff base ligand N-(thiophen-2-ylmethylene)benzo[d]thiazol-2-amine(NTBT) was prepared by adding 1:1 molar ratio of 2-aminobenzothiazole (0.01 M) drop wise to 2-thiophenecarboxaldehyde (0.01M) prepared in dilute solution of methanol and distilled water (70:30) with continuous stirring for half an hour. The resulting yellow coloured solution was again stirred for half an hour and then refluxed at 65-75^{o}C for one hour and cooled in refrigerator for two to three days till crystals appeared. Light yellow crystals were collected by filtering the reaction mixture. These crystals were dried and recrystallized with benzene and dried over $CaCl_2$ in a desiccator.

Synthesis of metal complexes: 0.01 M solution of the metal(II)chlorides (M= Zn) was added drop wise to 0.02 M solution of Schiff base ligand (1.22 g) in methanol with continuous stirring. The pH of resulting homo-geneous solutions was adjusted to 9 with triethylamine, and then refluxed for 2hrs till its colour changes. The precipitates formed were filtered and washed with methanol and dried over $CaCl_2$ in a desiccator.

Antibacterial activity: In vitro antibacterial activity of the Schiff base ligand N-(thiophen-2-ylmethylene) benzo[d]thiazol-2-amine and its metal complex with Zn (II) was investigated by zone inhibition method against the bacteria like *S. aureus*, *B. subtilis*, and *E. coli*. The inclination of the bacteria towards derived metal complexes were tested by measuring the zone of inhibition (in mm) and compared with the parent ligand.

RESULTS AND DISCUSSSIONS

The structures of Schiff base ligand and their complexes were confirmed by elemental analysis, IR, ^{1}HNMR and electronic spectra. Elemental analysis data, formula weight, and melting point of the ligand and the complexes are given in Table-1. The results of elemental analysis are in agreement with the theoretical values within the limits of experimental error.

Table 1: Analytical and physico-chemical data of Schiff base ligand and its complexes

Ligand/ Complex	Color	M.Pt. (^{o}C)	Mol. Wt.	Elemental analysis found (calcd.)%				
				C	H	N	S	Metal
NTBT $C_{12}H_8N_2S_2$	Light yellow	112	244.3	55.90 (55.96)	3.57 (3.68)	14.73 (14.82)	25.39 (25.47)	- -
Zn-$(NTBT)_2$ $C_{24}H_{16}N_4S_4ZnCl_2$	Yellow	217	554.1	42.85 (42.96)	3.42 (3.43)	12.86 (12.95)	13.75 (13.86)	13.08 (13.15)

Infrared spectra: The infrared spectrum for the present compounds was recorded in the range 400-4000 cm^{-1}. The peak between1644-1532 cm^{-1} in the Schiff base was assigned to the $\upsilon_{C=N}$ of azomethine and thiazole stretching vibrations[14]. These bands shows downward shift to lower wave numbers in the range 1608 cm–^{1} for $\upsilon_{C=N}$ band. This indicated the coordination of the imine nitrogen to metal ions. Similarly, the band for $\upsilon_{C=C}$ at 1498 cm^{-1} in the ligand was shifted to 1474cm^{-1} in the metal complex due to coordination. Symmetric vibrations of C-S were

observed, which were appeared near 715cm^{-1} in the ligand spectrum, has been shifted to lower frequencies after complexation. The sharp IR ligand bands at 833 cm^{-1} assigned as $\upsilon_{(C\text{-}S\text{-}C)}$ of thiophene moiety, shifted to 839 cm^{-1} for metal complexes[15]. Further the bonding is supported by the appearance of bands at 571-582 cm^{-1} and 438-441 cm^{-1} assigned to $\upsilon_{(M\text{-}N)}$ and $\upsilon_{(M\text{-}S)}$ vibrations respectively[16]. Therefore, from the IR spectra, it is concluded that the NTBT ligand behaves as a bidentate ligand coordinated to the metal ions via azomethine N, and thiophene S[17].

^{1}HNMR spectra: The^1 HNMR Spectra of the free ligand were recorded in DMSO. The^1 HNMR Spectra of free ligand and their diamagnetic Zn(II) complex show the SH signal appeared at 3.51ppm and completely disappeared in the spectrum of its Zn(II) complex that indicates the SH proton is removed by chelation with Zn(II) ions. The peak at 9.31-8.93 ppm was observed for the methine protons of the azomethine group are down fielded to 8.97-8.62 ppm[18]. The peaks in the region of 7.26-6.93 ppm were assigned to chemical shifts for protons of the aromatic ring are down fielded to 6.87-6.39ppm. Schiff base exhibited signals of the protons in their expected regions and these data are good agreement with that previously reported for similar compounds.

Electronic Spectra and Magnetic Moment Measurements: The electronic spectra of the complex was recorded in the solution state. In spectra the ligand showed a broad band at 358 nm which is assigned to n-π* transition of the C=N chromophore but on complexation this bond was shifted to the lower wave length suggesting the coordination of imine nitrogen with central metal ion. The UV spectra of Zn(II) complex showed absorption bands at 368nm, 358nm attributed to $T_1g^{(F)} \rightarrow A_1g^{(F)}$ transition respectively suggesting tetrahedral geometry for the complex. The magnetic moment value 3.81 B.M for Zn(II) complex confirmed their tetrahedral geometry and their slightly lower magnetic moment might be due to the slight deviation from the regular tetrahedral geometry.

Antibacterial activities: Schiff base ligand and its zinc complex was found active against all the bacteria used *S. aureus*, *B. subtilis*, and *E. coli* with inhibitory zones range of 5.0-11.0mm. The Zn(II) complex was active against *S. aureus* and *E. coli* with inhibitory zones range of 14.0-19.0 mm. Its noteworthy that the Zn(II) complex had broad spectrum anti-bacterial activity against the bacteria proving its potential as broad-spectrum antibacterial agent[19]. The Zone of inhibition of synthesized compounds is shown below in Table-2.

Table 2: Antimicrobial activities of ligand and its metal complexes

Sr. No.	Compound	Zone of inhibition diameter in (mm)		
		S. aureus	*B. subtilis*	*E. coli*
1	NTBT	07	06	10
2	$(NTBT)_2$-Zn	17	14	19

CONCLUSION

The present work describes the synthesis of Zn(II) complex of the Schiff base ligand N-(thiophen-2-ylmethylene)benzo[d]thiazol-2-amine.Schiff base ligand is coordinated to the metal ion via the imine nitrogen and thiophene sulphur respectively. Based on analytical and spectral data, tetrahedral geometry have been proposed for the complex. The complex exhibited good in-vitro antibacterial activities in comparison to Schiff base ligand.

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