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GREEN SYNTHESIS, CHARACTERISATION AND BIOLOGICAL STUDIES OF THIAZOLE DERIVED SCHIFF BASE COMPLEXES

J. Jeevitha Rani [1] , A.Mary Imelda Jayaseeli [2]

[1,2] PG and Research Center of Chemistry, Jayaraj Annapackiam College for Women (Autonomous), Periyakulam, Affiliated to Mother Teresa Women's University, Kodaikanal, Tamilnadu,(India)

ABSTRACT

A green route for synthesis of heterocyclic ligand and the schiff base complexes are followed to get minimization of time and solvent. Thiazolyl ligand is synthesized from benzaldehyde with 2- amino thiazole. Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) complexes are synthesized using the ligand by microwave irradiation method. The synthesized thiazolyl ligand and its complexes are characterized by UV-Visible and FT-IR spectral studies. The structure of thiazolyl ligand is confirmed by ^{1}H NMR. The schiff base and their complexes have been screened for their antibacterial and antifungal activities. The antimicrobial results show that the metal complexes are more active than the thiazolyl ligand.

Keywords: Antimicrobial Activities, Green Synthesis, Heterocyclic Ligand, Metal Complexes.

I. INTRODUCTION

Schiff base ligands are of significant importance in coordination chemistry, particularly in the development of schiff base complexes, due to their capablity of forming stable complexes with metal ions[1]. Transition metal complexes play an important and diversified role in biological systems. Metal complexes find interesting applications in the fields such as biology, analytical, industrial and medicine. Many of the schiff bases and their complexes have been revealed to exhibit a wide range of biological activities, including anti-tumor, anti-bacterial, anti-fungal and anticarcinogenic properties[2-5].

Heterocyclic schiff base metal complexes are important group of organic compounds which find potential drugs, due to the presence of multifunctional groups[6-9]. A biologically active thiazole analogue continues to be an area of intensive investigation in medicinal chemistry. It is proved useful for the design of future target and development of new drug molecule. Thiazoles like compounds and their derivatives are organic species which shows very good antibacterial and antifungal activities. They are biologically significant compounds which have the anticancer, antiviral and antidiabetic drugs [10-12].

Microwave assisted synthesis is a branch of green chemistry. Microwave reactions under solvent free conditions are attractive offering reduced pollution, low cost and higher yields following simplicity in processing and handling [13]. The salient features of microwave approach are shorter reaction times, simple reaction conditions and enhancement in yield. The usage of microwave oven for the synthesis of organic compounds has proved to be an efficient, safe and eco friendly method [14].

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Avinash Shinde et al synthesized schiff bases using Propane-1, 3-diamine with different halogen substituted benzaldehyde under microwave irradiation. The synthesized schiff bases are characterized by spectroscopic studies [15]. Rajendra Jain et al synthesized some new schiff base metal complexes of Cr (III), Co (II), Ni (II) and Cu (II) derived from heterocyclic schiff base ligands. The antimicrobial activities of the synthesized metal complexes are screened and reported [16]. The schiff base ligand using p-chlorobenzaldehyde with p-chloroaniline followed by reduction is synthesized which is used for preparation schiff base complexes by Pattanaik et al. The structures of these complexes are characterized by UV-Visible, FT- IR and H^1 NMR spectra [17].

In the present work, thiazole derived schiff base and Cu (II), Co (II), Ni (II) and Zn (II) and Cd (II) metal complexes are synthesized. The synthesized heterocyclic ligand and their metal complexes are characterized by different spectral techniques. The biological activities of the schiff base and its complexes are investigated.

II. EXPERIMENTAL

2.1 Materials and Methods

The chemicals and reagents are purchased commercially. The purification process done when there is necessity. The melting points of the synthesized compounds are recorded using melting point apparatus. Molar conductances of the complexes are measured at room temperature using a **Systronic Conductivity Bridge (OSWAL)**. FT-IR spectra are recorded using in **Shimadzu FT-IR-8400 spectrophotometer**. Electronic spectra are recorded in DMF using **Shimadzu UV-Visible spectrophotometer**. NMR spectrum of schiff base ligand is recorded in deuterated dimethylsulfoxide using a **Varian XL 200 NMR spectrometer**. Biological activities of the complexes are tested against different strains of bacteria and fungi by **Kirby-Bauer Method.**

2.2 Microwave Synthesis of Thiazolyl ligand

The preparation of thiazolyl ligand involves condensation of benzaldehyde and 2-amino thiazole in the ratio of 1:1 in an ethanolic medium. Two drops of acetic acid is added to keep acidic condition. The mixture of benzaldehyde (0.03 moles) and 2-amino thiazole (0.03 moles) in 5 ml of ethanol is subjected to microwave irradiation for 120 seconds. The mixture is cooled at room temperature. The yellow precipitate is collected and dried. The product obtained is recrystallized from ethanol.

Scheme 1. Microwave Synthesis of Thiazolyl ligand

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2.3 Microwave Synthesis of Metal – Thiazolyl complexes

An ethanolic solution of thiazolyl ligand is added to a solution of metal chloride or acetate salts in 2:1 ratio. The reaction mixture is irradiated by keeping in a microwave oven. The reaction is completed in a short time ranging from 2-6 minutes. The resulting precipitate is collected and dried. The crude sample is purified by recrystallization from ethanol. The same procedure is followed for synthesis of complexes **I-V**. **Fig.2.1** depicts the general form of structure of the complexes.

M = Cu, Co, Ni, Zn, Cd

Fig. 2.1. Structure of Metal – Thiazolyl Complexes

The reaction time taken for the completion of ligand and metal complexes are tabulated in **Table 2.1**

Table 2.1 Time taken for completion of reaction

Name	Complex	Reaction Time (sec)
Thiazolyl ligand	-	120
Copper Thiazolyl Complex	I	160
Cobalt Thiazolyl Complex	II	210
Nickel Thiazolyl Complex	III	250
Zinc Thiazolyl Complex	IV	360
Cadmium Thiazolyl Complex	V	250

III. RESULTS AND DISCUSSION

The spectral data analysis of the results are described below.

3.1 Physical properties

The synthesized thiazolyl schiff base and their metal complexes I-V are coloured complexes. A specific melting point is obtained for each complex. The molar conductance values of the synthesized complexes I-V ranges from 2.0 to 2.8 Ohm^{-1}, which indicate that complexes are non- electrolytes in nature.

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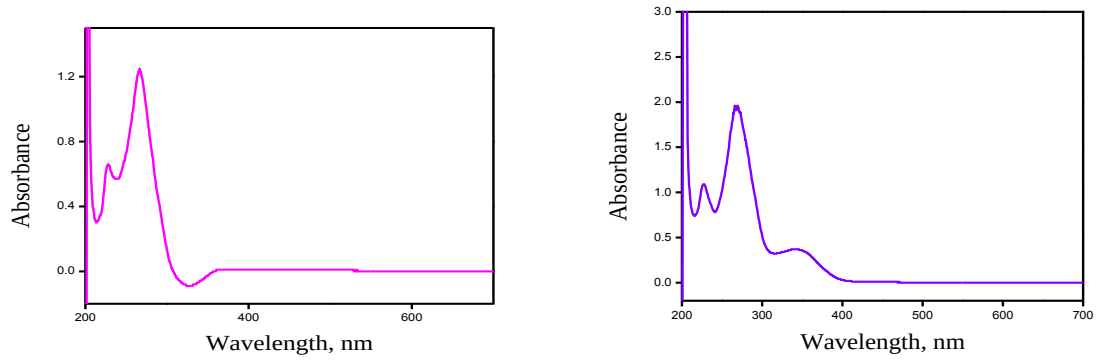
3.2 Characterization Techniques

3.2.1. Characterization by UV-Visible analysis

The synthesized thiazolyl ligand and their complexes are analyzed using UV-Visible spectrophotometer in DMF medium. The spectral values obtained are used to calculate the molar extinction coefficients. The values are useful to predict their transitions. The possible transitions are given tabulated in **Table 3.1**. The sample picture of electronic spectra of ligand and copper thiazolyl complex are shown in **Fig. 3.1 (a, b).**



a **b**

Fig.3.1. UV- Visible spectra of a) Thiazolyl ligand b) Complex I

Table 3.1 UV- Visible spectral transitions of ligand and the complexes I-V

Ligand / Complexes	Molar extinction coefficient	Transitions
Thiazolyl Ligand	29940	ILCT
Complex I	17452	$^3T_1$ (F)→$^3T_{1g}$(P)
Complex II	39063	ILCT
Complex III	19685	$^3A_{2g}$(F)→$^3T_{1g}$(F)
Complex IV	15174	$^3A_{2g}$(F)→$^3T_{1g}$(F)
Complex V	29940	ILCT

3.2.2. FT- IR spectra

The FT-IR spectra of the ligand and their complexes I-V are represented in **Table 3.2.** In the IR spectrum of the thiazolyl ligand, the band appeared at 1646 cm^{-1} is assigned to the formation of azomethine group. The stretching frequency of the azomethine group corresponds to the complexes I-V appears in the range 1618 to 1610 cm^{-1}. The decrease in stretching frequency of complexes than the ligand indicates the coordination of ligand to the metal site. The bands in the region 621 to 702 cm^{-1} are due to M-N stretching frequencies which show the coordination through N atom to the metal. The sample figures of FT-IR spectra of thiazolyl ligand and nickel complex are shown in **Fig.3.2. (a, b).**

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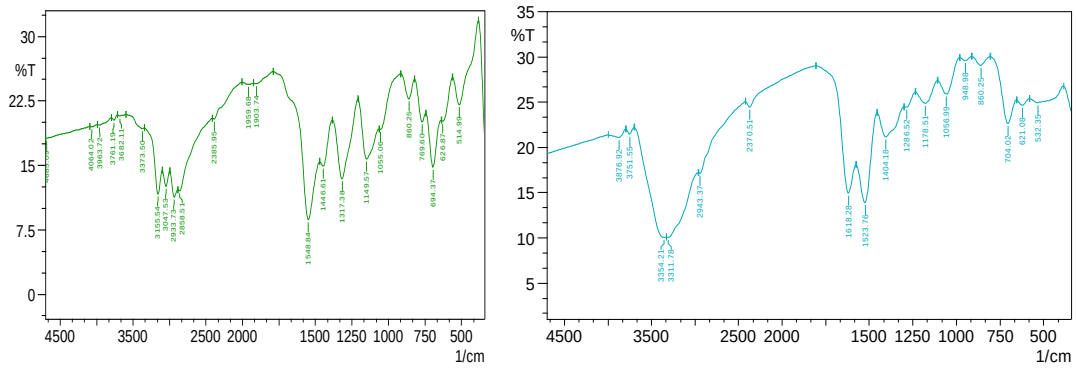
Table 3.2. FT-IR stretching frequencies of the ligand and complexes (I-V)

Ligand / Complexes	-CH=N (cm^{-1})	M-N (cm^{-1})
Thiazolyl Ligand	1646	-
Complex I	1618	621
Complex II	1610	702
Complex III	1612	621
Complex IV	1615	630
Complex V	1617	625



a **b**

Fig. 3.2. FT-IR spectra of a) Thiazolyl ligand b) Complex III

3.2.3. ^{1}H NMR spectra

The ^{1}H NMR spectrum of the thiazolyl ligand is recorded in DMSO. The data obtained is analyzed for their proton environment. The azomethine protons exhibit a singlet at δ7.1. The aromatic protons are observed as a multiplet in the range δ 6.8-7. ^{1}H NMR spectrum of the ligand is shown in **Fig. 3.3**.

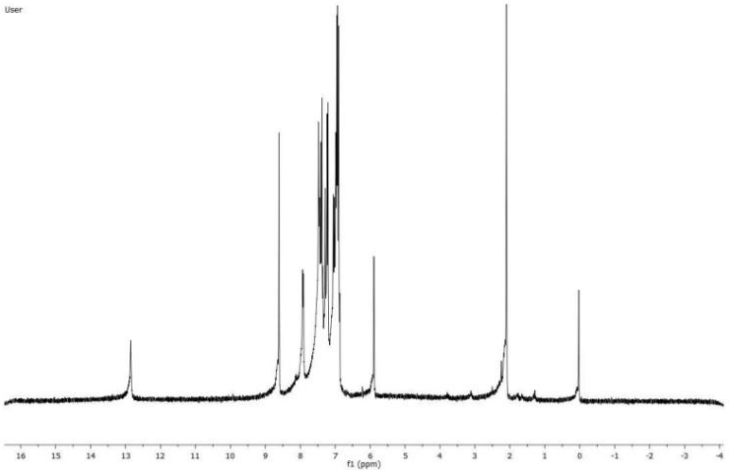


Fig.3.3. ^{1}H NMR spectrum of thiazolyl ligand

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3.2.4. Antimicrobial Activity

The antimicrobial activities of the investigated complexes are tested against the following strains of bacteria such as Escherichia Coli and Staphylococcus Aureus. The fungi, Candida Albicans and Aspergillus Flaves inhibition growth also screened. The inhibition zones are illustrated in **fig. 3.4.** The growth of inhibition zones after incubation is summarized in **Table 3.3.**

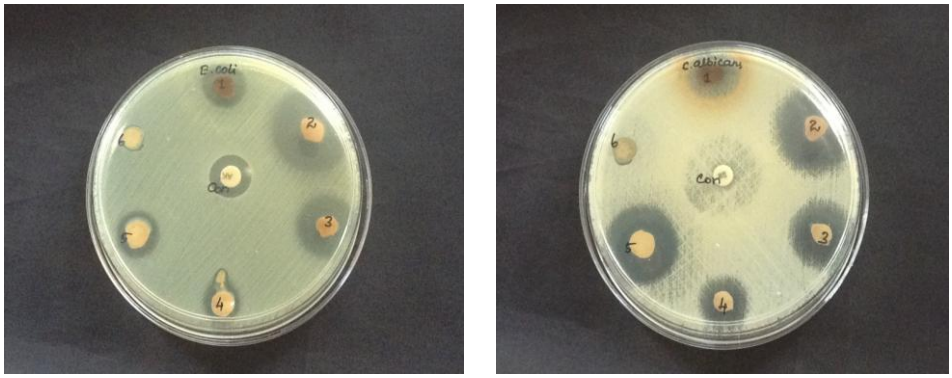

Fig. 3.4. Inhibition zones of E.Coli and C.Albicans

Table 3.3. Antimicrobial inhibition zone for the ligand and the complexes

Ligand / Complexes	Bacterial Inhibition in mm		Fungal Inhibition in mm	
	E. Coli	S.Aureus	C.Albicans	A.Flaves
Thiazolyl Ligand	8	8	9	9
Complex I	11	13	16	12
Complex II	14	17	18	13
Complex III	18	22	19	R
Complex IV	25	20	26	R
Complex V	14	12	23	11
Amikacin (Standard) bacteria	14	18	-	-
Flucanazole (Standard) fungi	-	-	24	16

Some complexes show moderate activity compared to the corresponding standard bacteria or standard fungi. The results of the screening indicate that cobalt and cadmium complexes show antibacterial activities towards E.Coli and S.Aureus. Cadmium complex exhibit antifungal activity against C.Albicans.

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IV. CONCLUSION

In this paper, a simple and convenient route is adopted for the synthesis of thiazolyl ligand and its complexes. The microwave assisted method is a green synthetic method for synthesis of ligands and complexes. The reaction time is very much reduced compared with the conventional method. The synthesized complexes are characterized using UV-Visible, FT-IR and H^1 NMR spectral techniques. The antimicrobial screening results suggest that the cobalt and cadmium complexes show moderate antibacterial activities towards E.Coli and S. Aureus. Cadmium complex is more active towards fungal C.Albicans.

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