

## Synthesis, Spectral and Antimicrobial Investigation of some Ternary Schiff Base Transition Metal Complexes

Badma Priya D<sup>1\*</sup>, Santha Lakshmi S<sup>2</sup>

<sup>1</sup>School of Advanced Sciences, VIT University, Vellore – 632014, Tamil Nadu, India.

<sup>2</sup>PG & Research Department of Chemistry, D. K.M. College for Women (Autonomous), Vellore – 632 001, Tamil Nadu, India.

\*Corres.author: <sup>1</sup>badmapriyad@gmail.com, <sup>2</sup>santhalakshmi\_s@yahoo.com

**Abstract:** In the present work a new ternary Schiff base transition metal complexes of general formula  $[ML^1L^2]$  were prepared by template synthesis. Where,  $L^1$  is a Schiff base ligand derived from L- tryptophan and 2' – hydroxyacetophenone,  $L^2$  is 2, 6- diaminopyridine and M is a transition metal ions (Cu(II), Ni(II), Co(II), Cd(II) and Zn(II) ). The ternary Schiff base transition metal complexes were characterized using spectroscopic techniques. The metal complexes were screened for antibacterial activity against *Salmonella enterica*, *Klebsiella pneumonia* and *E.coli* and antifungal activity against *Aspergillus flavus*, *Rhizopus nigricans*, and *Pencillium notatum*. The results revealed that the synthesized compounds were more potent against all the microbes under investigation.

**Keywords:** Schiff base transition metal complexes, spectroscopic techniques, antibacterial and antifungal activities.

### 1. INTRODUCTION

Schiff bases are one of the most prevalent and important of the mixed donor systems in the field of coordination chemistry. The first preparation of imines was reported in the 19<sup>th</sup> century by Schiff (1984), which are prepared by condensing primary amines with an aldehyde or a ketone under specific conditions[1]. Because of the relative easiness of preparation, synthetic flexibility and special property of C=N group, Schiff bases are considered as an excellent chelating agents. Schiff bases and its metal complexes have been found to exhibit biological activities including antifungal, antibacterial, antimalarial, antipyretic, larvicidal, antiviral and antitubercular activities [2-7]. Besides the biological activities, the metal complexes of Schiff bases are widely used as catalyst in the reactions like carbonylation, hydroformylation, reduction, oxidation, epoxidation and hydrolysis, corrosion inhibitor and as polymers [8-11].

Herein, we report the transition metal complexes of Schiff base derived from the condensation of 2'-hydroxyacetophenone and L-tryptophan. The ternary complexes were obtained by reaction with 2, 6-diaminopyridine. The structural features of these complexes were examined by analytical and spectral techniques. The *in vitro* antimicrobial behaviour of the complexes was studied by well diffusion method.

## 2. EXPERIMENTAL

### 2.1 Materials and Physical Measurement

All the chemicals used were of analytical grade. The molar conductivity of the complexes ( $10^{-3}$  M) was measured for the freshly prepared solution of the complexes in DMSO using DCM 900. The Ultraviolet-Visible spectra were recorded on a Systronics 2201 spectrophotometer using DMSO as solvent in the wavelength range of 200–800 nm. The IR spectra of the synthesized complexes were recorded using Shimadzu spectrometer in the range of 4000 – 500  $\text{cm}^{-1}$  using KBr pellet. The magnetic moments of the complexes were recorded for the solid samples using Lakshore VSM 7410 at room temperature.

### 2.2 Antimicrobial Studies

#### 2.2.1 Test Micro-organisms

The bacterial species *Escherichia coli*, *Klebsiella pneumonia* and *Salmonella enteric* and fungal species *Aspergillus flavus*, *Rhizopus nigricans* and *Penicillium notatum* were used as test organisms. The bacteria were sub cultured on nutrient agar whereas fungi on Sabourauds dextrose agar [12].

#### 2.2.2 Antibacterial activity

The antibacterial activities of ternary Schiff base complexes were evaluated by the agar well diffusion method. Mueller Hinton agar medium (20 mL) was poured into each Petri plate and plates were swabbed with 100  $\mu\text{L}$  inocula of the test microorganism and kept for 15 min for adsorption. Using sterile metallic borer of 8 mm diameter, wells were bored into the seeded agar plates and these were loaded with a 100  $\mu\text{L}$  solution of each complexes in dimethylsulphoxide (DMSO) with concentration of 4.0 mg/mL. All the plates were incubated at 37°C for 24 h. Antibacterial activity of each synthesized complexes was evaluated by measuring the zone of growth inhibition against the test organisms and ampicillin was used as positive control.

#### 2.2.3 Antifungal activity

The antifungal activities of ternary Schiff base complexes were also evaluated by the agar well diffusion method. Sabouraud dextrose agar was prepared, sterilized and prepared the culture plates same like Muller Hilton Agar. After solidification of media, respective fungal spore suspensions were transferred to petri plates. Using sterile metallic borer of 8 mm diameter, wells were bored into the seeded agar plates and these were loaded with a 100  $\mu\text{L}$  solution of each complexes in dimethylsulphoxide (DMSO) with concentration of 4.0 mg/mL. All the plates were incubated for 72 h. Antifungal activity of each synthesized complexes was evaluated by measuring the zone of growth inhibition against the test organisms and polymyxin B sulphate was used as positive control.

### 2.3 Synthesis of Schiff base transition metal complexes

The complexes of Cu (II), Ni (II), Co (II), Cd (II) and Zn (II) were prepared by the following procedure: An ethanolic solution (25 mL) of 2'-hydroxyacetophenone (3 mmol) was added to an aqueous solution of L-tryptophan (3mmol) and potassium hydroxide (2 mmol). The reaction mixture was stirred at 60°C for two hours. The solution turned yellow colour. Then the appropriate metal salt (3 mmol) (where M=  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ) was added and stirred for one hour. Then 2,6- diaminopyridine (6 mmol) was added and stirred for another additional two hours. The resultant solid product was filtered, washed with ethanol and dried.

### 3. RESULTS AND DISCUSSION

All synthesized ternary Schiff complexes are non hygroscopic solid, stable in air, insoluble in water and they are soluble in DMSO and DMF and partially soluble in ethanol.

#### 3.1 Molar conductance

The magnetic moments and molar conductivity data are summarized in Table 1. The molar conductance values are in the range of 30- 35  $\text{ohm}^{-1}\text{cm}^{-2}\text{mol}^{-1}$  indicating the non electrolytic nature of the complexes [13, 14]. The  $\mu_{\text{eff}}$  values lie within the range normally found for all of the metal complexes. The results indicate that  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  complexes are diamagnetic whereas  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  complexes are paramagnetic in nature. The results are also in good agreement with the theoretical value.

**Table: 1 Some physical and analytical data of synthesized transition metal complexes**

Compound/ Molecular Formula	Molecular weight	Color	Melting point	Molar conductance ( $\text{Ohm}^{-1}\text{cm}^{-2}\text{mol}^{-1}$ )	$\mu_{\text{eff}}$ BM
$[\text{CuL}^1\text{L}^2]$ $\text{CuC}_{24}\text{H}_{23}\text{N}_5\text{O}_3$	493.017	Dark green	234° C	35	1.2
$[\text{NiL}^1\text{L}^2]$ $\text{NiC}_{24}\text{H}_{23}\text{N}_5\text{O}_3$	488.161	Dark brown	> 320° C	35	2.86
$[\text{CoL}^1\text{L}^2]$ $\text{CoC}_{24}\text{H}_{23}\text{N}_5\text{O}_3$	488.404	Dark brown	> 320° C	38	3.24
$[\text{CdL}^1\text{L}^2]$ $\text{CdC}_{24}\text{H}_{23}\text{N}_5\text{O}_3$	541.881	Dark brown	> 320° C	40	-
$[\text{ZnL}^1\text{L}^2]$ $\text{ZnC}_{24}\text{H}_{23}\text{N}_5\text{O}_3$	494.851	Dark brown	> 320° C	37	-

#### 3.2 Electronic spectra

The electronic spectral data of the complexes are given in table 2. The electronic absorption spectral data shows the d-d transitions of the transition metal complexes in the range of 600-700 nm for copper, nickel and cobalt complexes. No d-d transition were observed for cadmium, and zinc complexes [15]. The absorption band observed in the range of 300 nm are due to  $n \rightarrow \pi^*$  transition of imine moiety and in the range of 200 nm are due to  $\pi - \pi^*$  transition. Based on the data a square planar geometry was suggested for all the complexes [16, 17].

**Table 2: The electronic absorption spectra of Schiff base transition metal complexes**

Compound	Absorption( $\lambda_{\text{max}}$ nm)		
	$n-\pi^*$ (azomethine)	$\pi-\pi^*$ (benzene)	d- d
$[\text{CuL}^1\text{L}^2]$	351	214	614
$[\text{NiL}^1\text{L}^2]$	385	250	672
$[\text{CoL}^1\text{L}^2]$	412	322	617
$[\text{CdL}^1\text{L}^2]$	362	286	-
$[\text{ZnL}^1\text{L}^2]$	423	297	-

### 3.3 IR spectra

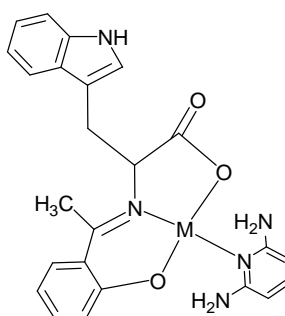
The characteristic IR bands of the complexes (Fig. 4- 8) are given in Table 3. The IR absorption bands appeared in the range of  $3300\text{ cm}^{-1}$ , may be due to the presence of coordinated/ lattice water molecule for all synthesized complexes. The weak bands appeared in the range of  $3200\text{ cm}^{-1}$  are due to the free  $\text{NH}_2$  group of 2, 6- diaminopyridine present in complexes [18]. The strong bands around  $1618\text{ cm}^{-1}$  are related to the  $\nu(\text{C}=\text{N})$  of the Schiff base moiety owing to the imino group [19-21] of the complexes. The  $\nu_{\text{as}}(\text{COO}^-)$  of carboxylate group of the transition metal complexes were observed in the range of  $1416\text{ cm}^{-1}$ . Whereas the  $\nu_{\text{s}}(\text{COO}^-)$  is attributed around  $1353\text{ cm}^{-1}$  bands is due to coordinated to the metals complexes to form as ternary complexes. The separation ( $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$ ) between  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  bands of these complexes are consistent with a monodentate coordination of the carboxylate group [20, 22] of L- tryptophan.

**Table 3: Characteristic IR absorption frequencies in ( $\text{cm}^{-1}$ ) of the Schiff base transition metal complexes**

Compound	$\nu$ (coordinated $\text{H}_2\text{O}/$ lattice)	$\text{NH}_2$	$\nu(\text{C}=\text{N})$ azomethine	carboxylate group		$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
				$\nu_{\text{as}}$ ( $\text{COO}^-$ )	$\nu_{\text{s}}$ ( $\text{COO}^-$ )		
$[\text{Cu L}^1\text{L}^2]$	3390 (b)	3274 (w)	1624	1575	1353	690	583
$[\text{Ni L}^1\text{L}^2]$	3325 (b)	3200 (w)	1614	1413	1350	663	619
$[\text{Co L}^1\text{L}^2]$	3312 (b)	3175 (w)	1618	1434	1374	668	585
$[\text{Cd L}^1\text{L}^2]$	3326 (b)	3198 (w)	1613	1416	1250	647	600
$[\text{Zn L}^1\text{L}^2]$	3328 (b)	3403 (w)	1618	1409	1352	650	599

The strong bands of  $\nu(\text{C}-\text{H})$  out of plane bending obtained in the range of  $743\text{ cm}^{-1}$  are due to pyridyl ring of 2, 6- diaminopyridine present in the complexes [23]. The bands  $\nu(\text{M}-\text{N})$  observed around  $650\text{ cm}^{-1}$  for all synthesized metal complexes indicated the formation of metal nitrogen linkage [24]. Also the bands  $\nu(\text{M}-\text{O})$  observed around  $583\text{ cm}^{-1}$  for complexes indicated the formation of metal to oxygen linkage [24, 25].

Based on the spectral data the proposed structure of the Schiff base transition metal complexes is given below (Fig. 1).



**Fig: 1 The proposed structure of ternary Schiff base metal complexes**

(Where, M = Cu (II), Ni (II), Co (II), Cd (II) and Zn (II))

### 3.4 Antimicrobial studies

The results of the antimicrobial studies (Fig. 2-3) are given in table 4 and 5.  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  complexes shows good antibacterial activity against *Salmonella enteric* with the zone of inhibition values were 25 mm, 28 mm, and 26 mm respectively.  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  complexes shows moderate antibacterial activity against *Salmonella enterica* were observed with 22 mm and 21 mm respectively.

**Table 4: Antibacterial activity data for the Schiff base transition metal complexes**

S.No	Organism (bacteria)	Zone of inhibition (mm)					Ampicillin Standard
		[Cu L <sup>1</sup> L <sup>2</sup> ]	[Ni L <sup>1</sup> L <sup>2</sup> ]	[Co L <sup>1</sup> L <sup>2</sup> ]	[Cd L <sup>1</sup> L <sup>2</sup> ]	[Zn L <sup>1</sup> L <sup>2</sup> ]	
1	<i>Salmonella enterica</i>	25	28	26	22	21	39
2	<i>Klebsiella pneumonia</i>	31	24	25	23	20	43
3	<i>E.coli</i>	11	-	10	-	-	16

$\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  complexes showed very good antibacterial activity against *Klebsiella pneumonia* with the zone of inhibition values were 31 mm, 24 mm, and 25 mm respectively.  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  complexes shows moderate antibacterial activity against *Klebsiella pneumonia* having 23 mm and 20 mm zone of inhibition respectively.  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  complexes showed good antibacterial activity against *E.coli* with the zone of inhibition values were 11 mm, and 10 mm respectively. Among the synthesized complexes  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  metal shows good antibacterial activity against, *Klebsiella pneumonia* and *Salmonella enteric* when compared with standard drug ampicillin.

**Table 5: Antifungal activity data for the Schiff base- transition metal complexes**

S. no	Organism (fungi)	Zone of inhibition (mm)					Polymyxin B sulphate
		[Cu L <sup>1</sup> L <sup>2</sup> ]	[Ni L <sup>1</sup> L <sup>2</sup> ]	[Co L <sup>1</sup> L <sup>2</sup> ]	[Cd L <sup>1</sup> L <sup>2</sup> ]	[Zn L <sup>1</sup> L <sup>2</sup> ]	
1	<i>Aspergillus flavus</i>	12	10	15	15	11	11
2	<i>Rhizopus nigricans</i>	12	16	10	14	11	11
3	<i>Penicillium Notatum</i>	-	-	-	-	-	11

$\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  complexes shows very good antifungal activity against *Aspergillus flavus* having the zone of inhibition values are 15 mm, 15 mm and 12 mm respectively whereas  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  complexes shows moderate antifungal activity against *Aspergillus flavus* having 10 mm and 11 mm zone of inhibition respectively.  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  complexes shows very good antifungal activity against *Rhizopus nigricans* with the zone of inhibition values are 12 mm, 16 mm and 14 mm respectively whereas  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  complexes shows moderate antifungal activity against *Rhizopus nigricans* having 10 mm and 11 mm zone of inhibition respectively. All the synthesized metal complexes did not shows antifungal activity against *Penicillium notatum* because of its resistance. Among the synthesized metal complexes  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$  shows very good antifungal activity against *Aspergillus flavus* when compared with antifungal drug polymyxin B sulphate.

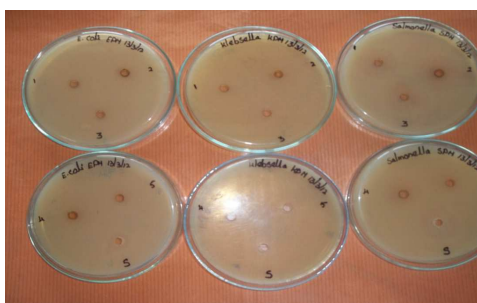


Fig: 2 Antibacterial studies of Schiff base transition metal complexes against tested bacteria



Fig: 3 Antifungal studies of Schiff base transition metal complexes against tested fungi  
 [1- [Cu L<sup>1</sup>L<sup>2</sup>]; [Ni L<sup>1</sup>L<sup>2</sup>]; 3- [Co L<sup>1</sup>L<sup>2</sup>]; 4- [Cd L<sup>1</sup>L<sup>2</sup>]; 5- [Zn L<sup>1</sup>L<sup>2</sup>];  
 S- Ampicillin, polymyxin B sulphate (standard)]

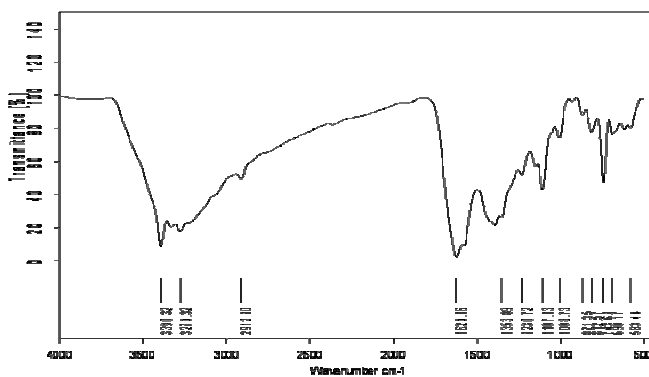


Fig. 4 FTIR spectra of [Cu L<sup>1</sup>L<sup>2</sup>]

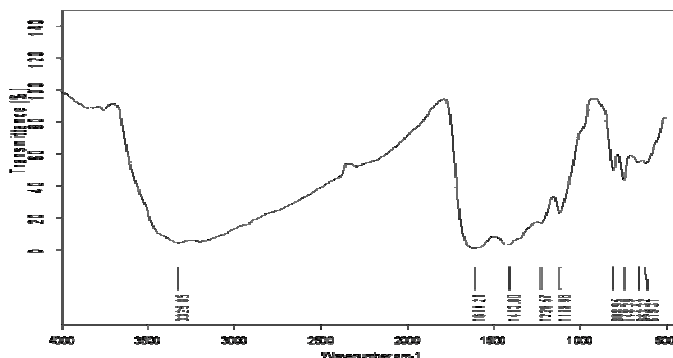
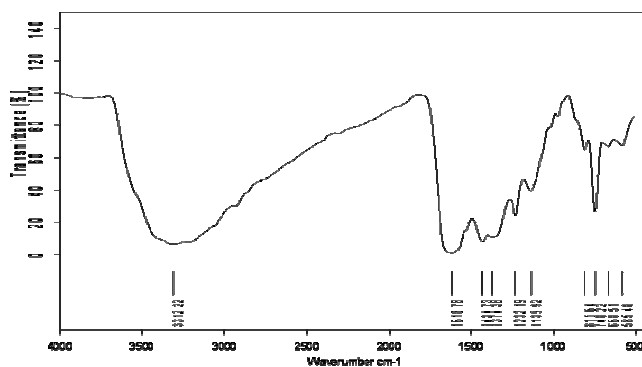
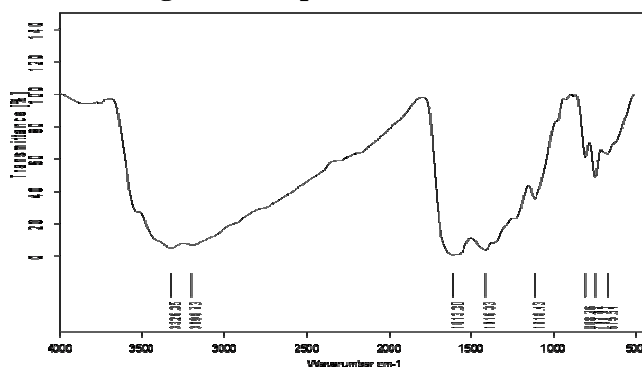
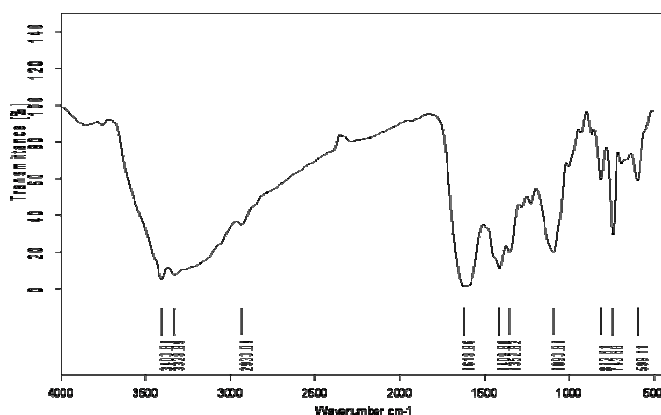


Fig. 5 FTIR spectra of [Ni L<sup>1</sup>L<sup>2</sup>]

Fig. 6 FTIR spectra of [Co L<sup>1</sup>L<sup>2</sup>]Fig.7 FTIR spectra of [Ni L<sup>1</sup>L<sup>2</sup>]Fig. 8 FTIR spectra of [Zn L<sup>1</sup>L<sup>2</sup>]

#### 4. CONCLUSION

In conclusion, the synthesis and spectroscopic investigation of ternary Schiff base transition metal complexes have been reported herein. The spectral data concluded the tridentate nature of the Schiff base ligand and the complexes are four coordinated and the complexes were found to be non-electrolyte. The *in vitro* investigation of the synthesized complex revealed that all the complexes showed very good results against the selected micro organisms under investigation except *Penicillium notatum*.

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