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## SYNTHESIS, CHARACTERIZATION AND ANTIMICROBAL STUDIES OF Ni (II) COMPLEXES OF BIDENTATE SCHIFF BASE



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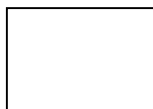
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### Abstract

The transition metal complex of Ni (II) was prepared from bidentate Schiff base. The Schiff base ligand synthesized from the condensation of P-methylbenzaldehyde and 2-amino -4,6 dihydroxypyrimidine (L<sub>4</sub>) in alcohol medium. These metal complexes were characterized on the basis of their micro analytical data, molar conductance, magnetic susceptibility, IR, UV-Vis, <sup>1</sup>H NMR, X-ray diffraction, therogravimetric analysis. The ligand and their metal complexes were screened for fungicidal activity against various fungi like *Aspergillus niger*, *Penicillium chrysogenum*, *Fusarium moneliforme* and *Aspergillus flavus*. and antibacterial activity against various bacteria like *Escherichia coli*, *Salmonellatyphi*, *Staphylococcus aurious*, *B.subtilis*. The result indicated that the complexes exhibited good antifungal and antibacterial activities.

**Keywords:** Schiff bases, Transition metal complexes, Thermal analysis, Powder X-ray diffraction, Antimicrobial activity.

**Subject Classification:** Subject Classification 2018

## INTRODUCTION

Schiff bases are quite valuable chemicals that have the usage properties in the area of medicine, chemistry, pharmaceutical chemistry and industry. Especially in recent years, active research fields have included their use in anticancer,[1] antibacterial,[2-3] antifungal,[4]anti- . [8]. According to many reports that after complexation with transition metal ions have shown that an increase in microbial activity. [9]. Metal complexes derived from Schiff base ligands of pyrimidine have been mostly researched in these days on account of their lot of biological activities, which have usually been related to their chelating ability with trace metal ions. [10]

A search of literature reveals that no work has been done on the transition metal complexes of the Schiff bases derived from 2-amino -4,6 dihydroxypyrimidine and P-methylbenzaldehyde. In this communication we report the synthesis of bidentate Schiff bases formed by the condensation of 2-amino -4,6 dihydroxypyrimidine and P-methylbenzaldehyde (Fig.3). The solid complexes of Ni (II) with these ligands

have been prepared and characterized by different physico-chemical methods.

## MATERIALS AND METHODS

### Reagents and solvents

2-amino-4,6 dihydroxypyrimidine(Aldrich sigma), P-methylbenzaldehyde, metal nitrate of AR grade was used for synthesis of ligand and metal complex .

### Synthesis of ligand

The ligand was prepared by a modification of the reported methods [11-13]. The Schiff base ligand has been synthesized by refluxing a mixture of 0.01 mol (1.2015g) of P-methylbenzaldehyde and 0.01 mol (1.2710g) of 2-amino-4, 6-dihydroxypyrimidine in 50 ml super dry ethanol refluxed for about 4h. Schiff base thus formed was cooled to room temperature and collected by filtration, followed by recrystallization in ethanol and dried *in vacuo* over anhydrous calcium chloride (Yield:70%).

### Synthesis of metal complexes

To a hot ethanol solution (25ml) of the ligand (2 mol) and (25ml) of metal Nitrate (1mol) was added with constant stirring. The pH of reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 3 h. The



precipitated solid metal complex was filtered off in hot condition and washed with hot ethanol and dried over calcium chloride in vacuum desiccators. (Yield: 65%)

### Physical Measurement

IR spectra were recorded on FTIR(ATR)-BRUKER -TENSOR37 spectrometer using KBr pellets in the range of 4000-400  $\text{cm}^{-1}$ .  $^1\text{H}$ - NMR Varian mercury 300MHZ spectra of ligand were measured in  $\text{CDCl}_3$  using TMS as internal standard. X-RD was recorded on BRUKER D8 Advance. TGA-DTA was recorded on Shimadzu. The carbon, hydrogen and nitrogen contents were determined on Elementar model vario EL-III. The UV-visible spectra of the complexes were recorded on model UV-1800, SHIMADZU spectrometer. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using  $10^{-4}$  M solution in DMSO. Magnetic susceptibility measurements of the metal chelates were done on a Guoy balance at room temperature using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as a calibrant.

## RESULTS AND DISCUSSION

Schiff bases of 2-amino- 4,6 dihydroxypyrimidine and its complexes have a variety of applications including

biological, clinical and analytical. The coordinating possibility of 2-amino- 4,6 dihydroxypyrimidine has been improved by condensing with a variety of carbonyl compounds. An attempt has been made to synthesize Schiff bases from 2-amino- 4,6 dihydroxypyrimidine with P-methylbenzaldehyde. Physical characteristics, micro analytical, and molar conductance data of ligand and metal complexes are given in (Table 1 and 2).The analytical data of complexes reveals 2:1 molar ratio (ligand: metal) and corresponds well with the general formula  $[\text{ML}(\text{H}_2\text{O})_2]$  (where  $\text{M} = \text{Ni}(\text{II})$ ). The magnetic susceptibilities of  $\text{Ni}(\text{II})$  complexes at room temperature are consistent with high spin octahedral structure with two water molecules coordinated to metal ion. The presence of two coordinated water molecules was confirmed by TG-DTA analysis. The metal chelate solutions in DMSO show low conductance and supports their non-electrolyte nature.(Table 1)

### $^1\text{H}$ -NMR spectra of ligand

The  $^1\text{H}$ -NMR. spectra of free ligand at room temperature shows the following signals. 2.36  $\delta$  (s, 3H, Methyl hydrogen bonded to phenyl ring), 4.47  $\delta$  (s, 2H,



Phenolic (OH) hydrogen of pyrimidine ring), 5.90  $\delta$ (s, 1H, Hydrogen bonded to pyrimidine ring ), 7.83  $\delta$  (s, 1H, hydrogen bonded to azomethine carbon), 7.09-7.42  $\delta$  (D,4H, Aromatic Ha, Hb, protons of phenyl ring).

### IR Spectra

The IR spectra of the complexes are compared with that of the ligand to determine the changes that might have taken place during the complexation. The bands at 3331, 1660, 1514, 1300, and 1211  $\text{cm}^{-1}$  assignable to  $\nu$  OH (intramolecular hydrogen bonded),  $\nu$  C=C(aromatic),  $\nu$  C=N (azomethine),  $\nu$  C-N (aryl azomethine) and  $\nu$  C-O (phenolic) stretching modes respectively[12-14] The absence of a weak broad band in the 3200-3400  $\text{cm}^{-1}$  region, in the spectra of the metal complexes suggests deprotonation of the intramolecular hydrogen bonded OH group on complexation and subsequent coordination of phenolic oxygen to the metal ion. This is further supported by downward shift in  $\nu$  C-O (phenolic) [15]with respect to free ligand. On complexation, the  $\nu$  (C=N)[16]band is shifted to lower wave number with respect to free ligand, denoting that the nitrogen of

azomethine group is coordinated to the metal ion. The  $\nu$  C-N band is shifted to lower wave number with respect to free ligand, The IR spectra of metal chelates showed new bands in between the 500-800 and 400-500  $\text{cm}^{-1}$  regions which can be assigned to  $\nu$  M-O and M-N[17] vibrations respectively The IR spectra of Ni (II) show a strong band in the 3050-3600  $\text{cm}^{-1}$  region, suggesting the presence of coordinated water in these metal complexes. The presence of coordinated water is further confirmed by the appearance of non-ligand band in 830-840  $\text{cm}^{-1}$  region, assignable to the rocking mode of water The presence of coordinated water is also established and supported by TGA/DTA analysis of these complexes. Hence it is concluded that the coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule.

### Thermogravimetric analysis

The dynamic TGA with the percentage mass loss at different steps have been recorded. The simultaneous TGA/DTA analysis of Ni(II) was studied from ambient temperature to 1000  $^{\circ}\text{C}$  in nitrogen atmosphere using  $\alpha\text{-Al}_2\text{O}_3$  as reference. An analysis of the



thermogram of the complexes indicated that Ni(II) complexes shows two step decomposition. The first weight loss 6.31%, in between temp. 50-150°C could be correlated with the loss of two coordinated water (calculated 6.51 %). The anhydrous compound does not remain stable at higher temperature, it undergoes rapid decomposition in the range 150-775°C, with 78.16 % mass loss corresponds to decomposition of the complex (calcd. 79.98%) in second step. The decomposition is completed leading to the formation of stable residue of metal oxide NiO obs. 12.63 % (calcd. 13.50 %). kinetic and thermodynamic viz the energy of activation ( $E_a$ ), frequency factor ( $Z$ ), entropy change ( $-\Delta S$ ) and free energy change ( $\Delta G$ ) for the non-isothermal decomposition of complexes have been determined by employing Horowitz-Metzger method [18] values are given in Table 3. The Calculated values of the given activation energy of the complexes are relatively low, indicating the autocatalysis effect of metal ion on the thermal decomposition of the complex. The negative value of activation entropy indicates that the activated complexes

were more ordered than the reaction was slow. The more ordered nature may be due to the polarization of bonds in the activated state, which might occur through charge transfer transitions [19].

### **Magnetic measurements and electronic absorption spectra**

The electronic spectral studies of metal complexes of Ni (II) with Schiff bases were carried out in DMSO solution. The absorption spectrum of the Ni(II) complexes shows bands at 13812 $\text{cm}^{-1}$  and 24875 $\text{cm}^{-1}$  are assigned to  $^1A_{1g} \rightarrow ^1T_{2g}$  and charge transfer transitions. The absence of band below 10,000  $\text{cm}^{-1}$  and All Ni(II) complexes were diamagnetic in nature indicates octahedral geometry[20].

### **Molar Conductivity Measurements**

The metal(II) complexes were dissolved in DMSO and the molar conductivity of  $10^{-4}\text{M}$  of their solution at room temperature were measured. The lower conductance values of the complexes support their non-electrolytic nature of the compounds.

### **Powder x-ray diffraction**

The x-ray diffractogram of Ni (II) complexes of L<sub>4</sub> was scanned in the range 20-80° at wavelength 1.540 Å.(Fig.1). The



diffraction pattern and associated data depict the  $2\theta$  value for each peak, relative intensity and inter-planar spacing ( $d$ -values). The diffraction pattern of Ni(II) complex of  $L_4$  had fourteen reflections with maxima at  $2\theta = 6.64^\circ$  corresponding to  $d$  value  $6.68\text{\AA}$ . The x-ray diffraction pattern of these complexes with respect to major peaks of relative intensity greater than 10% has been indexed by using computer programmed [21]. The above indexing method also yields Miller indices (hkl), unit cell parameters and unit cell volume.. The unit cell of Ni(II) complex of  $L_4$  yielded values of lattice constants,  $a=6.8760\text{\AA}$ ,  $b=9.2456\text{\AA}$ ,  $c = 24.234\text{\AA}$  and unit cell volume  $V=1334.21763\text{\AA}^3$ . In concurrence with these cell parameters, the condition such as  $a \neq b \neq c$  and  $\alpha = \beta = 90^\circ \neq \gamma$  required for sample to be monoclinic. Hence it can be concluded Ni (II) complex of  $L_4$  has monoclinic crystal system. The experimental density values of the complexes were determined by using specific gravity method [22] and found to be  $1.1022\text{ gcm}^{-3}$  for Ni (II) complexes respectively. By using experimental density values, molecular weight of complexes, Avogadro's number and volume of the unit cell were calculated.

Number of molecules per unit cell were calculated by using equation  $\rho = nM/NV$  and was found Ni (II) complexes respectively. With these values, theoretical density were computed and found to be  $1.2444\text{ gcm}^{-3}$  for respective complexes. Comparison of experimental and theoretical density shows good agreement within the limits of experimental error [23].

### **Antibacterial activity**

Antifungal activity and Antibacterial activity of ligand and metal complexes were tested *in vitro* against fungal such as *Aspergillus niger*, *Penicillium chrysogenum*, *Fusarium moniliforme*, *Aspergillus flavus* and bacteria such as *E. Coli*, *B.Subtilis*, *S. Aurious* And *Bacillus subtilis* by paper disc plate method [24-27]. The compounds were tested at the concentrations 1% and 2% in DMSO and compared with known antibiotics *viz* *Griseofulvin* and *Penicilin*. (Table 4 and 5), it is found that the inhibition by metal chelates is higher than that of a ligand and results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes [28].

**Table 1. Physical characterization, analytical and molar conductance data of compounds**

Compound Molecular formula	Mol.Wt.	M.P. Decomp temp. °C	Colour	Molar Conduc. Mho Cm <sup>2</sup> mol <sup>-1</sup>
L <sub>4</sub>	229.24	165	Yellow	----
Ni L <sub>4</sub>	553.19	>300	Faint Yellow	26.65

**Table 2. Elemental Analysis of Co(II)Complex:-**

Compound	Found (Calculated)			
	C	H	N	M
L <sub>4</sub>	62.87 (62.87)	4.84 (4.84)	18.33 (18.33)	--
NiL <sub>4</sub>	52.10 (52.00)	4.73 (4.67)	15.19 (15.11)	10.60 (10.44)

**Table: 3 The kinetic and thermodynamic parameters for**

Complex	Step	Decomp. Temp. (°C)	n	E <sub>a</sub> (kJmole <sup>-1</sup> )	Z (S <sup>-1</sup> )	ΔS (JK <sup>-1</sup> mole <sup>-1</sup> )	ΔG (kJmole <sup>-1</sup> )	Correl - ation coefficient
Ni-L <sub>4</sub>	I	230	0.0	5.33	6.47 × 10 <sup>3</sup>	-176.34	15.99	0.988
	II	510	0.1	12.91	1.56 × 10 <sup>4</sup>	-172.66	29.17	0.969

**decomposition of metal complexes**

Test Compound	Antifungal growth							
	<i>Aspergillus niger</i>		<i>Penicillium chrysogenum</i>		<i>Fusarium moneliforme</i>		<i>Aspergillus flavus</i>	
	1%	2%	1%	2%	1%	2%	1%	2%
L <sub>4</sub>	-ve	-ve	-ve	-ve	-ve	-ve	RG	+ve
Ni- L <sub>4</sub>	-ve	RG	RG	-ve	-ve	RG	+ve	RG
<b>+ve control</b>	+ve	+ve	+ve	+ve	+ve	+ve	+ve	+ve
<b>-ve control (Griseofulvin)</b>	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve

**Table 4 Antifungal activity of ligands**

Ligand& Metal : +ve – Growth

(Antifungal Activity absent )

-ve - Growth

(Antifungal Activity present )

RG - Reduced Growth (More than

50% reduction in growth observed)



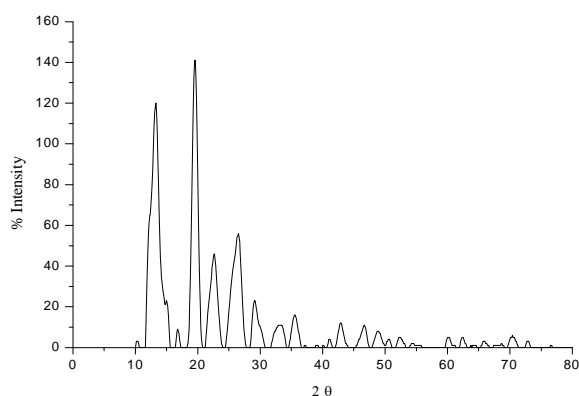
**Table 5 Antibacterial activity of ligands and their metal complexes**

Test Compound	Diameter of inhibition zone (mm)							
	<i>E. Coli</i>		<i>Salmonella typhi</i>		<i>Staphylococcus aureus</i>		<i>Bacillus subtilis</i>	
	1%	2%	1%	2%	1%	2%	1%	2%
L <sub>4</sub>	13mm	13mm	-ve	-ve	14mm	17mm	11mm	14mm
Ni- L <sub>4</sub>	10mm	13mm	-ve	12mm	-ve	17mm	-ve	11mm
DMSO	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve
Penicillin	14mm	14mm	17mm	17mm	30mm	30mm	19mm	19mm

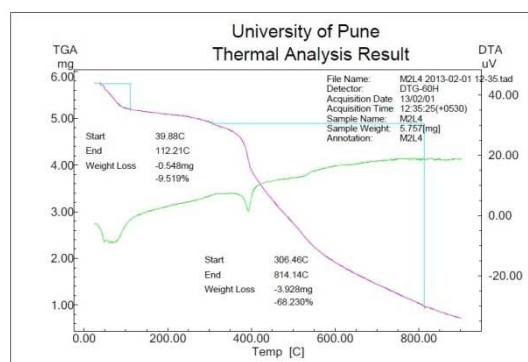
Ligand & Metal: - ve

- No Antibacterial Activity

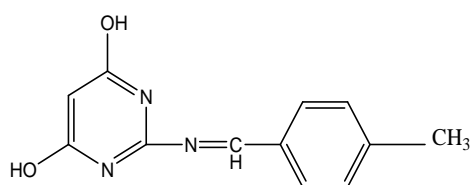
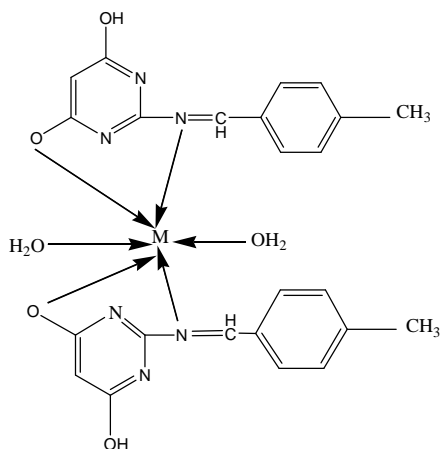
Zone of inhibition - --mm



**Fig 1 X-ray Diffractogram of Ni (II) complex of L<sub>4</sub>**



**Fig. 2 TGA-DTA Curve of Ni (II) Complex of Ligand L<sub>4</sub>**

**Figure 3. Structure of ligand****Figure 4. The proposed Structure of the complexes**

When M= Ni (II).

## CONCLUSION

In the light of above discussion we have proposed octahedral geometry for Ni (II) complexes. On the basis of the physico-chemical and spectral data discussed above, one can assume that the ligand behave as dibasic, NO bidentate, coordinating via phenolic oxygen and imino nitrogen as illustrated in Fig.4. The complexes are biologically active and show enhanced antimicrobial activities compared to free ligand. Thermal study reveals thermal stability of complexes. The X-ray study suggests monoclinic crystal system for Ni (II) complexes.



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