

## Synthesis, characterization of some transition metal complexes of bidentate Schiff base and their antifungal and antimicrobial studies

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### ABSTRACT

A new series of Cu(II), Ni(II), and Co(II) complexes with bidentate Schiff base ligand derived from 2-amino 4,6 dihydroxypyrimidine and P- chlorobenzaldehyde have been reported. The complexes have been characterized by elemental analysis, magnetic susceptibility measurements, conductrometry, electronic and infrared spectra, X-ray diffraction, <sup>1</sup>H-NMR spectra and thermogravimetric analysis. The ligand and its complexes were screened for their antifungal and antibacterial activity against *Aspergillus niger*, *Penicillium chrysogenum*, *Fusarium moniliforme* and *Aspergillus flavus* and *Escherichia coli*, *Salmonella typhi*, *Staphylococcus aureus*, *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.

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### INTRODUCTION

Coordination chemistry is undoubtedly the most active research area in inorganic chemistry. Several thousands of coordination complexes have been synthesized and investigated during the past few decades. Ever since the importance of coordination phenomenon in biological processes was realized, lot of metal containing macromolecules have been synthesized and studied to understand the role of these ligands in biological systems, and they also contribute to the development of new metal-based chemotherapeutic agents. These have resulted in the emergence of an important branch of inorganic chemistry viz. bioinorganic chemistry because in several cases, the metal chelates have been found to be more antimicrobial than the chelating agents themselves.[1] The importance of pyrimidine derivatives arises from their biological, medicinal and agricultural applications.[2-4] Metal complexes of pyrimidine have been extensively studied in recent years owing to their great variety of biological activity ranging from antimalarial, antibacterial, antitumor, antiviral activities etc.[5,6]

Bidentate Schiff bases are well known to co-ordinate with various metal ions and have attracted a great deal of interest in recent years due to their rich co-ordination chemistry Schiff bases of 2-amino- 4,6 dihydroxypyrimidine and P- chlorobenzaldehyde reported to have variety of applications including biological, clinical and analytical fields [7-10]. Metal complexes make the compounds effective as stereospecific catalysts towards oxidation, reduction, hydrolysis, biological activity and other transformations of organic and inorganic chemistry. Schiff base complexes play a vital role in designing metal complexes related to synthetic and natural oxygen carriers. [8,11-13] Many bidentate Schiff bases of amines with different aldehyde have been prepared and studied intensively. However much less attention has been focused on bidentate Schiff bases derived from amines and different

aldehydes / ketones. In particular, those derived from heterocyclic amines have been under-investigated. It is worthwhile to mention here that symmetrical Schiff bases of this type are difficult to obtain and not easily isolated. 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- chlorobenzaldehyde. In this communication we report the synthesis of symmetrical bidentate Schiff bases formed by the condensation of 2-amino- 4,6 dihydroxypyrimidine and P- chlorobenzaldehyde (Fig.1). The solid complexes of Cu(II) ,Ni(II) and Co(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) and P- chlorobenzaldehyde (AR grade) were used for synthesis of ligand. AR grade metal nitrate were used for the complex preparation.

### Synthesis of ligand

The ligand was prepared by a modification of the reported methods [14-16]. The Schiff base ligand has been synthesized by refluxing a mixture of 0.01 mol (1.4057 g) of, P- chlorobenzaldehyde and 0.01 mol (1.2710 g) 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: 60%)

### 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 DMSO 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 Elemental 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-chlorobenzaldehyde. 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 M= Cu(II) ,Ni(II) and Co(II). The magnetic susceptibilities of Cu(II) ,Ni(II) and Co(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 show the following signals. 5.9  $\delta$  (s, 2H, Phenolic (OH) hydrogen of pyrimidine ring), 6.66  $\delta$ (s, 1H, Hydrogen bonded to pyrimidine ring ), 7.94  $\delta$  (s, 1H, hydrogen bonded to azomethine carbon), 7.69-7.28  $\delta$  (D,4H, Aromatic Ha, Hb, protons of phenyl ring).

### IR Spectra

The IR spectrum of free ligands shows characteristic bands at 3331, 1641, 1487, 1207 and 1091  $\text{cm}^{-1}$  assignable to  $\nu$  OH (intramolecular hydrogen bonded),  $\nu$  C=N (azomethine),  $\nu$  C=C (aromatic),  $\nu$  C-N (aryl azomethine) and  $\nu$  C-O (Enolic) stretching modes respectively [14,16,17]. 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 intermolecular 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) [18] with respect to free ligand. On complexation, the  $\nu$  (C=N) [19] 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 500-600 and 400-500  $\text{cm}^{-1}$  regions which can be assigned to  $\nu$  M-O and M-N [20,21] vibrations respectively. The IR spectra of Cu(II), Ni(II), and Co(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 TG/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

Thermal decomposition studies of complex have been carried out as to corroborate the information obtained from the IR spectral studies to know the presence of water molecule in these complexes as well as to know their decomposition pattern. The simultaneous TGA/DTA analysis of Cu(II) and 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 Cu(II) complexes shows two step decomposition. The first weight loss 6.56 %, in between temp. 55-230 $^{\circ}\text{C}$  could be correlated with the loss of two coordinated water (calculated 6.01 %). The anhydrous compound does not remain stable at higher temperature; it undergoes rapid decomposition in the range 230-650 $^{\circ}\text{C}$  with 79.72 % mass loss corresponds to decomposition of the complex (calcd. 80.70%) in second step. The decomposition is completed leading to the formation of stable residue of metal oxide CuO obs. 13.12 % (calcd. 13.28 %). An analysis of the thermogram of the complexes indicated that Ni(II) complexes shows two step decomposition. The first weight loss 5.56 %, in between temp. 50-225 $^{\circ}\text{C}$  could be correlated with the loss of two coordinated water (calculated 6.06 %). The anhydrous compound does not remain stable at higher temperature, it undergoes rapid decomposition in the range 225-740 $^{\circ}\text{C}$ , and with 79.75% mass loss corresponds to decomposition of the complex (calcd. 81.36%) in second step. The decomposition is completed leading to the formation of stable residue of metal oxide NiO obs. 11.12 % (calcd. 12.57 %). The 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 [22,23] 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 [24].

### Magnetic measurements and electronic absorption spectra

The electronic absorption spectrum of the Cu(II) complexes in DMSO solution shows the region 13812 $\text{cm}^{-1}$  and 36764 $\text{cm}^{-1}$  assignable to the transition  $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$  and charge transfer bands. All Cu(II) complexes were diamagnetic in nature. These data and magnetic moment suggest octahedral geometry around Cu(II) [25]. The electronic absorption spectrum of the Ni(II) complexes shows bands at 29411 $\text{cm}^{-1}$  assignable to the charge transfer bands. All Ni(II) complexes were diamagnetic in nature. These data and magnetic moment suggest octahedral geometry around Ni(II) [26]. Co(II) complexes shows bands at 13477 $\text{cm}^{-1}$  and 20408 $\text{cm}^{-1}$  assignable to  $^6\text{T}_{1g} \rightarrow ^4\text{A}_{2g}(\text{F})$  and charge transfer transitions. All Co(II) complexes were diamagnetic in nature. These data and magnetic moment suggest octahedral geometry around Co(II) [27].

### Molar Conductivity Measurements

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

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>1</sub>	249.66	82	Yellow	-----
Cu-L <sub>1</sub>	598.88	>300	Dark Gray	27.25
Ni-L <sub>1</sub>	594.03	>300	Reddish Brown	43.69
Co-L <sub>1</sub>	594.33	>300	Dark Brown	24.15

Table 2. Elemental Analysis of Cu(II), Ni(II) and Co(II) Complex

Compound	Found (Calculated)			
	C	H	N	M
L <sub>1</sub>	52.92 (43.20)	3.23 (3.95)	16.83 (16.93)	-
Cu-L <sub>1</sub>	44.12 (44.10)	3.36 (3.20)	14.03 (13.95)	10.61 (10.50)
Ni-L <sub>1</sub>	44.48 (44.33)	3.39 (3.22)	14.14 (14.02)	9.87 (9.77)
Co-L <sub>1</sub>	44.46 (44.35)	3.39 (3.29)	14.14 (14.15)	9.92 (9.88)

### Powder x-ray diffraction

The x-ray diffractogram of Cu(II), Ni(II) and Co(II) complexes of L<sub>1</sub> was scanned in the range 20-80° at wavelength 1.543 Å. The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). The diffractogram of Cu(II) complex of L had twelve reflections with maxima at 2θ = 6.63° corresponding to d value 6.68 Å. The diffractogram of Ni(II) complex of L had fifteen reflections with maxima at 2θ = 13.28° corresponding to d value 6.65 Å. The diffractogram of Co(II) complex of L had twelve reflections with maxima at 2θ = 13.18° corresponding to d value 6.70 Å. 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 programme [28]. The above indexing method also yields Miller indices (hkl), unit cell parameters and unit cell volume. The unit cell of Cu(II) complex of L yielded values of lattice constants, a=9.59 Å, b=9.34 Å, c = 13.61 Å and unit cell volume V=1219.0558 Å<sup>3</sup>. In concurrence with these cell parameters, the condition such as a = b = c and α = β = γ = 90° required for sample to be Orthorhombic were tested and found to be satisfactory. Hence it can be concluded that Cu(II) complex has Orthorhombic crystal system. The unit cell of Ni(II) complex of L yielded values of lattice constants, a=8.97 Å, b=13 Å, c= 19.99 Å and unit cell volume V=2331.03394 Å. In concurrence with these cell parameters, the condition such as a = b = c and α = β = γ = 90° required for sample to be Orthorhombic. The unit cell of Co(II) complex of L yielded values of lattice constants, a=9.45 Å, b=9.91 Å, c = 18.99 Å and unit cell volume V=11778.40392 Å<sup>3</sup>. In concurrence with these cell parameters, the condition such as a = b = c and α = β = γ = 90° required for sample to be Orthorhombic. Hence it can be concluded Cu(II), Ni(II) and Co(II) complex of L has Orthorhombic and monoclinic crystal system. The experimental density values of the complexes were determined by using specific gravity method [29] and found to be 1.08, 1.08 and 1.08 gcm<sup>-3</sup> for Cu(II), Ni(II) and Co(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 Cu(II), Ni(II) and Co(II) complexes respectively. With these values, theoretical density were computed and found to be 1.07, 1.07 and 1.06 gcm<sup>-3</sup> for respective complexes. Comparison of experimental and theoretical density shows good agreement within the limits of experimental error [30]

Table: 3 The kinetic and thermodynamic parameters for decomposition of metal complexes

Complex	Step	Decomp. Temp. (°C)	n	Ea (kJmole <sup>-1</sup> )	Z (S <sup>-1</sup> )	ΔS (KJ <sup>-1</sup> mole <sup>-1</sup> )	ΔG (kJmole <sup>-1</sup> )	Correlation coefficient
Cu-L <sub>1</sub>	I	370	1.3	11.88	2.26 × 10 <sup>4</sup>	-167.97	24.86	0.933
Ni-L <sub>1</sub>	I	390	0.3	12.63	2.40 × 10 <sup>4</sup>	-167.72	25.99	0.959

### 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 moneliforme*, *Aspergillus flavus* and bacteria such as *E. Coli*, *B.Subtilis*, *Staphylococcus aureus* and *Bacillus subtilis* by paper disc plate method [31-34] The compounds were tested at the concentrations 1% and 2% in DMSO and compared with known antibiotics viz *Griseofulvin* and *Penicillin*. (Table 4 and 5). From Table 4 and 5, it is clear 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 [35] Such enhanced activity of metal chelates is due to the increased lipophilic nature of the metal ions in complexes. The increase in activity with concentration is due to the effect of metal ions on the normal cell

process. The action of compounds may involve the formation of hydrogen bond with the active centre of cell constituents, resulting in interference with the normal cell process.

Table 4 Antifungal activity of ligands

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

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>1</sub>	-ve	12mm	-ve	11mm	-ve	17mm	-ve	15mm
Cu- L <sub>1</sub>	10mm	11mm	-ve	-ve	14mm	14mm	10mm	23mm
Ni- L <sub>1</sub>	12mm	14mm	-ve	-ve	12mm	18mm	-ve	11mm
Co -L <sub>1</sub>	12mm	14mm	-ve	14mm	20mm	20mm	14mm	14mm
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 - --m

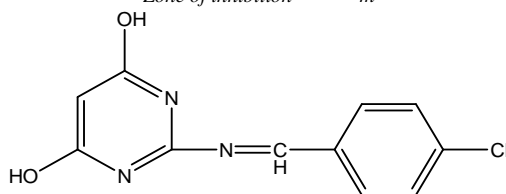


Figure 1. Structure of ligand

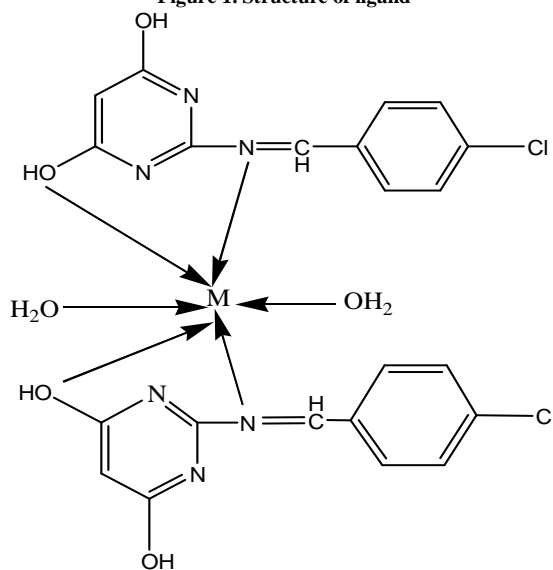


Figure 2. The proposed Structure of the complexes

When M= Cu(II) ,Ni(II) and Co(II)

### CONCLUSION

In the light of above discussion we have proposed octahedral geometry for Cu(II) ,Ni(II) and Co(II) complexes. On the basis of the physico-chemical and spectral data discussed above, one can assume that the ligand behave as dibasic, NNO bidentate, coordinating via phenolic oxygen and imino nitrogen as illustrated in Fig.2. 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 Cu(II) ,Ni(II) and Co(II) complexes.

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