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Syntheses, characterization of some transition metal complexes of bidentate schiff base and their antimicrobial activities

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ABSTRACT

The solid complexes of Cu (II), Ni (II) and Co (II) were prepared from bidentate Schiff base. The Schiff base ligand synthesized from the condensation of P-nitrobenzaldehyde and 2-amino -4,6 dihydroxypyrimidine (L_2) in alcohol medium. These metal complexes were characterized on the basis of their micro analytical data, molar conductance, magnetic susceptibility, IR, UV-Vis, ^{1}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 Aspergllus flavus. and antibacterial activity against various bacteria likes Escherichia coli, Salmonellatyphi, 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.

INTRODUCTION

Pyrimidines have been known to be one of the most important six membered heterocyclic compounds containing two nitrogen atoms. They occur in the living system in form of nucleic acids (RNA and DNA), in anti-malaria drugs and folic acid [1-5]. The chemistry of Pyrimidines has been of interest to many researchers including us due to their various biological activities such as antimicrobial, anticancer and HIV inhibitors [6-8]. Schiff bases play important role in co-ordination chemistry as they easily form stable complexes with most transition metal ions. Many biologically important Schiff bases and their complexes have been reported in literature possessing, analytical, industrial, biological, clinical, biochemical, antimicrobial, anticancer, antibacterial, antifungal and antitumor activity[9-12] in addition with important roles in ranging from anticorrosion, soil treatment agents and medicinal agents [10,12,13]. Schiff bases and their metal complexes have been used as carries in the preparation of potentiometric sensors of determining cations and anions, catalysts in several industrial redox process, oxidation reaction, vitamin B_6, Metal alkoxides. It's important and diversified roles in biological systems. The role of chlorophyll, hemoglobin, carbonic anhydrase, vitamin B_{12}, xanthine oxides and haemocyanin, illustrates the intimate linkage between inorganic chemistry and biology [14-20]. A search of literature revels that no work has been done on the transition metal complexes of the Schiff bases derived from 2-amino -4,6 dihydroxypyrimidine and P-nitrobenzaldehyde. In this communication we report the synthesis of bidentate Schiff bases formed by the condensation of 2-amino -4,6 dihydroxypyrimidine and P-nitrobenzaldehyde (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), P-nitrobenzaldehyde, 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 [21-23]. The Schiff base ligand has been synthesized by refluxing a mixture of 0.01 mol (1.5110g) of, P- nitrobenzaldehyde 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:72%).

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 cm^{-1}. ^{1}H- NMR Varian mercury 300MHZ spectra of ligand were measured in CDCl3 using TMS as internal standard. X-RD were recorded on BRUKER D8 Advance. TGA- DTA were 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 $Hg[Co(SCN)_4]$ 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-nitrobenzaldehyde. 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 revels 2:1 molar ratio (ligand: metal) and corresponds well with the general formula $[ML(H_2O)_2]$ (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)

1H-NMR spectra of ligand

The ^{1}H-NMR. Spectra of free ligand at room temperature show the following signals. 3.79 δ (s, 2H, Phenolic (OH) hydrogen of pyrimidine ring), 6.07 δ(s, 1H, Hydrogen bonded to pyrimidine ring), 8.07 δ (s, 1H, hydrogen bonded to azomethine carbon), 7.369-8.18 δ (D,4H, Aromatic H_a, H_b, protons of phenyl rin

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 3327, 1672, 1516, 1346, and 1197 cm^{-1} assignable to ν OH (intramolecular hydrogen bonded), ν C=C(aromatic), ν C=N (azomethine), ν C-N (aryl azomethine) and ν C-O (phenolic) stretching modes respectively[21-24] The absence of a weak broad band in the 3200-3400 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 υ C-O (phenolic) [25] with respect to free ligand. On complexation, the ν (C=N)[26]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 ν 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 cm^{-1} regions which can be assigned to ν M-O and M-N[27] vibrations respectively The IR spectra of Cu (II), Ni (II) and Co (II) show a strong band in the 3050-3600 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 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 Co(II) was studied from ambient temperature to 1000 ^{0}C in nitrogen atmosphere using α-Al_2O_3 as reference. An analysis of the thermogram of the complexes indicated that Co(II) complexes shows two step decomposition. The first weight loss4.78%,in between temp. 75-160^{0}C could be correlated with the loss of two coordinated water (calculated 5.85 %). The anhydrous compound does not remain stable at higher temperature, it undergoes rapid decomposition in the range 160-650°C, with 81.30 % mass loss corresponds to decomposition of the complex (calcd. 81.96%) in second step. The decomposition is completed leading to the formation of stable residue of metal oxide CoO obs. 11.95 % (calcd. 12.18 %). kinetic and thermodynamic viz the energy of activation (Ea), frequency factor (Z), entropy change (-ΔS) and free energy change (ΔG) for the non-isothermal decomposition of complexes have been determined by employing Horowitz-Metzger method [28] 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 [29].

Magnetic measurements and electronic absorption spectra

The electronic spectral studies of metal complexes of Cu (II), Ni (II) and Co (II) with Schiff bases were carried out in DMSO solution .The absorption spectrum of the The absorption spectrum of the Cu(II)complex shows bands at 36764cm^{-1} attributed to charge transfer respectively in an octahedral field[30]. Ni(II) complexes shows bands at 13812cm^{-1} and 24875cm^{-1} are assigned to $^1A_{1g}\rightarrow {}^1T_{2g}$ and charge transfer transitions. The absence of band below 10,000 cm^{-1} and All Ni(II) complexes were diamagnetic in nature indicates octahedral geometry[31]. The absorption spectrum of the Co(II)complex shows bands at 19920 and 29069 cm^{-1} attributed to $^4T_{1g}\rightarrow {}^4A_{2g}$(F) and charge transfer in an octahedral field[32]. All the Cu (II), Ni (II) and Co (II) complexes were diamagnetic in nature.

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. ^{0}C	Colour	Molar Conduc. Mho Cm^2mol^{-1}
L_2	260.21	110	Yellow	----
Cu -L_2	619.99	>300	Brown	23.05
Ni- L_2	615.13	>300	Reddish Brown	28.96
Co -L_2	615.43	>300	Dark Brown	22.75

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

Compound	Found (Calculated)			
	C	H	N	M
L_2	50.78 (39.29)	3.10 (3.67)	21.53 (17.55)	-
Cu-L_2	42.62 (42.30)	3.25 (3.10)	18.07 (18.00)	10.24 (10.10)
Ni-L_2	42.95 (42.77)	3.27 (3.12)	18.21 (18.11)	9.54 (9.43)
Co-L_2	42.93 (42.47)	3.27 (3.24)	18.20 (18.10)	9.58 (9.45)

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

Complex	Step	Decomp. Temp. (^{0}C)	n	Ea (kJmole^{-1})	Z (S^{-1})	ΔS ($JK^{-1}mole^{-1}$)	ΔG (kJmole^{-1})	Correlation coefficient
Co-L_2	I	430	0.9	10.41	1.26×10^4	-173.56	25.08	0.969

Table 4. Antifungal activity of ligands

Test Compound	Antigungal growth							
	Aspergillus niger		*Penicillium chrysogenum*		*Fusarium moneliforme*		*Aspergillus flavus*	
	1%	2%	1%	2%	1%	2%	1%	2%
L_2	+ve	RG	RG	-ve	RG	-ve	+ve	+ve
Cu- L_2	+ve	+ve	-ve	RG	-ve	-ve	+ve	RG
Ni- L_2	-ve	RG	RG	RG	-ve	RG	+ve	RG
Co- L_2	-ve	-ve	-ve	-ve	-ve	-ve	RG	+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)							
	E. coli		*Salmonella typhi*		*Staphylococcu saureus*		*Bacillus subtlis*	
	1%	2%	1%	2%	1%	2%	1%	2%
L_2	-ve	14mm	-ve	15mm	-ve	19mm	-ve	19mm
Cu- L_2	-ve	14mm	12mm	12mm	17mm	18mm	15mm	18mm
Ni- L_2	-ve	13mm	-ve	-ve	-ve	17mm	-ve	11mm
Co- L_2	12mm	13mm	12mm	14mm	18mm	20mm	11mm	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 - --mm

Powder x-ray diffraction

The x-ray diffractogram of Cu (II), Ni (II) and Co (II) complexes of L_2 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_2 had eight reflections with maxima at 2θ = 6.58° corresponding to d value 6.70Å. The diffractogram of Ni(II) complex of L_2 had twelve reflections with maxima at 2θ = 6.63° corresponding to d value 6.67Å. The diffractogram of Co(II) complex of L_2 had sixteen reflections with maxima at 2θ = 6.65° corresponding to d value 6.64Å. The diffractogram of Mn(II) complex of L_2 had eleven reflections with maxima at 2θ = 6.65° corresponding to d value 6.64Å. The diffractogram of Fe(III) complex of L_2 had ten reflections with maxima at 2θ = 6.64° corresponding to d value 6.66Å. 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[33]. 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_2 yielded values of lattice constants, a= 6.789Å, b=10.678 Å, c = 14.567 Å and unit cell volume V=914.52695 $Å^3$. In concurrence with these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \beta = 90^0 \neq \gamma$ required for sample to be Monoclinic were tested and found to be satisfactory. Hence it can be concluded that Cu(II) complex has Monoclinic crystal system. The unit cell of Ni(II) complex of L_2 yielded values of lattice constants, a=12.123 Å, b=7.459Å, c = 15.678Å and unit cell volume V=1227.99043 $Å^3$. In concurrence with these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \beta = 90° \neq \gamma$ required for sample to be monoclinic. The unit cell of Co(II) complex of L_2 yielded values of lattice constants, a=9.564 Å, b=10.456 Å, c = 11.234Å and unit cell volume V=972.90452$Å^3$.In concurrence with these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \beta = 90° \neq \gamma$ required for sample to be monoclinic. Hence it can be concluded Cu (II), Ni (II) and Co (II) complex of L_2 has monoclinic crystal system. The experimental density values of the complexes were determined by using specific gravity method [32] and found to be 1.0870, 1.1098, 1.0412, 1.0808 and 1.1000 gcm^{-3} 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 ρ = 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 1.0760, 1.0988, 1.0302, 1.0698 and 1.0890 gcm^{-3} for respective complexes. Comparison of experimental and theoretical density shows good agreement within the limits of experimental error [34].

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, S. aureus* And *Bacillus subtlis* by paper disc plate method [35-38] 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)., 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 [39]

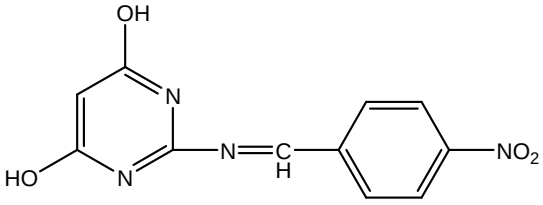

Figure 1. Structure of ligand

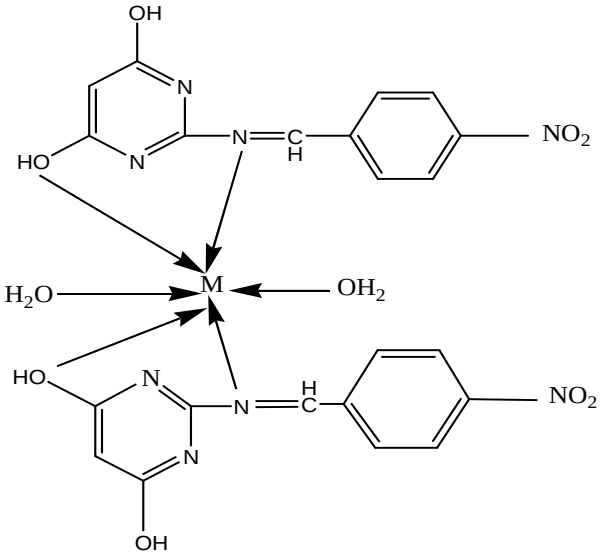

Figure 2. The proposed Structure of the complexes
When M= Cu (II), Ni (II) and Co (II)

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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