



Synthesis, characterization and antimicrobial activities of some Mn(II) and Fe(III) complexes of biologically active bidentate ligands

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ABSTRACT

A new solid complexes of Mn(II) and Fe(III) complexes with bidentate Schiff base ligand derived from 2-amino 4,6 dihydroxypyrimidine and P- methoxybenzaldehyde, have been reported. The complexes have been characterized by elemental analysis, magnetic susceptibility measurements, conductrometry, electronic and infrared spectra, X-ray diffraction, ¹H-NMR spectra. The ligand and its complexes were screened for their antifungal and antibacterial activity against *Aspergillus niger*, *Penicillium chrysogenum*, *Fusarium moneliforme* and *Aspergillus flavus* and *Escherichia coli.*, *Salmonellatyphi*, *Staphylococcus aurious*, *B.subtilis*. The result indicated that the complexes exhibited good antifungal and antibacterial activities. The Schiff base commonly coordinates through the oxygen atom of phenolic OH group and the nitrogen atom of azomethine group, which is confirmed by IR spectral data. Further conclusive evidence of the co-ordination of the Schiff bases with the metal ions was shown by the appearance of new bands due to $\nu(M-N)$ and $\nu(M-O)$ in the metal complexes.

Keywords: Schiff bases, Transition metal complexes, Powder X-ray diffraction, Antifungal and Antimicrobial activity.

INTRODUCTION

Schiff bases named after *Hugo Schiff* described the condensation between an aldehyde and an amine. Schiff base ligands are able to coordinate metals through imine nitrogen and another group usually linked to aldehyde. Schiff bases are an important class of ligands in coordination chemistry and find extensive application [1-2]. Schiff bases are straightforward to prepare thus being versatile [3] Modern chemists still prepare Schiff bases. In present time active and well-designed Schiff base ligands are considered to be privileged ligands [4] due to their ability to form complexes with a wide range of transition metal ions. These complexes have played an important role in the development of coordination chemistry [5]. Schiff bases are considered to be very good chelating agents [6], specially when -OH functional group closed with azomethine group. In recent years, there has been enhanced interest in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands due to their importance as catalysts in many reactions [7-12]. The chemistry of metal complexes including ordinary complexes, chelates and mixed ligand complexes has been extensively studied till date for their bioinorganic relevance as well as a wide range of physicochemical properties [13-14]. Here, we present the synthesis and properties of a new heterocyclic ligand containing pyrimidine ring and their Mn(II) and Fe(III) complexes. All the synthesized compounds were investigated for physiochemical properties and antimicrobial activities. The aim of

present investigation is to synthesize transition metal complexes of Schiff base condensed from 2-amino 4, 6 dihydroxypyrimidine and P-methoxybenzaldehyde.

EXPERIMENTAL SECTION

Reagents and solvents

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

Synthesis of ligand

The ligand L₄ was prepared by a modification of the reported methods [15-17]. The Schiff base ligand L₄ has been synthesized by refluxing a mixture of 0.01 mol (1.2015 g) of,

P-methoxybenzaldehyde 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%).

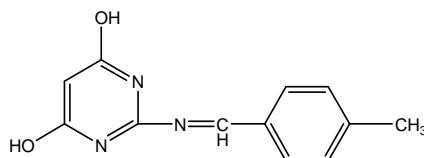


Figure1. Structure of ligand

Synthesis of metal complexes

To a hot ethanol solution (25ml) of the ligand L₄ (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. ¹H- NMR (varian mercury 300MHZ) spectra of ligand were measured in CDCl₃ 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 Hg[Co(SCN)₄] as a calibrate.

RESULTS AND DISCUSSION

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 [ML(H₂O)₂] (where M= Mn(II) and Fe(III)). The magnetic susceptibilities of Mn(II) and Fe(III)complexes at room temperature are consistent with two water molecules coordinated to metal ion. The metal chelate solutions in DMSO show low conductance and supports their non-electrolyte nature.

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

Compound	Mol. Wt.	M.P. Decomp temp. °C	Colour	μ _{eff} B.M.	Molar Conduc. Mho. Cm ² mol ⁻¹
L ₄	229.24	165	Yellow	--	----
Mn-L ₄	549.44	>300	Faint Brown	3.68	18.14
Fe-L ₄	550.35	>300	Pale Brown	3.92	33.57

Table 2. Elemental Analysis of Mn (II) and Fe(III) Complex

Compound	Found (Calculated)			
	C	H	N	M
L ₄	62.87 (62.87)	4.84 (4.84)	18.33 (18.33)	--
Mn-L ₄	52.46 (52.73)	4.76 (4.73)	15.29 (15.10)	9.99 (9.81)
Fe-L ₄	52.37 (52.20)	4.76 (4.72)	15.27 (15.10)	10.14 (10.05)

¹H-NMR spectra of ligand

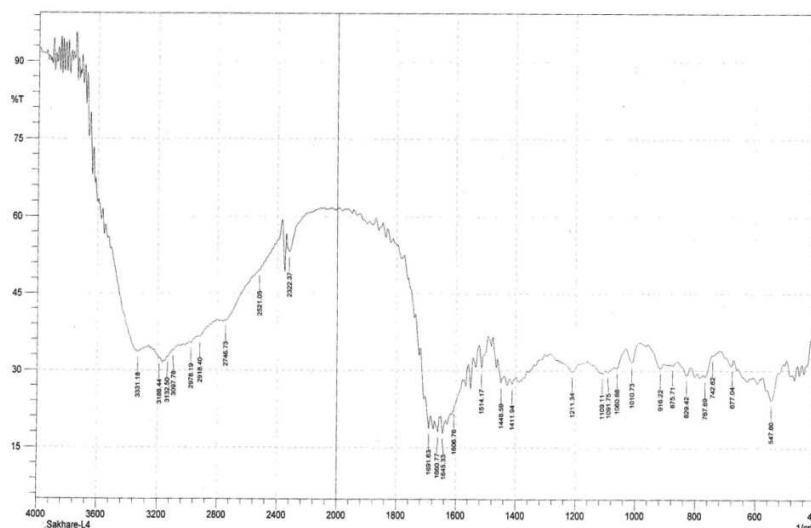
The ¹H-NMR. Spectra of free ligand L₄ at room temperature shows the following signals. 2.36 δ (s, 3H, Methyl hydrogen bonded to phenyl ring), 4.47 δ (s, 2H, Phenolic (OH) hydrogen of pyrimidine ring), 5.90 δ (s, 1H, Hydrogen bonded to pyrimidine ring), 7.83 δ (s, 1H, hydrogen bonded to azomethine carbon), 7.09-7.42 δ (D, 4H, Aromatic H_a, H_b, protons of phenyl ring).

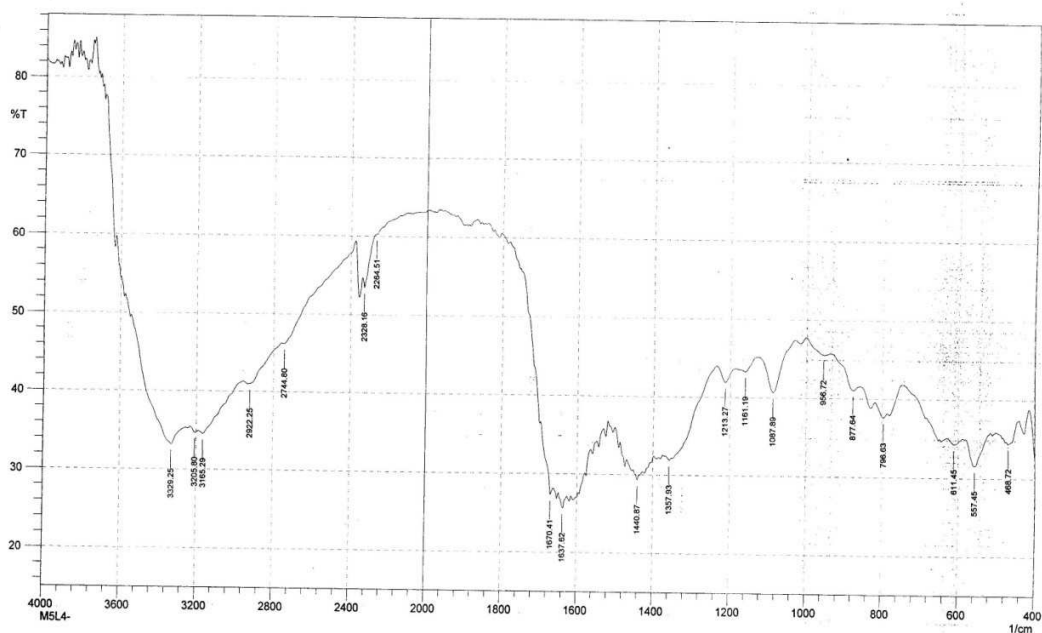
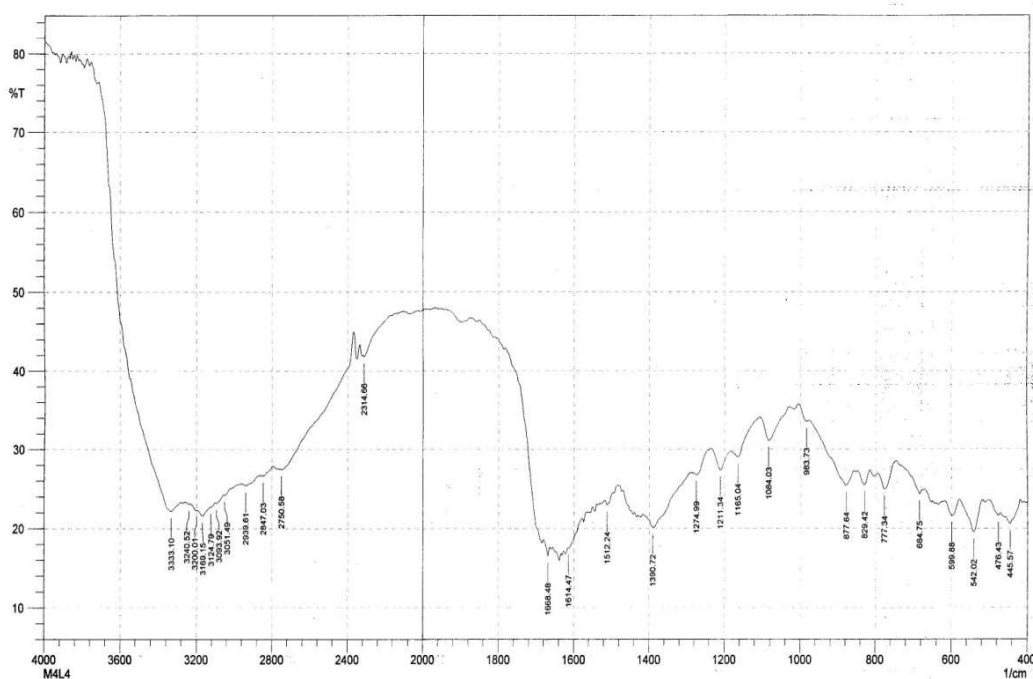
IR Spectra

The characteristic IR frequencies (cm⁻¹) of the ligand L₄ and their metal complexes are shown in Table 3. The IR spectra of ligand and metal complexes are presented in Fig. 2, 3 and 4. The IR spectrum of the free ligands show a broad weak band 3331 cm⁻¹ attributed to intramolecular bonding ν(OH). The bands 1660-1211 cm⁻¹ are assigned to ν (C=N) (azomethine), ν (C=C) (Aromatic double bond), ν (C-N) (aryl azomethine) and ν (C-O) (enolic) stretching modes, respectively. The disappearance of IR band at 3100-3300 cm⁻¹ (intramolecular hydrogen bonding) in the spectra of all the complexes indicates deprotonation of enolic oxygen and azomethine nitrogen in coordination to the metal ion. It is further supported by an downward shift in ν (C-O) by 52-61 cm⁻¹ in all complexes [18]. A upward shift in ν (C=N) by 6-31 cm⁻¹ indicates participation of azomethine nitrogen in complex formation [19]. The IR spectra of the metal complexes showed new bands in the 510-542 cm⁻¹ and 425-445 cm⁻¹ region, which can be assigned to ν (M-O) and ν (M-N) vibrations respectively. [20-22].

Table 3. Characteristic IR frequencies (cm⁻¹) of the ligands and their complexes

Compound	ν (C=N)	ν (C=C)	ν (C-N)	ν (C-O)	ν (M-O)	ν (M-N)
L ₄	1660	1514	1300	1211	---	---
Mn-L ₄	1637.62	1440.87	1345.15	1235.12	510.35	425.00
Fe-L ₄	1614.47	1425.12	1345.18	1274.99	542.02	445.57

Fig. 2 Infrared Spectra of Ligand L₄

Fig. 3 Infrared Spectra of Mn(II) Complex of Ligand L₄Fig. 4 Infrared Spectra of Fe(III) Complex of Ligand L₄

Magnetic measurements and electronic absorption spectra

The electronic absorption spectrum of the L₄ Mn(II) complexes shows bands at 13966 cm⁻¹ and 24875 cm⁻¹ are assigned to ⁶A_{1g} → ⁴T_{2g} and charge transfer transitions. All Mn(II) complexes were paramagnetic in nature indicates octahedral geometry[23,24]. The electronic absorption spectrum of the L₄ Fe(III) complexes shows bands at 29239cm⁻¹. These transitions may be assigned to charge transfer transitions. All Fe(III) complexes were paramagnetic in nature indicates octahedral geometry[25-27]. All the Mn (II) and Fe (III) complexes were paramagnetic in nature.

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. Aurious* and *Bacillus subtilis* by paper disc plate method [28-31,35]. 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 [32] 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 moneliforme</i>		<i>Aspergillus flavus</i>	
	1%	2%	1%	2%	1%	2%	1%	2%
L ₄	-ve	-ve	-ve	-ve	-ve	-ve	RG	+ve
Mn- L ₄	-ve	+ve	RG	RG	RG	RG	-ve	RG
Fe-L ₄	+ve	RG	+ve	-ve	RG	RG	+ve	+ve
+ve control	+ve	+ve	+ve	+ve	+ve	+ve	+ve	+ve
-ve control (<i>Griseofulvin</i>)	-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>Escheria Coli</i>		<i>Salmonella typhi</i>		<i>Staphylococcus aureus</i>		<i>Bacillus subtilis</i>	
	1%	2%	1%	2%	1%	2%	1%	2%
L ₄	13mm	13mm	-ve	-ve	14mm	17mm	11mm	14mm
Mn- L ₄	11mm	11mm	-ve	11mm	17mm	19mm	14mm	17mm
Fe-L ₄	-ve	-ve	-ve	-ve	19mm	21mm	18mm	18mm
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 Mn(II) and Fe(III) complexes of L₄ 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 Mn(II) complex of L₄ had fifteen reflections with maxima at 2θ = 12.77A° corresponding to d value 3.48Å. The diffractogram of Fe(III) complex of L₄ had ten reflections with maxima at 2θ = 6.66A° corresponding to d value 6.64Å. 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 [33] The above indexing method also yields Miller indices (hkl), unit cell parameters and unit cell volume. The unit cell of Mn(II) complex of L₄ yielded values of lattice constants, a=8.789 Å, b=9.456 Å, c = 15.456Å and unit cell volume V=1112.43507Å³. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β = 90° ≠ γ required for sample to be monoclinic. The unit cell of Fe(III) complex of L₄ yielded values of lattice constants, a=10.456 Å, b=8.567 Å, c = 14.674Å and unit cell volume V=1138.34398Å³. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β = 90° ≠ γ required for sample to be monoclinic were tested and found to be satisfactory. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β = 90° ≠ γ required for sample to be monoclinic. Hence it can be concluded Mn(II) and Fe(III) complex of L₄ has monoclinic crystal system. The experimental density values of the complexes were determined by using specific gravity method [34] and found to be 1.1084, 1.0600 gcm⁻³ for Mn(II) and Fe(III) 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 Mn(II) and Fe(III) complexes respectively. With these values, theoretical density were computed and found to be 1.10974, 1.0490 gm^{-3} for respective complexes. Comparison of experimental and theoretical density shows good agreement within the limits of experimental error [35, 36].

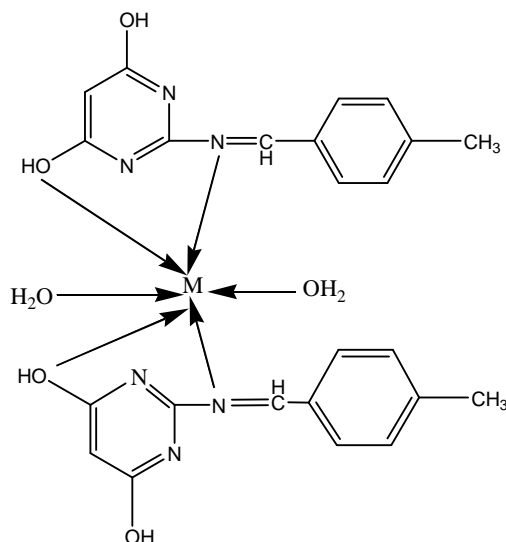


Figure 5. The proposed Structure of the complexes
When $M = \text{Mn(II)}$ and Fe(III) .

CONCLUSION

Based on the physicochemical and spectral data discussed above octahedral geometry for the Mn(II) and Fe(III) complexes are proposed. The ligand behave as bidentate, coordinating through phenolic oxygen and imino nitrogen as illustrated in Fig.5. The complexes are biologically active and show enhanced antimicrobial activities compared to free ligand. The X-RD study suggests monoclinic crystal system for Mn(II) and Fe(III) complexes.

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