



SYNTHESIS AND CHARACTERIZATION OF SOME Cr(III), Fe(III) AND Co(II) COMPLEXES OF UNSYMMETRICAL TETRADENTATE SCHIFF BASE

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ABSTRACT

The synthesis of Cr(III), Fe(III) and Co(II) complexes derived from Schiff base ligand. Obtained by the condensation of Dehydroacetic acid, 6-methyl-1,3,5-triazine-2,4-diamine and 4-hydroxybenzaldehyde is presented. The complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility, IR, Uv-Vis spectral data and X-RD analyses. The complexes were found to be electrolytic in nature on the basis of value of molar conductance. From the spectral data an octahedral geometry has been proposed for all the complexes. The metal complexes have been screened for their antibacterial activity against bacterium *Staphylococcus aureus*, *B. subtilis* (Gram positive) and *Escherichia coli*, *K. pneumoniae* (Gram negative). The result indicated that the complexes exhibited good antibacterial activities.

Keywords: Dehydroacetic acid, Unsymmetrical Schiff bases, Transition metal complexes, IR, Powder X-ray diffraction.

INTRODUCTION

Tetradentate 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 chemistry¹. Schiff bases of 6-methyl-1,3,5-triazine-2,4-diamine reported to have variety of applications including biological, clinical and analytical fields²⁻⁵. Metal complexes make the compounds effective as a 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.^{4,6-8} Many asymmetrical tetradentatebis-Schiff bases of 1, 2-diamines with different aldehyde/ketone have been prepared and studied intensively. However much less attention has been focused on asymmetrical tetradentateSchiffbases derived from 1, 2-diamines and different aldehydes / ketones. In particular, those derived from heterocyclic 1, 2- diamines have been under-investigated. It is worthwhile to mention here that asymmetrical 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 asymmetrical Schiff bases derived from 6-methyl-1,3,5-triazine-2,4-diamine, dehydroacetic acid and 4-hydroxybenzaldehyde. In this communication we report the synthesis of asymmetrical tetradentateSchiff bases formed by the condensation of 6-methyl-1,3,5-triazine-2,4-diamine, dehydroacetic acid and 4-hydroxybenzaldehyde (Fig.1). The solid complexes of Cr(III), Fe(III) and Co(II), with these ligands have been prepared and characterized by different physico-chemical methods.

MATERIALS AND METHODS

Reagents and solvents

4-hydroxybenzaldehyde, 6-methyl-1,3,5-triazine-2,4-diamine, metal nitrate of AR grade and Dehydroacetic acid obtained from Merck was used for synthesis of ligand and complex.

Synthesis of ligand

The ligand was prepared by a modification of the reported methods⁹⁻¹⁵. Asymmetric tetradentateSchiff base ligand has been synthesized via a stepwise approach. In the first step mono-Schiff base compound was prepared by refluxing 50 ml solution of 10 mmol of dehydroacetic acid and 10 mmol6-methyl-1,3,5-triazine-2,4-diamine in super dry ethanol for about 4h. Mono-Schiff base thus formed was then refluxed with 10mmol 4-hydroxybenzaldehyde to prepare asymmetric ligand. Asymmetric Schiff base thus formed was cooled to room temperature and collected by filtration, followed by recrystallization in ethanol. (Yield: 74%).



Synthesis of metal complexes

To a hot ethanol solution (25ml) of the ligand (0.005mol), methnolic solution (25ml) of metal Nitrate (0.005mol) 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 methanol, ethanol, petroleum ether (40°-50°) and dried over calcium chloride in vacuum desiccator.(yield: 57%)

Physical Measurement

IR spectra were recorded on FTIR(ATR)-BRUKER -TENSOR37 spectrometer using KBr pellets in the range of 4000-400 cm^{-1} . $^1\text{H-NMR}$ varian mercury 300MHZ spectra of ligand were measured in CDCl_3 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 $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant.

RESULTS AND DISCUSSION

Schiff bases of 6-methyl-1,3,5-triazine-2,4-diamine and its complexes have a variety of applications including biological, clinical and analytical .The Co-ordinating possibility of 6-methyl-1,3,5-triazine-2,4-diamine has been improved by condensaing with a variety of carbonyl compounds. An attempt has been made to synthesize asymmetric Schiff bases from 6-methyl-1,3,5-triazine-2,4-diamine anddehydroacetic acid with 4-hydroxybenzaldehyde.

Physical characteristics, micro analytical, and molar conductance data of ligand and metal complexes are given in Table1. The analytical data of complexes revels 1:1 molar ratio (metal:ligand) and corresponds well with the general formula $[\text{ML}(\text{H}_2\text{O})_2]$ (where M = Cr(III), Fe(III) and Co(II)). The magnetic susceptibilities of Cr(III), Fe(III) and Co (III) 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)

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

Compound Molecular formula	Mol.Wt.	M.P. Decomp temp. 0C	Colour	Molar Conduc. Mho Cm ² mol ⁻¹
L	379.37	>300	White	----
L Cr	431.37	>300	Gray	22.5
L Fe	435.21	>300	Brown	29.05
LCo	438.30	>300	Pink	30.96

Elemental Analysis of Cr(III) Complex:-

Compound	Found (Calculated)			
	C	H	N	M
L	60.84	5.09	18.22	0
	(60.15)	(4.51)	(18.46)	
L-Cr	52.86	3.9	16.27	11.96
	(52.9)	(3.97)	(16.23)	(12.05)

¹H-NMR spectra of ligand

The ¹H-NMR. spectra of free ligand at room temperature shows the following signals. 2.14δ (s, 3H, C₆-CH₃), 2.50δ (s, 3H, N=C-CH₃), 4.33δ (s, 1H, phenolic OH), 6.95 and 7.59δ (d, 2H, Aromatic H_a, H_a, H_b, H_b, protons of phenyl ring).

IR Spectra

The characteristic IR frequencies (cm⁻¹) of the ligand and their complexes are shown in Table 2. The IR spectrum of the free ligands show a broad weak band 3332 cm⁻¹ attributed to intramolecular bonding ν(OH). The bands 1635-1180 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) in all complexes¹⁶. A downward shift in ν (C=N) indicates participation of azomethine nitrogen in complex formation¹⁷. The IR spectra of the metal complexes showed new band at 609 cm^{-1} and 489 cm^{-1} region, which can be assigned to ν (M-O) and ν (M-N) vibrations respectively.¹⁸⁻²⁰

Table 2. 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	1635	1540	1270	1180	----	----
L-Cr	1633	1413	1062	976	609	489

Powder x-ray diffraction

The x-ray diffractogram of Cr(III), Fe(III) and Co(II) complexes of L was scanned in the range $20\text{-}80^\circ$ at wavelength 1.543 \AA . The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). The diffractogram of Cr(III) complex of L had eighteen reflections with maxima at $2\theta = 32.96^\circ$ corresponding to d value 1.41 \AA . The diffractogram of Fe(III) complex of L had nineteen reflections with maxima at $2\theta = 13.46^\circ$ corresponding to d value 3.30 \AA . The diffractogram of Co(II) complex of L had twenty reflections with maxima at $2\theta = 39.97^\circ$ corresponding to d value 1.19 \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 programme.²¹ The above indexing method also yields Miller indices (hkl), unit cell parameters and unit cell volume. The unit cell of Cr(III) complex of L yielded values of lattice constants, $a=9.6773\text{ \AA}$, $b=10.8920\text{ \AA}$, $c = 14.8959\text{ \AA}$ and unit cell volume $V=1359.76\text{ \AA}^3$. 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 were tested and found to be satisfactory. Hence it can be concluded that Cr(III) complex has Monoclinic crystal system. The unit cell of Fe(III) complex of L yielded values of lattice constants, $a=9.9511\text{ \AA}$, $b=9.9511\text{ \AA}$, $c = 15.5881\text{ \AA}$ and unit cell volume $V=1599.39\text{ \AA}^3$. 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. The unit cell of Co(II) complex



of L yielded values of lattice constants, $a=9.9893 \text{ \AA}$, $b=10.7608 \text{ \AA}$, $c = 14.9714 \text{ \AA}$ and unit cell volume $V=1609.32 \text{ \AA}^3$. In concurrence with these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ required for sample to be Orthorombhic.

Hence it can be concluded Cr(III), Fe(III) and Co(II) complex of L has monoclinic and Orthorombhic crystal system. The experimental density values of the complexes were determined by using specific gravity method²² and found to be 1.02, 1.06 and 1.2 g cm^{-3} for Cr(III), Fe(III) 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 Cr(III), Fe(III) and Co(II), complexes respectively. With these values, theoretical density were computed and found to be 1.02, 1.06 and 1.2 g cm^{-3} for respective complexes. Comparison of experimental and theoretical density shows good agreement within the limits of experimental error.²³

Magnetic measurements and electronic absorption spectra

The electronic spectral studies of metal complexes of Cr(III), Fe(III) and Co(II) with Schiff bases were carried out in DMSO solution. The absorption spectrum of the Cr(III) complex shows band at 29498 cm^{-1} attributed to charge transfer transition respectively in an octahedral field.²⁴ Fe(III) complex exhibits electronic spectral band at 39682 cm^{-1} which can be assigned to charge transfer in an octahedral field.²⁵ The absorption spectrum of the Co(II) complex shows bands at 38759 cm^{-1} attributed to charge transfer in an octahedral field²⁶. All the Cr(III), Fe(III) and Co(II) complexes were diamagnetic in nature.

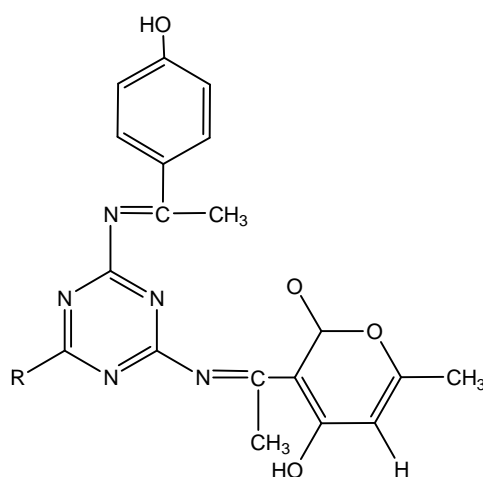
Antibacterial activity

Synthesized Schiff bases and their metal complexes were screened against bacteria such as *E. Coli*, *B. Subtilis*, *S. Aurious* And *K. Pneumonaeb* by paper disc plate method.²⁷ The compounds were tested at the concentration 1250ppm 2500ppm 5000ppm and 10000ppm. DMSO and compared with known antibiotics *viz* Tetracyclin. From Table 3, 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 3: Antibacterial activity of compound

Bacterium	Diameter of inhibition zone (mm)				
	(L)				<i>Tetracyclin</i>
	1250 ppm	2500 ppm	5000 ppm	10000 ppm	1000 ppm
<i>E. coli</i>	6	8	3	2	13
<i>S.Auriosus</i>	7	9	5	5	11
<i>B.Subtilis</i>	8	4	6	3	15
<i>K.Pneumoniae</i>	9	5	3	2	14

Bacterium	Diameter of inhibition zone (mm)				
	(LM)				<i>Tetracyclin</i>
	1250 ppm	2500 ppm	5000 ppm	10000 ppm	1000 ppm
<i>E. coli</i>	16	14	8	7	25
<i>S.Auriosus</i>	18	14	11	10	25
<i>B.Subtilis</i>	20	13	10	8	40
<i>K.Pneumoniae</i>	15	13	10	8	25



R= CH₃

Fig.1The proposed Structure of the ligand, a) R= CH₃

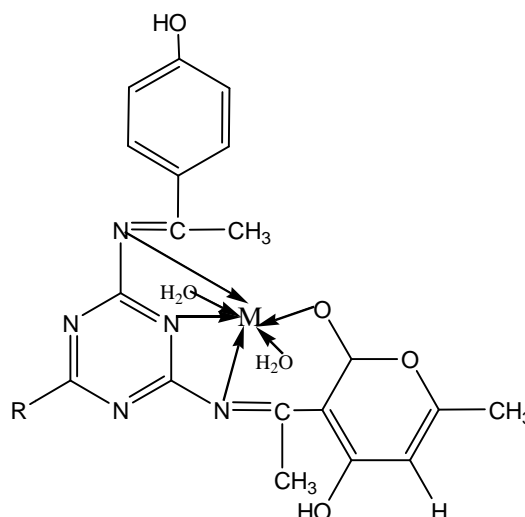


Figure 2. The proposed Structure of the complexes

a) R= CH₃ and b) M=Cr(III), Fe(III) and Co(II).

CONCLUSION

In the light of above discussion we have proposed octahedral geometry for Cr(III), Fe(III) 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, NNNO tetradentate, co-ordinating 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. The X-ray study suggests monoclinic crystal system for Cr(III), Fe(III) and Co(II) complexes.

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