



## Synthesis, characterization and antimicrobial activities of some transition metal complexes of biologically active asymmetrical tetradentate ligands

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### ABSTRACT

The synthesized metal complexes Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) of Schiff base have been condensed by Dehydroacetic acid, cinnamaldehyde and 6-methyl-1,3,5-triazine-2,4-diamine. The metal complexes were obtained as a result of interaction of Schiff base ligand. Schiff base have been synthesized and characterized on the basis of elemental analysis, Infrared, <sup>1</sup>H NMR analysis, magnetic susceptibility measurements, conductometry, electronic spectra, X-ray diffraction. The ligand and its complexes were 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. 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. © 2015 Trade Science Inc. - INDIA

### KEYWORDS

Dehydroacetic acid;  
Unsymmetrical schiff bases;  
Transition metal complexes;  
Thermal analysis;  
Powder X-ray diffraction.

### INTRODUCTION

Schiff base was first reported by Hugo Schiff<sup>[1,2]</sup> in 1864. Schiff bases are formed by the condensation of primary amine with compounds containing active carbonyl group<sup>[3-6]</sup>. The Schiff bases are also called imines<sup>[1,7]</sup> anils, azomethine ( $>C=N$ )<sup>[8]</sup>. Schiff bases are used for preparation of metal complexes having a series of different structures with different metal. These complexes having a importance and role of co-ordination compounds in living systems is well established. The co-ordination complexes which are found in min-

erals, plants and animals are of great significance because they exhibit important functions in the environment. The synthesis of newer and newer organic chelating agents that can co-ordinate with transition metal ions has tempted the researchers to synthesize more and more co-ordinated compounds and have become a challenge to the present day chemist.<sup>[9]</sup> 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

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and natural oxygen carries.<sup>[10-13]</sup> The aim of present investigation is to synthesize various transition metal complexes of Schiff base condensed from Dehydroacetic acid, cinnamaldehyde and 6-methyl-1,3,5-triazine-2,4-diamine.

### MATERIALS AND METHODS

#### Reagents and solvents

Dehydroacetic acid obtained from Merck was used as supplied cinnamaldehyde and 6-methyl-1,3,5-triazine-2,4-diamine of 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<sup>[9,14]</sup>. Asymmetric tetradentate Schiff 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 20mmol 6-methyl-1,3,5-triazine-2,4-diamine in super dry ethanol for about 4 h. Mono-Schiff base thus formed was then refluxed with 10mmol cinnamaldehyde to prepare asymmetric ligand. Asymmetric Schiff base thus formed was cooled to room temperature and collected by filtration, followed by recrystallization in ethanol. (Yield: 71.50%).

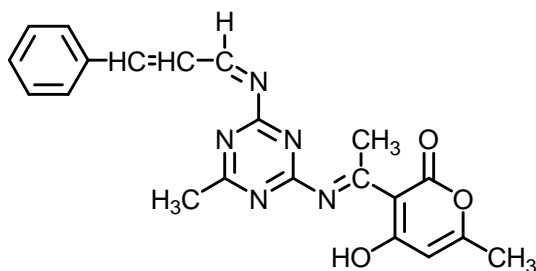


Figure 1 : Structure of ligand

#### Synthesis of metal complexes

To a hot ethanol solution (25ml) of the ligand (0.005mol), methanolic solution (25ml) of metal Nitrate (0.0025mol) 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: 63.62%)

#### Physical measurement

IR spectra were recorded on FTIR(ATR)-BRUKER -TENSOR37 spectrometer using KBr pellets in the range of 4000-400 cm<sup>-1</sup>. <sup>1</sup>H- NMR (varian mercury 300MHZ ) spectra of ligand were measured in CDCl<sub>3</sub> 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)<sub>4</sub>] as a calibrant.

### RESULTS AND DISCUSSION

Physical characteristics, micro analytical and molar conductance data of ligand and metal complexes are given in TABLE 1. The analytical data of complexes reveals 1:2 molar ratio (metal : ligand ) and corresponds well with the general formula [ML] where M= Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II). the magnetic susceptibilities of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes at room temperature are consistent with octahedral structure with two water molecule coordinated to metal ion. The metal chelate solutions in

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	389.41	>300	white	----
L Cr	441.40	>300	Gray	28.05
L Fe	445.25	>300	Brown	19.23
L Co	448.34	>300	Pink	41.68
L Ni	448.10	>300	Green	26.45
L Cu	452.95	>300	Blue	15.43
L Zn	454.80	>300	White	46.69

DMSO Show low conductance and supports their non-electrolyte nature.

### Elemental analysis of Co(II) complex

Compound	Found (Calculated)			
	C	H	N	M
L	65.10 (64.77)	4.45 (4.91)	18.20 (17.98)	0
L-Fe	56.66 (56.64)	4.33 (4.30)	15.69 (15.72)	12.59 (12.54)

### <sup>1</sup>H-NMR spectra of ligand

The <sup>1</sup>H-NMR. spectra of free ligand at room temperature shows the following signals. 2.13 δ (s, 3H, C<sub>6</sub>-CH<sub>3</sub>), 2.50δ (s, 3H, N=C-CH<sub>3</sub>), 7.00 to 7.90δ (m, 5H, Aromatic protons of phenyl ring).

### IR spectra

The characteristic IR frequencies (cm<sup>-1</sup>) of the ligand and their complexes are shown in TABLE 2. The IR spectrum of the free ligands show a broad weak band 3273 cm<sup>-1</sup> attributed to intramolecular bonding ν(OH). The bands 1663-1123 cm<sup>-1</sup> 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<sup>-1</sup> (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<sup>-1</sup> in all complexes<sup>[15]</sup>. A upward shift in ν(C=N) by 6-31 cm<sup>-1</sup> indicates participation of azomethine nitrogen in complex formation<sup>[16]</sup>. The IR spectra of the metal complexes showed new bands in the 508-612 cm<sup>-1</sup> and 468-510 cm<sup>-1</sup> region, which can be assigned to ν(M-O) and ν(M-N) vibrations respectively.<sup>[17-19]</sup>

### Magnetic measurements and electronic absorption spectra

The electronic absorption spectrum of the Cr(III)

complexes in DMSO solution shows the region 13661 cm<sup>-1</sup> and 31055 cm<sup>-1</sup> assignable to the transition <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub> and charge transfer bands. All Cr(III) complexes were dimagnetic in nature. these data and magnetic moment suggest octahedral geometry around Cr(III)<sup>[20]</sup>. The electronic absorption spectrum of the Fe(III) complexes shows bands at 28818 cm<sup>-1</sup> assignable to the charge transfer bands. All Fe(III) complexes were dimagnetic in nature. these data and magnetic moment suggest octahedral geometry around Fe(III)<sup>[21]</sup>. Co(II) complexes shows bands at 18214 cm<sup>-1</sup> and 36764 cm<sup>-1</sup> assignable to <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub>(F) and charge transfer transitions. All Co(II) complexes were dimagnetic in nature. these data and magnetic moment suggest octahedral geometry around Co(II)<sup>[22]</sup>. Ni(II) complexes shows bands at 13262 cm<sup>-1</sup> and 37735 cm<sup>-1</sup> are assigned to <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub> and charge transfer transitions. The absence of band below 10,000 cm<sup>-1</sup> and All Ni(II) complexes were dimagnetic in nature indicates octahedral geometry<sup>[23]</sup>. Cu(II) complexes shows bands at 12903 cm<sup>-1</sup> and 39062 cm<sup>-1</sup>. These transitions may be assigned to <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>A<sub>1g</sub> and charge transfer transitions. All Cu(II) complexes were dimagnetic in nature indicates octahedral geometry<sup>[24]</sup>. Zn(II) complexes did not show any d-d bands and their spectra were dominated by the charge transfer bands at 38314 cm<sup>-1</sup>. All Zn(II) complexes were dimagnetic in nature indicates octahedral geometry<sup>[25]</sup>.

### Antibacterial activity

In the present investigation, biological activity of the ligand and their asymmetrical complex with Co(II) have been screened for antimicrobial activity against *E. Coli*, *B.Subtilis*, *S. Aurious* And *K.Pneumoniae* by paper disc method.<sup>[26]</sup> The compounds were tested at the concentrations 1250ppm 2500ppm 5000ppm and 10000ppm. DMSO and compared with known antibiotics viz *Tetracyclin*. comparisons of the biological activity of the synthesized compounds with some known antibiotics presented in TABLE 3. it is clear that the

TABLE 2 : Characteristic IR frequencies (cm<sup>-1</sup>) 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	1663	1547	1393	1123	--	--
L-Ni	1657	1538	1263	1062	612	510
L-Cu	1632	1407	1269	1071	508	468

TABLE 3 : Antibacterial activity of compounds

Bacterium	Diameter of inhibition zone (mm)				
	(L)				Tetracyclin
	1250 ppm	2500 ppm	5000 ppm	10000 ppm	1000 ppm
<i>E. coli</i>	09	06	05	03	16
<i>S. Aurious</i>	06	07	02	08	14
<i>B.Subtilis</i>	05	04	04	07	12
<i>K.Pneumoniae</i>	04	03	06	10	10

Bacterium	Diameter of inhibition zone (mm)				
	(LM)				Tetracyclin
	1250 ppm	2500 ppm	5000 ppm	10000 ppm	1000 ppm
<i>E. coli</i>	15	13	08	08	25
<i>S. Aurious</i>	16	14	09	15	28
<i>B.Subtilis</i>	18	09	10	16	40
<i>K.Pneumoniae</i>	10	08	11	17	20

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 complex.<sup>[27]</sup>

### Powder x-ray diffraction

The x-ray diffractogram of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of L 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 Cr(III) complex of L had eighteen reflections with maxima at 2θ = 14.74° corresponding to d value 3.02 Å. The diffractogram of Fe(III) complex of L had seventeen reflections with maxima at 2θ = 14.77° corresponding to d value 3.01 Å. The diffractogram of Co(II) complex of L had nineteen reflections with maxima at 2θ = 32.87° corresponding to d value 1.41 Å. The diffractogram of Ni(II) complex of L had seventeen reflections with maxima at 2θ = 10.70° corresponding to d value 4.14 Å. The diffractogram of Cu(II) complex of L had seventeen reflections with maxima at 2θ = 14.78° corresponding to d value 3.01 Å. The diffractogram of Zn(II) complex of L2 shows twenty reflections with maxima at 2θ = 10.75° corresponding to d value 4.12 Å. The xray diffraction pattern of these complexes with respect to major peaks of relative intensity greater than 10% has been indexed by using computer programme<sup>[28]</sup> 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=8.9853 Å, b=9.6261 Å, c = 14.9519 Å and unit cell volume V=1119.98 Å<sup>3</sup>. 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. 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=9.8961 Å, b=8.9681 Å, c = 14.6085 Å and unit cell volume V=1122.80 Å<sup>3</sup>. 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 Co(II) complex of L yielded values of lattice constants, a=10.3413 Å, b=9.8876 Å, c = 12.6863 Å and unit cell volume V=1123.40 Å<sup>3</sup>. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and c required for sample to be monoclinic. The unit cell of Ni(II) complex of L yielded values of lattice constants, a=10.9770 Å, b=8.7018 Å, c = 14.9943 Å and unit cell volume V=1240.37 Å<sup>3</sup>. 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 Cu(II) complex of L yielded values of lattice constants, a=9.6292 Å, b=8.9800 Å, c = 14.2619 Å and unit cell volume V=1233.24 Å<sup>3</sup>. 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 orthorhombic. The unit cell of Zn(II) complex of L yielded values of lattice constants,  $a=10.1281\text{\AA}$ ,  $b=8.9693\text{\AA}$ ,  $c = 18.6868\text{\AA}$  and unit cell volume  $V=1470.14\text{\AA}^3$ . In concurrence with these cell parameters, the condition such as  $a \neq b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ \neq \gamma$  required for sample to be monoclinic were tested and found to be satisfactory. Hence it can be concluded Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complex of L has monoclinic crystal system. The experimental density values of the complexes were determined by using specific gravity method<sup>[29]</sup> and found to be 0.96, 1.14, 1.0, 1.1, 0.98 and 1.36  $\text{gcm}^{-3}$  for Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(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), Co(II), Ni(II), Cu(II) and Zn(II) complexes respectively. With these values, theoretical density were computed and found to be 0.96, 1.14, 1.0, 1.1, 0.98 and 1.36  $\text{gcm}^{-3}$  for respective complexes. Comparison of experimental and theoretical density shows good agreement within the limits of experimental error<sup>[30]</sup>.

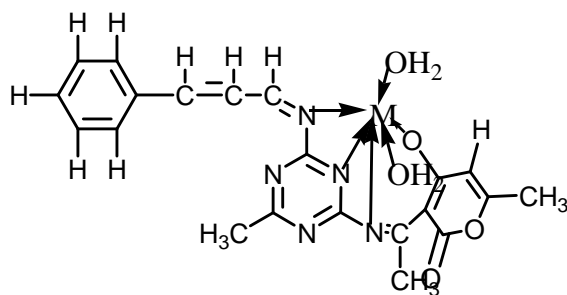


Figure 2 : The proposed structure of the complexes

when  $M = \text{Cr(III)}$ ,  $\text{Fe(III)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cu(II)}$  and  $\text{Zn(II)}$

## CONCLUSION

Based on the physicochemical and spectral data discussed above octahedral geometry for the

Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes are proposed. The ligand behave as tetradentate, coordinating through enolic oxygen and imino nitrogen of dehydroacetic acid moiety. The com-

plexes are biologically active and show enhanced antimicrobial activities compared to free ligand. The X-RD study suggests monoclinic crystal system for Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes.

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