



# SYNTHESIS AND CHARACTERIZATION OF SOME TRANSITION METAL COMPLEXES OF BIDENTATE LIGAND

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## ABSTRACT

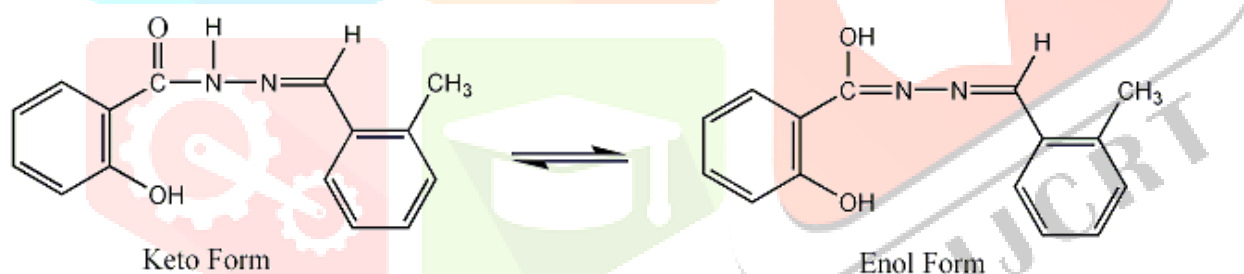
The solid complexes of Mn(II), Fe(III), Ni(II) and Cu(II) have been synthesized Schiff base derived from 2-hydroxybenzohydrazide and 2-Methyl benzaldehyde. And characterized by spectral and other physicochemical techniques such as <sup>1</sup>H-NMR, UV-vis molar conductivity, magnetic susceptibility, thermal analysis, X-ray diffraction, FTIR, and mass spectroscopy. The analytical data of these metal complexes showed metal: ligand ratio (1:2). The physico-chemical study supports the presence of square planar geometry around Cu(II) and Ni(II) and octahedral geometry around Mn(II), and Fe(III). The IR spectral data reveal that the ligand behaves as bidentate with ON donor atom sequence towards central metal ion. The molar conductance values of metal complexes suggest their non electrolyte nature. The X-ray diffraction data suggest orthorhombic crystal system for these complexes. Thermal behavior (TG/DTA) and kinetic parameters calculated by Coats-Redfern method are suggestive of more ordered activated state in complex formation. The ligand and their metal complexes were screened for antibacterial activity against *Staphylococcus aureus*, *Escherichia coli* and fungicidal activity against *Aspergillus Niger* and *Trichoderma*.

**KEYWORDS:** Bidentate Schiff base, Metal complexes, Thermal analysis, XRD, Antimicrobial study.

## INTRODUCTION

Many organic compounds, heterocyclic aromatic compounds in particular like benzimidazoles, benzothiazoles are reported to possess a variety of physiological activities such as fungicidal, insecticidal, antimicrobial and anesthetic properties. Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields like biological, inorganic and analytical chemistry [1-2]. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes since it has been recognized that many of these complexes may serve as models for biologically important species [3-5]. The study of ligands involving such hydrazones is interesting as they demonstrate versatility in coordination, a tendency to yield stereochemistry of higher coordination number [6] an ability to behave as neutral or deprotonated ligands and flexibility in assuming different conformations. Recently, several metal complexes of Schiff bases containing N, S and N, O donors have been synthesized and studied [7-9].

In the present article Mn(II), Fe(III), Ni(II), and Cu(II), complexes with Schiff base derived from 2-hydroxybenzohydrazide and 2-Methyl benzaldehyde. These have been characterized on the basis of physicochemical and spectral analysis. The antibacterial and antifungal activities of the ligand and its metal complexes were also tested. Unfortunately most Schiff bases are chemically unstable and show a tendency to be involved in various equilibria, like tautomeric interconversion hydrolysis or formation of ionised species [1, 2]



**Figure1.** Keto and enol form of ligand.

## EXPERIMENTAL

### Materials

All chemicals used were of the analytical grade (AR) and of highest purity. Methyl 2-hydroxybenzoate, hydrazine and benzaldehyde were purchased from E-Merk (AR grade) and were used for synthesis of ligand. AR grade metal chlorides of S. D. Fine chemicals were used for complex preparation. Spectral grade solvents were used for spectral measurements. The carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CHNS analyzer. IR spectra for ligand and metal complexes were recorded on Jasco FT-IR-4100 spectrometer using KBr pellets in the range of 4000-400  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  spectra of the ligand was measured in  $\text{CDCl}_3$  using TMS as an internal standard. The TG/DTA analysis was recorded on Perkin Elmer TA/SDT-2960 with heating rate  $10^\circ\text{C}/\text{min}$ . XRD was recorded on Philips 3701 employing  $\text{CuK}\alpha$  radiation ( $\lambda=1.541\text{\AA}$ ) in the range  $20^\circ$  to  $90^\circ$ . The UV-vis spectra of the complexes were recorded on Jasco UV-530 Spectrophotometer. Magnetic susceptibility measurements were carried out on Guoy balance at

room temperature using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as a calibrant. Conductance was measured on Elico CM-180 conductometer using 1 mM solution in dimethyl sulphoxide.

### *Synthesis of Ligand*

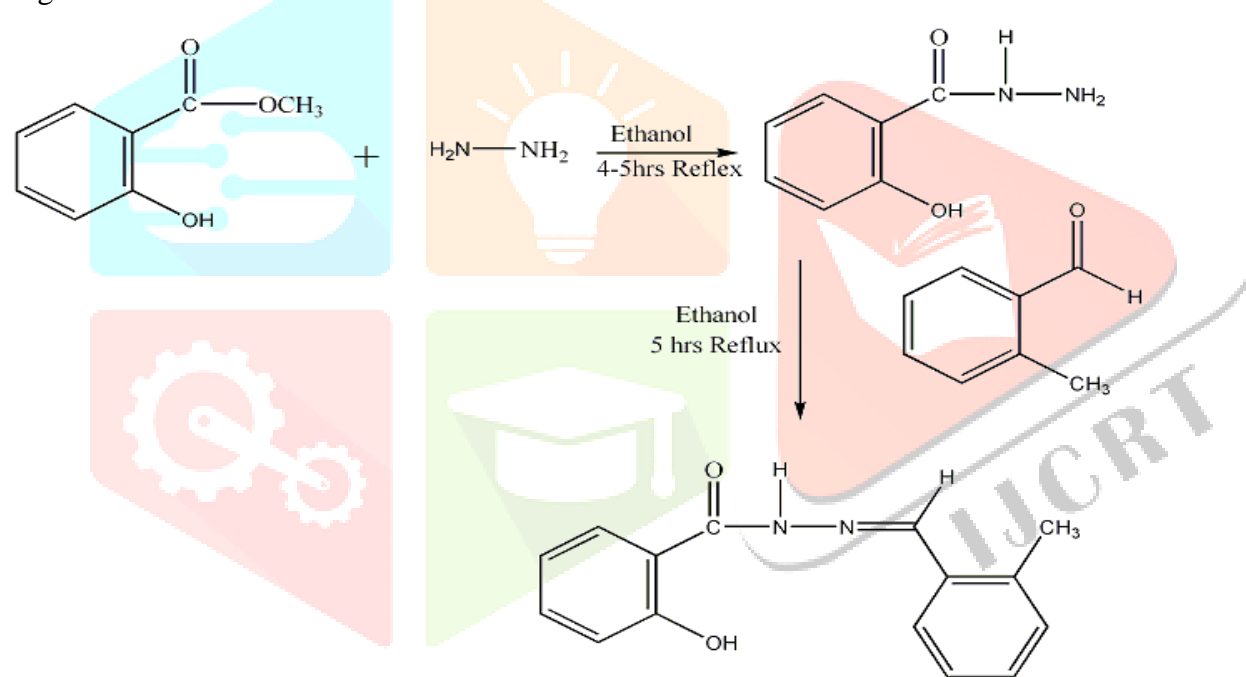
#### *Step-I*

50 mL ethanolic solution of 0.001 mol (0.168g.) of methyl salicylate was taken in round bottomed flask and to this 0.001 mol (0.108g.) of hydrazine in ethanol was added slowly under stirring. The resulting mixture was refluxed for about 4-5 h. It was naturally cooled to room temperature. After cooling, the solid residue was washed with hot ethanol and used for further study. (Yield 75%)

#### *Step-II*

Above synthesised intermediate 0.001 mol was refluxed with 0.001 mol of 2-methyl benzaldehyde in super dry ethanol for 5 h. The precipitate thus formed was filtered, dried in vacuum in presence of  $\text{CaCl}_2$  and recrystallised in ethanol (yield: 79%).

Fig. 2



**Figure 2.** Synthesis of ligand.

### *Preparation of Complexes*

To a hot solution of ligand (0.02 mol) in chloroform (25mL), methanolic solution of metal chloride (0.01 mol) was added under constant stirring. The pH of the reaction mixture was adjusted to 7.5-8.5 by adding 10 % ethanolic ammonia solution and refluxed for about 5 h. The precipitated solid metal complex was filtered and washed with hot methanol, followed by petroleum ether, ethyl acetate and dried over  $\text{CaCl}_2$  in vacuum desiccator (yield 61%).

## RESULT AND DISCUSSION

All the complexes are coloured solids, air stable and are having line solubility in polar solvents DMF and DMSO. The elemental analysis show 1:2 (metal: ligand) stoichiometry for all the complexes. Micro analytical data and molar conductance values are given in Table I. The metal contents in complexes were estimated by gravimetric analysis [10]. All the complexes show low conductance which indicates their non-electrolytic nature. The magnetic measurement studies suggest paramagnetic behavior of all these complexes

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

Compound	F.W.	M.P./ Decom Temp °C	Colour	Molar conduc tance Mho cm <sup>2</sup> mol <sup>-1</sup>	%C (calcd.)	%H (calcd.)	%N (calcd.)	%M (calcd.)
H <sub>2</sub> L	266	258	White		70.10 (70.85)	5.45 (5.54)	11.25 (11.01)	
[MnL]	544.93	>300	Yellow	4.74	63.59 (63.94)	4.95 (5.00)	9.60 (9.94)	10.01 (9.74)
[FeL]	545.84	230	Black	5.2	63.95 (63.84)	4.58 (4.99)	9.72 (9.92)	9.59 (9.89)
[NiL]	548.69	270	Brown	4.86	63.22 (63.52)	4.88 (4.97)	9.42 (9.87)	10.30 (10.36)
[CuL]	553.54	280	Pale green	17.66	62.22 (62.98)	4.88 (4.93)	9.42 (9.79)	10.38 (10.34)

### *<sup>1</sup>H-NMR spectra*

<sup>1</sup>H-NMR spectra of synthesised ligand was recorded in CDCl<sub>3</sub>. It shows signals at 7.59 δ (s, 1H, -C-N-H), 7.08 δ (dd, 2H, Ar-H), 7.22 δ (dd, 2H, Ar-H), 7.01-7.75 δ (dd, 4H, Ar-H), 7.85 δ (s, 1H, N=C-H), 2.50 δ (s, 3H, Ar-H) and 6.10 δ (s, 1H, Ar-OH).

### *Mass spectra of the ligand*

Mass spectra of the ligand H<sub>2</sub>L has been recorded which show the molecular ion peak (M<sup>+</sup>) at m/z = 255.28 corresponding to its molecular mass.

## *IR spectra*

The FT-IR spectrum of the free ligand shows four characteristic bands at 3240-3210, 3260, 1651 and 1615  $\text{cm}^{-1}$  assignable to ( $\nu$  -N-H), free (-O-H) stretching phenolic moiety, amide carbonyl ( $-\text{C}=\text{O}$ ) and azomethine ( $-\text{C}=\text{N}$ ), stretching modes respectively. The absence of a weak broad band in 3270-3300  $\text{cm}^{-1}$  region, noted in the spectra of the metal complexes indicates deprotonation of bonded (-NH) group during the complexation and subsequent coordination of the oxygen of amide carbonyl to metal ion enolization[11]. The  $\nu(\text{C}=\text{N})$  band is shifted to lower frequency with respect to free ligand, indicating that the nitrogen of the azomethine group is coordinated to the metal ion, which was further confirmed by observation of the red shift in the  $\nu(\text{N}-\text{N})$  stretching frequency from 923  $\text{cm}^{-1}$  to 953  $\text{cm}^{-1}$  regions[12-14]. New bands observed in the complexes at 1621 and 1624  $\text{cm}^{-1}$  are attributed to the  $>\text{C}=\text{N}-\text{N}=\text{C}<$  group[13]. The spectra of metal chelates showed new bands in the 460-540 and 407-478  $\text{cm}^{-1}$  regions which can be assigned to  $\nu$  (M-O) and (M-N) vibrations respectively[15]. The spectra of Mn(II) and Fe(III). showed a strong band at 3020-3500  $\text{cm}^{-1}$  region, suggesting the presence of coordinated water in these metal complexes[10]. The presence of coordinated water is further confirmed by the appearance of non-ligand band in 827-846  $\text{cm}^{-1}$  region[16]. The presence of coordinated water is also established and supported by TG/DTA analysis of these complexes. Hence co-ordination takes place via oxygen of amide and nitrogen of azomethine group of ligand molecule [17].

## *Electronic absorption spectra and magnetic measurements*

The electronic spectra of Mn(II) complex in DMSO show bands at 12225, 16009, 27823  $\text{cm}^{-1}$  assignable to a  ${}^4\text{T}_{1g} \rightarrow \text{T}_{2g}$ ,  ${}^4\text{T}_{1g} \rightarrow \text{A}_{2g}$  transition and charge transfer respectively. The electronic spectral data coupled with observed magnetic moment 5.8 B.M. suggest octahedral geometry for Mn(II) complex [18,19]. Fe(III) complex exhibits three bands at 16501, 24280 and 27871  $\text{cm}^{-1}$  assignable to  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$  (F) transitions and charge transfer respectively. These transitions and observed magnetic moment 5.7 B.M indicate square planer geometry of the complex[20]. Ni(II) complex exhibits three bands at 12280, 16118 and 27270  $\text{cm}^{-1}$  assignable to  ${}^4\text{T}_{1g} \rightarrow \text{T}_{2g}$ ,  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$  transitions and charge transfer respectively. These transitions and observed magnetic moment 2.6 B.M indicate octahedral geometry of the complex[17,21]. The electronic spectra of Cu(II) complex .show bands at 12600, 17980, 23475  $\text{cm}^{-1}$  assignable to a  ${}^6\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$  transition and charge transfer respectively. The electronic spectral data coupled with observed magnetic moment 1.8 B.M. suggest square planar geometry for Cu(II) complex.[17].

Table II. Magnetic and Electronic absorption spectral data of compounds.

Compound	Magnetic moment $\mu_{\text{eff}}$ (B.M.)	Frequency in $\text{cm}^{-1}$	Band Assignment	Geometry
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> ] H <sub>2</sub> L	-	32870 33940 34251	INCT <sup>a</sup> INCT dxy → dx <sup>2</sup> -y <sup>2</sup>	
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Mn]	5.8	12225 16009 27823	<sup>4</sup> T <sub>1g</sub> → T <sub>2g</sub> (F) <sup>4</sup> T <sub>1g</sub> → <sup>4</sup> A <sub>2g</sub> (F) I N C T	Octahedral
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Fe]	5.7	16501 24280 27871	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> I N C T	Octahedra
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Ni]	2.7	12280 16118 27270	<sup>4</sup> T <sub>1g</sub> → T <sub>2g</sub> (F) <sup>4</sup> T <sub>1g</sub> → <sup>4</sup> A <sub>2g</sub> (F) I N C T	Square planar
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Cu]	1.9	12600 17980 23475	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>2g</sub> I N C T I N C T	Square planar

### X-ray diffraction study

The X-ray diffractogram of a representative metal complex Mn(II) was scanned in the range 10-80° at wavelength 1.54 Å (Fig. 3). The diffractogram and associated data depict 2θ values for each peak, relative intensity and inter planar spacing (d-values). The diffractogram of Mn(II) complex showed fourteen reflections with maxima at 2θ (68.61°) corresponding to d value 1.36 Å. The X-ray diffraction pattern of the complex with respect to major peaks having relative intensity greater than 10 % have been indexed by using computer programme[22]. The above indexing method also yields Miller indices (hkl), unit cell parameters and volume. The unit cell of Mn(II) complex yielded values of lattice constants, a = 7.59 Å, b = 7.64 Å, c = 8.12 Å and unit cell volume, V = 471.24 (Å)<sup>3</sup>. In concurrence with these cell parameters of Mn(II) complex, the condition a ≠ b ≠ c and α = β = γ = 90° required for the compound to be orthorhombic lattice type. The diffractogram of Fe(III) complex shows eight reflections with maxima at 2θ = 61.81 corresponding to d value 1.50 Å. The observed values of lattice constants, a = 4.71 Å, b = 4.91 Å, c = 5.40 Å and α = β = 90° γ = 120°. Fe(III) complex satisfies the condition a ≠ b ≠ c and α = β = 90° γ = 120° required for the compound to be monoclinic lattice type. The diffractogram of Ni(II) complex shows eight reflections with maxima at 2θ = 62.38 corresponding to d value 1.43 Å. The observed values of lattice constants, a = 9.70 Å, b = 9.70 Å, c = 6.63 Å and α = β = γ = 90° Ni(II) complex satisfies the condition a = b ≠ c and α = β = γ = 90° required for the compound to be tetragonal lattice type. The diffractogram of Cu(II) complex shows thirteen reflections with maxima at 2θ = 31.00 corresponding to d value 2.88 Å. The observed values of lattice constants, a = 7.23 Å, b = 7.48 Å, c = 6.31 Å and α = β = 90° γ = 120° Cu(II) complex satisfies the condition a ≠ b ≠ c and α = β = 90° γ = 120° required for the compound to be monoclinic lattice type. The above values indicate that the metal

complex has orthorhombic crystal system. Experimental density value of the complex was determined by using specific gravity method [23].

Fig.III. The proposed structure of the complexes

a. when  $M = \text{Cu(II)}$  and  $\text{Fe(III)}$

b. when  $M = \text{Mn(II)}$  and  $\text{Ni(II)}$

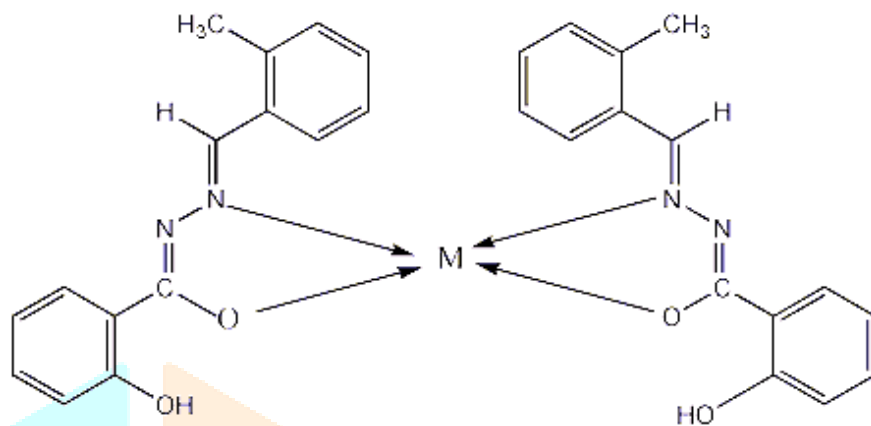


Fig.III.a

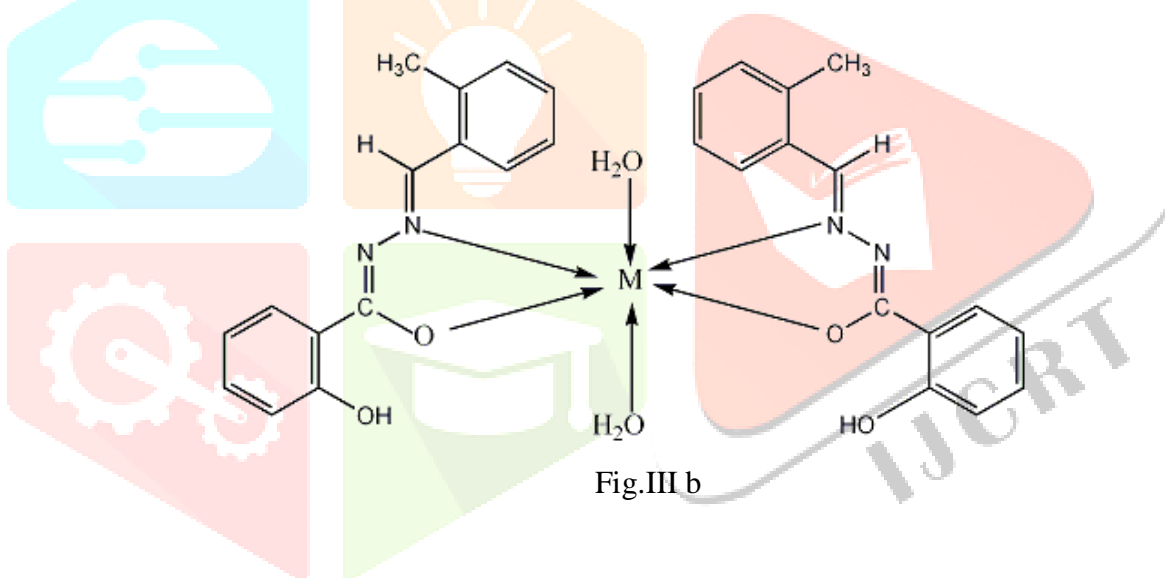
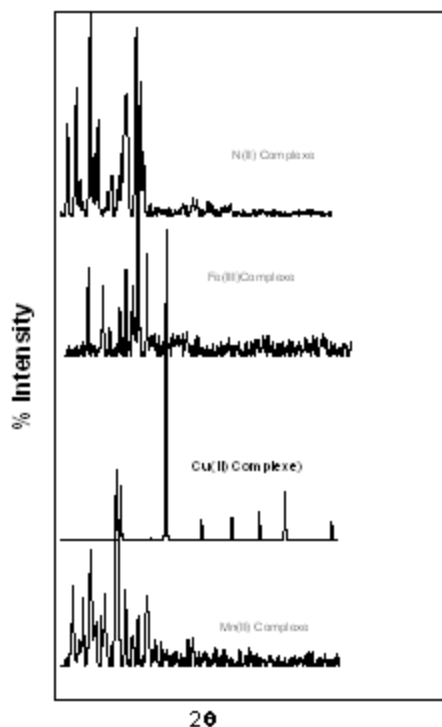


Fig.III b



**Fig. 3.** X-ray diffractogram of Mn(II), Cu(II), Fe(III) and Ni(II) complexes.

### **Thermal analysis.**

The simultaneous TG/DT analysis of metal complexes was studied from ambient temperature to 1000 °C in nitrogen atmosphere using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as reference. The thermogram curve of Cu(II) metal complex shows mass loss 5.7 % (calcd.5.85 %) representative in the range 160-230°C. An endothermic peak in this region  $\Delta T_{\max} = 120^{\circ}\text{C}$  indicating presence of two coordinated water molecules[10]. The TG curve of Cu(II) complex, then show slow decomposition from 270°C to 480°C with mass loss 52.10% (calcd.51.20%). An exothermic peak  $\Delta T_{\max} = 310^{\circ}\text{C}$  in DTA may be attributed to the decomposition of non coordinated part of ligand. The second slow step from 510 to 790°C with mass loss of 21.20% (calcd.21.50%) corresponds to decomposition of coordinated part of ligand. A broad endotherm  $\Delta T_{\max} = 740^{\circ}\text{C}$  in DTA is observed for this. The mass of final residue 15.90 % (calcd.16.10 %) corresponds to stable CuO. All other metal complexes show similar behavior.

### **Kinetic calculations**

The kinetic and thermodynamic parameters *viz* order of reaction (n), energy of activation ( $E_a$ ), pre-exponential factor (z), entropy of activation ( $\Delta S$ ) and free energy change ( $\Delta G$ ) together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Horowitz-Metzer (HM) approximation method and Coats-Redfern integral method[24] [34]. The data is given in Table III. The results show that the value obtained by two methods is comparable. The calculated value of energy of activation of the Co(II) and Ni(II) complexes is relatively low indicating the autocatalytic effect of metal ion on thermal decomposition of the metal complex[25,26]. The negative value of entropy of activation indicates that the activated complex is more ordered than the reactant and that the reaction is



slow. The more ordered nature may be due to the polarization of bonds in activated state which might happen through charge transfer electronic transition.

Table III. The kinetic parameter of metal complexes calculated by the methods Horowitz-Metzger (HM) and Coats-Redfern (CR).

Complex	Step	n	Method	E <sub>a</sub> (kJmol <sup>-1</sup> )	Z S <sup>-1</sup>	ΔS# JK <sup>-1</sup> mol <sup>-1</sup>	ΔG# (kJmol <sup>-1</sup> )	Corelation coefficient (r)
Ni(II)	I	1.3	HM	12.25	3.7 × 10 <sup>5</sup>	-175	50.23	0.9989
			CR	16.45	4.2 × 10 <sup>4</sup>	-195	47.25	0.9990
	II	1.1	HM	21.45	3.7 × 10 <sup>3</sup>	-161	61.47	0.9989
			CR	16.15	5.2 × 10 <sup>4</sup>	-198	52.40	0.9989
Cu(II)	I	1.3	HM	24.47	6.6 × 10 <sup>6</sup>	-214	41.35	0.9988
			CR	22.40	8.2 × 10 <sup>4</sup>	-242	38.11	0.9995
	II	1.1	HM	11.35	8.6 × 10 <sup>5</sup>	-236	40.41	0.9992
			CR	14.40	6.2 × 10 <sup>4</sup>	-283	39.33	0.9995

### Antimicrobial activity

The antimicrobial activity of ligand and its metal complexes were tested *in vitro* against bacteria such as *Staphylococcus aureus* and *Escherichia coli* by paper disc plate method [27]. The compounds were tested at the concentration 500 and 1000 μg cm<sup>-3</sup> in DMF and compared with known antibiotics *viz* ciproflaxin (Table IV). For fungicidal activity, compounds were screened *in vitro* against *Aspergillus Niger* and *Trichoderma* by mycelia dry weight method [28] with glucose nitrate media. The compounds were tested at the concentration 250 and 500 μg cm<sup>-3</sup> in DMF and compared with control (Table V). From Table 4 and 5, it is clear that the inhibition by metal chelates is higher than that of a ligand and metal salts. The results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes [17,20]. The metal chelates have higher antibacterial activity than the corresponding free ligand and control against the same microorganism under identical experimental conditions. Such enhanced activity of metal chelates is due to increased lipophilic nature of the metal ions in complexes [29]. The increase in activity with concentration is due to the effect of metal ions on the normal process.

The microbial results are presented in Tables IV and V. In case of antibacterial studies it was observed that, the ligand is moderately active towards *Staphylococcus* and less active towards *E.Coli*. Comparison of activities of the ligand and its metal chelates showed that the copper complex is approximately found to be more active than the ligand Cu(II) complex show higher activity than other metal complexes. The cobalt and manganese complexes show the activity comparable to copper complex. However Fe(III) and Ni(II) complexes show less activity against *E.Coli* and *Staphylococcus*. The activity of these complexes follow the order Cu>Co>Mn>Ni>Fe. This high antibacterial activity of ligand and its metal complexes can be explained on the basis of Overtone's concepts and Tweedy's concept. According to these concepts, chelation tends to make a liquid more potential bacterial agent. The increased activity depends upon chelation is attributed to the positive charge of the metal partially shared with donor atom present on

the ligand and possible  $\pi$ -electron delocalization over the whole chelate. This in turn, increases the lipophilic character of the metal chelate and favours its permeation through the lipid layer of the bacterial membranes. Inhibition was found to increase with increasing concentration of metal complex.

Investigation of antifungal activity of the ligand and its metal complexes revealed that all metal chelates are more fungi toxic than their parent ligand *Table V*. The antifungal activity of the ligand is found to enhance several times on being coordinated with metal ions. The activity of these complexes follow the order of *Aspergillus Niger*  $Cu > Ni > Mn > Fe$  and that of *Trichoderma*  $Cu > Ni > Mn > Fe$ .

As a result, metal complexes of Cu(II) and Mn(II) show good antibacterial and Cu > Ni show good antifungal activity, whereas Fe(III) complex shows comparatively less activity.

*Table IV*. Antibacterial activity of ligand and its metal complexes.

Test Compound	inhibition zone (mm)			
	<i>E. Coli</i>		<b>Staphylococcus</b>	
	500ppm	1000ppm	500ppm	1000ppm
<i>Ciproflaxin</i>	29	32	31	35
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> ] (H <sub>2</sub> L)	12	15	13	17
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Mn]	17	20	16	19
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Fe]	12	16	13	17
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Ni]	14	16	12	18
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Cu]	17	24	16	20

*Table V*. Antifungal activity of compounds yield of mycelial dry weight in mg (% inhibition)

Test Compound	<b>A.niger</b>		<b>Trichoderma</b>	
	250ppm	500ppm	250ppm	500ppm
Control	79	79	70	70
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> ] H <sub>2</sub> L	61 (22)	27 (65)	40 (42)	20 (72)
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Mn]	53 (32)	15 (81)	32 (54)	08 (87)
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Fe]	50 (36)	20 (74)	32 (54)	07 (90)
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Ni]	45 (43)	14 (82)	21 (70)	05 (93)
[C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Cu]	41 (48)	12 (84)	23 (68)	05 (93)

## CONCLUSIONS

In the light of above discussion we have proposed square-planar geometry for Cu(II) and Ni(II) complex and octahedral geometry for Mn(II) and Fe(III) complexes. On the basis of the physico-chemical and spectral data discussed above, one can assume that the ligand behave as monobasic, ON bidentate, coordinating via amide oxygen and azomethine nitrogen as illustrated in Fig.4. The complexes are biologically active and are having enhanced antimicrobial activities compared to free ligand. Thermal study reveals thermal stability of metal complexes. The XRD study suggests monoclinic crystal system for Cu (II) and Fe(III) complex, Mn(II) complex show orthorhombic crystal structure, and Ni(III) shows tetragonal crystal structure.

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