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Synthesis, Characterization and Antimicrobial studies of Some transition metal complexes of N-(5-chloro-2-hydroxyacetophenone)-N'-(2-hydroxyacetophenone)-ethylenediamine

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ABSTRACT

A new series of Mn(II), Co(II), Ni(II), Cu(II), Cr(III) and Fe(III) complexes with tetradentate unsymmetrical Schiff base ligand derived from o-hydroxyacetophenone, 5-chloro-2-hydroxyacetophenone and ethylenediamine have been reported. The complexes have been characterized by elemental analyses, magnetic susceptibility measurements, electronic and infrared spectra and thermogravimetric analyses. The ligand and its complexes were screened for their antimicrobial activities against the bacteria Staphalococcus aureus, Bacillus Subtilis, Salmonella typhimurium and Escherichia coli and fungi Aspergillus oryzae and Fusarium species. The results indicated that the complexes exhibited good antimicrobial activities.

Keywords: Unsymmetrical Schiff base, Transition metal complexes, Antimicrobial activity.

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INTRODUCTION

Metal complexes of Schiff base derived from aromatic carbonyl compounds have been widely studied because of the versatility of their steric and electronic properties, which can be modified by selecting the suitable amine precursors and ring substituent [1]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest for their ability to possess unusual configurations, structural lability and their sensitivity to molecular environments [2-4]. Amongst them, tetradentate Schiff bases with N_2O_2 donor atoms are well known to coordinate with various metal ions and have attracted great deal of interest due to their rich co-ordination chemistry [5, 6]. Many symmetrical tetradentate bis-type Schiff base ligands, usually obtained by the condensation of 1, 2-diamines with *o*-hydroxy aldehyde/ketone have been prepared and studied intensively. However much less attention has been focused on unsymmetrical tetradentate Schiff base derived from 1, 2-diamines and different aldehyde/ketones and allows for tuning of electronic properties and steric effects on one side and/or the other side of the complex. Unsymmetrical complexes are very important in biological systems as well as in industrial catalysis and interesting also from theoretical point a view. Unsymmetrical Schiff bases are very important as they can bind one, two or more metal centers, involving various coordination modes [7]. A search of the literature revealed that no work has been done on the transition metal complexes of unsymmetrical Schiff base derived from diamines, *o*-hydroxyacetophenone and 5-chloro-2-hydoxyacetophenone. Therefore, a new unsymmetrical Schiff base ligand derived from ethylenediamine, *o*-hydroxyacetophenone and 5-chloro-2-hydroxyacetophenone and its transition metal complexes are synthesized and characterized.

MATERIALS AND METHOD

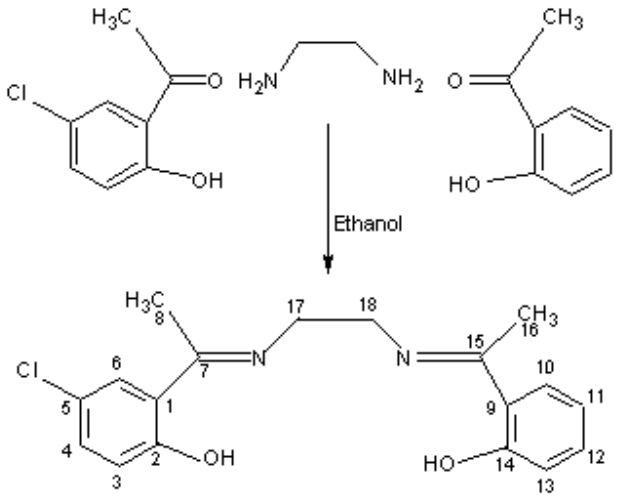
All chemicals used were of analytical grade and were used without purification. *o*-hydoxyacetophenone and ethylenediamine were obtained from Merck and S. D. fine chemicals. 5-chloro-2-hydoxyacetophenone was prepared according to the literature method [8].

The microanalyses of carbon, hydrogen and nitrogen were performed on a Carlo Erba 1108 elemental analyzer at Central Drug Research Institute (CDRI), Lucknow, India. The metal contents of the complexes were determined by standard methods after decomposing the organic matter with a mixture of $HClO_4$, H_2SO_4 and HNO_3 (1:1.5:2.5). The infrared spectra of ligand and its complexes were recorded on Perkin-Elmer spectrophotometer 597 as KBr pellets at SAIF, Panjab University, Chandigarh, India. The ^1H NMR and ^{13}C NMR spectra of ligand were measured in $CDCl_3$ using TMS as internal standard on Bruker Auance-II 400 NMR spectrometer

at SAIF, Panjab University, Chandigarh, India. Mass spectrum of ligand was recorded on Mass Spectrometer Jeol SX-102(FAB) at CDRI, Lucknow**,** India. Magnetic susceptibilities were determined on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were calculated from Pascal's constants. Thermograms of the complexes were recorded on a Metzsch STA 409 thermal analyzer in the temperature range 40-700^{O}C with a heating rate of 20^{O}C /min. The electrical conductivity was measured in pellet form using Zentech resistivity meter. Diffuse reflectance spectra of the solid complexes suitably diluted with magnesium carbonate were recorded on a Varien Cary 5E UV-NIR spectrophotometer at RSIC, IIT Madras, Chennai, India. SEM images of complexes were recorded at VNIT, Nagpur, India.

SYNTHESIS OF N- (5- CHLORO- 2-HYDROXYACETOPHENONE) -N'- (2-HYDROXYACETOPHENONE)- ETHYLENEDIAMINE (H_2L)

Equimolar amount of 5-chloro-2-hydroxyacetophenone (3.31 g, 2 mmol.) and *o*-hydroxyacetophenone (2.732 g, 2 mmol) were dissolved in absolute ethanol (25mL) with stirring and kept for 30 min in an ice bath. To this resulting solution, an ethanolic solution of ethylenediamine (1.2 g, 2 mmol) was added drop wise with continuous stirring .The resulting yellow solid obtained was filtered, washed with ethanol and crystallized from ethanol and air dried. TLC studied on silica gel confirmed the formation of only one compound. Yield = 82.54%.



Scheme 1: Synthesis of N-(5-chloro-2-hydroxyacetophenone)-N'-(2-hydroxyacetophenone)-ethylenediamine (H_2L)

Synthesis of Complexes

Complexes of Mn(II), Co(II), Ni(II), Cu(II), Cr(III) and Fe(III) with this ligand were synthesized using chloride salts of these metals. Equimolar quantity of ligand and desired metal chloride salt

was dissolved separately in minimum quantity of DMF (25mL). Both the solutions were filtered and mixed in hot condition. The resulting mixture was refluxed for 1h on sand bath. The pH of the reaction mixture was adjusted to 7.5-8.00 by adding 10% alcoholic ammonia solution and resulting solution was further refluxed for 3 h. The resulting colored product so obtained was filtered, washed well with DMF and hot ethanol and dried over calcium chloride in a desiccator.

Biological Assay

The antibacterial activities of the ligand and the complexes have been carried out against the bacteria *Staphalococcus aureus*, *Bacillus Subtilis*, *Salmonella typhimurium* and *Escherichia coli* using nutrient agar medium by the disc diffusion method. The compounds were tested at the concentration 100, 200 and 300 ppm in DMSO was used for the studies and compared with standard (Streptomycin). These discs were placed on the already seeded plates and incubated at 35^0C for 24h. The diameter (mm) of the inhibition zone around each disc was measured after 24h.

The antifungal activity was evaluated by the same disc diffusion method using potato dextrose agar medium containing starch 20g. Dextrose 20g and agar-agar powder 15g dissolved in 1000 mL distilled water. Same concentrations of compounds were used and compare with standard. The organisms used were *Aspergillus oryzae* and *Fusarium species.* The fungicidal activity of the compounds was recorded after 7 days.

RESULTS AND DISCUSSION

Unsymmetrical Schiff base ligand N-(5–chloro-2-hydroxyacetophenone)-N'-(2-hydroxyacetophenone)-ethylenediamine (H_2L) was prepared by refluxing appropriate acetophenone and ethylene diamine as per Scheme 1. The ^{1}H NMR spectrum of the ligand exhibits signals at 12.1 and 15.9 ppm, due to the phenolic protons [9]. The spectrum also exhibits multiplets in the range 6.8-7.54 ppm, due to aromatic protons. The singlet signals at 2.4 and 3.99 ppm were observed due to methyl and ethylene protons. The ^{13}C NMR spectrum of ligand shows chemical shift for C_{17} and C_{18} of =N-CH_2-CH_2-N= at 50.15 and for imine group –N=C< at 171.89 and 172.72 [10]. The IR spectrum of the ligand showed band at 3057cm^{-1} assigned to the hydrogen bonded O-H stretching. The bands present at 1613 and 1290 cm^{-1} were assigned to the C=N and C-O stretchings, respectively [11]. Mass spectrum of ligand exhibits two peak at m/z 331 $(M)^+$ and 333 $(M+2)^+$. The elemental analysis and spectral data are in consistent with the formula of the ligand ($C_{18}H_{19}O_2N_2Cl$). The reaction of the ligand (H_2L) with desired metals in 1:1 molar ratio in DMF gives unsymmetrical coordination compounds. The colors, spectral and micro-

analytical data of the complexes are listed in Table 1. The complexes are colored solid, air stable, insoluble in most of the organic solvents, but easily soluble in DMSO.

Anal. Calc. for $C_{18}H_{19}O_2N_2Cl$ (%): C, 65.35; H, 5.79; N, 8.47. Found: C, 64.36; H, 5.26; N, 8.49, m.p., 130^{O}C. UV/Vis: 327 nm (n→π*), 248 nm (π→ π*). IR (KBr, cm^{-1}) 3057 (O-H stretching of hydrogen bonded), 1613 (C=N stretching) 1290 (C-O phenolic stretching), ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 2.40 (s, 6H, Ar-CH_3), 3.99 (s, 4H, N-CH_2), 6.8- 7.5 (m, 7H, ArH), 12.1 (s, 1H, Ar-OH), 15.9 (s, 1H, Ar-OH). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm) 14.76(C8, C16), 50.15 (C17, C18), 117.41 (C13), 118.44 (C9), 119.69 (C11), 120.05 (C1), 121.9 (C3), 127.59 (C6), 128.12(C5), 132.28 (C6, C10), 132.35 (C4, C12), 161.72 (C2), δ = 163.04 (C14), 171.89 (C15) and 172.72 (C7). FAB-MS m/z 331 (M^+), 333 $(M+2)^+$.

IR spectra of complexes

In order to give conclusive idea about the structure of the metal complexes, the main IR bands were compared with those of free ligand. The Schiff base exhibits a medium intensity band at ~ 3057 cm^{-1} due to intramolecular hydrogen bonded υ (O-H). The absence of this band in the complexes indicates the deprotonation of the phenolic group and coordination of the oxygen atom to the metal ion. The ligand shows the υ (C=N) stretching band at 1613 cm^{-1} which shifted to lower frequency 1611-1564 cm^{-1} in the complexes indicating the involvement of the azomethine nitrogen in coordination [12]. This is further supported by the shift of the υ (C-O) (phenolic) band from 1290 cm^{-1} of the free ligand to 1339-1295 cm^{-1} in the spectra of complexes, indicating the coordination of phenolic oxygen atom to the metal ion [13]. This shift to higher frequency is expected due to the main tenure of ring currents arising from electron delocalization in the chelate ring. The bonding through oxygen and nitrogen is further supported by the appearance of new bands in the region 622- 459 cm^{-1} assigned to υ (M-O) and υ (M-N) bending vibrations, respectively [14]. The IR spectra of Fe(III), Cr(III), Mn(II), Co(II) and Cu(II) complexes show a strong band in the 3240-3560 cm^{-1} region, indicating the presence of coordinated water in these complexes. The presence of coordinated water is further confirmed by the appearance of a non-ligand band in the 830-850 cm^{-1} region, assignable to the rocking mode of water. The presence of coordinated water was also established and supported by TG analysis of complex. On the basis of these results, it can be concluded that in the complexes, the Schiff base behaves as dibasic tetradentate ligand.

Table 1. Analytical and spectral data of ligand and its complexes.

Compound	Color	% of yield	Dec. temp/ M. P. (^{O}C)	Elemental Analysis (%Found/Calcd.)					IR cm^{-1}			
				C	H	N	Cl	M	υC=N)	υ (C-O)	υ (M-O)	υ (M-N)
(H_2L)	Yellow	82.54	130	64.36 (65.35)	5.26 (5.79)	8.49 (8.47)	10.54 (10.57)	-	1613	1290	-	-
[$MnL(H_2O)_2$]	Copper leaf	68.41	>300	51.26 (51.50)	4.98 (5.01)	6.69 (6.68)	8.42 (8.46)	13.04 (13.10)	1600	1313	622	517
[$CoL(H_2O)_2$]	Ming Red	61.82	>300	50.96 (51.01)	4.94 (4.96)	6.64 (6.61)	8.33 (8.38)	13.88 (13.92)	1564	1339	551	493
[NiL]	Orange Vision	63.59	>300	55.68 (55.79)	4.38 (4.39)	7.25 (7.23)	9.14 (9.17)	15.12 (15.15)	1578	1328	516	473
[$CuLH_2O)_2$]	Maroon	61.58	>300	50.39 (50.46)	4.89 (4.91)	6.55 (6.54)	8.27 (8.29)	14.81 (14.85)	1611	1329	516	482
[CrLCl(H_2O)]	Sandstone	62.82	>300	51.81 (51.86)	5.01 (5.04)	6.77 (6.72)	8.49 (8.52)	12.46 (12.48)	1602	1315	523	500
[FeLCl (H_2O)]	Coffee	67.79	>300	49.28 (49.33)	4.33 (4.34)	6.42 (6.39)	16.21 (16.22)	12.72 (12.76)	1603	1295	602	459

Table 4. Antimicrobial activities of ligand and its complexes.

Compound	Diameter of inhibition zone (mm) (Concentration in ppm)																	
	Antibacterial Screening Data												Antifungal Screening Data					
	Staphalococcus aureus			*Bacillus Subtilis*			*Salmonella typhimurium*			*Escherichia coli*			*Aspergillus oryzae*			*Fusarium species*		
	100	200	300	100	200	300	100	200	300	100	200	300	100	200	300	100	200	300
LH_2	6	6	7	6	7	8	7	7	9	6	9	10	-	-	6	-	6	7
[$MnL(H_2O)_2$]	-	7	10	7	8	9	-	7	10	8	10	13	-	6	7	7	7	9
[$CoL(H_2O)_2$]	-	7	16	7	9	12	7	8	9	6	8	10	6	6	8	7	8	10
[NiL]	8	9	11	6	8	13	7	9	11	7	10	12	-	-	7	-	6	8
[$CuL(H_2O)_2$]	6	8	9	6	6	8	-	6	8	-	-	8	6	7	9	6	6	8
[CrLCl(H_2O)]	9	11	12	-	6	7	8	10	12	7	11	11	-	6	7	-	7	8
[FeLCl(H_2O)]	10	10	12	8	8	11	7	8	12	6	8	12	6	8	9	8	9	11
Standard	10	13	17	8	10	14	11	14	18	9	12	15	7	8	10	8	10	13

Magnetic and Electronic spectral studies

The magnetic and electronic spectral data of the complexes are given in Table 2.

Table 2. Magnetic and electronic spectral bands of complexes and their assignments

Compound	μ_{eff}	Bands (nm)	Assignment	Geometry
$[MnL(H_2O)_2]$	5.80	700	$^6A_{1g} \rightarrow {}^4T_{1g}$ (^4G)	Octahedral
		539	$^6A_{1g} \rightarrow {}^4T_{2g}$, $^4A_{1g}$ (^4G)	
		368	$^6A_{1g} \rightarrow {}^4Eg$ (^4D)	
$[CoL(H_2O)_2]$	4.75	755	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	Octahedral
		531	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
		405	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
[NiL]	Diamagnetic	800	$^1A_{ig} \rightarrow {}^3A_{2g}$	Square planer
		575	$^1A_{1g} \rightarrow {}^1A_{2g}$	
		370	$^1A_{1g} \rightarrow {}^1B_{1g}$	
$[CuLH_2O)_2]$	2.03	806	$^2B_{1g} \rightarrow {}^2A_{1g}$	Distorted octahedral
		581	$^2B_{1g} \rightarrow {}^2E_g$	
		358	LMCT	
[CrLCl(H_2O)]	3.84	800	$^4A_{2g} \rightarrow {}^4T_{2g}$ (F)	Octahedral
		593	$^4A_{2g} \rightarrow {}^4T_{1g}$ (F)	
		431	$^4A_{2g} \rightarrow {}^4T_{1g}$ (P)	
[FeLCl (H_2O)]	5.78	812	$^6A_{1g} \rightarrow {}^4T_{1g}$ (G)	Octahedral
		600	$^6A_{1g} \rightarrow {}^4T_{2g}$ (G)	
		356	$^6A_{1g} \rightarrow {}^4A_{1g}$ (G)	

The reflectance spectrum of Mn(II) complex exhibits three bands at 700, 539 and 368 nm, which are assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$ (^4G), $^6A_{1g} \rightarrow {}^4T_{2g}$, $^4A_{1g}$ (^4G) and $^6A_{1g} \rightarrow {}^4A_{1g}$, ^4Eg (^4D) transitions, respectively, in an octahedral symmetry [15]. The Mn(II) complex exhibits magnetic moment 5.80 B.M. is also in consistent with octahedral stereochemistry. The Co(II) complex showed three bands at 755, 531 and 405 nm which may be assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, respectively expected for an octahedral geometry [16]. The measured value of magnetic moment of 4.75 B.M. for Co(II) complex which lie in the range of octahedral compound. The electronic spectrum of Ni(II) complex exhibits bands at 800, 575 and 370 nm which may be due to $^1A_{ig} \rightarrow {}^3A_{2g}$, $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$, transitions, respectively and suggest square planer geometry [17]. The Ni(II) complex was found to be diamagnetic is also supporting its square planer geometry of complex [18]. The reflectance spectrum of Cu(II) chelates exhibited a broad band centered at 581 nm. The Cu(II) ion(d^9) split under the influence of the tetragonal distortion and the distortion can be such as to cause the three transitions. The Cu(II) complex display absorption bands at 806, 581 and 358 nm corresponding to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_g$ and charge transfer transitions, respectively for distorted octahedral geometry around Cu(II) ion [19]. The value of magnetic moment of Cu(II)

complex was found to be 2.03 B.M. which lie at the higher end of the range which confirm tetragonally distorted octahedral structure. Magnetic moment of chromium(III) complex was found to be 3.84 B.M. The electronic spectrum of chromium complex shows bands at 800, 593 and 431 nm which may be attributed to the $^4A_{2g} \rightarrow {}^4T_{2g}$ (F), $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) and $^4A_{2g} \rightarrow {}^4T_{1g}$ (P), transitions, respectively in an octahedral geometry [20]. The electronic spectrum of Fe(III) complex exhibits bands at 812, 600 and 356 nm assignable to $^6A_{1g} \rightarrow {}^4T_{1g}$ (G), $^6A_{1g} \rightarrow {}^4T_{2g}$ (G) and $^6A_{1g} \rightarrow {}^4A_{1g}$ (G) transitions, respectively expected for Fe(III) ion in octahedral environment [21]. The Fe(III) complex has magnetic moment 5.78 B.M. This value is within the range expected for high spin magnetically dilute Fe(III) complex.

Thermogravimetric analysis

Thermal decomposition studies of complex have been carried out as to corroborate the information obtained from the IR spectral studies to know the presence of water molecules in these complexes as well as to know their decomposition pattern. The complexes remain almost unaffected upto ~ 130^OC. An analysis of the thermogram of the complexes indicated that Mn(II), Co(II), Cu(II), Cr(III) and Fe(III) complexes show two step decomposition whereas Ni(II) complex shows only one step decomposition. The complexes of Cr(III) and Fe(III) show loss of one coordinated water molecule in the temperature range 140- 280^OC, whereas Mn(II), Co(II) and Cu(II) complexes losses their two coordinated water molecules in this range [% wt. loss obs/ calcd: Mn(II): 16.58/ 15.82, Co(II): 16.23/ 15.69 and Cu(II): 16.42/ 15.52]. The anhydrous complexes remain stable upto ~ 310^OC and thereafter a rapid loss in weight has been observed presumably due to decomposition of organic constituents of the complex molecule as indicated by the step fall in the percentage weight loss. The decomposition continues upto ~ 650^OC in each complex as indicated by the consistency in weight in the plateau of the thermogram. The kinetic and thermodynamic *viz* the energy of activation (Ea), frequency factor (Z), entropy change ($-\Delta S$) and free energy change (ΔF) for the non-isothermal decomposition of complexes have been determined by employing Horowitz-Metzger method [22] and 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 reactant and that the reactions were slow. The more ordered nature may be due to the polarization of bonds in the activated state, which might occur through charge transfer transitions.

Table 3. Electrical conductivity and Thermal decomposition data of complexes

Complex	Electrical Conductivity ($\Omega^{-1}cm^{-1}$)	Half Decomposition Temp (^{O}C).	Activation Energy Ea $kJmol^{-1}$	Frequency factor Z sec^{-1}	Entropy change ($-\Delta S$) $JmolK^{-1}$	Free energy change (ΔF) $kJmol^{-1}$
$[MnL(H_2O)_2]$	4.03×10^{-9}	310.	21.97	311.08	202.80	84.84
$[CoL(H_2O)_2]$	7.71×10^{-9}	340	15.43	165.52	208.47	86.31
[NiL]	3.61×10^{-9}	381	21.55	218.34	206.70	100.30
$[CuL(H_2O)_2]$	5.14×10^{-10}	337	18.35	180.83	207.68	88.34
$[CrLCl(H_2O)]$	2.02×10^{-6}	410	32.15	112.36	212.69	119.35
[FeLCl (H_2O)]	5.90×10^{-6}	252	11.33	101.52	211.24	64.56

Scanning Electron Micrographs

The structural studies of the complexes are also supported by scanning electron microscopy (SEM) as shown in Figure 1a-c. The Scanning electron micrograph (SEM) of metal complexes indicates the presence of well-defined crystals free from any shadow of the metal ion on their external surface. The morphology and particle size of the unsymmetrical Schiff base metal complexes have been illustrated by SEM. Figure. 1 depict the SEM photograph of the synthesized Co(II), Ni(II) and Cr(III) complexes as representative example. There is a uniform matrix of the synthesized complexes in the pictograph, which leads to dealing with homogeneous phase material. Co(II) complex is ice ball shaped morphology with 2-2.5 µm particle size and ~ 2 µm pore size Figure.1a. A single phase formation of Ni(II) complex having fiber morphologies in the form of a bundle with particle size 2-3 µm and ~ 1.5 µm pore size is displayed in Figure.1b. However Cr(III) complex is rock like shape morphology with 2-3 µm particle size and ~ 2µm pore size Figure. 1c.

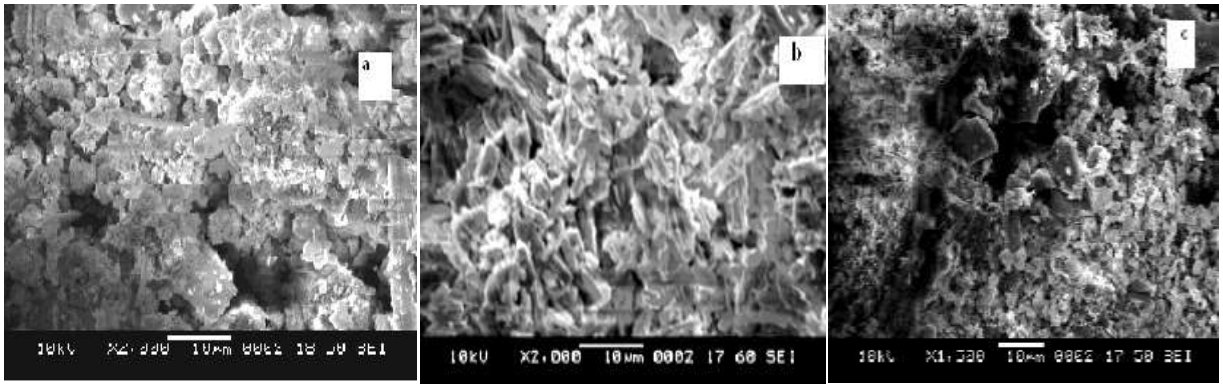


Figure. 1. SEM image of metal complexes

Electrical Conductivity

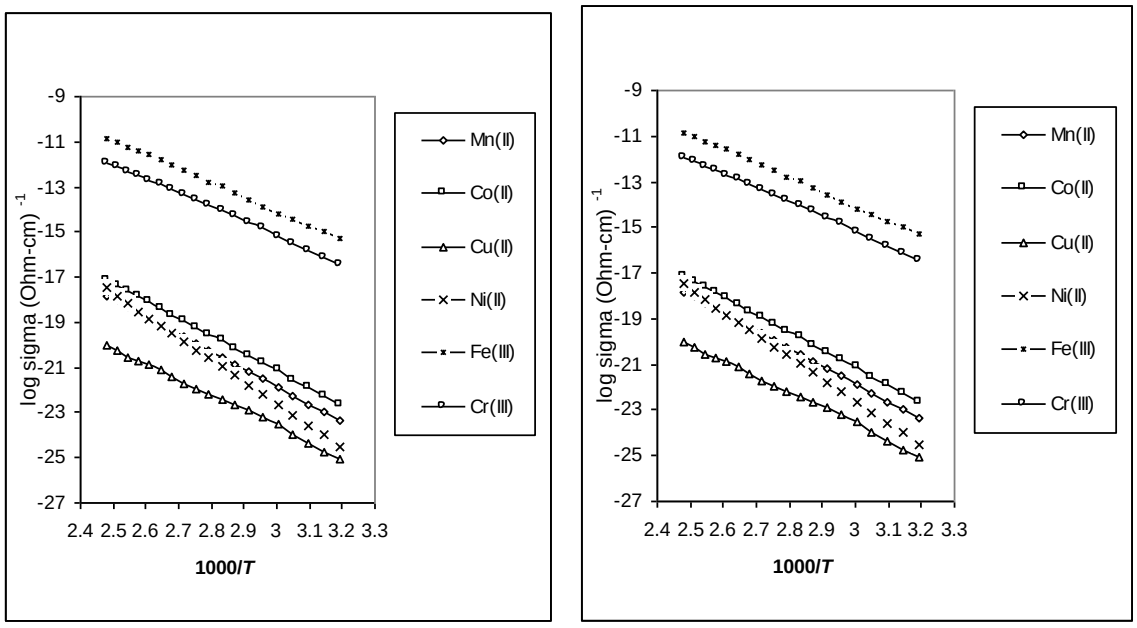


Figure 2. Plot of log sigma *vs.* 1000/*T*

The solid state electrical conductivity of the ligand and its complexes has been studied in the temperature range 313 K < T < 403 K using the two-probe method (Table 3). The value of the solid-state electrical conductivity of the complexes were found to be in the range of 10^{-10}-10^{-6} $\Omega^{-1}cm^{-1}$ and they are semiconductor in nature [23], because their conductivity increases with increase in temperature and decreases upon cooling over the studied temperature range. The data obtained obeyed the Arrehenius relation over the studied temperature range 40-130^{O}C

$\sigma = \sigma_0 \exp(- Ea/ kT)$..

Where σ_0, Ea and k a and k are conductivity constants, activation energy and the Boltzman constant, respectively. The plots of log σ vs. 1000/T (Figure 2) for all the compounds are found to be linear over the entire temperature range. The activation energy of the compounds lays in the range 0.543-845 eV.

Antimicrobial Screening

The Schiff base and its metal complexes were screened for their antimicrobial activity against two strain Gram +ve bacteria (*Staphalococcus aureus*, *Bacillus subtilis*), Gram –ve bacteria (*Salmonella typhimurium*, *Escherichia coli*) and fungus (*Aspergillus oryzae*, *Fusarium species*). The antimicrobial screening results are given in Table 4 and comparison of ligand and its metal complexes antimicrobial screening data depicted in Figure. 3. These observations show that the most of the complexes are quite active as compared to free ligand [24, 25]. The increased activity of the metal chelates can be explained on the basis of chelation theory [26]. It is known that chelation tends to make the ligand act as a more powerful and potent bactericidal agent, thus killing more

of the bacteria than the ligand. It is observed that, in the complex, the positive charge of the metal is partially shared with the donor atoms present in the ligand and there is may be π-electron delocalization over the whole chelating. This increases the lipophilic character of the metal chelate and favors its permeation through the lipoid layer of the bacterial membrane. Generally it is suggested that the chelated complexes deactivate various cellular enzymes, which play vital role in various metabolic pathways of these organisms. Other factors such as solubility, conductivity and dipole moment which affected by the presence of metal ions, may also be possible reasons for increasing the biological activity of the metal complexes as compared to the corresponding ligand [27]. The biological activity of the ligand and its complexes was less than the standard used. The Co(II), Cr(III) and Fe(III) complexes exhibit good antibacterial activity against *Staphylococcus aureus* and *Bacillus subtilis*. Whereas Mn(II), Ni(II) and Fe(III) complexes show good activity against Escherichia coli. The fungicidal screening shows that Cu(II) and Fe(III) complexes are more effective against *Aspergillus oryzae*. However Mn(II), Co(II) and Fe(III) complexes are more effective against *Fusarium species*.

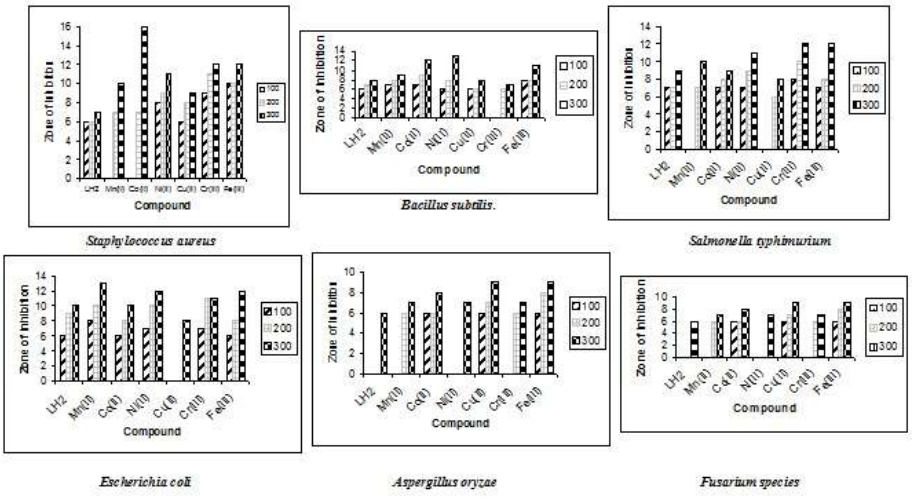


Figure. 3. Comparison of Antimicrobial screening data for ligand and its complexes

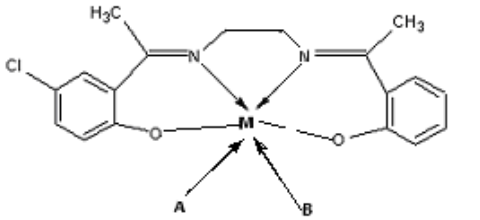
A- *Staphylococcus aureus,* B- *Bacillus subtilis,* C- *Salmonella typhimurium*

D- *Escherichia coli,* E- *Aspergillus oryzae,* F- *Fusarium species*

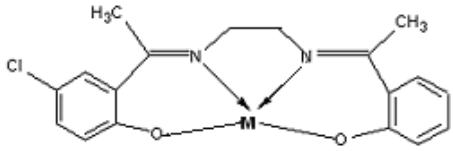
CONCLUSION

In the present paper coordination chemistry of a unsymmetrical Schiff base ligand, obtained from the reaction of *o*-hydroxyacetophenone, 5-chloro-2-hydroxyacetophenone and ethylenediamine, is described. Mn(II), Co(II), Ni(II), Cu(II), Cr(III) and Fe(III) complexes have been synthesized using above Schiff base ligand and characterized on the basis of analytical, magnetic and spectral

data. The Schiff base coordinates through its azomethine nitrogens and phenolic oxygens to the metal ion and act as a tetradentate ligand. All the complexes except Ni(II) and Cu(II) complexes exhibit regular octahedral geometry (Figure 4). Ni(II) and Cu(II) complexes indicate square planer and distorted octahedral geometry respectively. Thermal behavior, electrical conductivity and antimicrobial activity of all the complexes are investigated. All the complexes are semiconducting in nature. SEM image of the complexes indicate homogeneous phase material. It has been suggested that chelation/coordination enhance or suppress the biochemical potential of bioactive organic species.



A = B = H_2O (For M = Mn(II), Co(II) and Cu(II))
A = H_2O B = Cl (For M = Cr(III) and Fe(III))



M = Ni(II)

Figure 4. Proposed geometries of complexes

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