

Synthesis, Characterization and Biological Activity of Cr (III), Mn(III) And Fe(III) Complexes of Schiff Bases Ligands

A.D.Bansod

Department of Chemistry, Rajarshee Shahu Science College, Chandur Rly444904 (M.S.) India

Abstract

Metal complexes of Cr(III), Mn(III) and Fe(III) with symmetrical Schiff bases (derived from the *p*-phenylenediamine with 2-4 dihydroxyacetophenone or 2-5 dihydroxyacetophenone) have been prepared and characterized by physical-chemical methods. On the basis of electronic spectra and magnetic susceptibility measurement in conjugation with infrared spectra six coordinated octahedral structure have been proposed to Cr(III) and Fe(III) complexes, while Mn(III) complex may have a square pyramidal structure. Thermal stability of the complexes have been tested for their antibacterial activity against the bacteria *E. coli*, *Bacillus sp.*, *Staphylococcus* and *Pseudomonas* sp. The solid state conductivity of ligand and complexes were also measured in their compressed pellet in the temperature range 310-450 K and all complexes were found to be semiconducting in behaviour.

Key words: Schiff bases, Complexes, Biological activity

Introduction

The transition metal complexes with bidentate and tetradentate ligand containing both hard and soft donor groups, have been extensively in coordination and organometallic chemistry¹. Schiff bases containing polyfunctional groups not only produced stable metal complexes of transition, non-transition, inner-transition and actinide metal ion, but these ligands and their metal complexes have also played a significant role in the domains of stereochemistry, structure isomerism, magnetism, spectroscopy, kinetics and mechanisms of reactions, reaction of coordinated ligands, model system of biochemical interest, analytical chemistry, catalysis stabilizers, polymers, pigments and dyes. electro-optical display devices and agriculture²⁻⁴. In view of the growing interest in the biological and electrical properties of Schiff base complexes in this communication, synthesis, characterization, biological and electrical properties of Cr(III), Mn(III) and Fe(III) complexes containing dibasic tetradentate Schiff bases derived by condensing substituted acetophenones with *p*-phenylenediamine, has been reported.

Experimental and Methods

All of the reagents used were of analytical or chemical pure grade. Solvents were purified and dried according to standard procedures. The substituted acetophenones were prepared by Fridal-Craft reaction. Mn(OAc) 2H₂O was prepared by the reported method⁵.

Preparation of H₂L¹ and H₂L²

A hot ethanolic solution (10 mL) of *p*-phenylenediamine (0.01 mol) was added to a hot solution of 2-4 dihydroxyacetophenone or 2-5 dihydroxyacetophenone (0.02 mol) in 60 mL ethanol and the reaction mixture was refluxed for 2-3 h on a water bath. After reducing the solvents to *ca* 20 mL, it was kept overnight, the

separated solid was filtered, washed with ethanol and dried at ambient temperature. Finally both ligands were recrystallized from ethanol yield 70% m.p. 178 and 164^oC.

Synthesis of Complexes

The complexes were prepared by the reaction of the appropriate ligand with metal salts as follows.

To a hot ethanolic solution of appropriate ligands (H_2L^1 and H_2L^2) (0.01mol) a solution of the metal salt (0.01mol) in ethanol (25mL) was added with constant stirring. The reaction mixture was refluxed on a hot water bath for 3-4h. To this a few drops of alcoholic sodium acetate were added to improve the yield and further refluxed for one hour and left overnight. The prepared solid was filtered, washed with hot water and ethanol and dried at 80^oC in an electric oven. Yield 60-65%.

Elemental analyses were carried out using Carlo 1186 Perkin-Elmer-240CNH analyzer at CDRI Lucknow. ¹H NMR of ligands were recorded on a 300 MHz instrument using TMS as an internal standard. IR spectra were recorded with Perkin-Elmer FTIR-1601 spectrophotometer in the range 4000-400cm⁻¹. Diffuse reflectance spectra were recorded on a Carry 17D spectrophotometer in the range 350-1200nm. The magnetic measures were performed on a Gouy balance at room temperature using mercury tetrathiocyanato cobalt (II) as calibrating agents. Metal contents were determined gravimetrically/ volumetrically by literature methods⁶. Thermogravimetric analyses of the compounds were carried out on a simple manually operated thermo balance constructed in our laboratory. Instrument was calibrated using crystalline copper (II) sulphate pentahydrate run under dynamic air atmosphere with heating rate 10^oC min⁻¹. The antibacterial activity studies were carried out at department of Microbiology, Sant Gadge Baba Amravati University. The solid state conductivity was measured in their compressed pellet from over 310-420K temperature range by conventional two-probe method.

Results and discussion

The condensation of substituted with *p*-phenylenediamine in dry ethanol yielded the Schiff base H_2L^1 and H_2L^2 . Reaction of metal salts with Schiff base yielded the complexes. The analytical data given in Table 1 confirm the molecular formula for the new complexes formed. All the complexes are colored and are stable in air, non-hygroscopic and sparingly soluble in hot DMSO and DMF. The insolubility of the complexes in common organic solvents and their decomposition temperatures, indicate their polymeric nature. The ¹H NMR spectra of Schiff base signals δ 12.85, (C₂-OH), δ 10.44 (C₅-OH), δ 7.38 (Phenyl) and δ 3.25 (methyl) indicated the formation of Schiff bases. The downfield shift attributed to the existence of hydrogen bonding in Schiff base⁴.

The infrared spectra of Schiff base and of the corresponding complexes have been compared in order to fix mode of binding of the Schiff base ligands to the metal ions in the complexes. The Schiff bases show a strong band 1620-1610cm⁻¹, characteristic of the azomethine group. It is expected that the coordination of the nitrogen atom of the ligand to the metal ions would reduce the electronic density from ligands to the metal ions in the complexes. The Schiff base in the azomethine link would reduce the electronic density in the azomethine link and thus lower (C=N) frequency. In the infrared spectra of all complexes, the band is shifted to lower frequency region 1605-1595cm⁻¹ indicating the coordination of the Schiff base through nitrogen to metal ion⁵. A strong band observed at 1280-1265cm⁻¹ in the free Schiff base has been assigned to phenolic (C-O) stretching. On complexation, the band has been shifted to a higher frequency range (1305-1295cm⁻¹) indicating that the other coordinated to the Schiff bases in through the phenolic oxygen in all complexes. The ν (OH) absorption band at 3515cm⁻¹ ν (OH) at (C₅) and at 3300cm⁻¹ ν (OH) intramolecular H-bonded at (C₂) seen as broad band in the free ligands due to intermolecular H-bonded disappeared completely in the

complexes, indicating deprotonation of the phenolic protons prior to coordination which confirms that the phenolic oxygen is the second donor atom⁶⁻⁷. The infrared spectra of aceto complexes display two bands near $1620-1630\text{cm}^{-1}$ and $1425-1435\text{cm}^{-1}$ and these are assigned $\nu_{asym}(\text{CO}_2)$ and $\nu_{syn}(\text{CO}_2)$, respectively. The separation of these peaks by 195cm^{-1} indicates the monodentate coordination of acetato groups. A few medium band at about 3600cm^{-1} observed in the spectra of Cr(III) and Fe(III) complexes indicates the presence of either coordinated of lattice water molecule.

The diffusion spectra Cr(III) complexes show two at $12500-12700$ and $15384-15920\text{cm}^{-1}$. The band at $15384-15920\text{cm}^{-1}$ may be assigned to the ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{V}_1)$ transition. The weak band at $12000-12700\text{cm}^{-1}$ may be spin forbidden in nature and corresponds to ${}^4\text{A}_{2g} \rightarrow {}^2\text{E}_g$ transition. The room temperature magnetic moment (4.30 and 4.20 B.M.) of Cr(III) complexes is a little higher than the spin only value but still within the range required for octahedral stereochemistry⁸. The Mn(III) Complexes exhibits bands at $13970, 16810, 20090$ and 25525cm^{-1} , while are assigned ${}^5\text{B}_1 \rightarrow {}^5\text{B}_2, {}^5\text{B}_1 \rightarrow {}^5\text{A}_1, {}^5\text{B}_1 \rightarrow {}^5\text{E}$ and LMCT transition, respectively suggesting square pyramidal geometry. The Mn(III) complexes exhibits magnetic moments of 4.88 and 4.91 B.M., respectively corresponding to four paired electrons. The diffuse reflectance spectra of Fe(III) complex show that the d-d transition appear mostly as weak shoulder around at $18520-18540$ and $20000-20100\text{cm}^{-1}$ along with high energy bands at $21510, 22290$ and 25050cm^{-1} . The former two shoulders may be assigned to the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{D})$ transitions, respectively in an octahedral stereochemistry, while the latter high energy band may be the ligand bands admixed with the charge transfer process⁹. The observed magnetic moments at room temperature are 5.92 and 8.81 B.M. respectively, while are also within the range of high spin octahedral stereochemistry of the complexes⁹.

The thermal decomposition results revealed that the complexes mainly decompose in two stages. The weight loss calculations reveal that Cr(III) and Fe(III) complexes lose one water molecules (weight loss found 2.51 and 2.61g) during the first stage decompositions between temperature range $140-190^\circ\text{C}$. The Mn(III) complexes showed weight loss 4.51g at $230-235^\circ\text{C}$ equivalent to one acetate molecule per unit¹⁰. The second step of decomposition starts at 240°C for the former complexes whereas it starts at 260°C for the latter. This step in all the complexes may be due to the breakdown of the Schiff base subsequent removal of the constituents above 350°C . A gradual but continuous mass loss up to $600-700^\circ\text{C}$ occurs in all complexes and finally horizontal curves were observed corresponding to the final pyrolysis products $\text{Cr}_2\text{O}_3, \text{Fe}_2\text{O}_3$ and Mn_3O_4 respectively¹¹. The decompositions follows first order kinetic and activation energy (E_a) of all complexes lies between $18-35\text{kJmol}^{-1}$.

A close examination of the solid state conductance values (Table-1 and Fig 1-2) shows that the conductance in all the case increases with increasing temperature. At room temperature, the value less between 10^{-8} to $10^{-11}\Omega^{-1}\text{cm}^{-1}$. This shows that the conductivity of complexes is low at room temperature and increase regularly with increase in the temperature. The negative logarithm of conductivity for the complexes is found to be a linear function of reciprocal of temperature in the range studied, which indicates, their semiconducting nature. The electrical activation energies lies in between 0.34-0.72 eV, as calculated from Arrhenius plots¹².

Antimicrobial activities of the ligands and the complexes have been carried out, against the bacteria *E. coli, Bacillus sp., Staphylococcus and Pseudomonas sp.* using nutrient agar medium by the disc diffusion method. The test solution were prepared in DMSO to a final concentration of 0.01% and 0.02% and soaked in filter paper of 5mm diameter and 1 mm thickness. These discs were placed on the already seeded plates and incubated at 35°C for 24 hours¹³. The diameter (mm) of the inhibition zone around each disc was

measured after 24 hours and results are listed (Table-2 and Fig.3) Streptomycin was used as standard. It was observed from these studies that the metal complexes have a higher activity than the free ligands against the same microorganism under the identical experimental conditions. The mode of action of the complexes may involve the formation of hydrogen bonds involving the azomethine group with microbial or ribosomes of microbial cells resulting in interference with normal cell processes. The toxicity increases with increasing concentration of the complexes¹⁴⁻¹⁵.

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Table -1 Analytical and physical data of complexes

Compound	Colour	Decomp.Temp. (⁰ C)	Analysis Found		Electrical Conductivity ($\Omega^{-1}\text{cm}^{-1}$)	Activation Energy (eV)
			N	M		
H ₂ L ¹	Yellow	180	7.40 (7.48)	---	6.52x10 ⁻⁹	0.62
[CrL ¹ (Cl)H ₂ O]	Grey	305	5.02 (5.45)	9.12 (9.96)	9.25x10 ⁻⁹	0.42
[MnL ¹ OAc	Pale Brown	310	5.68 (5.78)	10.82(11.08)	2.45x10 ⁻⁹	0.54
[FeL ¹ (Cl)H ₂ O]	Black	312	4.92 (5.41)	9.82 (10.00)	6.24x10 ⁻⁹	0.68
H ₂ L ²	Yellow	189	7.38 (7.48)	--	3.45x10 ⁻⁸	.072
[CrL ² (Cl)H ₂ O]	Greenish Brown	310	5.00 (5.45)	9.10 (9.93)	2.18x10 ⁻⁹	0.72
[MnL ² OAc	Brown	320	5.59 (5.74)	9.89 (110.8)	7.28x10 ⁻⁹	0.39
[FeL ² (Cl)H ₂ O]	Black	315	5.18 (5.41)	9.75 (10.01)	6.25x10 ⁻⁹	0.34

Table -2 Antimicrobial data of ligand and their complexes.

Compound	<i>E coli</i> (mm)	<i>Bacillus sp</i> (mm)	<i>Pseudomonous</i> sp.(mm)	<i>Staphylocous</i> (mm)
H ₂ L ¹	6.8	5.6	6.7	6.9
CrL ¹	9.12	8.10	9.11	9.10
MnL ¹	10.11	10.13	12.13	10.12
FeL ¹	9.11	8.12	9.12	11.12
H ₂ L ²	8.10	6.7	6.9	7.9
CrL ²	9.12	10.11	12.14	10.11
MnL ²	11.14	10.14	11.19	10.12
FeL ²	10.12	12.14	12.13	10.13
Streptomycin	18.21	20.23	18.21	18.22

Fig .1 : Solid State Conductivity of H₂L¹ and Cr(III), Mn(III) and Fe(III) Complexes .

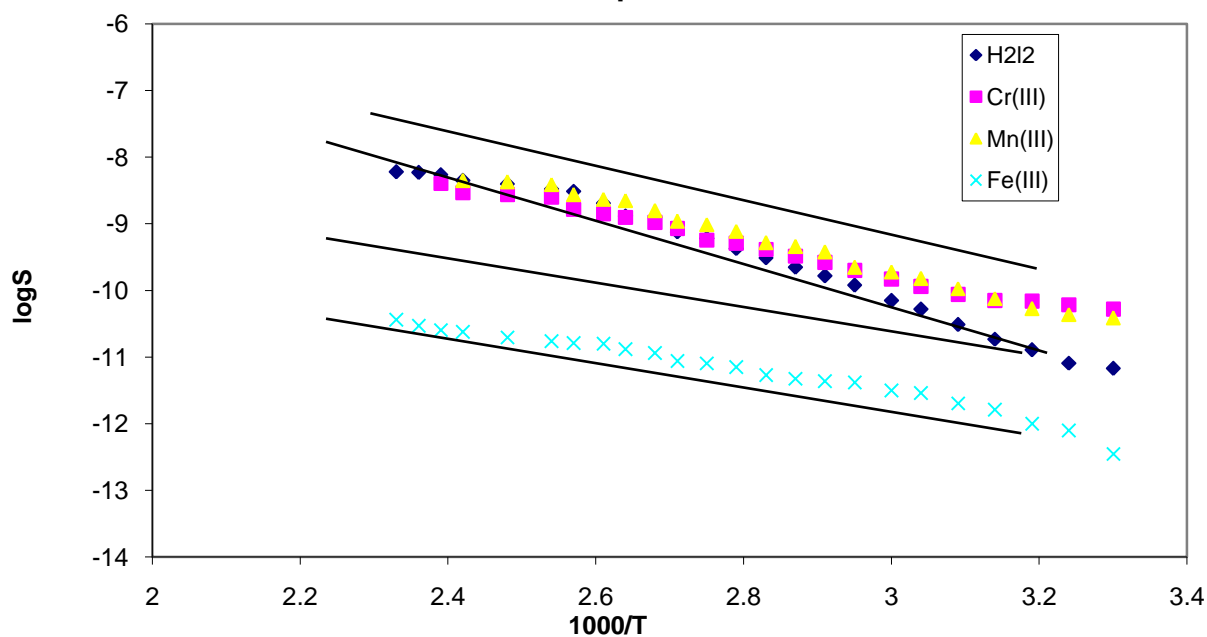


Fig .2 : Solid State Conductivity of H₂L¹ and Cr(III), Mn(III) and Fe(III) Complexes .

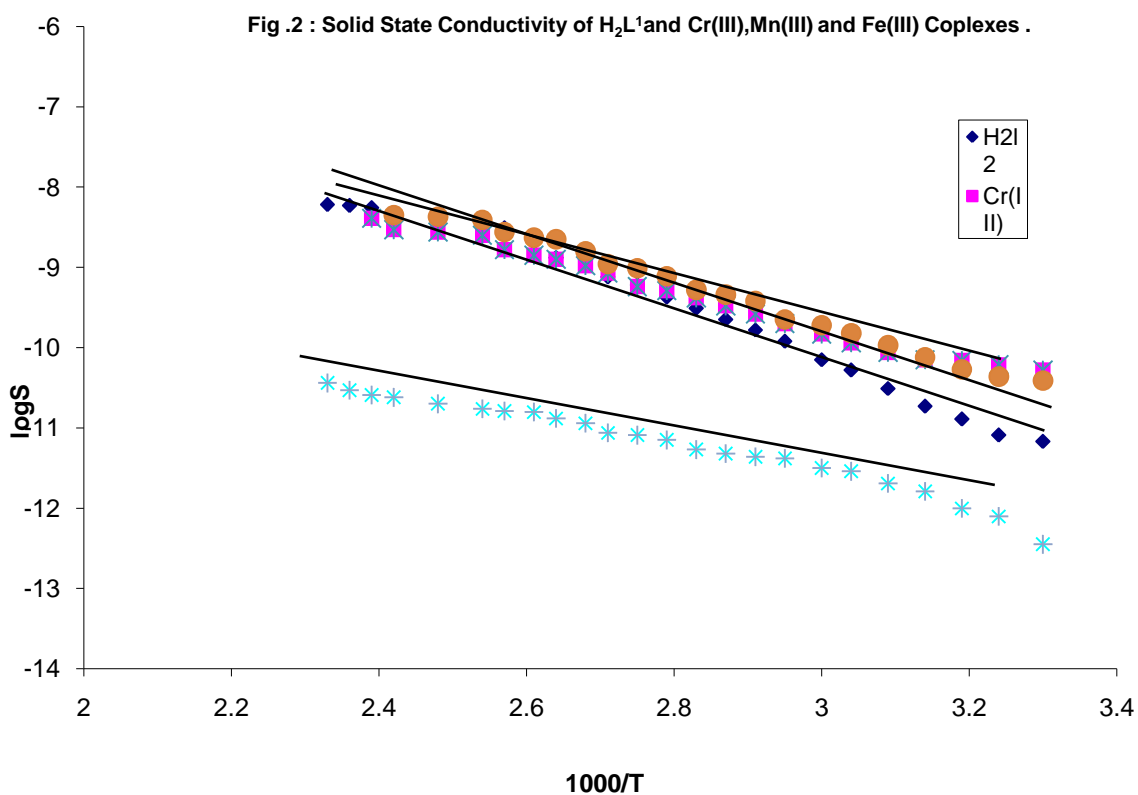


Fig.3 Biological studies of ligand and their complexes

