

## **SYNTHESIS AND CHARACTERISATION OF COMPLEXES OF SCHIFF BASES DERIVED FROM HYDRAZINE CARBOXAMIDE & THIOSEMICARBAZIDE**

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In this paper, coordination complexes of Cr(III), Fe(III) and Mn(III) with Schiff bases derived from 2, 5-dihydroxynaphthaldehyde and hydrazinecarboxamide [DHNAPHC]/thiosemicarbazidehydrochloride [DHNAPTSC] have been prepared and characterized by physicochemical and spectroscopic methods. The chelates are coloured solids and electrolytes of the type  $[ML_2]^+.Cl^-$ . Various physicochemical data suggest a six-coordinated octahedral geometry for all the complexes. The ligands and their respective complexes were also screened for their antibacterial activity.

**KEYWORDS :** Metal Complexes, Hydrazine Carboxamide and Thiosemicarbazide

### **INTRODUCTION**

The metal complexes of semicarbazones and thiosemicarbazones have aroused considerable interest in view of their industrial and biological importance. Many of these compounds possess a wide spectrum of medicinal properties. The multifarious roles of transition metals in biochemistry [1], suggest that considerable potential exists for the development of new chemistry with these metals in ligand system, specifically designed to serve these roles. Thiosemicarbazides and thiosemicarbazones react as chelating agents with transition metal ions by bonding through the sulphur and hydrogenic nitrogen atom [2, 3].

Keeping the above facts in mind and in continuation of our earlier research work [4-6] on transition metal complexes with Schiff bases, the present paper describes the synthesis and characterization of Chromium(III), Iron(III) and Manganese(III) complexes with the ligands.

### **EXPERIMENTAL**

All chemicals used were of AR grade (Aldrich, Lancaster and E. Merck). The ligands as well as metal complexes were analyzed by standard methods. The solvents and chemicals were purified and dried before use by standard techniques. The elemental analyses were carried out at RSIC, CDRI, Lucknow. The electronic spectra were recorded on a Hitachi 200-

20 spectrophotometer and the IR spectra (KBr/Nujol/HCB) on a Perkin-Elmer 1330 spectrophotometer. The molar conductance was measured using an Elico conductivity bridge. The magnetic susceptibility was determined by Gouy method. The analytical data, colour, magnetic moment and important IR spectral bands are recorded in table-1 and table-2 respectively.

**Table-1. Analytical data & physical data of the metal complexes**

Compound (colour)	Decomp. Temp. (°C)	Elemental Analysis(%): Found (Calculated)							Mag. moment (B.M.)
		C	H	N	O	M	Cl	S	
[Cr(DHNAPHC) <sub>2</sub> ].Cl (Dark brown)	261	50.00 (50.04)	3.50 (3.47)	14.57 (14.59)	16.60 (16.68)	8.96 (9.03)	6.11 (6.16)	----	3.83
[Cr(DHNAPTSC) <sub>2</sub> ].Cl (Green)	290	47.35 (47.39)	3.24 (3.29)	13.78 (13.82)	10.49 (10.53)	8.51 (8.55)	5.79 (5.84)	10.51 (10.55)	3.96
[Fe(DHNAPHC) <sub>2</sub> ].Cl (Orange)	240	49.67 (49.71)	3.41 (3.45)	14.47 (14.49)	16.52 (16.57)	9.60 (9.64)	6.15 (6.12)	----	4.98
[Fe(DHNAPTSC) <sub>2</sub> ].Cl (Dark red)	275	47.00 (47.09)	3.21 (3.27)	13.68 (13.73)	10.41 (10.46)	9.10 (9.13)	5.76 (5.80)	10.43 (10.48)	5.20
[Mn(DHNAPHC) <sub>2</sub> ].Cl (Dark green)	280	49.75 (49.78)	3.39 (3.45)	14.47 (14.52)	16.51 (16.59)	9.43 (9.49)	6.09 (6.13)	----	4.80
[Mn(DHNAPTSC) <sub>2</sub> ].Cl (Pale yellow)	310	47.12 (47.16)	3.23 (3.27)	13.70 (13.75)	10.45 (10.48)	8.91 (8.99)	5.73 (5.81)	10.47 (10.50)	4.90

**Table 2. Key ir spectral bands of ligands/metal complexes**

Compound	Key IR spectral bands (cm <sup>-1</sup> )			
	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}=\text{S})$
(DHNAPHC)	1590	1670	1510	----
(DHNAPTSC)	1597	----	1495	785
[Cr(DHNAPHC) <sub>2</sub> ].Cl (Dark Brown)	1595	1679	1516	----
[Cr(DHNAPTSC) <sub>2</sub> ].Cl (Green)	1605	----	1500	789
[Fe(DHNAPHC) <sub>2</sub> ].Cl (Orange)	1597	1683	1523	----
[Fe(DHNAPTSC) <sub>2</sub> ].Cl (Dark red)	1611	----	1513	792
[Mn(DHNAPHC) <sub>2</sub> ].Cl (Dark green)	1610	1690	1530	----
[Mn(DHNAPTSC) <sub>2</sub> ].Cl (Pale yellow)	1620	----	1527	797

**Preparation of the Ligands:** The schiff bases were prepared by the condensation of carbonyl and amino-compounds. The amino compound was dissolved in ethanol and refluxed for about half an hour. Now, the requisite amount of carbonyl compound was added to the flask and this mixture was refluxed for about 3-4hr. and kept for about 24hr. The crystals of

ligand were obtained and purified by recrystallisation in the same solvent. The purity of ligand was checked by elemental analysis and melting point.

**Preparation of Metal Complexes:** Metal complexes were synthesized by refluxation precipitation method. To the hot methanolic solution of ligand, methanolic solution of metal salts was added dropwise from dropping funnel and the resulting mixture was refluxed for 6hr. on a water bath and cooled. The pH of the solution was adjusted. The metal complexes obtained were filtered, washed with water and then with hot methanol and dried in an electrical oven.

## RESULTS AND DISCUSSION

All the complexes are coloured, stable in air and decompose at higher temperature. The elemental analyses of metal complexes suggest 1 : 2 metal to ligand stoichiometry. The solid complexes were found to be soluble in DMSO and DMF and the molar conductance was measured at  $10^{-3}$  M dilution (at  $25^{\circ}\text{C}$ ). The values of molar conductance in these solvents suggest 1:1 electrolytic nature for Cr(III), Mn(III) and Fe(III) complexes. Magnetic measurements and the electronic spectra of these complexes were also obtained in order to have information on their probable geometries.

The Cr(III) complexes show magnetic moment in the range  $3.82\text{-}3.96 \mu_{\beta}$  which indicates octahedral geometry corresponding to three unpaired electrons. Magnetic measurements support octahedral symmetry of the molecules [7, 8]. Structural information is further supported from d-d spectral band in the complexes. Complexes exhibit three spin allowed transitions  ${}^2_{g}A \rightarrow {}^4_{1g}T(F)$  ( $16200 - 18600$ )  $\text{cm}^{-1}$ ,  ${}^2_{g}A \rightarrow {}^4_{1g}T(F)$  ( $21000 - 24040$ )  $\text{cm}^{-1}$  and  ${}^2_{g}A \rightarrow {}^4_{1g}T(P)$  ( $25125 - 33000$ )  $\text{cm}^{-1}$ . These are consistent with octahedral symmetry of Cr(III) complexes[9]. The Fe(III) complexes show magnetic moment in the range  $4.98\text{-}5.20 \mu_{\beta}$  which indicates high spin octahedral geometry corresponding to five unpaired electrons. The complexes show bands corresponding to  ${}^6_{1g}A \rightarrow {}^4_{1g}T$  ( $16667 - 17666$ )  $\text{cm}^{-1}$ ,  ${}^6_{1g}A \rightarrow {}^4_{2g}T$  ( $23529 - 23825$ )  $\text{cm}^{-1}$  and  ${}^6_{1g}A \rightarrow {}^4_{g}E$  ( $29410 - 29880$ )  $\text{cm}^{-1}$  transitions, respectively [10]. Magnetic moment for Mn(III) complexes lie in the range  $4.80\text{-}4.90 \mu_{\beta}$  revealing the high spin nature of the complexes, corresponding to four unpaired electrons. Electronic spectra show a strong band at  $19680\text{-}20000 \text{ cm}^{-1}$  which can be assigned due to ligand to metal charge transfer and a shoulder at  $18000\text{-}180540 \text{ cm}^{-1}$  may be assigned to the  ${}^5E \rightarrow {}^5T$  transition.

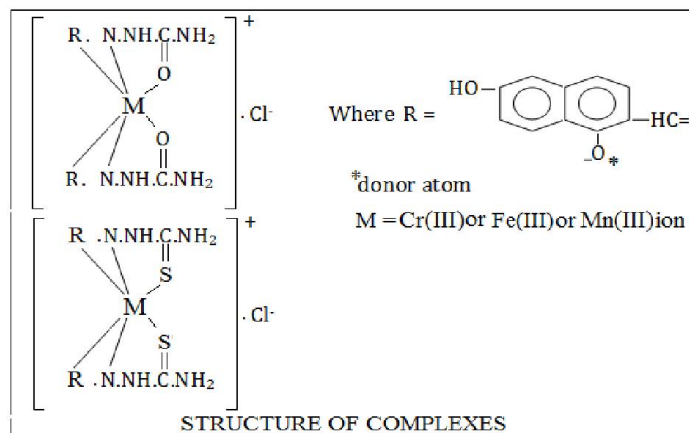
The characteristic infrared bands for the free ligands [DHNAPHC] and [DHNAPTSC] when compared with those of its Cr(III), Fe(III) and Mn(III) complexes provide meaningful information regarding the bonding sites of the ligands (given in table-2).

In the IR spectra the bands at  $1590 \text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  and  $1670 \text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{O})$  in [DHNAPHC] have shifted to a higher wave number, indicating coordination through the azomethine nitrogen and carbonyl oxygen of the ligand to the central metal ion, respectively. While the bands at  $1597 \text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  and  $785 \text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{S})$  in [DHNAPTSC] have shifted to a higher wave number, indicating coordination through the azomethine nitrogen and thionyl sulphur of the ligand to the central metal ion, respectively.

The free ligands ([DHNAPHC] & [DHNAPTSC]) display two sharp bands at  $3448 \text{ cm}^{-1}$  and  $3321 \text{ cm}^{-1}$ , assignable to asymmetric and symmetric  $\text{NH}_2$  groups, respectively, which remain at almost the same positions in all the metal complexes, suggesting that the amino group is not involved in chelation. The bands at  $1510 \text{ cm}^{-1}$  in [DHNAPHC] and at  $1495 \text{ cm}^{-1}$  in

[DHNAPTSC] due to  $\nu(\text{C-O})$  phenolic oxygen have shifted to higher wave numbers in their complexes respectively, suggesting deprotonation and complexation of phenolic oxygen during complex formation.

Based on the above discussion, octahedral structures are proposed for all the complexes.



All synthesized compounds were evaluated for their antibacterial activities by inhibition zone technique[11] against different gram positive and gram negative bacteria e.g. Escherichia coli, Staphylococcus aureus, Bacillus subtilis etc. All the ligands were found to be less potent than their corresponding metal complexes.

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