



## Preparation and Characterisation of Trivalent Metal Complexes With Schiff Bases

## KEYWORDS

Co(III), Cr(III), Coordination Complexes

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**ABSTRACT** In this paper coordination complexes of Co(III) and Cr(III) with Schiff bases derived from 1,3-diaminopropanol-2 and 5-chloro-2-hydroxynaphthaldehyde [DAPCHN]/5-chloro-2,4-dihydroxyacetophenone [DAPCDHAP] have been prepared and characterized by elemental analysis, electrical conductance, magnetic moment and spectral data. The chelates are coloured solids and non-electrolytes of the type  $[ML(H_2O)_6]$ . Various physicochemical data suggest a six-coordinated octahedral geometry for all the complexes. Ligands and their complexes have been tested for their antimicrobial activity. The detailed results will be displayed at the venue of congress meet.

### INTRODUCTION

Schiff bases [1] are useful ligands because of their ease of preparation, structural variety, varied denticities and subtle steric and/or electronic effects. Chromium(III) complexes containing Schiff bases have attracted many workers [2-4] due to their biological, pharmacological, clinical and analytical importance. The biologically important form of chromium is the trivalent ion, Cr(III), which is required for proper carbohydrate and lipid metabolism in mammals. Coordination compounds of cobalt in its varied oxidation states are of immense importance because of their interesting structural, magnetic, electronic and optoelectronic behaviours [5-9]. Keeping the above facts in mind and in continuation of our earlier research work [10-12] on transition metal complexes with Schiff bases, the present paper describes the synthesis and characterization of Chromium(III) and Cobalt(III) complexes with the ligands.

### EXPERIMENTAL

All chemicals used were of AR grade (Aldrich, Lancaster, Sisco and E. Merck). The ligands as well as metal complexes were analyzed by standard methods. Conductivity measurements were carried out on Philips Conductivity Bridge model PR9500 using  $10^{-3}$ M DMF solution. The IR spectra were recorded on Perkin-Elmer spectrometer using KBr pellets. Electronic spectra were recorded on Beckmann DU-2-spectrophotometer in the range of 750-350  $\text{cm}^{-1}$ . Magnetic-Susceptibility was measured on a Gouy-balance using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as a calibrant. The analytical data, colour, magnetic moment and important IR spectral bands are recorded in Table-1 and Table-2 respectively.

### PREPARATION OF THE LIGANDS

The Schiff bases were prepared by the condensation of carbonyls 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 6hr. and kept for 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 high temperature. The elemental analysis of metal complexes suggest 1:1 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°C). The values of molar conductance for Cr(III) and Co(III) complexes in these solvents are very low as compared to the values for 1:1 electrolytes. Therefore complexes of Cr(III) and Co(III) are non-electrolytic in nature. Magnetic measurements and the electronic spectra of Cr(III) and Co(III) complexes were also obtained in order to have information on their probable geometries. The Cr(III) complexes show magnetic moment in the range 3.82-3.96  $\mu_B$  consistent with other octahedral Cr(III) species [13] corresponding to three unpaired electrons. Magnetic measurements support octahedral symmetry of the molecules [14]. Structural information is further supported from d-d spectral band in the complexes. Complexes exhibit three spin allowed transitions  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  (F) (16200-18600)  $\text{cm}^{-1}$ ,  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  (F) (21000-24040)  $\text{cm}^{-1}$  and  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  (P) (25125-33000)  $\text{cm}^{-1}$ . These are consistent with octahedral symmetry of Cr(III) complexes [15]. The Co(III) complexes are diamagnetic as expected for a low spin  $d^6$  ion. The electronic spectra of Co(III) complexes display bands at 15110-15450  $\text{cm}^{-1}$ , 21095-21640  $\text{cm}^{-1}$  and 23370-23860  $\text{cm}^{-1}$ . These are similar to those reported for other six coordinated Co(III) complexes [16] and may be assigned to  ${}^1A_{1g} \rightarrow {}^3T_{2g}$ ,  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transitions, respectively.

The characteristic infrared bands (4000-200)  $\text{cm}^{-1}$  for the free ligands [DAPCHN] and [DAPCDHAP] when compared with those of its Cr(III) and Co(III) complexes provide meaningful information regarding the bonding sites of the ligands (given in Table-2).

The presence of secondary alcoholic (-OH) group in the ligands ([DAPCHN] and [DAPCDHAP]) has been indicated by the appearance of a band around 3400  $\text{cm}^{-1}$ . The broad nature of the bands suggest hydrogen bonding [17]. The  $\nu_{\text{C-O}}$  (secondary alcohol) appeared around 1350  $\text{cm}^{-1}$  in the free ligands and remained unchanged in the metal complexes indicating non-involvement of this group in the complexes [18]. The bands at 1610-1625  $\text{cm}^{-1}$  due to  $\nu_{\text{C=N}}$  (azomethine) shifted to lower frequencies by about 15-25  $\text{cm}^{-1}$  compared to the free ligand ([DAPCHN] and [DAPCDHAP]) values, indicating bonding through N. The  $\nu_{\text{C-O}}$  (phenolic) of the ligands ([DAPCHN] and [DAPCDHAP]) observed around 1510  $\text{cm}^{-1}$ , shifted to lower frequencies in the metal complexes. This,

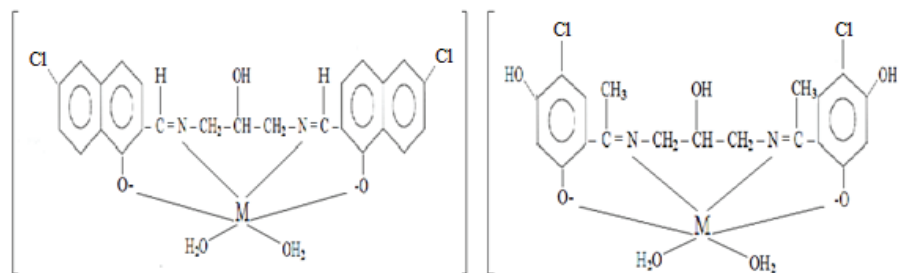
along with the disappearance of bands for  $\nu$ O-H (phenolic), suggest deprotonation and complexation of phenolic oxygen during complex formation [19]. The presence of coordinated water in the complexes  $[M(H_2O)_2]$  is indicated by a broad trough in the region  $3200-3400\text{ cm}^{-1}$ .

On the basis of available evidences, octahedral geometry

may be suggested for all Cr(III) and Co(V) complexes.

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STRUCTURE OF COMPLEXES  
WHERE M = Co (III) & Cr (III)

Table-1: ANALYTICAL DATA AND PHYSICAL DATA OF THE METAL COMPLEXES

Compound (colour)	M.P. (°C)	Elemental Analysis (%): Found (Calculated)						Mag.Moment (B. M.)
		C	H	N	O	Cl	M	
[Cr(DAPCHN)(H <sub>2</sub> O) <sub>2</sub> ] (Brown)	125	54.27 (54.20)	3.98 (3.87)	5.06 (4.90)	14.47 (14.37)	12.80 (12.75)	9.39 (9.30)	3.86
[Cr(DAPCDHAP)(H <sub>2</sub> O) <sub>2</sub> ] (Light Brown)	133	44.47 (44.40)	4.29 (4.22)	5.46 (5.40)	21.84 (21.79)	13.80 (13.70)	10.12 (10.06)	3.93
[Co(DAPCHN)(H <sub>2</sub> O) <sub>2</sub> ] (Yellow)	142	53.60 (53.51)	3.93 (3.80)	5.00 (4.90)	14.29 (14.19)	12.64 (12.59)	10.52 (10.45)	Diamagnetic
[Co(DAPCDHAP)(H <sub>2</sub> O) <sub>2</sub> ] (yellowish Brown)	153	43.87 (43.78)	4.23 (4.19)	5.38 (5.28)	21.55 (21.48)	13.62 (13.50)	11.33 (11.27)	Diamagnetic

Table-2: KEY IR SPECTRAL BANDS OF LIGANDS AND THEIR METAL COMPLEXES

Compound	Key IR spectral bands (cm <sup>-1</sup> )		M:L ratio
	$\nu$ (C=N)	$\nu$ (C-O)	
(DAPCHN)	1610	1510	----
(DAPCDHAP)	1625	1530	----
[Cr(DAPCHN)(H <sub>2</sub> O) <sub>2</sub> ]	1595	1500	1:1
[Cr(DAPCDHAP)(H <sub>2</sub> O) <sub>2</sub> ]	1590	1497	1:1
[Co(DAPCHN)(H <sub>2</sub> O) <sub>2</sub> ]	1623	1525	1:1
[Co(DAPCDHAP)(H <sub>2</sub> O) <sub>2</sub> ]	1617	1519	1:1

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