



## STUDY OF PREPARATION OF DITHIOCARBAMATE OF Cr(III), Co(III), Ni(II), Cu(II) AND THEIR THERMAL STUDIES

**S.S. Sakhare**

M. M. College of Science, Nagpur

sakhare.suresh@rediffmail.com

### Abstract:

The dimethyl dithiocarbamate complexes of Cr(III), Co(III), Ni(II) and Cu(II) have been prepared and characterised by elemental analysis and Infrared studies. The thermal studies of these complexes have been carried out. It was observed from the thermograms that of Ni(II) and Cu(II) complexes decompose without any break to sulphide and oxide respectively as the final products where as Co(III) complex directly decomposes to the mixture of cobaltic oxide cobaltic sulphate. The Cr(III) complex first loses two molecules of water followed by decomposition resulting to sulphate as the end product. Some thermodynamic parameters, e.g.,  $\Delta H$ ,  $\Delta S$ ,  $\Delta G$  and energy of activation were computed from Sharp-Wentworth plots.

### Introduction

Thermal studies on metal dithiocarbamate complexes have been reported [1], but very little work has been done on determination of thermodynamic parameters of these complexes [2,3]. The present paper deals with the TGA studies and determination of thermodynamic parameters of dimethyl dithiocarbamate (DMDC) complexes of Cr(III), Co(III), Ni(II) and Cu(II).

### Experimental

Copper, nickel, chromium and cobalt complexes were prepared [4] by adding ethanolic solution of the metal chlorides to the ethanolic solution of the sodium salt of the ligand and refluxed for two hours. The metal ligand ratio was kept 1:2 for Ni(II) and Cu(II) while that in case of Cr(III) and Co(III) was 1:3. The complexes were filtered, washed with ethanol and ether and dried and preserved in a desiccator over fused calcium chloride. The complexes were characterised by elemental and IR analyses. Thermogravimetric analyses were carried out in air as carrier gas using TGS-2 Thermogravimetric Analyser with TADS Computer System (Perkin-Elmer). The sample size were 5 to 10 mg and heating rate was 100C/min.

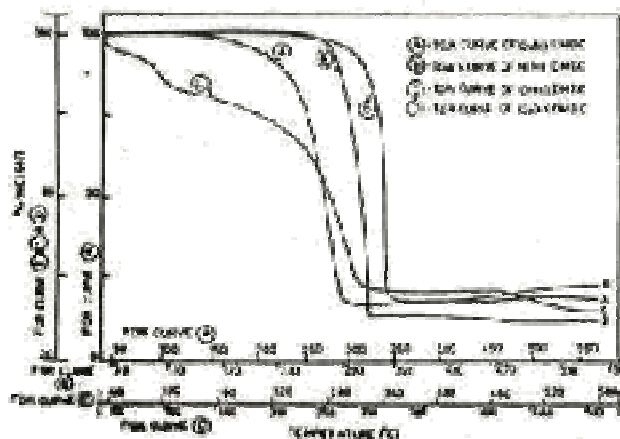
### Results and Discussion

Data on Physical character, elemental analyses and Thermo-gravimetric analyses of the complexes are listed in Table 1. The thermograms of DMDC complexes of Co(III), Ni(II) and Cu(II) between 50 and 5000C are similar in nature.

Lippard and presented in figure 1 and expected end product are as shown in Table 1. It was observed from the thermogram that the complexes of Ni, Cu Co do not contain water of hydration and decompose to yield final products nickel sulphide and copper oxide

respectively but in case of Co(III) complex a mixture of cobaltic oxide and cobaltic sulphate are obtained. On the other hand, Cr(III) complex loses two molecules of water of hydration around 100°C followed by decomposition giving to chromic sulphate [5].

Various thermodynamic parameters were calculated from the Sharp-Wentworth plots and shown in Table 2. The change of entropy of decomposition of all the four complexes are seen to be negative which indicates that the formation of activated complexes are less probable than the normal and decomposition is induced on application of heat which may convert rotational degree of freedom into vibrational degree of freedom in the activated complexes [6].



**Figure 1** Thermograms of DMDC complexes of Cr(III), Co(III), Ni(II) and Cu(II).

**Table 1.** Physical character, elemental and TG analyses of DMDC complexes of Cr(III), Co(III), Ni(II) & Cu(II)

Complex	Colour	%N	%S	End product
Cr <sub>3</sub> DMDC.2H <sub>2</sub> O	Dark blue	9.0	8.74	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
Co <sub>3</sub> DMDC	Dark green	10.0	9.4	Co <sub>2</sub> O <sub>3</sub> and Co <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
Ni <sub>2</sub> DMDC	Pale green	9.4	8.6	NiS
Cu <sub>2</sub> DMDC	Brown	9.2	8.3	CuO

### References

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G.D. Ascenzo and W.W. Wendlendt, J. (Figure 1) that the complexes of Ni, Cu and Thermal Analysis, 1(1969) 423.

**Table 2.** Thermodynamic parameters of thiocarbamate complexes of Cr(III), Co(III), Ni(II) and Cu(II)

Complexes	Activation energy (kJ/mole)	Frequency factor	$\Delta H$ (kJ/mole)	$\Delta S$ (kJ/mole)	$\Delta G$ (kJ/mole)
Cr <sub>3</sub> DMDC.2H <sub>2</sub> O	45.7	5.06 × 10 <sup>4</sup>	-41.0	-100.00	-50.7
Co <sub>3</sub> DMDC	127.6	1.86 × 10 <sup>12</sup>	-122.6	-10.8	-116.0
Ni <sub>2</sub> DMDC	150.8	3.46 × 10 <sup>4</sup>	-145.7	-10.9	-139.1
Cu <sub>2</sub> DMDC	95.5	9.76 × 10 <sup>9</sup>	-91.0	-59.00	-57.2

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