

## Thermal Properties of some Nitrogen Ligated Complexes of Co(II)

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**Summary:** The thermal behaviour of some nitrogen-ligated complexes of 2-Guanidinobenzimidazole (GBM), 1,2 dimorpholinoethane (DME), 1,3 dimorpholinopropane (DMP) with Co(II) have been studied by thermogravimetry and differential thermal analysis. Complete decomposition of the chelates, obtained from the above ligands, was accomplished generally in two stages. All DMP complexes studied in the present investigations were found to be thermally less stable than the corresponding DME complexes. While most of the GBM and DME complexes were observed to be of comparable stability. The differential thermal analysis of Co(II) complexes are also reported. The reaction found in DTA curves corresponded to those found in the TGA curves.

### Introduction

Systematic investigation of the ability of the ligands 1,2 dimorpholinoethane (DME) (1-5) and 1,3 dimorpholinopropane (DMS) (6-7) to form complexes with dipositive first row transition metal halides and non transition metal halides were studied in the past. The ligands behaved as bidentate chelating agents and coordinate through only two Nitrogen atoms (2-7). These chelating agents were used as a selective reagent for gravimetric and spectrophotometric analysis of various metals (8-14). DME was also used as a catalyst for the preparation of polyurethane foams (15).

The coordination Chemistry of another ligand 2-guanidinobenzimidazole (GBM) has also been studied in the past (16-19). It acts as a bidentate ligand and forms mono, bis and tris complexes with various metals. The mode of coordination through i.r studies has been found through secondary amine and terminal imide group forming a six membered ring (18-19). However no work has been reported so far on the thermal analysis of the complexes derived from ligands DME, DMP and GBM. Therefore, it was thought of interest to investigate the thermal behaviour of Co(II) complexes with a view to find out the mechanism of thermal decomposition and to study the thermal stability.

### Experimental

#### *Thermobalance*

Thermogravimetric analysis were carried out in an open crucible under atmospheric pressure on stanton automatic recording thermobalance model HT/SM. The crucible employed was calibrated by running a blank on empty crucible and recording the appropriate change in weight due to bouyancy.

#### *Differential thermal analysis:*

These results were obtained using the apparatus described previously (20). Sample sizes ranged in weight from 28.5 mg to 80.5 mg against alumina as reference. The furnace heating rate was about 50C per minute. The temperature rise and sensitivity of instrument was checked by quartz sample. Area of the peaks were calculated by planimeter and Sodium nitrate (Analar) having heat of fusion,  $H_f = 44.7 \text{ cal/gm}$  at  $315^\circ\text{C}$  was used as the standard.

#### *Preparation of Complexes*

All GBM complexes studied in this investigation were prepared by the procedure as previously described (18-19). DME and DMP complexes were prepared by the procedure reported earlier (6-7). Satisfactory elemental analysis (C, H & N) were obtained for all complexes. Elemental analysis were done at micro analytical Laboratories, Harwell (England).

## Results and Discussion

### Thermogravimetric studies of 2-Guanidinobenzimidazole (GBM) Complexes.

The thermal dissociation of a number of Co(II) Guanidinobenzimidazole complexes of the type  $\text{Co}(\text{GBM})_2\text{X}_2$ , when  $\text{X} = \text{Br}, \text{I}, \text{NO}_3$  and  $\text{Ac}$  and of  $\text{Co}(\text{GBM})_2\text{SO}_4$  were studied by thermogravimetric techniques. The weight loss curves for Co (II) GBM complexes are given in Fig-1. In all these complexes dissociation occurred in a particular sequence i.e. GBM-ligand evolved in the second stage of dissociation. The weight loss curve of  $\text{Co}(\text{GBM})_2(\text{NO}_3)_2$  Fig (1)/A indicated that one mole of nitrogen pentoxide was evolved per mole of the complex at temperature 170-300°C, (Found, 14.0 mg theor. 14.00 mg). The initial weight of the complex taken was 70.25 mg.

In the second step, at temperature 350-700°C, two moles of Guanidinobenzimidazole were evolved per mole of the complex. (Found, 43.0 mg Thero. 45.4 mg). No further loss was observed above 700°C. The weight of residue corresponded to CoO which was formed by oxidation of Co metal. (Found 12.0 mg Theor, 13.0

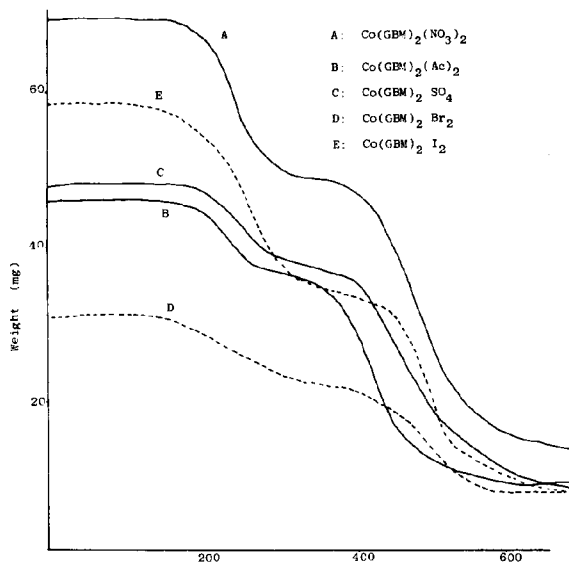
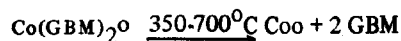
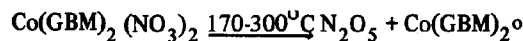


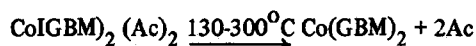
Fig.1: Thermograms of GBM complexes.

mg). The above data suggest the following decomposition sequence.



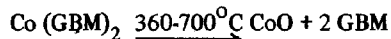
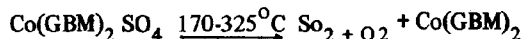
The mechanism of dissociation of  $\text{Co}(\text{GBM})_2(\text{Ac})_2$  Fig(1)/B was just the same, except that it was less stable than  $\text{Co}(\text{GBM})_2(\text{NO}_3)_2$ . The decomposition of the complex started at a lower temperature (130°C). The second weight loss was noted in the range 350-600°C. The observed loss was found to be in good agreement to the calculated value.

The thermal decomposition sequence appears to be:



The thermogram of  $\text{Co}(\text{GBM})_2\text{SO}_4$  Fig. (1)/C showed that one mole of sulphur dioxide and one mole of oxygen were evolved in the first stage, at temperature 170-325°C Fig (1/C) Initial weight of the complex taken was 48.5 mg. A loss of 10.0 mg was observed in the first step which corresponded to  $\text{SO}_2 + \text{O}_2$  against calculated weight of 10.2 mg. At the second stage, at temperature 360-700°C, two moles of guanidinobenzimidazole were evolved. (Found, 31.5 mg, Theor. 31.9 mg).

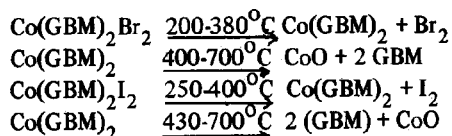
The mechanism of dissociation for this complex is:



The weight loss curves of  $\text{Co}(\text{GBM})_2\text{Br}_2$  and  $\text{Co}(\text{GBM})_2\text{I}_2$  are given in Fig. (1/D) and 1/E)

The decomposition sequence of both the complexes were about the same. In the first stage  $\text{Br}_2$  and  $\text{I}_2$ , while in the second stage 2 GBM moles were evolved respectively.

The decomposition sequent appears to be:



*Thermogravimetric studies of 1,2-Dimorpholinoethane (DME) Complex*

The weight loss studies of Co(II) complexes with 1,2-dimorpholinoethane are given in Fig.2.

The weight loss curve of Co(DME)Br<sub>2</sub>. (Fig. 2/B) indicates that decomposition took place in tow steps. Initial weight of the complex taken was 28.5 mg. In the first stage at 200-350°C 6.0 mg loss was observed which corresponded to the calculated weight of morpholinium ion, calculated to be 5.85 mg. The intermediate product formed was stable upto 400°C. The decomposition of the intermediate product was observed at 400-620°C.

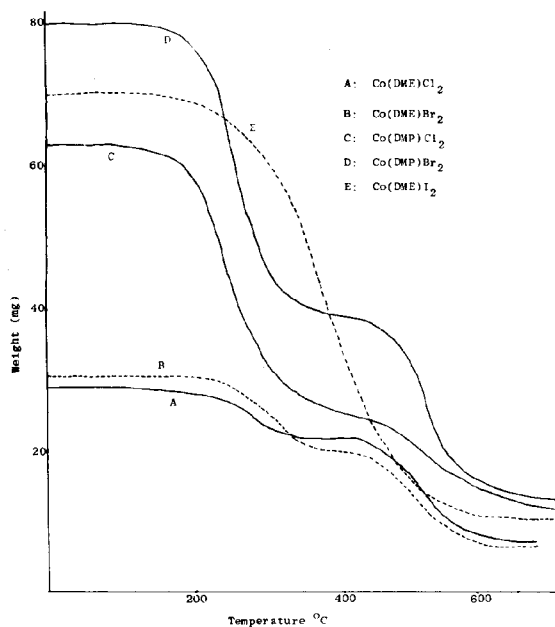
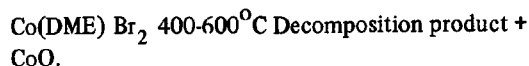
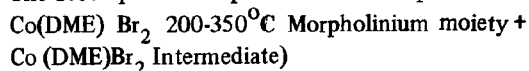


Fig. 2: Thermograms of DME & DMP complexes.

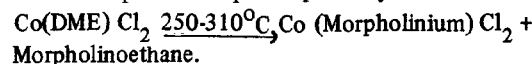
The observed weight loss being 17.5 mg against the calculated weight of 18.6 mg. No further loss in weight was observed above 620°C as indicated by the constant weight level in thermogram. The residue formed was CoO. (Found 6.0 mg. Theor, 5.1 mg).

The decomposition sequence for the complex is:

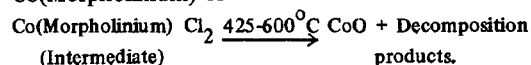


The thermogram of Co (DME) Cl<sub>2</sub> (Fig. 2/A) shows that the first step a loss of 10.0 mg was observed at 250-310°C, which corresponded to the calculated weight morpholinoethane anion to be 10.4 mg. The intermediate product formed was decomposed at 425-600°C. The observed weight of residue CoO, formed was 6.5 against the calculated weight of 6.9 mg.

The decomposition sequence probably is:

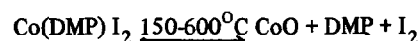


Co(Morpholinium) Cl



In case of Co(DME) I<sub>2</sub>. (Fig. 2/E) the weight of the complex taken was 70.5 mg. Decomposition take place in a single step and residue formed was CoO found to be 9.0 mg, against the calculated weight of 10.0 mg.

The decomposition mechanism may be :



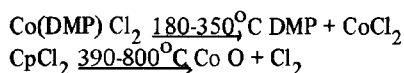
*Thermogravimetric studies of 1,3-Dimorpholinopropane (DMP) complexes.*

The weight loss studies of Co(II) Complexes with 1,3-Dimorpholinopropane are given in fig. 2.

The weight loss curve of Co(DMP)Cl<sub>2</sub>, (Fig. 2/C) indicates that decomposition take place in two steps. The initial weight of the complex taken was 63.0 mg. In

the first stage at 180-350°C, 38.0 mg loss was observed which corresponded to the calculated weight of ligand dimorpholinopropane (Theor: 39.3 mg). In the second stage of dissociation chlorine was evolved, resulting in the loss of 12.0 mg, against the calculated weight loss of 13.0 mg. The residue formed was CoO. (Theor: 13.5 mg, Found 13.0 mg).

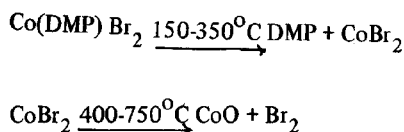
The probable sequence of decomposition is:



Similarly Co(DMP)Br<sub>2</sub> (Fig. 2/D) shows that first dissociation of the ligand DMP took place at 150-350°C. The observed weight loss being 40.0 mg. against the calculated weight loss of 39.8 mg.

In the second stage of dissociation, at 400-750°C, a loss of 31.0 mg was observed, which corresponded to the calculated weight loss of 29.7 mg, due to chlorine.

The possible sequence of decomposition is:



#### Differential Thermal analysis (DTA) studies of GBM Complexes.

The DTA curves for the GBM Complexes are given in Fig. 3 while the corresponding TGA curves are given in Fig. 1.

the DTA curve of Co(GBM)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, Fig. 3/A indicated two endothermic peaks. The first endothermic peak with a peak maximum at temperature 200°C, corresponded to the loss of N<sub>2</sub>O<sub>5</sub>. The exothermic peak at 275°C, may be due to the evolution of N<sub>2</sub>O<sub>5</sub> (21-22).

The second endothermic peak and peak maximum at 450°C corresponded to the decomposition of GBM ligand as indicated by TGA studies Fig. 1 and Table-1.

The DTA curves of Co(GBM)<sub>2</sub>SO<sub>4</sub>, Fig. 3/B showed two endothermic peaks with peak maximum at 240°C and 435°C which corresponded to the TGA curve in

Fig. 1.

The first peak at 240°C corresponded to the evolution of SO<sub>2</sub>+O<sub>2</sub> while the second peak at 435°C corresponded to the loss of GBM ligand.

The compound Co(GBM)<sub>2</sub>B<sub>4</sub> and Co(GBM)<sub>2</sub>I<sub>2</sub> Fig. 3/C and 3/D gave two endothermic peaks (7). In case of Co(GBM)<sub>2</sub>Br<sub>2</sub>, the first endothermic peak at temperature 250°C corresponded to the decomposition of Br<sub>2</sub>, as indicated by TGA Studies Table-1.

The second endothermic peak at 470°C is due to the thermal decomposition of the GBM-ligand.

In Co(GBM)<sub>2</sub>I<sub>2</sub> two endothermic peaks were observed at peak maximum temp. 250°C and 460°C. The first corresponded to the loss of I<sub>2</sub> while the second to the loss of the ligand GBM, as indicated by TGA studies Fig. 1.

#### Differential thermal analysis of 1,2 dimorpholinoethane complexes.

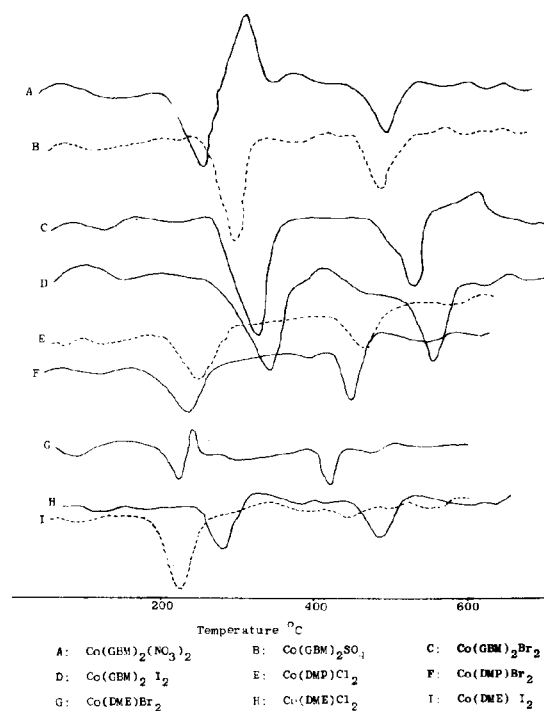


Fig. 3: Differential thermal analysis

The differential thermal analysis curves of  $\text{Co(DME)Cl}_2$  and  $\text{Co(DME)Br}_2$  are given in Fig. 3.

$\text{Co(DME)Cl}_2$  Fig. 3/H gave an endothermic peak at  $220^\circ\text{C}$  which is due to the dissociation of morpholinoethane anion as recorded by the TGA curve Fig. 2/A. A small exothermic peak at  $240^\circ\text{C}$  was formed, the origin of which is not known at present but it may be due to re-arrangement reactions or crystalline transition of some type.

The second endothermic peak was observed at  $430^\circ\text{C}$ , which corresponded to the dissociation reaction of intermediate product at  $400\text{--}620^\circ\text{C}$  as indicated by thermobalance curve Fig. 2/A.

The curve of  $\text{Co(DME)Br}_2$  is given in Fig. 3/G. The first endothermic peak was observed at  $200^\circ\text{C}$  which corresponded to the TGA curve Fig. 2/B. In this case also an exothermic peak was recorded at  $240^\circ\text{C}$ .

The second endothermic peak was observed at  $430^\circ\text{C}$ , as indicated by the TGA curve in Fig. 2/B.

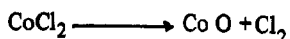
The DTA curve of  $\text{Co(DME)I}_2$ , Fig. 3/I indicated a single endothermic peak at  $220^\circ\text{C}$  (8). Taking into account, the thermogram of the complex Fig. 2/E it was found that the complex decomposed in a single step resulting in the formation of  $\text{Co O}$ .

#### Differential Thermal Analysis of DMP Complexes:

The differential thermal analysis of curves of  $\text{Co(DMP)Cl}_2$  and  $\text{Co(DMP)Br}_2$  are given in Fig. 3. In  $\text{Co(DMP)Cl}_2$  Fig. 3/E and endothermic peak was observed at  $210^\circ\text{C}$  which is due to the decomposition of the ligand as noted by TGA Curve, Fig. 2/C.



The second endothermic peak was recorded at  $450^\circ\text{C}$ , due to the decomposition of  $\text{CoCl}_2$  resulting in the formation of  $\text{CoO}$ .



$\text{Co(DMP)Br}_2$  Fig. 3/F also gave two endothermic peaks with peak maximum at temperature  $200^\circ\text{C}$  and  $430^\circ\text{C}$ . The reactions found in the DTA curve corres-

ponded to those found in the TGA curve.

The first peak corresponded to the loss of ligand DMP, while the second to the loss of bromine as indicated by TGA curve in Fig. 2/D.

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