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THERMAL STUDIES ON COPPER(II) AND COBALT(II) SEMICARBAZONE COMPLEXES

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ABSTRACT

The thermal decomposition of two new complexes of the general formula $ML \cdot 2H_2O$ (M = Cu, Co; L = *o*-hydroxynaphthaldehyde semicarbazone) has been studied by TG and DTA techniques. Dehydration takes place in the temperature range 165–210 and 141–226°C for the copper and cobalt complexes, respectively, two moles of water being lost in both complexes. The decomposition of ligand occurs in three steps between 210 and 466°C for the Cu and between 226 and 660°C for the Co complex giving metal oxide as end product. The end product in each case has been characterized by X-ray analysis. The order of thermal stability is Co > Cu.

INTRODUCTION

Salicylaldehyde semicarbazone has attracted the attention of chemists because of its analytical use in the determination of zinc by the luminescence method [1]. During the past few years, a plethora of references describing the transition metal complexes of semicarbazones have appeared in the literature [2–4]. Semicarbazone and thiosemicarbazone derivatives of diorganotin have also been reported recently [5]. Metal complexes of thiosemicarbazide and thiosemicarbazones have also recently drawn special attention due to their activity against smallpox, virus diseases and certain kinds of tumours [6–8]. However, nothing is known about the detailed thermal decomposition of the ligand in the complexes, except the dehydration process of the complexes. In continuation to previous spectral studies on Co(II), Ni(II) and Cu(II) complexes of semicarbazones [9], this paper reports the thermal studies of only two complexes of *o*-hydroxynaphthaldehyde semicarbazone. The end product is found to be metal oxide.

EXPERIMENTAL

The complexes were prepared by a previously reported method [9]. Thermogravimetric analyses (TG) were carried out on a Stanton-Redcroft

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TG770 thermobalance. Samples of 5–10 mg were used for TG and the heating rate was 2°C min^{-1}. For DTA, about 20-mg samples were used and the heating rate was 10°C min^{-1}. Both studies were carried out in an atmosphere of dry nitrogen. IR spectra were recorded in KBr matrix on a Beckman IR-20 double-beam instrument in the range 250–4000 cm^{-1}. The X-ray diffraction patterns were taken on a Philips diffractometer using Cu K_α radiation.

RESULTS AND DISCUSSION

The complexes lose their water molecules in one step which is immediately followed by a three-stage decomposition of the ligand to give the end

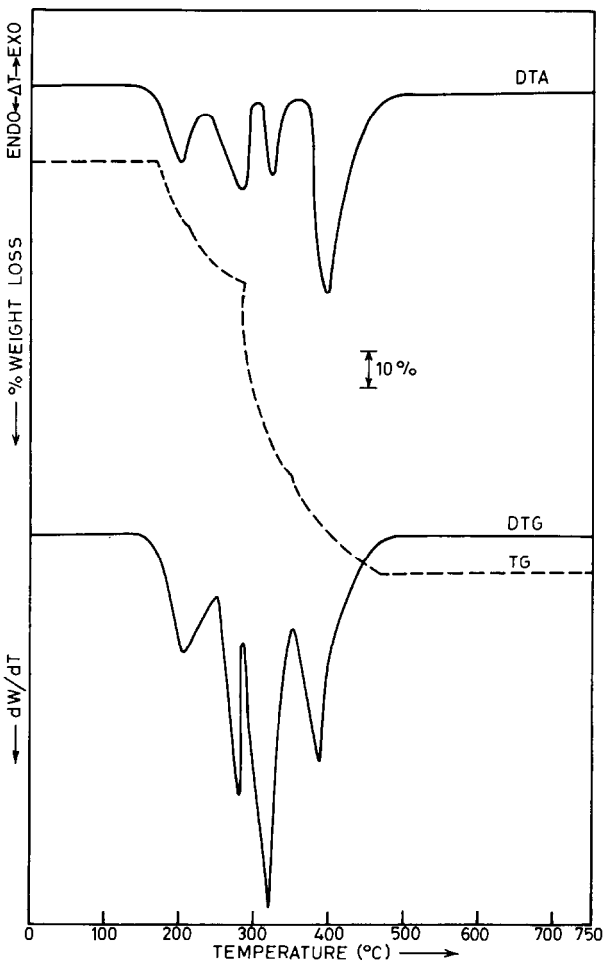


Fig. 1. DTA, TG and DTG of $CuL \cdot 2H_2O$ in dry nitrogen.

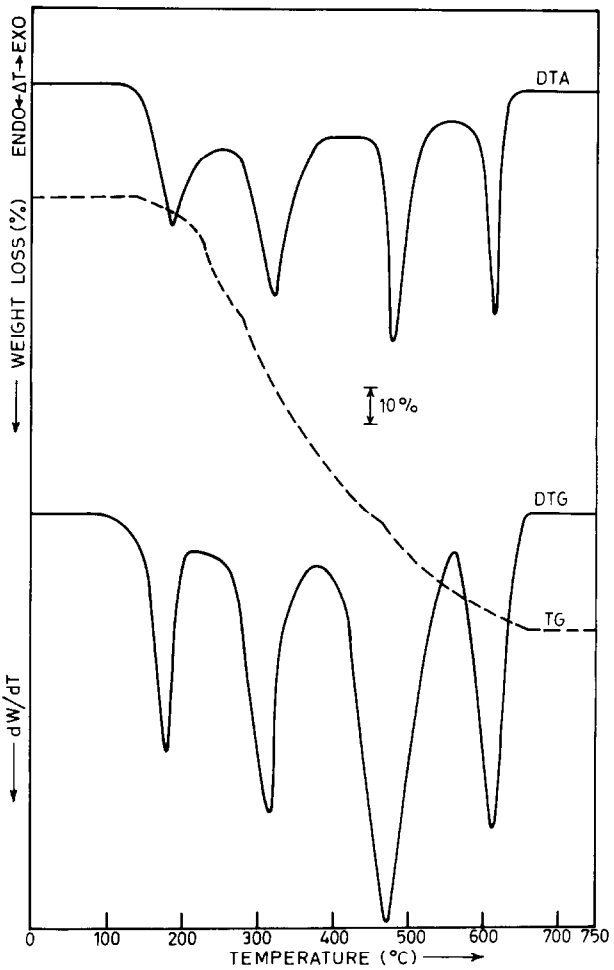


Fig. 2. DTA, TG and DTG of $CoL \cdot 2H_2O$ in dry nitrogen.

product. Figures 1 and 2 give the TG, DTA and differential thermogravimetric (DTG) curves of $ML \cdot 2H_2O$. The various stages are discussed in detail below.

Dehydration

It is evident from the TG curves (Figs. 1 and 2) that the copper complex is stable up to 165°C whereas the cobalt complex is stable up to 141°C and weight losses are 10.67 and 11.68%, while the calculated values are 11.02 and 11.18% for the Cu and Co complexes, respectively. This stage extends up to 210°C for the copper and 226°C for the cobalt complex indicating the presence of two molecules of water of coordination. This is observed in DTA

and DTG as peaks at about 200 and 205°C for $CuL \cdot 2H_2O$ and 185 and 180°C for $CoL \cdot 2H_2O$, giving ML as an intermediate (**I**).

Decomposition of ligand

The decomposition of the ligand takes place immediately after the dehydration in three steps. The first stage extends up to 286 and 318°C for $CuL \cdot 2H_2O$ and $CoL \cdot 2H_2O$, respectively, and corresponds to the loss of one mole of carbon monoxide, nitrogen and hydrogen each per mole of ML to give an intermediate (**II**) having the tentative composition $M(C_{11}H_7NO)$. The observed weight losses are 19.49 and 20.64% against the calculated values of 19.97 and 20.29% for the copper and cobalt complexes, respectively. Both DTA and DTG show peaks at 280°C for the copper complex, whereas peaks at 315 and 320°C are observed in DTG and DTA of the cobalt complex. The second stage occurs at 286–350°C for $CuL \cdot 2H_2O$ and 318–500°C for $CoL \cdot 2H_2O$ and involves the loss of a naphthalene ring to give another intermediate (**III**) with the tentative composition $M(CH_3NO)$. The observed weight losses are 53.12 and 54.28% while the calculated values are 53.34 and 54.43%, and DTA and DTG show peaks at 320 ± 5 and 470 ± 5°C for the copper and cobalt complexes, respectively.

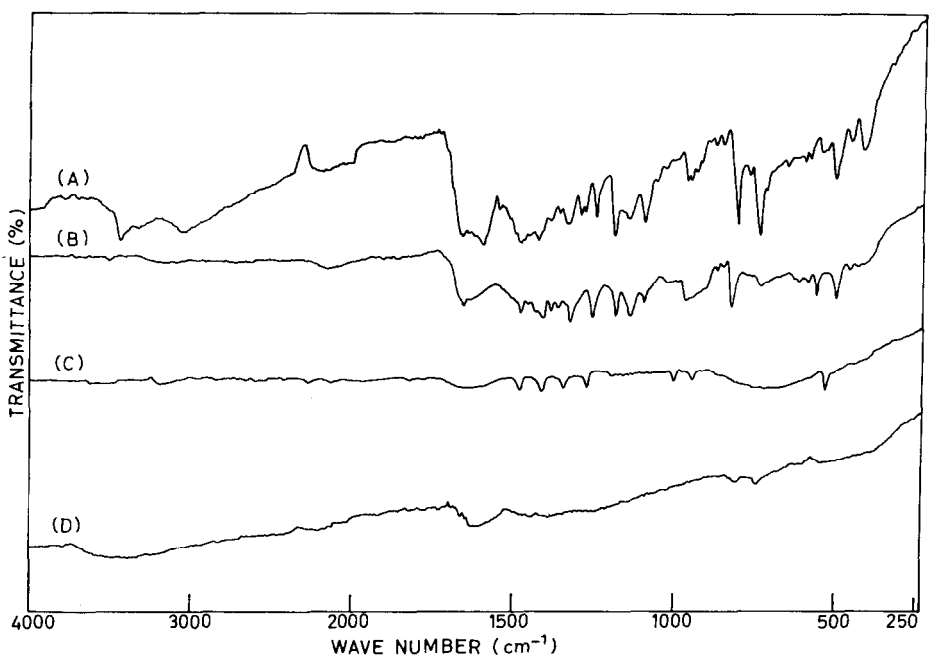


Fig. 3. IR spectra of $CuL \cdot 2H_2O$ (A), $CuL \cdot 2H_2O$ heated to 210°C (B), 285°C (C) and 350°C (D).

The third stage extends up to 466°C for the copper and 660°C for the cobalt complex. It involves the further loss of 1 mole of carbon monoxide, 1/2 mole of nitrogen and 3/2 moles of hydrogen to give the end product (**IV**). The observed weight losses are 26.67 and 28.11% against the calculated values of 26.81 and 28.49% along with the DTA and DTG peaks at 390 ± 5 and at 615°C for $CuL \cdot 2H_2O$ and $CoL \cdot 2H_2O$, respectively.

The compositions assigned to the intermediates are well supported by the IR spectra of samples obtained by heating $ML \cdot 2H_2O$ isothermally at 210 and 226°C (Figs. 3B and 4B), 286 and 318°C (Figs. 3C and 4C) and 350 and 500°C (Figs. 3D and 4D) for the copper and cobalt complexes, respectively.

Intermediate **I** does not show peaks of the coordinated OH group at ~ 3510 ± 5 (νOH), 1600 (δO–H) and 725 ± 5 cm^{-1} (rocking mode of coordinated water) [10,11]. In the intermediate **II**, νC–N + δNH_2 at ~ 1295 ± 10 and νC–O at 1655 ± 5 cm^{-1} are not observed in the IR spectrum (Figs. 3C and 4C) [11]. Intermediate **III** does not show the aromatic CH stretching and bending vibrations characteristic of the naphthalene ring [10,11]. The end product in both case is metal(II) oxide which is characterised by X-ray analysis. All *d* values together with their intensities (measured by peak height) are in accord with the reported values [12].

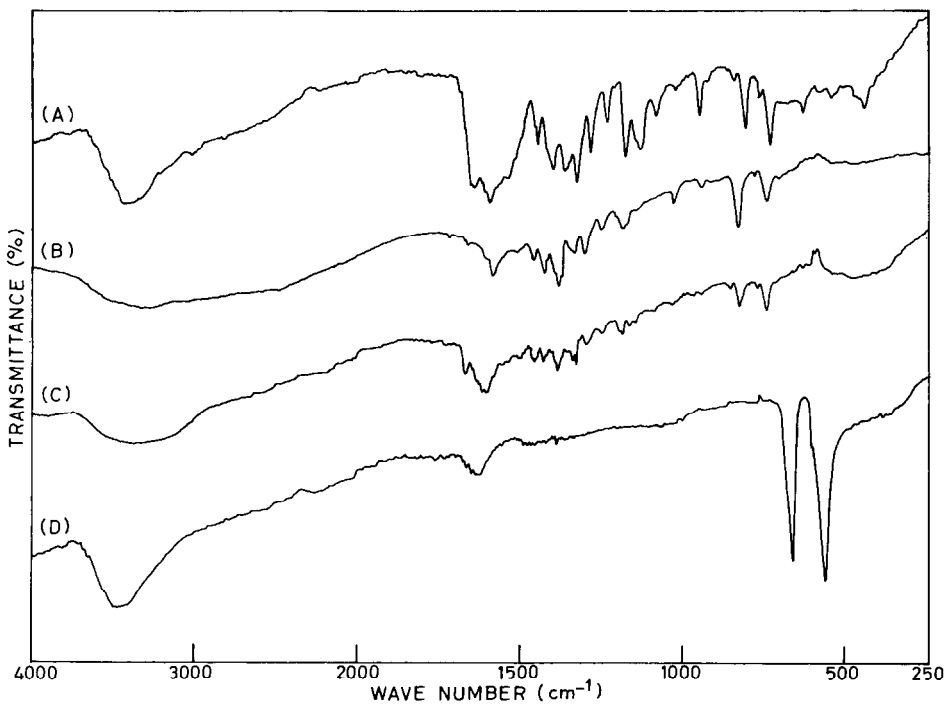
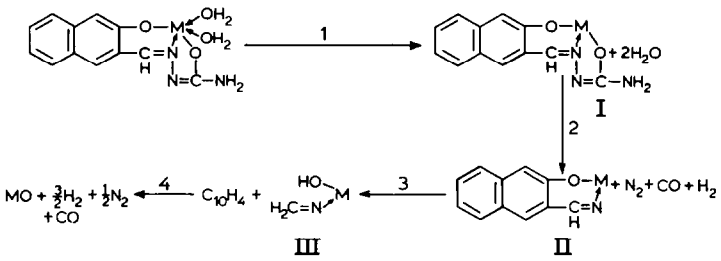


Fig. 4. IR spectra of $CoL \cdot 2H_2O$ (A), $CoL \cdot 2H_2O$ heated to 230°C (B), 320°C (C) and 500°C (D).

On the basis of the above-mentioned results, the following tentative scheme is proposed for the thermal decomposition of $ML \cdot 2H_2O$.



M = Cu or Co, and the temperatures above the arrows are:

	$CuL \cdot 2H_2O$	$CoL \cdot 2H_2O$
(1)	165–210°C	141–226°C
(2)	210–286°C	226–318°C
(3)	286–350°C	318–500°C
(4)	350–466°C	500–660°C

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