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Note

THERMAL STUDIES OF BIS-MORPHOLINE COMPLEXES OF COPPER(II) CARBOXYLATES

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INTRODUCTION

The thermal decomposition of hydrated metal(II) carboxylates has been studied extensively [1—6], but little work has been done on complexes of nitrogen donors with copper(II) carboxylates [7—9]. The present communication deals with the thermal decomposition of bis(acetato)bis(morpholine) copper(II) dihydrate, bis(benzoato) and bis(*o*-chlorobenzoato)bis(morpholine)copper(II) by TG and DTA techniques in an atmosphere of static air. These studies were undertaken with a view to isolating their mono-morpholine complexes which could not be obtained using their usual preparation procedures.

EXPERIMENTAL

Bis-morpholine complexes were prepared as reported earlier [10,11]. Thermogravimetry was carried out on a thermo-recording balance (Stanton Instruments, Model No. AD-2) at a heating rate of 4°C min^{-1}. Nearly 300 mg of each of the compounds were used for this study. Differential thermal analysis curves were recorded on a DTA-02-Universal apparatus at the same heating rate using alumina as reference material. As far as possible, identical conditions were maintained during these studies. The nature of the thermolysis curves was independent of the amount of sample used. Weight loss data are presented in Table 1.

RESULTS AND DISCUSSION

Bis-morpholine complexes are blue, stable in air and quite soluble in common organic solvents. Their analytical, molecular weight, magnetic and spectral studies indicate that they are monomeric distorted octahedral molecules containing bidentate chelating carboxylate groups [11]. In the bis-acetato complex the additional two molecules of water are hydrogen bonded. The TG curve of this complex (Fig. 1) reveals that the complex is stable up

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TABLE 1

Weight loss data of the complexes

Starting complex	Intermediates/products proposed	Temp. (K)	Weight loss (%)	
			Found	Calcd.
$Cu(O_2CCH_3)_2(C_4H_9ON)_2 \cdot 2H_2O$	$Cu(O_2CCH_3)_2 \cdot 2C_4H_9ON$	383	9.42	9.23
	$Cu(O_2CCH_3)_2 \cdot C_4H_9ON$	413	32.04	31.47
	$Cu(O_2CCH_3)_2$	458	54.26	53.72
	CuO	533	79.11	79.23
$Cu(O_2CC_6H_5)_2 \cdot 2C_4H_9ON$	$Cu(O_2CC_6H_5)_2 \cdot C_4H_9ON$	503	18.86	18.19
	$Cu(O_2CC_6H_5)_2$	558	37.02	36.35
	$CuCO_3$	688	74.46	74.26
	CuO	873	83.22	83.42
$Cu(O_2CC_6H_4Cl\text{-}o)_2 \cdot 2C_4H_9ON$	$Cu(O_2CC_6H_4Cl\text{-}o)_2 \cdot C_4H_9ON$	438	16.60	15.89
	$Cu(O_2CC_6H_4Cl\text{-}o)_2$	498	32.22	31.78
	$CuCO_3$	678	76.18	77.49
	CuO	798	85.72	85.51

to 323 K, after which it starts to slowly decompose, finally forming CuO at 533 K. However, the smoothness of the TG curve is disturbed at three points; 383, 413 and 458 K. These disturbances correspond to three intermediate species, $Cu(O_2CCH_3)_2 \cdot 2C_4H_9ON$, $Cu(O_2CCH_3)_2 \cdot C_4H_9ON$ and $Cu(O_2CCH_3)_2$, respectively. The formation of these intermediates confirms the weight loss data. None of the intermediates could be isolated, as they start to decompose even before they are completely formed. The most probable mode of decomposition of the complex is

$$Cu(O_2CCH_3)_2(C_4H_9ON)_2 \cdot 2\,H_2O \xrightarrow{323\text{—}383K} Cu(O_2CCH_3)_2 \cdot 2\,C_4H_9ON \tag{1}$$

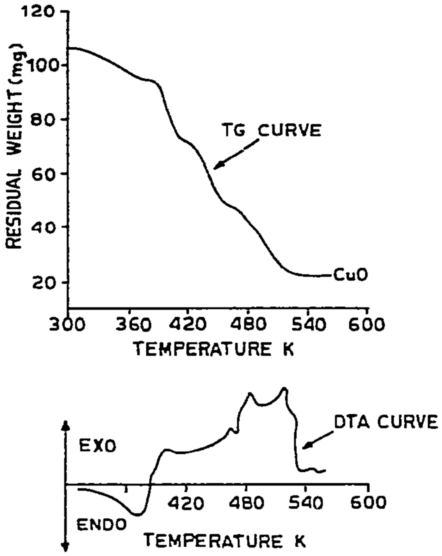
$$Cu(O_2CCH_3)_2 \cdot 2\,C_4H_9ON \xrightarrow{383\text{—}413K} Cu(O_2CCH_3)_2 \cdot C_4H_9ON \tag{2}$$

$$Cu(O_2CCH_3)_2 \cdot C_4H_9ON \xrightarrow{413\text{—}458K} Cu(O_2CCH_3)_2 \tag{3}$$

$$Cu(O_2CCH_3)_2 \xrightarrow{413\text{—}458K} CuO + \text{volatile products} \tag{4}$$

The DTA curve of this complex (Fig. 1) shows one endothermic broad band centred at 373 K corresponding to decomposition reaction (1). It also shows one exothermic band at 463 K having a shoulder at 403 K which corresponds to a successive loss of two morpholine molecules as shown in reactions (2) and (3) and two more exothermic peaks at 483 and 518 K which correspond to the decomposition reaction (4). The shape of these exotherms indicates that the decomposition of cupric acetate is a highly complex multistep process.

The TG curve of bis(benzoato)bis(morpholine) copper(II) (Fig. 2) shows that the complex is stable up to 373 K, after which it starts to decompose to give CuO as the final product at 873 K. However, the curve shows three dis-



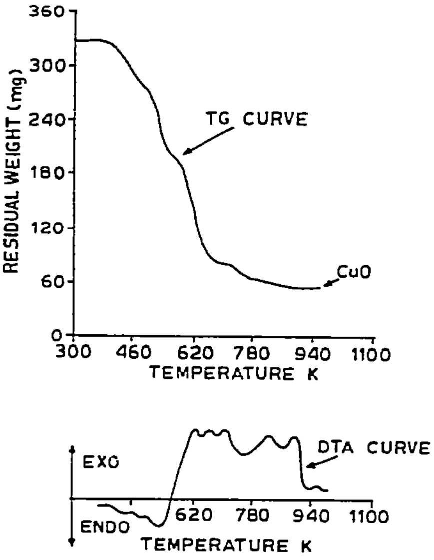


Fig. 1. Thermolysis curves of bis(acetato)bis(morpholine)copper(II) dihydrate.

Fig. 2. Thermolysis curves of bis(benzoato)bis(morpholine)copper(II).

turbances at 503, 558 and 688 K which correspond to the formation of three intermediates, $Cu(O_2CC_6H_5)_2 \cdot C_4H_9ON$, $Cu(O_2CC_6H_5)_2$ and $CuCO_3$, respectively. Weight loss data support these conclusions. The intermediates were too unstable to be isolated. This shows that the complex decomposes in four stages (5—8) to give CuO as the final product.

$$Cu(O_2CC_6H_5)_2 \cdot 2\ C_4H_9ON \xrightarrow{373\text{—}503K} Cu(O_2CC_6H_5)_2 \cdot C_4H_9ON \quad (5)$$

$$Cu(O_2CC_6H_5)_2 \cdot C_4H_9ON \xrightarrow{503\text{—}558K} Cu(O_2CC_6H_5)_2 \quad (6)$$

$$Cu(O_2CC_6H_5)_2 \xrightarrow{558\text{—}688K} CuCO_3 + \text{volatile product} \quad (7)$$

$$CuCO_3 \xrightarrow{688\text{—}873K} CuO \quad (8)$$

The DTA curve of this complex (Fig. 2) shows a broad endothermic band split into two peaks at 483 and 528 K corresponding to decomposition reactions (5) and (6), respectively. The remaining DTA curves shows two major broad exotherms observed in the regions 558—688 and 688—873 K. These exotherms are further split into a number of components suggesting that the decomposition of this complex is a complex multistep process.

The TG curve of bis(*o*-chlorobenzoato)bis(morpholine)copper(II) (Fig. 3) is similar to that of the bis-benzoato complex and follows the same pattern of decomposition. Weight loss data and relevant intermediates are presented in Table 1. The DTA curve of this complex (Fig. 3) shows two endotherms at 418 and 468 K and two composite exotherms in the regions 498—723 and 723—795 K. This curve is similar to the bis-benzoato DTA curve, indicating

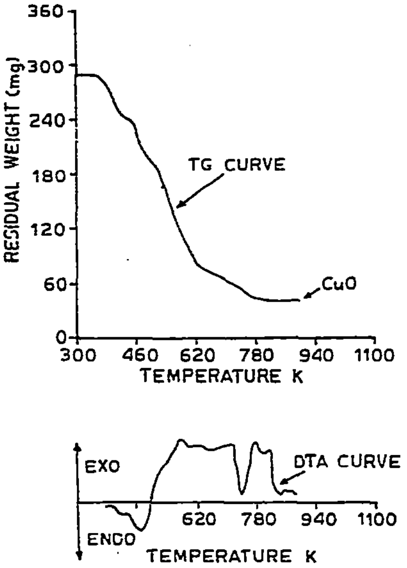


Fig. 3. Thermolysis curves of bis(*o*-chlorobenzoato)bis(morpholine) copper(II).

that the general mode of decomposition of these two complexes is similar in nature.

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