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PREPARATION AND THERMAL DECOMPOSITION OF COPPER(II) COMPLEXES WITH 4-METHYLIMIDAZOLE

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Abstract

Simple and mixed compounds of the formulae $Cu(4\text{-}Meim)_2$, CuSal(4-Meim), $CuSal(4\text{-}Meim)_2$ and $CuSalox(4\text{-}Meim)_2$, where *4-Meim*=4-methylimidazole, *Sal*=$(OC_6H_4COO)^{2-}$, *Salox*=$(OC_6H_4CHNO)^{2-}$ have been prepared. Thermal decomposition reactions have been established on the basis of thermal and X-ray analyses of these compounds. The pyrolysis proceeds in several (3–4) stages connected with the mass loss and exothermic effects. As a result of the last stage of decomposition CuO is formed.

Keywords: copper(II) compounds, 4-methylimidazole complexes of copper(II), mono(*o*-hydroxybenzaldoxime) of Cu(II), mono(*o*-hydroxy-benzoate) of Cu(II), thermal decomposition

Introduction

The imidazole group is of great importance in biochemistry because of its presence in histamine and histidine. The interactions of imidazole and its 4-methyl derivative with the copper(II) ion were described in several papers [1–6]. The thermal characteristics of two mixed coordination compounds obtained by a reaction of Cu(II) with 4-methylimidazole and NO_3^- were determined [7]. $Cu(4\text{-}Meim)_6(NO_3)_2$ and $Cu(4\text{-}Meim)_4(NO_3)_2$ decompose in two stages. In the first stage 4-methylimidazole groups are lost. The residual $Cu(4\text{-}Meim)(NO_3)_2$ decomposes and oxidizes to CuO. Thermal and spectral analyses have been reported for the organometallic complexes of copper(II) with 4-methylimidazole and succinate [8], adipate [9], benzoate [10], malate [11] and cinnamate [12]. The course of thermal decomposition differs for each of the compounds but in all cases it finally leads to CuO formation.

The aim of the present work was to synthesize complexes of copper(II) mono(*o*-hydroxybenzoate) or copper(II) mono(*o*-hydroxybenzaldoximate) with 4-methylimidazole and to investigate of thermal decomposition reactions of these compounds.

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Experimental

Preparation

$Cu(4\text{-Meim})_2$

4-Methylimidazole was dissolved in water and mixed with aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (the molar ratio of Cu: 4-Meim was 1:4). The solution with a beige precipitate was heated for 1 h at 60–70°C, cooled, filtered off, washed with water and dried on filter paper at room temperature.

CuSal(4-Meim), $CuSal(4\text{-Meim})_2$, $CuSalox(4\text{-Meim})_2$

0.328 g of 4-methylimidazole (L) was dissolved in 40 ml of toluene and mixed with solid CuSal (A) or CuSalox (A') in the molar ratio of A or A' to L 1:1 (for CuSal(4-Meim)) and 1:2 (for $CuSal(4\text{-Meim})_2$ and $CuSalox(4\text{-Meim})_2$). The mixtures were stirred at 60°C for 20 h, filtered off, washed with toluene and dried on filter paper at room temperature. Dark green compounds were obtained.

In order to obtain CuSal and CuSalox, $Cu(OH)_2 \cdot 2CuCO_3$ was gradually added to a solution of salicylic acid or salicylaldoxime [13, 14]. The mixture was heated for 3–4 h, stirred and filtered off. The precipitate was washed with hot water and dried at room temperature. The reactions are described by the following equations:

$$Cu(OH)_2 \cdot 2CuCO_3 + 3H_2Sal \rightarrow 3CuSal + 2H_2CO_3 + 2H_2O \quad (1)$$

$$Cu(OH)_2 \cdot 2CuCO_3 + 3H_2Salox \rightarrow 3CuSalox + 2H_2CO_3 + 2H_2O \quad (2)$$

Chemical analysis

Copper(II) was determined by complexometric titration with EDTA and carbon, hydrogen and nitrogen by elemental analysis. The results of the analyses are presented in Table 1.

Table 1 Results of chemical analysis of the compounds

Compound	Cu		C		H		N	
	found/	calc./	found/	calc./	found/	calc./	found/	calc./
	%							
$Cu(4\text{-Meim})_2$	27.91	28.15	41.90	42.56	4.49	4.43	24.95	24.82
CuSal(4-Meim)	22.09	22.55	45.96	46.88	3.79	3.55	9.89	9.94
$CuSal(4\text{-Meim})_2$	17.25	17.47	49.27	49.48	4.52	4.40	15.48	15.40
$CuSalox(4\text{-Meim})_2$	17.12	17.51	48.56	49.64	4.76	4.68	19.35	19.30

Thermal analysis

Thermal studies were carried out on an OD-102 derivatograph (MOM, Budapest). The measurements were made in air, over the temperature range 20–1000°C, the heating rate was 5°C min^{-1}, the mass of samples 100 mg, the reference substance α-Al_2O_3. The TG and DTG curves were also recorded using thermobalance C. I. Electronics within the temperature range 20–800°C. Table 2 lists the temperature ranges of the decomposition stages and the corresponding mass losses.

Table 2 Temperature ranges of the decomposition stages and the mass losses of copper(II) 4-methylimidazolate

Compound	Beginning of the decomposition/ °C	Ranges of decomposition stages/ °C		Mass loss/%
$Cu(4\text{-}Meim)_2$	190	I	190–250	6.0
		II	250–350	30.5
		III	420–605	28.5
			Total	65.0
CuSal(4-Meim)	70	I	70–195	5.0
		II	195–275	27.1
		III	275–370	9.3
		IV	370–480	27.2
			Total	68.6
$CuSal(4\text{-}Meim)_2$	80	I	80–160	7.0
		II	160–295	36.5
		III	295–330	14.5
		IV	390–480	21.0
			Total	79.0
$CuSalox(4\text{-}Meim)_2$	60	I	60–235	11.3
		II	255–510	62.9
			Total	74.2

Preparation and X-ray analysis of sinters

Samples (100 mg) of the salts were heated in an electric furnace under conditions similar to those of the thermal analysis. X-ray analysis was carried out on a Siemens D 5000 powder diffractometer using CuK_α radiation. The diffractograms of the sinters were compared with data base to confirm the presence of copper(II) salts. Figure 1 shows the powder diffractograms of $Cu(4\text{-}Meim)_2$ and CuSal(4-Meim) sinters.

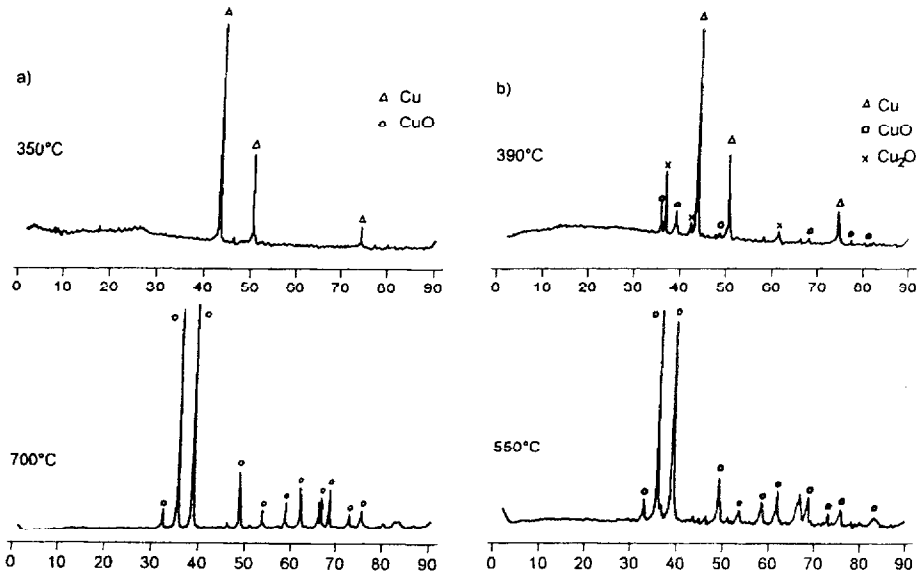

Fig. 1 X-ray patterns of: a) $Cu(4\text{-Meim})_2$ sinters; CuSal(4-Meim) sinters

Discussion

The thermal decomposition of copper(II) salts proceeds in 2–4 stages corresponding to mass loss and exothermic effects. Over the wide temperature range the TG and DTG curves indicate some differences. In some cases the analysis of the thermal curves allows only an approximate determination of the temperature ranges and mass losses of the pyrolysis stages. The general decomposition scheme of the complexes can be illustrated by the following equations:

$$Cu(4\text{-Meim})_2 \xrightarrow{350^\circ C} [Cu(4\text{-Meim})] \xrightarrow{605^\circ C} CuO \quad (3)$$

$$CuSal(4\text{-Meim}) \xrightarrow{275^\circ C} [CuSal] \xrightarrow{370^\circ C} [Cu+Cu_2O+CuO \xrightarrow{480^\circ C} CuO \quad (4)$$

$$CuSal(4\text{-Meim})_2 \xrightarrow{330^\circ C} [CuSal] \xrightarrow{480^\circ C} CuO \quad (5)$$

$$CuSalox(4\text{-Meim})_2 \xrightarrow{235^\circ C} [CuSalox(4\text{-Meim})_{1.5}] \xrightarrow{510^\circ C} CuO \quad (6)$$

The intermediate compounds in brackets were not isolated. The mass losses corresponding to the pyrolysis stages of the complexes (Eqs 3–6) were in good agreement with those calculated from the TG curves. On the basis of X-ray analysis of the sinters we assume that in the first stage the intermediate products

correspond to the mixtures of amorphous organic residues and metallic Cu. IR analysis of the sinters confirmed the destruction of the crystalline structure of the salts under investigation. In the IR spectra of the sinters no bands related to the characteristic vibrational frequencies of the organic ligands were observed. The presence of the intermediate organic compounds has been previously suggested in literature [8–12].

A further increase of temperature results is the decomposition of the intermediate products and evaporation of the volatile compounds. Metallic copper oxidizes to form Cu_2O (Eq. 4) and finally CuO.

The thermal stability of the mixed complexes in very similar. The beginning of the decomposition is observed at 60–80°C (Table 2). The stability of Cu(4-Meim)$_2$ is higher (190°C).

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