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THERMAL INVESTIGATION OF THE COMPOUNDS OF THE COPPER(II) MONO(*o*-HYDROXYBENZOATE) WITH CHELATE LIGANDS

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Abstract

Heteroligand complexes of copper(II) were obtained as a result of the reaction of Cu(II) mono (*o*-hydroxybenzoate) (monohydrate) with 8-hydroxyquinoline (HOx), *o*-aminophenol (NH_2Ph) and 2,2'-dipyridyl (2,2'-dipy). The mixture of the mono compound with: Cu(II) di(*o*-aminobenzoate) or Cu(II) di(*o*-hydroxybenzaldoximate) were obtained by the reaction with *o*-aminobenzoic acid (H_2A) and *o*-hydroxybenzaldoxime (H_2Salox). The obtained compounds and their sinters were subjected to chemical, X-ray and thermal analyses.

Keywords: copper(II) complexes, copper(II) mono(*o*-hydroxybenzoate), thermal analysis, X-ray analysis

Introduction

A number of divalent metals form compounds with *o*-hydrobenzoic acid (H_2Sal), where the molar ratio between metal and ligand is 1:2 [$M(HSal)_2$] or 1:1 [MSal] (M^{2+}-metal ion; $HSal^-$-$OHC_6H_4COO^-$; Sal^{2-}-$OC_6H_4COO^{2-}$). The latter compounds are formed primarily as a result of thermal decomposition of di-compounds [1–3] and may be used as substrates to obtain heteroligand complexes [4]. Thermal decomposition of Cu(II) di(*o*-hydroxybenzoate) does not lead to formation of a mono-complex [5] as it is in the case with Mn(II), Co(II), Ni(II), Zn(II) or alkaline earth metals [5, 6]. However, according to Babko and Szewczenko, it can be obtained by precipitation from a solution [7].

The subject of the present work was preparation and examination of thermal properties of compounds which are formed in the reaction of Cu(II) mono(*o*-hydroxybenzoate) (monohydrate) with 8-hydroxyquinoline, *o*-aminophenol, *o*-aminobenzoic acid, *o*-hydroxybenzaldoxime and 2,2'-dipyridyl.

Experimental

$Cu(OC_6H_4COO)\cdot H_2O$ was prepared according to a previously described method [7]. The heteroligand complexes were obtained as a result of a reaction

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between the solid mono-compound and a solution of the next ligand in toluene. The molar ratio of the reacting substances was 1:1. The suspension was heated to 70°C and stirred at this temperature for several hours. The precipitate was filtered off, washed with toluene and dried at room temperature. Light green compounds which were obtained, were subjected to elemental and X-ray analyses. After mineralization of the samples copper was determined by complexometric titration.

Results of chemical analysis:

$Cu(OC_6H_4COO)\cdot H_2O$

calculated: C 38.60%; H 2.76%; Cu 29.22%; H_2O 8.27%;
found: C 38.6%; H 2.5%; Cu 29.4%; H_2O 8.5% (from TG curve); **Cu(Sal)·H_2O**

$Cu(HOC_6H_4COO)(C_9H_6NO)$

calculated: C 55.72%; H 3.19%; N 4.06%; Cu 18.46%;
found: C 56.1%; H 3.6%; N 4.0%; Cu 18.5%; **Cu(HSal)(Ox)**

$Cu(HOC_6H_4COO)(NH_2C_6H_4O)$

calculated: C 50.55%; H 3.56%; N 4.54%; Cu 20.61%;
found: C 48.9%; H 3.4%; N 4.6%; Cu 21.1%; **Cu(HSal)(NHPh)**

$Cu(HOC_6H_4COO)(2,2'\text{-}C_{10}H_{10}N_2)$

calculated: C 57.23%; H 3.37%; N 7.87%; Cu 17.87%;
found: C 55.9%; H 3.4%; N 7.6%; Cu 18.2%; **Cu(Sal)(2,2'-dipy)**

The results of chemical analysis confirmed the formulae proposed for the obtained complexes*.

The chemical analysis did not confirm the formation of heteroligand compounds in the reaction between Cu(II) mono(*o*-hydroxybenzoate) and *o*-aminobenzoic acid or *o*-hydroxybenzaldoxime. However it indicated the formation of mixtures of Cu(Sal)·H_2O and $Cu(HA)_2$ (HA^-–$NH_2C_6H_4COO^-$) or Cu(Sal)·H_2O and $Cu(HSalox)_2$ ($HSalox^-$–OC_6H_4CHNOH).

Thermal analysis

The measurements were performed by means of a C.J. Electronics thermobalance with computer control and an OD-102 Derivatograph (MOM Budapest). Temperature range 20–1000°C, heating rate 10° min^{-1}, air atmosphere, sample mass 100 mg.

Investigation of sinters

Sinters were obtained under conditions similar to those of the thermal analysis. The TG curves were used to select the temperatures at which the sinters were

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* The course of the reaction is the same irrespective of whether the substrate is a hydrated or anhydrous monocomplex.

Table 1 Results of thermal analysis

Compound	Stage	T/°C	Mass loss/%	Peak nature
$CuSal{\cdot}H_2O$	I	155–210	8.5	endo
	II	240–580	60.5	exo
Cu(HSal)(Ox)	I	215–245	14.0	endo
	II	255–285	32.0	exo
	III	285–440	43.5	exo
	IV	440–690	78.0	exo
Cu(HSal)(NHPh)	I	185–270	21.0	exo
	II	270–580	73.0	exo
Cu(Sal)(2,2'-dipy)	I	290–340	44.0	endo
	II	440–570	74.0	exo
$CuSal{\cdot}H_2O+Cu(HA)_2$	I	155–205	3.0	endo
	II	245–295	34.0	exo
	III	295–575	73.0	exo
$CuSal{\cdot}H_2O+Cu(HSalox)_2$	I	160–280	30.0	endo, exo
	II	280–615	73.0	exo

obtained. Table 1 lists the temperature ranges of the decomposition stages, the corresponding mass losses and thermal effects.

X-ray analysis

Diffraction patterns of the obtained compounds and their sinters were prepared on the Siemens D5000 powder diffractometer on the CuK_α radiation. Diffractometric analysis confirmed the formation of heteroligand complexes with: 8-hydroxyquinoline, *o*-aminophenol and 2,2'-dipyridyl. It demonstrated that in the reaction of $Cu(Sal){\cdot}H_2O$ with *o*-aminobenzoic acid and *o*-hydroxybenzaldoxime mixtures of the initial compounds and copper(II) di(*o*-aminobenzoate) (1) or di(*o*-hydroxybenzaldoximate) (2) are formed. Diffraction patterns of $Cu(OHC_6H_4COO)(NH_2C_6H_4O)$ and its sinters are presented in Fig. 1.

Results and discussion

Thermal decomposition of the compounds under study proceeds in several stages and confirms formation of both heteroligand complexes and mixtures. The mass losses are accompanied by endothermic effects in the first stage decomposition (except in Cu(HSal)(NHPh)) and by exothermic effects in the following stages (Table 1).

The proposed scheme of decomposition of the examined compounds is:

$$1.\quad \mathrm{Cu(Sal)\cdot H_2O} \xrightarrow{155^{0}} \mathrm{CuSal} \xrightarrow{580^{0}} \mathrm{CuO}$$

$$2.\quad \mathrm{Cu(HSal)(Ox)} \xrightarrow{215^{0}} \begin{array}{c}\text{of the compound}\\ \text{partial decomposition}\end{array} \xrightarrow{255^{0}} \mathrm{Cu + Cu_2O + CuO} +$$

$$\begin{array}{c}\text{organic}\\ \text{fragments}\end{array} \xrightarrow{285^{0}} \mathrm{Cu + Cu_2O + CuO} \xrightarrow{440^{0}} \mathrm{CuO}$$

$$3.\quad \mathrm{Cu(HSal)(NHPh)} \xrightarrow{185^{0}} \mathrm{Cu} + \begin{array}{c}\text{organic}\\ \text{fragments}\end{array} \xrightarrow{270^{0}} \mathrm{CuO + Cu_2O}$$

$$4.\quad \mathrm{Cu(Sal)(2,2'\text{-}dipy)} \xrightarrow{290^{0}} \mathrm{Cu + Cu_2O} + \begin{array}{c}\text{organic}\\ \text{fragments}\end{array} \xrightarrow{440^{0}} \mathrm{CuO}$$

The analysis of the TG curves demonstrated that the temperature of the onset of decomposition $T_{\alpha=0.01}$ of the heteroligand complexes is considerably higher than $T_{\alpha=0.01}$ of the initial mono-compound and increases in the following order:

$$\mathrm{Cu(HSal)(NHPh) < Cu(HSal)\,(Ox) < CuSal(2,2'\text{-}dipy)}$$

The thermal decomposition of $\mathrm{Cu(Sal)\cdot H_2O}$ proceeds in two stages. Dehydratation of the hydrated compound is the first pyrolysis stage, the second one leads to the formation of the copper(II) oxide (reaction 1).

Diffractometric analysis of the sinters of the heteroligand complexes showed that reduction of $\mathrm{Cu^{2+}}$ ion to metallic copper causes the decomposition of these compounds. In the case of Cu(HSal)(Ox), metallic copper (and $\mathrm{Cu_2O}$, CuO) is formed in the second stage, while in the case of Cu(HSal)(NHPh) and

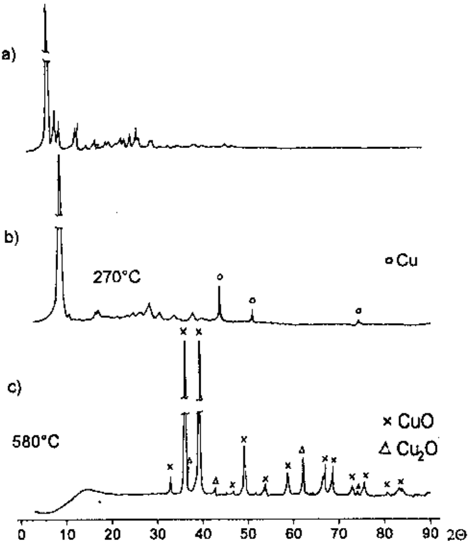

Fig. 1 X-ray analysis: a) $\mathrm{Cu(OHC_6H_4COO)(NH_2C_6H_4O)}$ complex; b) sinter 270°C; c) sinter 580°C

Cu(Sal)(2,2'-dipy) complexes copper formation is observed in the first stage. In the following stages organic residue escapes, metallic copper and Cu_2O are oxidized to CuO completely (reaction 2 and 4) or partly (reaction 3).

The process of decomposition of mixtures begins at a temperature characteristic of a less stable Cu(II)mono(*o*-hydroxybenzoate)(monohydrate) (Table 1) ($T_{\propto=0.01}$ $Cu(HA)_2$–245°C; $T_{\propto=0.01}$ $Cu(HSalox)_2$–225°C). The mixture (1) decomposes in three stages. After the stage of dehydration a simultaneous decomposition of anhydrous compounds Cu(Sal) and $Cu(HA)_2$ proceeds, resulting in the formation of Cu_2O and solid organic fragments in the second stage and CuO in the third.

Mixture (2) decomposes in two stages. Dehydration is combined with partial decomposition of $Cu(HSalox)_2$. The inorganic compound of copper does not appear until the second and final stage of decomposition.

References

1 K. Kishora and R. Nagarajanc, J. Thermal Anal., 22 (1981) 25.
2 F. P. Emmenegger, Thermochim. Acta, 112 (1987) 63.
3 P. Kokkonen, L. H. J. Lajunen, A. Jeakkola and H. Routsalainen, Thermochim. Acta, 79 (1984) 289.
4 F. P. Emmenegger, J. Thermal Anal., 33 (1988) 997.
5 K. Rissanen, J. Valkonen, P. Kokkonen and M. Leshela, Acta Chem. Scand., A41 (1987) 299.
6 A. Radecki and M. Wesołowski, J. Thermal Anal., 9 (1976) 29.
7 A. K. Babkó, and Ł. L. Szewczenko, Zh. Neorg. Khim., 9 (1964) 42.