THERMAL ANALYSIS OF COPPER(II) COMPLEXES OF GENERAL FORMULA [Et$_4$N]$_2$[CuBr$_n$Cl$_{4-n}$]

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Thermal decomposition of compounds consisting of tetrahalogenocuprate(II), [CuBr$_n$Cl$_{4-n}$]$^{2-}$ (*n*=0–4) anions and a tetraethylammonium cation has been studied using TG-FTIR, TG-MS, DTA and DTG techniques. The measurements were carried out in an argon and air atmospheres over the temperature range 293–1073 K. The products of the thermal decomposition were identified by IR and Far Infrared (FIR) spectroscopy as well as X-ray powder diffractometry.

Introduction

First reports on compounds containing halogenocuprate anions, [CuX$_4$]$^{2-}$, where X$^-$=Cl or Br, appeared in 1959 [1–5]. In addition to complexes with monohalide anions, also those with mixed anions, [CuBr$_n$Cl$_{4-n}$]$^{2-}$ have subsequently been published [6]. Owing to the possibility of occurrence of the central ion in different geometric environments consisting of four halide ligands, those compounds have become interesting subjects for spectroscopic [7–16] and magnetic [17, 18] exploration.

Many tetrahalogenocuprates exhibit thermochromic properties. For instance, a green R$_2$[CuCl$_4$], where *R*=(CH$_3$)$_2$CHNH$_3^+$ [9] or (C$_2$H$_5$)$_2$NH$_2^+$ [11], has a square planar geometry, whereas its yellow modification is tetrahedral. Roberts *et al.* [8] have found that thermochromism frequently occurs in compounds incorporating N–H····Cl hydrogen bonds.

Our study has been focused on copper(II) compounds with [CuBr$_n$Cl$_{4-n}$]$^{2-}$ (*n*=0–4) anions stabilized by a quaternary cation. Elimination of the hydrogen bonds has been intended to exclude the thermochromism in order to be able to preserve physical properties of the compounds up to their thermal decomposition points. Moreover, thermal decomposition of the tetraethylammonium cation could be determined [19] thus facilitating correct interpretation of the thermal decomposition steps of the inorganic constituent.

In the preceding reports, the series of analogous compounds with Co(II) [20] and Fe(III) [21, 22] as the central ion have been studied. The complexes of general formula [Et$_4$N]$_2$[CoBr$_n$Cl$_{4-n}$], underwent thermal decomposition in three steps independent of the composition of the anion and oven atmosphere. However, the atmosphere affected decomposition residues. In an inert atmosphere, CoCl$_2$ and Co$_2$C were the final products, whereas in an oxidative atmosphere Co$_3$O$_4$ was left behind. In this contribution, copper(II) has been chosen to determine the influence of the central ion on thermal stability of the halide complexes of metals(II) of the first row of transition elements.

By inspection of the TG, DTG and DTA curves and using the IR, FIR and MS techniques as well as the results of elemental analyses and X-ray powder diffractometry of polycrystalline samples, products of successive steps of thermal decomposition of the [Et$_4$N]$_2$[CuBr$_n$Cl$_{4-n}$] compounds have been identified. As previously, the measurements were run in argon and static air.

Experimental

Materials

The copper(II) complex salts were obtained by a procedure described in the literature, by mixing together stoichiometric quantities of a copper(II) halide with tetraethylammonium chloride and/or bromide in ethanol [1, 6].

Synthesis of [Et$_4$N]$_2$[CuCl$_4$]

CuCl$_2$·2H$_2$O (0.05 mol) was dissolved in a small quantity of ethanol and the solution was added to ethanolic solution of Et$_4$NCl (0.1 mol). (Found:

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C, 41.1; N, 6.0; H, 8.8; Cl, 30.3. Calcd. for [Et$_4$N]$_2$[CuCl$_4$], C, 41.2; N, 6.0; H, 8.7; Cl, 30.5%).

Synthesis of [Et$_4$N]$_2$[CuBr$_4$]

[Et$_4$N]$_2$[CuBr$_4$] was also prepared as described, by using CuBr$_2$ (0.05 mol) and Et$_4$NBr. (Found: C, 30.0; N, 4.4; H, 6.2; Br, 49.2. Calcd. for [Et$_4$N]$_2$[CuBr$_4$], C, 29.9; N, 4.4; H, 6.3; Br, 49.6%).

Synthesis of [Et$_4$N]$_2$[CuBrCl$_3$]

CuCl$_2$·2H$_2$O (0.05 mol) was dissolved in a small quantity of ethanol and the solution was added to an equimolar mixture (0.05 mol each) of Et$_4$NCl and Et$_4$NBr in ethanol. (Found: C, 37.5; N, 5.5; H, 8.0; Br, 18.0; Cl, 20.0. Calcd. for [Et$_4$N]$_2$[CuBrCl$_3$], C, 37.7; N, 5.5; H, 7.9; Br, 15.7; Cl, 20.9%).

Synthesis of [Et$_4$N]$_2$[CuBr$_3$Cl]

[Et$_4$N]$_2$[CuBr$_3$Cl] was prepared as described, but CuBr$_2$ (0.05 mol) was used as a copper halide. (Found: C, 32.1; N, 4.7; H, 6.8; Br, 40.0; Cl, 5.9. Calcd. for [Et$_4$N]$_2$[CuBr$_3$Cl], C, 32.1; N, 4.7; H, 6.7; Br, 40.0; Cl, 5.9%).

Synthesis of [Et$_4$N]$_2$[CuBr$_2$Cl$_2$]

CuBr$_2$ (0.05 mol) was dissolved in a small quantity of ethanol and the solution was added to an ethanolic solution of Et$_4$NCl (0.01 mol). (Found: C, 34.9; N, 5.1; H, 7.4; Br, 29.1; Cl, 12.9. Calcd. for [Et$_4$N]$_2$[CuBr$_2$Cl$_2$], C, 34.6; N, 5.0; H, 7.3; Br, 28.8; Cl, 12.8%).

The compounds were dried in a desiccator over P$_2$O$_5$. Upon storage at ambient temperature over a couple of weeks their structure did not change.

Methods

Potentiometric titrations were carried out using standard electrodes, SCE (indicator electrode) and silver electrode (the reference one). The IR spectra were recorded on a BRUKER IFS 66 spectrophotometer in a KBr pellet over the 4400–650 cm^{-1} range and the FIR spectra (650–50 cm^{-1}) were taken in PE.

Thermogravimetric measurements (TG-DTG-DTA) were run in static air on a model OD-103 derivatograph of Hungarian origin (range 293–1073 K, Pt crucible, sample mass ca. 500 mg, Al$_2$O$_3$ as reference, heating rate 5 K min^{-1}).

The TG-FTIR analyses in argon (Ar 5.0) were run on a Netzsch TG 209 apparatus coupled with a Bruker FTIR IFS66 spectrophotometer (range 293–1073 K, corundum crucible, sample mass ca. 15 mg, heating rate 15 K min^{-1}, flow rate of carrier gas 18 mL min^{-1}).

The TG-DTG-DTA measurements in helium were run on a Setsys 16/18 thermoanalyzer (Setaram) coupled with a Thermostar quadrupole mass spectrometer (range 293–1123 K, corundum crucible, sample mass ca. 4–5 mg, heating rate 5 K min^{-1}, flow rate of the carrier gas 15 mL min^{-1}).

The course of thermal analysis was broken at points corresponding to the main steps of decomposition and the residues in the crucible were quickly cooled in the stream of argon. This enabled to analyze the residues at a strictly pre-determined step of decomposition. The analysis was carried out using the IR and FIR spectroscopic techniques and the X-ray powder diffractometry as well as elemental analysis (C, H, N).

The presence of crystalline phases was checked by X-ray diffraction with the use of a Philips X'Pert diffractometer system. The XRD patterns were re-

Table 1 Results of analysis of the decomposition products in argon

Complexes	Stage	Temp. range/K	DTG$_{min}$/K	Mass loss/%	
				found	calcd.
[Et$_4$N]$_2$[CuCl$_4$]	1	533–563	543	34	36
	2	563–673	603	39	36
	3	673–1173	–	14	14
[Et$_4$N]$_2$[CuBrCl$_3$]	1	523–593	553	32	33
	2	593–673	–	30	41
	3	673–813	774	14	14
[Et$_4$N]$_2$[CuBr$_2$Cl$_2$]	1	503–548	523	37	30
	2	548–608	573	26	30
	3	608–1023	–	10	29
[Et$_4$N]$_2$[CuBr$_3$Cl]	1	488–543	509	30	28
	2	543–653	566	37	35
	3	653–853	807	11	26
[Et$_4$N]$_2$[CuBr$_4$]	1	503–548	510	37	33
	2	548–673	596	25	33
	3	673–853	787	19	24

corded at room temperature with CuK$_\alpha$ radiation (λ=1.540 Å). Qualitative analysis of diffraction spectra was carried out with an ICDD PDF database [23].

Results and discussion

The results of thermal analysis of the complexes in inert and oxidative atmospheres are collected in Tables 1 and 2.

Thermal decomposition of the [Et$_4$N]$_2$[CuBr$_n$Cl$_{4-n}$] compounds occurs in three steps. Both the temperatures corresponding to particular steps of decomposition as well as the shapes of the TG curves (Fig. 1) are alike. For clarity, only TG curves of three compounds are shown in Fig. 1.

At the onset of melting of the compounds, their rapid decomposition begins as indicated by a massive loss in mass (Fig. 1). The process is strongly endoenergetic, manifesting itself by sharp peaks in the DTG and DTA curves (Fig. 2). The thermal processes are exemplified by the TG, DTG and DTA curves of the decomposition of [Et$_4$N]$_2$[CuCl$_4$] shown in Fig. 2.

On the basis of the mass losses taken from the TG curve as well as the IR and MS spectra of the volatile products, a sequence of concurring reactions can be suggested. For the first step of the thermal decomposition of the series of compounds of general formula [Et$_4$N]$_2$[CuBr$_n$Cl$_{4-n}$] the sequence is as follows:

First step of decomposition of the [Et$_4$N]$_2$[CuBr$_n$Cl$_{4-n}$] compounds:

$$[Et_4N]_2[CuCl_4] \rightarrow [Et_4N][CuCl_3]_{(s)} + EtCl_{(g)} + Et_3N_{(g)}$$

$$[Et_4N]_2[CuBrCl_3] \rightarrow [Et_4N][CuBrCl_2]_{(s)} + EtCl_{(g)} + Et_3N_{(g)}$$

$$[Et_4N]_2[CuBr_2Cl_2] \rightarrow [Et_4N][CuBr_2Cl]_{(s)} + EtCl_{(g)} + Et_3N_{(g)}$$
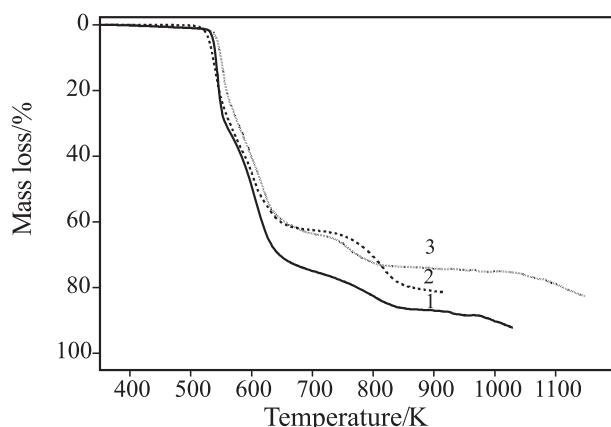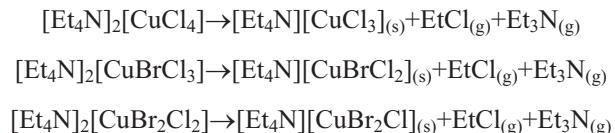
Fig. 1 TG curves of 1 – [Et$_4$N]$_2$[CuCl$_4$], 2 – [Et$_4$N]$_2$[CuBr$_4$] and 3 – [Et$_4$N]$_2$[CuBrCl$_3$] taken in argon

$$[Et_4N]_2[CuBr_3Cl] \rightarrow [Et_4N][CuBr_3]_{(s)} + EtCl_{(g)} + Et_3N_{(g)}$$

$$[Et_4N]_2[CuBr_4] \rightarrow [Et_4N][CuBr_3]_{(s)} + EtBr_{(g)} + Et_3N_{(g)}$$

During the first step, both the organic cation and the inorganic anion undergo decomposition.

Second step:

$$[Et_4N][CuCl_3] \rightarrow CuCl_{2(s)} + EtCl_{(g)} + Et_3N_{(g)}$$

$$[Et_4N][CuBrCl_2] \rightarrow CuCl_{2(s)} + EtBr_{(g)} + Et_3N_{(g)}$$

$$[Et_4N][CuBr_2Cl] \rightarrow CuBr_{2(s)} + EtCl_{(g)} + Et_3N_{(g)}$$

$$[Et_4N][CuBr_3] \rightarrow CuBr_{2(s)} + EtBr_{(g)} + Et_3N_{(g)}$$

$$[Et_4N][CuBr_3] \rightarrow CuBr_{2(s)} + EtBr_{(g)} + Et_3N_{(g)}$$

Reliability of the proposed equations of the thermal decomposition is supported by the results of elemental analyses of the solid residues of particular compounds. Moreover, ethyl halides and

Table 2 Results of analysis of the decomposition products in air

Complexes	Stage	Temp. range/K	DTG$_{min}$/K	Mass loss/%	
				found	calcd.
[Et$_4$N]$_2$[CuCl$_4$]	1	463–493	473	30	36
	2	493–623	513	31	36
	3	623–1093	–	15	14
[Et$_4$N]$_2$[CuBrCl$_3$]	1	513–588	523	38	33
	2	588–713	673	42	41
	3	713–1003	833	17	14
[Et$_4$N]$_2$[CuBr$_2$Cl$_2$]	1	493–543	513	44	30
	2	543–653	–	11	30
	3	–	–	–	29
[Et$_4$N]$_2$[CuBr$_3$Cl]	1	483–613	513	58	28
	2	613–713	–	10	35
	3	713–913	883	22	26
[Et$_4$N]$_2$[CuBr$_4$]	1	493––	513	–	33
	2	––673	593	62	33
	3	673–893	863	30	24
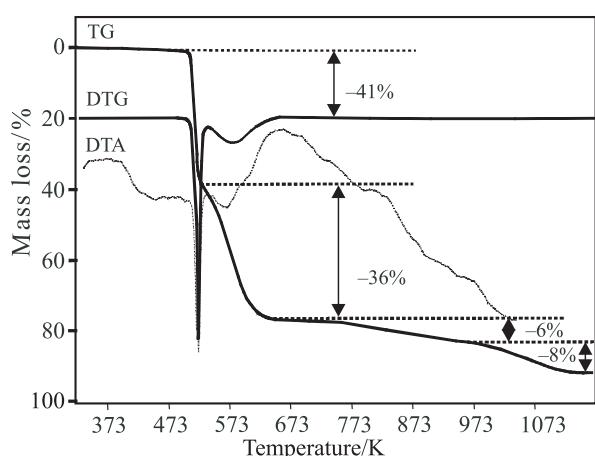
**Fig. 2** TG, DTG and DTA curves of the decomposition of [Et$_4$N]$_2$[CuCl$_4$] taken in the inert atmosphere

triethylamine were detected in the IR spectra of the volatiles (Fig. 3).

The IR bands over the range 650–700 cm^{-1} (C–Cl) seen in the volatile products of decomposition of [Et$_4$N]$_2$[CuBr$_2$Cl$_2$] collected during the first step at 533 and 593 K reveal volatilization of ethyl chloride. At 653 K (2nd step), other bands emerge between 665 and 670 cm^{-1} assigned to the C–Br bond. Their presence suggests cleavage of the Cu–Br bond during that step. These findings are supported by ionic currents of the volatile products. Thus, EtCl (*m/z* 66) and EtBr (*m/z* 110) appear over the ranges 483–573 and 533–653 K, respectively.

A comparison of the FIR spectra of the solid products of successive decomposition steps (Fig. 4) enables to identify structural changes of the anion.

Minor changes in the environment of the central ion, Cu(II), occur as soon as during the first step of decomposition as indicated by different bands emerging below 150 cm^{-1} in the spectrum of unheated [Et$_4$N]$_2$[CuBrCl$_3$] (Fig. 4) and in that of a sample
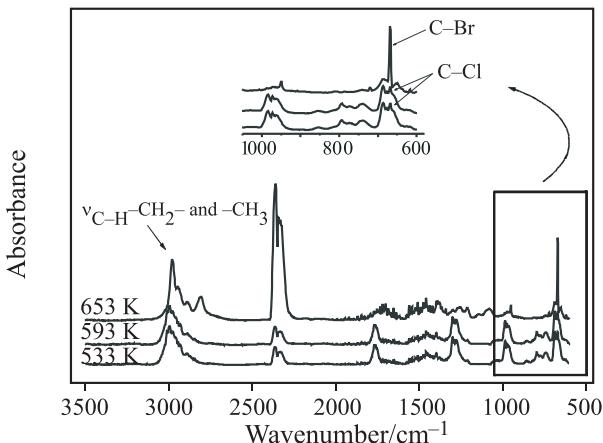
**Fig. 3** IR spectra of the volatile products of decomposition of [Et$_4$N]$_2$[CuBr$_2$Cl$_2$] in the inert gas atmosphere
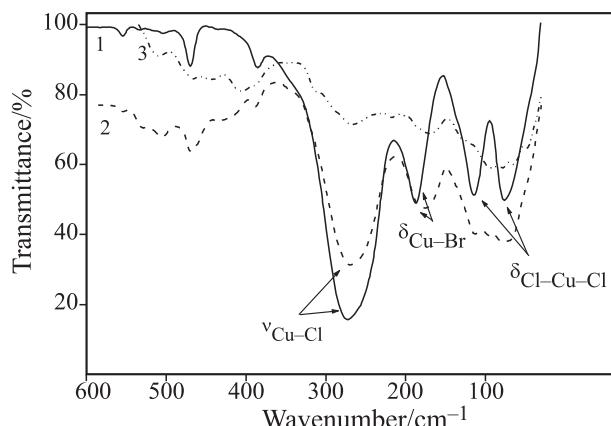
**Fig. 4** FIR spectra of the solid decomposition products of [Et$_4$N]$_2$[CuBrCl$_3$] at 2 – 563 K and 3 – 633 K compared to that of the 1 – unheated compound

heated up to 563 K (Fig. 4). Again, in the product of the first step, the Cu–Br and Cu–Cl bonds are present.

As the initial thermal processes of the compounds are very fast and accompanied by a series of consecutive reactions, unambiguous identification of the products becomes difficult. The difficulty consists in co-existence in the analyzed samples of the products of both the first and second steps.

Total decomposition of the anion occurs during the next step as indicated by missing Cu–X (*X*=Br, Cl) bands in the FIR spectrum of the compound heated up to 633 K (Fig. 4).

The mass losses recorded by the TG curves enable to identify a copper(II) halide as a decomposition product of the compounds at 673 K. In this context it is interesting to note that the X-ray diffraction patterns of polycrystalline samples obtained at that temperature in both atmospheres indicate unambiguously the presence of Cu(I) (Figs 5 and 6).
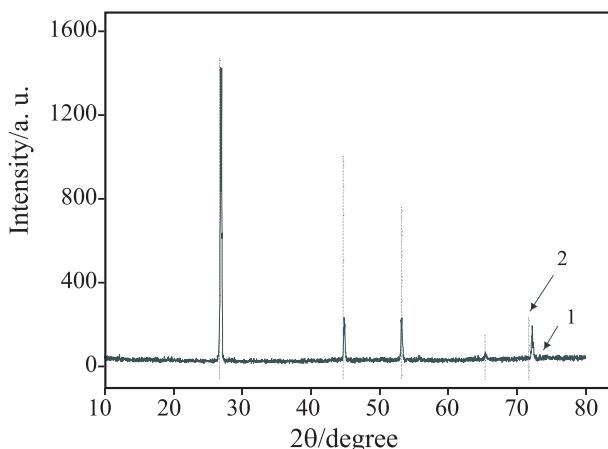

Fig. 5 XRD spectra of the decomposition products of 1 – [Et$_4$N]$_2$[CuBr$_2$Cl$_2$] at 673 K, in argon. For comparison, the XRD reflexes of the 2 – CuBr are shown

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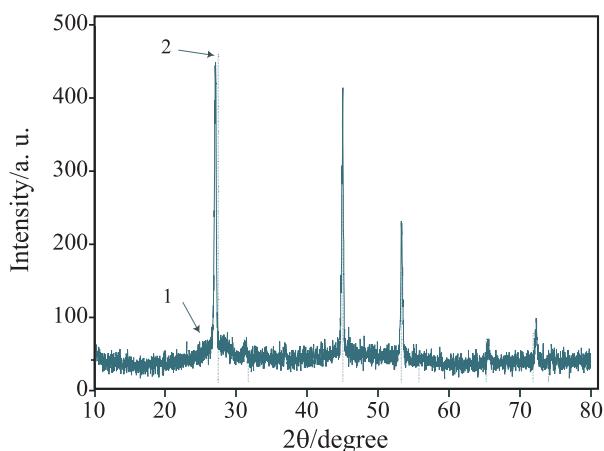
Fig. 6 XRD spectra of the decomposition products of 1 – [Et$_4$N]$_2$[CuBr$_4$] at 733 K, in air. For comparison, the XRD reflexes of the 2 – CuBr are shown
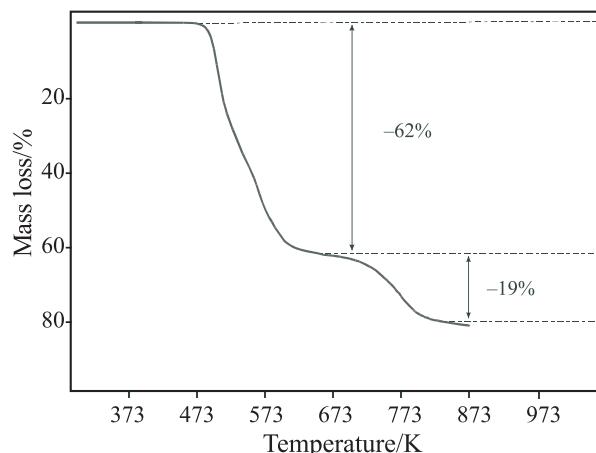
**Fig. 7** TG curves of [Et$_4$N]$_2$[CuBr$_4$] recorded in argon
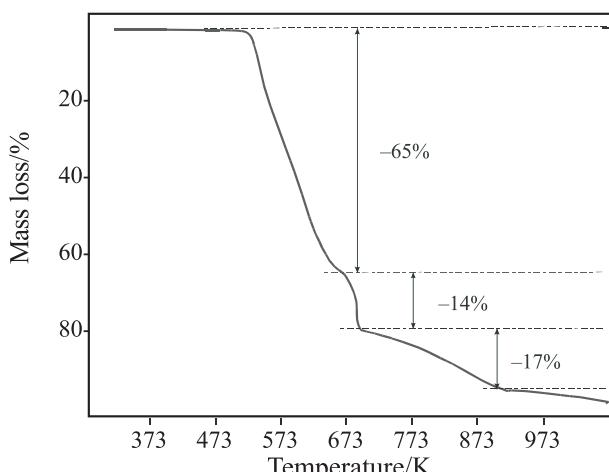
Fig. 8 TG curves of [Et$_4$N]$_2$[CuBr$_4$] recorded in air
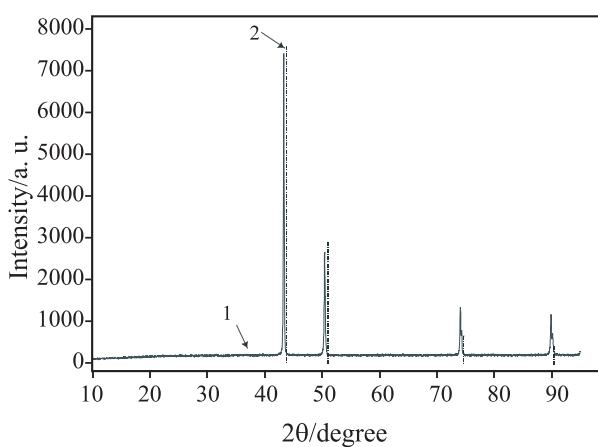
Fig. 9 XRD spectra of the decomposition products of 1 – [Et$_4$N]$_2$[CuCl$_4$] at 1073 K, in argon. For comparison, the XRD reflexes of the 2 – Cu are shown

Most probably, during the third step a Cu(II) halide undergoes decomposition to elemental copper according to the reaction:

$$CuX_2 \rightarrow Cu_{elemental} + X_{2(g)} \qquad X = Br, Cl$$
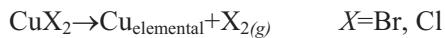
Subsequently, elemental copper reduces copper(II) to copper(I) halide:

$$CuCl_2 + Cu \rightarrow 2CuCl$$
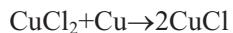
This conclusion is based on the presence of the reduced copper in a sinter generated from reactions occurring among the decomposition products rather than from direct decomposition of the compound.

Up to 673 K, the oven atmosphere has no significant influence on the course of decomposition. Both in the inert atmosphere as well as in the oxidative one, a copper(II) halide is the main product of the second step. However, the influence becomes appreciable in the next step as indicated also by the shape of the TG curves (Figs 7 and 8).

This process is much slower than the first two ones as seen in the shape of the TG curve.

In the inert atmosphere elemental copper is the final product of decomposition (Fig. 9).

In the oxidative atmosphere, the following reactions also occur [24]:

$$2CuCl_2 + O_2 \rightarrow 2CuO + 2Cl_{2(g)}$$

$T > 1073$ K $\qquad CuO \rightarrow Cu_2O$
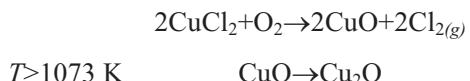
Conclusions

The [Et$_4$N]$_2$[CuBr$_n$Cl$_{4-n}$] compounds undergo thermal decomposition in three steps. During the first step, thermal transformations are not affected by oven atmosphere. Also the kind of the halogenocuprate(II) anion

has only insignificant influence. This notwithstanding, there is a markedly higher stability of the Cu–Br bond as compared to that of Cu–Cl. For instance, just during the first step of the decomposition of the bromochlorocuprates(II), EtCl emerges at a lower temperature than does EtBr. Such a course of decomposition is further confirmed by solid residues left during the second step in the inert atmosphere. A significant influence on the course of this step and the composition of solid residues has the oven atmosphere. In the inert atmosphere, elemental copper is deposited as found in a sample heated up to 1073 K, whereas in the air atmosphere CuO and Cu_2O were left behind.

A comparison of the results of this work with those dealing with analogous series of the Co(II) counterparts, $[Et_4N]_2[CoBr_nCl_{4-n}]$ [20], reveals a distinct influence of the kind of the central ion on the composition of the residue obtained in the inert atmosphere. Thus, among the solid decomposition products of the Co(II) compounds in argon, Co_2C and CoX_2 (*X*=Br, Cl) were identified, whereas in those of their copper(II) counterparts, elemental copper.

More meaningful conclusions about the influence of the central ion on the thermal processes will be drawn after inspection of the results of ongoing investigations into complex compounds of other bivalent transition metals.

Acknowledgements

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