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A THERMOANALYTICAL STUDY OF COPPER(I) THIOCARBAMIDE COMPOUNDS

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Abstract

Hydrated isostructural 1:3 complexes of copper(I) chloride and bromide with thiourea were synthesised and their thermal decomposition studied by simultaneous TG/DTA complemented by ex situ FTIR and XRD studies. The decomposition of $Cu(tu)_3Cl{\cdot}H_2O$ is initiated by dehydration around 100°C, followed by a total multi-step degradation of the structure in the temperature range of 200–600°C. The counter ion has some influence on the temperatures and composition of the solid residue. The results were compared with those obtained with the 1:1 complex $Cu(tu)Cl\ 1/2H_2O$.

Keywords: copper thiocarbamide complex, DTA, spray pyrolysis, TG

Introduction

Thermoanalytical studies of thiourea model compounds [1, 2] yield useful information for the development of chemical spray pyrolysis (CSP) processes for depositing thin films of binary and ternary metal sulphides which can be used, for instance, in photovoltaic applications. It is obvious that the CSP process parameters determine the properties of the resulting thin films [3, 4]. In spray pyrolysis the molar ratio of the precursor solution (sulfur/metal) together with the process temperature largely determines the stoichiometry of the product as recently shown for $Cu_{1-x}S$ [5].

In our previous investigation the thermal decomposition mechanism of the 1:1 copper chloride-thiourea (tu) complex, $Cu(tu)Cl{\cdot}1/2H_2O$, was studied by TG, DTA and EGA [2]. In order to obtain information on the effects of the metal to thiourea ratio and the counter-ion, we have now extended the investigation to the 1:3 complexes formed by copper chloride and bromide with thiourea.

Experimental

The preparation and characterization of $Cu(tu)Cl{\cdot}1/2H_2O$ (**1**) are presented in our previous study [2]. $Cu(tu)_3Cl{\cdot}H_2O$ (**2**) and $Cu(tu)_3Br{\cdot}H_2O$ (**3**) were prepared by add-

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ing solid copper(I) chloride and bromide, respectively, into 1 mol dm^{-3} aqueous solution of thiourea in a molar ratio of 1:3 at 70°C. In both cases transparent prisms with sizes up to some millimeters were precipitated. The compounds (**2**) and (**3**) were identified by chemical analysis (Cu by AAS in (**2**) 18.4%, calc.: 18.4%; and in (**3**) 16.2%, calc.: 16.3%). Single crystal X-ray diffractometer data measured at 193 K revealed the crystals of (**2**) to be monoclinic with space group P2/c and a=11.671, b=8.184, c=14.032 Å and β=98.2°. The structure was refined to a final R value of 2.84% for 2360 reflections. The corresponding bromide compound (**3**) is isostructural as shown by the unit cell data (a=12.075, b=8.232, c=14.029 Å and β=98.2°). The results of a full structural characterization of (**2**) will be presented elsewhere [6].

For the thermoanalytical studies of (**1**)–(**3**) a Seiko simultaneous TG/DTA 320 instrument was used. The sample mass was 15–20 mg and the heating rate 10°C min^{-1}. The measurements were carried out in dynamic air and helium (99.9995%) atmospheres (flow rates of 80 cm^{3} min^{-1}). Some additional heat treatments of the precursors in air were made isothermally in a laboratory oven at temperatures determined on the basis of the dynamic TG runs. The sample mass was in these cases 50–100 mg. The TG and DTA results were compared to an EGA-FTIR investigation carried out for (**1**) [2].

FTIR and powder diffraction were used *ex situ* to characterize the precursors, intermediates and final products of the thermal decomposition. IR spectra were obtained in the region 4000–400 cm^{-1} with a Nicolet Magna FTIR 750 Spectrometer using KBr pellet technique. The X-ray diffraction (XRD) patterns were recorded by a Philips MPD 1880 diffractometer using CuK$_\alpha$ radiation. The phases were identified using reference samples and JCPDS files.

Results and discussion

Thermal decomposition of copper chloride–thiocarbamide 1:3 complex

The TG curves of (**2**) show four mass loss steps in helium and five steps in air (Figs 1 and 2). The three first steps up to 400°C are strikingly similar in both atmospheres. In helium all processes are endothermic. The observed mass loss up to 1200°C is 80.0%. Cu_2S and Cu are the final decomposition products according to XRD and the last two endothermic effects on the DTA curve correspond to the melting of Cu and Cu_2S, respectively (Fig. 1).

Due to the reactive atmosphere the degradation in air is more complex and this case will be discussed in more detail. In air the decomposition steps 1, 4 and 5 are clearly endothermic. The second decomposition step, involving the largest mass loss, contains both endo- and exothermic reactions while the third step is exothermic (Fig. 2). According to XRD data Cu_2O is the final decomposition product at 1070°C (Table 1). The total mass loss up to 1200°C is 80.9% (calc. 79.3%).

The first mass loss in the temperature range 20–140°C is 4.9%, also in helium. This corresponds to the dehydration of (**2**) (calc. 5.2%):

$$Cu(tu)_3Cl\cdot H_2O_{(s)} \rightarrow Cu(tu)_3Cl_{(s)} + H_2O_{(g)} \qquad (1)$$

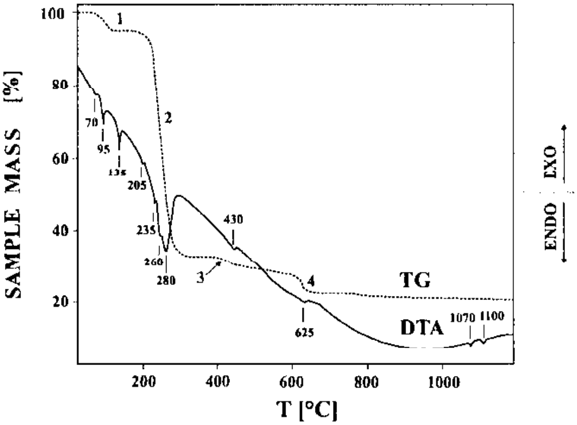

Fig. 1 TG and DTA curves of $Cu(SCN_2H_4)_3Cl{\cdot}H_2O$ recorded in flowing helium at the rate of 10°C min^{-1}. The sample mass is 19.9 mg

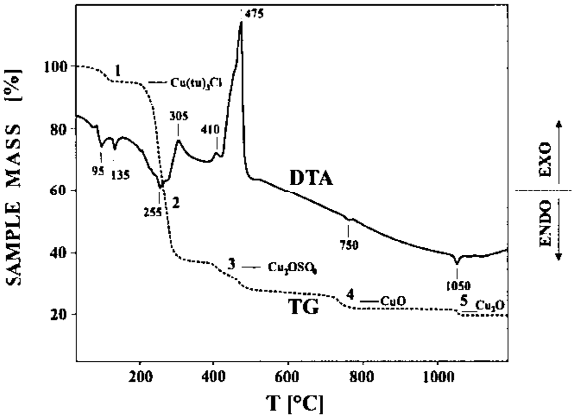

Fig. 2 TG and DTA curves of $Cu(SCN_2H_4)_3Cl{\cdot}H_2O$ recorded in flowing air at the rate of 10°C min^{-1}. The sample mass is 20.7 mg

The endothermic effect at 135°C (Figs 1 and 2) is probably due to the melting of dehydrated compound $Cu(tu)_3Cl$. Its thermal decomposition starts at 200°C, i.e. somewhat lower than in the case of the 1:1 complex (220°C) [2]. The decomposition step no. 2 between 200 and 320°C is a complex multistep process as seen in the Figs 1 and 2. In air four endothermic reactions occur followed by an exothermic one with a maximum at 305°C. This is a more complex decomposition mechanism than in the case of (**1**), where only two endothermic steps were observed. According to EGA the first endothermic reaction for (**1**) was interpreted as decomposition with evolution of HCl while the second one corresponded to the decomposition of the released thiourea ligand [2]. This mode of decomposition is also probable for (**2**).

Table 1 Crystalline decomposition products of $Cu(tu)_3Cl{\cdot}H_2O$ and $Cu(tu)_3Br{\cdot}H_2O$ as detected by XRD

$Cu(tu)_3Cl{\cdot}H_2O$		$Cu(tu)_3Br{\cdot}H_2O$	
T/°C	Main crystalline phases and JCPDS reference files	*T*/°C	Main crystalline phases and JCPDS reference files
255	Cu_9S_5 (26–476) $Cu(SCN)_{0.333}$ (38–498) unidentified phase	260	CuS (6–464) $Cu(SCN)_{0.333}$ (38–498)
280	CuS (6–464) Cu_7S_4 (33–439) $Cu(SCN)_{0.333}$ (38–498)	360	CuS (6–464) Cu_7S_4 (33–489)
350	CuS (6–464) Cu_7S_4 (33–489)	500	$Cu_{1.8}S$ (23–962) CuBr (6–262, 6–310)
460	Cu_2OSO_4 (13–189) $Cu_{1.8}S$ (23–962)	580	CuBr (6–262, 6–310) Cu_2OSO_4 (13–189)
750	CuO (5–661)	640	Cu_2OSO_4 (13–189) CuO (5–661)
1070	Cu_2O (5–667)	900	CuO (5–661)

XRD data of solid residues confirm the complete degradation of (**2**) at temperatures higher than 200°C (Table 1). The FTIR spectra of the samples heated at 220 and 250°C show vibrations at 2070–2130 cm^{-1} which weaken and shift to 2110–2175 cm^{-1} at 280°C (Fig. 3). These vibrations are characteristic for isothiocyanate

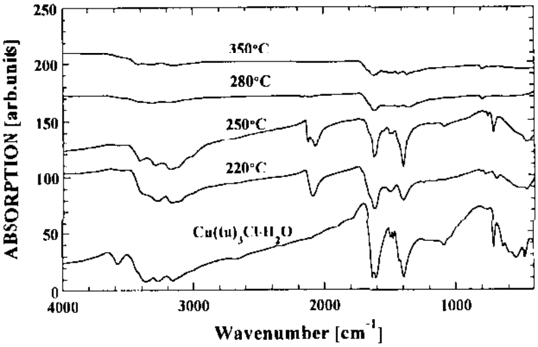

Fig. 3 FTIR spectra of $Cu(SCN_2H_4)_3Cl{\cdot}H_2O$ and its decomposition products in air (220, 250, 280 and 350°C)

(–N=C=S) and thiocyanate (–S–C≡N) groups [7], formed by isomerization of thiourea [1]. The FTIR data support the XRD results that the products contain SCN groups.

The third decomposition step in air at 390–520°C involves two exothermic processes at 410 and 475°C. The exothermic process at 410°C is obviously connected with oxidation of copper sulphide and formation of sulphate. The oxosulphate Cu_2OSO_4 is the main solid residue at 460°C as detected by XRD. The highly exothermic process close to 475°C is connected with the decomposition and oxidation of condensed organic matter confirmed earlier by EGA for the 1:1 complex [2]. Finally, the last decomposition steps at 700–770°C and 1030–1060°C correspond to the decomposition of Cu_2OSO_4 and CuO, respectively.

Thermal decomposition of copper bromide–thiocarbamide 1:3 complex

The TG curve of the bromide complex (**3**) in air shows six decomposition steps (Fig. 4). The total mass loss determined from TG curve up to 1200°C is 86%, which is somewhat higher than the theoretical value (81.6%), calculated on the basis of the presumption that all copper is converted into Cu_2O. It appears that the total observed mass loss for all investigated thiourea complexes is slightly (2–4%) higher than the theoretical values indicating possible nonstoichiometry of the product. Except for the temperatures, at which they occur the first and second mass loss steps are similar to those of compound (**2**), but the solid decomposition products contain CuBr whereas CuCl was not detected with compound (**2**) (Table 1). The third decomposition step at 540–600°C is accompanied by evolution of large amount of heat with a DTA maximum at 580°C. CuBr and Cu_2OSO_4 are the main crystalline products at 580°C. The decomposition step no. 4 at 620–650°C is an endothermic process and CuO together with Cu_2OSO_4 are the solid residues at 650°C. The endothermic effects at 740 and 1050°C are similar to those for complex (**2**) and correspond to the decomposition of Cu_2OSO_4 and CuO, respectively.

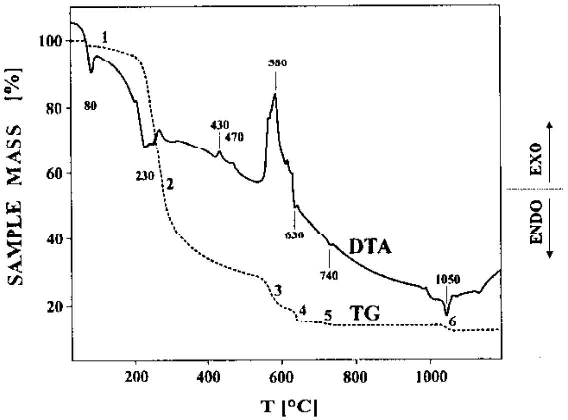

Fig. 4 TG and DTA curves of $Cu(SCN_2H_4)_3Br{\cdot}H_2O$ recorded in flowing air at the rate of 10°C min^{-1}. The sample mass is 17.0 mg

Conclusions

A comparison of thermal degradation of copper chloride thiourea 1:1 and 1:3 complexes shows that the dehydration as well as the destruction of the anhydrous 1:3 complex starts at lower temperatures than in the case of the 1:1 complex. This is probably caused by different structure [6]. The main decomposition processes in air and in inert atmosphere are similar for the both chloride complexes. The multistep decomposition mechanism of the 1:3 complex at 200–320°C and the observed highly exothermic reactions in air at 470°C are connected with its higher ligand-to-metal ratio compared to the 1:1 complex which leads also to a higher amount of condensed organic matter in the decomposition intermediates.

There seems to be no significant effect of counter ion on the decomposition of 1:3 complexes during the first and final decomposition steps. The difference is noticed in the intermediate temperature range of 470–570°C, where intensive exothermic reactions are shifted to higher temperatures in the case of copper bromide complex. The effect of counter ion is also visible in the solid residue of (**3**) which contains CuBr at 500°C while no chloride was detected by XRD in the case of (**2**).

The present results suggest that in spite of higher decomposition temperature it is better to use a lower ligand-to-metal ratio precursor in a spray pyrolysis process of Cu_xS or $CuInS_2$ in order to avoid excessive carbon contamination. The use of bromide as a counter ion would probably lead to CuBr impurities in the films and should therefore be avoided.

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