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Evolved gas analyses on a mixed valence copper(I,II) complex salt with thiosulfate and ammonia by in situ TG-EGA-FTIR and TG/DTA-EGA-MS

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Abstract Thermal decomposition of a mixed valence copper salt, $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2{\cdot}0.5NH_3$ (**1**) prepared from pentahydrates of sodium thiosulfate and copper sulphate of various molar ratios in 1:1 v/v aqueous ammonia solution, has been studied up to 1,000 °C in flowing air by simultaneous thermogravimetric and differential thermal analysis coupled online with quadrupole mass spectrometer (TG/DTA-MS) and FTIR spectrometric gas cell (TG-FTIR), in comparison. Compound **1** releases first but very slowly some of the included ammonia till 170 °C, then simultaneously ammonia (NH_3) and sulphur dioxide (SO_2) from 175 to 225 °C, whilst the evolution of SO_2 from thiosulfate ligands continues in several overlapping stages until 410 °C, and is escorted by explicit exothermic heat effects at around 237, 260, 358 and 410 °C. The former two exothermic DTA-peaks correspond to the simultaneous degradation and air oxidation processes of excess thiosulfate anions not reacted by formation of copper sulfides (both digenite, $Cu_{1.8}S$ and covellite, CuS, checked by XRD) and sodium sulfate, while the last two exothermic peaks are accompanied also by considerable mass gains, as the result of two-step oxidation of copper sulfides into various oxosulfates. The mass increase continues further on until 580 °C, when the sample mass begins to decrease slowly, as a continuous decomposition of the intermediate copper oxosulfates, indicated also by re-evolution of SO_2. At 1,000 °C, a residual mass value of 64.3% represents a stoichiometric formation of $Cu^{II}O$ and anhydrous Na_2SO_4.

Keywords Evolved gas analysis (EGA) · Mass spectrometry (MS) · FTIR-spectroscopic gas cell · Simultaneous thermogravimetry and differential thermal analysis (TG/DTA) · Mixed valence copper(II) and (I) complex · Formation of SO_2 and NH_3 · Digenite · Covellite · Copper(II)-oxo-sulfates

Introduction

The chemistry of the ammonia–thiosulfate–copper system is complicated due to the simultaneous presence of complexing ligands such as ammonia and thiosulfate, the Cu(II)–Cu(I) redox couple and the possibility of oxidative decomposition reactions of thiosulfate involving the formation of tetrathionate and other additional sulfur compounds [1, 2]. It has importance either in the ammoniacal thiosulfate leaching process for gold and silver extraction, which is catalyzed by copper and has several advantages over the conventional cyanidation process [1] or it can be applied in design of chemical oscillators [3]. Thiosulfate leaching of gold or silver can be considered as a non-toxic process. Nevertheless, the thiosulfate leaching catalyzed by copper is reported in the literature with high reagent consumption. One of the reasons of high consumption of thiosulfate might be the reduction of Cu^{2+} into Cu^+ with formation tetrathionate ($S_4O_6{}^{2-}$) and following precipitation of mixed valence copper(II)–copper(I) species [1].

Structure of such a solid mixed valence Cu(II)–Cu(I) salt, $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2$, named as tetrasodium tetraamminecopper(II) di-catena-di-μ-thiosulphato cuprate(I), were found to consist of cations of Na^+ and $[Cu^{II}(NH_3)_4]^{2+}$, and polymeric catena-anions, $\left[Cu^I(S_2O_3)_2\right]_n^{3n-}$, and in the

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crystal the univalent Cu^{I} atoms are tetrahedrally coordinated by four thiosulfato groups [4, 5]. An independent refinement of published single crystal data revealed also a presence of one additional water or rather ammonia molecule in the periodic voids in between the square planar $[Cu^{II}(NH_3)_4]^{2+}$ cations [5], along with the *c* crystallographic axis (space group *I*4/*m*, no. 87). Hathaway and Stephens [6] has even reported synthesis of both monoaquo and mono-ammoniac ($Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2{\cdot}L$, where L = H_2O or NH_3) adducts.

Electronic [6, 7], e.s.r. [7, 8], infrared [6, 9, 10] spectra, magnetic susceptibility and magnetic moments data [8] are available for characterization of these mixed valence complex, anyhow study of its thermal stability and decomposition seems to be missing. Thus, we decided to study the thermal behaviour of this interesting mixed valence copper salt, actually prepared in its hemi-ammoniac form, $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2{\cdot}0.5NH_3$ (**1**), as a potential source also for copper sulphide depositions, up to 1000 °C in flowing air by simultaneous thermo-gravimetric and differential thermal analysis coupled online with quadrupole mass spectrometer (TG/DTA-MS) and FTIR spectrometric gas cell (TG-FTIR), especially in order to explore thermal gas release processes occurring during pyrolytic fabrication techniques aiming various copper sulphides.

Experimental

Samples and methods

Samples of title compound are prepared by filtering out the violet-blue crystals after 30 min from 1:1 v/v aqueous ammonia solution of copper sulphate pentahydrate formed after addition of sodium thiosulfate pentahydrate applied either in 1:1, 1:2, and 1:4 molar ratios. Theoretically the formation stoichiometry of $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2{\cdot}0.5NH_3$ shows, that the Cu(II) and thiosulfate reagents are expected to be equivalent in 3:6(=1:2) molar ratio (Eq. 1):

$$\begin{aligned} &3\,Cu^{II}SO_4 + 6Na_2S_2O_3 + 4.5NH_3 \\ &\quad = Na_4\left[Cu^{II}(NH_3)_4\right]\left[Cu^{I}(S_2O_3)_2\right]_2 * 0.5NH_3 \qquad (1) \\ &\qquad + 3Na_2SO_4 + Na_2S_4O_6 \end{aligned}$$

FTIR spectra of samples **1** (1:1, 1:2, and 1:4) were measured by Excalibur Series FTS 3000 (Biorad) FTIR spectrophotometer in KBr between 700 and 4,000 cm^{-1}, while the XRD patterns of the samples and also their decomposition products obtained at various temperatures in the thermal balances, were recorded on X'pert Pro MPD (PANalytical, The Netherlands) X-ray diffractometer using Cu K_α radiation with Ni filter and X'celerator detector.

In situ EGA by coupled TG/DTA-MS

A simultaneous thermogravimetric and differential thermal analysis (TG/DTA) apparatus (STD 2960 Simultaneous DTA-TG, TA Instruments Inc., USA), a heating rate of 10 °C min^{-1}, an air flow rate of 130 ml/min, sample sizes between 11–19 mg, and open Pt crucible was used. The mixture of gaseous species could reach the ThermoStar GDS 200 (Balzers Instruments) quadrupole mass spectrometer equipped with Chaneltron detector, through a heated 100% methyl deactivated fused silica capillary tubing kept at $T = 200$ °C. Data collection was carried out with QuadStar 422v60 software with Multiple Ion Detection (MID) mode monitoring 64 selected channels ranging mostly between m/z 12–78. Measuring time was ca. 0.5 s for one channel, resulting in time of measuring of each cycle in ca. 30 s.

In situ EGA by coupled TG-FTIR

A TGA 2050 Thermogravimetric Analyzer (TA Instruments, USA) with a heating rate of 10 °C min^{-1}, with air flow rate of 120 ml/min, (and an extra 10 ml/min air as a balance purge) and sample size 37.27 mg of samples in open Pt crucible were used. Gaseous species evolved from the sample were led into FTIR gas cell of the BioRad TGA/IR Accessory Unit equipped with cooled DTGS detector through a heated stainless steal transfer line ($l = 90$ cm, $d_{in} = 2$ mm) kept at $T = 180$ °C. FTIR spectra (550–4,000 cm^{-1}) were collected in every 30 s after accumulation of 29 interferograms by a BioRad Excalibur Series FTS 3000 spectrometer using Win IR Pro 2.7 FTIR (Bio-Rad) data collection and evaluation software.

FTIR spectroscopic and mass spectrometric identification of various gaseous species

The components of released gaseous mixtures were monitored and identified mostly on the basis of their FTIR and MS reference spectra available on world wide web in the public domain spectral libraries of NIST [11] and collected from the special literature [12].

Results and discussion

FTIR and XRD characterization of samples 1

FTIR spectra of samples **1** (1:1), **1** (1:2), and **1** (1:4) as crystallized from aqueous 1:1 v/v ammonia solution of copper sulphate ($CuSO_4{\cdot}5H_2O$) and sodium thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$)·applied either in 1:1, 1:2, and 1:4 molar ratios, respectively, are shown in Fig. 1.

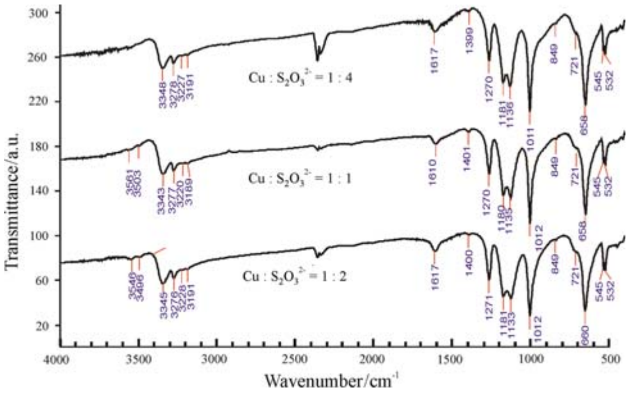

Fig. 1 FTIR(KBr) spectra of sample **1** (1:4), **1** (1:1), and **1** (1:2) as prepared with initial molar reagent ratio of Cu^{2+}:S_2O_3 = 1:4, 1:1, and 1:2, respectively. No significant effect of the initial reagent ratio on the FTIR-spectra of crystalline samples is obtained

The spectra of all samples are strikingly similar, independently on the initial reagent ratios of Cu^{2+}:S_2O_3 applied, what indicates that the same product is formed and crystallized in all the cases. The filtrated mother liquid remained dark blue in case of 1:1, only light blue for 1:2, while colourless in case of 1:4, what indicates that in the letter cases almost all the Cu(II) is consumed. The FTIR spectra of all samples are in harmony with spectrum details reported for $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2$ in the range of 400–1,300 cm^{-1} [9]. A not yet reported feature of spectra of samples **1,** worth to mention, is that in the 3,150–3,400 cm^{-1} range there are two doublets of NH stretching vibrations, a strong doublet at 3345, 3277 and a weaker one at 3227, 3190 cm^{-1}. The former one corresponds to the four square-planarly coordinated ammonia ligands, while the latter one might belong to some apically coordinated ammonia molecules. The lowered wavenumbers indicate, that these otherwise loosely coordinated ammonia molecules are involved even stronger hydrogen bond than the formal tetragonally coordinated ones, unfortunately, neither IR-data and in this way nor explanation were reported earlier on this type of ammoniacal stretching vibration in $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2{\cdot}NH_3$ by Hathaway and Stephens [6]. In addition, a weak doublet of free OH groups occurred in our samples also at around 3,550 and 3,500 cm^{-1}. It seems to be in agreement with suggestion of free rotating molecules of water, as it is in $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2{\cdot}H_2O$ [6], anyhow in ref. [6] the higher wavenumber of 3,600 cm^{-1} was reported. With aging of samples at open air conditions, these bands of OH groups become more significant and are accompanied with an increasing occurrence of a new band at 1,400 cm^{-1} (characteristic for NH_4^+ cations), indicating a slow simultaneous formation of ammonium and hydroxide ions (or NH_4OH) within, or at least on the surface of the samples.

The XRD patterns of all the samples are similar to each other and to those calculated ones, which are originated from single crystal coordinates of anhydrous $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2$ [4, 13] and $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2{\cdot}NH_3$ [5, 13]. Actually, the patterns, corresponding to these two reference phases, (PDF-01-71-2180 and PDF-01-76-792, respectively [14]) do not seem to differ significantly from each others.

Thermal behavior of Sample 1 ($Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2{\cdot}0.5NH_3$) measured in situ by TG/DTA-EGA-MS system and TG-FTIR spectrometric gas cell

Simultaneous thermogravimetric (TG) and differential thermal analytical (DTA) curves of sample **1** (1:4) are shown in Fig. 2. Meanwhile the in situ observed gas-evolution curves, represented either by ion currents of various mass spectroscopic ion fragments or by integrated absorbances of the characteristic wavenumber regions of evolved gases, are displayed on Figs. 3 and 4, respectively. The temperature limits of various stages of the complex decomposition processes taking place are marked on the thermogravimetric TG curve (Fig. 2), based on the

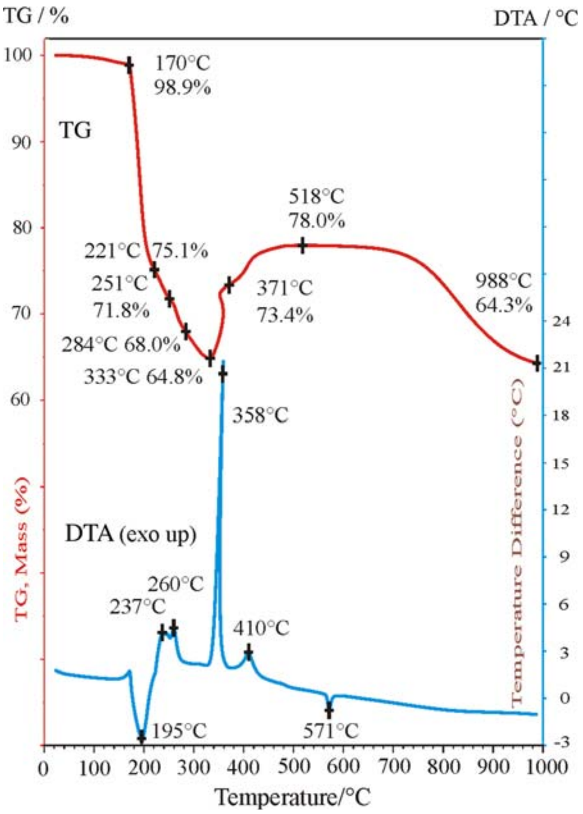

Fig. 2 Simultaneous TG/DTA curves of sample **1** ($Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2{\cdot}0.5NH_3$, 1:4). (Air flow 130 ml/min, heating rate 10 °C/min, initial mass 18.79 mg)

observed local minimal values of derivative TG (i.e. DTG) curve (not shown).

The first step of air decomposition can be characterized by a slow elongated mass loss of 1.1% up to 170 °C, which process is slightly endothermic and can be assigned to slow evolution of ammonia, based on mainly the FTIR spectral observations of evolving gases. The 1.1% mass loss corresponds to about half a molecule of ammonia (theoretical value 1.05%) in the formula unit of **1** ($Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2 \cdot 0.5NH_3$. This formulation might reflect shared square pyramidal [15] coordination of the fifth ammonia molecule rather then a tetragonal-octahedral one suggested earlier [5, 6].

Between 170 and 335 °C four consecutive decomposition steps are occurred (see TG and DTA curves in Fig. 2). The first one comes with a relative quick and large mass loss and an endothermic heat effect centered at 195 °C, while the second and third ones with much lowered mass loss rates and slightly exothermic heat effects observed to be centered at around 237 and 260 °C. The fourth step does not show an explicit heat effect. In the first endothermic step, an intense evolution of ammonia could be observed, while evolution of sulfur dioxide has been observed over the whole 170–335 °C temperature range shown by the in situ EGA-MS (Fig. 3).

Essentially the same gas evolution dynamics has been detected by the TG-FTIR spectroscopic gas cell system, except that during the initial simultaneous evolution of ammonia and SO_2 resulted in virtual loss of sulfur dioxide, probably because of spectral overlappings in the 1300–1400 cm^{-1} range (Fig. 4).

In these stages the obvious source of ammonia is the degradation process of the $[Cu(NH_3)_4]$ complex cation, while the formation of SO_2 is considered through various chemical processes taking place, including at least two of the various disproportional degradation processes of thiosulfate anions:

$$2\ S_2O_3^{2-} = 2\ S^{2-} + 2\ SO_{2(g)} + O_{2(g)} \tag{2}$$

$$S_2O_3^{2-} = SO_3^{2-} + S \tag{3}$$

and also at least two of the partial oxidation processes of the degradation products by air or even by the oxygen formed according to Eq. 2:

$$2\ SO_3^{2-} + O_{2(g)} = 2\ SO_4^{2-} \tag{4}$$

$$S + O_{2(g)} = SO_{2(g)} \tag{5}$$

The two exothermic effects observed between 220 and 285 °C are considered as results of the latter two oxidation processes (Eqs. 4, 5).

According to the phase analysis carried out on residues of sample **1** (1:4) obtained at the temperature of maximal mass loss (333 °C, 35.2% loss), the solid residue contains the following crystalline phases: copper(II) ion stabilized sodium sulfate (PDF 00-29-1290), anhydrous Na_2SO_4 (PDF 01-89-4751), CuS (covellite, PDF 01-74-1234), and $Cu_{1.8}S$ (digenite, PDF 01-73-8624). Formation of a mixture of copper(I) and (II) sulfides is not unusual in the Cu–S

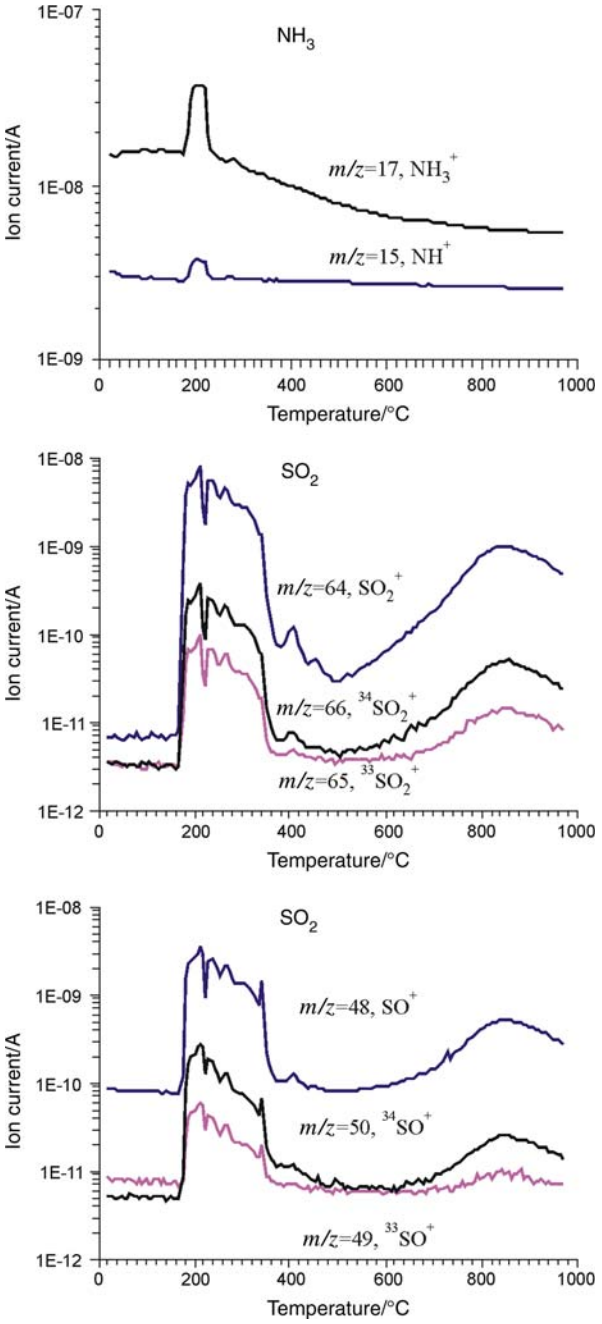

Fig. 3 Gas-evolution curves represented by various mass spectroscopic ion fragments of ammonia (NH_3) and sulfur dioxide (SO_2) formed from sample **1** ($Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2 \cdot 0.5NH_3$, 1:4) measured in situ by online coupled TG/DTA-EGA-MS system (air flow 130 ml/min, heating rate 10 °C/min, initial mass 18.79 mg)

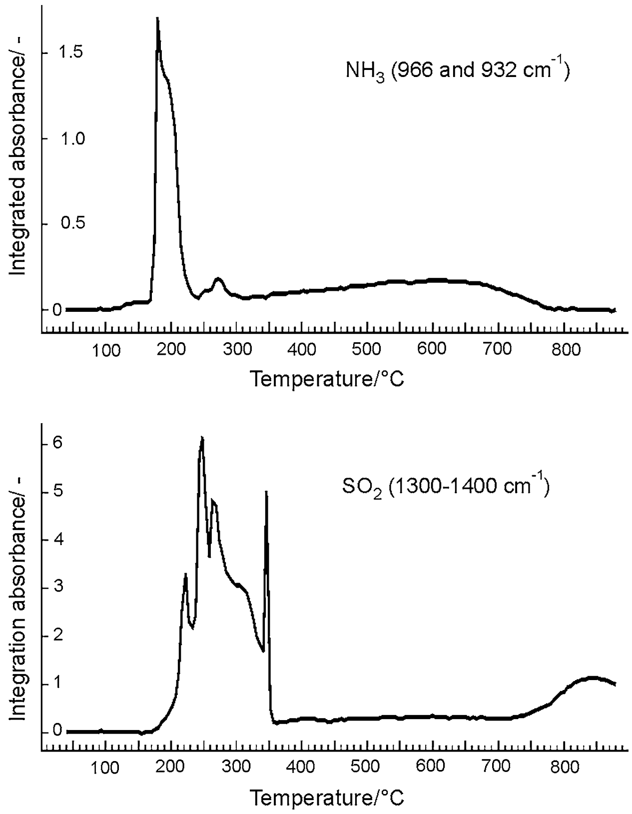

Fig. 4 Evolution courses of ammonia (NH_3) and sulfur dioxide (SO_2) formed from sample **1** ($Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2 \cdot 0.5NH_3$, 1:4) as observed by in situ TG-EGA-FTIR measurement. (Integrated absorbance in the characteristic wavenumber regions, 10 °C/min heating rate, 130 ml/min air flow, initial mass 37.27 mg)

system [16], anyhow the Cu species with both valences are originally present in our sample. Nevertheless, significant amount of sulfite species should also be present, as according to the mass loss calculation, (a residue level of Na_2SO_3: Na_2SO_4: CuS: $CuS_{0.555} = 1.5:0.5:1:2$, the mass loss is 34.83%, being rather comparable with the observed one (35.2%). Afterall, it does not seem that any oxidation of Cu(I) into Cu(II) would have taken place at the given stage.

Above 335 °C, two consequent oxidative processes take place till 500 °C, indicated by two exothermic heat effects (centered at 350 and 410 °C) and significant mass gains (altogether more then 13%). The first one is sudden and highly exothermic, raising the temperature of sample in the crucible to almost 15–20 °C higher than the programmed one. It is attributed to the oxidation of all of Cu(I) to Cu(II) by air and the mass gains are explained by simultaneous sulfate and oxosulfate formation. Various coordination complexes of thiourea with copper(I) chlorides [17–19], showed also formation of oxosulfate, Cu_2OSO_4 from digenite. For oxidation of covellite $\left[\mathrm{CuS} = 1/6\mathrm{Cu}^{\mathrm{I}}_4(\mathrm{S}_2)_2(\mathrm{CuS})_2\right]$ see the recent research studies [20, 21 and references therein; 22–24].

Between 500 and 700 °C a virtual plateau (probably as a compensated result of simultaneous mass gains and losses) is observed showing a more or less stabilized mass lever of 78% for the solid residues. Meanwhile an endothermic heat effect at 571 °C indicates a high temperature polymorphic transition of the readily formed anhydrous Na_2SO_4 (from monoclinic to hexagonal modification).

Above 700 °C a slow but definite decomposition of copper oxosulfates takes place, what is almost completed near 1,000 °C. Meanwhile evolution of SO_2 is continuously going on according to both TG/DTA-MS and TG-FTIR (Fig. 3b, c and Fig. 4b).

The identity and evolution course of the observed gaseous species by the parallel mass spectroscopic gas-evolution curves of various ion fragments of ammonia (NH_3) and sulfur dioxide (SO_2) as released from sample **1** ($Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2 \cdot 0.5NH_3$) are confirmed by both the online coupled TG/DTA-EGA-MS and TG-EGA-FTIR systems. The EGA-FTIR curve of ammonia (Fig. 4a) provides more detailed course than does the weak signals of *m/z* 15 (NH^+, Fig. 3a, bottom curve). The isotopic distribution of S with mass number of 32, 33, and 34 in the EGA-MS spectra fully confirm the evolution courses of SO_2 by ion fragments of *m/z* 48, 50, and 49 (SO^+ from SO_2, Fig. 3c) and the *m/z* 64, 66, and 65 ($SO_2{}^+$, Fig. 3b) molecular ions, and indicates definite release of SO_2, despite the fact that a parallel evolution of ammonia at around 200–250 °C seems to disturb, technically, somehow the EGA-FTIR detection of sulfur dioxide (Fig. 4b).

The final residue at 1,000 °C is consist of CuO (tenorite, PDF 00-48-1548) and copper(II) ion stabilized sodium sulfate (PDF 00-29-1290), while none of the simulated patterns for Cu_2OSO_4 (PDF 01-074-1590, 01-076-0754, 01-078-0612) occurred according to the XRD phase analysis.

Conclusions

Mixed valence copper(I,II) salt, $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2 \cdot 0.5NH_3$ has been successfully synthesized, and its excessive (half a mol of) ammonia content has been confirmed as one of the results of simultaneous TG and EGA measurements by FTIR and MS. The detailed mass loss and XRD phase analyses show that till 333 °C mainly decomposition steps occur and lead to formation of various copper (I and II) sulphides, which are represented by a local minimum on the TG curve and by the corresponding evolution courses of ammonia and sulphur dioxide. The oxidation of Cu(I) ions into Cu(II) takes only place above 335 °C reaching a certain mass plateau between 500 and 700 °C indicating also formation of certain crystalline Cu(II) oxosulfate species, whose identity unfortunately could not be determined (not matching with appropriate references). Nevertheless, they slowly begin to decompose above 700 °C with release of SO_2 again. Formation of sodium sulphate seems to start already in the initial decomposition stages of the title compound, anyhow its presence is proven by occurrence of endothermic phase transition at 571 °C. This latter compound is water-soluble and easily separable from copper sulphides by dissolution in water.

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