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TWO NOVEL COPPER COORDINATION COMPOUNDS WITH THIOSULFATE ANIONS AS LIGANDS
Solid state and reaction medium thermal decomposition

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Abstract

Thermal investigations of two novel coordination compounds, potential precursor of copper sulfides, namely $[Cu_2(S_2O_3)_2(NH_3)_4]\cdot 5H_2O$ and $Na_2[Cu_4(S_2O_3)_5(NH_3)_8]\cdot 2H_2O$ were performed either in solid state (static air atmosphere), as well as in reaction medium. During both decompositions, Cu^{2+} reduction occurs. In solid state decomposition, a mixture containing sulfides and sulfates is observed. In the reaction medium, CuS_y compounds with sulfur content y ($0.66<y<1$) dependent on thiosulfate concentration are obtained.

Keywords: copper sulfide, thermal decomposition, thiosulfate–copper coordination compounds

Introduction

The discovery of the nonlinear optical properties of copper sulfides Cu_xS_y ($1\leq x\leq 2$, $2\geq y\geq 1$) [1–2] directs the investigations to the synthesis of suitable precursors, coordination compounds being among them. The chemistry of Cu^{2+} is dominated by its reducing tendency ($Cu^{2+}\rightarrow Cu^{+}$) by even mild reducing agent. In the presence of ligands [3], Cu^{2+} ion may be stabilized by complex formation. Cu–S bonds are less more common than Cu–P bonds [4], being limited to thiosulfate [5], thiocarbamate [6] and dimercaptomalonitrile [7] type ligands.

The present paper deals with the synthesis, the characterization and the thermal decomposition study (both solid state and reaction medium) of two novel coordination compounds, namely $[Cu_2(S_2O_3)_2(NH_3)_4]\cdot 5H_2O$ and $Na_2[Cu_4(S_2O_3)_5(NH_3)_8]\cdot 2H_2O$ obtained in the system:

$$Cu^{2+}\text{– S source } (Na_2S_2O_3) \text{ – L } (L=NH_3)$$

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Table 1 Elemental analysis of the obtained coordination compounds

Cu^{2+}:nS_2O_3	Cu/%		Na/%		S/%		N/%		H/%		Molecular formula
	exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.	
1	24.80	24.76	–		25.26	25.17	11.41	10.91	2.40	4.28	$[Cu_2(S_2O_3)_2(NH_3)_4]\cdot 5H_2O$ (**I**) *FW*=513.08
2	25.89		4.12		31.80		12.45		2.65		
4	24.75	24.62	4.27	4.45	32.13	31.00	11.58	10.84	2.80	2.71	$Na_2[Cu_4(S_2O_3)_5(NH_3)_8]\cdot 2H_2O$ (**II**) *FW*=1032.12
6	24.59		4.80		33.11		11.93		2.77		

Experimental

Coordination compounds synthesis

As starting materials $Cu(CH_3COO)_2\cdot H_2O$, $Na_2S_2O_3\cdot 5H_2O$ and NH_4OH (25%) reagent grade, in a molar ratio $Cu(CH_3COO)_2\cdot H_2O:Na_2S_2O_3\cdot 5H_2O=1:n$ with n=1, 2, 4, 6 were used. Into NH_4OH solution, the metallic salts in the corresponding ratio were added. An immediate color change from blue to violet blue occurs. The solution was stirred vigorously one hour at room temperature at a pH~10–11 till the solution became colorless. Further, two variants of the synthesis were performed. Firstly, the violet-blue compounds were isolated, washed with ethanol and vacuum dried. Secondly, the violet compounds were maintained in the reaction medium, the temperature was risen up to ~80°C and the stirring was continued. The precipitates' color changes violet blue→dark brown→black. After 48 h, the compounds were isolated, washed with ethanol and vacuum dried.

Elemental analysis

The metal content Cu, Na was determined by atomic absorption, S_{total} and S in SO_4^{2-} by gravimetric technique and H, N content by microcombustion techniques. The elemental analysis results of the final compounds are summarized in Tables 1 and 2. It is worth to specify that no mention of Cu(II) coordination compounds containing both NH_3 and S_2O_3 as ligands was found in the analyzed literature data. Gmelin Handbuch [8, 9] mentioned the synthesis of some Cu(I)–NH_3–S_2O_3 coordination compounds.

Table 2 Elemental analysis of the obtained compounds after decomposition in reaction medium decomposition

$Cu^{2+}:nS_2O_3$	Cu/%		S/%		H/%		Molecular formula
	exp.	theor.	exp.	theor.	exp.	theor.	
1	73.06	73.32	26.66	26.68	–		$CuS_{0.71}$
2	74.07	74.86	24.89	25.13	–		$CuS_{0.66}$
3	61.79	62.29	23.67	24.13	2.02	1.88	$CuS_{0.76}H_2O$
4	67.66	66.50	32.78	33.49	–		CuS

Thermal measurements

The decomposition curves (TG, DTG, DTA) were recorded by a Q-1500 Paulik–Paulik–Erdey derivatograph in a static air atmosphere, at heating rates in the range 2.5–10°C min^{-1} with sample mass of ~50 mg. As inert reference material α-Al_2O_3 was used. IR spectra (400–4000 cm^{-1}) were recorded with a BIO-RAD FTIR 125 type spectrophotometer in KBr pellets. UV-VIS spectra (11 000–54 000 cm^{-1}) in diffuse reflectance technique were recorded with a JASCO V550 device.

Magnetic susceptibility

Magnetic susceptibility at room temperature was determined using a Faraday balance with Ni as calibrant. The TEM investigations were performed on a CM 120 microscope.

Results and discussion

Synthesis and characterization of the coordination compounds

Depending on the $S_2O_3^{2-}$ content (quantified through the *n* content parameter) the following two coordination compounds were isolated:

for *n*=1: $[Cu_2(S_2O_3)_2(NH_3)_4]\cdot 5H_2O$ **(I)**

for *n*=2, 4, 6 $Na_2[Cu_4(S_2O_3)_5(NH_3)_8]\cdot 2H_2O$ **(II)**

The IR spectra of the coordination compounds containing thiosulfate as ligand are usually dominated by two absorption bands assigned to $\nu_{asym}(SO)$ and $\nu_{sym}(SO)$. On the basis of spectroscopic criteria [10], the shift of $\nu_{asym}(SO)$ and $\nu_{sym}(SO)$ in comparison with the corresponding ones of anhydrous $Na_2S_2O_3$, (chose as reference due to its weak interactions between Na^+ and $S_2O_3^{2-}$ and absence of hydrogen bonds) may represent an indication for establishing the different coordination modes of $S_2O_3^{2-}$ ion.

Thus, a value of $\nu_{asym}(SO)>1130$ cm^{-1} suggests a coordination through S atom, a bridging one [11] if $\nu_{asym}(SO)$ is higher than 1175 cm^{-1} and a simple one [12–13] if $\nu_{asym}(SO)$ value is included in the range 1130–1175 cm^{-1}. Values of $\nu_{asym}(SO)<1130$ cm^{-1} are characteristic for coordination through oxygen atom. Correspondingly, $\nu_{sym}(SO)<1000$ cm^{-1} indicates a sulfur coordination, while $\nu_{sym}(SO)>1000$ cm^{-1} an oxygen one.

The IR spectra of synthesized compounds (Figs 1 and 2 curves (a)), suggest a different bonding of $S_2O_3^{2-}$ ligand. For the $[Cu_2(S_2O_3)_2(NH_3)_4]\cdot 5H_2O$ compound the location of ν_{asym} and ν_{sym} at ~1144 and 1011 cm^{-1} respectively, indicates a sulfur atom coordination and M–S simple bonds. For the $Na_2[Cu_4(S_2O_3)_5(NH_3)_8]\cdot 2H_2O$ compound, ν_{asym} is

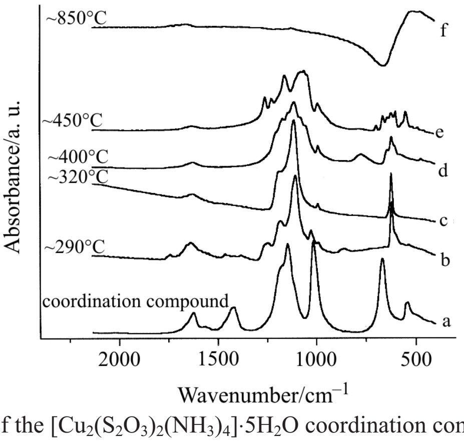


Fig. 1 IR spectra of the $[Cu_2(S_2O_3)_2(NH_3)_4]\cdot 5H_2O$ coordination compounds and its decomposition intermediates

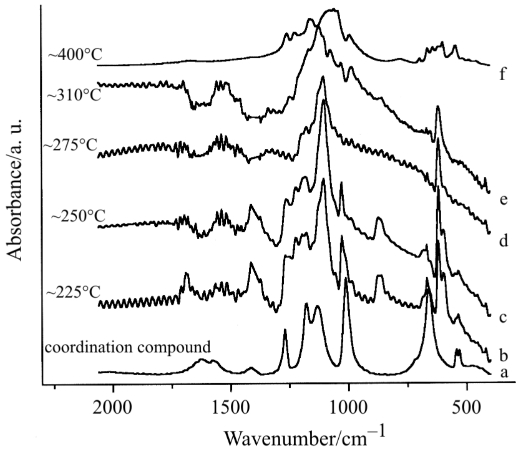


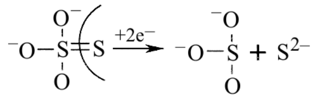
Fig. 2 IR spectra of the $[Cu_2(S_2O_3)_2(NH_3)_4]\cdot5H_2O$ coordination compounds and its decomposition intermediates

splitted into three strong bands in the range 1300–1130 cm^{-1} (1268, 1178 and 1130 cm^{-1}) and ν_{sym} vibration is found at 1003 cm^{-1}. This outcome denotes the existence of $S_2O_3^{2-}$ bridges coordinated to Cu^{2+}, bonded through both sulfur and oxygen atoms.

In the electronic spectra, the band assigned to Cu^{2+} in an octahedral configuration was evidenced. The transition at 650–750 nm (maximum at 690 nm) can be interpreted as $^2E_g \rightarrow {}^2T_{2g}$.

Thermal decomposition investigations

It is known that, in certain experimental conditions, the S–S bond of thiosulfate anion may be broken with electron capture [14], leading to sulfite and sulfide formation:



Scheme I

Solid state decomposition

The thermal curves of the compounds I and II (Figs 3 and 4) reveal eight or nine (compound(I)/compound(II)) decomposition steps, respectively.

The decomposition starts with two/one processes of water release (61–145/ 80–152°C compound(I)/(II)), followed by ammonia evolving (145–270/ 152–210°C (I)/(II)).

On further heating (270–320/210–310°C (I)/(II)), the thiosulfate decomposed in one/two step(s) through sulfite intermediates leading to a mixture of sulfides and sulfate. Either the calculated mass losses and magnetic results support the assumption of copper reduction, Cu^+ being present as sulfides. Thus, magnetic moments of

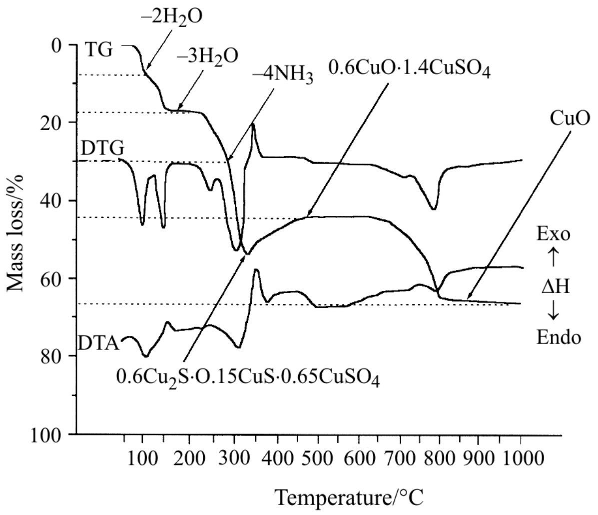


Fig. 3 Thermoanalytical curves (TG, DTG and DTA) of the polynuclear compound $[Cu_2(S_2O_3)_2(NH_3)_4]\cdot 5H_2O$ (heating rate of 5°C min^{-1}, the dotted line represents the theoretical mass loss)

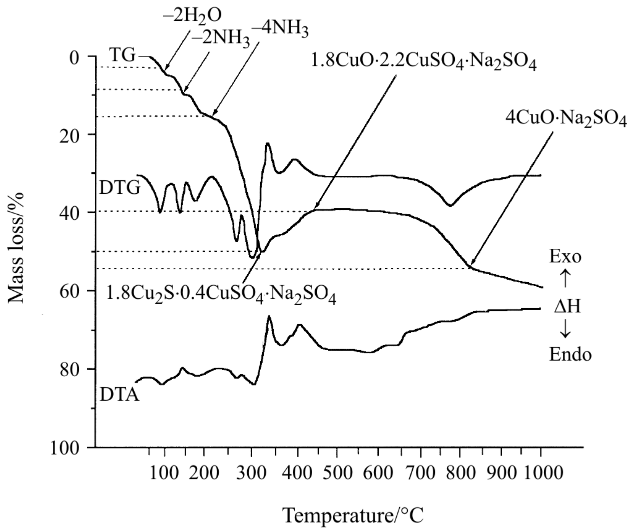


Fig. 4 Thermoanalytical curves (TG, DTG and DTA) of the polynuclear compound $Na_2[Cu_4(S_2O_3)_5(NH_3)_8]\cdot 2H_2O$ (heating rate of 5°C min^{-1}, the dotted line represents the theoretical mass loss)

μ=0.78/0.47 BM (I/II) were obtained for the two intermediates isolated at the end of this decomposition step (T=320/310°C). The values are in agreement [15] with the existence 0.8 and 0.4 Cu^{2+} ions. The IR spectra of the reaction intermediates show a gradual disappearance of the bands characteristic to $S_2O_3^{2-}$ and the appearance of the sulfite group characteristic vibration at ~610, ~860 and ~1005 cm^{-1} (Figs 1 and 2 curves (b) and respectively (b)–(d)). Rising the temperature, a sulfite→sulfate conversion occurs. The disappearance of the band from ~860 cm^{-1} and its shift towards a higher frequencies of the stretching vibrations $\nu_{sym,asym}$ (1105→1113 cm^{-1}, 609→610 cm^{-1} and 1104→1120 cm^{-1}, 615→625 cm^{-1}, compound (I)/(II)) characterizes this transformation (Figs 1 and 2 curves (c) and respectively (e)). It is important to mention here, that the bands identified for sulfates are typical for free $S_2O_4^{2-}$.

The reaction mixtures, stable in a narrow temperature range 320–330/310–330°C ((I)/(II)), undergo on further heating an exothermic two/one stepped mass gain process (330–500/330–472°C, (I)/(II)) assigned to $Cu^+ \rightarrow Cu^{2+}$ and $S^{2-} \rightarrow SO_4^{2-}$ oxidation. An increase of the magnetic moment is detected for the isolated compounds at ~400°C (μ=0.87/0.91 BM, (I/II)). The splitting of the SO_4^{2-} representative vibrations in the IR spectra (Figs 1 and 2 curves (d)–(e) and respectively (f)), denote two different binding modes of this group: a bidentate and bridging one [16].

The next region of mass loss (620–842/580–880°C ((I)/(II)) corresponds to sulfates decomposition in one/two stage(s) process. As final decomposition product of compound (I), CuO (theoretical/experimental mass loss=68.49/68.99%) was identified (Fig. 1 curve (e)). In the case of compound (II) at temperatures higher than 880°C the evaporation of Na_2SO_4 occurs.

Reaction medium decomposition

The maintenance of the synthesized coordination compounds in the reaction medium 48 h at 80°C with continuous stirring, induces their hydrolytic decomposition with the formation of the following sulfides:

$$CuS_{0.71} \quad n=1$$

$$CuS_{0.66} \quad n=2$$

$$CuS_{0.76}\cdot H_2O \quad n=4$$

$$CuS \quad n=6$$

The products of the hydrolytic reaction show quite different Cu and S to contents, probably due to the presence of a mixture of different copper sulfides, namely CuS (covellite, ASTM=60464), Cu_7S_4 (anilite, ASTM= 24-58) and $Cu_{1.8}$ (digenite, ASTM 23-962). Based on X-ray diffraction patterns of the products, CuS seems to be the main product.

The obtained compounds are characterized by quasi-spherical shaped particles with mean particle diameter included in the range 8.77–22.42 nm. The distribution of the particles dimensions are given in Fig. 5.

Two observations concerning the hydrolytic decomposition of the $Na_2[Cu_4(S_2O_3)_5(NH_3)_8]\cdot 2H_2O$ compound have to be pointed out: the increase of thiosulfate concentration in reaction medium favors the synthesis of higher sulfur content sulfides and an increase of particles size.

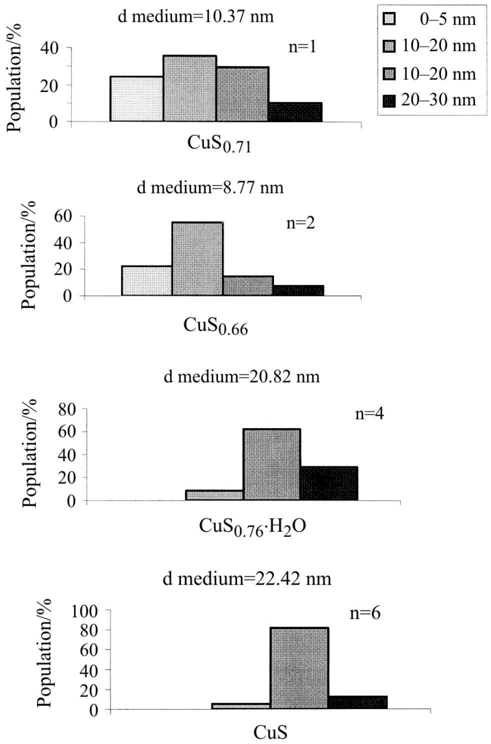


Fig. 5 The distribution of CuS_y particles dimensions obtained after hydrolytic decomposition

Conclusions

Although is unanimous recognized the role of sodium thiosulfate in Cu_xS_y synthesis, the sulfides formation mechanism is not yet elucidate. The thermal decomposition of the investigated system (Cu^{2+}–$S_2O_3^{2-}$–NH_3) is rather complicated involving a combination of decomposition and redox processes. The main reaction is represented by the thermal decomposition of the coordination compound synthesized in the above mentioned system, respectively $[Cu_2(S_2O_3)_2(NH_3)_4]\cdot5H_2O$ and $Na_2[Cu_4(S_2O_3)_5(NH_3)_8]\cdot2H_2O$. The decomposition occur differently in the solid state and in the reaction medium. Solid state decomposition performed in air static atmosphere does not generate clean copper sulfide, sulfates compounds are also obtained. In reaction medium, the coordination compounds – thiosulfate solution acts as precursors in copper sulfides synthesis, the concentration of sulfure increasing with thiosulfate one. A partial reduction of Cu^{2+} is identified in all cases.

The next step of our study will consist in the thermal investigations in inert and reducing atmosphere analyzing also the evolved gaseous decomposition products.

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