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THERMAL DECOMPOSITION OF RUBIDIUM-SODIUM HALIDOTHIOCYANATOBISMUTHATES(III)

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Abstract

Mono- and binuclear rubidium-sodium halidothiocyanatobismuthates(III) have been prepared. Thermal, chemical and X-ray analyses were used to establish the thermal decomposition course of these complexes. The pyrolysis occurs in three stages connected with the mass loss and exothermic effects. The decomposition temperatures of the title salts are 190–210°C.

Keywords: bismuth(III) complexes, halidothiocyanatobismuthates(III) of rubidium-sodium, thermal decomposition

Introduction

Among the halidothiocyanatobismuthates(III) alkali metals the thermal decomposition reactions of caesium-sodium salts with chlorides, bromides [1], fluorides, iodides and caesium-potassium iodothiocyanatobismuthates(III) [2] have been examined. The results have shown that all these complexes decompose in main three stages with the mass loss and exothermic peaks in the DTA curves. In the first stage an intermediate compound of the formula $BiS_xC_yN_8X_z$, Bi_2S_3 and/or $Cs_3Bi_2X_9$ ($Cs_3Bi_2F_9$ have not been established) and halides, thiocyanates and sulphates of alkali metals are formed. Then thiocyanates oxidize to form sulphates and in the last stage $BiS_xC_yN_8X_z$ decomposes to BiOX, Bi_2S_3 and/or $(BiO)_2SO_4$.

The aim of the present work was synthesis of halidothiocyanatobismuthates(III) of the rubidium-sodium group and examination of the thermal decomposition reactions of these heteroligand complexes.

Experimental

Rubidium-sodium halidothiocyanatobismuthates(III) were obtained in reaction of solid $Rb[Bi(SCN)_4]$ (prepared according to method described by Cygański [3]) with an aqueous solution of the respective sodium halide. The mixtures of these reagents:

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$Rb_2Na[Bi(SCN)_5Cl]$: 2.0 ml of a 5.5 $mol \cdot l^{-1}$ NaCl solution, 3.0 g $Rb[Bi(SCN)_4]$;

$Rb_2Na[Bi(SCN)_5Br]$: 1.5 ml of a 4.0 $mol \cdot l^{-1}$ NaBr solution, 2.5 g $Rb[Bi(SCN)_4]$;

$Rb_2Na[Bi_2(SCN)_7I_2]$: 2.0 ml of a 3.0 $mol \cdot l^{-1}$ NaI solution, 3.0 g $Rb[Bi(SCN)_4]$;

$Rb_2Na[Bi_2(SCN)_6I_3]$: 2.0 ml of a 5.5 $mol \cdot l^{-1}$ NaI solution, 3.0 g $Rb[Bi(SCN)_4]$;

$Rb_2Na[Bi_2(SCN)_5I_4]$: 2.0 ml of a 8.5 $mol \cdot l^{-1}$ NaI solution, 3.0 g $Rb[Bi(SCN)_4]$

were shaken for 2 h (mononuclear complexes) or 0.5 h (binuclear complexes), filtered and dried on filter paper at room temperature. Orange (chloro- and bromosalts) and brown (iodosalts) precipitates were obtained. Yield of the reaction was 60–75% (yield was calculated with regard to the amount rubidium used).

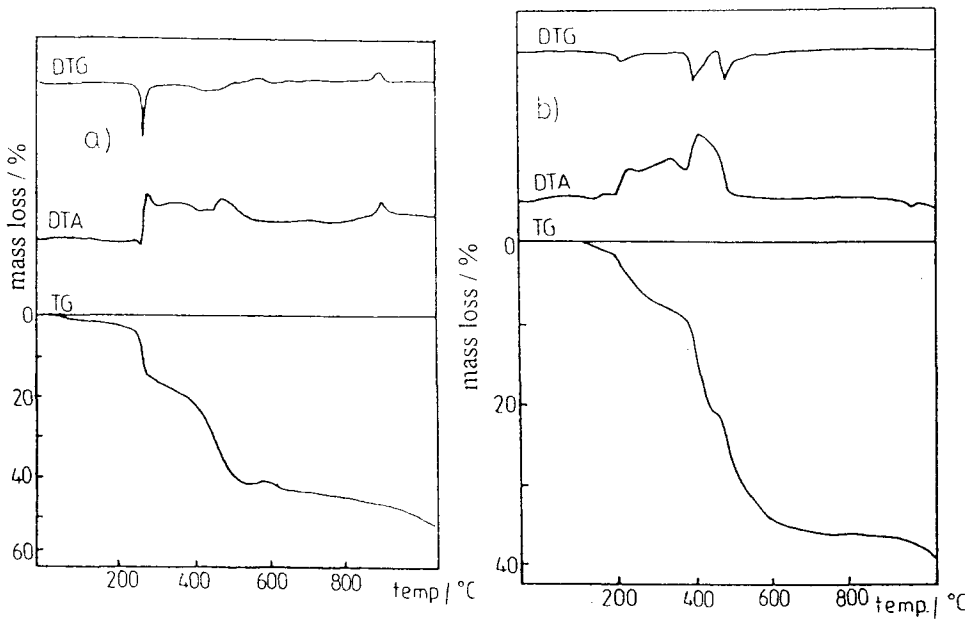

Fig. 1 Thermal analysis curves of: a) $Rb_2Na[Bi(SCN)_5Cl]$; b) $Rb_2Na[Bi_2(SCN)_7I_2]$

Thermal analysis

Thermal studies were carried out in air on an OD-102 derivatograph (MOM, Budapest). The temperature range was 20–1000°C, a heating rate 5 deg·min^{-1}, the weight of samples 200 mg, the reference substance α-Al_2O_3. Thermal curves of some complexes are presented in Fig. 1.

Preparation of sinters

Sinters were prepared under conditions similar to those of the thermal analysis. Samples (200 mg) of the complexes were heated in an electric furnace. The TG curves were used to choose appropriate temperatures for preparation of the sinters. Table 1 lists the temperature ranges of the decomposition stages and the corresponding mass losses. Table 2 presents the results of chemical analysis of the sinters of $Rb_2Na[Bi(SCN)_5Cl]$ and $Rb_2Na[Bi_2(SCN)_7I_2]$.

Table 1 Temperature ranges of the decomposition stages and the mass losses of rubidium-sodium halidothiocyanatobismuthates(III)

Compound	Beginning of the decomposition / °C	Ranges of decomposition stages / °C		Mass loss / %
$Rb_2Na[Bi(SCN)_5Cl]$	210	I	210–265	7.7
		II	265–360	2.0
		III	360–520	9.6
$Rb_2Na[Bi(SCN)_5Br]$	200	I	200–280	7.0
		II	280–380	3.1
		III	380–480	9.1
$Rb_2Na[Bi_2(SCN)_7I_2]$	200	I	200–280	5.5
		II	280–360	2.0
		III	360–460	12.0
$Rb_2Na[Bi_2(SCN)_6I_3]$	190	I	190–270	4.5
		II	270–365	2.0
		III	365–460	13.5
$Rb_2Na[Bi_2(SCN)_5I_4]$	200	I	200–280	4.0
		II	280–350	1.2
		III	350–420	11.8

X-ray analysis of sinters

X-ray analysis was carried out on a Siemens D 5000 powder diffractometer using CuK_α radiation. The diffractograms of $Rb_2Na[Bi(SCN)_5Cl]$ and its sinters are given in Fig. 2.

Table 2 Results of chemical analysis of sinters

Compound	T / °C	Composition of sinter / %		Eq.
		Calculated	Found	
$Rb_2Na[Bi(SCN)_5Cl]$	265	31.21 Bi	32.4 Bi	
		12.76 S	12.8 S	
		4.21 C	4.3 C	
		6.41 N	6.0 N	
		5.29 Cl	5.0 Cl	
				(1)
	520	34.95 Bi	36.0 Bi	
		9.38 S	9.1 S	
		0.0 C	0.0 C	
		0.0 N	0.0 N	
		4.94 Cl	4.7 Cl	
$Rb_2Na[Bi_2(SCN)_7I_2]$	360	35.74 Bi	34.1 Bi	
		8.56 S	8.5 S	
		3.51 C	3.3 C	
		7.63 N	7.7 N	
		21.34 I	21.8 I	
				(2)
	460	40.62 Bi	39.6 Bi	
		6.49 S	6.2 S	
		0.0 C	0.0 C	
		0.0 N	0.0 N	
		18.50 I	17.7 I	

Discussion

A comparison of the results of thermal, chemical and X-ray analyses allows us to suggest that the thermal decomposition of rubidium-sodium halidothiocyanatobismuthates(III) proceeds in three stages. The general scheme of pyrolysis of these compounds is similar. Equations (1, 2) represent the decomposition reactions for example:

$$6Rb_2Na[Bi(SCN)_5Cl] \xrightarrow{\text{stage I}} 4\ BiS_{1.0}C_{3.0}N_{4.1}Cl_{1.0} + Bi_2S_3$$

$$+ 2MCl + 2MNCS + 7M_2SO_4$$

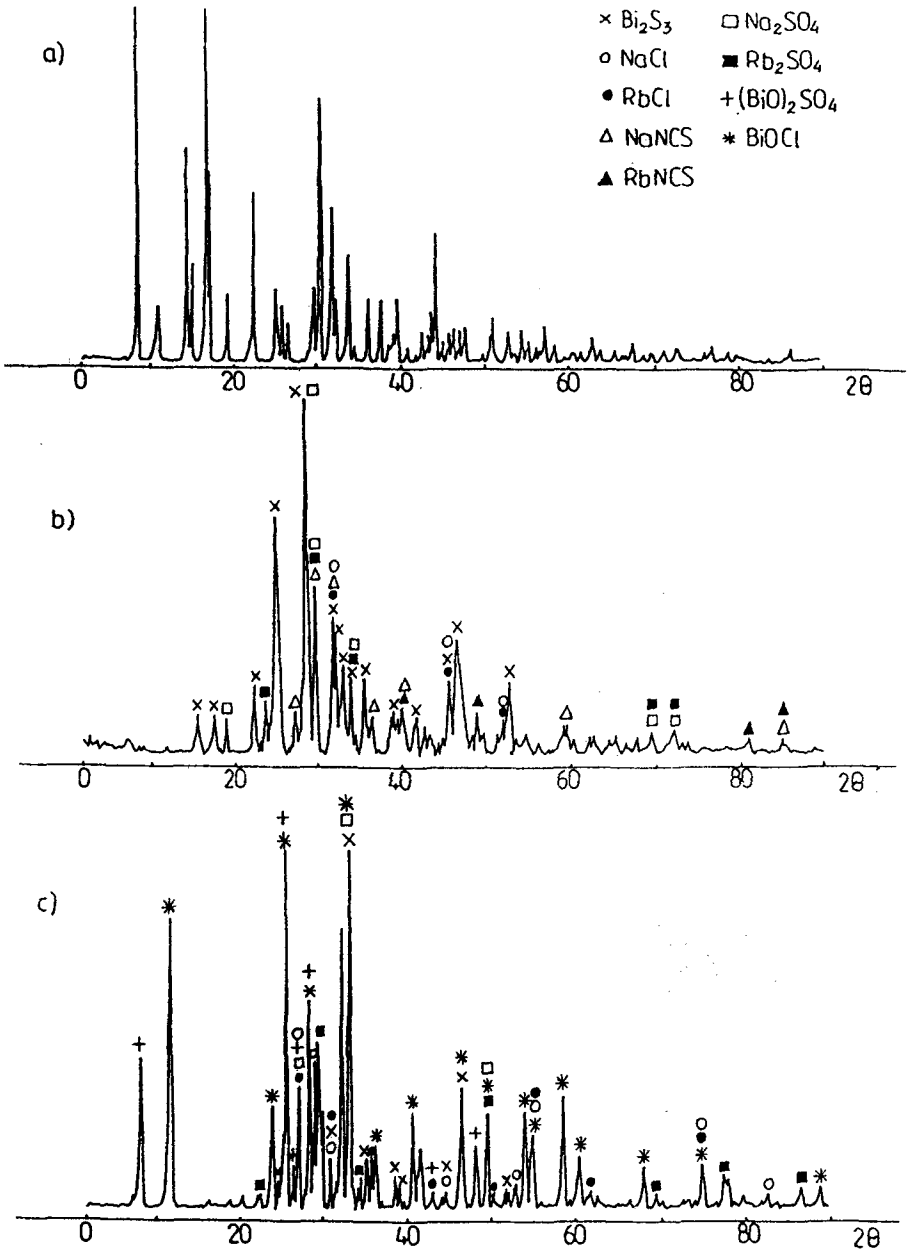

Fig. 2 X-ray patterns of: a) $Rb_2Na[Bi(SCN)_5Cl]$ and its sinters b) at 265°C c) 520°C

$$\xrightarrow{\text{stage III}} 0.5\,Bi_2S_3 + (BiO)_2SO_4 + 3\,BiOCl + 2MCl + 8\,M_2SO_4 \qquad (1)$$

$$6Rb_2Na[Bi_2(SCN)_7I_2] \xrightarrow{\text{stage II}} 8\,BiS_{0.6}C_{2.4}N_{4.9}I_{1.1} + 2Bi_2S_3 + 3MI + 7.5M_2SO_4$$

$$\xrightarrow{\text{stage III}} Bi_2(SO_4)_3 + 2(BiO)_2SO_4 + 6BiOI + 3MI + 7.5M_2SO_4 \qquad (2)$$

where: M=Rb or Na; the sum of alkali metal atoms is 18; in the reaction only solid products are given; the composition of the gaseous products was not examined.

The analysis of the thermal curves allows only an approximate determination of the temperature ranges of the decomposition stages. Some stages partly overlap. The shape of the TG curves (Fig. 1) did not allow us to prepare sinters of $Rb_2Na[Bi(SCN)_5Cl]$ (II stage) and $Rb_2Na[Bi_2(SCN)_7I_2]$ (I stage). The thermal decomposition of rubidium-sodium halidothiocyanatobismuthates(III) is connected with the mass losses in the TG curves corresponding to the exothermic peaks in the DTA curves. In the first stage the title compounds decompose rapidly with the mass decrease of about 4–8%. In the sinters halides, thiocyanates and sulphates of alkali metals, Bi_2S_3 and an intermediate product $BiS_xC_yN_sX_z$ have been found. At about 265–380°C (II stage) thiocyanates of rubidium and sodium oxidize to form corresponding sulphates. The last stage of decomposition is rapid with the mass losses of 10–14%. The main reaction in the third stage is decomposition of the intermediate product to BiOX and $(BiO)_2SO_4$. The mass of the sinters decrease after the third stage. This is caused by evaporation of MX and transformation of Bi_2S_3 or $Bi_2(SO_4)_3$ into $(BiO)_2SO_4$. The thermal stability of rubidium-sodium halidothiocyanatobismuthates(III) is very similar. All compounds decompose at 190–210°C. These temperatures are lower a little than that for $Rb_2Na[Bi(SCN)_6]$ [4]. No dependence of the thermal stability upon the radius of the halide ligand has been observed. On the basis of our earlier works we can suggest that all halidothiocyanatobismuthates(III) of alkali metals decompose in the same way. The only difference is that in the case of rubidium-sodium salts no $Rb_3Bi_2X_9$ complexes are formed. The literature data [5] confirms this observation.

References

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Zusammenfassung — Es wurden ein- und zweikernige Rubidium-natrium-halidothiocyanato-bismutate(III) hergestellt. Zur Ergründung des Weges für die thermische Zersetzung dieser Komplexe wurden Thermo-, Chemische- und Röntgenanalyse eingesetzt. Die Pyrolyse erfolgt in drei Schritten, verbunden mit Masseverlust und exothermen Effekten. Die Zersetzungstemperaturen der Titelsalze liegen zwischen 190 und 210°C.