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STUDIES ON THERMAL DECOMPOSITION REACTIONS OF COBALT, NICKEL AND ZINC THIOCYANATOBISMUTHATES (III)

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ABSTRACT

On the basis of thermal and chemical analysis and X-ray analysis of solid decomposition products and determination of gaseous products (sulfur dioxide) the mechanism of thermal decomposition was established for the following compounds:

$$Co_3[Bi(SCN)_6]_2 \cdot 12H_2O,\ Ni_3[Bi(SCN)_6]_2 \cdot 11H_2O,\ Zn_3[Bi(SCN)_6]_2$$

INTRODUCTION

The course of the thermal decomposition of alkali metal hexathiocyanatobismuthates (III) has been previously investigated[1-2]. The thermal decomposition of caesium and rubidium tetrathiocyanatobismuthates (III)[3] is the basis for the method of determination of caesium in the presence of rubidium or the method of determination of caesium and rubidium[4]. In the hitherto examined thiocyanatobismuthates (III) the cations of the outer coordination sphere do not exhibit complex forming properties. In the present work it was found that the outer coordination sphere cations have strong complex forming properties and they form an isothiocyanate complex with the SCN^- group, coordinating it by the nitrogen atom.
Cobalt, nickel and zinc hexathiocyanatobismuthates (III) were obtained for the first time by Pociello and Pod[5] by evaporation of combined solutions of bismuth thiocyanate (III) and thiocyanates of the respective metals at 40°C.

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EXPERIMENTAL

Preparation method

Hexathiocyanatobismuthates were obtained by neutralizing $H_3Bi(SCN)_6$ acid with cobalt, nickel or zinc carbonate. Hexathiocyanatobismuthic acid solution was obtained by dissolving basic bismuth carbonate in thiocyanic acid [6] taken in such an amount that the molar ratio SCN:Bi equalled approximately six [10g of $(BiO)_2CO_3$ were treated with 80 ml 18 % HNCS][2].

Thermal analysis

Thermal curves were determined on a M O N derivatograph, Budapest, 00-102/1500°C type with a heating rate of 5°/min. and using α-Al_2O_3 as a standard. The sensitivity of galvanometers was: DTA-1/15, DTG-1/20 and TG-200.

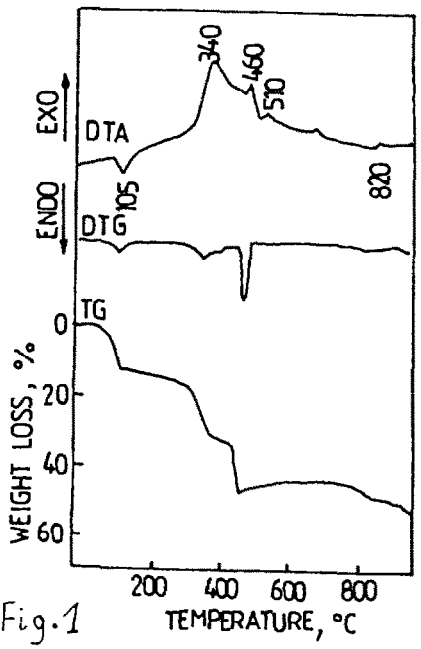

Fig.1

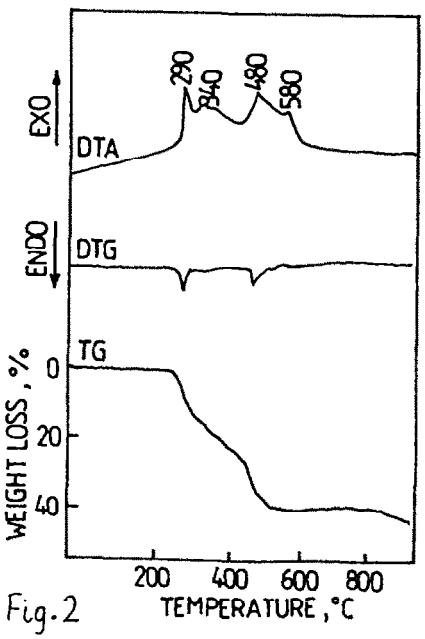

Fig.2

Thermal curves of $Ni_3[Bi(SCN_6)]_2 \cdot 11\ H_2O$

Thermal curves of $Zn_3[Bi(SCN)_6]_2$

Thermal curves for cobalt thiocyanatobismuthate have a course similar to those for nickel thiocyanatobismuthate.

Chemical analysis of decomposition products

To study the nature of reactions which are taking place, sinters of the compounds were prepared in conditions similar to those in which the derivatograms were obtained.
Weighed samples of about 250 mg were heated in a silite furnace at a rate of 5°/min up to temperatures determined from the thermal curves. To control the process of sinter preparation, mass losses were determined and then compared with the values resulting from the TG curve.
The obtained sinters were divided into water soluble and insoluble fractions by boiling with water for several hours. The fractions were analyzed by determining the content of thiocyanates, sulfates and the outer coordination sphere cation in the soluble fraction, and by determining bismuth and sulfur in the insoluble fraction. The elementary analysis (determination of carbon and nitrogen) of the insoluble fraction obtained as a result of the second decomposition stage (approx. 380°C) was also carried out. Sulfur dioxide evolved in the second and third stages of decomposition was determined by absorbing it in tetrachloromercurate (II) solution and titration of the formed hydrochloric acid with sodium hydroxide solution[7].
The results of the analyses are presented in table 1.

X-ray analysis of sinters

The diffraction patterns of sinters of the compounds under study were obtained by means of a DRON-1 diffractometer produced in the USSR. The analysis revealed the presence of bismuth sulfide in the sinters obtained at temperatures corresponding to the second decomposition stage. In the sinters obtained at temperatures corresponding to the third stage of decomposition,

Table 1. Results of chemical analysis of sinters of zinc hexathiocyanatobismuthate

Temperature of sinter preparation	Loss of mass in %	Evolved SO_2 %	Analysis of sinters	
			Soluble fraction	Insoluble fraction
360°	determined, %		4.20% SCN 2.61% SO_4 3.73% Zn	43.60% Bi 18.80% S 6.74% C 9.76% N
	21.50	28.50		
	calculated equation 2			
	21.41	26.06		
580°	determined, %		0% SCN 1.69% SO_4 1.20% Zn	57.22% Bi 8.93% S
	40.0	47.2		
	calculated equation 3			
	43.73	48.17		

X-ray analysis revealed the presence of bismuth sulfide, bismuth and oxides of respective cations /Co, Ni, Zn/. As an example, Fig. 3 presents the diffraction of $Co_3[Bi(SCN)_6]_2 \cdot 12H_2O$ sinter obtained at 580°C.

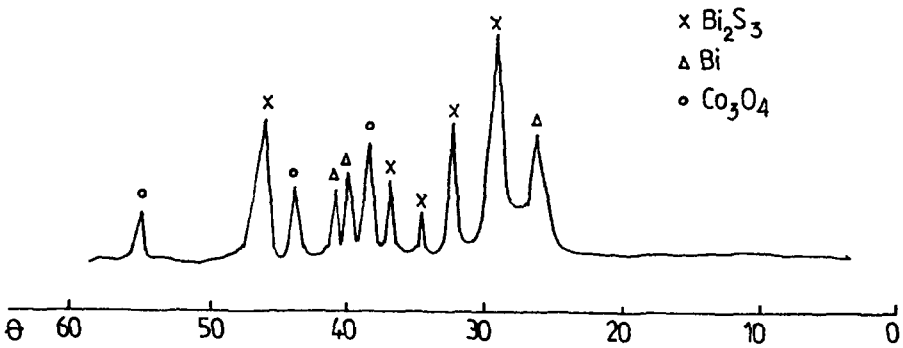

Fig. 3 X-ray analysis of $Co_3[Bi(SCN)_6]_2 \cdot 12H_2O$ after sintering at 580°C

DISCUSSION

Three stages are observed in the decomposition process of cobalt (III) and nickel (II) thiocyanatobismuthates (III), whereas in the decomposition of zinc thiocyanatobismuthate two stages can be observed.
In the first decomposition stage of $Ni_3[Bi(SCN)_6]_2 \cdot 11H_2O$ and $Co_3[Bi(SCN)_6]_2 \cdot 12H_2O$ occurring at 120°C the compounds are dehydrated, which is expressed by the following equation:

$$\text{I} \quad M_3[Bi(SCN)_6]_2 \cdot xH_2O \longrightarrow M_3[Bi(SCN)_6]_2 + xH_2O \qquad (1)$$

when M = Co, x = 12
when M = Ni, x = 11,

An intensive exothermic peak /in the case of nickel compound (Fig. 1)/, or two exothermic peaks close to each other/in the case of cobalt and zinc (Fig. 2)/ correspond to the second decomposition stage, in which the decomposition proper of thiocyanatobismuthates occurs according to the following reaction:

$$\text{II} \quad 3M_3[Bi(SCN)_6]_2 \xrightarrow{O_2} Bi_2S_3 + 4M_nBiS_xC_yN_z + aM(SCN)_2 + bMSO_4 +$$
$$+ /33-4x-2a-b/SO_2 + /36-4y-2a/CO_2 + /18-2z-a/N_2 \qquad (2)$$

The values of factors in the equation determined on the basic of analyses /Table 1/ are equal e.g. for the zinc compound: n = 1.68 x = 3.47, y = 4.03, z = 5.01, a = 1.14, b = 0.86. From the value of n,x,y,z factors it follows that the intermediate decomposition product may also be expressed by the approximate formula $M_{12}Bi_7S_{24}C_{28}N_{33}$.

The occurence of the intermediate compound of tne formula $BiS_xC_yN_z$ was observed during the examination of thermal decomposition reaction of thiocyanatobismuthates of alkali metals[2] and bismuth thiocyanate[8]. The formation of the intermediate compound of the general formula $M_nBiS_xC_yN_z$ in the course of decomposition of cobalt, nickel and zinc thiocyanato-bismuthates can be explained by the fact that SCN groups are bound by these cations far stronger than by any of the alkali metal cations. The high vibration frequency /CN/ about 2150 cm^{-1}/ in iron group and zinc

thiocyanatobismuthates[9] indicates the formation of bridge coordination[10] of the M-SCN-M type.

In alkali metal thiocyanatobismuthates[9] the frequency is considerably lower equalling approx. 2080 cm^{-1}, which is characteristic of compounds of M-SCN type.

As a result of decomposition at about 360°C /second stage of decomposition/ apart from the intermediate compound $M_nBiS_xC_yN_z$, bismuth sulfide and a small amount of cobalt, nickel or zinc thiocyanate and sulfate are formed.

In the third decomposition stage two processes take place:

a/ Decomposition of the intermediate decomposition product together with the formation of further amounts of bismuth sulfide, of cobalt, nickel or zinc oxide and bismuth.

b/ Oxidation of cobalt, nickel or zinc thiocyanate to form a sulfate and partial or total decomposition of the sulfate.

The general equation of the decomposition reaction in the third decomposition stage /460°C for the nickel compound, 520° for the cobalt compound (3), 550°C for the zinc compound is presented below:

$$3M_3[Bi(SCN)_6]_2 \xrightarrow{O_2} 2\,Bi_2S_3 + 2Bi + (9-m)MO + mMSO_4 + (30-m)SO_2 + 18N_2 \qquad (3)$$

The value of the factor m for zinc thiocyanatobismuthate is 0.43. The calculated loss of mass according to equation (3) is higher than determined (table). It could be due to previous oxidation of bismuth sulfide.

In the case of $Co_3[Bi(SCN)_6]_2$ decomposition, Co_3O_4 is formed (Fig. 3)

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