

Thermal decomposition of caesium–potassium iodothiocyantobismuthates(III)

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Abstract

New double complex bismuth salts of the general formula $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_x\text{I}_{6-x}]$ where $x = 1, 2$ and $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_y\text{I}_{9-y}]$ where $y = 5, 6, 7$ have been obtained by dissolving $\text{Cs}[\text{Bi}(\text{SCN})_4]$ in KI solutions of various concentrations. The mechanism of the thermal decomposition of these compounds has been determined on the basis of thermal curves, chemical and diffractometric analyses of the solid pyrolysis products. The decomposition was found to proceed in three stages.

INTRODUCTION

Previous work [1, 2] presented a discussion of the results of the study on hexathiocyantobismuthates(III) of alkali metals. The caesium–sodium salt was found to be the most stable of the double complexes. This fact was used in thermal examination of heteroligand salts. The group of caesium–sodium halidothiocyantobismuthates(III) (the derivatives of $\text{Cs}_2\text{Na}[\text{Bi}(\text{SCN})_6]$) was examined in order to determine the influence of the type of ligand on thermal stability of a mixed complex [3, 4]. The mechanism of pyrolysis was established, together with the dependence of thermal stability on ionic radius of the halide.

To continue the study on heteroligand bismuth(III) salts the following salts were obtained and their thermal properties examined: $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})\text{I}_5]$, $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_2\text{I}_4]$, $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_7\text{I}_2]$, $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_6\text{I}_3]$ and $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_5\text{I}_4]$. The compounds are derivatives of $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_6]$, the second complex in the thermal stability order of double hexathiocyantobismuthates(III) of the caesium group. The purpose of the present work is to determine the mechanism of decomposition and thermal stability of the above mentioned compounds, and then to compare them with caesium–sodium complexes.

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EXPERIMENTAL

Preparation

The principle of the method is the reaction of solid caesium tetrathio-cyanatobismuthate(III) with an aqueous KI solution of a given concentration. In order to obtain $\text{Cs}[\text{Bi}(\text{SCN})_4]$, Cs_2CO_3 or CsNO_3 was added to a solution of $\text{H}[\text{Bi}(\text{SCN})_4]$ [5]. Tetrathiocyanatobismuthate(III) acid was obtained by dissolving basic bismuth carbonate in HNCS (10 g of $(\text{BiO})_2\text{CO}_3$ was dissolved in 45 ml of 15% HNCS solution, prepared by vacuum distillation of NH_4NCS and H_2SO_4 [6]).

To obtain caesium–potassium iodothiocyanatobismuthates(III), 3 g of $\text{Cs}[\text{Bi}(\text{SCN})_4]$ was treated with 2 ml of KI of various concentrations. For $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})\text{I}_5]$ a saturated solution was used; for $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_2\text{I}_4]$ a 5 M KI solution (and 3.3 g $\text{Cs}[\text{Bi}(\text{SCN})_4]$); for $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_5\text{I}_4]$ a 4 M KI solution; for $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_6\text{I}_3]$ a 3 M KI solution; and for $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_7\text{I}_2]$ a 2 M KI solution were used. The mixtures of reagents were shaken for 0.5 h, then filtered and precipitates were dried at room temperature.

Thermal analysis

Thermal analysis of complex salts was conducted in air using a MOM Budapest type OD-102/1500°C derivatograph. The measurements were performed within the temperature range 20–1000°C, at the heating rate of 5°C min⁻¹. The sensitivity of the galvanometer for the DTA curve was 1/15 and that for the DTG curve was 1/20. The TG sensitivity was 200 mg. α -Alumina was used as reference material. Each sample weighed 200 mg.

The thermal analysis curves of $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})\text{I}_5]$ are presented in Fig. 1. The TG curve of $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})\text{I}_5]$ shows a constant slight decrease of mass up to 440°C. These changes correspond to a small exothermic peak (the DTA curve). Over the range 440–555°C the mass of the compound decreases rapidly (TG, DTG curves), with no clear energetic effects (a very small endothermic peak at 555°C), and then does not change up to 670°C. At 670–920°C the compound is further decomposed (total mass loss at 920°C is 63%). The mass of the sinter remains unchanged over the range 920–1000°C.

Figure 2 presents thermal curves of $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_2\text{I}_4]$. The shape of the TG curve is similar to the previous one, although the fragment corresponding to temperatures from 190 to 450°C shows more clearly the stages of decomposition. These changes are connected with energy release (two clear exothermic peaks at 230 and 430°C, and a broad peak at 340°C). At temperatures higher than 450°C the mass of the sinter drops rapidly (TG, DTG curves), remains unchanged over the range of 570–680°C, and then

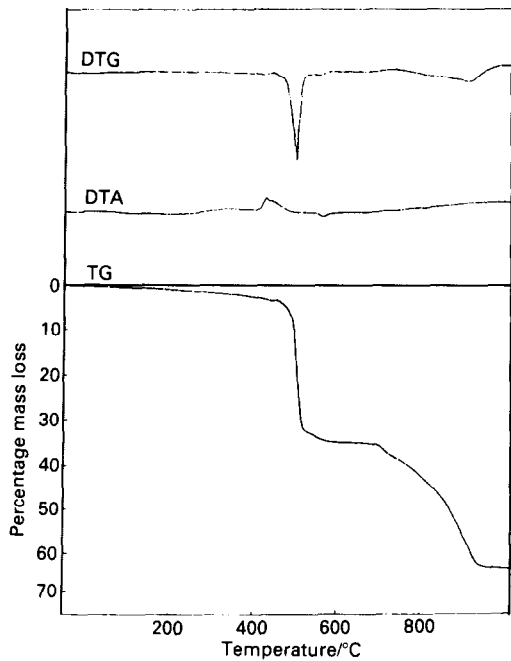


Fig. 1. Thermal analysis curves of $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})\text{I}_5]$.

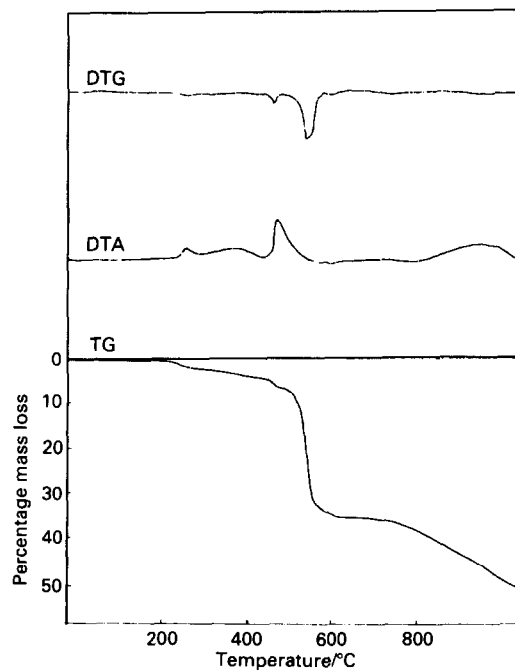


Fig. 2. Thermal analysis curves of $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_2\text{I}_4]$.

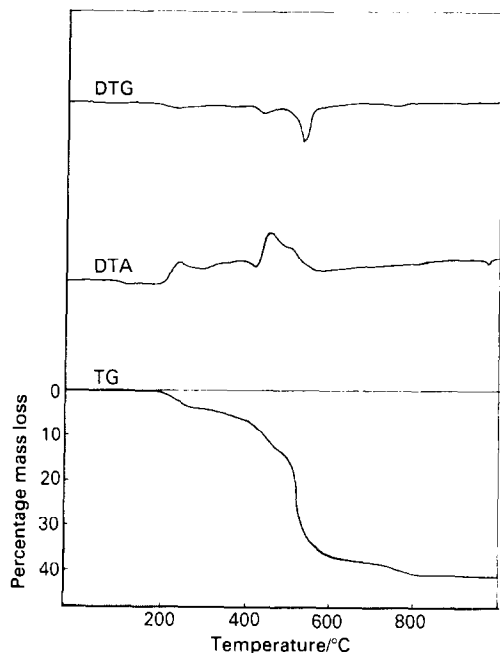


Fig. 3. Thermal analysis curves of $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_5\text{I}_4]$.

decreases again (the process is slower than in the case of $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})\text{I}_5]$) up to 980°C . The loss in mass observed at 1000°C is 51%.

The shape of thermal curves of $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_5\text{I}_4]$ (Fig. 3) is slightly different from those described above (Figs. 1, 2). The loss in mass observed on the TG curve ($190\text{--}465^\circ\text{C}$) is approximately twice as high as that observed in mononuclear salts. Over the range $465\text{--}760^\circ\text{C}$ the decomposition proceeds, rapidly at first, and slowly above 540°C . The mass of the sample remains unchanged at $760\text{--}1000^\circ\text{C}$ (a weak endothermic peak appears on the DTA curve at 950°C). The total loss of mass at 1000°C is 41%.

Figure 4 presents thermal curves of $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_6\text{I}_3]$. The individual stages of decomposition are more distinct than in the case of $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_5\text{I}_4]$ (the TG curve) whereas the exothermic peaks are less clear, broad and split.

The thermal analysis curves of $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_7\text{I}_2]$ have a shape similar to that for $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_6\text{I}_3]$. The thermal characteristics of the compounds under study are given in Table 1.

The solid products of the thermoanalysis of iodothiocyantobismuthates(III) were identified on the basis of the TG curves, chemical, elementary and diffractometric analyses. In order to study the thermal decomposition reactions, sinters were prepared under conditions similar to those in the derivatograph. The salts were heated up to the temperature determined

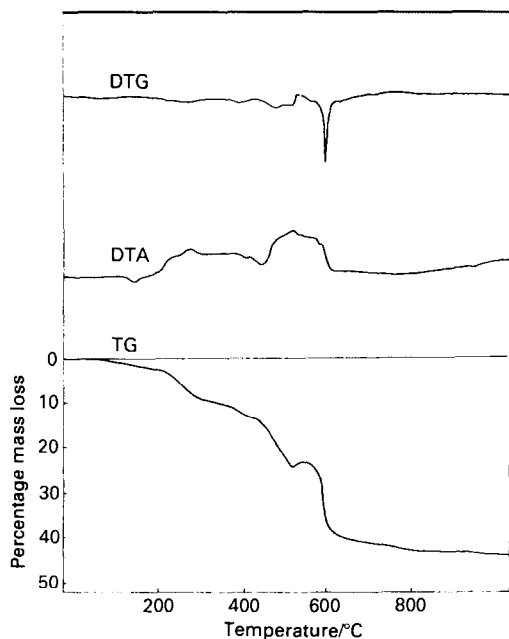
Fig. 4. Thermal analysis curves of $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_6\text{I}_3]$.

TABLE 1

DTA peaks and temperature ranges of decomposition stages of caesium–potassium iodothiocyanatobismuthates(III)

DTA peaks/°C	Ranges of decomposition stages/°C	DTA peaks/°C	Ranges of decomposition stages/°C
$\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})\text{I}_5]$		$\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_6\text{I}_3]$	
425 exo	180–440	140 endo	
555 endo		250 exo	180–270
790 endo		320 exo	270–370
		480 exo	370–490
$\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_2\text{I}_4]$		$\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_5\text{I}_4]$	
230 exo	190–265	230 exo	190–260
340 exo	265–395	360 exo	260–385
430 exo	395–450	440 exo	385–465
560 endo		950 endo	
$\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_7\text{I}_2]$			
140 endo			
190 exo	140–280		
240 exo			
300 exo	280–380		
430 exo	380–440		

TABLE 2

Results of chemical analysis of $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_4\text{I}_2]$ and $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_6\text{I}_3]$

Compound	Temp./°C	Composition of sinter/%		Eqn.
		Detected	Calculated	
$\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_2\text{I}_4]$	395	21.2 Bi	19.11 Bi	(5)
		2.4 S	2.05 S	
		1.1 C	1.11 C	
	600	1.3 N	1.28 N	(8)
		46.3 I	45.64 I	
		Mass loss 4.0%	Mass loss 3.97%	
$\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_6\text{I}_3]$	270	30.8 Bi	29.05 Bi	(2)
		3.2 S	2.97 S	
		28.9 I	29.39 I	
	490	Mass loss 35.5%	Mass loss 36.76%	(6)
		32.7 Bi	30.75 Bi	
		8.7 S	8.65 S	
		3.5 C	3.71 C	
		5.7 N	5.67 N	
		27.4 I	28.01 I	
		Mass loss 6.5%	Mass loss 6.26%	
		36.4 Bi	34.90 Bi	
		7.1 S	7.81 S	
	0 C	0 C		
	0 N	0 N		
	25.78 I	26.49 I		
		Mass loss 18.0%	Mass loss 17.52%	

from the derivatogram, the mass decrements being controlled simultaneously. Up to a temperature of 300°C the samples were heated in a drier, but at higher temperatures they were heated in an electrical resistance furnace with SiC heating elements. The chemical composition of solid sinters was established on the basis of the determination of bismuth, thiocyanate, iodide, total sulphur, carbon and nitrogen. The results of the analysis of the sinters for $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_2\text{I}_4]$ and $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_6\text{I}_3]$ are given in Table 2.

The diffractometric analysis of sinters was carried out on the Siemens D 5000 powder diffractometer. The intensity data were collected using Cu K α radiation within the range $2\theta = 2-70^\circ$. The diffractograms of $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})\text{I}_5]$ and its sinter are given in Fig. 5.

DISCUSSION

Thermal, chemical and diffractometric analyses allowed us to establish the mechanism of thermal decomposition of caesium-potassium iodothio-

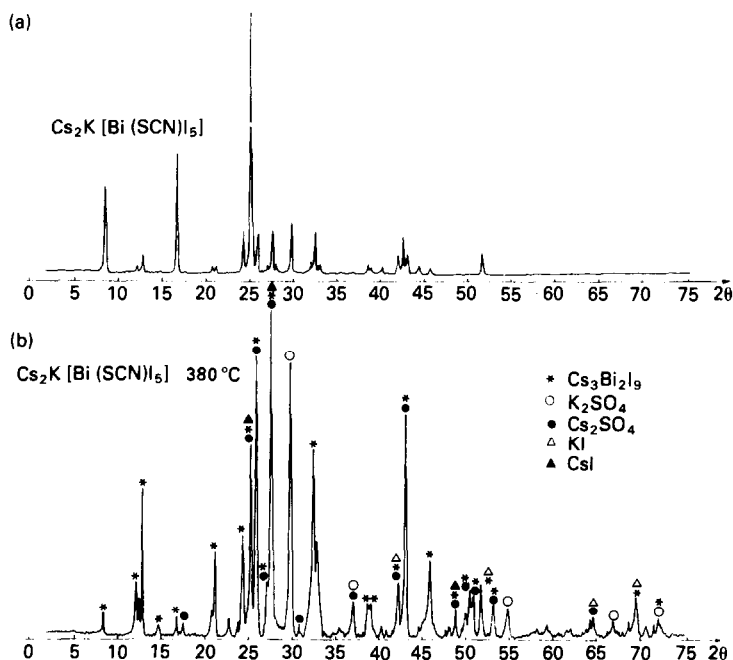
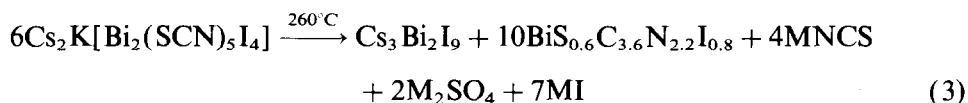
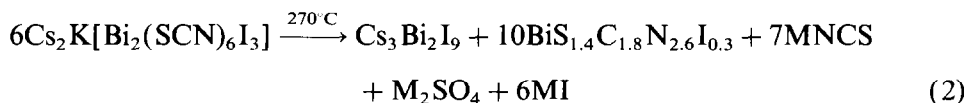
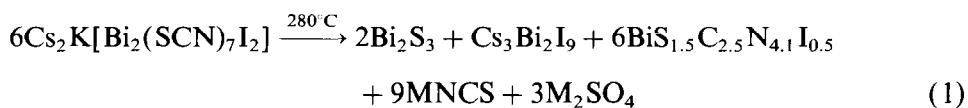


Fig. 5. X-ray patterns of (a) $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})\text{I}_5]$ and (b) its sinter at 380°C .

cyanatobismuthates(III). As in the case of caesium–sodium complexes [3, 4], it was assumed that there are three basic stages of pyrolysis, corresponding to exothermic effects (DTA) and mass loss (TG). It is possible to determine only approximate temperature ranges corresponding to particular stages, because the mass of the samples decreases continuously, and no horizontal fragments are observed on the TG curves.

Stage I

The proposed mechanism of pyrolysis in Stage I is presented in eqns. (1–3) (solid products of decomposition are given in the equations).

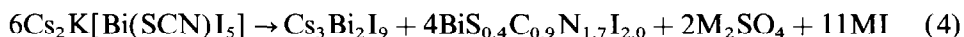


Here M is Cs or K; the sum of Cs and K atoms is 18 (the number of caesium atoms is 12, and potassium atoms is 6).

Considering the shape of the TG curves and slight mass losses up to 400°C, no sinters were made and no equations are given for mononuclear salts. The above presented equations show that in the first stage, a mixture of bismuth, caesium and potassium salts of different stoichiometric composition is formed. In all sinters an intermediate product $\text{BiS}_x\text{C}_y\text{N}_s\text{I}_z$ is present.

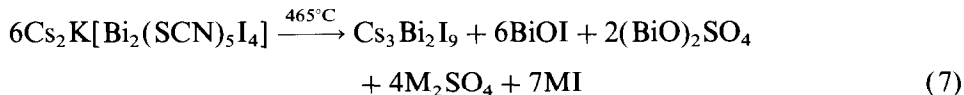
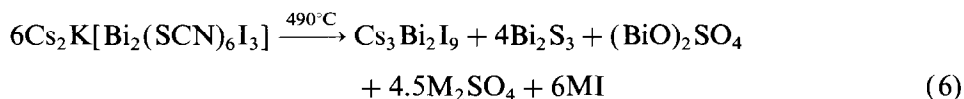
Stage II

In the next stage, the basic reactions are the oxidation of alkali metal thiocyanates to the respective sulphates, and partial decomposition of the intermediate product. The changes in the mass of the sinters in this stage are slight. Equations (4) and (5) represent the reactions in the sinters of mononuclear salts at 400°C.



Stage III

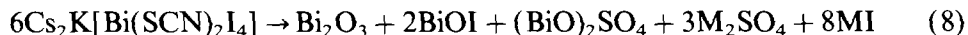
The last stage is the decomposition of the intermediate compound and the resulting formation of bismuthyl iodide, bismuth sulphide or bismuthyl sulphate (Bi_2S_3 oxidation product). The form of the TG curves of mono- and binuclear complexes above 400°C is slightly different. Literature data [7] show that above 400°C, the decomposition of $\text{Cs}_3\text{Bi}_2\text{I}_9$ also begins (Bi_2O_3 , CsI and I_2 are formed). In the case of mononuclear salts these processes overlap (Figs. 1, 2), whereas in binuclear complexes these stages are distinctly separated. Equations (6) and (7) present examples of reactions in Stages I–III.



After completion of the third stage of pyrolysis, the mass of binuclear complexes remains unchanged.

The analysis of $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_2\text{I}_4]$ sinter prepared at 450°C (the point at which the TG curve bends) indicates incomplete decomposition of the intermediate product. In the range 555–670°C for $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})\text{I}_5]$ and 570–680°C for $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_2\text{I}_4]$ the mass of the sinters is constant, and

then it decreases again. Equation (8) presents the decomposition of $\text{Cs}_2\text{K}[\text{Bi}(\text{SCN})_2\text{I}_4]$ at 600°C .



The differences in the course of TG curves of mono- and binuclear salts at temperatures above 400°C result from different rates of decomposition of caesium iodobismuthate(III), oxidation of bismuth sulphide and evaporation of caesium iodide and iodine.

The thermal stabilities of the examined salts, determined on the basis of the temperature at which their decomposition starts (TG curve), are similar ($180\text{--}190^\circ\text{C}$). Only the temperature of decomposition of $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_7\text{I}_2]$ is lower (140°C), which may result from deformation of the structure of the compound, compared with the other salts.

The comparison of the result of thermal analysis of caesium–potassium iodothiocyantobismuthates(III) with the results of previous studies on caesium–sodium halidothiocyantobismuthates(III) [3, 4] leads to the conclusion that the mechanism of decomposition of these compounds is similar. There are three basic stages of pyrolysis. In the first stage, the compounds decompose and an intermediate compound $\text{BiS}_x\text{C}_y\text{N}_z\text{X}_r$ is formed; in the second stage, thiocyanates of alkali metals are oxidized to form corresponding sulphates; and in the last stage, the intermediate compound is decomposed (to form bismuthyl halide, bismuth sulphide or bismuthyl sulphate). The equations representing the process of decomposition of complexes of the same molecular formula differ in proportions in which the compounds included in the sinter occur. Some differences result from different rate of oxidation of bismuth sulphide, and therefore bismuth sulphide, bismuth sulphate or bismuthyl sulphate may occur in the third stage. The shape of TG curves of mono- and binuclear salt at higher temperatures is slightly different both in the group of caesium–sodium and caesium–potassium complexes. This probably results from the different rate of decomposition of $\text{Cs}_3\text{Bi}_2\text{X}_9$ and evaporation of caesium halide.

The thermal stabilities of the corresponding caesium–sodium and caesium–potassium iodothiocyantobismuthates(III) are similar. The difference in thermal stabilities of caesium–sodium and caesium–potassium group halidothiocyantobismuthates(III) is far smaller than in the case of the corresponding homoligand salts. As mentioned in the Introduction, caesium–sodium hexathiocyantobismuthate(III) is the most stable of all the double alkali metal thiocyantobismuthates(III). Its thermal decomposition begins at 230°C [2]. Thus mononuclear iodothiocyantobismuthates(III) are a little less stable ($200\text{--}210^\circ\text{C}$), and the difference in stability of $\text{Cs}_2\text{Na}[\text{Bi}(\text{SCN})_6]$ and $\text{Cs}_2\text{Na}[\text{Bi}_2(\text{SCN})_5\text{I}_4]$ is as much as 75°C . The temperatures at which the decomposition of hexathiocyantobismuthate(III) [2] and iodothiocyantobismuthates(III) of caesium–potassium begins are very similar, $180\text{--}190^\circ\text{C}$ (except for $\text{Cs}_2\text{K}[\text{Bi}_2(\text{SCN})_7\text{I}_2]$ which starts to decom-

pose at 140°C). From the above data it follows that the structure of the inner sphere has a strong influence upon the thermal stability of heteroligand complexes. The replacement of thiocyanate ligands with halide ones causes reduction of the influence of outer sphere cations.

REFERENCES

- 1 A. Cygański, *Pol. J. Chem.*, 52 (1978) 2321.
- 2 A. Cygański and J. Kobyłecka, *Thermochim. Acta*, 178 (1991) 321.
- 3 A. Cygański and A. Turek, *Thermochim. Acta*, 137 (1989) 337; 164 (1990) 269.
- 4 A. Turek and A. Cygański, *Thermochim. Acta*, 197 (1992) 225.
- 5 A. Cygański, *Rocz. Chem.*, 39 (1965) 193.
- 6 W. Glund, K. Keller and W. Klempt, *Ber. Dtsch. Chem. Ges.*, 59 (1926) 1384.
- 7 K. Bogusławska, A. Cygański and J. Krystek, *J. Therm. Anal.*, 31 (1986) 605.