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STUDIES ON THERMAL DECOMPOSITION OF CAESIUM–SODIUM CHLOROTHIOCYANATOBISMUTHATES(III)

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ABSTRACT

The decomposition reactions of caesium–sodium chlorothiocyanatobismuthates(III) of the formulae $Cs_2Na[Bi(SCN)_4Cl_2]$, $Cs_2Na[Bi(SCN)_3Cl_3]$ and $Cs_2Na[Bi(SCN)_2Cl_4]$ have been investigated. The mechanism of the thermal decomposition of these compounds has been determined on the basis of their thermal curves together with the chemical, diffractometric and IR spectrophotometric analyses of the pyrolysis products. The results are used to determine the three stages of the thermal decomposition. The courses of decomposition and the thermal stabilities of alkali metal chlorothiocyanatobismuthates(III) and thiocyanatobismuthates(III) are compared.

INTRODUCTION

In previous papers [1–5] thermal decompositions of the following thiocyanatobismuthates(III) have been investigated: $Bi(SCN)_3$; BiOSCN, $M[Bi(SCN)_4]$ where $M = Rb^+$, Cs^+; $M_3[Bi(SCN)_6]$ where $M = Li^+$, K^+, Na^+, Rb^+, NH_4^+; and $M_2M'[Bi(SCN)_6]$ where $M = NH_4^+$, K^+, Rb^+, Cs^+, $M' = Na^+$, K^+, Li^+.

The subject of this paper is the thermal decomposition of caesium–sodium chlorothiocyanatobismuthates(III): $Cs_2Na[Bi(SCN)_4Cl_2]$, $Cs_2Na[Bi(SCN)_3Cl_3]$ and $Cs_2Na[Bi(SCN)_2Cl_4]$. The compounds were obtained by treating $Cs[Bi(SCN)_4]$ with NaCl solutions of different concentrations [6].

EXPERIMENTAL

Thermal analysis

Thermal analyses were carried out using a thermal analyzer (MOM, Budapest, type OD-102/1500 °C). The measurements were made in air, over the temperature range 20–1000 °C at a heating rate of 5 °C min^{-1}. The sensitivity of the galvanometer for the DTA curve was 1/15 and for the

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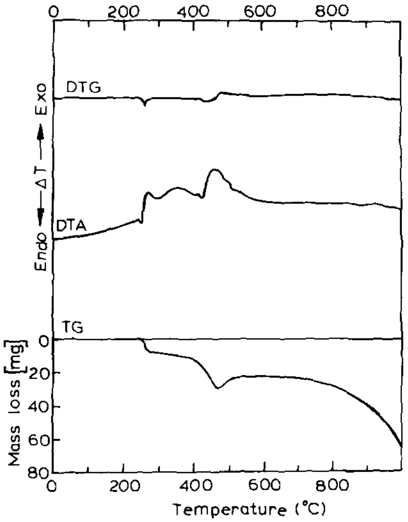

Fig. 1. Thermal analysis curves of $Cs_2Na[Bi(SCN)_4Cl_2]$.

DTG curve 1/20. TG sensitivity was 200 mg. α-Al_2O_3 was used as the reference material. Each sample weighed 200 mg.

The thermal analysis curves of caesium–sodium dichlorotetrathiocyanatobismuthate(III) $Cs_2Na[Bi(SCN)_4Cl_2]$, caesium–sodium trichlorotrithiocyanatobismuthate(III) $Cs_2Na[Bi(SCN)_3Cl_3]$ and caesium–sodium tetrachlorodithiocyanatobismuthate(III) $Cs_2Na[Bi(SCN)_2Cl_4]$ are shown in Figs. 1–3.

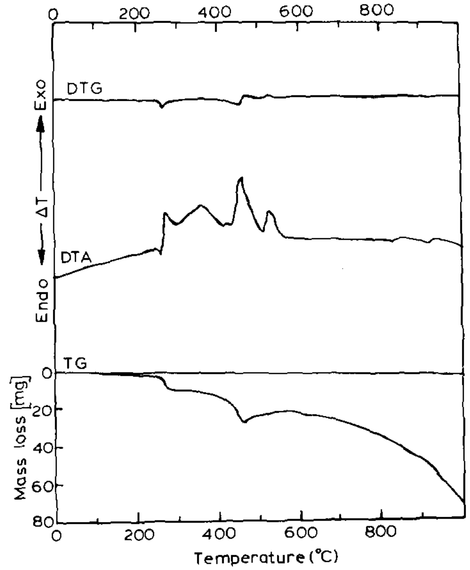

Fig. 2. Thermal analysis curves of $Cs_2Na[Bi(SCN)_3Cl_3]$.

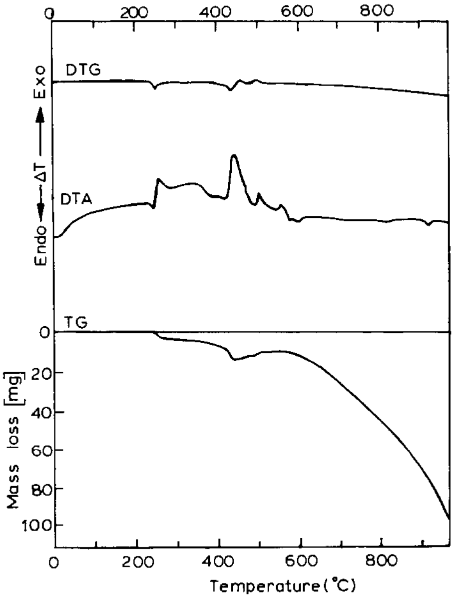

Fig. 3. Thermal analysis curves of $Cs_2Na[Bi(SCN)_2Cl_4]$.

The DTA curve of $Cs_2Na[Bi(SCN)_4Cl_2]$ (Fig. 1) has a small endothermic peak at 240 ° C and three distinct exothermic peaks: the first intense peak at 260 ° C corresponds to a rapid mass loss observed in the TG and DTG curves, the second broad peak at 340 ° C corresponds to a slight decrease in the mass of the sample and the third peak at 460 ° C involves rapid mass loss and then slow mass growth, visible in the TG and DTG curves. At temperatures > 620 ° C a loss of mass, slow at first, and rapid after 840 ° C, occurs.

The DTA curve of $Cs_2Na[Bi(SCN)_3Cl_3]$ (Fig. 2) is different from the curve described above in that it has one more exothermic peak at 500 ° C corresponding to a slight increase in the mass of the compound, visible on the TG curve, and two weak endothermic peaks at 810 and 900 ° C.

The DTA curve of $Cs_2Na[Bi(SCN)_2Cl_4]$ (Fig. 3) is similar to that of $Cs_2Na[Bi(SCN)_3Cl_3]$. A difference may be seen in the fifth exothermic peak, however, connected with a slight increase in the mass of the compound. The curve also has a weak endothermic peak at 600 ° C.

Analysis of the derivatograms indicates that caesium–sodium chlorothiocyanatobismuthates(III) decompose in three stages, each accompanied by a considerable loss of mass. From the differences between mass losses and the forms of the DTA curves of individual compounds it may be seen that the mechanisms of their thermal decompositions are slightly different. Details of the temperatures at which all the decomposition stages of the caesium–sodium chlorothiocyanatobismuthates(III) plus $Cs_2Na[Bi(SCN)_6]$

TABLE 1

Temperatures and DTA peaks of caesium–sodium chlorothiocyanatobismuthates(III)

Formula	Endothermic peak (° C)	Beginning of the first exothermic peak (° C)	Exothermic peaks (° C)					Endothermic peaks (° C)		
			I	II	III	IV	V	II	III	IV
$Cs[Bi(SCN)_4]$	160	160	190	330	470	600				
$Cs_2Na[Bi(SCN)_6]$	–	250	280	370	480	610		710		
$Cs_2Na[Bi(SCN)_4Cl_2]$	240	240	260	340	460					
$Cs_2Na[Bi(SCN)_3Cl_3]$	240	240	260	340	440	500		810	900	
$Cs_2Na[Bi(SCN)_2Cl_4]$	240	240	260	340	450	500	560	600	820	930

and Cs[Bi(SCN)$_4$] were investigated and the DTA peaks which correspond to these reactions are presented in Table 1.

Analysis of the sinters confirmed the differences between reactions occurring in the course of the thermal decomposition of the different caesium–sodium chlorothiocyanatobismuthates(III). The sinters were obtained under conditions similar to those used in the thermal analysis, i.e. 200-mg weighed samples of the compound were heated in an electric silite furnace at a heating rate of 5° min^{-1}. To test the validity of the sinter preparation, the mass loss was determined and compared with that observed from the TG curve. The sinters were obtained at 260, 460 and 750 °C.

TABLE 2

Results of chemical analysis of caesium–sodium chlorothiocyanatobismuthate(III) sinters prepared at 260, 460 and 750 °C

Formula	Temp. (°C)	Composition of sinter (%)		Eqn.
		Detected	Calculated	
Cs$_2$Na[Bi(SCN)$_4$Cl$_2$]	260	29.13 Bi	27.59 Bi	(1)
		9.17 S	9.82 S	
		3.93 C	3.93 C	
		5.56 N	5.55 N	
	460	31.78 Bi	30.56 Bi	(5)
		6.95 S	7.81 S	
		0 C	0 C	
		0 N	0 N	
	750	30.17 Bi	29.19 Bi	(9)
		6.61 S	6.20 S	
Cs$_2$Na[Bi(SCN)$_3$Cl$_3$]	260	30.02 Bi	28.05 Bi	(2)
		6.96 S	7.37 S	
		2.89 C	2.82 C	
		4.38 N	4.42 N	
	460	31.16 Bi	30.00 Bi	(6)
		4.41 S	4.22 S	
		0 C	0 C	
		0 N	0 N	
	750	32.16 Bi	31.24 Bi	(10)
		4.61 S	4.39 S	
Cs$_2$Na[Bi(SCN)$_2$Cl$_4$]	260	27.93 Bi	28.63 Bi	(3)
		4.60 S	4.65 S	
		1.89 C	1.84 C	
		2.95 N	2.95 N	
	460	29.25 Bi	30.26 Bi	(7)
		2.98 S	3.09 S	
		0 C	0 C	
		0 N	0 N	
	750	32.53 Bi	32.93 Bi	(11)
		2.95 S	3.37 S	

Chemical analysis

The sulphur contained in the sinters was determined in the form of $BaSO_4$ by a gravimetric method after oxidation with a mixture of HNO_3, HCl and Br_2 (in the ratio 9 : 3 : 1) and separation of bismuth by precipitation with $NH_3 + (NH_4)_2CO_3$ solution [7]. Bismuth was determined in the form of Bi_2S_3 by precipitation with thioacetamide. Elemental analysis was also carried out to determine the contents of sulphur, carbon and nitrogen. To analyse the composition of the sinters more completely and to determine the properties of the compounds of which the sinters consist, the latter were divided into water-soluble and water-insoluble fractions by leaching for 4 h. In the insoluble fraction bismuth, sulphur, carbon and nitrogen were determined by the above mentioned methods. In the soluble fraction sulphates were determined in the form of $BaSO_4$, thiocyanates were determined by bromatometry, total thiocyanates and chlorides by Volhard's method and acids by acid–base titration.

Table 2 presents the results of the sinter analyses of caesium–sodium chlorothiocyanatobismuthates(III), and Table 3 the results of the analysis of water soluble and insoluble fractions of $Cs_2Na[Bi(SCN)_3Cl_3]$ sinters.

TABLE 3

Results of chemical analyses of soluble and insoluble fractions of $Cs_2Na[Bi(SCN)_3Cl_3]$ sinters prepared at 260, 460 and 750 °C

Temp. (°C)	Soluble fraction (%)		Insoluble fraction (%)		Eqn.
	Detected	Calculated	Detected	Calculated	
260	3.63 S_{SCN}	3.66 S_{SCN}	69.15 Bi	67.91 Bi	(4)
	3.53 S_{SO_4}	3.66 S_{SO_4}	7.89 S	7.43 S	
	18.75 Cl	17.56 Cl	4.88 C	4.89 C	
	in this	in this	7.85 N	8.43 N	
	5.62 Cl_{HCl}	5.40 Cl_{HCl}	m.fr.43.05	m.fr.41.30	
	m.fr.56.95	m.fr.58.70			
460	7.56 S_{SO_4}	6.74 S_{SO_4}	77.13 Bi	80.24 Bi	(8)
	14.79 Cl	14.90 Cl	0 S	0 S	
	in this	in this	m.fr.39.02	m.fr.37.37	
	5.39 Cl_{HCl}	5.41 Cl_{HCl}			
	m.fr.60.98	m.fr.62.63			
750	6.44 S_{SO_4}	7.19 S_{SO_4}	80.00 Bi	80.24 Bi	(12)
	17.51 Cl	17.36 Cl	0 S	0 S	
	in this	in this	m.fr.31.55	m.fr.38.93	
	5.56 Cl_{HCl}	5.78 Cl_{HCl}			
	m.fr.58.45	m.fr.61.07			

X-ray analysis

X-ray analyses of the sinters were carried out on a DRON-1 diffractometer using Cu*Kα* radiation with a nickel filter. The diffraction curves were recorded over the range $2\theta = 2\text{–}60°$. Diffraction patterns of the compounds under investigation were obtained, along with those of their sinters and the insoluble fractions of their sinters. The division of the sinters into soluble and insoluble fractions was thus also significant in X-ray analysis. It made it possible to eliminate the reflections due to the soluble fraction of a sinter from the diffraction patterns due to the insoluble fraction.

The diffractograms of $Cs_2Na[Bi(SCN)_4Cl_2]$ and its sinters are given in Fig. 4. A comparison of the reflections occurring in the diffractogram of the

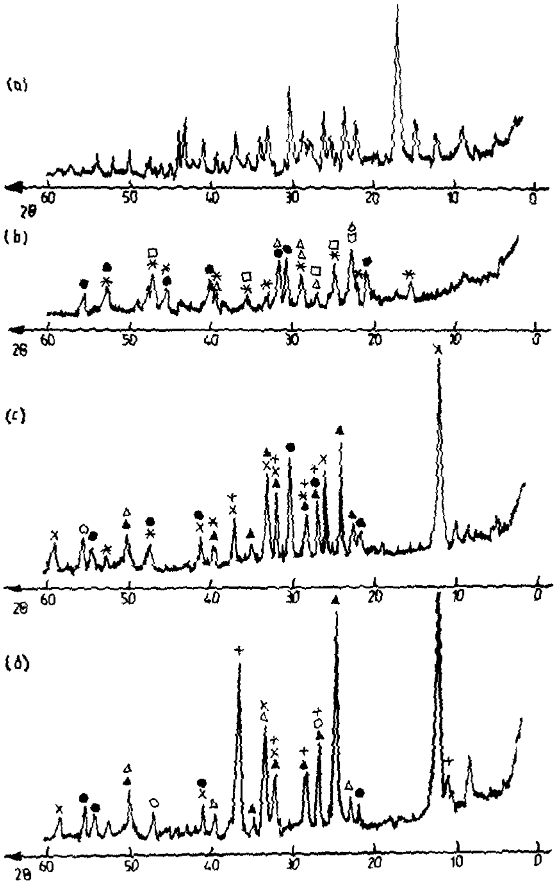

Fig. 4. X-ray pattern of: (a) $Cs_2Na[Bi(SCN)_4Cl_2]$ and its sinters prepared at (b) 260 °C, (c) 460 °C, (d) 750 °C. *, Bi_2S_3; ×, BiOCl, +, $(BiO)_2SO_4$; ■, CsNCS; □, NaNCS; ●, CsCl; ○, NaCl; ▲, Cs_2SO_4; △, Na_2SO_4.

TABLE 4

X-ray identification of $Cs_2Na[Bi(SCN)_3Cl_3]$ sinter prepared at 260 °C

Date from X-ray pattern of the sinter		Literature data		
2θ (°)	d/n (Å)	d/n (Å)	Compound	Intensity of lines %
13.7	6.46	Unidentified		
14.3	6.19	Unidentified		
20.4	4.35	Unidentified		
21.6	4.11	4.12	CsCl	45
23.0	3.86	3.88	CsNCS	20
23.3	3.81	3.78	$Cs_3Bi_2Cl_9$	100
25.1	3.54	3.56	Bi_2S_3	94
		3.53	Bi_2S_3	60
		3.49	NaNCS	53
27.4	3.25	3.27	CsNCS	100
		3.28	Cs_2SO_4	100
		3.20	NaNCS	100
28.6	3.11	3.12	Bi_2S_3	100
		3.14	Cs_2SO_4	100
30.0	2.98	2.96	NaNCS	53
30.8	2.90	2.92	CsCl	100
31.7	2.82	2.82	NaCl	100
		2.78	Na_2SO_4	100
33.2	2.70	2.68	$Cs_3Bi_2Cl_9$	41
		2.65	Na_2SO_4	48
39.5	2.28	2.27	Cs_2SO_4	45
		2.27	Bi_2S_3	36
40.2	2.24	2.24	CsCl	17
40.9	2.20	2.20	Cs_2SO_4	53
		2.19	$Cs_3Bi_2Cl_9$	46
45.7	1.98	1.99	NaCl	55
		1.98	$Cs_3Bi_2Cl_9$	52
46.9	1.93	1.93	Bi_2S_3	20
47.6	1.91	1.90	$Cs_3Bi_2Cl_9$	32
		1.86	Na_2SO_4	31
52.7	1.73	1.68	CsCl	25

sinter of $Cs_2Na[Bi(SCN)_3Cl_3]$ obtained at 260 °C with the literature data is given in Table 4.

IR analysis

Infrared spectra were recorded on a UR-10 Zeiss spectrophotometer. Suspensions of powders in Nujol were studied in the 2200–600 cm^{-1} range.

Infrared spectral absorption bands and the corresponding vibrations of $Cs_2Na[Bi(SCN)_4Cl_2]$ and its sinters prepared at 260 and 460 °C are given in

TABLE 5

Frequencies of the fundamental valence vibrations

Compound	Frequencies of vibration (cm^{-1})				
	δ(OSO); F [a]	ν(CS)	ν(SO); A [a]	ν(SO); F [a]	ν(CN)
$Cs_2Na[Bi(SCN)_4Cl_2]$		728			2095
260 °C sinter	618; 637	728; 755; 810	1000	1110; 1125	2085
460 °C sinter	618; 635		1000	1115; 1120	
$Bi(SCN)_3$		731			2100; 2125
CsNCS		752			2062
NaNCS		758			2080
Na_2SO_4	618; 640		983	1106	
Cs_2SO_4	620		990	1120; 1180	

[a] The band assignments for tetrahedral XY_4 molecules [8].

Table 5. Frequencies of fundamental vibrations of $Bi(SCN)_3$, NaNCS, CsNCS, Cs_2SO_4 and Na_2SO_4 are also given for comparison.

DISCUSSION

On the basis of the results of the thermal, chemical, diffractometric and IR spectrophotometric analyses it has been concluded that the thermal decomposition of caesium–sodium chlorothiocyanatobismuthates(III) is a three-stage process. The course of the decomposition, involving the decomposition of individual intermediate compounds at each stage, is described below.

Stage I

The first stage of thermal decomposition of caesium–sodium chlorothiocyanatobismuthates(III) is melting. The occurrence of endothermic peaks at 240 °C on the DTA curves indicates this process. Exothermic peaks at 260 °C on the DTA curves accompanied by rapid mass losses on the TG and DTG curves (Figs. 1–3) correspond to further decomposition of the compounds. The greatest mass loss occurs in the $Cs_2Na[Bi(SCN)_4Cl_2]$ sinter, and the smallest in $Cs_2Na[Bi(SCN)_2Cl_4]$. Equations (1)–(3) represent the reactions which occur at 260 °C

$$6Cs_2Na[Bi(SCN)_4Cl_2] \xrightarrow{O_2} Bi_2S_3 + 4BiS_{0.73}C_{2.72}N_{3.5}Cl_{1.5} + 6(Cs, Na)Cl$$
$$+ 4(Cs, Na)NCS + 4(Cs, Na)_2SO_4 + \text{gaseous products} \qquad (1)$$

$$6Cs_2Na[Bi(SCN)_3Cl_3] \xrightarrow{O_2} Bi_2S_3 + 2BiS_{0.64}C_{3.76}N_{5.56}Cl_{1.5} + Cs_3Bi_2Cl_9 \\ + 6(Cs, Na)Cl + 3(Cs, Na)NCS + 3(Cs, Na)_2SO_4 + \text{gaseous products} \quad (2)$$

$$6Cs_2Na[Bi(SCN)_2Cl_4] \xrightarrow{O_2} Cs_3Bi_2Cl_9 + 4BiS_{0.59}C_{1.18}N_{1.81}Cl_{1.5} \\ + 9(Cs, Na)Cl + 2(Cs, Na)NCS + 2(Cs, Na)_2SO_4 + \text{gaseous products} \quad (3)$$

The total number of caesium and sodium atoms involved in the decomposition reaction is 18 (12 caesium atoms, 6 sodium atoms).

The notation in parentheses (Cs, Na) means that both caesium and sodium may occur in the compound. The number in front of the parentheses represents the total number of caesium and sodium atoms, e.g. 6 (Cs, Na)Cl means that the total number of caesium and sodium atoms in the compound is equal to 6. This notation has been used because the ratio in which caesium chloride and sodium chloride occur is not known.

The composition of the sinters at 260 °C is in accordance with the results of chemical analyses of the solid products of caesium–sodium chlorothiocyanatobismuthate(III) pyrolysis (Table 2). X-ray analysis of the sinters at 260 °C confirmed the presence of caesium and sodium thiocyanates, chlorides and sulphates, bismuth sulphide (for $Cs_2Na[Bi(SCN)_4Cl_2]$ and $Cs_2Na[Bi(SCN)_3Cl_3]$) and caesium chlorobismuthate $Cs_3Bi_2Cl_9$ (for $Cs_2Na[Bi(SCN)_3Cl_3]$ and $Cs_2Na[Bi(SCN)_2Cl_4]$). While comparing eqns. (1)–(3) attention should be paid to the absence of Bi_2S_3 in the $Cs_2Na[Bi(SCN)_2Cl_4]$ sinter obtained at 260 °C (eqn. (3)) resulting from the small amount of thiocyanate groups in the compound. Similarly, the absence of $Cs_3Bi_2Cl_9$ in $Cs_2Na[Bi(SCN)_4Cl_2]$ sinter obtained at 260 °C can be explained by the small amount of chlorides in the complex compound. The sinters obtained at 260 °C were also studied in infrared. Analysis of the spectra (Table 5) proves that in the first stage of decomposition caesium sulphates (a characteristic splitting of the absorption band ν(SO)) and sodium sulphates (splitting of δ(OSO)) are formed. As compared with the spectra of the compounds before heating, the spectra of the sinters exhibit increased vibrational frequency for ν(CS) and decreased vibrational frequency for ν(CN). From the increase of ν(CS) in the sinter compared with that in the initial compound it follows that the Bi–SCN bond is ruptured and alkali metal thiocyanates M–NCS are formed (decrease in ν(CN)) [1]. The occurrence of a weak absorption band at 728 cm^{-1} suggests the existence of an intermediate compound in which bismuth is coordinated with the rest of the group by a sulphur atom.

The division of sinters into soluble- and insoluble-in-hot-water fractions confirms the formation of caesium and sodium chlorides, thiocyanates and sulphates as a result of pyrolysis of chlorothiocyanatobismuthates(III). The results of analyses of the soluble fractions indicate quantitative lixiviation of the compounds. The presence of $Cs_3Bi_2Cl_9$ in the sinters was also confirmed by leaching the sinters with water. Caesium chlorobismuthate is then decomposed into CsCl, BiOCl and HCl. The hydrolysis reaction occurring in the $Cs_2Na[Bi(SCN)_3Cl_3]$ sinter is described by

$$\begin{aligned} &Bi_2S_3 + Cs_3Bi_2Cl_9 + 2BiS_{0.64}C_{3.76}N_{5.56}Cl_{1.5} + 6(Cs, Na)Cl + 3(Cs, Na)NCS \\ &\quad + 3(Cs, Na)_2SO_4 + 2H_2O \rightarrow Bi_2S_3 + 2BiOCl + 2BiS_{0.64}C_{3.76}N_{5.56}Cl_{1.5} \\ &\quad + 9(Cs, Na)Cl + 3(Cs, Na)NCS + 3(Cs, Na)_2SO_4 + 4HCl \qquad (4) \end{aligned}$$

This decomposition is confirmed by the presence of BiOCl identification lines and the absence of $Cs_3Bi_2Cl_9$ reflexes in the diffraction pattern of the compounds present in the insoluble fraction and the analysis of the composition of the insoluble and soluble fractions (Table 3).

Stage II

Further oxidation of caesium and sodium thiocyanates takes place in the second stage of decomposition in the range 280–410 ° C. The main products are caesium and sodium sulphates, as confirmed by analysis of the composition of the soluble fraction (increased content of sulphate and decreased amount of thiocyanate). In the second stage a slow decomposition of the intermediate compound begins. These changes are associated with a slow loss in the masses of the samples, observed in the TG curves and as an exothermic peak at 340 ° C in the DTA curves.

Stage III

The third stage begins at 410 ° C. The reactions reach the highest rate at 460 ° C (for $Cs_2Na[Bi(SCN)_4Cl_2]$), 440 ° C (for $Cs_2Na[Bi(SCN)_3Cl_3]$) and 450 ° C (for $Cs_2Na[Bi(SCN)_2Cl_4]$). Exothermic peaks on the DTA curves and the rapid losses in mass observed in the TG and DTG curves correspond to these temperatures. The greatest mass loss was observed for the $Cs_2Na[Bi(SCN)_4Cl_2]$ sinter and the smallest for $Cs_2Na[Bi(SCN)_2Cl_4]$. The main process in the third stage of decomposition is the breaking down of the intermediates $BiS_xC_yN_sCl_z$. In the case of $Cs_2Na[Bi(SCN)_4Cl_2]$ this decomposition probably results in the formation of Bi_2S_3 and BiOCl, and in the cases of $Cs_2Na[Bi(SCN)_3Cl_3]$ and $Cs_2Na[Bi(SCN)_2Cl_4]$ in the formation of BiOCl and $(BiO)_2SO_4$. In the third stage bismuth sulphide is oxidized to bismuthyl sulphate. The changes occurring at 460 ° C are illustrated by the following equations:

$$\begin{aligned} &6Cs_2Na[Bi(SCN)_4Cl_2] \xrightarrow{O_2} Bi_2S_3 + 2BiOCl + (BiO)_2SO_4 + 6(Cs, Na)_2SO_4 \\ &\quad + 6(Cs, Na)Cl + \text{gaseous products} \qquad (5) \end{aligned}$$

$$6Cs_2Na[Bi(SCN)_3Cl_3] \xrightarrow{O_2} 2BiOCl + Cs_3Bi_2Cl_9 + (BiO)_2SO_4 + 4.5(Cs, Na)_2SO_4 + 6(Cs, Na)Cl + \text{gaseous products} \quad (6)$$

$$6Cs_2Na[Bi(SCN)_2Cl_4] \xrightarrow{O_2} Cs_3Bi_2Cl_9 + 2BiOCl + (BiO)_2SO_4 + 9(Cs, Na)Cl + 3(Cs, Na)_2SO_4 + \text{gaseous products} \quad (7)$$

The composition of sinters obtained at 460 °C is consistent with the results of chemical analysis of the solid products of decomposition of caesium–sodium chlorothiocyanatobismuthates(III) (Table 2). The diffractometric examination showed that in the sinters obtained at 460 °C the following compounds are present: caesium and sodium sulphates and chlorides, bismuthyl chloride, $Cs_3Bi_2Cl_9$ (does not occur in $Cs_2Na[Bi(SCN)_4Cl_2]$) and bismuth sulphide (present only in $Cs_2Na[Bi(SCN)_4Cl_2]$). The absence of $Cs_3Bi_2Cl_9$ in the sinter of $Cs_2Na[Bi(SCN)_4Cl_2]$ obtained at 460 °C results from the small chloride content of the compound. Similarly, the absence of bismuth sulphide in $Cs_2Na[Bi(SCN)_3Cl_3]$ and $Cs_2Na[Bi(SCN)_2Cl_4]$ (eqs. (6) and (7)) is a result of the low content of thiocyanate groups in the complex compounds. The sinters obtained at 460 °C were also analysed in infrared. Analysis of the spectra (Table 5) indicates that both caesium sulphate (split absorption band ν(SO)) and sodium sulphate (split band δ(OSO)) are present in the examined sinters.

The presence of alkali metal chlorides and sulphates was confirmed when the compounds in the sinters obtained at 460 °C were divided into soluble- and insoluble-in-water fractions, and when the composition of both fractions was analysed. Analysis of hydrolysis products indicates also the presence of $Cs_3Bi_2Cl_9$ in the sinters of $Cs_2Na[Bi(SCN)_3Cl_3]$ and $Cs_2Na[Bi(SCN)_2Cl_4]$. As a result of leaching, caesium chlorobismuthate decomposes and caesium chlorides, bismuthyl chlorides and hydrochloric acid are formed. Moreover, as the sinters are leached with water bismuthyl sulphate changes into bismuthyl chloride. Equation (8) illustrates the hydrolysis reaction of the $Cs_2Na[Bi(SCN)_3Cl_3]$ sinter obtained at 460 °C

$$2BiOCl + Cs_3Bi_2Cl_9 + (BiO)_2SO_4 + 4.5(Cs, Na)_2SO_4 + 6(Cs, Na)Cl + 2H_2O \rightarrow 6BiOCl + 7(Cs, Na)Cl + 5.5(Cs, Na)_2SO_4 + 4HCl \quad (8)$$

The above reaction is confirmed by the analyses of the soluble and insoluble fractions (Table 3) and the presence of the BiOCl identification lines in the diffraction pattern of the compounds present in the insoluble fraction. No NaCl identification lines were observed in the diffraction pattern of the $Cs_2Na[Bi(SCN)_4Cl_2]$ sinter obtained at 460 °C and no NaCl or Cs_2SO_4 reflexes occurred in the diffraction pattern of that of $Cs_2Na[Bi(SCN)_2Cl_4]$. This can be explained by the formation of amorphous forms of sodium chloride and caesium sulphate.

At temperatures > 460 °C (in the case of $Cs_2Na[Bi(SCN)_4Cl_2]$), > 440 °C ($Cs_2Na[Bi(SCN)_3Cl_3]$) and > 450 °C ($Cs_2Na[Bi(SCN)_2Cl_4]$) a slow increase of the mass of the sinter occurs (greatest in the case of $Cs_2Na[Bi(SCN)_4Cl_2]$ and the least in that of $Cs_2Na[Bi(SCN)_2Cl_4]$. The increase in mass is probably associated with the formation of bismuthyl sulphate. The differences between the increases in the masses of the individual chlorothiocyanatobismuthates(III) result from the different thiocyanate contents. The more thiocyanate groups in the compound the greater the increase in the sinter mass observed in the TG curve (more bismuthyl sulphate is formed).

At 500 ° C (in the cases of $Cs_2Na[Bi(SCN)_3Cl_3]$ and $Cs_2Na[Bi(SCN)_2Cl_4]$) and at 560 ° C ($Cs_2Na[Bi(SCN)_2Cl_4]$) exothermic peaks occur in the DTA curves, accompanied by a slight increase in the sinter mass.

The mass of the $Cs_2Na[Bi(SCN)_4Cl_2]$ sinter remains the same from 510 to 620 ° C. The masses of other compounds begins to diminish rapidly after it reaches maximum values on the TG curves. The loss in mass has the highest rate in the case of $Cs_2Na[Bi(SCN)_2Cl_4]$ (the rapid decomposition at temperatures > 570 ° C may result from $Cs_3Bi_2Cl_9$ pyrolysis). It is a little slower for $Cs_2Na[Bi(SCN)_3Cl_3]$ (decomposition begins at 580 ° C) and the slowest for $Cs_2Na[Bi(SCN)_4Cl_2]$ (no caesium chlorobismuthate).

The sinters of caesium–sodium chlorothiocyanatobismuthates(III) obtained at 750 ° C were analysed in order to study the decomposition reactions of pyrolysis products formed in the third stage. Equations (9)–(11) represent the processes occurring in these sinters:

$$6Cs_2Na[Bi(SCN)_4Cl_2] \xrightarrow{O_2} 2BiOCl + 2(BiO)_2SO_4 + 6(Cs, Na)_2SO_4 + 6(Cs, Na)Cl + \text{gaseous products} \quad (9)$$

$$6Cs_2Na[Bi(SCN)_3Cl_3] \xrightarrow{O_2} 2BiOCl + Cs_3Bi_2Cl_9 + (BiO)_2SO_4 + 4.5(Cs, Na)_2SO_4 + 5(Cs, Na)Cl + CsCl\uparrow + \text{gaseous products} \quad (10)$$

$$6Cs_2Na[Bi(SCN)_2Cl_4] \xrightarrow{O_2} 2BiOCl + (BiO)_2SO_4 + Cs_3Bi_2Cl_9 + 3(Cs, Na)_2SO_4 + 7(Cs, Na)Cl + 2CsCl\uparrow + \text{gaseous products} \quad (11)$$

These mechanisms were confirmed by analyses of the sinters obtained at 750 ° C (Table 2), of the soluble and insoluble fractions of the sinters, and by diffractometric examination of the insoluble fractions and of sinters which were not leached.

The results of the analyses indicate that at 750 ° C caesium chloride evaporates (melting point 640 ° C). Comparison of eqns. (9)–(11) indicates that the rate of caesium chloride evaporation depends on the content of chlorides in the complex compounds. At 750 ° C two moles of CsCl evaporate from $Cs_2Na[Bi(SCN)_2Cl_4]$, 1 mole evaporates from $Cs_2Na[Bi(SCN)_3Cl_3]$, whereas the dissociation of caesium chloride from $Cs_2Na[Bi(SCN)_4Cl_2]$ does not occur at this temperature.

Leaching of the sinters obtained at 750 °C with hot water results, like before, in the change of bismuthyl sulphate into bismuthyl chloride and in the decomposition of $Cs_3Bi_2Cl_9$ resulting in the formation of BiOCl, CsCl and HCl. The hydrolysis reaction of $Cs_2Na[Bi(SCN)_3Cl_3]$ sinter obtained at 750 °C takes the following course:

$$\begin{aligned} &2BiOCl + Cs_3Bi_2Cl_9 + (BiO)_2SO_4 + 4.5(Cs, Na)_2SO_4 + 5(Cs, Na)Cl \\ &\quad + 2H_2O \rightarrow 6BiOCl + 6(Cs, Na)Cl + 5.5(Cs, Na)_2SO_4 + 4HCl \qquad (12) \end{aligned}$$

The mechanism of the leaching reaction was confirmed by fraction analysis (Table 3) and diffractometric examination. Only BiOCl identification lines were observed in the diffraction patterns of the insoluble fractions. Further increase in temperature brings about the formation of Bi_2O_3 as a result of the oxidation of bismuth compounds [9] and the further evaporation of CsCl.

At 810 and 900 °C (in the case of $Cs_2Na[Bi(SCN)_3Cl_3]$) and at 600, 820 and 930 °C ($Cs_2Na[Bi(SCN)_2Cl_4]$) weak endothermic peaks occurred in the DTA curves. They probably correspond to the decomposition of $Cs_3Bi_2Cl_9$. No endothermic peaks were observed in the derivatogram of $Cs_2Na[Bi(SCN)_4Cl_2]$.

The results of chemical analysis of the sinters and their water-soluble and insoluble fractions indicate that the increase in the amount of chlorine in caesium–sodium chlorothiocyanatobismuthates(III) in the sinters obtained at 260 °C is associated with increases in the contents of chlorine bound to bismuth, bismuth in the insoluble fraction, chlorides in the soluble fraction, and with the decrease in the amounts of thiocyanates and sulphates in the soluble fraction. The same applies to the composition of the soluble fraction of the sinters obtained at 460 and 750 °C (though no differences in the content of bismuth in the insoluble fraction of these sinters were observed). The smallest content of chlorine in the intermediate compounds, calculated relative to the mass of the sinter and the mass of the insoluble fraction, occurs in the sinters obtained at 260 °C in $Cs_2Na[Bi(SCN)_3Cl_3]$, whereas in the other compounds the amount of chlorine in $BiS_xC_yN_sCl_z$ is similar (about 4.7% relative to the mass of the sinter and about 11% relative to the mass of the insoluble fraction).

To sum up the results of the examination of the thermal decomposition it should be observed that the analysis of the thermal curves and mass losses (Table 6) indicates a similar mechanism of the decomposition of individual caesium–sodium chlorothiocyanatobismuthates(III). In the first stage, which occurs at about 260 °C, decomposition of the complexes occurs and caesium and sodium thiocyanates, chlorides and sulphates, Bi_2S_3 or $Cs_3Bi_2Cl_9$ and an intermediate product of the general formula $BiS_xC_yN_sCl_z$ are formed. In the second stage sulphates are formed as a result of oxidation of thiocyanates. This process occurs at 340 °C. In the last stage the intermediate compound

TABLE 6

Mass changes in the thermal decomposition of caesium–sodium chlorothiocyanatobismuthates(III)

Compound	Mass losses (%)					
	260 ° C		460 ° C		750 ° C	
	Det.	Calc.	Det.	Calc.	Det.	Calc.
$Cs_2Na[Bi(SCN)_4Cl_2]$	5.69	5.42	15.26	14.63	13.13	13.96
$Cs_2Na[Bi(SCN)_3Cl_3]$	4.50	4.23	11.03	10.46	14.97	14.06
$Cs_2Na[Bi(SCN)_2Cl_4]$	3.10	3.41	9.94	9.17	15.82	16.59

is decomposed, bismuth sulphate is oxidized and bismuthyl sulphate results (at about 450 ° C). At temperatures > 600 ° C bismuth compounds formed in the third stage are gradually oxidized resulting in the formation of Bi_2O_3 and caesium chloride evaporates.

By comparison of the results of the thermal analysis of caesium–sodium chlorothiocyanatobismuthates(III) with those of the previously analysed thiocyanatobismuthates(III) [2,5] it follows that the compounds have a similar mechanism of decomposition. Decomposition of the salts proceeds in three stages (corresponding to three exothermic peaks on the DTA curves): in the first stage the complex is decomposed and an intermediate compound is formed; in the second stage sulphates of alkali metals are the main products; and in the third stage the intermediate compound is decomposed. The basic difference consists in the occurrence of chlorine in the intermediate compounds of caesium–sodium chlorothiocyanatobismuthates(III) and the formation of chlorides of alkali metals, bismuthyl chloride and caesium chlorobismuthate $Cs_3Bi_2Cl_9$. Moreover, one of the products of pyrolysis of the intermediate compound formed in the process of thiocyanatobismuthate(III) decomposition is free bismuth. This does not occur for caesium–sodium chlorothiocyanatobismuthates(III).

As caesium–sodium chlorothiocyanatobismuthates, $Cs_2Na[Bi(SCN)_6]$ and $Cs[Bi(SCN)_4]$ (the initial compound for obtaining chlorothiocyanatobismuthates) are compared, it is evident that the most stable compound is $Cs_2Na[Bi(SCN)_6]$ (its decomposition begins at 250 ° C) and the least stable is $Cs[Bi(SCN)_4]$ (160 ° C). The stability of the chlorothiocyanatobismuthates(III) under discussion is identical (240 ° C) and the same as the stability of $Rb_2Na[Bi(SCN)_6]$ [5]. Among double salts $K_2Na[Bi(SCN)_6]$ is a little less stable (220 ° C). The decomposition temperatures of the other complexes are in the range 190–210 ° C.

By comparing the thermal decomposition temperatures it follows that the exchange of some of the thiocyanate groups for chloride ones does not involve considerable changes in the stability of bismuth(III) complexes with similar outer sphere structure.

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REFERENCES

1 A. Cygański, Rocz. Chem., 51 (1977) 869.
2 A. Cygański, Talanta, 24 (1977) 361.
3 A. Cygański, Rocz. Chem., 50 (1976) 391.
4 A. Cygański, Rocz. Chem., 51 (1977) 2061.
5 A. Cygański, Rocz. Chem., 52 (1978) 2321.
6 A. Cygański and A. Turek, Polish J. Chem., in press.
7 A. Cygański, Chem. Anal., 3 (1958) 807.
8 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2nd edn., John Wiley, New York, 1970.
9 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1953.