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STUDIES ON THE THERMAL DECOMPOSITION OF CAESIUM SODIUM BROMOTHIOCYANATOBISMUTHATES(III)

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ABSTRACT

The thermal decomposition reactions of caesium sodium bromothiocyanatobismuthates(III), $Cs_2Na[Bi(SCN)_3Br_3]$, $Cs_2Na[Bi(SCN)_2Br_4]$, $Cs_2Na[Bi_2(SCN)_7Br_2]$ and $Cs_2Na[Bi_2(SCN)_6Br_3]$, were investigated using thermal analysis. The mechanism of the thermal decomposition of these compounds was determined based on the chemical and X-ray analysis of the solid products of the pyrolysis. The decomposition was found to occur in three stages. The decomposition courses and thermal stabilities of caesium sodium bromothiocyanatobismuthates(III), caesium sodium chlorothiocyanatobismuthates(III), caesium sodium hexathiocyanatobismuthate(III) and caesium tetrathiocyanatobismuthate(III) were compared.

INTRODUCTION

In a previous paper [1], the thermal decomposition reactions of caesium sodium chlorothiocyanatobismuthates(III) of general formula $Cs_2Na[Bi(SCN)_xCl_{6-x}]$, where $x = 2$, 3 and 4, were discussed. The aim of the present work is to determine the mechanism of the thermal decomposition of the following caesium sodium bromothiocyanatobismuthates(III): $Cs_2Na[Bi(SCN)_3Br_3]$, $Cs_2Na[Bi(SCN)_2Br_4]$, $Cs_2Na[Bi_2(SCN)_7Br_2]$ and $Cs_2Na(Bi_2(SCN)_6Br_3]$. The compounds were obtained by treating $Cs[Bi(SCN)_4]$ with NaBr solutions of different concentrations [2]. The thermal stabilities of chlorothiocyanatobismuthates(III), bromothiocyanatobismuthates(III) and thiocyanatobismuthates(III), $Cs_2Na[Bi(SCN)_6]$ and $Cs[Bi(SCN)_4]$, were compared. Caesium tetrathiocyanatobismuthate(III) is the starting compound for all the above complex salts.

EXPERIMENTAL

Thermal analysis

Thermal analyses were carried out in air using a MOM Budapest OD-102/1500 °C thermal analyser over the temperature range 20–1000 °C at a

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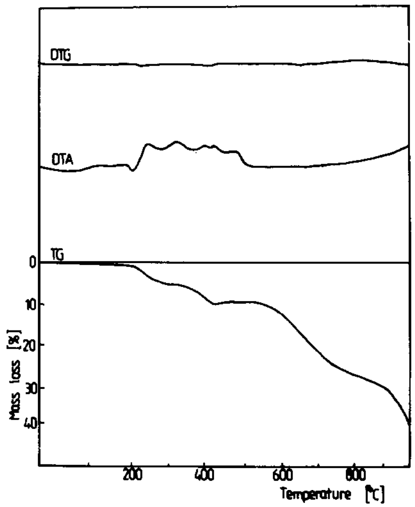

Fig. 1. Thermal analysis curves of $Cs_2Na[Bi(SCN)_3Br_3]$.

heating rate of 5 °C min^{-1}. The sample mass was 200 mg. α-Al_2O_3 was used as the reference material. The galvanometer sensitivity for the DTA curve was $\frac{1}{15}$, for the DTG curve $\frac{1}{20}$ and for the TG curve 200 mg. The thermal analysis curves of caesium sodium tribromotrithiocyanatobismuthate(III), tetrabromodithiocyanatobismuthate(III), dibromoheptathiocyanatobismu-

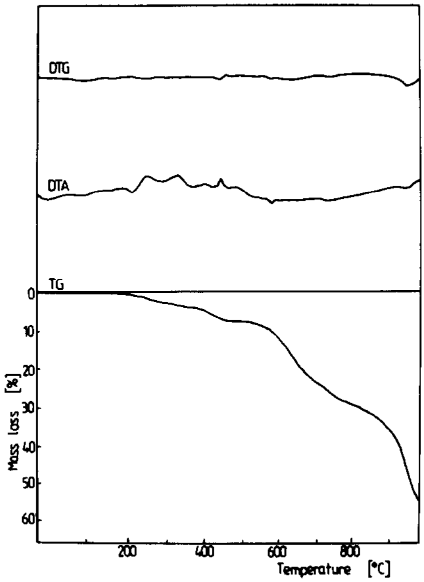

Fig. 2. Thermal analysis curves of $Cs_2Na[Bi(SCN)_2Br_4]$.

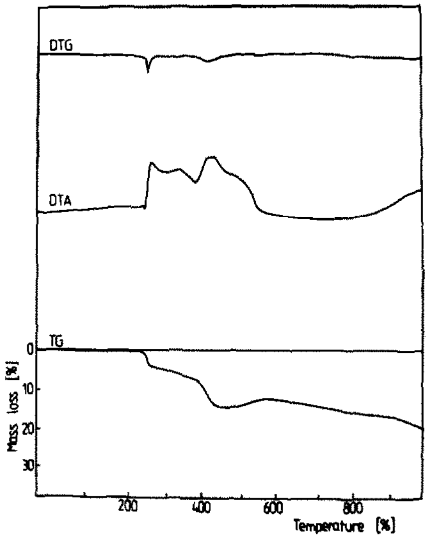

Fig. 3. Thermal analysis curves of $Cs_2Na[Bi_2(SCN)_7Br_2]$.

thate(III) and tribromohexathiocyanatobismuthate(III) are shown in Figs. 1–4.

The DTA curve of $Cs_2Na[Bi(SCN)_3Br_3]$ (Fig. 1) has an endothermic peak at 210 °C and less intense exothermic peaks at 250, 330, 400 and 430 °C, corresponding to a mass loss observed in the TG and DTG curves. There is a slight increase in mass over the temperature range 430–540 °C. The increase is related to the occurrence of a very broad exothermic peak in the DTA curve. Above 540 °C the sample mass decreases rapidly.

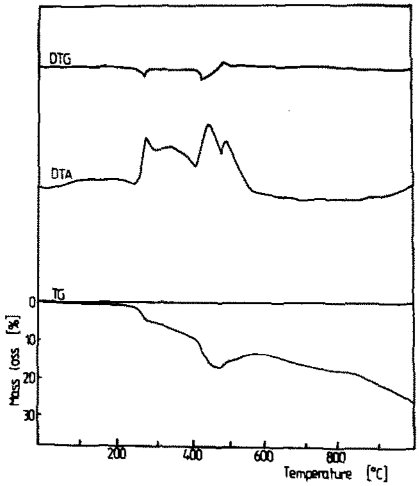

Fig. 4. Thermal analysis curves of $Cs_2Na[Bi_2(SCN)_6Br_3]$.

TABLE 1

Temperatures and DTA peaks of caesium sodium bromothiocyanatobismuthates(III)

Formula	Endothermic peak (°C)	Beginning of the first exothermic peak (°C)	Exothermic peaks (°C)				Endothermic peaks (°C)		
			I	II	III	IV	II	III	IV
$Cs_2Na[Bi(SCN)_3Br_3]$	210	210	250	330	400	430	–	–	–
$Cs_2Na[Bi(SCN)_2Br_4]$	210	210	250	330	400	440	580	730	950
$Cs_2Na[Bi_2(SCN)_7Br_2]$	240	240	260	330	430	–	–	–	–
$Cs_2Na[Bi_2(SCN)_6Br_3]$	240	240	260	330	450	500	–	–	–

The DTA curve of $Cs_2Na[Bi(SCN)_2Br_4]$ (Fig. 2) is different from the curve described above in that its exothermic peak at 400 ° C is broader. In addition, there are small endothermic peaks at 580, 730 and 950 ° C. In the temperature range 440–540 ° C, the mass is stable. At 540 ° C, a loss of mass, slow at first and very rapid after 580 ° C, is observed.

The DTA curve of $Cs_2Na[Bi_2(SCN)_7Br_2]$ (Fig. 3) shows a very slight endothermic peak at 240 ° C. The exothermic peaks are much more intense than those of the two previous compounds. The first exothermic peak is sharp and occurs at 260 ° C, while the exothermic peaks at 330 and 430 ° C are not sharp. The exothermic peaks are accompanied by a continuous mass loss in the TG and DTG curves, which is considerably greater than in the mononuclear complex salts. Above 450 ° C, an increase in mass is observed in the TG curve, accompanied by a very broad exothermic peak in the DTA curve. Above 600 ° C, a slow mass loss occurs. The loss of mass is considerably smaller than in the compounds discussed previously.

The DTA curve of $Cs_2Na[Bi_2(SCN)_6Br_3]$ (Fig. 4) is similar to that of $Cs_2Na[Bi_2(SCN)_7Br_2]$. The difference lies in the occurrence of two sharp exothermic peaks at 450 and 500 ° C. The first peak corresponds to a loss in mass, the second to an increase in mass, in the TG and DTG curves. Above 600 ° C, the sample mass gradually decreases, the mass loss being slightly greater than that for $Cs_2Na[Bi_2(SCN)_7Br_2]$.

The analysis of the thermal curves suggests three stages of thermal decomposition for caesium sodium bromothiocyanatobismuthates(III) associated with the mass loss. The differences in the course of the DTA curves and in the mass losses testify to a slightly different mechanism of thermal decomposition for each particular complex salt. The temperatures and their corresponding peaks in the DTA curves for the compounds investigated are presented in Table 1.

The analysis of the sinters has confirmed the differences in the reactions occurring during the decomposition of the caesium sodium bromothiocyanatobismuthates(III). The sinters were obtained under conditions similar to those used for the thermal analysis. The 200 mg samples were heated in a silite furnace at a heating rate of 5 ° C min^{-1} up to the appropriate temperatures determined from the thermal curves. The samples tested were those whose changes in mass were similar to those calculated from the TG curves.

Chemical analysis

The chemical analyses of the solid products of the pyrolysis were by standard chemical methods [1]. Table 2 presents the results of the analyses of the caesium sodium bromothiocyanatobismuthate(III) sinters.

TABLE 2

Results of chemical analyses of caesium sodium bromothiocyanatobismuthate(III) sinters

Formula	Temperature (° C)	Composition of sinter (%)		Equation no.
		Detected	Calculated	
$Cs_2Na[Bi(SCN)_3Br_3]$	270	23.93 Bi	23.86 Bi	(1)
		8.40 S	8.69 S	
		2.85 C	2.80 C	
		2.96 N	3.09 N	
	430	26.76 Bi	25.90 Bi	(6)
		5.54 S	5.63 S	
		0 C	0 C	
		0 N	0 N	
	760	27.02 Bi	26.13 Bi	(11)
		5.64 S	5.21 S	
$Cs_2Na[Bi(SCN)_2Br_4]$	270	24.61 Bi	23.00 Bi	(2)
		5.60 S	5.32 S	
		2.72 C	2.25 C	
		2.02 N	2.47 N	
	440	24.99 Bi	24.60 Bi	(7)
		1.57 S	1.89 S	
		0 C	0 C	
		0 N	0 N	
	760	26.96 Bi	26.06 Bi	(12)
		2.21 S	2.40 S	
$Cs_2Na[Bi_2(SCN)_7Br_2]$	270	35.87 Bi	34.50 Bi	(3)
		14.45 S	14.33 S	
		5.28 C	5.15 C	
		7.42 N	7.23 N	
	430	39.34 Bi	38.32 Bi	(8)
		8.51 S	8.82 S	
		0 C	0 C	
		0 N	0 N	
	760	39.30 Bi	39.28 Bi	(13)
		7.73 S	8.03 S	
$Cs_2Na[Bi_2(SCN)_6Br_3]$	270	33.94 Bi	34.00 Bi	(4)
		11.42 S	11.31 S	
		4.66 C	4.62 C	
		5.45 N	5.32 N	
	450	38.54 Bi	38.32 Bi	(9)
		8.18 S	8.08 S	
		0 C	0 C	
		0 N	0 N	
	760	39.22 Bi	38.89 Bi	(14)
		5.14 S	5.22 S	

TABLE 3

X-ray identification of $Cs_2Na[Bi(SCN)_3Br_3]$ sinter (270 °C)

Data from X-ray patterns of the sinter		Literature data		
2θ (deg)	d/n (Å)	d/n (Å)	Compound	Intensity of lines (%)
9.6	9.21	Unidentified		
13.3	6.66	6.70	NaNCS	8
16.5	5.37	5.37	CsNCS	6
19.1	4.65	4.66	Na_2SO_4	73
20.5	4.33	Unidentified		
22.4	3.97	3.99	$Cs_3Bi_2Br_9$	72
24.0	3.71	3.68	Cs_2SO_4	35
26.1	3.41	3.45	NaBr	64
26.6	3.35	3.32	NaNCS	20
27.2	3.28	3.27	CsNCS	100
		3.28	Cs_2SO_4	100
		3.27	$Cs_3Bi_2Br_9$	72
27.5	3.24	3.20	NaNCS	100
		3.24	$Cs_3Bi_2Br_9$	61
29.0	3.08	3.11	Bi_2S_3	100
		3.07	Na_2SO_4	47
29.6	3.02	3.04	CsBr	100
		2.99	NaBr	100
30.5	2.93	2.96	NaNCS	53
31.8	2.81	2.78	Na_2SO_4	100
		2.81	$Cs_3Bi_2Br_9$	100
		2.81	Bi_2S_3	63
32.9	2.72	2.72	Cs_2SO_4	10
33.3	2.69	2.64	Na_2SO_4	48
		2.65	Cs_2SO_4	20
34.6	2.59	2.62	CsNCS	12
35.6	2.52	2.52	Bi_2S_3	35
36.7	2.45	2.47	CsNCS	10
38.2	2.35	2.33	Na_2SO_4	21
39.3	2.29	2.30	$Cs_3Bi_2Br_9$	37
		2.27	Cs_2SO_4	45
41.8	2.16	2.11	NaBr	63
		2.15	CsBr	54
44.0	2.06	2.04	NaNCS	53
45.6	1.99	1.95	Bi_2S_3	55
		1.99	$Cs_3Bi_2Br_9$	43
49.1	1.85	1.86	Na_2SO_4	31
		1.85	Bi_2S_3	17
50.2	1.82	1.80	NaBr	21
51.9	1.76	1.75	CsBr	68

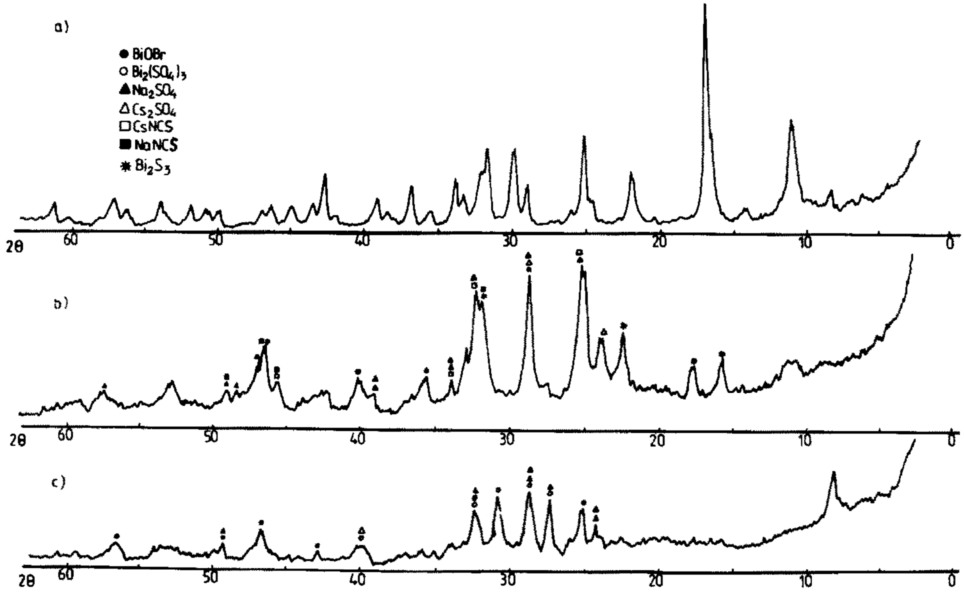

Fig. 5. X-ray patterns of: a, $Cs_2Na[Bi_2(SCN)_7Br_2]$; and its sinters obtained at: b, 270 °C; and c, 430 °C.

X-ray analysis

The X-ray analysis of the sinters was carried out on a DRON-1 diffractometer using Cu $K\alpha$ radiation with a nickel filter. The diffraction curve was recorded over the range $2\theta = 2\text{–}70°$. Diffraction patterns of the compounds under investigation, along with those of their sinters and the insoluble fractions of the sinters, were obtained. The division of the sinters into insoluble and soluble fractions allows the elimination of reflections due to the soluble fraction of a sinter in the insoluble fraction diffractograms. The diffractograms of caesium sodium dibromoheptathiocyanatobismuthate(III) and its sinters are shown in Fig. 5.

Table 3 presents a comparison of the reflections occurring in the diffractogram of the sinter of caesium sodium tribromotrithiocyanatobismuthate(III) obtained at 270 °C with the literature data.

DISCUSSION

From the thermal analysis, it has been found that the thermal decomposition of caesium sodium bromothiocyanatobismuthates(III) occurs in three stages. The course of the decomposition of these compounds in particular stages has been established by chemical and X-ray analyses.

Stage I

The decomposition of caesium sodium bromothiocyanatobismuthates(III) is preceded by their melting. The endothermic peak in the DTA curves (Figs. 1–4) is related to this process. Immediately following melting, the complexes decompose with a loss in mass being indicated on the TG curves. In the DTG curves of the polynuclear complexes, sharp peaks associated with a slightly greater loss of mass can be observed.

Equations (1)–(4) show the reactions occurring at 270 ° C

$$\begin{aligned} 6\mathrm{Cs_2Na[Bi(SCN)_3Br_3]} &\xrightarrow{O_2} \mathrm{Bi_2S_3 + 2BiS_{0.62}C_{1.62}N_{1.30}Br_{2.5} + Cs_3Bi_2Br_9} \\ &\quad \mathrm{+\,9MNCS + M_2SO_4} \\ &\quad \mathrm{+\,4MBr + (C_{5.76}N_{6.40}S_{3.76})}\ ^{*} \end{aligned} \tag{1}$$

$$\begin{aligned} 6\mathrm{Cs_2Na[Bi(SCN)_2Br_4]} &\xrightarrow{O_2} \mathrm{4BiS_{0.76}C_{1.05}N_{0.90}Br_{1.5} + Cs_3Bi_2Br_9 + 6MNCS} \\ &\quad \mathrm{+\,9MBr + (C_{1.80}N_{2.40}S_{2.96})}\ ^{*} \end{aligned} \tag{2}$$

$$\begin{aligned} 6\mathrm{Cs_2Na[Bi_2(SCN)_7Br_2]} &\xrightarrow{O_2} \mathrm{3Bi_2S_3 + 6BiS_{1.25}C_{2.86}N_{3.92}Br_{2.0} + 14MNCS} \\ &\quad \mathrm{+\,2M_2SO_4 + (C_{10.84}N_{4.48}S_{9.50})}\ ^{*} \end{aligned} \tag{3}$$

$$\begin{aligned} 6\mathrm{Cs_2Na[Bi_2(SCN)_6Br_3]} &\xrightarrow{O_2} \mathrm{2Bi_2S_3 + 6BiS_{1.17}C_{2.90}N_{2.84}Br_{1.5} + Cs_3Bi_2Br_9} \\ &\quad \mathrm{+\,11MNCS + 2M_2SO_4 + (C_{7.60}N_{7.96}S_{9.98})}\ ^{*} \end{aligned} \tag{4}$$

where M ≡ Cs or Na, the sum of the caesium and sodium atoms being 18 (12 caesium atoms, 6 sodium atoms).

The quantitative composition of the sinters (270 ° C) is in agreement with the chemical analysis of the solid pyrolysis products (Table 2) while the qualitative composition was confirmed by diffractometry. The ratio of caesium and sodium thiocyanates, sulphates and bromides in the sinters is not known. Comparing eqns. (1)–(4), it can be seen that Bi_2S_3 and sulphates are absent from the $Cs_2Na[Bi(SCN)_2Br_4]$ sinter obtained at 270 ° C, see eqn. (2); this is caused by a small amount of thiocyanate in the starting compound. In the $Cs_2Na[Bi_2(SCN)_7Br_2]$ sinter obtained at 270 ° C, eqn. (3), there was no $Cs_3Bi_2Br_9$, which is related to a small amount of bromide in the complex salt. The absence of alkali metal bromides in the $Cs_2Na[Bi_2(SCN)_7Br_2]$ and $Cs_2Na[Bi_2(SCN)_6Br_3]$ sinters obtained at 270 ° C can be explained in a similar way. In the sinters of all the caesium sodium bromothiocyanatobismuthates(III) one of the products of stage I of the pyrolysis is an intermediate compound of general formula $BiS_xC_yN_sBr_z$. The

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* The composition of the gaseous products was not studied. The reaction equation presents a summary formula of the gaseous products resulting from the difference in the mass of the substrates and reaction products.

composition of this compound is different for different complex salts and, in addition, it depends on the conditions of the decomposition, e.g. the heating rate.

To test the validity of the mechanism suggested, the sinters were divided into fractions that were soluble and insoluble in hot water. The reaction occurring in the leaching of the $Cs_2Na[Bi(SCN)_3Br_3]$ sinter (270 °C) with water is

$$\begin{aligned} &Bi_2S_3 + 2BiS_{0.62}C_{1.62}N_{1.30}Br_{2.5} + Cs_3Bi_2Br_9 + 9MNCS + M_2SO_4 + 4MBr \\ &\quad + 2H_2O \rightarrow Bi_2S_3 + 2BiS_{0.62}C_{1.62}N_{1.30}Br_{2.5} + 2BiOBr + 9MNCS \\ &\qquad\qquad + M_2SO_4 + 7MBr + 4HBr \end{aligned} \tag{5}$$

As a result of the leaching, $Cs_3Bi_2Br_9$ decomposes, and caesium and bismuthyl bromide and hydrobromic acid are formed. Caesium and sodium bromides, thiocyanates and sulphates pass into the soluble fraction, while bismuth sulphide and the intermediate products of the decomposition remain undecomposed in the insoluble fraction. The leaching process proceeds quantitatively. The presence of $Cs_3Bi_2Br_9$ was demonstrated by its X-ray diffraction pattern, found in the sinter prior to leaching. An increase in the concentration of bromides in the soluble fraction as a result of leaching and the presence of BiOBr reflections in the insoluble fraction of the sinter provide additional evidence.

Stage II

The processes occurring in the first stage of the decomposition partly coincide with the reactions of the second stage. From the analysis of the shape of the thermal curve, one can only approximate the temperature limits of the second stage of pyrolysis (Table 4). The main reaction occurring in this stage is the further oxidation of the sodium and caesium thiocyanates to the corresponding sulphates: a decrease in thiocyanate content and an increase in the sulphates in the soluble fraction was found. A slow decomposition of the intermediate compound probably also takes place. These

TABLE 4

Temperature ranges of particular decomposition stages of caesium sodium bromothiocyanatobismuthates(III)

Compound	Stage I (°C)	Stage II (°C)	Stage III (°C)
$Cs_2Na[Bi(SCN)_3Br_3]$	210–280	280–340	340–430
$Cs_2Na[Bi(SCN)_2Br_4]$	210–280	280–360	360–440
$Cs_2Na[Bi_2(SCN)_7Br_2]$	240–300	300–380	380–430
$Cs_2Na[Bi_2(SCN)_6Br_3]$	240–300	300–400	400–450

processes occur simultaneously, so that an accurate interpretation of the thermal curves is impossible. In stage II there is a slow loss in mass of the samples under investigation observed in the TG curves. These changes have an exothermic character, confirmed by the presence of a broad peak in the DTA curves, which reaches its maximum at 330 °C. (In the case of $Cs_2Na[Bi(SCN)_3Br_3]$ and $Cs_2Na[Bi(SCN)_2Br_4]$ there is an additional slight, broad exothermic peak at 400 °C).

Stage III

The last stage in the thermal decomposition of caesium sodium bromothiocyanatobismuthates(III) begins immediately after completion of stage II, see Table 4. The reactions are accompanied by a continuous loss in mass observed in the TG curves (much greater for the polynuclear compounds than for the mononuclear compounds). The mass losses of $Cs_2Na[Bi_2(SCN)_7Br_2]$ and $Cs_2Na[Bi_2(SCN)_6Br_3]$ correspond to sharp, distinct peaks in the DTG curves, while these peaks are indistinct, broad and difficult to identify for the remaining salts. In the third stage, the main process is decomposition of the intermediate compound $BiS_xC_yN_sBr_z$, which leads to formation of BiOBr, and in the case of $Cs_2Na[Bi_2(SCN)_6Br_3]$, to formation of BiOBr and $Bi_2(SO_4)_3$. The reactions occurring in the third stage of the decomposition are

$$6Cs_2Na[Bi(SCN)_3Br_3] \xrightarrow{O_2} Bi_2S_3 + 2BiOBr + Cs_3Bi_2Br_9 + 4MBr + 5.5M_2SO_4 + (C_{18}N_{18}S_{9.5}Br_3)^{*} \quad (6)$$

$$6Cs_2Na[Bi(SCN)_2Br_4] \xrightarrow{O_2} 4BiOBr + Cs_3Bi_2Br_9 + 3M_2SO_4 + 9MBr + (C_{12}N_{12}S_9Br_2)^{*} \quad (7)$$

$$6Cs_2Na[Bi_2(SCN)_7Br_2] \xrightarrow{O_2} 6BiOBr + 3Bi_2(SO_4)_3 + 9M_2SO_4 + (C_{42}N_{42}S_{24}Br_6)^{*} \quad (8)$$

$$6Cs_2Na[Bi_2(SCN)_6Br_3] \xrightarrow{O_2} 2Bi_2S_3 + Bi_2(SO_4)_3 + Cs_3Bi_2Br_9 + 7.5M_2SO_4 + 4BiOBr + (C_{36}N_{36}S_{19.5}Br_5)^{*} \quad (9)$$

The mechanism of the decomposition reaction of the caesium sodium bromothiocyanatobismuthates(III) is consistent with the results of the chemical analyses of the pyrolysis solid products (Table 2) and was confirmed by diffractometric examination of these sinters and their insoluble fractions. The sinters were divided into fractions soluble and insoluble in hot water and the composition of both fractions was analysed. The decomposition reaction occurring in the caesium sodium tribromotrithiocyanatobis-

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* See footnote on p. 277.

muthate(III) sinter (430 °C) is described by

$$\mathrm{Bi_2S_3 + 2BiOBr + Cs_3Bi_2Br_9 + 5.5M_2SO_4 + 4MBr + 2H_2O}$$
$$\rightarrow \mathrm{Bi_2S_3 + 4BiOBr + 5.5M_2SO_4 + 7MBr + 4HBr} \qquad (10)$$

This reaction is confirmed by the results of the analysis of both fractions and the presence of identification lines of the corresponding bismuth compounds in the diffractogram of the insoluble fraction.

As has already been mentioned, particular stages of the pyrolysis of the caesium sodium bromothiocyanatobismuthates(III) partly overlap and they cannot be precisely separated. Therefore, under different conditions of decomposition, the proportions of particular compounds in the sinters (different rates of oxidation) can change.

Above 430 °C for $\mathrm{Cs_2Na[Bi(SCN)_3Br_3]}$ and $\mathrm{Cs_2Na[Bi_2(SCN)_7Br_2]}$, and above 450 °C for $\mathrm{Cs_2Na[Bi_2(SCN)_6Br_3]}$, there is a slow increase in the sinter mass: highest for tribromohexathiocyanatobismuthate(III), and lowest for caesium sodium tribromotrithiocyanatobismuthate(III). This is observed in the TG curves, and is just perceptible in the DTG curves. The increase in mass is probably caused by the oxidation reactions. The $\mathrm{Cs_2Na[Bi(SCN)_2Br_4]}$ sinter mass remains stable over the temperature range 440–540 °C: this can be explained by its low thiocyanate group content and rapid oxidation. The masses of the sinters of the remaining compounds begin decreasing after they have reached the maximum in the TG curves. Above 540 °C for mononuclear complex salts and above 600 °C for polynuclear ones, the products of stage III of the pyrolysis decompose, accompanied by the loss in mass of the sinters (much more rapid and greater for $\mathrm{Cs_2Na[Bi(SCN)_3Br_3]}$ and $\mathrm{Cs_2Na[Bi(SCN)_2Br_4]}$.

To examine the decomposition of the pyrolysis products formed in the third stage, the sinters of the salts obtained at 760 °C were analysed. Equations (11)–(14) describe the reactions occurring in the sinters (760 °C)

$$\mathrm{6Cs_2Na[Bi(SCN)_3Br_3]} \xrightarrow{\mathrm{O_2}} \mathrm{2BiOBr + Cs_3BiBr_6 + (BiO)_2SO_4 + 5.5M_2SO_4}$$
$$\mathrm{+ 2MBr + BiBr_3}\uparrow \mathrm{+ 2CsBr}\uparrow$$
$$\mathrm{+ (C_{18}N_{18}S_{11.5}Br_3)}\ * \qquad (11)$$

$$\mathrm{6Cs_2Na[Bi(SCN)_2Br_4]} \xrightarrow{\mathrm{O_2}} \mathrm{4BiOBr + Cs_3BiBr_6 + 3M_2SO_4 + 6MBr}$$
$$\mathrm{+ BiBr_3}\uparrow \mathrm{+ 3CsBr}\uparrow \mathrm{+ (C_{12}N_{12}S_9Br_2)}\ * \qquad (12)$$

$$\mathrm{6Cs_2Na[Bi_2(SCN)_7Br_2]} \xrightarrow{\mathrm{O_2}} \mathrm{6BiOBr + 2Bi_2(SO_4)_3 + (BiO)_2SO_4 + 9M_2SO_4}$$
$$\mathrm{+ (C_{42}N_{42}S_{26}Br_6)}\ * \qquad (13)$$

$$\mathrm{6Cs_2Na[Bi_2(SCN)_6Br_3]} \xrightarrow{\mathrm{O_2}} \mathrm{4BiOBr + Cs_3Bi_2Br_9 + 3(BiO)_2SO_4}$$
$$\mathrm{+ 7{,}5M_2SO_4 + (C_{36}N_{36}S_{25{,}5}Br_5)}\ * \qquad (14)$$

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* See footnote on p. 277.

TABLE 5

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

Compound	Mass losses (%)					
	270 °C		450 °C		760 °C	
	Detd.	Calc.	Detd.	Calc.	Detd.	Calc.
$Cs_2Na[Bi(SCN)_3Br_3]$	4.16	3.94	11.40	11.49	27.21	26.89
$Cs_2Na[Bi(SCN)_2Br_4]$	2.58	2.68	8.72	9.01	28.56	28.42
$Cs_2Na[Bi_2(SCN)_7Br_2]$	4.90	4.84	14.89	14.32	16.42	16.41
$Cs_2Na[Bi_2(SCN)_6Br_3]$	4.94	5.08	15.61	15.77	17.44	17.01

The decomposition mechanisms postulated are consistent with the results of the analysis of the sinters (760 ° C), see Table 2, the soluble and insoluble fractions of these sinters and the diffractometric studies. From eqns. (11)–(14), it can be seen that for $Cs_2Na[Bi(SCN)_3Br_3]$ and $Cs_2Na[Bi(SCN)_2Br_4]$ at 760 ° C, $Cs_3Bi_2Br_9$ decomposes to form Cs_3BiBr_6 and gaseous $BiBr_3$. This is in agreement with previous studies [3,4]. The authors of these works have established the mechanism of the thermal decomposition of $Cs_3Bi_2Br_9$ and have found that in the first stage over the temperature range 520–680 ° C, $Cs_3Bi_2Br_9$ decomposes, Cs_3BiBr_6 is formed and 1 mol of $BiBr_3$ evaporates. In stage II (680–920 ° C), Cs_3BiBr_6 decomposes to form CsBr, and $BiBr_3$ evaporates. For the pyrolysis of the mononuclear caesium sodium bromothiocyanatobismuthates(III), it has been observed that Cs_3BiBr_6 does not decompose at 760 ° C. (It is likely that the temperature at which the beginning of stage II of the $Cs_3Bi_2Br_9$ decomposition begins increases under these conditions.) Based on the chemical and X-ray analysis, undecomposed $Cs_3Bi_2Br_9$ has been found in the $Cs_2Na[Bi_2(SCN)_6Br_3]$ sinter obtained at 760 ° C. An analysis of losses in mass of the complex salts at 760 ° C (Table 5), confirms the observations concerning the decomposition of $Cs_3Bi_2Br_9$. The losses in mass of the mononuclear compounds are nearly 1.5 times greater than those of the remaining complexes. The other conclusion resulting from the analysis of eqns. (11)–(14) is that the caesium bromide evaporation rate depends on the bromide content of the starting compound. At 760 ° C, 3 mol of CsBr evaporate from $Cs_2Na[Bi(SCN)_2Br_4]$ and 2 mol of CsBr evaporate from $Cs_2Na[Bi(SCN)_3Br_3]$. As the processes of decomposition and evaporation of the compounds occur simultaneously, the temperatures of CsBr evaporation, of $Cs_3Bi_2Br_9$ decomposition or of other changes cannot be determined. The endothermic peak at 580 ° C in the DTA curve for $Cs_2Na[Bi(SCN)_2Br_4]$ can be associated with the melting of $Cs_3Bi_2Br_9$ (620 ° C cited in refs. 3 and 4), while the endothermic peak at 730 ° C probably corresponds to the transformation of Cs_2SO_4 from the orthorhombic to the hexagonal system (710 ° C cited in ref. 5). A further increase in the temperature results in the decomposition of Cs_3BiBr_6, the oxidation of bismuth compounds to Bi_2O_3 [6] and the evaporation of CsBr.

The analysis results presented above indicate that the decomposition mechanisms of each caesium sodium bromothiocyanatobismuthate(III) are similar. In the first stage the complexes decompose to form caesium and sodium thiocyanates, sulphates or bromides, the intermediate product having the general formula $BiS_xC_yN_sBr_z$, and Bi_2S_3 or $Cs_3Bi_2Br_9$. The main process occurring in stage II is oxidation of thiocyanates to the corresponding sulphates, while in stage III the intermediate compound decomposes to form BiOBr, whereas Bi_2S_3 is oxidised to $Bi_2(SO_4)_3$.

A comparison of the results of the thermal analyses of caesium sodium bromothiocyanatobismuthates(III) and the results of caesium sodium chlorothiocyanatobismuthates(III) studied earlier [1], leads to the conclusion that these compounds have a similar decomposition mechanism,. The pyrolysis of the salts proceeds in three stages with three corresponding distinct peaks in the DTA curve. In the first stage the complexes decompose to form an intermediate product; in the second stage the alkali metal thiocyanates oxidise to the corresponding sulphates; and in the last stage the intermediate compound decomposes (to form bismuthyl halide, bismuth sulphide or bismuth sulphate). The equations describing the decomposition processes in caesium sodium halidothiocyanatobismuthates(III) of the same general formula differ mainly in the proportions of the particular compounds making up the sinters: slight differences are due to different oxidation rates of Bi_2S_3, and, hence, the possibility of forming of bismuth sulphide, bismuth sulphate or bismuthyl sulphate in stage III of the decomposition; more marked differences appear only after the completion of stage III. The analysis of the sinters obtained at 760 °C has confirmed the presence of $Cs_3Bi_2Cl_9$ in the sinters of chlorothiocyanatobismuthates(III), while $Cs_3Bi_2Br_9$ occurs at this temperature only in the $Cs_2Na[Bi_2(SCN)_6Br_3]$ sinter. According to literature data [3,4], stage I of the decomposition of $Cs_3Bi_2Cl_9$ proceeds over the temperature range 460–803 °C. It is supposed that the decomposition of $Cs_3Bi_2Cl_9$ occurs under these conditions at a higher temperature than that of the pure compound. A similar explanation can be given for the presence of $Cs_3Bi_2Br_9$ in caesium sodium tribromohexathiocyanatobismuthate(III). Cs_3BiBr_6 occurs in the $Cs_2Na[Bi(SCN)_3Br_3]$ and $Cs_2Na[Bi(SCN)_2Br_4]$ sinters (eqns. (11) and (12)). It should be pointed out that for these salts the decomposition of the products of stage III of the pyrolysis begins at 540 °C and approximates to the beginning of stage I of the decomposition of $Cs_3Bi_2Br_9$ (520 °C), while in the remaining complexes the decomposition occurs at a temperature much higher than the beginning of stage I of the decomposition of $Cs_3Bi_2X_9$.

The evaporation rate of caesium halide is faster the more halide there is in the starting compound. The differences in the course of the thermal curves and in the sinter mass-losses testify to a slightly different decomposition mechanism.

While comparing the thermal decomposition of hetero- and homoligand complexes [7], differences can be observed in the course of the third stage of the pyrolysis. In the case of homoligand complexes, the intermediate compound decomposes to form bismuth sulphide and free bismuth.

The thermal stability of the complex salts changes in the following order: $Cs_2Na[Bi(SCN)_6]$ (decomposition begins at 250 °C) > $Cs_2Na[Bi(SCN)_4Cl_2]$ = $Cs_2Na[Bi(SCN)_3Cl_3]$ = $Cs_2Na[Bi(SCN)_2Cl_4]$ = $Cs_2Na[Bi_2(SCN)_7Br_2]$ = $Cs_2Na[Bi_2(SCN)_6Br_3]$ (240 °C) > $Cs_2Na[Bi(SCN)_3Br_3]$ = $Cs_2Na[Bi(SCN)_2Br_4]$ (210 °C) > $Cs[Bi(SCN)_4]$ (160 °C).

From the data presented it can be seen that replacement of some of the thiocyanate groups with chloride or, especially, with bromide ions, reduces the thermal stability of the caesium sodium hexathiocyanatobismuthate(III).

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