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Thermal dehydration of hexathiocyanatobismuthates(III) of lanthanides

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Abstract

The thermal dehydration of hexathiocyanatobismuthates(III) of lanthanides of the general formula $Ln[Bi(SCN)_6] \cdot nH_2O$, where Ln is La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Y and n is 3–5, has been examined. The thermal analysis curves of the complexes and the results of chemical and X-ray analyses of the products are presented. From these results, the mechanism of the thermal dehydration was established. The reaction order and activation energy were calculated by the Coats–Redfern and Zsakó methods.

INTRODUCTION

The majority of reports concerning the study of lanthanide complexes deal with compounds in which the Ln^{3+} cation is the central ion and focus primarily on lanthanide salts with organic ligands or complexes containing both organic groups and simple inorganic anions. The latter group includes complex compounds with thiocyanate ions.

Methods of preparation and the thermal properties of complexes of the following formulae have been reported: with dipyridyl, $Ln(NCS)_3(2\text{-dipy})_3$ [1,2], $La(NCS)_3(2\text{-dipy})_2 \cdot H_2O$, $Ln(NCS)_3(2\text{-dipy})_2 \cdot 5H_2O$ [2], $Ln(NCS)_3(4\text{-dipy})_2 \cdot 5H_2O$ [3,4]; with *o*-phenanthroline, $Ln(NCS)_3phen_2$, $Ln(NCS)_3phen_3$ [5,6]; and with hexamethylenetetramine, $Ln(NCS)_3 \cdot 2HMTA \cdot nH_2O$ [7–9].

Serebrennikov et al. [10] carried out the decomposition of $[CeL_6][Cr(NCS)_6]$, where L is pyridine or quinoline, under isothermic conditions. There are far fewer reports concerning thermal studies of lanthanide complexes with inorganic ligands. More data have been obtained about double salts of nitritolanthanidates. The mechanism of decomposition and thermal stability of complexes of formula $Cs_2Ag[Ln(NO_2)_6]$, where Ln is La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Y [11] and of double nitritolanthanidates of the sodium and lithium group $M_2M'[Ln(NO_2)_6] \cdot nH_2O$

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where M′ is Na or Li, M is K, Rb or Cs; and Ln is La or Nd, have been determined [12].

The purpose of the present study is to examine the thermal dehydration of lanthanide hexathiocyanatobismuthates(III) where the Ln^{3+} cation belongs to the outer sphere. The preparation and properties of compounds of $Ln[Bi(SCN)_6] \cdot nH_2O$ type have been described previously [13]. In the present work, the thermal stability of lanthanide hexathiocyanatobismuthates(III) is determined and the stages of their thermal dehydration are described.

EXPERIMENTAL

The preparation methods of lanthanide hexathiocyanatobismuthates(III) have been reported previously [13].

Thermal analysis

Thermal curves were obtained using a MOM Budapest-type OD-102 derivatograph. The compounds were heated over the temperature range 20–1000°C in air, in the presence of α-Al_2O_3 as reference material. The heating rate was 5°C min^{-1}, TG sensitivity was 200 mg, DTA and DTG sensitivity was 1/10 and the sample weights were 250 mg.

The dehydration of lanthanide hexathiocyanatobismuthates(III) of the general formula $Ln[Bi(SCN)_6] \cdot 5H_2O$, where Ln is La, Ce, Pr, Nd, Sm, Gd, proceeds in several stages. The first pyrolysis stage at 50–120°C is associated with a decrease in the mass shown in the TG curves and with endothermic effects in the DTA curves (minimum at 90–120°C). The thermal analysis curves are different over the temperature range 100–230°C. For the lanthanum, cerium, praseodymium and neodymium salts, one endothermic peak (minimum at 170°C) is observed. For the samarium and gadolinium compounds there are three endothermic peaks (samarium 150, 200, 220°C; gadolinium 110, 150, 210°C). These effects are related to a continuous mass loss of the complexes as indicated in the TG curves. The thermal curves of $La[Bi(SCN)_6] \cdot 5H_2O$ and $Gd[Bi(SCN)_6] \cdot 5H_2O$ are shown in Figs. 1 and 2, respectively.

The thermal analysis curves of the 4- and 3-hydrous complexes are slightly different from those described above. Three small, endothermic peaks are observed in the DTA curves (110–190°C). The thermal curves of $Y[Bi(SCN)_6] \cdot 3H_2O$ are shown in Fig. 3. Table 1 lists the DTA peak temperatures and the temperature ranges of the thermal dehydration stages of the compounds under study. Table 2 gives the mass changes of the dehydration stages.

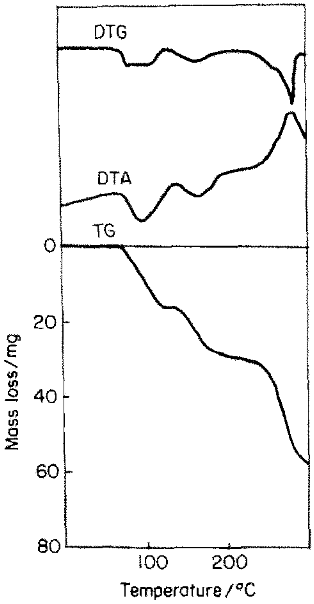

Fig. 1. Thermal analysis curves of La[Bi(SCN)$_6$] · 5H$_2$O.

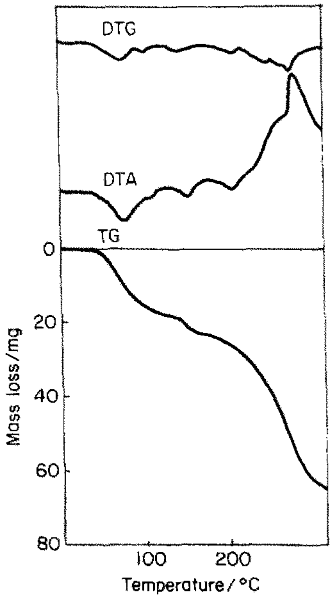

Fig. 2. Thermal analysis curves of Gd[Bi(SCN)$_6$] · 5H$_2$O.

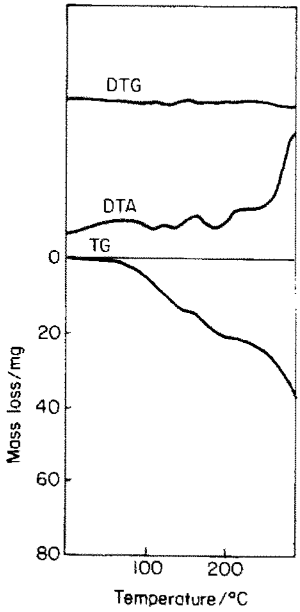

Fig. 3. Thermal analysis curves of $Y[Bi(SCN)_6] \cdot 3H_2O$.

Chemical analysis

Quantitative analyses were carried out by various methods. Lanthanides were determined by complexometry, bismuth by gravimetry and thiocyanate by bromatometry. Table 3 presents the results of the analysis of the anhydrous lanthanum, neodymium and erbium salts.

X-ray diffractometry

X-ray diffraction analysis was carried out on a Siemens D 5000 powder diffractometer using Cu K_α radiation. The diffraction curves were recorded over the 2Θ range of 2–60°. The diffractograms of $Nd[Bi(SCN)_6] \cdot 5H_2O$ and its sinters are given in Fig. 4.

Kinetic parameters

The order of reaction n and activation energy E_a were calculated for the thermal dehydration stages of the hexathiocyanatobismuthates(III). The calculations were made using the Zsakó [14] and Coats–Redfern [15] methods. The results for the calculated kinetic parameters are presented in Table 4.

TABLE 1

Temperatures, DTA peaks and temperature ranges of dehydration stages of the lanthanide hexathiocyanatobismuthates(III)

Compound	DTA peaks/°C	Ranges of decomposition stages/°C
$La[Bi(SCN)_6] \cdot 5H_2O$	100, endo	70–120
	170, endo	130–190
$Ce[Bi(SCN)_6] \cdot 5H_2O$	110, endo	80–120
	170, endo	150–200
$Pr[Bi(SCN)_6] \cdot 5H_2O$	100, endo	75–120
	170, endo	150–190
$Nd[Bi(SCN)_6] \cdot 5H_2O$	100, endo	70–120
	170, endo	140–190
$Sm[Bi(SCN)_6] \cdot 5H_2O$	120, endo	75–120
	150, endo	140–155
	200, endo	170–200
	220, endo	200–230
$Gd[Bi(SCN)_6] \cdot 5H_2O$	90, endo	55–100
	110, endo	100–130
	150, endo	130–170
	210, endo	170–210
$Dy[Bi(SCN)_6] \cdot 4H_2O$	100, endo	50–110
	120, endo	110–140
	180, endo	140–190
$Er[Bi(SCN)_6] \cdot 3H_2O$	105, endo	50–120
	110, endo	
	130, endo	120–155
	180, endo	155–200
$Y[Bi(SCN)_6] \cdot 3H_2O$	110, endo	80–115
	130, endo	115–155
	190, endo	160–190

RESULTS AND DISCUSSION

The thermal examination and analysis of sinters elucidated the course of the thermal dehydration of the lanthanide hexathiocyanatobismuthates(III). The evaporation of water molecules proceeds in several stages, depending on the compound under investigation.

Dehydration of 5-hydrous salts

Dehydration of $Ln[Bi(SCN)_6] \cdot 5H_2O$ complexes where Ln is La, Ce, Pr, Nd proceeds in two stages. In the first stage, 3 moles, and in the second, 2 moles of H_2O are released. In the case of samarium and gadolinium salts, a slightly different course of dehydration was observed. In the first stage

TABLE 2

Mass losses for the thermal dehydration of lanthanide hexathiocyanatobismuthates(III)

Compound	Temp./°C	Mass loss/%			Eqn.
		TG	Calcd.	Detd.	
$La[Bi(SCN)_6] \cdot 5H_2O$	120	6.8	6.87	6.66	(1)
	190	11.2	11.45	10.94	
$Nd[Bi(SCN)_6] \cdot 5H_2O$	120	6.8	6.82	6.72	(4)
	190	11.6	11.37	11.49	
$Gd[Bi(SCN)_6] \cdot 5H_2O$	100	4.4	4.47	4.68	(6)
	130	7.0	6.71	6.86	
	170	9.2	8.95	8.77	
	210	12.0	11.18	11.35	
$Dy[Bi(SCN)_6] \cdot 4H_2O$	115	2.0	2.27	2.23	(7)
	150	4.6	4.54	4.70	
	190	7.0	6.82	6.60	
	–	–	9.09	–	
$Er[Bi(SCN)_6] \cdot 3H_2O$	120	2.4	2.31	2.52	(8)
	155	4.8	4.62	4.72	
	200	7.2	6.93	6.91	
$Y[Bi(SCN)_6] \cdot 3H_2O$	110	3.0	2.57	2.87	(9)
	150	5.6	5.14	5.32	
	190	8.4	7.71	8.06	

TABLE 3

Results of chemical analyses of the anhydrous salts

Compound	Composition		Eqn.
	Detected	Calculated	
$Nd[Bi(SCN)_6] \cdot 5H_2O$	30.27% Bi	29.78% Bi	(4)
	21.03% Nd	20.55% Nd	
	48.39% SCN	49.66% SCN	
$Gd[Bi(SCN)_6] \cdot 5H_2O$	30.65% Bi	29.24% Bi	(6)
	20.45% Gd	21.99% Gd	
	48.98% SCN	48.76% SCN	
$Dy[Bi(SCN)_6] \cdot 4H_2O$	30.50% Bi	28.32% Bi	(7)
	23.78% Dy	22.02% Dy	
	46.97% SCN	47.22% SCN	
$Er[Bi(SCN)_6] \cdot 3H_2O$	30.11% Bi	28.84% Bi	(8)
	24.32% Er	23.08% Er	
	47.52% SCN	48.08% SCN	

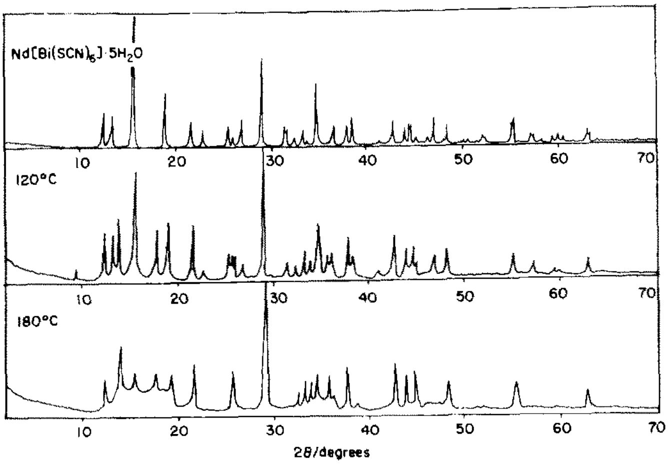

Fig. 4. X-ray diffraction patterns of $Nd[Bi(SCN)_6] \cdot 5H_2O$ and its sinters.

two moles of H_2O are eliminated, and the remaining molecules of water evaporate in the next three stages

$$LaX \cdot 5H_2O \xrightarrow{120°C} LaX \cdot 2H_2O \xrightarrow{190°C} LaX \tag{1}$$

$$CeX \cdot 5H_2O \xrightarrow{120°C} CeX \cdot 2H_2O \xrightarrow{200°C} CeX \tag{2}$$

$$PrX \cdot 5H_2O \xrightarrow{120°C} PrX \cdot 2H_2O \xrightarrow{190°C} PrX \tag{3}$$

$$NdX \cdot 5H_2O \xrightarrow{120°C} NdX \cdot 2H_2O \xrightarrow{190°C} NdX \tag{4}$$

$$SmX \cdot 5H_2O \xrightarrow{120°C} SmX \cdot 3H_2O \xrightarrow{155°C} SmX \cdot 2H_2O \xrightarrow{200°C}$$
$$SmX \cdot H_2O \xrightarrow{230°C} SmX \tag{5}$$

$$GdX \cdot 5H_2O \xrightarrow{100°C} GdX \cdot 3H_2O \xrightarrow{130°C} GdX \cdot 2H_2O \xrightarrow{170°C}$$
$$GdX \cdot H_2O \xrightarrow{210°C} GdX \tag{6}$$

where X is $[Bi(SCN)_6]^{3-}$

TABLE 4

Kinetics parameters of thermal dehydration of $Ln[Bi(SCN)_6] \cdot nH_2O$

Compound	First stage				Second stage				Third stage				Fourth stage			
	C–R		Z		C–R		Z		C–R		Z		C–R		Z	
	n	*E*	*n*	*E*	*n*	*E*	*n*	*E*	*n*	*E*	*n*	*E*	*n*	*E*	*n*	*E*
$La[Bi(SCN)_6] \cdot 5H_2O$	1.2	20.9	1.2	21.0	0.3	30.1	0.3	30.0								
$Ce[Bi(SCN)_6] \cdot 5H_2O$	1.7	30.5	1.7	31.0	1.7	55.4	1.7	56.0								
$Pr[Bi(SCN)_6] \cdot 5H_2O$	1.4	28.1	1.4	28.0	0.8	26.5	0.8	27.0								
$Nd[Bi(SCN)_6] \cdot 5H_2O$	1.99	33.5	1.9	33.0	1.3	39.7	1.3	40.0								
$Sm[Bi(SCN)_6] \cdot 5H_2O$	1.6	37.3	1.6	37.0	1.2	65.7	1.2	65.0	1.99	67.1	1.9	66.0	1.5	85.7	1.5	87.0
$Gd[Bi(SCN)_6] \cdot 5H_2O$	1.3	26.7	1.3	27.0	1.99	91.8	1.9	90.0	0.7	36.2	0.7	37.0	1.0	43.2	1.0	43.0
$Dy[Bi(SCN)_6] \cdot 4H_2O$	1.8	16.7	1.8	17.0	0.0	18.3	0.0	18.0	0.2	32.4	0.2	32.0				
$Er[Bi(SCN)_6] \cdot 3H_2O$	1.5	30.1	1.5	30.0	1.3	44.2	1.3	44.0	0.8	34.6	0.9	36.0				
$Y[Bi(SCN)_6] \cdot 3H_2O$	1.99	40.0	1.9	39.0	1.99	65.9	1.9	64.0	1.8	60.6	1.8	60.0				

Dehydration of 4- and 3-hydrous salts

Dehydration of the dysprosium salt proceeds in three stages

$$DyX \cdot 4H_2O \xrightarrow{110^\circ C} DyX \cdot 3H_2O \xrightarrow{140^\circ C} DyX \cdot 2H_2O \xrightarrow{190^\circ C} DyX \cdot H_2O \tag{7}$$

The absence of a fourth endothermic DTA peak indicates that the evaporation of the last molecule of water and the further decomposition of the complex occur simultaneously. Not can a separate stage be observed in the TG curve: the mass of the compound decreases continuously up to 440°C, which may indicate that the final dehydration stage and a decomposition stage of the anhydrous compound overlap. Only in the DTG curve can a splitting of the peaks at the temperature corresponding with the exothermic DTA peak be observed.

The erbium and yttrium complexes release their water molecules as follows

$$ErX \cdot 3H_2O \xrightarrow{120^\circ C} ErX \cdot 2H_2O \xrightarrow{155^\circ C} ErX \cdot H_2O \xrightarrow{200^\circ C} ErX \tag{8}$$

$$YX \cdot 3H_2O \xrightarrow{115^\circ C} YX \cdot 2H_2O \xrightarrow{155^\circ C} YX \cdot H_2O \xrightarrow{190^\circ C} YX \tag{9}$$

The dehydration stages partly overlap, which makes it difficult to determine precisely the corresponding temperature ranges and may be the reason for certain discrepancies between the theoretical mass losses determined on the basis of the TG curves, and the mass losses measured. The shape of the TG curve (no horizontal segments in the curve) and the change in the colour of the anhydrous salt show that the anhydrous salt decomposes as soon as water is released. Diffractometric analysis (Fig. 4) demonstrates that the structure of the salt changes as a result of dehydration. A precise determination of the structure of the complexes may help to explain the differences in the course of dehydration.

The salts under study can be divided into two groups with respect to the dehydration temperatures: I, La, Ce, Pr, Nd, Sm, Y complexes (70–80°C); II, Gd, Dy, Er complexes (50–55°C). This division is similar to the classification of complexes with respect to their resistance to hydrolytic decomposition [13], but no clear relation has been observed between the temperature of decomposition of the hydrated compounds and the ionic radius of the lanthanide compound. Furthermore, as regards stability, $Y[Bi(SCN)_6] \cdot 3H_2O$ should be classified in group I; its dehydration temperature is 80°C.

The activation energy of the dehydration process in group I increases as the radius of the cation decreases in the order La → Sm (as in the case of resistance to hydrolysis), while in group II, no regular changes in E_a with ionic radius of the lanthanide are observed. The activation energy of the yttrium salt is similar to that of samarium (Table 4).

In conclusion, the way in which the electronic shell of the outer sphere cations is packed influences the changes in the thermal properties of the complexes. This influence is, however, less distinct than in the case of solubility and resistance to hydrolysis [13]. Particular lanthanide hexathiocyanatobismuthates(III) exhibit different mechanisms of dehydration.

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