

THERMAL DECOMPOSITION OF 4,4'-DIPYRIDYL COMPLEXES OF LIGHT RARE-EARTH THIOCYANATES IN AIR ATMOSPHERE

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Abstract

The thermal decompositions of $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ were studied, where $\text{Ln} = \text{La, Pr, Nd, Sm, Eu}$ and Y , and 4-dipy \approx 4,4'-dipyridyl. The compounds are first dehydrated. During the thermal decomposition of $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2$, deamination takes place. The transient products decompose with the formation of $\text{Ln}_2\text{O}_2\text{SO}_4$. The energies of activation for the first step of dehydration of the La, Pr, Nd, Sm and Eu complexes were determined.

Keywords: complexes, light rare-earth thiocyanates

Introduction

Dipyridyl complexes of rare-earth thiocyanates are little known. Hart and Laming [1] obtained complexes of the type $\text{Ln}(\text{NCS})_3(2\text{-dipy})_3$ ($\text{Ln} = \text{La}$ and Ce(III) , Dy; 2-dipy = 2,2'-dipyridyl). The decomposition points are 160–170°C for La, 210–220°C for Ce(III) and 215–225°C for Dy.

Eremin and Bondarenko [2] isolated $\text{Ln}(\text{NCS})_4(2\text{-dipy})_2 \cdot 2\text{-dipyH}$ ($\text{Ln} = \text{La, Sm, Yb}$ and Y). These complexes were characterized by their thermal properties.

We earlier reported the preparation and thermal properties of complexes $\text{La}(\text{NCS})_3(2\text{-dipy})_3 \cdot \text{H}_2\text{O}$, $\text{Ln}(\text{NCS})_3(2\text{-dipy})_3$ ($\text{Ln} = \text{Ce(III), Pr}$ and Nd) $\text{Ln}(\text{NCS})_3(2\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ ($\text{Ln} = \text{Sm, Eu}$ and Gd) [3].

We have also studied compounds of the type $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$, where $\text{Ln} = \text{Y}$ and La-Lu (except Pm and Tm) [4, 5]. The conditions of thermal decomposition of these compounds for $\text{Ln} = \text{Gd-Lu}$ and Ce(III) were investigated.

In the present paper, the thermal decompositions of the following compounds were studied: $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ ($\text{Ln} = \text{La, Pr, Nd, Sm, Eu}$ and Y).

Experimental

The preparation of $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ and the analytical methods are described in [3–5].

The thermal stabilities of the complexes were studied by means of TG, DTA and DTG techniques. The measurements were made with a derivatograph-C with a TG sensitivity of 50 mg, using Al_2O_3 as reference material. Samples of 50 mg were heated to 1000°C at a heating rate of $5 \text{ deg} \cdot \text{min}^{-1}$, in ceramic crucibles in air atmosphere.

The solid products of thermal decomposition were identified on the basis of the TG curves and were verified via chemical analysis and the IR spectra.

Results and discussion

When heated in air atmosphere, the complexes $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ undergo dehydration in various ways.

The thermal curves were recorded for the studied complexes, and the analytical data on the dehydration are presented in Table 1.

$\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ ($\text{Ln} = \text{Sm, Eu}$ and Y) are dehydrated progressively. The complexes of Sm and Eu lose 4 water molecules at $100\text{--}175^\circ\text{C}$ and at $100\text{--}160^\circ\text{C}$, respectively, and the monohydrates formed lose the residual water molecule during deamination. For $\text{Y}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$, 1 mol of water is split off in the first stage ($50\text{--}100^\circ\text{C}$), the next 2 moles of water are split off at $105\text{--}135^\circ\text{C}$, and the residual water is lost at $135\text{--}190^\circ\text{C}$. The multistep dehydration of the Sm , Eu and Y complexes suggests that the crystallization-water molecules are bonded in various modes. The water lost at higher temperature is probably inner-sphere water, while that lost at lower temperature is outer-sphere water [3, 6–10]. The water molecules are also bonded in different ways in $\text{Ce}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$, $\text{Ln}(\text{NCS})_3(2\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ ($\text{Ln} = \text{Sm, Eu}$ and Gd) and other lanthanide complexes [3, 4, 7].

Table 1 Dehydration of $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ in air atmosphere

Ln	Loss of H_2O molecules	E / $\text{kJ}\cdot\text{mol}^{-1}$	Temp. range of dehydration reaction/ $^{\circ}\text{C}$	Endothermic effects/ $^{\circ}\text{C}$	Mass loss/%	
					Calcd.	Found
La	5	96	70-190	118	12.59	12.0
Ce[4]	4	67	60-158	90	10.05	10.0
	1	-	158-220	125	2.51	2.0
Pr	5	64	95-200	130	12.55	12.6
Nd	5	89	95-140	130	12.49	12.0
Sm	4	81	100-175	118	9.92	10.5
Eu	4	124	100-160	135	9.85	9.6
Y	1	-	50-100	70	2.52	-
	2	-	105-135	115	5.41	5.2
	2	-	135-190	160	5.41	5.2

The complexes of La, Pr and Nd lose all the water molecules in one stage on heating, within the temperature range 70–190°C for La, 95–200°C for Pr, and 95–140°C for Nd. These results lead us to conclude that all the water molecules in the La, Pr and Nd complexes are present in the outer sphere. We have obtained similar results for $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ ($\text{Ln} = \text{Gd-Lu}$, except Tm) [5].

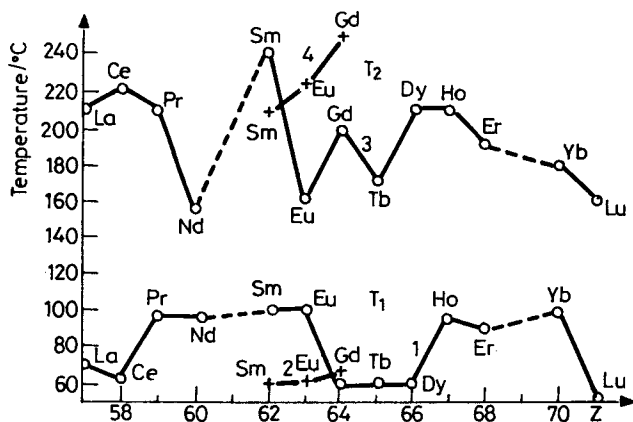


Fig. 1 Relationship between temperature T_1 , T_2 and Z . T_1 - initial temperature of the dehydration process: 1 - for $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$; 2 - for $\text{Ln}(\text{NCS})_3(2\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$. T_2 - initial temperature of the decomposition process: 3 - for $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2$ ($\text{Ln} = \text{La, Pr, Nd, Y}$) and $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Sm, Eu}$); 4 - for $\text{Ln}(\text{NCS})_3(2\text{-dipy})_2$ [3]

The initial temperature T_1 of the dehydration process does not change regularly with atomic number Z (Fig. 1, curve 1). The values T_1 are higher for Pr, Nd, Sm, Eu, Ho, Er and Yb than for La, Ce, Tb, Dy and Lu. The initial temperature T_2 of the decomposition for $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2$ and for $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Sm}$ and Eu) likewise does not change regularly with the atomic number of the element (Fig. 1, curve 3). For comparison, curves 2 and 4 correspond to the initial temperatures of dehydration (T_1) and of deamination (T_2) for the complexes with an isomeric ligand (2-dipy) [3].

The dehydration of $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ is accompanied by a strong endothermic effect at about 130°C for Pr, Nd and Eu, and at about 118°C for La and Sm. The DTA curve for the Y complex exhibits several endothermic peaks.

From the TG and DTA curves, the activation energies (E_d) of the dehydration reactions (the first stage of dehydration) for La, Pr, Nd, Sm and Eu were calculated by means of the Pilojan and Novikova method [11]. The results obtained are given in Table 1. Figure 2 shows the values of E_d for $\text{Ln}(\text{NCS})_3(4\text{-$

dipy)₂·5H₂O (for heavy lanthanides [5]) as a function of the atomic number. There was no regular variation in the activation energy of dehydration with the lanthanide atomic number.

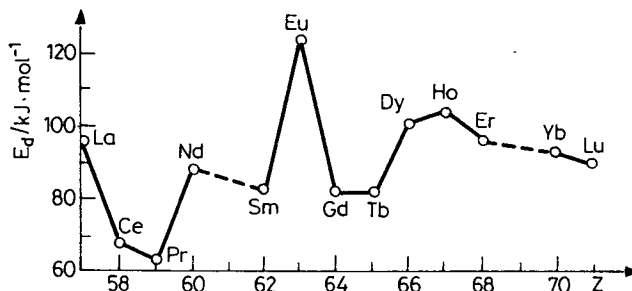


Fig. 2 Relationship between activation energy of dehydration E_d (the first stage) and Z

Thermal decomposition data obtained for the anhydrous complexes of La, Pr, Nd and Y, and for $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2\cdot\text{H}_2\text{O}$ ($\text{Ln} = \text{Sm}$ and Eu), are listed in Table 2.

During the thermal decomposition of the complexes of La, Pr, Nd, Sm, Eu and Y, partial deamination takes place. The thermal curves for La, Pr and Nd have similar patterns. In the first stage, 1.5 mol of 4-dipy is eliminated to yield $\text{Ln}(\text{NCS})_3(4\text{-dipy})_{0.5}$ (temperature range 210–310°C for La, 210–310°C for Pr and 155–332°C for Nd).

DTA curve minima are observed at 282 for La, 280 and 302 for Pr, and 208 and 300°C for Nd.

In the second stage, these compounds lose the remaining 4-dipy, and the main process of thiocyanate decomposition takes place. The intermediates in the thermal decomposition of lanthanide thiocyanates are difficult to identify. The transient products can have various compositions (the solid product contain thiocyanate, sulfide and sulfate ions), but only $\text{La}(\text{NCS})_3$ was identified. The lanthanide thiocyanates probably decompose via $\text{LnS}(\text{NCS})$ and oxysulfides to oxysulfates. Sulfides and sulfates were also identified as the major transient decomposition products for the thiocyanate complexes of other metals [12–14] and for $\text{Ln}(\text{NCS})_3(2\text{-dipy})_2$ [3]. The DTA curves exhibit several exothermic peaks, of which the first one at about 350°C is very strong. $\text{Ln}_2\text{O}_2\text{SO}_4$ is detected in the TG curves in the temperature range 780–900°C for Pr and 700–900°C for Nd. On temperature elevation, $\text{Ln}_2\text{O}_2\text{SO}_4$ decomposes through $\text{Ln}_2\text{O}_{3-x}(\text{SO}_4)_x$, where $0 < x < 3$ (these compounds, of variable composition, are known in the literature [15, 16]), to the corresponding oxides.

Table 2 Thermal decomposition data of $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$) and $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Sm}, \text{Eu}$)

Compound	Temperature range / °C	Mass loss* / %		Peak temp. in DTA / °C
		Calcd.	Determ.	
$\text{Ln}(\text{NCS})_3(4\text{-dipy})_2$				
↓	210–310	32.75	33.2	282 endo
$\text{Ln}(\text{NCS})_3(4\text{-dipy})_{0.5}$				
↓	310–340	10.92	11.8	320 endo
$\text{Ln}(\text{NCS})_3$				
↓	340–680	14.28	13.6	350, 425, 550 exo 415 endo
$\text{La}_2\text{O}_2\text{SO}_4$				
$\text{Pr}(\text{NCS})_3(4\text{-dipy})_2$				
↓	210–310	32.65	32.2	280, 302 endo
$\text{Pr}(\text{NCS})_3(4\text{-dipy})_{0.5}$				
↓	310–780	26.68	26.5	350, 418 exo 400 endo
$\text{Pr}_2\text{O}_2\text{SO}_4$				
↓	900–1000	4.84	5.0	
Pr_6O_{11}				
$\text{Nd}(\text{NCS})_3(4\text{-dipy})_2$				
↓	155–332	32.49	33.0	208, 300 endo
$\text{Nd}(\text{NCS})_3(4\text{-dipy})_{0.5}$				
↓ a/	332–700	25.89	25.0	350, 392, 540 exo 460 endo
$\text{Nd}_2\text{O}_2\text{SO}_4$				
↓ b/	>900			
Nd_2O_3				
$\text{Sm}(\text{NCS})_3(4\text{-dipy})_2 \cdot \text{H}_2\text{O}$				
↓	240–346	34.7	34.2	275, 300 endo
$\text{Sm}(\text{NCS})_3(4\text{-dipy})_{0.5}$				
↓ a/	346–662	25.90	25.1	365, 428, 590 exo 450 endo
$\text{Sm}_2\text{O}_2\text{SO}_4$				
↓ b/	>720			

Table 2 Continued

Compound	Temperature range $^{\circ}\text{C}$	Mass loss* / %		Peak temp. in DTA $^{\circ}\text{C}$
		Calcd.	Determ.	
Eu(NCS) ₃ (4-dipy) ₂ ·H ₂ O				
↓	160–240	18.55	18.2	198, 216 endo
Eu(NCS) ₃ (4-dipy) _{1.25}				
↓	240–427	40.86	40.5	317, 415 exo 387 endo
Eu ₂ O(S)SO ₄				
↓	427–585	1.10	1.2	
Eu ₂ O ₂ SO ₄				
↓ b/	>800			
Eu ₂ O ₃				
Y(NCS) ₃ (4-dipy) ₂				
↓	220–280	17.60	17.4	205 endo
Y(NCS) ₃ (4-dipy) _{1.25}				
↓	290–323	11.70	11.5	255, 290 endo
Y(NCS) ₃ (4-dipy)				
↓ a/	323–660	34.19	33.8	340, 370, 445 exo 460 endo
Y ₂ O ₂ SO ₄				
↓ b/	>700			
Y ₂ O ₃				

* in comparison with the weight of the hydrated compounds Ln(NCS)₃(4-dipy)₂·5H₂O

a/ probably via compound containing sulfide and sulfate ions

b/ very slowly, probably via Ln₂O_{3-x}(SO₄)_x

Sm(NCS)₃(4-dipy)₂·H₂O loses 1 mol of H₂O and 1.5 mol of 4-dipy within the temperature range 240–346 $^{\circ}\text{C}$. With increase of the temperature, it loses the remaining 4-dipy and forms Sm₂O₂SO₄, probably via Sm₂O(S)SO₄ (the intermediate solid contains both sulfide and sulfate ions).

Similar interpretations were made for Eu(NCS)₃(4-dipy)₂·H₂O, which loses 1 mol of H₂O and 0.75 mol of 4-dipy in the first stage, and Eu₂O(S)SO₄ was identified as transition compound.

The yttrium complex loses 4-dipy in three steps. The postulated intermediates are Y(NCS)₃(4-dipy)_{1.25} and Y(NCS)₃(4-dipy). On increase of the temperature, the intermediate Y(NCS)₃(4-dipy) decomposes to Y₂O₂SO₄.

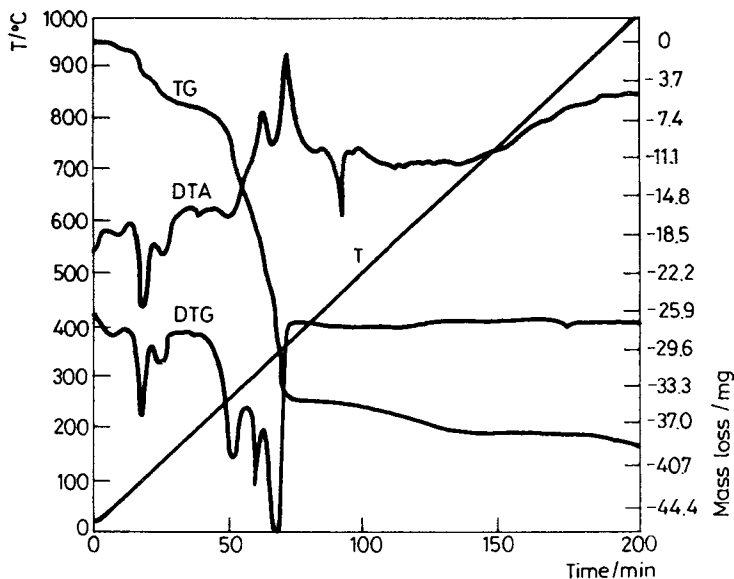


Fig. 3 Thermoanalytical curves of $Y(NCS)_3(4-dipy)_2 \cdot 5H_2O$

$Ln_2O_2SO_4$ is formed in the temperature range $662\text{--}720^\circ$ for Sm, $585\text{--}800^\circ$ for Eu and $660\text{--}800^\circ$ for Y. The first exothermic maximum occurs at 365 (Sm), 317 (Eu) and 340° (Y).

Thermal decomposition curves for $Y(NCS)_3(4-dipy)_2 \cdot 5H_2O$ are shown as examples in Fig. 3.

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Zusammenfassung — Es wurde die thermische Zersetzung von $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ mit $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Y}$ und 4-dipy = 4,4'-Dipyridyl untersucht. Die Verbindungen werden zuerst dehydratiert. Bei der thermischen Zersetzung von $\text{Ln}(\text{NCS})_3(4\text{-dipy})_2$ findet eine Desaminierung statt. Die Übergangprodukte zersetzen sich unter Bildung von $\text{Ln}_2\text{O}_2\text{SO}_4$. Die Aktivierungsenergie für den ersten Schritt der Dehydratation der La-, Pr-, Nd-, Sm- und Eu-Komplexe wurde ermittelt.