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STUDIES ON THE THERMAL DECOMPOSITION OF RARE EARTH ELEMENT COMPLEXES WITH 2-NAPHTHOIC ACID

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Abstract

The rare earth element 2-naphthoates were prepared as crystalline solids sparingly soluble in water (10^{-5}–10^{-6} mol·dm^{-3}), with general formula $Ln(C_{10}H_7COO)_3 \cdot nH_2O$, where $n = 3$ for La–Gd, $n = 2$ for Tb and Dy, and $n = 0$ for Y and Ho–Lu. During heating, the di- and trihydrated rare earth 2-naphthoates lose the crystallization water molecules and the anhydrous complexes then decompose directly to Ln_2O_3, CeO_2, Pr_6O_{11} or Tb_4O_7. Formation of an intermediate is observed only in the case of the anhydrous lanthanum complex, which decomposes to La_2O_3 via $La_2O_2CO_3$. The anhydrous complexes of Ho–Lu decompose directly to Ln_2O_3 in one step when heated. The anhydrous rare earth 2-naphthoates are very stable (up to 578–683 K).

Keywords: complexes, rare earth elements

Introduction

2-Naphthoic acid ($C_{10}H_7COOH$) is a crystalline solid sparingly soluble in water. Its compounds with metal ions are little known. The literature contains some notes on the 2-naphthoates of Na(I), K(I), Ca(II), Ba(II), Ag(I) [1] and Cu(II) [2]. The thermal decompositions of K(I) 2-naphthoate [3, 4] and Cu(II) naphthoate [5] have been studied. These compounds are used in organic synthesis in industry. The structure and mode of coordination of Mo(II) in its complex with 2-naphthoic acid have also been studied [6]. The complexes of rare earth elements with 2-naphthoic acid have not been studied so far.

The aim of our work was to prepare the complexes of Y, La and lanthanide(III) 2-naphthoates in the solid state and to examine some of their properties, including the thermal stability, during heating in an air atmosphere.

Experimental

The complexes of 2-naphthoic acid with Y, La and the lanthanides from Ce(III) to Lu(III) were prepared in aqueous solutions at room temperature by

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adding an equivalent amount of ammonium 2-naphthoate solution (*pH* 5.2) to a solution of rare earth chloride (Ce(III) was used as nitrate). The precipitate formed was stirred in the mother liquor for 0.5 h, and then filtered off, washed with water to remove NH_4^+ and Cl^- and dried at 303 K to constant mass.

The contents of carbon and hydrogen in the prepared complexes were determined on the basis of elemental analysis, using V_2O_5 as oxidizing agent. The contents of rare earth elements were determined by heating the complexes to Ln_2O_3, CeO_2, Pr_6O_{11} or Tb_4O_7 at 1173 K, and also from the TG curves. The crystallization water contents were determined by isothermal heating of the complexes obtained at definite temperature, and from the TG curves.

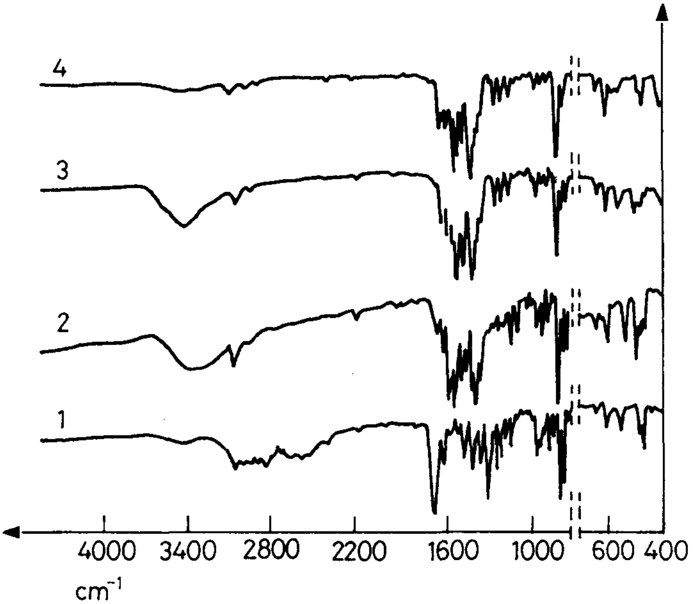

Fig. 1 IR spectra of: 1:2-naphthoic acid, 2-naphthoates of 2:Na, 3:Pr(III), 4:Er(III)

The IR spectra of 2-naphthoic acid and the prepared 2-naphthoates of rare earths and sodium were recorded in the range 4000–400 cm^{-1} on a UR-20 spectrophotometer. Samples were prepared as KBr discs. The X-ray patterns of the prepared hydrated and anhydrous complexes were recorded on a DRON-2 diffractometer, using CuK_α (Ni-filtered) radiation. The measurements were made by means of the Debye–Scherrer method over the range $2\theta = 4–80°$.

The thermal stabilities and products of decomposition of the rare earth 2-naphthoates were studied. The measurements were made on a Q-1500 D derivatograph (Paulik-Paulik-Erdey). Samples of 100 mg were heated in an air atmosphere in platinum crucibles at a heating rate of 10 deg·min^{-1} to 1273 K.

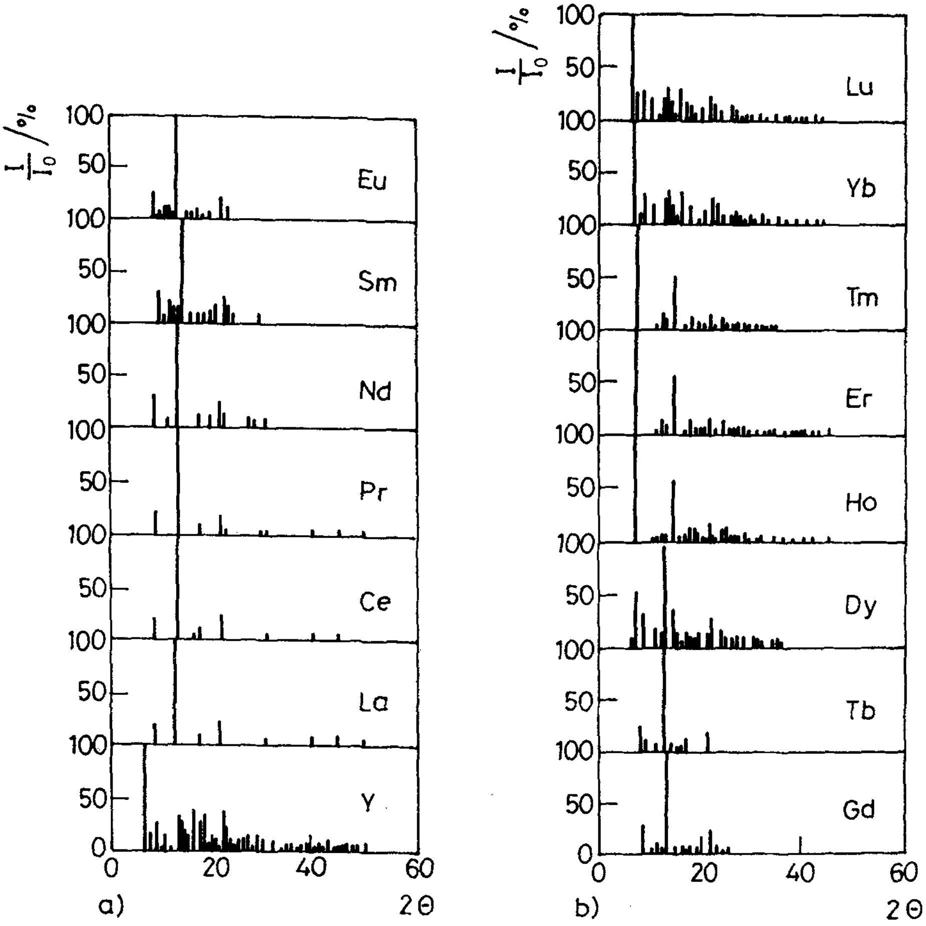

Fig. 2 Radiogram sheets of 2-naphthoates of a) Y, La and light lanthanides, b) heavy lanthanides

Al_2O_3 was used as standard. The curves for the La, Ce, Nd and Tm complexes as examples are presented in Figs 4–8. From the thermal curves of the prepared complexes, the temperatures of thermal decomposition were evaluated and are presented in Table 2. The decomposition products obtained during heating were established from the TG curves and confirmed by recording IR and X-ray spectra.

The solubilities of the prepared complexes in water at 293 K were determined. The saturated solutions were prepared under isothermal conditions. Samples of 1, 2 and 5 cm^3 were taken from the solutions and the concentrations of Ln^{3+} were determined spectrophotometrically, using arsenazo-III. The measurements were made on a Specord M-40 spectrophotometer.

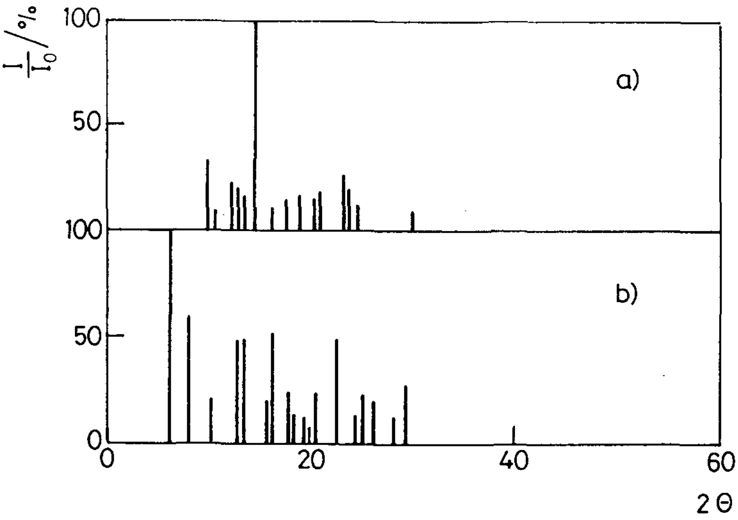

Fig. 3 Radiogram sheets of a) $Sm(C_{10}H_7COO)_3{\cdot}3H_2O$, b) $Sm(C_{10}H_7COO)_3$

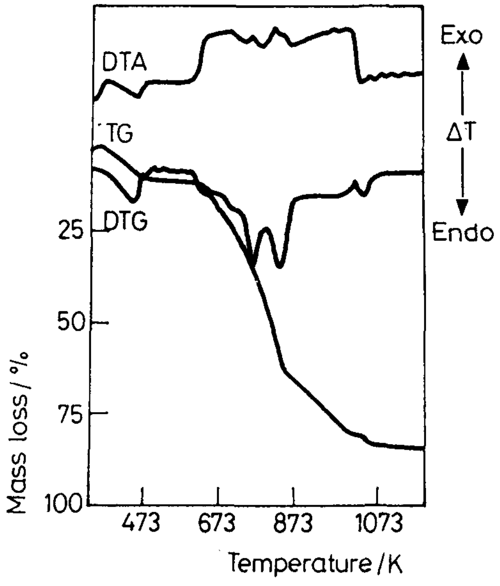

Fig. 4 TG, DTG and DTA curves of $La(C_{10}H_7COO)_3{\cdot}3H_2O$

Results and discussion

The rare earth element 2-naphthoates were prepared as crystalline solids with colours characteristic of the Ln^{3+} ions, and with a ratio of metal to ligand of 1:3, with general formula $Ln(C_{10}H_7COO)_3{\cdot}nH_2O$, where $n = 3$ for La, Ce, Pr, Nd, Sm, Eu and Gd; $n = 2$ for Tb and Dy; $n = 0$ for Ho, Er, Tm, Yb, Lu and Y.

For confirmation of the obtained data and determination of the metal-ligand coordination mode, the IR spectra of 2-naphthoic acid, its sodium salt and the prepared complexes were recorded. The IR spectra of two complexes as examples are presented in Fig. 1.

The IR spectrum of 2-naphthoic acid contains the absorption band of the –COOH group at 1710–1690 cm^{-1}, the bands of aromatic ring vibrations at 1635, 1585, 1505 and 1480 cm^{-1}, the bands of C–H deformation vibrations at 1240, 1205, 1160 and 1020 cm^{-1} and the bands of C–H out-of-plane vibrations at 870, 780, 765 and 730 cm^{-1}, characteristic of the aromatic system. When the acid is converted into a complex, the absorption band of the –COOH group disappears.

The spectra of the 2-naphthoates display the absorption bands of the asymmetric and symmetric vibrations of the OCO^- group at 1540–1535 cm^{-1} and 1425–1415 cm^{-1}, respectively. The absorption bands of the deformation vibration of the C–H group (out-of-plane and in-plane) of the aromatic ring in the spectra of the prepared complexes are not changed in position or are displaced only a little (≈5 cm^{-1}) in comparison with the spectrum of the free acid. The ab-

Table 1 Frequency of absorption bands of OCO^- ion of Na and rare earth 2-naphthoates (cm^{-1})

Complex	$\nu_{as}COO^-$	ν_sCOO^-	$\Delta\nu COO^-$
NaL*	1545	1425	120
$LaL_3 \cdot 3H_2O$	1535	1420	115
$CeL_3 \cdot 3H_2O$	1535	1425	110
$PrL_3 \cdot 3H_2O$	1535	1425	110
$NdL_3 \cdot 3H_2O$	1535	1425	110
$SmL_3 \cdot 3H_2O$	1535	1425	110
$EuL_3 \cdot 3H_2O$	1535	1420	115
$GdL_3 \cdot 3H_2O$	1540	1425	115
$TbL_3 \cdot 2H_2O$	1540	1425	115
$DyL_3 \cdot 2H_2O$	1540	1420	120
HoL_3	1535	1415	120
ErL_3	1535	1415	120
TmL_3	1535	1415	120
YbL_3	1535	1415	120
LuL_3	1535	1415	120
YL_3	1535	1415	120

* $L - C_{10}H_7COO^-$

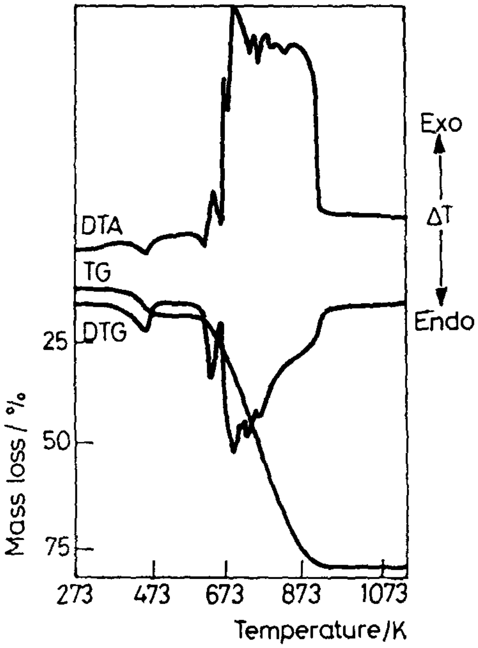

Fig. 5 TG, DTG and DTA curves of $Ce(C_{10}H_7COO)_3 \cdot 3H_2O$

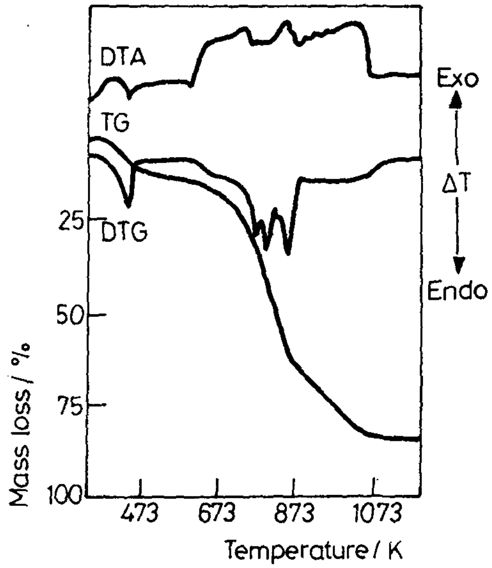

Fig. 6 TG, DTG and DTA curves of $Nd(C_{10}H_7COO)_3 \cdot 3H_2O$

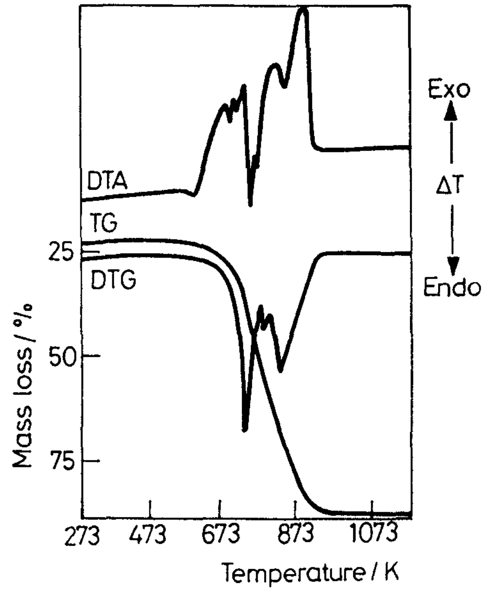

Fig. 7 TG, DTG and DTA curves of $Nd(C_{10}H_7COO)_3$

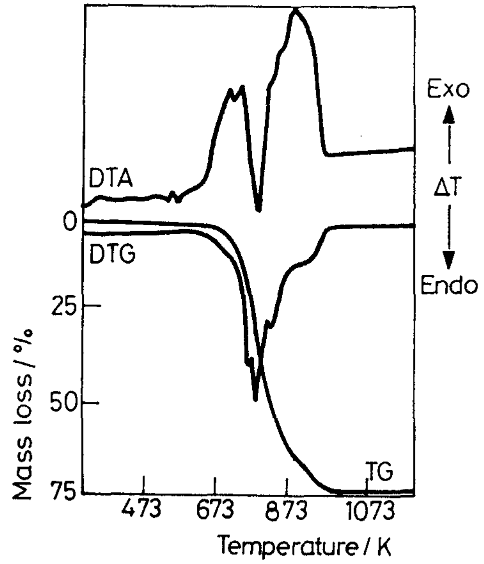

Fig. 8 TG, DTG and DTA curves of $Tm(C_{10}H_7COO)_3$

sorption bands of the metal–oxygen bonds are situated at frequencies lower than 400 cm^{-1}, which is why they are not observed in the recorded spectra. In the IR spectra of the hydrated 2-naphthoates of La(III) and the lanthanides from Ce(III) to Dy(III), a broad absorption band appears with maximum at 3440–3430 cm^{-1} and a narrow band at 1605 cm^{-1}; this confirms the presence of crystallization water molecules. These bands are not observed in the spectra of the anhydrous 2-naphthoates of Y and the heavy lanthanides from Ho(III) to Lu(III).

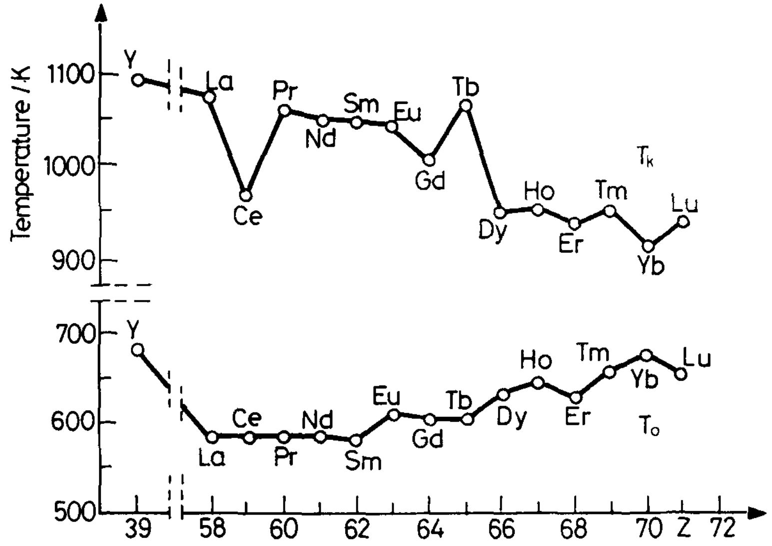

Fig. 9 Relationship between temperature of complex decomposition (T_o) and oxide formation (T_k) and Z

The frequencies of the asymmetric (ν_{as}) and symmetrical (ν_s) bands of the OCO^- group of the studied complexes and of the sodium salt are given in Table 1. The separation of the absorption bands of the asymmetric and symmetric vibrations of the carboxylate group ($\Delta\nu = \nu_{as}-\nu_s$) of the rare earth 2-naphthoates in comparison with those for the sodium salt suggests that the bonding is a little more ionic in the Y and heavy lanthanide complexes than in those of the light lanthanides. The absorption bands of $\nu_{as}OCO^-$ are shifted to lower frequencies than for the sodium salt, and the absorption bands of ν_s shift to lower frequencies or are unchanged. Thus, it may be concluded that the carboxylate ion is bidentate.

In order to confirm the crystalline structure of the rare earth 2-naphthoates, the X-ray spectra were recorded (Fig. 2). Analysis of the diffractograms revealed that the obtained complexes are crystalline compounds of low symmetry with large unit cells. They have different structures and are isostructural in the groups La–Ce, Pr–Nd, Eu–Gd–Tb, Ho–Er–Tm and Yb–Lu–Y. The diffractograms were also recorded for the 2-naphthoates of La and the lanthanides from

Table 2 Data of thermal decomposition of Y, La and lanthanide 2-naphthoates

Complex	ΔT_1	Weight loss/ %		n/	ΔT_2	Weight loss/ %		T_k	Peak temperature
		calc.	found	H_2O		calc.	found		of DTG/K
$LaL_3^*\cdot 3H_2O$	333-448	7.64	7.5	3	593-1073	76.93	77.1	1073	448,713,758,833
$CeL_3\cdot 3H_2O$	333-458	7.63	7.5	3	593- 963	75.67	76.0	963	458,633,783,838
$PrL_3\cdot 3H_2O$	323-438	7.62	7.5	3	593-1058	75.97	76.2	1058	438,763,773,823
$NdL_3\cdot 3H_2O$	333-438	7.58	7.7	3	593-1048	76.36	76.8	1048	428,753,778,838
$SmL_3\cdot 3H_2O$	323-438	7.52	7.5	3	578-1043	75.70	76.3	1043	433,743,778,828
$EuL_3\cdot 3H_2O$	333-438	7.51	7.5	3	608-1043	75.54	75.4	1043	433,698,788,833
$GdL_3\cdot 3H_2O$	323-423	7.45	7.0	3	603-1003	74.99	75.3	1003	423,738,773,818
$TbL_3\cdot 2H_2O$	313-408	5.08	5.0	2	698-1063	73.63	74.0	1063	398,758,783,818
$DyL_3\cdot 2H_2O$	318-413	5.06	5.0	2	628- 948	73.80	74.2	948	403,753,783,823
HoL_3					643- 953	72.15	72.0	953	773,783,823
ErL_3					623- 933	71.94	72.0	933	778,788,828
TmL_3					658- 948	71.67	72.0	948	768,778,823
YbL_3					673- 908	71.30	72.0	908	763,778,828
LuL_3					648- 938	71.10	70.8	938	778,803,828
YL_3					683-1093	81.25	82.4	1093	773,803,838

*L – $C_{10}H_7COO^-$

ΔT_1 – temperature range of dehydration / K

ΔT_2 – temperature range of decomposition / K

T_k – temperature of oxide formation / K

Ce(III) to Dy(III) after heating at 573 K. The results indicate that the anhydrous complexes obtained by heating are also crystalline compounds, but their structures are different from those of the hydrated complexes of the respective elements. Figure 3 presents the diffractograms of Sm(III) 2-naphthoate trihydrate and its anhydrous form as examples.

When heated, the rare earth element 2-naphthoates decompose in various ways (Table 2, Figs 4–8). The hydrated complexes of La and the lanthanides from Ce(III) to Dy are stable in air up to 317–333 K, and are then dehydrated in the temperature range 313–458 K (Table 2, Figs 4–6). The low temperature of dehydration and the total dehydration in a narrow range of temperature show that the crystallization water molecules are in the outer coordination sphere. The decompositions of the anhydrous light lanthanide 2-naphthoates begin at 573–598 K, while those Y and heavy lanthanide 2-naphthoates do so at 623–673 K. On heating, the anhydrous complexes of Y and the lanthanides decompose directly to the oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7, whereas the anhydrous La(III) complex decomposes to La_2O_3 with intermediate formation of $La_2O_2CO_3$. The temperatures of formation of the oxide obtained during heating of the complexes of Y, La and the light lanthanides (without CeO_2) are notably higher (1003–1093 K) than that for the heavy lanthanides (908–948 K) (Fig. 9). As usual, $CeO_2$is formed at a lower temperature than for the oxides of the other light lanthanides.

Table 3 Solubilities of rare earth 2-naphthoates in water at 293 K

Complex	Solubility $mol\cdot dm^{-3}\cdot 10^{-5}$	Complex	Solubility $mol\cdot dm^{-3}\cdot 10^{-5}$
$LaL_3\cdot 3H_2O$	4.10	$DyL_3\cdot 2H_2O$	11.64
$CeL_3\cdot 3H_2O$	1.98	HoL_3	11.51
$PrL_3\cdot 3H_2O$	1.81	ErL_3	10.33
$NdL_3\cdot 3H_2O$	3.28	TmL_3	9.89
$SmL_3\cdot 3H_2O$	1.76	YbL_3	8.13
$EuL_3\cdot 3H_2O$	3.53	LuL_3	6.09
$GdL_3\cdot 3H_2O$	4.26	YL_3	7.45
$TbL_3\cdot 2H_2O$	4.52		

The solubilities of the rare earth 2-naphthoates in water at 293 K were studied. The prepared complexes are sparingly soluble in water (Table 3). Their solubilities are of the order of 10^{-5}–10^{-6} $mol\cdot dm^{-3}$, with higher values for the heavy lanthanide 2-naphthoates than for those of the light lanthanides. The solubilities of the heavy lanthanide complexes decrease from Dy to Lu with increasing atomic number of the metal. The solubility of Y 2-naphthoate is similar to those of the heavy lanthanide complexes. The solubilities of the rare earth element 2-naphthoates are notably lower than those of the corresponding benzoates [7], which is connected with the different structures of the complexes, the larger molecular size and molecular mass, and the lower polarity.

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Zusammenfassung — Mit der allgemeinen Formel $Ln(C_{10}H_7COO)_3 \cdot nH_2O$ (wobei $n=3$ für La-Gd, $n=2$ für Tb und Dy und $n=0$ für Y und Ho-Lu) wurden 2-Naphthoate von Seltenerdenelementen als wenig in Wasser lösliche (10^{-5}–10^{-6} mol/dm^3) kristalline Feststoffe hergestellt. Beim Erhitzen verlieren die di- und trihydratisierten Seltenerden-2-naphthoate ihr Kristallwasser und die wasserfreien Komplexe zersetzen sich dann direkt zu Ln_2O, CeO_2, Pr_6O_{11} oder Tb_4O_7. Die Bildung eines Zwischenproduktes wurde lediglich im Falle des wasserfreien Lanthankomplexes beobachtet, der sich zu über $La_2O_2CO_3$ zu L_2O_3 zersetzt. Die wasserfreien Komplexe von Ho-Lu zersetzen sich beim Erhitzen in einem Schritt direkt zu Ln_2O_3. Wasserfreie Seltenerden-2-naphthoate sind sehr stabil (bis 578–683 K).