

# Crystal Structures and Thermal Behaviour of Lanthanide(III) Hexanoate 1,10-Phenanthroline Complexes, $[M(C_5H_{11}CO_2)_3(phen)]$ and $[Tm(C_5H_{11}CO_2)_2(NO_3)(phen)]$

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**Abstract.** Lanthanide(III) hexanoate 1,10-phenanthroline complexes crystallise in the space group  $P2_1/n$ . The compounds consist of dimers, whereby two lanthanide ions are held together by two bidentate bridging and two tridentate bridging carboxylate groups. The first coordination sphere of the lanthanide ions is completed by one bidentate chelating carboxylate group and by one bidentate 1,10-phenanthroline molecule, resulting in the coordination number 9. The dimers have a spherical form, which has important consequences for the thermal properties of complexes. The basic idea behind the preparation of this type of compounds is the stabilisation of the ionic lanthanide layer, so that the smaller lanthanide ions (from which the normal alkanooates do not show mesomorph-

ism because they are too small) show liquid crystallinity. The stabilisation of the ionic layer was successful, expressed by the high melting temperatures, but mesomorphism is not observed. The absence of mesomorphism is related to the isotropic structure of the compounds. A lower symmetry is obtained when a hexanoate group is replaced by a nitrate group. Thulium(III) dihexanoate nitrate 1,10-phenanthroline crystallises in the space group  $P\bar{1}$ . However, this compound also shows a spherical dimeric structure, but no mesomorphism.

**Keywords:** Rare earths; Lanthanides; Metal soaps; Crystal structure

## Kristallstrukturen und thermisches Verhalten von Hexanoat-1,10-Phenanthrolin-Komplexen der dreiwertigen Lanthanide, $[M(C_5H_{11}CO_2)_3(phen)]$ und $[Tm(C_5H_{11}CO_2)_2(NO_3)(phen)]$

**Inhaltsübersicht.** Die Hexanoat-1,10-Phenanthrolin-Komplexe der dreiwertigen Lanthanide, kristallisieren in der Raumgruppe  $P2_1/n$ . Strukturbestimmendes Merkmal der Verbindungen ist ein Dimer, welches von zwei zweizählig angreifenden und zwei dreizählig angreifenden Carboxylatgruppen verknüpft wird. Die Koordinationssphäre jedes Kations wird durch eine zweifach koordinierende Carboxylatgruppe sowie durch ein ebenfalls zweifach angreifendes 1,10-Phenanthrolin-Molekül vervollständigt, so dass die Koordinationszahl neun für die  $M^{3+}$ -Ionen resultiert. Diese dimeren Einheiten haben eine kugelförmige Gestalt, was sich in hohem Maße in den thermischen Eigenschaften widerspiegelt. Die Intension für die

Darstellung der Verbindungen war die Stabilisierung der kationischen Schichten, so dass diese auch mit kleinen Lanthanidionen flüssigkristalline Eigenschaften aufweisen. In der Tat findet man hohe Schmelzpunkte, was auf eine Stabilisierung hinweist, jedoch konnte kein Mesomorphismus beobachtet werden, was auf die Isotropie der Struktur zurückzuführen ist. Wird eine Hexanoat-Gruppe durch eine Nitrat-Gruppe ersetzt, ergibt sich eine Erniedrigung der Symmetrie. So kristallisiert Thulium-Dihexanoat-Nitrat-1,10-Phenanthrolin mit der Raumgruppe  $P\bar{1}$ . Auch diese Verbindung kristallisiert mit dimeren Einheiten, aber auch in diesem Fall konnte kein Mesomorphismus beobachtet werden.

### Introduction

Although lanthanide(III) alkanooates have been known since the early sixties [1–2], it was not before 1998 that their ther-

mal behaviour, and in particular their mesomorphic behaviour, was investigated. *Marques* et al. found liquid crystallinity in cerium(III) alkanooates [3]. They suggested a lamellar mesophase, although they could not assign the exact mesophase. In 1999, the mesophase behaviour of lanthanide(III) alkanooates was confirmed by *Binnemans* et al. [4, 5]. They found that lanthanum(III) tetradecanoate and the homologues with longer alkyl chains exhibit a smectic A phase. *Jongen* made a systematic study on the thermal behaviour of lanthanide(III) alkanooates and investigated the influence of the size of the lanthanide ion and the alkyl chain length on the thermal behaviour [6–10]. It was found that a mesophase could only be formed for the alkanooate complexes with the larger lanthanide ions (*i.e.*  $La^{III}$ ,  $Ce^{III}$ ,

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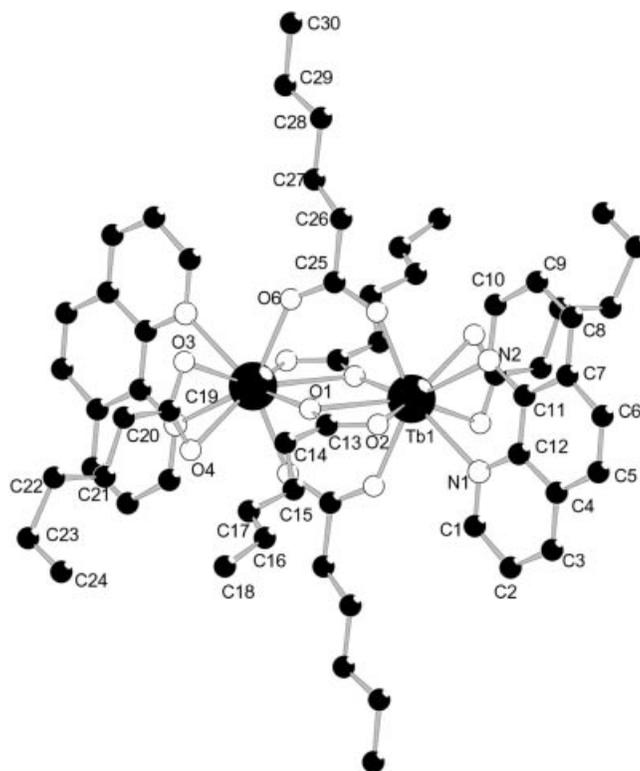
Supporting information for this article is available on the WWW under <http://www.wiley-vch.de/home/zaac> or from the author

Pr<sup>III</sup> and Nd<sup>III</sup>). Alkanoate complexes with smaller lanthanide ions (Sm<sup>III</sup> – Lu<sup>III</sup>) do not show any mesomorphism. This difference in phase behaviour depending on the ionic size could be explained by taking into account unfavourable electrostatic interactions between the carboxylate groups at elevated temperatures.

The structures of lanthanide(III) alkanoates were also investigated. Meyer made a systematic study on the crystal structures of lanthanide(III) acetates. The larger lanthanide ions (*i.e.* La<sup>III</sup> and Pr<sup>III</sup>) form network structures. The acetates of smaller lanthanide ions (*i.e.* Ho<sup>III</sup>, Lu<sup>III</sup>) show several chain structures depending on the lanthanide ion [11–13]. Praseodymium(III) propionate exhibits a chain structure [14]. The crystal structure of lanthanum(III) and neodymium(III) butyrate monohydrate is also known [7, 15]. Both compounds form infinite layers of lanthanide ions connected by carboxylate groups. The alkyl chains are placed perpendicular to these layers and are in the *all trans* conformation. By comparison of X-ray powder diffractograms at room temperature and of IR spectra of several compounds with the data of the lanthanide(III) butyrates, this bilayer structure could be extrapolated to all of the lanthanide(III) alkanoates [7].

Because just so few of the lanthanide(III) alkanoates are mesomorphic, mesophase induction experiments were carried out by mixing a mesogenic and a non-mesogenic compound [16]. The thermal behaviour of complexes with the formula  $[La_xLn_{1-x}(C_{11}H_{23}CO_2)_3]$  was investigated (Ln = Eu<sup>III</sup>, Tb<sup>III</sup>, Ho<sup>III</sup>, and Yb<sup>III</sup>). In the case of lanthanum-europium mixtures only a small amount of lanthanum was needed to induce mesomorphism in the mixtures. The minimum amount of lanthanum necessary for mesophase induction increased with decreasing ionic size of the lanthanide ion.

Another possibility to stabilise the ionic layer is the introduction of a neutral ligand like 1,10-phenanthroline (phen) [17, 18]. With the synthesis of phen adducts of lanthanide(III) alkanoates, we tried to stabilise the ionic lanthanide layer so that possibly a mesophase can be found for lanthanide(III) alkanoates which normally do not show any mesomorphism. Lebedev synthesised  $[Eu(C_5H_{11}CO_2)_3(phen)]$  [19]. This compound crystallises in the space group  $P2_1/n$ . The crystals are built of centrosymmetric dimeric molecules, whereby three different carboxylate groups are present. The coordination of the europium atom is supplemented by the bidentate phen molecule, resulting in the coordination number nine. The structures of  $[Ce(CH_3CO_2)_3(phen)]$  and of  $[Gd(CH_3CO_2)_3(phen)]$  are also known [20].  $[Eu(C_5H_{11}CO_2)_3(phen)]$  has been studied in detail because of its strong photoluminescence [20–24]. However, the crystal structures of hexanoate adducts with other lanthanide ions are not known. Moreover, no studies on the thermal behaviour of this kind of compounds have been done. Here we report the results of a systematic study of the structures and thermal behaviour of lanthanide(III) hexanoate phen complexes.



**Figure 1** Molecular structure of the dimeric complex  $[Tb(C_5H_{11}CO_2)_3(phen)]$ .

## Results and Discussion

### *Crystal Structure of $[Ln(C_5H_{11}CO_2)_3(phen)]$ ( $Ln = Pr, Nd, Sm, Tb$ )*

Although we were able to solve the crystal structure of the praseodymium(III), neodymium(III), samarium(III) and terbium(III) hexanoate phen complexes, we will only discuss the terbium homologue. However, a comparison of the cell parameters will be made. In Table 1 a summary of crystallographic data of  $[Tb(C_5H_{11}CO_2)_3(phen)]$  is given. In Table 2 selected bond lengths are listed.

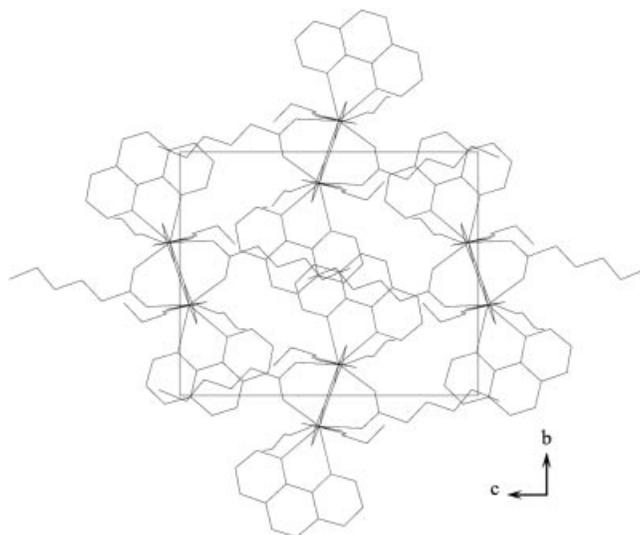
$[Tb(C_5H_{11}CO_2)_3(phen)]$  crystallises in space group  $P2_1/n$  (no. 14). The unit cell contains two dimeric molecules, so a better formula for this compound would be  $[Tb(C_5H_{11}CO_2)_3(phen)]_2$  (see Figure 1). In these dimers the terbium atoms are nine-coordinated. Each atom is surrounded by seven oxygen atoms of carboxylate groups and by two nitrogen atoms of one phen group. The coordination polyhedron of the terbium atoms is a distorted tricapped trigonal prism. Two bidentate bridging and two tridentate bridging carboxylate groups link the terbium atoms. Further coordination of each terbium atom occurs by one bidentate chelating carboxylate and one bidentate phen group. These phen groups are both placed almost parallel to (100) (see Figure 2). The alkyl chains of the bidentate chelating and tridentate bridging carboxylate groups are placed nearly perpendicular to the plane of the phen groups, the bidentate bridging ones are placed in a parallel way. The bidentate and tridentate bridging carboxylate

**Table 1** Summary of crystallographic data for [Tb(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)] and [Tm(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)(phen)].

Chemical formula	C <sub>30</sub> H <sub>41</sub> N <sub>2</sub> O <sub>6</sub> Tb	C <sub>24</sub> H <sub>30</sub> N <sub>3</sub> O <sub>7</sub> Tm
Formula weight	684.24	641.44
Crystal system	monoclinic	triclinic
Space Group (No.)	P2 <sub>1</sub> /n (No.14)	P1̄ (No.2)
Unit Cell Dimensions	a = 16.111 (6) Å b = 12.683 (3) Å c = 16.632 (7) Å β = 110.84 (4)°	a = 8.782 (3) Å b = 12.242 (5) Å c = 12.496 (5) Å α = 87.08 (2)° β = 73.16 (2)° γ = 78.66 (3)°
V	3176.3 (19) Å <sup>3</sup>	1260.7 (9) Å <sup>3</sup>
Z	4	2
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.431	1.690
T	293 (2) K	110 (1) K
λ/Å	0.7107 (Mo-Kα graphite)	0.7107 (Mo-Kα, graphite)
θ limits/deg	2.07 – 24.09	2.57 – 25.68
μ/mm <sup>-1</sup>	2.138	3.566
No. of Parameters	352	318
F (000)	1392	640
Reflections collected/unique	24226/4916 [R <sub>int</sub> = 0.0899]	11435/4427 [R <sub>int</sub> = 0.070]
Goodness-of-fit on F <sup>2</sup>	0.836	1.049
Final R indices [I <sub>0</sub> > 2σ(I <sub>0</sub> )]	R <sub>1</sub> = 0.0377, wR <sub>2</sub> = 0.0675	R <sub>1</sub> = 0.0503, wR <sub>2</sub> = 0.1364
R indices (all data)	R <sub>1</sub> = 0.0870, wR <sub>2</sub> = 0.0764	R <sub>1</sub> = 0.0524, wR <sub>2</sub> = 0.1341
Crystal size	0.1 x 0.3 x 0.6 mm	0.05 x 0.2 x 0.2 mm

**Table 2** Selected bond lengths/Å for [Tb(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)] and [Tm(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)(phen)].

[Tb(C <sub>5</sub> H <sub>11</sub> CO <sub>2</sub> ) <sub>3</sub> (phen)]		[Tm(C <sub>5</sub> H <sub>11</sub> CO <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> )(phen)]	
<i>Tridentate chelating carboxylate</i>		<i>Tridentate chelating carboxylate</i>	
Tb(1)-O(1)	2.326(5)	Tm(1) – O(1)	2.350 (4)
Tb(1)-O(2)	2.467(5)	Tm(1) – O(2)	2.546 (5)
Tb(1)-O(1)	2.602(5)	Tm(1) – O(2)	2.277 (4)
<i>Bidentate chelating carboxylate</i>		<i>Bidentate chelating carboxylate</i>	
Tb(1)-O(3)	2.398(5)	Tm(1) – O(3)	2.309 (4)
Tb(1)-O(4)	2.505(5)	Tm(1) – O(4)	2.254 (4)
<i>Bidentate bridging carboxylate</i>		<i>Bidentate chelating nitrate</i>	
Tb(1)-O(5)	2.335(4)	Tm(1) – O(5)	2.484 (5)
Tb(1)-O(6)	2.386(4)	Tm(1) – O(6)	2.424 (5)
<i>Phen</i>		<i>Phen</i>	
Tb(1)-N(2)	2.577(5)	Tm(1) – N(1)	2.519 (5)
Tb(1)-N(1)	2.604(5)	Tm(1) – N(2)	2.548 (5)

**Figure 2** Projection of the structure of [Tb(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)], along [100].

alkyl chains are in their *all trans* conformation, whereas the end of the bidentate chelating carboxylate alkyl chain is in *cis*. The alkyl chains point in three directions, resulting in a pseudospherical dimeric molecule. The temperature factors of some of the methylene and methyl groups are relatively large, which is due to relatively large thermal vibrations of the alkyl chains at room temperature.

These compounds show two main differences with the normal lanthanide(III) alkanoates. First, these compounds do not form infinite layers where all the lanthanide ions are connected by carboxylate groups, secondly, not all the alkyl chains are in *all trans* conformation. The entire dimer is pseudospherical which implicates some important features for the thermal behaviour of this kind of complexes.

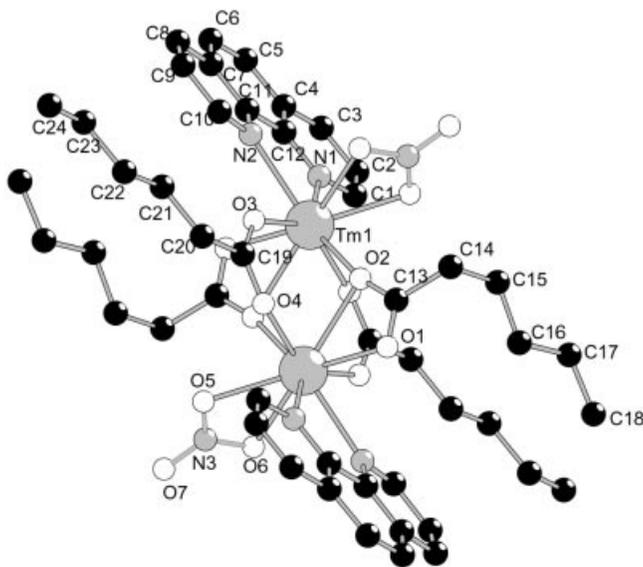
The crystal structures of the compounds of the series [Ln(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)] with Ln<sup>III</sup> = Pr<sup>III</sup>, Nd<sup>III</sup>, Sm<sup>III</sup> and Tb<sup>III</sup> is isomorphic, which is evident from Table 3. However, we prefer to describe the crystal structure of the Tb<sup>III</sup> hom-

ologue, rather than one of the other lanthanide(III) hexanoate phen complexes. The Tb<sup>III</sup> complex does not have any absorption problems. The crystal structure of the other complexes were more difficult to refine due to their strong absorption ( $\mu(\text{Cu-K}\alpha) = 12\text{--}15\text{ mm}^{-1}$ ) and the lathlike shape of the crystals. One should expect that the unit cell dimensions of the different compounds should decrease with decreasing ionic radius (*i.e.* from Pr<sup>III</sup> to Tb<sup>III</sup>). However this is not the case. The reason for this is that [Tb(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)] was measured at room temperature, whereas the other compounds were measured at  $-163\text{ }^\circ\text{C}$ .

The crystal structure of [Eu(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)] as described by *Lebedev* [19] is also isomorphic to the com-

**Table 3** Summary of unit cell dimensions for  $[\text{Ln}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$  complexes.

	$a / \text{Å}$	$b / \text{Å}$	$c / \text{Å}$	$\beta / ^\circ$	$T / \text{K}$
$[\text{Pr}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	15.422 (8)	12.7653 (7)	16.5305 (8)	112.162 (3)	110
$[\text{Nd}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	15.448 (2)	12.764 (2)	16.607 (3)	112.611 (7)	110
$[\text{Sm}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	15.397 (2)	12.681 (9)	16.527 (1)	112.427 (6)	110
$[\text{Tb}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	16.111 (6)	12.683 (3)	16.632 (7)	110.84 (4)	273

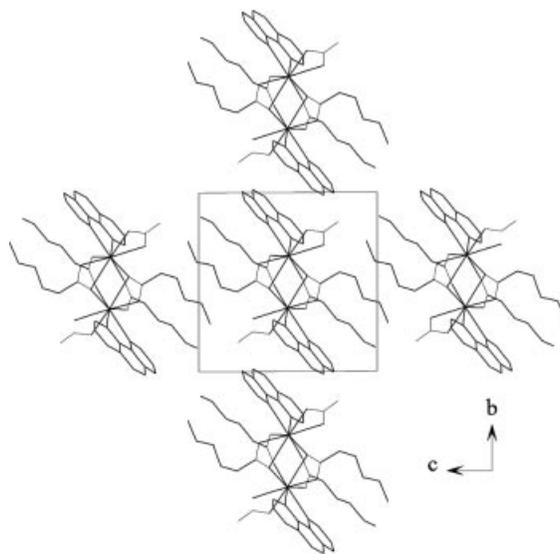
**Figure 3** Molecular structure of the dimeric complex  $[\text{Tm}(\text{C}_5\text{H}_{11}\text{CO}_2)_2(\text{NO}_3)(\text{phen})]$ .

pounds described in this paper. This means that the ionic size of the lanthanide has a minor effect on the synthesis and the structures of the complexes. This isomorphism throughout the lanthanide series has also been observed for lanthanide(III) butyrates [7, 15, 25]. However, in the case of anhydrous lanthanide(III) acetates different crystal structures were observed for different lanthanide(III) ions. Whereas the larger lanthanide ions (*i.e.*  $\text{La}^{\text{III}}$  and  $\text{Pr}^{\text{III}}$ ) give rise to network structures, the acetates of the smaller lanthanide ions (*i.e.*  $\text{Ho}^{\text{III}}$ ,  $\text{Lu}^{\text{III}}$ ) show several chain structures. [11–13]

#### Crystal Structure of $[\text{Tm}(\text{C}_5\text{H}_{11}\text{CO}_2)_2(\text{NO}_3)(\text{phen})]$

In the case of non-stoichiometric amounts of hexanoic acid, a complex with the formula  $[\text{Tm}(\text{C}_5\text{H}_{11}\text{CO}_2)_2(\text{NO}_3)(\text{phen})]$  was formed. In Table 1 a summary of crystallographic data of  $[\text{Tm}(\text{C}_5\text{H}_{11}\text{CO}_2)_2(\text{NO}_3)(\text{phen})]$  is given. In Table 2 selected bond lengths are listed.

$[\text{Tm}(\text{C}_5\text{H}_{11}\text{CO}_2)_2(\text{NO}_3)(\text{phen})]$  crystallises in the space group  $\text{P}\bar{1}$  (no. 2). The unit cell contains one dimeric molecule. So a better formula of this compound would be  $[\text{Tm}(\text{C}_5\text{H}_{11}\text{CO}_2)_2(\text{NO}_3)(\text{phen})]_2$ . In the dimer both thulium atoms are nine-coordinated. Each atom is surrounded by seven oxygen atoms, originating from two carboxylate groups and one nitrate group, and by two nitrogen atoms from one bidentate phen group. The overall coordination

**Figure 4** Projection of the structure of  $[\text{Tm}(\text{C}_5\text{H}_{11}\text{CO}_2)_2(\text{NO}_3)(\text{phen})]$ , along  $[100]$ 

polyhedron of the thulium atoms is a distorted tricapped trigonal prism.

The thulium atoms are held together by two bidentate bridging and two tridentate bridging carboxylate groups. Further coordination of each thulium atom occurs by one bidentate chelating nitrate group and by one phen group.

Whereas in the  $[\text{Ln}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$  complexes the alkyl chains of the hexanoate groups are more or less fully stretched, here the tridentate bridging carboxylate group is folded. This gives rise to a structure where the alkyl chains are placed nearly parallel to each other. The nitrate groups are placed perpendicular to the alkyl chains. However, the overall structure is still pseudospherical.

#### Thermal Behaviour

There is a single melting peak above  $180^\circ\text{C}$  for all compounds of the series  $[\text{Ln}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$ . The melting temperature increases from praseodymium to europium and decreases from europium to lutetium (see Table 4). It is possible that the interaction between the europium ion and the phen group is ideal, whereas for the larger or smaller lanthanide ions this interaction is less favourable, so the structure breaks down at lower temperatures. At the melting point the compounds are transformed into an isotropic liquid. This became evident from XRD measurements at high temperatures. No diffraction peak is observed after

**Table 4** Transition temperatures and melting enthalpies for the series  $[\text{Ln}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$ 

Compound	Transition <sup>a)</sup>	T/°C	$\Delta H/\text{kJ mol}^{-1}$
$[\text{Pr}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	Cr → I	220	40.48
$[\text{Nd}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	Cr → I	234	43.41
$[\text{Sm}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	Cr → I	238	44.29
$[\text{Eu}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	Cr → I	246	42.20
$[\text{Gd}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	Cr → I	241	47.66
$[\text{Tb}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	Cr → I	236	43.74
$[\text{Dy}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	Cr → I	230	43.77
$[\text{Ho}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	Cr → I	225	48.16
$[\text{Er}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	Cr → I	216	37.54
$[\text{Tm}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	Cr → I	207	41.03
$[\text{Yb}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	Cr → I	194	43.55
$[\text{Lu}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$	Cr → I	185	45.15

<sup>a)</sup> Cr = crystalline state, I = isotropic liquid

melting, so a totally isotropic phase must be formed. Decomposition starts at temperatures above 260 °C.

There is no evidence for mesomorphism, neither in DSC, neither in thermo-optical microscopy, nor in X-ray diffraction at high temperatures.

The high melting point and the absence of a mesophase are in contrast with the normal lanthanide(III) alkanooates where at least one mesophase is present with  $\text{Ln}^{\text{III}} = \text{La}^{\text{III}}, \text{Ce}^{\text{III}}, \text{Pr}^{\text{III}}$  and  $\text{Nd}^{\text{III}}$  and where the melting point is much lower. The reason for the absence of any mesomorphism can be related to the structure of the complexes. Lanthanide(III) hexanoate phen adducts form pseudospherical dimeric molecules. There is no interaction between the dimers. Hence, it is rather logical that these compounds do not form a mesophase because molecular anisotropy is a condition for the existence of a mesophase.

Thulium(III) dihexanoate nitrate phen shows a similar thermal behaviour as the lanthanide(III) trihexanoate phen complexes. It has a single high melting point at 231 °C. Decomposition starts immediately after melting. In comparison to the homologous lanthanide(III) hexanoate phen complex, the melting point is higher, but the compound has a lower thermal stability caused by the introduction of a nitrate group.

## Conclusion

The introduction of a phen group in lanthanide(III) alkanooates has a pronounced effect not only on their thermal behaviour, but also on the synthesis and structure of the complexes.

The basic idea behind the synthesis of this type of compounds was the stabilisation of the ionic lanthanide layer so that the smaller lanthanide(III) ions (from which the normal alkanooates do not show mesomorphism because they are too small) show mesomorphism.

The stabilisation of the ionic layer was successful (cfr. high melting temperatures) but none of the compounds is mesomorphic, not even the complexes with the lanthanide(III) ions that normally show a mesophase. This can be explained by the fact that the compounds do not show any

molecular anisotropy, but they form spherical dimers. There is a rigid centre present and there are flexible alkyl chains, but these chains point in all directions and can not be oriented in an anisotropic way, nor can the dimers be oriented in layers or columns because there is no interaction between them.

When in the lanthanide(III) hexanoate phen complexes a carboxylate group is replaced by a nitrate group, a decrease of symmetry is observed. However, thulium(III) dihexanoate nitrate phen is still a spherical dimeric molecule. The introduction of a nitrate group gives rise to a higher melting point and a lower thermal stability. Thulium(III) dihexanoate nitrate phen does not show mesomorphism.

## Experimental Section

### General

CH elemental analyses were performed on a CE Instruments EA-1110 elemental analyser. Differential scanning calorimetry (DSC) measurements were made on a Mettler-Toledo DSC 821e module. Optical textures were observed with an Olympus BX60 polarized optical microscope equipped with a Linkam THMS 600 hot stage and a Linkam TMS 93 programmable temperature controller.

Intensities of a single crystal of  $[\text{Tb}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$  were measured with an image plate diffractometer (IPDS, Stoe) at 293 K. Monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) was obtained with a graphite monochromator.

Intensities of single crystals of  $[\text{Pr}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$ ,  $[\text{Nd}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$  and  $[\text{Sm}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$  were measured with a SMART 6000 CCD detector (Bruker) at 100 K. Monochromatic Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) was obtained with Göbel mirrors.

Intensities of a single crystal of  $[\text{Tm}(\text{C}_5\text{H}_{11}\text{CO}_2)_2(\text{NO}_3)(\text{phen})]$  were measured with a *mar345* imaging plate (MARRResearch) at 110 K. Monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) was obtained with a graphite monochromator.

The data were processed with the program systems SHELX-97.[26] Scattering factors were taken from the International Tables, Volume C.[27] Figures of crystal structures were drawn using the graphical software Diamond, Version 2.

High temperature X-ray diffractograms of  $[\text{Eu}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$  and of  $[\text{Tb}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$  were measured on a STOE transmission powder diffractometer system STADI P, with a high-temperature attachment and using monochromatic Cu K $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation.

Reagents and solvents were used as received without further purification. Analytical grade solvents were used for the synthesis and washing of the complexes. Hydrated lanthanide(III) nitrates were purchased from Aldrich.

### Synthesis of $[\text{Tb}(\text{C}_5\text{H}_{11}\text{CO}_2)_3(\text{phen})]$

Hexanoic acid (0.400 g, 3.44 mmol) and phen (0.207 g, 1.15 mmol) were dissolved in absolute ethanol. The solution was heated till boiling. 6.89 mL of a 0.5M NaOH solution in absolute ethanol was added dropwise (3.44 mmol).

Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.500 g, 1.15 mmol) was dissolved in absolute ethanol and heated. The hot lanthanide(III) solution was added dropwise to the phen – hexanoate solution. The reaction mixture must be clear; when a precipitate is formed, the solution must be decanted. The remaining clear solution was refluxed during 1 hour.

The hot solution was cooled down immediately in a refrigerator (–25 °C). After two days the precipitate was filtered off, washed with absolute ethanol and dried in vacuum. The compound was recrystallised from absolute ethanol. The dissolved product was decanted and the insoluble residue was thrown away. The hot solution was put in the refrigerator. The compound was filtered off after two days, washed with absolute ethanol and dried in vacuum.

Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanolic solution of the complex at room temperature. Yield: 0.632 g (80 %)

In the same way the following adducts were synthesised: [Pr(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)], [Nd(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)], [Sm(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)], [Eu(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)], [Gd(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)], [Tb(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)], [Ho(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)], [Er(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)], [Yb(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)] and [Lu(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)]. The compounds were obtained as needle like crystals, with the typical colour of the lanthanide ion. The purity of all the compounds was checked with elemental analysis. Reliable analytical data could only be obtained after purification of the adducts by recrystallisation. C<sub>30</sub>H<sub>41</sub>N<sub>2</sub>O<sub>6</sub>Ho (FW: 684.24): C: 50.46 % (calc. 50.85 %), H: 5.65 % (6.12 %), N: 4.51 % (3.95 %)

### Synthesis of [Tm(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)(phen)]

[Tm(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)(phen)] was synthesised in the same way as described above, except that non-equimolar amounts of hexanoic acid were used.

C<sub>24</sub>H<sub>30</sub>N<sub>3</sub>O<sub>7</sub>Tm (FW: 641.44): C: 44.10 % (calc. 44.94 %), H: 4.66 % (4.71 %), for N: 6.51 % (6.55 %).

### Supporting Information

X-ray crystallographic file in CIF format ([Tb(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)]: CCDC 192043; [Tm(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)(phen)]: CCDC 192044); drawings of the dimers of [Tb(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>3</sub>(phen)] and of [Tm(C<sub>5</sub>H<sub>11</sub>CO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)(phen)] showing the thermal vibration ellipsoids (50 % probability).

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### References

[1] S. N. Misra, T. N. Misra, R. C. Mehrotra, *J. Inorg. Nucl. Chem.* **1963**, 25, 195.

- [2] S. N. Misra, T. N. Misra, R. C. Mehrotra, *J. Inorg. Nucl. Chem.* **1963**, 25, 201.
- [3] E. F. Marques, H. D. Burrows, M. da Graça Miguel, *J. Chem. Soc., Faraday Trans.* **1998**, 94, 1729.
- [4] K. Binnemans, C. Görrler-Walrand, *Chem. Rev.* **2002**, 101, 2303.
- [5] K. Binnemans, B. Heinrich, D. Guillon, D. W. Bruce, *Liq. Cryst.* **1999**, 26, 1717.
- [6] K. Binnemans, L. Jongen, C. Görrler-Walrand, W. D'Olieslager, D. Hinz, G. Meyer, *Eur. J. Inorg. Chem.* **2000**, 1429.
- [7] K. Binnemans, L. Jongen, C. Bromant, D. Hinz, G. Meyer, *Inorg. Chem.*, **2000**, 39, 5938.
- [8] L. Jongen, K. Binnemans, D. Hinz, G. Meyer, *Liq. Cryst.* **2001**, 28, 819.
- [9] L. Jongen, K. Binnemans, D. Hinz, G. Meyer, *Mater. Sci. Eng. C* **2001**, 18, 199.
- [10] L. Jongen, K. Binnemans, D. Hinz, G. Meyer, *Liq. Cryst.* **2001**, 28, 1727.
- [11] G. Meyer, D. Gieseke-Vollmer, *Z. Anorg. Allg. Chem.* **1993**, 619, 1603.
- [12] A. Lossin, G. Meyer, *Z. Anorg. Allg. Chem.* **1994**, 620, 438.
- [13] A. Lossin, G. Meyer, *Z. Anorg. Allg. Chem.* **1993**, 619, 1609.
- [14] D. Deiters, G. Meyer, *Z. Anorg. Allg. Chem.* **1996**, 622, 325.
- [15] L. Jongen, G. Meyer, K. Binnemans, *J. Alloys Comp.* **2001**, 323–324, 142.
- [16] L. Jongen, D. Hinz, G. Meyer, K. Binnemans, *Chem. Mater.* **2001**, 13, 2243.
- [17] A. M. Giroud-Godquin, *Coord. Chem. Rev.* **1998**, 180, 1485.
- [18] K. Binnemans, K. Lodewyckx, *Angew. Chem. Int. Ed.* **2001**, 40, 242.
- [19] M. A. Poraikoshits, A. S. Antsyshkina, G. G. Sadikov, E. N. Lebedeva, S. S. Korovin, R. N. Shchelokov, V. G. Lebedev, *Russian J. Inorg. Chem.* **1995**, 40, 748.
- [20] A. Panagiotopoulos, T. F. Zafiroopoulos, S. P. Perlepes, E. Bakalbassis, E. Masson-Ramade, O. Kahn, A. Terzis, C. Raptopoulou, *Inorg. Chem.* **1995**, 34, 4918.
- [21] B. Yan, H. J. Zhang, S. B. Wang, J. Z. Ni, *Spectrosc. Lett.* **1998**, 31, 603.
- [22] R. F. Wang, L. S. Li, S. Z. Lu, *J. Rare Earths* **1998**, 16, 149.
- [23] V. Tsaryuk, V. Zolin, J. Legendziewicz, *Spectrochim. Acta A.* **1998**, 54, 2247.
- [24] Z. M. Wang, L. J. van de Burgt, G. R. Choppin, *Inorg. Chim. Acta* **1999**, 293, 167.
- [25] M. A. Nibar, S. D. Barve, *J. Appl. Crystallogr.* **1984**, 17, 39.
- [26] G. M. Sheldrick, SHELX-97 manual, University of Göttingen, Germany 1997.
- [27] A. J. C. Wilson, *International Tables for Crystallography, Vol. C, Mathematical, Physical and Chemical Tables*, Kluwer Dordrecht, The Netherlands, 1995.