Lanthanide(III) Dodecanoates: Structure, Thermal Behaviour, and Ion-Size Effects on the Mesomorphism

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Rare-earth salts of dodecanoic acid (lauric acid) have been prepared and characterized. The compounds have the stoichiometry $Ln(C_{11}H_{23}COO)_3$, where Ln = Y, La, Ce–Lu (except Pm). The thermal behaviour of these rare-earth dodecanoates has been investigated by hot-stage polarized optical microscopy, differential scanning calorimetry (DSC), thermogravimetry (TG), and high-temperature X-ray diffraction analysis. The compounds have a lamellar bilayer structure in the solid state, with the alkyl chains in an *all-trans* conformation normal to the ionic sublayer. The size of the trivalent lanthanide ion has proved to be a critical factor with regard to the existence of mesophases of this type of metallomesogens bearing carboxylate ligands. Thus, it was found that a mesophase can only be formed with the light lanthanide ions having large ionic radii. The mesophase stability range decreases rapidly on traversing the lanthanide series. Whereas a smectic A phase has been observed for the La^{III}, Ce^{III}, Pr^{III}, and Nd^{III} dodecanoates, no mesomorphism is apparent for the other lanthanide complexes.

Introduction

Although rare-earth containing metal soaps have long been studied,[1−15] their mesomorphism was discovered only recently. Thus, Marques et al.[16] found liquid-crystallinity in Ce^{III} soaps and, based on the textures observed by hot-stage polarized optical microscopy, the authors suggested that Ce^{III} tetradecanoate and its higher homologues formed disordered smectic mesophases, whereas more complex mesophase behaviour was observed for Ce^{III} soaps with shorter chain lengths. By high-temperature X-ray diffraction analysis, Binnemans et al.[17] identified the mesophase formed by La^{III} tetradecanoate and its higher homologues as a smectic A (SmA) phase. These compounds were found to adopt a lamellar bilayer structure. The layer spacing in the crystalline lamellar phase at moderate temperature was close to the calculated thickness of a bilayer with the *all-trans* alkyl tails *normal* to the ionic sublayer.

Since Binnemans et al.[18] observed a very pronounced effect of the contraction of the lanthanide ion radius on the transition temperatures of lanthanide-containing metallomesogens with Schiff-base ligands, we were interested in ascertaining whether a similar effect could be found for the lanthanide(III) dodecanoates. For the Schiff-base complexes, the mesophase stability range decreases on traversing the lanthanide series (broad mesophase range for the La^{III} compound → a very narrow mesophase range for the Lu^{III} compound). We have found that in the case of the lanthanide(III) dodecanoates, the ionic radius of the trivalent lanthanide ion has a critical effect on the transition temperatures in that a mesophase can only be formed with the lighter lanthanide elements. Since there have been several reports on the industrial applications of lanthanide(III) soaps as catalysts,[19,20] polymer stabilizers,[21] and photosensitizers,[22,23] as well as on their medicinal applications,[12] a good understanding of the structural properties of compounds of this type is clearly desirable.

In this paper, we report on the structures and thermal behaviour of these lanthanide(III) dodecanoates. The structures of the compounds have been studied by IR and X-ray powder diffraction analysis. Their thermal behaviour has been investigated by hot-stage polarized optical microscopy, differential scanning calorimetry (DSC), thermogravimetry (TG), and high-temperature X-ray diffraction analysis.

Results and Discussion

The dodecanoates of all the trivalent rare-earth ions other than Sc^{III} and the radioactive Pm^{III} have been synthesized. The compounds were prepared by a metathesis reaction between the sodium salt of dodecanoic acid and the appropriate rare-earth salt (hydrated nitrate or chloride) in aqueous ethanol solution (ethanol/water, 1:1). The crude soaps were recrystallized from 1-pentanol/ethanol (5:1). The yield after recrystallization ranged from 68 to 87%.

The carbon and hydrogen contents of the rare-earth soaps were determined by C/H elemental microanalysis (combustion analysis), whereas the rare-earth contents were determined by complexometric titrations with EDTA using xylenol orange as an indicator. The fatty acid contents were measured titrimetrically using a standardized NaOH solution. For all the rare-earth dodecanoates, the ratio of the

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Table 1. Analysis results for the rare-earth dodecanoates

Ln^{III}	% C[a]	% H[a]	% Ln[a]	$C_{11}H_{23}COOH/Ln$	# mol H_2O
Y^{III}	61.8 (62.1)	10.1 (10.1)	12.7 (12.8)	3.04	0.5
La^{III}	57.8 (58.0)	9.3 (9.5)	18.6 (18.6)	2.93	0.5
Ce^{III}	57.3 (57.2)	9.5 (9.5)	18.5 (18.5)	3.04	1
Pr^{III}	57.7 (57.8)	9.4 (9.4)	19.0 (18.8)	2.98	0.5
Nd^{III}	57.6 (57.6)	9.4 (9.4)	19.4 (19.2)	2.96	0.5
Sm^{III}	56.6 (56.4)	9.3 (9.3)	20.1 (19.6)	3.01	1
Eu^{III}	56.3 (56.3)	9.3 (9.3)	20.4 (20.4)	2.90	1
Gd^{III}	56.5 (56.6)	9.3 (9.2)	20.8 (20.6)	2.98	0.5
Tb^{III}	56.3 (56.5)	9.3 (9.2)	20.9 (20.8)	2.98	0.5
Dy^{III}	55.7 (55.5)	9.2 (9.2)	21.3 (20.9)	3.03	1
Ho^{III}	55.9 (56.0)	9.1 (9.1)	21.9 (21.4)	2.96	0.5
Er^{III}	55.8 (55.8)	9.0 (9.1)	22.3 (21.6)	2.96	0.5
Tm^{III}	54.9 (55.1)	9.0 (9.1)	22.2 (21.5)	2.94	1
Yb^{III}	55.3 (55.4)	9.1 (9.0)	22.4 (22.2)	3.01	0.5
Lu^{III}	55.1 (55.3)	9.0 (9.0)	22.6 (22.4)	3.05	0.5

[a] The calculated values are given in brackets. For the calculations, the stoichiometries $Ln(C_{11}H_{23}COO)_3 \cdot 1/2\ H_2O$ or $Ln(C_{11}H_{23}COO)_3{\cdot}H_2O$ were used, depending on the water content. The theoretically expected $C_{11}H_{23}COOH/Ln$ ratio is 3.00 in all cases.

dodecanoic acid content to the rare-earth content was found to vary between 2.84 and 3.05, which is close to the theoretically expected value of 3.00 for the stoichiometry $Ln(C_{11}H_{23}COO)_3$. C, H, and Ln analyses were supportive of these findings, but also indicated that, under the reaction conditions used, the compounds could not be obtained in completely anhydrous form. Water molecules were present in all the rare-earth dodecanoates; the compounds were found to be hemihydrates, $Ln(C_{11}H_{23}COO)_3 \cdot 1/2\ H_2O$, or monohydrates, $Ln(C_{11}H_{23}COO)_3 \cdot H_2O$. The analysis results of the soaps are presented in Table 1. However, on heating, the water molecules were lost before or at the melting point and hence anhydrous lanthanide(III) dodecanoates could be obtained by cooling the melts. The water loss and the subsequent thermal decomposition of the compounds were studied by thermogravimetry in combination with DTA (heating to 1000 °C in a static air atmosphere). The TG curves show that, in general, less than 1 mol water is lost per mol of rare-earth soap. The greatest water loss is observed for Ce^{III} dodecanoate, i.e. 1.04 mol. All the rare-earth dodecanoates, with the exception of Ce^{III} dodecanoate, decompose between 360 and 380 °C. The final decomposition product is the rare-earth oxide. In the case of the Ce^{III} dodecanoate, thermal decomposition was found to commence at 200 °C. The lower thermal stability of the cerium soap may be attributed to oxidation of Ce^{III} to Ce^{IV}, which was evident from the orange colour of the ash after decomposition (CeO_2).

The lanthanide(III) dodecanoates are powders that are waxy to the touch and take on the characteristic colour of the corresponding trivalent lanthanide ion.[24] Not unexpectedly, these metal soaps have very low solubilities in water. The compounds are hydrophobic and have low wetting abilities. At room temperature, no organic solvent could dissolve appreciable quantities of these metal soaps. Their solubilities in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-octanol, hexane, chloroform, dichloromethane, toluene, benzene, ethylene glycol, DMSO, DMF, and pyridine were tested. At elevated temperatures, the lanthanide(III) dodecanoates proved to be fairly soluble in the higher alcohols (1-pentanol, 1-hexanol, 1-octanol) and in the aromatic solvents (toluene, benzene). 1-Pentanol was preferred as the crystallization solvent as the product separated from solutions in this solvent as a powder rather than as a gel (as is often the case when toluene or benzene is employed). Moreover, 1-pentanol is easier to remove from the purified product than 1-hexanol or 1-octanol. The crystallinity of the product was improved when some ethanol was added to the 1-pentanol (i.e. using 1-pentanol/ethanol, 5:1).

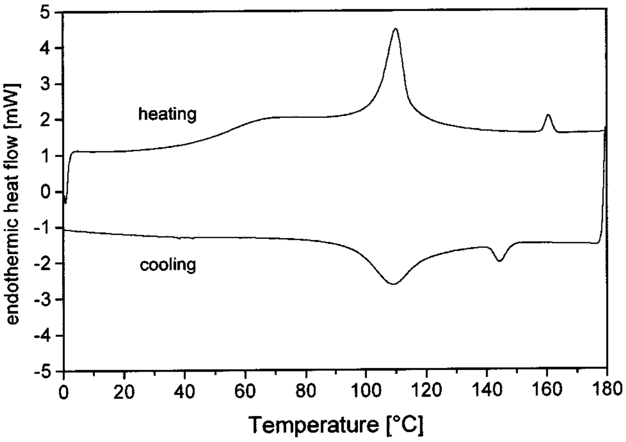

Figure 1. DSC thermogram of La^{III} dodecanoate (first heating−cooling cycle); endothermic peaks are shown pointing upwards

The melting points of the rare-earth dodecanoates $Ln(C_{11}H_{23}COO)_3$ were determined by hot-stage polarized optical microscopy, by the capillary melting technique, and by differential scanning calorimetry (DSC). Whereas in the DSC thermograms of the $Ln(C_{11}H_{23}COO)_3$ compounds with Ln = Sm−Lu, Y just a single peak is observed (corresponding to the melting point), the DSC thermograms of the dodecanoates of La^{III}, Ce^{III}, Pr^{III}, and Nd^{III} show an additional weaker peak above the melting point, indicating that these compounds form a mesophase on heating. In Figure 1, the first heating and cooling cycle in the DSC thermogram of $La(C_{11}H_{23}COO)_3$ is shown. It can be seen that the melting peak is rather broad and shows a much higher enthalpy change than the clearing peak. Before the melting peak, a broad, weak endothermic transition is observed, which is due to the loss of water (as can be proved by thermogravimetry). In the cooling run, a slight supercooling is observed for the clearing transition. At high cooling rates (> 10 °C min^{-1}), no crystallization is observed and the samples are supercooled to a glassy state. The formation of a mesophase was also evident from the melting point determinations by hot-stage polarized optical microscopy and the capillary melting technique. Whereas the compounds showing only one peak in their DSC thermograms melted directly in a heated capillary tube to give a clear liquid (of rather low viscosity), the $\mathrm{La^{III}}$, $\mathrm{Ce^{III}}$, $\mathrm{Pr^{III}}$, and $\mathrm{Nd^{III}}$ dodecanoates first melted to a highly viscous, turbid liquid and then, upon further heating, the viscosity decreased markedly and the melt became clear. Such a turbid melt is typical of a liquid-crystalline phase (i.e. a mesophase). Under the microscope, the compounds exhibited first a soft, waxy appearance and then melted to a birefringent liquid. However, it proved very difficult to obtain a good defect texture, even by cooling the isotropic liquid, as the compounds showed a very strong tendency to align homeotropically. By pressing with a needle on the cover glass it was possible to observe birefringence, but the molecules quickly re-orientated to the homeotropic alignment. The texture was suggestive of a smectic mesophase, most probably a smectic A phase (considering the presence of regions with a homeotropic alignment). It was not easy to visually observe the melting points of the mesomorphic lanthanide(III) dodecanoates owing to the high viscosities of the mesophases. The melting temperatures are thus quoted as the temperature at which the compound showed some fluidity. These temperatures are corroborated by the DSC thermograms and correspond to the maxima of the endothermic melting peaks. The clearing points were detected by hot-stage polarized optical microscopy. The transition temperatures and the corresponding enthalpy and entropy changes are listed in Table 2. For the enthalpy and entropy changes of the melting peak, the values of both the first and the second heating runs are listed. Large differences are observed between the first and the second heating runs; this is due to the fact that the evaporation enthalpy of water in the hydrated lanthanide soaps contributes to the transition enthalpy of the first heating run, whereas in the second heating run the enthalpy values are likely to be smaller owing to the fact that the samples are not completely crystalline (i.e. that they are partially amorphous). However, the enthalpy values of the clearing peak are consistent for the various compounds.

Room-temperature X-ray powder diffractograms were recorded for all of the synthesized compounds. Up to 4 peaks are observed in the low-angle region of the X-ray powder diffractograms of the solid lanthanide(III) dodecanoates, with the peak at the lowest angle showing by far the greatest intensity. The *d*-spacing values are in the ratio $1:{}^{1}/_{2}:{}^{1}/_{3}: \ldots :{}^{1}/_{n}$. These peaks correspond to the successive (00*l*) reflections and indicate the presence of a lamellar structure. Because the *d*-spacing is about twice the calculated length of the dodecanoate molecule, a bilayer structure can be postulated. The maximum average *d*-spacing of the bilayer structure was calculated for an *all-trans* conformation of the dodecanoate chain perpendicular to the metal ion base plane using Equation (1):[16]

$$d_{\mathrm{max}} = 2d_{\mathrm{C-H}} + 2(n-1)d_{\mathrm{C-C}}\sin 55^\circ + 2d_{\mathrm{C-O}} + 2r_{\mathrm{Ln}^{3+}} \quad (1)$$

where $n = 12$ (total number of carbon atoms), $d_{\mathrm{C-H}} = 1.09$ Å, $d_{\mathrm{C-C}} = 1.54$ Å, and $d_{\mathrm{C-O}} = 1.36$ Å. For the ionic radii $r_{\mathrm{Ln}^{3+}}$ of the trivalent lanthanide ions, we took the values reported by Shannon for rare-earth complexes with a coordination number of six.[25] The calculated and experimental d_{max} values, which correspond to two consecutive $\mathrm{Ln^{III}}$

Table 2. Transition temperatures, enthalpies, and entropies of the rare-earth dodecanoates $\mathrm{Ln(C_{11}H_{23}COO)_3}$

$\mathrm{Ln^{III}}$[a]	Transition[b]	Temperature/°C	ΔH/kJ $\mathrm{mol^{-1}}$[c]	ΔS/J $\mathrm{K^{-1}\ mol^{-1}}$[c]
$\mathrm{Y^{III}}$	Cr → I	85	114.7 (26.9)	320.4 (75.1)
$\mathrm{La^{III}}$	Cr → SmA	110	63.7 (23.2)	116.3 (60.6)
	SmA → I	161	1.3	3.0
$\mathrm{Ce^{III}}$	Cr → SmA	106	113.5 (30.3)	299.5 (79.9)
	SmA → I	138	0.9	2.2
$\mathrm{Pr^{III}}$	Cr → SmA	98	89.6 (26.1)	241.5 (70.4)
	SmA → I	128	1.3	3.2
$\mathrm{Nd^{III}}$	Cr → SmA	91	57.1 (26.5)	156.9 (72.8)
	SmA→ I	117	1.3	3.3
$\mathrm{Sm^{III}}$	Cr → I	91	103.2 (21.3)	283.5 (63.5)
$\mathrm{Eu^{III}}$	Cr → I	90	84.8 (20.9)	233.6 (57.6)
$\mathrm{Gd^{III}}$	Cr → I	93	89.2 (20.4)	243.7 (55.7)
$\mathrm{Tb^{III}}$	Cr → I	90	95.9 (17.5)	264.2 (48.2)
$\mathrm{Dy^{III}}$	Cr → I	87	109.8 (20.3)	305.0 (56.4)
$\mathrm{Ho^{III}}$	Cr → I	85	108.3 (23.4)	302.5 (65.4)
$\mathrm{Er^{III}}$	Cr → I	84	116.6 (27.2)	326.6 (76.2)
$\mathrm{Tm^{III}}$	Cr → I	83	117.9 (33.3)	331.2 (93.5)
$\mathrm{Yb^{III}}$	Cr → I	81	117.5 (33.6)	331.9 (94.9)
$\mathrm{Lu^{III}}$	Cr → I	78	104.9 (31.8)	298.9 (90.6)

[a] The molecular masses have been calculated assuming that the soap is anhydrous as water is lost before or at the melting point. − [b] Cr: crystalline phase; SmA: smectic A phase; I: isotropic liquid. − [c] The values are those for the first heating run, the values in brackets those for the second heating run. The values for the clearing point are the same in both heating runs.

Table 3. Calculated and experimental layer spacings d_{max} (in Å) of the rare-earth dodecanoates $Ln(C_{11}H_{23}COO)_3$ at room temperature

Ln^{III}	d_{max} (calcd.) [Å]	d_{max} (expt.) [Å]
Y^{III}	34.45	34.38
La^{III}	34.74	34.67
Ce^{III}	34.67	33.87
Pr^{III}	34.65	34.34
Nd^{III}	34.62	34.34
Sm^{III}	34.57	34.44
Eu^{III}	34.55	34.74
Gd^{III}	34.52	34.83
Tb^{III}	34.50	34.32
Dy^{III}	34.48	34.28
Ho^{III}	34.45	34.56
Tm^{III}	34.41	34.24
Yb^{III}	34.39	34.24
Lu^{III}	34.37	33.98

basal planes, are given in Table 3. Good agreement is found between the experimental and calculated values, any differences invariably amounting to less than 1% of the calculated value. As the ionic radii of the trivalent lanthanide ions decrease smoothly on traversing the lanthanide series ($r_{La}{}^{3+}$ = 1.045 Å, $r_{Lu}{}^{3+}$ = 0.861 Å for CN = 6), a corresponding decrease in the layer spacing might be expected, but this is not found experimentally. The small difference in ionic radius between La^{3+} and Lu^{3+} is outweighed by the experimental error in the determination of the *d*-values from the rather broad diffraction peaks. That the *d*-spacing does not follow the expected decrease on traversing the lanthanide series can be attributed to small variations in the conformations of the alkyl chains in the different compounds. For the calculation of the *d*-spacing, we assume an *all-trans* conformation for the alkyl chains, but random deviations can occur due to the flexibility of the alkyl chains.

The size of the lanthanide ion does have a very significant effect on the thermal behaviour of the lanthanide(III) dodecanoates. As the ionic radius of the lanthanide cation decreases, the distance between the carboxylate groups mutually opposite with respect to the plane containing the lanthanide ions also decreases. The thermal vibrations increase in amplitude at increasing temperatures and thereby induce unfavourable electrostatic interactions (repulsions) between the carboxylate groups, not only of the two opposing layers, but also between adjacent carboxylate groups within the same layer. When the repulsive forces between the negative charges are stronger than the attractive forces between the negative (carboxylate groups) and positive charges (lanthanide ions), the bilayer structure of the solid metal soap is no longer stable and breaks down. In this case, a rearrangement of the carboxylate groups and lanthanide ions to obtain a more stable solid-state structure (i.e. a crystal−crystal transition) might be expected. However, melting of the compounds is observed. The alkyl chains have sufficient thermal energy such that when the layer structure breaks down, their *all-trans* conformation is lost and they adopt a less extended conformation (which is more or less random). On melting, the metal soaps are transformed into ionic liquids with rather low viscosities. In such an ionic liquid, the total negative charge (due to the carboxylate groups) is, of course, equal to the total positive charge (due to the lanthanide ions), but the oppositely charged species can move independently of one another.

The melting points of the lanthanide(III) dodecanoates decrease over the lanthanide series; the smaller the lanthanide ion, the more unstable the layer structure becomes, and hence less thermal energy is required to break down the solid-state structure. The influence of the ion size on the melting point is also evident from the melting points of Y^{III} dodecanoate (m.p. 85 °C) and Ho^{III} dodecanoate (m.p. 85 °C), these similar values reflecting the similar ionic radii of Y^{3+} and Ho^{3+}.

A mesophase is formed when, at the melting point of the alkyl chains, the electrostatic interactions between the lanthanide ions and the carboxylate groups are still sufficiently favourable to maintain a layer structure. This is the case for the La^{III}, Ce^{III}, Pr^{III}, and Nd^{III} dodecanoates. The thermal behaviour of these compounds has been investigated by high-temperature X-ray diffraction analysis. Although the general features of the X-ray diffractograms remained the same in comparison to those of the solid compounds (except for the disappearance of the peaks of an order higher than 2), decreases in the *d*-spacings were observed at the melting points (vide infra). The X-ray diffractogram of each mesophase was consistent with a disordered smectic mesophase, indicating that the layered structure present in the solid phase is retained in the mesophase, whereas the in-plane ordering is largely lost. The loss of the in-plane ordering is reflected by the disappearance of the peak at large angles (at $2\theta \simeq 21°$, equivalent to $d \simeq 4.2$ Å) and the appearance of a much broader one, which is typical for disordered alkyl chains. Thus, the bilayer structure seen in the solid phase still represents an energetically favourable packing of the carboxylates in the mesophase. Additionally, the ratio of the peak positions in the low-angle region is $1:{}^{1}/_{2}$, indicating a one-dimensional stacking of the layers. The mesophase can be identified as a smectic A mesophase in that the layer spacing decreases slightly with increasing temperature. For a smectic C phase, an increase in layer spacing would be expected with increasing temperature.[26] The presence of an SmA phase is further supported by the homeotropically aligned regions in the optical texture observed by hot-stage polarized optical microscopy. After the clearing point, only one weak broad band is observed in the X-ray diffractograms. This is typical for the X-ray diffractogram of a liquid, indicating that the melts are isotropic. The mesophases have very high viscosities as, unlike in neutral organic molecules, the layers in the metal soaps are held together by electrostatic forces. It is difficult to shear the layers. In this sense, the mesophases can be considered as partially solid compounds, the alkyl chains exhibiting a molten behaviour, while to some extent the ionic part the structure remains intact. Consequently, sharp melting points are not observed for the lanthanide(III) dodecanoates forming a mesophase, but rather melting processes that occur over certain temperature ranges. Not all the alkyl chains melt at the same temperature. This became evident

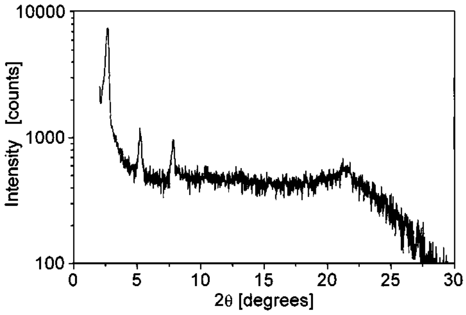

Figure 2. X-ray powder diffractogram of La^{III} dodecanoate at 50 °C

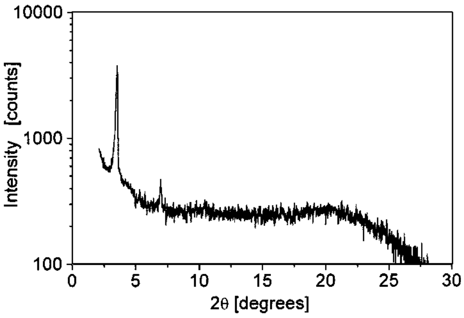

Figure 3. X-ray diffractogram of La^{III} dodecanoate in the mesophase at 135 °C

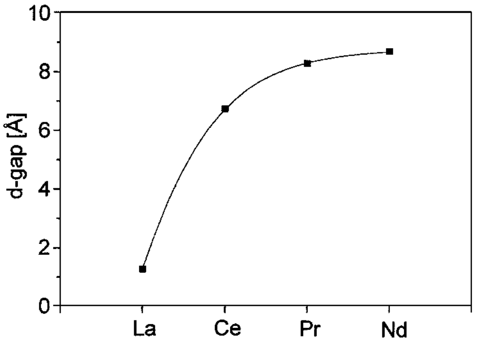

Figure 4. Variation of the change in the *d*-spacing at the melting point for the mesomorphic lanthanide(III) dodecanoates

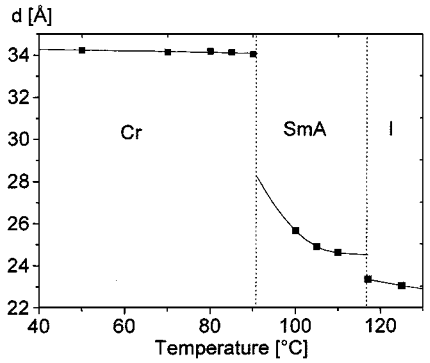

Figure 5. Evolution of the *d*-spacing of Nd^{III} dodecanoate as a function of temperature

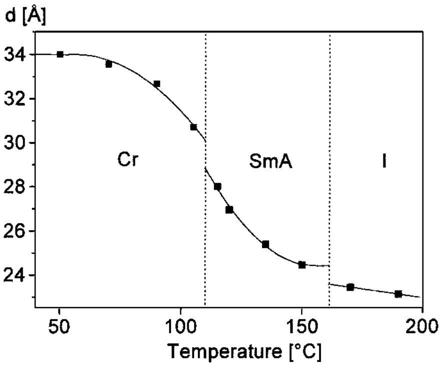

Figure 6. Evolution of the *d*-spacing of La^{III} dodecanoate as a function of temperature

when X-ray diffractograms of the compounds forming a mesophase were recorded close to their melting points. Such X-ray diffractograms show more peaks than those of the solid phase or the mesophase and it turned out that they were in fact a superposition of these respective diffractograms. In Figure 2, the X-ray diffractogram of solid La^{III} dodecanoate at 50 °C is shown; Figure 3 shows the corresponding diffractogram of the mesophase (135 °C).

The La^{III}, Ce^{III}, Pr^{III}, and Nd^{III} dodecanoates all form mesophases, which can be identified by high-temperature X-ray diffraction analyses as smectic A phases, although some structural differences between the mesophases can be observed. For La^{III} dodecanoate, the structure of the mesophase is much closer to that of the corresponding solid compound than in the case of the Ce^{III}, Pr^{III}, and Nd^{III} compounds. This is evident from the smaller change in layer spacing upon melting of the La^{III} compound as compared with the decreases in layer spacing at the melting points of the other compounds. The change in layer spacing gradually increases from 1.28 Å for La^{III} dodecanoate, through 6.73 Å for Ce^{III} dodecanoate and 8.26 Å for Pr^{III} dodecanoate, to 8.67 Å for Nd^{III} dodecanoate (Figure 4). The decrease in *d*-value upon melting may either be due to more vigorous thermal movements of the alkyl chains giving rise to larger tilts (the average tilt remains at zero, however, and the alkyl chains are perpendicular to the layer planes) or to a curling of the chains. For Nd^{III} dodecanoate in the solid phase, the *d*-layer spacing shows a very small temperature dependence and remains virtually constant between room temperature and the melting point (Figure 5). For solid La^{III} dodecanoate, however, another phenomenon is observed: close to the melting point, a distinct decrease in the layer spacing is seen (Figure 6). For Ce^{III} and Pr^{III} dodecanoate, intermediate behaviour is observed. This indicates differences in the pre-melting behaviour of the metal complexes.[27]

The layer structure is gradually lost in the compounds that form a mesophase, whereas it is lost much more abruptly in the compounds that melt without forming a mesophase. It must be emphasized that in the compounds forming a mesophase, the layer structure breaks down at the clearing point, whereas in the case of the non-mesogenic compounds total break-down of the layer structure occurs

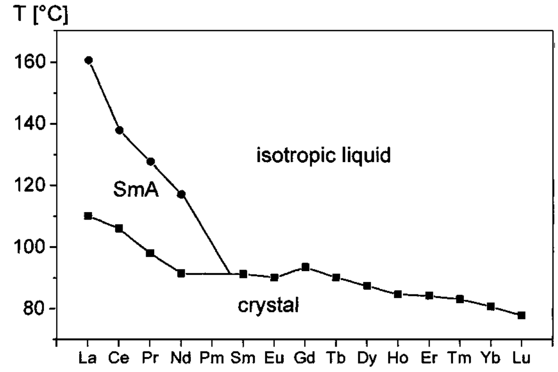

Figure 7. Phase diagram for the lanthanide(III) dodecanoates

only at the melting point. The phase diagram for the lanthanide(III) dodecanoates is shown in Figure 7.

The bilayer structure described herein is not restricted to lanthanide soaps. In fact, this mesophase structure was first described by Skoulios and Luzatti for alkali metal soaps in the "neat soap" lamellar mesophase.[28] The liquid-crystallinity of ionic metal soaps has been reviewed by Mirnaya et al.,[29] by Polishchuk and Timofeeva,[30] and by Giroud-Godquin.[31]

Although X-ray powder diffraction experiments revealed a bilayer structure for the solid lanthanide(III) dodecanoates, this technique did not give any information concerning the coordination of the lanthanide(III) ions. All that is known is that the metal ions form a layer that is sandwiched between two layers of carboxylate groups. From the stoichiometry $Ln(C_{11}H_{23}COO)_3$, it could be deduced that three carboxylate groups are present for each lanthanide ion, and that the lanthanide ions cannot be confined to one single carboxylate group (as in the case of the carboxylates of monovalent cations). We investigated the coordination around the lanthanide ion by IR spectroscopy.

The IR spectra of the various rare-earth dodecanoates proved to be all very similar. Moreover, the absorption maxima due to vibrations of the aliphatic chain of dodecanoic acid are not modified upon formation of the metal soaps. However, the IR absorptions due to the carboxyl group do change drastically. The IR spectrum of dodecanoic acid indicates the presence of a localized C=O bond and an OH bond within the COOH unit. The carbonyl (C=O) stretching vibration is observed as a very strong transition at 1700 cm^{-1}, whereas the OH stretching vibration at ca. 2660 cm^{-1} is broad due to intermolecular hydrogen bonding between two molecules of dodecanoic acid (dimeric structure). In the rare-earth dodecanoates, these transitions disappear and are replaced by the symmetric and asymmetric stretching vibrations of the carboxylate group (COO^-): ν_{symm} is seen at 1410 cm^{-1} and ν_{asymm} at 1540 cm^{-1}, giving a splitting of $\Delta\tilde{\nu} = \nu_{asymm} - \nu_{symm} =$ 130 cm^{-1}. This splitting is comparable to that seen for sodium soaps ($\Delta\tilde{\nu}$ = 138 cm^{-1}), in which the metal−carboxylate bonding is essentially ionic.[16] Since in the rare-earth compounds the positions of the bands are shifted to smaller wavenumbers in comparison to the sodium soaps, there is a strong evidence to suggest that the carboxylate groups coordinate in a bidentate fashion. However, there is insufficient evidence to discriminate between a chelating bidentate or a bridging bidentate coordination mode, and even a mixture of both coordination types within the same compound cannot be ruled out. Marques et al.[16] have discussed in detail all the other transitions observed in the IR spectra of Ce^{III} carboxylates, and our results are in agreement with theirs. Recently, Corkery and Martin investigated Eu^{III} dodecanoate and Eu^{III}-doped La^{III} dodecanoate by high-resolution luminescence spectroscopy.[32] These authors found that at least two symmetrically distinct Eu^{III} sites are present in samples obtained by slow cooling of melts.

Conclusion

The lanthanide(III) dodecanoates are waxy compounds with a stoichiometry corresponding to $Ln(C_{11}H_{23}COO)_3 \cdot x\,H_2O$ ($0 \leq x \leq 1$). Water is often present in non-stoichiometric amounts, with compositions being close to the hemihydrate (x = 0.5) or the monohydrate (x = 1). TG-DTA has revealed that on heating the water molecules are lost before or at the melting point, and that cooling of the melts results in the anhydrous compounds (albeit often in a glass-like state). The X-ray powder diffraction patterns are consistent with a bilayer structure, in which an infinite layer of lanthanide ions is separated by a double layer of dodecanoate groups. The dodecanoate groups are arranged tail-to-tail. The experimentally determined layer spacing d_{max} is close to the calculated length of the dodecanoate group with the $C_{11}H_{23}$ chain in an *all-trans* conformation. The melting points of the lanthanide(III) dodecanoates decrease smoothly on traversing the lanthanide series, ranging from 110 °C for La^{III} dodecanoate to 78 °C for Lu^{III} dodecanoate. This can be attributed to an ion-size effect; the behaviour of Y^{III} dodecanoate is very similar to that of Ho^{III} dodecanoate, in accordance with the similarity of the radii of these cations. The dodecanoate salts of La^{III}, Ce^{III}, Pr^{III}, and Nd^{III} form mesophases, and the mesophase stability range decreases rapidly on traversing the lanthanide series. On the basis of hot-stage polarized optical microscopy observations and high-temperature X-ray diffraction measurements, the mesophase could be identified as a smectic A phase (SmA). The smectic phase has a very high viscosity owing to the strong electrostatic interactions between the anionic and cationic layers. Just above the melting point, the structure of the mesophase formed by La^{III} dodecanoate is close to that of the solid compound, but on proceeding towards Nd^{III} dodecanoate, the respective mesophases exhibit more liquid-like behaviour. This is reflected by the changes in d-spacing at the melting points. For Sm^{III} dodecanoate and the other dodecanoates, no mesomorphism is observed, not even monotropic mesomorphism. The difference in thermal behaviour between the dodecanoates of the light and heavy lanthanides can be quantitatively explained in terms of a model that takes into account the size of the lanthanide ion and the electrostatic repulsions between the carboxylate groups. Although the present study confirms the results of earlier work on the thermal and structural properties Ce^{III} and La^{III} carboxylates,[16,17] the observation of an SmA mesophase only for the larger lanthanides La^{III}−Nd^{III} is somewhat surprising and was not expected. A decrease in the mesophase stability ranges over the lanthanide series has been found for Schiff-base complexes,[18] but the lanthanide(III) dodecanoates show that small differences in ionic radius between the lanthanide ions are critical with regard to the formation or absence of a mesophase.

Experimental Section

General Remarks: Elemental analyses (CHN) were performed on a CE Instruments EA-1110 elemental analyzer. − Differential scanning calorimetry (DSC) measurements were made on a Mettler-Toledo DSC821e module. Solid samples weighing 2−5 mg were placed in aluminium pans (40 μL) with pierced lids and heated or cooled at a scan rate of 10 °C min^{-1} under a nitrogen flow. Indium metal was used as a standard to calibrate the instrument (T_m = 156.6 ± 0.3 °C, ΔH_m = 28.45 ± 0.6 J g^{-1}). − The optical textures of the mesophases were observed with an Olympus BX60 polarized optical microscope equipped with a LINKAM TMS600 hot-stage and a LINKAM TMS93 programmable temperature-controller. − High-temperature X-ray diffraction was measured on a STOE transmission powder diffractometer system STADI P with a high-temperature attachment version 0.65.1 (temperature range from room temp. to 1000 °C). Monochromatic Cu-$K_{\alpha 1}$ radiation (λ = 1.54 Å) was obtained with the aid of a curved germanium primary monochromator. Diffracted X-rays were measured by a linear position-sensitive detector (PSD). The sample was placed in a quartz capillary (outer diameter 0.3 mm, wall thickness 0.01 mm) and spun during the measurement. In general, data were collected in the range $1 \leq 2\theta \leq 30°$. − Melting points were measured on an Apotec melting-point apparatus using samples in capillaries. − Thermogravimetric curves were obtained using a Polymer Laboratories STA 1000H TG-DTA apparatus. The sample (ca. 15 mg) was heated in a static air atmosphere from 30 to 1000 °C at a rate of 10 °C min^{-1}. − FT-IR spectra were recorded on a Bruker IFS-66 spectrometer with samples in KBr pellets or as Nujol mulls. − All chemicals were used as received, without further purification. Dodecanoic acid (lauric acid) was obtained from Acros. Hydrated rare-earth nitrates were purchased from Aldrich.

Synthesis of La^{III} Dodecanoate: Dodecanoic acid (2.75 g, 13.8 mmol) was dissolved in 1:1 ethanol/water (100 mL) and converted to sodium dodecanoate by adding an equivalent amount of a standardized 0.5 M NaOH solution by means of a burette. Lanthanum nitrate hexahydrate (2.00 g, 4.6 mmol) was also dissolved in 1:1 ethanol/water (100 mL). The solution of sodium dodecanoate was then added dropwise with stirring to the solution of lanthanum nitrate at ambient temperature, which led to the immediate deposition of a white precipitate. After the addition was complete, the mixture was stirred for 1 h at ambient temperature. The precipitate was then collected by filtration through a Büchner funnel, and washed with water (3 × 100 mL), ethanol (3 × 50 mL), and acetone (3 × 50 mL) in order to remove residual traces of the lanthanum salt or of dodecanoic acid. The crude lanthanum(III) dodecanoate was dried for 24 h in vacuo at 50 °C and then recrystallized from 1-pentanol/ethanol (5:1). Crystallization was completed by placing the solution in a refrigerator. The purified soap was collected by filtration, washed with ethanol (25 mL) to remove most of the 1-pentanol, and then dried in vacuo (10^{-3} mbar) at 50 °C for at least 24 h. Lanthanum(III) dodecanoate was obtained as a white powder. Yield: 2.25 g (87%). − Elemental analysis: calcd. for $C_{36}H_{69}O_6La \cdot {}^1/_2\ H_2O$: C 58.0, H 9.5, La 18.6; found C 57.8, H 9.3, La 18.6; ratio $C_{11}H_{23}COOH$/Ln: theoretical for $La(C_{11}H_{23}COO)_3$: 3.0; found 2.93. − IR (KBr): $\tilde{\nu}$ = 1540 (s, COO^-, asymm. C−O stretch), 1410 cm^{-1} (m, COO^-, symm. C−O stretch).

All the other lanthanide(III) dodecanoates were prepared by the same method.

Analysis Procedures: − 1. Determination of Rare-Earth Content: The compound (200 mg) was dissolved in hot 0.1 M H_2SO_4 solution (15 mL). After cooling, the solution was extracted with diethyl ether to remove dodecanoic acid. An aliquot (5 mL) of the aqueous solution was transferred to a beaker by means of a volumetric pipette and its pH was adjusted to 6 by adding hexamethylenetetraamine buffer. Xylenol orange was added as an indicator and the solution was titrated with standardized 0.01 M EDTA solution until the indicator changed color from purple to yellow. Titrations were performed at 60 °C, at which temperature the color change was more easily observed. − **2. Determination of the Dodecanoic Acid Content:** The combined diethyl ether extracts containing dodecanoic acid (obtained by extracting the H_2SO_4 solution after decomposition of the soap; see above) were washed with saturated brine and then the solvent was removed under reduced pressure. The residual dodecanoic acid was redissolved in ethanol and this solution was titrated with 0.025 M NaOH solution using phenolphthalein as indicator.

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