Structure and Mesomorphism of Neodymium(III) Alkanoates

Koen Binnemans,*,† Liesbet Jongen,† Claudia Bromant,‡ Dirk Hinz,‡ and Gerd Meyer‡

Katholieke Universiteit Leuven, Department of Chemistry, Celestijnenlaan 200F,
B-3001 Leuven, Belgium, and Universität zu Köln, Institut für Anorganische Chemie, Greinstrasse 6,
D-50939 Köln, Germany

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The structural and thermal behavior of all members of the homologous series of neodymium(III) alkanoates, ranging from neodymium(III) butyrate to neodymium(III) eicosanoate are described. Neodymium(III) butyrate monohydrate, $Nd(C_3H_7COO)_3 \cdot H_2O$ crystallizes in space group $P\bar{1}$ (No. 2), $Z = 2$. The lattice parameters are $a = 9.824(2)$ Å, $b = 11.974(2)$ Å, $c = 14.633(2)$ Å, $\alpha = 86.21(2)°$, $\beta = 75.92(2)°$, $\gamma = 77.97(2)°$. The crystal structure consists of ionic layers of neodymium ions, separated by bilayers of butyrate anions. In the ionic layers, the neodymium ions are connected by bridging tridentate carboxylate groups to zigzag chains, whereas the chains are connected among themselves by bridging bidentate carboxylate groups. The two crystallographically different neodymium ions are both having coordination number 9, with a geometry close to a monocapped square antiprism. The structure of the higher homologues can be derived from the structure of neodymium butyrate by extending the alkyl chains. These compounds have a lamellar bilayer structure with planes of neodymium(III) ions coordinated to the carboxylate groups and with the alkyl chains in an *all-trans* conformation. All homologous compounds from neodymium(III) pentanoate to neodymium(III) pentadecanoate display a thermotropic mesophase, which was identified by high-temperature X-ray diffraction as a smectic A phase. For the series from neodymium(III) pentanoate to neodymium(III) undecanoate an additional high viscosity mesophase is present between the crystalline state and the smectic A mesophase.

Introduction

The structural chemistry of metal carboxylates is quite fascinating, because carboxylate groups can coordinate in different ways to the central metal ion.[1] Ouchi *et al.* pointed to the fact that often dimeric and polymeric forms are observed for these compounds.[2] In the past, many studies on the crystal structure of rare-earth carboxylates have been reported. The structure of the hydrated rare-earth acetates $Ln(CH_3COO)_3 \cdot xH_2O$ ($x = 1, 1.5, 3, 4$) is well-known, because these complexes can easily be obtained in crystalline form by evaporation of aqueous solutions containing rare-earth acetates.[3] In all of these crystals, the acetate groups are bridging two rare-earth ions, either forming dimers ($x = 3, 4$), chains ($x = 1$), or a mixture of both ($x = 1.5$). Besides these structural features, coordinating water molecules are incorporated in the crystal structure. The coordination numbers of the rare-earth ions in hydrated rare-earth acetates are 9 or 10. On the other hand, the structures of the anhydrous rare-earth acetates have been studied less intensively, because most of these compounds could be obtained in a powder form only. The structure of $Sc(CH_3COO)_3$ was determined by Fuchs and Strähle,[4] later followed by the crystal structure of the anhydrous lanthanide acetates (determined by Meyer and co-workers).[5,6] It was found that $Pr(CH_3COO)_3$ forms a three-dimensional network.[7] Hardly any crystal structure of the higher homologues of the lanthanide alkanoates is available. Nabar and Barve determined the structural parameters of the lanthanide(III) butyrate dihydrates, $Ln(CH_3CH_2CH_2COO)_3 \cdot 2H_2O$ (Ln = Nd, Tb, Er, Tm, Yb, and Y) by X-ray powder diffraction and found that they have a monoclinic symmetry with space group $P2_1/m$ ($Z = 4$).[8] To our knowledge, the only crystal structure which has been described is that of praseodymium(III) propionate trihydrate, $Pr(CH_3CH_2COO)_3 \cdot 3H_2O$, the crystal structure of which consists of chains parallel to [100].[9] Two crystallographically different praseodymium ions are coordinated by four bidentate bridging propionate groups. Additionally, Pr1 is coordinated by three water molecules and Pr2 by two bidentate propionate groups. It can be expected that by increasing the length of the alkyl chain of the lanthanide alkanoates, other structural types can be obtained. Indeed, the longer the alkyl chain, the more the structural characteristics are determined by these chains. X-ray powder diffraction of the lanthanide alkanoates with long alkyl chains (also called *lanthanide soaps*) shows that these compounds have a lamellar bilayer structure.[10−15] Interestingly, this lamellar structure is preserved for several

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† Katholieke Universiteit Leuven.
‡ Universität zu Köln.

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compounds at temperatures above the melting point, leading the formation of a mesophase.[15] Binnemans *et al.* identified this mesophase of lanthanum(III) alkanoates as a smectic A phase.[16] Unexpectedly, liquid crystallinity was observed for lanthanum(III), cerium(III), praseodymium(III), and neodymium(III) dodecanoates only, not for the heavier lanthanide soaps.[17] Corkery and Martin were able to proof the presence of two symmetrically distinct europium sites in europium(III) dodecanoate.[18]

In this paper, we report on the structural and thermal properties of the compounds of the homologous series Nd($C_nH_{2n+1}COO)_3$ ($n = 3-19$). The single-crystal X-ray structure of neodymium(III) butyrate monohydrate is described, and the results are compared with those of neodymium(III) alkanoates with longer chain lengths. All members of the series Nd(C_4H_9-$COO)_3$−Nd($C_{14}H_{29}COO)_3$ display liquid crystallinity, and the mesophase structure is discussed.

Experimental Section

Materials and Methods. Elemental analyses (CHN) were carried out on a CE Instruments EA-1110 elemental analyzer. Differential scanning calorimetry (DSC) measurements were performed on a Mettler-Toledo DSC821e module. Samples of 2−5 mg in the solid state were put in aluminum crucibles (40 μL) with a pierced lid and were heated or cooled at a scan rate of 10 °C min^{-1} under a nitrogen flow. Indium metal was used as standard for the calibration of the instrument ($T_m = 156.6 \pm 0.3$ °C, $\Delta H_m = 28.45 \pm 0.6$ J g^{-1}). Optical textures of the mesophases were observed with an Olympus BX60 polarized optical microscope equipped with a LINKAM THMS600 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 temperature to 1000 °C). Monochromatic Cu Kα radiation ($\lambda = 1.5406$ Å) was obtained with the aid of a curved germanium (111) primary monochromator. Diffracted X-rays were measured by a linear Position Sensitive Detector (PSD). The sample was placed in a quartz glass capillary (outer diameter 0.3 mm, wall thickness 0.01 mm) and spinned during the measurement. In general, data were collected in the range $1 \le 2\theta \le 30°$. Room-temperature X-ray diffractograms were measured on the same apparatus, but without the high-temperature attachment. In this case the sample was mounted on a flat plastic foil. Melting points of samples in a capillary tube were determined on an Apotec melting-point apparatus. Thermogravimetric curves were obtained by 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}. FTIR spectra were recorded on a Bruker IFS-66 spectrometer, using the KBr pellet method or a Nujol mull. All chemicals were used as received, without further purification. The carboxylic acids were from ACROS, Aldrich, or Fluka. The purity of the carboxylic acids was higher than 99%. Hydrated rare-earth nitrates (99.9%) were purchased from Aldrich.

Synthesis of Neodymium(III) Butyrate. Neodymium(III) butyrate was prepared by reaction between neodymium(III) hydroxide and butyric acid. Pure Nd$(OH)_3$ was obtained through hydrothermal synthesis. Neodymium nitrate hexahydrate, Nd$(NO_3)_3 \cdot 6H_2O$, (1.00 g, 2.28 mmol), and NaOH (3.00 g, 25 mmol) were dissolved in water (15 mL), and the resulting solution was heated in a Teflon bomb for 4 days at 220 °C. Afterward, the solution was left to slowly cool to room temperature, at a cooling rate of 4 °C/h. Crystalline Nd$(OH)_3$ was obtained, and its purity was checked by X-ray powder diffraction. The pure hydroxide was dissolved in diluted butyric acid (butyric acid:water 1:1). Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solution in air. The transparent crystals were lath-like and had the typical purple color of the trivalent neodymium ion.[19]

Synthesis of Neodymium(III) Pentanoate. Pentanoic acid (1.02 g, 10.0 mmol) and triethylamine (1.02 g, 10.0 mmol) were dissolved in toluene (50 mL), and NdCl$_3 \cdot 6H_2O$ (0.60 g, 1.67 mmol) was added. Triethylamine is used as a base to trap the evolved hydrogen chloride. An excess of pentanoic acid was used to avoid the formation of mixed chloride−pentanoate complexes. The solution was heated at reflux for 48 h. After leaving the solution to cool to room temperature, water was added to the toluene solution to dissolve triethylammonium chloride. The precipitate was filtered and washed with water and ethanol to remove traces of the neodymium salt, the fatty acid or triethylammonium chloride. Neodymium(III) pentanoate was dried for 24 h in vacuo at 50 °C. Yield: 0.14 g (19%).

Synthesis of Neodymium(III) Dodecanoate. Dodecanoic acid (2.75 g, 13.8 mmol) was dissolved in 100 mL of an ethanol: water mixture (1:1), and transformed into sodium dodecanoate by adding an equivalent amount of a 0.5 M NaOH standard solution (addition via a buret). Nd$(NO_3)_3 \cdot 6H_2O$ (2.00 g, 4.56 mmol) was dissolved in 100 mL of an ethanol:water mixture (1:1). The solution of sodium dodecanoate was added dropwise with stirring to the solution of neodymium(III) nitrate (at ambient temperature). A light blue-purple precipitate immediately formed. After addition was complete, the solution was stirred for 1 h at ambient temperature. Subsequently, the precipitate was filtered on a Büchner funnel and washed with water (3× 100 mL), ethanol (3× 50 mL), and acetone (3× 50 mL) to remove traces of the neodymium(III) salt or of the dodecanoic acid. The crude neodymium(III) dodecanoate was dried for 24 h in vacuo at 50 °C and recrystallized from a 1-pentanol:ethanol (5:1) mixture. It was found empirically that this mixture gave the best crystalline precipitate. Crystallization was made complete by placing the solution in a refrigerator. The purified soap was filtered on a funnel, washed with ethanol (25 mL) to remove most of the 1-pentanol, and dried in vacuo (10^{-3} mbar) at 50 °C for at least 24 h. Neodymium(III) dodecanoate was obtained as a blue-violet powder. Yield: 2.85 g (84%). Anal. Calcd for $C_{36}H_{69}O_6Nd \cdot 0.5H_2O$: C, 57.6; H, 9.4; Nd, 19.2%. Found: C, 57.6; H, 9.4; Nd, 19.4. IR (KBr, cm^{-1}): 1550 (s, COO$^-$, asymm. C−O stretch), 1420 (s, COO$^-$, symm. C−O stretch).

All other neodymium(III) alkanoates were prepared by a similar method.

Determination of Neodymium Content. The compound (200 mg) was dissolved in 15 mL of a hot 0.1 M H_2SO_4 solution. After cooling, the solution was extracted with diethyl ether to remove dodecanoic acid; 5 mL of the aqueous solution was transferred with a volumetric pipet to a beaker, and the pH was adjusted by a hexamethylenetetramine buffer to pH = 6. Xylenol orange was added as an indicator, and the solution was titrated with a 0.01 M EDTA standard solution, until the indicator changed from purple to yellow. The solution was heated to 60 °C to make the color change better visible.

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Collection and Reduction of X-ray Data. Intensities of a small crystal of neodymium butyrate monohydrate (0.15 × 0.04 × 0.75 mm) were measured with an image plate diffractometer (IPDS, Stoe) at 293 K. Data acquisition: Mo Kα (graphite monochromator, $\lambda = 0.7107$ Å), $2.50° < \theta < 28.13°$, $\varphi = 0-250°$, $\Delta\varphi = 2°$, 125 images, 15 616 measured reflections, 7255 unique ($R_{int} = 0.0667$). Data processing: program systems SHELXS-97 and SHELXL-97, scattering factors according to the International Tables, Volume C.[20-22] Reliability factors: R_1/wR_2 (5339 reflections with $I_o > 2\sigma(I)$) 0.0879/0.2494; R_1/wR_2 (all data) 0.1063/0.2626. Goodness-of-fit on F^2: 1.096.

Results and Discussion

Synthesis. The series of homologous neodymium(III) alkanoates from neodymium(III) butyrate, $Nd(C_3H_7COO)_3$, to neodymium(III) eicosanoate, $Nd(C_{19}H_{39}COO)_3$, was synthesized by a metathesis reaction between the sodium salt of the corresponding fatty acid and neodymium(III) nitrate hexahydrate in an aqueous ethanol solution (ethanol:water 1:1). For the neodymium(III) alkanoates with short chain lengths (neodymium(III) octanoate and shorter homologues), water was the reaction medium, because the neodymium(III) soaps are too soluble in an ethanol:water mixture. For the compounds with the longest chain lengths (neodymium(III) tetradecanoate and the higher homologues), it was necessary to carry out the reaction in ethanol due to solubility problems with the corresponding sodium salts. The reactions are pH-dependent, in the sense that for the reactions the pH of the sodium alkanoate solution has to be adapted between 7 and 12. When pH < 6, no complexes are formed because the alkanoate anion is transformed into the corresponding fatty acid. At pH > 12, mixed hydroxy complexes of the type $Nd(OH)_x(C_nH_{2n+1}COO)_{3-x}$ are formed. For the synthesis of neodymium(III) butyrate and neodymium(III) pentanoate, the synthesis procedure had to be adapted (see Experimental Section). The carbon and hydrogen content of the neodymium(III) soaps was determined by CH elemental microanalysis (combustion analysis), whereas the neodymium content was determined titrimetrically with EDTA as complex forming reagent and xylenol orange as the indicator. The analysis results are consistent with an alkanoic acid to neodymium(III) ratio of 3:1, but also indicate that under the given reaction conditions the compounds cannot be obtained in a total anhydrous form. In nearly all neodymium alkanoates, water molecules were present. The compounds were hemihydrates, $Nd(C_nH_{2n+1}COO)_3{\cdot}0.5H_2O$, or monohydrates, $Nd(C_nH_{2n+1}COO)_3{\cdot}H_2O$. The analysis results of the neodymium(III) soaps are available as Supporting Information. Upon heating, water molecules were lost before or at the melting point. Anhydrous neodymium(III) alkanoates were obtained by cooling the melt. The loss of water and the thermal decomposition of the compounds were studied by TG-DTA. The TG-curves show that in general less than 1 mol of water is lost per mole of neodymium(III) soap. A good agreement was found between the water content obtained via thermogravimetry and the values calculated from elemental analysis data. The neodymium(III) alkanoates are waxy, blue-violet powders.

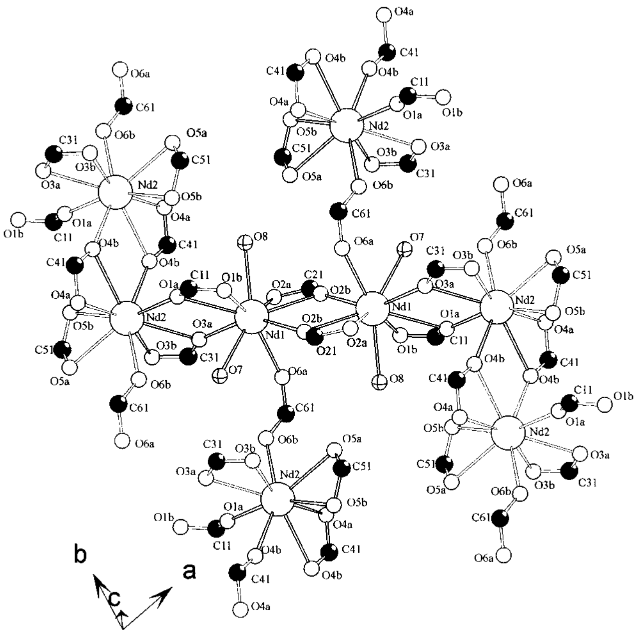

Figure 1. Drawings of the coordination sphere of Nd1 and Nd2 in neodymium(III) butyrate monohydrate.

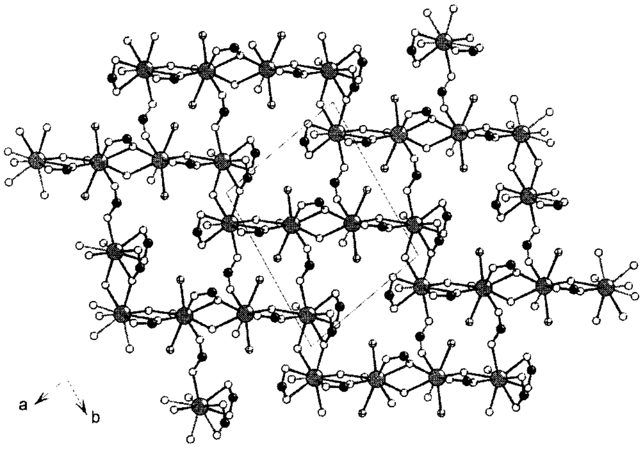

Figure 2. Zigzag chains of neodymium(III) ions in neodymium(III) butyrate monohydrate.

Crystal Structure of Neodymium(III) Butyrate Monohydrate. Neodymium butyrate monohydrate, $Nd(C_3H_7COO)_3{\cdot}H_2O$, crystallizes in the triclinic space group $P\bar{1}$ (No. 2). In the crystal structure, two crystallographically different neodymium ions are present, both having coordination number 9 (nine oxygen atoms). The coordination polyhedra can be described as monocapped square antiprisms (Figure 1). Nd1 is surrounded by two water molecules and by five carboxylate groups. Four of these carboxylate groups are bridging tridentate and one is *Z*,*E*-type bridging bidentate. Nd2 is coordinated by four bridging tridentate carboxylates, one *Z*,*E*-type bridging bidentate carboxylate group and one chelating-type bidentate. The coordination polyhedra are connected via common edges to zigzag chains (Figure 2). These common edges consist of two oxygen atoms, each belonging to a bridging tridentate carboxylate group. In the bridging tridentate carboxylate groups, one of the oxygen atoms is bound to two neodymium atoms, whereas the second oxygen atom is bound directly to a neodymium atom. Such a bridging tridentate coordination of carboxylate groups is discussed by Ouchi *et al.*[2] and was also found for $Lu(CH_3COO)_3$, $Ho(CH_3COO)_3$, and $Pr(CH_3CH_2COO)_3{\cdot}3H_2O$.[4,7] The chains are connected to one another by *Z*,*E*-type bridging bidentate carboxylate groups. A schematic representation of the different carboxylate coordination modes is available as Sup-

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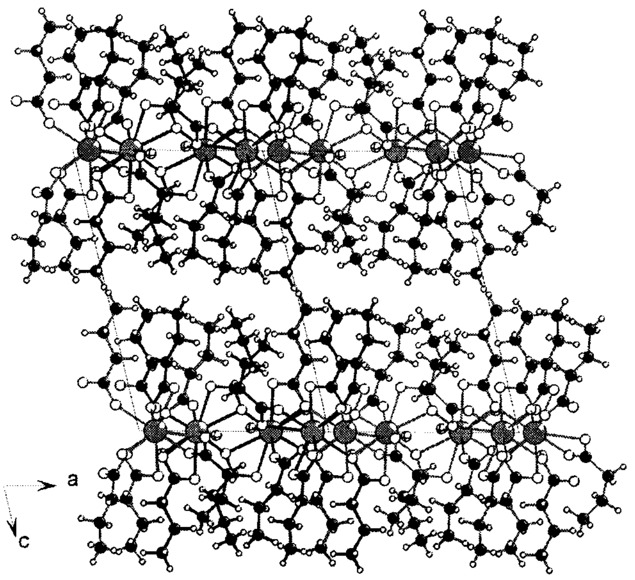

Figure 3. Crystal structure of neodymium(III) butyrate monohydrate viewed down the *b* axis.

Table 1. Crystallographic Data for Neodymium(III) Butyrate Monohydrate

chemical formula	$C_{24}H_{42}Nd_2O_{14}$
fw	842.72
space group (No.)	$P\bar{1}$ (No. 2)
a, Å	9.824(2)
b, Å	11.974(2)
c, Å	14.633(2)
α, deg	86.21(2)
β, deg	75.95(2)
γ, deg	77.97(2)
V, Å^3	1633.0(5)
Z	2
ρ_{calcd}, g cm^{-3}	1.714
T, K	293
μ, cm^{-1}	30.18
GOF on F^2	1.046
R_1/wR$_2$ [$I_o > 2\sigma(I)$][a]	0.0879/0.2494
R_1/wR$_2$ (all data)[a]	0.1063/0.2626

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.1705P)^2 + 16.8096P$, where $P = (F_o^2 + 2F_c^2)/3$.

porting Information. The alkyl chains of the butyrate groups are in an all-trans conformation (Figure 3).

The temperature factors of the ending methyl group are relatively large, which is due a strong disorder of the ends of the alkyl chains. The large *R* values of the structure can be explained by the fact that it is very difficult to obtain good crystals for structure analysis from layered structures. Crystallographic information and data collection parameters for neodymium(III) butyrate monohydrate are summarized in Table 1 and in the Experimental Section, and selected bond lengths and angles are included in Table 2.

The layerlike structure of $Nd(C_3H_7COO)_3 \cdot H_2O$ contrasts to the infinite chains of $Pr(CH_3CH_2COO)_3 \cdot H_2O$. The alkyl chains of the propionate groups are not long enough to force themselves to a parallel alignment in layers. The butyrate compounds are thus the first members in the series of lanthanide(III) alkanoates with the typical bilayer structure of metal soaps.

Structure of the Higher Neodymium(III) Alkanoates. Room-temperature X-ray powder diffractograms were recorded for all of the synthesized compounds. Up to eight peaks were observed in the low-angle region of the X-ray powder diffractograms of the solid neodymium(III) alkanoates, with the peak at the lowest angle bearing by far the highest intensity. The X-ray diffractogram of neodymium(III) tetradecanoate is shown in Figure 4. The large number of reflections points on a high crystallinity of the compound. The *d*-spacing values are in the ratio 1:1/2:1/3 ... 1/*n*. These diffraction peaks correspond to the successive (00*l*) Bragg reflections and indicate the presence of a lamellar structure. The polar groups of the neodymium(III) alkanoates are localized in infinite, parallel, and equidistant planes. These planes are separated from each other by a bilayer of alkyl chains in the all-trans conformation. The interplanar layer spacing *d* corresponds to the distance between two successive layers of neodymium(III) ions. The fact that the alkyl chains are in the all-trans conformation is supported by the good agreement between experimental and calculated maximal average *d*-spacing values (d_{max}) (see Supporting Information). The maximal average *d*-spacing of the bilayer structure was calculated for an all-trans conformation of the alkyl chain perpendicular to the metal ion base plane using the formula:[15]

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Neodymium(III) Butyrate Monohydrate

Bridging Tridentate Carboxylates			
Nd(1)−O(1a)	2.659(10)	O(1a)−C(11)	1.263(15)
Nd(1)−O(1b)	2.514(9)	O(1b)−C(11)	1.226(17)
Nd(1)−O(2a)	2.505(10)	O(2a)−C(21)	1.274(16)
Nd(1)−O(2b)	2.444(10)	O(2b)−C(21)	1.284(15)
Nd(1)−O(2b)	2.546(9)	O(3a)−C(31)	1.307(15)
Nd(1)−O(3a)	2.447(10)	O(3b)−C(31)	1.243(16)
Nd(2)−O(1a)	2.460(9)	O(4a)−C(41)	1.266(15)
Nd(2)−O(3a)	2.577(10)	O(4b)−C(41)	1.296(14)
Nd(2)−O(3b)	2.519(9)		
Nd(2)−O(4a)	2.482(9)		
Nd(2)−O(4b)	2.452(9)		
Nd(2)−O(4b)	2.658(9)		
O(1a)−C(11)−O(1b)	120.7(12)		
O(2b)−C(21)−O(2a)	117.2(11)		
O(3b)−C(31)−O(3a)	118.5(11)		
O(4a)−C(41)−O(4b)	117.9(11)		
Chelating Bidentate Carboxylate			
Nd(2)−O(5a)	2.582(8)	O(5a)−C(51)	1.248(18)
Nd(2)−O(5b)	2.490(10)	O(5b)−C(51)	1.281(17)
O(5a)−C(51)−O(5b)	116.2(13)		
Bridging Bidentate Carboxylates			
Nd(1)−O(6a)	2.421(9)	O(6a)−C(61)	1.243(16)
Nd(2)−O(6b)	2.470(9)	O(6b)−C(61)	1.273(15)
O(6a)−C(61)−O(6b)	123.3(12)		
Coordinated Water			
Nd(1)−O(7)	2.556(9)		
Nd(1)−O(8)	2.502(9)		

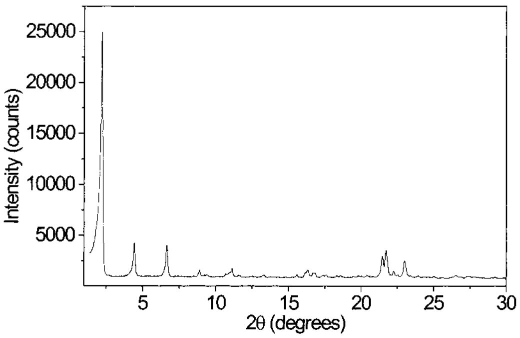

Figure 4. Room-temperature X-ray diffractogram of neodymium(III) tetradecanoate.

where n = total number of carbon atoms, $d_{C-H} = 1.09$ Å, $d_{C-C} = 1.54$ Å, and $d_{C-O} = 1.36$ Å, $r_{Nd^{3+}} = 1.163$ Å (CN = 9).[23] The increment in d-spacing due to addition of a CH_2-group is 2.52 Å when the chain are in the *all-trans* conformation. Experimentally, we find an average increment of 2.41 Å. This constant increment is also an indication that the crystal structure of the compounds does not change drastically when varying the alkyl chain length. Our value for the d-spacing of neodymium(III) tetradecanoate (39.66 Å) corresponds well with the value reported by Upadhyaya and Sharma (39.58 Å) for the same compound.[11] For the series $Nd(C_4H_9COO)_3$−$Nd(C_8H_{17}COO)_3$ the (00*l*) reflection is split in two peaks, and the second peak has a d-spacing which is 1 to 4 Å shorter than the d-spacing corresponding to the (00*l*) peak with the highest intensity (see Supporting Information). The splitting is not observed for the higher order peaks, because of their low intensity. This splitting of the (00*l*) peak is an indication that more than one crystal modification is present in our samples. The most likely explanation for the shorter d-spacing in the second modification is that the methyl end groups of the alkyl chains in one layer partially penetrate into the adjacent layer. Because of the high purity (+99%) of the fatty acids used for the synthesis of the alkanoates in which this splitting occurs, the possibility that the satellite peaks are due to impurities of compounds with shorter chain lengths can be neglected.

In the wide-angle region ($2\theta \approx 22°$) a broad weak band is observed for the compounds with long alkyl chains. This indicates absence of long-range order of the alkyl chains in the bilayers.

The powder diffractograms of $Nd(C_3H_9COO)_3$ and $Nd(C_4H_9COO)_3$ are not typical for lanthanide soaps, in the sense that the (001) reflection is not much intenser than the (002) reflection. This is because the crystallinity of these compounds is much higher than for the other compounds. The weaker the (002) reflection is with respect to the (001) reflection, the worse the layers are defined.

The fact that the neodymium(III) alkanoates have a different degree of hydration (hemihydrate or monohydrate) could give the impression that the series of neodymium(III) alkanoates is not a real homologous series. However, no differences are observed in the X-ray powder diffractograms of the hemihydrate in comparison with the diffractograms of the monohydrate. Thus, $Nd(C_{14}H_{29}COO)_3 \cdot 0.5H_2O$ gives the same diffractograms as $Nd(C_{13}H_{27}COO)_3 \cdot H_2O$, except for the expected shift in the peak positions due to the addition of a CH_2 group. The presence or absence of water molecules can give rise to structural differences in the ionic layers, but the differences are not reflected in the X-ray powder diffractograms. Half of the water molecules can be lost without the need of the Nd1 ions to change coordination number (we assume that the coordination sphere of the neodymium atoms in the higher homologues is comparable to that in neodymium(III) butyrate monohydrate). Indeed, if one of the two water molecules coordinated to the Nd1 ions is removed, the bidentate bridging carboxylate groups can be transformed into tridentate carboxylate groups. The Nd chains are then brought closer to each other and the neodymium polyhedra will now have more than two common edges. The chain structure of the Nd atoms will be replaced by a two-dimensional network. Transformation of the hemihydrate to an anhydrous compound can without structural changes in the overall structure, but the coordination number of Nd1 will be reduced from 9 to 8. This hypothesis is valid also if the coordination number of Nd1 is decreased by the loss of the first water molecule and consecutively the bidentate carboxylate groups are transformed into tridentate ones upon loss of the second water molecule.

Infrared spectra in the spectral region from 400 to 4000 cm^{-1} were recorded for all the neodymium(III) alkanoates and are available as Supporting Information. The most remarkable difference between the infrared spectra is the number of CH_2 wagging progression bands, observable in the 1350−1150 cm^{-1} spectral region as a set of regularly spaced peaks. These bands are a further indication that the chains are in the all-trans conformation.[24] For an even number of carbon atoms in the alkyl chain, the number of IR bands is $n/2$ (n being the number of carbon atoms). For an odd number of carbon atoms, the number of IR bands is equal to $(n+1)/2$. The C═O stretching vibration observed in the alkanoic acid around 1700 cm^{-1} disappears in the neodymium(III) alkanoates and is replaced by two new absorption bands. These bands correspond the symmetric stretching vibration of the carboxylate anion (1410−1420 cm^{-1}) and the asymmetric stretching vibration (1520−1550 cm^{-1}). The interaction between the neodymium(III) ion and the carboxylate group can be evaluated by considering the splitting of the two carboxylate bands, being 120−130 cm^{-1} in our complexes. This splitting remains constant for complexes with different chain lengths. In comparison to the carboxylate stretching vibrations in sodium alkanoates (ν_s at ca. 1427 cm^{-1} and ν_{as} at ca. 1563 cm^{-1}, $\Delta\nu = 138$ cm^{-1}),[25] both infrared bands are shifted to lower wavenumbers and the splitting is reduced. Although the splitting $\Delta\nu$ is often used to probe the carboxylate coordination,[26] we do not think that this approach is very suitable for the neodymium(III) alkanoates, because the single-crystal structure of neodymium(III) butyrate monohydrate indicates that more than one type of carboxylate coordination is present in each compound. The fact that the splitting $\Delta\nu$ is independent of the alkyl chain length is an indication that no major structural changes occur when extending the alkyl chain length toward the higher homologues. The other transitions in the infrared spectra corresponds to vibrations due to the alkyl chains,[15] except for a broad band at ca. 3450 cm^{-1} (OH-stretching vibration of water molecules).

Thermal Behavior. The thermal behavior of the neodymium(III) alkanoates was investigated by hot-stage polarized optical microscopy, by melting point determination in capillary tubes, by differential scanning calorimetry (DSC), and by high-temperature X-ray diffraction. The DSC thermograms and microscopy studies of compounds of the series $Nd(C_{11}H_{23}COO)_3$−$Nd(C_{14}H_{29}COO)_3$ reveal the presence of one mesophase. Neodymium(III) butyrate has a single high melting point (166 °C); neodymium(III) hexadecanoate and the higher homologues melt directly to an isotropic liquid at temperatures between 107 and 116 °C. For the series $Nd(C_4H_9COO)_3 \rightarrow Nd(C_{10}H_{21}COO)_3$ more than one mesophase is observed. It was not easy to obtain a good optical texture by hot-stage polarized optical microscopy. In general, the compounds softened close to the melting point and they became more or less fluid at a temperature which correspond to the peak temperature of the corresponding transition in the DSC thermogram. The low-temperature mesophase of the short-chain homologues has a high viscosity and even the high-temperature mesophase (i.e., the unique mesophase in the $Nd(C_{11}H_{23}COO)_3$−$Nd(C_{14}H_{29}COO)_3$ series) is not very fluid. We label the high viscosity

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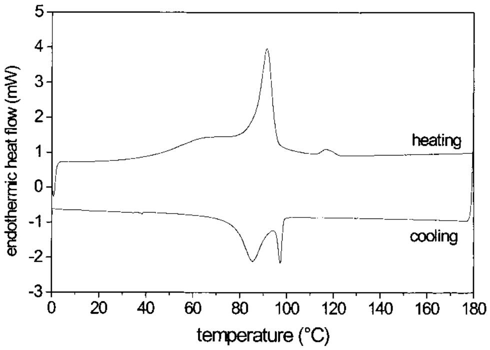

Figure 5. DSC thermogram of neodymium(III) dodecanoate (first heating−cooling cycle). Endothermic peaks are pointing upward.

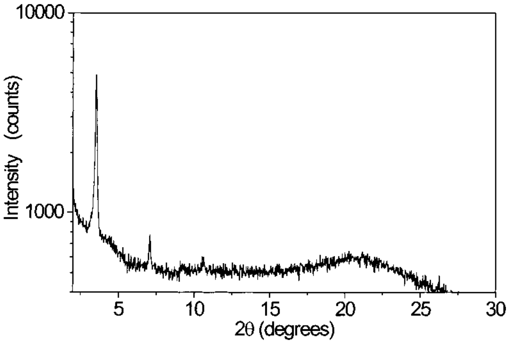

Figure 6. High-temperature X-ray diffractogram of neodymium(III) dodecanoate at 105 °C.

mesophase as an M phase. The textures of the high-temperature mesophase were the same as described by Marques et al.[15] for cerium(III) alkanoates. Most often, the textures had a grainy appearance with white-yellow zones on a dark background. When the mesophase was obtained by cooling the isotropic liquid, birefringence could be observed only by pressing with a needle on the cover glasses. Often the birefringence disappeared when the pressure was released. In other cases, birefringence was visible only at the borders of the melt or around air bubbles entrapped in the melt. This shows that the compounds have a very strong tendency to align homeotropically (with the alkyl chains perpendicularly to the cover glasses). In Figure 5 the DSC thermogram of neodymium(III) dodecanoate is shown (first heating−cooling cycle). The broad endothermic peak before the melting point indicates the loss of water of hydration (which was proved also by thermogravimetry). Both melting and clearing peak are quite distinct. In the cooling run, a supercooling of more than 20 °C was observed for the clearing peak. Such a supercooling is often observed for ionic metallomesogens. The mesophase stability range in the cooling run was less than the stability range observed in the heating run. The mesophase could only be determined unambiguously by high-temperature X-ray diffraction. The X-ray diffractogram of neodymium(III) dodecanoate in the mesophase at 105 °C is given in Figure 6. In the mesophase, the lamellar bilayer structure of the solid state is retained, but a distinct decrease in *d*-spacing is observed at the solid-mesophase transition (Figure 7). This indicates that the alkyl chains loose their *all-trans* conformation. To our opinion, no tilting of the chains occur, but some kind of folding. In fact, the solid-to-mesophase transition can be considered as the melting of the alkyl chains. The transition of the mesophase to the isotropic liquid at the clearing point corresponds to destruction of the ionic layers and the formation of an ionic salt melt. The temperature dependence of the *d*-spacing in the mesophase (decrease of *d*-spacing at increasing temperatures) corresponds to the behavior expected for a smectic A phase. In this kind of mesophase the molecules are ordered in layers and on average the long molecular axis is perpendicular to the layer planes. In the case of a smectic C mesophase, where the long molecular axis is tilted to the layer planes, the *d*-spacing increases with increasing temperature. Because no discrete molecules are present in the mesophase of neodymium(III) alkanoates, the smectic A phase is not totally the same as the one observed for classic organic rodlike liquid crystals. In the neodymium(III) alkanoates, the neodymium(III) ions are arranged in layers (sheets) separated by double-layers of alkanoate groups with the alkyl chains perpendicularly to the neodymium(III) ion layers. Due to the polymeric nature of the ionic layers, no orientation of the mesophase could be observed in a magnetic field.[27,28] No monotropic mesomorphism is observed for the higher homologues (neodymium(III) hexadecanoate to neodymium(III) eicosanoate). The compounds show either enantiotropic mesomorphism or no mesomorphism at all. The SmA phase as we describe here, is very comparable to that observed for the alkali metal soaps in the "neat soap" lamellar mesophase.[29] The mesophase behavior in ionic metal alkanoates is discussed in the review articles of Mirnaya *et al.*,[30] Akanni *et al.*,[31] Polishchuk and Timofeeva,[32] and Giroud-Godquin.[33]

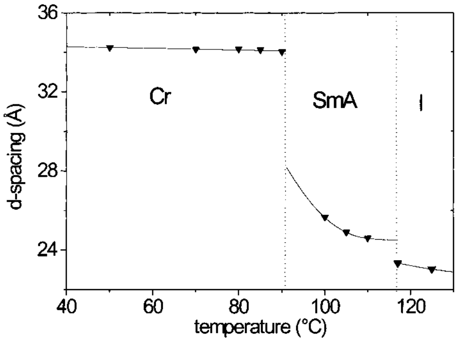

Figure 7. Change of the *d*-spacing of neodymium(III) dodecanoate as a function of the temperature.

The M mesophase observed for the neodymium(III) alkanoates up to neodymium(III) undecanoate can be considered as a phase with partially molten alkyl chains, in contrast to the SmA phase with totally molten alkyl chains. The M phase is a highly viscous liquid and cannot be considered as a solid phase. However, high-temperature X-ray diffraction data do not indicate the presence of ordering within the smectic layers (which is the case for the highly order smectic phases or crystal phases). Only a change in interplanar layer spacing could be observed, together with disappearance of most of the higher-order (00*l*) reflections. The interplanar layer spacing of the M

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Table 3. Thermal Behavior of the Neodymium(III) Alkanoates

compound	transition[a]	temp./°C[b]	ΔH/kJ mol^{-1} [c]
$Nd(C_3H_7COO)_3$	Cr → I	166	9.90
$Nd(C_4H_9COO)_3$	Cr → M	77	34.51
	M → SmA	95	n.d.[d]
	SmA → I	113	6.32
$Nd(C_5H_{11}COO)_3$	Cr → M	81	57.42
	M → SmA	94	n.d.
	SmA → I	128	1.80
$Nd(C_6H_{13}COO)_3$	Cr → M	86	59.91
	M → SmA	101	n.d.
	SmA → I	133	2.31
$Nd(C_7H_{15}COO)_3$	Cr → M	83	64.51
	M → SmA	92	n.d.
	SmA → I	126	1.20
$Nd(C_8H_{17}COO)_3$	Cr → M	82	68.86
	M → SmA	90	n.d.
	SmA → I	127	1.03
$Nd(C_9H_{19}COO)_3$	Cr → M	85	88.08
	M → SmA	94	n.d.
	SmA → I	125	1.10
$Nd(C_{10}H_{21}COO)_3$	Cr → M	90	94.08
	M → SmA	97	n.d.
	SmA → I	120	1.19
$Nd(C_{11}H_{23}COO)_3$	Cr → SmA	91	26.74
	SmA → SmI	117	1.14
$Nd(C_{12}H_{25}COO)_3$	Cr → SmA	101	36.23
	SmA → I	116	1.94
$Nd(C_{13}H_{27}COO)_3$	Cr → SmA	98	45.94
	SmA → I	111	1.28
$Nd(C_{14}H_{29}COO)_3$	Cr → SmA	108	54.20
	SmA → I	114	1.21
$Nd(C_{15}H_{31}COO)_3$	Cr → I	107	82.39
$Nd(C_{16}H_{33}COO)_3$	Cr → I	111	71.46
$Nd(C_{17}H_{35}COO)_3$	Cr → I	112	90.45
$Nd(C_{18}H_{37}COO)_3$	Cr → I	116	101.60
$Nd(C_{19}H_{39}COO)_3$	Cr → I	115	109.91

[a] Cr = crystalline phase; M = unidentified smectic phase; SmA = smectic A phase; I = isotropic liquid. [b] The reported transition temperatures correspond to the peak temperatures in the DSC thermogram and these agree with the values determined by polarizing microscopy. [c] First heating run. [d] n.d. = not determined.

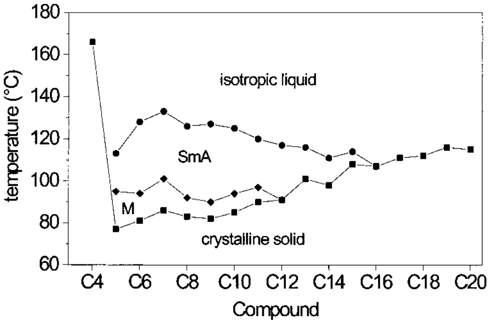

Figure 8. Phase diagram of the neodymium(III) alkanoates. The compounds are labeled with the number of carbon atoms in the alkanoate groups (e.g., C12 stands for neodymium(III) dodecanoate).

phase is intermediate between that of the crystalline solid and that of the SmA mesophase. Although no textural changes can be observed for the M-to-SmA transition, the viscosity decreases markedly when going from the M to the SmA mesophase. The higher homologues go directly from the solid state to a SmA phase, without going through a M phase. The transition temperatures and enthalpies of the neodymium(III) alkanoates are summarized in Table 3. The corresponding phase diagram is shown in Figure 8.

The neodymium(III) alkanoates can be divided into two groups depending on the magnitude of the transition enthalpies: (I) $Nd(C_4H_9COO)_3$−$Nd(C_{10}H_{21}COO)_3$ and (II) $Nd(C_{11}H_{23}COO)_3$−$Nd(C_{19}H_{39}COO)_3$. Neodymium(III) butyrate monohydrate was not considered, because it is nonmesomorphic and has a much higher melting point than the other compounds. In each group the enthalpy change ΔH (in kJ mol^{-1}) increases with increasing alkyl chain length, but a discontinuity is observed between $Nd(C_{10}H_{21}COO)_3$ and $Nd(C_{11}H_{23}COO)_3$. This is at the point where the M phase ceases to exist (the M phase is observed for $Nd(C_{10}H_{21}COO)_3$, but not for $Nd(C_{11}H_{23}COO)_3$). Linear regression was applied to the two data sets in order to determine the increase in ΔH, but the correlation coefficient of the best fit was much higher for the group II ($r = 0.9807$) than for group I ($r = 0.9652$). For the mesomorphic compounds, the enthalpy changes for the melting and the clearing transition were summed. The slopes of the two fitted curves are 2.75 kJ (mol CH_2)$^{-1}$ for group I and 3.45 kJ (mol CH_2)$^{-1}$ for group II. These values can be compared with the enthalpy change of 3.8 kJ (mol CH_2)$^{-1}$ observed for complete fusion of aliphatic chains from the fully crystalline state[34] and are higher than the 2.5 kJ (mol CH_2)$^{-1}$ found by Marques *et al.* for cerium(III) soaps.[15] The main difference between the two groups is the enthalpy change for extrapolation to zero CH_2 groups: 11.18 kJ (mol CH_2)$^{-1}$ for group I and −85.84 kJ (mol CH_2)$^{-1}$ for group II. For the series of cerium(III) soaps ranging between cerium(III) octanoate and cerium(III) octadecanoate, Marques *et al.* found a value of −49 kJ (mol CH_2)$^{-1}$ and the authors contributed the negative value to electrostatic interactions.[15] When the compounds melt the repulsive electrostatic interactions are reduced, leading to a stabilization of the system. The positive intercept for group I can be attributed to the fact that part of the enthalpy change is due to the loss of water of hydration and this contribution overwhelms the negative contribution due to electrostatic interaction.

It should be noticed that the thermal behavior of the compounds depends on the thermal history of the compounds, in the sense that samples obtained by crystallization from an organic solvent have different thermal behavior than samples obtained by crystallization from the melt. This difference is very obvious from the differences in the first and the second heating runs in the DSC thermograms. In nearly every case, the enthalpy change of the melting peak was smaller in the second heating run than in the first heating run, indicating that the samples did not totally crystallize from the melt, but have the tendency to form glasses. Additionally, in the second heating run, water of crystallization was no longer present. In general, the DSC thermograms of the second heating run contain less solid−solid transitions. Differences could be observed in the *d*-spacing for “fresh” samples and samples recrystallized from the melt. In the glasslike samples, the alkyl chains are not in the all-trans conformation, but in a less symmetric conformation. Such a complicated thermal behavior was not only observed by Marques *et al.*[15] for cerium(III) alkanoates but also for other metal soaps (e.g., for the higher lead(II) alkanoates[35]).

Conclusion

A single-crystal X-ray diffraction study of neodymium butyrate monohydrate shows the presence of two crystallographically different neodymium ions, both with coordination number 9 and a geometry which can be considered as a distorted monocapped antiprism. The alkyl chains of the carboxylate groups are in the all-trans conformation, giving raise to a

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layerlike structure. The higher homologues have a lamellar bilayer structure with planes of neodymium(III) ions coordinated to the carboxylate groups. It can be assumed that the coordination sphere of neodymium(III) in the higher alkanoates is comparable to the surroundings of neodymium(III) in neodymium butyrate monohydrate. However, structural changes will occur in the ionic layer when water of hydration is lost by heating the compounds. Loss of water will not affect the conformation of the hydrophobic alkyl chains. The members of the series from $Nd(C_4H_9COO)_3-Nd(C_{14}H_{29}COO)_3$ display a thermotropic mesophase, which was identified by high-temperature X-ray diffraction as a smectic A phase. The compounds of the series $Nd(C_4H_9COO)_3-Nd(C_{10}H_{21}COO)_3$ show an additional mesophase between the crystalline state and the SmA mesophase. This high viscosity mesophase M could not be fully characterized yet. Although it was expected that the short-chain homologue $Nd(C_3H_7COO)_3$ does not show liquid crystalline properties, the absence of a mesophase for neodymium(III) hexadecanoate and the higher homologues was unforeseen. Indeed a mesophase was found by Binnemans *et al.*[16] for the $La(C_{13}H_{27}COO)_3-La(C_{17}H_{35}COO)_3$ series, and Marques *et al.*[15] describe similar results for the corresponding cerium(III) alkanoates. Present results are complementary to the findings of Binnemans *et al.*[17] that the mesophase stability range decreases over the lanthanide series. Further studies are being undertaken to determine the whole phase diagram of the rare-earth alkanoates.

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Supporting Information Available: Tables of chemical analysis results of the neodymium(III) alkanoates, atomic coordinates and equivalent isotropic temperature factors for neodymium(III) butyrate monohydrate, experimental and calculated *d*-spacings; figures of coordination spheres of Nd1 and Nd2 in neodymium(III) butyrate monohydrate showing thermal vibration ellipsoids (50% probability); figure illustrating the different coordination modes of carboxylate groups in neodymium(III) butyrate monohydrate; IR spectra of selected neodymium(III) alkanoates; and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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