

# Lanthanide-Containing Liquid Crystals and Surfactants

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## I. Introduction

### A. What Are Liquid Crystals?

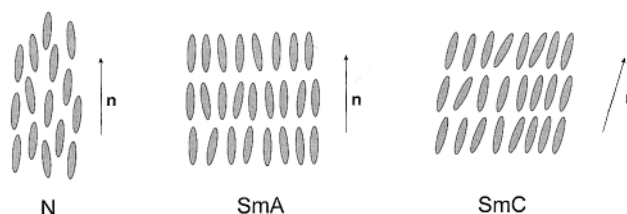
Molecules in a crystalline lattice possess both orientational and positional order. In noncubic crys-

tals, the physical properties depend on the direction in which they are measured; i.e., these properties are anisotropic. In a perfect crystal, the order effects extend over a quasi-indefinite distance (or in practice to the borders of the crystal). In general, the orien-

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tational and positional order are retained when the crystal is heated, and the effect of heating is an increase in the vibrational energy of the molecules. When the compound is heated further, the melting point will be reached. At this point, all long-range order is suddenly lost and the crystal is transformed into an isotropic liquid state. However, not all compounds show this simple behavior. When some particular structural features are present in the molecule, the melting process is a stepwise process; i.e., the crystal lattice is transformed into the isotropic liquid (the melt) in more than one step. These compounds can be considered as having more than one melting point. They possess one or more intermediate states between the ordered crystalline state and the disordered liquid state. Such an intermediate state is called a "mesophase". When a crystal consisting of molecules with a spherical shape is heated, the molecules will retain their positional order up to the melting point, but they will lose their orientational order below the melting point. Rather than staying at a fixed orientation, they will start to tumble around (but they will keep their position in the crystal lattice). This type of mesophase is called the "plastic state" and the compounds forming such a mesophase are said to be "plastic crystals". From the name plastic crystal it can be derived that these compounds have a very high viscosity and show little or no fluidity.

Molecules with a rodlike shape (*calamitic molecules*) show a different behavior. When a crystal consisting of such molecules is being heated, the molecules retain their orientational and positional order up to the melting point. At the melting point, the molecules lose their 3D positional order, but not all their orientational order. This phase with partial orientational order is called "liquid-crystalline state" and compounds forming such liquid-crystalline state are termed "liquid crystals" (or *mesomorphic compounds* or *mesogens*).<sup>1</sup> Depending on the degree of orientational order, different types of liquid-crystalline states or mesophases can be distinguished. The least ordered liquid-crystalline phase is the *nematic phase* (N), in which the molecular axis of the molecules has some preferential average direction (which is called the *director*,  $\mathbf{n}$ ). The nematic phase has quite a low viscosity and is therefore very fluid. Because the orientation of the molecules can be changed by applying an external electric field, liquid crystals in the nematic phase have found several technological applications. The best-known application is the *liquid-crystal display* (LCD), which is being used in displays of calculators and in the screen of laptop computers. In the *smectic phases*, the molecules possess more order than in the nematic phase. Just as in the nematic phase, the molecules have their long molecular axis more or less parallel to the director. Additionally, the molecules are confined into layers. One can consider that the molecules have some degree of 2D positional order (in contrast to the 3D order in a crystal). Of the many types of smectic mesophases, we will consider here only two: the *smectic A phase* (SmA) and the *smectic C phase* (SmC). In the smectic A phase, the director is parallel to the normal to the

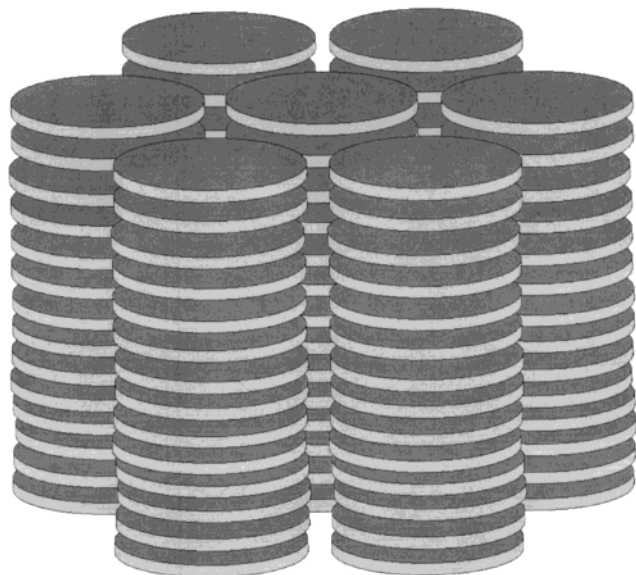


**Figure 1.** Arrangement of rodlike molecules in the nematic phase (N), the smectic A phase (SmA), and in the smectic C phase (SmC). The director is denoted as  $\mathbf{n}$ .

smectic layers. The individual molecules can be tilted with respect to the normal, but the average tilt angle is zero. In the smectic C phase, the director makes a tilt angle  $\theta$  with the normal. Both the SmA and the SmC phase have some fluidity, but their viscosity is much higher than that of the nematic phase. In Figure 1, the arrangement of molecules in the nematic, smectic A, and smectic C phase is shown schematically.

Molecules with a disklike shape (*discotic molecules*) can also form liquid-crystalline phases upon heating. The best known of these mesophases are the *columnar phases*, in which the molecules are stacked into columns. Depending on the type of 2D lattice in which the molecules are being stacked, one can make a distinction between the *hexagonal columnar phase* (Col<sub>h</sub>), the *tetragonal columnar phase* (Col<sub>t</sub>), and the *rectangular columnar phase* (Col<sub>r</sub>). Other ways of stacking are possible, but they will not be considered here. Sometimes a difference is made between ordered and disordered columnar mesophases. In the *ordered columnar phase* (e.g., Col<sub>ho</sub>) there is some degree of ordering within the column, whereas no order inside the columns exists in the *disordered columnar phase* (e.g., Col<sub>hd</sub>). Notice that we use the modern way of labeling (Col<sub>h</sub>, Col<sub>t</sub>, Col<sub>r</sub>), rather than the old-fashioned one (D<sub>h</sub>, D<sub>t</sub>, D<sub>r</sub>; D referring to "discotic"), since these mesophases can be formed too by molecules with a shape other than disklike. Besides the columnar arrangement of the molecules, there are two other types of stacking of discotic molecules. In the *discotic nematic phase* (D<sub>N</sub>), the molecules are with their short molecular axis parallel to the director. This way of ordering is comparable with that of a heap of coins spread on a flat surface. In the *columnar nematic phase* (Col<sub>N</sub>), molecules stacked into short columns behave like rods and the order in this mesophase is analogous to that of the nematic phase of calamitic molecules. Figure 2 presents schematically the stacking of the molecules in the hexagonal columnar phase.

Liquid crystals that form a mesophase upon heating are called "*thermotropic liquid crystals*". Up to now, we considered the heating process. When thermotropic liquid crystals are heated to the *isotropic state* (I) and subsequently cooled, the molecules will arrange to a mesomorphic state at the clearing point. These are so-called "*enantiotropic liquid crystals*", forming a liquid-crystalline state both on heating and cooling. "*Monotropic liquid crystals*" do not form a liquid-crystalline state when heated to a temperature above their melting point. However, they will form a liquid-crystalline state when the isotropic liquid is



**Figure 2.** Arrangement of disklike molecules in the hexagonal columnar phase ( $\text{Col}_h$ ).

supercooled to a temperature below the melting point. Monotropic phases are thermodynamically unstable.

Whereas rod-shaped and disk-shaped molecules form a mesophase upon heating them, amphiphilic molecules can form a mesophase in the presence of a solvent. *Amphiphilic molecules* have of a polar headgroup (the *hydrophilic part* of the molecule) and an apolar tail (the *hydrophobic part* of the molecule; typically the tail consists of a long alkyl chain). Typical examples of amphiphilic molecules are the surfactants, which can be classified into cationic, anionic, or nonionic surfactants. When a surfactant is put into a polar solvent, it will readily dissolve when the surfactant concentration is low. When the concentration is increased above a certain point, the *critical micelle concentration* (cmc), the surfactant molecules will arrange to spherical or rodlike entities, called *micelles*. In a polar solvent, the hydrophilic headgroups are situated on the surface of the micelle, whereas the hydrophobic tails are in the inner part of the micelle. When the surfactant concentration is still further increased, the micelle concentration will increase accordingly and at a certain point the micelles will start to arrange themselves into *lyotropic mesophases*. Depending on the type of surfactant or solvent and the temperature and surfactant concentration, different types of lyotropic mesophases can be formed: hexagonal, lamellar, or cubic phases. Micelles and lyomesophases can be formed in a nonpolar solvent, too, but then *inverse micelles* are present, with the hydrophobic tails on the outside of the micelle.

## B. Why Put Lanthanides into Liquid Crystals?

Because of the desire to combine the properties of liquid crystals and metal complexes, a substantial amount of research has been devoted in the last 25 years to the design of liquid-crystalline–metal complexes (*metallomesogens*). The development of this research domain has been described in several re-

views.<sup>2</sup> The first discovered classes of metallomesogens incorporate metal ions that form either linear complexes ( $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ) or square planar complexes ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$ ). In the former case, the coordination number (CN) of the central metal ion is 2, in the latter case it is 4. At that time, it was thought that only classes of coordination compounds that mimic the classical organic rod-shaped liquid crystals would exhibit mesomorphism. Later studies illustrated the possibility to include octahedral metal centers (CN = 6) into liquid crystals. However, obtaining high coordination number liquid crystals remains a challenge.<sup>3</sup> The next logical step toward metallomesogens with a coordination number higher than 6, was the design of liquid crystals containing *lanthanide ions* (or *rare-earth ions* in general). The coordination number of these trivalent ions is typically 8 or 9.

The quest for metallomesogens with a high coordination number is not the only reason people are looking for new lanthanide-containing liquid crystals, although, in principle, the differences in coordination behavior between lanthanide ions and the d-group transition metal ions open the way to liquid crystals with new geometries. The main driving forces for the development of this type of advanced materials are the unique physical properties of lanthanide ions. Several of the lanthanide ions show a very intense luminescence (photo- or electroluminescence). Europium(III) compounds emit in the red, terbium(III) compounds in the green, and thulium(III) compounds in the blue spectral region. By incorporating lanthanide ions into liquid crystals, one can obtain luminescent liquid crystals, which are useful for the design of emissive LCDs. Most of the trivalent lanthanide ions are paramagnetic, due to the unfilled 4f subshell. They have a high magnetic moment, and what is more important, often they exhibit a large magnetic anisotropy. Together with a low viscosity, a high magnetic anisotropy is one of the factors that reduce the threshold magnetic field for the alignment of molecules in an external magnetic field. Switching of molecules by a magnetic field can have some advantages over switching by an electric field. First of all, due to the presence of the electrode on the walls of the liquid crystal cell (LC cell), molecules in an external electric field can only be oriented with their long molecular axis either parallel or perpendicular to the LC cell walls. In principle, a magnetic field can be applied in any given direction, independent of the LC cell walls, and thus magnetic alignment is possible in any desired direction, too. Unwanted charge separation or redox reactions can occur when metallomesogens are placed in a strong electric field. These problems are absent in the case of magnetic switching. Although magnetic switching will never replace electric switching in LCDs, one can think about the possibilities in the field of magneto-optical data storage.

## C. Scope of This Review

In this review, for the first time a comprehensive overview of lanthanide-containing liquid crystals is given. The literature has been covered up to Decem-

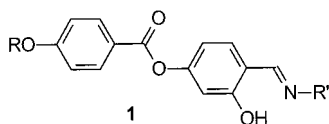
ber 2001. In the past, a few short reviews have been devoted to his topic, but their scope was very limited.<sup>4,5</sup>

In this review, the compounds have been classified according to their chemical composition. The Schiff's base complexes, the alkanooates, and the phthalocyanines are discussed in depth, because these classes of lanthanide-containing liquid crystals have been studied in detail. Also reviewed are the lanthanide-containing surfactants, with emphasis on the behavior of lanthanide ions and complexes in micellar systems. Additionally, we cover work on lanthanide complexes in Langmuir–Blodgett films (LB films), on lanthanide-doped bilayer membranes, and on lipophilic MRI contrast agents. A separate section has been devoted to the magnetic alignment of calamitic liquid-crystalline lanthanide complexes. Finally, the potential application of lanthanide complexes in emissive LCDs is discussed.

## II. Calamitic Liquid Crystals

### A. Schiff's Base Complexes

Because Schiff's base complexes have been used so often for the design of metallomesogens,<sup>2</sup> and because the trivalent lanthanides are known to form complexes with these ligands,<sup>6</sup> it was expected that Schiff's bases could be used to prepare liquid-crystalline lanthanide complexes. Whereas the major part of the Schiff's base metallomesogens described in the literature are complexes of *N*-aryl substituted salicylaldehydes, one failed up to present to obtain lanthanide complexes of this type of ligand. The first calamitic lanthanide-containing liquid crystals were reported in 1991 by Galyametdinov and co-workers. In their very short, yet seminal paper, the authors describe the synthesis and thermal behavior of lanthanide complexes with an *N*-alkyl salicylaldehyde ligand **1** ( $R = C_7H_{15}$ ,  $R' = C_{12}H_{25}$ ).<sup>7</sup> The stoichiometry



of the complexes was believed to be  $[LnL_3X_2]$ . It is noteworthy that no base was used to deprotonate the ligand. The ligand itself is mesogenic, exhibiting a nematic mesophase. The lanthanide complexes form a highly viscous smectic mesophase, which was later identified as a smectic A phase. Much lower transition temperatures were observed for complexes with nitrate counterions in comparison with complexes with chloride counterions. Except for the mesophase behavior, no other physical properties have been reported for this type of compounds. Exploration of the physical properties is hampered by the very high viscosity of the mesophase and by the low thermal stability of the lanthanide complexes (in general, they decompose at the clearing point). An X-ray diffraction study of these compounds has been published by Binnemans and co-workers.<sup>8</sup> By placing an additional alkoxy chain on the benzoyloxy group, Bruce and co-

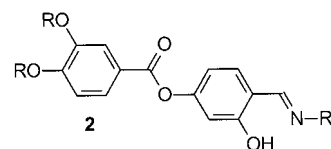
**Table 1. Thermal Behavior of Lanthanide Compounds with Two-Ring Schiff's Base Ligands LH**

compound	R	R'	temperatures (°C)	ref
[La(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>6</sub> H <sub>13</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 70 SmA 184 dec	8
[Tb(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>6</sub> H <sub>13</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 75 SmA 172 dec	8
[La(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>6</sub> H <sub>13</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 71 SmA 191 I (dec)	8
[Pr(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 96 SmA 181 I	7
[Gd(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 98 SmA 192 I	7
[Dy(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 92 SmA 186 I	7
[La(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 66 SmA 199 I (dec)	8
[La(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>10</sub> H <sub>21</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 87 SmA 178 dec	8
[La(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>10</sub> H <sub>21</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 70 SmA 177 dec	8
[Nd(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>10</sub> H <sub>21</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 74 SmA 173 dec	8
[La(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 87 SmA 187 dec	8
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 96 SmA 164 dec	8
[La(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 88 SmA 169 dec	8
[Nd(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 85 SmA 170 dec	8
[Eu(LH) <sub>2</sub> LCI <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 146 SmA 236 I	7
[La(LH) <sub>2</sub> L(DOS) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 113 SmA 132 I	19
[Gd(LH) <sub>2</sub> L(DOS) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 106 SmA 113 I	19
[Tb(LH) <sub>2</sub> L(DOS) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 106 SmA 126 I	19
[Dy(LH) <sub>2</sub> L(DOS) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 102 SmA 124 I	19

**Table 2. Thermal Behavior of the Lanthanide Complexes of the *N*-Alkyl-4-(3,4-dialkoxybenzoyloxy)salicylaldehyde Schiff's Bases**

compound	R	R'	temperatures (°C)	ref
[Nd(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 84 Col <sub>h</sub> 112 I	9
[Dy(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 85 Col <sub>h</sub> 146 I	9
[Er(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 77 Col <sub>h</sub> 128 I	9
[Nd(LH) <sub>2</sub> L(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 57 Col <sub>h</sub> 88 I	9
[Gd(LH) <sub>2</sub> L(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 51 Col <sub>h</sub> 89 I	9
[Tb(LH) <sub>2</sub> L(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 48 Col <sub>h</sub> 88 I	9
[Dy(LH) <sub>2</sub> L(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 51 Col <sub>h</sub> 88 I	9
[Er(LH) <sub>2</sub> L(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 51 Col <sub>h</sub> 88 I	9

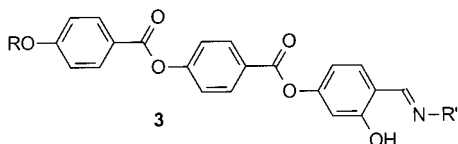
workers were able to obtain lanthanide complexes with a hexagonal columnar mesophase (ligand **2**).<sup>9</sup> The authors also showed that substantially lower



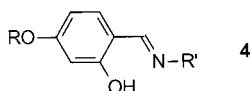
transition temperatures could be achieved by making use of the triflate group as the counterion. An overview of the lanthanide complexes of the two-ring Schiff's base ligands and their transition temperatures is given in Tables 1 and 2.

Binnemans et al. prepared lanthanide complexes of a Schiff's base ligand with three aromatic rings (**3**,  $R = C_6H_{13}$ ,  $R' = C_{18}H_{37}$ ).<sup>10</sup> The influence of the lanthanide ion on the transition temperatures is marginal, although it was found that the nematic

phase of the ligand was suppressed, in favor of the smectic C phase.



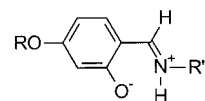
Taking the unfavorable physical properties of the first generation Schiff's base complexes (high viscous mesophase, low thermal stability) into account, research in calamitic lanthanide complexes would have died silently if no better systems had been found. A major breakthrough came in 1994, when again Galyametdinov and co-workers discovered lanthanide Schiff's base complexes with an enhanced thermal stability and exhibiting a smectic A phase with a relatively low viscosity.<sup>11</sup> The ligands in these complexes are remarkable, because they contain one aromatic ring only and they do not form a mesophase themselves (ligand **4**); mesomorphism is induced by



the lanthanide ion. Such a behavior is quite unique. In many cases the mesophase of organic ligands is destroyed upon complexation, or at least the mesophase is greatly destabilized. Determination of the stoichiometry and the structure of the complexes turned out to be a challenge, since no single crystals suitable for single-crystal X-ray diffraction could be obtained. The first report compounds gave analytical results in agreement with the stoichiometry  $[\text{Ln}(\text{LH})_2\text{LX}_2]$ , where LH is the salicylaldimine Schiff's base, L is its deprotonated form, and X is the counterion.<sup>11,12</sup> The complexes were prepared by reaction of the Schiff's base ligand with an excess of the lanthanide salt in absolute ethanol. Because the complexes are insoluble in ethanol—in contrast to the ligand and lanthanide salts—the complexes precipitate upon formation. The complexes can be purified by extensive washing with ethanol, not by recrystallization. They are soluble in halogenated organic solvents, such as chloroform, dichloromethane, or carbon tetrachloride. The complexes with chloride counterions have a much lower solubility than the nitrate complexes.

Just as in the case of the two-ring Schiff's base complexes, a complex with a chloride counterion was found to have much higher transition temperatures than analogous compounds with nitrate counterions. Soon after the discovery of this type of metallomesogens, it became evident that they have very interesting magnetic properties, such as a huge magnetic anisotropy.<sup>13</sup> Due to the high magnetic anisotropy, the mesophase formed by these compounds can be much easier aligned in an external magnetic field than organic liquid crystals. The magnetic behavior of the Schiff's base complexes is discussed in detail in section VII.A.

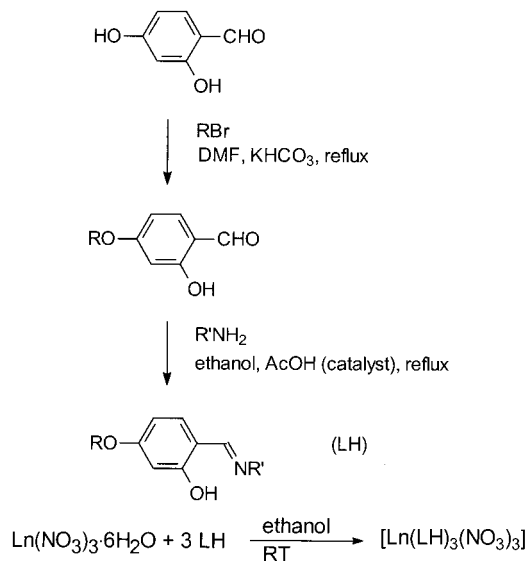
Further work done by the research groups of Galyametdinov, Bruce, and Binnemans gave more



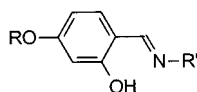
**Figure 3.** In the lanthanide complexes, the Schiff's bases are present in zwitterionic form. The phenolic proton has been transferred to the imine nitrogen.

insight in the structure of these Schiff's base complexes.<sup>4,14</sup> By performing the complex formation at room temperature or just above, compounds could be obtained with a stoichiometry consistent with  $[\text{Ln}(\text{LH})_3(\text{NO}_3)_3]$  (Scheme 1). <sup>1</sup>H NMR studies on

#### Scheme 1



diamagnetic lanthanum(III) complexes showed that in the complexes the Schiff's base ligand is present in a *zwitterionic form*, i.e., the phenolic oxygen has been transferred to the imine nitrogen (Figure 3).<sup>4</sup> It was found that the <sup>1</sup>H signal corresponding to the imine hydrogen (CH=N) is broadened in the lanthanum(III) complex in comparison with the same signal in the Schiff's base ligand. In some cases, even a splitting of the imine signal was observed. The value of the coupling constant was on the same order of magnitude as the expected value for a trans-coupling in H-C=N<sup>+</sup>-H. This and the fact that the signal at  $\delta \approx 12.29$  ppm belongs to a NH resonance and not to an OH resonance could be determined by a homonuclear decoupling experiment. Irradiation of the NH signal leads to a collapse of the CH=N doublet. Further evidence for the existence of a zwitterionic form in the metal complexes is given by infrared spectra, and more particularly by the band frequencies of the C=N vibration. The shift to higher wavenumbers in the complexes compared to the corresponding values in the ligands indicates that the nitrogen atom is not involved in the complex formation and that a C=N<sup>+</sup> group is present. The best piece of evidence is the single crystal X-ray structure of homologous nonmesogenic complexes formed by ligands with short alkyl chains (Figure 4). The crystal structure shows that three ligands and three nitrate groups are present for each metal ion. The Schiff's base ligands are indeed in the zwitterionic form, as

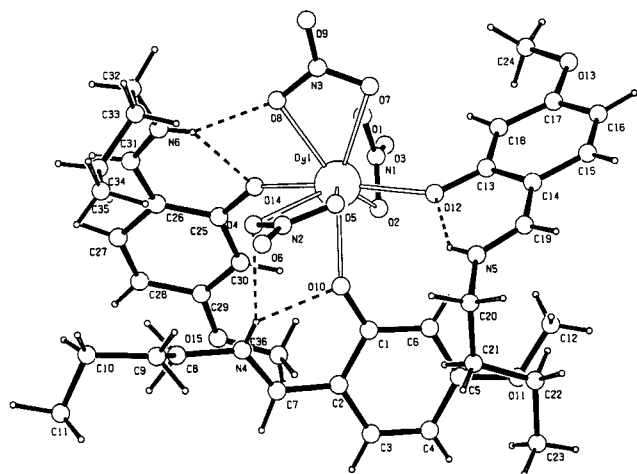
**Table 3. Thermal Behavior of the Lanthanide Complexes of the One-Ring Schiff's Base Ligands**

compound	R	R'	temp (°C)	ref	compound	R	R'	temp (°C)	ref
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	CH <sub>3</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 119 SmA 127 A	14	[Tb(LH) <sub>3</sub> (C <sub>18</sub> H <sub>37</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 75 SmA 84 I	21
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>2</sub> H <sub>5</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 132 SmA 147 A	14	[Tb(LH) <sub>3</sub> (C <sub>19</sub> H <sub>39</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 72 SmA 89 I	21
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>3</sub> H <sub>7</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 112 SmA 149 A	14	[Er(LH) <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 90 SmA 129 I	21
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>4</sub> H <sub>9</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 119 SmA 158 A	14	[Er(LH) <sub>3</sub> (C <sub>6</sub> H <sub>17</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 100 SmA 113 I	21
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>5</sub> H <sub>11</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 115 SmA 155 A	14	[Er(LH) <sub>3</sub> (C <sub>18</sub> H <sub>37</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 70 SmA 90 I	21
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>6</sub> H <sub>13</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 110 SmA 156 A	14	[La(LH) <sub>3</sub> {CF <sub>3</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 110 SmA 121 I	22
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ] <sup>a</sup>	C <sub>7</sub> H <sub>15</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 104 SmA 155 A	14	[Pr(LH) <sub>3</sub> {CF <sub>3</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 113 SmA 120 I	22
[Tb(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ] <sup>a</sup>	C <sub>7</sub> H <sub>15</sub>	C <sub>14</sub> H <sub>29</sub>	Cr 141 (SmA 139) I	12	[Nd(LH) <sub>3</sub> {CF <sub>3</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 114 SmA 122 I	22
[Dy(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ] <sup>a</sup>	C <sub>7</sub> H <sub>15</sub>	C <sub>14</sub> H <sub>29</sub>	Cr 143 (SmA 142) I	12	[Eu(LH) <sub>3</sub> {CF <sub>3</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 110 SmA 125 I	22
[La(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 128 SmA 149 I	5	[Gd(LH) <sub>3</sub> {CF <sub>3</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 106 SmA 119 I	22
[Gd(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 128 SmA 146 I	5	[Tb(LH) <sub>3</sub> {CF <sub>3</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 103 SmA 119 I	22
[Dy(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 140 SmA 142 I	5	[Ho(LH) <sub>3</sub> {CF <sub>3</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 96 SmA 120 I	22
[La(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ] <sup>a</sup>	C <sub>7</sub> H <sub>15</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 146 (SmA 145) I	11	[Er(LH) <sub>3</sub> {CF <sub>3</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 98 SmA 125 I	22
			Cr 127 SmA 165 I	23	[La(LH) <sub>3</sub> {CHF <sub>2</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 111 SmA 131 I	22
[Nd(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 135 SmA 146 I	23	[Ce(LH) <sub>3</sub> {CHF <sub>2</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 114 SmA 131 I	22
[Eu(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 140 SmA 153 I	23	[Pr(LH) <sub>3</sub> {CHF <sub>2</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 115 SmA 135 I	22
[Gd(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 135 SmA 146 I	11	[Nd(LH) <sub>3</sub> {CHF <sub>2</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 109 SmA 133 I	22
			Cr 148 SmA 155 I	23	[Sm(LH) <sub>3</sub> {CHF <sub>2</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 106 SmA 131 I	22
			Cr 148 SmA 151 I	23	[Eu(LH) <sub>3</sub> {CHF <sub>2</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 106 SmA 132 I	22
[Tb(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 182 SmA 203 I	23	[Gd(LH) <sub>3</sub> {CHF <sub>2</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 108 SmA 126 I	22
[Tb(LH) <sub>2</sub> LCl <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 151 (SmA 150) I	23	[Tb(LH) <sub>3</sub> {CHF <sub>2</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 99 SmA 128 I	22
[Dy(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ] <sup>a</sup>	C <sub>7</sub> H <sub>15</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 138 SmA 141 I	11	[Dy(LH) <sub>3</sub> {CHF <sub>2</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 102 SmA 125 I	22
			Cr 151 (SmA 150) I	23	[Ho(LH) <sub>3</sub> {CHF <sub>2</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 98 SmA 125 I	22
[Y(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 132 SmA 141 I	16	[Er(LH) <sub>3</sub> {CHF <sub>2</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 98 SmA 140 I	22
[La(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 83 SmA 165 I	16	[Yb(LH) <sub>3</sub> {CHF <sub>2</sub> (CF) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 103 SmA 138 I	22
[Pr(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 90 Sm 163 I	16	[Gd(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 115 SmA 147 I	13
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 95 SmA 159 I	14, 16	[Tb(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 114 SmA 147 I	13
[Sm(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 105 SmA 154 I	16	[La(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 81 SmA 138 I	12
[Eu(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 108 SmA 151 I	16	[La(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 81 SmA 138 I	14
[Gd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 121 SmA 150 I	16	[La(LH) <sub>2</sub> L(DOS) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 78 SmA 92 I	19
[Tb(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 128 SmA 148 I	16	[Nd(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 100 SmA 151 I	12
[Dy(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 131 SmA 146 I	16	[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 100 SmA 158 I	14
[Ho(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 134 SmA 144 I	16	[Nd(LH) <sub>2</sub> LCl <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 162 SmA 187 I	18
[Er(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 135 SmA 142 I	16	[Nd(LH) <sub>2</sub> L(DOS) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 61 SmA 98 I	18
[Tm(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 139 SmA 142 I	16	[Eu(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 113 SmA 147 I	12
[Yb(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 138 SmA 141 I	16	[Gd(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 112 SmA 144 I	12
[Lu(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 135 SmA 139 I	16	[Gd(LH) <sub>2</sub> LCl <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 164 SmA 185 I	12
[Y(LH) <sub>3</sub> Cl <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 175 SmA 192 I	17	[Gd(LH) <sub>2</sub> LCl <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 164 SmA 188 I	18
[Pr(LH) <sub>3</sub> Cl <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 158 SmA 187 I	17	[Gd(LH) <sub>2</sub> L(DOS) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 59 SmA 112 I	18
[Sm(LH) <sub>3</sub> Cl <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 168 SmA 161 I	17				Cr 61 SmA 110 I	19
[Eu(LH) <sub>3</sub> Cl <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 170 SmA 193 I	17	[Tb(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 114 SmA 148 I	12
[Gd(LH) <sub>3</sub> Cl <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 171 SmA 194 I	17				Cr 96 SmA 148 I	19
[Tb(LH) <sub>3</sub> Cl <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 169 SmA 191 I	17				Cr 137 SmA 186 I	19
[Dy(LH) <sub>3</sub> Cl <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 174 SmA 192 I	17	[Tb(LH) <sub>2</sub> L(DOS) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 71 SmA 86 I	19
[Ho(LH) <sub>3</sub> Cl <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 174 SmA 191 I	17	[Tb(LH) <sub>2</sub> L(Pr <sup>+</sup> SO <sub>4</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 102 SmA 138 I	19
[Er(LH) <sub>3</sub> Cl <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 174 SmA 188 I	17	[Dy(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 130 SmA 144 I	12
[Tm(LH) <sub>3</sub> Cl <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 174 SmA 190 I	17	[Dy(LH) <sub>2</sub> LCl <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 166 SmA 186 I	18
[Yb(LH) <sub>3</sub> Cl <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 176 SmA 193 I	17	[Dy(LH) <sub>2</sub> L(DOS) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 61 SmA 89 I	18
[Lu(LH) <sub>3</sub> Cl <sub>3</sub> ]	C <sub>8</sub> H <sub>17</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 175 SmA 190 I	17				Cr 61 SmA 90 I	19
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>9</sub> H <sub>21</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 100 SmA 158 I	14				Cr 129 SmA 143 I	12
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>10</sub> H <sub>21</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 101 SmA 158 I	14	[Ho(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 168 SmA 185 I	18
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>11</sub> H <sub>23</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 103 SmA 157 I	14	[Ho(LH) <sub>2</sub> LCl <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 59 SmA 81 I	18
[Pr(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 105 SmA 148 I	14	[Ho(LH) <sub>2</sub> L(DOS) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 127 SmA 146 I	12
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 105 SmA 147 I	14	[Yb(LH) <sub>2</sub> LCl <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 169 SmA 185 I	18
[Gd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 107 SmA 145 I	14	[Yb(LH) <sub>2</sub> L(DOS) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 59 SmA 111 I	18
[Tb(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 107 SmA 147 I	14	[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>13</sub> H <sub>27</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 100 SmA 158 I	14
[Er(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 107 SmA 147 I	14	[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>8</sub> H <sub>17</sub>	Cr 116 SmA 158 I	15
[Tb(LH) <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 85 SmA 123 I	21	[Gd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>8</sub> H <sub>17</sub>	Cr 125 SmA 143 I	15
[Tb(LH) <sub>3</sub> (C <sub>3</sub> H <sub>7</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 102 SmA 138 I	21	[Ho(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ] <sup>a</sup>	C <sub>14</sub> H <sub>29</sub>	C <sub>8</sub> H <sub>17</sub>	Cr [143 SmA] 133 I	15
[Tb(LH) <sub>3</sub> (C <sub>4</sub> H <sub>9</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 107 SmA 142 I	21	[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 106 SmA 160 I	15
[Tb(LH) <sub>3</sub> (C <sub>5</sub> H <sub>11</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 103 SmA 138 I	21	[Gd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 130 SmA 150 I	15
[Tb(LH) <sub>3</sub> (C <sub>6</sub> H <sub>13</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 100 SmA 131 I	21	[Ho(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 138 SmA 144 I	15
[Tb(LH) <sub>3</sub> (C <sub>7</sub> H <sub>15</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 106 SmA 140 I	21	[La(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr	

**Table 3 (Continued)**

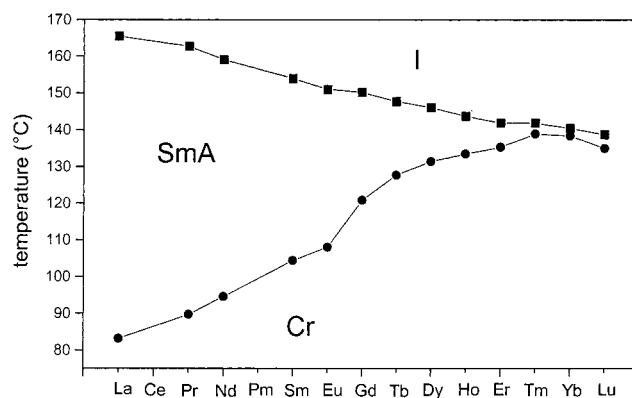
compound	R	R'	temp (°C)	ref	compound	R	R'	temp (°C)	ref
[Ce(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 66 SmA 80 I	20	[Yb(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 60 SmA 87 I	20
[Pr(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 66 SmA 80 I	20	[Lu(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 59 SmA 86 I	20
[Nd(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 65 SmA 79 I	20	[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>15</sub> H <sub>31</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 103 SmA 154 I	14
[Sm(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 62 SmA 78 I	20	[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>16</sub> H <sub>33</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 103 SmA 152 I	14
[Eu(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 62 SmA 78 I	20	[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>17</sub> H <sub>35</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 104 SmA 150 I	14
[Gd(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 61 SmA 77 I	20	[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>18</sub> H <sub>37</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 101 SmA 150 I	14
[Tb(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 61 SmA 80 I	20	[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>19</sub> H <sub>39</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 101 SmA 146 I	14
[Dy(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 61 SmA 82 I	20	[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>20</sub> H <sub>41</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 100 SmA 144 I	14
[Ho(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 62 SmA 84 I	20	[Tm(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 61 SmA 86 I	20
[Er(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 61 SmA 85 I	20	[Yb(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 60 SmA 87 I	20
[Tm(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 61 SmA 86 I	20					

<sup>a</sup> Monotropic liquid crystal.



**Figure 4.** Crystal structure of complex [Dy(LH)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>]. LH is the Schiff's base ligand shown in Figure 3, with R = CH<sub>3</sub> and R' = C<sub>4</sub>H<sub>9</sub> (Reprinted from ref 14. Copyright 2000 American Chemical Society).

assumed from the spectroscopic data. The ligands coordinate to the metal ion via the negatively charged phenolic oxygen only. No binding occurs between the lanthanide ion and the imine nitrogen, and the three nitrate groups coordinate in a bidentate fashion. The coordination number of the lanthanide ion is 9, and the coordination polyhedron can be described as a distorted monocapped square antiprism. The phenolic proton is transferred to the imine nitrogen, but two of the three transferred protons in the complex form a double hydrogen bond (with the phenolic oxygen and with an oxygen atom of a nitrate group), whereas the third proton only forms a single hydrogen bond (with the phenolic oxygen). The formation of a zwitterionic form can be rationalized by the tendency of the lanthanide ions to coordinate to negatively charged ligands (with a preference for O-donor ligands). By transfer of the phenolic proton to the imine nitrogen, the phenolic oxygen becomes negatively charged and can coordinate to the lanthanide ion. The *N*-alkyl-substituted imine nitrogen has sufficient basic character to take up the proton. However, under the same reaction conditions, no lanthanide complexes are formed with *N*-aryl Schiff's bases. In this type of ligand, the imine nitrogen is probably not basic enough for the uptake of the proton (and thus no zwitterion can be formed). It should be noticed that it is not feasible to deprotonate the Schiff's base ligand, because in the complexes formed no counter-

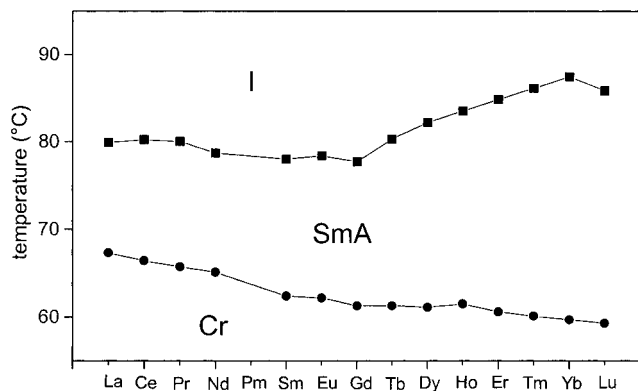


**Figure 5.** Influence of the lanthanide ion on the transition temperatures of [Ln(LH)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>] complexes. LH is the Schiff's base ligand shown in Figure 3, with R = C<sub>8</sub>H<sub>17</sub> and R' = C<sub>18</sub>H<sub>37</sub>. Cr = crystalline solid, SmA = smectic A mesophase, I = isotropic liquid. (Drawn using the data in Table 1 of ref 16.)

ions will be present and probably they will have a polymeric structure. It turned out that the stoichiometry of these complexes is variable. Although the complexes prepared at room temperature have the [Ln(LH)<sub>3</sub>X<sub>3</sub>] stoichiometry, for complexes prepared at higher temperatures, often the stoichiometry [Ln(LH)<sub>2</sub>LX<sub>2</sub>] is observed. This can be explained by an increased dissociation of the phenolic proton of the Schiff's base ligand at higher temperatures. The temperature is thus a critical factor in the synthesis. One should not heat the ethanolic solution above 40 °C, if formation of [Ln(LH)<sub>3</sub>X<sub>3</sub>] complexes is desired.

All the lanthanide complexes with the one-ring salicylaldimine Schiff's base ligands exhibit without exception a smectic A phase. An overview of these complexes and their transition temperatures is given in Table 3. Neither the alkoxy chain length<sup>14</sup> nor the *N*-alkyl chain length has a substantial influence on the transition temperatures.<sup>15</sup> However, for the nitrate series, the lanthanide ion influences the mesophase behavior greatly (Figure 5).<sup>16</sup> Whereas the melting point increases over the lanthanide series, the clearing decreases simultaneously, so the overall effect is a decrease of the mesophase stability range over the lanthanide series.

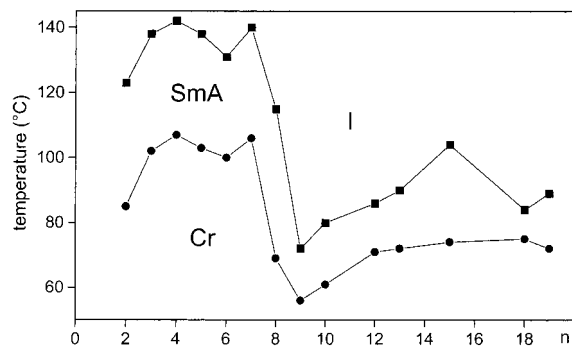
Counterions other than the nitrate group have been investigated, but much less is known about their structural features, except that always zwitterionic Schiff's base ligands are present. It has already been mentioned that the chloride complexes have higher



**Figure 6.** Influence of the lanthanide ion on the transition temperatures of  $[\text{Ln}(\text{LH})_3(\text{DOS})_3]$  complexes. LH is the Schiff's base ligand shown in Figure 3, with  $\text{R} = \text{C}_{14}\text{H}_{29}$ ,  $\text{R}' = \text{C}_{18}\text{H}_{37}$ , and  $\text{DOS} = \text{C}_{12}\text{H}_{25}\text{SO}_4$ . Cr = crystalline solid, SmA = smectic A mesophase, I = isotropic liquid. (Drawn using the data in Table 2 of ref 20.)

transition temperatures than the corresponding nitrate complexes. Because chloride ions act as a monodentate ligand only and because the lanthanide ions prefer high coordination numbers (typically 8 or 9), complexes of the type  $[\text{Ln}(\text{LH})_3\text{Cl}_3]$  are most likely dimeric or even oligomeric.<sup>17</sup> In contrast to the nitrate complexes, the type of lanthanide ion has a much less pronounced influence on the transition temperatures of the chloride complexes: both melting and clearing points are virtually unchanged over the lanthanide series.

An interesting class of compounds are the Schiff's base complexes with dodecyl sulfate counterions (or with alkyl sulfate counterions in general), because their transition temperatures are much lower than those of the nitrate or chloride complexes. Complexes with dodecyl sulfate counterions were first prepared by Binnemans et al. via a metathesis reaction between the corresponding chloride complex and Ag-DOS (DOS = dodecyl sulfate).<sup>18</sup> However, Galyametdinov et al. found a more elegant synthetic route, namely the reaction of  $\text{Ln}(\text{DOS})_3 \cdot x\text{H}_2\text{O}$  salts with the Schiff's base ligand.<sup>19</sup> The transition temperatures of the complexes are greatly reduced in comparison with those of the chloride complexes: the melting points are reduced from ca. 160 to ca. 60 °C and the clearing points from ca. 180 to ca. 100 °C. These Schiff's base complexes have an opposite temperature dependence on the lanthanide ion in comparison with the nitrate complexes, in the sense that the mesophase stability range increases over the lanthanide series (Figure 6).<sup>20</sup> The influence of the alkyl chain length on the transition temperatures of terbium(III) and erbium(III) complexes was investigated by Galyametdinov and co-workers (Figure 7).<sup>21</sup> The transition temperature increases when the chain length is increased from ethyl sulfate to butyl sulfate and then decreases sharply to nonyl sulfate (the heptyl sulfate being an exception). Again, from nonyl sulfate to nonadecyl sulfate the transition temperatures decrease gradually. Because both the melting point and the clearing point are influenced by the same extent, the mesophase stability range does not depend largely on the alkyl chain length. Although the perfluoroalkyl sulfate complexes have slightly



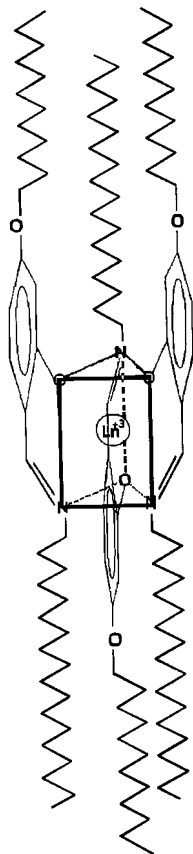
**Figure 7.** Influence of the alkyl sulfate chain length on the transition temperatures of  $[\text{Tb}(\text{LH})_3(\text{C}_n\text{H}_{2n+1}\text{SO}_4)_3]$  complexes. LH is the Schiff's base ligand shown in Figure 3, with  $\text{R} = \text{C}_{12}\text{H}_{25}$  and  $\text{R}' = \text{C}_{16}\text{H}_{33}$ . Cr = crystalline solid, SmA = smectic A mesophase, I = isotropic liquid. (Drawn using the data in Table 1 of ref 21.)

higher transition temperatures than the alkyl sulfate complexes, they have the great advantage that their mesophase has a much lower viscosity.<sup>22</sup> The low viscosity is most probably due to the immiscibility of the alkyl chains of the Schiff's base ligand and the perfluoroalkyl chains of the counterion. These complexes can be aligned much more easily in an external magnetic field. Replacement of the  $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{SO}_4^-$  counterion by  $\text{CHF}_2(\text{CF}_2)_2\text{CH}_2\text{SO}_4^-$  has a significant influence on the transition temperatures.

A disadvantage of metallomesogens is their low thermal stability in comparison with the classic organic liquid crystals. Many metallomesogens decompose at the clearing point (or they even decompose in the mesophase without clearing at all). In this context the thermal stability of the Schiff's base complexes is remarkable. Thermal decomposition starts more than 100 °C above the clearing point. This makes these compounds well-suited for physical studies, because alignment can in most cases only be achieved by heating the compounds to the isotropic liquid and cooling them into the mesophase. In general, no supercooling is observed for the clearing point of liquid crystals, so that clearing is observed both on cooling and heating at the same temperature. However, for the Schiff's base complexes and especially those with alkyl sulfate counterions, supercooling can be as large as 5–25 °C.<sup>21</sup> The Schiff's base complexes have a low tendency to crystallize when their mesophase is being cooled. Most probably this is due to the high viscosity of the smectic A phase. The mesophase can be supercooled into a glass state.<sup>12</sup> In this way, anisotropic glasses can be obtained. Glass formation is especially evident in thin microscope preparates, where the defect texture can be retained at room temperature. The vitrified mesophase is stable for several days, but they tend to crystallize over a longer time period.

Although the crystal structures of the nonmesomorphic Schiff's base complexes have been determined, much less is known about the actual structure of the mesomorphic lanthanide complexes themselves. The presence of a smectic A phase dictates that the Schiff's base ligands have to be arranged around the central metal ion in such a way that the

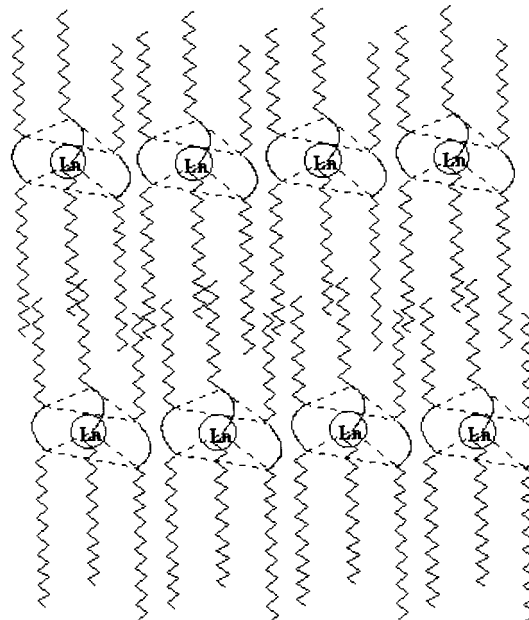




**Figure 8.** Molecular structure of the  $[\text{Ln}(\text{LH})_3(\text{NO}_3)_3]$  Schiff's base complexes, as suggested by Galyametdinov et al.<sup>12</sup> The nitrate groups have been omitted for clarity (Reprinted from ref 12. Copyright 1996 American Chemical Society).

formation of a layered structure is possible. Spectroscopic data indicate that the first coordination sphere around the lanthanide ion is not changed by elongation of the alkyl chains. Therefore, it was anticipated that the bonding in the nonmesogenic complexes is the same as in the mesogenic complexes. Of course, changes in the packing of the molecules can be assumed. A molecular structure has been proposed by Galyametdinov and co-workers that can be described as a trigonal prism where the nitrate groups occupy equatorial or axial positions (Figure 8).<sup>12,23</sup> Because the smectic layer thickness  $d$  (as determined by X-ray diffraction) was found to be shorter than the calculated length of the Schiff's base ligand, it was assumed that the molecules of each layer penetrate the adjacent layer to a limited depth. Although we know that, in contrast to the proposed structure, the nitrogen atoms in the Schiff's base ligands do not coordinate to the lanthanide ion, it is likely that the proposed molecular arrangement of the lanthanide complexes in the smectic layer is close to reality (Figure 9). This view is supported by the existence of a class of compounds, called "epitaxigen" by Simon.<sup>24</sup>

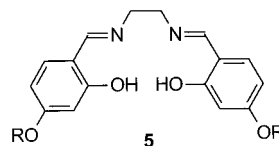
The magnetic properties of the Schiff's base complexes are discussed in section VII.A. The spectroscopic properties have been investigated much less intensively. Because of the presence of the  $\text{N}^+-\text{H}$  group in the zwitterionic ligand, which can effectively deactivate the excited states of the lanthanide ions,



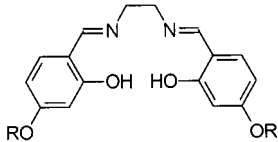
**Figure 9.** Schematic representation of the  $[\text{Ln}(\text{LH})_3(\text{NO}_3)_3]$  Schiff's base complexes in a smectic A phase. The nitrate groups have been omitted for clarity.

most of the complexes show a weak photoluminescence only or do not luminesce at all. Interestingly, the europium complexes with the perfluorinated alkyl sulfate counterions do show a strong luminescence.<sup>22</sup> It was found that the europium complexes feel in these complexes a very strong crystal field. In fact, the  $B_0^2$  crystal-field parameter for these compounds are among the largest ever reported for europium complexes. The absorption spectra of the Schiff's base complexes dissolved in chloroform give evidence for  $f-f$  transitions with a much enhanced intensity for the so-called *hypersensitive transitions*.<sup>25</sup> Temperature-dependent absorption and linear dichroism spectra of neodymium(III), terbium(III), and erbium(III) complexes have been recorded from the crystalline to the isotropic state, through the mesophase.<sup>26</sup>

In all the Schiff's base complexes described so far, no base was used to deprotonate the Schiff's base ligand. Therefore, the Schiff's base binds in a neutral, albeit a zwitterionic, form to the central metal ion, resulting in complexes with stoichiometry  $[\text{Ln}(\text{LH})_3\text{X}_3]$ . It was also mentioned that, in some complexes, only one of the ligands loses spontaneously a proton, giving complexes of stoichiometry  $[\text{Ln}(\text{LH})_2\text{LX}_2]$ . With dimeric salen-type ligands (salen = 2,2'-*N,N*-bis(salicylidene)ethylenediamine) it was possible to form, by use of piperidine as the base, neutral complexes in which the lanthanide ion was bound to one monoanionic ligand and one dianionic ligands (ligand 5).<sup>4,27</sup> The ligands themselves are

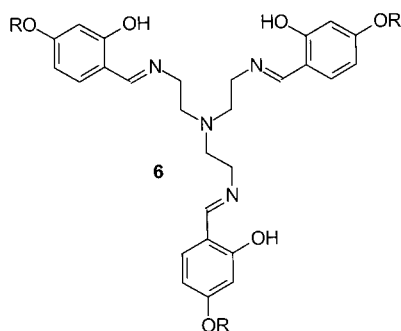


mesomorphic (SmC or SmA) and the bis(salen) complexes exhibit a highly viscous smectic meso-

**Table 4. Thermal Behavior of the Lanthanide Complexes of the Salen-Type Schiff's Base Ligands LH<sub>2</sub>**


compound	R	temperatures (°C)	ref
[La(LH <sub>2</sub> ) <sub>2</sub> Cl <sub>3</sub> ]·4H <sub>2</sub> O	C <sub>12</sub> H <sub>25</sub>	Cr 220 SmX 288 dec	27
[La(LH <sub>2</sub> ) <sub>2</sub> (CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub> ]·4H <sub>2</sub> O	C <sub>12</sub> H <sub>25</sub>	Cr 170 SmX 240 I	27
[La(LH)(LH <sub>2</sub> )]·4H <sub>2</sub> O	C <sub>12</sub> H <sub>25</sub>	Cr 176 SmX 190 I	27
[Nd(LH)(LH <sub>2</sub> )]	C <sub>12</sub> H <sub>25</sub>	Cr 182 SmX 209 I	27
[Eu(LH)(LH <sub>2</sub> )]·2H <sub>2</sub> O	C <sub>12</sub> H <sub>25</sub>	Cr 150 SmX 190 I	4
[Er(LH)(LH <sub>2</sub> )]·3H <sub>2</sub> O	C <sub>12</sub> H <sub>25</sub>	Cr 165 SmX 230 I	4
[Nd(LH)(LH <sub>2</sub> )]	C <sub>12</sub> H <sub>25</sub> O-C <sub>6</sub> H <sub>4</sub> CO	Cr 140 SmX 200 dec	4

phase. In the absence of a base, the salen-type ligands form complexes with three counterions, but with two ligands for each lanthanide ion. An overview of the transition temperatures is given in Table 4. The ligand design was taken a step further and encapsulation of the lanthanide ion in a tripodal Schiff's base ligand **6** was attempted.<sup>4</sup> Lanthanide

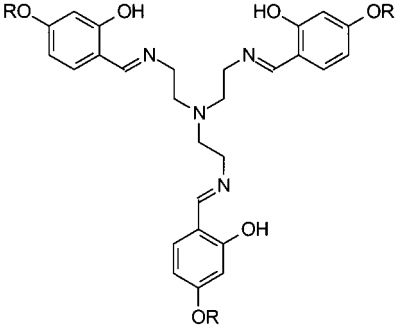


complexes were obtained as neutral species, for which, on the basis of the crystal structure of an analogous compound with short alkyl chains, a dimeric complex has been proposed. The complexes show a mesophase that could not yet be unequivocally identified, but which is most probably a smectic phase. The transition temperatures are quite high: the majority of the complexes melt only above 200 °C, with clearing points up to 280 °C (Table 5).

All the Schiff's base complexes discussed so far are low-molecular weight complexes. An erbium(III)-containing methacrylate metallo-polymer was prepared by free-radical polymerization of a Schiff's base monomer, followed by complex formation with hydrated erbium nitrate.<sup>28</sup> By XRD, the presence of a smectic mesophase was shown. A special feature of the polymer is that the complexing group is an *N*-aryl-substituted Schiff's base, rather than an *N*-alkyl-substituted one. No further structural data have been reported.

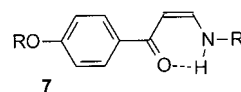
## B. β-Enaminoketonates

Although β-enaminoketonates (β-aminovinyl ketones) are structurally closely related to the Schiff's bases, their lanthanide complexes have been investigated

**Table 5. Thermal Behavior of the Lanthanide Complexes of the Tripodal Schiff's Base Ligands LH<sub>3</sub>**


compound	R	temperatures (°C)	ref
[LaL <sub>3</sub> ]·H <sub>2</sub> O	C <sub>12</sub> H <sub>25</sub>	Cr 209 SmX 221 I	4
[GdL <sub>3</sub> ]·H <sub>2</sub> O	C <sub>12</sub> H <sub>25</sub>	Cr 205 SmX 278 I	4
[ErL <sub>3</sub> ]·2H <sub>2</sub> O	C <sub>12</sub> H <sub>25</sub>	Cr 230 SmX 270 I	4
[LaL <sub>3</sub> ]·4H <sub>2</sub> O	C <sub>12</sub> H <sub>25</sub> OC <sub>6</sub> H <sub>4</sub> CO	Cr 216 SmX 230 I	4
[LaL <sub>3</sub> ]·H <sub>2</sub> O	3,4-(C <sub>12</sub> H <sub>25</sub> O)C <sub>6</sub> H <sub>3</sub> CO	Cr 122 SmX 180 I	4

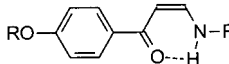
much less intensively (ligand **7**).<sup>29–31</sup> Upon reaction with lanthanide nitrates or chlorides in ethanol, the



β-enaminoketonates form complexes with stoichiometry [Ln(LH)<sub>2</sub>LX<sub>2</sub>] (X = NO<sub>3</sub>, Cl). The <sup>1</sup>H NMR spectrum of a lanthanum(III) compound shows that two ligands (LH) have the ketoamine structure, whereas the third ligand (L) has the enolimine structure.<sup>31</sup> A coordination number of 8 was proposed for the complexes with nitrate ions, the three β-enaminoketonate ligands being bidentate and the two nitrates being monodentate. The latter assumption is unlikely to be true, because in lanthanide complexes nitrate ions are nearly always bidentate. A coordination number of 7 is more realistic (three monodentate β-enaminoketonate ligands and two bidentate nitrates). Further studies are necessary to elucidate this problem. The length-to-width ratio of the rotation cylinder of the complexes was calculated to vary between 2.9 and 3.8, depending on the length of the alkyl chain lengths. The ligands do not form a liquid-crystal phase, but the lanthanide complexes exhibit a SmA phase. The transition temperatures of the complexes are given in Table 6. As in the case of the Schiff's base complexes, an increase in transition temperatures was observed when the nitrate ions were substituted for chloride ions. The influence of the lanthanide ion on the mesophase behavior has not been investigated yet. The layer spacings of a lanthanum(III) and a dysprosium(III) complex (R = C<sub>7</sub>H<sub>15</sub>, X = NO<sub>3</sub>) are respectively 30.7 and 30.0 Å, which is smaller than the length of the ligand with the alkyl chains in the all-trans conformation (estimated to be ~40 Å by molecular modeling calculations).<sup>30</sup> The magnetic properties of the β-enaminoketonate complexes are discussed in section VII.A.

## C. β-Diketones

The trivalent lanthanide ions form three distinct types of complexes with 1,3-diketones (β-diketones):

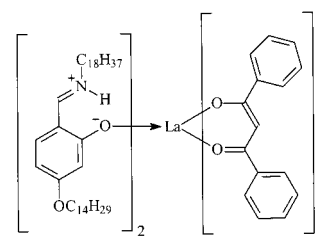
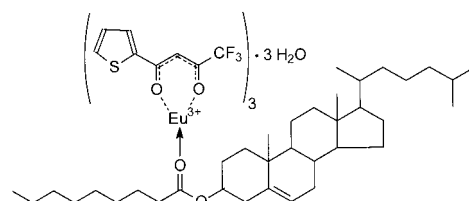
**Table 6. Thermal Behavior of  $\beta$ -Enaminoketone Compounds**


compound	R	R'	temperatures (°C)	ref
[La(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>12</sub> H <sub>12</sub>	Cr 142 SmA 153 I	31
[La(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 82 SmA 140 I	30
[Dy(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>7</sub> H <sub>15</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 121 SmA 135 I	30
[La(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 121 SmA 149 I	31
[Gd(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 127 SmA 152 I	31
[Tb(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 123 SmA 147 I	31
[Dy(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>12</sub> H <sub>25</sub>	Cr 125 SmA 147 I	31
[La(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 153 SmA 164 I	31
[Tb(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 143 SmA 154 I	31
[Dy(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 131 SmA 160 I	31
[Er(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	Cr 124 SmA 158 I	31
[La(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 96 SmX 160 I	29
			Cr 101 SmA 143 I	30
[Eu(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>27</sub>	Cr 140 SmA 160 I	31
[Gd(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 89 SmX 139 I	29
			Cr 105 SmA 146 I	30
[Tb(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 109 SmA 139 I	30
[Dy(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 84 SmX 134 I	29
			Cr 116 SmA 151 I	30
[Er(LH) <sub>2</sub> L(NO <sub>3</sub> ) <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 110 SmA 145 I	30
[Gd(LH) <sub>2</sub> LCl <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 159 SmA 173 I	30
[Tb(LH) <sub>2</sub> LCl <sub>2</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	Cr 161 SmA 165 I	30

(a) tris-complexes, (b) Lewis-base adducts of tris-complexes, and (c) tetrakis-complexes.<sup>32</sup> It is very difficult to obtain pure monomeric tris-complexes, because the coordination number of the lanthanide ion in this type of compounds is 6 and this is too low for saturation of the first coordination sphere of a trivalent lanthanide ion (except for tris-complexes of very bulky 1,3-diketones). Therefore, most of the tris-complexes form either dimeric (or even oligomeric or polymeric) complexes, or they form hydrates. The water molecules act as Lewis bases, and by adding two water molecules to a tris-complex, the coordination number can be increased to 8 and the coordination sphere will be saturated. The tris-complexes can also form adducts with other Lewis bases that have oxygen or nitrogen donor atoms, e.g. 2,2'-bipyridine, 1,10-phenanthroline, tri-*n*-octylphosphine. In the tetrakis complexes, four  $\beta$ -diketonate ligands result in a complex with coordination number 8 for the lanthanide ion and with a counteraction to balance the negative charge of the complex.

Although  $\beta$ -diketones are well-known as ligands of metallomesogens<sup>2</sup> and Swager and co-workers showed that  $\beta$ -diketones could be used to obtain eight-coordinate metallomesogens with zirconium(IV) as the central metal ion,<sup>33</sup> all attempts to synthesize liquid-crystalline lanthanide complexes with these mesogenic ligands failed up to now. The main reason is that the commonly used synthetic routes to  $\beta$ -diketonate complexes do not work for the mesogenic  $\beta$ -diketones, mainly due to solubility problems (the solvents in which the ligands are soluble do not dissolve the lanthanide precursor salts).

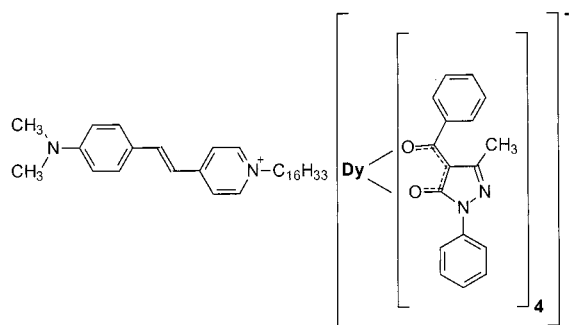
Binnemans and Lodewyckx showed that it is possible to obtain mesomorphic lanthanide complexes by forming Lewis-base adducts of simple tris( $\beta$ -diketonato)lanthanide(III) complexes with mesogenic ligands. More particularly, they studied bis-adducts

**Figure 10.** Lewis base adduct of the tris( $\beta$ -diketonato)-lanthanum(III) complex [La(dbm)<sub>3</sub>] and a nonmesomorphic salicylalimine Schiff's base.<sup>34</sup> The compound exhibits a monotropic smectic A phase: Cr 95 (SmA 81) I.**Figure 11.** Adduct of cholesteryl nonanoate to [Eu(tta)<sub>3</sub>] $\cdot$ 3H<sub>2</sub>O.

of [Ln(dbm)<sub>3</sub>] complexes (Hdbm = 1,3-diphenyl-1,3-propanedione or dibenzoylmethane) with the one-ring Schiff base ligands discussed in section II.A. (Figure 10).<sup>34</sup> The adducts are monotropic liquid crystals, exhibiting a smectic A phase upon cooling of the isotropic liquid.

Other attempts to obtain liquid-crystalline lanthanide complexes via Lewis-adduct formation to tris( $\beta$ -diketonato)lanthanide(III) complexes failed. Hapiot and Boyaval studied adducts of [Ln(tta)<sub>3</sub>] (Htta = thenoyltrifluoroacetone) and cholesteryl nonanoate and cholesteryl tetradecanoate (Figure 11).<sup>35,36</sup> By means of IR and <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectroscopy, including 2D NMR and relaxation techniques, they were able to show that a 1:1 adduct was formed between [Ln(tta)<sub>3</sub>] (Ln = Nd, Sm, Eu) and the cholesteryl ester and that bonding of the cholesteryl ester and the metal ion occurs through both oxygen atoms of the ester. This type of bonding can be considered as a pseudo-chelate type. The association constant *K* of the europium(III) complexes was estimated to be 22 mol<sup>-1</sup> L. The authors argue that the absence of a mesophase in the adducts is not only due to the large size of the [Ln(tta)<sub>3</sub>] moiety but also to a twisted conformation of the ligands (so the overall structure of the adduct is not rodlike). Optical properties of the corresponding europium(III) complexes in a cholesteric liquid crystal mixture have been investigated.<sup>37</sup> The authors measured refractive index, wavelength-dependent light scattering, optical absorption, and luminescence spectra.

Wang et al. reported the mesomorphic properties of lanthanide complexes of (*E*)-*N*-hexadecyl-4-(*N,N*-dimethylamino)stilbazolium tetrakis(1-phenyl-3-methyl-4-benzoyl-5-pyrazolonato)lanthanides(III), where the lanthanide was lanthanum(III), neodymium(III), dysprosium(III), and ytterbium(III) (Figure 12).<sup>38</sup> The complexes were investigated by differential scanning calorimetry (DSC), TG-DTA, and polarized optical microscopy. (*E*)-*N*-hexadecyl-4-(*N,N*-dimethylamino)stilbazolium bromide (*hemicyanine bromide*) was found to exhibit an unidentified smectic mesophase



**Figure 12.** Dysprosium(III) complex 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone with a hemicyanine counterion.

with a focal conical texture, melting at 96.3 °C and clearing at 246.3 °C. The lanthanide complexes except that of lanthanum(III) were also reported to be mesomorphic, showing a mosaic texture. In comparison with the stilbazolium bromide, both the melting and clearing points were reduced in the lanthanide complexes, but the mesophase range was narrower. The authors state that it ought to be possible to obtain interesting metallomesogens by the combination of the stilbazolium chromophore having large second-order molecular hyperpolarizability with functional lanthanide complexes. However, these results could not be reproduced by other workers.<sup>39</sup>

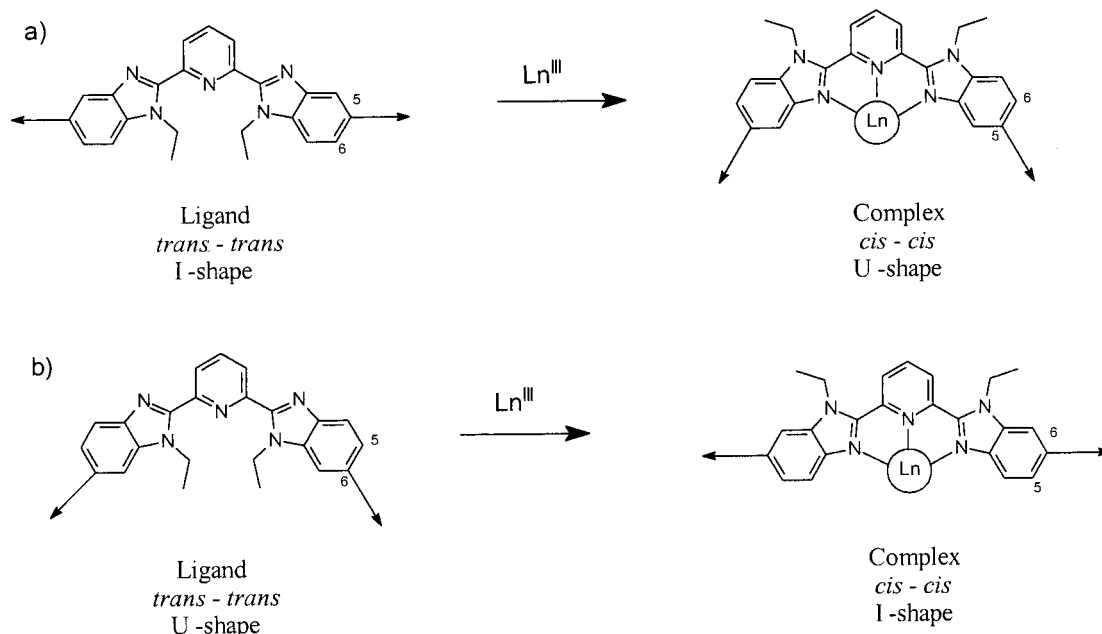
The lanthanide tris-complexes of higher homologues of acetylacetone are in general anhydrous, because steric crowding inhibits the bonding of water molecules. Complexes of 2,4-decanedione have been prepared by reaction between the corresponding lanthanide hydrate and the sodium salt of 2,4-decanedione.<sup>40</sup> XRD studies revealed a very low crystallinity. The melting point of the complexes decrease over the lanthanide series, from neodymium (120 °C) to lutetium (96 °C), but the decrease in melting point is not monotonic. Thermogravimetry shows that thermal decomposition starts above 150

°C. Extraction studies of neodymium and europium with 2,4-decanedione have been performed.<sup>41</sup>

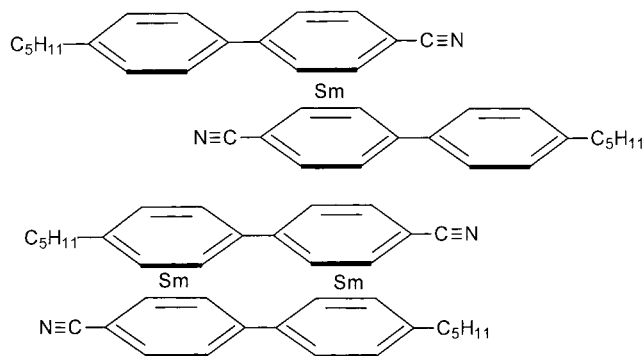
A cerium(IV) complex of stearylacetone (2,4-heneicosandione) was prepared by adding ammonia to an ethanolic solution of cerium(III) nitrate hexahydrate and stearylacetone.<sup>42</sup> Cerium(III) was oxidized to cerium(IV) by passing air through the solution. After precipitation, the compounds were purified by recrystallization from an acetonitrile/ethyl acetate mixture. Elemental analysis revealed that the composition was  $\text{Ce}(\text{C}_{21}\text{H}_{39}\text{O}_2)_4$ . The red brown waxy complex melted at 36.0 °C.

#### D. Miscellaneous Calamitic Liquid Crystals

Piguet and co-workers investigated 5- and 6-substituted 2,6-bis(benzimidazol-2-yl)pyridines and the corresponding lanthanide complexes  $[\text{LnL}(\text{NO}_3)_3]$ .<sup>43,44</sup> Conformational changes (trans,trans  $\rightarrow$  cis,cis) occurred upon complexation to lanthanide ions: the I-shaped 5-substituted ligands are transformed into U-shaped lanthanide complexes, whereas the U-shaped 6-substituted ligands give I-shaped lanthanide complexes (Figure 13). The 5-substituted 2,6-bis(benzimidazol-2-yl)pyridines are calamitic liquid crystals and exhibit a rich mesomorphism (SmC, SmA, and/or N). Although it was reported that the lanthanide complexes essentially retain the mesomorphism of the ligands, further studies showed that the lanthanide complexes having a low thermal stability are not mesomorphic.<sup>45</sup> Structurally, the bent 6-substituted ligands have the same shape as banana liquid crystals. However, no mesomorphism was detected. The corresponding lanthanide complexes have the shape of calamitic liquid crystals, but they decompose around 180–200 °C, without evidence for mesomorphism. The photophysical properties of all the ligands and lanthanide complexes have been studied in detail.



**Figure 13.** Conformational changes (trans,trans  $\rightarrow$  cis,cis) occurring upon complexation to trivalent lanthanide ions for (a) 5-substituted and (b) 6-substituted 2,6-bis(benzimidazol-2-yl)pyridines.<sup>44</sup> Linear substituents have been schematized by rods.



**Figure 14.** Suggested structures of the complexes  $[\text{Sm}(5\text{CB})_2]$  and  $[\text{Sm}_2(5\text{CB})_2]$ , 5CB being the liquid crystal 4-pentyl-4'-cyanobiphenyl.

*N*-(2-hydroxy-4-alkoxybenzaldehydeimino)-2-benzamidoethanamide (habbe) forms with lanthanide ions complexes of the type  $[\text{Ln}(\text{habbe})_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$ ).<sup>46</sup> The ligands exhibit a smectic A and a smectic B phase. The corresponding lanthanide complexes have been reported to exhibit a smectic C and a nematic phase.

Cocondensates between metallic samarium and 4-pentyl-4'-cyanobiphenyl (5CB) in the solid phase have been obtained via joint atomic/molecular beam deposition on a cooled calcium fluoride surface at liquid nitrogen temperature.<sup>47,48</sup> The film samples have been studied by IR and UV/vis spectroscopy in the temperature range from 80 to 300 K. Two types of complexes were detected, one complex with a metal-to-ligand ratio of 1:1,  $[\text{Sm}_2(5\text{CB})_2]$ , and another complex with a 1:2 ratio,  $[\text{Sm}(5\text{CB})_2]$ . The solid-phase transformation of the 1:2 complex to the 1:1 complex took place when the compound was heated to 183–200 K. The complexes are samarium  $\pi$  complexes, in which a samarium atom interacts with the aromatic ring of 5CB (Figure 14).

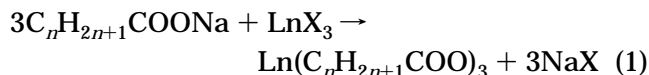
### III. Layered Compounds

Layered compounds with mesophase behavior consist of ionic sheets separated by long alkyl chains, so compounds are structurally related to smectic liquid crystals. They can be considered as mesomorphic compounds, because they show a multiple melting behavior upon heating. Not all long-range structure is lost at the melting point. First, the alkyl chain melts, whereas at the clearing point the ionic layers break down. The layered compounds with long alkyl chains differ from classic liquid crystals, because they do not contain discrete molecules but rather ionic compounds having 2D structure. For this reason, these compounds cannot be aligned by external electric or magnetic fields.

#### A. Alkanoates

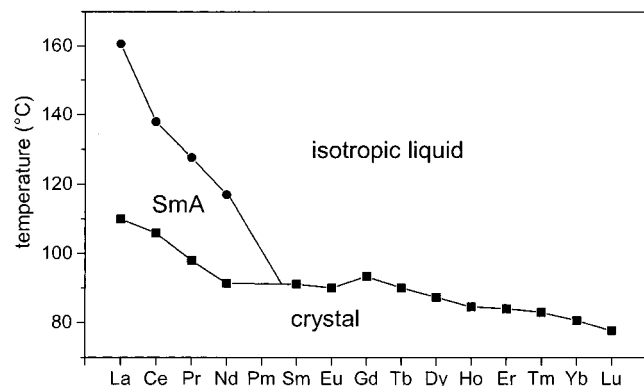
Lanthanide(III) alkanoates are salts of alkanic acids (or fatty acids). They are also known under the term “lanthanide soaps”. Their general formula is  $[\text{Ln}(\text{C}_n\text{H}_{2n+1}\text{COO})_3]$ . The first examples of lanthanide salts of the higher alkanic acids were described by Mehrotra and co-workers,<sup>49,50</sup> although the shorter homologues were known much earlier.<sup>51</sup> The lan-

thanide(III) alkanoates are prepared by a metathesis reaction between the corresponding sodium alkanoate and the lanthanide salt (nitrate or chloride) in ethanol/water solution:



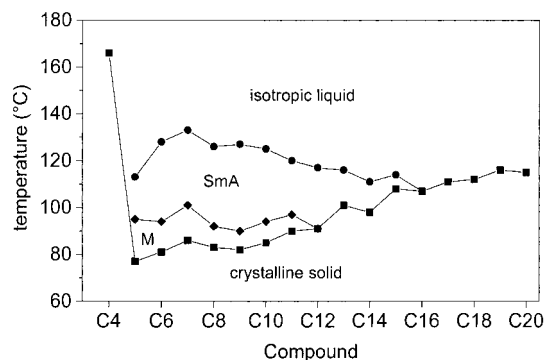
The crude metal soaps can be purified by recrystallization from 1-pentanol. The pH of the solution is of importance, because at low pH the alkanic acid precipitates and at high pH values mixed hydroxy compounds of the type  $[\text{Ln}(\text{OH})_x(\text{C}_n\text{H}_{2n+1})_{3-x}]$  are formed.<sup>52,53</sup> For the short chain homologues, the experimental procedures had to be adapted, because of too high a solubility of the compounds in the solvents mentioned. The butyrates were obtained by reaction between the lanthanide(III) hydroxide and butyric acid in 1:3 molar ratio.<sup>54</sup> Another method is the reaction between a lanthanide(III) isopropoxide and butanoic acid in 1:3 molar ratio in benzene.<sup>55</sup> Typically the lanthanide soaps with a short chain length are obtained as dihydrates, those with an intermediate chain length as mono- or hemihydrates, and the homologues with a long chain length as anhydrous compounds. The water of crystallization is lost upon heating before or at the melting point, so compounds obtained from cooling of the melt are always anhydrous. Anhydrous soaps can be synthesized by reaction between the alkanic acid and anhydrous lanthanide(III) chloride in dry toluene.<sup>56</sup> By changing the stoichiometric ratio, it is possible to obtain mixed compounds of the type  $[\text{LnCl}_x(\text{C}_n\text{H}_{2n+1}\text{COO})_{3-x}]$ . Misra and co-workers prepared lanthanide(III) alkanoates with three different alkyl chain within one and the same compounds by stepwise substitution of isopropoxide groups in lanthanide(III) isopropoxides.<sup>57</sup> The lanthanide(III) alkanoates can form adducts with neutral nitrogen donor ligands such as 1,10-phenanthroline (phen).<sup>58</sup> The long-chain homologues are insoluble in water and have a low solubility in all organic solvents at room temperature. They are soluble at elevated temperatures in the higher *n*-alcohols (1-butanol, 1-pentanol, etc.) and in aromatic solvents (benzene, toluene, etc.). For crystallization, the *n*-alcohols are preferable over the aromatic solvents, because in the former a well-filterable precipitate is obtained, whereas in the latter the compounds come out of solution as a gel. The best filterable precipitates can be obtained with 1-pentanol–ethanol mixtures. The solubility of the homologues with shorter alkyl chains is much higher than those with the long chains. The solubility of lanthanide(III) octanoates ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$ ) is on the order of  $10^{-4}$  M at room temperature.<sup>59</sup> The lanthanide(III) alkanoates have a much better resistance toward hydrolysis than the extremely hydrolyzable aluminum(III) alkanoates.<sup>49,57</sup> Only very limited data about scandium(III) alkanoates are available.<sup>60</sup> Perfluorinated alkanic acids too form metal soaps with trivalent lanthanides.<sup>61</sup>

Mesomorphism of the lanthanide soaps was first observed by Burrows and co-workers in a series of cerium(III) alkanoates.<sup>62</sup> These authors found by

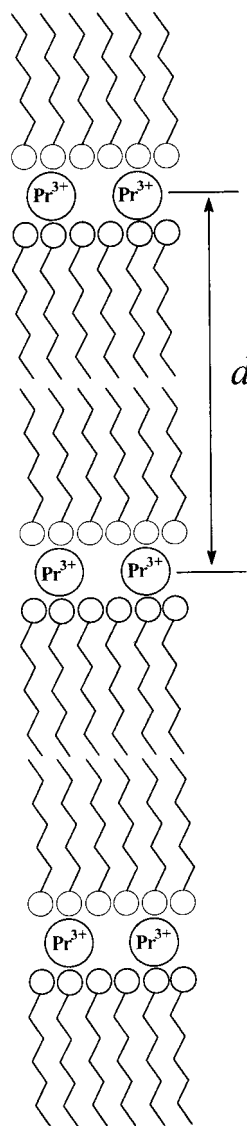


**Figure 15.** Phase diagram of the lanthanide(III) dodecanoates. (Drawn using the data in Table 2 of ref 65.)

polarized optical microscopy and DSC that the compounds exhibit a viscous mesophase that was tentatively assigned as a SmA-like mesophase. Without high-temperature X-ray diffraction, it is difficult to determine the mesophase type unambiguously, because the optical textures of these compounds are not diagnostic. It was also observed that the compounds showed a complex thermal behavior in the sense that the second heating run of the DSC differed markedly from the first heating run (especially the  $\Delta H$  values are different between the two different heating runs). On the basis of the transition enthalpies, it was concluded that electrostatic interactions in the polar region (due to the essentially ionic character of the metal–carboxylate bond) play an important role in the melting process. In the series of homologous cerium(III) alkanooates, each  $\text{CH}_2$  group contributes  $2.5 \text{ kJ mol}^{-1}$  to the melting enthalpy. This value is lower than the  $3.8 \text{ kJ mol}^{-1}$  associated with complete fusion of aliphatic chains in their fully crystalline state.<sup>63</sup> An analysis of the corresponding entropy data showed that the chains melt incompletely, so molecular aggregates are present in the melt. The identity of the mesophase of lanthanum(III) tetradecanoate was identified as a smectic A phase by Binnemans et al. via XRD studies.<sup>64</sup> Shortly later, an in-depth study of the thermal behavior of the lanthanide(III) alkanooates was started by Jongen and Binnemans. Both metal ion and the alkyl chain were varied in a systematic way. This work revealed that, of the series of lanthanide(III) dodecanoates, only the lanthanum(III), cerium(III), praseodymium(III), and neodymium(III) compounds form a mesophase, but not samarium(III) dodecanoate and the dodecanoates of the heavier lanthanides (Figure 15).<sup>65</sup> It was also observed that the change in  $d$ -spacing at the crystal-to-mesophase transition increased over the lanthanide series. The alkyl chain length has been found to have an influence on the thermal behavior, too. For the neodymium(III) alkanooates, a mesophase is present for the homologous series  $[\text{Nd}(\text{C}_4\text{H}_9\text{COO})_3]$ – $[\text{Nd}(\text{C}_{14}\text{H}_{29}\text{COO})_3]$ , but not for neodymium(III) hexadecanoate and the higher homologues (Figure 16).<sup>54</sup> The compounds with short alkyl chains exhibit two mesophases, the smectic A phase at high temperature and an unidentified high-ordered smectic phase at lower temperature. For the lanthanum(III),<sup>66</sup> cerium(III),<sup>67</sup> and praseodymium(III) alkanooates,<sup>68</sup> a very comparable mesophase behavior to that of the neody-



**Figure 16.** Phase diagram of the neodymium(III) alkanooates. The compounds are labeled with the total number of carbon atoms in the alkanooate groups; e.g., C12 stands for neodymium(III) dodecanoate. M = unidentified mesophase; SmA = smectic A phase (Reprinted from ref 54. Copyright 2000 American Chemical Society).



**Figure 17.** Schematic structural representation of praseodymium(III) heptanoate at room temperature (Reprinted from ref 68 with permission. Copyright 2001 Taylor & Francis; <http://www.tandf.co.uk>).

mium(III) alkanooates was observed, except that these compounds also have a mesophase present for the hexadecanoates and the higher homologues. In Table

**Table 7. Thermal Behavior of Lanthanide(III) Alkanoates**

compound	temperatures (°C) <sup>a</sup>	ref	compound	temperatures (°C) <sup>a</sup>	ref
[La(C <sub>3</sub> H <sub>7</sub> COO) <sub>3</sub> ]	Cr 188.4 I	66	[Pr(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 102 SmA 129 I	68
[La(C <sub>4</sub> H <sub>9</sub> COO) <sub>3</sub> ]	Cr 93.8 M 139.2 SmA 190.2 I	66	[Pr(C <sub>12</sub> H <sub>25</sub> COO) <sub>3</sub> ]	Cr 105 SmA 124 I	68
[La(C <sub>5</sub> H <sub>11</sub> COO) <sub>3</sub> ]	Cr 94.4 M 137.9 SmA 189.9 I	66	[Pr(C <sub>13</sub> H <sub>27</sub> COO) <sub>3</sub> ]	Cr 106 SmA 122 I	68
[La(C <sub>6</sub> H <sub>13</sub> COO) <sub>3</sub> ]	Cr 97.7 M 133.5 SmA 189.3 I	66	[Pr(C <sub>14</sub> H <sub>29</sub> COO) <sub>3</sub> ]	Cr 110 SmA 120 I	68
[La(C <sub>7</sub> H <sub>15</sub> COO) <sub>3</sub> ]	Cr 94.6 M 122.4 SmA 175.9 I	66	[Pr(C <sub>15</sub> H <sub>31</sub> COO) <sub>3</sub> ]	Cr 112 SmA 120 I	68
[La(C <sub>8</sub> H <sub>17</sub> COO) <sub>3</sub> ]	Cr 98.1 M 121.0 SmA 179.8 I	66	[Pr(C <sub>16</sub> H <sub>33</sub> COO) <sub>3</sub> ]	Cr 113 SmA 118 I	68
[La(C <sub>9</sub> H <sub>19</sub> COO) <sub>3</sub> ]	Cr 95.6 M 122.1 SmA 172.3 I	66	[Pr(C <sub>17</sub> H <sub>35</sub> COO) <sub>3</sub> ]	Cr 115 SmA 119 I	68
[La(C <sub>10</sub> H <sub>21</sub> COO) <sub>3</sub> ]	Cr 106.9 SmA 165.9 I	66	[Pr(C <sub>18</sub> H <sub>37</sub> COO) <sub>3</sub> ]	Cr 116 SmA 120 I	68
[La(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 110.0 SmA 160.6 I	66	[Pr(C <sub>19</sub> H <sub>39</sub> COO) <sub>3</sub> ]	Cr 117 SmA 122 I	68
[La(C <sub>12</sub> H <sub>25</sub> COO) <sub>3</sub> ]	Cr 116.4 SmA 154.6 I	66	[Nd(C <sub>3</sub> H <sub>7</sub> COO) <sub>3</sub> ]	Cr 166 I	54
[La(C <sub>13</sub> H <sub>27</sub> COO) <sub>3</sub> ]	Cr 120.3 SmA 157.1 I	66	[Nd(C <sub>4</sub> H <sub>9</sub> COO) <sub>3</sub> ]	Cr 77 M 95 SmA 113 I	54
[La(C <sub>14</sub> H <sub>29</sub> COO) <sub>3</sub> ]	Cr 121.4 SmA 157.0 I	66	[Nd(C <sub>5</sub> H <sub>11</sub> COO) <sub>3</sub> ]	Cr 81 M 94 SmA 128 I	54
[La(C <sub>15</sub> H <sub>31</sub> COO) <sub>3</sub> ]	Cr 123.4 SmA 148.2 I	66	[Nd(C <sub>6</sub> H <sub>13</sub> COO) <sub>3</sub> ]	Cr 86 M 101 SmA 133 I	54
[La(C <sub>16</sub> H <sub>33</sub> COO) <sub>3</sub> ]	Cr 123.9 SmA 149.7 I	66	[Nd(C <sub>7</sub> H <sub>15</sub> COO) <sub>3</sub> ]	Cr 83 M 92 SmA 126 I	54
[La(C <sub>17</sub> H <sub>35</sub> COO) <sub>3</sub> ]	Cr 125.9 SmA 148.0 I	66	[Nd(C <sub>8</sub> H <sub>17</sub> COO) <sub>3</sub> ]	Cr 82 M 90 SmA 127 I	54
[La(C <sub>18</sub> H <sub>37</sub> COO) <sub>3</sub> ]	Cr 126.7 SmA 126.7 I	66	[Nd(C <sub>9</sub> H <sub>19</sub> COO) <sub>3</sub> ]	Cr 85 M 94 SmA 125 I	54
[La(C <sub>19</sub> H <sub>39</sub> COO) <sub>3</sub> ]	Cr 140.1 SmA 140.1 I	66	[Nd(C <sub>10</sub> H <sub>21</sub> COO) <sub>3</sub> ]	Cr 90 M 97 SmA 120 I	54
[La(C <sub>20</sub> H <sub>41</sub> COO) <sub>3</sub> ]	Cr 128.1 SmA 143.6 I	66	[Nd(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 91 SmA 117 I	54
[Ce(C <sub>5</sub> H <sub>11</sub> COO) <sub>3</sub> ]	Cr 74 M 110 SmA 159 I	67	[Nd(C <sub>12</sub> H <sub>25</sub> COO) <sub>3</sub> ]	Cr 101 SmA 116 I	54
[Ce(C <sub>6</sub> H <sub>13</sub> COO) <sub>3</sub> ]	Cr 73 M 106 SmA 161 I	67	[Nd(C <sub>13</sub> H <sub>27</sub> COO) <sub>3</sub> ]	Cr 98 SmA 111 I	54
[Ce(C <sub>7</sub> H <sub>15</sub> COO) <sub>3</sub> ]	Cr 75 M 102 SmA 152 I	67	[Nd(C <sub>14</sub> H <sub>29</sub> COO) <sub>3</sub> ]	Cr 108 SmA 114 I	54
[Ce(C <sub>8</sub> H <sub>17</sub> COO) <sub>3</sub> ]	Cr 81 M 96 SmA 148 I	67	[Nd(C <sub>15</sub> H <sub>31</sub> COO) <sub>3</sub> ]	Cr 107 I	54
[Ce(C <sub>9</sub> H <sub>19</sub> COO) <sub>3</sub> ]	Cr 86 M 93 SmA 148 I	67	[Nd(C <sub>16</sub> H <sub>33</sub> COO) <sub>3</sub> ]	Cr 111 I	54
[Ce(C <sub>10</sub> H <sub>21</sub> COO) <sub>3</sub> ]	Cr 101 SmA 142 I	67	[Nd(C <sub>17</sub> H <sub>35</sub> COO) <sub>3</sub> ]	Cr 112 I	54
[Ce(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 106 SmA 142 I	67	[Nd(C <sub>18</sub> H <sub>37</sub> COO) <sub>3</sub> ]	Cr 116 I	54
[Ce(C <sub>12</sub> H <sub>25</sub> COO) <sub>3</sub> ]	Cr 107 SmA 133 I	67	[Nd(C <sub>19</sub> H <sub>39</sub> COO) <sub>3</sub> ]	Cr 115 I	54
[Ce(C <sub>13</sub> H <sub>27</sub> COO) <sub>3</sub> ]	Cr 111 SmA 131 I	67	[Sm(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 91 I	65
[Ce(C <sub>14</sub> H <sub>29</sub> COO) <sub>3</sub> ]	Cr 115 SmA 130 I	67	[Eu(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 90 I	65
[Ce(C <sub>15</sub> H <sub>31</sub> COO) <sub>3</sub> ]	Cr 116 SmA 129 I	67	[Gd(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 93 I	65
[Ce(C <sub>16</sub> H <sub>33</sub> COO) <sub>3</sub> ]	Cr 119 SmA 127 I	67	[Tb(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 90 I	65
[Ce(C <sub>17</sub> H <sub>35</sub> COO) <sub>3</sub> ]	Cr 120 SmA 129 I	67	[Dy(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 87 I	65
[Pr(C <sub>5</sub> H <sub>11</sub> COO) <sub>3</sub> ]	Cr 86 M 109 SmA 142 I	68	[Ho(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 85 I	65
[Pr(C <sub>6</sub> H <sub>13</sub> COO) <sub>3</sub> ]	Cr 90 M 111 SmA 144 I	68	[Er(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 84 I	65
[Pr(C <sub>7</sub> H <sub>15</sub> COO) <sub>3</sub> ]	Cr 90 M 112 SmA 144 I	68	[Tm(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 83 I	65
[Pr(C <sub>8</sub> H <sub>17</sub> COO) <sub>3</sub> ]	Cr 86 M 95 SmA 135 I	68	[Yb(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 81 I	65
[Pr(C <sub>9</sub> H <sub>19</sub> COO) <sub>3</sub> ]	Cr 90 SmA 136 I	68	[Lu(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 78 I	65
[Pr(C <sub>10</sub> H <sub>21</sub> COO) <sub>3</sub> ]	Cr 99 SmA 133 I	68	[Y(C <sub>11</sub> H <sub>23</sub> COO) <sub>3</sub> ]	Cr 85 I	65

<sup>a</sup> Cr = crystalline phase; M = unidentified smectic phase; SmA = smectic A phase; I = isotropic liquid.

7, the transition temperatures of the lanthanide(III) alkanooates are listed.

Although samarium(III) dodecanoate and the dodecanoates of the heavier lanthanides do not exhibit a mesophase, it was found that a mesophase could be induced by preparing binary mixtures of these compounds with lanthanum(III) dodecanoate (or with cerium(III), praseodymium(III), or neodymium(III) dodecanoates).<sup>69</sup> The mole fraction of lanthanum(III) dodecanoate required to induce the mesophase increased over the lanthanide series. Whereas 4 mol % lanthanum(III) dodecanoate is sufficient to induce mesomorphism in europium(III) dodecanoate, this amount increased to 48 mol % for ytterbium(III) dodecanoate.

A melt of the higher homologues of the lanthanide(III) alkanooates can be easily supercooled into a transparent glass, although the samples tend to crystallize after a period of 1 year or longer. Spectroscopic studies of vitrified lanthanide soaps have been reported by Corkery and Martin (luminescence study of europium(III) dodecanoate)<sup>70</sup> and by Jongen et al. (Judd–Ofelt intensity parameters of lanthanide(III) octadecanoates).<sup>71</sup> Binnemans et al. discuss the spectroscopic properties of neodymium(III) alkanooates dissolved in 1-pentanol.<sup>72</sup>

In the solid state, the structure of the lanthanide(III) alkanooates can be described as an infinite ionic

sheet of lanthanide ions and carboxylate groups, separated by a bilayer of alkyl chains (Figure 17).<sup>54,62,73–78</sup> The alkyl chains are in the all-trans conformation and perpendicular to the ionic layer. It is possible to calculate the *d*-spacing using the formula<sup>62</sup>

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

where *n* is the total number of carbon atoms in the chain, *d*<sub>C-H</sub> = 1.09 Å, *d*<sub>C-C</sub> = 1.54 Å, and *d*<sub>C-O</sub> = 1.36 Å. *r*<sub>Ln<sup>3+</sup></sub> is the radius of the trivalent lanthanide ion. The coordination mode of the carboxylate groups in the mesomorphic lanthanide alkanooates is not known in detail, although some structural details can be derived from the crystal structures of lanthanum(III) butyrate hydrate and neodymium(III) butyrate hydrate (Figure 18).<sup>54,79</sup> For these compounds it was observed that different types of lanthanide–carboxylate coordination modes are present. Although it is in principle possible to deduce the type of lanthanide–carboxylate bonding by infrared spectroscopy, these studies could not give an unambiguous answer (probably because of the presence of multiple coordination types). In the hydrated compounds, loss of water does not change the bilayer structure. Of

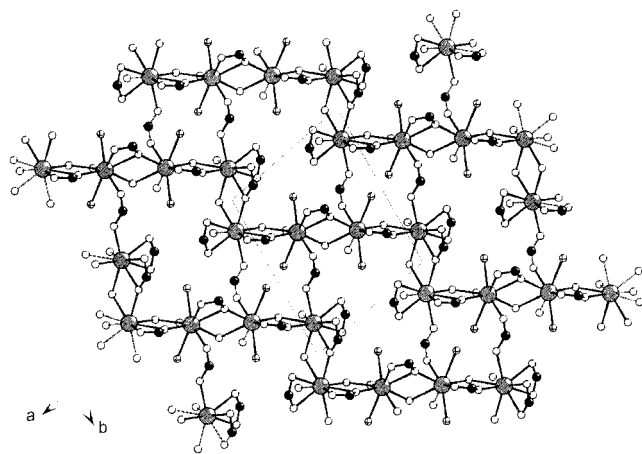
**Table 8. Critical Micelle Concentration (cmc) of Lanthanide(III) Alkanoates and Yttrium(III) Alkanoates in Nonaqueous Solvents**

compound	solvent	T(°C)	method	cmc (mol L <sup>-1</sup> )	ref			
lanthanum(III) hexanoate	methanol–DMF (3:1 v/v)	40	conductivity	0.0265	95			
			methanol–DMF (1:1 v/v)	40	conductivity	0.0265	95	
lanthanum(III) octanoate	benzene–methanol (3:7 v/v)	40	conductivity	0.006	89			
			benzene–methanol (1:1 v/v)	40	conductivity	0.006	89	
lanthanum(III) decanoate	benzene–methanol (7:3 v/v)	40	conductivity	0.0027	81			
			conductivity	0.0027	81			
			conductivity	0.0027	81			
	benzene–methanol (1:1 v/v)	40	ultrasonic velocity	0.0026	82			
			conductivity	0.0027	81			
lanthanum(III) dodecanoate	benzene–methanol (5:5 v/v)	40	ultrasonic velocity	0.0016	82			
			cerium(III) octanoate	benzene–methanol (3:7 v/v)	40	ultrasonic velocity	0.00049	98
cerium(III) decanoate	benzene–methanol (1:1 v/v)	40	conductivity	0.00049	98			
			viscosity	0.00049	98			
			ultrasonic velocity	0.00033	98			
			conductivity	0.00033	98			
			viscosity	0.00033	98			
	benzene–DMF (1:1 v/v)	40	conductivity	0.00056	101			
			benzene–DMF (1:1 v/v)	30	conductivity	0.0670	102	
	cerium(III) dodecanoate	benzene–DMF (1:1 v/v)	30	conductivity	0.0710	102		
				conductivity	0.0760	102		
				conductivity	0.0810	102		
conductivity				0.0560	102			
conductivity				0.0600	102			
conductivity				0.0650	102			
praseodymium (III) octanoate	1-pentanol	40	ultrasonic velocity	0.06	86			
			viscosity	0.06	87			
			praseodymium (III) decanoate	1-pentanol	40	ultrasonic velocity	0.05	86
praseodymium (III) hexadecanoate	benzene–DMSO (6:4 v/v)	40	ultrasonic velocity	0.00101	88			
			neodymium(III) butyrate	methanol	40	ultrasonic velocity	0.021	83
			conductivity	0.021	83			
neodymium(III) pentanoate	methanol	40	conductivity	0.021	90			
			viscosity	0.021	83			
			ultrasonic velocity	0.018	83			
			conductivity	0.018	83			
			conductivity	0.018	90			
neodymium(III) hexanoate	benzene–methanol (1:1 v/v)	40	ultrasonic velocity	0.017	83			
			ultrasonic velocity	0.0205	91			
			ultrasonic velocity	0.015	83			
	methanol	40	conductivity	0.015	83			
			conductivity	0.015	90			
			viscosity	0.015	83			
			ultrasonic velocity	0.0183	91			
neodymium(III) octanoate	benzene–methanol (1:1 v/v)	40	ultrasonic velocity	0.0175	91			
			ultrasonic velocity	0.00046	101			
			conductivity	0.0170	91			
neodymium(III) decanoate	benzene–methanol (1:1 v/v)	40	ultrasonic velocity	0.00112	88			
neodymium(III) hexadecanoate	benzene–DMSO (6:4 v/v)	40	ultrasonic velocity	0.0190	106			
samarium(III) pentanoate	methanol	30	conductimetry	0.0165	106			
samarium(III) hexanoate	methanol	30	conductimetry	0.0133	106			
samarium(III) octanoate	methanol	30	conductimetry	0.00040	101			
samarium(III) dodecanoate	benzene–DMF (1:1 v/v)	40	conductivity	0.00040	101			
			benzene–DMSO (7:3 v/v)	40	ultrasonic velocity	0.005	100	
	benzene–DMSO (1:1 v/v)	40	viscosity	0.005	100			
			ultrasonic velocity	0.0068	100			
europium(III) octanoate	benzene–methanol (3:2 v/v)	40	viscosity	0.0069	100			
			molar volume	0.07	103			
			ultrasonic velocity	0.07	103			
europium(III) dodecanoate	benzene–methanol (3:2 v/v)	40	molar volume	0.06	103			
			ultrasonic velocity	0.06	103			
gadolinium(III) octanoate	benzene–methanol (1:1 v/v)	35	conductivity	0.0250	99			
			conductivity	0.0270	99			
			conductivity	0.0310	99			
			conductivity	0.0350	99			
			conductivity	0.0225	99			
gadolinium(III) decanoate	benzene–methanol (1:1 v/v)	40	conductivity	0.0250	99			
			conductivity	0.0280	99			
			conductivity	0.0280	99			
			conductivity	0.0325	99			
			ultrasonic velocity	0.0059	107			
gadolinium(III) dodecanoate	benzene–methanol (7:3 v/v)	40	ultrasonic velocity	0.0054	107			
gadolinium(III) tetradecanoate	benzene–methanol (7:3 v/v)	40	ultrasonic velocity	0.0047	94			
			conductivity	0.0047	94			
			viscosity	0.0047	94			



**Table 8 (Continued)**

compound	solvent	$T$ (°C)	method	cmc (mol/L)	ref	
gadolinium(III) octadecanoate	benzene–methanol (7:3 v/v)	40	ultrasonic velocity	0.0040	94	
			conductivity	0.0044	94	
			viscosity	0.0045	94	
terbium(III) dodecanoate	benzene–methanol (7:3 v/v)	40	conductimetry	0.027	104	
			viscosity	0.028	104	
			ultrasonic velocity	0.027	104	
terbium(III) tetradecanoate	benzene–methanol (7:3 v/v)	40	molar volume	0.0045	105	
			viscosity	0.0045		
			ultrasonic velocity	0.0045		
terbium(III) hexadecanoate	benzene–methanol (7:3 v/v)	40	molar volume	0.0040	105	
			viscosity	0.0039		
			ultrasonic velocity	0.0040		
terbium(III) octadecanoate	benzene–methanol (7:3 v/v)	40	molar volume	0.0033	105	
			viscosity	0.0034		
			ultrasonic velocity	0.0034		
yttrium(III) butyrate	benzene–DMF (6:4 v/v)	40	ultrasonic velocity	0.019	92	
yttrium(III) pentanoate	benzene–DMF (6:4 v/v)	40	ultrasonic velocity	0.018	92	
yttrium(III) hexanoate	benzene–DMF (6:4 v/v)	40	ultrasonic velocity	0.0135	92	
		1-propanol	30	conductivity	0.025	97
		1-propanol	40	conductivity	0.027	97
		1-propanol	50	conductivity	0.031	97
		1-butanol	30	conductivity	0.029	97
		1-butanol	40	conductivity	0.033	97
		1-butanol	50	conductivity	0.036	97
		yttrium(III) octanoate	benzene–DMF (6:4 v/v)	40	ultrasonic velocity	0.0130
yttrium(III) decanoate	benzene–DMF (6:4 v/v)	40	viscosity	0.0130	93	
			ultrasonic velocity	0.0120	93	
			viscosity	0.0120	93	
yttrium(III) dodecanoate	benzene–DMSO (1:1 v/v)	40	ultrasonic velocity	0.0062	96	
	benzene–DMF (6:4 v/v)	40	ultrasonic velocity	0.0113	93	
			viscosity	0.0115	93	
yttrium(III) tetradecanoate	benzene–DMSO (1:1 v/v)	40	ultrasonic velocity	0.0057	96	
	benzene–DMSO (1:1 v/v)	40	ultrasonic velocity	0.0050	96	

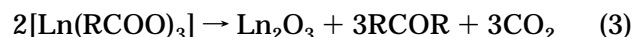


**Figure 18.** Crystal structure of neodymium(III) butyrate monohydrate (Reprinted from ref 54. Copyright 2000 American Chemical Society).

course, it can be expected that the structure within the ionic layer changes.

In comparison with the alkanooates of the alkaline and earth-alkaline metals, the thermal behavior of the lanthanide(III) alkanooates is less complex.<sup>80</sup> As mentioned, in most cases only one mesophase is present (smectic A), although sometimes a second mesophase is detected for the short chain homologues. This is in marked contrast to the alkaline soaps, where the compounds go upon heating through a series of mesophases. This less complex behavior is most probably due to the higher carboxylate-to-metal ratio in the metal soaps of highly valent metal ions, which makes the ionic layer more rigid. The

lanthanide(III) alkanooates decompose thermally to the lanthanide(III) oxide, a symmetric ketone, and carbon dioxide:<sup>74</sup>



Despite their low solubility, the solution behavior of the compounds in organic solvents has been extensively studied, mainly by Mehrotra and co-workers. It was observed that the lanthanide(III) alkanooates form inverse micelles in nonaqueous solvents (benzene–methanol, benzene–DMF, benzene–DMSO mixtures, etc.). The cmc was determined by plotting different physical quantities as a function of the surfactant concentration (ultrasonic velocity, molar volume, electric conductivity, viscosity). The physical properties of the metal soap solutions exhibit a discontinuity at the cmc. The cmc values are summarized in Table 8.<sup>81–107</sup> It is difficult to compare the values of the different compounds in the table, because different solvent mixtures have been used. For one and the same solvent mixture, the cmc values were found to decrease with decreasing chain length of the lanthanide soap and to decrease over the lanthanide series.

For a long time, the formation of Langmuir–Blodgett films made of fatty acids and trivalent metal ions was considered to be problematic, mainly because of the strong tendency of trivalent metal ions to hydrolyze in aqueous solution (e.g.,  $\text{Al}^{3+}$ ). Moreover, trivalent ions tend to produce more rigid films than monovalent and divalent ions. Blodgett made the statement that monolayers formed on solutions

of these ions would not be successfully transferred to solid substrates.<sup>108</sup> Because of the stronger resistance of trivalent rare-earth ions toward hydrolysis, the choice of these ions for obtaining Langmuir–Blodgett films with trivalent ions can be understood. Derué et al. investigated an elaidic acid monolayer prepared on a terbium-containing subphase by scanning force microscopy.<sup>109</sup> Among the first Langmuir–Blodgett films of lanthanide(III) alkanooates were those of lanthanum(III) octadecanoate.<sup>110</sup> Silva and co-workers studied monolayers and Langmuir–Blodgett films formed by spreading arachidic acid on aqueous solutions of europium(III) and terbium(III).<sup>111</sup> By transferring these films to a solid support, luminescent multilayer films could be obtained. Several authors investigated the influence of pH and lanthanide ion concentration on the formation of monolayers and multilayers. Arslanov et al. propose two mechanisms for the conversion of octadecanoic acid into octadecanoate.<sup>112,113</sup> At low pH values and low metal salt concentration in the subphase, the main mechanism is ion exchange between the hydrogen atoms of the nonionized acid groups and the metal ions. At higher pH values, the ionized carboxylate groups react directly with the metal ions. At high pH values, the formation of the basic yttrium salt  $[Y(OH)(C_{17}H_{35}COO)_2]$  was detected. On the other hand, other authors report on the presence of only  $[Y(\text{arachidate})_3]$  in the yttrium/arachidic acid system.<sup>114</sup> Xu et al. prepared by a conventional Langmuir–Blodgett method multilayers and Y-type bilayers of pure and mixed erbium(III) hexadecanoate, erbium(III) nonadecanoate, and erbium(III) behenate on calcium fluoride substrates.<sup>115</sup> Gadolinium(III)-containing Langmuir–Blodgett films were prepared with the aim to prepare planar magnetic materials.<sup>116,117</sup> Even less information than on LB films of lanthanide(III) alkanooates is available on LB films of lanthanide(III) complexes of aromatic carboxylic acids. Li and co-workers described the synthesis, spectroscopic properties, and LB-film formation of lanthanide complexes of mono-octadecyl phthalate (MOP).<sup>118</sup> These complexes had the stoichiometry  $[Ln(\text{MOP})_2Cl]$ , and a strong luminescence was observed for the corresponding europium and terbium compounds. Closely related to the alkanooic acids are the amides formed by reaction between a small amino acid and an alkanooic acid (*N*-acyl amino acids). Du and Liang described Langmuir–Blodgett films of *N*-octadecanoyl-L-alanine deposited from an aqueous subphase containing  $\text{La}^{3+}$ .<sup>119</sup> Although mesophases were observed when LB films containing  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$  were heated, no thermal data have been reported for the  $\text{La}^{3+}$ -containing film.

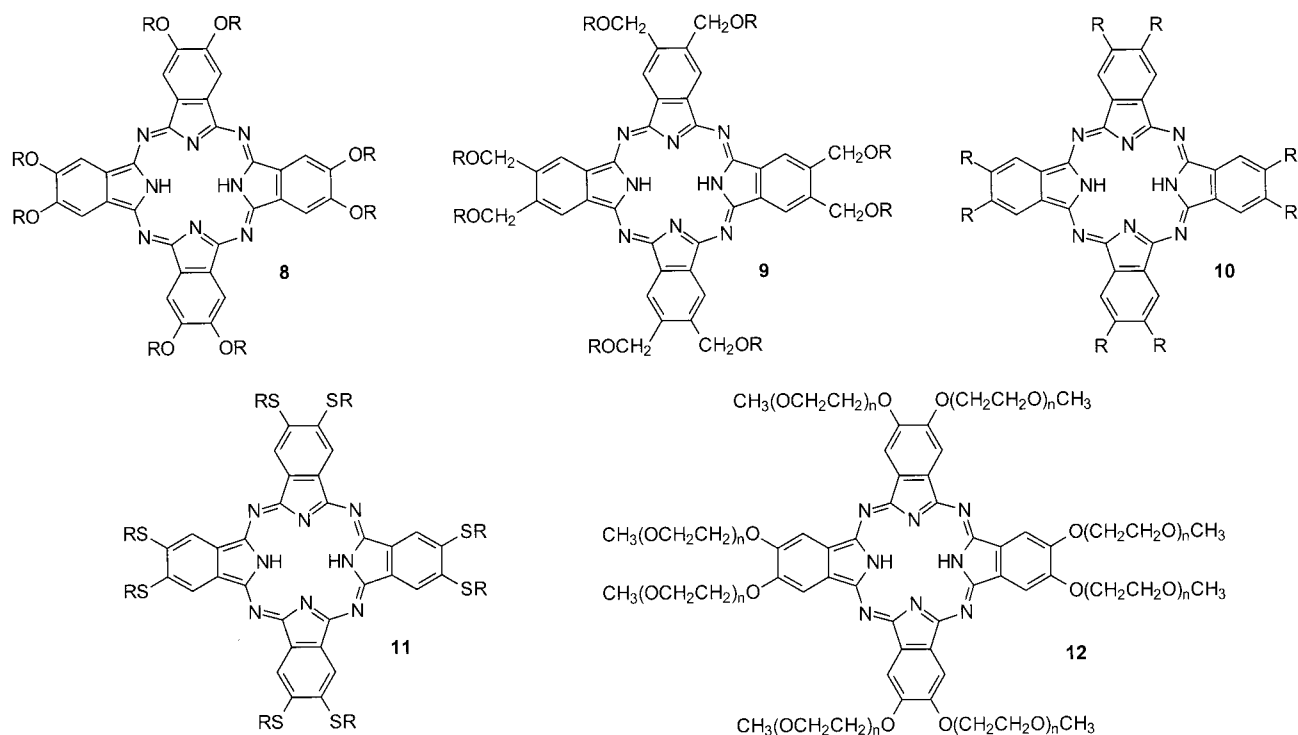
There is an industrial interest in lanthanide(III) alkanooates, and especially cerium(III) alkanooates, mainly because of the potential catalytic applications of these compounds. Cerium(III) alkanooates are being added to diesel fuel in order to improve the combustion and to reduce the emission of soot particles.<sup>120–122</sup> Cerium(III) octanoate has been tested as an additive to alkyd–resin-based paints as a paint drier.<sup>120</sup> Technical advantage of the use of cerium(III) com-

pounds over classic dryers such as classic lead compounds are the much higher drying rate (cerium is more effective in the body of the paint than at the surface, in contrast to lead), the need for a smaller amount of paint drier, and the nontoxicity. Cerium(III) octadecanoate can be added to PVC as a stabilizer. The role of the stabilizer is to decrease the rate of dehydrochlorination of PVC.<sup>120</sup> Different mixtures of cerium(III) and zinc(II) octadecanoate have been tested as a stabilizer in various PVC formulations. In addition, cerium(III) octadecanoate improves the rheological effects of PVC melts. Also elements other than cerium can stabilize PVC polymers.<sup>123,124</sup> Whereas PVC is stabilized by cerium(III) alkanooates, the same compounds cause accelerated photooxidative degradation of polyethylene (both LDPE and HDPE),<sup>125–133</sup> polypropylene,<sup>128,129</sup> and polystyrene.<sup>134</sup> The photosensitive activity of cerium(III) alkanooates on UV photooxidative degradation decreases with decreasing alkyl chain length. The role of cerium(III) octadecanoate in the oxidation of *n*-pentadecane has been investigated.<sup>135</sup> Lanthanide(III) alkanooates have been intensively investigated as catalysts for the stereospecific polymerization of 1,3-butadiene. They allow the yield of polybutadiene with a very high *cis*-1,4 content.<sup>136</sup> Not all the lanthanide(III) ions are equally efficient. In most cases, neodymium(III) compounds are the best choice. It was reported that europium(III) compounds do not initiate the polymerization and that a very low catalytic activity was found for samarium(III) compounds.<sup>137</sup> There might be a correlation between the poor catalytic activity and the tendency of these latter two ions to be reduced to the divalent state. The polymer yields depend on the solvent. A study using a mixed catalyst containing neodymium(III) octanoate reports that the yield decreases in the order olefinic  $\geq$  paraffinic  $\gg$  aromatic solvent.<sup>138</sup> Often not a pure catalyst but a mixed catalyst system is used.<sup>139,140</sup> An example is the ternary system consisting of neodymium(III) octanoate, diethylaluminum sesquichloride ( $\text{AlEt}_2\text{Cl}$ ), and triisobutylaluminum. Samarium(III) and ytterbium(III) alkanooates were shown to be useful as replacement of the corresponding oxides in dosage forms for radiolabeling with  $\gamma$ -emitting isotopes (samarium-153 and ytterbium-175) for scintigraphic image acquisition.<sup>141–143</sup> Neodymium(III) octanoate has been used to dope PMMA fibers with neodymium(III) ions.<sup>144,145</sup> The choice of the octanoate salt is mainly due to its relatively high solubility in the PMMA matrix. The absorption spectrum of  $\text{PMMA:Nd}^{3+}$  was found to be similar to that of  $\text{Nd}^{3+}$  in silica glass, although a slight blue shift was found in the  $\text{PMMA:Nd}^{3+}$  spectrum. Application of neodymium(III)-doped optical fiber for optical amplification has been proposed. The use of gadolinium(III) octanoate in a scintillation counter for recording neutrons has been described.<sup>146</sup>

## B. Phosphonates

Lanthanide(III) alkylphosphonates have the stoichiometry  $[LnH(\text{O}_3\text{PC}_n\text{H}_{2n+1})_2]$  and form a 2D continuous lattice structure.<sup>147,148</sup> Langmuir–Blodgett films of lanthanide(III) octadecylphosphonate ( $\text{Ln} =$

Chart 1



La, Ce, Sm, Gd) have been prepared by Y-type deposition on hydrophobic surfaces.<sup>149,150</sup> The LB films form at lower pH than those of divalent metal ions. X-ray photoelectron spectroscopy (XPS) of the films revealed a 1:2 metal/phosphorus ratio, just as in the solid-phase stoichiometry. XRD patterns were consistent with a layered structure. Several orders of 00/ reflections were observed, and these correspond to an interlayer spacing of 51 Å. Although the lamellar alkylphosphonate salts of zinc(II), [Zn(O<sub>3</sub>-PC<sub>n</sub>H<sub>2n+1</sub>)] (*n* = 8, 14, 18), were found to exhibit a mesophase behavior,<sup>151</sup> no data on the thermal behavior of the lanthanide(III) alkylphosphonates are available yet. Trivalent lanthanide ions form, with the azobenzene-derivatized phosphonic acid (4-(4'-tetradecyloxyphenyldiazenyl)phenyl)butylphosphonic acid, Langmuir-Blodgett films of the same type as those with octadecylphosphonic acid.<sup>152</sup> The interlayer spacing was 67 Å. Irradiation with UV light induced an inefficient trans-cis isomerization of the azobenzene chromophores.

#### IV. Discotic Liquid Crystals

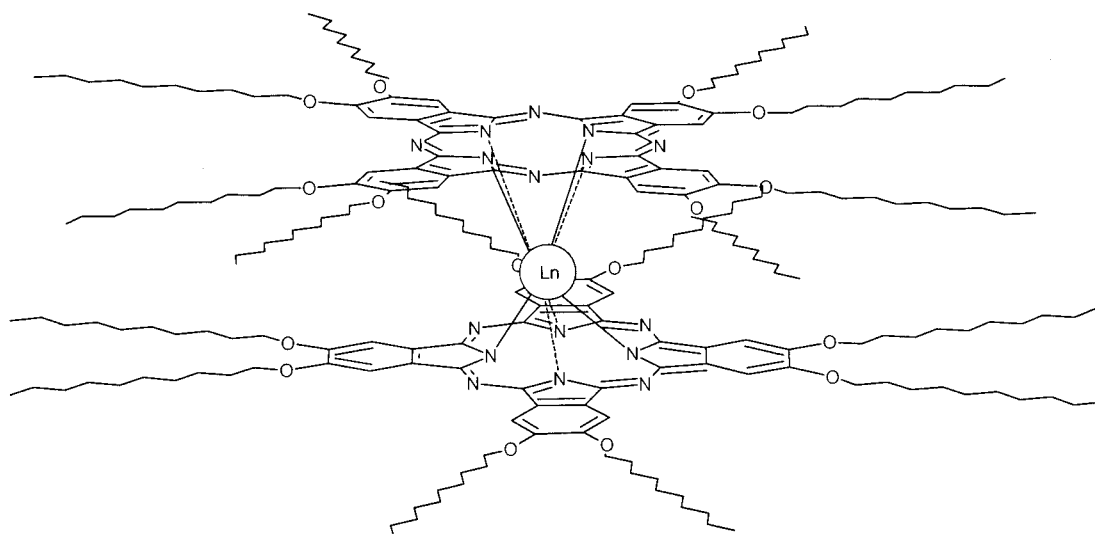
##### A. Bis(Phthalocyaninato)lanthanide(III) Complexes

The first lanthanide-containing metallomesogens were the substituted bis(phthalocyaninato)lutetium(III) complexes described by Simon and co-workers in 1985.<sup>153</sup> In these compounds, the lanthanide(III) ion is sandwiched between two macrocycles (see further). These authors were trying to obtain one-dimensional molecular semiconductors. The conductivity behavior of the bis(phthalocyaninato)lutetium(III) sandwich complexes was known previously, but only at that time it was realized that aligned columnar mesophases formed by such metallophthalocyanines can be considered as electrical wires at a

molecular level. The molten alkyl chains are acting as insulating layers. The phthalocyanine ring is one of the most stable macrocycles. Although different substitution patterns are possible on the macrocycle ring, the easiest compounds to obtain are the octakis-substituted phthalocyanines. Different substitution patterns are found in bis(phthalocyaninato)lanthanide(III) complexes (Chart 1): alkoxy substitution (**8**), alkoxymethyl substitution (**9**), alkyl substitution (**10**), alkylthio substitution (**11**), and poly(oxyethylene) substitution (**12**). The structure of an octakis-alkoxy-substituted bis(phthalocyaninato)lanthanide(III) sandwich complex is shown in Figure 19.

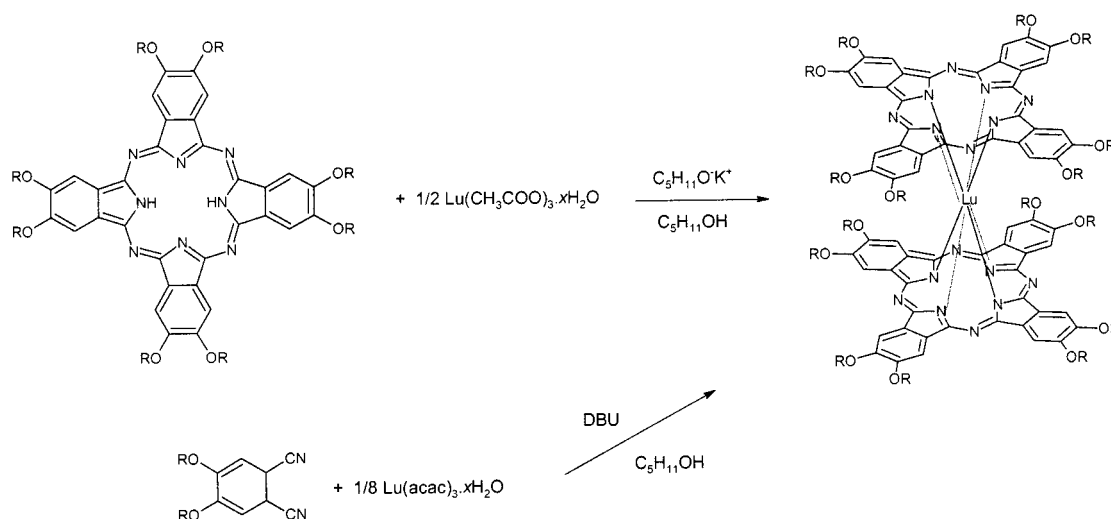
There are different synthetic routes possible to the bis(phthalocyaninato)lanthanide(III), which can be divided into two general methods: (a) reaction between a metal free phthalocyanine and a lanthanide salt, and (b) reaction between phthalocyanine precursors and a lanthanide salt (*template reaction*). The different routes are shown in Scheme 2.

Piechocki et al. obtained the alkoxymethyl-substituted complexes [(C<sub>n</sub>H<sub>2n+1</sub>OCH<sub>2</sub>)<sub>8</sub>Pc]<sub>2</sub>Lu (*n* = 8, 12, 18) by reaction between the corresponding metal-free phthalocyanines and lutetium(III) acetate, in 1-pentanol at 150 °C.<sup>153,154</sup> To form the phthalocyanine dianion, Pc<sup>2-</sup>, a very large excess of potassium pentanolate was necessary (50 times the stoichiometric amount). Before reaction, the lutetium salt was dissolved in refluxing 1,2-propanediol. During the reaction mainly [(C<sub>n</sub>H<sub>2n+1</sub>OCH<sub>2</sub>)<sub>8</sub>Pc]<sub>2</sub>Lu-K<sup>+</sup> (blue-green) was formed, with a small amount of [(C<sub>n</sub>H<sub>2n+1</sub>OCH<sub>2</sub>)<sub>8</sub>Pc]<sub>2</sub>Lu (green). By treatment of the organic phase with a diluted aqueous solution of hydrochloric acid, the green [(C<sub>n</sub>H<sub>2n+1</sub>OCH<sub>2</sub>)<sub>8</sub>Pc]<sub>2</sub>Lu complex was regenerated from [(C<sub>n</sub>H<sub>2n+1</sub>OCH<sub>2</sub>)<sub>8</sub>Pc]<sub>2</sub>Lu-K<sup>+</sup>, and this was also the form that was isolated. Probably first the protonated form [(C<sub>n</sub>H<sub>2n+1</sub>OCH<sub>2</sub>)<sub>8</sub>Pc]<sub>2</sub>LuH



**Figure 19.** Structure of an octakis-alkoxy-substituted bis(phthalocyaninato)lanthanide(III) sandwich complex.

**Scheme 2**



was formed, which was subsequently oxidized by air oxygen to  $[(C_nH_{2n+1}OCH_2)_8Pc]_2Lu$ . The compounds could be purified by flash chromatography on a silica column. The red oxidized form  $[(C_nH_{2n+1}OCH_2)_8Pc]_2Lu^+SbCl_6^-$  was prepared by reaction in dichloromethane of  $[(C_nH_{2n+1}OCH_2)_8Pc]_2Lu$  with a stoichiometric amount of the mild oxidizing reagent phenoxathiine hexachloroantimonate.

An alternative synthetic route to these sandwich complexes is via a *template reaction*. By treatment of 4,5-bis(octyloxy)phthalonitrile with  $Ln(acac)_3 \cdot nH_2O$  ( $Hacac = acetylacetonate$ ) in the ratio 6:1 using the sterically hindered organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the catalyst in refluxing 1-pentanol, the protonated forms  $[(C_8H_{17}O)_8Pc]_2LnH$  ( $Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Y$ ) were obtained as the initial products.<sup>155</sup> Except for  $Ln = Ce$ , the protonated forms underwent oxidation upon exposure of the chloroform solutions to air to give the  $[(C_8H_{17}O)_8Pc]_2Ln$  complexes. This process could be monitored by UV-vis spectra. The conversion was found to be accelerated by the acidity of the silica gel used for chromatographic purification. Depending on the lanthanide ion, differences in the

reaction products were found. Whereas for lanthanum(III), the bis(phthalocyaninato)lanthanum(III) complex was only formed in small quantities (the metal-free phthalocyanine being the major product), the amount of metal-free phthalocyanines gradually decreased in favor of the bis(phthalocyaninato)lanthanide(III) complex when going in the lanthanide series from lanthanum(III) to neodymium(III). From samarium(III) to thulium(III), no metal-free phthalocyanine  $PcH_2$  could be isolated. However, a large amount of monomeric  $[(C_8H_{17}O)_8Pc](acac)Tm$  was found in the case of thulium(III). In general, it is difficult to obtain good C, H, N microanalysis data for the phthalocyanine complexes, and these compounds are most often characterized by UV-vis spectra and by MALDI-TOF mass spectra.

Jiang et al. prepared the substituted bis(phthalocyaninato)cerium(IV) complexes  $[(C_7H_{15})_8Pc]_2Ce$  and  $[(C_5H_{11}O)_8Pc]_2Ce$  by reaction of a mixture of  $Ce(acac)_3 \cdot H_2O$ , DBU, and the corresponding dicyanobenzene in 1-pentanol.<sup>156</sup> The authors report that these compounds could not be obtained by reaction of  $Ce(acac)_3 \cdot H_2O$  with  $[(C_7H_{15})_8Pc]Li$  or  $[(C_5H_{11}O)_8Pc]Li$ .

Li. Instead, the metal-free phthalocyanines were obtained.

The  $[(C_nH_{2n+1})_8Pc]_2Lu$  compounds are soluble in *n*-hexane, benzene, toluene, chloroform, dichloromethane, diethyl ether, and tetrahydrofuran.<sup>157</sup> They are insoluble in DMF, acetonitrile, acetone, methanol, and ethanol. The best solvent for recrystallization was reported to be ethyl acetate. On the other hand, the poly(oxyethylene)-substituted lutetium phthalocyanines are soluble in chloroform, dichloromethane, methanol, ethanol (and higher alcohols), acetone, ethyl acetate, diethyl ether, DMF, and water (up to  $10^{-4}$  M) but insoluble in alkanes.<sup>158</sup>

The compound  $[(C_{18}H_{37}OCH_2)_8Pc]_2Lu$  melts at 51 °C to a mesophase and the clearing point is at 56 °C [ref 153]. The mesophase behavior was investigated by temperature-dependent XRD measurements. In the small-angle region, a series of five sharp Bragg reflections was observed. The reciprocal spacings were in the ratio  $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$ , which is characteristic for a hexagonal columnar mesophase (Col<sub>h</sub>). The intercolumnar distance is 37 Å, and the lutetium to lutetium spacing (intracolumnar distance) is about 7.3 Å. The broad peak due to the molten paraffinic chains was split into two peaks ( $d = 4.1$  and 4.3 Å). This behavior might be due to the partial crystallization of the alkyl chains. The XRD pattern remained unchanged for the temperature range from room temperature up to the isotropic liquid, indicating very similar structures for the solid state and the mesophase. In the solid state, the aliphatic chains are at least partially crystallized, whereas they are molten in the mesophase. No mesophase was found for  $[(C_8H_{17}OCH_2)_8Pc]_2Lu$ , whereas  $[(C_{12}H_{25}OCH_2)_8Pc]_2Lu$  exhibits a mesophase over a narrow temperature range and only after a full cycle of heating to the isotropic liquid and cooling to the crystal state has been performed. The small mesophase stability range of the neutral forms can be due to the concave form of the phthalocyanine macrocycles. For the oxidized forms  $[(C_nH_{2n+1}OCH_2)_8Pc]_2Lu^+SbCl_6^-$ , the melting point was found to increase strongly with the length of the alkoxyethyl chain, whereas the mesophase stability range varies much less as a function of the chain length. Although the oxidized forms exhibit a mesophase over a much larger temperature range than the neutral forms, the former are relatively unstable: after several cycles of heating to the isotropic state and cooling to the crystalline state, the compounds change color from red to green.<sup>154</sup> The green color is that of the neutral species. Not the pure neutral form is reobtained, but a mixture. Even when only 10% of the neutral form is present, the mixture already has a green appearance. No XRD data are available for the oxidized forms. In comparison with the metal-free phthalocyanines, the enthalpy changes of the  $[(C_nH_{2n+1}OCH_2)_8Pc]_2Lu$  complexes are large.<sup>154</sup> In the case of  $[(C_{12}H_{25}OCH_2)_8Pc]_2Lu$ ,  $\Delta H = 167.2$  kJ mol<sup>-1</sup> for the melting process and  $\Delta H = 58.5$  kJ mol<sup>-1</sup> for the clearing process. The values for  $(C_{12}H_{25}OCH_2)_8PcH_2$  are respectively 112.9 and 4.6 kJ mol<sup>-1</sup>. This could indicate that the degree of molecular organization is much higher for the lutetium complex than for the metal-free phthalocyanine and that the

intermolecular interactions in the mesophase are more important than in the isotropic state.

The alkoxy-substituted compound  $[(C_{12}H_{25}O)_8Pc]_2Lu$  forms a mesophase over a more extended temperature range (from 85 to 189 °C) than the corresponding alkoxyethyl-substituted analogues.<sup>159</sup> The mesophase of oxidized species and  $[(C_{12}H_{25}O)_8Pc]_2Lu^+BF_4^-$  is even more stable than that of the neutral compound. The stabilization of the mesophase in the ionic derivative was attributed to electrostatic contributions or to partial orbital overlap within the columns. The solid phase of  $[(C_{12}H_{25}O)_8Pc]_2Lu$  has an orthorhombic unit cell ( $a = 29$  Å,  $b = 24.6$  Å), whereas  $[(C_{12}H_{25}O)_8Pc]_2Lu^+BF_4^-$  is a liquid at room temperature. For  $[(C_{12}H_{25}O)_8Pc]_2Lu$ , a crystal-to-crystal transition was observed at 42 °C. In the mesophase both compounds exhibit an ordered hexagonal columnar mesophase (Col<sub>h</sub>), with an intercolumnar distance of 34.6 Å. The oxygen linkage leads to significantly larger intercolumnar distances than the oxymethyl linkage. The conjugation of the oxygen atom with the aromatic macrocycle stiffens the anchoring point of the paraffinic chain. The ordered character of the mesophase is evidenced by the presence of a fairly narrow peak at large angles in the XRD patterns. The stacking period along the columns is 3.3 Å for both compounds, whereas the correlation length of the disordered side chains is in the range 4.5–4.6 Å. The stacking period along the columns is in this case less than half of the value observed for  $[(C_{18}H_{37}OCH_2)_8Pc]_2Lu$  and seems to be related to a regular intermacrocylic spacing uncorrelated to the position of the lutetium ion. This was attributed to the presence of impurities in the percent range of the monocyclic  $(C_{18}H_{37}OCH_2)_8PcH_2$ , which introduce a dephasing in the position of the lutetium ions. If the concentration of the impurity leads to unperturbed column lengths smaller than the spatial coherent domain of the incident X-ray beam (200–300 Å), XRD will only detect the intermacrocylic distance that is not changed by the presence of impurities. The mesophase behavior of  $[(C_{12}H_{25}O)_8Pc]_2Lu$  was reinvestigated by van de Craats et al.<sup>160</sup> They found nearly the same transition temperatures as Belarbi et al.,<sup>159</sup> but the crystal-to-crystal transition at 61 °C was considered as a crystal-to-mesophase transition ( $\Delta H = 202$  kJ mol<sup>-1</sup>), which involves only partial melting of the alkyl chains. Melting is complete at the transition of this Col<sub>x</sub> mesophase to the hexagonal columnar mesophase Col<sub>h</sub> ( $\Delta H = 70$  kJ mol<sup>-1</sup>). The clearing point is at 196 °C ( $\Delta H = 5.9$  kJ mol<sup>-1</sup>). Upon cooling, no supercooling is observed for the isotropic-to-Col<sub>h</sub> transition, but a supercooling of 10 °C for the Col<sub>h</sub>-to-Col<sub>x</sub> transition is seen. The Col<sub>x</sub> mesophase crystallizes at 35 °C to another crystalline solid than the virgin sample. In the second heating run, the crystal-to-Col<sub>x</sub> transition is found at 45 °C (instead of 61 °C in the first heating run). In the Col<sub>h</sub> phase, the phthalocyanine macrocycles adopt a planar geometry and are equidistant within the columnar stacks (and uninfluenced by the presence or absence of a Lu<sup>3+</sup> ion between alternate pairs). Indeed, the lack of correlation in the spacing of the phthalocyanine macrocycles with the position

of the lutetium ion is evident from the absence of a reflection corresponding to a distance of 6.6 Å, which would have been expected for orthogonal stacking of  $\text{Pc}_2\text{Ln}$  molecular units. All Pc macrocycles are equivalent. There is a gradual change from a well-ordered columnar structure at a temperature close to 90 °C to an increasingly disordered columnar structure as the temperature is raised. This is evident from the gradual decrease of the intensity of the 3.3 Å reflection, which is the characteristic cofacial contact distance between aromatic moieties. The  $\text{Col}_x$  phase was reinvestigated by Naido et al. and was established as a new type of  $\text{Col}_{10}$  phase ( $P2_1/a$  symmetry) with two different stacking distances.<sup>161</sup> Steven et al. found an increase of both the melting and clearing point over the lanthanide series for  $[(\text{C}_{12}\text{H}_{25}\text{O})_8\text{Pc}]_2\text{Ln}$  complexes (Ln = Nd, Eu, Er, Lu).<sup>162</sup>

In contrast to  $[(\text{C}_8\text{H}_{17}\text{OCH}_2)_8\text{Pc}]_2\text{Lu}$ ,  $[(\text{C}_8\text{H}_{17})_8\text{Pc}]_2\text{Lu}$  is a liquid crystal and exhibits a disordered hexagonal columnar phase in the 79–82 °C temperature range ( $a = 25.0$  Å at 80 °C), the melting enthalpy being 47.2 kJ mol<sup>-1</sup> and the clearing enthalpy 13.8 kJ mol<sup>-1</sup>.<sup>157</sup> A virgin sample of  $[(\text{C}_{12}\text{H}_{25})_8\text{Pc}]_2\text{Lu}$  showed an oblique disordered columnar phase at room temperature, indicating that the phthalocyanine macrocycles are tilted with respect to the stacking axis of the column. On heating of this mesophase, it cleared at 32 °C to an isotropic liquid but soon relaxed into an disordered hexagonal columnar phase ( $a = 31.5$  Å at 42 °C). This mesophase cleared slowly to an isotropic liquid at 44 °C. A sample rapidly cooled from the isotropic liquid gave the disordered oblique columnar phase. When this sample was heated again, it showed the same thermal behavior as the virgin sample. However, a slowly cooled sample from the isotropic liquid gave the disordered hexagonal columnar phase (with horizontal stacking of the macrocycles). This behavior was explained using a Gibbs energy versus temperature diagram. A virgin sample of  $[(\text{C}_{18}\text{H}_{37})_8\text{Pc}]_2\text{Lu}$  gave at room temperature a discotic lamellar phase ( $\text{D}_L$ ), which cleared at 30 °C to an isotropic liquid but soon relaxed to a disordered hexagonal columnar phase ( $a = 32.9$  Å at 40 °C). The sample cleared slowly to an isotropic liquid at 43 °C. When the sample in the isotropic state was cooled, it gave a mixture of  $\text{D}_L$  and  $\text{Col}_{\text{hd}}$  phases, independent of the cooling rate.

A  $\text{Pc}_2\text{Lu}$  compound substituted by eight 4-octadecyloxyphenyl groups showed a tetragonal columnar phase at room temperature ( $a = 40.0$  Å), which transformed at 46.9 °C into a hexagonal columnar phase ( $a = 43.5$  Å at 230 °C) and cleared at 242 °C.<sup>163</sup> Decomposition of the isotropic liquid was observed at ca. 283 °C. The isotropic liquid sample cooled to room temperature gave a mesophase that was different from that of the virgin sample, but its XRD pattern could not be indexed. This unknown mesophase is transformed at 34 °C to a hexagonal columnar phase. In the virgin sample at room temperature in the tetragonal columnar phase, the phthalocyanine core is not able to rotate. When this mesophase is heated, the thermal mobility of the alkyl side chains increases, causing the packing of the columns to loosen. The phthalocyanine rings start

to rotate, resulting in the transformation of the two-dimensional tetragonal lattice in the more stable two-dimensional hexagonal lattice of the hexagonal columnar phase.

The poly(oxyethylene)-substituted lutetium phthalocyanine complex  $[(\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{O})_8\text{Pc}]_2\text{Lu}$  exhibits a tetragonal columnar phase ( $\text{Col}_t$ ) between 53 and 57.6 °C ( $a = 26.7$  Å).<sup>158</sup> The high-temperature XRD pattern consists of a series of Bragg reflections that correspond to reciprocal distances in the ratio  $1:\sqrt{2}:\sqrt{4}:\sqrt{8}$ . Around 4.2 Å, a halo due to the molten poly(oxyethylene) chains is observed both in the mesophase and in the isotropic liquid. The melting enthalpy is 1.6 J g<sup>-1</sup> and the clearing enthalpy 6.4 J g<sup>-1</sup>. The low-temperature phase is crystalline with an orthorhombic unit cell ( $a = 25.4$  Å,  $b = 19.2$  Å,  $c = 13.75$  Å). Analogous compounds with shorter or longer chain length do not show a mesophase, either being crystalline and melting directly to the isotropic liquid or being liquid at room temperature.

All the members of a series of octakis(alkylthio)-substituted complexes  $[(\text{C}_n\text{H}_{2n+1}\text{S})_8\text{Pc}]_2\text{Ln}$  (Ln = Eu, Tb, Lu;  $n = 8, 10, 12, 14, 16, 18$ ) exhibit a hexagonal columnar phase over a broad temperature range.<sup>164</sup> A novel pseudo-hexagonal phase with  $P2_1/a$  symmetry (labeled as  $\text{D}_{\text{rh}}$ ) was found for the complexes with the decylthio and with the dodecylthio chain (and also for the terbium(III) complex with the tetradecylthio chain). This mesophase has a two-dimensional rectangular lattice (having a relationship  $a = \sqrt{3}b$ ) for the whole molecules and a two-dimensional hexagonal lattice for the central core disks. On heating, the tilted molecules become stepwise cofacially stacked on heating. In the large angle region of the XRD diffractograms, two peaks due to the stacking distances  $h_1$  (ca. 3.5 Å, corresponding to a single decker) and  $h_2$  (ca. 7 Å, corresponding to a double decker) could be observed. The stacking distance at ca. 3.5 Å was attributed to rapid thermal fluctuations that extinguish the differences between the upper and lower macrocycles in the sandwich compound. Thermal fluctuations may cause trampoline movements of the phthalocyanine rings. Indeed, the phthalocyanine ring bearing the unpaired electron is not aromatic and not flat. It bends just like a dome. On increasing the temperature, the trampoline movement may occur faster, to give apparent single deckers on the time average. The thermal behavior of the substituted bis(phthalocyaninato)lanthanide(III) complexes has been summarized in Table 9.

Electron paramagnetic resonance measurements have been carried out for the  $[(\text{C}_n\text{H}_{2n+1}\text{OCH}_2)_8\text{Pc}]_2\text{Lu}$  compounds ( $n = 8, 12, \text{ and } 18$ ) as a function of the temperature.<sup>153,154</sup> In chloroform solution, the EPR signal is inhomogeneous (10 G), with a  $g$  factor corresponding to a free electron ( $g = 2.0021$ ). In the solid state, the EPR signal is much narrower (2 G) and the band shape can be described by a Lorentzian function instead of a Gaussian function. The compounds follow the Curie–Weiss law until 4.2 K, which indicates that the interactions between the spins are weak. The intensity of the signal, both for the sample in solution and in the solid state, corresponds to about one spin per molecule. The spin

**Table 9. Thermal Behavior of Substituted Bis(phthalocyaninato)lanthanide(III) Compounds**

compound	temperatures (°C)	ref
[(C <sub>8</sub> H <sub>17</sub> OCH <sub>2</sub> ) <sub>8</sub> Pc] <sub>2</sub> Lu	Cr 25 I	4152
[(C <sub>8</sub> H <sub>17</sub> OCH <sub>2</sub> ) <sub>8</sub> Pc] <sub>2</sub> Lu <sup>+</sup> SbCl <sub>6</sub> <sup>-</sup>	Cr 10 Col <sub>h</sub> 130 I	4152
[(C <sub>12</sub> H <sub>25</sub> OCH <sub>2</sub> ) <sub>8</sub> Pc] <sub>2</sub> Lu	Cr 24 Col <sub>h</sub> 30 I	4152
[(C <sub>12</sub> H <sub>25</sub> OCH <sub>2</sub> ) <sub>8</sub> Pc] <sub>2</sub> Lu <sup>+</sup> SbCl <sub>6</sub> <sup>-</sup>	Cr 13 Col <sub>h</sub> 118 I	4152
[(C <sub>18</sub> H <sub>37</sub> OCH <sub>2</sub> ) <sub>8</sub> Pc] <sub>2</sub> Lu	Cr 51 Col <sub>h</sub> 56 I	4152
[(C <sub>18</sub> H <sub>37</sub> OCH <sub>2</sub> ) <sub>8</sub> Pc] <sub>2</sub> Lu <sup>+</sup> SbCl <sub>6</sub> <sup>-</sup>	Cr 56 Col <sub>h</sub> 132 I	4152
[(C <sub>10</sub> H <sub>21</sub> O) <sub>8</sub> Pc] <sub>2</sub> Er	Cr 63 Col <sub>h</sub> 180 I	162
[(C <sub>12</sub> H <sub>25</sub> O) <sub>8</sub> Pc] <sub>2</sub> Nd	Cr 57 Col <sub>h</sub> 167 I	162
[(C <sub>12</sub> H <sub>25</sub> O) <sub>8</sub> Pc] <sub>2</sub> Eu	Cr 60 Col <sub>h</sub> 173 I	162
[(C <sub>12</sub> H <sub>25</sub> O) <sub>8</sub> Pc] <sub>2</sub> Er	Cr 54 Col <sub>h</sub> 174 I	162
[(C <sub>12</sub> H <sub>25</sub> O) <sub>8</sub> Pc] <sub>2</sub> Lu	Cr <sub>I</sub> 41 Cr <sub>II</sub> 85 Col <sub>h</sub> 189 I	159
	Cr 45 Col <sub>x</sub> 90 Col <sub>h</sub> 196 I	160
	Cr 85 Col <sub>h</sub> 185 I	162
[(C <sub>12</sub> H <sub>25</sub> O) <sub>8</sub> Pc] <sub>2</sub> Lu <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	Cr-3 Col <sub>h</sub> 253 I	159
[(C <sub>18</sub> H <sub>37</sub> O) <sub>8</sub> Pc] <sub>2</sub> Er	Cr 61 Col <sub>h</sub> 154 I	162
[(C <sub>8</sub> H <sub>17</sub> ) <sub>8</sub> Pc] <sub>2</sub> Lu	Cr 79 Col <sub>h</sub> 82 I	157
[(C <sub>12</sub> H <sub>25</sub> ) <sub>8</sub> Pc] <sub>2</sub> Lu	see text	157
[(C <sub>18</sub> H <sub>37</sub> ) <sub>8</sub> Pc] <sub>2</sub> Lu	see text	157
[(C <sub>18</sub> H <sub>37</sub> OPh) <sub>8</sub> Pc] <sub>2</sub> Lu	Col <sub>t</sub> 46.9 Col <sub>h</sub> 242 I	163
[(CH <sub>3</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> O) <sub>8</sub> Pc] <sub>2</sub> Lu	Cr 53 Col <sub>t</sub> 57.6 I	158
[(C <sub>8</sub> H <sub>17</sub> S) <sub>8</sub> Pc] <sub>2</sub> Eu	Cr 98 Col <sub>h</sub> 252 I	164
[(C <sub>8</sub> H <sub>17</sub> S) <sub>8</sub> Pc] <sub>2</sub> Tb	Cr 102 Col <sub>h</sub> 242 I	164
[(C <sub>8</sub> H <sub>17</sub> S) <sub>8</sub> Pc] <sub>2</sub> Lu	Cr <sub>I</sub> 45 Cr <sub>II</sub> 84 Col <sub>h</sub> 219 I	164
[(C <sub>10</sub> H <sub>21</sub> S) <sub>8</sub> Pc] <sub>2</sub> Eu	X 1 M 68 Col <sub>h</sub> 209 I	164
[(C <sub>10</sub> H <sub>21</sub> S) <sub>8</sub> Pc] <sub>2</sub> Tb	X 3 M 56 Col <sub>h</sub> 205 I	164
[(C <sub>10</sub> H <sub>21</sub> S) <sub>8</sub> Pc] <sub>2</sub> Lu	X 6 M 40 Col <sub>h</sub> 192 I	164
[(C <sub>12</sub> H <sub>25</sub> S) <sub>8</sub> Pc] <sub>2</sub> Eu	X 22 M 64 Col <sub>h</sub> 181 I	164
[(C <sub>12</sub> H <sub>25</sub> S) <sub>8</sub> Pc] <sub>2</sub> Tb	X 20 M 53 Col <sub>h</sub> 172 I	164
[(C <sub>12</sub> H <sub>25</sub> S) <sub>8</sub> Pc] <sub>2</sub> Lu	X 27 M 38 Col <sub>h</sub> 167 I	164
[(C <sub>14</sub> H <sub>29</sub> S) <sub>8</sub> Pc] <sub>2</sub> Eu	Cr 13 Col <sub>h</sub> 152 I	164
[(C <sub>14</sub> H <sub>29</sub> S) <sub>8</sub> Pc] <sub>2</sub> Tb	X 22 M 47 Col <sub>h</sub> 144 I	164
[(C <sub>14</sub> H <sub>29</sub> S) <sub>8</sub> Pc] <sub>2</sub> Lu	Cr 38 Col <sub>h</sub> 146 I	164
[(C <sub>16</sub> H <sub>33</sub> S) <sub>8</sub> Pc] <sub>2</sub> Eu	Cr 50 Col <sub>h</sub> 134 I	164
[(C <sub>16</sub> H <sub>33</sub> S) <sub>8</sub> Pc] <sub>2</sub> Tb	Cr 46 Col <sub>h</sub> 132 I	164
[(C <sub>16</sub> H <sub>33</sub> S) <sub>8</sub> Pc] <sub>2</sub> Lu	Cr 46 Col <sub>h</sub> 126 I	164
[(C <sub>18</sub> H <sub>37</sub> S) <sub>8</sub> Pc] <sub>2</sub> Tb	Cr 33 Col <sub>h</sub> 116 I	164
[(C <sub>18</sub> H <sub>37</sub> S) <sub>8</sub> Pc] <sub>2</sub> Lu	Cr <sub>I</sub> 32 Cr <sub>II</sub> 53 Col <sub>h</sub> 110 I	164

density of the lutetium ion is negligible. The free ion is delocalized on the macrocycles and not on the metal ion. The intensity of the signal, both for the sample in solution and in the solid state, corresponds to about one spin per molecule. The EPR signal line width of a  $\pi$ -radical system depends on the strength of the spin exchange interaction ( $J_s$ ) and on the degree of order. The EPR line width of [(C<sub>18</sub>H<sub>37</sub>OCH<sub>2</sub>)<sub>8</sub>Pc]<sub>2</sub>Lu is very similar in the mesophase and in the isotropic liquid (5 G) but much smaller in the crystalline state (2 G, as mentioned above).

For [(C<sub>12</sub>H<sub>25</sub>O)<sub>8</sub>Pc]<sub>2</sub>Lu, no change in EPR line width is observed at the crystal-to-mesophase transition, but an important line broadening from 3.2 to 4.7 G occurs at the mesophase-to-isotropic transition.<sup>159</sup> It was concluded that the solid-state and mesophase structure are closely related in this compound. The change in line width between the mesophase and the isotropic liquid is due to the difference in dipolar interaction associated with the structural change. The difference in EPR line width behavior between the alkoxymethyl- and the alkoxy-substituted compounds indicates strong differences in ordering within the columns for these two types of compounds. In contrast to the neutral complexes, no EPR signal could be observed for the oxidized forms

[(C<sub>n</sub>H<sub>2n+1</sub>OCH<sub>2</sub>)<sub>8</sub>Pc]<sub>2</sub>Lu<sup>+</sup>SbCl<sub>6</sub><sup>-</sup> and [(C<sub>12</sub>H<sub>25</sub>O)<sub>8</sub>Pc]<sub>2</sub>Lu<sup>+</sup>BF<sub>4</sub><sup>-</sup>.<sup>154,159</sup> No conclusion was possible whether these compounds can be described as a strongly coupled biradical or as a diamagnetic system.<sup>159</sup>

The free electron in the both the unsubstituted and substituted bis(phthalocyaninato)lutetium(III) is associated with the extensive  $\pi$ -system of the phthalocyanine macrocycles. The individual Pc<sub>2</sub>Lu units can be considered nominally as Lu<sup>3+</sup>Pc<sub>2</sub><sup>3-</sup>. There remains some discussion whether the unpaired electron is localized on a single Pc macrocycle at a given time, thus with formula Pc<sup>2-</sup>-Lu<sup>3+</sup>Pc<sup>-</sup>,<sup>165</sup> or can be considered to be completely delocalized between the two macrocycles.<sup>166</sup> It has been suggested that one Pc macrocycle is slightly more distorted than the other.<sup>167</sup> In any case, the lutetium ion is in its trivalent state (Lu<sup>3+</sup>) and not in the (impossible) tetravalent state.

The substituted bis(phthalocyaninato)lutetium(III) complexes are intrinsic molecular semiconductors. In such materials, the generation of charge carriers can be represented by the reaction AAA  $\rightleftharpoons$  A<sup>+</sup>A<sup>-</sup>A  $\rightleftharpoons$  free carriers, where A is the molecular unit. The ionized pair A<sup>+</sup>A<sup>-</sup> is photochemically or thermally activated. The self-organization of the discotic phthalocyanine compounds into columnar stacks provides a one-dimensional pathway for charge transport. The ac electric properties of [(C<sub>18</sub>H<sub>37</sub>OCH<sub>2</sub>)<sub>8</sub>Pc]<sub>2</sub>Lu were studied by Belarbi et al. over a large frequency range (10<sup>-3</sup>–10<sup>5</sup> Hz), in the solid state, in the mesophase, and in the isotropic liquid.<sup>168</sup> In the solid state and in the mesophase, a  $\omega^{0.8}$  frequency dependence is observed, with a very low activation energy of conduction (0.05 eV). The conductivities at 10<sup>4</sup> Hz are 8.2  $\times$  10<sup>-10</sup>  $\Omega^{-1}$  cm<sup>-1</sup> in the solid state at room temperature and 1.8  $\times$  10<sup>-9</sup>  $\Omega^{-1}$  cm<sup>-1</sup> in the mesophase at 52 °C. A capacitance increase associated with ionic conductivity is detected below 10 Hz. The very low activation energy is attributed to intercolumnar electron hopping of trapped charge carriers. Because of the smallness of the homogeneous solid or liquid-crystalline domains, the conductivity at low frequencies is limited by intercrystallite or intercolumnar hopping processes. In the isotropic liquid, the electric conduction is frequency independent. At 60 °C and below 10<sup>4</sup> Hz, the electric conductivity is 4  $\times$  10<sup>-11</sup>  $\Omega^{-1}$  cm<sup>-1</sup>. At higher frequencies, a dipolar relaxation mechanism characterized by a  $\omega^2$  frequency dependence is observed. The thermal activation energy of the conduction (0.4 eV) corresponds to the energy required for energy hopping between the [(C<sub>18</sub>H<sub>37</sub>OCH<sub>2</sub>)<sub>8</sub>Pc]<sub>2</sub>Lu molecular subunits through the quasi-liquid paraffinic continuum. The electric conductivity in the solid state, in the mesophase, and in the isotropic liquid could be increased by partial oxidation of the compound with phenoxathiine hexachloroantimonate. An increase of the amount of oxidized species makes the ionic conductivity occur at higher frequencies.

The electric studies were later extended by the same authors to [(C<sub>12</sub>H<sub>25</sub>O)<sub>8</sub>Pc]<sub>2</sub>Lu, and the oxidized species [(C<sub>12</sub>H<sub>25</sub>O)<sub>8</sub>Pc]<sub>2</sub>Lu<sup>+</sup>BF<sub>4</sub><sup>-</sup>.<sup>159</sup> It was shown that the frequency dependence of the electric conductivity is determined by the intercolumnar order:  $\omega^{0.8}$  for

the disordered columnar mesophase and  $\omega^{0.5}$  for the ordered columnar mesophase. Because the ionization potentials and electron affinities of paraffinic and aromatic moieties are very different, it was concluded that the charge carriers are entirely localized on the aromatic subunits and that therefore the electronic charge processes involve the aromatic cores of the columns. It was estimated that for the same activation energy, the intracolumnar hopping probability is  $10^7$  times greater than the intercolumnar one. For,  $[(C_{12}H_{25}O)_8Pc]_2Lu$ , the intracolumnar mobility of the charge carriers is in the range  $10^{-4}$ – $10^{-2}$   $cm^2 V^{-1} s^{-1}$ , with the number of charge carriers being about  $10^{11}$  carriers/cm<sup>3</sup>. At 10 GHz, the charge migration occurs over less than 1 Å and involves hops between only two localized sites, whereas multiple sites were postulated in the low-frequency range. Most of the electric studies have been done on lutetium(III) complexes. However, studies on unsubstituted  $Pc_2-Ln$  complexes have revealed major differences between the bisphthalocyanine complexes of lutetium ( $Pc_2Lu$ ) and thulium ( $Pc_2Tm$ ).<sup>169,170</sup> Whereas  $Pc_2Lu$  is an intrinsic molecular semiconductor (as discussed above),  $Pc_2Tm$  is an extrinsic molecular semiconductor.

Van de Craats et al. used the *pulse-radiolysis time-resolved microwave conductivity technique* (PR-TRMC) to study the charge transport properties of  $[(C_{12}H_{25}O)_8Pc]_2Lu$ .<sup>160</sup> The results indicated an increase in charge carrier mobility at the crystalline solid-to-Col<sub>x</sub> mesophase transition and another strong increase by a factor of 3 at the transition to the higher temperature mesophase Col<sub>h</sub>. In the mesophase above 90 °C, the charge carrier mobility gradually decreases and an abrupt decrease by a factor of about 2 was observed at the Col<sub>h</sub> to isotropic liquid transition. In the solid state, the charge carrier mobility is more than 1 order of magnitude lower than in the solid state of other alkoxy-substituted phthalocyanines. This is possibly due to the sandwich structure of the individual molecules. The increase at the crystal-to-mesophase transition was attributed to a change from a tilted to an orthogonal stacking. The increase at the Col<sub>x</sub>-to-Col<sub>h</sub> transition is attributed to the equivalence of the Pc macrocycles within the columns, which leads to delocalization of the radical site between neighboring molecular units and results in additional intracore binding over and above the electrostatic and  $\pi$ - $\pi$  interactions normally responsible for columnar self-aggregation. The intracolumnar mobility determined just above the Col<sub>x</sub>-to-Col<sub>h</sub> transition at 90 °C is  $0.17 \times 10^{-4}$   $m^2 V^{-1} s^{-1}$  and was at that time the highest yet determined using the PR-TRMC technique for a liquid crystal forming a columnar mesophase. The increase in charge mobility at the crystal-to-mesophase transition is in contrast to what is observed for other discotic molecules, such as porphyrins, perylenes, triphenylenes, and even other alkoxy-substituted phthalocyanines. Because of the fast time response and ultrahigh-frequency involved in the PR-TRMC technique, the mobilities obtained are thought to be intrinsic, trap-free values associated with organized domains within the material.<sup>164</sup> Therefore, these

mobilities can be considered to be close to the maximum value that can be obtained with well-organized monodomain layers.

Replacement of the oxygen atoms of alkoxy-substituted  $Pc_2Lu$  phthalocyanine complexes by sulfur atoms (giving alkylthio-substituted phthalocyanines) results in an increase of more than one order of magnitude in the intramolecular charge mobility to values in the range of 0.15–0.3  $cm^2 V^{-1} s^{-1}$ .<sup>164</sup> The pronounced positive effect on the charge transport properties of sulfur compared with oxygen as chain-to-core coupling group was attributed to the larger size of the sulfur atom, which hinders rotational and translational displacements of the phthalocyanine macrocycles within the cores of the columns. The resulting decrease in structural disorder within the stacks of the alkylthio-substituted compounds is favorable for fast charge transport. The higher charge mobility can also be explained by the differences in electronegativity between oxygen and sulfur atoms (K. Ohta, personal communication). Whereas the alkoxy group is electron-donating to the phthalocyanine ring, the alkylthio group is in a first approximation neither electron-donating nor electron-withdrawing. Therefore the HOMO–LUMO gap is smaller in the alkylthio-substituted compounds, and hence, the charge mobility is higher. The one-dimensional intracolumnar charge carrier mobilities exhibit only a weak temperature dependence, except for an abrupt decrease by a factor of ca. 3 at the crystal-to-mesophase transition. This decrease can be attributed to the melting of the alkylthio chains, with a resulting increase in the disorder within the columns. The mobility remains high in the isotropic state, which indicates that a high degree of columnar order still exists and allows charge transport to occur via intermolecular charge-transfer rather than by molecular ion diffusion. Because of the high charge mobility in the isotropic state, these compounds are considered as the first liquid-phase organic semiconducting materials.

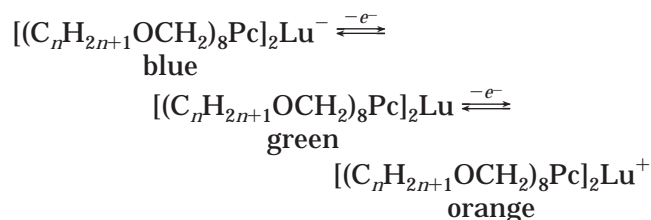
The photoconductivity of the  $[(C_{16}H_{33}S)_8Pc]_2Ln$  ( $Ln = Eu, Tb, Lu$ ) complexes is very weak.<sup>171</sup> Non-radiative relaxation of the photoexcitations is dominating. A significant enhancement of the photoconductivity was observed after doping with C<sub>60</sub>. In the case of the lutetium(III) complex, the photoconductivity parallel with the columns was 2 orders of magnitude larger than in the case of the undoped sample.

The transitions in the absorption spectrum arise from the phthalocyaninato ligands and are essentially  $\pi \rightarrow \pi^*$  transitions. The main features are the B (Soret) absorption band at about 315 nm due to the electronic transition  $\pi(b_{2u}) \rightarrow \pi^*(e_g^*)$ , an absorption band at about 460 nm due to the  $\pi(2e_g) \rightarrow \pi(a_{2u})$  transition, and the Q-band at about 670 nm due to the  $\pi(a_{2u}) \rightarrow \pi^*(e_g^*)$  transition. Due to the radical nature of the compound, a band at about 900 nm is assigned to a  $\pi(e_g) \rightarrow \pi(a_{2u})$  transition. An intramolecular charge transfer between the two moieties leads to a near-infrared transition at about 1400 nm. The position of the Q-band determines the color of the complexes. The band is around 670 nm in the green complexes  $Pc_2Lu$  and around 640 nm in the



blue complexes  $\text{Pc}_2\text{LnH}$  and  $\text{Pc}_2\text{Ln}^-$ . Upon decrease of the lanthanide ion size from lanthanum(III) to thulium(III), all the corresponding absorption bands (except the ones around 900 and 1425 nm) are systematically blue-shifted.<sup>155</sup> The photoluminescence of the  $[(\text{C}_{16}\text{H}_{33}\text{S})_8\text{Pc}]_2\text{Ln}$  ( $\text{Ln} = \text{Eu}, \text{Tb}, \text{Lu}$ ) is very weak.<sup>171</sup> In chloroform solution, two photoluminescence bands were observed around 400–650 nm and 720–800 nm, corresponding to the Soret- and Q-bands in the absorption spectrum. No characteristic f–f emission lines could be observed for the europium(III) and the terbium(III) complexes, only ligand-centered emission.

The bis(phthalocyaninato)lanthanide(III) complexes show electrochromism: in solution or deposited as thin films they exhibit different colors according to the applied potential.<sup>172</sup> For this reason, the potential of these materials for display applications has been investigated. The electrochromic behavior of the octaalkoxymethyl-substituted  $\text{Pc}_2\text{Lu}$  has been investigated and it has been shown that they have similar properties in solution as the unsubstituted  $\text{Pc}_2\text{Lu}$  complexes.<sup>173,174</sup> Even so, the substituted compounds are far more stable under electrochemical cycling (cyclic voltammetry) than the unsubstituted ones.<sup>175</sup> The green neutral form can be transformed via a one-electron oxidation step into an orange form and via a one-electron reduction step into a blue form:



The redox processes are reversible. In the blue complex, the Q-band is at about 631 nm, in the green complex at about 671 nm, and in the orange complex at about 704 nm. The total oxidation of  $[(\text{C}_8\text{H}_{17}\text{OCH}_2)_8\text{Pc}]_2\text{Lu}$  or  $[(\text{C}_{12}\text{H}_{25}\text{OCH}_2)_8\text{Pc}]_2\text{Lu}$  films to form an orange cation or reduction to form a blue anion could be achieved when the electrode potential was held for several minutes at 0.6 or  $-0.1$  V, respectively. It was shown that the potential of the oxidation step depends on the anion of the aqueous electrolyte in contact with the film. The oxidized and reduced compounds are stable in solution. In the presence of an external potential, the orange and blue species remain unchanged over at least 2 days. Without external potential, the colors remain for several hours or days, depending on the impurity concentration. An increase in the chain length makes both the reduction and the oxidation process more difficult.<sup>175</sup> For  $[(\text{C}_{18}\text{H}_{37}\text{OCH}_2)_8\text{Pc}]_2\text{Lu}$  films, it was necessary to heat the film at 55 °C and to increase the potential to overcome the Ohmic drop (typical potential were 1.4 and  $-1.0$  V). Ohta and co-workers pointed to the fact that substituents on the phthalocyanine ring have hardly any influence on the colors of the neutral green complex and the reduced blue species.<sup>157</sup> However, the colors of the oxidized species showed remarkable differences (in dichloromethane solution). The oxidized form of the unsubstituted

$\text{Pc}_2\text{Lu}$  was yellowish green,  $[(\text{C}_{12}\text{H}_{25}\text{OCH}_2)_8\text{Pc}]_2\text{Lu}^+$  and  $[(\text{C}_{12}\text{H}_{25}\text{O})_8\text{Pc}]_2\text{Lu}^+$  were orange, whereas  $[(\text{C}_{12}\text{H}_{25})_8\text{Pc}]_2\text{Lu}^+$  solution was red. With respect to the alkoxy- and alkoxymethyl-substituted  $\text{Pc}_2\text{Lu}$ , the Q-band of the alkyl-substituted  $\text{Pc}_2\text{Lu}$  is shifted more than 8 nm to longer wavelengths (and is found at 712 nm). The oxidation potential in the  $[(\text{C}_n\text{H}_{2n+1})_8\text{Pc}]_2\text{Lu}$  is at  $-0.17$  V and the reduction potential is at 0.28 or 0.29 V. The electrochromism of these alkyl-substituted  $\text{Pc}_2\text{Lu}$  exhibits the three primary colors (blue, green, red), so it is possible to construct a full-color display using one single compound. The drawback of this type of display is the long response time: color changes require several hundreds of seconds. On the other hand, once an image is formed by an electrochromic process, no further energy input is required to retain it.

By incorporating electron-donating groups on the phthalocyanine ring, the complexes become more reducing and less oxidizing.<sup>176</sup> This was illustrated by attaching pentyloxy or *n*-heptyl groups on the macrocycle ring. However, the difference between the oxidation and reduction potentials, which are a good estimate of the thermal activation energy in the  $\text{Pc}_2\text{Ln}$  complexes, remained relatively constant at ca. 0.40 V.

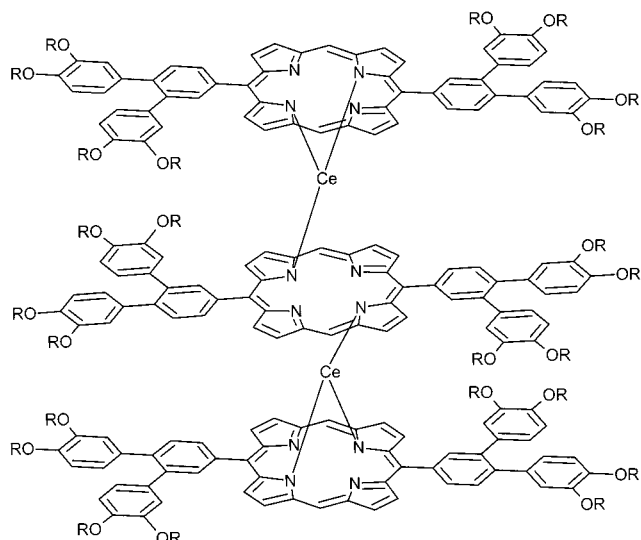
It should be mentioned that the theoretical explanation of the electrochromic behavior of  $\text{Pc}_2\text{Lu}$  compounds is not without controversies. Some authors claim that the color changes are acid–base in nature and not due to redox processes involving the phthalocyanine rings. Daniels et al. reported that in acetonitrile solution and in the absence of an applied potential, the color change from blue over green to red could be obtained by the addition of acid and then quantitatively reversed by the addition of base.<sup>177,178</sup> The blue species is  $\text{Pc}_2\text{Ln}^-$ , the green  $\text{Pc}_2\text{LnH}$ , and the red species  $\text{Pc}_2\text{LnH}_2$ .

A poly(oxyethylene)-substituted bis(phthalocyaninato)lutetium(III) complex has been incorporated in the alignment layer of an optically addressed spatial light modulator (OASLM), and this device has been shown to be able to memorize a gray scale image.<sup>179</sup>

The phenyl ring of the phthalocyanine ring can be replaced by a naphthalene ring. In this way, naphthalocyanines are obtained. In analogy with phthalocyanines, naphthalocyanines form sandwich complexes with the lanthanides. Nyokong et al. described two substituted bis(naphthalocyaninato)europium(III) complexes, i.e., bis(octakis(dodecylthio)2,3-naphthalocyaninato)europium(III) and bis(tetra-*tert*-butyl-2,3-naphthalocyaninato)europium(III).<sup>180</sup> Although it can be expected that the dodecylthio-substituted compound exhibits mesomorphism, the thermal behavior has not been investigated by these authors. A series of bis(tetra-*tert*-butyl-2,3-naphthalocyaninato)lanthanide(III) complexes ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Er}, \text{Y}$ ) has been prepared by Jiang et al.<sup>181</sup>

## B. Porphyrin Complexes

Triple-decker sandwich complexes consisting of two cerium(III) ions and three 5,15-diarylporphyrins were prepared by reaction between the parent porphyrins

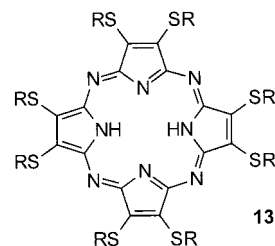


**Figure 20.** Structural model of a porphyrinato triple-decker cerium(III) complex.<sup>182</sup>

and  $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$  (Hacac = acetylacetonate) in 1,2,4-trichlorobenzene at reflux temperature (Figure 20).<sup>182</sup> The work was focused on finding the border on the molecular structure between a discotic mesogen and a calamitic mesogen, when the molecular shape is continuously changed from disklike to rodlike. The parent porphyrins have a striplike shape, but they can aggregate into columnar structures. The thermal behavior of the triple-decker complexes has been investigated in detail. The complexes containing dialkoxyphenyl groups in the 5,15-positions of the parent porphyrin show a mesophase possessing both lamellar and columnar structures at lower temperatures (discotic lamellar columnar mesophase,  $D_{LC}$ ) and a rectangular columnar mesophase ( $\text{Col}_r$ ) at higher temperatures. The  $D_{LC}$  phase could only be observed in virgin samples. The X-ray pattern of this mesophase gave reciprocal Bragg spacings in the ratio 1:2:3:4 (corresponding to a lamellar structure) and a broad peak around  $2\theta = 20^\circ$  (corresponding to the molten alkyl chains). Additionally, a relatively broad peak could be observed at ca.  $3.6 \text{ \AA}$  ( $h_1$ ), which agrees with a stacking distance of  $3.2\text{--}3.5 \text{ \AA}$  between the porphyrin monomers in a columnar structure. Two peaks, one at  $7.9 \text{ \AA}$  ( $h_2$ ) and one at  $10.4 \text{ \AA}$  ( $h_3$ ), are close to 2 and 3 times  $3.6 \text{ \AA}$  ( $h_1$ ), respectively. Complexes containing tetraalkoxylated terphenyl groups at the 5,15-position of the parent porphyrin show only a hexagonal columnar phase ( $\text{Col}_h$ ) with a single stacking distance. On the basis of the extinction rules for two-dimensional lattices, the rectangular columnar phase was found to have  $P2/a$  symmetry. The differences in mesomorphism are explained by differences in the steric hindrance of the side chains for rotation along the axis connecting the center of the three porphyrins. In addition to the mesomorphic properties, the electrochemical and spectroscopic properties of the triple-decker complexes have been reported too.

The synthesis and characterization of the bis-(2,3,7,8,12,13,17,18-octylthio)-5,10,15,20-tetraazaporphyrinato)lutetium(III) has been described.<sup>183</sup> The compounds, abbreviated to  $\text{Lu}(\text{OOTTAP})_2$  were pre-

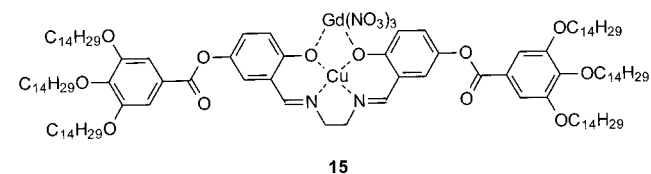
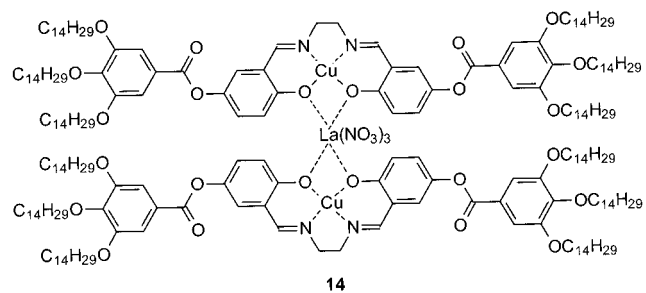
pared by reaction of  $\text{H}_2\text{OOTTAP}$  (**13**) with hydrated lutetium(III) acetate in a 2:1 molar ratio for 1 week



in refluxing 1-hexanol. EPR, NMR, UV-vis, and NIR data were consistent with a deprotonated and radical structure of the complex. The authors conclude that there is no evidence for a preferential localization of the unpaired electron on the two tetraazaporphyrinato rings. Deep green solutions of the compound in acetone, in alcohols, and in a various series of organic solvents were found to be stable over months. Both the redox and UV-vis spectroscopic properties are comparable with those of the substituted bis(phthalocyaninato)lutetium(III) complexes, whereas the NIR vibrational spectra better resemble those of bis-(porphyrinato)lutetium(III) complexes. Although this compound and especially analogous compounds with long alkyl chain have a good potential to exhibit a liquid-crystalline phase, the thermal properties of this class of compounds has not been explored yet. Langmuir-Blodgett films of the butylthio analogue of  $\text{Lu}(\text{OOTTAP})_2$  could only be obtained after mixing the compound with cadmium stearate.<sup>184</sup>

### C. Mixed f-d Metallomesogens

All the liquid-crystalline-metal complexes described so far contain one single lanthanide ion as the central metal ion. It was shown by Binnemans et al. that it is also possible to design metallomesogens containing both a lanthanide ion and a transition metal ion.<sup>185</sup> Mixed f-d metallomesogens **14** and **15** were obtained by adduct formation be-



tween a mesomorphic  $\text{Cu}(\text{salen})$  complex (salen = 2,2'-N,N-bis(salicylidene)ethylenediamine) and a lanthanide nitrate. The trinuclear copper-lanthanum-copper complex and the binuclear copper-gadolinium complex both exhibit a hexagonal columnar phase.

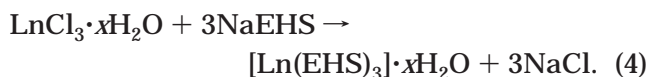
## V. Micellar Solutions and Lyomesophases

### A. Surfactants as Counter Anions for Lanthanide(III) Cations

Although many studies have been devoted to lanthanide ions in micellar systems, only few of these are dealing with well-characterized lanthanide surfactants and even fewer consider the aggregation behavior and lyomesophases formed by these compounds. Often these lanthanide(III) complexes have a low or very low solubility in water, so they have to be dissolved in organic solvents. The lanthanide(III) alkanoates described in section III.A. can be considered as anionic surfactants. As shown in Table 8, the critical micelle concentration has been determined for many compounds in organic solvents.

The only system for which the lyotropic behavior has been studied are the lanthanide(III) alkyl sulfates, especially the lanthanide(III) dodecyl sulfates,  $\text{Ln}(\text{DOS})_3$ . These compounds were known previously, because they are being used as starting materials for the synthesis of liquid-crystalline Schiff's base complexes of the lanthanides with DOS counterions (see section II.A). Lyotropic mesophases were observed for lanthanide trisdodecyl sulfates,  $\text{Ln}(\text{C}_{12}\text{H}_{25}\text{SO}_4)_3$  ( $\text{Ln} = \text{Y}, \text{La}, \text{Ce}-\text{Lu}$ , except  $\text{Pm}$ ) in the presence of ethylene glycol or water (or mixtures thereof) as the solvent.<sup>186</sup> In ethylene glycol, a normal hexagonal phase and a cubic phase could be detected, whereas in water a normal hexagonal phase and a lamellar phase were found. By changing the solvent, it is thus possible to obtain different supramolecular organizations within a series of lanthanide-containing metallocenes. The catalytic properties of these compounds are discussed in section V.D. and their use as templates for mesoporous oxides in section V.E.

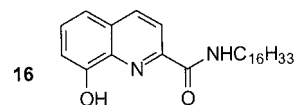
Mwalupindi et al. synthesized the surfactant complexes  $[\text{Eu}(\text{EHS})_3] \cdot x\text{H}_2\text{O}$  and  $[\text{Tb}(\text{EHS})_3] \cdot x\text{H}_2\text{O}$ , where EHS is bis(2-ethylhexyl)sulfosuccinate, by reaction between the respective hydrated chloride and sodium bis(2-ethylhexyl)sulfosuccinate:<sup>187-189</sup>



NaEHS is known by the name Aerosol OT (AOT). AOT is a classic reverse-micelle forming surfactant that gives spherical aggregates of about 15 molecules in nonpolar organic solvents. The micelle swells by addition of water. Replacement of the  $\text{Na}^+$  ions by  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  ions, decreases the cmc from  $4.6 \times 10^{-4}$  to  $7.1 \times 10^{-5}$  M for  $[\text{Eu}(\text{EHS})_3]$  and  $6.4 \times 10^{-5}$  M for  $[\text{Tb}(\text{EHS})_3]$ . In the presence of small amounts of water, the surfactant complexes aggregate in cyclohexane to form reverse micelles with  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  counterions. Small-angle neutron scattering indicated that  $[\text{Ln}(\text{EHS})_3]$  ( $\text{Ln} = \text{Nd}, \text{Eu}, \text{Tb}$ ) compounds form spherical inverse micelles in cyclohexane.<sup>190</sup> The luminescence lifetime of the lanthanide ions inside the micelles was found to depend on the loading,  $w$ , which is defined as the molar ratio  $[\text{water}]/[\text{AOT}^-]$ . In "dry micelles" the lanthanide ions are complexed by the AOT anions. Addition of water results in progressive hydration of the lanthanide ions and a

smooth decrease of the luminescence lifetime. Extraction of lanthanide ions by *p-tert*-butylcalix[4]-arene has been conducted in an AOT–isooctane micellar solution.<sup>191</sup>

8-Hydroxyquinoline is a well-known reagent for gravimetric analysis of trivalent rare-earth ions. In general, neutral complexes with stoichiometry  $\text{LnL}_3$  are formed. Ouyang and co-workers prepared a lanthanum(III) and a gadolinium(III) complex of the amphiphilic 8-hydroxyquinoline derivative 2-(*N*-hexadecylcarbamoyl)-8-hydroxyquinoline (LH, **16**).<sup>192</sup>



The stoichiometry of these complexes is  $[\text{LnL}_2(\text{H}_2\text{O})_4\text{-Cl}]$  ( $\text{Ln} = \text{La}, \text{Gd}$ ), and it is assumed that they are monomeric with the lanthanide ion coordinating by eight donor atoms: two phenolic O atoms, two heterocyclic N atoms, two carbonyl O atoms, and two water O atoms. The chloride ion and the other two water molecules are present in the outer sphere. The complexes show a strong ligand-centered photoluminescence and electroluminescence.<sup>193</sup> It is suggested that these complexes can be used as a light-emitting layer in electroluminescent devices. They form stable monolayers and can be deposited as Langmuir–Blodgett films. These LB films have been studied by X-ray photoelectron spectroscopy (XPS).<sup>194</sup> Evidence was found that the lanthanum(III) ion is coordinated by two ligand molecules.

As written in section II.C., the trivalent lanthanide(III) ions can form tetrakis complexes with  $\beta$ -diketone ligands:  $[\text{Ln}(\beta\text{-diketonato})_4]^-$ . The complexes have an overall negative charge, which can be neutralized by cations such as  $\text{Na}^+$ ,  $\text{K}^+$ , but also by organic cations such as a piperidinium or a quaternary ammonium ion. Amphiphilic complexes can be obtained by using cation surfactants as counteranion. Typical examples are the dimethyldihexadecylammonium or dimethyldioctadecylammonium ions. Another example is the *N*-alkylpyridinium salts. By combining these amphiphilic counteranion with tetrakis( $\beta$ -diketonato) complexes of europium(III) and terbium(III), it is possible to prepare luminescent materials of which it is rather easy to obtain Langmuir–Blodgett films.<sup>195-204</sup> The pyridinium or quaternary ammonium cation can be replaced by an amphiphilic hemicyanine (or azo dye).<sup>205-223</sup> In these amphiphilic lanthanide compounds deposited into Langmuir–Blodgett films, the lanthanide complex anions act both as the counterion of hemicyanine and as the spacer within the Langmuir–Blodgett film. These complexes show that not only the film-forming properties can be improved if the appropriate  $\beta$ -diketone ligands were chosen but also the molecular hyperpolarizability,  $\beta$ , can be enhanced compared with the corresponding hemicyanine bromide or iodide. This effect may be in part due to the local field effect, but primarily to molecular ordering and ordered segregation of hemicyanine chromophores by the bulky lanthanide complexes' anions. The hemicyanine complexes exhibit interesting NLO effects in

solution too. In these systems (both in the solid state and in solution), only ligand-centered photoluminescence is observed, with no luminescence by the lanthanide ion. The supposed liquid crystallinity of these complexes has been discussed in section II.C.

## B. Photophysics

Lanthanide ions are well-known for their narrow-line luminescence. The luminescence behavior of lanthanide complexes can be influenced by adding surfactant to the solution in which the lanthanide complexes is dissolved. In micelles it is also possible to dissolve lanthanide complexes that are themselves not soluble in aqueous solution. The micelles can modify transition intensities (absolute and relative), the luminescence lifetime, and the energy transfer. Micelles can influence the energy transfer largely by bringing the donor and acceptor in close proximity to each other. Dong and Flint have studied the photophysical properties of anionic  $[\text{Ln}(\text{dpa})_3]^{3-}$  (dpa = pyridine-1,6-dicarboxylate or dipicolinate) complexes in aqueous solution containing the cationic surfactant cetyltrimethylammonium bromide (CTAB).<sup>224,225</sup> The authors were able to show that the complexes associate strongly with the surface of CTAB micelles so that most of the bromide anions have been replaced by the complex  $[\text{Ln}(\text{dpa})_3]^{3-}$  anions. The electrostatic interactions between the  $[\text{Ln}(\text{dpa})_3]^{3-}$  ions were sufficiently strong to distort these complexes significantly. For  $[\text{Tb}(\text{dpa})_3]^{3-}$  on the micelle surface, it was found that the luminescence lifetime of the  $^5\text{D}_4$  state is reduced, due to this distortion. Only little changes in the luminescence spectra could be detected. In general, the transition probability is higher for lanthanide ions located at a site of low symmetry when compared to a lanthanide ion located at a site of high symmetry. Precise measurements of the luminescence lifetime allowed differentiation between  $[\text{Tb}(\text{dpa})_3]^{3-}$  complexes in bulk solution and those bound to the micelle surface. For the  $[\text{Eu}(\text{dpa})_3]^{3-}$ , a different behavior was observed, in the sense that the luminescence lifetime of the  $^5\text{D}_0$  state is longer for the complex ion on the surface of the micelles than for the same complex ions in the bulk aqueous solution.<sup>226</sup> The most important effect of association of complex ions to the micelle surface is that more water molecules are excluded from the second coordination sphere than when the  $[\text{Ln}(\text{dpa})_3]^{3-}$  complexes are present in the bulk aqueous solution. This exclusion causes a decrease of the radiationless decay rate, which more than compensates for the increase in the radiative decay rate due to the distortion of the complex. Because the energy difference between the excited state and the ground state is larger for  $\text{Tb}^{3+}$  than for  $\text{Eu}^{3+}$ , exclusion of water molecules from the second coordination sphere has a more pronounced influence on  $\text{Eu}^{3+}$  than on  $\text{Tb}^{3+}$ . Indeed, the probability of radiationless deactivation depends exponentially on the number of O–H vibration phonons necessary to bridge the gap between the excited state and the ground state. The triply negative  $[\text{Eu}(\text{dpa})_3]^{3-}$  complex anions have to compete with the bromide anions for the sites on the surface of the micelle. Measurements have shown

that the micellar surface is essentially covered with  $[\text{Eu}(\text{dpa})_3]^{3-}$  complexes when the surfactant:  $[\text{Eu}(\text{dpa})_3]^{3-}$  ratio is ca. 4:1 (provided that the surfactant concentration is above the cmc). This is before electrical neutrality of the micelle complex would be achieved in the absence of other anions. Two factors are discussed for the distortion of the  $[\text{Eu}(\text{dpa})_3]^{3-}$  complexes on the surface of the micelle: (1) penetration of the pyridine rings in the micelle to bring the carbonyl oxygens in close contact with the  $\text{N}^+(\text{CH}_3)_3$  groups and (2) repulsive interaction between adjacent complex ions on the micelle surface at high  $[\text{Eu}(\text{dpa})_3]^{3-}$  concentrations. The distortion can be studied by monitoring the intensity of the  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  transition: forbidden in the  $D_3$  symmetry of an undistorted  $[\text{Eu}(\text{dpa})_3]^{3-}$  complex but allowed by distortion to a lower symmetry. The same authors measured the energy transfer from  $[\text{Tb}(\text{dpa})_3]^{3-}$  to other  $[\text{Ln}(\text{dpa})_3]^{3-}$  complexes (Ln = Pr, Nd, Sm, Eu, Ho, Er, Y).<sup>227</sup> In homogeneous aqueous solution, energy transfer between  $[\text{Tb}(\text{dpa})_3]^{3-}$  and  $[\text{Ln}(\text{dpa})_3]^{3-}$  complex is inefficient, because of the large distance between the  $[\text{Tb}(\text{dpa})_3]^{3-}$  donor complex and the  $[\text{Ln}(\text{dpa})_3]^{3-}$  acceptor complex, due to the repulsion between the triply negative charges. Association of the complexes on the micellar surface brings the anionic complexes close enough to each other so that energy transfer can occur via an electric dipole–electric dipole mechanism. The mean distance between the complexes on the surface of the micelle is only slightly larger than the distances in crystalline complexes.<sup>228</sup> The rate of energy transfer depends on the spectral overlap between the emissive transition from the  $^5\text{D}_4$  state of  $\text{Tb}^{3+}$  and the absorption transition of the quenching complex ion. The energy transfer rate was the fastest from  $[\text{Tb}(\text{dpa})_3]^{3-}$  to  $[\text{Nd}(\text{dpa})_3]^{3-}$  but was also large for  $[\text{Sm}(\text{dpa})_3]^{3-}$ ,  $[\text{Eu}(\text{dpa})_3]^{3-}$ , and  $[\text{Y}(\text{dpa})_3]^{3-}$ . The energy transfer rate from  $[\text{Tb}(\text{dpa})_3]^{3-}$  to  $[\text{Nd}(\text{dpa})_3]^{3-}$  was found to be reduced by addition of other anions to the micellar solution. These anions compete with  $[\text{Ln}(\text{dpa})_3]^{3-}$  complexes for a place on the micellar surface. The effect of the added anions decreased in the order  $\text{NO}_3^- > \text{Br}^- > \text{Cl}^-$ , reflecting the binding efficiency of the anions.

Whereas the charged  $[\text{Ln}(\text{dpa})_3]^{3-}$  complexes cannot be introduced to the hydrophobic interior of a micelle, neutral complexes such as Lewis-base adducts of tris( $\beta$ -diketonato)lanthanide(III) complexes can. Wong and Flint were able to show that one or two  $[\text{Tb}(\text{acac})_3\text{phen}]$  complexes (Hacac = acetylacetonate; phen = 1,10-phenanthroline) can be solubilized in the interior of a sodium dodecyl sulfate (SDS) micelle, provided that the molar ratio of SDS to  $[\text{Tb}(\text{acac})_3\text{phen}]$  is larger than 25.<sup>229</sup> Intermolecular energy transfer can occur between the  $[\text{Tb}(\text{acac})_3\text{phen}]$  complexes inside the micelle and  $[\text{Ln}(\text{dpa})_3]^{3-}$  complexes (Ln = Pr, Nd, Ho, Er) associated with the surface of the micelle. Little energy transfer (and thus little quenching of the terbium luminescence) was observed for Ln = Eu, Sm.  $[\text{Nd}(\text{acac})_3\text{phen}]$  quenches the emission of  $[\text{Tb}(\text{acac})_3\text{phen}]$  when one molecule of each is introduced in the hydrophobic region of the micelle. The energy transfer between

phenanthrene solubilized in cetyltrimethylammonium bromide micelles and  $[\text{Ln}(\text{dpa})_3]^{3-}$  complexes ( $\text{Ln} = \text{Eu}, \text{Tb}, \text{Dy}$ ) associated with the micelle surface has been measured.<sup>230</sup> The mechanism of energy transfer depends on the relative energy of the aromatic triplet states and the lanthanide excited states. For the  $[\text{Eu}(\text{dpa})_3]^{3-}$  and  $[\text{Dy}(\text{dpa})_3]^{3-}$  complexes, the energy transfer is from the aromatic triplet state  $T_1$  to the lanthanide excited states ( ${}^5D_2$  for  $\text{Eu}^{3+}$  and  ${}^4F_{9/2}$  for  $\text{Dy}^{3+}$ ). For the  $[\text{Tb}(\text{dpa})_3]^{3-}$  complex, the energy transfer is from the  ${}^5D_4$  excited state of  $\text{Tb}^{3+}$  to the coexcited phenanthrene lowest triplet  $T_1$  (excitation with the 347 nm line of a ruby laser), thereby exciting the phenanthrene to a higher triplet  $T_2$ . De Schryver and co-workers reported an investigation of fluorescence quenching of solubilized pyrene and pyrene derivatives by  $\text{Eu}^{3+}$  ions in SDS micelles.<sup>231</sup> They concluded that, due to the low solubility of  $\text{Eu}(\text{DOS})_3$ , only one ion per micelle can be present. The results are discussed using a kinetic model.

The photophysics of lanthanide ions in inverse micellar systems have been investigated, too. Most of these studies were focused to the energy transfer between organic molecules dissolved in the bulk nonpolar organic phase and lanthanide ions in the aqueous solution entrapped inside the inverse micelle. Correll et al. observed intermolecular energy transfer from the pyrene triplet to the terbium ion for cyclohexane solutions of substituted pyrene molecules with dodecylammonium inverse micelles containing aqueous terbium ions.<sup>232</sup> These results look strange, because the pyrene lowest triplet is below the lowest excited state of  $\text{Tb}^{3+}$ . Comparable results were obtained using  $\omega$ -naphthyl-substituted alkanic acids, but in this case the triplet level is above the lowest excited state of the  $\text{Tb}^{3+}$  ion.<sup>233</sup> Energy transfer was observed from naphthalene, phenanthrene, and biphenyl solubilized in SDS micelles to  $\text{Tb}^{3+}(\text{aquo})$ ,<sup>234,235</sup> but no energy transfer could be observed from phenanthrene to the  $\text{Eu}^{3+}(\text{aquo})$ .<sup>235</sup>

### C. Analytical Applications

Neutral lanthanide complexes can be dissolved in micelles formed by nonionic surfactants such as polyoxyethylene isooctylphenol (Triton X-100) or nonaoxyethylene dodecyl ether (BL-9EX). This approach is useful to obtain highly luminescent aqueous lanthanide solutions. The free aqueous lanthanide ions are only very weakly luminescent, because of the low molar absorptivities  $\epsilon$  of the lanthanide f-f transitions ( $\epsilon \leq 10 \text{ mol}^{-1} \text{ L cm}^{-1}$ ) and because the water molecules in the first coordination sphere quench the excited states very efficiently. By forming coordination complexes with strongly absorbing organic ligands, the luminescence efficiency can be increased. The organic ligand absorb light via intense  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  transitions. The ligand absorption is then followed by an intramolecular ligand-to-metal energy transfer. The energy transfer is efficient in the case that the lowest ligand triplet level is at the same energy as an excited lanthanide level. By complex formation with organic ligands, water molecules can be expelled from the first coordination sphere, too. Three bidentate monocharged ligands

result in a neutral 6-coordinate complex. Classical examples are the tris( $\beta$ -diketonato)lanthanide(III) complexes. Coordination number 6 is low for lanthanide ions (CN 8 or 9 is more common), so it is very likely that the coordination sphere is expanded by taking up two or three water molecules. The water molecules can be removed from the first coordination sphere by forming Lewis-base adducts with neutral molecules, such as 1,10-phenanthroline (phen) or tri-*n*-octylphosphine (topo). However, these neutral Lewis-base adducts have a very low solubility in water. They can be solubilized by addition of a surfactant. As mentioned above, a nonionic surfactant is often used.

Highly luminescent lanthanide complexes dissolved inside micelles have found application in the spectrofluorimetric determination of lanthanide ions ( $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Dy}^{3+}$ ). Micellar systems provide a means of much faster and easier analysis than when the highly luminescent, but hydrophobic, lanthanide complexes have to be separated from the aqueous solution in a separate solvent extraction step. Arnaud and Georges showed that by using the ternary complex  $[\text{Eu}(\text{tta})_3(\text{topo})_2]$  ( $\text{Htta} = 2$ -thenoyltrifluoroacetone) in a micellar solution of Triton X-100 detection limits as low as  $6 \times 10^{-12} \text{ mol L}^{-1}$  can be achieved.<sup>236</sup> The luminescence intensity was a linear function of the europium(III) concentration over 6 orders of magnitude from  $10^{-11}$  to  $10^{-5} \text{ mol L}^{-1}$ . It is interesting to note that most of the Htta exists outside the micelle, in the bulk aqueous phase, whereas the  $[\text{Eu}(\text{tta})_3]$  and  $[\text{Eu}(\text{tta})_3(\text{topo})_2]$  complexes were found to exist inside the micelle.<sup>237</sup> Trace analysis of  $\text{Eu}^{3+}$  is important in fluoroimmunoassay.<sup>238</sup> It is possible to determine by spectrofluorimetry simultaneously traces of samarium and europium,<sup>239,240</sup> or even of a ternary mixture of samarium, europium, and terbium.<sup>241,242</sup> The method can also be adapted for analysis by flow injection spectrofluorimetry.<sup>243,244</sup> The most often used  $\beta$ -diketone in analytical determination of europium or samarium is 2-thenoyltrifluoroacetone (Htta),<sup>236,245–248</sup> because this ligand is known to form strongly luminescent complexes with europium(III), although also other  $\beta$ -diketones have been investigated. For determination of terbium(III), it is more advisable to use benzoate complexes, because these are much more luminescent than the tris( $\beta$ -diketonato)terbium(III) complexes.<sup>249–251</sup> Tetracyclines can be detected by europium luminescence in micellar solutions.<sup>252–254</sup> By adding sodium dodecyl sulfate to solution containing  $[\text{Eu}(\text{dpa})_3]^{3-}$  or  $[\text{Tb}(\text{dpa})_3]^{3-}$ , the detection limit was hardly changed, but the linear dynamic range could be extended to higher concentrations.<sup>255</sup> It has been illustrated that lanthanide luminescence in micellar solutions can be used to detect additives such as benzoic acid, terephthalic acid, or saccharin in soft drinks.<sup>256,257</sup> The luminescence enhancement by topo of lanthanide complexes with trimesic acid was found to depend strongly on the pH.<sup>258</sup> In comparison to europium(III), terbium(III), and samarium(III), reports on the spectrofluorimetric determination of dysprosium(III) in surfactant systems are much scarcer.<sup>259</sup> Lanthanide(III) ions and espe-

cially terbium(III) are of interest for the detection of biological molecules after separation by HPLC or capillary electrophoresis.<sup>260–263</sup>

Instead of using luminescence, the lanthanide ion concentration can be determined by absorption spectroscopy. Because the *f*–*f* transitions of lanthanide ions are too weak for analytical purposes, a complexometric indicator is used. An example is the determination of lanthanide ions with xylenol orange in the presence of a surfactant.<sup>264,265</sup> Slightly acidic solutions of xylenol orange are yellow, showing an absorption maximum at 435 nm. In the presence of lanthanide ions, intensively red complexes with an absorption maximum in the 570–575 nm range are formed. The sensitivity of the reaction can be increased by adding a surfactant. At the same time, a shift of the absorption bands to longer wavelength can be observed. Complexometric reagents other than xylenol orange have been investigated, too.<sup>266–268</sup>

*Micellar ultrafiltration* has been used to determine the extraction yield of europium(III) by a series of micelle-solubilized extractants derived from 5-pyrazolone as a function of the pH.<sup>269</sup> The extractants were solubilized inside CTAB micelles. Because no anionic europium(III) species are formed, association of the cationic surfactant molecules to the europium(III) complexes is considered unlikely.

Europium(III)–DTPA complexes (DTPA = diethylenetriaminepentaacetic acid) have been incorporated into liposomes doped with biotin (for a definition of liposome, see section VI).<sup>270</sup> It was shown that the Eu<sup>3+</sup> ion needs to be complexed by a chelate in order to obtain stable liposomal encapsulation.<sup>270,271</sup> This is thought to be due to the interaction between the phospholipid headgroup and the Eu<sup>3+</sup> ion, interfering with the formation of liposomes. The resulting europium(III)-loaded liposomes bind specifically to streptavidin. The potential of this system for time-resolved fluorometric assay has been demonstrated. The sensitivity of the assay allowed for the detection of 10<sup>–18</sup> M quantities of liposomes.

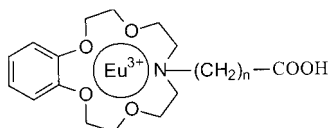
#### D. Catalytic Applications

Lewis acids are extensively being used as reagents or catalysts for organic reactions. Reactions such as the Friedel–Crafts acylation of aromatic compounds require at least a stoichiometric amount of a Lewis acid (e.g. AlCl<sub>3</sub> or FeCl<sub>3</sub>), due to complex formation of the Lewis acid with the carbonyl groups in the reagents. Because of the industrial importance of Friedel–Crafts reactions, there is a need for Lewis acids that are required in catalytic amounts only. An additional disadvantage of strongly reactive Lewis acids is that they cannot be used in aqueous solutions, because the Lewis acid is decomposed by water. Possible alternatives for AlCl<sub>3</sub> or FeCl<sub>3</sub> are salts of trivalent lanthanide ions.<sup>272,273</sup>

Kobayashi and co-workers showed that water-stable Lewis-acid catalysts can be obtained by combining Lewis acids with surfactants.<sup>274</sup> The Lewis acids are incorporated in micelles, so that they retain their catalytic activity in the organic medium inside the micelle. The first example of these combined Lewis acid–surfactant systems consisted of a mixture

of scandium(III) triflate as Lewis acid and sodium dodecyl sulfate as surfactant.<sup>275,276</sup> Also, aromatic anionic surfactants have been mixed with scandium(III) triflate.<sup>277</sup> Scandium(III) dodecyl sulfate and scandium(III) dodecanesulfonate can be used as a monocomponent catalyst.<sup>278,279</sup> In contradiction to organic solvents, where Lewis acids catalyze both Diels–Alder reactions and aldol condensations, scandium(III) dodecyl sulfate and scandium(III) dodecanesulfonate have no influence on the rate of Diels–Alder reactions in aqueous solution.<sup>280</sup> However, these compounds are an excellent catalyst for Mukaiyama aldol reactions,<sup>281</sup> for Michael reactions,<sup>282</sup> for Mannich reactions,<sup>274</sup> and for allylation reactions.<sup>274</sup> In the aldol reactions, a remarkable enhancement of the reactivity was observed after addition of a Brønsted acid such as HCl.<sup>283</sup> Studies on aldol reactions of benzaldehyde with a thioketene silyl acetal in water in the presence of various dodecyl sulfate and dodecanesulfonate salts revealed that scandium(III) and ytterbium(III) salts are more suitable than transition metal salts, because of their ability to suppress the hydrolysis of the thioketene silyl acetal.<sup>279</sup> An investigation of the effect of the alkyl chain length of the scandium(III) alkane-sulfonates on their catalytic activity in aldol reaction showed that the maximal yield is obtained for scandium(III) dodecanesulfonate.<sup>274</sup> A similar variation of the solvent with scandium(III) dodecyl sulfate as catalyst indicated that water is by far the best solvent.<sup>274</sup> In the workup procedure, it was demonstrated that centrifugation of the reaction mixture led to phase separation without the addition of any organic solvent. So, in principle, the removal of the surfactant type catalyst is easy. Another application of scandium(III) dodecyl sulfate is to catalyze three-component reactions of aldehydes, amines, and triethyl phosphite to  $\alpha$ -amino phosphonates.<sup>284</sup>

It is well-known that lanthanide ions facilitate the hydrolysis of phosphodiester.<sup>285,286</sup> These compounds can be considered as RNA or DNA model compounds. An often used standard phosphodiester substrate is bis(*p*-nitrophenyl)phosphate (BNPP). Rapid cleavage of this compound could be obtained by Ce<sup>4+</sup> in aqueous micellar solution.<sup>287</sup> Of the trivalent lanthanide ions, Tm<sup>3+</sup> was reported to be the most effective.<sup>288</sup> The cleavage of the liposomal phosphodiester 1,2-dipalmitoyl-3-glyxceryl *p*-nitrophenyl phosphate by Eu<sup>3+</sup> or La<sup>3+</sup> in the presence of H<sub>2</sub>O<sub>2</sub> is 50–70 times faster than the cleavage of BNPP.<sup>289</sup>  $\beta$ -Hydroxyhexadecyl *p*-nitrophenyl phosphate forms micelles in water (cmc = ca. 4.5  $\times$  10<sup>–5</sup>M) and is cleaved by Eu<sup>3+</sup> 7–11 times faster than a nonmicellar  $\beta$ -hydroxypropyl analogue.<sup>290</sup> The hydrolytic activity of Eu<sup>3+</sup> of *N*-carboxyalkyl benzoaza-15-crown-5 ethers toward the BNPP and plasmid DNA has been investigated (Figure 21).<sup>291</sup> The rate of BNPP hydrolysis was found to vary dramatically with the chain length of the methylene spacer, with the longest spacer being the most efficient one. On the other hand, the hydrolysis rate of plasmid DNA is virtually independent of the chain length.



**Figure 21.** Europium(III) complexes of *N*-carboxyalkylbenzoaza-15-crown-5 ethers, which are able to hydrolyze phosphate esters.<sup>291</sup>

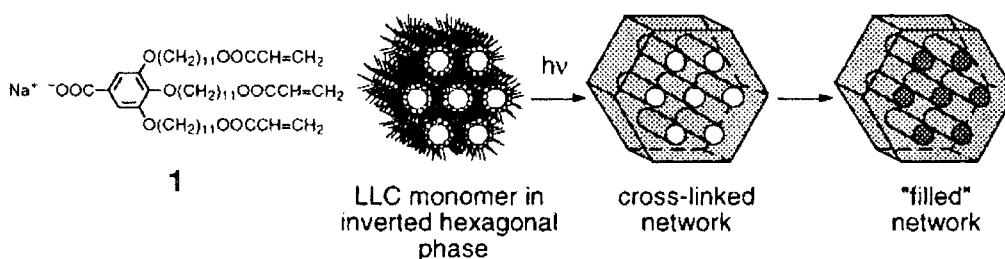
### E. Mesoporous Materials by LC Templating

Gin and co-workers studied europium(III) and cerium(III) salts of 3,4,5-tris(11'-acroyloxyundecyl-oxy)benzoic acid.<sup>292</sup> An inverted hexagonal lyotropic mesophase was obtained by mixing the metal complexes with distilled water and a xylene solution of the photoinitiator 2-hydroxy-2-methylpropiophenone. The nature of the lyotropic mesophase was determined by X-ray diffraction. By photopolymerization of the lyotropic mesophase, the mesophase order remained intact and a nanostructured polymer network was obtained (Figure 22). The dimensions of the inverted hexagonal mesophase could be controlled by changing the nature of the metal ion and by varying the alkoxy chain length. The unit cell dimensions of the cerium(III)- and europium(III)-containing mesophases were substantially smaller than those of comparable mesophases containing divalent transition metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ) or containing sodium ions. It was concluded that the nature of the metal-carboxylate interaction has a

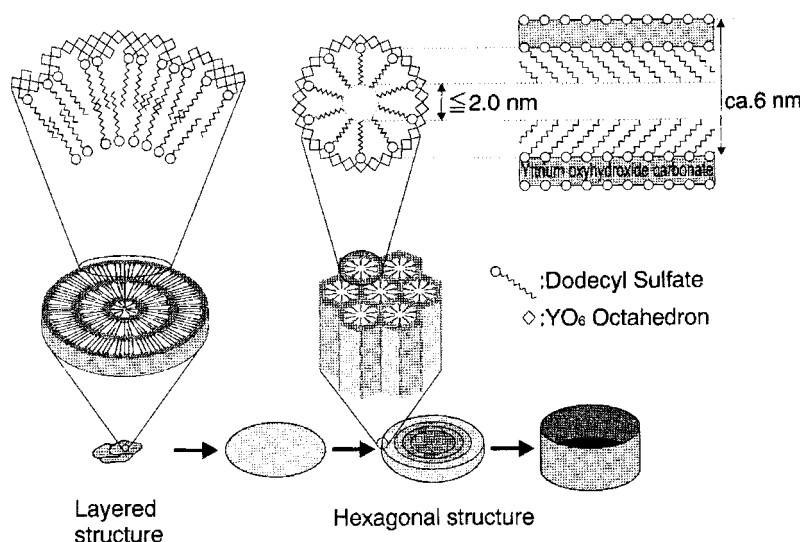
larger influence on the size of the amphiphilic head-group than the size of the metal ion has. Stronger metal-carboxylate interactions reduce the overall size of the headgroup, resulting in a more efficient packing and hence smaller unit cell dimensions. The europium(III)-containing polymer network exhibited a strong photoluminescence, the strongest emission bands being situated at 593 and 615 nm. These bands correspond to the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition, respectively. This is an indication that only few water molecules are present in the first coordination sphere of the lanthanide ion, because water molecules quench  $\text{Eu}^{3+}$  luminescence efficiently.

A nanostructured ion-exchange resin containing sulfonate groups was prepared by photocross-linking of an inverted hexagonal lyotropic liquid-crystal phase of a monomeric precursor with sodium counterions.<sup>293</sup> By replacing the  $\text{Na}^+$  ions by  $\text{Sc}^{3+}$  ions, a heterogeneous Lewis acid catalyst was obtained. This catalyst was tested for Mukaiyama aldol reactions and Mannich reactions in water. A recent review describes the possibilities of lyotropic mesophases to create nanostructured polymers binding metal ions (including lanthanide ions).<sup>294</sup>

Yada and co-workers synthesized layered and hexagonal mesostructured yttrium oxides using anionic surfactants (alkyl sulfates or alkylsulfonates) as the template (Figure 23).<sup>295</sup> The mesoporous



**Figure 22.** Cerium(III) and europium(III) analogues of the sodium compound **1** have been studied as polymerizable lyotropic liquid crystals, which could be converted into nanostructured lanthanide-containing polymers (Reprinted from ref 292. Copyright 1998 American Chemical Society).



**Figure 23.** Structure models proposed for the layered and hexagonal forms of the yttrium dodecyl sulfate containing mesophases and their transformation in mesoporous oxides (Reprinted from ref 295. Copyright 1998 American Chemical Society).

compounds were precipitated by a homogeneous precipitation method using urea. The hydrolysis of urea slowly raises the pH. The yttrium-based material formed by hydrolysis of the mesophase was shown to exist as a mixture of yttrium oxide, hydroxide, carbonate, and alkyl sulfate (or alkylsulfonate) species. The porosity of the compounds could be increased markedly by replacing the anionic surfactant by acetate groups (via anion exchange). This method was extended to the synthesis of a whole series of porous rare earth oxides.<sup>296</sup> It is also possible to obtain mixed oxides, such as yttrium aluminum oxide,<sup>297,298</sup> yttrium zirconium oxide,<sup>299</sup> or yttrium gallium oxide.<sup>300</sup>

A micellar phase has been used to obtain fine disklike particles of the red-emitting phosphor  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ .<sup>301</sup> A mixed ethanolic of  $\text{YCl}_3$  and  $\text{EuCl}_3$  was added to a micellar ethanolic solution of the cationic surfactant  $\text{C}_{12}\text{H}_{25}\text{NH}_3\text{Cl}$ . Although not characterized, the precipitate is most likely a perovskite-type layer compound of formula  $(\text{C}_{12}\text{H}_{25}\text{NH}_3)_3(\text{LnCl}_6)$ . The product was calcinated at 600 °C and further annealed at 1350 °C. The europium complex  $[\text{Eu}(\text{tta})_3]$  ( $\text{Htta} = 2$ -thenoyltrifluoroacetone) has been encapsulated into the MCM-41 mesoporous molecular sieve by a sol-gel process.<sup>302</sup> MCM-41 was synthesized using the surfactant cetyltrimethylammonium bromide (CTAB) as the template. With the same surfactant, mixed yttrium zirconium oxides have been prepared.<sup>303,304</sup>

## VI. Phospholipid Bilayers

In aqueous solution, phospholipids self-assemble to lipid bilayers rather than to micelles. The reason is that phospholipids, such as phosphatidyl choline, have two fatty acid chains that are more or less parallel to one another. The overall shape of a phospholipid molecule is approximately rectangular, so these molecules are too bulky to fit in the interior of micelles. The lipid bilayers can form lipid vesicles (also called liposomes) in which an aqueous compartment is enclosed by the bilayer. Liposomes can be considered as bilayer micelles, in which a volume of water is entrapped inside the micelles. Lipid bilayers can also exist in the form of planar bilayer membranes. Such bimolecular sheets can have macroscopic dimensions, up to 1 mm. The well-defined synthetic membranes are being studied as model systems for biological membranes.

Although phosphatidyl choline (lecithin) in membranes is an electrically neutral zwitterion at physiological pH values, it can bind di- and trivalent cations at the membrane surface. In a biological environment, binding of  $\text{Ca}^{2+}$  to phosphatidyl choline is of great importance. It is known that the stability of the membrane bilayers is affected by the presence of cations. Because the trivalent lanthanide ions often mimic the properties of divalent calcium, the interaction of lanthanide ions with the membrane component phosphatidyl choline has been investigated by several research groups. Most often, phosphatidyl choline is obtained from egg yolk. Because coordination of  $\text{Ln}^{3+}$  to phosphatidyl choline takes place via the phosphate groups, <sup>31</sup>P NMR has proved to be a

useful tool in these studies.<sup>305–308</sup> The binding strength of the lanthanide ions to the membrane depends on the type of anion present. The order of bonding enhancement is  $\text{Cl}^- < \text{Br}^- < \text{NO}_3^-$ .<sup>307</sup> The smaller the lanthanide ion, the stronger is the interaction with the phosphatidyl choline membranes (so the strongest interaction is observed for the ions at the end of the lanthanide series).<sup>309</sup> The lanthanide ions show a much stronger interaction than  $\text{Ca}^{2+}$ . Competition experiments between  $\text{Eu}^{3+}$  and the cationic form of amphiphilic drugs (procaine, tetracaine, metoprolol, alprenolol, and propofanol) for absorption to phosphatidyl choline membranes have been carried out.<sup>307</sup> The binding constants of the drugs in the competition experiments followed the same order as in the absence of  $\text{Eu}^{3+}$ , but the numerical values were reduced.

The effect of lanthanide ions on the phase behavior of dipalmitoylphosphatidylcholine (DPPC) liposomes has been investigated in detail.<sup>309–316</sup> Free lanthanide ions are able to displace  $\text{Ca}^{2+}$  bound on DPPC liposomes, but  $\text{Ln-DTPA}$  coordination complexes cannot. Also, citrate complexes have little effect on the liposomes.<sup>312</sup> Pure DPPC liposomes exhibit a sharp gel to liquid crystal phase transition at 315.2 K with a pretransition at 308.8 K. Both lanthanide and calcium ions increase the phase transition temperature of DPPC, and the pretransition peak disappears. This means that the cations increase the membrane rigidity. The strongest effect is observed for the heavy lanthanides. The DTPA complexes of the lanthanide ions and of calcium effect the phase transition temperatures, too, but the effect is less distinct than in the case of the chloride salts. Long-range ordered stripes domain structures were observed in a DPPC Langmuir-Blodgett film that was spread on an europium(III)-containing aqueous solution and transferred to a freshly cleaved mica substrate.<sup>314</sup> The ordered domain structures have been studied by atomic force microscopy.<sup>316</sup> The influence of gadolinium ions on the phase behavior of dimyristoylphosphatidyl serine (DMPS) has been investigated by DSC.<sup>317</sup> At low ionic strengths, the gel-to-liquid crystal phase transition appeared as one peak, which broadened and shifted to higher temperatures as the total concentration of  $\text{Gd}^{3+}$  was increased. At high ionic strengths, a more complicated behavior was observed. On the other hand, the gel-to-liquid crystal transition temperatures of dielaidoylphosphatidylethanolamine (DEPE) liposomes were found not to change upon addition of  $\text{La}^{3+}$  ions.<sup>318</sup> The same authors mention that  $\text{Gd}^{3+}$  is able to shift the phase transition temperature in these DEPE liposomes. The different behavior is attributed to differences in the interaction strength for these ions.  $\text{La}^{3+}$  ions promote the formation of the hexagonal II phase ( $\text{H}_{\text{II}}$ ) at temperatures lower than those of pure egg phosphatidylethanolamine. Thus, the mesophase stability range of the lamellar phase ( $\text{L}_\alpha$ ), which occurs at lower temperatures than the hexagonal II phase, is reduced upon addition of  $\text{La}^{3+}$  ions.

Polymerized luminescent liposomes containing  $\text{Tb}^{3+}$  ions have been obtained by combining an EDTA chelating group with a polymerizable lipid.<sup>319</sup> Studies



of lanthanide-doped magnetically alignable phospholipid bilayers are discussed in section VII.B.

## VII. Magnetic Properties

### A. Magnetic Anisotropy and Magnetic Alignment of Liquid Crystals

The molecules in a mesophase can be aligned by applying an external magnetic field. An important factor dictating how the liquid crystal will be oriented in a magnetic field is the *magnetic anisotropy*,  $\Delta\chi$ , which is defined as  $\chi_{\parallel} - \chi_{\perp}$ . Here,  $\chi_{\parallel}$  and  $\chi_{\perp}$  are the components of the magnetic susceptibility tensor parallel and perpendicular to long molecular axis, respectively. The higher the value of  $\Delta\chi$ , the easier the liquid crystal can be aligned in a magnetic field (i.e., the weaker the magnetic field has to be for obtaining magnetic alignment). The sign of  $\Delta\chi$  determines how the director, and thus the long molecular axis, will be aligned in a magnetic field. If  $\Delta\chi$  is positive, the molecules will be oriented with their molecular long axes parallel to the magnetic field. If  $\Delta\chi$  is negative, the molecules will be aligned with their long molecular axis perpendicular to the magnetic field. Whereas it is in principle possible to obtain a monodomain liquid crystal when the director aligns parallel to the applied magnetic field ( $\Delta\chi > 0$ ), this is not the case when the director aligns perpendicular to the magnetic field ( $\Delta\chi < 0$ ); there is only one direction parallel to the magnetic field, but if  $\Delta\chi < 0$ , the director can have any orientation in a plane perpendicular to the magnetic field. A polydomain is obtained when the different microdomains are randomly oriented, with the only restriction that the director is situated within a plane.<sup>320</sup> A monodomain can be obtained by applying a second magnetic field perpendicular to the first magnetic field. If  $\Delta\chi < 0$ , the director will be oriented perpendicular to both magnetic field directions.

The trivalent lanthanides ions (especially Tb<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>) have a very large magnetic anisotropy in comparison with other paramagnetic ions (e.g., Cu<sup>2+</sup> or V=O<sup>2+</sup>), so the diamagnetic contributions to  $\Delta\chi$  can be neglected in comparison to the paramagnetic contribution. An exception is the Gd<sup>3+</sup> ion, which is almost magnetically isotropic due to the S ground state <sup>8</sup>S<sub>7/2</sub>. The large magnetic anisotropy of liquid-crystalline lanthanide complexes was discovered soon after the first calamitic lanthanide-containing metallomesogens had been prepared.<sup>321</sup> Because the sign of the magnetic anisotropy depends on the lanthanide ion, it is possible to obtain, with the same kind of ligand and with the proper choice of the lanthanide ion, compounds that can either be aligned perpendicular or parallel to the magnetic field. Analysis of the experimental magnetic susceptibility data shows that these compounds can be classified into two distinct groups, depending on the sign of  $\Delta\chi$ .<sup>322</sup> The first group contains Ce<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup>, and Ho<sup>3+</sup> compounds, while the second group contains Eu<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, and Yb<sup>3+</sup> compounds. Two compounds not belonging to the same group always have opposite sign of  $\Delta\chi$ . For instance, if  $\Delta\chi$  is negative for the first group of

lanthanide compounds,  $\Delta\chi$  is positive for the second group, and vice versa. All experimental results obtained so far for lanthanide-containing liquid crystals are in agreement with a negative  $\Delta\chi$  value for the first group and a positive  $\Delta\chi$  value for the second group. But recent theoretical work shows that the reverse situation can be expected, too.<sup>322</sup> The highest values of the magnetic anisotropy are observed for the heavy lanthanides Tb<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, and Tm<sup>3+</sup>, because these ions have a high magnetic moment. There is no one-to-one relationship between a high magnetic moment and a large magnetic anisotropy, but if the magnetic moment is small, it is impossible to have a large magnetic anisotropy. The magnitude of the magnetic anisotropy for a series of isostructural lanthanide-containing metallomesogens can be estimated on the basis of the crystal-field splitting of the <sup>7</sup>F<sub>1</sub> multiplet in the corresponding europium(III) compound.<sup>323</sup> This splitting is accessible via photoluminescence measurements. Model calculations have been used to relate the magnetic anisotropy to the type of coordination polyhedron around the central lanthanide ion.<sup>324</sup> Another approach to rationalize the magnetic anisotropy is based on the Bleaney theory (which is used to predict the lanthanide-induced shift in NMR spectra).<sup>325</sup>

It should be remembered that the magnetic moment is related to the magnetic anisotropy by the relationship

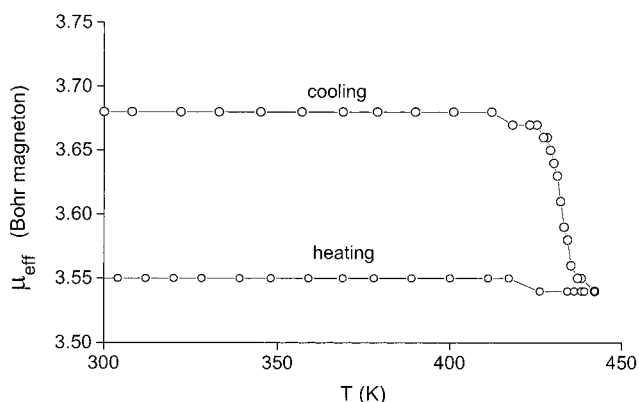
$$\mu_{\text{eff}} = \sqrt{\frac{3k}{N_A}} \cdot \sqrt{\chi T} = 2.828 \sqrt{\chi T} \quad (5)$$

where  $\mu_{\text{eff}}$  is the effective magnetic moment (in Bohr magneton,  $\mu_B$ ),  $k$  is the Boltzmann constant,  $N_A$  Avogadro's number,  $\chi$  the magnetic susceptibility, and  $T$  the absolute temperature. Another requirement for a high magnetic anisotropy (except a large magnetic moment) is that the crystal-field perturbation is strong. The <sup>2S+1</sup>L<sub>J</sub> ground-state splits under the influence of the crystal-field potential in a number of crystal field levels, at maximum  $2J+1$  for integer  $J$  (even number of f electrons), and  $J + 1/2$  for half-integer  $J$  (odd number of f electrons). The magnetic anisotropy arises from the fact that when the crystal-field splitting is large, not all the crystal-field levels are statistically populated at a given temperature. The magnetic anisotropy increases when the temperature is lowered. At temperatures above room temperature, the magnetic behavior becomes more and more isotropic and approaches the predictions in the free ion approximation. However, when the crystal-field perturbation is large, it is possible to have a large magnetic anisotropy, even at temperatures at which the mesophase of lanthanide-containing liquid crystals is stable.

The main problem to cope with is the high viscosity of the mesophase, which prevents fast switching. In general, cooling rates of less than 1 °C/min are necessary to achieve good alignment in a magnetic field when going from the isotropic liquid to the mesophase. All the Schiff's base complexes reported up to present display a smectic A phase. The smectic

A phase has an intrinsically higher viscosity than the nematic phase. Therefore, obtaining liquid-crystalline lanthanide complexes exhibiting a nematic phase is a major research goal. This goal is not easy to achieve, because the structure of the Schiff's base complexes tends to promote formation of layered structures (and this means smectic mesophases). However, by a proper choice of the counterion, the viscosity of the mesophase can be reduced considerably. For instance, a smectic A phase with a low viscosity is found for Schiff's base complexes with perfluorinated alkyl sulfates as counterions.<sup>22</sup>

$\chi_{||}$  and  $\chi_{\perp}$  can be measured directly by orienting an aligned liquid crystal with the director parallel or perpendicular to the magnetic field. This implies that the measurements are carried out in a magnetic field that is not strong enough to reorient the liquid crystal. Alternatively, the aligned mesophase can be frozen into the glassy state. The  $\chi_{||}$  and  $\chi_{\perp}$  values of a glassy (aligned) mesophase can be measured as one would measure that on a single crystal (orienting the sample with its long molecular axis parallel or perpendicular to the magnetic field lines). The situation is quite different for a mesophase in a magnetic field above a certain threshold strength  $H_0$ , because in this case, the mesophase will be aligned by the magnetic field. A nematic phase can be oriented at any temperature within the mesophase, because of the low viscosity of this phase. Because of the intrinsic higher viscosity, the smectic A phase can only be oriented at a temperature close to the clearing point. The orientation at this point will be retained when the mesophase is cooled further. The magnetic anisotropy  $\Delta\chi$  cannot be obtained via the relation  $\Delta\chi = \chi_{||} - \chi_{\perp}$ , because only one of the two components  $\chi_{||}$  or  $\chi_{\perp}$  can be determined. This problem can be overcome by measuring the magnetic susceptibility in the isotropic phase and in the mesophase. In the isotropic phase,  $\chi_{iso}$  will be measured. It is assumed that  $\chi_{iso}$  is equal to the average magnetic susceptibility  $\bar{\chi}$ , which is defined as  $\bar{\chi} = (\chi_{||} + 2\chi_{\perp})/3$ . In the mesophase, the molecules will be oriented in such a way that the axis of maximal magnetic susceptibility will be parallel to the magnetic field. Because of alignment of the paramagnetic molecules, an increase in magnetic susceptibility will be observed (in comparison to  $\bar{\chi}$ ), and the measured value is denoted as  $\chi_{max}$ . If  $\Delta\chi > 0$ ,  $\chi_{max}$  corresponds to  $\chi_{||}$  and  $\Delta\chi = 3/2(\chi_{max} - \bar{\chi})$ . If  $\Delta\chi < 0$ ,  $\chi_{max}$  corresponds to  $\chi_{\perp}$  and  $\Delta\chi = 3(\bar{\chi} - \chi_{max})$ . The sign of  $\Delta\chi$  cannot be determined by magnetic susceptibility measurements and has to be obtained by an independent measurement, for instance via EPR (angle dependence of the EPR-signal) or X-ray diffraction in a magnetic field (distribution of the diffraction maxima with respect to the external magnetic field). It should be realized that the maximal value for the magnetic anisotropy  $\Delta\chi$  can only be measured on completely aligned samples. For real samples, alignment is never complete, so the measured value of  $\Delta\chi$  is smaller than the value that can be theoretically expected. In Figure 24 the alignment of a praseodymium(III)-containing liquid crystal is illustrated. The sample exhibited a Curie–Weiss behavior for the tempera-



**Figure 24.** Effective magnetic moments  $\mu_{eff}$  of the liquid-crystalline praseodymium(III) complex  $[\text{Pr}(\text{LH})_3(\text{NO}_3)_3]$  (LH being the Schiff's base ligand shown in Figure 3, with  $\text{R} = \text{C}_{12}\text{H}_{25}$  and  $\text{R}' = \text{C}_{16}\text{H}_{33}$ ) in the temperature range of 300–442 K (Reprinted from ref 14. Copyright 2000 American Chemical Society).

ture dependence of their magnetic properties, when heated from the solid state through the smectic A phase until the isotropic phase was reached. When the samples were cooled from the isotropic phase to the mesophase (in the presence of a magnetic field), in the vicinity of the clearing point, a drastic increase in the magnetic moment  $\mu_{eff}$  was observed in comparison to the initial values recorded by heating of the samples. The increase takes place over a narrow temperature range, and upon further cooling, the magnetic properties vary according to the Curie–Weiss law, but with a different higher  $\mu_{eff}$  than in the heating cycle. This behavior can be referred to a magnetic-field-induced orientation in the liquid-crystalline phase of a magnetically anisotropic sample with its axis of maximal magnetic susceptibility parallel to the magnetic field. The experimental values for the magnetic anisotropy in lanthanide-containing liquid crystals are summarized in Table 10. The  $\Delta\chi$  values depend on the counterion. The highest  $\Delta\chi$  values have been observed for complexes with perfluorinated counterions.<sup>22</sup> The studies have been largely restricted to Schiff's base complexes. A few data for  $\beta$ -enaminoketone complexes are available.<sup>30</sup> The values for the magnetic anisotropy reported in Table 10 are often much smaller than the theoretically predicted values and have to be considered as lower limit values (minimal values). The discrepancy between theoretical and experimental values has been discussed in detail in ref 322.

## B. Lanthanide-Assisted Alignment of Bicelles and Membranes

Magnetically oriented phospholipid bilayered micelles or "bicelles" are used as membrane mimics for structural and dynamic studies of integral and peripheral membrane polypeptides by different spectroscopic methods (NMR, EPR, etc.). These membrane systems are composed of a mixture of a bilayer-forming phospholipid and a short chain phospholipid that breaks up the extended bilayers into bicelles.<sup>326</sup> A typical phospholipid mixture consists of a long chain bilayer forming 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (dimyristoylphosphatidylcholine,

**Table 10. Magnetic Properties of Mesogenic Schiff's Base Complexes<sup>a</sup>**

compound	R	R'	$\mu_{\text{eff}}$ (BM)	$\chi_{\text{iso}}$	$\chi_{\text{or}}$	$(\chi_{\text{or}} - \chi_{\text{iso}})$	$\Delta\chi_{\text{min}}$	ref
[La(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>		-1440	-1380	60	90	325
[Pr(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	3.60	3850	4160	310	-930	14
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	3.55	3750	4020	270	-810	14
[Nd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	3.75	3270	3530	260	-780	325
[Eu(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	3.70	3010	3140	130	195	325
[Gd(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	7.80	18200	18200	~0	~0	14
[Eu(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	8.10	20280	20330	50	75	325
[Tb(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.65	27980	29830	1850	-5550	14
[Tb(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	9.95	32010	33860	1850	-5500	325
[Tb(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>					4665	22
[Dy(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>					-4756	22
[Dy(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	10.80	34670	35790	1120	-3360	325
[Ho(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	10.90	35440	36400	960	-2880	325
[Ho(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>14</sub> H <sub>29</sub>	C <sub>18</sub> H <sub>37</sub>					-7794	22
[Er(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.55	27270	28345	1075	1610	14
[Er(LH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	9.95	29540	29930	390	585	325
[La(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>		-2110	-2030	80	120	325
[Nd(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	3.75	3200	3420	220	-660	325
[Gd(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	8.45	24010	24080	70	105	325
[Tb(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	10.25	37070	39090	2020	-6060	325
[Dy(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	11.20	44940	46000	1060	-3180	325
[Ho(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	11.20	44980	46020	1040	-3120	325
[Er(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	10.20	36860	37350	490	735	325
[Yb(LH) <sub>3</sub> (DOS) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>18</sub> H <sub>37</sub>	4.85	6610	6810	200	300	325
[Tb(LH) <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.64			760	-2280	21
[Tb(LH) <sub>3</sub> (C <sub>8</sub> H <sub>17</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.71			970	-2910	21
[Tb(LH) <sub>3</sub> (C <sub>10</sub> H <sub>21</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.29			1040	-3120	21
[Tb(LH) <sub>3</sub> (C <sub>18</sub> H <sub>37</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.31			1125	-3375	21
[Er(LH) <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.19			2465	3700	21
[Er(LH) <sub>3</sub> (C <sub>8</sub> H <sub>17</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.44			2085	3130	21
[Er(LH) <sub>3</sub> (C <sub>18</sub> H <sub>37</sub> SO <sub>4</sub> ) <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.76			670	1000	21
[Tb(LH) <sub>3</sub> {CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.29			2280	-6840	22
[Ho(LH) <sub>3</sub> {CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	10.24			3035	-9100	22
[Nd(LH) <sub>3</sub> {CHF <sub>2</sub> (CF <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	3.62			195	-580	22
[Eu(LH) <sub>3</sub> {CHF <sub>2</sub> (CF <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	3.79			470	700	22
[Tb(LH) <sub>3</sub> {CHF <sub>2</sub> (CF <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.44			2740	-8220	22
[Dy(LH) <sub>3</sub> {CHF <sub>2</sub> (CF <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	10.10			6490	-19470	22
[Ho(LH) <sub>3</sub> {CHF <sub>2</sub> (CF <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.97			4280	-12840	22
[Er(LH) <sub>3</sub> {CHF <sub>2</sub> (CF <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> SO <sub>4</sub> } <sub>3</sub> ]	C <sub>12</sub> H <sub>25</sub>	C <sub>16</sub> H <sub>33</sub>	9.58			3985	5980	22

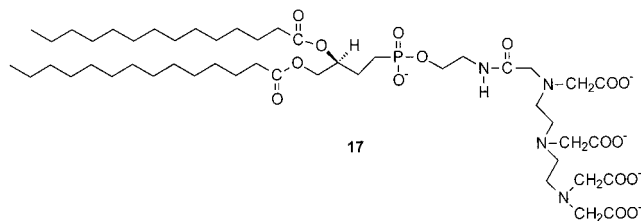
<sup>a</sup> All the susceptibility values are expressed in  $10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  units at the melting point. A structure of the salicyldimine Schiff's base ligand LH is shown in Figure 3.

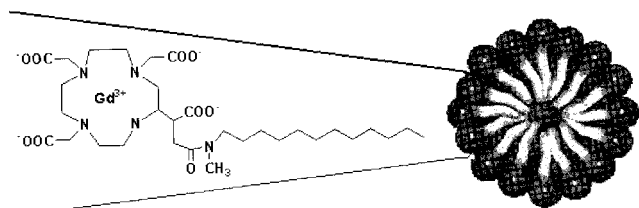
DMPC) phospholipids and short-chain 1,2-dihexanoyl-*sn*-glycero-3-phosphocholine (dihexanoylphosphatidylcholine, DHPC) phospholipids. The structural geometry of the bicelle depends on the molar ratio  $q = [\text{DMPC}]/[\text{DHPC}]$ . When the  $q$  ratio is reduced, the bicelle diameter is correspondingly reduced. Below a certain threshold value of the diameter, the bicelles are no longer able to maintain the magnetic alignment and an isotropic solution is observed. When  $2 < q < 5$ , a magnetically aligned phase is readily formed. Approximate dimensions of disklike bicelles used in membrane studies are  $200 \times 40 \text{ \AA}^2$ .

The magnetic alignment of bicelles is due to the magnetic anisotropy of the system. The bicelles are diamagnetic and the sign of their magnetic anisotropy is negative ( $\Delta\chi < 0$ ), so the bicelles align with the bicelle normal perpendicular to the direction of the external magnetic field. By incorporation of paramagnetic lanthanide ions with a large positive magnetic anisotropy (especially  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$ , and to a lesser extent  $\text{Eu}^{3+}$  and  $\text{Er}^{3+}$ ) in the bicelles, the bicelles can obtain an overall positive magnetic anisotropy, and they will flip over  $90^\circ$ , so the bicelle normal is on average parallel to the external magnetic field.<sup>327,328</sup> The lanthanide ions bind to the lipid

phosphate groups. The bicelles for which an orientation of the normal parallel to the external magnetic field are more suitable for studies of predominantly  $\alpha$ -helical membrane-spanning proteins. The use of lanthanide ions allows the structure determination of larger membrane proteins than when no lanthanide ions are added to the bicelles.

Because  $\text{Tm}^{3+}$  has the largest  $\Delta\chi$  value among the above-mentioned lanthanide ions, the magnetic alignment can be obtained with low  $\text{Tm}^{3+}$  concentrations. As little as one  $\text{Tm}^{3+}$  ion per 155 DMPC molecules is required for sufficient alignment. However, in practice,  $\text{Yb}^{3+}$  is the most suitable lanthanide ion for magnetic alignment of bicelles in NMR studies, because it gives minimal paramagnetic shifts and line broadening at acceptable low concentrations. Prosser and co-workers found that by addition of a phospho-





**Figure 25.** Schematic representation of a micelle formed by amphiphilic  $[\text{Gd}(\text{DOTA-C}_{12})(\text{H}_2\text{O})]^-$  complexes. (Reprinted from ref 351 with permission. Copyright 1999 Wiley-VCH).

lipid chelate 1,2-dimyristoyl-*sn*-glycero-3-phosphoethanolamine–diethylenetriaminepentaacetic acid (DMPE–DTPA, **17**), the paramagnetic line broadening can be reduced significantly, probably because direct lanthanide–protein interactions are avoided.<sup>329,330</sup> The chelate DMPE–DTPA:Yb<sup>3+</sup>, obtained by reaction between equimolar amounts of DMPE–DTPA and an ytterbium(III) salt, is currently being commercialized by Avanti Polar Lipids for magnetic alignment of biological membranes (Figure 25). Typically, either a 25% aqueous (w/w) dispersion of DMPC/DHPC/DMPG/DMPE–DTPA:Yb<sup>3+</sup> in a 2.75/1.00/0.1375/0.0306 mole ratio or a 40% (w/w) aqueous dispersion of DMPC/DHPC/DMPG/DMPE–DTPA:Yb<sup>3+</sup> in a 2.75/0.458/0.1375/0.0306 mole ratio is used. The 25% mixture often results in the smallest line widths, whereas the latter combination yields larger order parameters and chemical shift offsets. Furthermore, the use of the negatively charged lipid dimyristoyl-*sn*-glycero-3-[phosphorac-(1-glycerol)] (DMPG) and the chelate stabilizes the liquid crystalline phase as a function of temperature and seems to prevent long-term sample degradation. The use of the negatively charged lipid DMPG in combination with the chelate is essential, because in the absence of DMPG, precipitation of the chelate can occur. Using *small-angle neutron scattering* (SANS) Nieh et al. determined the morphology of Tm<sup>3+</sup>-doped bicelles formed by mixtures of DMPC/DHPC and DMPC/DHPC/DMPG, over a wide range of temperatures and lipid concentrations.<sup>331</sup> Below about 25 °C, the systems form disklike bicelles over a wide concentration range. At elevated temperatures (above 35 °C), an unilamellar vesicular phase is formed at low lipid concentrations and a perforated lamellar phase at high lipid concentrations. The lyotropic DMPC/DHPC/water system undergoes upon addition of Tm<sup>3+</sup> a nematic → smectic transition.<sup>332</sup> Although this transition is common in thermotropic liquid crystals, it is seldomly observed in lyotropic systems.

The greatest potential of magnetically aligned phospholipid membranes is in the field of both solution and solid-state NMR studies of membrane proteins. This topic has been reviewed recently by Prosser and Shiyanovskaya.<sup>333</sup> Also in EPR spectroscopy, oriented spin-labeled phospholipid bilayers provide much more structural and dynamic information about membrane-associated molecules than randomly dispersed bilayers can.<sup>334–336</sup> In oriented phospholipid bilayers, the EPR spectra reveal orientational-dependent changes in the hyperfine splitting of the spin label with respect to the magnetic field, as well as reduction of the spectral line widths. Smaller line

widths improve the spectral resolution and allow the *g* tensors to be determined with greater precision. It should be stressed that in these studies the EPR signal of the lanthanide ion is not measured but that of an organic spin label, such as 3 $\beta$ -doxyl-5 $\alpha$ -cholestane or 5-doxylstearic acid. Because the magnetic field strength in EPR experiments is less than that of NMR experiments, it is more difficult to obtain a good magnetic alignment of the bicelles in EPR experiments.

Whereas in NMR and EPR work mostly only lanthanide ions with a positive anisotropy are added to the bicelles (Eu<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, Yb<sup>3+</sup>), in some studies also lanthanide ions with a large negative magnetic anisotropy (especially Dy<sup>3+</sup>) are added to increase the overall negative magnetic anisotropy of the bicelles.<sup>336–338</sup>

### C. Lipophilic MRI Contrast Agents

An important noninvasive medical diagnostic technique is *magnetic resonance imaging* (MRI). MRI is based on the acquisition of images that are topological representations of NMR parameters, including the  $1/T_1$  and  $1/T_2$  relaxivity rates of water protons. Certain chemicals, called *contrast agents* (CA) can be used to increase the contrast between the target organ and the surrounding tissues. Most contrast agents are gadolinium(III) chelates.<sup>339,340</sup> Paramagnetic Gd<sup>3+</sup> complexes cause a marked increase of the water proton relaxation rates in the body regions where they distribute. To create liver-specific contrast agents, lipophilic Gd<sup>3+</sup> are being investigated. Because of their low solubility in aqueous solution, they are often incorporated on the surface of liposomes. Paramagnetic micelles have not only the advantage of being liver-specific but also because of their large size they have an enhanced proton relaxivity, too.

With the aim to design liver-specific contrast agents, Kabalka et al. modified DTPA by attaching two octadecyl chains via an amide, ester, or thioester bond,<sup>341</sup> according to a method first described by Hnatowich et al.<sup>342</sup> An alternative synthetic route to the bis(amide) ligands has been reported.<sup>343</sup> Gadolinium complexes have been synthesized and incorporated into liposomes. The  $1/T_1$  relaxation rate is invariant with vesicle size within the range 50–400 nm average diameter.<sup>344</sup> However, it was reported that octadecylamine is neurotoxic.<sup>345</sup> Therefore, other hydrophobic chains have been attached to DTPA. For instance, Zhao et al. synthesized octadecyl esters of L-tyrosine and L-phenylalanine and prepared the respective Gd<sup>3+</sup> and Yb<sup>3+</sup> complexes.<sup>346</sup> These complexes have been incorporated into the membrane of liposomal vesicles. The paramagnetic liposomes showed a high proton relaxation rate. As can be expected, the relaxivity of the Yb<sup>3+</sup> complexes is lower than that of the corresponding Gd<sup>3+</sup> complexes. The same lipophilic complexes that are being explored for MRI contrast agent can also be used as complexing agents for radiolanthanides. Nepveu and co-workers bound Gd<sup>3+</sup> to the *N,N*-bis(octadecyl)amide of DTPA<sup>347</sup> and to the *N*-(monodipalmitoylphosphatidylethanolamide of EDTA or DTPA.<sup>347,348</sup> They de-

scribe a procedure to label the ligands with the radioisotope  $^{153}\text{Gd}$ .<sup>347</sup> Another application of this type of complexes is for neutron capture therapy.<sup>349,350</sup>

Complexes of  $\text{Gd}^{3+}$  with the macrocycle DOTA (DOTA = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) have been commercialized as MRI contrast agents (DOTAREM). The complexes are thermodynamically very stable and kinetically inert. Merbach and co-workers prepared an amphiphilic analogue by attaching a dodecylamide chain to the macrocycle, leaving the  $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^-$  unit intact.<sup>351</sup> The compound behaves like an anionic surfactant. The critical micelle concentration was determined by surface-pressure measurements and found to be  $3.5 \times 10^{-4}$  M. A schematic representation of the micellar structure formed by  $[\text{Gd}(\text{DOTA}-\text{C}_{12})(\text{H}_2\text{O})]^-$  in aqueous solution is shown in Figure 25. The  $^{17}\text{O}$  NMR, EPR, and NMRD measurements show that the micellar structure does not affect the water exchange. This is due to the fact that the gadolinium(III) chelate points toward the hydrophilic exterior (bulk water phase) and the access from the bulk water to the paramagnetic  $\text{Gd}^{3+}$  ion is not limited. Although the  $[\text{Gd}(\text{DOTA}-\text{C}_{12})(\text{H}_2\text{O})]^-$  has the same rate of water exchange as  $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^-$ , its proton relaxivity is much higher. The relaxivity could be increased further by adding cholesterol. The mixed micelles are more rigid than the ones formed by  $[\text{Gd}(\text{DOTA}-\text{C}_{12})(\text{H}_2\text{O})]^-$  alone.  $\text{Gd}(\text{DTPA}-\text{bisamide})$ -alkyl copolymers form rigid intramolecular micelle-like structures in aqueous medium.<sup>352</sup> Just as in the case of  $[\text{Gd}(\text{DOTA}-\text{C}_{12})(\text{H}_2\text{O})]^-$ , the micellar structure does not affect the water exchange rate.

#### D. NMR Shift Agents in LC Solvents

In the 1970s and 1980s, before the general availability of high-field NMR spectrometers, lanthanide shifts reagents were extensively used to make  $^1\text{H}$  NMR spectra more easily interpretable by reducing complex spectra to first-order spectra. And even at present, these shifts reagents, and especially chiral shift reagents, are being used in some specific studies.<sup>353</sup> On the other hand, much more information on the molecular geometry can be extracted from the NMR spectra of molecules partially aligned in a nematic liquid-crystalline solvent.<sup>354</sup> However, very little research effort has been devoted to the use of lanthanide shifts reagents in anisotropic solvents such as nematic liquid crystals. This limited attention is probably due to the fact that early work indicated that shift reagents have no practical value for solving NMR spectra of oriented molecules. The influence of shift reagents on the NMR spectra of pyridine and of methanol dissolved in nematic solvents has been reported.<sup>355,356</sup>

Zaev studied the influence of lanthanide ions on the  $^1\text{H}$  NMR spectra of micellar aqueous solutions of the anionic surfactant sodium dodecyl sulfate.<sup>357</sup> Different aromatic solvents and cyclohexane were solubilized inside the micelle. It was investigated how the proton NMR signals of the constituents of the micelles were shifted upon absorption of the lanthanide salts on the surface of the micelle. The authors found that  $\text{Eu}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Tm}^{3+}$  ions shift

the NMR signals downfield, whereas  $\text{Dy}^{3+}$  and  $\text{Tb}^{3+}$  shift these signals upfield. The shift capacity of the ions decreased in the series  $\text{Tb}^{3+} > \text{Tm}^{3+} > \text{Dy}^{3+} > \text{Er}^{3+} > \text{Eu}^{3+}$ . The same authors studied the lanthanide-induced  $^1\text{H}$  NMR shift of acetone in the second coordination sphere of hydrated lanthanide salts. They used micelles of nonionic and cationic surfactants as NMR standard (the  $\text{CH}_3$  or  $\text{CH}_2$  signals of the alkyl chains in the center of the micelles were monitored). Because the lanthanide ions cannot penetrate into the micelles, the micelles can be considered as diamagnetic spheres inside a paramagnetic solution.<sup>358</sup> A mesophase formed by uranyl fluoride in water–acetone solutions was investigated by  $^1\text{H}$  NMR.<sup>359</sup> This is up to now the only example among the lanthanide and actinide series of a simple inorganic compound exhibiting a lyotropic mesophase. It was shown that uranyl fluoride occurs as dimeric complexes in the mesophase.

#### VIII. Lanthanides in LCD Applications

*Liquid crystal displays* (LCDs) are being widely used for several technological applications, such as the display of calculators or in the screen of laptop computers. LCDs have the advantage of low power consumption and they are flat (in contrast to the cathode ray tube monitors), but they have some disadvantages, too. The main disadvantages of LCDs—the restricted viewing angle and the low brightness—are mainly due to the use of dichroic sheet polarizers and absorbing color filters in the LC cell. Those optical components are inefficient in the sense that they lose a large part of the incident light. Major improvements in LCD performance can be expected when an LC cell without polarizers and color filters is designed. A very promising concept is the *luminescent LCD*, which is an emissive type of display, just as the cathode ray tube is. Luminescent lanthanide complexes can play an important role in the development of this type of display. The idea of a luminescent LCD is not new. The first one to explore this concept was Larrabee, who added luminescent molecules to a nematic liquid crystal.<sup>360,361</sup> These luminescent molecules were excited with an UV source and emission was controlled electrically by the alignment of the liquid crystal (the *nematic “guest–host effect”*). Yu and Labes suggested the use of an electric-field-induced cholesteric-to-nematic phase transition as the basis of a luminescent LCD.<sup>362,363</sup> The cholesteric off state absorbs the excitation light stronger than the nematic on state, so that the emission of the luminescent additive is intense in the off state and is reduced in the on state. The authors used the red-emitting europium(III) complex  $\text{Eu}(\text{tta})_3 \cdot 2\text{H}_2\text{O}$  ( $\text{Htta} = 2$ -thenoyltrifluoroacetone) as the luminescent additive and could reach a contrast ratio of 9:1 (differences in intensities between the off and the on state). A third approach to luminescent LCDs is replacement of the absorbing color filter by a luminescent layer. However, the development of luminescent LCDs slowed. At that time the quality of the LCD was high enough to fit for all the needs. Second, there were no convenient UV sources available (except the mercury discharge lamp). Presently,

the situation is different. The growing market for flat computer monitors makes luminescent LCDs attractive again. The newly developed UV-LEDs have advantages as LCD backlights: light, thin, Hg-free, and noiseless. Yamaguchi et al. designed a luminescent LC full-color display using a guest–host LC–UV shutter and polymer sheets incorporating inorganic phosphors.<sup>364</sup> The application of UV-LED as backlights for luminescent LCDs was explored by Sato et al. and by Yamaguchi et al.<sup>365,366</sup> Recent work done in the Philips Research Laboratories describes the use of organic lanthanide-containing phosphors ( $\beta$ -diketonato complexes) incorporated in a polymer sheet, excited by UV-LEDs.<sup>367,368</sup>

## IX. Conclusions

The research field of lanthanide-containing liquid crystals is still in its infancy. Although many different types of metallomesogens incorporating d-group transition metals are known, only few liquid-crystalline lanthanide complexes have been described in the literature. Among these, the most intensively studied compounds are the Schiff's base complexes, the alkanooates, and the phthalocyanine complexes. However, no complexes of mesogenic analogues of the classic ligands for lanthanides such as  $\beta$ -diketonates, bipyridines, phenanthrolines, or aminopolycarboxylic acids are known yet. Here, a lot of work remains to be done. The quest is for new types of stable lanthanide-containing metallomesogens, with low transition temperatures and lowly viscous mesophases. Although a mesophase with a low viscosity was observed for Schiff's base complexes with perfluorinated counterions, all these compounds exhibit a smectic mesophase that has intrinsically a higher viscosity than the nematic phase. Therefore, obtaining liquid-crystalline lanthanide complexes with a nematic phase is a major goal in this research field. The design of lanthanide-containing liquid crystals is a challenge. Because of the high coordination number of trivalent lanthanide ions in complexes (typically 8 or 9), it is difficult to obtain complexes of these ions that have sufficient structural anisotropy to stabilize mesophases.

By incorporating paramagnetic and/or luminescent lanthanide ions in liquid crystals, it is possible to create materials with unique physical properties. Due to the huge anisotropy of metallomesogens containing terbium(III), dysprosium(III), or thulium(III), such compounds can be reoriented in relatively weak magnetic fields. Magnetic alignment studies also renewed the theoretical interest in the magnetic properties of lanthanide coordination compounds.<sup>322,324</sup> Lanthanide-assisted magnetic alignment of bicelles and other model membranes have found application for the study of membrane proteins via spectroscopic methods (NMR, EPR). Luminescent lanthanide-containing liquid crystals have the advantage of narrow line emission and thus a high coloric purity. It is very likely that the objective of obtaining the luminescent materials will not be achieved by pure compounds but rather by dissolving nonmesogenic lanthanide complexes in liquid-crystalline solvents.

In the past, quite a lot of work has been done in the field of lanthanide ions in micellar solutions. In aqueous micellar solutions, it is possible to solubilize lanthanide complexes of hydrophobic ligands that are otherwise only soluble in organic solvents. Lanthanide ions have been added to surfactant solutions to study their influence on the aggregation behavior of surfactant molecules to micelles. Trivalent lanthanide ions have a high electric charge but are much more readily hydrolyzed than smaller trivalent ions such as  $Al^{3+}$ . Lanthanide complexes solubilized in micellar solutions have interesting photophysical properties, and they have possible analytical and photophysical applications. Lyotropic mesophases formed by lanthanide complexes can be useful for the synthesis of mesoporous lanthanide-containing materials via LC templating.

## X. Abbreviations

$\chi$	magnetic susceptibility
$\Delta\chi$	magnetic anisotropy
$\mu_{\text{eff}}$	effective magnetic moment
AOT	Aerosol OT
BNPP	bis( <i>p</i> -nitrophenyl)phosphate
CA	contrast agent
cmc	critical micelle concentration
CN	coordination number
Col	columnar phase
Col <sub>h</sub>	hexagonal columnar phase
Col <sub>r</sub>	rectangular columnar phase
Col <sub>t</sub>	tetragonal columnar phase
Col <sub>x</sub>	unidentified columnar phase
Cr	crystalline solid
CTAB	cetyltrimethylammonium bromide
<i>d</i>	smectic layer thickness
D	discotic phase
D <sub>L</sub>	discotic lamellar phase
D <sub>N</sub>	discotic nematic phase
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dec	decomposition
DEPE	dielaidoylphosphatidylethanolamine
DHPC	dihexanoylphosphatidylcholine
DMPC	dimyristoylphosphatidylcholine
DMPG	dimyristoyl- <i>sn</i> -glycero-3-[phosphorac-(1-glycerol)]
DMPS	dimyristoylphosphatidyl serine
DOS	dodecyl sulfate
DOTA	1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid
dpa	pyridine-1,6-dicarboxylate, -dipicolinate
DPPC	dipalmitoylphosphatidylcholine
DTPA	diethylenetriaminepentaacetic acid
EHS	bis(2-ethylhexyl)sulfosuccinate
G	gauss
habbe	<i>N</i> -(2-hydroxy-4-alkoxybenzaldehydeimino)-2-benzamidoethanamide
Hdbm	1,3-diphenyl-1,3-propanedione or dibenzoyl-methane
H <sub>2</sub> OOTTAP	(2,3,7,8,12,13,17,18-octylthio)-5,10,15,20-tetraazaporphyrine
Htta	2-thenoyltrifluoroacetone
I	isotropic liquid
LB	Langmuir–Blodgett
LED	light-emitting diode
LC	liquid crystal
LCD	liquid crystal display
MRI	magnetic resonance imaging
N	nematic phase
NLO	nonlinear optics

Pc	phthalocyanine
phen	1,10-phenanthroline
PMMA	poly(methyl methacrylate)
R, R'	linear alkyl chains, $C_nH_{2n+1}$
salen	2,2'-N,N-bis(salicylidene)ethylenediamine
SANS	small-angle neutron scattering
SDS	sodium dodecyl sulfate
SmA	smectic A phase
SmC	smectic C phase
topo	tri- <i>n</i> -octylphosphine
XRD	X-ray diffraction

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