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Trimetallic Nickel–Lanthanum and Nickel–Gadolinium Metallomesogens

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The Future of Supramolecular Chemistry

Supramolecular chemistry is a rapidly growing branch of chemistry, each year attracting the interest of more and more scientists. Intense research in the field has led to many discoveries, and different principles have been demonstrated: self-assembly, recognition of cations, anions and neutral molecules, biomimetic systems, supramolecular crystal engineering, molecular machines and so on. However, very few supramolecular systems lead to (industrial) applications. Before supramolecular compounds can be transformed into competitive new materials, more efficient synthetic routes to self-assembling building blocks have to be developed. Compounds which are accessible only after multiple tedious synthesis steps will be too expensive for applications. I think that a major goal in supramolecular chemistry should be the development of easy and cheap methods for the synthesis of target compounds.

The quest for new synthetic routes and of new materials is also of importance in the subfield of supramolecular chemistry I am working in: metal-containing liquid crystals (metallomesogens). This research field has been dominated by chemists, not by physicists. During the last two decades, many different classes of metallomesogens have been discovered. At present, only a limited number of metals have not yet been incorporated in liquid crystals: hafnium, tantalum, niobium, scandium, gallium and indium (not to mention the radioactive elements). It is to be expected that the methodology which leads to the development of metallomesogens with the lanthanides or zirconium as the central metal ion can also be successfully applied to the design of metallomesogens containing the above-mentioned metal ions. There is still a need to develop new types of ligands for metallomesogens, because many of the metallomesogens described in the literature have very high transition temperatures or are thermally unstable. In comparison with the classic liquid crystals, very little is known about the physical properties of metallomesogens. Workers in the field of metallomesogens should encourage physicists to look in more detail at the properties of metal-containing liquid crystals. Because of the presence of a (transition) metal ion, metallomesogens can exhibit very interesting electrochemical, electronic or magnetic behaviour. Other properties of interest could be thermochromism, information storage and switching ability (in electric and/or magnetic fields). Most of the metallomesogens described in the literature are thermotropic liquid crystals. Lyotropic metallomesogens have been largely neglected so far. Many transition complexes have the right chemical structure to exhibit lyomesomorphism, not only in polar solvents but also in apolar solvents.



Prof. Dr Koen Binnemans was born in Geel, Belgium, in 1970. He obtained his M.Sc. (1992) and Ph.D. (1996) in Chemistry at the Catholic University of Leuven (Belgium), under the supervision of Prof. C. Görller-Walrand. In 1996, he became a Postdoctoral Fellow of the Fund for Scientific Research Flanders (Belgium). He did postdoctoral work with Prof. J. Lucas (Rennes, F) and Prof. D. W. Bruce (Exeter, UK). In 2000, he received the first ERES Junior Award (ERES: European Rare-Earth and Actinide Society), and since 2002, he has been Associate Professor of Chemistry at the Catholic University of Leuven. Koen Binnemans is an author of more than 100 papers in international scientific journals. His current research interests are metal-containing liquid crystals (metallomesogens), MRI contrast reagents, lanthanide-doped sol-gel glasses, lanthanide spectroscopy and applications of lanthanide compounds as reagents for organic synthesis. Other interests include reading, collecting minerals, Egyptology and history of artificial lighting.

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Adducts were formed between a mesomorphic Ni(salen) complex [salen = 2,2'-N,N'-bis(salicylidene)ethylenediamine] with six terminal alkoxy chains and a lanthanide nitrate (Ln = La, Gd). Different alkoxy chain lengths were used: OC₁₂H₂₅, OC₁₄H₂₉, OC₁₆H₃₃ and OC₁₈H₃₇. Trinuclear nickel–lanthanum and nickel–gadolinium complexes [Ln(NO₃)₃{Ni(salen)}₂] were obtained. The compounds exhibit a wide-temperature-range hexagonal columnar mesophase (Col_H) with rather low melting points. The mesophase stability ranges of both the parent nickel complexes and the nickel–lanthanide complexes decrease with increasing chain length. A decrease in the mesophase stability range over the lanthanide series was also observed. The results are compared with those of similar copper–lanthanide complexes. A marked difference is the higher thermal stability of the nickel–lanthanide complexes in comparison with the copper–lanthanide complexes.

Keywords: Liquid crystals; Metallomesogens; Columnar mesophases; Rare earths; Lanthanides

INTRODUCTION

Transition metal ions and lanthanide ions are being incorporated into liquid crystal to combine the properties of both the metal ion (electronic and magnetic properties, redox behaviour) and a liquid crystal (anisotropy of physical properties, fluidity) into one single type of new material [1–8]. The first examples of metal-containing liquid crystals (*metallomesogens*) were complexes of d⁸ transition metal ions (Pd^{II}, Pt^{II}, Rh^I, Ir^I) or d⁹ transition metal ions (Ag^I, Cu^{II}) with mesomorphic ligands, i.e. with ligands which are already liquid crystals themselves [1–7]. The choice of d⁸ or d⁹ transition metal ions was inspired by the fact that these metal ions prefer a square planar or a linear coordination geometry, so that when the ligands are complexed in a *trans*-position, the linear shape of the mesomorphic ligands is retained in the metal complexes. The working hypothesis at that time was that only rod-like or disk-like metal complexes would display liquid-crystalline behaviour. However, gradually it became clear that also metal complexes with other geometries could be transformed into liquid crystals and that the molecular order in these complexes can be different from the order in the classic organic liquid crystals. For example, mesomorphism has been achieved in non-conventional metal complexes, with octahedral [9–13], square-antiprismatic [14], trigonal-bipyramidal [15,16] and tetrahedral [17–20] coordination geometry. Typical examples of metallomesogens with high coordination number are the lanthanide-containing liquid crystals [8,21–28]. The synthesis of mesomorphic metallacrowns [29,30], butterfly compounds [31],

metallo dendrimers [32] and polynuclear systems [33–36] opened up the field for the construction of original structures able to contain a large number of metallic centres.

Recently, we reported the first examples of metallomesogens which contain both a transition metal ion and a lanthanide ion [37]. Adducts were formed between a mesomorphic Cu(salen) complex [salen = 2,2'-N,N'-bis(salicylidene)ethylenediamine] and a lanthanide nitrate. Different stoichiometries were found, depending on the lanthanide ion: a trinuclear copper–lanthanum–copper complex and a binuclear copper–gadolinium complex. The compounds exhibit a wide-temperature-range hexagonal columnar mesophase (Col_H). In this paper, we extend our previous work, in the sense that we present data on nickel–lanthanide complexes and the nickel-containing ligands (Fig. 1). The influence of the chain length of the alkoxy substituents on the Ni(salen) complex on the thermal behaviour of the nickel and nickel–lanthanide complexes has been investigated. Comparison with the mesophase properties of the copper–lanthanide complexes will be made.

RESULTS AND DISCUSSION

The well-known salen ligand [salen = 2,2'-N,N'-bis(salicylidene)ethylenediamine] is often used to form f–d complexes by adduct formation of a transition-metal salen complex and a lanthanide salt [38]. Most often, copper(II) is chosen as the transition metal (because Cu^{II} is paramagnetic), but other divalent d-metal ions such as Ni^{II}, Pd^{II}, Co^{II} or vanadyl can be used to prepare f–d complexes. Because we knew that liquid-crystalline copper–lanthanide complexes can be obtained [37], our next target was the nickel–lanthanide complexes. For the nickel–lanthanide complexes, we followed the same approach as for the corresponding copper–lanthanide complexes [37]. The salen ligand was modified by coupling a gallic acid derivative with three long alkoxy chains to the both ends of the salen molecule, so that a total of six alkoxy chains were attached to each salen molecule. The tris(alkoxy)benzoic acids were synthesized according to a literature method [39]. Different chain lengths were used: C₁₂H₂₅, C₁₄H₂₉, C₁₆H₃₃ and C₁₈H₃₇. It is expected that by using such ligands, metal complexes with a disk-like shape could be obtained (for which the formation of a columnar mesophase is likely). The synthesis of the nickel–lanthanide complexes is outlined in Scheme 1. First, the substituted salen-type ligands have been prepared by synthesis of the corresponding 3,4,5-tris(alkoxy)benzoic acid, coupling this compound by esterification to 2,5-dihydroxybenzaldehyde in

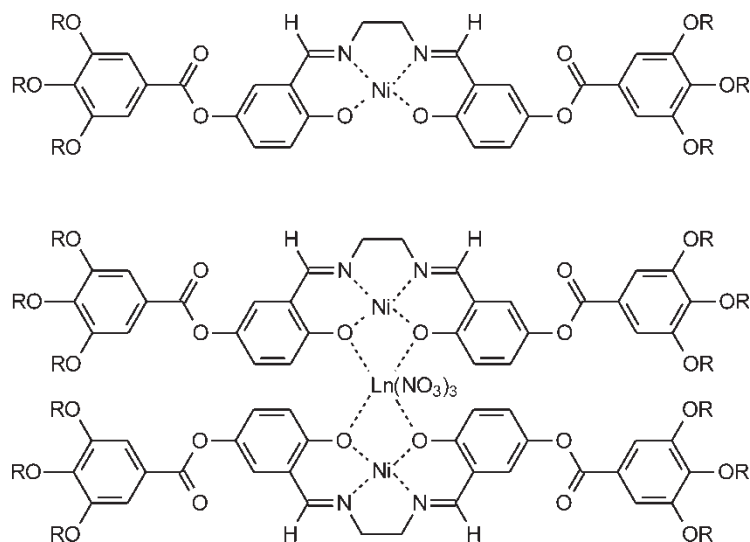
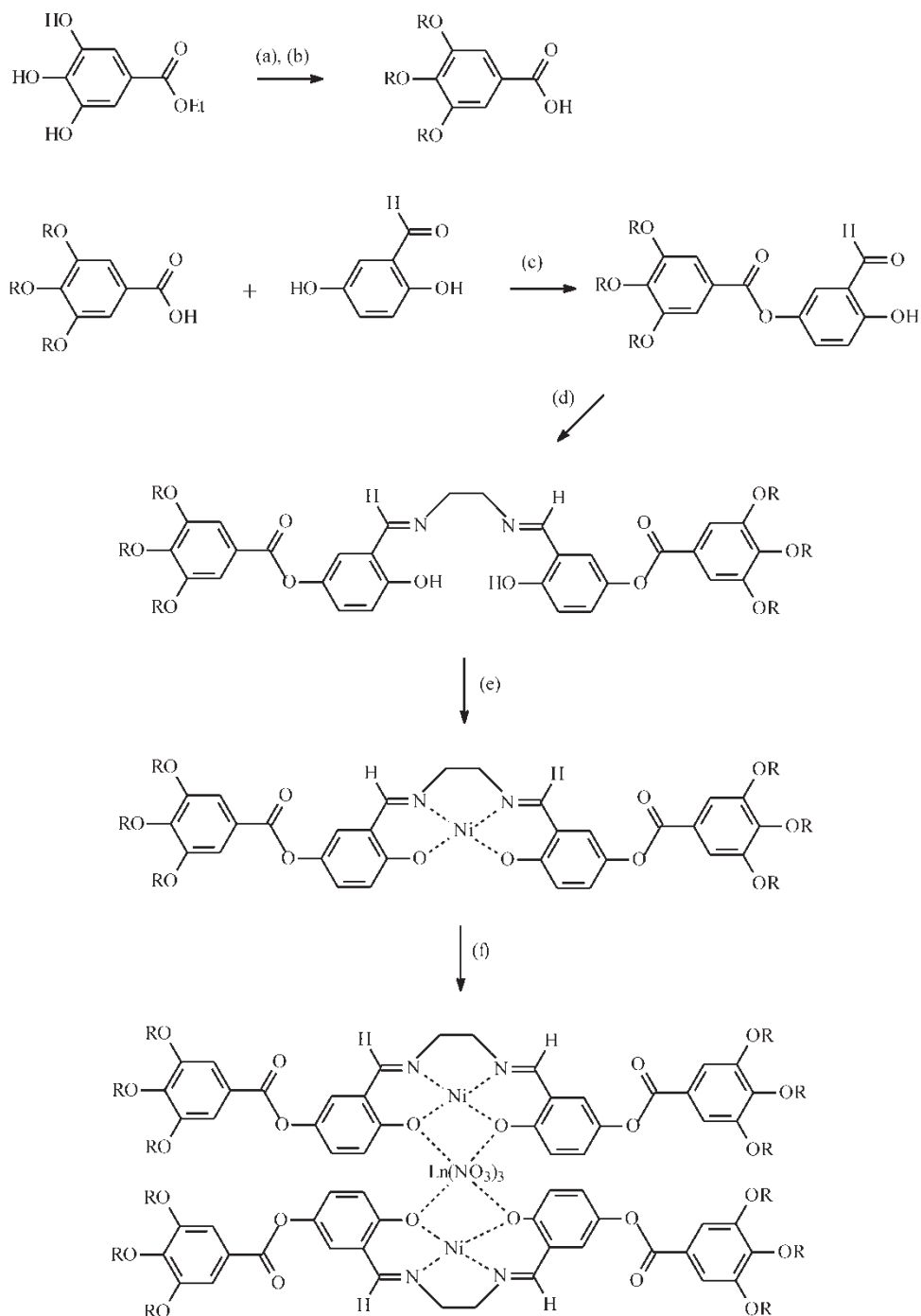


FIGURE 1 Structure of the nickel and nickel-lanthanide complexes (Ln = La, Gd; R = C₁₂H₂₅, C₁₄H₂₉, C₁₆H₃₃, C₁₈H₃₇).

the 5-position and condensing two equivalents of the resulting aldehyde with one equivalent of ethylenediamine to the Schiff's base. The nickel complex of the salen-type ligands could be obtained by reaction of the ligand with nickel acetate tetrahydrate. Reaction of the Ni(salen) complexes with a hydrated lanthanide nitrate gave the nickel-lanthanide complexes. The metal complexes were characterized by CHN elemental analysis and by IR spectroscopy. By comparing the stoichiometry of the previous described copper-lanthanide complexes with the nickel complexes, a remarkable difference can be seen. In the mixed complexes with a copper(II) ion, the size of the lanthanide(III) ion is a determining factor for the structure of the complexes. We found that a lanthanum(III) ion is large enough to bind two Cu(salen) complexes, resulting in a trinuclear Cu-La-Cu complex, while the gadolinium(III) ion is too small and only binds one Cu(salen) complex, resulting in a binuclear Cu-Gd complex. The situation is different in the case of the nickel-containing complexes. All of the studied mixed complexes were trinuclear. This could be assigned to the fact that the nickel(II) ion fits better in the salen core than the copper(II) ion and results in a less distorted complex. These findings are confirmed by IR measurements. While, in the Cu-Ln complexes, the C=N stretching bond increases from 1639 cm⁻¹ for La to 1647 cm⁻¹ for Gd, this value remains constant (within the accuracy of the apparatus) at 1628 cm⁻¹ for the Ni-Ln complexes. The similar IR spectra in the Ni-Ln complexes suggest that they have similar, thus trinuclear, structures: [Ln(NO₃)₃{Ni(salen)}₂] (Fig. 1).

The thermal behaviour of the metal complexes was studied by polarizing optical microscopy (POM)

and by differential scanning calorimetry (DSC). All the metal complexes are enantiotropic liquid crystals. The mesophases were identified as a hexagonal columnar mesophase Col_H on the basis of the optical textures. On cooling from the isotropic phase, dendritic features seem to grow slowly, resulting in a columnar phase. Good optical textures could be obtained in this way, whereas on heating, the texture contains no typical features. Whereas the copper-lanthanide complexes decompose upon heating [37], the corresponding nickel-lanthanide complexes can be heated above the clearing point without thermal decomposition. However, the thermal stability ranges of the mesophase of both these types of complexes are comparable. The viscosity of the mesophases is quite high, but a gradual decrease in viscosity can be observed with increasing temperature. At the melting point, the mesophase does not flow. However, when one presses with a needle on the cover glass of the sample, fluidity is observed. The fact that we observe a hexagonal columnar mesophase is also in agreement with our findings for the corresponding copper-lanthanide complexes (for which an XRD study is available) [37]. The thermal data have been summarized in Table I and in Figs. 2 and 3. It can be seen that the mesophase stability range decreases with increasing alkoxy chain length for all metal complexes; the melting points increase, and the clearing points decrease. The melting points of the nickel-lanthanide complexes are comparable with those of the parent nickel complexes. However, the nickel-lanthanide complexes exhibit the mesophase over a larger temperature range than do the corresponding nickel complexes. The nickel-lanthanum complexes have a larger mesophase stability



SCHEME 1 Synthesis of the modified salen ligand and the corresponding nickel and nickel-lanthanide complexes. Reagents and conditions: (a) RBr (3 eq.), K₂CO₃ (6 eq.), DMF, KI (catalytic amount), reflux overnight; (b) NaOH, ethanol, reflux for 4 h; acidification by dilute HCl solution; (c) DCC, DMAP, dichloromethane, 24 h at RT; (d) ethylenediamine (1/2 eq.), glacial acetic acid (catalyst), toluene, Dean-Stark trap, 3 h at reflux; (e) Ni(OOCCH₃)₂·4H₂O (1 eq.), methanol/chloroform, reflux overnight; (f) Ln(NO₃)₃·6H₂O, acetone, RT, 24 h.

range than the gadolinium complexes. This is the same trend as that observed for salicylaldehyde Schiff's base complexes with nitrate counterions [40].

Although several types of metallomesogens based on salen-type Schiff's base ligands have been described in the literature [37,41–52], it is difficult to compare our results with these literature data

because of the differences in substitution pattern. Most of these mesomorphic metal complexes exhibit smectic mesophases (smectic A, smectic C, smectic E or unidentified smectic phases), because these metal complexes have a linear molecular shape. Our trinuclear nickel-lanthanide complexes with 12 terminal alkoxy chains have a disk-like shape.

TABLE I Thermal behaviour of the nickel and nickel-lanthanide complexes

Compound*	Transitions (°C) [†]	$\Delta H_{\text{melting}}^{\ddagger}$ (kJ mol ⁻¹) [‡]	$\Delta H_{\text{clearing}}^{\ddagger}$ (kJ mol ⁻¹) [‡]
Ni-C ₁₂	Cr:52-Col _H :174-I	59.8	0.7
Ni-C ₁₄	Cr:65-Col _H :139-I	62.0	5.7
Ni-C ₁₆	Cr:71-Col _H :111-I	65.9	2.1
Ni-C ₁₈	Cr:74-Col _H :94-I	106.6	1.8
Ni-La-C ₁₂	Cr:59-Col _H :230-I	-	-
Ni-La-C ₁₄	Cr:81-Col _H :206-I	-	-
Ni-La-C ₁₆	Cr:90-Col _H :192-I	-	-
Ni-Gd-C ₁₂	Cr:59-Col _H :230-I	66.0	12.4
Ni-Gd-C ₁₈	Cr:69-Col _H :224-I	-	-

* The complexes are shown in Fig. 1. Ni-La-C₁₂ stands for the [La(NO₃)₃{Ni(salen)}₂] complex with terminal dodecyloxy (C₁₂H₂₅O) terminal chains.
[†] Transition temperatures were determined by optical microscopy. Abbreviations: Cr = crystalline phase; Col_H = hexagonal columnar mesophase; I = isotropic liquid. [‡] The enthalpy changes were determined by DSC. When the values could not be determined unambiguously (overlapping peaks, very weak transitions), they are not listed.

The molecules are disk-like rather than polycatenar-like [53], because of the broad rigid core. The mesophase behaviour of the nickel-lanthanide complexes is comparable with that of the copper-lanthanide metallomesogens, with the difference that the nickel-lanthanide complexes have a higher thermal stability than the copper-lanthanide complexes [37]. Indeed, a clearing point could be observed for the nickel-lanthanide complexes that we present here, but not for the copper-lanthanide complexes.

EXPERIMENTAL

General Procedures

CHN elemental analyses were performed on a CE Instruments EA-1110 elemental analyser. FTIR

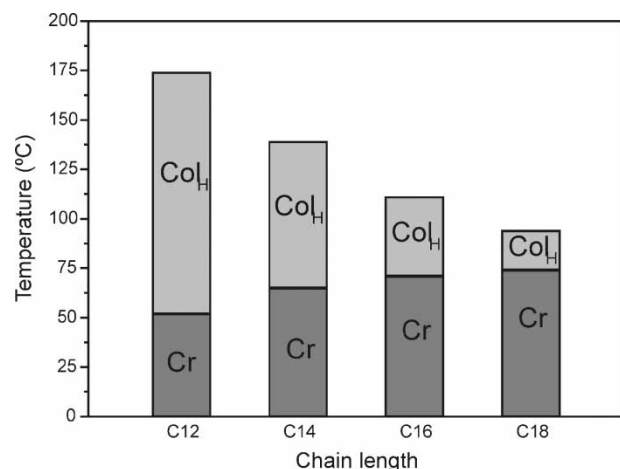


FIGURE 2 Dependence of the transition temperatures of the nickel complexes (Ni-C₁₂, Ni-C₁₄, Ni-C₁₆, Ni-C₁₈) on the alkoxy chain length.

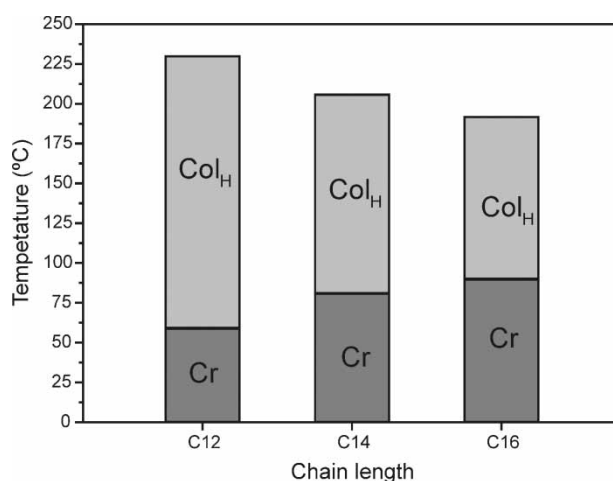


FIGURE 3 Dependence of the transition temperatures of the nickel-lanthanum complexes (Ni-La-C₁₂, Ni-La-C₁₄, Ni-La-C₁₆) on the alkoxy chain length.

spectra were recorded on a Bruker IFS-66 spectrometer, using the KBr pellet method. ¹H NMR spectra were recorded on Bruker Avance 300 spectrometer. Optical textures of the mesophase were observed with an Olympus BX60 polarizing optical microscope equipped with a Linkam THMS 600 hot stage and a Linkam TMS 93 programmable temperature-controller. All chemicals were used as received, without further purification. Organic reagents were obtained from ACROS, Aldrich or Fluka. 3,4,5-Tris(dodecyloxy)benzoic acid (**1**) was purchased from the Laboratory of Macromolecular and Organic Chemistry (Eindhoven University of Technology, The Netherlands).

Synthesis

3-Formyl-4-hydroxyphenyl-3,4,5-tris(dodecyloxy)-benzoate (**2**)

3,4,5-Tridodecyloxybenzoic acid **1** (6.75 g; 0.01 mol) and DMAP [= 4-(*N,N*-dimethylamino)pyridine] (0.12 g; 0.001 mol) were added to a mixture of 2,5-dihydroxybenzaldehyde (1.38 g; 0.01 mol) and DCC (= *N,N'*-dicyclohexylcarbodiimide) (2.30 g; 0.012 mol) in 600 mL of dichloromethane. The solution was stirred at room temperature for a period of 24 h. The precipitated *N,N'*-dicyclohexylureum was filtered off and washed with a saturated NaHCO₃ solution (2 × 200 mL) and water (2 × 200 mL). The aqueous layers were back-extracted with dichloromethane (100 mL). The combined organic layers were dried over MgSO₄, and the solvent was removed using a rotavap. The crude compound was purified by column chromatography (silica, with dichloromethane as the eluent). Yield: 64% (5.12 g). ¹H-NMR (δ_H, CDCl₃, 300 MHz): 0.88 (9H, t, CH₃), 1.26 (48H, m, CH₂), 1.49 (6H, m, CH₂CH₂CH₂O), 1.84 (6H, m, CH₂CH₂O), 4.04 (6H, t,

CH₂O), 7.06 (1H, dd, H-aryl), 7.35 (1H, d, H-aryl), 7.39 (2H, d, H-aryl), 7.43 (1H, dd, H-aryl), 9.88 (1H, s, CHO), 10.95 (1H, s, OH). Elemental analysis: calcd. for C₅₀H₈₂O₇ (MW = 795.18): C, 75.52%; H, 10.40%; found: C, 75.47%; H, 10.47%.

4-Hydroxy-3-[(12-[(E)-{2-hydroxy-5-[(3,4,5-tritridecyloxybenzoyloxy]phenyl)methylidene]amino]ethyl]imino)methyl]phenyl 3,4,5-tritridecyloxybenzoate (3)

Ethylenediamine (0.06 g; 0.001 mol) and 5 drops of glacial acetic acid (as the catalyst) were added to a solution of 3-formyl-4-hydroxyphenyl-3,4,5-tritridecyloxybenzoate **2** (1.59 g; 0.002 mol) in 250 mL of toluene. The mixture was heated for 3 h at reflux, and water formed by the reaction was removed azeotropically (Dean–Stark trap). After leaving to cool to room temperature, the solvent was removed at reduced pressure. The crude product was purified by recrystallization from absolute ethanol. Yield: 90% (1.45 g). ¹H-NMR (δ_H, CDCl₃, 300 MHz): 0.88 (18H, t, CH₃), 1.26 (96H, m, CH₂), 1.48 (12H, m, CH₂CH₂CH₂O), 1.83 (12H, m, CH₂CH₂O), 4.04 (16H, m, CH₂O, CH₂N), 6.98 (2H, dd, H-aryl), 7.12 (2H, d, H-aryl), 7.14 (2H, dd, H-aryl), 7.38 (4H, d, H-aryl), 8.36 (2H, s, CHN), 13.10 (2H, s, OH). IR (KBr, cm⁻¹): 1638 (C=N), 1203 (C–O). Elemental analysis: calcd. for C₁₀₀H₁₆₂O₁₂N₂ (MW = 1584.36): C, 75.81%; H, 10.31%; N, 1.77%; Found: C, 75.72%; H, 10.62%; N, 1.59%.

Ni Complex with C₁₂ Chains (4)

A hot solution of Ni(OOCCH₃)₂·4H₂O (0.622 g; 2.5 mmol) in methanol was added dropwise to a hot solution of **3** (3.229 g; 2.0 mmol) in chloroform. The reaction mixture was then refluxed overnight. After leaving to cool to room temperature, the solvent was removed at a reduced pressure. The crude product was recrystallized from ethyl acetate, washed with methanol. Yield: 92% (3.07 g). Thermal behaviour: Cr-52-Col_H-174-I. IR (KBr, cm⁻¹): 1626 (C=N), 1201 (C–O). Elemental analysis: calcd. for C₁₀₂H₁₆₆O₁₂N₂Ni (MW = 1671.11): C, 73.31%; H, 10.01%; N, 1.68%; found: C, 72.98%; H, 10.35%; N, 1.70%.

La–Ni Complex with C₁₂ Chains (5)

A solution of La(NO₃)₃·6H₂O (0.095 g; 0.22 mmol) in acetone was added to a solution of **4** (0.334 g; 0.2 mmol) in acetone. The reaction mixture was stirred at room temperature for a period of 24 h, and the precipitate was filtered, washed with cold methanol and dried *in vacuo*. Yield: 78% (287 mg). Thermal behaviour: Cr-59-Col_H-230-I. IR (KBr, cm⁻¹): 1628 (C=N), 1200 (C–O). Elemental analysis: calcd. for C₂₀₄H₃₃₂O₃₃N₇Ni₂La (MW = 3667.14): C, 66.12%;

H, 9.13%; N, 2.67%; found: C, 66.04%; H, 9.42%; N, 2.40%.

Gd–Ni Complex with C₁₂ Chains (6)

A solution of Gd(NO₃)₃·6H₂O (0.992 g; 0.22 mmol) in acetone was added to a solution of **4** (0.334 g; 0.2 mmol) in acetone. The reaction mixture was stirred at room temperature for a period of 24 h, and the precipitate was filtered, washed with cold methanol and dried *in vacuo*. Yield: 62% (229 mg). Thermal behaviour: Cr-69-Col_H-224-I. IR (KBr, cm⁻¹): 1628 (C=N), 1200 (C–O). Elemental analysis: calcd. for C₂₀₄H₃₃₂O₃₃N₇Ni₂Gd (MW = 3685.48): C, 66.48%; H, 9.08%; N, 2.66%; found: C, 66.80%; H, 9.44%; N, 2.30%.

3,4,5-Tritetradecyloxybenzoic Acid (7)

1-bromotetradecane (91.50 g; 0.33 mol) and a spatula point of KI were added to a mixture of gallic acid ethyl ester (19.82 g; 0.1 mol) and K₂CO₃ (82.93 g; 0.6 mol) in 700 mL of DMF, and the solution was refluxed overnight. The resulting mixture was poured into water and the precipitate was filtered. This crude product was refluxed for 4 h with NaOH (6.40 g; 0.16 mol) in 300 mL of ethanol. The reaction mixture was poured into water, acidified with dilute HCl and the precipitate filtered and recrystallized from ethyl acetate and acetone. Yield: 86% (60.87 g). ¹H-NMR (δ_H, CDCl₃, 300 MHz): 0.89 (9H, t, CH₃), 1.27 (60H, m, CH₂), 1.49 (6H, m, CH₂CH₂CH₂O), 1.81 (6H, m, CH₂CH₂O), 4.03 (6H, t, CH₂O), 7.33 (2H, d, H-aryl). Elemental analysis: calcd. for C₄₉H₉₀O₅ (MW = 759.24): C, 77.52%; H, 11.95%; found: C, 77.56%; H, 11.98%.

3-Formyl-4-hydroxyphenyl-3,4,5-tritetradecyloxybenzoate (8)

7 (15.16 g; 0.02 mol) and DMAP [= 4-(*N,N*-dimethylamino)pyridine] (0.24 g; 0.002 mol) were added to a mixture of 2,5-dihydroxybenzaldehyde (2.76 g; 0.02 mol) DCC (= *N,N'*-dicyclohexylcarbodiimide) (4.60 g; 0.022 mol) in 600 mL of dichloromethane, and the solution was stirred at room temperature for a period of 24 h. The precipitated *N,N'*-dicyclohexylurea was filtered and washed with a saturated NaHCO₃ solution (2 × 400 mL) and water (2 × 400 mL). The aqueous layers were back-extracted with dichloromethane (200 mL). The combined organic layers were dried over MgSO₄, and the solvent was removed using a rotavap. The crude compound was purified by column chromatography (silica, with dichloromethane as the eluent). Yield: 49% (8.60 g). ¹H-NMR (δ_H, CDCl₃, 300 MHz): 0.89 (9H, t, CH₃), 1.27 (60H, m, CH₂), 1.50 (6H, m, CH₂CH₂CH₂O), 1.81 (6H, m, CH₂CH₂O),

4.05 (6H, t, CH₂O), 7.06 (1H, dd, H-aryl), 7.36 (1H, d, H-aryl), 7.40 (2H, d, H-aryl), 7.44 (1H, dd, H-aryl), 9.89 (1H, s, CHO), 10.96 (1H, s, OH). Elemental analysis: calcd. for C₅₆H₉₄O₇ (MW = 879.34): C, 76.49%; H, 10.77%; found: C, 76.56%; H, 10.83%.

4-Hydroxy-3-[(2-[(E)-(2-hydroxy-5-[(3,4,5-tritetradecyloxybenzoyl)oxy]phenyl)methylidene]amino]ethyl]imino)methyl]phenyl 3,4,5-tritetradecyloxybenzoate (9)

Ethylenediamine (0.12 g; 0.002 mol) and five drops of glacial acetic acid (as the catalyst) were added to a solution of **8** (3.52 g; 0.004 mol) in 250 mL of toluene. The mixture was then heated for 3 h at reflux, and water formed by the reaction was removed azeotropically (Dean–Stark trap). After leaving to cool to room temperature, the solvent was removed at reduced pressure. The crude product was purified by recrystallization from absolute ethanol. Yield: 89% (3.17 g). ¹H-NMR (δ_H, CDCl₃, 300 MHz): 0.88 (18H, t, CH₃), 1.27 (120H, m, CH₂), 1.49 (12H, m, CH₂CH₂CH₂O), 1.81 (12H, m, CH₂CH₂O), 4.04 (16H, m, CH₂O, CH₂N), 7.00 (2H, dd, H-aryl), 7.12 (2H, d, H-aryl), 7.15 (2H, dd, H-aryl), 7.39 (4H, d, H-aryl), 8.37 (2H, s, CHN), 13.12 (2H, s, OH). IR (KBr, cm⁻¹): 1637 (C=N), 1203 (C–O). Elemental analysis: calcd. for C₁₁₄H₁₉₂O₁₂N₂ (MW = 1782.75): C, 76.80%; H, 10.86%; N, 1.57%; found: C, 76.72%; H, 11.01%; N, 1.56%.

Ni Complex with C₁₄ Chains (10)

A hot solution of Ni(OOCCH₃)₂·4H₂O (0.27 g; 0.0011 mol) in methanol was added dropwise to a hot solution of **9** (1.78 g; 0.001 mol) in chloroform, and the reaction mixture was refluxed overnight. After leaving to cool to room temperature, the solvent was removed at reduced pressure. The crude product was crystallized from ethyl acetate and washed with methanol. Yield: 89% (1.64 g). Thermal behaviour: Cr-65-Col_H-139-I. IR (KBr, cm⁻¹): 1624 (C=N), 1203 (C–O). Elemental analysis: calcd. for C₁₁₄H₁₉₀O₁₂N₂Ni (MW = 1839.43): C, 74.44%; H, 10.41%; N, 1.52%; found: C, 74.13%; H, 10.47%; N, 1.51%.

La–Ni Complex with C₁₄ Chains (11)

A solution of La(NO₃)₃·6H₂O (0.072 g; 0.17 mmol) in acetone was added to a solution of **9** (0.277 g; 0.15 mmol) in acetone, and the reaction mixture was stirred at room temperature for a period of 24 h. The precipitate was filtered, washed with cold methanol and dried *in vacuo*. Yield: 36% (108 mg). Thermal behaviour: Cr-81-Col_H-206-I. IR (KBr, cm⁻¹): ν = 1627 (C=N), 1201 (C–O). Elemental analysis: calcd. for C₂₂₈H₃₈₀O₃₃N₇Ni₂La (MW = 4003.78): C, 68.40%; H,

9.56%; N, 2.56%; found: C, 68.18%; H, 10.02%; N, 2.25%.

3,4,5-Trihexadecyloxybenzoic Acid (12)

1-Bromohexadecane (100.65 g; 0.33 mol) and a spatula point of KI were added to a mixture of gallic acid ethyl ester (19.82 g; 0.1 mol) and K₂CO₃ (82.93 g; 0.6 mol) in 700 mL of DMF. The solution was then refluxed overnight. The resulting mixture was poured into water, and the precipitate was filtered. This crude product was refluxed for 4 h with NaOH (6.40 g; 0.16 mol) in 300 mL of ethanol. The reaction mixture was poured into water, acidified with dilute HCl and the precipitate filtered and recrystallized from ethyl acetate and acetone. Yield: 76% (63.78 g). ¹H-NMR (δ_H, CDCl₃, 300 MHz): 0.88 (9H, t, CH₃), 1.26 (72H, m, CH₂), 1.48 (6H, m, CH₂CH₂CH₂O), 1.82 (6H, m, CH₂CH₂O), 4.02 (6H, t, CH₂O), 7.32 (2H, d, H-aryl). Elemental analysis: calcd. for C₅₅H₁₀₂O₅ (MW = 843.40): C, 78.32%; H, 12.19%; found: C, 78.31%; H, 12.28%.

3-Formyl-4-hydroxyphenyl-3,4,5-trihexadecyloxybenzoate (13)

3,4,5-Trihexadecyloxybenzoic acid **12** (8.43 g; 0.01 mol) and DMAP [= 4-(*N,N'*-dimethylamino)-pyridine] (0.12 g; 0.001 mol) were added to a mixture of 2,5-dihydroxybenzaldehyde (1.38 g; 0.02 mol) DCC (= *N,N''*-dicyclohexylcarbodiimide) (2.30 g; 0.012 mol) in 600 mL of dichloromethane. The solution was stirred at room temperature for a period of 24 h. The precipitated *N,N''*-dicyclohexylureum was filtered and washed with a saturated NaHCO₃ solution (2 × 200 mL) and water (2 × 200 mL). The aqueous layers were back-extracted with dichloromethane (100 mL). The combined organic layers were dried over MgSO₄, and the solvent was removed using a rotavap. The crude compound was purified by column chromatography (silica, with dichloromethane as the eluent). Yield: 61% (5.92 g). ¹H-NMR (δ_H, CDCl₃, 300 MHz): 0.88 (9H, t, CH₃), 1.26 (72H, m, CH₂), 1.49 (6H, m, CH₂CH₂CH₂O), 1.84 (6H, m, CH₂CH₂O), 4.04 (6H, t, CH₂O), 7.05 (1H, dd, H-aryl), 7.35 (1H, d, H-aryl), 7.39 (2H, d, H-aryl), 7.43 (1H, dd, H-aryl), 9.88 (1H, s, CHO), 10.94 (1H, s, OH). Elemental analysis: calcd. for C₆₂H₁₀₆O₇ (MW = 963.50): C, 77.29%; H, 11.09%; found: C, 77.54%; H, 11.32%.

4-Hydroxy-3-[(2-[(E)-(2-hydroxy-5-[(3,4,5-trihexadecyloxybenzoyl)oxy]phenyl)methylidene]amino]ethyl]imino)methyl]phenyl 3,4,5-trihexadecyloxybenzoate (14)

Ethylenediamine (0.15 g; 25 mmol) and five drops of glacial acetic acid (as the catalyst) were added to

a solution of **13** (4.82 g; 0.005 mol) in 300 mL of toluene. The mixture was heated for 3 h at reflux, and water formed by the reaction was removed azeotropically (Dean–Stark trap). After leaving to cool to room temperature, the solvent was removed at reduced pressure. The crude product was purified by recrystallization from absolute ethanol. Yield: 96% (4.68 g). $^1\text{H-NMR}$ (δ_{H} , CDCl_3 , 300 MHz): 0.88 (18H, t, CH_3), 1.26 (144H, m, CH_2), 1.48 (12H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.82 (12H, m, $\text{CH}_2\text{CH}_2\text{O}$), 4.04 (16H, m, CH_2O , CH_2N), 6.97 (2H, dd, H-aryl), 7.11 (2H, d, H-aryl), 7.14 (2H, dd, H-aryl), 7.38 (4H, d, H-aryl), 8.36 (2H, s, CHN), 13.10 (2H, s, OH). IR (KBr, cm^{-1}): 1637 (C=N), 1203 (C–O). Elemental analysis: calcd. for $\text{C}_{126}\text{H}_{216}\text{O}_{12}\text{N}_2$ (MW = 1951.07): C, 77.57%; H, 11.16%; N, 1.44%; found: C, 77.94%; H, 11.01%; N, 1.43%.

Ni Complex with C_{16} Chains (15)

A hot solution of $\text{Ni}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.27 g; 0.0011 mol) in methanol was added dropwise to a hot solution of **14** (1.95 g; 0.001 mol) in chloroform, and the reaction mixture was then refluxed overnight. After leaving to cool to room temperature, the solvent was removed at reduced pressure. The crude product was crystallized from ethyl acetate and washed with methanol. Yield: 85% (1.72 g). Thermal behaviour: Cr-71-Col_H-111-I. IR (KBr, cm^{-1}): 1626 (C=N), 1203 (C–O). Elemental analysis: calcd. for $\text{C}_{126}\text{H}_{214}\text{O}_{12}\text{N}_2\text{Ni}$ (MW = 2007.75): C, 75.38%; H, 10.74%; N, 1.40%; found: C, 75.60%; H, 10.78%; N, 1.30%.

La–Ni Complex with C_{16} Chains (16)

A solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.052 g; 0.12 mmol) in acetone was added to a solution of **14** (0.186 g; 0.1 mmol) in acetone. The reaction mixture was then stirred at room temperature for a period of 24 h. The precipitate was filtered and washed with cold methanol and dried under reduced pressure. Yield: 47% (203 mg).

Thermal behaviour: Cr-90-Col_H-192-I. IR (KBr, cm^{-1}): 1628 (C=N), 1201 (C–O). Elemental analysis: calcd. for $\text{C}_{252}\text{H}_{428}\text{O}_{33}\text{N}_7\text{Ni}_2\text{La}$ (MW = 4340.41): C, 69.73%; H, 9.94%; N, 2.26%; found: C, 69.42%; H, 10.07%; N, 2.04%.

3,4,5-Trioctadecyloxybenzoic Acid (17)

1-Bromo-octadecane (109.89 g; 0.33 mol) and a spatula point of KI were added to a mixture of gallic acid ethyl ester (19.82 g; 0.1 mol) and K_2CO_3 (82.93 g; 0.6 mol) in 700 mL of DMF. The solution was refluxed overnight, the resulting mixture was poured into water, and the precipitate was filtered. This crude product was refluxed for 4 h with NaOH (6.40 g;

0.16 mol) in 300 mL of ethanol. The reaction mixture was poured into water, acidified with dilute HCl and the precipitate filtered and recrystallized from ethyl acetate and acetone. Yield: 54% (50.34 g). $^1\text{H-NMR}$ (δ_{H} , CDCl_3 , 300 MHz): 0.88 (9H, t, CH_3), 1.26 (84H, m, CH_2), 1.42 (6H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.72 (6H, m, $\text{CH}_2\text{CH}_2\text{O}$), 3.91 (6H, t, CH_2O), 7.22 (2H, d, H-aryl). Elemental analysis: calcd. for $\text{C}_{61}\text{H}_{114}\text{O}_5$ (MW = 927.56): C, 78.99%; H, 12.39%; found: C, 78.61%; H, 12.48%.

3-Formyl-4-hydroxyphenyl-3,4,5-trioctadecyloxybenzoate (18)

3,4,5-Trioctadecyloxybenzoic acid **16** (18.52 g; 0.02 mol) and DMAP [= 4-(*N,N'*-dimethylamino)pyridine] (0.24 g; 0.002 mol) were added to a mixture of 2,5-dihydroxybenzaldehyde (2.76 g; 0.02 mol) DCC (= *N,N'*-dicyclohexylcarbodiimide) (4.60 g; 0.024 mol) in 600 mL of dichloromethane. The solution was stirred at room temperature for a period of 24 h. The precipitated *N,N'*-dicyclohexylurea was filtered and washed with a saturated NaHCO_3 solution (2×400 mL) and water (2×400 mL). The aqueous layers were back-extracted with dichloromethane (200 mL). The combined organic layers were dried over MgSO_4 , and the solvent was removed using a rotavap. The crude compound was purified by column chromatography (silica, with dichloromethane as the eluent). Yield: 56% (11.75 g). $^1\text{H-NMR}$ (δ_{H} , CDCl_3 , 300 MHz): 0.88 (9H, t, CH_3), 1.26 (84H, m, CH_2), 1.48 (6H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.79 (6H, m, $\text{CH}_2\text{CH}_2\text{O}$), 4.03 (6H, t, CH_2O), 6.74 (1H, dd, H-aryl), 7.08 (1H, d, H-aryl), 7.39 (2H, d, H-aryl), 7.44 (1H, dd, H-aryl), 9.89 (1H, s, CHO), 10.94 (1H, s, OH).

Elemental analysis: calcd. for $\text{C}_{68}\text{H}_{118}\text{O}_7$ (MW = 1047.66): C, 77.96%; H, 11.35%; found: C, 77.94%; H, 11.64%.

*4-Hydroxy-3-[(2-[(*E*)-{2-hydroxy-5-[(3,4,5-trioctadecyloxybenzoyl)oxy]phenyl}methylidene)-aminoethyl]imino)methyl]phenyl 3,4,5-trioctadecyloxybenzoate (19)*

Ethylenediamine (0.135 g; 0.00225 mol) and five drops of glacial acetic acid (as the catalyst) were added to a solution of 3-formyl-4-hydroxyphenyl-3,4,5-trioctadecyloxybenzoate **18** (4.71 g; 0.0045 mol) in 500 mL of toluene. The mixture was heated during 3 h at reflux, and water formed by the reaction was removed azeotropically (Dean–Stark trap). After leaving to cool to room temperature, the solvent was removed at reduced pressure. The crude product was purified by recrystallization from absolute ethanol. Yield: 89% (4.26 g). $^1\text{H-NMR}$ (δ_{H} , CDCl_3 , 300 MHz): 0.88 (18H, t, CH_3), 1.26 (168H, m, CH_2),

1.46 (12H, m, CH₂CH₂CH₂O), 1.80 (12H, m, CH₂CH₂O), 3.98 (16H, m, CH₂O, CH₂N), 6.74 (2H, dd, H-aryl), 6.98 (2H, d, H-aryl), 7.11 (2H, dd, H-aryl), 7.38 (4H, d, H-aryl), 8.36 (2H, s, CHN), 13.12 (2H, s, OH). IR (KBr, cm⁻¹): ν = 1641 (C=N), 1203 cm⁻¹ (C-O). Elemental analysis: calcd. for C₁₃₈H₂₄₀O₁₂N₂ (MW = 2119.39): C, 78.21%; H, 11.41%; N, 1.32%; found: C, 78.55%; H, 11.31%; N, 1.53%.

Ni Complex with C₁₈ Chains (20)

A hot solution of Ni(OOCCH₃)₂·4H₂O (0.30 g; 0.0012 mol) in methanol was added dropwise to a hot solution of **19** (2.12 g; 0.001 mol) in chloroform, and the reaction mixture was refluxed overnight. After leaving to cool to room temperature, the solvent was removed at reduced pressure. The crude product was crystallized from ethyl acetate and washed with methanol. Yield: 60% (1.30 g). Thermal behaviour: Cr-74-Col_H-94-I. IR (KBr, cm⁻¹): 1628 (C=N), 1203 (C-O). Elemental analysis: calcd. for C₁₃₈H₂₃₈O₁₂N₂Ni (MW = 2176.07): C, 76.17%; H, 11.02%; N, 1.29%; found: C, 75.85%; H, 11.53%; N, 1.44%.

Gd-Ni Complex with C₁₈ Chains (21)

To a solution of **19** (0.141 g; 0.1 mmol) in acetone was added a solution of Gd(NO₃)₃·6H₂O (0.054 g; 0.12 mmol) in acetone. The reaction mixture was stirred at room temperature for a period of 24 h. The precipitate was filtered and washed with cold methanol and dried under reduced pressure. Yield: 40% (188 mg). Thermal behaviour: Cr-82-Col_H-177-I (dec). IR (KBr, cm⁻¹): 1626 (C=N), 1201 (C-O). Elemental analysis: calcd. for C₂₇₆H₄₇₆O₃₃N₇Ni₂Gd (MW = 4695.40): C, 70.60%; H, 10.22%; N, 2.09%; found: C, 70.09%; H, 10.70%; N, 2.09%.

CONCLUSIONS

In this paper, the first examples of liquid-crystalline nickel-lanthanide complexes have been presented. We followed the same approach as that successfully used to obtain liquid-crystalline copper-lanthanide complexes [37]. However, whereas the stoichiometry of the copper-lanthanide complexes depended on the size of the trivalent lanthanide ion (trinuclear copper-lanthanide-copper species for the light lanthanides and dinuclear copper-lanthanide species for the heavy lanthanides), only one stoichiometry was found for the nickel-lanthanide complexes: [Ln(NO₃)₃{Ni(salen)}₂]. Both the nickel and nickel-lanthanide complexes exhibited a hexagonal columnar mesophase (Col_H). Complex formation with a lanthanide nitrate increases

the mesophase stability range of the mesomorphic Ni(salen) complexes, although the melting point of the nickel-lanthanide complexes is comparable with that of the parent nickel complex. In contrast to the copper-lanthanide complexes which decompose before the clearing point is reached, the thermal stability of the nickel-lanthanide complexes is higher, and a clearing point can be observed. The mesophase stability range of both the nickel and the nickel-lanthanide complexes decreases with increasing alkoxy chain length. Smaller lanthanide ions stabilize the mesophase: a larger mesophase range was observed for the nickel-lanthanum complexes than for the corresponding nickel-gadolinium complexes. Further work is in progress to incorporate other transition metal ions in the salen-type ligand and to make the corresponding f-d complexes, and experiments in varying the number and position of the alkoxy chain lengths are also being done.

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