

Anisotropic molecular magnetic materials based on liquid-crystalline lanthanide complexes

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Abstract

The alignment of liquid crystals in an external magnetic field is discussed. Special attention is paid to paramagnetic metallomesogens containing trivalent lanthanide ions. The huge magnetic anisotropy of rare-earth compounds is favourable to achieve easy magnetic alignment. The principle of orientation of liquid-crystalline lanthanide complexes is illustrated for Schiff base complexes of the type $[\text{Ln}(\text{LH})_3(\text{NO}_3)_3]$, where Ln is a trivalent lanthanide ion and LH is a salicylaldimine. The compounds exhibit a smectic A phase. By a proper choice of the lanthanide ion, it is possible to align the director either parallel or perpendicular to the magnetic field. When the aligned mesophase is cooled in the presence of a magnetic field, the mesophase order is frozen into the glass state and an anisotropic molecular magnetic material is obtained. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Most of the commercial applications of liquid crystals (such as LCDs) are based on the behaviour of liquid crystals in an electric field. Liquid-crystalline molecules can be oriented with their director perpendicular or parallel to the electric field lines [1–3]. It is much less known that it is also possible to switch liquid crystals by applying an external magnetic field. The anisotropy of the magnetic susceptibility can be considered as the driving force for the alignment of the molecules in a magnetic field. Pioneering work in this field has been done by Foëx [4–8]. Hitherto, most of the alignment studies of conventional liquid crystals in a magnetic field were aimed to determine the order parameter S of nematic liquid crystals [9–15], although some studies have been devoted to magnetic alignment of smectic mesophases [16–21].

In order to obtain mesophases with a high magnetic anisotropy, liquid crystals containing paramagnetic transition metal ions or lanthanide ions have been synthesised [22–31]. Especially lanthanide-containing metallomesogens are of interest to design magnetic liquid crystals because it is well known that several lanthanide compounds have a very large magnetic anisotropy [32]. Not many types of liquid-crystalline lanthanide complexes have been described in the literature yet [33] and, of these compounds, the Schiff base complexes are the most promising for obtaining magnetic liquid crystals [34–43] (Fig. 1). In fact, for this type of compounds, values of the magnetic anisotropy have been measured which are one or two orders of magnitude larger than for conventional liquid crystals [42–46]. Recently, a theoretical model for the magnetic anisotropy of lanthanide-containing metallomesogens has been developed [47].

In this paper, we give an overview of the structural data available for the lanthanide complexes with salicylaldimine ligands and nitrate counter ions. The alignment of lanthanide-containing liquid crystals in an external magnetic field is discussed in detail. It will be shown how anisotropic molecular magnetic materials can be obtained

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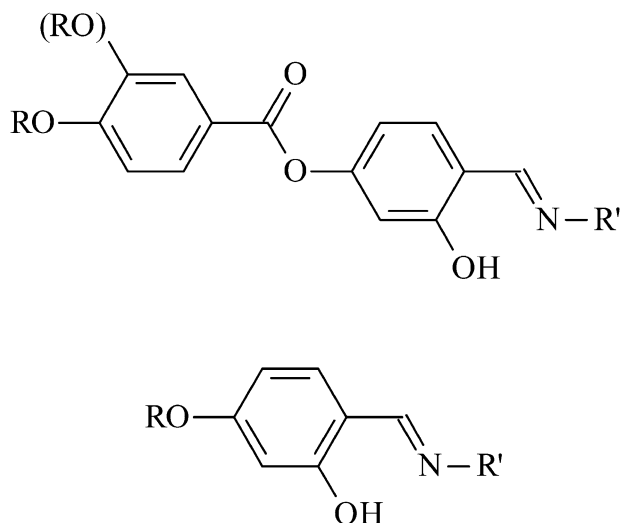


Fig. 1. Overview of salicylaldehyde Schiff base used to design liquid-crystalline lanthanide complexes. *R* and *R'* are alkyl chains. Especially the ligands with one aromatic ring are very suitable for obtaining thermally stable magnetic liquid crystals.

by cooling the aligned mesophase of these compounds in the presence of a magnetic field.

2. Structure of Schiff base complexes with nitrate counter ions

The only fully characterised type of liquid-crystalline lanthanide complexes with Schiff base ligands are those with nitrate counter ions [42]. The determination of the stoichiometry of these mesogenic complexes turned out to be a difficult task. On the basis of CHN elemental analysis, vapour pressure osmometry and magnetic moment measurements, the stoichiometry was claimed as $[\text{LnL}(\text{LH})_2(\text{NO}_3)_2]$. Thus, the complexes were thought to have a metal:ligand ratio 1:3; however, only one of the Schiff base complexes was considered to be deprotonated, whereas the other ligands coordinate to the rare-earth ion in their neutral form [43]. In this case, two nitrate counter ions would be required to guarantee electrical neutrality. Only a few rare-earth complexes with comparable ligands have been described in the literature. Yamada and coworkers reported on complexes of Schiff bases derived from salicylaldehyde [48,49]. Depending on the method of preparing the complexes, these authors found different stoichiometries. By grinding a mixture of the hydrated lanthanide chlorides and the Schiff base (ratio 1:3) in the absence of a solvent, complexes of the type $\text{Ln}(\text{L})_3 \cdot n\text{H}_2\text{O}$ ($n = 3-4$) were obtained. In these complexes, the OH group in the Schiff base ligand was deprotonated and no counter ions were present in the complexes. By refluxing the same mixture in ethanol, the stoichiometry of the formed yttrium(III) complexes was $[\text{Y}(\text{LH})_3\text{Cl}_3]$. More data are available for complexes with the *N,N'*-ethylene

bis(salicylideneimine) ligand (H_2salen) [50–58]. The stoichiometry of the Schiff base complexes is strongly dependent on the reaction conditions. Due to the relatively high molecular weight of the metal complexes, CHN microanalysis alone is not accurate enough to discriminate between the different possible stoichiometries: $[\text{LnL}(\text{LH})_2(\text{NO}_3)_2]$, $[\text{LnL}(\text{LH})_2(\text{NO}_3)_2] \cdot x\text{H}_2\text{O}$ or $[\text{L}(\text{LH})_3(\text{NO}_3)_3]$. In principle, a molecular weight determination could give the answer. However, the error on the molecular mass measurements with vapour osmometry leaved the question open which of the three stoichiometries given above is the right one. Mass spectrometry was not able to give the answer either because it was impossible to decide whether or not a nitrate group was split off by ionization.

The first key to the solution of the problem was given by the ^1H NMR spectra of the diamagnetic lanthanum(III) derivatives [38]. We found that the ^1H signal corresponding to the imine hydrogen ($\text{CH}=\text{N}$) was broadened in the lanthanum(III) complex when compared with the same signal in the Schiff base ligand. In first instance, we thought that this broadening could be attributed to paramagnetic impurities (i.e. other lanthanide ions) in the starting lanthanum(III) salt. However, sometimes a very distinct splitting of the imine signal could be observed. The value of the coupling constant is of the same order of magnitude as the expected value for a trans-coupling in $\text{H}-\text{C}=\text{N}^+-\text{H}$. This and the fact that the signal at $\delta \approx 12.3$ ppm belonged to a NH resonance and not to an OH resonance could be proved by a homonuclear decoupling experiment. Irradiation of the NH signal lead to a collapse of the $\text{CH}=\text{N}$ doublet. The Schiff base is present in a zwitterionic form, with the phenolic oxygen deprotonated and the imine nitrogen protonated (Fig. 2). Further evidence for the existence of a zwitterionic form in the metal complexes was given by infrared spectroscopy and, more particularly, by the band frequencies of the $\text{C}=\text{N}$ 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 $\text{C}=\text{N}^+$ group is present.

The best evidence for this model was given by the single crystal X-ray structure of analogous nonmesogenic complexes formed by ligands with short alkyl chains (Fig. 3) [42]. The crystal structure showed that three ligands and three nitrate groups are present for each metal ion. The

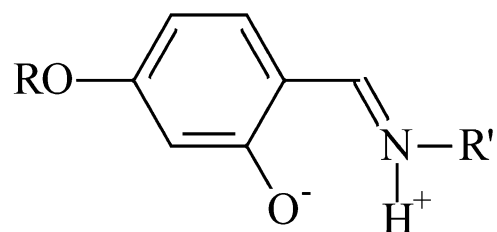


Fig. 2. Schiff base ligand in a zwitterionic form.

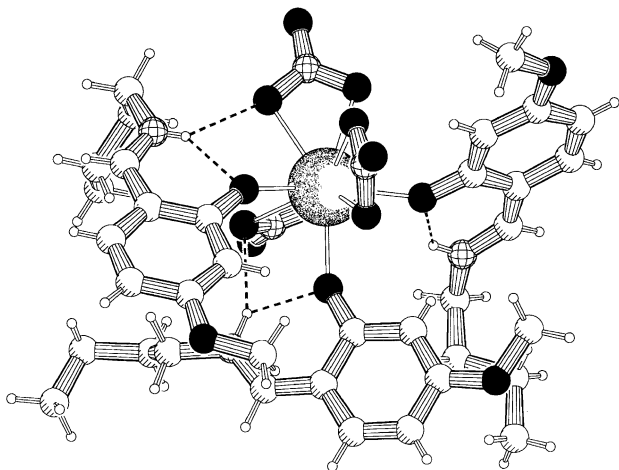


Fig. 3. Molecular structure of $[\text{Nd}(\text{LH})_3(\text{NO}_3)_3]$, where LH is *N*-butyl-2-hydroxy-4-methoxybenzaldimine. Atomic coordinates were taken from Ref. [42].

Schiff base ligands are indeed in the zwitterionic form, as 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; however, 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 spectroscopic data (luminescence spectra) indicate that the first coordination sphere around the lanthanide ion is not changed by elongation of the alkyl chains. Therefore, we can anticipate that the bonding in the nonmesogenic complexes is the same as in the mesogenic complexes. Of course, the packing of the molecules is changed.

Although the lanthanides are sometimes called “inner transition elements”, the coordination chemistry of these *4f*-block elements is essentially different from the coordination chemistry of the *d*-block transition metals [59–63]. In fact, the bonding properties of the lanthanides are more comparable with those of the alkali and earth-alkaline metal ions. The main difference between *4f*-block elements and *d*-block elements is that the *4f*-orbitals do not participate in complex formation while the *d*-orbitals do. Therefore, metal–ligand bond has an appreciable covalent character in the *d*-block complexes, whereas metal ion and

ligands are held together largely by electrostatic interactions in lanthanide complexes. Most of the *d*-block complexes have a well-defined geometry (ideal or distorted tetrahedra or octahedra) and coordination number (CN = 4 for tetrahedral coordination, CN = 6 for octahedral coordination). Because of the lack of directional covalent bonding, the coordination polyhedra are much less defined in lanthanide complexes and the coordination number ranges from 6 to more than 12. However, many lanthanide complexes have coordination number 8 or 9, and the coordination sphere can be defined as one of the following idealized polyhedra: dodecahedron (CN = 8), square antiprism (CN = 8), tricapped trigonal prism (CN = 9) and monocapped square antiprism (CN = 9). Octahedral lanthanide complexes (CN = 6) do exist; however, they are very difficult to obtain. The best known example is formed by the tris(β -diketonato) complexes. Lanthanide complexes with coordination number 6 are coordinatively unsaturated and will expand their coordination sphere either by polymerisation or by adduct formation. In polymerised products, each ligand is shared by two or more metal ions and infinite chains, sheets or even a three-dimensional network is formed. Thus, the coordination number in lanthanide alkanoates, $(\text{C}_n\text{H}_{2n+1}\text{COO})_3\text{Ln}$ is not 6, but 8 or 9 [64]. In adducts, the coordination sphere of the trivalent lanthanide ion is expanded by adding neutral molecules. Because the lanthanide ions are hard Lewis acids, hard Lewis bases are preferred for adduct formation. Most of the molecules which add to lanthanide ions are oxygen donors and, to a lesser extent, nitrogen donors. A very common ligand, which forms adducts with lanthanide ions, is water. When tris(β -diketonato) complexes are prepared in an aqueous solution, they are most often obtained as dihydrates. In this way, the coordination number of the lanthanide ion will be 8, not 6. Adducts are often formed by aprotic polar organic solvents such as DMSO or acetone. Polydentate ligands with N-donor atoms (e.g. 2,2'-bipyridine) are also able to form adducts with tris(β -diketonato) complexes.

It is much less known that the lanthanides can also form *salt adducts*. In these compounds, the coordination sphere of the lanthanide ion is essentially formed by small inorganic anions such as perchlorates, chlorides, bromides, acetates, or nitrates. Much of the pioneering work on lanthanide salt adducts has been performed by Vicentini and coworkers [65–67], studying adducts with *N,N*-dimethylurea (DMA). Another adduct forming compounds is 4-aminoantipyrene [68]. The crystal structure of $[\text{Eu}(\text{TMU})_3(\text{NO}_3)_3]$, where TMU is tetramethylurea, has been described by Chieh et al. [69], showing that europium has a coordination number of 9 with three nitrates coordinated in a bidentate way and with three DMU molecules bonded via the oxygen atoms. The first coordination sphere of $[\text{Eu}(\text{TMU})_3(\text{NO}_3)_3]$ is very analogous to the first coordination sphere in the Eu(III) compound $[\text{Eu}(\text{LH})_3(\text{NO}_3)_3]$ described in this work. In fact, our Schiff base complexes can be considered as *salt adducts*.

Although we used a threefold excess of the lanthanide nitrate (to compensate for the unknown quantity of crystal water in the hygroscopic lanthanide nitrates and to avoid coprecipitation of the ligand), we always observed the formation of tris-adducts and not of mono- or bis-adducts. It is important not to use a base during synthesis of the lanthanide compounds because salt adducts can only be formed with neutral ligands. Adduct formation of salicylaldehyde Schiff bases to lanthanide nitrates is promoted by the existence of a zwitterion. The imine nitrogen is basic enough for uptake of the proton. This is not the case if a 4-substituted aniline is used for Schiff base formation instead of an *n*-alkylamine. Until now, it was not possible to obtain salt adducts of the latter Schiff bases. If the ligand is deprotonated by a base, complexes of the type LnL_3 will be formed. Such compounds are very likely to be polymeric because with a stoichiometry of LnL_3 , there are only six donor atoms available which is less than that required to satisfy the lanthanide's coordination requirements. With two-ring Schiff base ligands, sometimes complexes of the type $[\text{Ln}(\text{LH})_2\text{L}(\text{NO}_3)_2]$ are formed, the lanthanide ion having coordination number 7.

The *salt adduct formation* is the driving force for the existence of a mesophase in the salicylaldehyde Schiff base complexes. Because the Schiff base ligands only have one aromatic ring, their structural anisotropy is not high enough to form a mesophase by themselves. In general, at least two aromatic rings are required for stabilisation of a thermotropic mesophase of rodlike (calamitic) molecules. The lanthanide nitrate subunit $\text{Ln}(\text{NO}_3)_3$ is holding the ligands together, and can be considered as a pivoting point. Because of the monodentate character of the Schiff base ligands, one can expect that the ligands are able to rotate around the Ln–O axis. However, the bulkiness of the nitrate groups could put some constraints to this rotation ability. The main question is how the phenyl rings are situated with respect to each other in the adducts: are the phenyl rings more or less parallel to each other or not? This problem has not been solved yet.

3. Alignment of liquid crystals by a magnetic field

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, χ_{\parallel} and χ_{\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 it will be to align a liquid crystal in a magnetic field (i.e. the weaker the magnetic field can be for obtaining magnetic alignment). The sign of $\Delta\chi$ determines how the director and, thus the molecular long 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 molecular long 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; however, if $\Delta\chi < 0$, the director can take any orientation in a plane perpendicular to the magnetic field. A polydomain is obtained where the different microdomains are randomly oriented, with the only restriction that the director is situated within a plane [70]. 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.

Diamagnetic calamitic liquid crystals have, in general, a positive magnetic anisotropy and diamagnetic discotic liquid crystals a negative magnetic anisotropy. Therefore, calamitic molecules will align with the director parallel to the external magnetic field, while discotic molecules will align with the director perpendicular to the magnetic field. It is sometimes difficult to predict the direction of alignment of paramagnetic liquid crystals because there is a competition between the diamagnetic ($\Delta\chi_{\text{dia}}$) and the paramagnetic contributions ($\Delta\chi_{\text{para}}$) to the overall magnetic anisotropy $\Delta\chi$. The diamagnetic contribution, $\Delta\chi_{\text{dia}}$, is nearly always positive (for calamitic molecules); however, $\Delta\chi_{\text{para}}$ can be either positive or negative. In the case of oxovanadium ($\text{V}=\text{O}$) complexes $\Delta\chi_{\text{para}}$ is positive so that $\Delta\chi$ is always positive. Therefore, all oxovanadium complexes align with the director parallel to the magnetic field [70–74]. In the case of copper(II) complexes, the situation is more complicated because $\Delta\chi_{\text{para}}$ is negative. It was found for liquid-crystalline Cu^{II} complexes with Schiff base ligands that the sign of $\Delta\chi$ depends on the number of benzene rings present in the molecule [70,75,76]. If two benzene rings are present in the ligand, $\Delta\chi_{\text{para}} > \Delta\chi_{\text{dia}}$ and $\Delta\chi < 0$ (perpendicular orientation to the magnetic field). In ligands with three or more benzene rings, $\Delta\chi_{\text{para}} < \Delta\chi_{\text{dia}}$ and $\Delta\chi > 0$ (parallel orientation to the magnetic field). Due to geometric effects, deviations for these rules may occur. The diamagnetic contribution to the magnetic anisotropy can be calculated using an additive scheme (Pascal's scheme) [13] and the paramagnetic contribution can be found by subtracting the calculated $\Delta\chi_{\text{dia}}$ value from the experimental measured $\Delta\chi$ value.

The situation is quite different in the case of lanthanide-containing liquid crystals because the trivalent ions of the lanthanides (especially Tb^{III} , Dy^{III} , Ho^{III} , Er^{III}) have a very large magnetic anisotropy in comparison with other paramagnetic ions (e.g. Cu^{II} or $\text{V}=\text{O}$) [32]. In the case of the paramagnetic lanthanide ions (all the ions of the lanthanide series except La^{III} , Lu^{III} , and the rare earths Y^{III} and Sc^{III}), the diamagnetic contributions to $\Delta\chi$ can be neglected in comparison to the paramagnetic contri-

bution. An exception is the Gd^{III} ion, which is almost magnetically isotropic due to the S ground state $^8S_{7/2}$. 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 which 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 $\Delta\chi$ [47]. The first group contains Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Tb^{III}, Dy^{III}, and Ho^{III} compounds, while the second group contains Eu^{III}, Er^{III}, Tm^{III}, and Yb^{III} 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 for lanthanide-containing liquid crystals and for phospholipid bilayers doped with lanthanide chelates [77–81] are in agreement with a negative $\Delta\chi$ value for the first group and a positive $\Delta\chi$ value for the second group. However, recent theoretical work shows that the reverse situation can be expected too [47]. The highest values of the magnetic anisotropy are observed for the heavy lanthanides Tb^{III}, Dy^{III}, Ho^{III}, Er^{III}, Tm^{III} because these ions have a high magnetic moment. There is no one-on-one relationship between a high magnetic moment and a large magnetic anisotropy; however, if the magnetic moment is small, it is impossible to have a huge magnetic anisotropy. It should be remembered that the magnetic moment is related to the magnetic anisotropy by the relationship:

$$\mu_{\text{eff}} = \sqrt{\frac{3k}{N_A}} \sqrt{\chi T} = 2.828\sqrt{\chi T}, \quad (1)$$

where μ_{eff} is the effective magnetic moment (in Bohr magneton, μ_B), k is the Boltzmann constant, N_A Avogadro's

adro's number, χ 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 should be strong. The $^{2S+1}L_J$ 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 behaviour 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. A summary of the theoretically expected value of μ_{eff} for the trivalent lanthanide ions in the free-ion approximation is given in Table 1. Experimentally, only small deviations from these predicted values are observed at room temperature.

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-base complexes reported up to present display a smectic A mesophase. The smectic A phase has an intrinsic higher viscosity than the nematic phase. Therefore, obtaining liquid-crystalline lanthanide complexes exhibiting a nematic phase is a major goal in our research. This goal is not easy to achieve because the structure of the Schiff base complexes tends to promote formation of layered structures (and this means smectic mesophases). However, by a proper choice of the counter ion, the viscosity of the

Table 1
Magnetic properties of the trivalent lanthanide ions Ln³⁺ [62,84]

Ln ³⁺	Electronic configuration	Ground state	μ_{eff} Calculated (Bohr magnetons)	μ_{eff} Observed (Bohr magnetons)
Ce ³⁺	[Xe]4f ¹	$^2F_{5/2}$	2.56	2.3–2.5
Pr ³⁺	[Xe]4f ²	3H_4	3.58	3.4–3.6
Nd ³⁺	[Xe]4f ³	$^4I_{9/2}$	3.62	3.5–3.6
Pm ³⁺	[Xe]4f ⁴	4I_4	2.68	–
Sm ³⁺	[Xe]4f ⁵	$^6H_{5/2}$	1.55–1.65	1.4–1.7
Eu ³⁺	[Xe]4f ⁶	7F_0	3.40–3.51	3.3–3.5
Gd ³⁺	[Xe]4f ⁷	$^8S_{7/2}$	7.94	7.9–8.0
Tb ³⁺	[Xe]4f ⁸	7F_6	9.72	9.5–9.8
Dy ³⁺	[Xe]4f ⁹	$^6H_{15/2}$	10.65	10.4–10.6
Ho ³⁺	[Xe]4f ¹⁰	5I_8	10.60	10.4–10.7
Er ³⁺	[Xe]4f ¹¹	$^4H_{15/2}$	9.58	9.4–9.6
Tm ³⁺	[Xe]4f ¹²	3H_6	7.56	7.1–7.5
Yb ³⁺	[Xe]4f ¹³	$^2F_{7/2}$	4.54	4.3–4.9
Lu ³⁺	[Xe]4f ¹⁴	1S_0	0	0

mesophase can be reduced considerably. For instance, a smectic A mesophase with a low viscosity is found for Schiff base complexes with perfluorinated alkyl sulphates as counter ions [82]. Recently, Kumar and Pisipati [83] observed a nematic mesophase in lanthanide complexes of *N*-(2-hydroxy-4-alkoxybenzaldehydeimino)-2-benzamidoethanamide.

χ_{\parallel} and χ_{\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 which is not strong enough to reorient the liquid crystal. Alternatively, the aligned mesophase can be frozen into the glassy state. The χ_{\parallel} and χ_{\perp} values of a glassy (aligned) mesophase can be measured as if one would measure 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 SmA phase can only be oriented at a temperature close to the clearing point. The orientation at this point will be retained when the mesophase will be cooled further. The magnetic anisotropy, $\Delta\chi$, cannot be obtained via the relation $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ because only one of the two components, χ_{\parallel} or χ_{\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, χ_{iso} will be measured. It is assumed that χ_{iso} is equal to the average magnetic susceptibility, $\bar{\chi}$, which is defined as $\bar{\chi} = (\chi_{\parallel} + 2\chi_{\perp})/3$. In the mesophase, the molecules will be oriented in such a way that the axis of maximum 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 χ_{max} . If $\Delta\chi > 0$, χ_{max} corresponds to χ_{\parallel} and $\Delta\chi = 3/2(\chi_{\text{max}} - \bar{\chi})$. If $\Delta\chi < 0$, χ_{max} corresponds to χ_{\perp} and $\Delta\chi = 3(\bar{\chi} - \chi_{\text{max}})$. The sign of $\Delta\chi$ cannot be determined by magnetic susceptibility measurements and should be obtained by an independent measurement, for instance, via EPR (angle dependence of the EPR signal) or via 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 that the measured value of $\Delta\chi$ is smaller than the value which can be theoretically expected. In Fig. 4, the alignment of a neodymium(III)-containing liquid crystal is illustrated. The sample exhibited a Curie–Weiss behaviour for the temperature dependence of their magnetic properties, when heated from the solid state through the SmA phase until the

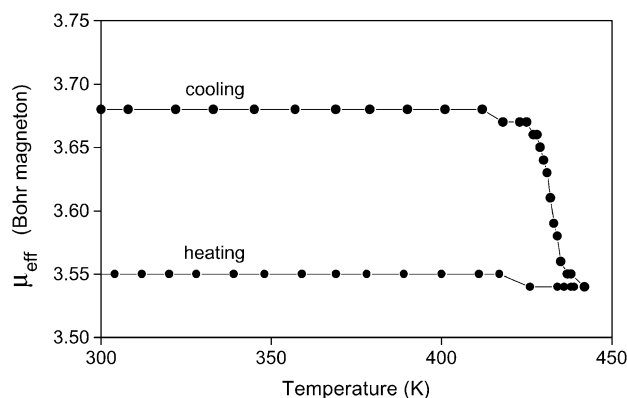


Fig. 4. Magnetic alignment of the praseodymium(III) containing liquid crystal $[\text{Pr}(\text{LH})_3(\text{NO}_3)_3]$, where LH is 4-dodecyloxy-*N*-hexadecyl-2-hydroxybenzalimine. Adapted from Ref. [42].

isotropic phase was reached. When the samples were cooled down 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, μ_{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 μ_{eff} than in the heating cycle. This behaviour can be referred to a magnetic-field-induced orientation in the liquid-crystalline phase of a magnetically anisotropic sample with its axis of maximum magnetic susceptibility parallel to the magnetic field.

What are the advantages of switching liquid crystals by an external magnetic field over switching the same compounds by an external electric field? By switching metal-omesogens by an electric field, some problems can arise because of unwanted electrochemical reactions. Due to the electric conductivity of ionic metallomesogens, an electric double layer can be formed in an electric field so that switching will be difficult. It is evident that one will not have these problems in the case of a magnetic field. By an electric field, liquid crystals can be aligned only parallel or perpendicular to the electrodes. Because these electrodes are ITO glass plates and, thus, also the walls of the LC cell, the liquid crystal can be oriented only parallel or perpendicular to the wall of the LC cell. With a magnetic field, it is possible to align a liquid crystal with its director parallel or perpendicular to the magnetic field; however, this direction can be independent of the orientation of the walls of the LC cell. Of course, magnetically switched liquid crystals will never replace electrically switched liquid crystals in LCDs; however, one can imagine some possible applications. Metallomesogens can often be super-cooled to a glassy mesophase. When a liquid crystal is aligned in a magnetic field, the mesophase can be frozen into a glassy state and the position of the orientation of the molecules can be retained in the vitreous mesophase. In

this way, all the spins will be oriented more or less parallel. If such an aligned glassy mesophase is heated locally (for instance, by a laser), the alignment can be destroyed in some places. It is also possible to realign the molecules by using a magnetic field opposite to the previous used magnetic field direction. By cooling liquid crystals with a high magnetic anisotropy in a magnetic field, it is possible to obtain anisotropic magnetic materials. Otherwise, much more expensive single crystals have to be used to obtain the same properties. It is interesting to note that Foëx [6,8] was also able to obtain anisotropic molecular magnetic materials. He heated a nematic compound to a temperature just above the melting point so that a small quantity of the solid is in equilibrium with the nematic phase. The nematic phase was oriented by the external magnetic field. When the compound was cooled, it crystallized forming a solid with the same orientation of the molecules as in the nematic phase. In this case, the molecular magnetic material consists of aligned small crystallites, whereas for our compounds, we obtained aligned molecules in a glass phase. In polycrystalline solids, the value of the magnetic susceptibility, χ , is very close to the value χ_{iso} of the isotropic liquid.

4. Conclusions

By taking advantage of the very large magnetic anisotropy of the elements of the lanthanide series (especially Tb^{III}, Dy^{III}, Ho^{III}, Er^{III} and Tm^{III}), it is possible to design paramagnetic liquid crystals which can be switched by an external magnetic field. Depending on the sign of the magnetic anisotropy, the rod-like molecules can be oriented with their long molecular axis parallel or perpendicular to the magnetic field lines. We illustrated magnetic alignment of mesomorphic Schiff base complexes of the type [Ln(LH)₃(NO₃)₃], where Ln is the trivalent lanthanide ion and LH is a salicylaldehyde Schiff base. The compounds exhibit an enantiotropic smectic A mesophase. When the magnetically aligned mesophase is cooled in the presence of a magnetic field, the mesophase order can be frozen into a glass state. In this way, anisotropic molecular magnetic materials can be obtained.

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References

- [1] D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds.), Handbook of Liquid Crystals, vol. 1, Wiley-VCH, Weinheim, 1998.
- [2] L.V. Blinov, Electro-Optical and Magneto-Optical Properties of Liquid Crystals, Wiley, Chichester, 1983.
- [3] P.J. Collins, J.S. Patel (Eds.), Handbook of Liquid Crystal Research, Oxford Univ. Press, Oxford, 1997.
- [4] G. Foëx, L. Royer, Compt. Rend. 180 (1925) 1912.
- [5] G. Foëx, Compt. Rend. 184 (1927) 147.
- [6] G. Foëx, Compt. Rend. 187 (1928) 822.
- [7] G. Foëx, J. Phys. Radium 10 (1929) 421.
- [8] G. Foëx, Trans. Faraday Soc. 29 (1933) 958.
- [9] H. Kelker, R. Hatz, Handbook of Liquid Crystals, Verlag Chemie, Weinheim, 1980, Chap. 4.
- [10] D. Dunmur, K. Toriyama, in: D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds.), Magnetic Properties of Liquid Crystals, Handbook of Liquid Crystals, vol. 1, Wiley-VCH, Weinheim, 1998, p. 204.
- [11] H. Gasparoux, B. Regaya, J. Prost, C. R. Acad. Sci. Paris 272 (1971) 1168.
- [12] I.H. Ibrahim, W. Haase, Z. Naturforsch. 31A (1976) 1644.
- [13] I.H. Ibrahim, W. Haase, J. Phys. Colloque C3 (France) 40 (1979) 164.
- [14] I.H. Ibrahim, W. Haase, J. Phys. 44 (1983) 1209.
- [15] T. Dries, E.W. Fischer, M. Ballauff, J. Appl. Phys. 69 (1991) 7539.
- [16] B. Bahadur, S. Chandra, N.K. Sanyal, Phys. Status Solidi A 35 (1976) 387.
- [17] B. Bahadur, J. Chem. Phys. 67 (1977) 3272.
- [18] F. Hardouin, M.F. Achard, S. Sigaud, H. Gasparoux, Mol. Cryst. Liq. Cryst. 39 (1977) 241.
- [19] G. Illian, H. Knepe, F. Schneider, Z. Naturforsch. 40A (1985) 46.
- [20] M. Harada, S. Ohno, J. Phys. Soc. Jpn. 54 (1985) 998.
- [21] P.I. Ktorides, D.L. Uhrich, Mol. Cryst. Liq. Cryst. 87 (1982) 69.
- [22] A.M. Giroud-Godquin, P.M. Maitlis, Angew. Chem., Int. Ed. Engl. 30 (1991) 375.
- [23] P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, E. Sola, Coord. Chem. Rev. 117 (1992) 215.
- [24] S.A. Hudson, P.M. Maitlis, Chem. Rev. 93 (1993) 861.
- [25] D.W. Bruce, J. Chem. Soc., Dalton Trans. (1993) 2983.
- [26] A.P. Polishchuk, T.V. Timofeeva, Russ. Chem. Rev. 62 (1993) 291.
- [27] J.L. Serrano (Ed.), Metallomesogens, Synthesis, Properties and Applications, VCH, Weinheim, 1996.
- [28] D.W. Bruce, in: D.W. Bruce, D. O'Hare (Eds.), Inorganic Materials, 2nd edn., Wiley, Chichester, 1996, p. 429, Chap. 8.
- [29] B. Donnio, D.W. Bruce, Struct. Bonding 95 (1999) 193.
- [30] S.R. Collinson, D.W. Bruce, in: J.P. Sauvage (Ed.), Transition Metals in Supramolecular Chemistry, Wiley, New York, 1999, p. 285, Chap. 7.
- [31] W. Haase, M.A. Athanassopoulou, SPIE 4147 (2000) 1.
- [32] E.A. Boudreaux, L.N. Mulay (Eds.), Theory and Applications of Molecular Paramagnetism, Wiley, New York, 1976.
- [33] K. Binnemans, Mater. Sci. Forum 315–317 (1999) 169.
- [34] Yu.G. Galyametdinov, G.I. Ivanova, I.V. Ovchinnikov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 40 (1991) 1109.
- [35] Yu.G. Galyametdinov, G.I. Ivanova, A.V. Prosvirin, O. Kadkin, Russ. Chem. Bull. 43 (1994) 938.
- [36] K. Binnemans, Yu.G. Galyametdinov, S.R. Collinson, D.W. Bruce, J. Mater. Chem. 8 (1998) 1551.

- [37] K. Binnemans, R. Van Deun, D.W. Bruce, Yu.G. Galyametdinov, *Chem. Phys. Lett.* 300 (1999) 509.
- [38] K. Binnemans, D.W. Bruce, S.R. Collinson, R. Van Deun, Yu.G. Galyametdinov, F. Martin, *Philos. Trans. R. Soc. London, Ser. A* 357 (1999) 3063.
- [39] R. Van Deun, K. Binnemans, *J. Alloys Compd.* 303–304 (2000) 146.
- [40] Yu.G. Galyametdinov, G.I. Ivanova, I.V. Ovchinnikov, K. Binnemans, D.W. Bruce, *Russ. Chem. Bull.* 48 (1999) 385.
- [41] F. Martin, S.R. Collinson, D.W. Bruce, *Liq. Cryst.* 27 (2000) 859.
- [42] K. Binnemans, Yu.G. Galyametdinov, R. Van Deun, D.W. Bruce, S.R. Collinson, A.P. Polishchuk, I. Bikchantaev, W. Haase, A.V. Prosvirin, L. Tinchurina, I. Litvinov, A. Gubajdullin, A. Rakhmatullin, K. Uytterhoeven, L. Van Meervelt, *J. Am. Chem. Soc.* 122 (2000) 4335.
- [43] Yu. Galyametdinov, M.A. Athanassopoulou, K. Griesar, O. Kharitonova, E.A. Soto Bustamante, L. Tinchurina, I. Ovchinnikov, W. Haase, *Chem. Mater.* 8 (1996) 922.
- [44] I.V. Ovchinnikov, Yu.G. Galyametdinov, A.V. Prosvirin, *Russ. Chem. Bull.* 44 (1995) 768.
- [45] Yu.G. Galyametdinov, M. Atanasopoulou, V. Haase, I.V. Ovchinnikov, *Russ. J. Coord. Chem.* 21 (1995) 718–719.
- [46] A.N. Turanov, I.V. Ovchinnikov, Yu.G. Galyametdinov, G.I. Ivanova, V.A. Goncharov, *Russ. Chem. Bull.* 48 (1999) 690.
- [47] V.S. Mironov, Yu.G. Galyametdinov, A. Ceulemans, K. Binnemans, *J. Chem. Phys.* 113 (2000) 10293.
- [48] S. Yamada, K. Yamanouchi, H. Kuma, *Bull. Chem. Soc. Jpn.* 44 (1971) 1448.
- [49] H. Kuma, S. Yamada, *Inorg. Chim. Acta* 15 (1975) 213.
- [50] N. Dutt, K. Nag, *Inorg. Nucl. Chem.* 30 (1968) 2493.
- [51] J.I. Bullock, H.A. Tajmir-Riahi, *J. Chem. Soc. Dalton Trans.* (1978) 36.
- [52] S. Afshar, J.I. Bullock, *Inorg. Chim. Acta* 38 (1980) 145.
- [53] L. Huang, C. Huang, G. Xu, *J. Struct. Chem.* 8 (1989) 1.
- [54] S. Mangani, A. Takeuchi, S. Yamada, P. Orioli, *Inorg. Chim. Acta* 155 (1989) 149.
- [55] L. Huang, G. Xu, *J. Struct. Chem.* 9 (1990) 100.
- [56] R.D. Archer, H. Chen, L.C. Thompson, *Inorg. Chem.* 37 (1998) 2089.
- [57] J.P. Costes, A. Dupuis, J.P. Laurent, *Inorg. Chim. Acta* 268 (1998) 125.
- [58] W. Xie, J. Heeg, P.G. Wang, *Inorg. Chem.* 38 (1999) 2541.
- [59] T. Moeller, *The Chemistry of the Lanthanides*. Chapman & Hall, London, 1965.
- [60] Z.S. Yu, M.B. Chen (Eds.), *Rare Earth Elements and Their Applications*, Metallurgical Industry Press, Beijing, 1995.
- [61] S. Cotton, *Lanthanides and Actinides*. Macmillan Education, Houndmills, 1991.
- [62] N. Kaltsoyannis, P. Scott, *The f Elements*. Oxford Univ. Press, Oxford, 1999.
- [63] K. Binnemans, L. Jongen, C. Görrler-Walrand, W. D’Olieslager, D. Hinz, G. Meyer, *Eur. J. Inorg. Chem.* (2000) 1429.
- [64] J.-C.G. Bünzli, N. André, M. Elhabiri, G. Muller, C. Piguet, *J. Alloys Compd.* 303–304 (2000) 66.
- [65] G. Vicentini, E. De Carvalho Filho, *J. Inorg. Nucl. Chem.* 28 (1966) 2987.
- [66] G. Vicentini, R. Najjar, *J. Inorg. Nucl. Chem.* 30 (1968) 2771.
- [67] G. Vicentini, L.B. Zinner, A.M.P. Felicissimo, K. Zinner, *J. Inorg. Nucl. Chem.* 41 (1979) 1661.
- [68] T.A. Malikova, M.G. Lutfullina, *Russ. J. Inorg. Chem.* 22 (1977) 1474.
- [69] C. Chieh, G.E. Toogood, T.D. Boyle, C.M. Burgess, *Acta Crystallogr., Sect. B* 32 (1976) 1008.
- [70] J. Barberá, X-ray studies of metallomesogens, in: J.L. Serrano (Ed.), *Metallomesogens, Synthesis, Properties and Applications*, VCH, Weinheim, 1996, pp. 336–338, Chap. 8.
- [71] E. Campillos, M. Marcos, J.L. Serrano, J. Barberá, P.J. Alonso, J.I. Martínez, *Chem. Mater.* 3 (1993) 1518.
- [72] M. Marcos, J.L. Serrano, *Adv. Mater.* 3 (1991) 256.
- [73] P.J. Alonso, M.L. Sanjuán, P. Romero, M. Marcos, J.L. Serrano, *J. Phys.: Condens. Matter.* 2 (1990) 9173.
- [74] I. Bikchantaev, Yu.G. Galyametdinov, A. Prosvirin, K. Griesar, E. Soto-Bustamante, W. Haase, *Liq. Cryst.* 18 (1995) 231.
- [75] J. Barberá, A.M. Levelut, M. Marcos, P. Romero, J.L. Serrano, *Liq. Cryst.* 10 (1991) 119.
- [76] P.J. Alonso, J.I. Martínez, *Liq. Cryst.* 21 (1996) 597.
- [77] R.S. Prosser, S.A. Hunt, J.A. DiNatale, R.R. Vold, *J. Am. Chem. Soc.* 118 (1996) 269.
- [78] R.S. Prosser, J.S. Hwang, R.R. Vold, *Biophys. J.* 74 (1998) 2405.
- [79] R.S. Prosser, V.B. Volkov, I.V. Shiyonovskaya, *Biophys. J.* 75 (1998) 2163.
- [80] R.S. Prosser, V.B. Volkov, I.V. Shiyonovskaya, *Biochem. Cell Biol.* 76 (1998) 443.
- [81] R.S. Prosser, H. Bryant, R.G. Bryant, R.R. Vold, *J. Magn. Reson.* 141 (1999) 256.
- [82] Yu.G. Galyametdinov, W. Haase, L. Malykhina, A. Prosvirin, I. Bikchantaev, A. Rakhmatullin, K. Binnemans, *Chem. Eur. J.* 7 (2001) 99.
- [83] P.A. Kumar, V.G.K.M. Pisipati, *Synth. React. Inorg. Met-Org. Chem.* 30 (2000) 1099.
- [84] J.H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford Univ. Press, Oxford, 1966.