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Preliminary communication

Formation of lanthanide ion networks by orientation of the mesophases of their complexes in magnetic fields

YURY G. GALYAMETDINOV†‡*, WEN WAN‡, LARISA MALYKHINA†,
MICHAEL DARIUS‡ and WOLFGANG HAASE‡

†Physical-Technical Institute, Russian Academy of Sciences, Sybirski Tract 10/7,
420029 Kazan, Russia
‡Institute of Physical Chemistry, Darmstadt University of Technology,
Petersenstrasse 20, D-64287 Darmstadt, Germany

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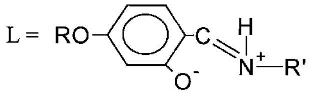
A complex of a Tm(III) perfluoroalkylsulsphate with salicylaldimine Schiff's base was synthesized and its liquid crystallinity characterized by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction. An additional phase transition was detected. 2D or 3D anisotropically-organized media were obtained by cooling of the lanthanide complex from different phases in an applied magnetic field. A huge positive magnetic anisotropy was observed for the resulting material.

In contrast to conventional diamagnetic liquid crystals (LCs), which can be oriented only in strong magnetic fields, paramagnetic metallomesogens can be oriented in rather weak magnetic fields as shown in [1]. At the present time lanthanide derivatives attract much attention as promising high luminescence dopants for organic light emitting diodes and amplifiers [2, 3]. In this connection, to have predetermined organized, uniformly oriented, defect-free layers with linearly polarized luminescence and lanthanide ions is also of interest. The above references awakened our interest in the magnetic field-induced alignment of lanthanide metallomesogens in different types of mesophase. The mesophases of perfluorinated lanthanide derivatives exhibit much more pronounced values of magnetic anisotropy [4], and most of the investigated compounds which demonstrate high magnetic anisotropy show negative signs ($\Delta\chi < 0$) and are oriented with their molecular long axes perpendicular to the external magnetic field. According to theoretical predictions the highest values of positive anisotropy in a lanthanide series should involve compounds of Tm^{3+} [5]. Here we describe the preparation, liquid crystallinity and orientational behaviour of an L_3TmX_3 complex of the Schiff's base ligand (L), 4-tetradecyloxy-*N*-octadecyl-2-hydroxybenzaldimine ($R = C_{14}H_{29}$; $R' = C_{18}H_{37}$ as shown in the structure below) with dodecafluoroheptyl sulphate as counter ion (X).



The ligand L and the lanthanide complex were obtained according to previously described procedures [1, 4]. The structure of the compound was confirmed by elemental analysis and effective magnetic moment measurements. It is found that the complex exhibits at 110°C a fan-shaped texture observed by optical microscopy and this is typical for an SmA mesophase. It is noteworthy that the substance obtained in the present work exhibits a more fluid SmA mesophase in comparison with that previously described for non-fluorinated lanthanide metallomesogens [1]. The DSC curve of the complex shows three endothermic peaks, at 92.5, 98.2 and 133.8°C. Although the sample does not become fluid between the first two transition points, microscopic investigation showed that the material behaves like a wax.

The phase transitions to the lanthanide complex were also characterized by X-ray diffraction (XRD) at elevated temperatures. The XRD patterns of the complex at different temperatures are shown in figure 1.

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*Author for correspondence; e-mail: yugals@rambler.ru

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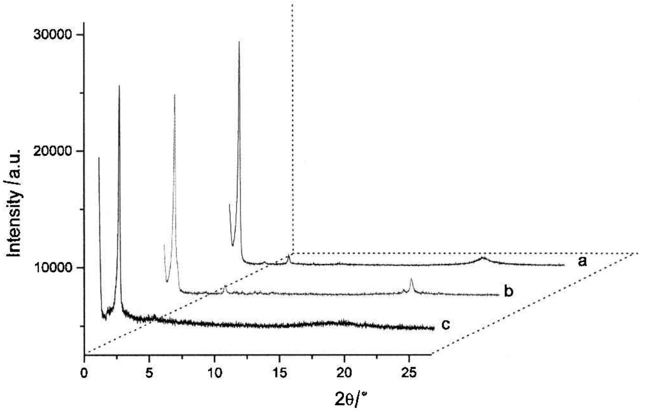


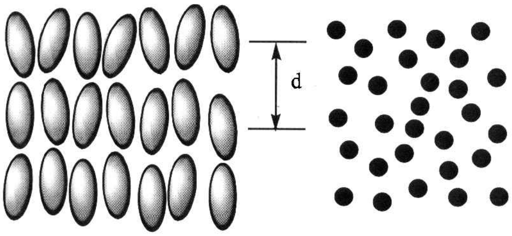
Figure 1. XRD patterns of the Tm^{3+} complex at different temperatures: (*a*) starting materials, $T = 25^{\circ}C$, $d = 46.1$ Å; (*b*) 'soft' crystal E, $T = 94^{\circ}C$, $d = 45.7$ Å; (*c*) SmA phase, $T = 112^{\circ}C$, $d = 33.5$ Å.

The appearance of two weak reflections at 4.5 and 4.4 Å in the wide angle region at $2\theta = 20^{\circ}$, figure 1 (*b*), indicates that a highly ordered phase is formed in the lower temperature region ($\sim 94^{\circ}C$). It is found that the thickness of the smectic layers d, obtained by application of Bragg's law to the small angle peak, is 45.7 Å. The lengths of the Schiff's base ligand L and of the complex were calculated by molecular modelling to be 45.4 and 49.0 Å, respectively. The differences between the calculated and experimental data at low temperatures can be explained in terms of the layers evolving by penetration of the alkyl chains of one layer into another. This kind of pattern indicates a three-dimensional (3D) crystal E phase, which can be considered as being a 'soft' crystal [6–8].

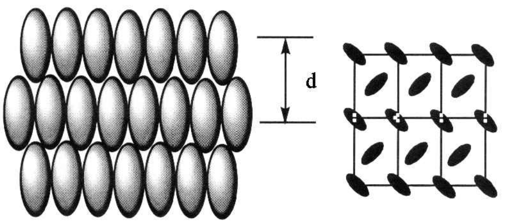
Further heating shows that these sharp peaks in the small angle region begin to shift. The shift of the interlayer peak from 45.7 to 33.5 Å, figure 1 (*c*), indicates a profound rearrangement of the phase structure by the inclination of the alkyl chains of the molecules by 20–30° due to the rotation and/or mutual penetration of the alkyl chains. Similar behaviour was observed for the nitrate derivatives of mesogenic lanthanide complexes [9]. Transition to the SmA phase ($\sim 112^{\circ}C$) is accompanied by a strong broadening of the peak at 4.5 Å which implies the complete disordering of the molecules inside the smectic layers. As shown by Stoebe *et al.* transition from a highly ordered mesophase to an SmA phase occurs as a continuous layer-by-layer conversion [10], and the transformation for the substance investigated probably takes place in an analogous way. Transition to the isotropic phase is accompanied by a sharp decrease in the intensity and a broadening of both peaks at 4.5 and 33 Å. After cooling again to 25°C, the peak for the interlayer distance of 45.7 Å is recovered in the spectrum. Therefore, after cooling, the compound does not crystallize and has a (CrE) short range ordered structure, figure 2 (*b*).

In order to investigate the orientational behaviour of the complex in different magnetic fields, we carried out temperature-dependent magnetic susceptibility measurements. The substance was initially heated to the isotropic phase and then cooled slowly to the smectic phase in applied magnetic fields of 1.2, 0.9, 0.6 and 0.3 T. Typical plots of temperature against the effective magnetic moment (μ_{eff}) of the mesogenic Tm^{3+} derivative are presented as curves in figure 3.

On cooling the sample from the isotropic to the smectic A phase, we observed a noticeable increase in μ_{eff}. This change is caused by the magnetic field-induced orientation of the mesophase such that the axis of maximal magnetic susceptibility is arranged parallel to the magnetic field direction. The second notable jump in the magnetic moment, which was not detected in previous experiments, take place in the temperature region of the transition from the 2D-organized SmA (as detected by the DSC and XRD measurements) to the highly 3D-ordered 'soft' crystal E orthogonal phase. On further cooling, the magnetic moment does not change its value even at room temperature. The resulting magnetically anisotropic sample kept its organization during several days until the next experiment, as can be

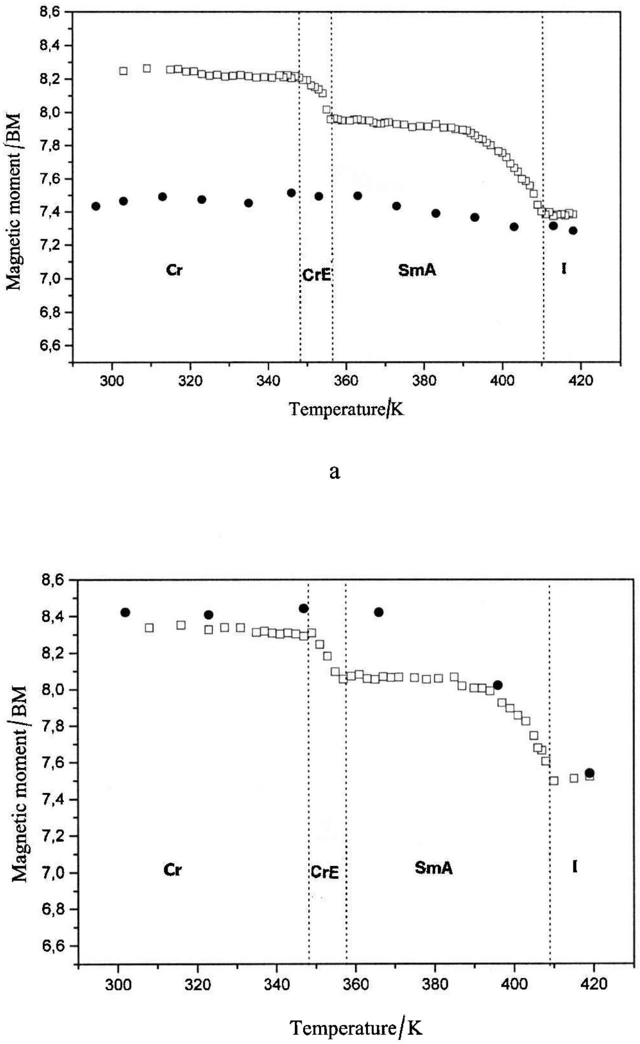


a) Smectic A phase



b) 'Soft' Crystal E phase

Figure 2. Molecular packing in: (*a*) smectic A, calc length 49.0 Å and $d = 33.5$ Å; (*b*) 'soft' crystal E, $d = 45.7$ Å.



a

Figure 3. Temperature dependent magnetic moments of the L_3TmX_3 complex in applied magnetic fields: (*a*) 1.2 T; (*b*) 0.6 T. ● Heating run, □ cooling run, Cr = crystal, CrE = 'soft' crystal E, SmA = smectic A, I = isotropic phases observed on cooling.

seen from figure 3(*a*, *b*). In subsequent experiments we observed the same reversible behaviour. These procedures have strengthened the stability of the oriented mesophase. To calculate the magnitude of the magnetic anisotropy of the resulting sample, $\Delta\chi_{min}$, we need to know the sign of $\Delta\chi$, but this cannot be determined by magnetic susceptibility measurements. It is possible to determine this by direct observation of XRD patterns in a magnetic field as described in [4]. As is apparent from the patterns for the thulium complex, it is oriented with the molecular long axis parallel to the magnetic field. Therefore, for the compound investigated we have a positive sign and in this case $\Delta\chi_{min} = 1.5\ (\chi_{or} - \chi_{iso})$, where χ_{or} is the maximum susceptibility parallel to the magnetic field and χ_{iso} is the isotropic susceptibility in the isotropic phase. The experimental $\chi_{or} - \chi_{iso}$ data and the estimated values of the magnetic anisotropy $\Delta\chi_{min}$ for the L_3TmX_3 compound in different strengths of magnetic field are $\chi_{min} = 7615 \times 10^{6}$ (**H** = 1.2 T) and $7106 \times 10^{6}\ cm^{3}\ mol^{-1}$ (**H** = 0.3 T).

Finally, due to the strong *positive* magnetic anisotropy of the Tm^{3+} ion, the complex can be aligned by an external magnetic field down to 0.3 T. Two jumps in the magnetic susceptibility curve are measured in the magnetic field due to the alignment of the materials. When the formation is carried out in presence of a magnetic field, it is possible to obtain anisotropic (magnetically and optically) materials with long range order. When application of the magnetic field during the cooling process is stopped in the SmA mesophase, it is possible to obtain 2D-organized material. Magnetically and optically 3D-organized materials will be the result of fast cooling of the mesogenic lanthanide from the oriented CrE phase.

Finally, temperatures and textures of phase transitions were determined using a polarizing optical microscope equipped with a hot stage and a computer-driven temperature controller giving an accuracy better than ± 0.05°C. Differential scanning calorimetry measurements were carried out using a Perkin Elmer DSC-2 (scan rate of 10 K min^{-1} under a nitrogen flow). The high temperature X-ray measurements where made with a STOE STADI 2 diffractometer and a linear position sensitive detector (STOE mini PSD). Monochromatic CuK_α radiation was obtained uing a curved germanium detector (1 1 1 plane).

The thulium complex L_3TmX_3 was prepared by adding thulium tris[1H,1H-dodecafluoroheptyl] sulphate (0.069 g, 0.01 mmol) to an ethanol solution of the ligand L (0.11 g, 0.03 mmol) at 40°C. The precipitate was filtered off and dried *in vacuo*. The yield was 0.09 g (80%) of a yellow powder. Elemental analysis for $C_{144}H_{231}F_{39}N_3S_3O_{18}Tm$ (3298.5): calc. C 52.44, H 7.06, N 1.27; found C 52.61, H 7.26, N 1.33%.

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