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## Liquid Crystals

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# On the reported mesomorphism of lanthanide complexes containing the hemicyanine structural unit

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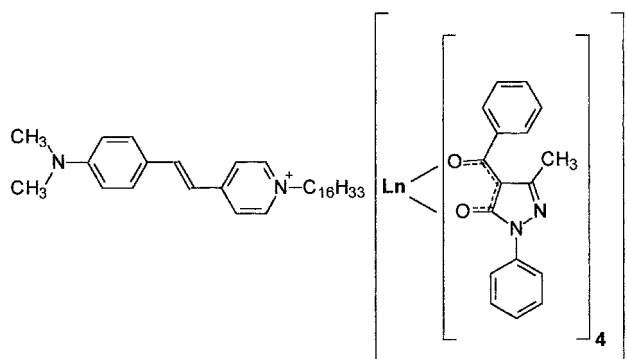
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Close examination of the thermal behaviour of the (*E*)-*N*-hexadecyl-4-*N,N'*-dimethylamino-stilbazolium tetrakis(1-phenyl-3-methyl-4-benzoyl-5-pyrazolonato)lanthanide(III) complexes has revealed that these compounds are not mesomorphic, in contradiction to an earlier report in the literature (K. Z. Wang *et al.*, 1995, *Solid State Commun.* **95**, 223). By replacing the bromide of the hemicyanine precursor (see the scheme) by a tetrakis( $\beta$ -diketonato)lanthanide(III) anion, new complexes were synthesized, but none shows a mesophase. Reasons for the absence of mesomorphism are discussed. Transition temperatures for the mesomorphic hemicyanine bromides are reported.

## 1. Introduction

Liquid crystalline metal complexes (metallomesogens) offer the opportunity to combine the properties of classic organic liquid crystals with properties due to the presence of a metal centre [1, 2]. Because of their interesting optical and magnetic properties, the trivalent lanthanide ions are intriguing candidates for the core of metal-containing liquid crystals. However, to date rather few examples of lanthanide-containing metallomesogens have been described in the literature. The first mesomorphic lanthanide compounds were the columnar bis-(phthalocyaninato)lutetium(III) complexes, described by Piechocki *et al.* [3]. These compounds exhibit columnar mesophases. Later, Galyametdinov and co-workers described calamitic lanthanide complexes with Schiff's bases [4, 5] and  $\beta$ -enaminoketones [6] as the ligands; these showed a smectic A mesophase. In 1995, Wang *et al.* [7] reported the mesomorphic properties of lanthanide complexes—(*E*)-*N*-hexadecyl-4-*N,N'*-dimethylamino-stilbazolium tetrakis(1-phenyl-3-methyl-4-benzoyl-5-pyrazolonato)lanthanides(III) (where the lanthanide was La, Nd, Dy and Yb):



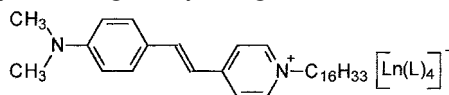
Ln(III) complexes 3–7 (see table).

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 with a focal-conic texture, melting at 96.3°C and clearing at 246.3°C. The lanthanide complexes except that of La(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

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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.

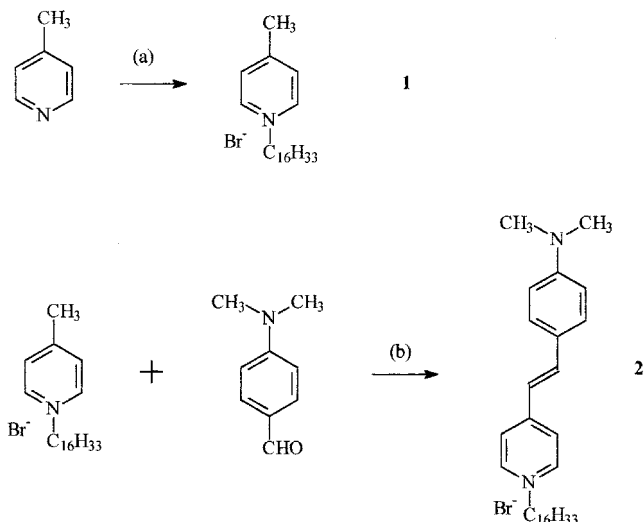
Inspired by the work of Wang *et al.* [7] we wanted to develop new lanthanide-containing metallomesogens. The idea was simply to replace the bromide ion in the stilbazolium bromide by a negatively charged tetrakis-( $\beta$ -diketonato)lanthanide(III) complex to give materials of the general structure shown below. Since the nature of the  $\beta$ -diketone and the terminal alkyl groups of the stilbazole can be varied, this approach seemed very promising for fine-tuning the mesomorphic properties of the lanthanide complexes. This could open the door for replacement of the tetrakis( $\beta$ -diketonato)lanthanide(III) anion by other negatively charged lanthanide complexes.



General structure of the Ln(III) complexes 3–9 (see table).

## 2. Experimental

We first began to repeat the work of Wang *et al.* [7]. *N*-Hexadecyl-4-methylpyridinium bromide **1** (see the scheme) was synthesized by heating 4-picoline and 1-bromohexadecane in ethanol at reflux. Compound **1** was transformed to the stilbazolium bromide **2** by heating with 4-dimethylamino benzaldehyde in ethanol under reflux with piperidine as the catalyst (see the scheme). The lanthanide complexes 3–9 were prepared by mixing the stilbazolium bromide **2**, the appropriate



Scheme. Synthesis of compounds **1** and **2**. Experimental conditions: (a)  $C_{16}H_{33}Br$  (1 equiv.), ethanol, reflux 24 h; (b) piperidine (catalyst), ethanol, reflux 4 h.

$\beta$ -diketone and the lanthanide salt (nitrate or chloride) in the molar ratio 1:4:1, in ethanol and in the presence of 4 equivalents of NaOH.

All the ligands and complexes gave satisfactory analytical data. Although our DSC curves show the same transitions as those described by Wang *et al.* [7], observation of the samples by polarized optical microscopy leads to other conclusions. For the stilbazolium bromide **2**, the DSC spectrum shows in the first heating cycle (25–300°C) three endothermic peaks at 99, 249 and 268°C. After the second peak, a distinct increase in the baseline is observed. The peak at 99°C, does not correspond to the melting peak as indicated by Wang *et al.* [7], but to a crystal–crystal transition. The peak at 249°C is the melting peak and clearing is observed at 268°C. Close to the clearing point, decomposition started and the decomposition is very pronounced thereafter (evident from the formation of gas bubbles in the melt). The mesophase exhibited a focal-conic texture. Due to the presence of both homeotropic and homogeneous regions in the texture between untreated glass slides, the mesophase has been identified as smectic A. The phase behaviour of compound **2** (with a  $C_{16}$  chain) can be summarised as:  $Cr_1 \cdot 99 \cdot Cr_2 \cdot 249 \cdot SmA \cdot 268 \cdot I$  (decomp.) (°C). It should be noted that the enthalpy change of the crystal–crystal transition is nearly as large as the melting enthalpy. The transition temperatures for the corresponding  $C_{14}$  and  $C_{18}$  ligands are  $Cr_1 \cdot 99 \cdot Cr_2 \cdot 251 \cdot SmA \cdot 265 \cdot I$  (decomp.) (°C) for the  $C_{14}$ , and  $Cr_1 \cdot 100 \cdot Cr_2 \cdot 255 \cdot SmA \cdot 271 \cdot I$  (decomp.) (°C) for the  $C_{18}$  stilbazolium bromide.

Complexes of the type studied by Wang *et al.* [7] using 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one as the  $\beta$ -diketone (BMPP) were prepared from all members of the lanthanide series (except Pm). None was mesomorphic as described below and as illustrated by the five examples (complexes 3–7) in the table, dealing with complexes 3–9.

For the complexes 3–9, the DSC curve generally shows several endothermic peaks, with the peak at the highest temperature being the largest. Polarizing optical microscopy reveals that this large peak corresponds to the melting point. The compounds clear to the isotropic state directly without showing a mesophase. When cooling the isotropic liquid at a moderate speed (5–20°C min<sup>-1</sup>), a mosaic texture is formed which could give the impression of the presence of a highly ordered smectic phase. On rotating the two crossed polarizers together, different parts of the mosaic texture are extinguished. However, closer inspection of the texture reveals that in fact a solid phase has been formed instead of a mesophase. Thus pressing with a needle on the cover glass, resulted in cracks in the texture, and not deformation as would be expected in the case of a

Table. Thermal behaviour of examples of the lanthanide(III) complexes investigated.

Compound	L <sup>a</sup>	Ln	Transition temperatures in °C (and $\Delta H$ in kJ mol <sup>-1</sup> )
3	BMPP	Pr	Cr <sub>1</sub> • 58 (6.2) • Cr <sub>2</sub> • 92 (-9.2) • Cr <sub>3</sub> • 149 (11.2) • I
4	BMPP	Sm	Cr <sub>1</sub> • 75 (-3.1) • Cr <sub>2</sub> • 90 (-0.7) • Cr <sub>3</sub> • 159 (11.9) • I
5	BMPP	Gd	Cr <sub>1</sub> • 65 (4.0) • Cr <sub>2</sub> • 162 (13.23) • I
6	BMPP	Dy	Cr <sub>1</sub> • 80 (1.0) • Cr <sub>2</sub> • 167 (13.30) • I
7	BMPP	Ho	Cr <sub>1</sub> • 74 (8.6) • Cr <sub>2</sub> • 159 (12.2) • I
8	DBM	Gd	Cr <sub>1</sub> • 112 (23.4) • Cr <sub>2</sub> • 206 (51.9) • I
9	acac	Eu	Cr <sub>1</sub> • 98 (19.7) • Cr <sub>2</sub> • 226 (52.4) • I (decomp.)

<sup>a</sup> Abbreviations: BMPP 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one; DBM dibenzoylmethane (1,3-diphenyl-1,3-propanedione); acac acetylacetonone (2,4-pentanedione).

mesophase. Cooling from the isotropic liquid at a low rate (1°C min<sup>-1</sup>) allowed the formation of larger crystals in the melt and often a solidification front was observed, starting at one place in the melt and gradually spreading out over the whole field view. High cooling speeds resulted in the formation of a large number of tiny crystallites.

The observations by optical microscopy were supported by high temperature X-ray diffraction—for the Gd(III) complex **5** and the Dy(III) complex **6**. At room temperature, the diffractogram is typically that of an amorphous or highly disordered crystalline solid (Cr<sub>1</sub>). At the first endothermic peak for **6** around 80°C, crystallization to a more ordered crystalline phase (Cr<sub>2</sub>) occurred. Around 160°C, the crystalline phase melted directly to an isotropic liquid. When cooling the isotropic liquid, no mesophase was formed, but rather a crystalline phase with a structure different from that present before melting.

Also when 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone was replaced by different  $\beta$ -diketones, e.g. acetylacetonone, dibenzoylmethane, the resulting lanthanide salt of the stilbazolium cation (complexes **8** and **9**) did not exhibit any mesophase. Under the microscope, the compounds melted directly to an isotropic liquid, without passing through a mesophase. Cooling of the isotropic liquid resulted simply in crystallization. The thermal behaviour of the different lanthanide(III) complexes are summarized in the table.

### 3. Discussion

Ionic mesogens show a strong tendency to form smectic mesophases, because of the electrostatic attractive forces. Therefore, the formation of a smectic A mesophase by the hemicyanine bromide **2** is explainable. However, the lanthanide-containing anions are probably too bulky to maintain the necessary organization of the cationic hemicyanine moieties in layers and with their long axis parallel to each other. Because of the absence of the necessary conditions for molecular organization, no mesophase can be formed. Even with small  $\beta$ -diketones,

e.g. acetylacetonone (acac) and dibenzoylmethane (DBM), the anionic tetrakis  $\beta$ -diketonate complexes are too voluminous to result in mesomorphism. Some complexes with acetylacetonone decomposed before melting. Therefore, it is not possible to obtain mesogens with anionic macromolecular lanthanide complexes as the counter-ion for mesogenic hemicyanine cations.

In conclusion, the claim of Wang *et al.* [7] to have obtained liquid crystalline lanthanide complexes containing hemicyanine should be discarded. The complexes do not show any mesophase. The approach of designing metallomesogens by substituting the bromide ion in (*E*)-*N*-hexadecyl-4-*N*',*N*'-dimethylaminostilbazolium bromide by negatively charged coordination complexes is not successful. At present, the only remaining mesomorphic lanthanide complexes are those with Schiff's base and  $\beta$ -enaminoketone ligands and the substituted bis(phthalocyaninato)lutetium(III) compounds. In the course of this work, the transition temperatures and mesophase behaviour of three mesomorphic hemicyanine bromides have been determined.

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