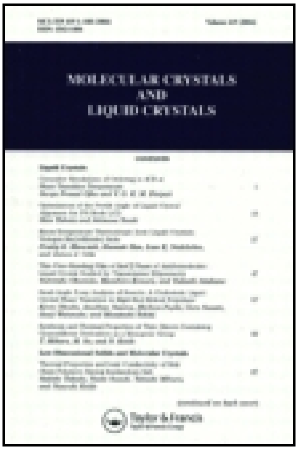

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Optically Active Homogeneous Mixtures of Cholesteric Liquid Crystals and a New Coordination Compound: Eu(Thenoyltrifluoroacetonate)$_3$.(Cholesteryl Tetradecanoate or Nonanoate)

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Optically Active Homogeneous Mixtures of Cholesteric Liquid Crystals and a New Coordination Compound: Eu(Thenoyltrifluoroacetonate)$_3$. (Cholesteryl Tetradecanoate or Nonanoate)

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The reactions of cholesteryl pelargonate (**P**) or myristate (**M**) with Eu(thenoyltrifluoroacetonate)$_3$.3H_2O (**EuTTA$_3$**) at room temperature give the corresponding complexes Eu(thenoyltrifluoroacetonate)$_3$. (Cholesteryl pelargonate), n H_2O (**1**) and Eu(thenoyltrifluoroacetonate)$_3$. (Cholesteryl myristate), n H_2O (**2**) respectively. When adding these two fluorescent complexes to liquid crystal compounds, optically active and aggregate free mixtures are obtained, containing up to 2.5 molar percent of dopant without loosing the mesogenic properties. The different phases exhibited by these mixtures have been identified. The luminescence properties of these Eu^{3+}complexes in cholesteric phases have been investigated.

Keywords: Cholesteric liquid crystal; rare earth complex; fluorescence

INTRODUCTION

Some works have already been done on the use of cholesteric liquid crystal (CLC) as components in optical devices such as laser end mirrors[1-3], polarizers, isolators and filters [4]. In most of these applications they play the part of passive constituents. When mixed with dopants, in most cases organic dyes, they can also behave as active elements [5]. This particular kind of active optical mediums can also be realized on the basis of a rare earth-CLC mixture. As it is well known, due to the peculiar compactness of the 4f orbital, rare earth complexes exhibit fluorescence characteristics very similar to those of the free ions [6]. Dispersed as dopants in a host medium, these rare earth ions support the high energy rate of a laser with no damage, even being not especially cooled down. However, if one mixes the $EuTTA_3$ within the liquid crystal host using mechanical stirring procedures we are left with aggregates of lanthanide salt. In order to overcome this difficulty, we report here the synthesis of some complexes, dubbed **1** and **2** in the following, which can be homogeneously added to a CLC mixture. These new materials exhibit a coordination bond between the ester ligand and the europium atom. This has been checked by NMR, IR and visible spectroscopy as reported below. In addition, the different phases presented by the mixtures of these complexes with CLC have been identified. Finally, we report also the study of the fluorescence properties of these new Eu^{3+} complexes.

EXPERIMENTAL

FT-IR spectra have been recorded at room temperature with a Bruker model IFS55 spectrometer in the 4000-400cm^{-1} spectral range, using the KBr pellets technique. NMR spectra have been recorded in benzene-d_6 on a Bruker AC300 spectrometer at ambient probe temperature and referenced to $Si(CH_3)_4$ (^1H, δ 0.00), Benzene-d_6 (^{13}C, 128 ppm). The transition phases have been observed using an Olympus model BH2 polarizing microscope equipped with a Mettler model FP90 heating stage. The doped liquid crystal is introduced by capillarity in a wedge formed by two microscope slides preliminarly cleaned with methanol and rubbed with diamond paste (0.25µm grain size). The fluorescence has been excited using the 488nm line of an Ar^+ Coherent Radiation Innova 300 CW laser. The corresponding spectra have been recorded using a SOPRA model F1500 spectrometer equiped with a 600 groves mm^{-1} grating, a Hamamatsu R928 photomultiplier and a Stanford Research model SR830 Lock-in amplifier.

RESULTS AND DISCUSSION

Synthesis and characterization of cholesteryl alkanoate complexes.

Complex **1** (Fig.1) was prepared as follow : a 100 mL round-bottom flask was charged with **P** (0.418g, 7 10^{-4} mol) (Aldrich), **EuTTA₃**[7] (0.608g, 7 10^{-4} mol) and 120 mL toluene (Fig.1). The reaction mixture was stirred at room temperature. Over the course of 4 days, the ligand slowly coordinates to the metal. The solvent was then removed from the solution by rotary evaporation. An orange-yellow solid was obtained and dried *in vacuo* leading to complex **1**.

M (0.418g, 7 10^{-4} mol) and **EuTTA₃** (0.608g, 7 10^{-4} mol) were combined in a procedure analogous to that given for **1**. An identical workup gave complex **2** as an orange-yellow.

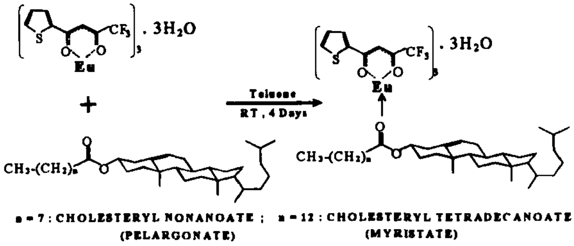
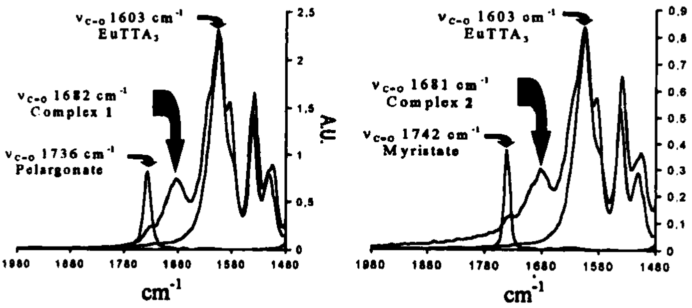


FIGURE 1 Synthesis of complexes **1** (n = 7) and **2** (n = 12).

The IR spectroscopy allowed the formal identification of the coordination bond between the carbonyl group of the ester and the metal. Actually, the displacements of the C=O stretching from 1736 cm^{-1} in the free ester ligand to 1682cm^{-1} in the complex **1** and from 1742 cm^{-1} in the free ester ligand to 1681cm^{-1} in the complex **2** provide a good evidence that the metal ion is coordinated through the oxygens (Fig.2).



2a 2b

FIGURE 2 IR spectra of complexes **1** (2a) and **2** (2b).

However, a small quantity of free ligand is observed, suggesting that a partial dissociation of the ester ligand can not *a priori* be excluded. Actually, although experiments have shown that the complex do not undergo ligand dissociation over extended period, increase of the concentration of complexes **1** and **2** in toluene yields to the precipitation of **EuTTA$_3$**, suggesting a weak coordination bond between the alkanoate and the metal.

In order to get further evidence that only one ester ligand is coordinated to the europium atom, a synthesis has been performed with two equiv. of **P** or **M** and one equiv. of **EuTTA$_3$**. After work up, the IR spectrum showed two $\nu_{C=O}$ stretching at 1736cm^{-1} (free **P**) or at 1742cm^{-1} (free **M**) and 1682cm^{-1} or 1681cm^{-1} (coordinated ligand) respectively in a 1:1 ratio, suggesting that only one **P** or **M** ligand coordinated to the metal. Actually, complex **1** was subject to important steric structural perturbations. Accordingly, two ligands could not be coordinated, though 8 to 10 coordination sites were available on the europium ion.

Another synthesis was carried out with 10 equiv. of cholesteryl alkanoate and 1 equiv. of **EuTTA$_3$** and showed that the coordination to the metal occured rapidly (< 2h) proving, as expected, that the coordination speed depends on the alkanoate concentration.

The NMR spectroscopy further supports the conclusions of the IR spectra.

The C=O and CF_3 ^{13}C NMR resonances of complexes **1** and **2** were assigned by analogy to shielding trends exhibited by free ligand and **$EuTTA_3$** (Table 1). Two of the three C=O resonances (162/145 ppm) and one of the two CF_3 resonances (92 ppm) were slightly downfield of those of the free ligand ($\delta_{C=O}$ 173 ppm) and **$EuTTA_3$** ($\delta_{C=O}$ 167 ppm, δ_{CF_3} 98 ppm), whereas the opposite shielding trend was observed for the second CF_3 resonance (102 ppm). This indicates that the metal exerts a shielding effect upon the C=O and various effects upon the CF_3, suggesting two types of CF_3 groups. One or several TTA ligand could probably coordinate to the metal through only one oxygen atom.

$^{13}C\{^1H\}$ NMR (ppm. C_6D_6)	C = O ester	C = O TTA	C_5	$C_{arom.}$	C_6	CF_3	C_3	$C_{cholesteryl}$	C_{-H} TTA
complex **1** (n = 7)	173	163 146	141	135 ; 129 ; 126 ; 124	123	103 92	84	58 - 11	52 49
complex **2** (n = 12)	175	165 149	141	136 ; 129 ; 125 ; 123	122	92	86	58 - 11	52 49

TABLE 1 ^{13}C $\{^1H\}$ NMR results of complexes **1** (n = 7) and **2** (n = 12).

The ^1H resonance patterns were considerably more complex. Actually, the paramagnetism of the metal broaden signals. Numerous modifications of the spectra of complexes **1** and **2** compared with those of the reagents confirm the coordination of the esters to the metal (Table 2).

^1H NMR (ppm. C_6D_6)	H_{TTA}	- C = C<u>H</u>	- O - C<u>H</u>	- CH_2 - CO -	$H_{cholesteryl}$
complex **1**(n = 7)	4.5 ; 5.6 ; 6.9 ; 7.2 ; 7.5 ; 7.7 ; 11.7	5.4	5.2	3.6	0.4 - 2.2
complex **2**(n = 12)	5.4 ; 5.9 ; 6.5 ; 7.5 ; 7.8 ; 8.0 ; 11.8	5.3	5.1	4.0	0.3 - 2.3

TABLE 2 ^1H NMR results of complexes **1** (n = 7) and **2** (n = 12).

Because of the weakness of the coordination bond, we have up to now been unable to obtain a pure sample of these complexes. All attempts to crystallize the product were unsuccessful. Currently, additional types of analysis based on ligand field theory are underway to further define the exact structure of complexes **1** and **2**. However, we provisionally conclude that the general formula of these complexes is $EuTTA_3$. Cholesteryl alkanoate, n H_2O.

Realization of a doped cholesteric liquid crystal mixture.

To prevent any crystallization at room temperature and to obtain a cholesteric phase with a selective reflection band located in the visible region, **P** was blended with an empirically determined amount of **M**, in the respective molar proportions of 77 and 23%. Both compounds are left-handed cholesteryl esters. The used nematic medium (**N**) was the ternary mixture ZLI 1083 by Merck. Depending on the added amount of **N**, the left-handed chiral **PMN** mixture exhibits a pitch ranging from 0.5 to 40 µm.

Finally, complexes **1** and **2** were added in a variable molar ratio to a **PMN** mixture. The center of the reflection band (SRB) of the resulting CLC depends on the dopant concentration (Table 3).

dopant * (molar percent)	cholesteryl pelargonate (**P**) (molar percent)	cholesteryl myristate (**M**) (molar percent)	nematic ZLI 1083 (**N**) (molar percent)	λ_{BRAGG} (nm)	label
0	24.6	7.2	68.2	638	**PMN**
0.2	24.4	7.2	68.2	662	**Eu$_{0.2}$PMN**
1	23.5	6.9	68.6	693	**Eu$_1$PMN**
2	22.4	6.6	69	795	**Eu$_2$PMN**
2.5	27.8	8.1	61.6	615	**Eu$_{2.5}$PMN**

TABLE 3 Bragg wavelength for different **EuPMN** mixtures.

* the dopant is a mixture of complex **1** / complex **2** ratio of 2/3.

A rudimentary study of the different phases exhibited by **EuPMN** reveals a cholesteric texture (Photo 1) from room temperature to 50°C approximately. The transition from the cholesteric to the isotropic phase looks complex (possibly via an other phase) but this is beyond the scope of this paper.

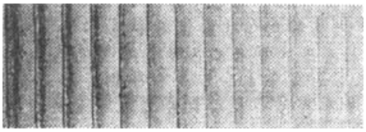
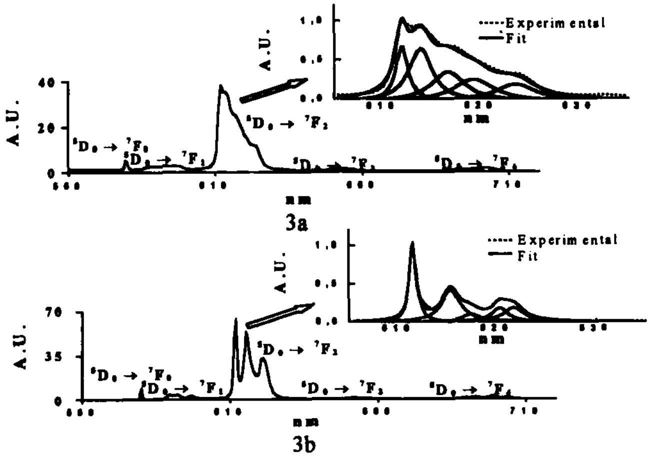


PHOTO 1 Defects lines Grandjean-Cano for **Eu$_{2.5}$PMN** (T = 23°C).

Laser stimulated fluorescence experiments have shown that the new obtained coordination complexes exhibit the expected strong fluorescence emission of the Eu^{3+} rare earth ion around 611 nm (Fig.3a). The high resolution spectra have evidenced a shift of the stark components of each observed transition when compared with those of **$EuTTA_3$** (Fig.3b).

This shift can be ascribed to a local electric field modification in the near environment of the Eu^{3+} ion. This perturbation corroborates the existence of a bond between **$EuTTA_3$** and the added cholesteric molecules.



3a

3b

FIGURE 3 Fluorescence spectra of complex **1** (3a) and **$EuTTA_3$** (3b).

Complexes **1** and **2** are not mesogenic, which is not surprising accordingly to their structure. However, when mixing these complexes (up to 2.5 molar percent) with **P**, **M** and **N**, the liquid crystalline state is restored with no aggregates as opposed to the materials obtained by mechanical mixing. Moreover, the main feature of this system lies in the nature of the ester ligands coordinated to the metal, which are either the pelagargonate (**P**) or the myristate (**M**). In other words, when added in a **PMN** cholesteric mixture, the complexes will unlikely suffer from being decoordinated or will experience ligand exchange **P/M**, being sunk in an almost saturated solution. Actually, the existence of the complexes in solution in **EuPMN** allows to avoid migration of dopant to the surface of the mixture.

CONCLUSION

We have evidenced the formation of the coordination complexes **(EuTTA$_3$).(P)** or **(M)** that form room temperature optically active cholesteric mediums when mixed with appropriate cholesteric liquid crystals. These complexes are designed to be the basic elements of a new generation of optically active devices.

Acknowledgments

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