Synthesis and mesogenic properties of azomethine complexes of lanthanides with alkyl sulfate anions

Yu. G. Galyametdinov,[a]* **G. I. Ivanova,**[a] **I. V. Ovchinnikov,**[a] **K. Binnemans,**[b] **and D. V. Bruce**[c]

[a]E. K. Zavoisky Kazan' Physico-Technical Institute, Russian Academy of Sciences,
10/7 ul. Sibirskii Trakt, 420029 Kazan', Russian Federation.
Fax: +7 (483 2) 76 5075. E-mail: galyametdinov@kcn.sci.ru
[b]Department of Chemistry, Coordination Chemistry Division,
Celestjnenlaan 200F, B-3001 Heverlee (Leuven), Belgium
[c]Department of Chemistry, University of Exeter,
Stocker Road, Exeter EX4 4QD, England

Liquid-crystalline cationic complexes of lanthanides with azomethines containing the alkyl sulfate anion as the counterion were synthesized. The temperatures of existence of the mesophase of the complexes with the alkyl sulfate anion were by 80—100 °C lower than those of similar complexes with the Cl^- and NO_3^- counterions.

Key words: lanthanides, complexes with azomethines, synthesis, mesogenic properties.

The majority of works on liquid-crystalline metal complexes are devoted to their synthesis.[1—3] High temperatures (often higher than 200 °C) of existence of their mesophases, resulting in the decomposition of the compounds in the mesophase or on going to the isotropic liquid, is a substantial disadvantage of thermotropic metallomesogens. The problem of decreasing temperatures of phase transitions is especially urgent for liquid-crystalline complexes of lanthanides with azomethines $[L(LH)_2Ln]X_2$,[3] possessing a high anisotropy of magnetic susceptibility.[4,5] The study of these compounds has shown[4,6] that their temperatures of phase transitions decrease by 30—40 °C when the Cl^- counterion is replaced by the NO_3^- anion; however, they remain sufficiently high.

In this work, we describe the synthesis of lanthanide complexes containing the alkyl sulfate group $RO—SO_3^-$ as the counterion and possessing substantially lower temperatures of phase transitions, and their mesogenic properties were studied.

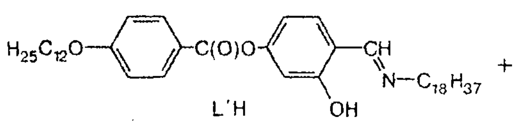
The complexes were obtained by the reaction of sodium alkyl sulfate with $LnCl_3$ followed by the interaction of equimolar amounts of the corresponding ligand with lanthanide alkyl sulfate in ethanol (scheme 1) (H_2SO_4 formed during the reaction is not indicated). The precipitate formed was washed from admixtures with ethanol and dried *in vacuo*. The structures of the ligand and the diamagnetic La^{III} complex were confirmed by the ^1H NMR spectroscopic data, and the compositions of other complexes were established by elemental analysis.

When we attempted to obtain coordination compounds of lanthanide alkyl sulfates with β-aminovinyl ketones, we could not isolate the expected products, although the mesogenic complexes of β-aminovinyl ketones based on rare-earth elements have been synthesized successfully.[7]

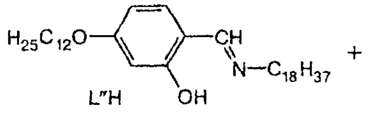
Scheme 1

$$LnCl_3 + 3\ R—OSO_3Na \longrightarrow Ln(R—OSO_3)_3 + 3\ NaCl,$$

where Ln = La, Tb, Dy, Gd; R = $C_{12}H_{25}$, Pr^i



$$+ Ln(R—SO_4)_3 \longrightarrow [LnL'(L'H)_2](SO_4—R)_2$$



$$+ Ln(R—SO_4)_3 \longrightarrow [LnL''(L''H)_2](SO_4—R)_2$$

The liquid-crystalline properties of the compounds obtained were studied by polarization microscopy and differential scanning calorimetry.

As can be seen from the data presented in Table 1, the compounds of different lanthanides possess similar liquid-crystalline properties: they have close temperatures of phase transitions, the fan-like texture is observed in polarized light, and all compounds studied exhibit smectic A mesomorphism.

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Table 1. Elemental analysis data and temperatures of phase transitions in the $L(LH)_2M(C_{12}H_{25}—OSO_3)_2$ lanthanide complexes

M	L	Found/Calculated (%)		Temperatures of phase transitions/°C*		
		C	H	$C \to S_A$	$S_A \to I$	ΔT
La	L′	71.00 71.04	9.88 9.94	113	132	19
La	L″	71.25 71.39	11.00 11.32	78	92	14
Tb	L′	70.55 70.50	9.81 9.87	106	126	20
Tb	L″	70.32 70.58	10.70 10.89	71	86	15
Dy	L′	70.12 70.40	9.80 9.85	102	124	22
Dy	L″	70.25 70.47	10.81 10.87	61	90	29
Gd	L′	70.06 70.56	9.75 9.88	106	113	7
Gd	L″	70.41 70.65	10.85 10.90	61	110	49

* C is the crystalline, S_A is the smectic *A*, and I is the isotropic phase.

On going from the complexes with 4-(*n*-alkyloxy-4′-benzoyloxy)-2-hydroxybenzaldehyde (L′) to the compounds containing 4-*n*-alkyloxy-2-hydroxybenzaldehyde (L″) as the ligand, the temperatures of both phase transitions decrease by 35—40 °C.

Comparison of the results obtained with the published data[4—6] makes it possible to estimate the effect of the X^- counterion on the character of phase transitions in the compounds studied (Table 2).

A sharp decrease in the temperatures of phase transitions of the complexes with the long-chain alkyl sulfate structure is an especially significant result of this work. As shown previously,[5] when the Cl^- counterion is replaced by NO_3^- in the lanthanide complexes with Schiff bases of the L″ type, the temperatures of phase transitions decrease by ~40 °C. Our data show that the use of the dodecyloxysulfate counterion $C_{12}H_{25}—OSO_3$ (see Table 2) results in a sharp decrease in the temperatures of existence of the mesophase. In this case, the temperature of the isotropic transition decreased more sharply (by 100 °C), whereas the temperature of the crystal — smectic transition decreased by 66 °C. As a result, the interval of existence of the mesophase (ΔT) decreased by 34 °C. Perhaps, this is due to a stronger intermolecular interaction of the complexes with the chloride ion in the mesophase as compared to that with the alkyl sulfate group. The mobility of alkyl chains in the sulfate group increases on heating; they "loosen" the liquid-crystalline system, which is more rapidly disordered. The degree of temperature decrease depends on the length of the alkyl fragment in the sulfate counterion (see Table 2, Pr^i—OSO_3 and $C_{12}H_{25}—OSO_3$).

Table 2. Effect of the X^- counterion on temperatures of phase transitions in the $L''(L''H)_2TbX_2$ complexes

X^-	Temperatures of phase transitions/°C		
	$C \to S_A$	$S_A \to I$	ΔT
Cl	137	186	49*
NO_3	96	148	52*
$Pr^i—OSO_3$	102	138	36
$C_{12}H_{25}—OSO_3$	71	86	15

* By the data in Ref. 4.

The enthalpies of melting ($\Delta H_{C \to S}$ = 75.2 kJ mol^{-1}) and isotropic transition ($\Delta H_{S \to I}$ = 5.9 kJ mol^{-1}) for the Tb^{III} complex (see Table 1, TbL′) were calculated from the data of differential scanning calorimetry.

Thus, the introduction of long-chain alkyl-containing counterions makes it possible to considerably decrease the temperature of existence of the mesophase in the liquid-crystalline lanthanide complexes.

Experimental

Temperatures and types of phase transitions were determined on a polarization microscope with an automated temperature unit. The accuracy of temperature determination was ±0.1 °C. ^1H NMR spectra were recorded on a Varian-300 instrument (300 MHz).

The synthesis of the ligands has been described previously.[4,5] The lanthanide complexes were obtained under conditions analogous for all ions.

Sodium isopropyl sulfate. Pr^iOH (3.5 mL, 45 mmol) was added to concentrated H_2SO_4 (3.5 mL, 65 mmol) at room temperature with stirring. The mixture was stored at 50 °C for 5 min and poured into 50 mL of ice-cold water. The solution obtained was neutralized by powdered $BaCO_3$ to pH 7. The $BaSO_4$ precipitated was filtered off, and the filtrate was concentrated. Dried barium isopropyl sulfate (4.5 g, 10^{-2} mol) was dissolved in water and added to a solution of $Na_2CO_3 \cdot 10\ H_2O$ (5.72 g, 20 mmol). The $BaCO_3$ precipitated was filtered off. The solution was concentrated, and the sodium isopropyl sulfate was dried above P_2O_5.

Tb^{III} isopropyl sulfate. Equimolar amounts of alcohol solutions of $TbCl_3$ (0.17 g, 0.64 mmol) and sodium isopropyl sulfate (0.31 g, 1.9 mmol) were mixed at room temperature. The NaCl that precipitated was filtered off, the filtrate was concentrated to dryness, and the residue was dried *in vacuo* above P_2O_5 to obtain the product in 92% yield (3 g). Found (%): C, 18.81; H, 3.62. $C_9H_{21}O_{12}S_3Tb$. Calculated (%): C, 18.65; H, 3.60.

La^{III} didodecyl sulfate [bis(4-dodecyloxy-*N*-octadecyl)benzaldimino-2-ol][(4-dodecyloxy-*N*-octadecyl)benzaldimino-2-olate]. A solution of the ligand (0.36 g, 0.65 mmol) in EtOH was added dropwise with stirring at 50 °C to an alcohol solution of lanthanum dodecyl sulfate (0.26 g, 0.25 mmol). The reaction mixture was stirred at room temperature for 2 h. A yellow precipitate that formed was filtered off, washed with ethanol two times, and dried *in vacuo* above P_2O_5. The yield was 0.40 g (80%). Found (%): C, 71.25; H, 11.00. $C_{135}H_{250}O_{14}N_3La$. Calculated (%): C, 71.39; H, 11.32. ^1H NMR ($CDCl_3$), δ: 1.0—2.2 (214 H, alkyl); 3.50 (6 H, $N—CH_2$); 3.81 (6 H, $O_{Ph}—CH_2$); 4.00

(4 H, S—OCH$_2$); 6.23 (d, 3 H, 3-Ar, $^3J_{35}$ = 7.8 Hz); 6.41 (3 H, 5-Ar); 6.96 (d, 3 H, 2-Ph, $^3J_{35}$ = 7.8 Hz); 7.83 (3 H, CH=N); 13.25 (2 H, OH).

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