Liquid Crystalline *N*-Aryl-β-aminovinyl Ketones and Their Complexes with Lanthanides

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Abstract—Liquid crystalline lanthanide complexes with *N*-aryl-substituted β -aminovinyl ketones were synthesized for the first time. The complexes give rise to smectic *A* mesophase and are stable only in the solid state; in going to solution, they dissociate with formation of the initial ligand. **DOI:** 10.1134/S1070363206070152

Studies in the field of liquid crystalline coordination compounds (metallomesogens) constitute an interdisciplinary line appearing at the junction of coordination chemistry and physics of liquid crystals. The series of available metallomesogens has been extended considerably due to diversity of ligands (uni-, bi-, and multidentate) and variation of metals (s, p, d, and f) used in complex formation. The presence of a metal ion in coordination liquid crystals endows them with unique electric and magnetic properties [1, 2]. Therefore, metallomesogens together with organic liquid crystals are widely used in modern technics (displays, optical trsnducers, etc.). Lanthanide-containing liquid crystals are advantageous due to their strong magnetic anisotropy and easy control by weak magnetic fields [3]. Apart from liquid crystalline properties, lanthanide adducts exhibit efficient luminescence [4]. A drawback of such systems is difficult generation of geometric anisotropy (anisometry) of their molecules owing to high coordination numbers of lanthanides. It is known that anisometry is a necessary condition for the appearance of liquid crystalline properties: smectic, nematic, discotic, etc.

Up to now, liquid crystalline coordination compounds of some lanthanides with Schiff bases have been studied in detail [1], and adducts of lanthanide β -diketonates with Schiff bases [5], bipyridine, and phenanthroline [4] have been obtained. Previously, only *N*-alkyl-substituted ligands were involved in complex formation with f elements. Coordination of lanthanides to *N*-aryl-substituted ligands was questioned [6]. Only a few publications are available on related compounds with Schiff bases [7, 8].

In the present article we describe our successful attempt to synthesize liquid crystalline *N*-aryl-substituted β -aminovinyl ketones and their complexes with lanthanum and dysprosium. The ligands were obtained in several steps according to Scheme 1. The first step was alkylation of phenol with alkyl bromides. The reactions were carried out following the Claisen procedure, in anhydrous acetone in the presence of potassium carbonate. The resulting alkoxybenzenes were acetylated with acetic anhydride using 60% perchloric acid as catalyst.

Intermediately formed acetyl perchlorate is an

$$HO - \underbrace{\bigcirc}_{-HBr} RO - \underbrace{\bigcirc}_{CH_{3}CO_{2}, HCIO_{4}} RO - \underbrace{\bigcirc}_{O} C_{-CH_{3}COOH} RO - \underbrace{\bigcirc}_{O} C_{-CH_{3}COOH} C_{-CH_{3}COOH} RO - \underbrace{\bigcirc}_{O} C_{-CH_{3}COOH} C_{-CH_{3}COOH} RO - \underbrace{\bigcirc}_{O} C_{-CH_{3}COOH} RO - \underbrace{O}_{-CH_{3}COOH} RO - \underbrace{O}_{-CH_{$$

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$$\mathbf{R} = \mathbf{C}_{9}\mathbf{H}_{19}, \ \mathbf{C}_{12}\mathbf{H}_{25}, \ \mathbf{C}_{14}\mathbf{H}_{29}; \ \mathbf{R}' = \mathbf{C}_{4}\mathbf{H}_{9}, \ \mathbf{C}_{8}\mathbf{H}_{17}, \ \mathbf{C}_{10}\mathbf{H}_{21}, \ \mathbf{C}_{11}\mathbf{H}_{23}.$$

R	R'	Ln	Found, %				Formula	Calculated, %			
			С	Н	Ln	N	Formula	С	Н	Ln	N
C ₉ H ₁₉	C ₄ H ₉	_	76.89	8.92	_	3.48	C ₈₄ H ₁₁₇ N ₆ O ₁₈	76.85	8.98	_	3.20
$C_{9}H_{19}$	C_4H_9	Dy	60.85	6.94	9.93	4.99	C ₈₄ H ₁₁₇ DyN ₆ O ₁₈	60.73	7.10	9.78	5.06
$C_{9}H_{19}$	$C_{10}H_{21}$	-	78.32	9.87	_	2.58	C ₁₀₂ H ₁₅₃ N ₆ O ₁₈	78.27	9.85	—	2.68
$C_{9}H_{19}$	$C_{10}H_{21}$	Dy	64.12	8.16	8.63	4.59	C ₁₀₂ H ₁₅₃ DyN ₆ O ₁₈	64.01	8.06	8.49	4.39
$C_{9}H_{19}$	$C_{10}H_{21}$	La	64.49	8.45	7.89	4.56	C ₁₀₂ H ₁₅₃ LaN ₆ O ₁₈	64.81	8.16	7.35	4.45
$C_{9}H_{19}$	$C_{11}H_{23}$	-	78.49	9.99	-	2.89	C ₁₀₅ H ₁₅₉ N ₆ O ₁₈	78.46	9.97	_	2.61
$C_{9}H_{19}$	$C_{11}H_{23}$	La	65.72	8.37	7.01	4.40	C ₁₀₅ H ₁₅₉ LaN ₆ O ₁₈	65.26	8.29	7.19	4.35
$C_{12}H_{25}$	C_8H_{17}	-	78.59	9.83	_	2.39	C ₁₀₅ H ₁₅₉ N ₆ O ₁₈	78.46	9.97	-	2.61
$C_{12}H_{25}$	$C_{8}H_{17}$	Dy	64.12	8.35	8.57	4.48	C ₁₀₅ H ₁₅₉ DyN ₆ O ₁₈	64.48	8.19	8.31	4.30
$C_{14}H_{29}$	$C_{8}H_{17}$	_	78.93	10.21	_	2.32	C ₁₁₁ H ₁₇₁ N ₆ O ₁₈	78.81	10.19	_	2.48
C ₁₄ H ₂₉	C ₈ H ₁₇	Dy	65.47	8.63	8.12	4.33	$C_{111}H_{171}DyN_6O_{18}$	65.35	8.45	7.97	4.12

Table 1. Elemental analyses of β -aminovinyl ketones LH and their complexes with lanthanides Ln(LH)₃(NO₃)₃

acetylating agent which ensures higher yield of the acetylation product and considerably shortens the reaction time [9]. The use of aluminum chloride as a catalyst in such reactions also provides good results. The next stage was the synthesis of β -hydroxymethylideneacetophenone sodium salt. The reaction was carried out by heating the reactants in anhydrous benzene. The product was a yellow powder which was recrystallized from benzene. The use of a large excess of ethyl formate allowed us to raise the yield to 90% and reduce the reaction temperature.

Substituted β -hydroxymethylideneacetophenone sodium salts were then brought into reaction with palkoxyaniline hydrochlorides to obtain the desired β -aminovinyl ketones LH as ligands (Scheme 1). The reactions were performed by heating the reactants in boiling ethanol. After cooling, the precipitate was filtered off and recrystallized from alcohol, or reprecipitated from chloroform with ethanol. β -Aminovinyl ketones thus obtained were stable in air, as well as on heating to isotropic melt and subsequent cooling.

We previously reported on liquid crystalline lanthanide complexes with nonmesogenic *N*-alkyl-substituted β -aminovinyl ketones [10]. Surprisingly, our attempt to obtain coordination compounds with mesogenic *N*-aryl-substituted ligands, following an analogous procedure, was unsuccessful. Presumably, complex formation was hampered for steric reasons owing to the presence of an additional benzene ring on the nitrogen atom. We found that more severe conditions are necessary to obtain the desired complexes (heating of the reactants in boiling ethanol at 80°C for 4–5 h, Scheme 2). It should be noted that complexes with *N*-alkyl-substituted ligands decompose under these conditions. After heating, the solvent was immediately and completely removed from the reaction mixture. If the mixture was allowed to cool down before removal of the solvent or even traces of the latter were present in the residue, the complex formation equilibrium was displaced completely toward the initial components. The products were isolated as yellow powders. The complexes can not be recrystallization reprecipitapurified bv or tion; in both cases their decomposition occurred. Such instability in solution is inherent in the complexes derived from both N-aryl- and N-alkyl-substituted ligands. Analogous results were discussed previously while studying coordination compounds of lanthanides with Schiff bases [11, 12].

Scheme 2.

$$3LH + Ln(NO_3)_3 \cdot 6H_2O \longrightarrow Ln(LH)_3(NO_3)_3.$$

Since no single crystal could be grown, the structure of the ligands and their complexes was determined on the basis of their elemental analyses (Table 1) and ¹H NMR and IR spectra. According to the ¹H NMR and IR data, most of the synthesized β -aminovinyl ketones have ketoenamine structure which is favored by formation of stable quasiaromatic ring via intramolecular O···H hydrogen bonding. The presence of an H-chelate ring with conjugated double bonds is confirmed by displacement of the IR bands belonging to the stretching vibrations of the N–H (3310 and 3435 cm⁻¹), C–O, and C–C bonds (1640 and 1602 cm⁻¹, respectively) toward lower frequencies. The chemical shift of the NH proton ($\delta \sim 12$ ppm) and splitting of its signal due to coupling with the vinyl proton ($J \sim 12$ Hz) in the ¹H NMR spectra also suggest the presence of a strong intramolecular hydrogen bond in the ligand.

$$R - O - C \sim N - R'$$

It is known that biphenyl rod-like structures are prone to form mesophases [13, 14]. Introduction of an *N*-aryl substituent into aminovinyl ketone molecule gives rise to conjugation between the aromatic rings and enaminoketone moiety, which stabilizes a rigid rod-like structure and leads to appearance of the desired liquid crystalline properties.

In the IR spectra of the complexes (in mineral oil) we observed a slight narrowing of absorption bands due to stretching vibrations of the NH group (3304, 3442 cm⁻¹) involved in the intramolecular hydrogen bond; this pattern indicates that the ligand structure remained essentially the same on complex formation {the proton on the nitrogen atom is retained, though it is usually replaced upon complex formation with d elements, e.g., in copper(II) complexes [15]. In addition, displacement of the C-O and C-C stretching vibration bands toward higher frequencies (1653 and 1605 cm⁻¹, respectively) was observed. Analogous IR spectra were reported for coordination compounds of dioxomolybdenum(VI) dichloride with β -aminovinyl ketones [16]. Four bands in the IR spectra, in particular at 1465, 1261, 1106, and 847 cm⁻¹ for the lanthanum complex, were assigned to stretching vibrations of the nitro group (v_4 , v_1 , v_2 , and v_6 , respectively). The difference in the v_4 and v_1 frequencies (204 cm^{-1}) is typical for bidentane nitrate groups.

Analysis of the ¹H NMR spectrum of the diamagnetic lanthanum complex showed that in solution it undergoes dissociation to the initial components. The ¹H NMR spectrum contained a dublet of dublets at δ 7.44 ppm, which belongs to the CHN proton. The position of the NH doublet (δ 12.15 ppm) corresponds to the free ligand. Complexes with *N*-alkyl-substituted ligands, which are stable in solution, are characterized by splitting of the NH signal into a multiplet and its displacement to a stronger field (δ 10.38 ppm) [17]. Thus the ¹H NMR spectra confirm that liquid crystalline lanthanide complexes with *N*-aryl-substituted ligands are stable only in the absence of a solvent.

Mesogenic properties of the synthesized compounds (phase transition temperatures and types of mesophases) were studied by polarizing microscopy. Both initial ligands and the complexes are thermotropic liquid crystals giving rise to a fan texture typical of smectic A mesophase on heating. All

nectic	Α	mesophase	on	heating.	All	line	lanthanide	con

Table 2. Phase transition temperatures and mesophase temperature ranges ΔT of ligands LH and their complexes with lanthanides with the composition Ln(LH)₃(NO₃)₃

R	R'	Ln	Phase temperat	ΔT ,	
			$Cr-S_A$	$S_A(N)-I$	
C ₉ H ₁₉ ^b	C ₄ H ₉ ^b	_ ^b	129	195	66
C_9H_{19}	C_4H_9	Dy	178	217	39
$C_{9}H_{19}$	$C_{10}H_{21}$	-	118	189	71
$C_{9}H_{19}$	$C_{10}H_{21}$	Dy	173	216	43
$C_{9}H_{19}$	$C_{10}H_{21}$	La	175	210	35
C_0H_{10}	$C_{11}H_{23}$	_	106	184	78
$C_0 H_{10}$	$C_{11}^{11}H_{23}^{23}$	La	178	218	40
$C_{12}H_{25}$	$C_{8}H_{17}$	_	140	180	40
$C_{12}^{12}H_{25}^{23}$	$C_{8}H_{17}^{17}$	Dy	177	212	35
$C_{14}^{12}H_{20}^{23}$	$C_{8}H_{17}^{17}$	_	139	182	43
$C_{14}^{14}H_{29}^{29}$	$C_{8}^{\circ}H_{17}^{17}$	Dy	169	208	40

^a Cr stands for crystalline, S_A for smectic A, N for nematic, and I for isotropic. ^b S_A -N phase transition temperature 186°C.

compounds are thermally stable: they did not change after several heating–cooling cycles. The phase transition temperatures and temperature ranges of mesophases formed by β -aminovinyl ketones and their complexes with lanthanides are given in Table 2.

Increase in the number of benzene rings in the ligand favors additional π -electron interactions between the phenyl fragments; as a result, the phase transition temperature increases. On the average, it becomes by 50–60°C hygher than the corresponding parameter found for *N*-alkyl-substituted analogs [17]. The phase transition temperatures also increase in going from the ligands to their lanthanide complexes; their ability to form smectic phase increases in parallel.

Insofar as the behavior and liquid crystalline properties of lanthanide complexes with Schiff bases and β -aminovinyl ketones are very similar, we presume that these compounds have similar structures and that their molecules in the mesophase are packed in the same mode [18]. The data of elemental analysis and spectral and liquid crystalline properties of the synthesized compounds suggest that the complexes have the composition Ln(LH)₃(NO₃)₃ where the nearest environment of the rare-earth metal ion includes three oxygen atoms of the ligands and six oxygen atoms of the bidentate nitrate groups to form a one-cap square antiprism.

Thus we were the first to synthesize liquid crystalline lanthanide complexes with *N*-aryl-substituted β -aminovinyl ketones, whose phase transition temperatures (or thermal stability) exceed by 50–60°C those typical of *N*-alkyl-substituted analogs. The complexes are stable only as neat substances, and they undergo dissociation into the initial ligand and metal salt on dissolution.

EXPERIMENTAL

The textures and phase transition temperatures were determined using a Boetius polarizing microscope equipped with a computer-guided temperature-control unit. The temperatures were measured with an accuracy of $\pm 0.1^{\circ}$ C. The IR spectra were recorded in mineral oil on a Specord IR-75 spectrometer. The ¹H NMR spectra were obtained on a Varian Unity-300 spectrometer from solutions in CDCl₃ using TMS as reference.

The ligands and complexes were synthesized according to the general procedure described below. All initial reagents and solvents were preliminarily purified by recrystallization or distillation until their physical constants coincided with reference values.

Nonyloxybenzene. A mixture of 0.53 mol of phenol, 0.53 mol of nonyl bromide, and 0.53 mol of finely powdered potassium carbonate in 100 ml of anhydrous acetone was heated for 8 h under reflux on a water bath. During the reaction, KBr precipitated. The mixture was cooled, 300 ml of water was added, and the product was extracted into diethyl ether. The extract was washed with a 10% solution of sodium hydroxide and dried over K₂CO₃. The solvent was distilled off, and the residue was distilled under reduced pressure, a fraction boiling in the temperature range from 100 to 110°C (3 mm) being collected. Yield 43.3 g (40%), $n_D^{20} = 1.4857$.

1-(4-Nonyloxyphenyl)ethanone. Nonyloxybenzene, 0.1 mol, was mixed with 0.1 mol of acetic anhydride, and 60 drops of 60% perchloric acid were added. The solution warmed up and turned dark red. It was heated for 30 min on a boiling water bath and poured into 100 ml of cold water, and the mixture was left to stand for 1 h to remove excess of acetic anhydride. In order to accelerate this process, 8 g of sodium carbonate can be added, followed by heating to the boiling point. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The extract was combined with the organic phase, treated with a solution of sodium carbonate to neutral reaction, washed with water, and dried over K_2CO_3 . The solvent was distilled off, and the residue was distilled under reduced pressure. Yield 8.71 g (33%), bp 150–160°C (3 mm), $n_{\rm D}^{20} = 1.4890$. **Sodium 1-(4-nonyloxyphenyl)-3-oxoprop-1-en-1-olate.** A mixture of 0.01 mol of 1-(4-nonyloxyphenyl)ethanone, 0.01 mol of ethyl formate, and 0.01 mol of metallic sodium in anhydrous benzene was heated for 5 h under reflux. The precipitate was filtered off, washed with hot diethyl ether, and recrystallized from benzene. Yield 3.39 g (72%), mp 221°C (decomp.). The reaction occurred under milder conditions and the yield was greater in the presence of excess ethyl formate.

1-(4-Nonyloxyphenyl)-3-(4-undecyloxyphenylamino)prop-2-en-1-one. A solution of 0.35 mmol of sodium 1-(4-nonyloxyphenyl)-3-oxo-1-propen-1-olate in ethanol was mixed with a solution of 0.35 mmol of 4-undecyloxyphenylamine hydrochloride in the same solvent, and the mixture was heated for 10 min. After cooling, the yellow precipitate was filtered off and recrystallized from ethanol. Yield 0.09 g (64%). ¹H NMR spectrum (CDCl₃), δ , ppm (*J*, Hz): 0.90–0.94 m (6H, CH₃), 1.31–1.48 m (14H, CH₂), 1.65–1.90 m (4H, CH₂CH₂O), 4.01 d.t (4H, CH₂O, *J* 6.8, 24.6), 5.97 d [1H, C(O)CH, *J* 7.9], 6.90–6.98 m (4H, OC₆H₄C), 7.07 d and 7.96 d (2H each, NC₆H₄O, *J* 9.01), 7.44 d. d (1H, CHN, *J* 12.4, 7.8), 12.15 d (1H, NH, *J* 12.1).

Tris[1-(4-nonyloxyphenyl)-3-(4-undecyloxyphenylamino)-2-propen-1-one]trinitrolanthahexahydrate. num(III). Lanthanum(III) nitrate 0.07 mmol, was added to a solution of 0.20 mmol of 1-(4-nonyloxyphenyl)-3-(4-undecyloxyphenylamino)prop-2-en-1-one in ethanol, and the mixture was heated for 5 h under reflux. The solvent was removed under reduced pressure to obtain a yellow finely crystalline powder. IR spectrum (mineral oil), v, cm⁻¹: 3304, 3342 (NH); 1653 (CO); 1605 (C=C). ¹H NMR spectrum (CDCl₃), δ, ppm (J, Hz): 0.90–0.94 m (6H, CH₃), 1.31–1.48 m (14H, CH₂), 1.65–1.90 m (4H, CH₂CH₂O), 4.01 d.t (4H, CH₂O, J 6.8, 24.6), 5.97 d $[1H, C(O)CH, J 7.9], 6.90-6.98 \text{ m} (4H, OC_6H_4C),$ 7.07 d and 7.96 d (2H each, NC_6H_4O , J 9.01), 7.44 d.d (1H, CHN, J 12.4, 7.8), 12.15 d (1H, NH, J 12.1).

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