Liquid-crystal complexes of some lanthanides with a nonmesogenic β-enaminoketone

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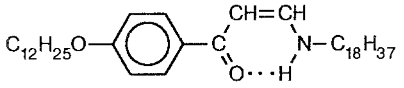
When lanthanides are introduced into liquid-crystal compounds, the polarizability and the magnetic anisotropy of the systems increase. For this reason, the resulting media should possess interesting magnetooptical properties.[1]

We have previously obtained liquid-crystal complexes of lanthanides with Schiff bases.[2] It was of interest to investigate coordination compounds formed from rare-earth elements and β-aminovinyl ketone as the ligand. For this purpose we synthesized a series of mesogenic complexes of Dy, Gd, and La with 1-(4-dodecyloxyphenyl)-3-octadecylamino-2-propen-1-one (LH). Unlike the β-aminovinyl ketones used previously for the synthesis of some metallomesogenes,[3,4] this ligand has no liquid-crystal properties. The shifts in the frequencies of the N—H and C=O stretching vibrations in the IR spectrum of LH indicate the presence of a strong intramolecular hydrogen bond, which appears due to the formation of a stable chelate cycle.



The IR spectra (in vaseline oil) of the complexes obtained display slightly shifted C=O and C=C bands (at 1620 and 1585 cm^{-1}, respectively). According to the magnetic susceptibility and elemental analysis data, the metallomesogenes have the compositions $LHL_2M(NO_3)_2$. Polythermic microscopy shows that the complexes contain an S_a-mesophase. The phase transition temperatures and the magnetic susceptibilities (298 K, $\chi_g \cdot 10^6$/cm^{-3} g^{-1}) are as follows: *for the ligand*, C76i (−0.75); *for the complexes*, M = Dy, C84S134i (23.35); M = Gd, C89S139i (12.99); M = La, C96S160i (−0.676), where "C" is the crystalline phase, "S" is the smectic phase, and "i" is the isotropic phase.

1-(4-Dodecyloxyphenyl)-3-octadecylamino-2-propen-1-one (LH). An ethanolic solution of octadecylamine hydrochloride (0.22 g, 0.72 mmol) was added to an ethanolic solution of sodium 2-(4-dodecyloxybenzoyl)vinyloxide (0.25 g, 0.72 mmol), and the mixture was heated for 5 min. The yellow precipitate was filtered off and recrystallized from ethanol to give 0.4 g (95 %) of the product. Found (%): C, 80.29; H, 11.83; N, 2.40. $C_{39}H_{69}NO_2$. Calculated (%): C, 80.24; H, 11.80; N, 2.34. IR (vaseline oil), ν/cm^{-1}: 3310 (N—H); 1640 (C=O); 1605 (C—C).

The $LHL_2Dy(NO_3)_2$ complex. Dysprosium nitrate (0.12 g, 0.23 mmol) was added at 30 °C to an ethanolic solution of the LH ligand (0.20 g, 0.34 mmol). The precipitate was filtered off and dried *in vacuo* to give 0.19 g (80 %) of the product. Found (%): C, 69.07; H, 10.08; N, 3.50. $C_{117}H_{205}N_5O_{12}Dy$. Calculated (%): C, 69.01; H, 10.05; N, 3.40. The derivatives of Gd and La were obtained by a similar procedure.

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