

Synthesis and Magnetic Investigations on Rare-Earth-Containing Liquid Crystals with Large Magnetic Anisotropy

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A new series of liquid-crystalline Schiff base lanthanide compounds of the general formula $(L'H)_2L'MX_2$ was prepared ($L'H = H_{2n+1}C_nOC_6H_3(OH)CHNC_mH_{2m+1}$; $n = 7, 12$; $m = 14, 18$; $M = La, Tb, Dy, Er, Nd, Ho, Eu, Pr,$ and Gd ; $X = NO_3$ or Cl). The thermal behavior of these complexes was examined by polarizing microscopy, differential scanning calorimetry, and X-ray diffraction experiments. The ligands $L'H$ are nonmesomorphic, but all lanthanide complexes show smectic A mesophases. Further, temperature-dependent magnetic susceptibility measurements were carried out in order to obtain information about the magnetic anisotropy of the lanthanide compounds. The Tb(III) and Dy(III) derivatives could be oriented by a magnetic field. These liquid-crystalline lanthanide complexes display magnetic anisotropies which are two orders of magnitude greater than those of known liquid crystals.

Introduction

The interest in the synthesis of metallomesogens has increased enormously during the past few years.¹⁻³ The new features of this kind of material combine the optical and electrical properties of conventional liquid crystals with the magnetic and electronic properties of transition-metal complexes.

The aim of this work was to synthesize new liquid-crystalline rare-earth-containing compounds with large magnetic anisotropy and to investigate their orientation behavior in a magnetic field. A necessary condition for the orientation of the molecules in a magnetic field is the existence of molecular magnetic anisotropy. Simon et al.^{4,5} reported on the first discotic alkoxy-substituted bis(phthalocyaninato)lutetium derivatives $((C_n)_8Pc)_2Lu$ ($n = 8, 12, 18$). In 1991 the synthesis of the first calamitic liquid-crystalline lanthanide complexes derived from (*N*-dodecyl-4-(4'-heptyloxy)benzoyloxy)salicylaldehyde $[L'H]$ with general structure $(L'H)_2L'MX_2$ ($M = Eu, Gd, Dy,$ and Pr ; $X = NO_3$ or Cl) was described in the literature.⁶ These compounds show smectic A mesophases. The orientation of the lanthanide complexes by a magnetic field was difficult due to the high viscosity of the liquid-crystalline phases. Recently, preliminary results of magnetic investigations of lan-

thanide-containing mesogens with Schiff's base ligands^{7,8} and β -enamino ketone ligands⁹ were presented.

In this paper we report on the synthesis, the characterization, and the magnetic investigations of the mesogenic lanthanide complexes based on 4-(alkyloxy)-*N*-alkyl-2-hydroxybenzaldehyde $[L'H]$ of the general formula $(L'H)_2L'MX_2$. It is noteworthy that the Schiff base ligands $[L'H]$ are nonmesomorphic alone. The chemical structure of the ligands $[L'H]$ and $[L''H]$ is presented in Figure 1. Previously investigations^{10,11} showed that copper(II), nickel(II), and oxovanadium(IV) complexes derived from $[L''H]$ are nonmesogenic, whereas the corresponding copper(II), nickel(II), and oxovanadium(IV) complexes of $[L'H]$ form smectic C, smectic A, and nematic phases, respectively.

Experimental Section

Preparation of ligand $[L'H]$. 4-(Dodecyloxy)-*N*-octadecyl-2-hydroxybenzaldehyde. For the preparation of ligand a mixture of equivalent amount of 4-(dodecyloxy)-2-hydroxybenzaldehyde and octadecylamine in ethanol was refluxed for 2 h. The precipitate was recrystallized from ethanol; yield 80%.

Elemental anal. calcd for $C_{37}H_{67}O_2N$: C, 79.65%; H, 12.10%; N, 2.51%. Found: C, 80.05%; H, 11.98%; N, 2.48%.

¹H NMR (δ ppm in $CDCl_3$) 0.9 (t, 6H, CH_3); 1.1–1.68 (m, 52H, CH_2); 3.49 (m, 2H, $N-CH_2$); 3.74 (t, 2H, OCH_2); 6.28 (d, 1H, Ph); 6.39 (s, 1H, Ph); 6.93 (d, 1H, Ph); 8.12 (s, 1H, $CH=N$); 13.18 (s, 1H, OH); $J_0 = 8.7$ Hz; $J_m = 2.1$ Hz.

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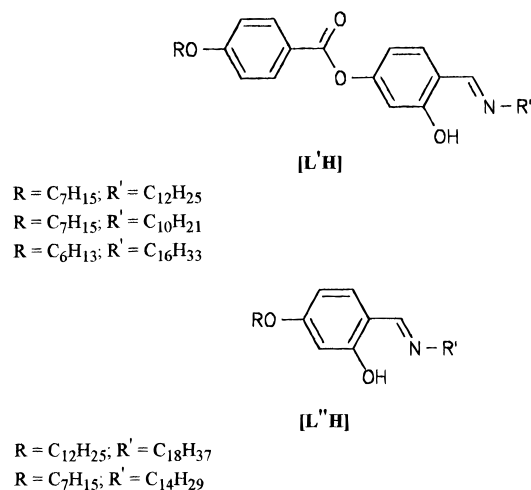


Figure 1. Chemical structure of the ligands [L'H] and [L''H].

Preparation of Lanthanide Complexes. The synthesis of the lanthanide complexes was carried out as described previously⁶ by reaction of the Schiff base ligand L''H with the corresponding lanthanide trinitrate or trichloride in ethanol. All lanthanide compounds were prepared using a similar procedure as presented below for the lanthanum(III) compound 1.

Dinitrate[bis[4-(dodecyloxy)-N-octadecylbenzaldimino-2-hydroxy][4-(dodecyloxy)-N-octadecylbenzaldimino-2-olate]]lanthanum(III). A solution of $La(NO_3)_3 \cdot H_2O$ (0.2 g, 0.62 mmol) was added dropwise to a stirred ethanolic solution of L''H (0.34 g, 0.61 mmol). The reaction mixture was stirred for 5 h. The precipitate was collected by filtration, washed with ethanol, and dried by vacuum; light yellow powder, yield 0.32 g (80%).

Elemental anal. calcd: for $C_{111}H_{200}O_{12}N_5La$: C, 70.63%; H, 10.68%; N, 3.71%. Found: C, 68.89%; H, 10.00%; N, 3.63%.

¹H NMR (δ ppm in $CDCl_3$) 0.88 (t, 6H, CH_3); 1.3–1.67 (m, 52H, CH_2); 3.51 (m, 2H, $N-CH_2$); 3.71 (t, 2H, OCH_2); 6.23 (d, 1H, Ph); 6.37 (s, 1H, Ph); 6.97 (d, 1H, Ph); 7.75 (s, 1H, $CH=N$); 12.58 (s, 1H, OH); $J_0 = 8.6$ Hz; $J_m = 1.9$ Hz.

Techniques. ¹H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer in deuteriochloroform solutions. Infrared spectra were obtained using a Perkin-Elmer 580B spectrophotometer. The spectra of the lanthanide compounds were recorded in the 200–4000 cm^{-1} spectral range.

The phase behavior of all lanthanide complexes was observed with a polarizing microscope (Leitz Orthoplan Pol) equipped with a heating stage (Mettler FP-84). A differential scanning calorimeter (Perkin-Elmer DSC-2M) was also used for this purpose as well as for determining the enthalpies of the phase transitions.

X-ray diffraction measurements were performed by a focusing horizontal two circle diffractometer^{12,13} (Stoe Stadi 2) equipped with a modified oven. The $Cu K\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) is focused by a curved Ge(111) monochromator. For the fast diffractometry a linear position-sensitive detector (Stoe Mini PSD) was used.

Magnetic susceptibility data for lanthanide compounds over the temperature range 4.2–300 K were obtained with a Faraday-type magnetometer using a computer controlled Cahn D-200 electrobalance and a Bruker B-MN 200/60 power supply. Magnetic susceptibility measurements in the temperature range 300–460 K were carried out using the heating mode of the system designed for this range. Details of the apparatus are described elsewhere.^{14,15} The applied field was approxi-

Table 1. IR Data (cm^{-1}) of the Lanthanide Complexes with General Structure $(L''H)_2L''MX_2$ and the Ligand [L''H]

vibration	M: X:	Dy NO ₃	Gd Cl	Gd NO ₃	Er NO ₃	Pr NO ₃	L''H
$\nu(OH)$		3400	3100	3350	3100	3400	2850
$\nu(C=N)$		1620	1626	1626	1620	1624	1612
$\nu(C=C)$		1580	1580	1580	1580	1580	1580
$\nu(C_{Ph}-O)$		1300	1300	1305	1300	1298	1288
$\nu_{as}(C-O-C)$		1240	1245	1250	1250	1240	1245
$\nu_s(C-O-C)$		1052	1056	1060	1067	1056	1050
$\nu_1(NO_3)$		1475		1476	1474	1475	
$\nu_2(NO_3)$		1285		1287	1288	1289	
$\nu_3(NO_3)$		1035		1032	1028	1030	
$\nu_4(NO_3)$		775		780	780	775	
$\nu(M-O, M-N)$		425	424	424	424	420	
		584	584	584	584	582	

mately 1.2 T. Diamagnetic corrections of the molar magnetic susceptibility of the compounds were applied using Pascal's constants.¹⁶

Results and Discussion

Characterization of the Lanthanide Compounds.

The structures of all new lanthanide compounds were characterized by elemental analysis, IR spectroscopy, ¹H NMR spectroscopy, and magnetic susceptibility measurements at room temperature. The analytical data confirm the $(L''H)_2L''MX_2$ composition of the lanthanide compounds.

The IR data of some lanthanide complexes of the general formula $(L''H)_2L''MX_2$ and the ligand [L''H] are summarized in Table 1. The ligand [L''H] exhibits a stretching vibration at 1612 cm^{-1} assigned to the C=N bond. In the case of the lanthanide compounds, this band is slightly shifted to higher wavenumbers (1620–1626 cm^{-1}), indicating that the nitrogen atom is involved in metal–nitrogen bond formation. The infrared spectrum of the ligand shows a broad band at 2850 cm^{-1} which was assigned to the stretching vibration of the hydroxy group. This band is apparently shifted to higher wavenumbers (3100–3400 cm^{-1}) in the lanthanide compounds, caused by the breaking of the intramolecular hydrogen bond $OH \cdots N$ on complexation. In addition, a stretching band at 1288 cm^{-1} corresponding to the phenolic bond $C_{Ph}-O$ for the ligand is observed and is slightly shifted to higher wavenumbers (1300 cm^{-1}) in the rare-earth-containing compounds. The shift of the frequencies of the stretching vibrations $\nu(C_{Ph}-O)$ and $\nu(OH)$ shows that the oxygen atom is also coordinated to the rare-earth ion. Four absorption bands within the region 1476–775 cm^{-1} corresponding to the nitrate groups of the complexes are observed. The infrared spectra of the lanthanide compounds show two bands at 425 and 584 cm^{-1} which can be attributed to the stretching vibrations of $\nu(M-O)$ and $\nu(M-N)$.¹⁷

Magnetic susceptibility studies at room temperature were carried out essentially in order to obtain information about the composition of the lanthanide compounds. Often, magnetic susceptibility measurements at room temperature are used as a valuable analytical tool to confirm the composition of metal complexes, especially in case of metal ions with a well-defined high-temperature limit of the spin-only value. The experimental

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Table 2. Thermodynamic Data of the Lanthanide Complexes of the General Formula (L'H)₂L'MX₂

compound	R	R'	X	M	C → S _A			S _A → I			μ _{eff} [μB]		
					T [°C]	ΔH [kJ/mol]	ΔS [10 ⁻² kJ/mol K]	T [°C]	ΔH [kJ/mol]	ΔS [10 ⁻² kJ/mol K]	ΔT [°C]	exp	theor
1 ^a	C ₁₂ H ₂₅	C ₁₈ H ₃₇	NO ₃	La	81	3.74	1.05	138	10.3	2.50	57	0	0
2	C ₁₂ H ₂₅	C ₁₈ H ₃₇	NO ₃	Tb	114	15.9	4.32	148	9.69	2.30	34	9.8	9.7
3	C ₁₂ H ₂₅	C ₁₈ H ₃₇	NO ₃	Dy	130.3	22.7	5.63	144.2	9.86	2.36	13.9	10.6	10.6
4	C ₁₂ H ₂₅	C ₁₈ H ₃₇	NO ₃	Er	127	22.8	5.70	146	10.3	2.47	19	9.1	9.5
5	C ₁₂ H ₂₅	C ₁₈ H ₃₇	NO ₃	Nd	100	16.7	4.48	151	9.63	2.27	51	3.4	3.6
6	C ₁₂ H ₂₅	C ₁₈ H ₃₇	NO ₃	Ho	129.2	19.5	4.86	143	9.34	2.25	13.8	10.6	10.6
7	C ₁₂ H ₂₅	C ₁₈ H ₃₇	NO ₃	Eu	112.5	20.8	5.39	147	12.6	3.00	34.5	3.3	3.5
8	C ₁₂ H ₂₅	C ₁₈ H ₃₇	NO ₃	Gd	112	22.3	5.79	144	11.1	2.67	32	7.9	7.9
9	C ₁₂ H ₂₅	C ₁₈ H ₃₇	Cl	Gd	164	26.0	5.98	185	7.89	1.72	21	8.0	7.9
10	C ₇ H ₁₅	C ₁₄ H ₂₉	NO ₃	Tb	141	42.3	10.2	[139]	11.5	2.78	[2]	9.8	9.7
11	C ₇ H ₁₅	C ₁₄ H ₂₉	NO ₃	Dy	143.3	39.7	9.54	[142]	10.5	2.54	[1.3]	10.3	10.6

^a Phase transition C₁ → C₂ at 52 °C.

Table 3. Comparison of Observed (μ_{eff}[exp]) and Calculated (μ_{eff}[theor]) Effective Magnetic Moments at Room Temperature for the Investigated Lanthanide Compounds^a

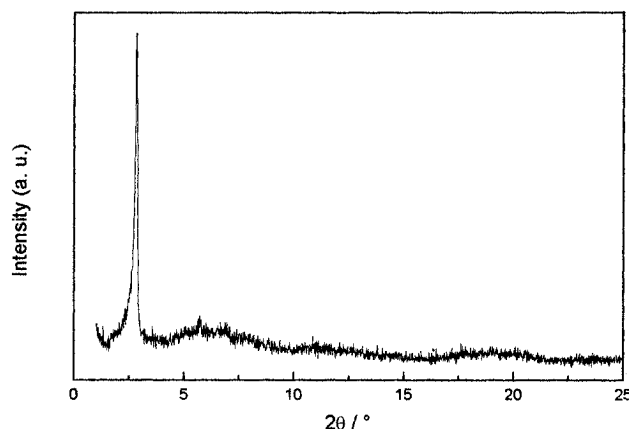
compound	L	M	R	R'	μ _{eff} [μB]		g _J	J	Θ [K]
					theor	exp			
2	L''	Tb	C ₁₂ H ₂₅	C ₁₈ H ₃₇	9.72	9.88	3/2	6	-2.6
3	L''	Dy	C ₁₂ H ₂₅	C ₁₈ H ₃₇	10.63	10.69	4/3	15/2	
8	L''	Gd	C ₁₂ H ₂₅	C ₁₈ H ₃₇	7.94	7.91	2	7/2	-1.3
12	L'	Dy	C ₇ H ₁₅	C ₁₀ H ₂₁	10.63	10.30	4/3	15/2	
13	L'	Gd	C ₆ H ₁₃	C ₁₆ H ₃₃	7.94	7.95	2	7/2	

^a The Θ values result from a Curie-Weiss fit of the magnetic susceptibility data.

effective magnetic moments at room temperature determined for the lanthanide complexes as well as the calculated magnetic moments using the free-ion approximation^{18,19} are given in Tables 2 and 3, respectively. The experimental magnetic moments of the rare-earth compounds are in agreement with the calculated values. Consequently, the magnetic susceptibility studies of the lanthanide compounds confirm also the composition (L'H)₂L'MX₂ as suggested by the analytical experiments.

Mesogenic Properties. The transition temperatures, enthalpies, and entropies determined for the lanthanide complexes are reported in Table 2. It was found out that the ligand L'H showed no liquid-crystalline behavior. The mesophases of all lanthanide compounds were investigated by optical microscopy. All lanthanide complexes exhibit smectic A phases which were clearly identified by the characteristic fan-shaped textures. Lanthanide derivatives with R = C₇H₁₅ and R' = C₁₄H₂₉ (**10** and **11**) exhibit only monotropic smectic A phases. Further increase of the alkyl chain length (R = C₁₂H₂₅ and R' = C₁₈H₃₇) leads to enantiotropic smectic A phases. These new liquid-crystalline rare-earth compounds have the remarkable ability to form supercooled mesophases. During several heating and cooling cycles in the temperature range -20 to +50 °C, the mesogenic structure of the lanthanide compounds is conserved.

The melting points and clearing temperatures of the lanthanide compounds with nitrate groups are similar. The complex with X = Cl (**9**) has significant higher

**Figure 2.** X-ray diffraction pattern of compound **2** in the smectic A phase.

phase transition temperatures compared to compound **8**. An increase in the phase transition temperatures was observed when substituting the NO₃⁻ ion by the Cl⁻ ion.

The mesophases of the derivatives **2** and **8** were also characterized by X-ray diffraction at several temperatures. As an example, the X-ray diffraction pattern of the terbium complex **2** at 142 °C is shown in Figure 2. Two sharp reflections in the small angle region (2θ = 2.838° and 5.660°) and a diffuse reflection around 2θ = 19° are visible. This pattern indicates a low ordered smectic phase. The thickness of the smectic layer *d* amounts to 31.1 Å obtained by application of Bragg's law to the small-angle peak. The length of the ligand [L'H] *l* was calculated to be 44 Å. The comparison between the value of *d* and *l* showed that the thickness of the smectic layer is smaller than the calculated length of the molecules. An explanation of the shorter distance between the smectic layers may be that the molecules of each layer penetrate the adjacent layer to a limited depth. The molecular structure suggested for the lanthanide compounds as well as their molecular arrangement in the smectic A phase are represented in Figure 3. The proposed molecular structure of the lanthanide compounds can be described as a trigonal prismatic structure where the nitrate groups occupy the equatorial or axial positions.

Magnetic Properties. Magnetic susceptibility measurements in the temperature range 4.2–460 K were carried out in order to detect possible exchange interactions between the spin centers. The molar magnetic susceptibilities and effective magnetic moments versus

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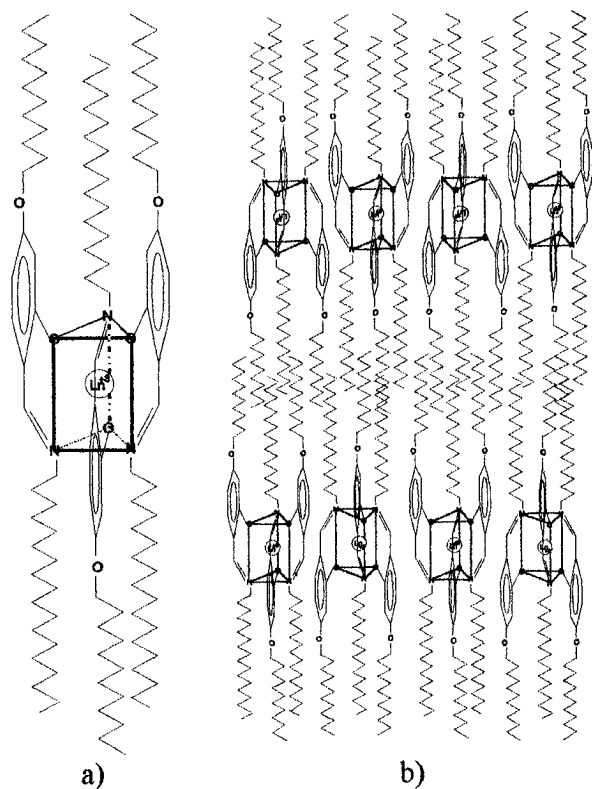


Figure 3. (a) Molecular structure suggested for lanthanide compounds. (b) Molecular arrangement of the lanthanide compounds in the smectic A phase (nitrate groups and hydrogen atoms are not shown).

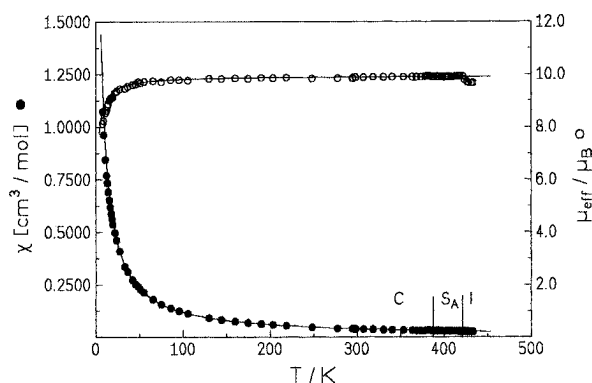


Figure 4. Magnetic susceptibilities χ and magnetic moments μ_{eff} versus temperature for compound **2** [(L'H)₂L'Tb(NO₃)₂] (heating process). The lines represent the Curie-Weiss fit.

temperature for the complexes **2** and **8** are presented in Figures 4 and 5, respectively. The Θ values of the Tb(III) and Gd(III) compounds given in Table 3 result from a Curie-Weiss fit of the magnetic susceptibility data according to eq 1. This is rather a phenomenologi-

$$\chi = \frac{N_L g_J^2 \mu_B^2}{3k(T - \Theta)} J(J + 1) \quad \frac{\mu_{\text{eff}}}{\mu_B} = 2.828 \sqrt{\chi^* T} \quad (1)$$

cal description of the temperature dependency of the molar susceptibility than a quantitative analysis. The magnetic behavior of lanthanide compounds is mainly influenced by crystal-field effects and dipole-dipole interactions, whereas superexchange interactions are relatively unimportant.²⁰ Some models have been developed for cubic or axial environments,^{18,19} but rare-earth-containing molecular compounds possess usually

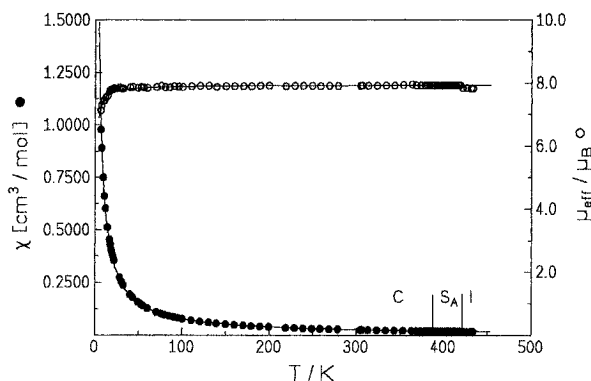


Figure 5. Magnetic susceptibilities χ and magnetic moments μ_{eff} versus temperature for compound **8** [(L'H)₂L'Gd(NO₃)₂] (heating process). The lines represent the Curie-Weiss fit.

lower symmetries and a precise interpretation of their magnetic behavior is still very difficult. Especially, a clear separation of crystal-field effects and exchange interactions remains difficult in most cases. The influence of dipole-dipole interactions can be described by a Curie-Weiss law. No maximum in the magnetic susceptibility curves for complexes **2** and **8** was observed. It is evident that the existence of strong exchange interactions between the spin centers can be excluded. The high coordination number of eight of the investigated lanthanide compounds hinders the strength of efficient superexchange paths. Therefore, the lanthanide compounds can be considered as magnetically isolated spin centers.

Further, an aim of our work was to investigate the orientation behavior of the rare-earth compounds in a magnetic field in order to obtain quantitative information about the degree of the magnetic anisotropy. In case of an orientation of the sample in the liquid-crystalline phase with the axis of maximum susceptibility parallel to the magnetic field, an increase of the magnetic susceptibility associated with the isotropic-to-liquid crystalline phase transition can be observed. By comparison of the isotropic value of susceptibility χ_{iso} measured in the isotropic phase with the value of maximum susceptibility χ_{max} (maximum susceptibility tensor component) observed in the oriented liquid-crystalline phase, we can obtain useful information about the degree of magnetic anisotropy of the lanthanide compounds. For a detailed interpretation, the structural connections between the relative orientation of the χ tensor with respect to the molecular frame must be considered.

Temperature-dependent magnetic susceptibility measurements of some representative lanthanide complexes **2**, **3**, **8**, and **12** were carried out in the liquid-crystalline phases. The effective magnetic moments versus temperature for complexes **2**, **3**, and **12** are displayed in Figures 6–8, respectively. The substances were initially heated up to the isotropic phase and then cooled slowly to the smectic phase in an applied magnetic field of 1.2 T. In the case of the compounds **2**, **3**, and **12** an alignment of the molecules in the magnetic field was observed during the cooling process. In general, for liquid crystals an orientation of the molecules can be realized more easily during the cooling procedure than

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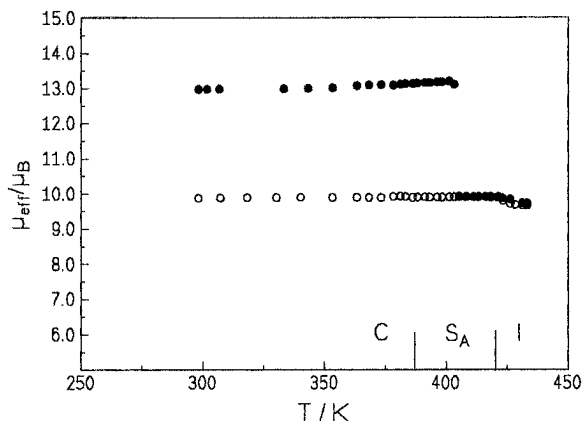


Figure 6. Magnetic moments μ_{eff} versus temperature for compound **2** [(L'H)₂L''Tb(NO₃)₂] (○, heating process; ●, cooling process).

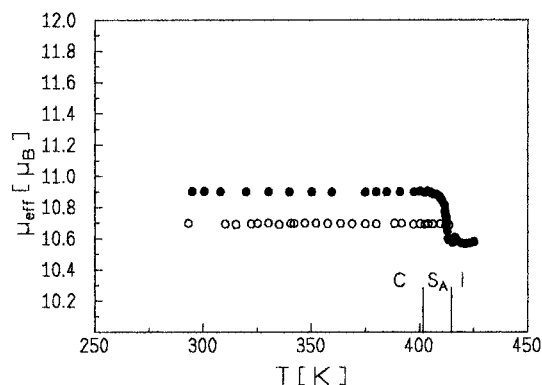


Figure 7. Magnetic moments versus temperature for complex **3** [(L'H)₂L''Dy(NO₃)₂] (○, heating process; ●, cooling process).

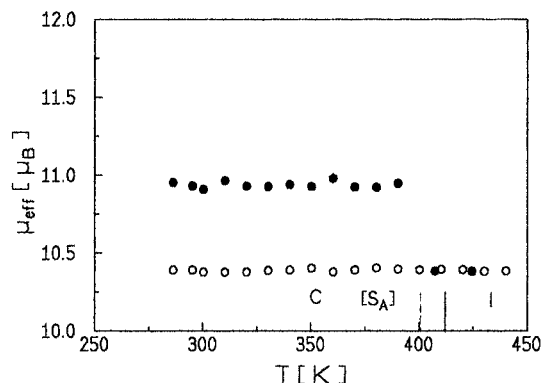


Figure 8. Magnetic moments μ_{eff} versus temperature for compound **12** [(L'H)₂L''Dy(NO₃)₂] (○, heating process; ●, cooling process).

the heating one. Accordingly, no orientation behavior was observed during the heating process for the complexes. A drastic increase of the susceptibility values on cooling compared with the initial ones recorded during the heating process were found for complexes **2**, **3**, and **12**. This behavior indicates a magnetic-field-

Table 4. Experimental Values for χ_{iso} , χ_{max} , and $\chi_{\text{iso}} - \chi_{\text{max}}$ (Magnetic Susceptibility χ in Units of [10^{-6} cm³/mol])

compound	T [K]	χ_{iso}	χ_{max}	$\chi_{\text{max}} - \chi_{\text{iso}}$
2 (L'H) ₂ L''Tb(NO ₃) ₂	404	30500	53300	22800
3 (L'H) ₂ L''Dy(NO ₃) ₂	417	33445	35933	2488
12 (L'H) ₂ L''Dy(NO ₃) ₂	401	33596	37319	3723

induced orientation of the molecules with the axis of maximum susceptibility χ_{max} parallel to the magnetic field. The experimental data χ_{iso} , χ_{max} as well as $\chi_{\text{max}} - \chi_{\text{iso}}$ determined for the lanthanide compounds **2**, **3**, and **12** at the phase transition temperature are shown in Table 4.

The orientation behavior of metal-free liquid crystals^{21,22} has been well investigated. In the case of organic liquid crystals the anisotropy is mainly produced by diamagnetic phenyl groups (axis of maximum susceptibility parallel to the director): The molecules orient with the director parallel to the magnetic field. For organic liquid crystals the magnitude of the magnetic anisotropy is approximately 50×10^{-6} cm³/mol.

In a previous paper¹⁰ we presented the results of EPR and magnetic susceptibility investigations on metal-omesogens (copper and oxovanadium complexes). The direction of the orientation (director parallel or perpendicular to the magnetic field) was detected by angular-dependent EPR measurements. The magnetic anisotropy of metallomesogens includes the anisotropy of the diamagnetic ligand (caused by the phenyl groups) and the anisotropy of the paramagnetic metal ion.²³ The magnitude of the paramagnetic anisotropy of copper or oxovanadium ions is comparable to the diamagnetic anisotropy of the ligands, the magnitude of the overall magnetic anisotropy is in the range $(20-130) \times 10^{-6}$ cm³/mol. However, due to the extremely high paramagnetic anisotropy of the terbium and dysprosium ions, the observed experimental values of $\chi_{\text{max}} - \chi_{\text{iso}}$ for the lanthanide compounds **2**, **3**, and **12** exceed clearly the corresponding values for copper and oxovanadium complexes. These liquid-crystalline rare-earth compounds display magnetic anisotropies which are 2 orders of magnitude greater than those of other known liquid crystals.

In the case of the gadolinium derivative **8** no orientation behavior was observed. The compound cannot be oriented by a magnetic field due to the low magnetic anisotropy of the gadolinium ion.

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