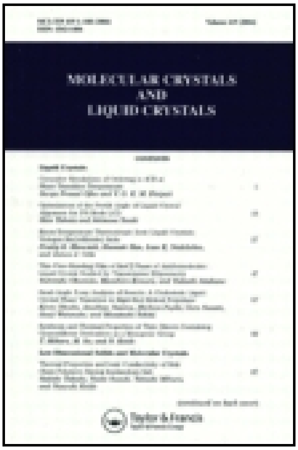

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Investigations on the Liquid Crystalline Phase of Schiff's Base Complexes of Copper(II) and Their Corresponding Ligands

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Some new liquid crystalline Schiff's base complexes with copper(II) have been prepared. Microscopic observations and D.S.C. measurements reveal broad nematic mesophases. X-ray investigations on magnetically oriented samples confirm the nematic mesophase and indicate a cybotactic one.

Anisotropic magnetic susceptibility data of a mixture of Schiff's base complexes of copper(II) are presented. An orientation with the longitudinal axis parallel to the magnetic field is caused by the dominating diamagnetic anisotropy of the phenyl groups of these metallo-mesogens. The order parameter of bis[4-((4-hexyloxybenzoyloxy)-*N*-(4-butylphenyl)-salicylaldiminato] copper(II) solved in 5CB is investigated. Values up to $S = 0.575$ have been obtained. We report on D.S.C. measurements and microscopic observations on a series of N-(4-(4′-n-alkoxybenzoyloxy)salicylidene)-4-n-alkyl- or alkyloxy-anilines. Temperature dependent X-ray investigations on magnetically oriented samples show skewed cybotactic nematic phases for these ligands.

INTRODUCTION

The synthesis and study of transition metal containing liquid crystals is rapidly in progress[1] due to the possibility of getting interesting magnetic or optical properties combined with those of liquid crystals. Of special interest are samples with nematic or smectic mesophases like some β-diketonato complexes of copper(II)[2,3] or some Schiff's base complexes of copper(II).[4–17] Specially on the field of mesogenic Schiff's base complexes of copper(II) the research is increasing rapidly.[4–17] Up to now, the research is concentrated on synthesis and phase characterizations mainly. Other physical data like order parameters, X-ray measurements on oriented samples,[16,17] investigations of guest-host mixtures[18,19] or magnetic data[4,9,20–26] are limited. The aim of this work is to present some physical data as well as the chemical synthesis of these metallo-mesogens and their corresponding ligands. We report on thermal data and phase characterizations as well as some X-ray investigations on magnetically oriented samples. Anisotropic magnetic susceptibility measurements of a mixture of Schiff's base copper(II) complexes are also presented. The behaviour

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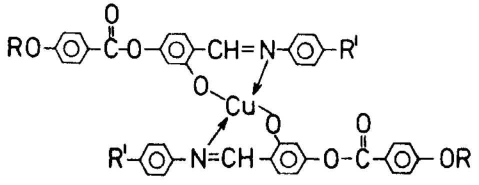
† Part of Dr-Ing. thesis of Bettina Borchers, D17, Technische Hochschule Darmstadt.

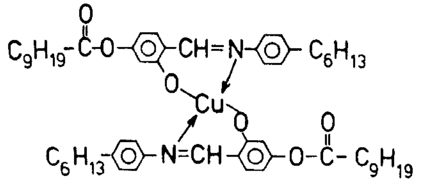
of metallo-mesogens solved in common liquid crystals is of interest too. The order parameter of a Schiff's base complex of copper(II) solved in 5CB is presented too.

EXPERIMENTAL

The investigated compounds are shown in Figure 1. They were prepared with slight variations according to procedures described in literature.[14,15] The N-(4-4′-n-alkoxybenzoyloxy)salicylidene)-4-n-alkyl-or alkyloxy-anilines (6–9) were obtained from the reaction of resorcylaldehyde with 4-alkoxybenzoylchlorids followed by a condensation with 4-alkyl or alkyloxyanilines. The copper(II) complexes (1–4) were prepared with copper(II)-acetate in ethanolic solution. Recrystallization from toluene gave brown crystals. A similar synthesis has been carried out but with decanoic acid instead of the 4-alkyloxybenzoic acids (5). The elemental analysis data are consistent with the proposed structures (the theoretically calculated values are given



	R	R'
1	C_6H_{13}	C_4H_9
2	C_6H_{13}	OCH_3
3	C_4H_9	C_4H_9
4	C_4H_9	OCH_3



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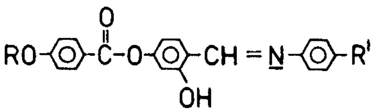

	R	R'
6	C_6H_{13}	C_4H_9
7	C_6H_{13}	OCH_3
8	C_4H_9	C_4H_9
9	C_4H_9	OCH_3

FIGURE 1 Investigated compounds.

in parentheses): 1 C:71.61(71.44), H:6.85(6.80), N:2.69(2.76); 2 C:68.04(68.80), H:5.89(5.90), N:2.97(2.93); 3 C:70.62(70.61), H:6.30(6.35), N:2.93(2.94); 4 C:66.45(66.69), H:5.31(5.37), N:3.08(3.11); 5 C:72.30(72.20), H:8.34(8.36), N:3.02(2.90); 6 C:75.97(76.08), H:7.43(7.45), N:2.93(2.96); 7 C:72.32(72.46), H:6.55(6.53), N:3.09(3.13); 8 C:75.08(75.48), H:6.93(7.01), N:3.13(3.14); 9 C:71.49(71.58), H:5.98(6.01), N:3.28(3.34).

For phase characterization of the metallo-mesogens and the ligands a polarizing microscope (Leitz Orthoplan-Pol) equipped with a hot stage and a controller (Mettler FP82 and FP80) was used. The transition temperatures were determined using a D.S.C. equipment (DuPont Thermal Analyzer 990, calibrated with pure indium as standard). In case of the copper(II) complexes a heating rate of 10 K/min was used for determining the melting points and 20 K/min for the clearing points. For the ligands a heating rate of 10 K/min was used for the determination of both transition temperatures.

For X-ray investigations the substances were put in 1.0 mm Lindemann glass capillaries. The samples were oriented within a magnetic field of about 0.6 Tesla. Because of thermal decomposition by heating above the clearing temperature an orientation in the cooling mode was not possible. Nevertheless a good alignment parallel to the magnetic field has been observed for the copper(II) Schiff's base complexes and their corresponding ligands. A specially constructed oven allowed temperature dependent measurements. Cu-K_α-radiation perpendicular to the glass capillaries was used for these experiments. Flat plate photographs were taken in the mesophase. A Joyce MKIIIC-microdensitometer was used to analyze the observed patterns. From the cybotactic spots the molecular tilt angle (β) was obtained and the interplanar distance was calculated by using the Bragg equation. The modified Bragg equation (Equation (3))

$$2 \cdot D \cdot \sin\theta = 1.117 \cdot \lambda \tag{3}$$

was used for the equatorial reflections to calculate the intermolecular distance (D).

The magnetic susceptibilities of a nearly eutectic mixture of 1 (61 mol%) and 2 (39 mol%) with $T_m = 453$ K were investigated in the heating mode with a Faraday System[27] modified for the temperature range of 300–500 K. The mixture was pulverised to obtain isotropic data for the solid phase. Because of thermal decomposition no data of the isotropic phase could be observed. The molecular susceptibilities were corrected for isotropic diamagnetism ($-\chi_{dia}/10^{-6}$ cm^3 mol^{-1} = 602.3). The paramagnetic anisotropy of the copper(II) center was estimated from magnetic susceptibility data of single crystals described in literature.[28]

The preparation of the mixture of 1 in 5CB was done within a little tube with a side tube. In the side tube there was a filter of grade 4 porosity. After closing the tubes and heating the system up to about 50°C for the intermixing of the metallomesogen and the nematic liquid crystal the mixture was standing at room temperature for some days. Then the solution was sucked through the filter. After this filtration we could be sure, that no solid amount of 1 exists in the sample volume.

The order parameters of 1 (1.9 w%) solved in 5CB were obtained from the extinctions of the polarized spectra at the absorption maximum of 1 ($\lambda_{\parallel} = 380$ nm,

$\lambda_\perp = 375$ nm) with a Cary-17 spectrometer (Varian). The dichroitic ratio R is given by Equation (1)

$$R = A_{\parallel}/A_{\perp}. \tag{1}$$

Where $A_{\parallel}$ and $A_{\perp}$ are the absorbances with the incident light parallel and perpendicular to the director of the nematic host. From this value R we obtained the order parameter S from Equation (2)

$$S = (R - 1)/(R + 2). \tag{2}$$

RESULTS AND DISCUSSION

The copper(II) Schiff's base compounds 1–4 exhibit a nematic mesophase. The average value of the transition temperatures as well as the enthalpies are given in Table I. We have found nematic phases of a wide thermal range $\Delta T = 47–65$ K. In case of 4 we observed a second solid phase additionally (Table I). The textures were similar to those of a nematic phase shown by classical rod-like molecules. A progress concerning the thermal stability of these compounds caused by their high melting and clearing temperatures is compound 5. Microscopic observations of the particular substance show a monotropic fan-shaped texture which is typical for smectic mesophases.

The observed thermal data of the compounds 6–9 are shown in Table I. The transition temperatures of 6 and 8 are in good agreement with the literature.[33] The magnitude of the obtained enthalpies for the transition nematic-isotropic phase are in the expected range (1.5–2.3 kJ/mol). Microscopic observations on the mesophase show a Schlieren-texture of the nematic mesophase. The monotropic S_c-phase could be determined by means of polarizing microscopy and D.S.C. measurements also.

X-ray experiments on magnetically oriented samples of 1, 2 and 4 confirm the nematic mesophase. An orientation of the molecular length axes parallel to the

TABLE I

Transition temperatures and enthalpies for compounds 1–9. Thermal data for 1 and 3[15] and 6 and 8[33] as far as reported are given in parentheses. In case of 6 a monotropic S_c-phase at T = 77°C (77) was observed

	T_m[°C]	ΔH_m[kJ/mol]	T_c[°C]	ΔH_c[kJ/mol]
1	219(213)	46.4	275(258)	1.9
2	226	65.5	291	—
3	238(231)	52.1	285(261)	2.0
4	219	41.3		
	229	16.0	292	1.2
5	179.5	55.6	164.0	—
6	82.5(80)	24.5	227(227)	1.6
7	111.0	37.8	268.5	2.3
8	90.5(89)	23.6	243(242)	1.5
9	113.5	27.6	283.5	1.7

magnetic field was observed. The small angle reflections split up into four points, a typical phenomena for skewed cybotactic nematic phases. Figure 2 gives a schematic representation of the observed diffraction patterns. For 3 it was impossible to obtain a X-ray pattern because of the high melting point of this compound. The phase characterization for 3 could be done by thermomicroscopy only. The obtained data for the molecular length (d_l), the molecular tilt angle (β) and the intermolecular distance (D) are given in Table II. In case of 4 the meridional reflections do not split up into the typical cybotactic arrangement. This is caused by a worse orientation of this compound. The molecular length (d_{calc}) is calculated from standard bond length and angles including van der Waals radii. A significant difference between the experimental (d_l) and theoretically calculated data (d_{calc}) was observed which could not be caused by the molecular tilt angle only. A similar behaviour has been observed recently for a comparable system[16,17] and was explained as an interdigitated arrangement.

X-ray experiments on magnetically oriented samples of 6–9 show the typical cybotactic spots. A flat plate photograph for 8 is shown in Figure 3. The obtained data for the molecular tilt angle (β), the intermolecular distance (D) and the molecular length (d_l) are given in Table II. The temperature dependence of the molecular tilt angle (β) is shown in Figure 4. A linear dependence was observed in the investigated temperature interval. This was described for some *p*-azoxybenzenes which exhibit S_c-phases with a similar diffraction patterns before.[34] In contrast

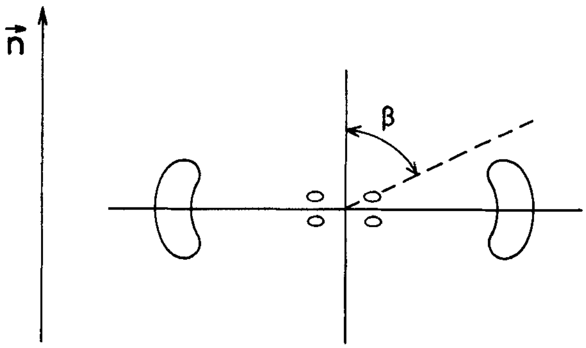

FIGURE 2 Schematic representation of the X-ray diffraction patterns for the skewed cybotactic nematic phases.

TABLE II

The obtained values for the molecular length (d_l), the intermolecular distance (D), the molecular tilt angle (β) and the calculated molecular length (d_{calc})

	T[°C]	d_l[Å]	β[°]	D[Å]	d_{calc}[Å]
1	220	32.4	28	5.2	42.6
2	228	31.5	31	5.1	42.6
4	230	28.0	—	5.1	37.6
6	111	32.5	46.5	5.0	32.2
7	113	33.1	49.5	5.0	29.8
8	112	32.6	49.0	4.9	29.7
9	116	28.5	54.5	4.9	27.3

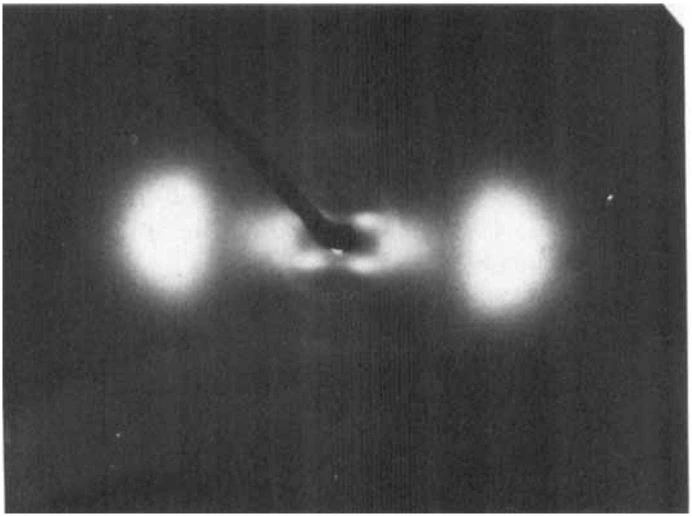

FIGURE 3 The X-ray diffraction pattern for the skewed cybotactic nematic phase of 8 at T = 84°C.

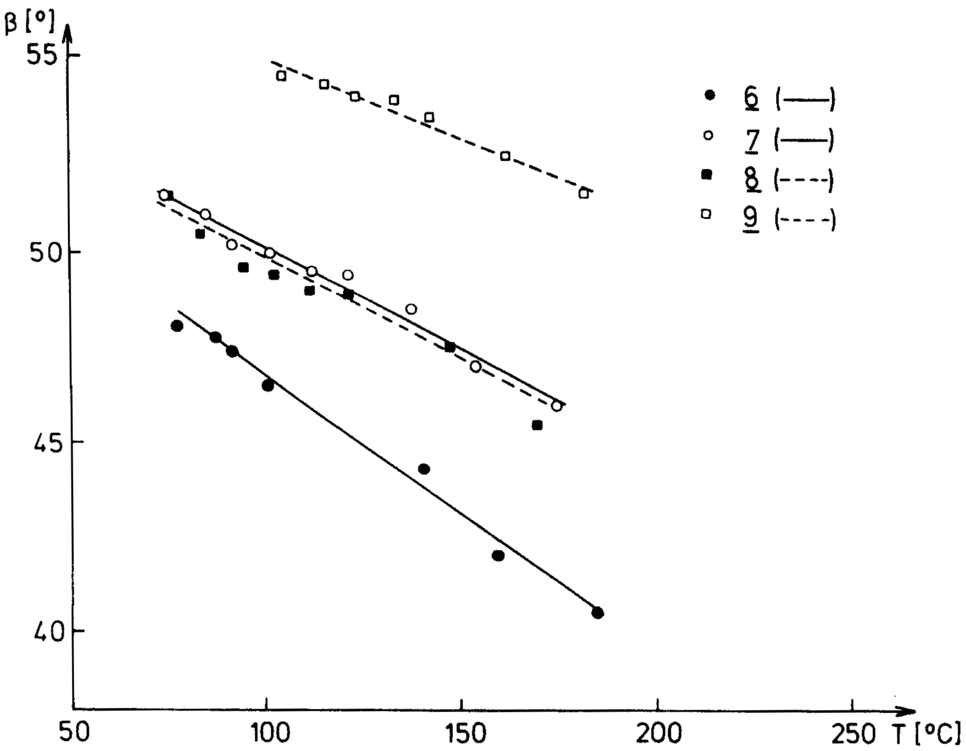

FIGURE 4 The observed molecular tilt angle (β) as a function of temperature for 6–9.

to the investigated copper(II) complexes a good agreement of the theoretically calculated data and the experimentally obtained molecular length was found.

The mesophase range of the Schiff's base complexes with copper(II) as well as those of the corresponding ligands is very broad. Yet the complexation of the Schiff's bases has reduced the mesophase range. This could be caused by the worse molecular anisotropy of the complexes compared with those of the ligands. Nevertheless a good orientation of the copper(II) complexes in magnetic fields (confirmed by X-ray investigations and magnetic measurements[9]) can be observed.

The experimental $\chi(T)$-data of the mixture of $\underline{1}$ and $\underline{2}$ are presented together with the phase transition temperatures in Figure 5. The solid phase magnetism ($\mu_{\mathrm{eff}}^{\mathrm{exp.}} = 1.878(8)\ \mu_B$; $g = 2.11(2)$) obeis the Curie-law. A $\Delta\chi > 0$ jump occurs at the phase transition crystalline (C) → nematic (N). For the description of the behaviour of a paramagnetic copper(II) containing liquid crystal within magnetic fields two different effects have to be taken into account. First the diamagnetic anisotropy which depends mainly on the number and the position of the phenyl groups within the molecule and usually is found to be more or less parallel to the director. Additionally the paramagnetic anisotropy arising from the copper(II) core has to be considered. In case of square planar Schiff's base complexes of copper(II) the main component of the paramagnetic susceptibility tensor is orthogonal to the plane of the copper(II) core.[28] This effect has been described for the liquid crystalline phase of Schiff's base complexes of copper(II) also.[5] Bikchantaev *et al.*[5] explain the orientation of their samples with the molecular long axes orthogonal to the direction of the magnetic field by a predominant paramagnetic anisotropy. Our samples show an orientation with the director parallel to the magnetic field. Therefore we suspect a predominant diamagnetic anisotropy in our case. The main difference within the molecular structure compared to Reference 5 are two additional phenyl groups and two carboxylate groups. An estimation for the paramagnetic anisotropy with respect to the director was done on the basis of single crystal susceptibility measurements[28] and E.P.R. investigations within the mesophase of similar copper(II) complexes[5] either. In case of the single crystal data $\Delta\chi$ was

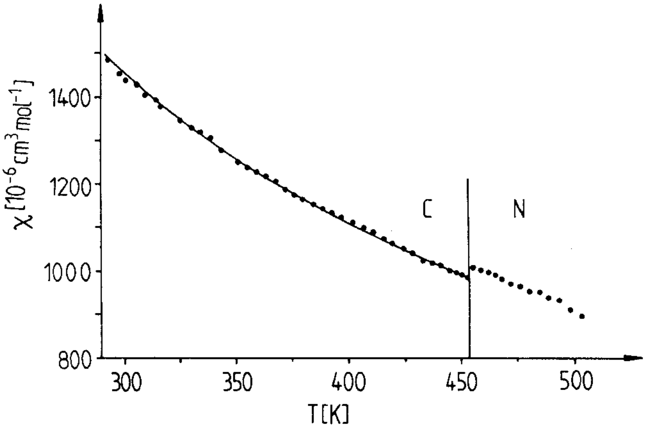

FIGURE 5 Experimental (·) and calculated (–) magnetic susceptibilities vs. temperature and phase transition T_{C-N} for the mixture of $\underline{1}$ and $\underline{2}$.

calculated from the given data parallel (K_1) and perpendicular (K_2, K_3) to the molecular long axes using Equation (4)

$$\Delta\chi = K_1 - \frac{1}{2}(K_2 + K_3). \tag{4}$$

A value of $\Delta\chi = -114 \cdot 10^{-6}$ cm^3 mol^{-1} was obtained. From E.P.R. investigations anisotropic g-factors have been obtained.[5] Using Equation (5) the anisotropic molar susceptibilities can be calculated:

$$\chi = \frac{N \cdot g^2 \cdot \mu_B^2}{3 \cdot k \cdot T} S \cdot (S + 1). \tag{5}$$

μ_B is the Bohr magneton, S is the total spin ($S = \frac{1}{2}$ for Cu^{2+}), N, k, and T are of the usual meaning. $\Delta\chi = -119 \cdot 10^{-6}$ cm^3 mol^{-1} was obtained for the E.P.R. experiments.[5] For the calculations of the molecular anisotropy we used an average value of $\Delta\chi = -117 \cdot 10^{-6}$ cm^3 mol^{-1}. Compared with the diamagnetic anisotropy arising from the six phenyl groups ($\Delta\chi = +29.85 \cdot 10^{-6}$ cm^3 mol^{-1} per phenyl group[29]; $\Delta\chi = +179.1 \cdot 10^{-6}$ cm^3 mol^{-1} per metallo-mesogen) within the molecule we obtained $\Delta\chi > 0$ ($\Delta\chi = 62.6 \cdot 10^{-6}$ cm^3 mol^{-1}). A parallel orientation of a diketonato copper(II) complex has been described by Chandrasekhar *et al.*[24] before. This molecule contains six phenyl groups also. In contrast to these results an orientation with the director perpendicular to the magnetic field has been observed for some Schiff's base complexes of copper(II) with only four aromatic rings.[5,12,16] Therefore it seems obvious that the orientation of these metallo-mesogens within magnetic fields is caused by a competition of the paramagnetic and diamagnetic anisotropy of the molecules.

From the above mentioned molecular anisotropic data ($\Delta\chi = 62.1 \cdot 10^{-6}$ cm^3 mol^{-1}) and our results from the anisotropic magnetic susceptibility measurements ($\Delta\chi = 38.5 \cdot 10^{-6}$ cm^3 mol^{-1}) we estimated an order parameter of about $S \approx 0.6$ ($T = 456$ K) which is in sufficient agreement with the data obtained from the extinction measurements in 5CB.

To investigate the behaviour of these metallo-mesogens within common liquid crystals a solution of $\underline{1}$ in 5CB was prepared. The solubility of $\underline{1}$ in 5CB was quite good. It was possible to obtain a solution of 1.9 w% of $\underline{1}$ in 5CB. Other liquid crystals have been tested also. In case of PCH7 the solubility was reduced (1.2 w%) and we got some problems with the reproduction of the obtained order parameters. A possible reason for this behaviour is the existence of microcrystallites within the mesophase of PCH7. The order parameter S of $\underline{1}$ in 5CB has been determined as a function of the reduced temperature (T_{red})

$$T_{red} = \frac{T}{T_{NI}}.$$

The result is shown in Figure 6. We also observed an increase of the transition temperature nematic-isotropic of about $\Delta T = 2.5$ K. This shows a significant

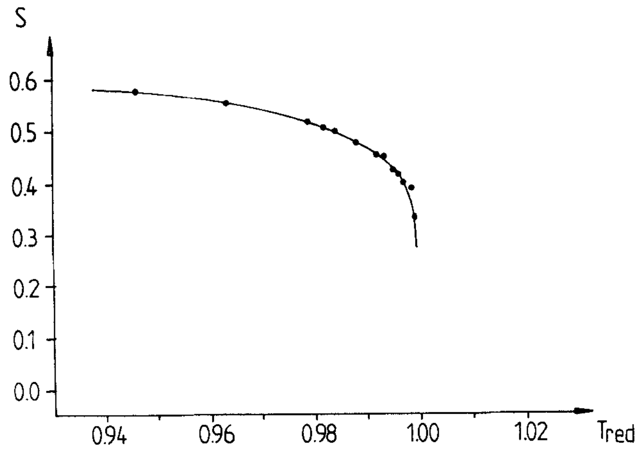

FIGURE 6 The order parameter of 1 in 5CB vs. reduced temperature.

stabilization of the liquid crystalline phase of 5CB which is possibly caused by the nematic phase of 1 and it's high clearing temperature of 275°C (Table I). An obvious stabilization of the mesophase range caused by the metallo-mesogen has been reported before.[19] In case of bis(4-n-butylstyryl-1,2-dithiolato)nickel an increase of the transition temperature nematic-isotropic of about 1.5 K (2 w%) was observed.[19] But the N-I transition temperature of the used metallo-mesogen was about 100 K below that of our compound. The maximum value of the observed order parameter (S = 0.575) is close to this observed for bis(4-n-butylstyryl-1,2-dithiolato)nickel in 5CB[19] and in the range of those observed for other guest-host systems.[30] The order parameter of pure 5CB obtained from polarized Raman scattering is in the range of about S = 0.55–0.65.[31,32] The data obtained for the metallo-mesogen solved in 5CB are nearly in the same magnitude.

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