

First Example of Coexistence of Thermal Spin Transition and Liquid-Crystal Properties

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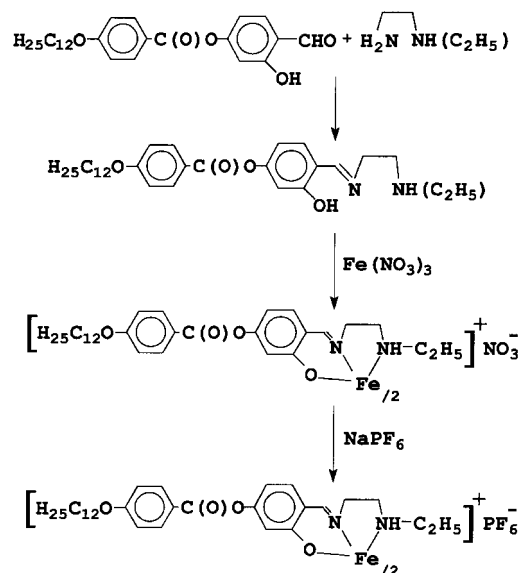
Dedicated to Professor Weyrich on the occasion of his 60th birthday

Flexibility in the synthesis of molecular assemblies based on molecular units is an important factor in achieving synergy of various interesting physical properties in modern materials. The fascinating peculiarities of spin-crossover (SC) compounds^[1] stimulated the idea of combining liquid-crystalline (LC) and SC behavior in a single material, which to the best of our knowledge has not yet been achieved.

To obtain highly ordered materials we chose the LC state as a basis for the elaboration of supramolecular organized systems with controlled physical properties.^[2] Earlier, similar approaches were used for the easy alignment by magnetic fields of LC compounds^[3] containing lanthanide ions with large magnetic moments and anisotropy.^[4] Liquid-crystalline materials with giant magnetic anisotropy were thus obtained.

The realization of synergistic SC and LC properties should lead to a combination of the sensitivity of the LC state to electromagnetic fields with the magnetic and optical properties of SC compounds, with their well-known characteristic responses to physical perturbation.^[1] The practical application of SC materials with LC properties as active media for memory storage and optical devices is appealing, and the whole traditional variety of LC technologies and techniques can be applied.

As model building blocks for systems with spin-variable properties we chose a complex of Fe^{3+} with an *N*-alkoxy-salicylidene-*N'*-ethyl-*N*-ethylenediamine ligand. Spin-crossover behavior for similar complexes was found and investigated previously.^[5] Pseudooctahedral complexes of Fe^{3+} with an N_4O_2 coordination core were prepared in a similar way to that described in ref. [5]. Schiff base ligands with elongated substituents were employed to provide the rodlike geometry and hence the LC properties of the complex, which was prepared from the condensation product of 4-(dodecyloxybenzoyloxy)-2-hydroxybenzaldehyde with *N*-ethylethylenediamine (Scheme 1). The synthesis of the complex was carried out without isolation of the intermediate products. The PF_6^-



Scheme 1. Synthesis of the liquid-crystalline Fe^{3+} complexes with an LC Schiff base ligand.

salt was obtained as black microcrystals by metathesis of the NO_3^- salt in CH_3OH , and its composition was confirmed by elemental analysis.

Liquid-crystalline properties were confirmed in the crystal state and mesophase by polarizing optical microscopy, differential scanning calorimetry (DSC), and X-ray scattering. The sample contains rodlike molecules (Figure 1) and, in the range 388–419 K, exhibits the fan-shaped texture usually attributed to the smectic A mesophase.



Figure 1. Computer simulation of the molecular structure of the LC Fe^{3+} complex (counterion omitted).

Proposed molecular packing in crystal and mesophase states, based on X-ray scattering data, are shown in Figure 2. The sharp reflection in the small-angle region ($d = 21.5 \text{ \AA}$) detected at room temperature corresponds to the length of $l = 22.6 \text{ \AA}$ of the rigid part of the molecule. Drastic changes

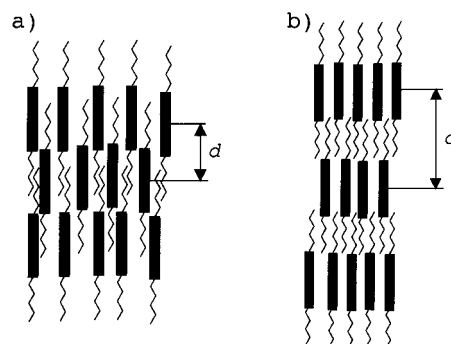


Figure 2. Proposed molecular packing of the Fe^{3+} complex in the crystal and mesophase states at different temperatures: a) starting material, crystal state: $T = 303 \text{ K}$, $d = 21.5 \text{ \AA}$; b) S_A phase, $T = 391 \text{ K}$, $d = 33.6 \text{ \AA}$.

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appear at 398 K. At this temperature the formation of the smectic layers is complete. A sharp reflection in the small-angle region ($d = 33.6 \text{ \AA}$) is detected at this temperature. This X-ray pattern indicates a disordered smectic phase. The length of the Schiff base complex, calculated by molecular modeling, is 55.3 \AA . The difference between the calculated and experimental data can be explained by interpenetration of alkyl chains of the layers (Figure 2). Alternatively, the smaller experimental smectic layer distances can be explained by strong thermal motion of the alkyl chains on heating in the mesophase and/or bilayer lamellar structure of the mesophase.

Magnetic properties were investigated in the temperature range 4.5–460 K (Figure 3). Clearly, the compound exhibits a gradual spin-crossover transition. According to the magnetic

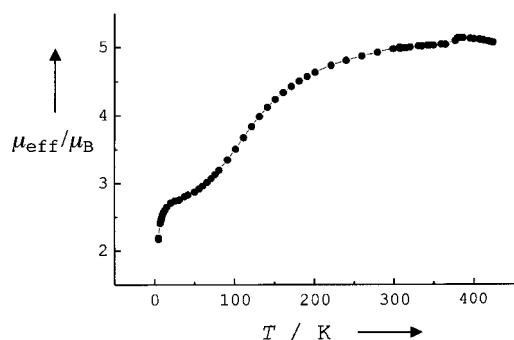


Figure 3. Temperature dependence of the effective magnetic moments $\mu_{\text{eff}} [\mu_B]$ of the Fe^{3+} complex.

susceptibility data, the transition should be almost complete both at high and low temperatures. The value of the effective magnetic moment per Fe ion, μ_{eff} , is $5.14 \mu_B$ at 400 K, instead of the $5.9 \mu_B$ expected for an Fe^{3+} complex in a high-spin state. A fraction of about 88% of low-spin Fe^{3+} follows from the magnetic susceptibility measured at $T = 4.6 \text{ K}$. The ^{57}Fe Mössbauer spectra measured in the range $4.2 < T < 293 \text{ K}$ reveal Fe^{3+} in high-spin (HS) and low-spin (LS) states and confirm the occurrence of thermal spin crossover between these states. The room-temperature spectrum (Figure 4a)

corresponds to the HS state only, whereas the Mössbauer spectrum measured at $T = 4.2 \text{ K}$ (Figure 4c) reveals two kinds of Fe^{3+} species and confirms the incompleteness of spin crossover at this temperature. The LS fraction of 86% is in good agreement with that derived from magnetic measurements; the rest is the HS fraction. The isomer shift and quadrupole splitting values at 4.2 K are $\delta = 0.26 \text{ mm s}^{-1}$, $\Delta E_q = 0.72 \text{ mm s}^{-1}$ for the HS state and $\delta = 0.01 \text{ mm s}^{-1}$, $\Delta E_q = -2.90 \text{ mm s}^{-1}$ for the LS state. The fractions of the HS and LS components, derived from the spectrum at $T = 125 \text{ K}$ (Figure 4b), are 52 and 48%, respectively. This means that the spin transition temperature $T_{1/2}$, at which both spin states are present to 50%, is around 125 K. Equal areas of both components of the LS spectra rule out the Goldanskii–Karyagin^[6] effect or texture influence. The observed pronounced asymmetry of the LS quadrupole doublet is caused by spin–spin relaxation, for which the observed temperature independence of the asymmetry is typical in the range 1.5–4.2 K. The relaxation effects are responsible for the broadening of lines of the HS component, too. The large quadrupole splitting for Fe^{3+} (LS) indicates strong distortion of the local N_2O_4 coordination environment of iron, which contributes to the electric field gradient in addition to a noncubic valence electron distribution in the split t_{2g} manifold.

A specific feature in the magnetic behavior of the studied system is the jump in the magnetic moment at $T = 380 \text{ K}$ associated with the crystal–liquid crystal phase transition. To clarify the reason for the observed magnetic anomaly, the compound was studied in the temperature range $293 < T < 425 \text{ K}$. The sample was heated in an external magnetic field of 1.5 T through the crystal–smectic phase transition. The jump of μ_{eff} from 5.04 to $5.14 \mu_B$ occurs in the range of crystal–smectic phase transition. Further heating leads to a decrease of μ_{eff} to $5.05 \mu_B$ in the isotropic phase. This value was preserved when the sample was cooled to room temperature in the presence of a magnetic field. Cooling in zero magnetic field led to the value of the magnetic moment at room temperature measured at the beginning of the experiment. The described feature was completely reproducible. Heating the sample in the temperature range $300 < T < 360 \text{ K}$ in a magnetic field of 1.5 T caused a gradual increase in the magnetic moment. This may be explained by increasing orientation of microcrystalline particles with anisotropic paramagnetic susceptibility, as the viscosity of intergrain boundaries in pre-translational regions decreases. This effect is similar to the known phenomenon of magnetic field induced texture formation (thermomagnetic processing) in paramagnetic powder samples.^[7] The orientation effect reaches its maximum in the vicinity of the transition from the crystalline (Cr) to smectic (S_A) phase because of a drastic decrease in viscosity in the pre-

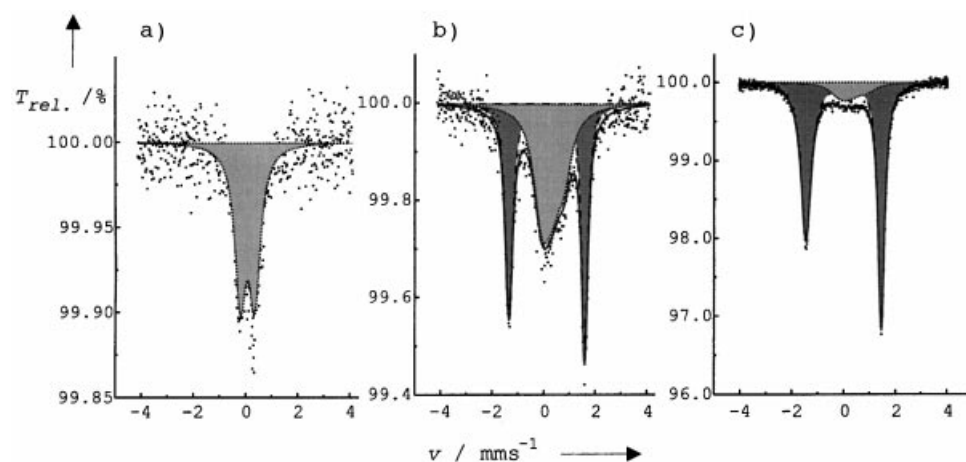


Figure 4. Mössbauer spectra at room temperature (a), 125 K (b), and 4.2 K (c). Shaded subspectra correspond to Fe^{3+} (HS) (••••) and Fe^{3+} (LS) (----).

transitional temperature range. In the smectic phase increasing temperature leads to the disappearance of long-range order, and hence the susceptibility decreases. The behavior of the magnetic susceptibility on cooling in a magnetic field of 1.5 T, with a change from the isotropic to liquid-crystalline phase (Figure 5) may be explained by magnetic anisotropy

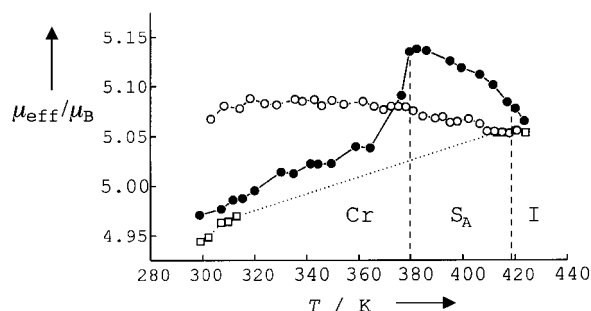


Figure 5. Effective magnetic moment μ_{eff} versus temperature for the Fe^{3+} complex in an applied magnetic field of 1.5 T. ● heating run; ○ cooling run at 1.5 T; □ cooling run at zero magnetic field. Cr: crystal, S_A : smectic A, I: isotropic phases.

caused by magnetic field induced orientation of the molecules. During the alignment of the molecules, the axis of maximum magnetic anisotropy orients itself parallel to the director in the smectic phase, and a macroscopic orientation of the sample appears. One cannot exclude the possibility that this process is accompanied by a change of the HS/LS ratio because of possible changes of elastic properties of the compound that occur during the rearrangement of the molecular packing.

In conclusion, the possibility of coexistence of spin cross-over and liquid-crystalline properties in a single compound has been demonstrated. Our efforts are directed towards enhancing the synergy between SC and LC phenomena. To achieve this we intend to chemically modify the system to increase the SC transition temperature and simultaneously decrease the transition temperature to the liquid-crystalline state. Furthermore, SC compounds containing thermochromic Fe^{2+} will be studied. Due to the presence of paramagnetic ions, the material reported here exhibits enhanced magnetic anisotropy and can be aligned by a magnetic field in the mesophase of a liquid crystal.

Experimental Section

N-ethylethylenediamine, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and KPF_6 were used as received from Aldrich. Aldehyde **1** was prepared according to the literature procedure.^[3]

2: *N*-Ethylethylenediamine (0.046 g, 0.52 mmol) was added in small portions to **1** (0.208 g, 0.52 mmol) in EtOH (30 mL). The mixture was heated for 20 min at 100 °C, and NaOH (0.021 g, 0.52 mmol) in H_2O (1 mL) was added. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1 g, 0.53 mmol) in EtOH (5 mL) was added to the resulting orange solution with stirring. A twofold excess of KPF_6 in methanol was added to the resulting suspension of the complex, which was then heated to reflux for 15 min. The product was filtered from the hot mixture. The brown precipitate was washed with methanol and dried in vacuo. Yield: 0.25 g (42%). Elemental analysis (%) calcd for $\text{C}_{30}\text{H}_{78}\text{N}_4\text{O}_8\text{PF}_6\text{Fe}$: C 59.21, H 6.87, N 4.93; found: C 59.02, H 6.94, N 5.11.

The temperatures and textures of phase transitions were determined with a polarization microscope, equipped with a hot stage and with temperature

control of better than ± 0.05 K. Differential scanning calorimetry measurements were carried out on a Perkin-Elmer DSC-2M differential scanning calorimeter (scan rate of 5 K min^{-1}).

The high-temperature X-ray measurements were obtained with a STOE STADI 2 diffractometer, equipped with a linear position-sensitive detector (STOE mini PSD). Monochromatic $\text{Cu K}\alpha$ radiation was obtained by using a curved germanium detector (111 plane). The temperature-dependent susceptibilities in the range 4.2–450 K of the powdered metallomesogen were recorded by using a Faraday-type magnetometer, equipped with an enhanced heating device operating in the range 300–450 K and an applied field of 1.5 T.^[8]

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Assembly of Encapsulated Transition Metal Catalysts**

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There is considerable interest in the encapsulation of guest molecules in the hollow framework of spherical host molecules. The first examples of containerlike molecules were obtained by performing the synthesis in the presence of the guest molecule.^[1] More recent strategies involve the construction of spherical hosts consisting of two self-complementary units held together by hydrogen bonds^[2–4] and multi-component assembly of capsules by using metal–ligand interactions.^[5, 6] Initially, only small guest molecules were

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