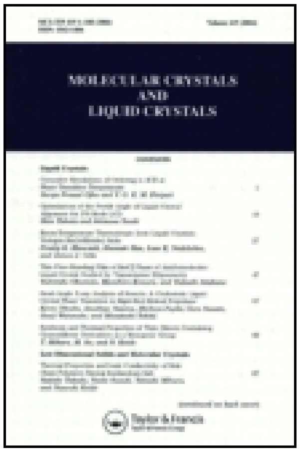

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Magnetic Investigations on a Liquid Crystalline Complex Showing Ferromagnetic Properties

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MAGNETIC INVESTIGATIONS ON A LIQUID CRYSTALLINE COMPLEX SHOWING FERROMAGNETIC PROPERTIES

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dedicated to Prof. Wolfgang Haase on the occasion of his 60th birthday

Abstract The possibility of combining the bulk magnetic properties of ferrimagnetic chains as observed for $Mn^{III}TPP(TCNE) \cdot 2$ toluene with the molecular stacking of mesogenic metal-containing meso-porphyrins prompted us to prepare and examine the dodecyloxy-substituted compound $Mn^{III}[((OC_{12}H_{25})_4TPP)](TCNE)\cdot 2$ toluene. This mesogenic complex exhibits ferrimagnetic properties below 21.4 K and considerable large coercive field of 5000 Gauss at 4.2 K.

INTRODUCTION

Interest in liquid crystals incorporating transition metal ions has primarily arisen from the special magnetic and electronical properties of these materials [1,2]. A great deal of current research has been devoted to metallomesogens on account of their magnetic properties [3,4,5,6,7]. The structural order in a mesogenic phase may provide the existence of magnetically ordered structures. However, materials which combine mesogenic with ferro- or ferrimagnetic exchange coupling or bulk properties such as ferro- or ferrimagnetism have not been reported.

Detailed investigations on porphyrin-based electron transfer compounds of the type $[Mn^{III}(TPP)](TCNE) \cdot 2$ toluene (TPP= tetraphenylporphyrin; TCNE= tetracyanoethylene) [8] were recently reported by Miller and Epstein.[9]. The structure determination identified a quasi-1-D alternating chain structure with $TCNE^-$ bridging two manganese(III) ions through nitrogen atoms in trans-position and the presence of two toluene solvate molecules per chain unit.

In this contribution, we present the results of the static and AC-susceptibility measurements as well as magnetization measurements on the mesogenic complex $[Mn^{III}((OC_{12}H_{25})_4TPP)](TCNE)\cdot 2$ toluene (see Figure 1).

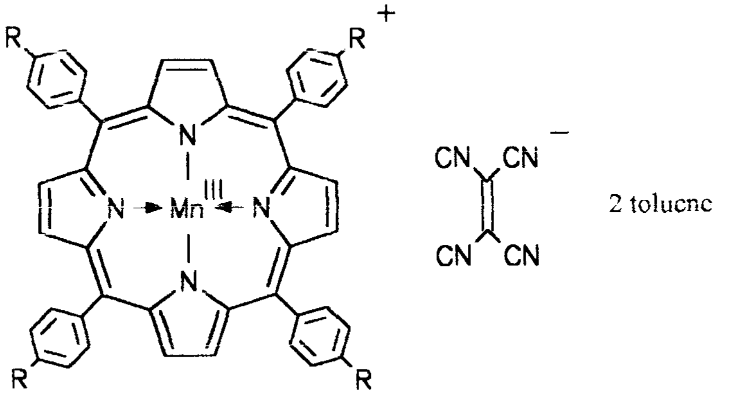

FIGURE 1 Chemical structure of the investigated mesogenic compound, R = $OC_{12}H_{25}$

EXPERIMENTAL PART

Synthesis

The synthesis of the complex was carried out according to the method described by Summerville et al. [8]. The ligand $(OC_{12}H_{25})_4TPP$ was synthesized as described by Thomas and Martell [10]. Details have been already published in a previous paper [11].

Liquid Crystalline Behaviour

The phase behaviour was observed with a polarizing microscope (Leitz Orthoplan Pol). A differential scanning calorimeter (Perkin Elmer DSC-2C) was also used for this purpose as well as for determining the enthalpies of phase transitions.

X-ray diffraction measurements were performed by a focusing horizontal two circle diffractometer (Stoe Stadi2) equipped with a modified oven. The $CuK_{\alpha 1}$ radiation (λ = 1.54056 Å) is focused by a curved Ge(III) monochromator. For the fast diffractometry a linear position sensitive detector (Stoe Mini PSD) was used.

Magnetic Susceptibility Measurements

Magnetic susceptibility data were collected in the temperature range 4.2-300 K using a Faraday system consisting of a CAHN D-200 microbalance. The applied field was ≈ 1.5 T. The magnetic susceptibilities in the temperature range of 300-460 K were measured in the heating mode by a similar equipment, modified for this range.

AC susceptibility measurements were obtained using a Lake Shore mutual inductance susceptometer. The real (χ') and the imaginary (χ'') components of the complex susceptibility were recorded with increasing temperature beginning from 4.2 K. The results presented here were obtained for the frequency ω_{ac} and the amplitude H_{ac} of the excited magnetic field equal to 111 Hz and 10 Oe, respectively at zero static magnetic field. Additional experiments were carried out varying frequency (ω_{ac}=33; 111; 666 Hz) and amplitude of the alternating field H_{ac} (1; 10 Oe) as well as the strength of the static field (H_{stat}=0; 100 Oe).

Magnetization Measurements

The magnetization measurements were performed by means of a Lake Shore 7225 versatile instrument using an extraction technique.

RESULTS AND DISCUSSION

Liquid Crystalline Behaviour

In contrary to the results published by Kugimiya and Takemura based on their DSC-investigations [12], our X-ray investigations could not confirm mesogenic behaviour for the free porphyrin ligand $(OC_{12}H_{25})_4TPP$ [11].

The investigated Mn(III)-containing compound exhibits a discotic mesophase in the temperature-range 108-155 °C, the thermodynamic data obtained by DSC- and polarizing microscope techniques are given in Figure 2:

$$\mathrm{C} \xrightarrow[(20.6)]{108} \mathrm{D_{ho}} \xrightarrow[(10.1)]{155} \mathrm{I}$$

FIGURE 2 Thermodynamic data of the investigated compound: Phase transition temperatures [°C] and -enthalpies [kJ/mol]

The complex displays well-behaved mesomorphism with relatively small mesophase-to-isotropic transition enthalpies.

Figure 3 shows the X-ray diffraction pattern at 123 °C.

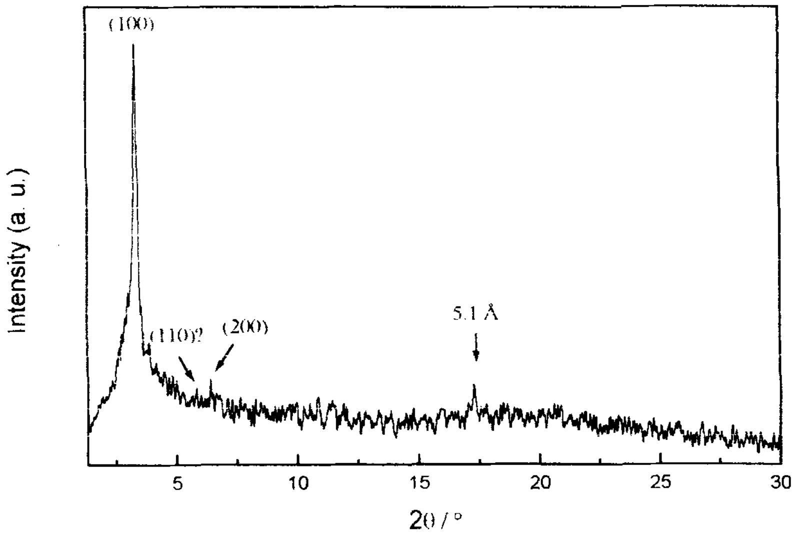

FIGURE 3 X-ray diffraction from the D_{ho} phase at 123 °C

The strong low angle peak indicates a lamellar structure and can be attributed to a hexagonal columnar lattice. It is hence assigned as the (100)-reflection corresponding to an intercolumnar distance of 30.8 Å. This spacing is in very good agreement with the expected length of the molecular "side" (from the end of one alkylchain to the end of an adjacent alkyl chain as reported in ref. 13). Further confirmation of the hexagonal structure is given by the other low angle peak at 13.7 Å, which is approximately where the (200)-reflection of a hexagonal lattice is expected. The (110)-reflection has a very weak intensity.

The weak wide angle peak at 5.1 Å can be most probably referred to the distance between porphyrin and the center of $TCNE^-$, which is similar in crystalline Mn(III)-Porphyrin / TCNE-complexes (≈5Å) [14]. It can be concluded from these results that the complex shows a discotic hexagonally ordered columnar (D_{ho}) mesophase.

Magnetic Susceptibility Measurements

As described in our previous publication[11], the compound exhibits essentially the same temperature dependency of the effective magnetic moment μ_{eff} as reported for $[Mn^{III}(TPP)](TCNE)\cdot 2toluene$ [9]:

To describe the strength of the intrachain coupling of such a 1-D- ferrimagnetic (S_A:S_B) chain, we used the analytical expression proposed by Drillon et al. [15]. The best parameters obtained from fitting the $\chi(T)$-data above 100 K are g=2.19 and J_{intra}=-123.7 cm^{-1}. The strength of the antiferromagnetic exchange interaction between Mn(III) and $TCNE^{-}$ is not essentially influenced by the phase transition crystalline to discotic, i.e. the antiferromagnetic exchange interaction between Mn(III) and $TCNE^{-}$ is maintained in the mesogenic phase[11]. In spite of the large distance between spins of adjacent chains (30.8 Å), the J-value of -123.7 cm^{-1} is surprinsingly high. Some work is in progress to investigate the nature of the inter-chain interaction.

In order to get a deeper insight in the nature of the long-range magnetic order of the mesogenic Mn(III)-porphyrin, we carried out AC susceptibility measurements. The most important feature of the AC-measurement is the onset of a pronounced out-of phase χ''-component at zero static magnetic field with maxima at 21 K (Fig. 4).

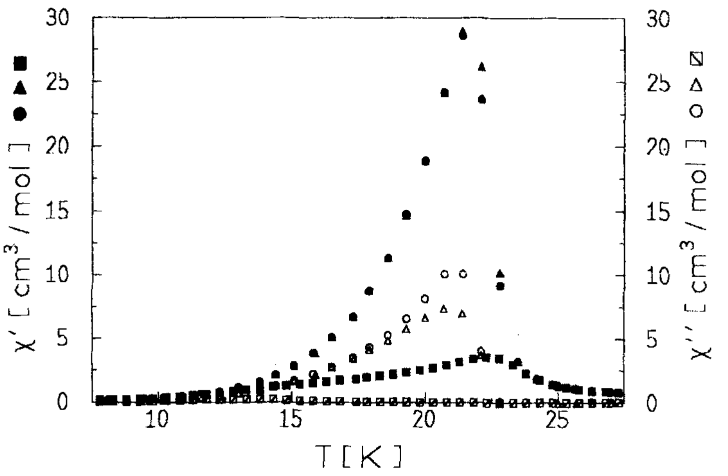

FIGURE 4 Temperature dependence of the χ' ((•): ω_{ac} = 10 Hz; (▲): H_{ac} = 1 Oe) and χ'' ac-susceptibility component ((o): ω_{ac}= 10 Hz; (Δ): ω_{ac} = 111 Hz) for the investigated compound at zero static magnetic field and applied static field (■):χ'; (□): χ''; H_{stat} = 100 Oe; ω_{ac}=111 Hz)

The $\chi'(T)$-curves exhibit relative sharp maxima at 21.4 K. These results clearly indicate the presence of net magnetic moments at zero applied field in the complex. The relative high values of χ'' with respect to the corresponding magnitude of χ' give strong evidence for the existence of a 3d-ferrimagnetic ordered state below 21.4 K (corresponding to the maximum of the $\chi'(T)$-curve).

The in-phase susceptibilty values $\chi'(T)$ in the temperature region T>70 K coincide with those obtained by static magnetic susceptibility measurements at 1.5 T. The decrease in $\chi'(T)$ below the maxima is probably connected with the increasing domain wall stiffness with decreasing temperature as common in molecular based ferromagnets exhibiting

anisotropy and low magnetic density. Such systems can be compared with weak ferromagnets and domain wall mobility is almost impossible so that χ' should drop rapidly from a maximum immediately below the T_c [16].
It should be mentioned that a similar situation was reported for $V(TCNE)_2 \cdot 1/2\, CH_2Cl_2$[17, 18, 19].

In order to obtain further informations about the nature of the long-range order, we carried out some additional AC-experiments varying the frequency ω_{ac} and the amplitude H_{ac} of the alternating field as well as the strength H_{stat} of the static field (Figures 4 and 5).

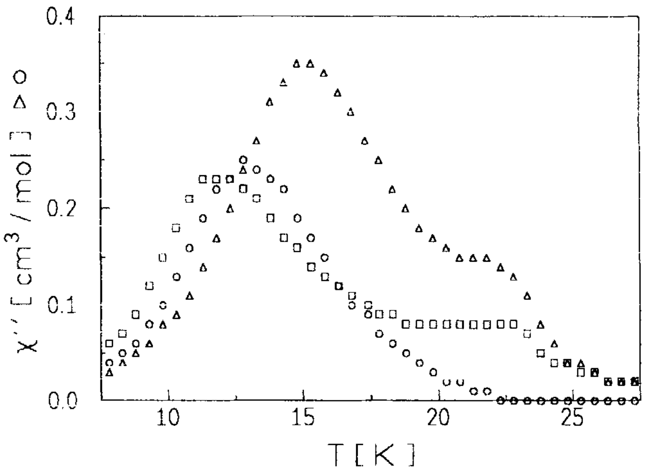

FIGURE 5 Temperature dependence of the χ'' ac-susceptibility component in the temperature region 7.5 - 27.5 K obtained at H_{ac} = 10 Oe for different amplitudes ω_{ac} ((□): ω_{ac} = 33 Hz; (O): ω_{ac} = 111 Hz; (Δ): ω_{ac} = 666 Hz), applying a static field of H_{stat} = 100 Oe

As expected, the absolute value of the $\chi'(T)$-maximum is only slightly influenced by the frequency ω_{ac} and is not affected by the amplitude H_{ac}. The magnitude of this $\chi'(T)$-maximum decreases, if one applies a static magnetic field (100 Oe), whereas its corresponding temperature remains unchanged (Figure 4). Applying a static magnetic field of 100 Oe, the χ''-signal at 21 K decreases and appears now as a shoulder in the $\chi''(T)$-curve (Figure 5).

The weak $\chi''(T)$-maximum at ≈12 K observed in the case H_{stat}=100 Oe (Figure 5) is most probably connected with a transition from a ferrimagnetic ordered state into a reentrant spin glass, as reported for $(Fe_{0.65}Ni_{0.25})_{1-x}Mn_x$ [20]. In accordance with this interpretation, we observed an increasing of magnitude as well as temperature of this $\chi''(T)$-signal with increasing frequency ω_{ac}.

The existence of a spin-glass-phase suggest that there is a frustration in the magnetic interactions, which originated from random exchange and random anisotropy.

In the discotic phase, the disk-like molecules tend to be parallel to the axis of the director n, the degree of structural order can be described by a order parameter $S<1$. If this structural disorder of the discotic phase is maintained even in the powdered state (i.e. glass-type behaviour), one can assume that topological disorder might be the origin for such randomness.

Therefore, the direction of the magnetic anisotropy is randomly distributed and compete with the exchange interaction to orient each moment in the network: At higher temperatures, the exchange interaction favors long-range ferromagnetic coupling. so there must be ferromagnetic clusters of spins at small distances. Below the freezing temperature, however, the anisotropy energy is larger than the exchange energy and the orientation of any spin is determined by the direction of the local anisotropy.

Figure 6 shows the M(H)-curves for different temperatures:

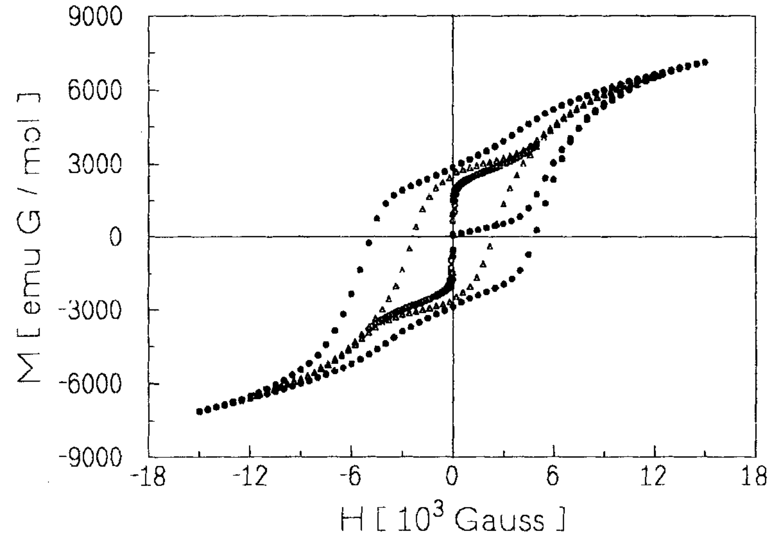

FIGURE 6 Magnetization vs. field for the mesogenic compound; (•): T= 4.2 K, (Δ): T= 5.7 K, (O): T= 15.7 K

Strong magnetic hysteresis is observed at 4.2 K. The shape of this hysteresis, especially the large H_C-field was found to be equal for different preparations of the sample. The coercitive-field at 4.2 K is about 5000 Gauss. After switching off the magnetic field, we observed a time-dependent magnetization, which indicates that the spin-state of the system is essentially metastable. The remanant magnetization continiously decreases from a initial value of about 3200 emu G / mol to a upper limite of 2500 emu G / mol. The S-shape virigin-magnetization curve may be attributed to a spin-flop-transition of a metamagnetic system. This is in agreement with a arrangement of coupled spins including entities carrying large net magnetic moments which are coupled in a antiferromagnetic fashion. If an external field is applied parallel to the easy axis of antiferromagnetic alignment, then at a certain field value the antiferromagnetic arrangement is broken up.

Figure 7 displays the isothermal remanent magnetization (IRM) as function of temperature, indicating compensation phenomena as suggested by Curely et al [21]. Since the single ion-anisotropy of Mn(III) is considerable high, the magnetic moment of the Mn(III)-ions could rotate toward the direction of the magnetic field and compensate the sublattice magnetization of the TCNE S=1/2-spins. For our mesogenic compound, we observed a compensation point at about 3 K below T_C, the sublattice magnetization within the two different spin systems vary differently under thermical activation.

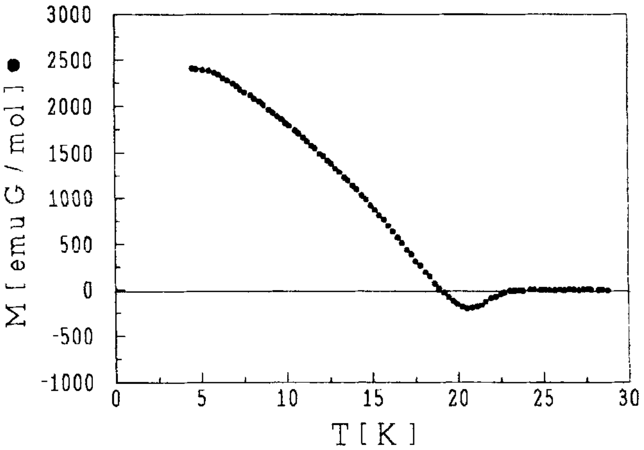

FIGURE 7 Isothermal remanent magnetization vs. temperature

CONCLUSION

For a first time, magnetic properties of a liquid crystalline metallomesogen were reported which are substantially combined with ferrimagnetic properties. Furthermore, this discotic complex shows a considerable high coercitive field.

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