

# MAGNETIC INVESTIGATIONS ON LIQUID CRYSTALLINE METALLOPOLYMERS

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**Abstract** In this contribution, magnetic investigations on materials, which essentially combine mesogenic and polymeric properties, were presented. In the glassy and the smectic phase of a copper(II) containing polymer we observed remarkable antiferromagnetic exchange interactions between the copper centers, whereas in the isotropic phase, the magnetism followed the Curie-Weiss law. The monomeric model compound showed Curie-Weiss behaviour. In addition, we describe the magnetic behaviour of mesogenic compounds, resulting from the incorporation of rare-earth ions in chelating units of the liquid-crystalline Schiff base polymer.

## INTRODUCTION

Our previous investigations dealing with magnetic properties of metallopolymers (A) 1,2 and metallomesogens (B) 3,4,5,6,7,8 have prompted us to prepare materials which combine both mesogenic and polymeric properties and examine their magnetic behaviour.

A) In some cases, polymers containing paramagnetic spin centers are found to exhibit magnetic exchange interactions, which take not place in related model compounds of non-polymeric structure 9,10,11. Although the strong role of structural features provided by the polymer backbone conformation and the existence of exchange pathways through atoms situated in the chain was pointed out, no systematic investigation to help for a full clarification of this phenomenon was presented. Therefore, our previous studies concerning the magnetic behaviour of metallopolymers with discrete transition metal complex units involved a detailed characterization of appropriate crystalline model compounds. In this way, we have analysed the magnetic behaviour of copper metallopolymers containing N-pyridoxalidene or N-salicylidene chelating units in their side chain 1,2. Considerable antiferromagnetic exchange interactions were established. The nature of these interactions were explained by

structural and magnetic investigations on the related low-molecular mass model compounds.

B) Magnetic susceptibility measurements can be used as a valuable tool for the structural characterization of liquid-crystalline transition metal complexes under several aspects:

- coordination type of the metal ion.
- detection of strong intramolecular exchange interactions.
- development of models for the arrangement of spin-coupled ions in the crystalline and mesogenic phases.

Up to date, however, we have observed no cooperative behaviours in the liquid-crystalline phase of these low-mass mesogenic compounds, although theoretical considerations suggest this<sup>12</sup>.

In this contribution, we report on the synthesis and magnetic investigation of methacrylate polymers with Schiff-base complexes in the side chain, exhibiting liquid crystalline behaviour. We focused our interest on the specific magnetic properties of materials which combine polymeric and mesogenic properties.

The strategy of synthesis of our polymers was to combine the high experience on preparation of Schiff-base complexes and long enough side chain alkyl substituent looking to reach liquid crystallinity and remarkable magnetic properties within a polymer structure after introducing a paramagnetic metal ion.<sup>13</sup>

Here, we present the results of our magnetic investigations on liquid-crystalline Cu(II)-, Nd(III)- and Er(III)-polymers obtained by complexation of chelating polymers as shown in Figure 1.

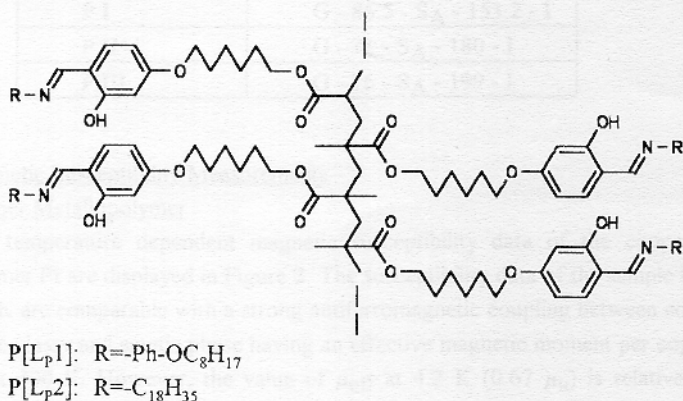


FIGURE 1 Schematic representation of the chemical structure of the polymers P[L<sub>p</sub>1] and P[L<sub>p</sub>2] used for complexation.

EXPERIMENTAL PARTSynthesis

For the preparation of liquid crystalline metallopolymers containing discrete transition metal complexes in their side chain, we used different functionalized polymethacrylates (see Figure 1) as starting materials. They contain N,O-bidentate pendent groups capable of forming stable complexes with different transition metal ions.

TABLE 1 Schematic representation of the essential composition of the investigated metallopolymers. Here  $L_p$  refers to a repeating unit of the polymer, containing one N,O-chelating group.

Compound	Composition
PI	$Cu(L_p1)_2$
PII	$Nd(L_p2)_2(NO_3)_2$
PIII	$Er(L_p1)_2(NO_3)_2$

The resulting polymers summarized in Table 1 are soluble in different organic solvents like Toluene or Tetrahydrofuran. The molecular weights for the starting material P[Lp1] and the Cu-metallopolymer PI were determined by Gel Permeation Chromatography using PMMA as standard and tetrahydrofuran as eluent. The weight averaged molar mass  $\bar{M}_w$  and polydispersity index were 81.500 (2.1) and 20.700 (1.2) respectively. Details of synthesis as well as elemental analysis and other analytical results will be presented in a separate paper.<sup>13</sup>

In the case of the copper polymer PI two different metal salts ( $Cu(OAc)_2$  and  $CuCl_2$ ) were used for complexation in order to investigate the influence of the counterions on the reaction and their possible inclusion in the final structure. Although both samples have a slight difference in the degree of polymerization, their physical properties are in principle identical. Here, we describe the properties of the Cu-polymer synthesized from  $Cu(OAc)_2$ , the data of the other polymer will be included in a separate paper.<sup>13</sup>

Liquid Crystalline Behaviour

The liquid crystalline properties were investigated by polarizing microscopy, Differential Scanning Calorimetry and X-ray diffraction techniques.<sup>13</sup>

### Magnetic Susceptibility Measurements

Temperature dependent susceptibilities of the samples were recorded using a Faraday-type magnetometer in the temperature range of 4.2-300 K. The measurements presented were done using a computer controlled Cahn D-200 microbalance and a Bruker B-MN 200/60 power supply<sup>14</sup>. The applied field was  $\approx 1.5$  T. The magnetic susceptibilities in the temperature range of 300-500 K were measured in the heating mode of an equipment described in ref. 15, modified for this range. Diamagnetic corrections of the molar magnetic susceptibilities of the compounds were applied using Pascal's constants.<sup>16</sup> The  $\chi(T)$ -fits were performed with programs developed in our group.

## RESULTS AND DISCUSSION

### Liquid Crystalline Behaviour

The phase transition temperatures of the liquid crystalline polymers PI, PII and PIII are summarized in Table 2.

TABLE 2 Transition Temperatures ( $^{\circ}\text{C}$ ) for the mesogenic polymers determined by differential scanning calorimetry.

Compound	Phase behaviour
P I	G - 86.5 - S <sub>A</sub> - 153.2 - I
P II	G - 78 - S <sub>A</sub> - 180 - I
P III	G - 76 - S <sub>A</sub> - 199 - I

### Magnetic Susceptibility Measurements

#### Copper Metallopolymer

The temperature dependent magnetic susceptibility data of the copper containing polymer PI are displayed in Figure 2. The susceptibility data of the sample between 4,2-420 K are comparable with a strong antiferromagnetic coupling between copper centers in the glassy and smectic phase having an effective magnetic moment per copper of  $1.55 \mu_{\text{B}}$  at 300 K. However, the value of  $\mu_{\text{eff}}$  at 4.2 K ( $0.67 \mu_{\text{B}}$ ) is relatively high with respect to the reduced magnetic moment at room temperature. This can be explained in terms of a remaining part of monomeric (i.e. non-coupled) copper sites, which obey a Curie- or Curie-Weiss law. It must be pointed out that in the isotropic phase of the polymer the antiferromagnetic exchange interactions disappeared and we observe the behaviour of magnetically isolated copper(II) ( $\mu_{\text{eff}}=1.87 \mu_{\text{B}}$  at 430 K).

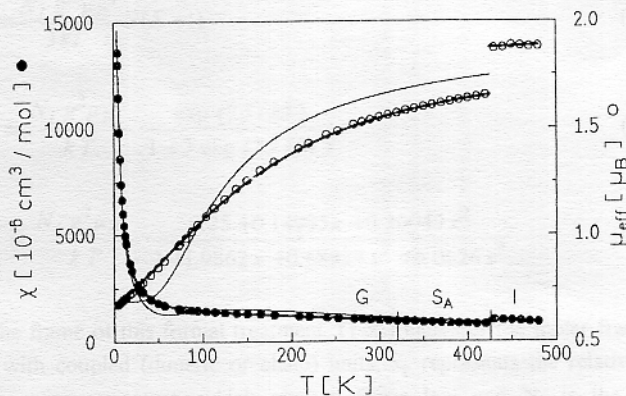


FIGURE 2 Magnetic susceptibilities and effective magnetic moments for PI in the range 4.2–480 K. In the glassy and smectic phase, the broad lines based on a fit using the chain model (Eq. (1)), whereas the narrow lines referred to a fit using the dimer model (Eq. (2)). A fit to the Curie-Weiss law was carried out for the data in the isotropic phase (for details see text).

The IR spectra in the region of 4000 to 200  $\text{cm}^{-1}$  of the crosslinked polymer PI synthesized from  $\text{Cu}(\text{OAc})_2$  completely correlates with the spectra of the polymer derived from  $\text{CuCl}_2^{13}$ , in both cases all ligands act as N,O-bidentate chelates. Accordingly, the temperature dependency  $\chi(T)$  for both polymers are comparable, although the starting copper salts are different. The counterion ( $\text{Cl}^-$  or  $\text{OAc}^-$ ) is not involved in the polymer structure and does consequently not influence the exchange interactions. Therefore, our structural proposal implies an arrangement such as shown in Figure 3 which is mainly related to  $\text{Cu}(\text{L}_p)_2$ -composition.

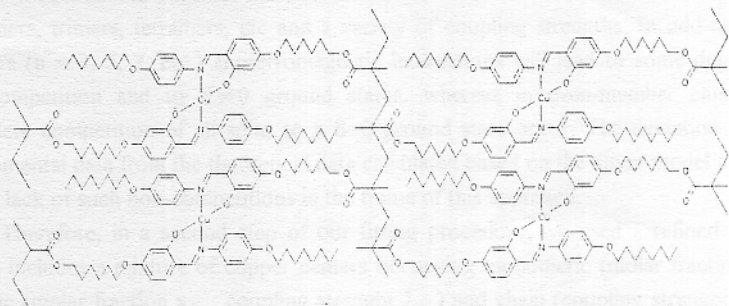


FIGURE 3 Proposal for the basic chemical structure  $\text{Cu}(\text{L}_p)_2$  of PI.

The proposed model given in Figure 3 implies the occurrence of square-planar coordinated monomeric, i.e. non-coupled copper ions. However, superexchange mechanism via axial interactions such as displayed in Figure 4 may provide an efficient pathway to realize spin-pairing and antiferromagnetic exchange interactions. Such kind of axial interactions are essentially connected with five or six-fold coordinated copper species in the polymer.

In principle, we can consider two possible selected structural arrangements based on axial interactions: the spin centers can be linked as dimers (Figure 4a) or in a more extended chain motive (Figure 4b). Moreover, an adequate model for the magnetic behaviour in the polymers involves a mixture of non-interacting and antiferromagnetic coupled copper species.

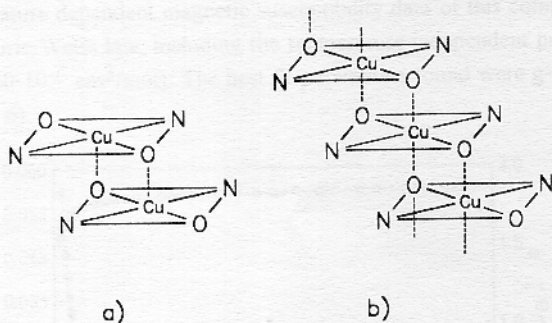


FIGURE 4 Schematic representation of different structural arrangements in the polymer: a) dimer; b) 1-D-Heisenberg linear-chain model.

Assuming that these axial interactions are most probably the origin of the antiferromagnetic coupling and keeping in mind the random polymeric structure which leads to some degree of structural disorder the magnetic data will be analyzed.

The simplest model allowing an interpretation is the assumption of a mixture of monomeric and coupled copper units, considering only one coupling strength  $J$ .

In accordance with this, we have fitted the magnetic data to Eq. (1) (dimer model) and Eq. (2) (1-D-Heisenberg, linear-chain model).

$$\chi = (1 - x_p) \chi'' + x_p \chi' + N_\alpha \quad (1)$$

$$\chi = (1 - x_p) \chi''' + x_p \chi' + N_\alpha \quad (2)$$

using

$$\chi^I = \frac{N_L g^2 \mu_B^2}{3kT} S(S+1) \quad (3)$$

$$\chi^{II} = \frac{N_L g^2 \mu_B^2}{kT} \cdot \frac{\exp(2J/kT)}{1 + 3 \exp(2J/kT)} \quad (4)$$

$$\chi^{III} = \frac{N_L g^2 \mu_B^2}{kT} \cdot \frac{0.25 + 0.14995x + 0.30049x^2}{1 + 1.9862x + 0.68854x^2 + 6.0626x^3} \quad (5)$$

In the frame of this formal treatment,  $(1-x_p)$  indicates the molar fraction of sites occupied with coupled (dimeric or chain) units;  $x_p$  represents the relative amount of monomeric copper centers, which obey a Curie law and  $N_\alpha$  is the temperature independent paramagnetism. The results are summarized in Table 3:

TABLE 3 Results of fitting of the susceptibility data in the glassy and smectic phase for PI according to dimeric (Eq. (1)) and 1-D-Heisenberg (Eq. (2)) model.

g	J(cm <sup>-1</sup> )	X <sub>p</sub> (%)	Equation
2.12	-84.1	15.5 %	1
2.12	-84.2	12.8 %	2

The better fit over the complete temperature range was obtained with the chain model (Eq. (2)). However, due to the relatively high amount of paramagnetic (i.e. monomeric) centers, it is difficult to exclude the existence of dimeric units only on the basis of an analysis of the magnetic data. By discussing the model used we have to keep in mind the random polymer backbone conformation in the metallopolymer. A more refined model should consider the existence of clusters with different nuclearities such as dimers, trimers, tetramers, etc and a variety of coupling strengths. In odd-member clusters ( $n = 3, 5, 7$ , etc.) antiferromagnetic interactions will lead to some degree of non-competition and to  $S \neq 0$  ground states, whereas in even-member clusters a complete competition of all spins to a  $S=0$  ground state occur. The deviation of the experimental data from the theoretical data calculated based on the dimer model are due to the lack of such non-competitions in the frame of this approach.

Therefore, in a second step of our fitting procedure, we used a refined model which includes a mixture of copper centers occupying monomeric (molar fraction  $x_p$ ), dimeric (molar fraction  $x_{\text{dim}}$ ; coupling strength  $J_{\text{dim}}$ ) and chain (coupling strength  $J_{\text{chain}}$ ) sites. The improved fit yield  $g=2.11$ ;  $J_{\text{chain}}=-84 \text{ cm}^{-1}$ ,  $J_{\text{dim}}=-87 \text{ cm}^{-1}$ ,  $x_{\text{dim}}=8.7\%$  and  $x_p=13.2\%$ .

It must be pointed out that in the monomeric non mesogenic Schiff-base compound M1 of similar structure (Figure 5), no comparable degree of antiferromagnetic exchange interaction was observed.

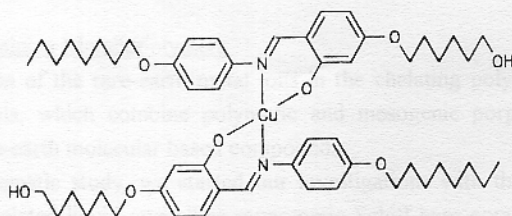


FIGURE 5 Chemical structure of the monomeric model compound M1.

The temperature dependent magnetic susceptibility data of this compound can be described by a Curie-Weiss law, including the temperature independent paramagnetism for Cu(II) ( $N_A = 60 \cdot 10^{-6} \text{ cm}^3/\text{mol}$ ). The best fit parameters found were  $g=2.12$  and  $\theta=-1,7 \text{ K}$  (see Figure 6).

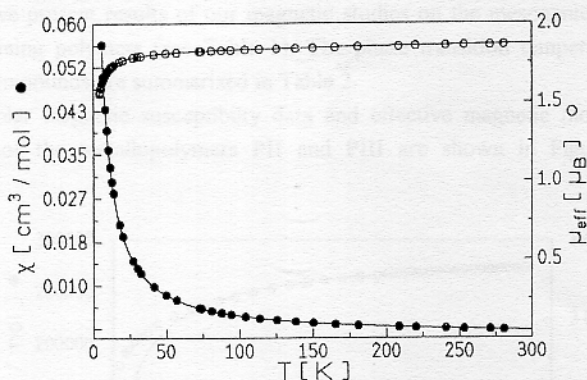


FIGURE 6 Magnetic Susceptibilities and effective magnetic moments for M1 in the temperature range of 4.2-300 K.

The occurrence of antiferromagnetic exchange interactions in a metallopolymer containing discrete transition metal complex units is worth to be discussed more in detail.

A similar situation was observed for polyacrylates containing triphenylporphinato-silver(II)<sup>10</sup>, tetraphenylporphinato-cobalt(II) or chloro-tetraphenylporphinato-iron(III) complexes<sup>11</sup> in their side chain. Although examinations on these compounds include no detailed structural analysis, the authors assume that pathways via atoms situated in the chain play an important role for the occurrence of the exchange interactions effects.



It must be pointed out that the relevant common feature of these representative examples and our copper(II) polymers is the attachment of square-planar- or five-fold-coordinated metal sites on a polymer backbone, but in our case, via a more flexible  $(\text{CH}_2)_6$ -spacer. We have to interpret the antiferromagnetic coupling behaviour either through superexchange or dipolar interactions, the former is most probably (Figure 4).

The magnitude of the exchange coupling constant  $J$  in a  $\text{Cu}-(\mu\text{-OR})_2\text{-Cu}$  bridged unit is mainly determined by the  $\text{Cu}-(\mu\text{-O})\text{-Cu}$ -angle, the influence of other sterical features such as the  $\text{Cu-O}$  or  $\text{Cu-Cu}$  distances is not so pronounced. It is well established that for  $\text{Cu}-(\mu\text{-OR})_2\text{-Cu}$ -bridges, the sign and strength of exchange interaction is very sensitive to variations of the  $\text{Cu}-(\mu\text{-O})\text{-Cu}$ -angles.<sup>17</sup>

Although most compounds which possess a  $\text{Cu}$ -arrangement such as shown in Figure 4 are dimers and have a ferromagnetic ground-state, it was pointed out that certain structural requirements must be met in order to obtain the  $S \neq 0$ -ground-state.<sup>18</sup>

Therefore, the large magnitude of  $J$  in our copper(II) metallopolymers is not essentially connected with closer axial  $\text{Cu-O}$ -contacts in the polymer compared to related monomeric compounds and can rather be explained in terms of relative large  $\text{Cu}-(\mu\text{-O})\text{-Cu}$  angles.

Moreover, the specific arrangement of the copper(II)-ions which leads to the 1-D-Heisenberg behaviour is connected with a combination of polymeric and liquid-crystalline properties: In the isotropic phase these interactions vanish and we observe a normal Curie-Weiss-behaviour ( $g=2.13$ ,  $\theta=-12.7$  K).

A structural model for the  $S_A$ -phase can be seen in Figure 7 as projection along the directors direction.

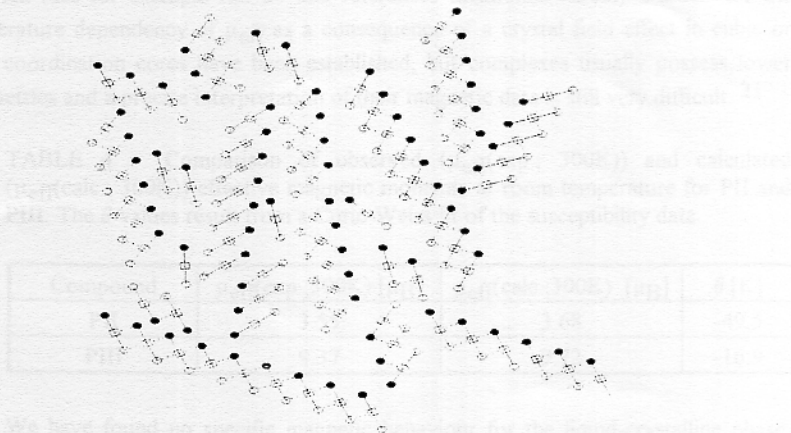


FIGURE 7 Structural model for the  $S_A$ -phase. The full and open circles represent the Schiff-base ligands oriented in two antiparallel directions, the squares represent the  $\text{Cu}$ -atoms.

May be, in the layered  $S_A$ -phase, oligomers with exchange coupled units are randomly ordered. Although there is no clear evidence for the pronounced far-range liquid-crystalline effect.

### Rare-Earth Containing Metallopolymers

The incorporation of the rare-earth metal ions in the chelating polymers  $L_{p1}$  or  $L_{p2}$  leads to materials, which combine polymeric and mesogenic properties with those expected for rare-earth molecular based compounds.

For a systematic study, we started our investigations with the preparation and examination of related liquid-crystalline monomeric Schiff-base complexes, the results will be reported elsewhere<sup>19</sup>. Magnetic susceptibility data and other analytical data of different  $M=Tb(III)$ ,  $Gd(III)$ ,  $Dy(III)$ -metallomesogens with  $N,O$ -bidentate Schiff base ligands  $L$  suggest a composition  $M(III)L_3(NO)_2$ . The temperature dependent magnetic susceptibility data are in agreement with those reported for molecular based rare-earth compounds.<sup>20</sup> For the  $Tb(III)$ -complex, we observed characteristic orientation behaviour from X-ray and magnetic investigations, governed by the paramagnetic anisotropy of the compound.

Here, we present results of our magnetic studies on the mesogenic  $Nd(III)$ - and  $Er(III)$ -containing polymers (see Table 1). The phase transition temperatures of this mesogenic compounds are summarized in Table 2.

The molar magnetic susceptibility data and effective magnetic moments versus temperature of the metallopolymers PII and PIII are shown in Figure 8 and 9, respectively.

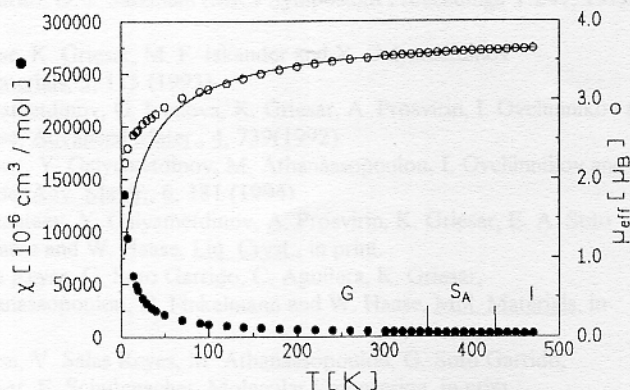


FIGURE 8 Magnetic susceptibilities and effective magnetic moments for the  $Nd(III)$ -containing polymer PII in the temperature range of 4.2-480 K.

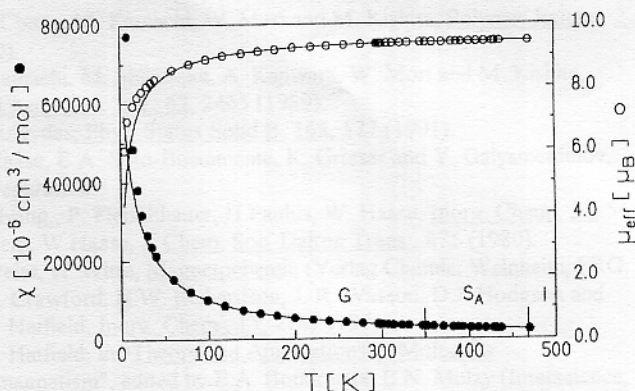


FIGURE 9 Magnetic susceptibilities and effective magnetic moments of the Er(III)-containing polymer PIII in the temperature range of 4.2-480 K.

The high-temperature limits of  $\mu_{\text{eff}}$  of both compounds are in agreement with the expected values calculated using the free-ion approximation<sup>20</sup> (see Table 3). This results confirm a composition  $M(\text{III})(L_p)_3(\text{NO})_2$  as suggested in Table 1, according to our studies on the monomeric compounds. The  $\theta$ -values given in Table 4 correspond to a Curie-Weiss fit and should give rather a phenomenological description of the temperature dependency of the molar susceptibility than a quantitative analysis. Such kind of treatment is quite usual in the field of rare-earth containing molecular based compounds and the  $\theta$ -values are in agreement with equivalent data which are already reported (see for example ref. 20 and references mentioned herein). Models for the temperature dependency of  $\mu_{\text{eff}}$  as a consequence of a crystal field effect in cubic or axial coordination cores have been established, but complexes usually possess lower symmetries and a precise interpretation of their magnetic data is still very difficult.<sup>21</sup>

TABLE 4 Comparison of observed ( $\mu_{\text{eff}}(\text{exp.}; 300\text{K})$ ) and calculated ( $\mu_{\text{eff}}(\text{calc.}; 300\text{K})$ ) effective magnetic moments at room temperature for PII and PIII. The  $\theta$ -values result from a Curie-Weiss fit of the susceptibility data.

Compound	$\mu_{\text{eff}}(\text{exp.}; 300\text{K})$ [ $\mu_B$ ]	$\mu_{\text{eff}}(\text{calc.}; 300\text{K})$ [ $\mu_B$ ]	$\theta$ [K]
PII	3.55	3.68	-49.5
PIII	9.37	9.72	-16.9

We have found no specific magnetic behaviour for the liquid-crystalline phase. From the first point of view, it is a little bit surprising that no orientation in a static magnetic field was observed, although the paramagnetic centers should offer a large paramagnetic anisotropy. However, the investigated polymers PII and PIII possess a

high viscosity which is responsible for the lack of orientation in the mesogenic phase. Most probably, the viscosity is due to the extended crosslinking in the polymer since the coordination core of the ion contains three bidentate Schiff base ligands attached on different sites of the polymer backbone.

## CONCLUSION

For a first time, magnetic properties of liquid crystalline metallopolymer were reported which substantially differ from the behaviour of monomeric model compounds. The problem, if only the polymeric backbone cause exchange effects or - by the same time - liquid crystalline properties are responsible is still a question of further investigation.

## ACKNOWLEDGEMENT

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