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Self-assembling Complexes with Magnetic Properties

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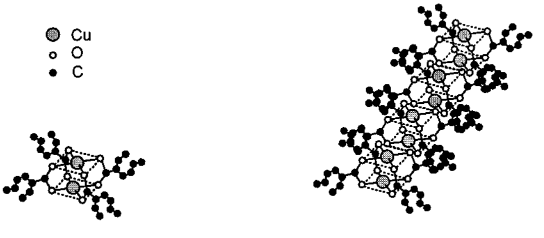
Summary: The magnetic properties and the nucleation capability of a self-assembling bicopper complex are reported. Attention is focused on the effect of the chirality of the bicopper complex. Comparison is made between the racemic mixture and the right-handed enantiomer.

Keywords: heterogeneous nucleation; gels; magnetic properties; self-assembling systems

Introduction

In the past few years, we have been involved in the study of a bicopper complex (copper II2-ethylhexanoate, noted CuS8[1]) with a self-assembling properties in organic solvent where it forms long filaments.[2,3] Also, we have studied the capability of these filaments to nucleate the growth of fibrils in thermoreversible gels from isotactic polystyrene.[4-6] Here, we report preliminary experiments showing the effect of the chirality of the basic bicopper complex molecule. Comparison is made between the racemic mixture and the right-handed enantiomer.



2-ethylhexanoate copper II complex　　*filaments of the complex*

Fig. 1. The 2-ethylhexanoate copper II complex (left) and the self-assembled filaments (right).

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Molecular Structure of the Bicopper Complex in Organic Solvents

As was reported earlier, the bicopper complex shown in Figure 1 possesses the propensity of piling up in dilute organic solutions. Long filaments are thus obtained as ascertained by SAXS experiments presented in Figure 2. As can be seen in the case of CuS8/cyclohexane a linear behaviour is observed. This is typical of long rod-like filaments which reads:

$$q^2 I(q) = C_{CuS8}\mu_L \varphi(q\sigma)\left(\pi q - \frac{2}{<L>}\right) \qquad (1)$$

in which C_{CuS8} is the bicopper complex concentration, μ_L the mass per unit length of the filaments, $<L>$ their mean-length and σ a dimension related to their cross-section. Here $\varphi(q\sigma) \approx 1$.

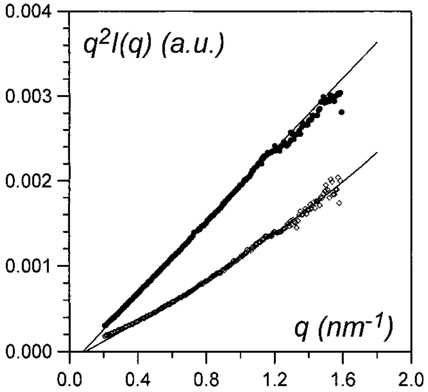

Fig. 2. Scattering curve in a Kratky representation ($q^2I(q)$ vs q) for jellies of CuS_8 in *trans*-decalin (◊) and in cyclohexane (•). In the case of CuS8/trans-decalin the intensity is fitted with a polynomial function of degree 3 as expected from relations (1) and (2). In both cases $C_{CuS8} = 0.02$ g/cm^3.

Here it is worth noticing that a linear behaviour is seen in cyclohexane whereas a curvature is seen in *trans*-decalin. This arises from a contrast effect. As a matter of fact, the term $\varphi(q\sigma)$ in relation 1 can be expressed in the present case through:[7,8]

$$\varphi(q\sigma) = \left[\frac{2A_{Cu}\gamma}{A_m q r_H} J_1(q\gamma r_H) + \frac{2A_{CH}}{A_m q r_H}\left(J_1(q r_H) - \gamma J_1(q\gamma r_H)\right)\right]^2 \qquad (2)$$

in which r_H the cross-section radius of the entire molecule (radius of the equivalent cylinder containing one filament), and γr_H the radius of the copper core. A_{Cu} and A_{CH} are the scattering amplitudes of the copper core and of the aliphatic wings with respect to the solvent, and $A_m = \gamma^2 A_{Cu} + (1-\gamma^2) A_{CH}$. In the case of X-rays A_{Cu} and A_{CH} are written:

$$A_i = \left(Z_i - \frac{v_i}{v_S} Z_S \right) \tag{3}$$

where Z_i and Z_s are the numbers of electrons in the considered structure and in the solvent molecule, v_i and v_s the molar volumes.

In the range where $qr_H < 1$, relation 2 reduces to:

$$\varphi(qr_H) = 1 - \frac{q^2}{4} \frac{r_H^2}{A_m} \left\{ A_{Cu}\gamma^4 + A_{CH}(1-\gamma^4) \right\} \tag{4}$$

and since the copper core is such that $\gamma \approx 0.1\text{-}0.15$:[2]

$$\varphi(qr_H) \approx 1 - \frac{q^2 r_H^2}{4} \left(\frac{A_{Cu}\gamma^4 + A_{CH}}{A_{Cu}\gamma^2 + A_{CH}(1-\gamma^2)} \right) \tag{5}$$

In the case of cyclohexane, A_{Cu} and A_{CH} are of the same signs and also $A_{Cu} >> A_{CH}$ so that the correction term due to the cross-section is negligeable. Conversely, if these amplitudes are of opposite signs, and as γ occurs as its 4th power, the effect of the correction term turns out to be not so negligeable, and in addition gives rise to an upturn at larger q values because the term in brackets in relation (5) is negative. Note that in neutron scattering such an effect cannot be seen as A_{Cu} and A_{CH} are virtually identical. Calculations by means of (3) of A_{CH} for cyclohexane and *trans*-decalin based on the density of equivalent aliphatic molecules yield $A_{CH} = -13$ and $A_{CH} = -27$ while A_{Cu} is but positive. Clearly, the effect is expected to be more pronounced with *trans*-decalin than with cyclohexane as is experimentally observed.

Magnetic Properties vs Chirality

This type of bicopper complex displays strong intramolecular and antiferromagnetic exchange interactions which depends on distances, on bond angles and on the aliphatic wings. The magnetic properties of these bicopper complex were studied in the powder state with a SQUID susceptometer which allows determination of the magnetic susceptibility χ. The variation of χ as a function of temperature are shown in Figure 3. In both cases the experimental data can be fitted by means of a Bleaney-Bowers law[9] for isolated two-spin ½ model [...], where the magnetic exchange coupling constant J corresponds to a Hamiltonian of the form $\mathcal{H} = -2JS_1S_2$ where S_1 and S_2 are the spins of each copper atoms (namely ±1/2).

$$\chi = \frac{N_A g^2 \mu_B^2}{kT} \frac{2\exp(2x)}{1+3\exp(2x)} \quad with \quad x = \frac{J}{kT} \tag{6}$$

in which N_A is Avogadro's number, g is the number of unpaired electrons in the molecule and μ_B Bohr's magneton.

Here, we have obtained $-2J = 202$ cm^{-1} for the racemic mixture and of $-2J = 346$ cm^{-1} for the right-handed enantiomer. The Curie tail observed at low temperature is due to a weak amount of paramagnetic impurities (0.08% to 0.15%).

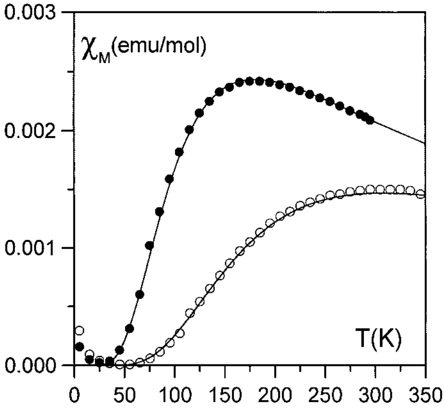

Fig. 3. Temperature dependence of the magnetic susceptibility χ for the racemic (●) and for the right-handed enantiomer (○). In both cases $H = 5000$ Gauss. The solid line represents the best fit to the experimental data with the Bleaney-Bowers equation (relation 6).

This shows that the antiferromagnetic interactions are more important in the right-handed enantiomer than in the racemic mixture. This is probably due to the fact that the piling is more regular with the enantiomers, especially as far as the organization between aliphatic wings belonging to neighbouring bicopper complex molecules is concerned. This is to some extent reminiscent of the formation of helical structures with stereoregular polymers. Such enhanced regularity in the piling process is also liable to occur in organic solutions.

Nucleation Properties vs Chirality. Encapsulation in Polymer Fibrils

It has been recently observed that the bicopper complex filaments act as a heterogeneous nucleating agent for the growth of the fibrils in gels prepared from isotactic polystyrene/*trans*-decalin solutions.[4-6] The nucleation behaviour is evidenced through an increase of the gelation threshold upon addition of bicopper complex to the iPS/*trans*-decalin solutions. Here we have performed the same type of experiments by comparing the nucleation capability of the racemic mixture with respect to that of the right-handed enantiomer.

As shown in Figure 4 we have also observed an increase of the gelation temperature upon addition of bicopper complex. The increase of the gelation temperature ΔT_{gel} is linear up to some critical bicopper complex molar fraction f^*_c, and then levels off. We have found that the maximum increase of T_{gel} is about 8°C against 15°C as reported by Lopez and Guenet.[4] This may arise from the use of different calorimeters. Interestingly, the increase of the gelation temperature ΔT_{gel} with the right-handed enantiomer is about 3°C more important than with the racemic mixture. This may be due to the higher level of organization within the bicopper complex filaments.

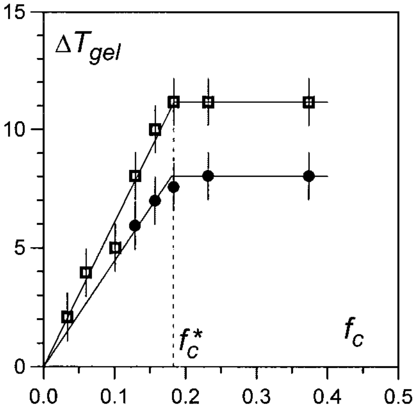

Fig. 4. Increase of the gelation temperature ΔT_{gel} as a function of the bicopper complex molar fraction f_c (with respect to the mixture polymer+complex) for C_{pol} = 0.04 g/cm^3, C_{Cu} varies from 0.01 g/cm^3 to 0.16 g/cm^3. f^*_c corresponds to the cross-over. (●) racemic mixture CuS_8; (□) right-handed enantiomer.

Concluding Remarks

These results suggest that the chirality of the bicopper complex molecule plays a significant role in its properties both in the solid state (magnetic properties) and in the solution state (nucleation capability). Further experiments are under way to assess the role of chirality in the self-assembling process.

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