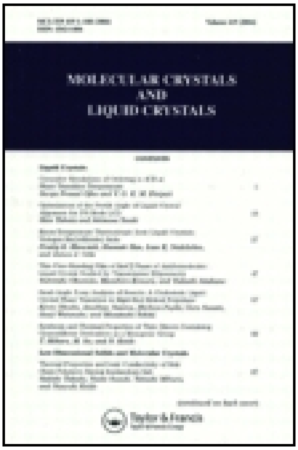

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Miguel Clemente-leon [a], Helene Soyer [b], Christophe Mingotaud [b], Carlos J. Gomez-garcia [a], Eugenio Coronado [a] & Pierre Delhaes [b]

[a] Dept. Quimica Inorganica, Universitat de Valencia, Dr Moliner 50, E-46100, Burjassot, SPAIN

[b] Centre de Recherche Paul Pascal-C.N.R.S., University of Bordeaux I, Avenue A. Schweitzer, 33600, Pessac, FRANCE

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MIGUEL CLEMENTE-LEON[a], HELENE SOYER[b],
CHRISTOPHE MINGOTAUD[b], CARLOS J. GOMEZ-GARCIA[a],
EUGENIO CORONADO[a] and PIERRE DELHAES[b]

[a]*Dept. Quimica Inorganica, Universitat de Valencia, Dr Moliner 50, E-46100 Burjassot, SPAIN and* [b]*Centre de Recherche Paul Pascal-C.N.R.S., University of Bordeaux I, Avenue A. Schweitzer, 33600 Pessac, FRANCE*

The mixed-valence manganese clusters $[Mn_{12}O_{12}(carboxylato)_{16}]$ have been organized in a multilayer architecture. Indeed, well-defined Langmuir-Blodgett (LB) films of the acetate and the benzoate Mn_{12} clusters can be obtained using behenic acid as organic matrix. Here, we report the magnetic properties of these multilayers, which present a marked hysteresis at 2 K.

Keywords: Langmuir-Blodgett film; clusters; molecular magnets; relaxation of magnetization; single molecule nanomagnets

INTRODUCTION

The mixed-valence manganese clusters $[Mn_{12}O_{12}(carboxylato)_{16}]$ are an interesting class of magnetic materials since the discovery that these individual molecules can act as magnets of nanometer size[1-6]. Thus, they exhibit large magnetic hysteresis comparable to that observed in hard magnets. In view of these properties, we have explored the possibility of organizing these Mn_{12} clusters in monolayers by using the Langmuir-Blodgett (LB) technique[7]. Although for the most part, this method has been used to organize organic molecules, very recently it has been shown that inorganic clusters, as the polyoxometalate anions[8], can also be organized in a LB film. Previously, we have shown that homogeneous LB films of the acetate and the benzoate Mn_{12} clusters can be obtained using behenic acid ($C_{21}H_{43}COOH$) as organic matrix[9]. Here, we report the magnetic properties of these films.

RESULTS AND DISCUSSION

A brief survey of the structural features of these LB films as deduced from infrared and X-ray diffraction should be presented. IR experiments show that the alkyl chains are somewhat fully extended and tilted versus the normal to the substrate. The tilt angle of the hydrophobic tails is easily evaluated from the dichroic behaviour of the bands associated to the alkyl chains[10]. Some differences appear between the benzoate and acetate derivatives: the tilt angle in the benzoate derivative is close to 22-24° for both the pure matrix and the different cluster / lipid mixtures, whereas it varies in the acetate cluster from 22° for the pure matrix to 29°-33° for 1/10 and 1/20 mixtures. It seems that only the Mn_{12} acetate modifies slightly the organization of the behenic acid matrix. When increasing the concentration of clusters, a relative decrease of intensity is observed in the band at 1700 cm^{-1}, associated to the COOH function of the behenic acid. This may be a consequence of a partial substitution around the Mn_{12} core of acetate ligands by behenate molecules. The same effect is observed for the benzoate derivative.

The X-ray diffraction allows us to calculate the periodicity of the LB films. In both cases, this periodicity is strongly dependent on the concentration of cluster. In the LB films of the acetate derivative, three Bragg peaks are observed for the different cluster / lipid ratios (1/20, 1/10 and 1/5; see figure 1). These data show an increase in the interlayer separation when the concentration of cluster is increased, reaching a maximum value of 67 Å for the 1/5 ratio. This distance corresponds closely to the intercalation of a monolayer of clusters between a bilayer of behenic acid. For diluted films, the Bragg peaks have the same position than for the LB films of pure behenic acid and corresponds to a periodicity of ca 53.5 Å. However, the height of each peak is lower and its width is much larger than in the pristine film. This indicates that the organic layer structure is still maintained but the coherence length has decreased in the material due to the insertion of the inorganic cluster.

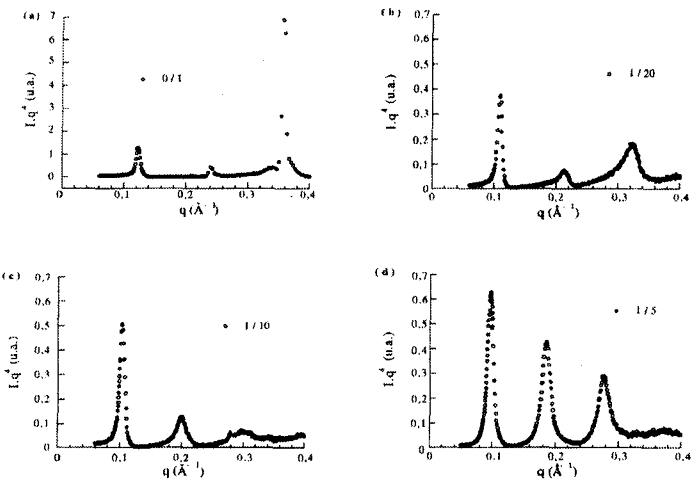

FIGURE 1 X-Ray diffraction patterns of LB films based on behenic acid / Mn_{12} acetate mixtures with cluster / lipid ratios: 0/1 (a), 1/20 (b), 1/10 (c) and 1/5 (d)

From the above discussion, we conclude that the degree of organization of the clusters within the films appears to be strongly dependent on the concentration of clusters in the LB film. For low concentrations, isolated clusters or partial monolayers of clusters are obtained, while for the higher concentrations (typically in the range 1/10 to 1/5) lamellar structures with the clusters organized in well-defined monolayers are obtained (see figure 2).

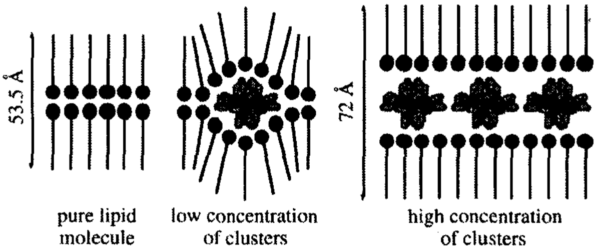

FIGURE 2 Schemes of the LB films when the lipid ratio is varied.

Therefore we focused the magnetic study on the 1/10 and 1/5 films which are those containing monolayers of clusters. The magnetic properties were measured after deposition of about 300 layers onto a diamagnetic mylar substrate fixing the film parallel or perpendicular to the magnetic field direction. Magnetic susceptibility measurements differ from the behavior observed on crystalline powders. Thus, while the microcrystalline samples show upon cooling down an increase in χT with a maximum at 10-20 K followed by a decrease, the LB films exhibit a constant value of χT whith a continuous decreases below 50 K (see figure 3). A possible explanation is that, in contrast to what has been observed for crystalline powders, the high compactness of the layer, the strong interactions between the alkyl chains together with the possible partial substitution of acetate or benzoate ligands by behenate molecules prevent the clusters to be oriented along the field direction. We have also seen that χT does not change significantly when the orientation of the film with respect to the applied magnetic field is modified.

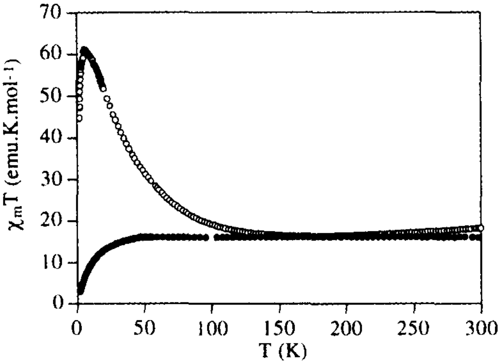

FIGURE 3 Plot of $\chi_m T$ versus temperature for the $Mn_{12}Bz$ cluster in the powder (open circles) and normalized value for the $Mn_{12}Bz$ / behenic acid (1/10) LB film.

A remarkable magnetic result comes from the magnetization data versus the applied magnetic field performed at temperatures below and above the blocking temperature of the cluster of 3.8 K (see figure 4). As for the parent crystalline salt, the LB films of the two Mn_{12} clusters show at 2 K a marked hysteresis loop with coercive field of ca. 0.1 Tesla (benzoate derivative) or 0.06 T (acetate derivative), which vanishes as the temperature is increased to 5 K (see inset of figure 4)[9]. We also observe that in the benzoate derivative the shape of the loop depends on the orientation of the film with respect to the applied magnetic field H. Thus, when H is parallel to the plane of the magnetic monolayer the loop is softer than when H is perpendicular.

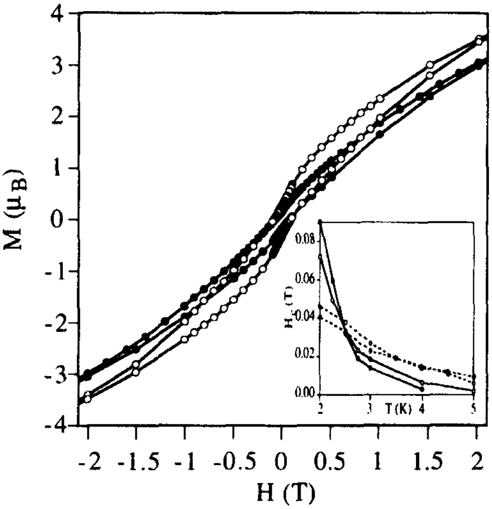

FIGURE 4 Hysteresis loops at 2 K of the Langmuir-Blodgett film prepared with the $Mn_{12}Bz$ cluster and behenic acid with a lipid / cluster ratio of 10 / 1. Magnetic field perpendicular (filled circles) or parallel (empty circles) to the film layer. Inset: temperature dependence of the coercive field for the LB films of benzoate (solid lines) and acetate (dotted lines). Filled and open circles refer to the orientation of the LB film with respect to the applied field (perpendicular and parallel respectively).

Such an anisotropy indicates a preferential orientation of these anisotropic clusters within the layers (with the axial axis of the disk-shape cluster perpendicular to the monolayer). This effect is not observed for the acetate film, in which the $Mn_{12}Ac$ clusters seem to be less oriented within the layer. A possible explanation is that the larger shape of the benzoate derivative makes more difficult an out-of-plane orientation of the cluster. The coercive field at 2 K is strongly reduced by an order of magnitude when comparing the film to the the crystal. This is surely related to the different spin dynamics of the Mn_{12} cluster in these two media, as it is submitted to different environments and packings. In fact, it is well known that the magnetic relaxation in the Mn_{12} cluster can be strongly affected by its surroundings[11].

This effect is clearly demonstrated by the study of the relaxation of magnetization versus time at different temperatures in the 1/10 LB films of $Mn_{12}Ac$/ behenic acid and $Mn_{12}Bz$/ behenic acid. The temperature and magnetic field dependences of the magnetization relaxation time on single crystals and microcrystalline samples of the Mn_{12} acetate were already studied by several groups[2,5,12,13]. The results indicated an exponential decay of the magnetization versus time with a single relaxation time given by $\tau = \tau_0 \exp(\Delta E/kT)$. The data obtained in LB films of the acetate derivative cannot be fitted to a single exponential equation but to a logarithmic equation (see figure 5a). In turn, in the LB film of the benzoate derivative an exponential law can be still used to fit the decay of the magnetization (see figure 5 b). Such a difference constitutes a further support on the higher degree of ordering of the benzoate cluster compared to the acetate one in the multilayers. In fact, a single-molecule magnet with its easy axis of magnetization parallel to the magnetic field would relax faster than a molecule with its easy axis of magnetization perpendicular to it; therefore, a distribution of energy barriers is expected to occur when the clusters are randomly oriented within the LB film. The situation resembles that found in a system of noninteracting single-domain particles of similar size but with a broad distribution of energy barriers. The theory predicts that such a system has a decay of the magnetization which follows a logarithmic law of the type[14,15] $M(t) = M(t_0)[1-S(T,H)\ln(t/t_0)]$ where S is the magnetic viscosity. Well below the blocking temperature, it can be expressed as $S(T)=kT/<U>$. In the film containing the acetate cluster a logarithmic behavior has been observed for M(t) measured at 2, 2.5 and 3 K.

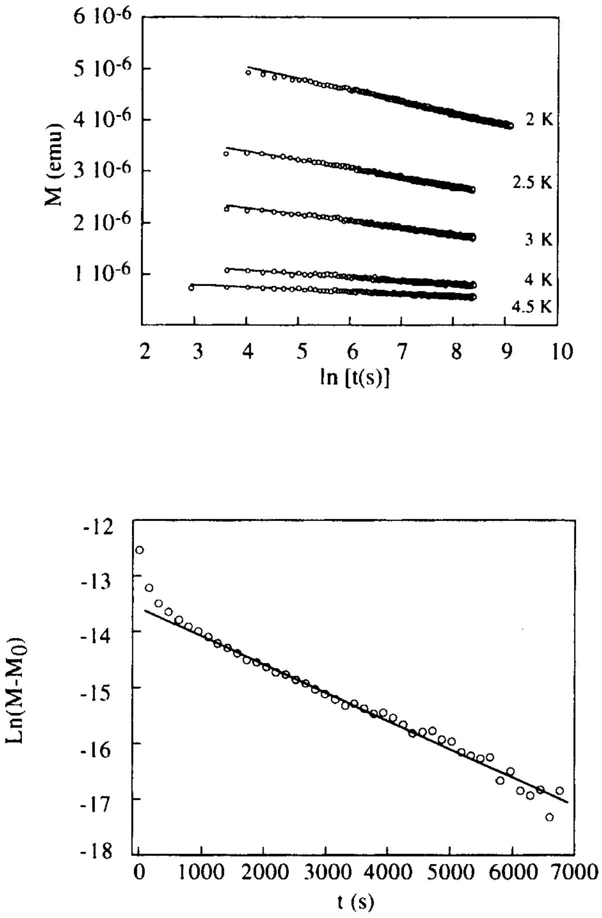

FIGURE 5 (a) Relaxation of magnetization at different temperatures for a $Mn_{12}Ac$ / behenic acid (1 / 10) LB film (up). (b) Relaxation of magnetization at 2 K for a $Mn_{12}Bz$ / behenic acid (1 / 10) LB film with the fitting to an exponential law (down).

Furthermore, a linear increase of the viscosity with the temperature has been observed in this range. At higher temperatures (4 and 4.5 K), there is the usual decrease of S(T). This behavior supports then a random orientation of the magnetic clusters of Mn_{12} acetate in the LB film. In order to compare the relaxation properties of the Mn_{12} clusters embedded in the LB films to those observed in the crystalline powders, we have fit the M(t) data of the benzoate derivative to an exponential law. Although a faster decay during the initial time (~1000 s) has been observed, data for higher times follow an exponential law. This allows us to calculate the relaxation time τ at temperatures below 3.5 K. At 2 K, τ is reduced by three orders of magnitude in the LB film comparing with measurements on powders. This faster relaxation accounts for the lower coercive field in the hysteresis curve observed in the LB films. The relaxation is even faster for the salt of the anionic cluster $[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]^-$ and an organic radical that shows a coercive field of ~20 G at 1.7 K[11]. In this last case the reason for this enhancement of the relaxation of the magnetization has been related to the presence of paramagnetic species around the cluster.

CONCLUSION

The LB technique has been used to obtain monolayers of Mn_{12} molecular clusters exhibiting hysteresis below the blocking temperature. However, this technique has not been able to completely orient the clusters within the monolayers. Only a preferential orientation has been achieved when the LB films contain the benzoate cluster. An explanation is that Van der Waals interactions between the fatty acids and the clusters are not strong enough to induce a preferential orientation of the clusters. Furthermore, partial substitution of benzoate or acetate groups from the clusters by behenate molecules can also result in an increase of the disorder. A possible strategy to solve these problems is the use of the anionic derivatives of Mn_{12} such as $[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]^-$ and a cationic amphiphilic molecule. The electrostatic interactions between them could improve the preferential orientation of the magnetic clusters as it has been already shown for LB films of polyoxometalate clusters.[8,16]. Currently we are investigating the use of anionic derivatives of Mn_{12} clusters to construct LB films.

Finally the molecular origin of the hysteresis in these LB films opens a very efficient way to design molecular multilayers with useful magnetic properties or combination of properties. Notice that a precedent of magnetic LB film showing a weak hysteresis with a coercive field of 0.02 T has been recently reported[17]. However, in that case the hysteresis has a cooperative origin as it requires the formation of a polymeric manganese phosphonate layer, which in the solid state is a weak ferromagnet.

Acknowledgements

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