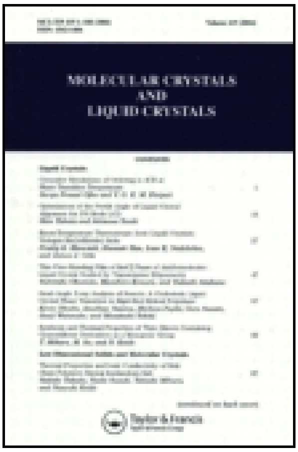

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Large Magnetic Anisotropy in High Spin Clusters; a Route to Magnetic Hysteresis at the Molecular Level

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To cite this article: Roberta Sessoli (1995): Large Magnetic Anisotropy in High Spin Clusters; a Route to Magnetic Hysteresis at the Molecular Level, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 274:1, 145-157

To link to this article: http://dx.doi.org/10.1080/10587259508031875

Mol. Cryst. Liq. Cryst., 1995, Vol. 274, pp. 145–157
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LARGE MAGNETIC ANISOTROPY IN HIGH SPIN CLUSTERS; A ROUTE TO MAGNETIC HYSTERESIS AT THE MOLECULAR LEVEL

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Abstract

New experiments on a well known compound, a dodecanuclear manganese cluster of formula $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$, are providing very exciting results. Recently this cluster was shown to have a huge magnetic anisotropy of the Ising type which, associated to the large spin of the ground state, S=10, is responsible of an unusually slow relaxation of the magnetization. This, on its turn, is the origin of hysteretic behavior at low temperature.
We have also looked at the relaxation properties in dilute frozen solutions of the cluster and we have found that the slow relaxation and hysteretic behavior persist, confirming that we are dealing with a molecular phenomenon.
The large spin ground state associated with the Ising type anisotropy have also been evidenced in a different type of clusters of formula $[Mn_{10}(biphen)_4O_4Br_{12}]^{4-}$ recently synthesized, in which four manganese(III) and six manganese(II) are present and the spin of the ground state is 12.

INTRODUCTION

Nanoscale magnetic particles are attracting increasing interest in fields that range from material science to biochemistry and to fundamental physics.[1,2] Very small particles of metals or metal oxides have been prepared by using sophisticated techniques,[3] but the molecular approach seems very promising. In fact, clusters of smaller dimensions can be obtained which are structurally well characterized without dispersion in size and orientation.

Beyond the difficulty of synthesizing large molecular clusters a second complication is associated with the interpretation of the magnetic properties. While the behavior of simple paramagnets is well understood and infinite assemblies of spins can be handled taking advantage of the translational symmetry of the lattices, large but finite clusters constitute a challenging problem. Our group has endeavored in this field because we feel that a rationale for the magnetic behavior is necessary to gain the ability to tune the magnetic problems of these materials.

One of the main interest in the mesoscopic phase of magnetism is that of understanding where is the threshold between paramagnetism and bulk magnetism. The study of clusters of increasing size should in principle provide the answer and recently superparamagnetic-like behavior has been detected in some high nuclearity iron clusters by using Mössbauer spectroscopy.[4]

A class of well known dodecanuclear mixed valence manganese clusters has,[5] however, shown more similarity with bulk behavior.[6-8] The clusters have the general formula, $[Mn_{12}O_{12}(RCOO)_{16}(H_2O)_4]$, where RCOO is acetate or benzoate, and a view of the core is reported in Figure 1. Four manganese(IV) are arranged on the vertexes of a tetrahedron and surrounded by eight manganese(III) connected through μ-oxo bridges that constitute the main pathway to magnetic exchange interaction.

Recently also a reduced form, where a Mn(III) has been replaced by a Mn(II) has been synthesized.[9]

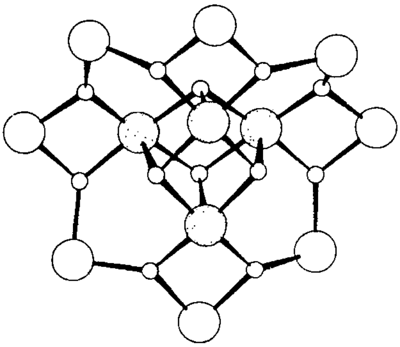

FIGURE 1 View of the core of Mn_{12} clusters. The dotted circles represent manganese(IV) atoms while the small empty circles oxygen atoms

MAGNETIC PROPERTIES OF Mn_{12} CLUSTERS.

A large amount of experimental work has been done on the acetate derivative,[6,8,10] $Mn_{12}Ac$, which has the advantage of crystallizing in a tetragonal group with the cluster lying on a S_4 symmetry axis. Moreover relatively large air stable crystals can be obtained.

The common feature of this type of clusters is the presence of very large spin states populated at low temperature. Ground states of S=10 and 9 have been observed for $Mn_{12}Ac$ and $Mn_{12}Benz$ respectively, while S=19/2 has been proposed for the

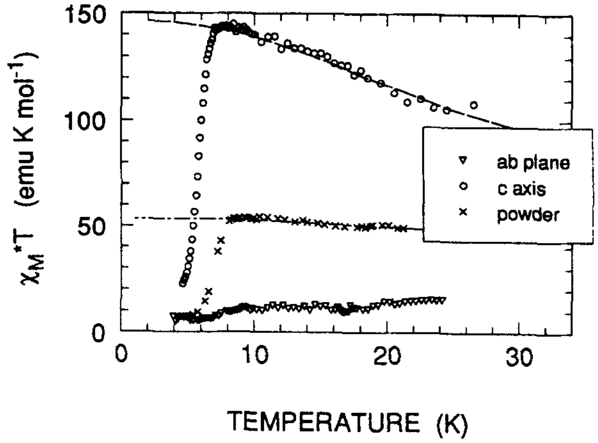

FIGURE 2 Temperature dependence of the product χT for powder and single crystals sample.The solid line represents the calculated values.

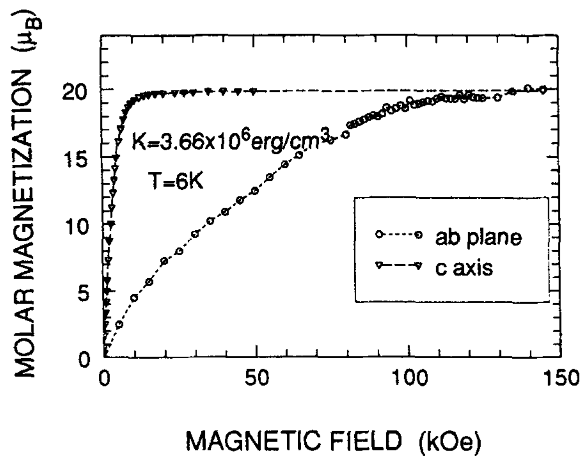

FIGURE 3 Magnetization curves measured with the field parallel and perpendicular to the *c* axis. The area between the two curves provides the anisotropy constant.

reduced cluster. The existence of high spin ground states have been rationalized by assuming that the antiferromagnetic exchange interactions between Mn(IV) and Mn(III) through a double μ-oxo bridge dominate and that interactions between Mn(III) through a single μ-oxo bridge are negligible. The role of the spin topology appears to be crucial when antiferromagnetic interactions are present.

The single crystal magnetic studies on $Mn_{12}Ac$ have confirmed previous results from high frequency EPR spectra and clearly evidenced the presence of a huge Ising type anisotropy. As shown in Figure 2, $\chi_{||}T$ measured with the field applied to the unique axis, the crystallographic *c* axis, reaches much higher value than those observed for the powder sample, while $\chi_{\perp}T$ decreases on lowering the temperature below 30 K.

The macroscopic magnetic anisotropy is better evaluated as the difference in the work required to saturate the magnetization along the hard plane and the easy axis. From Figure 3 we evaluated anisotropy constants $K_1=3.64\times10^6$ erg/cm^3 at 6.0 K. This value, which takes also into account the relatively small density of the magnetic moments, is only about 10 times smaller than that found for iron at room temperature.

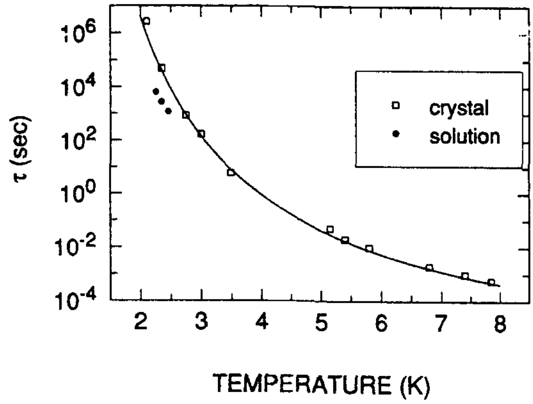

FIGURE 4 Temperature dependence of the relaxation time of crystals and frozen solution of $Mn_{12}Ac$. The solid line represents the best fit curve (see text).

The most spectacular property of these clusters is the presence of an unusual slow relaxation of the magnetization at low temperatures, which can be evidenced by the presence of out-of-phase susceptibility in ac experiments inzero static applied field and, at lower temperature, by the presence of remnant magnetization that decays with time.

By using these two techniques we have found that the relaxation time of $Mn_{12}Ac$ increases exponentially on decreasing temperature reaching at 2.1 K the value of 1 month, as shown in Figure 4. The slow relaxation is responsible of the magnetic hysteresis reported in Figure 5, whose origin is not, of course, the irreversibility in the deplacement of the domain walls, but simply the freezing of the spins in the aligned position. In fact a moderate field, in the present case 20 kOe, accelerates dramatically the relaxation process and the magnetic moments are able to align along the applied field. By decreasing the field the relaxation slows down and the spins are frozen in the aligned position until a negative field is reached, which is strong enough to accelerate again the relaxation.

Similar effects are observed on an oriented polycrystalline powder of $Mn_{12}Benz$, for which zero field cooled and field cooled susceptibilities are reported in Figure 6.

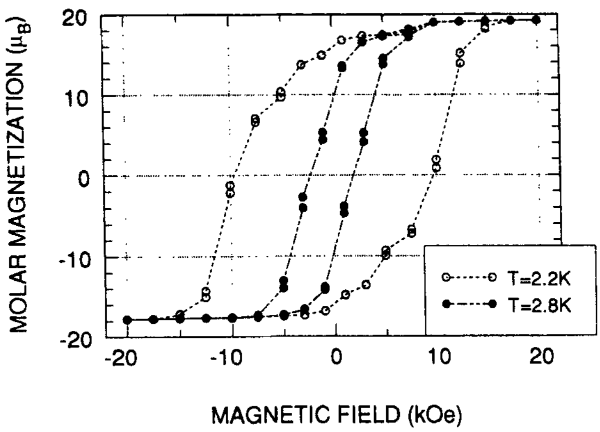

FIGURE 5 Magnetic hysteresis of $Mn_{12}Ac$ at two temperatures obtained by applying the field parallel to the *c* axis.

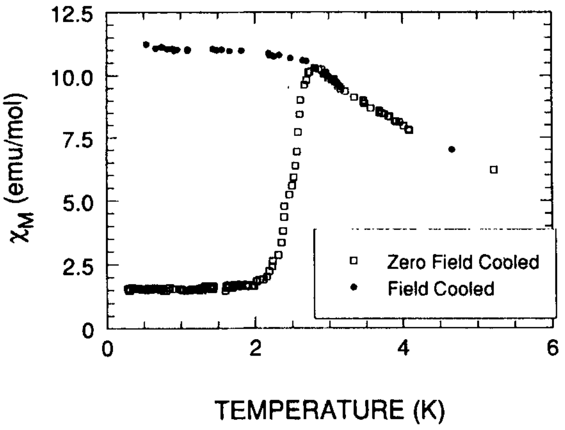

FIGURE 6 Hysteresis effects on the magnetization of an oriented powder sample of Mn12Benz

The magnetic hysteresis seems not to be originated by 3-d magnetic order as no anomaly in the specific heat has been observed down to 1.2 K.

The final confirmation has been provided by magnetic measurements in a dilute frozen solution of $Mn_{12}Ac$. This is indeed soluble without decomposition of the cluster in CH_3CN and we have investigated two solutions of concentration $5x10^{-4}$ M and $5x10^{-5}$M, respectively. The solutions were cooled abruptly in order to prevent the precipitation of the compound . After the measurements the solutions were immediately checked under a microscope to be sure that no precipitate had been formed. It is well established that a mixture of solvents is more suitable to perform frozen solution EPR experiments, as they form glasses that hamper the precipitation of the solute. Therefore we repeated the experiments with a 5x10^{-5}M solution by using CH_3CN, CH_2Cl_2 and toluene in the volume ratio 3:1:1. The experiments were performed by cooling the sample in 20 kOe, removing the field and looking at the decay of the magnetization. Even if the diamagnetism of the solvent overcomes the paramagnetic signal of the compound, in zero field the diamagnetic contribution of the solvent is zero and therefore does not affect the remnant magnetization.

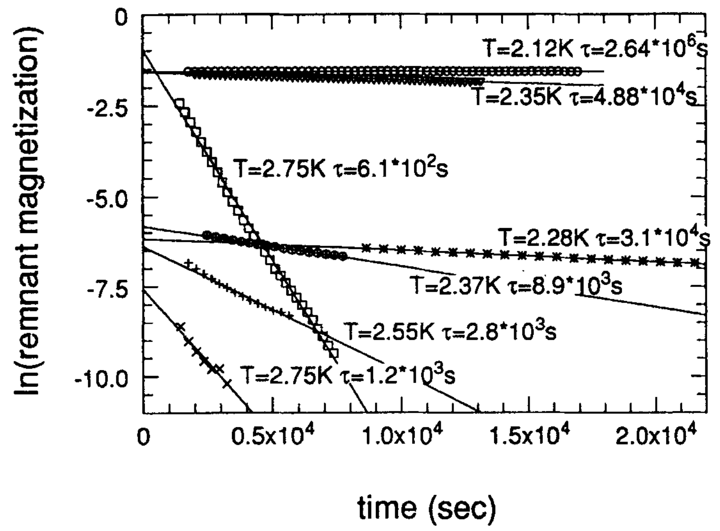

FIGURE 7. Decay of the remnant magnetization of $Mn_{12}Ac$ at different tempaeratures measured on a single crystal (curves in the upper part) and a frozen solution sample.

The results of the decay of the remnant magnetization of the mixed solvents solution are reported in Figure 7 in a semi- logarithmic scale as well as those on single crystals. It is aparent that the phenomenon of slow relaxation persists in frozen solution even if relaxation is a little faster than in the solid state.

We want to emphasize the novelty of this results as magnetic hysteresis has always been associated to cooperative behavior and then to the solid state of matter, even if hysteresis due to the freezing of the dynamic of the magnetic moments is well known in spin-glasses and superparamagnets, and it is interesting to rationalize this unprecedented behavior.

MECHANISM OF RELAXATION

The behavior of this class of clusters resembles the superparamagnetism of small magnetic particles where the magnetization fluctuates when the thermal energy overcomes the magnetic anisotropy, which is responsible of the orientation of the spins along the easy direction. In superparamagnets the relaxation time has found to follow the Arrhenius low:[11]

$$\tau = \tau_0 \exp(\Delta/k_B T) \qquad (1)$$

where Δ is the anisotropy energy, which is proportional to the volume of the particle, and τ_0 is the relaxation time at infinite temperature or in the absence of the barrier. τ_0 has always been found to be of the order 10^{-9}- 10^{-11} sec. By using eq. (1) to fit the temperature dependence of the relaxation time we obtained $\Delta = 61$ K and $\tau_0 = 2\times10^{-7}$ sec. This unusually long τ_0 suggests that we are dealing with a mesoscopic phase still far from bulk magnetism and that, perhaps, a molecular approach is more appropriate to describe the relaxation of the magnetization

In the case of $Mn_{12}Ac$ the system can be depicted as an atom with a S=10 ground state, which is splitted in zero field in such a way that m=±10 states lie lowest in energy. Given the tetragonal symmetry of the cluster the energy of the different states of the S=10 manifold is given by

$$E(m)=-D(m)^2 \qquad (2)$$

from which we can draw the energy diagram of Figure 8.

In the measurement of the decay of the remnant magnetization by applying a strong field the m=-10 state becomes selectively populated, and when the field is removed half of the population has to cross the barrier in order to reach the equilibrium. Villain et al.[12] have treated the problem assuming that at low temperature the relaxation occurs essentially through a modulation of the crystal field due to coupling with the phonons of the lattice and, according to a generalization of the Orbach process, the reversal of the magnetization involves 20 steps of the type

$$|-S\rangle \rightarrow |-S+1\rangle \rightarrow |-S+2\rangle \rightarrow \ldots\ldots \rightarrow |0\rangle \rightarrow \ldots\ldots \rightarrow |S-1\rangle \rightarrow |S\rangle$$

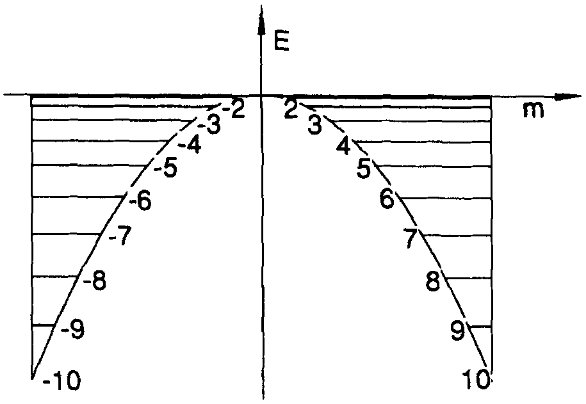

FIGURE 8 Energy diagram of the splitting of the S=10 ground manifold in zero field.

In the low temperature limit and in the absence of field the relaxation rate can be expressed as

$$1/\tau \approx \frac{3}{2\pi}\,\frac{v^2}{h^4\rho c^5}\left(\frac{\Delta}{S^2}\right)^3 \frac{\exp(-\Delta//k_BT)}{1-\exp(-\Delta//k_BT)} \qquad (3)$$

where Δ is the energy barrier, ρ is the density, v is the spin phonon interaction, and c is the velocity of sound in the crystal. Even if these last two parameters are not known it is clear that the pre-exponential factor has a strong dependence on the value of the spin, being $\tau_0 \propto S^6$. Assuming a given macroscopic anisotropy a much longer relaxation time is then expected for large spin molecules.

The height of the barrier, which correspond to E(m=0)-E(m=10), is therefore simply given by $-DS^2$. From the fit of the data of Figure 4 a D value of -0.6 K is evaluated which is not far from D=-0.75 K, provided by high field EPR spectra and single crystal magnetic susceptibility.

Our hypothesis of molecular origin of the hysteretic behavior is substantiated by the presence of an appropriate model. Also the difference in the results obtained from frozen solutions and reported in Figure 7 are in agreement with the proposed model. In fact, passing from crystal to solution experiments the spin-lattice coupling is expected to vary but not by several orders of magnitude.

QUANTUM TUNNELING OF THE MAGNETIZATION

Mesoscopic phases are characterized by the cohesistance of quantum and classic effects which are well known and exploited in superconducting devices based on Josephson junctions. In the last few years it has been evidenced that also the magnetization can display quantum behavior like the tunneling between two wells.

Leaving the details to a very rich literature on the subject[13] we can say that the simplest model corresponds to a single-domain ferromagnetic particle where the number of interacting atoms is sufficiently small that a coherent rotation of all the spins is favored compared to the individual rotation of the moments. In the case of uniaxial anisotropy that generates a barrier, the rotation occurs through a thermally activated process and the relaxation time follows the eq. (1).

If a basal plane anisotropy is present a mixing of the states occurs and below a characteristic temperature, T*, the escape of the magnetization from a metastable configuration through an underbarrier transition dominates over of the thermal activated process.

Below the cross-over temperature the relaxation rate becomes temperature independent

$$\Gamma_q=\nu_q\exp(-\Delta/k_BT^*) \qquad (4)$$

and a rough estimation of T* is given by

$$T^*\approx(K_{\parallel}K_{\perp})^{1/2} \qquad (5)$$

where $K_{\parallel}$ is the uniaxial anisotropy and $K_{\perp}$ the basal one. The tunneling of large spin was the first to be analyzed[14] and a fundamental difference has been found between integer and half-integer S values, the tunneling being forbidden in the last case.

Even if sophisticated experiments have been performed on nanoparticles with very narrow size distribution[15] and on ferritin,[16] which is well known to accommodate inside the proteic shell about 4500 atoms of iron, the precious contribution of experiments on well characterized molecules of large S is clearly evident. In fact by using molecular clusters not only the size but also the value of the spin, the anisotropy and the orientation are rigorously known and exact treatments are possible.

In recent experiments on $Mn_{12}Ac$[17] it has been evidenced that below 1.8 K the relaxation time becomes temperature independent. Evidences of thermally assisted quantum tunneling at higher temperature seem to be provided by the unusual field dependence of τ, which increases dramatically by applying a relatively weak magnetic field, in disagreement with the fact that the magnetic field reduces the height of the barrier. Experiments on this subject are still in progress.

The possibility of tuning the magnetic anisotropy is another appealing characteristic of molecular materials. In fact while $Mn_{12}Ac$ has a four-fold crystal imposed symmetry, and therefore only terms of the type Sx,y^4 of the Hamiltonian can be responsible of quantum tunneling, $Mn_{12}Benz$ crystallizes in the triclinic system and has a lower symmetry. From Figure 9 it is clear that below 2.5 K τ increases with a smaller slope than that expected from the Arrhenius law and experiments are in progress to evidence the presence of quantum tunneling.

The reduced form recently reported is even more interesting as it has an odd number of unpaired electrons and therefore a half-integer spin ground state.

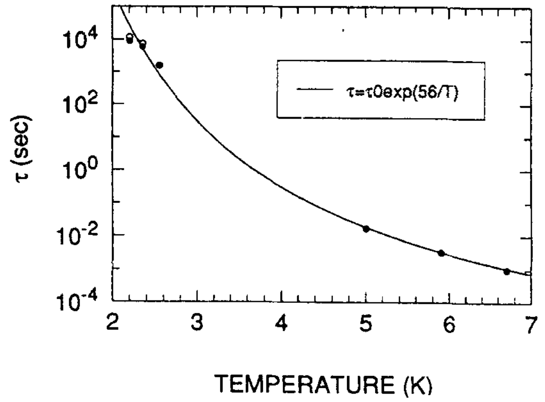

FIGURE 9 Temperature dependence of the relaxation time of $Mn_{12}Benz$. Full and empty circles represents the maximum and minimum τ evaluated from a non exactly monoexponetial decay of the remnant magnetization.

BEYOND Mn_{12} CLUSTERS

Even if it seems that we are able to rationalize the unprecedented magnetic behavior of the Mn_{12} clusters, they remain unique and we feel that, if our hypothesis is correct, similar phenomena should be observed in the presence of the appropriate conditions: a well isolated ground state with large S and a Ising type anisotropy. To achieve this combination, tripositive manganese seems to be the best candidate as it has a large spin and in the elongated octahedral environment has sizable negative z.f.s parameter.

Recently new decanuclear mixed valent manganese clusters of formula $[Mn_{10}(biphen)_4O_4X_{12}]^{4-}$(with X=Cl, Br) have been synthesized.[18] They comprise six manganese(II) and four manganese(III) connected by μ_4-oxo bridges as well as alcohoxo and halogeno bridges. The structure is reported in Figure 10 as well as a view of the spin topology. These clusters have shown to have very large spin states populated at low temperature, S=12-14, a fact that can be rationalized by the presence of competing antiferromagnetic interactions.

One of the members of this type of clusters crystallizes in a tetragonal space group and the single crystal magnetic susceptibility,[19] reported in Figure 11, has

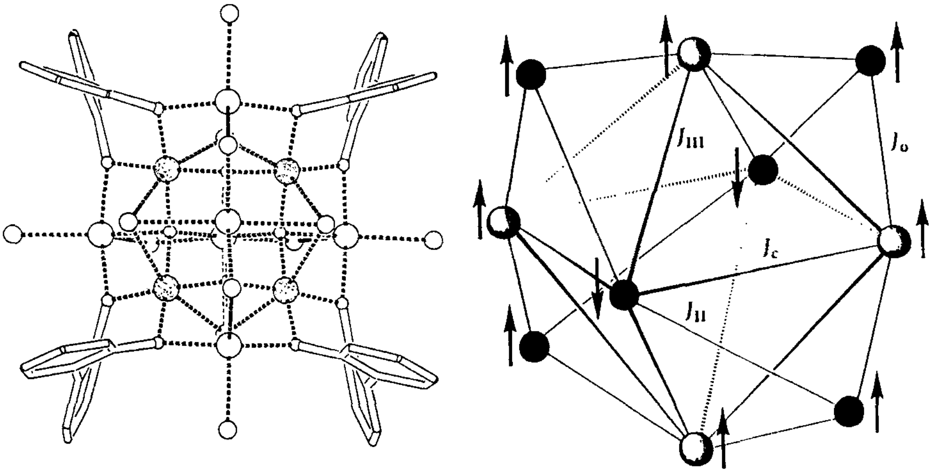

FIGURE 10 Left: view of the structure of $[Mn_{10}(biphen)_4O_4X_{12}]^{4-}$; the circles of decreasing size represent manganese, halogen, oxygen and carbon atoms respectivly, and. Mn^{3+} are evidenced by the dots. Right: spin topology of the cluster where Mn^{2+} are reported as full circles.

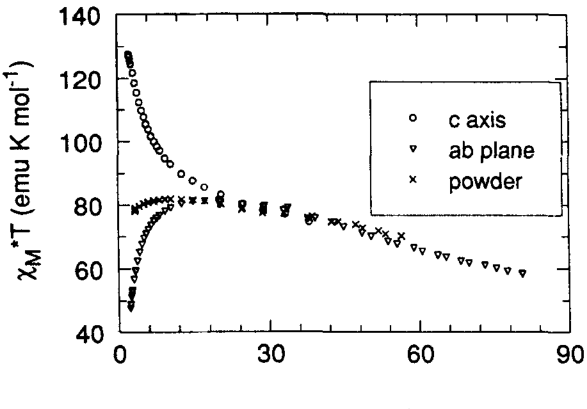

FIGURE 11 Temperature dependence of the χT product for a single crystal and a powder sample of the $[Mn_{10}(biphen)_4O_4Br_{12}]^{4-}$ cluster.

revealed a large Ising type anisotropy associated to a rather well isolated S=12 ground state. The value of D of the ground state, D=-0.050 K, has been unambiguously determined by single crystal EPR spectra and has been found in good agreement with the anisotropy constant evaluated by single crystal magnetization curves, which is about ten times smaller than that of $Mn_{12}Ac$. By using (4) and assuming a similar spin-phonon interaction relaxation effects on M should be observed at 1 K and experiments are in program.

CONCLUSIONS

We have shown that magnetic bistability and hysteresis can also be observed in isolated molecules, even if very strict prerequisite are necessary. Their application as molecular magnetic memories is in principle possible but very far in the realization essentially for the prohibitive temperatures at which these effects are detectable. Some other interesting uses can however anticipated. By mentioning an example, the molecular nature of the cluster could be exploited by attaching the cluster to other molecules of biological or pharmacological interest. A very interesting magnetic probe or contrasting medium could then be absorbed and reach the target site.

The main interest in this new class of molecular magnetic materials comes, however, from fundamental physics that can exploit them as test-book examples of magnetism in the nano-scale range of matter.

ACKNOWLEDGMENTS

The constant help of Prof. Dante Gatteschi is gratefully acknowledged as well as the contributions of Andrea Caneschi, Miguel A. Novak, and David P. Goldberg.

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