Slow Magnetic Relaxation of [Et₃NH]₂[Mn(CH₃CN)₄(H₂O)₂] [Mn₁₀O₄(biphen)₄Br₁₂] (biphen = 2,2′-biphenoxide) at Very Low Temperature

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The high-field EPR spectra of a mixed valence cluster compound of formula [Et₃NH]₂[Mn(CH₃CN)₄(H₂O)₂] [Mn₁₀O₄(biphen)₄Br₁₂] confirm that the high-spin ground state ($S = 12$) of the cluster has a negative zero-field splitting, $D = -0.037(1)$ cm^{-1}. The reversal of the magnetization at low temperature should therefore overcome an energy barrier corresponding to $|D|S^2$, which corresponds to ca. 7.7 K. Slow relaxation of the magnetization is detected below 1 K by ac magnetic susceptibility and the characteristic time follows approximately an Arrhenius law, where the height of the barrier is 7.0 K. The counterion, constituted by a manganese(II) complex, is easily oxidized, and aged samples seem to contain amorphous Mn₃O₄.

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INTRODUCTION

Molecular clusters comprising transition-metal ions bridged by anions, like oxides and halides, have been shown to give rise to novel magnetic behaviors, intermediate between those of simple paramagnets and bulk magnets (1). Under this respect manganese clusters (2) have been found to be particularly appealing after it was shown that the magnetization of the dodecanuclear cluster [Mn₁₂O₁₂ (CH₃COO)₁₆(H₂O)₄], Mn12Ac, which has a ground $S = 10$ state (3), relaxes very slowly at low temperature (3). In fact, at 2 K the relaxation time of the magnetization is on the order of some months, (4) and quantum effects have

been observed, like a stepped magnetic hysteresis and an anomalous field dependence of the relaxation of the magnetization (5). These properties are associated with the presence of an Ising type magnetic anisotropy, which is given by an axial zero field splitting of the ground $S = 10$ multiplet, $D \approx -0.5$ cm^{-1} (3, 6). The barrier for the reorientation of the magnetization is of the order $\Delta = DS^2 \sim 70$ K (7).

The appealing feature of the manganese clusters as possible candidates for observing similar properties is that they can comprise the metal ion in three different oxidation states all of them magnetic, namely manganese(II), $S = 5/2$, manganese(III), $S = 2$, and manganese(IV), $S = 3/2$. Further manganese(III) in octahedral environment is always strongly distorted given the instability of the ground ^5E_g state to Jahn–Teller distortions. This in general traps the valencies in mixed valence species, thus giving rise to compounds corresponding to Class I of Robin and Day classification (8), but it gives rise to strong anisotropy of the Ising type, which is necessary prerequisite for the observation of the slow relaxation of the magnetization of the clusters at low temperature.

As the height of the barrier depends on the square of the spin value of the ground state, very high spin molecules become very promising to achieve single-molecule magnets with high blocking temperature.

Recently, some of us reported a series of decanuclear manganese clusters of general formula [Mn₁₀O₄(biphen)₄ X_{12}]$^{4-}$, where $X =$ Cl, Br, and biphen is 2,2′-biphenoxide, whose structure is reported in Fig. 1 (9). Charge compensation and X-ray crystal structure data suggest that there are four manganese(III) and six manganese(II) ions in the cluster and that the valences are localized. The ground state of the cluster is characterized by a very large spin, $S = 12$.

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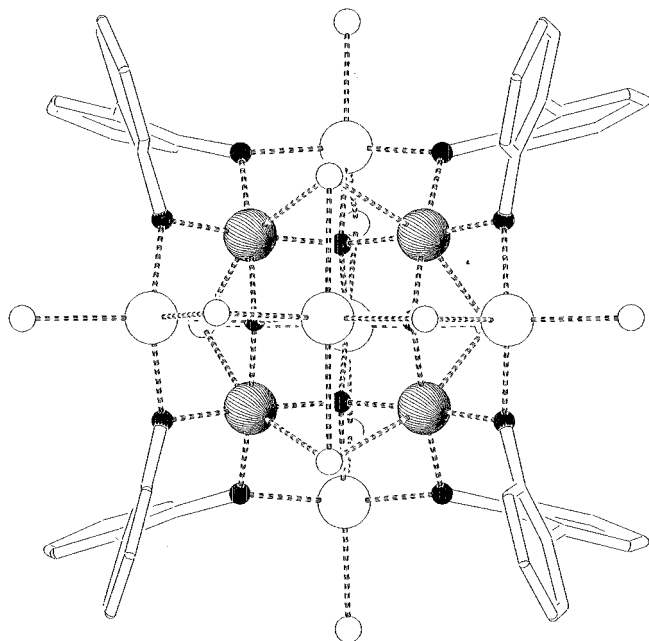
FIG. 1. Structure of the cluster $[Mn_{10}O_4(biphen)_4Br_{12}]^{4-}$. The large circles represent Mn and the tripositive sites are shown. The small filled circles are oxygen atoms and the empty circles are bromine atoms.

A zero field splitting parameter $D \approx -0.047$ cm^{-1} was reported for $[N(CH_3)_4]_4[Mn_{10}O_4(biphen)_4Cl_{12}]$ from high-frequency, HF-EPR, data (10). The clusters crystallize with different cations. Performing the reaction in CH_3CN, we isolate large crystals of a compound of formula $[Et_3NH]_2[Mn(CH_3CN)_4(H_2O)_2][Mn_{10}O_4(biphen)_4Br_{12}]$, Mn11, which comprise a paramagnetic manganese(II) cation. Single crystals polarized neutron diffraction through the analysis of the spin density map has recently confirmed a magnetization of 23.7 μB per cluster at 10 K and 5.5 T (11). The coupling scheme with all the manganese(III) spins aligned parallel to each other, previously suggested (9), has also been confirmed, and a spherical spin density around the metal cation is observed as expected for manganese(II), a d^5 ion (11).

Single-crystal magnetic anisotropy and conventional X-band EPR spectroscopy showed that the interaction between the isolated manganese(II) and the cluster is small, and that the ground $S = 12$ state has $D \sim |0.035|$ cm^{-1}. This suggests an upper limit to the barrier for the reorientation of the magnetization, $\Delta = DS^2$ of ca. 7 K. With this barrier, one should expect slow relaxation only at very low temperature, since this is about one tenth the barrier observed in Mn12Ac.

We have now measured the HF-EPR spectra together with the dynamic magnetic susceptibility of Mn11 at low temperature (lower than 1 K), and we wish to report here the evidence of slow relaxation of the magnetization in that range of temperature.

EXPERIMENTAL

Mn11 was prepared as previously described (9). Ac susceptibility measurements on polycrystalline samples were made with a home-built susceptometer based on a mutual inductance bridge, operating at various frequencies and equipped with an Oxford Instruments ^{3}He Heliox system capable of reaching 300 mK.

Dc magnetization measurements on polycrystalline samples were performed on a Metronique Ingegnerie M03 SQUID operating in the range 0–7 T, 1.5–280 K. The diamagnetic contributions of the compounds were estimated using Pascal's constants.

The HF-EPR spectra have been recorded on a freshly filtered microcrystalline powder by using a laboratory-made spectrometer based on a far-infrared laser and a InSb bolometer (12).

X-ray powder diffraction spectra were recorded on a Philips PW 1050/70 diffractometer equipped with copper radiation and Fe filter in the range $6 < 2\theta < 60°$.

RESULTS AND DISCUSSION

The HF-EPR spectra of a pellet of Mn11 at 10 K are shown in Fig. 2. The spectra were recorded with an exciting frequency of 245 GHz. The spectra are similar to those of an $S = \frac{1}{2}$ spin, with a feature, associated with crystallites with their unique axis parallel to the external field, at 8 T and a perpendicular feature at 9.2 T. This is the result of the
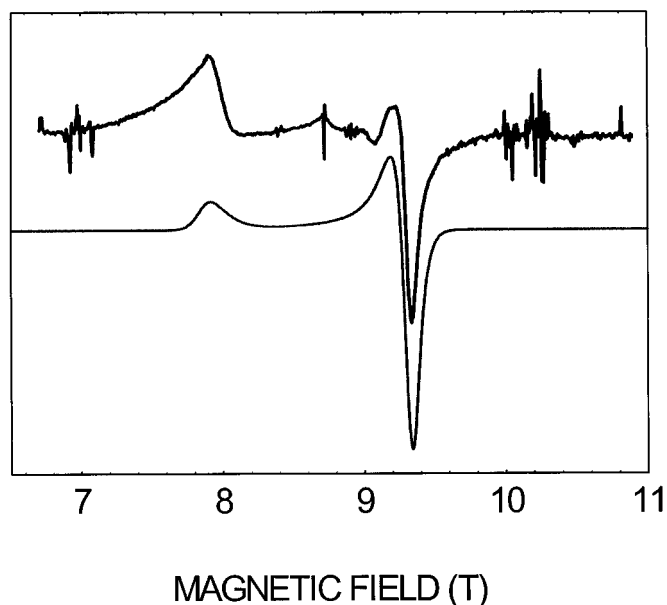

MAGNETIC FIELD (T)

FIG. 2. Polycrystalline powder EPR spectrum recorded at 245 GHz and 10 K (top) and calculated spectrum with $S = 12$, $D = -0.037$ cm^{-1} and $E/D = 0$. The g = 2 resonates at 8.75 T. The spikes are due to experimental artifacts.

depopulation of the excited Zeeman levels, which at low temperature allow one to see only the transitions starting from the lowest $M = -S$ state (13). The fact that the parallel feature is observed at low field is a clear indication of the fact that the zero field splitting parameter D is negative, i.e., the $M = \pm S$ states lie lowest in zero field. The fit of the spectra shown in Fig. 2 was performed using a described program which takes into account the thermal depopulation effect (14). The fit can be considered satisfactory as far as the position of the absorptions is concerned, the intensities as well as the line shape are not correctly simulated. Similar problems are often encountered using high-frequency spectrometers (6) and can be due to the experimental setup as well as to partial alignment of the crystallites in the high external field, even if the powder was pressed to reduce the alignment. The best-fit parameters assuming $S = 12$ are $g = 1.98$, $D = 0.037$ cm^{-1}. They are in good agreement with the values obtained from the analysis of single-crystal X-band EPR spectra (9) even if the last one presented a more pronounced signal at $g = 2$, which could be due to a larger content of Mn_3O_4 (vide infra). The D value is also similar but significantly smaller than that reported for $[N(CH_3)_4]_4$ $[Mn_{10}O_4(biphen)_4Cl_{12}]$ (10). The zero-field splitting of the cluster is expected to be due to a sum of contributions, including the individual zero-field splitting of the manganese(II) and manganese(III) ions and the through space and through bond magnetic interactions. In clusters comprising manganese(III) ions it is usually assumed that the single-ion zero-field splitting gives the largest contribution to D. The difference in the observed D values of Mn11 and $[N(CH_3)_4]_4[Mn_{10}O_4(biphen)_4Cl_{12}]$ may be due to the replacement of chloride with bromide in the coordination environment of manganese(III). The important result of the HF-EPR spectra of Mn11 is that it suggests an Ising-type anisotropy, with an upper limit to the barrier for the re-orientation of the magnetization of 7.7 K.

The temperature dependence of the in-phase, χ', and the out-of-phase, χ'', ac susceptibility of Mn11 is shown in Fig. 3. χ' dramatically drops below 1 K, in a frequency-dependent fashion, and at the same time χ'' becomes different from zero and goes through a maximum. This is a clear indication of the fact that the relaxation rate of the magnetization becomes of the same order of magnitude as the frequency of the ac field (15). Higher frequencies give rise to maxima at higher temperature. The relaxation time can be obtained from the position of the maxima in χ'' where $\tau \simeq \frac{1}{2\pi\gamma}$, being γ the frequency of the ac field. The results, shown in Fig. 4, can be fitted with an exponential law

$$\tau = \tau_0 \exp(\Delta/kT) \qquad [1]$$

with $\Delta/k = 7.0$ K, and $\tau_0 = 1.7 \times 10^{-9}$ s. The barrier is only slightly lower than that, 7.7 K, guessed from the zero-field splitting of the ground $S = 12$ state but almost within the
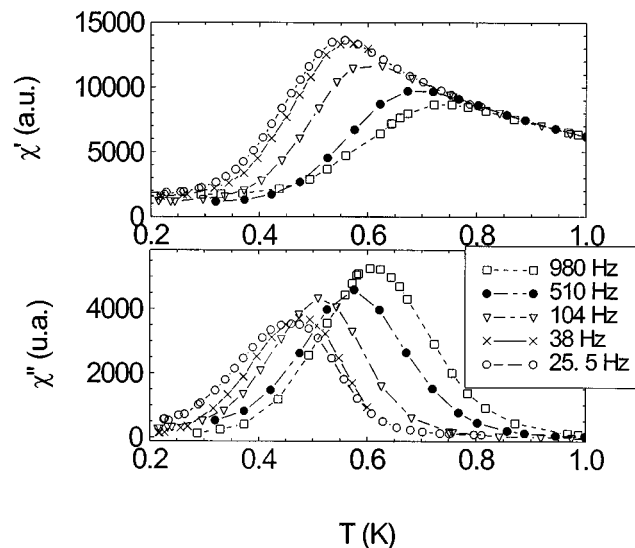

FIG. 3. Temperature dependence of the real (top) and imaginary (bottom) components of the ac magnetic susceptibility measured at five frequencies.

incertitude of the determination of D. A reduction of the height of the barrier compared to that estimated through the $\Delta = DS^2$ relation has been always experimentally found and has been attributed to quantum tunneling across the barrier involving the higher levels with a shortcut of the top of the barrier (17). In the present case, such a phenomenon is not very pronounced, suggesting that at these temperatures the mechanism of relaxation of the magnetization is mainly thermally activated, in agreement with the tetragonal symmetry of the cluster, the tunneling being driven by the transverse magnetic anisotropy. Other experiments at lower
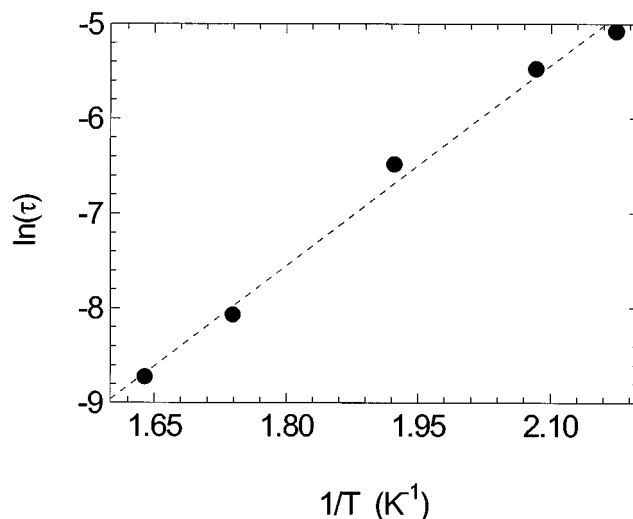

FIG. 4. Temperature dependence of the relaxation time of the magnetization. The solid line represents the best fit obtained using an Arrhenius law $\tau = \tau_0 \exp(\Delta E/k_B T)$ with $\tau_0 = 1.7 \times 10^{-9}$ s and $\Delta E = 7.0$ K.
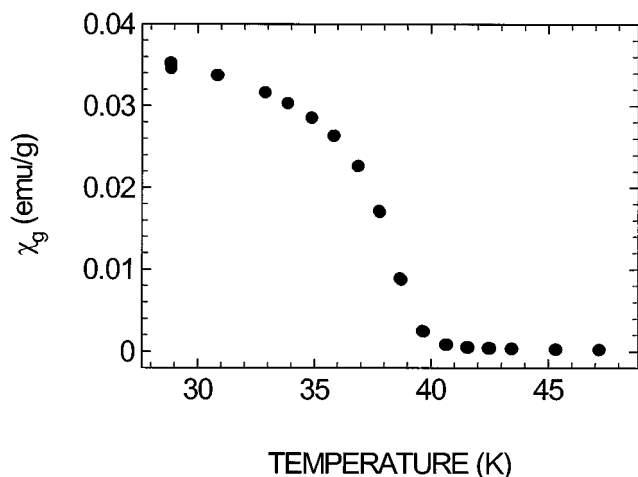
FIG. 5. Temperature dependence of the magnetic susceptibility in emu per gram of the inorganic fraction of an aged sample. A magnetic phase transition occurs at ca. 40 K.

temperature, still in progress, are required to speculate further on this point. The preexponential factor is much shorter than that observed in Mn12 (4) and in another cluster comprising manganese(III) and manganese(IV) ions showing slow relaxation of the magnetization at low temperature (2).

All the reported measurements were performed on freshly filtered samples. We measured the magnetic susceptibility also on samples left in standard atmosphere at room temperature for about one week and found different properties. In fact, the magnetic susceptibility showed sharp increase below 40 K, suggesting the presence of a magnetic phase transition. We were suspicious of the coincidence of the phase transition with that observed for haussmannite, Mn_3O_4 (18); therefore, we tried to confirm the possibility that the magnetic properties of the aged samples were due to this decomposition product. The aged sample was redissolved in acetonitrile and the insoluble fraction was filtered out. X-ray powder diffraction patterns showed that this material is essentially amorphous. Metal analysis showed the presence of ca. 69.5% of manganese and 29% of oxygen, to be compared to the expected 72 and 28%, respectively, of haussmannite. The temperature dependence of the magnetic susceptibility, shown in Fig. 5, agrees well with that observed for Mn_3O_4. From the solution it was possible to obtain the starting material in moderate yield. The formation of the haussmannite was observed to occur more rapidly if the material was gently warmed for few hours.

CONCLUSIONS

Mn11 represents a new example of very high spin single molecule magnet, and despite the low blocking temperature as compared to other systems, its characterization has provided an interesting confirmation of the molecular origin of the superparamagnetic behavior in this class of materials.

The agreement between the observed and calculated barrier to the reorientation of the magnetization shows that the slow relaxation can be successfully modeled within the simple spin-Hamiltonian approach. The presence of the uncoupled manganese(II) ions in the lattice is of great interest. In fact, while in the thermally activated regime it does not seem to affect the relaxation of the clusters, confirming the molecular origin of the phenomenon, it could play an important role in the tunneling mechanism due to the presence of fluctuating dipolar magnetic field inside the sample. Further investigations at lower temperatures are in progress to elucidate this point.

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