

Proton NMR study in hexanuclear manganese single-molecule magnets

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(Received 5 November 2006; published 12 February 2007)

We report a detailed proton NMR study, as a function of temperature and external magnetic field, of two hexanuclear manganese magnetic molecule clusters with chemical formula $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CMe})_2(\text{salox})_6(\text{EtOH})_4] \cdot 4\text{EtOH}$ (in short Mn_6 acetate) and $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_2(\text{salox})_6(\text{EtOH})_4] \cdot 4\text{EtOH}$ (henceforth Mn_6 benzoate). Both clusters are characterized by a ferrimagnetic ground state with total spin $S_T=4$ and a large uniaxial anisotropy, which gives rise to an effective energy barrier for the relaxation of the magnetization of the order of $U_{\text{eff}} \sim 28$ K. The main characteristics of the ^1H NMR spectra (measured between 1.5 K and room temperature for different fields) are explained in terms of the dipolar hyperfine interaction of the proton nuclei with the adjacent magnetic ions. At low temperatures ($T < 3.5$ K), the spectra broaden significantly and become structured due to the slowing down of the local fluctuating fields at the proton sites, caused by the gradual freezing of the Mn^{3+} moments into the $S_T=4$ collective ground state. The spin dynamics of the exchange coupled magnetic ions was also probed by proton spin-spin relaxation rate T_2^{-1} and spin-lattice relaxation rate T_1^{-1} measurements. On decreasing the temperature, a gradual enhancement of both relaxation rates is observed, followed by a significant decrease of the signal intensity (wipe-out effect). The low frequency regime of the spin fluctuations as probed by T_1^{-1} , can be described and analyzed in terms of a single characteristic correlation frequency $\omega_c(T)$, which is interpreted as the lifetime broadening of the discrete magnetic energy levels due to spin-phonon interactions.

DOI: [10.1103/PhysRevB.75.064414](https://doi.org/10.1103/PhysRevB.75.064414)

PACS number(s): 75.50.Xx, 76.60.-k, 75.75.+a

I. INTRODUCTION

The recent progress in the field of molecular chemistry has made feasible the synthesis of a large variety of crystalline structures built from identical molecular units. Each such unit contains a relatively small number of magnetic transition metal ions embedded in a large, nonmagnetic organic matrix. These ions are strongly coupled via intramolecular super-exchange interactions J of typical order of a few tens of Kelvin, while being magnetically “shielded” from ions belonging to adjacent molecular units due to the presence of the large organic matrices. Hence, the intermolecular magnetic interactions are typically of dipolar origin and thus, for most cases, can be neglected.¹ Accordingly, the measurements in bulk crystalline samples reflect the magnetic properties of each “single-domain particle.”

The research in the field of molecular magnetism has been very active with particularly emphasis being given to the study of molecular clusters with high spin ground states and large, negative magnetoanisotropy (such as the Mn_{12} , Fe_8 , and Fe_4). The interest in these so-called single molecule magnets (SMM’s), relies on the remarkable manifestation of purely quantum effects at low T , such as macroscopic quantum tunneling of the magnetization^{2–4} and quantum interference effects.⁵

Of particular experimental and theoretical interest has also been the study of the electronic spin correlations. One can follow the evolution of these correlations from the high temperature regime ($T \gg J/k_B$), where thermal fluctuations dominate and the ions behave independently (zero dimensional paramagnet), down to intermediate T ($T \sim J/k_B$), where correlations have been established by the exchange

interactions, and finally to very low T where each molecular unit occupies its collective ground state. In addition, and because of the discreteness of the magnetic energy spectrum, the effects of the various small interactions of the exchange coupled spins with the excitations of the thermal bath (for instance phonons) are also of great interest. Such small interactions cause a long-time decay of the spin fluctuations, which in turn can be probed by dynamic NMR measurements. For instance, for the so-called antiferromagnetic (AFM) ring systems, it has been found that the characteristic cut-off frequency of the long-time decay of the electronic spin correlations decreases by a few orders of magnitude when decreasing the temperature below J/k_B , and this is manifested in measurements of T_1^{-1} by an enhancement at $T \sim J/k_B$ (Refs. 6 and 7). In SMM’s, a similar enhancement has also been observed in T_1^{-1} and T_2^{-1} , but the corresponding analysis had been hindered by a simultaneous gradual loss of the signal intensity. A detailed analysis of this so called “wipe-out effect” in the SMM’s can be found in Ref. 8, which includes some of our data from the two present SMM’s. Here, we present and analyze the full body of our data and provide additional information on the static and dynamic properties of these two SMM’s.

The two hexanuclear molecular clusters of the present study belong to a class of SMM’s consisting exclusively of Mn^{3+} ions.⁹ Except for their different ligands and the fact that the Mn_6 benzoate comprises two nearly identical hexanuclear molecules per unit cell, these two samples have quite similar molecular structures. Each molecule consists of two exchange coupled triangular spin units. The competition between antiferromagnetic and ferromagnetic exchange interactions stabilizes a ferrimagnetic ground state of collective

total spin $S_T=4$.⁹ Both molecular clusters have a uniaxial anisotropy (with anisotropy constant $D=-1.75$ K), which gives rise to a zero-field splitting of the ground state that in turn is responsible for an energy barrier U_{eff} for the reorientation of the magnetization at low temperature.⁹ The relaxation time of the magnetization follows an Arrhenius type of equation, $\tau=\tau_0 e^{U_{eff}/kT}$, with $U_{eff}\sim 28$ K and the pre-exponential factor τ_0 is $\tau_0=3.6\times 10^{-8}$ s for the Mn_6 acetate, and $\tau_0=2.3\times 10^{-8}$ s for the Mn_6 benzoate.⁹

The organization of this paper is as follows. We begin, in Sec. II, by giving the experimental details about our NMR measurements. In Sec. III, we present and analyze the experimental results for the line shape, signal intensity, the nuclear spin-spin relaxation time T_2 , and the spin-lattice relaxation time T_1 , both as a function of temperature and applied magnetic field. A short summary of the present study with our conclusions is finally given in Sec. IV.

II. EXPERIMENTAL DETAILS

We have performed 1H NMR measurements on polycrystalline Mn_6 acetate and Mn_6 benzoate samples using standard Fourier transform (FT) pulse NMR spectrometers. Two continuous flow cryostats were employed for measurements in the range 4–300 K and a bath cryostat for measurements in the range (1.5–4.2) K. The NMR spectrum was obtained from the FT of the half echo spin signal whenever the whole line could be irradiated with one radio frequency (rf) pulse. In case of a large width resonance line the spectrum was obtained either by (i) the spin echo, point per point method at different values of the irradiation frequency or (ii) for extremely wide lines by changing the external magnetic field while keeping the irradiation frequency constant (see Fig. 3). The 1H spin lattice relaxation T_1^{-1} rate was measured at the center of the spectrum by monitoring the recovery of the nuclear magnetization following a saturating comb of rf pulses. Because of the presence of many inequivalent proton sites in the cluster the recovery of the nuclear magnetization was nonexponential. The T_1^{-1} values reported here have been calculated from the initial decay of the recovery curve, and thus correspond to an average relaxation rate of the non-equivalent protons. The proton spin-spin relaxation rate T_2^{-1} was obtained using a standard Hahn echo pulse sequence.

III. RESULTS AND DISCUSSION

A. Proton NMR spectra

1H NMR spectra for Mn_6 acetate and Mn_6 benzoate were acquired as a function of temperature at different magnetic fields. Typical proton NMR spectra are shown in Fig. 1(a) at 4.7 T for selected temperatures in case of Mn_6 acetate (similar lines were observed for Mn_6 benzoate). By decreasing temperature a continuous broadening of the NMR spectrum is observed while no appreciable frequency shift of the peak from the Larmor frequency was found indicating that the broadening mechanism is of dipolar origin.

At room temperature the full width at half maximum (FWHM) of the 1H NMR spectrum varies linearly with the magnetic field [see Fig. 1(b), for Mn_6 acetate], and its mag-

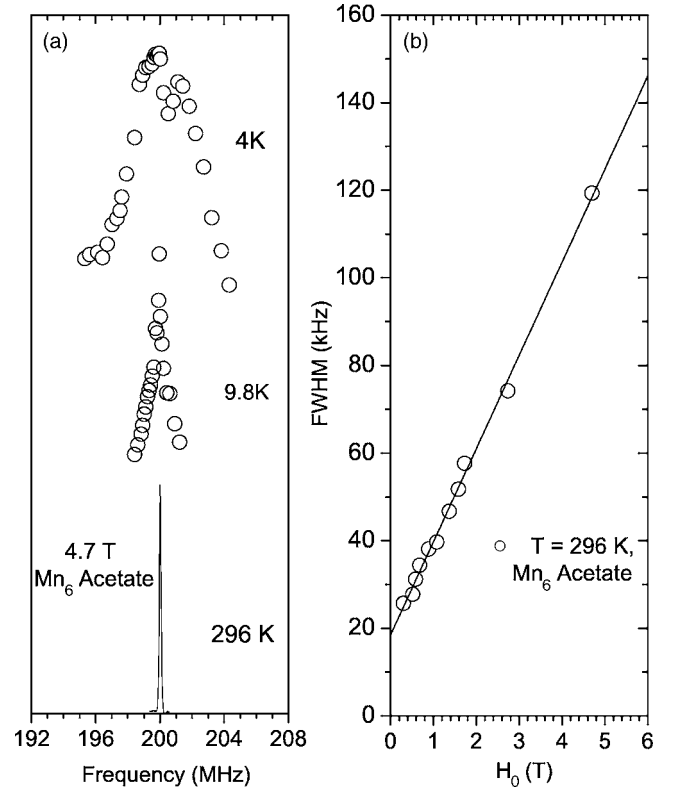


FIG. 1. (a) 1H NMR spectra at selected temperatures for Mn_6 acetate, at 4.7 T. The line at 296 K was obtained from the FT of the half echo spin signal while the lines at 4 and 9.8 K, were acquired by the point per point method. (b) 1H NMR linewidth $\Delta\nu$ (FWHM) vs field for Mn_6 acetate at room temperature. The solid line is linear fit according to Eq. (3), with parameters $A_z=3.47\times 10^{22}$ cm⁻³ and $\Delta\nu_0=18.5$ kHz.

nitude is of the order of a few kilohertz. The width of the proton NMR spectrum is a measure of (a) the dipolar interactions between the nuclei and (b) the dipolar hyperfine interactions of the nuclei with the neighboring magnetic ions. Due to the large number of protons in each molecule that have different dipolar hyperfine coupling with the adjacent Mn^{3+} ions, a distribution of paramagnetic shifts exists that broadens the NMR line inhomogeneously. In the presence of magnetic dipolar broadening and above the freezing temperature, the FWHM, $\Delta\nu$, can be written as^{10,11}

$$\Delta\nu = \Delta\nu_0 + (\Delta\nu)_{inh}. \quad (1)$$

The first term, $\Delta\nu_0$, is the intrinsic linewidth for dipolar interactions between the 1H nuclei and it is field and temperature independent. The second term, $(\Delta\nu)_{inh}$, is the inhomogeneous linewidth, which can be expressed in terms of the local susceptibility $\chi_M = \chi_{local}/N$ (N , the number of magnetic ions per molecule) as

$$\frac{(\Delta\nu)_{inh}}{\nu_L} = \frac{\gamma_N H_{local}^z}{2\pi \nu_L} = A_Z \chi_M \approx \frac{\langle \mu \rangle}{r^3 H_0}, \quad (2)$$

Here, $\nu_L = \frac{\gamma_N}{2\pi} H_0$, denotes the proton Larmor frequency, χ_M is the magnetic susceptibility, A_Z is the component of the hyperfine coupling constant along the applied magnetic field

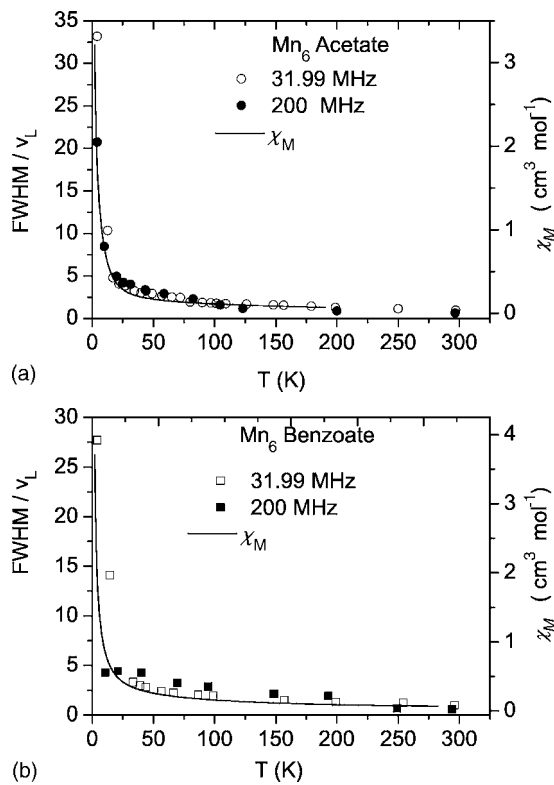


FIG. 2. Temperature dependence of the magnetic susceptibility χ_M (solid line) and the ^1H NMR full width at half maximum (FWHM) divided by the Larmor frequency, ν_L , for Mn_6 acetate in (a) and for Mn_6 benzoate in (b). The quantity FWHM/ν_L , is plotted at two different irradiation frequencies i.e., 31.99 MHz and 200 MHz, for each molecular cluster.

H_0 , and r is the mean distance between the ^1H and Mn^{3+} ions. According to Eqs. (1) and (2), the linewidth $\Delta\nu$ can be written as

$$\Delta\nu = A_Z \chi_M \nu_L + \Delta\nu_0, \quad (3)$$

i.e., the FWHM is field dependent and follows the temperature dependence of the magnetic susceptibility χ_M . At a given temperature, a linear frequency dependence of the FWHM is expected, as indeed observed in Fig. 1(b), for Mn_6 acetate. The experimental data were fitted by the Eq. (3), and the parameters $\Delta\nu_0$ and A_Z were estimated from the fit. Given that $\chi_M(295 \text{ K}) = 1.44 \times 10^{-26} \text{ cm}^3/\text{Mn-atom}$, we found $A_Z = 3.47 \times 10^{22} \text{ cm}^{-3}$ and $\Delta\nu_0 = 18.5 \text{ kHz}$. The value of $A_Z = 3.47 \times 10^{22} \text{ cm}^{-3}$ corresponds to an average distance $r = 3.1 \text{ \AA}$, between the H and Mn^{3+} ions which is of the correct order of magnitude, since the corresponding distances in the molecule cover a range from 2.37 \AA to 6.45 \AA .⁹

The temperature evolution of FWHM was studied for both samples, from room temperature to 4 K, for two different fields, i.e., 0.75 T and 4.7 T. The experimental data for the FWHM, were divided by the Larmor frequency and the results are presented in Fig. 2(a) for Mn_6 acetate and in Fig. 2(b) for Mn_6 benzoate. On decreasing the temperature, a monotonic increase of the FWHM is observed, and at low T , the FWHM becomes of the order of MHz. The temperature dependence of the FWHM can be understood in terms of the

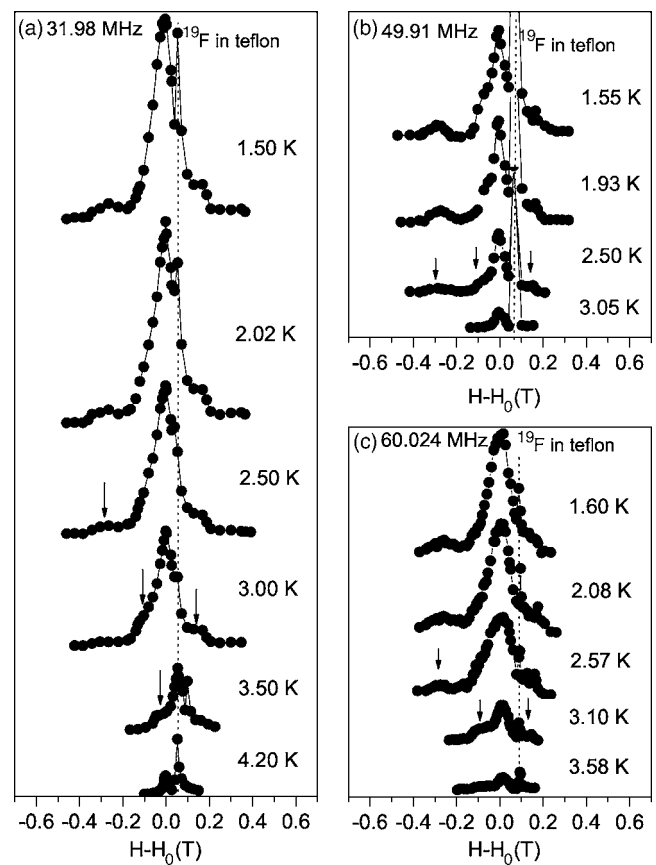


FIG. 3. ^1H line shape measurements at low temperature obtained at three different irradiation frequencies for Mn_6 acetate: (a) 31.984 MHz, (b) 49.91 MHz, and (c) 60.024 MHz. The vertical axis is the NMR signal intensity multiplied by the Boltzmann factor.

Eq. (3). After dividing the FWHM by the Larmor frequency ν_L the field dependence of the linewidth at low temperature is removed: $\frac{\Delta\nu}{\nu_L} = A_Z \chi_M + \frac{\Delta\nu_0}{\nu_L}$ and the T dependence of the linewidth arises from the T dependence of the susceptibility χ_M , as can be seen in Figs. 2(a) and 2(b).

The ^1H NMR spectrum of both Mn_6 samples, broadens and remains structureless, down to 4 K. Due to the extreme broadening (the spectrum covers a range of a few MHz at low T), the line shape measurements for the Mn_6 acetate at $T < 4.2 \text{ K}$ were performed by varying the magnetic field intensity while keeping constant the irradiation frequency ν_L . The measurements were acquired at three different irradiation frequencies, 31.98 MHz, 49.91 MHz, and 60.024 MHz, and the results are shown in Fig. 3. The main line of the spectrum remains unshifted down to the lowest measured temperature, for all the different irradiation frequencies, as expected for protons coupled to Mn^{3+} ions via dipolar interactions. Apart from this central line, three more weak and shifted peaks emerge at lower temperatures (their position is marked with arrows in Fig. 3). The shift $\Delta H_i = H_i - H_0$ of each peak from the Larmor field H_0 (H_i is the magnetic field at the center of each peak), is the same for all the different irradiation frequencies, as can be seen in Fig. 3, and the magnitude of the local field for each peak is $\Delta H_1 \approx -0.25 \text{ T}$, $\Delta H_2 \approx -0.07 \text{ T}$, and $\Delta H_3 \approx 0.17 \text{ T}$. The

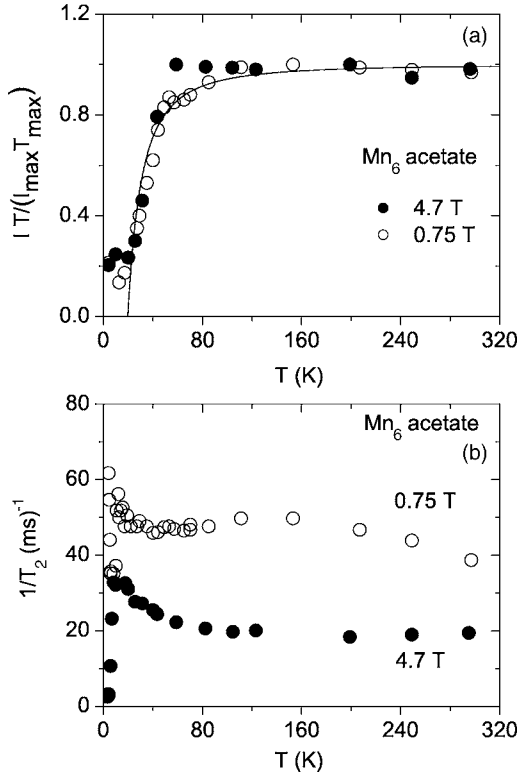


FIG. 4. (a) Normalized ^1H NMR signal intensity vs T at 0.75 T (open circles) and 4.7 T (filled circles) for Mn_6 acetate. The solid line is the fit to the data according to Eq. (4). (b) ^1H spin-spin relaxation rate T_2^{-1} vs temperature for Mn_6 acetate at 0.75 T (open circles) and 4.7 T (filled circles).

above experimental findings demonstrate that at low T (approximately 3.5 K) a spontaneous dipolar hyperfine field at the proton sites builds up, as the result of a frozen spin configuration of the Mn^{3+} moments in the $S_T=4$ ground state of the molecule. A static hyperfine field is anticipated providing that the lifetime of the corresponding magnetic state is longer than the inverse frequency shift of the proton NMR line from the Larmor frequency (estimated as 8×10^{-8} s from Fig. 3).^{12,13} An estimate of the average lifetime of the magnetic states according to our analysis (see below) gives that the average lifetime of the excited states is longer than 8×10^{-8} s below 10 K. The appearance of the shifted lines at even lower temperature is a result of the decreasing population of the excited states, and the subsequent increase of the population in the ground state, along with the progressive decrease of the frequency width of the magnetic states (see below).

B. Proton NMR signal intensity and spin-spin relaxation time T_2 measurements: wipeout effect

In order to investigate the dynamic spin freezing process and the related phenomena more thoroughly, we have performed detailed ^1H NMR signal intensity measurements as a function of temperature at two different external magnetic fields. The results are presented in Fig. 4(a) for Mn_6 acetate and in Fig. 5(a) for Mn_6 benzoate. Details about the calcu-

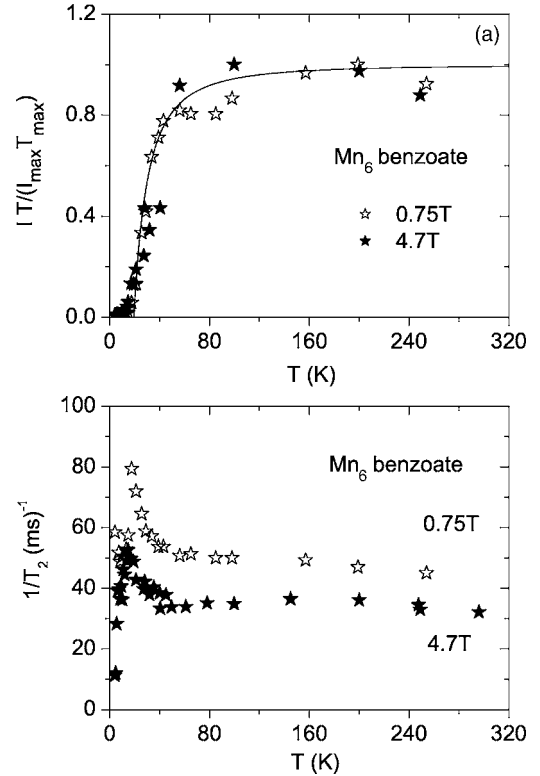


FIG. 5. (a) Normalized ^1H NMR signal intensity vs T at 0.75 T (open stars) and 4.7 T (filled stars) for Mn_6 benzoate. The solid line is the fit to the data according to Eq. (4). (b) ^1H spin-spin relaxation rate T_2^{-1} vs temperature for Mn_6 benzoate at 0.75 T (open stars) and 4.7 T (filled stars).

tion of the signal intensity can be found in Ref. 8. The freezing of the spin dynamics, as the system evolves towards its magnetic ground state, is accompanied by significant variation of the ^1H NMR signal intensity. In particular, a remarkable loss of the signal intensity (wipeout effect) is observed in the intermediate temperature range (from 80 K down to 4 K). The temperature dependence of the signal intensity was found to be field independent, according to measurements performed at 0.75 T and 4.7 T, for both samples, as can be seen in Figs. 4(a) and 5(a). The wipeout effect is due to the gradual enhancement of the spin-spin relaxation rate, $1/T_2$, which takes place below 80 K [see Fig. 4(b) for Mn_6 acetate and Fig. 5(b) for Mn_6 benzoate]. The temperature dependence of the spin-spin relaxation rate T_2^{-1} , and subsequently of the signal intensity, can provide useful information for the spin dynamics of the magnetic ions. The relaxation rate T_2^{-1} , in the fast motion approximation is related to the spectral density of the fluctuating hyperfine field at zero frequency, i.e., $T_2^{-1} = \gamma_N^2 \langle \delta H_z^2 \rangle \tau(T) = \gamma_N^2 \frac{\langle \delta \mu_z^2 \rangle}{\rho} \tau(T)$, where δH_z is the local longitudinal fluctuating field originating from the Mn^{3+} magnetic moment at a distance r apart from the proton spin, and $\tau(T)$ gives the correlation time, which is determined by the dynamics of the magnetic ions. The magnitude of the relaxation rate T_2^{-1} , varies among the nuclei since the local field δH_z depends on the relative distance, r , between the magnetic ion and the proton site. On decreasing the temperature a fraction of protons, in particular the ones

which are closer to the magnetic ions, attain relaxation times T_2 faster than the dead time of the spectrometer ($T_2 < \tau_d = 10 \mu\text{s}$) and thus, they do not contribute to the signal intensity, while the more distant protons have slower relaxation time ($T_2 > \tau_d$) and can be detected. The loss of the signal intensity (wipeout effect) has been found to be a common feature in the FM clusters,^{8,14} and has explained and analysed in Ref. 8, in terms of a simple and intuitive model. The number of the protons $n(T)$ that contribute to the NMR signal intensity at each temperature according to this model was found to be⁸

$$\frac{n(T)}{n_0} = 1 - \frac{\gamma_N \sqrt{\langle \delta \mu_e^2 \rangle} \sqrt{\tau_d}}{R^{*3}} \sqrt{\tau(T)}, \quad (4)$$

where n_0 is the total number of protons in each molecule, and R^* accounts for the distance between the magnetic ion and the more distant proton sites. The above formula was used to fit the signal intensity data in Figs. 4(a) and 5(a) (solid line) where for the temperature dependence of the correlation time $\tau(T)$ a power law of the form $\tau(T) = cT^{-3.5}$ (T in Kelvin) was used. This power law temperature dependence of the correlation time was originally obtained by an ^1H NMR study in a series of AFM molecular rings,⁶ and later used in Ref. 8 to reproduce both the signal intensity and the spin-lattice relaxation rate T_1 measurements in a series of SMM's. The adjustable parameters in Eq. (4) are the terms $\sqrt{\langle \delta \mu_e^2 \rangle}/R^{*3}$ and c [from the temperature dependence of $\tau(T)$]. The factor $\sqrt{\langle \delta \mu_e^2 \rangle}/R^{*3}$ can be considered as the local hyperfine field experienced by the most distant proton sites and is found to be 343 G for Mn_6 acetate and 331 G for Mn_6 benzoate, being of the correct order of magnitude for both samples. The value of the parameter c is found to be the same, $c = 4 \times 10^{-5} \text{ sec/rad}$, for both clusters.

The abrupt drop of the signal intensity is followed at even lower temperatures ($T_f \sim 3.5 \text{ K}$) by a recovery of intensity as can be observed in Fig. 3 for Mn_6 acetate. This recovery of the signal intensity occurs as the system enters in a frozen spin configuration, which is evident from the appearance of shifted peaks in the low T spectra (Fig. 3), and can be qualitatively explained as follows. For T lower than some characteristic temperature T_f , the correlation time $\tau(T)$ becomes so long that, $\tau\gamma\delta H_z \sim 1$, i.e., the fast motion approximation breaks down and the local field δH_z becomes static in the time scale of the Larmor precession period in the local field itself. As a consequence the line broadens inhomogeneously, the spin-spin relaxation time T_2 increases again towards the value corresponding to nuclear dipolar interactions, and the NMR signal intensity recovers, similar to what have been reported in other SMM's.^{8,15}

C. Spin-lattice relaxation time T_1

The spin-lattice relaxation rate, T_1^{-1} , is a unique microscopic probe of the low frequency (or long time) regime of the spin fluctuations of the exchanged coupled Mn^{3+} ions, since the dominant relaxation mechanism for the nuclear spins is the dipolar hyperfine interaction. In the weak collision perturbative approximation the spin-lattice relaxation

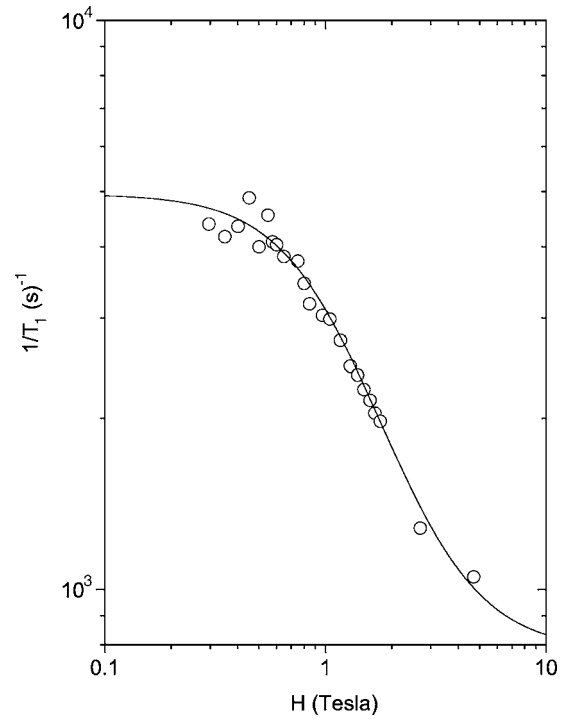


FIG. 6. ^1H spin-lattice relaxation rate T_1^{-1} as a function of the external magnetic field H measured at room temperature for Mn_6 acetate. The solid line is the fit to the data according to Eq. (6).

rate is proportional to the spectral density of the electronic spin fluctuations evaluated at the Larmor frequency, ω_L .^{6,16} Assuming isotropic Heisenberg interactions only and that in the long time regime the correlation functions decay exponentially with a single correlation time $\tau(T)$, one can express the relaxation rate T_1^{-1} as^{6,16,17}

$$\frac{1}{T_1} = A\chi T \frac{\omega_0(T)}{\omega_0^2(T) + \omega_L^2}. \quad (5)$$

Here the parameter A contains geometrical information about the relative distances and orientations of the protons with respect to the electronic spin sites, χ is the uniform magnetic susceptibility and $\omega_0(T) = \tau(T)^{-1}$ is the lifetime broadening of the discrete energy levels due to the transitions induced by the bath. Thus, by measuring the nuclear spin-lattice relaxation one can gain information about the relaxation processes of the electronic spin system driven by the interaction with the bath.

The proton spin-lattice relaxation rate T_1^{-1} for Mn_6 acetate is shown in Fig. 6 as a function of the external magnetic field at room temperature. The field dependence is well represented (solid line in Fig. 6) by the formula

$$\frac{1}{T_1} = A' \frac{\omega_0(T)}{\omega_0^2(T) + \omega_L^2} + C, \quad (6)$$

with $A' = 1.25 \times 10^{12} \text{ rad}^2/\text{sec}^2$, $\omega_0 = 3 \times 10^8 \text{ Hz}$, and $C = 7.8 \times 10^2 \text{ Hz}$. The prefactor A' corresponds to the product $A\chi T$ of Eq. (5) and is of the correct order of magnitude. The constant term C accounts for additional contributions to the spin-lattice relaxation related with the presence of aniso-

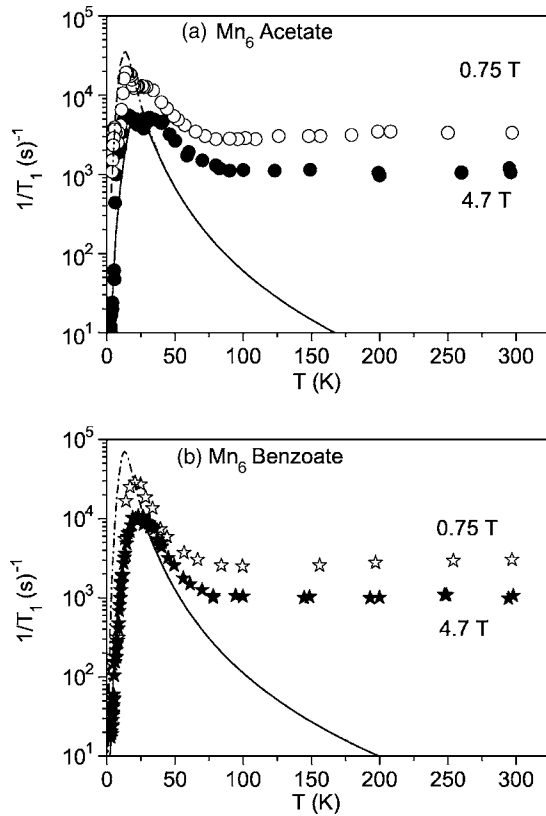


FIG. 7. (a) ^1H spin lattice relaxation rate T_1^{-1} vs temperature for Mn_6 acetate at 0.75 T (open circles) and 4.7 T (filled circles). (b) ^1H spin lattice relaxation rate T_1^{-1} vs temperature in Mn_6 benzoate at 0.75 T (open stars) and 4.7 T (filled stars). The lines are fits according to Eq. (5).

tropic interactions [e.g., anisotropic exchange, intercluster couplings, or single ion anisotropies⁷ not included in Eq. (5)]. More generally, the characteristic enhancement of T_1^{-1} at low fields is similar to what has been reported in other molecular nanomagnets,⁷ and according to Eq. (6), expresses the fact that the low frequency part of the electronic spin fluctuations is peaked at low fields.

The spin-lattice relaxation rate T_1^{-1} , was also studied as a function of temperature, in two different fields (0.75 T and 4.7 T), for Mn_6 acetate [Fig. 7(a)] and for Mn_6 benzoate [Fig. 7(b)] and was found to be strongly temperature dependent. Specifically, by decreasing T an enhancement of T_1^{-1} is observed below 100 K, followed by a broad maximum at $T \sim 20$ K, similarly to what has been observed in other FM clusters and antiferromagnetic (AFM) rings with local spins $s > 1/2$.^{6,8,18} The enhancement of T_1^{-1} appears simultaneously with the increase of the spin-spin relaxation rate T_2^{-1} [Figs. 4(b) and 5(b)] and is evidence of their common origin, namely the increase of the correlation time $\tau(T)$ (slowing down) by decreasing temperature. The spin-lattice relaxation data at intermediate T can be fitted according to Eq. (5) [solid lines in Figs. 7(a) and 7(b)], where we use for the temperature dependence of $\tau(T)$ the same expression

[$\tau(T) = cT^{-3.5}$] and the same values for the parameter c , we used before to fit the signal intensity measurements. Considering that the amplitude of the fluctuations of the electronic moment (χT) does not change appreciably in the temperature range of interest, we can treat the term $A\chi T$ as a fitting constant. The fit to our data is satisfactory [solid lines in Figs. 7(a) and 7(b)], considering that the enhancement of T_2^{-1} and the subsequent loss of the signal intensity introduces some uncertainty in the measured T_1^{-1} data. Specifically, by decreasing T and due to wipeout effect, the reported values of T_1^{-1} correspond to the average relaxation rate of only a fraction of the protons in the molecule, i.e., those with slow relaxation rate, and not all the nuclei as was the case for $T > 100$ K. The values of the average square frequency of the fluctuating transverse hyperfine field, $A\chi T$, was found to be $1.5 \times 10^{13} \text{ rad}^2/\text{sec}^2$ for the Mn_6 acetate and $2.8 \times 10^{13} \text{ rad}^2/\text{sec}^2$ for Mn_6 benzoate which are of the correct order of magnitude.

IV. SUMMARY AND CONCLUSIONS

In this work, we have presented a thorough ^1H NMR study in two new ferrimagnetic SMM's. From the ^1H NMR line shape measurements at different fields and temperatures, we have shown that the width of the spectrum is proportional to the magnetic susceptibility, demonstrating that NMR is a direct probe of the local magnetic properties. The source of the inhomogeneous broadening of the spectra is the dipolar coupling between the protons and the localized manganese ions. At very low temperatures ($T < 3.5$ K), the width of the ^1H NMR spectrum remains constant and additional lines appear whose relative shifts from the Larmor frequency are field independent. The appearance of the shifted lines and the recovery of the signal intensity imply the presence of local static hyperfine fields due to the thermal occupation by the molecules of the superparamagnetic ground state and the decrease of the lifetime time broadening parameter $\omega_c(T)$. The temperature dependence of $\omega_c(T)$ succeeds in explaining the signal intensity measurements and in reproducing the temperature dependence of T_1^{-1} at the intermediate temperature range. A significant result is that the electronic spin fluctuations can be described well by this single correlation frequency, having a similar power law T dependence, as found in a number of AFM rings,^{6,18} FM clusters¹⁸ and recently in a crystal of $\text{LiY}_{1-x}\text{Ho}_x\text{F}_4$ with very dilute Ho concentrations, $x = 0.002$.¹⁹ A theoretical justification for such a temperature dependence of $\omega_c(T)$ is still lacking, but its origin is believed to be related to the electron spin-phonon interactions.

ACKNOWLEDGMENTS

We would like to acknowledge fruitful discussions with I. Rousochatzakis, I. Papaefstathiou, and the experimental assistance of R. Vincent. Ames Laboratory is operated by the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

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