Persistent spin dynamics in the $S=1/2$ V_{15} molecular nanomagnet

Z. Salman,[1,2,*] R. F. Kiefl,[3,4,5] K. H. Chow,[6] W. A. MacFarlane,[7] T. A. Keeler,[4] T. J. Parolin,[7] S. Tabbara,[3] and D. Wang[4]
[1]*Clarendon Laboratory, Department of Physics, Oxford University, Parks Road, Oxford OX1 3PU, United Kingdom*
[2]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 0QX, United Kingdom*
[3]*TRIUMF, 4004 Wesbrook Mall, Vancouver, British Columbia, Canada V6T 2A3*
[4]*Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1*
[5]*Canadian Institute for Advanced Research, Toronto, Ontario, Canada M5G 1Z8*
[6]*Department of Physics, University of Alberta, Edmonton, Alberta, Canada T6G 2G7*
[7]*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1*
(Received 3 January 2008; revised manuscript received 28 March 2008; published 10 June 2008)

We present muon spin-lattice relaxation measurements in the V_{15} spin 1/2 molecular nanomagnet. We find that the relaxation rate in low magnetic fields (<5 kG) is temperature independent below ~ 10 K, implying that the molecular spin is dynamically fluctuating down to 12 mK. These measurements show that the fluctuation time increases as the temperature is decreased and saturates at a value of ~ 6 ns at low temperatures. The fluctuations are attributed to V_{15} molecular spin dynamics perpendicular to the applied magnetic-field direction, induced by coupling between the molecular spin and nuclear spin bath in the system.

DOI: 10.1103/PhysRevB.77.214415 PACS number(s): 76.60.−k, 75.45.+j, 76.75.+i

I. INTRODUCTION

Recent advances in the field of molecular magnetism, using a bottom up approach to synthesis, have produced magnetic systems based on molecules rather than metals or oxides. Example systems include single molecule magnets (SMMs) and high spin molecules,[1] photomagnets,[2,3] and room-temperature magnets.[4] The focus of the current work is SMMs and their interaction with the environment. These systems have been attracting much attention in recent years mainly due to the discovery of quantum tunneling of the magnetization (QTM) in Mn_{12} and Fe_8.[5,6] A SMM is composed of a small cluster of magnetic ions with strong magnetic interactions between them ($J\sim 10-100$ K), embedded in magnetically inactive organic or inorganic ligands. Each cluster is thus isolated from its neighbors, forming at low temperatures a lattice of noninteracting spins and allowing the study of the quantum behavior of isolated spins. SMMs are ideal objects to study phenomena of great scientific importance for mesoscopic physics, such as QTM,[5–7] topological quantum phase interference,[8,9] and quantum coherence.[10–15] They could also be applicable for the recording industry,[16,17] as well as for information transmission and quantum computing.[18–22]

The effective spin Hamiltonian describing a SMM is usually written as

$$\mathcal{H} = -DS_z^2 - g\mu_B \mathbf{S}\cdot\mathbf{H} + \mathcal{H}^t, \quad (1)$$

where the first term is the easy axis magnetocrystalline anisotropy term, which is the source of the double-well structure and degeneracy of spin-up and spin-down states, the second is the Zeeman term, and $\mathcal{H}^t$ includes additional crystal-field terms as well as the interaction between the molecular spin and its environment (including molecule-molecule dipolar[12,23] and molecule-nuclear-spin bath interactions[23,24]). In prototypical systems such as Mn_{12} and Fe_8, the anisotropy term is large and therefore $\mathcal{H}^t$ is only a perturbation, making it difficult to perform direct measurements to identify the detailed nature of $\mathcal{H}^t$. However, isotropic ($D\simeq 0$) systems provide an ideal system in which $\mathcal{H}^t$ can be probed directly. In this paper we present muon spin-relaxation (μSR) measurements on the spin 1/2 molecular magnet $K_6[V_{15}^{IV}As_6O_{42}(H_2O)]\cdot 8H_2O$, known as V_{15}.[25] Due to its spin 1/2 nature this molecule has no anisotropy, i.e., $D\equiv 0$. We find the molecular spin dynamics of V_{15} persists down to millikelvin temperatures, and there is no evidence of freezing even in an applied field of up to 10 kG.[26] The persistent spin dynamics are consistent with a previously reported μSR study;[27] however, our measurements were extended to lower temperatures and higher fields, allowing a more comprehensive understanding of the nature and source of V_{15} spin dynamics. The spin-fluctuation time measured is on the nanosecond scale and saturates at ~ 6 ns at low temperature. These molecular spin fluctuations are perpendicular to the applied field direction and are attributed to the interaction between the V_{15} molecular spin and its environment, in particular, nuclear spins.

The V_{15} complex consists of a lattice of molecules with 15 V^{IV} ions of spin 1/2 in a quasispherical layered structure formed of a triangle sandwiched between two hexagons (see Fig. 1). When the temperature is lower than ~ 100 K, the two hexagons of the V ions form a $S=0$ state due to antiferromagnetic interactions, leaving the three V ions on the triangle with an effective Hamiltonian[11,28]

$$\mathcal{H}_0 = -J_0(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_2\cdot\mathbf{S}_3 + \mathbf{S}_3\cdot\mathbf{S}_1) - g\mu_B\mathbf{H}\cdot\sum_{i=1}^{3}\mathbf{S}_i, \quad (2)$$

where $\mathbf{S}_i$ are the spins of the three V ions and $J_0\simeq -2.445$ K is the effective coupling between the spins, which is due to competing J_1 and J_2 interactions (see Fig. 1). At temperatures lower than 500 mK the ground state of each V_{15} molecule is $S=1/2$, with negligible dipolar interactions (few mK) between neighboring molecules. In contrast to Mn_{12} and Fe_8, the V_{15} molecule has no anisotropy barrier and a large tunneling splitting at zero field, $\Delta_0\simeq 80$ mK.[11,29]

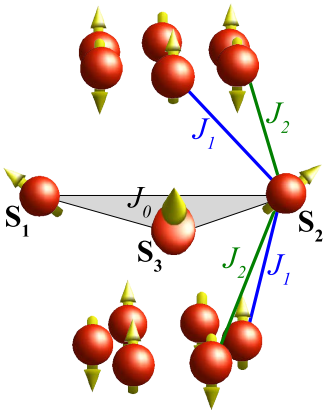

FIG. 1. (Color online) The core of the V_{15} molecule. Only V^{IV} ions are shown here. The arrows indicate the V^{IV} spins.

II. EXPERIMENT

The μSR experiments were performed on the M15 and M20 beamlines at TRIUMF in Vancouver, Canada. In these experiments 100% polarized (along z) positive muons are implanted in the sample. Each implanted muon decays (lifetime τ=2.2 μs), emitting a positron preferentially in the direction of its polarization at the time of decay. Using appropriately positioned detectors, one measures the asymmetry of the muon beta decay along z as a function of time $A(t)$, which is proportional to the time evolution of the muon spin polarization. $A(t)$ depends on the distribution of internal magnetic fields and their temporal fluctuations. Further details on the μSR technique may be found in Refs. 30 and 31.

The composition and structure of V_{15} single crystals were confirmed using x-ray diffraction and their magnetization was examined in a superconducting quantum interference device (SQUID) magnetometer. These single crystals were then crushed into a fine powder and used for the μSR measurements reported here. The fine powder was placed in a ^{4}He gas flow cryostat to measure the muon spin relaxation in the temperature range between 2.5 and 300 K. For the low-temperature measurements the sample was pressed into pellets and placed in a dilution refrigerator (DR) to measure the relaxation between 12 mK and 3.5 K. To ensure thermalization of the sample in the DR, the pellets were mounted on a silver plate using Apiezon grease, wrapped in a silver foil, and attached to the cold finger of the DR. The relaxation in the full temperature range was measured in magnetic fields up to 10 kG applied in the direction of the initial muon spin polarization.

III. RESULTS

The measured asymmetry at all temperatures and applied fields was found to fit best to a square-root exponential function (see Fig. 2)

$$A(t) = A_0 e^{-\sqrt{\lambda t}} + A_{\mathrm{Bg}}, \tag{3}$$

which reflects the dynamic nature of the local magnetic fields experienced by the muons as well as multiple muon stopping sites.[32,33] Here A_0 is the initial asymmetry and $\lambda = 1/T_1$ is the relaxation rate averaged over all stopping sites.[34] A_{Bg} is the nonrelaxing background signal due to muons missing the sample and stopping in the silver sample holder. The high-temperature measurements were performed using the low background setup.[35] Therefore, a nonzero background signal was found only in the measurements done in the DR. The values of λ in the full temperature range and various magnetic fields are presented in Fig. 3.

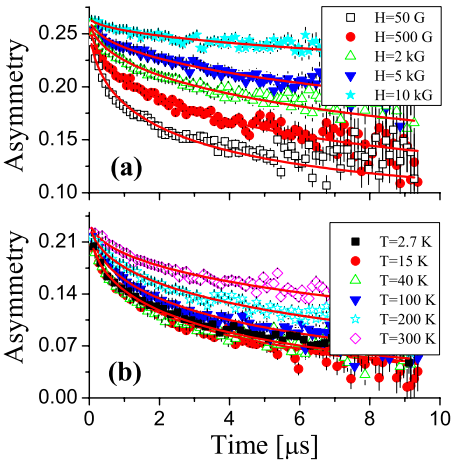

FIG. 2. (Color online) Example muon spin-relaxation curves at (a) T=15 mK and different magnetic fields and (b) H=50 G and different temperatures. The solid lines are fits to Eq. (3).

The relaxation rate increases as the temperature is decreased from room temperature down to ~50 K due to the slowing down of the thermally activated transitions between the different spin states.[32,36,37] This increase in the relaxation rate is a signature of the increased correlations between the V moments, as the temperature becomes comparable to the magnetic couplings inside the V_{15} core. Similar behavior is observed in many molecular magnets studied by μSR and NMR.[32,36–39] Most striking is the fact that the relaxation rate at temperatures below ~10 K and at fields lower than 5 kG becomes almost temperature independent, in agreement with similar ^{1}H NMR (Refs. 27, 40, and 41) and μSR (Ref. 27) studies. At higher fields (5 and 10 kG) and temperatures

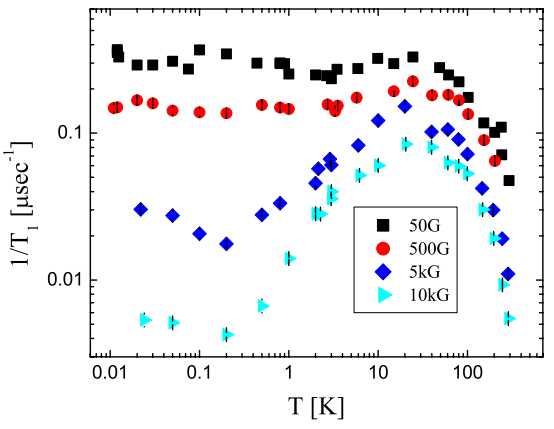

FIG. 3. (Color online) The muon spin-lattice relaxation rate as a function of temperature for different values of external magnetic field.

lower than 10 K, the relaxation rate decreases as the temperature is decreased down to 200 mK. Since at these temperatures the $S=1/2$ ground spin state is preferentially populated, we attribute the decrease in $1/T_1$ to the reduction in the thermally activated transitions between the (Zeeman) split $m=\pm 1/2$ states, in agreement with ^{1}H NMR measurements.[40,41] However, at even lower temperatures (less than ~200 mK) $1/T_1$ seems to saturate (within experimental accuracy) and become temperature independent even at high fields. Note that $1/T_1$ exhibits a strong-field dependence, which can be clearly seen in Fig. 2(a). In contrast, $1/T_1$ seems to be field independent up to 1.5 kG in Ref. 27. The source of discrepancy between these results and our results is still unclear.

A better understanding of the relaxation rate can be obtained by studying the eigenstates and eigenvalues of Hamiltonian (2). We rewrite the Hamiltonian as

$$\mathcal{H}_0 = -\frac{J_0}{2}\left(\mathbf{S}^2 - \frac{9}{4}\right) - g\mu_B \mathbf{H}\cdot\mathbf{S}, \tag{4}$$

where $\mathbf{S}=\Sigma_{i=1}^{3}\mathbf{S}_i$ and S are the total spin operator and spin number, respectively. The eigenstates of $\mathcal{H}_0$ are $|Sm\rangle$ with eigenvalues E_{Sm}, where S can be either 1/2 or 3/2 with $m=-S,-S+1,\cdots,S$. Note that the $S=1/2$ state is doubly degenerate. The energy-level scheme implies that at temperatures $T \ll -3J_0/2 \simeq 3.7$ K (i.e., the splitting between the $S=3/2$ and 1/2 states), only the ground spin state $S=1/2$ is appreciably populated. With the absence of additional terms in $\mathcal{H}_0$, the molecular spin and hence the resultant local field experienced by the muon should be static. However, as seen in Fig. 3 at low fields the relaxation rate is finite at these temperatures, and therefore the local field (and molecular spin) continues to fluctuate down to 12 mK, the lowest temperature measured. These results indicate that $\mathcal{H}_0$ cannot fully describe the system at low temperature. Rather, one expects the existence of an additional term in the spin Hamiltonian, $\mathcal{H}^t$, that mixes the unperturbed $|Sm\rangle$ eigenstates, hence inducing transitions between them.

We expect that the local magnetic field experienced by the implanted muons is proportional to the V_{15} neighboring spins. Hence, assuming that fluctuations of the V_{15} spins are described by exponential correlation functions,[42]

$$\langle S_z(t)S_z(0)\rangle = \frac{1}{3}S(S+1)\exp\left(-\frac{t}{\tau_z}\right), \tag{5}$$

$$\langle S_+(t)S_-(0)\rangle = \frac{2}{3}S(S+1)\exp(i\omega_e t)\exp\left(-\frac{t}{\tau_\pm}\right), \tag{6}$$

where τ_z and $\tau_\pm$ are the correlation times of the parallel and perpendicular (to the applied field) $\mathbf{S}$ components, respectively, and $\omega_e=g\mu_B H$ is the electronic resonance frequency. For simplicity we assume that the correlation times for both components are equal, $\tau_z=\tau_\pm=\tau$. In this case $1/T_1$ can be written as[42]

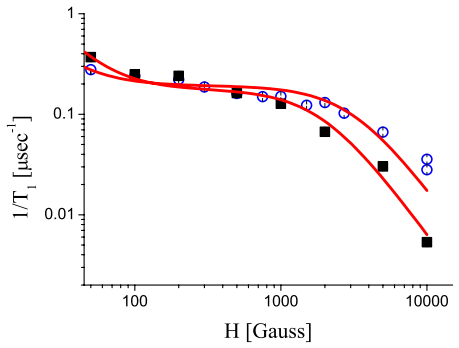

FIG. 4. (Color online) The spin-lattice relaxation rate as a function of the applied magnetic field for $T=15$ mK (squares) and $T=2.7$ K (circles). The solid lines are fits to Eq. (8).

$$\frac{1}{T_1} = \frac{2\Delta_z^2\tau}{1+\omega_\mu^2\tau^2} + \frac{2\Delta_+^2\tau}{1+(\omega_e+\omega_\mu)^2\tau^2} + \frac{2\Delta_-^2\tau}{1+(\omega_e-\omega_\mu)^2\tau^2}, \tag{7}$$

where $\omega_\mu=\gamma H$ is the muon Larmor frequency and Δ_i is an estimate of the coupling strength between the muon and the molecular spin, which depends on the nature of the coupling (e.g., exchange or dipolar). The first term in Eq. (7) originates from flipping of the muon while second and third terms are due to flip-flop and coflipping of the muon and molecular spins, respectively. Using $\omega_e \gg \omega_\mu$ one can rewrite Eq. (7) as[43]

$$\frac{1}{T_1} \approx 2f\frac{\Delta^2\tau}{1+\omega_\mu^2\tau^2} + 2(1-f)\frac{\Delta^2\tau}{1+\omega_e^2\tau^2}, \tag{8}$$

where $\Delta=\sqrt{\Delta_z^2+\Delta_+^2+\Delta_-^2}$ is a measure of the distribution of local magnetic field observed by muons, which depends on the coupling strength between the muon spin $\mathbf{I}$ and molecular spin $\mathbf{S}$, and $f=\Delta_z^2/\Delta^2$. Note the first term in Eq. (8) is due to fluctuations along the applied field (S_z), while the second is due to fluctuations in S_x and S_y. The value of f measures the relative size of parallel versus perpendicular local field. For example, using the assumptions above, for a dipolar interaction between $\mathbf{I}$ and $\mathbf{S}$ (which is fluctuating randomly in all directions) we expect on average $f\approx 0.3$. However, if our earlier assumption of $\tau_z=\tau_\pm$ in Eqs. (5) and (6) does not hold, f will contain also information on the importance of parallel versus perpendicular fluctuations, e.g., $f=0$ implies that $\tau_z \gg \tau_\pm$ and therefore $1/T_1$ is dominated by fluctuations perpendicular to the applied field.

Next, we evaluate the correlation time τ from the field dependence of $1/T_1$ using Eq. (8). Note that τ is the fluctuation time of the molecular spin. In Fig. 4 we present the relaxation rate as a function of applied magnetic field for two different temperatures. The solid lines are fits of the data to Eq. (8), from which the values of τ, Δ, and f for the corresponding temperature are extracted. By fitting the field dependence of $1/T_1$ for all temperatures, we obtain the values of these parameters as a function of temperature, shown in Fig. 5. In Fig. 5(a) the correlation time increases from $\tau \sim 1-2$ ns above $T=10$ K and saturates at $\tau \sim 6$ ns below 1 K. The value of this correlation time is similar to that mea-

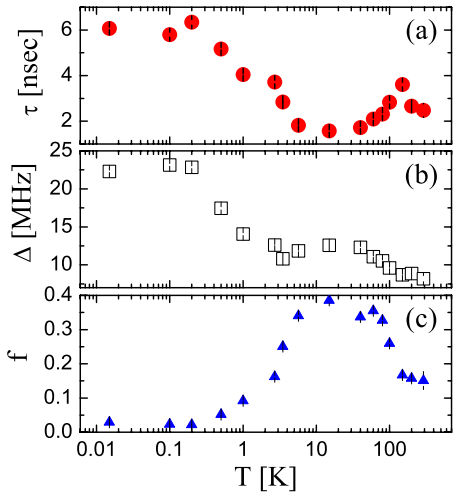

FIG. 5. (Color online) (a) The correlation time τ, (b) the size of the local field experienced by muons Δ, and (c) the value of f as a function of temperature.

sured earlier in other isotropic high spin molecule systems.[24,32,44] This similarity strongly suggests that a similar mechanism is responsible for the observed molecular spin fluctuations, namely, an interaction between the molecular spin and its environment, in particular the interaction with neighboring nuclear moments (nuclear-spin bath), inducing transitions between the different states.[24,32] In Ref. 27 the low-temperature dynamics were attributed to spin fluctuations between the two lowest lying $S=1/2$ doublet, whose energy difference is 80 mK. However, our measurement shows that the dynamics persist down to 12 mK, much lower than the splitting of the doublet. Therefore the proposed source of fluctuations in Ref. 27 cannot account for the dynamics observed in V_{15}.

The value of Δ, shown in Fig. 5(b), increases as the temperature is decreased from room temperature down to $\sim$100 K. This increase coincides with the observed decrease in the effective magnetic moment above 100 K.[11] Similarly, the increase below $\sim$1 K coincides with the additional decrease in the effective magnetic moment from $3\mu_B$ down to $1\mu_B$ at this temperature. Note that Δ is a measure of the distribution of the local magnetic fields experienced by muons and therefore is not simply proportional to the measured V_{15} magnetic moment. Instead, factors such as the local magnetization combined with the fluctuation rate as well as the type of interaction between the V_{15} moments and muons determine the value of Δ.

IV. SUMMARY AND CONCLUSIONS

As we mentioned earlier, if the parallel and perpendicular fluctuations are different, the value of f is related to the direction of fluctuations of **S**, perpendicular or parallel to the magnetic field (defined as z direction). Interestingly, we find $f\sim0.35$ at high temperatures (5–100 K) [see Fig. 5(c)], indicating that (I) the fluctuations of **S** are randomly oriented relative to the applied field as expected from thermal fluctuations and (II) the coupling between **I** and **S** is dipolar. As the temperature is reduced, thermal fluctuations between the spin states become less likely, especially when the temperature is much lower than the energy splitting between the levels (including Zeeman). Nevertheless, the fluctuations persist even at millikelvin temperatures. Note however, that at low temperatures $f\approx0$, i.e., the fluctuations are predominantly perpendicular to the z direction and do not originate from transitions between, e.g., $m=\pm1/2$ spin states, since these are indeed separated by the Zeeman energy. Instead they are most probably due to the finite-energy level broadening produced by the interaction between **S** and the nuclear-spin bath in the system. This occurs since in the presence of the nuclear moments (as a perturbation on $\mathcal{H}_0$), S_z is no longer a good quantum number, and therefore the m levels are split or broadened. The size of $\tau\sim6$ ns implies broadening of the levels on the scale of few tens of millikelvin, which is a reasonable size for such interactions.[24,32] Finally, since at $T>100$ K there are less correlations between the V ions in the magnetic core, the fluctuations measured by the muon are due to its interaction with multiple, uncorrelated V ions. This may be the reason for the decrease in f at $T>100$ K. Alternatively, it may also be due to diffusion of the muons in the sample at these temperatures.

In conclusion, we found that the muon spin-lattice relaxation rate is temperature independent at low temperatures and fields, in agreement with earlier NMR and μSR measurements.[27,40,41] This temperature independence exhibits the nonthermal/quantum nature of the V_{15} molecular spin fluctuations which persist down to 12 mK. The correlation time of the spin-spin autocorrelation functions was estimated to be $\sim$6 ns at low temperature. We believe that this low-temperature spin dynamics is due to broadening of the spin states introduced by the interactions between the V_{15} spin and the nuclear-spin bath.

ACKNOWLEDGMENTS

We would like to thank Achim Müller at the University of Bielefeld for providing the sample and Bernard Barbara at Institut Néel for helpful discussions. This work was supported by the CIAR, NSERC, and TRIUMF. We thank Syd Kreitzman, Rahim Abasalti, Bassam Hitti, and Donald Arseneau for technical support.

*Former address: TRIUMF, 4004 Wesbrook Mall, Vancouver, BC, Canada V6T 2A3; z.salman1@physics.ox.ac.uk

[1] D. Gatteschi and R. Sessoli, Angew. Chem., Int. Ed. **42**, 268 (2003).

[2] O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, Science **272**, 704 (1996).

[3] O. Sato, Y. Einaga, A. Fujishima, and K. Hashimoto, Inorg. Chem. **38**, 4405 (1999).

[4] S. Ferlay, T. Mallah, R. Ouahes, P. Villet, and M. Verdaguer, Nature (London) **378**, 701 (1995).

[5] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) **383**, 145 (1996).

[6] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).

[7] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. **78**, 4645 (1997).

[8] W. Wernsdorfer and R. Sessoli, Science **284**, 133 (1999).

[9] W. Wernsdorfer, R. Sessoli, A. Caneschi, D. Gatteschi, and A. Cornia, Europhys. Lett. **50**, 552 (2000).

[10] V. V. Dobrovitski, M. I. Katsnelson, and B. N. Harmon, Phys. Rev. Lett. **84**, 3458 (2000).

[11] B. Barbara, I. Chiorescu, W. Wernsdorfer, H. Bögge, and A. Müller, Prog. Theor. Phys. Suppl. **145**, 357 (2002).

[12] A. Morello, P. C. E. Stamp, and I. S. Tupitsyn, Phys. Rev. Lett. **97**, 207206 (2006).

[13] S. Hill, R. S. Edwards, N. Aliaga-Alcalde, and G. Christou, Science **302**, 1015 (2003).

[14] E. del Barco, A. D. Kent, E. C. Yang, and D. N. Hendrickson, Phys. Rev. Lett. **93**, 157202 (2004).

[15] S. Bertaina, S. Gambarelli, T. Mitra, B. Tsukerblat, A. Müller, and B. Barbara, Nature (London) **453**, 203 (2008).

[16] N. V. Prokof'ev and P. C. E. Stamp, J. Low Temp. Phys. **104**, 143 (1996).

[17] C. Joachim, J. K. Gimzewski, and A. Aviram, Nature (London) **408**, 541 (2000).

[18] D. Divincenzo, in *Quantum Tunneling of the Magnetizat—QTM'94*, edited by L. Gunther and B. Barbara (Kluwer, Dordrecht, 1995), p. 189.

[19] J. Tejada, E. M. Chudnovsky, E. del Barco, J. M. Hernandez, and T. P. Spiller, Nanotechnology **12**, 181 (2001).

[20] F. Troiani, M. Affronte, S. Carretta, P. Santini, and G. Amoretti, Phys. Rev. Lett. **94**, 190501 (2005).

[21] F. Troiani, A. Ghirri, M. Affronte, S. Carretta, P. Santini, G. Amoretti, S. Piligkos, G. Timco, and R. E. P. Winpenny, Phys. Rev. Lett. **94**, 207208 (2005).

[22] A. Ardavan, O. Rival, J. J. L. Morton, S. J. Blundell, A. M. Tyryshkin, G. A. Timco, and R. E. P. Winpenny, Phys. Rev. Lett. **98**, 057201 (2007).

[23] N. V. Prokof'ev and P. C. E. Stamp, Phys. Rev. Lett. **80**, 5794 (1998).

[24] A. Keren, O. Shafir, E. Shimshoni, V. Marvaud, A. Bachschmidt, and J. Long, Phys. Rev. Lett. **98**, 257204 (2007).

[25] A. Müller and J. Döring, Angew. Chem., Int. Ed. Engl. **27**, 157 (1991).

[26] One may expect that if the applied field is high enough, the spins align along its direction.

[27] D. Procissi, A. Lascialfari, E. Micotti, M. Bertassi, P. Carretta, Y. Furukawa, and P. Kögerler, Phys. Rev. B **73**, 184417 (2006).

[28] I. Chiorescu, R. Giraud, A. G. M. Jansen, A. Caneschi, and B. Barbara, Phys. Rev. Lett. **85**, 4807 (2000).

[29] I. Chiorescu, W. Wernsdorfer, A. Müller, S. Miyashita, and B. Barbara, Phys. Rev. B **67**, 020402(R) (2003).

[30] S. L. Lee, S. H. Kilcoyne, and R. Cywinski, *Muon Science* (SUSSP/IOP, Bristol, 1998).

[31] K. H. Chow, B. Hitti, and R. F. Kiefl, in *Semiconductors and Semimetals*, edited by M. Stavola (Academic, New York, 1998), Vol. 51, Pt. A, p. 137.

[32] Z. Salman, A. Keren, P. Mendels, V. Marvaud, A. Scuiller, M. Verdaguer, J. S. Lord, and C. Baines, Phys. Rev. B **65**, 132403 (2002).

[33] Y. J. Uemura, T. Yamazaki, D. R. Harshman, M. Senba, and E. J. Ansaldo, Phys. Rev. B **31**, 546 (1985).

[34] This relaxation function does not contradict that used in Ref. 27, however, transverse field muon precession measurements show no evidence for three inequivalent muon sites in the sample. Therefore we use this function to estimate the relaxation rate averaged over all sites.

[35] J. W. Schneider *et al.*, Phys. Rev. Lett. **71**, 557 (1993).

[36] S. J. Blundell and F. L. Pratt, J. Phys.: Condens. Matter **16**, R771 (2004).

[37] A. Lascialfari, Z. H. Jang, F. Borsa, P. Carretta, and D. Gatteschi, Phys. Rev. Lett. **81**, 3773 (1998).

[38] F. Borsa, A. Lascialfari, and Y. Furukawa, in *Novel NMR and EPR Techniques*, edited by J. Dolinsek, M. Vilfan, and S. Zumer (Springer, Berlin, 2006), pp. 297–349.

[39] F. Borsa, in *NMR-MRI, μSR and Mossbauer Spectroscopies in Molecular Magnets*, edited by P. Carretta and A. Lascialfari (Springer-Verlag, Berlin, 2007).

[40] H. Yoneda, T. Goto, Y. Fujii, B. Barbara, and A. Müller, Physica B (Amsterdam) **329-333**, 1176 (2003).

[41] Y. Furukawa, Y. Fujiyoshi, K. Kumagai, and P. Kögerler, Polyhedron **24**, 2737 (2005).

[42] I. J. Lowe and D. Tse, Phys. Rev. **166**, 279 (1968).

[43] S. R. Dunsiger, R. F. Kiefl, J. A. Chakhalian, J. E. Greedan, W. A. MacFarlane, R. I. Miller, G. D. Morris, A. N. Price, N. P. Raju, and J. E. Sonier, Phys. Rev. B **73**, 172418 (2006).

[44] Z. Salman, A. Keren, P. Mendels, A. Scuiller, and M. Verdaguer, Physica B (Amsterdam) **289-290**, 106 (2000).