55Mn NMR spectra of Mn12 single-molecule magnets: Single crystal versus aligned powder studies

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Abstract

X-ray structural, magnetization and 55Mn single crystal NMR investigations of Mn12O12(CH2BrCOO)16(4H2O)Æ4CH2Cl2 indicate that this highly symmetric (I4) lattice, devoid of hydrogen bonding of the Mn12-framework with the molecules of lattice hydration, might be an improved model for studying single-molecule magnetism. Single crystal NMR yield much enhanced NMR data as compared to magnetically oriented powders, enable determination of 55Mn hyperfine and quadrupole couplings, and show that the oriented powder samples do not represent an authentic crystal picture.

Keywords: Single-molecule magnets; 55Mn NMR; Single crystal; Aligned powder

1. Introduction

Single-molecule magnets (SMMs) are currently the subject of many theoretical and experimental investigations because of their surprising property of macroscopic quantum tunneling (MQT) at low temperatures [1]. Novel applications are possible since Mn12 and analogs have been proposed as potential materials for elements in quantum computation devices [1,2]. The family of [Mn12O12(O2CMe)16(H2O)4]·2MeCO2H·4H2O, henceforth Mn12-Ac [3], molecules contain an external crown of eight Mn3+ ions (S = 2), which are ferromagnetically coupled and an inner core of four Mn4+ ions (S = 3/2), also ferromagnetically coupled. The crown and core are antiferromagnetically coupled to produce a total spin of S = 10. The symmetry implies an effective Hamiltonian that is dominated by a strong easy-axis term H = D S_z^2, with D = −0.56 K, which splits the ground state such that the degenerate m_s = ±10 levels lie lowest. The fundamental question in this material so far concerns the nature of the basic mechanism underlying the MQT behavior. According to theory, MQT may be induced by fourth order transverse anisotropy, phonons effect, or dipolar interactions with dynamic hyperfine fields. Indeed, electron paramagnetic resonance [4–13] (EPR) and inelastic neutron scattering [14–17] experiments have shown the presence of a fourth order transverse anisotropy term [S_2^2 + S_3^2] in the spin Hamiltonian, however, this term cannot account for the observed odd tunneling resonances in magnetic relaxation. Besides, hyperfine and dipolar interactions are too weak to provide the actual tunneling rates. Recently, based on a detailed X-ray analysis, Cornia et al. [18] have suggested that the solvated molecules play a crucial role in the mechanism of the MQT phenomena, via strong hydrogen-bonding and
thus the lowering of the lattice symmetry, and the presence of the rhombic (E) term in the spin Hamiltonian. It is thus of interest to examine, by solid state NMR spectroscopy, the role of the lattice-solvated molecules in the overall magnetic symmetry and structure of Mn12–Ac and related compounds. To this effect, we have carried out 55Mn NMR measurements on the recently synthesized compound [Mn12O12(O2CCH2Br)16(H2O)4] · 4CH2Cl2 (Fig. 1), henceforth as Mn12–BrAc [19]. In particular, we examined the NMR spectra of single crystal as well as aligned powder of this compound. We found significant differences between the spectra from the single crystals versus aligned powder; specifically that the single crystals afford significantly higher spectral resolution than the aligned powder, and moreover, that the act of powdering introduces significant differences in the chemical structure of Mn12–BrAc. Furthermore, angular dependence studies are now possible because of the use of single crystals. We conducted such studies with rotations in the ac-plane.

2. Synthesis and crystal growth

Mn12–BrAc was synthesized by mixing Mn12–Ac in toluene and then adding an excess of HO2CCH2Br, as described elsewhere [19]. Once the initial crystals of Mn12–BrAc were formed, they were recrystallized by dissolving in dichloromethane and adding bromoacetic acid. Once dissolved, the solution was filtered and placed into small vials with a small amount of hexanes. A needle was pushed through the lid to assure slow evaporation. After a week, nice brick looking single crystals form.

3. NMR experimental details

55Mn NMR measurements were made using a home built MAGRes2000 Integrated Wideband NMR spectrometer with quadrature detection and a home built high frequency probe [20,21]. The crystal samples were prepared by removing the crystal from its mother liquor and immediately covering in 5-min epoxy to prevent the sample from drying. Immediately after the epoxy was set, the sample was mounted into the coil and cooled in a dewar of liquid Helium. Aligned powder samples were made by crushing the crystals and then mixing with Stycast 1266 epoxy. On crushing the sample, it was noticed that the crystals went from a dark wet looking brown color to a light brown, dry powdery sample. The epoxy was then allowed to cure overnight at room temperature in a field of 8.5 T. Data was acquired for both samples at ~2 K, below the blocking temperature, $T_B$, of ~3 K because of fast $T_2$ times above this temperature. A Hahn echo pulse sequence was used while the frequency was scanned from 220 to 400 MHz, usually taking 0.1–0.2 MHz steps. Frequency scans were necessary because of the large peak widths (~5–20 MHz). Pulse lengths were on the order of hundreds of nanoseconds giving a bandwidth of roughly ~2 MHz. After the scan, the data was processed using a Fast Fourier Transform Sum (FFT Sum).

4. Results

We present here the comparison of single crystal 55Mn NMR spectroscopic measurements of [Mn12O12(O2CCH2Br)16(H2O)4] · 4CH2Cl2 (Fig. 2, henceforth Mn12–BrAc) and an aligned powder sample of Mn12–BrAc. As will be seen, the ability to probe Mn sites represents a powerful tool to study factors such as symmetry-lower-
ing in SMMs due to extrinsic perturbations and the ground state at each Mn ion. Mn\textsubscript{12}–BrAc yield large single crystals suitable for \textsuperscript{55}Mn NMR studies. Fig. 2 shows a comparison of \textsuperscript{55}Mn NMR signals obtained from: (a) Mn\textsubscript{12}–BrAc powder and (b) a Mn\textsubscript{12}–BrAc single crystal, all in zero external field, \(H_0 = 0\).

The aligned powder spectrum of Mn\textsubscript{12}–BrAc, Fig. 2(a), shows three peaks corresponding to the three expected sites of the Mn ions [22,23]. The first peak (Mn(3)) at 227.7 MHz corresponds to the Mn\textsuperscript{4+} ions in the Mn\textsubscript{6}O\textsubscript{4} core and has Full Width at Half Maximum (FWHM) of 6.52 MHz. The second peak (Mn(2)) at 279.3 MHz, with a FWHM of 24.74 MHz, is a result of four of the Mn\textsuperscript{3+} ions located in the crown of the molecule. No quadrupolar splitting is noticed. The last four Mn\textsuperscript{3+} ions located in the crown of the molecule produce the third peak (Mn(1)) at 370.1 MHz and a FWHM of 6.52 MHz. The second peak is a result of four of the Mn\textsuperscript{3+} ions located in the crown of the molecule. No quadrupolar splitting is noticed. The last four Mn\textsuperscript{3+} ions located in the crown of the molecule produce the third peak (Mn(1)) at 370.1 MHz and a FWHM of 6.52 MHz. The second peak is expected sites of the Mn ions [22,23].

Upon examination of the single crystal data (Fig. 2(b)) a sharp distinction is noticed. Resolution is far superior to that of the aligned powder and the peaks are actually shifted, up to \(\sim 16\) MHz. The peak assignments are the same as the aligned powder. The narrow first peak has a frequency of 232.2 MHz, a FWHM of 2.89 MHz, and a hyperfine field of 22.11 T. The second quadrupolar split line has a central transition at 284.5 MHz, a FWHM of 2.89 MHz, and a hyperfine field of 22.11 T. The second quadrupolar splitting, the effective field, \(H_{\text{eff}}\), felt by the nuclei is just the sum of the projection of \(H_0\) onto the hyperfine field, \(H_N\) (\(H_{\text{eff}} = H_N \pm H_0 \cos \theta\)). Thus, a maximum in the splitting is noticed when \(H_0\) is parallel to the \(c\)-axis (\(\theta = 0^\circ\)) while a minimum in the splitting is noticed when \(H_0\) is perpendicular to the \(c\)-axis (\(\theta = 90^\circ\)). One interesting result is the splitting observed when the crystallographic \(c\)-axis is perpendicular to the external field, \(H_0\). The crystal is in this configuration and an external field is applied, we observe two peaks as opposed to the expected one. We tentatively assign this to two different orientations of the hyperfine fields at the Mn\textsuperscript{4+} sites.

\[ E_m = -\gamma_n \hbar H_0 m + \frac{e^2 q Q}{4I(2I-1)} \left( \frac{3\cos^2 \theta - 1}{2} \right) [3m^2 - I(I + 1)], \]

where \(I\) and \(m\) are the nuclear spin and its projection quantum numbers, and \(\theta\) the angle from the symmetry axis. From crystallographic data for Mn\textsubscript{12}–BrAc, it is known that the local Jahn–Teller axes, and hence the principal hyperfine field directions of Mn(2) and Mn(1) ions are canted away from the \(c\)-axis at angles of 7.9° and 34.0°, respectively. With \(I = \frac{5}{2}\), \(\Delta\nu_Q = 5.15 \pm 0.05\) MHz for the Mn(2) peak while \(\Delta\nu_Q = 3.3 \pm 0.10\) MHz for the Mn(1) peak resulting in \(e^2 q Q\) values of 35.33 \pm 0.35 and 41.43 \pm 1.26 MHz, respectively. No such information is obtainable from the oriented powder data (Fig. 2(a)).

Powdering the sample obviously changes the environment of the Mn ions, most likely due to the pressure and temperature change placed on the crystals when they are crushed. Further studies of these effects are underway to determine the exact cause of the transformation. More significant to this work is the knowledge that an aligned powder does not represent a statistical average of the crystal, as is seen by the large shift of the peaks in the aligned powdered spectra. It is thus suggested that work on aligned powders should be viewed with caution.

Yet another advantage to using single crystals is the ability to perform angular dependence studies. Angular dependence of the Mn(3) peak of Mn\textsubscript{12}–BrAc was conducted from the easy to hard axis, as shown in Fig. 3. Rotation in the \(ac\) plane was prepared by cooling the crystal in zero field, so signals from both \(m_s = \pm 10\) states are discernible, separated by twice the Zeeman frequency at the applied field (1 T here). The angular variation in the \(ac\)-plane is described by the following equation:

\[ \text{Peak Frequency} = \nu_{CF} \pm \left( \frac{5}{2} \right) \left( \frac{H_0}{2\pi} \right) (\cos \theta). \]

\(\nu_{CF}\) represents the central frequency and \(\theta\) being the angle between \(H_0\) and the \(c\)-axis. As the crystal is rotated, the effective field, \(H_{\text{eff}}\), felt by the nuclei is just the sum of the projection of \(H_0\) onto the hyperfine field, \(H_N\) (\(H_{\text{eff}} = H_N \pm H_0 \cos \theta\)). Thus, a maximum in the splitting is seen when \(H_0\) is parallel to the \(c\)-axis (\(\theta = 0^\circ\)) while a minimum in the splitting is noticed when \(H_0\) is perpendicular to the \(c\)-axis (\(\theta = 90^\circ\)). One interesting result is the splitting observed when the crystallographic \(c\)-axis is perpendicular to the external field, \(H_0\). When the crystal is in this configuration and an external field is applied, we observe two peaks as opposed to the expected one. We tentatively assign this to two different orientations of the hyperfine fields at the Mn\textsuperscript{4+} sites.

Fig. 3. Angular dependence in the \(ac\)-plane of a single crystal of Mn\textsubscript{12}–BrAc.
5. Conclusion

Loss of information from aligned powdered samples is obvious by the shifts in frequency and loss of quadrupolar splitting. Single crystal measurements offer a new way to probe the magnetic properties of SMM by providing more accurate measurements of hyperfine fields and quadrupolar information. Angular dependence studies show that there is more work to be done to understand the magnetic structure of this molecule. The higher symmetry of Mn$_{12}$–BrAc, as a result of having no waters of hydration to allow hydrogen bonding, produces a less convoluted spectrum than Mn$_{12}$–Ac, suggesting that Mn$_{12}$–BrAc is a model system to study for understanding magnetic tunneling in the Mn$_{12}$ family. Two recent studies [24–26] support this conclusion.

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References