

Single-Crystal  $^{55}\text{Mn}$  NMR Spectra of Two  $\text{Mn}_{12}$  Single-Molecule MagnetsAndrew G. Harter,<sup>†</sup> Nicole E. Chakov,<sup>‡</sup> Brian Roberts,<sup>†</sup> Randy Achey,<sup>†</sup> Arneil Reyes,<sup>†</sup> Philip Kuhns,<sup>†</sup> George Christou,<sup>\*,†</sup> and Naresh S. Dalal<sup>\*,†</sup>*Department of Chemistry and Biochemistry and National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306, and Department of Chemistry, University of Florida, Gainesville, Florida 32611*

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The initial application is reported of single-crystal  $^{55}\text{Mn}$  NMR spectroscopy, and associated orientation dependence studies, to single-molecule magnets (SMMs). The studies were performed on two members of the  $\text{Mn}_{12}$  family of SMMs,  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]\cdot 2\text{MeCO}_2\text{H}\cdot 4\text{H}_2\text{O}$  ( $\text{Mn}_{12}\text{-Ac}$ ) and  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Br})_{16}(\text{H}_2\text{O})_4]\cdot 4\text{CH}_2\text{Cl}_2$  ( $\text{Mn}_{12}\text{-BrAc}$ ). Single-crystal spectra give a dramatic improvement in the spectral resolution over oriented powder spectra, allowing the clear observation of quadrupolar splittings, the determination of quadrupole coupling parameters ( $e^2qQ$ ), and an assessment of the symmetry-lowering perturbation of the core of  $\text{Mn}_{12}\text{-Ac}$  by hydrogen-bonding interactions with lattice solvate molecules of crystallization. The results emphasize the utility of single-crystal NMR studies to probe the cores of these magnetic molecules.

We report the initial application of single-crystal  $^{55}\text{Mn}$  nuclear magnetic resonance (NMR) spectroscopy, and associated orientation dependence studies, to two members of the  $\text{Mn}_{12}$  family of single-molecule magnets (SMMs).<sup>1,2</sup> This technique opens up new avenues for directly probing the magnetic structure and individual metal ions of the cores of these interesting molecules. SMMs provide a molecular route to nanoscale magnetic materials and display magnetization hysteresis loops and steps due to quantum tunneling of the magnetization (QTM), rendering them potentially useful for memory storage at molecular dimensions as well as for quantum computation. Among the many SMMs now known, the most studied is  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]\cdot 2\text{MeCO}_2\text{H}\cdot 4\text{H}_2\text{O}$ , abbreviated  $\text{Mn}_{12}\text{-Ac}$ ,<sup>1,2</sup> partly because it has the highest blocking temperature and because its crystal structure was long thought to be the simplest, a tetragonal ( $I4$ ) lattice with  $Z = 2$  and each  $\text{Mn}_{12}\text{-Ac}$  molecule exhibiting axial ( $S_4$ ) symmetry.<sup>3</sup> Recently, however, Cornia et al.<sup>4</sup> have

reexamined the X-ray data and suggested that the average symmetry is much lower than tetragonal when taking into account the possible hydrogen-bonding interactions of the two  $\text{MeCO}_2\text{H}$  molecules of lattice solvation. This provides an easy rationalization for the detection of certain (odd-numbered) steps in the hysteresis loops, not expected for tetragonal symmetry. It also suggests that the molecules of lattice hydration, via their hydrogen bonding with the  $\text{Mn}_{12}$  subunit, have a major effect on the quantum tunneling process, and indeed, this is currently an area of much active research. The present paper reports (i) single-crystal  $^{55}\text{Mn}$  NMR spectroscopic measurements of  $\text{Mn}_{12}\text{-Ac}$  and  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Br})_{16}(\text{H}_2\text{O})_4]\cdot 4\text{CH}_2\text{Cl}_2$  (Figure 1, henceforth  $\text{Mn}_{12}\text{-BrAc}$ ), the latter also crystallizing in a tetragonal space group ( $I42d$ ), and (ii) the influence of the hydrogen bonding in  $\text{Mn}_{12}\text{-Ac}$  on the symmetry of the  $\text{Mn}_{12}$  core as reflected in the resulting NMR spectra and comparison with the spectra of  $\text{Mn}_{12}\text{-BrAc}$ , which has no significant hydrogen-bonding perturbation of its  $\text{Mn}_{12}$  core. As will be seen, the ability to probe individual Mn sites within the core represents a powerful new tool to study factors such as symmetry lowering in SMMs due to extrinsic perturbations.

Both  $\text{Mn}_{12}\text{-Ac}$  and  $\text{Mn}_{12}\text{-BrAc}$  yield high-quality single crystals large enough for  $^{55}\text{Mn}$  NMR studies. Single crystals of  $\text{Mn}_{12}\text{-BrAc}$  were grown from  $\text{CH}_2\text{Cl}_2$ /hexanes layerings as described elsewhere.<sup>5</sup> They were removed from the mother liquor and immediately covered in 5-minute epoxy to guard against solvent loss.  $^{55}\text{Mn}$  NMR measurements were made using a locally developed MagRes2000 spectrometer with quadrature detection, along with a home-built probe.<sup>6</sup> Crystal orientation was possible with a relative accuracy of  $0.2^\circ$ . All measurements were made below 3 K as the signal deteriorates rapidly above the blocking temperature of 2.7 K because of short  $T_2$  times. Because peak widths were  $\sim 2\text{--}20$  MHz,

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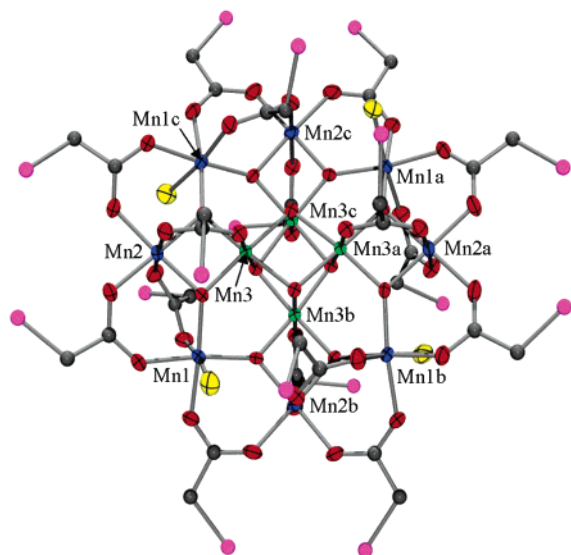


Figure 1. ORTEP representation in PovRay format of  $\text{Mn}_{12}\text{-BrAc}$ .

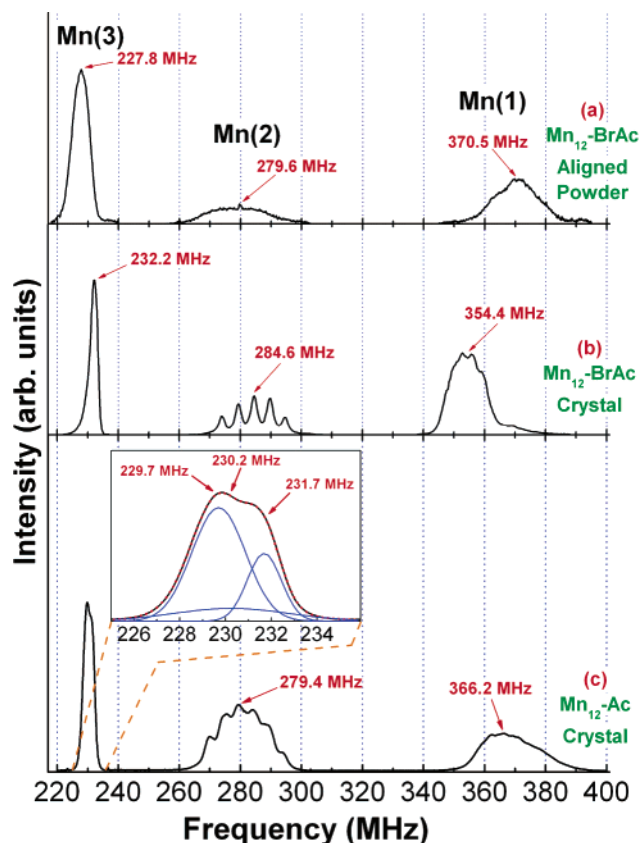


Figure 2. Comparison of zero-field  $^{55}\text{Mn}$  NMR spectra of (a)  $\text{Mn}_{12}\text{-BrAc}$  aligned powder, (b) single-crystal  $\text{Mn}_{12}\text{-BrAc}$ , and (c) single-crystal  $\text{Mn}_{12}\text{-Ac}$ .

the data were recorded by stepping the frequency at regular intervals using Hahn echoes and processed employing an FFT sum. For angular measurements of  $\text{Mn}_{12}\text{-BrAc}$  in its  $ab$  plane, the crystal was cooled to 2 K in a field of 5 T.

Figure 2 shows a comparison of  $^{55}\text{Mn}$  NMR signals obtained from (a)  $\text{Mn}_{12}\text{-BrAc}$  powder, (b) a  $\text{Mn}_{12}\text{-BrAc}$  single crystal, and (c) a  $\text{Mn}_{12}\text{-Ac}$  single crystal, all in zero external field. The observed peaks are assigned to the three main groups of Mn ions expected under  $S_4$  symmetry,

following Goto and co-workers<sup>7</sup> and Furukawa et al.,<sup>8</sup> who reported oriented powder NMR spectra for  $\text{Mn}_{12}\text{-Ac}$ . Specifically, the peak around 230 MHz [labeled Mn(3) in Figure 1] is assigned to the four  $\text{Mn}^{4+}$  ions located in the  $\text{Mn}_4\text{O}_4$  cubane core of the  $\text{Mn}_{12}$  molecules. The second peak around 284 MHz [labeled Mn(2)], with well-resolved quadrupolar splitting in the crystals, is assigned to four of the eight  $\text{Mn}^{3+}$  ions in the outer ring, and the broad signal around 355 MHz [labeled Mn(1)] is assigned to the remaining four  $\text{Mn}^{3+}$  ions. Two significant conclusions are evident from Figure 2:

(i) Comparison of the oriented powder (Figure 2a) and single-crystal (Figure 2b) spectra of  $\text{Mn}_{12}\text{-BrAc}$  demonstrates the impressive increase in the spectral resolution gained using a crystal. A significant broadening of all of the peaks in Figure 2a as compared to those in 2b and, in particular, the complete loss of quadrupolar splitting on the Mn(2) peak and up to 16 MHz shifts in the peak positions [e.g., for Mn(1)] provide clear evidence that aligned powders could lead to erroneous structural and magnetic information. Indeed, the single-crystal data enable us to measure the quadrupole coupling parameter  $e^2qQ$  through the quadrupole splitting,  $\Delta\nu_Q$ , and the equation for the energy<sup>7,8</sup>

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

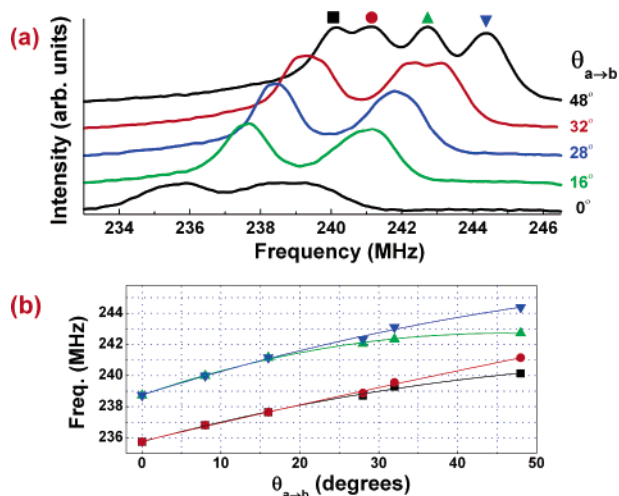
where  $I$  and  $m$  are the nuclear spin and its projection quantum numbers, respectively, and  $\theta$  is the angle from the symmetry axis. From crystallographic data for  $\text{Mn}_{12}\text{-BrAc}$ , it is known that the local Jahn–Teller axes, and hence the principal hyperfine field directions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

(ii) Comparison of the single-crystal spectrum of  $\text{Mn}_{12}\text{-Ac}$  (Figure 2c) with those reported earlier using oriented powders<sup>7</sup> shows qualitative differences. In particular, the splitting reported on the Mn(3) peak, at  $\sim 230$  MHz, was earlier assigned to a partially resolved quadrupolar interaction.<sup>7</sup> In contrast, our data demonstrate three Gaussian lines (inset of Figure 2c), instead of five lines expected from this interpretation. Rather, these peaks could originate from structural isomers of  $\text{Mn}_{12}\text{-Ac}$  (with very little or no quadrupolar splitting), as was inferred from X-ray analysis<sup>4</sup> and supported by recent high-field EPR<sup>9</sup> and magnetization data.<sup>10</sup> Additional measurements are needed to identify the origin of the powdering effects. From the line positions

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**Figure 3.** Angular dependence of  $^{55}\text{Mn}$  NMR in the  $ab$  plane of a single crystal of  $\text{Mn}_{12}\text{-BrAc}$  at 2T.

(obtained from fitting with three Gaussians) shown in the inset of Figure 2c and  $\gamma_n^{55}$ , we deduce that the three variants of  $\text{Mn}_{12}\text{-Ac}$  have internal fields of 21.89, 21.93, and 22.07 T for the  $\text{Mn}_4\text{O}_4$  core. These should be contrasted with the average value of 21.8 T reported by Goto and co-workers<sup>7</sup> and 22.11 T for  $\text{Mn}_{12}\text{-BrAc}$ .

The higher resolution afforded by the  $\text{Mn}_{12}\text{-BrAc}$  single crystal enabled us to investigate the anisotropic behavior of the hyperfine field of the Mn(3) site.<sup>7,8</sup> Measurements were made with a Zeeman field of 1 T in the  $ac$  plane and 2 T in the  $ab$  plane, which allows resolution for observing the critical structures in the spectra. For example, in Figure 3,

we observe an evolution of the zero-field single peak, splitting first into two at small angles and then into four distinct peaks when the field is at large angles with respect to the  $a$  or  $b$  axis. This result can only be attributed to four magnetically distinct (but crystallographically equivalent)  $\text{Mn}^{4+}$  ions in the  $\text{Mn}_4\text{O}_4$  core. Our preliminary analysis shows that the hyperfine fields at each of the atoms in the core are canted away from the  $c$  axis with a small but finite perpendicular component. Consequently, this implies that the interaction among the local electronic moments in the core leads to a spin structure that is not purely ferromagnetically aligned, as suggested earlier by EPR data.<sup>11</sup> Because  $\text{Mn}_{12}\text{-BrAc}$  is even more symmetric than  $\text{Mn}_{12}\text{-Ac}$ , our results imply that earlier conclusions based on the hyperfine fields being parallel to the easy axis need to be reexamined.

In conclusion, single-crystal  $^{55}\text{Mn}$  NMR spectroscopy affords a significant resolution enhancement over oriented powder spectroscopy, allowing information to be obtained that would otherwise not be achievable. It also shows that powdering of these SMM crystals introduces a significant structural perturbation. Thus single-crystal NMR spectroscopy opens a new window on the magnetic characterization of these novel magnetic materials.

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