A spectroscopic comparison between several high-symmetry $S=10$ Mn$_{12}$ single-molecule magnets

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We report angle-dependent high-field electron-paramagnetic-resonance data collected for single-crystal samples of Mn$_{12}$–Ac. The spectra reveal fine structures associated with various Mn$_{12}$ species corresponding to different disordered local environments. Each of the fine structures exhibits a distinct dependence on the field orientation, thereby highlighting the discrete nature of the disorder. We compare these data with the spectra obtained for two recently discovered analogs of Mn$_{12}$–Ac, differing only in their ligand and solvent molecules. None of the fine structures seen for Mn$_{12}$–Ac are found for the recently discovered Mn$_{12}$ complexes, thus confirming that the solvent significantly influences the magnetization dynamics in Mn$_{12}$–Ac.

51.5 GHz in each case (±0.3 GHz), and the temperature is 15 K. The dips in transmission through the cavity correspond to EPR. In order to correct for slight frequency differences between the measurements, as well as differences in the orientation of the field within the hard plane for the Mn$_{12}$–Ac sample, the magnetic-field axis is referenced to the average position of the α8 peak (see Ref. 5 for explanation of labeling), which occurs at about 6.1 T at 51.5 GHz. It is immediately apparent that the EPR peaks for the BrAc and tBuAc complexes are considerably sharper than those obtained for the Ac complex. Furthermore, the Mn$_{12}$–Ac resonances reveal clear fine structures (high- and low-field shoulders) which vary with the field orientation within the hard plane (dashed and solid curves). The behavior of these fine structures, which are caused by the different local solvent environments (E strain), has been discussed in great detail in our previous publications.\textsuperscript{3,5,6} We note that studies of the Mn$_{12}$–BrAc and Mn$_{12}$–tBuAc complexes for different field orientations within the hard plane indicate no evidence for these fine structures.

The key result in this paper is the absence of the EPR fine structures in the two Mn$_{12}$ complexes, thus suggesting that the QMT in Mn$_{12}$–BrAc and Mn$_{12}$–tBuAc may reflect the intrinsic $S_3$ symmetry of the Mn$_{12}$ molecule. This contrasts the situation for Mn$_{12}$–Ac where the QMT is significantly influenced by the hydrogen bonding to surrounding disordered acetic acid solvent molecules. The crystal-field parameters for the BrAc complex are almost identical to those of Mn$_{12}$–Ac (see Ref. 8). Comprehensive angle-dependent HFEPR studies for the tBuAc complex indicate a slightly larger $D$ value of 0.462(2) cm$^{-1}$; the remaining parameters are $B_{31}^0 = 2.5(2) \times 10^{-5}$ cm$^{-1}$, $B_{41}^0 = 4.3(5) \times 10^{-5}$ cm$^{-1}$, $g_z = 2.00(2)$, and $g_x = g_y = 1.94(2)$.

A further illustration of the differences between Mn$_{12}$–Ac and the BrAc and tBuAc complexes is illustrated in Fig. 2. The top panel (a) displays simulations of the out-of-plane angle dependence of the HFEPR absorption intensity for a spin $S = 10$ system with the Mn$_{12}$–BrAc Hamiltonian parameters, and no disorder; the angle corresponds to the field orientation relative to the easy axis of the crystal, and the darker regions represent EPR absorption (see also Fig. 1). In Fig. 2(b), actual experimental data are displayed for the Mn$_{12}$–BrAc complex. The data are in very good agreement with the simulations, i.e., the EPR intensity alternates between the α and β transitions as the field is tilted away from the hard plane, with clear gaps in between (see Ref. 5 for a detailed explanation for this behavior). Furthermore, most of the curvature associated with the bands of absorption is reproduced in the experiments, which is an indication that the molecular easy axes are very well aligned ($< \pm 0.5^\circ$); similar results are found for Mn$_{12}$–tBuAc. In contrast, the regions of absorption for Mn$_{12}$–Ac [Fig. 2(c)] are considerably broader, displaying clear streaks on the high- and low-field sides of the main absorption bands. These streaks correspond to the shoulders observed in Fig. 1 (solid curve). Also notable is the fact that each of the absorption bands for Mn$_{12}$–Ac is extremely flat, and they extend over angle ranges exceeding those in the simulations [Fig. 2(a)], as evidenced by the overlapping α and β EPR intensities. We note that the fine structures seen for Mn$_{12}$–Ac are completely reproducible. Indeed, the data in Fig. 2 were obtained for samples grown by a different group than those presented in Refs. 3, 5, and 6.

As we have already documented,\textsuperscript{5} the out-of-plane angle dependence of the EPR spectra for Mn$_{12}$–Ac can be understood as resulting from significant easy-axis tilting. To illustrate this point, Fig. 3 displays a simulation of the Mn$_{12}$–Ac data which consists of a superposition of spectra corresponding to the three main species in Cornia’s solvent disorder.
We assume that 50% of the molecules possess no E term, so that they contribute to the strongest central portions of the EPR absorption bands. Of the remaining 50%, half possess an E value of +0.014(2) cm⁻¹, and the other half an E value of −0.014 cm⁻¹ (a change in the sign of E is equivalent to a 90° rotation of the hard and medium directions).

These molecules contribute to the high- and low-field shoulders on the Mn₁₂−Ac EPR peaks (see Fig. 1) when the field is applied along either the hard or medium magnetic axes induced by the disordered solvent molecules. The flattening of the absorption bands is then reproduced by convoluting the individual contributions to the spectrum with a Gaussian function, \( \exp[-(\theta-90°)^2/2\sigma^2] \), where \( \theta \) is the orientation of the field relative to the global easy axis of the crystal. The full width at half maximum (FWHM) \( (\sim 2.35\sigma) \) of the distribution used in Fig. 3 is 2.6°. Overall agreement with the experimental spectrum in Fig. 2 is very good. The FWHM of the distribution is found to vary for different planes of rotation (to be published elsewhere), confirming our recent assertion that the easy-axis tilting is confined to orthogonal planes defined by the disorder-induced rhombic (E) zero-field tensor.

The above E value \( \pm 0.014(2) \) cm⁻¹, which was determined from separate in-plane angle-dependent measurements for Mn₁₂−Ac (to be published elsewhere), is larger than the value of 0.008(2) cm⁻¹ reported in Refs. 3–5. We note that the crystal used in the present study was transferred directly from the mother liquor to the experimental cryostat, whereas those used in earlier experiments were removed from the mother liquor long (up to two years) before performing the EPR measurements. We therefore speculate that the E strain may be reduced in older samples, possibly due to solvent loss. Most notably, the low-field shoulder seen in Fig. 1 for Mn₁₂−Ac is not resolved from the main peak in the earlier experiments, even though we suggested that it should exist.\(^3\)\(^5\)

In summary, we compare the HF-EPR data for Mn₁₂−Ac with the spectra obtained for two recently discovered Mn₁₂ analogs, differing only in their ligand and solvent structures. None of the fine structures seen for Mn₁₂−Ac are found for the recently discovered complexes, thus confirming that the solvent significantly influences the EPR spectra and, therefore, the QMT dynamics in Mn₁₂−Ac.

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