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From single-molecule magnetism to long-range ferromagnetism in Hpyr[Fe_{17}O_{16}(OH)_{12}(py)_{12}Br_{4}]Br_{4}


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I. INTRODUCTION

High-spin molecular compounds are crystalline aggregates of single-domain magnetic particles, for which the intramolecular coupling is such that each molecule carries a net magnetic moment (or “molecular spin”) at sufficiently low temperatures. A uniaxial molecular anisotropy due to the crystal field generated by the surrounding organic ligands may also be present and lead to a spin ground state that is parallel to the anisotropy axis. Molecular magnets are in many ways superior to similar sized magnetic particles as, by their nature, they exhibit ideal monodispersity in size, volume, shape, and charge. Furthermore, they are soluble in common solvents and their highly modular character opens up avenues for fine tuning of their magnetic properties. In addition, molecular magnets are of interest for possible technological applications, i.e., as bits for small magnetic memory units and qubits in quantum computing or as magnetic refrigerants for their enhanced magnetocaloric effect.

The intramolecular and intermolecular engineering of molecular magnets can lead to the observation of long-range magnetic ordering (LRMO). The large molecular spins in these crystals take the place of the individual magnetic ions in conventional materials. The intermolecular magnetic coupling results from either purely dipolar or weak superexchange interactions. The former are, in principle, much simpler to understand because magnetic phase transitions driven solely by long-range dipolar interactions can be predicted without involving any adjustable parameters. Unfortunately, very few examples of purely dipolar LRMO are known to date, and hence the investigation of magnetic phase transitions induced by dipolar interactions presents a most pertinent field of research in molecular nanomagnets.

A requirement for the experimental observation of LRMO is that the molecules should possess a large net spin ground state S to lead to accessible ordering temperatures. Indeed, the larger the spin, the stronger the intermolecular magnetic interaction is, likely yielding higher transition temperatures. However, S is also related to the anisotropy barrier given by $U = -D_S S_i^z (S_i^z + D/4)$ for (half-) integer spin, where D is the axial molecular anisotropy. If the anisotropy is strong enough, then this energy barrier dominates the low-temperature behavior.

The magnetic relaxation slows down notably inducing the molecular spins to freeze at temperatures much higher than the LRMO. The most obvious way to obtain a dipolarly ordered nanomagnet is thus to look for a high-spin molecule with a sufficiently low magnetic anisotropy. The latter condition is met by synthesizing molecular magnets of high symmetries and/or containing isotropic ions. The control of intramolecular interactions is indeed one of the main issues that has stimulated the research in molecular magnetism.

Using neutron diffraction to characterize magnetic order in molecular compounds is made difficult by two features of these materials: (i) they typically contain large numbers of hydrogen atoms, which leads to a substantial incoherent background; (ii) the very large number of nonmagnetic atoms in the molecules means that the nuclear scattering is far stronger than any potential magnetic signal. The first problem is readily avoided by using deuterated reagents, however, the second problem is intrinsic. In spite of this, some notable achievements have been reported. For example, single-crystal neutron diffraction was used to probe and characterize the LRMO in the organic molecular magnet $p$-NPNN, in which the ordered moment is highly delocalized. The propagation vector of the zero-field ordered magnetic structure (which can be observed unambiguously via neutron diffraction) was determined, as was the temperature...
The Fe$_{17}$ molecule is shown in Fig. 1. The occurrence of such a large spin ground state is due to the presence of the competing antiferromagnetic (AF) interactions between the Fe$^{3+}$ ions occupying the tetrahedral ($T$) and octahedral ($O$) sites. The Fe-O-Fe bridges that connect the five tetrahedral Fe$^{3+}$ ions (one central, and four capping) to the shell of 12 octahedral Fe$^{3+}$ ions are in the 125°–130° range, whereas the angles in the Fe-O-Fe bridges between the octahedral Fe$^{3+}$ ions are in the 97°–101° range. Assuming that the larger angles promote stronger antiferromagnetic interactions, we expect the $T$-$O$ interactions to be stronger than the $O$-$O$ interactions, so that the 12 octahedrally coordinated Fe$^{3+}$ ions form a ferromagnetic shell that is antiferromagnetically coupled to both the central Fe$^{3+}$ ion and the outer four capping Fe$^{3+}$ ions, leading to a ferrimagnetic molecule.$^{25,26}$

The Fe$_{17}$ molecules are bound together in the crystal solely by van der Waals forces, hence prohibiting any intermolecular superexchange pathway. An interesting and possibly unique characteristic of Fe$_{17}$ is that once the constituent ligands have been chosen, the molecules can be arranged in different crystal packings without affecting the individual molecules themselves,$^9$ keeping the surrounding ligands, the molecular high-spin ground state, and the magnetic anisotropy unaltered. In other words, the dipolar coupling between the molecules may be tuned with respect to single-molecular properties. The resulting interplay gives rise to behaviors ranging from superparamagnetic blocking to long-range magnetic order.$^9$ The present work focuses on the pyridine (pyr) derivative of the Fe$_{17}$ molecule based on Br$^-$ counterions, which adopts the $R3$ space group. This system is characterized by a uniaxial anisotropy of only $D=-0.02$ K, in addition to the $S=35/2$ giant-spin ground state. This combination of high spin and low anisotropy makes Fe$_{17}$ an ideal candidate for investigating dipolar-induced long-range magnetic order. In what follows, we shall present the magnetic structure of Fe$_{17}$ as induced by dipolar interactions solely and determined by means of neutron powder diffraction measurements. These are also accompanied by bulk magnetization, susceptibility, and magnetic field-dependent specific heat data measurements, as well as numerical simulations of the ground-state energy.

## II. SAMPLE PREPARATION

The Fe$_{17}$ molecules were obtained by dissolving FeBr$_3$ in a mixture of pyr and tetrahydrofuran. Crystallization (in the space group $R3$) was obtained from a slow evaporation of the filtered solution after a stirring period of approximately 1 h.

The resulting cluster has at its core a central tetrahedral Fe$^{3+}$ ion linked by O bridges to 12 outer octahedral Fe$^{3+}$ ions, which form a truncated tetrahedron: the octagonal faces of this tetrahedron are linked by other oxygen ligands. The inner Fe$^{3+}$ ion and the four outer Fe$^{3+}$ sit in the tetrahedral sites of the lattice with the others occupying the octahedral sites.$^{25,26}$ Displayed in Table I are the unit cell coordinates of the seven crystallographically distinct Fe atoms which are related by symmetry operations to make up the Fe$_{17}$ mol-

![Image](http://example.com/image.png)

**FIG. 1.** (Color online) Structure of Fe$_{17}$ (space group $R3$, $a=b$ = 16.1170(9) Å, $c$ = 69.928(6) Å, hexagonal setting). The molecule contains 17 magnetically coupled Fe$^{3+}$ atoms. Within the cluster core: brighter (yellow), darker (dark red), and smaller (red) balls represent Fe, Br, and O, respectively. CCDC-612322 contains the supplementary crystallographic data and can be obtained free of charge via the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/conts/retrieving.html).

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<td>2/3</td>
<td>0.131</td>
</tr>
</tbody>
</table>

TABLE I. Site symmetry and coordinates of the Fe$^{3+}$ atoms in the Fe$_{17}$ molecule.

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PHYSICAL REVIEW B 77, 224403 (2008)
ecule as well as the unit cell itself. Each molecule consists of 1 Fe$_{17}$, 3 Fe$_2$, 3 Fe$_3$, 3 Fe$_4$, 3 Fe$_5$, 3 Fe$_6$, and 1 Fe$_7$ atoms. The spin distribution within the cluster is thus Fe$_2$, Fe$_3$, Fe$_4$, and Fe$_5$ with spin up and Fe$_1$, Fe$_6$, and Fe$_7$ with spin down. This gives a net spin ground state of $S=35/2$ per molecule. Magnetization measurements on nondeuterated Fe$_{17}$ (Refs. 25 and 26) confirm this extraordinarily high-spin ground state.

For the neutron diffraction experiments, deuteration of the sample was necessary in order to avoid the enormous incoherent scattering from hydrogen ($\sigma_{\text{inc}}=80.3$ barns). This scattering leads to an unacceptably high background signal that dominates even the coherent nuclear scattering and makes it essentially impossible to observe any magnetic scattering. The incoherent background can be reduced to an acceptable level by partial replacement of hydrogen atoms by deuterium, for which $\sigma_{\text{inc}}=2.1$ barns. The degree of deuteration of the Fe$_{17}$ sample under investigation is estimated at approximately 80%–90%.

III. RESULTS AND DISCUSSION

Measurements of the magnetization down to 2 K and specific heat down to $\theta=0.3$ K on powder samples were carried out in a $0<B_0<7$ T magnetic field range. Magnetization, susceptibility, and relaxation measurements below 2 K were performed using home-made Hall microprobes. In this case, the grainlike samples consisted of collections of small crystallites of about $10^{-3}$ mm$^3$. For measurements performed on powder samples, the fits were obtained taking into account random spin orientations.

A. Magnetization and susceptibility

Figure 2 shows the low-temperature behavior of the magnetic susceptibility. For the 5 K$\leq T\leq 100$ K temperature range, the fit to the Curie–Weiss law $\chi=C/(T-\theta)$ provides $C=175.4$ emu K/mol and $\theta=0.9$ K. The Curie constant $C$ equals, within the error, the expected value of a (superpara-

FIG. 2. Inverse of the in-phase component of the ac magnetic susceptibility collected for $f=1730$ Hz together with the fit to the Curie–Weiss law (dashed line). Inset: low temperature behavior of the susceptibility collected using a Hall microprobe with an applied field of $B_0=2$ mT.

Figure 3 shows the low-temperature behavior of the magnetic susceptibility collected at $T=2$, 5, and 20 K. Full lines represent the fit results (see text), yielding a net molecular spin $S=35/2$ and an axial anisotropy $D=0.02$ K. Bottom: hysteresis loop measured at $T=0.5$ K with a magnification of the lowest applied-field range (inset). The susceptibility is corroborated by the field dependence of the magnetization $M(B)$, as depicted in Fig. 3. The $M(B)$ curves collected for $T=2$, 5, and 20 K can be well fitted using a net molecular spin of $S=35/2$, $g=2.06$, and zero-field splitting of only $D=-0.02$ K. Although smaller trigonal components could be present, the data do not justify a more sophisticated fitting. On basis of the estimated $D$, the activation energy of Fe$_{17}$ amounts to $D(S^2−1/4)=7$ K, i.e., nearly 1/9 of that in Mn$_{12}$ acetate. Accordingly, superparamagnetic blocking might be expected to occur at $T_g(Mn_{12})/9=0.5$ K if intermolecular interactions were absent.

Accordingly, superparamagnetic blocking might be expected to occur at $T_g(Mn_{12})/9=0.5$ K if intermolecular interactions were absent. Assuming that the phase transition to LRMO occurs at $T_C=1$ K (inset of Fig. 2), we collected a hysteresis loop in the ordered phase at $T=0.5$ K (inset of Fig. 3). We observe that Fe$_{17}$ appears to behave like a soft

FIG. 3. Top: isothermal molecular magnetization collected at $T=2$, 5, and 20 K. Bottom: hysteresis loop measured at $T=0.5$ K with a magnification of the lowest applied-field range (inset).
ferromagnet with a small coercivity of \(\sim 2\) mT. From the estimate, \(D = -0.02\) K, the anisotropy likely causes a pinning of the domain wall motions leading to the slow decrease in the experimental susceptibility below \(T_C\) (Fig. 2).

B. Specific heat

Figure 4 shows the specific heat \(C(T, B)\) as a function of temperature for applied fields of \(B_0 = 0, 1, \) and \(3\) T. In zero field, there is a prominent \(\lambda\)-type anomaly that develops below \(\sim 1.2\) K and reaches a maximum at \(\sim 0.85\) K, revealing the onset of a phase transition.\(^{28}\) The magnetic nature of this event is confirmed by its disappearance upon application of a magnetic field. It is clear that the \(\lambda\)-type anomaly sits on top of a much broader feature, which shifts with increasing applied field toward higher temperatures. Because of the small anisotropy (\(D = -0.02\) K), it is expected that the magnetic contribution to \(C(T, B)\) for \(B_0 \geq 1\) T is mainly due to a Schottky-type Zeeman splitting of the otherwise nearly degenerate spin states. Indeed, the calculated Schottky curves (solid lines in Fig. 4) arising from the field-split levels account very well for the experimental data. The lattice contributions (dashed lines in Fig. 4) were modeled as a sum of a Debye term for the acoustic low-energy phonon modes plus an Einstein term that likely arises from intramolecular vibrational modes. The fit yields \(\theta_D = 27\) K and \(\theta_E = 42\) K for the Debye and Einstein temperatures, respectively. Finally, we estimate the magnetic entropy change \(\Delta S_m\) using \(\Delta S_m / R = \int_0^T C_m(T) / (RT) dT\), where \(C_m(T)\) is the magnetic contribution obtained from \(C(T)\) after subtracting the lattice contribution. We find \(\Delta S_m = 3.7R\), in good agreement with the entropy expected \(R \ln(2S+1) = 3.6R\), given \(S = 35/2\). As already anticipated, we can therefore safely attribute the \(\lambda\) feature to a phase transition of the Fe\(_{17}\) molecular spins.

C. Neutron diffraction

Two sets of neutron diffraction measurements were performed. The first set was performed on the GEM time-of-flight diffractometer, located at the ISIS pulsed neutron source, Rutherford Appleton Laboratory, U.K. A sample weighing approximately \(2\) g was inserted in a 6 mm diameter vanadium sample can with a copper “cold finger” inserted from top to bottom for the length of the sample can in order to assist in the thermalization of the sample.

An “orange-type” cryostat and a \(^3\)He closed cycle system were used to cool the sample, and measurements were performed at four different temperatures: the ambient (293 K), an intermediate temperature (50 K), the low \(T\) (\(\sim 1.5\) K), and the base temperature of the \(^3\)He cryostat. Data were normalized to the wavelength distribution of the incident neutron beam. The most important part of the data is contained in the low-angle banks, which corresponds to the small values of the scattering vector \(Q\), where one can expect magnetic scattering.

No changes were observed in the scattering patterns between 293 and 1.5 K, confirming that the high-spin system remains paramagnetic, with no long-range magnetic order, down to at least 1.5 K. This is consistent with the bulk data, reported above, which indicate that magnetic correlations are not expected to set in above \(T \sim 1.2\) K. The unchanging nuclear scattering also shows that the material retains its \(R^3\) crystal symmetry on cooling. The first indication of magnetic ordering comes from a suppression of the paramagnetic background scattering for \(Q < 0.45\) Å\(^{-1}\) on cooling below 1.5 K, as seen in Fig. 5. This is typical of a transition from a disordered to an ordered state. The observed Bragg intensities are dominated by the nuclear scattering and any magnetic scattering is expected to be weak. In spite of this limitation, a discernible increase in intensity was noted on cooling from 1.5 K, particularly for \(Q \sim 0.48\) Å\(^{-1}\), which corresponds to the overlapping nuclear (101) and (102) reflections (Fig. 5). This increase in intensity with decreasing temperature is positive confirmation of the presence of magnetic Bragg scattering. Furthermore, as no new reflections were observed, the scattering from the magnetic structure is superimposed on the nuclear scattering, and the ordering wave vector \(k\) of the magnetic structure is therefore \(\{000\}\). This corresponds to either a commensurate ferromagnetic or commensurate antiferromagnetic structure. The peak shape is
of the expected double-exponential pseudo-Voigt type, commonly obtained on time-of-flight diffraction instruments, so that the ordering can be taken to be three-dimensional in nature.

The second set of neutron diffraction measurements consisted of a more complete and detailed temperature dependent survey of the magnetic signal and was performed on the constant wavelength C2 DualSpec spectrometer (located at the Canadian Neutron Beam Centre, Chalk River, Canada) on the same sample of deuterated Fe$_{17}$. An incident neutron wavelength of 2.3723 Å was used and a modified Oxford Instruments Heliox $^3$He cold stage was adapted to fit into an orange cryostat that was mounted on the spectrometer. This system enabled subkelvin temperatures down to 330 mK to be reached with typical holding times of ~48 h. Earlier experience with mounting powdered samples on this Heliox system showed that cooling time constants of several days can be observed unless significant efforts are taken to ensure thermalization. The following procedure, which has been found to yield thermalization times of less than 30 s, was therefore used. The 1.17 g of powder Fe$_{17}$ was mixed with 1.25 g of 99.99% pure copper powder and hydraulically pressed into a 6 mm inside diameter oxygen-free, high-conductivity copper can to form a 26 mm long solid rod inside the can. While this packing does not affect the properties of the Fe$_{17}$, it does add some fcc-Cu reflections, however, the first of these occur at $Q \sim 3$ Å$^{-1}$, well outside our region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest. Diffraction patterns were collected at temperatures from 0.33 to 1.4 K to follow the magnetic ordering region of interest.

The only constraints imposed on the magnetic structure are that all single-ion Fe$^{3+}$ spins in the molecule are nonzero and equal in magnitude to $\mathbf{S}=5/2$ and that each molecule consists of a well-defined collinear ferrimagnetic arrangement of spins. The present neutron data are restricted to a limited range of scattering vector. This implies that a traditional Rietveld refinement of the crystal and magnetic structures is not feasible. With the available neutron data and the above constraints, we have utilized the theory of irreducible representations for magnetic groups to define a magnetic structure compatible with the neutron and bulk macroscopic magnetic data. This theory is particularly valid for second order phase transitions. There are six possible irreducible representations of the space group $R^3$ for $\mathbf{k}=$\{000\}. For the two types of magnetic sites, 6c and 18f, which comprise the Fe$_{17}$ molecule, each of these six representations occur for both sites. The basis vectors of these representations for each of the magnetic sites were calculated using SARA $h$-representational analysis (downloadable at ftp://ftp.ill.fr/pub/dif/sarah/). The selected basis vectors belong to two of the six irreducible presentations, $\Gamma_1$ and $\Gamma_2$, which corre-
TABLE II. Basis vectors and basis vector components \((m_x, m_y, m_z)\) of the irreducible group representations for the space group \(R3\) with propagation vector \(\mathbf{k} = (000)\). The atom notations \(6c_1\) and \(6c_2\) refer to atom 1 and its symmetry equivalent atom 2 in an adjacent molecule.

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<td>((6c_2) 00−m_z)</td>
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respond to the magnetic structures with all moments aligned either parallel or antiparallel to the \(c\) axis, respectively. The other four, \(\Gamma_3\), \(\Gamma_4\), \(\Gamma_5\), and \(\Gamma_6\), represent various planar configurations. We can discard these latter configurations on the basis of the observed intensities, which clearly point to an axial configuration. Furthermore, some of the basis vectors for \(\Gamma_3\), \(\Gamma_4\), \(\Gamma_5\), and \(\Gamma_6\) give sites where a magnetic moment is not allowed. Table II lists the irreducible representations and their corresponding basis vectors for the magnetic structures compatible with our data. Figure 8 displays our simulations of the expected powder diffraction patterns for the two corresponding magnetic structures \(\Gamma_1\) and \(\Gamma_2\).

The ferromagnetic configuration \(\Gamma_1\) attributes a small intensity to the (101) reflection and a larger assignment of intensity to the (102) reflection. This is in stark contrast to the antiferromagnetic configuration \(\Gamma_2\), for which the intensity ratios of these two peaks are practically inverted. The representations corresponding to the four planar configurations all give intensity at the (003) position. Of the six possible models, only the axial ferromagnet is in accord with our data. We therefore conclude that dipolar interactions do, in fact, favor this configuration. As a further confirmation and anticipating Sec. IV, dipolar calculations indicate indeed that of the two ground states displayed in Fig. 9, the axial ferromagnet has a lower energy than the axial antiferromagnet.

The \(\text{Fe-O}\) cluster forming the core of the \(\text{Fe}_{17}\) molecule behaves as a single, exchange-coupled \(S = 35/2\) entity. The temperature dependence of the ordered magnetization below \(T_c\) reflects excitations of these giant-spin orderings in the mean field established by intercluster dipolar forces and manifests itself in the intensity of the (102) reflection. This peak intensity is directly proportional to the square of the ordered moment (Fig. 10). Fitting the observed magnetic intensity to a \(S = 35/2\) Brillouin function, neglecting any effects due to the small anisotropy, yields an ordering temperature of 1.13(2) K in good agreement with values obtained from both susceptibility and heat capacity measurements. We emphasize here that the neutron diffraction data do more than simply confirm the transition temperature; they unequivocally demonstrate that the magnetic order is long ranged and ferromagnetic in nature, with moments aligned parallel to the \(c\) axis.

IV. GROUND-STATE ENERGY CALCULATIONS

We calculated ground-state dipolar energies \(E_{\text{dip}}\) for the pointlike Heisenberg spins arranged in crystallographic lattice analogs to that of \(\text{Fe}_{17}\). In particular, the position of the spins was fixed accordingly to molecular centroids. The mo-
The calculations are carried out for the spin configurations depicted in Fig. 9, i.e., the ferroelectric (FE) and AF spin alignments along the c axis. We obtain $E_{\text{dip}} = 0.2$ and 2.0 K for FE and AF, respectively. Since they differ by 1 order of magnitude, we can clearly conclude that the most probable configuration is ferromagnetic, corroborating the neutron diffraction analysis.

V. CONCLUSIONS

The $Fe_{17}$ magnetic molecule represents a unique system, in which neutron scattering techniques can be successfully employed to assess the long-range ferromagnetically ordered structure induced by dipolar interactions. A highly symmetric molecular core and a correspondingly small uniaxial anisotropy combine to support the occurrence of magnetic ordering at accessible temperatures. Neutron diffraction measurements performed on powder samples of $Fe_{17}$ confirm the type of the order and the direction of the ordered magnetic moments with respect to the crystallographic unit cell. A small but clear magnetic signal is observed and successfully tracked in the temperature interval 0.33 K $\leq T \leq 1.4$ K. The transition temperature $T_c = 1.13(2)$ K is in good agreement with susceptibility and specific heat data. Furthermore, unlike most other examples of long-range ordered molecular magnets, it is possible to obtain the relatively large amounts of deuterated $Fe_{17}$ essential for a successful neutron diffraction experiment. Modeling the magnetic structure with a net spin $S = 35/2$ positioned in the molecular centroids shows a good agreement with the experimental data, indicating that the $Fe_{17}$ molecule behaves as an atom with a macrospin given by the sum of the contributions of the constituent $Fe^{3+}$ ions. This encouraging result should stimulate neutron powder diffraction experiments in other molecular superparamagnets where long-range order may be active.

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