Experimental report

13/02/2019

Proposal: 5-51-526 **Council:** 4/2018

Title: Magnetisation Density Mapping of Strongly Delocalized Giant Spin Hexa-iron Clusters Exhibiting Superparamagnetism

Research area: Chemistry

This proposal is a new proposal

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Samples: C126H90D58N30O11F18Fe12

Instrument	Requested days	Allocated days	From	To
D3 High field >1T	10	11	11/10/2018	22/10/2018
D19	6	6	05/10/2018	11/10/2018

Abstract:

Superparamagnetic metal clusters are of fundamental interest due to the quantum origin of their magnetic behavior, and they have been proposed for use in information storage and spintronics devices, but the small size of the spin reversal energy barriers limits applications. 1-D coordination polymers containing anisotropic paramagnetic molecules also exhibit spin reversal barriers whose magnitude depends on the spin state of the component molecules and the strength of the intrachain magnetic exchange. Thus, 1-D exchange coupled systems containing giant-spin metal clusters could exhibit higher spin reversal barriers. We have prepared a series of clusters that are uniquely suited to this challenge, featuring strong exchange leading to the highest reported thermally isolated spin ground states. We propose to map the spin density within the clusters using polarized neutron diffraction to gain insight into the role of electronic delocalization and short metal-metal distances in promoting the strong magnetic exchange and to better predict how the clusters will behave as building blocks in magnetic materials.

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Objective. The Betley lab has prepared many examples of superparamagnetic octahedral iron clusters in which very strong magnetic exchange leads to large spin ground states that are well-isolated from excited states up to room temperature. In the experiments conducted at ILL, we aimed to learn more about the nature of the unusually strong exchange and the resulting large spin ground states by constructing spin density maps of representative clusters from unpolarized and polarized neutron diffraction data.

Results: D19. After some additional crystallization trials, we were able to produce crystals of the metal cluster sample that were substantially larger than the crystals that we had obtained before we wrote the proposal (8 to 15 mm^3 compared to 2-3 mm^3). However, the crystals proved to be significantly less stable than expected with respect to loss of solvent, which posed an additional challenge for the sample preparation and shipment. We found that the crystals could retain high diffraction quality only if coated in oil or grease and kept at low temperature. For transportation to ILL, we coated the crystals with fluorinated oil and sealed them in capillaries. We took the largest crystal with us to D19 in a liquid nitrogen-cooled dry shipper and shipped the remainder of the crystals to the facility in a package cooled by dry ice. However, when we removed the crystal from the dry shipper at the beamline, the rapid increase in temperature caused the capillary to snap, resulting in the loss of the crystal.

The remainder of the samples that we shipped with dry ice did not arrive until several days after the beginning of the experiment, although they were scheduled to be delivered the day before the experiment. As a result, we were only able to use 1.5 out of the 6 days of beamtime to collect diffraction data. As indicated in Table 1, the crystal diffracted well, with good resolution and intensity and a relatively low R_{int} value considering the large atom% hydrogen. However, the 7000 unique reflections that we were able to measure in this short time yielded a low data-to-parameter ratio for the resulting model, which could not be refined to an acceptable value of R_1.

Table 1. Results of the D19 experiment.

Crystal dimensions	$2\theta_{max}$	Mean I/σ	R_{int}
5 x 2.5 x 1.5 mm	120.8°	19.1	0.0751
Completeness	Redundancy	R_1	wR_2
0.615	1.5	0.167	0.444

The model obtained is displayed in Figure 1 below. Notably, there are two cases of solvent disorder which cannot be adequately refined with this limited data set, and there are spurious negative peaks in the difference map throughout parts of the structure. We conclude that a more complete set of reflections will be required to produce an acceptable structural model.

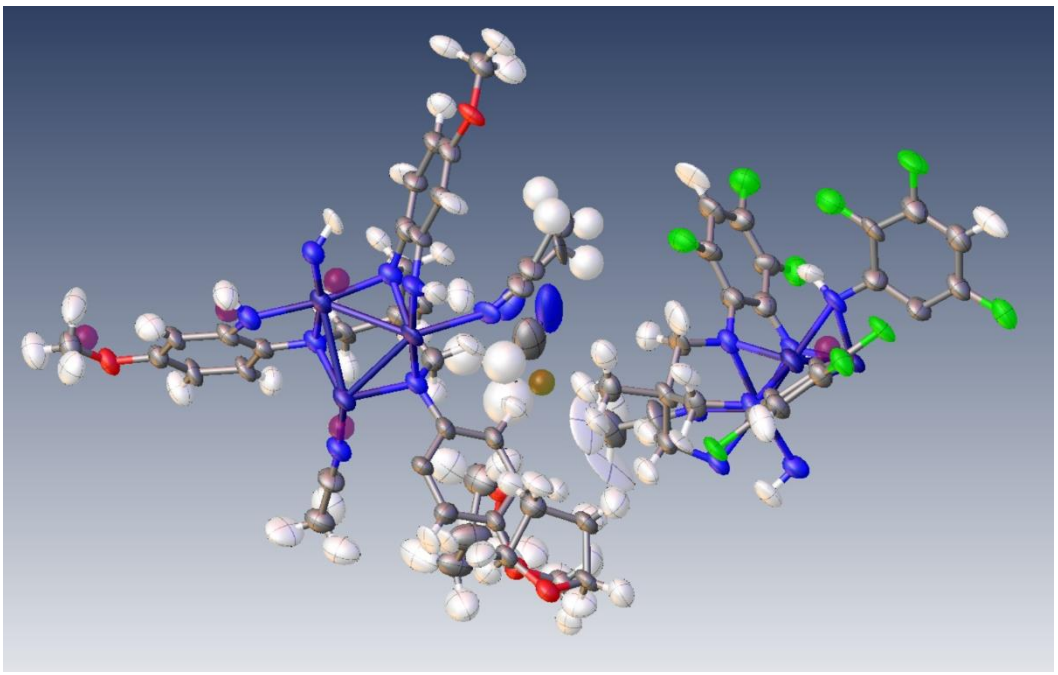

Figure 1. Structural model obtained from the D19 experiment. Purple = Fe, gray = C, blue = N, red = O, green = F, white = H. Negative difference map peaks are light purple and positive peaks are gold.

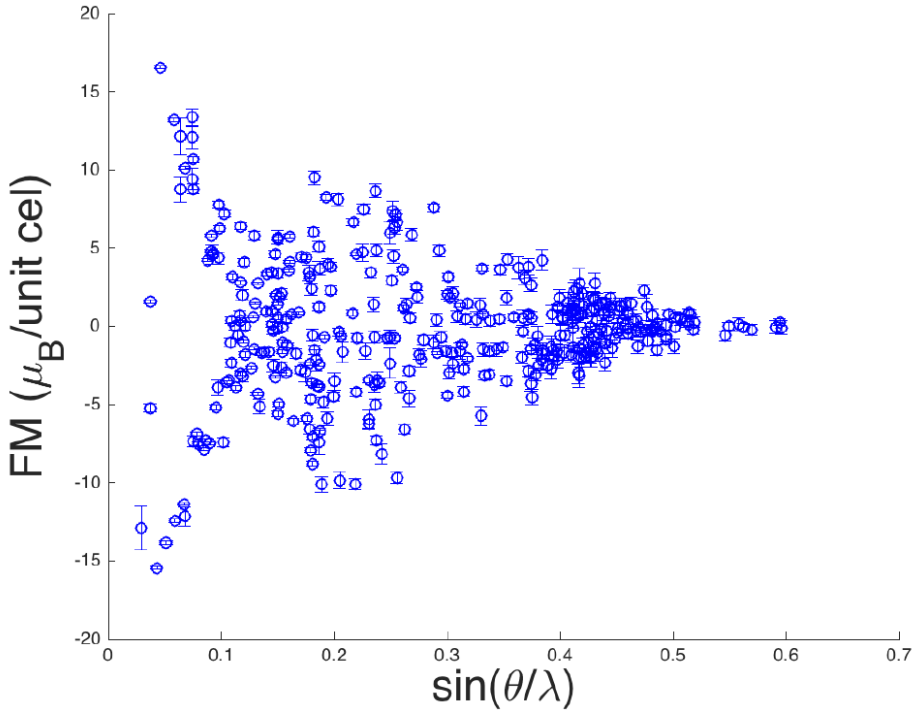

Figure 2. Magnetic structure factors obtained from the D3 experiment.

Results: D3. Although we were not able to obtain a satisfactory structural model from the D19 experiment, the orientation matrix of the crystal was sufficient to continue to the polarized

neutron diffraction experiment at D3. Here, we measured 384 flipping ratios up to $\sin(\theta/\lambda) = 0.6$ with a 9 T magnetic field parallel to the long axis of the crystal, and we extracted the magnetic structure factors using the nuclear structure factors calculated from the structural model (Fig. 2).

These magnetic structure factors were used to produce a spin density map for the two different clusters in the crystal using the maximum entropy method (Fig. 3). As expected, there is substantially more spin density on the anionic cluster (S = 19/2) than on the cationic cluster (S = 7/2). However, the superposition of the spin density map onto the structure indicates that the maxima of the spin density do not overlap well with the structure, particularly in the cationic cluster. Therefore, we cannot perform a model-based analysis to compare the amount of spin density at each iron site and gain more information about spin delocalization in these systems. Moreover, we find that the features of the spin density map depend strongly on the choice of nuclear structure factors, with maps produced using nuclear structure factors calculated from the X-ray model, nuclear structure factors calculated from the neutron model, or only the measured nuclear structure factors all differing significantly in the shape and location of the density maxima. We conclude that a more reliable set of nuclear structure factors from D19 is necessary to enable analysis of the spin density in this material.

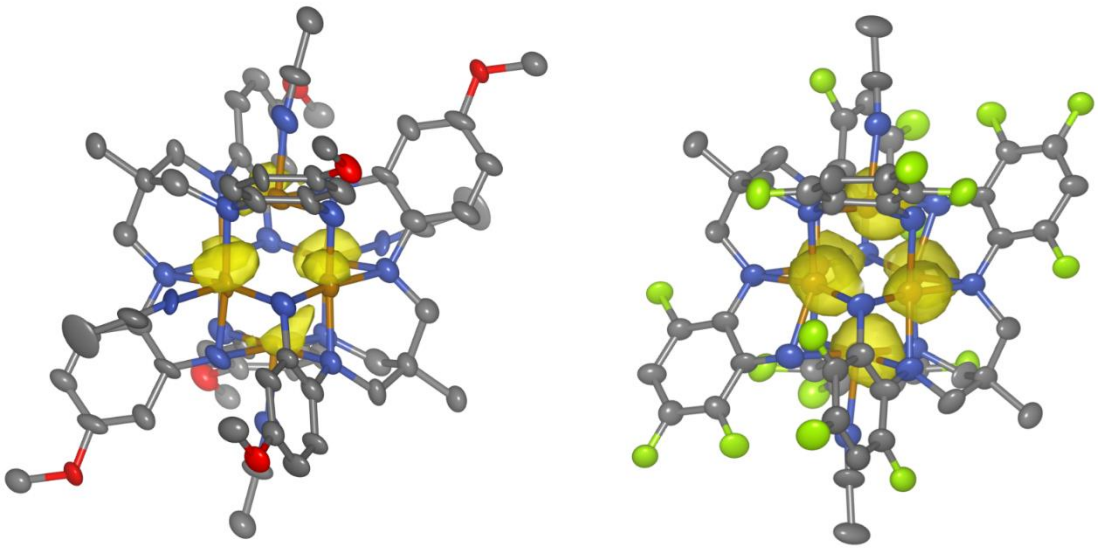

Figure 3. Superposition of the spin density map produced from the nuclear structure factors calculated from the neutron structural model onto the neutron structural model. Left: S = 7/2 cationic cluster. Right: S = 19/2 anionic cluster. Orange = Fe, gray = C, blue = N, red = O, yellow-green = F. Hydrogen atoms omitted. Isosurface cutoff 0.09 $\mu_B/Å^{-3}$.

Conclusion and future plans. We were not able to obtain a complete set of nuclear structure factors at D19, and analysis of the D3 data shows that the spin density map depends strongly on the quality of the nuclear structure factors used. Therefore, we plan to submit a continuation proposal to obtain a complete set of nuclear structure factors at D19 in order to produce a spin density map of sufficient quality to allow a detailed model-based analysis of the spin distribution in this material.