Inorganic Approach to Stabilizing Nanoscale Toroidicity in a Tetraicosanuclear $Fe_{18}Dy_6$ Single Molecule Magnet

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ABSTRACT: Cyclic coordination clusters (CCCs) are proving to provide an extra dimension in terms of exotic magnetic behavior as a result of their finite but cyclized chain structures. The $Fe_{18}Dy_6$ CCC is a Single Molecule Magnet with the highest nuclearity among Ln containing clusters. The three isostructural compounds $[Fe_{18}Ln_6(\mu\ OH)_6(ampd)_{12}(Hampd)_{12}(PhCO_2)_{24}](NO_3)_6\cdot 38MeCN$ for Ln = Dy^{III} (**1**), Lu^{III} (**2**), or Y^{III} (**3**), where H_2ampd = 2 amino 2 methyl 1,3 propanediol, are reported. These can be described in terms of the cyclization of six $\{Fe_3Ln(\mu OH)(ampd)_2(Hampd)_2(PhCO_2)_4\}^+$ units with six nitrate counterions to give the neutral cluster. The overall structure consists of two giant Dy_3 triangles sandwiching a strongly antiferromagnetically coupled Fe_{18} ring, leading to a toroidal arrangement of the anisotropy axis of the Dy ions, making this the biggest toroidal arrangement on a molecular level known so far.

The field of magnetically interesting molecules has remained on the forefront of research ever since the discovery of slow relaxation of magnetization in a Mn_{12} coordination cluster and the subsequent characterization of these compounds as single molecule magnets (SMMs).[1−7] Varying approaches to improve magnetic properties of SMMs have been investigated, with one being incorporating 3d and 4f ions into coordination clusters to exploit benefits of both types of ions. The approach used here can be characterized as "assisted self assembly" using preformed triangular building blocks.[8]

Currently, there is a relatively small number of 3d/4f cyclic coordination clusters (CCCs) reported[9−20] despite the finite chain nature of these compounds providing an opportunity to study phenomena induced by the interplay of coupling, periodic boundary conditions, and mesoscopic size. Out of the reported Fe containing examples, some turn out to be SMMs, mostly incorporating Dy as the 4f ion.[16−20] Here we describe an $Fe_{18}Ln_6$ system (Figure 1, Scheme S1) showing slow relaxation of magnetization at zero DC field characteristic of single molecule magnets (SMMs) for the Dy compound but also a nonmagnetic ground state characteristic of a single molecule toroic (SMT) system.[21,22]

This represents the largest Fe/4f SMM with a nonmagnetic ground state, as well as the physically largest molecule (Figure S2) showing a toroidal arrangement of anisotropy.

$[Fe_{18}Ln_6(\mu\ OH)_6(ampd)_{12}(Hampd)_{12}(PhCO_2)_{24}](NO_3)_6\cdot 38MeCN$ for Ln = Dy^{III} (**1**), Lu^{III} (**2**), or Y^{III} (**3**) and H_2ampd = 2 amino 2 methyl 1,3 propanediol, crystallize isomorphously in the orthorhombic space group *Pccn* with $Z = 4$ (see the Supporting Information). In contrast to a previously reported CCC with the same nuclearity,[19] the described compound here is far from planar. Figure 1a shows compound **1** viewed down its pseudo 3 fold axis, leading to the impression of planarity. In fact, the structure is better described as a planar Fe_6 ring, decorated with six triangular Fe_2Ln moieties, alternating above and below the plane (Figure 1b).

The cluster can be broken down into repeating Fe_2Dy triangles linked together via a benzoate bridged Fe to form a "modified delta chain"[9] (Figure S1a, b). The repeating unit within the chain is therefore an Fe_3Dy moiety. In other words, the cyclization of six of these units along with six nitrate counterions, which help to stabilize the structure, results in the cyclic coordination cluster.

In this modified delta chain model, the Fe_3Dy repeating units have the Fe_2Dy triangles positioned above and below the plane of the six central Fe's. This equates to a pseudo cubic close packing (ccp) arrangement with the sequence A (Dy_3 triangle above the Fe_6 plane), B (Fe_6 plane), and C (Dy_3 triangle below the Fe_6 plane, rotated by 60° compared to A); compare Figure 1b. This predisposes the Dy_3 triangles to show the toroidal arrangement as in previously reported examples[23−26] with two Dy_3 triangles sandwiching either a single ion or a trimesate. In this case we have two such triangles sandwiching an Fe_{18} ring. Note that due to the long $Dy_3\cdots Dy_3$ distance, a negligible interaction is expected between the Dy triangles.

Clearly, this makes the magnetic properties of this system of great interest. For $Fe_{18}Dy_6$ (**1**), the χT product at 300 K is 145.0 $cm^3\ K\ mol^{-1}$, which is lower than the expected value (163.8 $cm^3\ K\ mol^{-1}$) for 18 uncoupled Fe^{III} ions ($S = 5/2$, $g = 2$, $C = 4.375\ cm^3\ K\ mol^{-1}$) and six Dy^{III} ions ($^6H_{15/2}$, g = 4/3, *S*

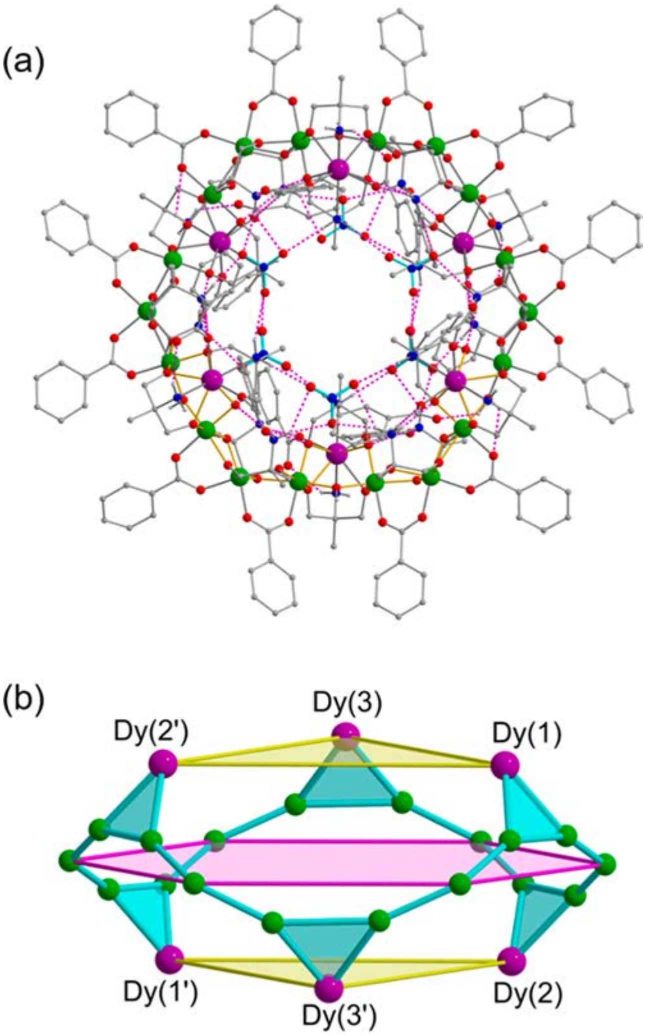

Figure 1. Molecular structure of $Fe_{18}Dy_6$ (**1**) (a) viewed along its pseudo 3 fold axis. Organic H atoms omitted for clarity; Dy−O and Fe−O bonds to bridging oxygens shown in orange, nitrate N−O bonds shown in cyan, and hydrogen bonds shown as dashed pink lines. Dy, purple; Fe, green; O, red; N, blue; C, dark gray; H, pale gray. (b) Modified delta chain and cubic close packing.

= 5/2, L = 5, J = 15/2, C = 14.17 cm^3 K mol^{-1}). This is consistent with the values for **2** and **3** (Ln = Lu, Y) (see below and Figure S7a,c,e), where the contribution of unpaired f electrons is not present and thus arises solely from the contribution of the Fe_{18} ring. The χT product for **1** gradually decreases from 300 to 50 K before rapidly decreasing to reach 49.4 cm^3 K mol^{-1} at 2 K, indicating dominant antiferromagnetic interactions within this $Fe_{18}Dy_6$ cluster. The magnetization value does not fully saturate (Figure S7b), which is expected assuming antiferromagnetic Fe−Fe exchange and given the presence of six anisotropic Dy ions.

Given that the central Fe_{18} ring is structurally very similar to the antiferromagnetically coupled ring of King et al.,[27] we were intrigued to discover whether the decoration of this ring with a triangle of dysprosiums above and below makes a difference to the magnetic properties. For this reason, we synthesized the Y and Lu analogues to check the magnetic properties for the situation where there is no contribution to the magnetism from Ln.

The magnetic data for **2** and **3** reveal that there must be substantial antiferromagnetic Fe−Fe nearest neighbor exchange. ALPS/QMC[28,29] complemented by magnetostructural calculations according to Cañada Vilalta et al.[30] suggests interactions following a weak−weak−strong pattern (J_1 = J_2 = 8K, J_3 = 29K) as shown in Figure 2 and Scheme S4. The unique strong interaction occurs between the two Fe at the base of the Fe_2Dy triangle. Using the same magnetostructural correlation approach on the Fe_{18} ring of King et al. leads to results in agreement with the original calculations,[31] taking into account that it has previously been shown that values obtained from such magnetostructural correlations tend to be overestimated by a value of approximately 4K.[32]

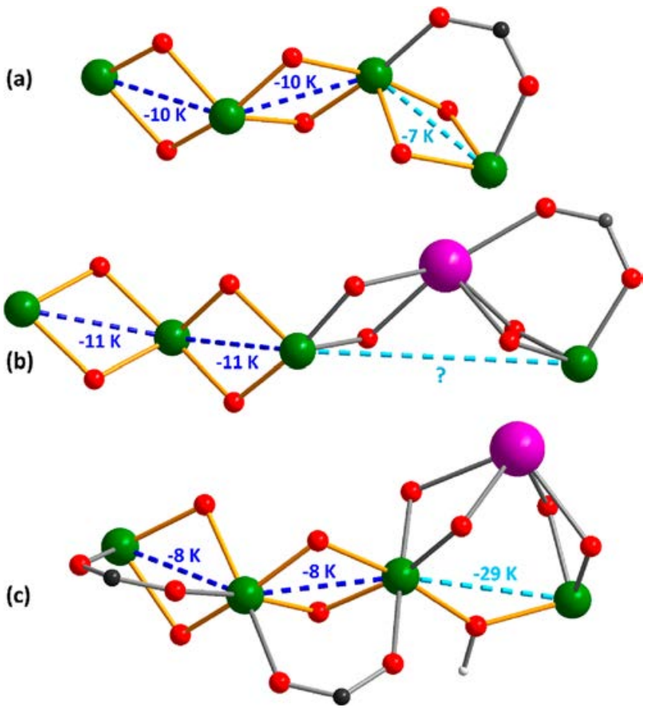

Figure 2. Repeating units from the Fe_{18} rings in (a) Fe_{18}, King et al.;[27] (b) $Fe_{18}Ln_6$, Botezat et al.;[19] and (c) $Fe_{18}Ln_6$, this work, showing the J_{FeFe} values calculated (for a $-2J(S_A{\cdot}S_B)$ Hamiltonian) using the magnetostructural correlation of Cañada Vilalta et al.[30] (Fe, green; Ln, purple; O, red; Fe bridging O bonds, orange). Note that in each repeating unit a J_1−J_1−J_2 coupling pattern is observed.

Replacing Lu/Y by Dy yields magnetic data that cannot be explained using a simple sum of the Fe_{18} ring and six noninteracting Dy ions (Figure S7g). We therefore assume that the anisotropic Dy ions interact with their two neighboring Fe ions (see Scheme S4 in the SI). Such a system is impossibly large for any quantum calculation and the strong spin−orbit interaction of the Dy moments renders a spin only model a poor approximation. In order to arrive at semiquantitative conclusions based on a full quantum calculation we model the system according to the following approximations: (1) The two Fe adjacent to a Dy mutually interact very strongly antiferromagnetically; we therefore assume that they are locked into a singlet dimer and do not contribute to the observables at low temperatures and small fields. (2) The remaining system is a sawtooth chain of alternating Dy and Fe ions coupled by an effective exchange J_1^{eff} and an additional next nearest neighbor exchange J_2^{eff} between adjacent Fe ions.(Schemes S2 and S4) The sign of J_1^{eff} is not known, but J_2^{eff} is antiferromagnetic in second order perturbation theory. In order to answer the question about the character of the ground state, the spin quantum numbers of Dy and Fe have been replaced by fictitious small values $s_{\mathrm{Dy}}^{\mathrm{eff}} = 1$ and $s_{\mathrm{Fe}}^{\mathrm{eff}} = 1/2$. This makes it possible to perform full diagonalization studies for arrangements of the Dy anisotropy (easy) axes as shown in Figure 4. These calculations reveal that the system is indeed toroidal. A large energy gap to excited states appears in the spectrum, compare Scheme S3. The ground state is ferrotoroidal as given by Dy−Dy spin−spin correlations, and it is 2 fold degenerate. The latter fact suggests a different behavior of rings with multiples of four Dy moments[32] compared to rings with even numbers of Dy moments that are not multiples of four. This difference is not uncommon in magnetism,[33] and our quantum calculations reproduce the 4 fold degeneracy found by Zhang et al.[34]

The dynamic behavior was explored using AC susceptibility measurements (see Figures 3 and S11), this compound shows clear peaks in the out of phase susceptibility without applied DC field, which is in stark contrast to the $Fe_{18}Dy_6$ compound reported by Botezat et al. which, although it has the same stoichiometry has a different topology and although the authors observed a peak in the out of phase susceptibility, this could not be attributed to slow magnetic relaxation.

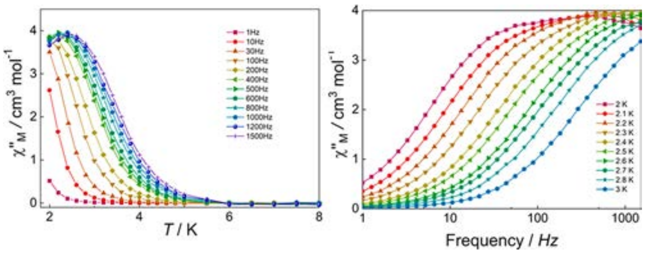

Figure 3. Out of phase temperature (left) and frequency dependence (right) of **1**.

In order to explore the possibility of a toroidal arrangement within the Dy triangles above and below the Fe_{18} ring, the system was explored using the Magellan software.[35] Although such an analysis is not watertight for 3d 4f systems, it does give a good indication from the electrostatic point of view of the anisotropy directions, which here are found to be in a characteristic propeller shaped toroidal arrangement for the Dy ions (see Figure 4).

To check whether the proposed toroidal arrangement within the Dy_3 triangles could be present we performed microSQUID measurements which revealed a behavior consistent with a toroidal moment[21] (Figures 5 and S13). In this particular case the strongly antiferromagnetically coupled Fe_{18} ring steers the direction of the Dy anisotropy axis through the Fe_2Dy sawtooth motifs which are necklaced by the interposed antiferromagnetically coupled Fe ions of the Fe_{18} ring (compare Schemes S2 and S4 in the SI). The long $Dy_3 \cdots Dy_3$ distances suggest that there will be negligible interaction within or, indeed, between the Dy. Out of the three possible organizations of two linked triangular toroidal systems, side by side,[25] sandwiching one paramagnetic 3d metal[26] or sandwiching a large organic moiety[24] this system is supramolecularly closest to the latter one, as the Dy···Dy distances are between 10.1 and 11.9 Å (within the Dy_3 triangles) and 15.5 Å (biggest Dy···Dy distance within the molecule) compared to 6.0 (intermolecular) to 10.3 Å (intramolecular) in the previously largest toroidal sandwich "Double Propeller" system.[24] However, in terms of magnetic behavior we show by providing a comparative figure (Figure S13) of the microSQUID data for the ferrotoroidal $CrDy_6$ complex that the magnetic signatures of both systems are very similar. As can be observed in the microSQUID loops for $CrDy_6$ and $Fe_{18}Dy_6$, an almost flat $M(H)$ profile is observed between ca. −0.5 and 0.5 T, characteristic of a nonmagnetic toroidal ground state.

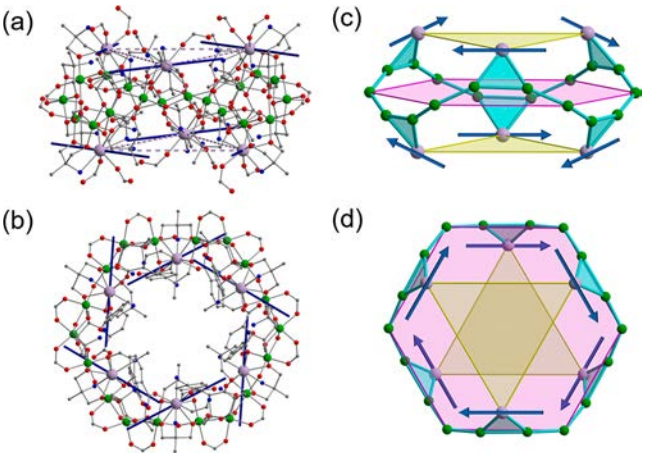

Figure 4. (a, b) Arrangement of anisotropy axis (dark blue) within the Dy_3 triangles sandwiching the Fe_{18} ring, note that the orientation of the axis is very close to being completely within the Dy_3 plane. Phenyl groups and hydrogen atoms are omitted for clarity. (c, d) Proposed rationalization of the spin arrangement within **1** taking the dominating antiferromagnetic interaction in the Fe_{18} ring into consideration. For clarity, only one of the possible degenerate classical states is shown here.

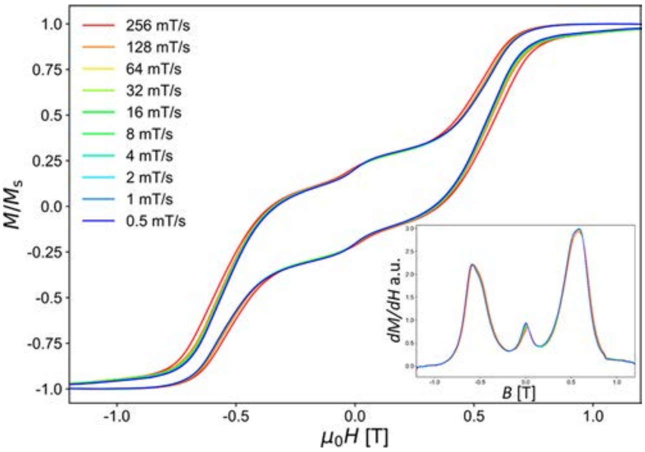

Figure 5. MicroSQUID data: magnetic hysteresis of $Fe_{18}Dy_6$ (**1**) at 30 mK under varying field sweep rates and derivative (inset). The loops show a plateau between −0.5 and 0.5 T, characteristic of a nonmagnetic toroidal ground state.

In conclusion we have synthesized a nanoscale cyclic coordination cluster, the structure of which can be described as two giant Dy_3 triangles sandwiching a strongly antiferromagnetically coupled Fe_{18} ring, such that the Fe_{18} ring achieves what the six Dy ions could not do on their own: organizes them toroidally. This toroidal arrangement is confirmed by microSQUID measurements. From quantum calculations it could be shown that the moments are arranged ferrotoroidally. The field needed to break the toroidal arrangement in the

$Fe_{18}Dy_6$ is nearly as large as that for the $CrDy_6$ sandwich,[26] and also comparable to those for the Dy_6 rings,[36] even though the Dy···Dy distances in our molecule are much larger and direct Dy···Dy dipolar interactions are likely to be at best negligible, a testimony to the very good job the unsung Fe_{18} ring is doing. The compound also shows slow relaxation of magnetization without the need to apply a DC field making it the largest Fe/4f SMM. Furthermore, this system also represents the biggest molecular based toroidal arrangement reported so far, making it a multiferroic.[23,26] These types of systems are especially interesting to study, and given the increased length scale for the current Dy_3 triangle it should be possible to achieve further exotic spin states such as molecular based Skyrmions.[37]

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CCC, cyclic coordination cluster; SMM, single molecule magnet; SMT, single molecule toroic

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