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A nested spin structure and single molecule magnet behaviour in an $\text{Fe}_8\text{Dy}_{12}$ heterometallic cyclic coordination cluster†

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The 20-nuclearity compound $[\text{Fe}_8\text{Dy}_{12}(\text{tea})_8(\text{teaH})_{12}(\text{NO}_3)_{12}] \cdot 8\text{MeCN}$ (where teaH_3 = triethanolamine) was synthesised and characterised through single crystal X-ray diffraction and magnetic measurements. The shape of the magnetic hysteresis in the microSQUID measurements was rationalised using the MAGELLAN program.

Investigations on coordination clusters (CCs) based on either 3d or 4f ions have attracted great attention over the past decades because of their beautiful molecular architectures and interesting magnetic properties, such as single molecule magnet (SMM) behaviour,^{1–3} the magnetocaloric effect^{4–8} and spintronics.⁹ Particular attention has been paid to cyclic coordination clusters (CCCs), whose closed but infinite electronic structure could have applications in molecular electronics/spintronics and have, for example, been identified as qubits.¹⁰ Pioneering research has shown many examples of homometallic wheel-shaped clusters such as $\{\text{Mo}_{154}\}$,¹¹ $\{\text{Mn}_{84}\}$,¹² $\{\text{Ni}_{24}\}$,¹³ $\{\text{Dy}_{21}\}$ ¹⁴ and $\{\text{Gd}_{140}\}$.¹⁵ However, heterometallic cyclic clusters containing cooperatively coupled 3d and 4f ions have rarely been reported. Most of the examples, including $\{\text{M}_4\text{Ln}_4\}$ ($\text{M} = \text{Fe}^{\text{III}}$, Cr^{III} , Mn^{III}),^{16–19} $\{\text{Fe}_4\text{Ln}_2\}$,^{20,21} $\{\text{Fe}_5\text{Yb}_3\}$,²¹ $\{\text{Fe}_3\text{Yb}_2\}$,²¹ $\{\text{Fe}_{16}\text{Ln}_4\}$,²² $\{\text{Fe}_{10}\text{Ln}_{10}\}$ ^{21,23,24} and $\{\text{Fe}_{18}\text{Dy}_6\}$ ^{25,26} complexes, were reported by Powell and co-workers. Examples of other 3d–4f wheel motifs include

$\{\text{Mn}_8\text{Ln}_8\}$,²⁷ $\{\text{Cr}_8\text{Ln}_8\}$,²⁸ $\{\text{Cu}_{36}\text{Ln}_{24}\}$ ²⁹ and $\{\text{Co}_{16}\text{Ln}_{24}\}$ ³⁰ complexes reported by other groups. It is noted that the common features in the synthesis of these 3d–4f cyclic structures are the use of amine polyalcohol ligands such as triethanolamine and *N*-butyldiethanolamine, and small bridging co-ligands, like acetate, benzoate and α -amino acids.

Cyclic systems containing paramagnetic ions, in particular Dy^{III} , have the possibility to show toroidal moments which lead to non-magnetic states. Such a toroidal moment can have a spin structure which is either a cyclic arrangement of the spin in the metal ion plane or a solenoidal arrangement, both of which lead to non-magnetic states. For coordination systems the first molecule to be identified showing such an arrangement was a Dy_3 triangle.^{31–33} Since then many more molecular systems have been identified, as recently summarised in Murray's book *Single Molecule Toroids*.³⁴

The compound we report here has the same overall nuclearity as the $\text{Fe}_{10}\text{Ln}_{10}$ clusters we previously described. These exhibited quantum properties such as proximity to the quantum critical point, exciton formation and intermolecular charge hopping.^{21,23} By slightly modifying the synthetic procedure we obtained an $\text{Fe}_8\text{Dy}_{12}$ coordination cluster and report here the investigation of its magnetic properties.

The reaction of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with teaH_3 in MeOH and MeCN in the presence of Et_3N at ambient temperature yielded $[\text{Fe}_8\text{Dy}_{12}(\text{Htea})_8(\text{tea})_{12}(\text{NO}_3)_{12}] \cdot 8\text{MeCN}$ (**1**). Single-crystal X-ray diffraction studies reveal that compound (**1**) crystallises in the tetragonal space group $I4_1/acd$ (Fig. 1). The molecule is on a twofold axis in the crystal and thus the asymmetric unit is half the molecule (Fig. S1†).

Compound **1** is related to the previously reported $[\text{Fe}_{10}\text{Ln}_{10}(\text{Me-tea})_{10}(\text{Me-teaH})_{10}(\text{NO}_3)_{10}]$.^{21,23,24} The repeating units of both nanoscale compounds are extremely similar as both show Dy–Fe–Dy–Fe–Dy chains (Fig. 2), but rather than the Fe^{III} ion that follows, leading to alternating Fe–Dy in the $\{\text{Fe}_{10}\text{Dy}_{10}\}$ ring, these units are linked by an additional Dy^{III} ion in $\{\text{Fe}_8\text{Dy}_{12}\}$ (**1**). This also influences the topology of the cluster. While $\{\text{Fe}_{10}\text{Dy}_{10}\}$ can be described as a cyclic standing

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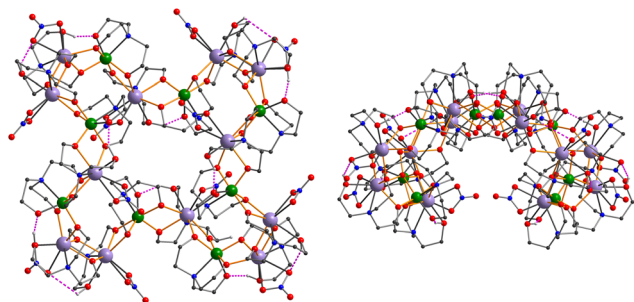


Fig. 1 Two views of the molecular structure of $\text{Fe}_8\text{Dy}_{12}$ (**1**).

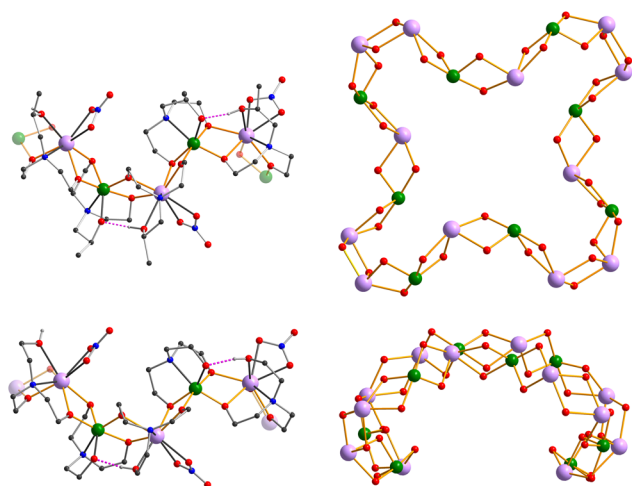


Fig. 2 Comparison of the repeating units of $\text{Fe}_{10}\text{Dy}_{10}$ (top, left) and $\text{Fe}_8\text{Dy}_{12}$ (**1**) (bottom, left) with the difference in the continuation of the chain having paler coloured Fe/Dy ions as appropriate. Two views of the saddle-like core structure of **1** (right).

wave, the presence of additional Dy^{III} ions leads to the cluster folding into a saddle shape (Fig. 2). Within **1**, the Fe^{III} ion is chelated by the nitrogen and three oxygen atoms of a fully deprotonated tea^{3-} ligand and the Dy^{III} ions by a doubly deprotonated teaH^{2-} ligand with one alcohol arm remaining protonated. The two deprotonated alcohol arms of each ligand form μ -alkoxo bridges to adjacent metal centres in the ring.

The static magnetic susceptibilities of compound **1** were collected over the temperature range 1.8–300 K under an applied magnetic field of 0.1 T. Magnetisation data were collected at fields of 0–7 T at temperatures of 2, 3 and 5 K. The χT value of **1** is $204.7 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K, close to the expected value of $205.1 \text{ cm}^3 \text{ K mol}^{-1}$ for eight uncoupled Fe^{III} and twelve Dy^{III} ions (Fig. 2). Upon cooling, the χT value stays nearly constant before increasing sharply below 30 K reaching a maximum value of $246.9 \text{ cm}^3 \text{ K mol}^{-1}$ at 4.3 K. This is followed by an abrupt decrease at lower temperature to $200.6 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. The increase of the χT value suggests ferromagnetic coupling between Fe^{III} and Dy^{III} ions, while the subsequent decrease is likely due to the presence of magnetic anisotropy and/or intermolecular weak antiferromagnetic interactions. The presence of dominant ferro-

magnetic intramolecular interactions is supported by the temperature dependence of the reciprocal susceptibility ($1/\chi$) over the whole temperature range following the Curie–Weiss law ($\chi = C/(T - \theta)$) with a Weiss constant $\theta = +0.54 \text{ K}$ and Curie Constant $C = 203 \text{ cm}^3 \text{ K mol}^{-1}$ (Fig. 3, top). The field-dependent magnetisation measurements for **1** (Fig. 3, bottom) increase sharply at low fields and reach $95.80 \mu_B$ at 7 T without reaching saturation, suggesting the presence of significant magnetic anisotropy.

To probe the magnetic anisotropy, ac susceptibility measurements were carried out under zero dc field for compound **1**. Out-of-phase signals were detected below 5 K (Fig. S3†) indicative of the slow relaxation of the magnetisation behaviour characteristic of potential SMMs. Under a small external dc field, the magnetic slow relaxation was still too fast for maxima to be observed (Fig. S4†) within the parameters of our SQUID.

MicroSQUID measurements were performed at different temperatures and scan rates (Fig. 4 and S5†). In order to investigate the energy barrier and relaxation time, dc magnetisation decay measurements were performed under zero applied field in the sub-kelvin temperature range (Fig. S5†). The relaxation times were fitted using the following equation:

$$\tau^{-1} = AT + B + CT^n + \tau_0^{-1} \exp(-U_{\text{eff}}/k_B T)$$

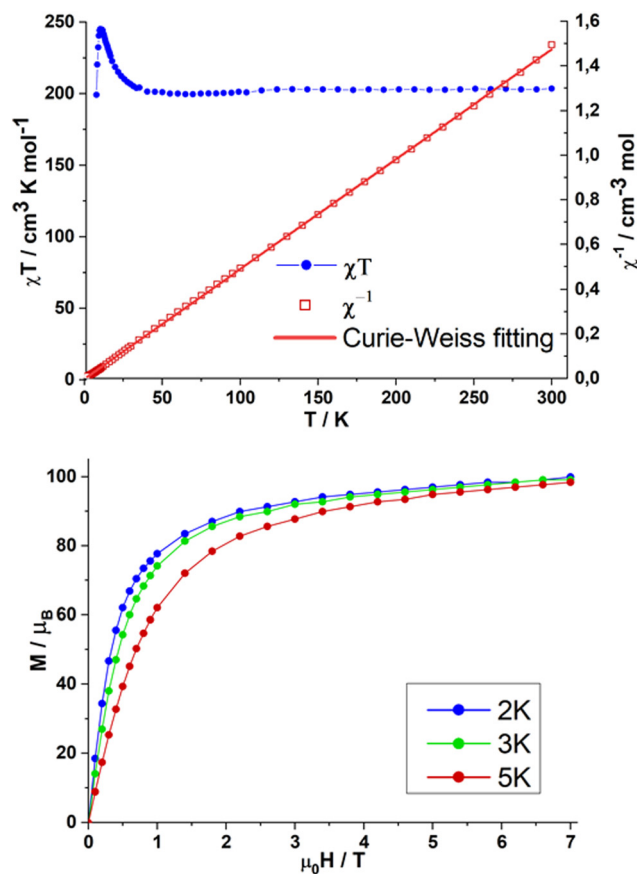


Fig. 3 Magnetic dc (top) and magnetisation data (bottom) for $\text{Fe}_8\text{Dy}_{12}$ (**1**).

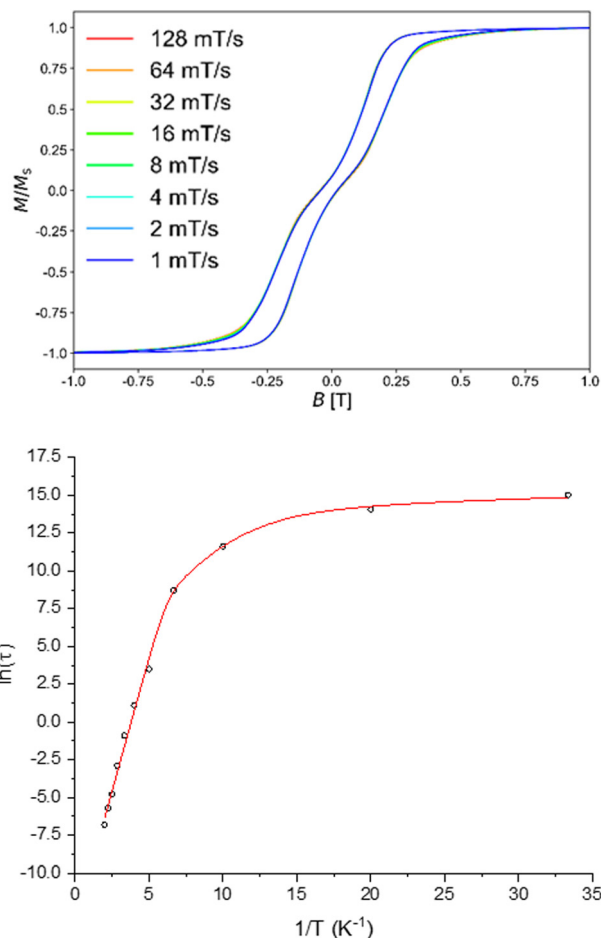


Fig. 4 MicroSQUID measurement of the sweep rate dependence of the magnetisation at $T = 30$ mK (top). Plot of relaxation time (τ) against T^{-1} for complex (**1**) using dc magnetisation decay data (bottom). The red line is a fit of the relaxation data to the equation described above.

where A describes the direct process, B describes the zero field quantum tunnelling (ZFQTM), C is the Raman process with the Raman exponent n , τ_0 is the preexponential factor and U_{eff} is the energy barrier related to the Orbach process. The relaxation times of **1** could be fitted without the need for the parameter B , thus excluding the presence of ZFQTM which is also clear from the absence of a vertical increase at 0 T in the microSQUID hysteresis loops. The parameters for the best fit are $A = 1.18 \times 10^{-5} \text{ s}^{-1} \text{ K}^{-1}$, $B = 0$, $C = 90.4 \text{ s}^{-1} \text{ K}^{-n}$, $n = 7.05$, $\tau_0 = 1.49 \times 10^{-6} \text{ s}$ and the extracted energy barrier U_{eff} is 3.54 K.

In order to understand the hysteresis behaviour seen in the microSQUID measurement we performed the electrostatic field-based MAGELLAN³⁵ analysis to locate the Ising easy-axes of the Dy^{III} ions. Although this program was designed for purely Dy^{III} containing molecules, nevertheless we have found that coordination clusters containing Fe^{III} and Dy^{III} can be safely analysed. Furthermore, a cluster of this size cannot be calculated using *ab initio* methods; therefore MAGELLAN provides the only opportunity to help rationalise the magnetic behaviour. Whereas in the Fe₁₀Dy₁₀ cluster the axes are

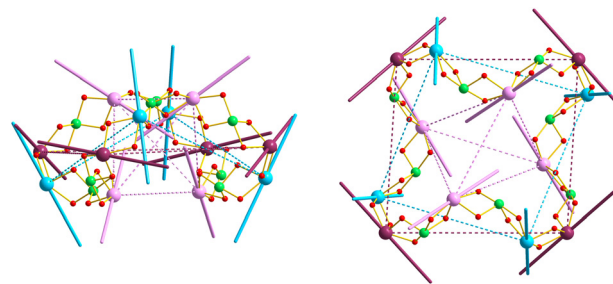


Fig. 5 Two views of the core structure of compound (**1**) showing the three sets of MAGELLAN axes. The pink set represents the spin-ice-like structure, the burgundy set represents the toroidal "square" and the cyan set represents the boat-like shape.

arranged in a regular arrangement (see Fig. S6†), the saddle-shape of **1** leads to an apparent jumble of directions (see Fig. 5). However, a closer analysis reveals that in fact the twelve Dy^{III} ions can be divided into three sets of four ions (see Fig. 5). The innermost set of four corresponds to a slightly distorted tetrahedron with its MAGELLAN axes oriented in a spin-ice-like arrangement (pink in Fig. 5).^{36,37} The middle set of axes form what can be described as a toroidal arrangement around a slightly distorted square as seen for Dy₄.³⁸ The "square" is neither completely planar nor completely square, but with angles of 86.3° and 93.7° as well as distances of 12.8 Å and 13.3 Å, and the deviation from planarity for each of the Dy^{III} ions of 0.32 Å is not far off (burgundy in Fig. 5). The outer set is arranged in a boat-like shape. Two of the axes are parallel and essentially perpendicular to the plane of the "square" of the middle layer. The other two are at an angle of 30.1° to the perpendicular ones (cyan in Fig. 5).

These arrangements may lead to the following characteristics of the microSQUID hysteresis curve. The easiest part to assess is the toroidal nature of the middle set which leads to a narrowing and a change in gradient near 0 T. The alignment of the outer set is likely responsible for the sharp increase in magnetisation at fields higher than 0.1 T. The inner spin-ice-like set remains a "dark horse" in the sense that its contribution to the magnetic hysteresis behaviour is impossible to judge but it might possibly be non-magnetic.

In conclusion, disrupting the alternating pattern of the ions in the Fe₁₀Ln₁₀ ring system through slightly altered reaction conditions leads to a folding of the ring into a saddle shape. This in turn alters the orientations of the MAGELLAN axes. These axes help rationalise the magnetic hysteresis observed in the microSQUID measurements.

Author contributions

Y.P. and Y.F.S.: synthesis and characterisation; J.B., H.K., C.E.A. and A.K.P.: paper conceptualisation and writing; C.E.A.: crystallography; M.S. and W.W.: microSQUID measurement and interpretation; and A.K.P.: supervision and funding acquisition.



Conflicts of interest

There are no conflicts to declare.

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