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EDGE ARTICLE

Symmetry related [$Dy^{III}_6Mn^{III}_{12}$] cores with different magnetic anisotropies†

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Two heterometallic [$Dy^{III}_6Mn^{III}_{12}$] clusters comprising of the same [$Mn^{III}_8O_{13}$] fragment, four isolated Mn^{III} ions and two linear [Dy^{III}_3] units have been synthesised. Except for the same composition, the main difference of these two cores lies in the coordination environment and the orientations of the linear [Dy^{III}_3] units. This difference leads to an alternation in the symmetry of the two cores that significantly modulates their magnetic properties including ground spin state and slow relaxation behavior.

Since the first [Mn_{12}] cluster that exhibits slow relaxation of the magnetization was discovered in the 1990's,[1–4] considerable effort has been focused on exploring single-molecule magnets (SMMs).[5,6] These unique complexes require both a high spin ground-state (S_T) and an appreciable uniaxial magnetic anisotropy ($D < 0$), leading to an energy barrier between the bistable states that slows down magnetization reversal.[4,7,8] Although numerous SMMs have been reported, finding an SMM with both high ground spin-state and large magnetic anisotropy is still a challenge for synthetic chemists.

The importance of both factors for an SMM can be well illustrated by the example of the [Mn_{19}] complex,[9] which holds a record ground spin state of $S = {}^{83}/_2$, but fails to be an SMM because of the nearly absent magnetic anisotropy.[10,11] By deliberately replacing the central eight-coordinate Mn^{II} ion with the highly anisotropic Dy^{III} ion, slow relaxation of the magnetization was observed.[12] Another example of the significance of the magnetic anisotropy on the energy barrier of the SMMs is the large-spin ($S = 37$) molecule with an energy barrier of only 13 K due to the very small magnetic anisotropy.[13]

Inspired by the large magnetic anisotropy of the heavier lanthanides, great synthetic efforts have been devoted to, not only the pure 4*f*,[14–17] but also 3*d*–4*f*[12,18–23] clusters in recent years. Although the magnetic interactions between the contracted 4*f* electrons are usually weak, the recently reported linear [Dy^{III}_3] and [Tb^{III}_3] complexes showed promising ferromagnetic coupling (up to $J = +7.5$ K) and thus, a high ground spin state.[15] Besides the ground state the control of the magnetic anisotropy is also very important as can be seen in a triangular [Dy^{III}_3] molecule with non-collinearity of the principle axes.[16f,16g] However, the intrinsic correlation between the spin-state and the magnetic anisotropy in these systems haven't been completely elucidated, which requires further exploration.

Herein we demonstrated two 3*d*–4*f* complexes by employing an extended *in situ* synthetic route we have isolated three new 3*d*–4*f* clusters (structures shown in Fig. 1), [$Dy_6Mn_{12}O_7(OH)_{10}(OAc)_{14}(mpea)_8$]·$20H_2O$·4MeOH (**1**) and [$Ln_6Mn_{12}O_9(OH)_8(OAc)_{10}(mpea)_8(mp)_2(MeOH)_2(H_2O)_2$]·solv (**2**. While Ln = Dy, solv = $26H_2O$·2MeOH **2-Dy**; Ln = Y, solv = $15H_2O$·4MeOH **2-Y**), where Hmp = 2-hydroxy-5-methyl-isophthalaldehyde and H_2mpea = 2-hydroxy-3-((2-hydroxyethylimino)methyl)-5-methylbenzaldehyde), with symmetry related [$Ln^{III}_6Mn^{III}_{12}$] cores. Interestingly, the two complexes **1-Dy** and **2-Dy** show different ground-state spins and slow magnetization behaviors, which may be influenced by the different symmetries of their cores (*vide infra*).

After the Schiff-base was synthesized *in situ*, it was added to $LnCl_3·6H_2O$, $Mn(OAc)_2·4H_2O$, and triethylamine in different solvents. Complex **1** crystallizes in the orthorhombic space group *Fddd* while **2** is of lower symmetry and crystallizes in the triclinic $P\bar{1}$ space group (see ESI†). As can be seen in Fig. 1, though isomeric, the [$Ln^{III}_6Mn^{III}_{12}$] cores possess D_2 site symmetry in **1** and C_1 symmetry in **2**. All of the Mn and Ln ions in both

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† Electronic supplementary information (ESI) available: The ESI contains experimental details of the synthesis of **1-Dy**, **2-Dy** and **2-Y** together with their X-ray structure determinations, magnetic susceptibility and ab initio calculations of the local magnetic properties on Dy sites in **1-Dy** and **2-Dy**. CCDC 779464 (**1-Dy**), 779465 (**2-Dy**), and 795483 (**2-Y**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1sc00166c

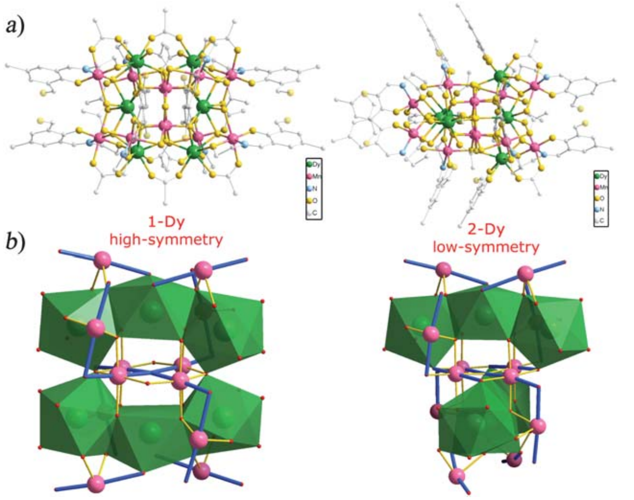

Fig. 1 a) Molecule structures of **1-Dy** (*left*) and **2-Dy** (*right*). b) The cluster cores of **1-Dy** (*left*) and **2-Dy** (*right*). Each Ln^{III} is highlighted as a green polyhedron and the Jahn–Teller axes of Mn^{III} ions are highlighted as blue sticks. Hydrogen atoms and lattice solvent molecules have been omitted for clarity.

compounds are trivalent, which are confirmed by bond-valence-sum (BVS) calculations (Table S1†),[24] charge considerations, and the observation of Jahn–Teller distortion around the Mn^{III} centers.

The cores can be described as being composed of five parts; ABCBA for **1** and AB′CB″A for **2** (Figures S1 and S2†). Two isolated Mn^{III} ions capping a linear $[Ln^{III}_3]$ trimer form fragment AB, while fragment C comprises a $[Mn^{III}_8O_{13}]$ unit that contains a twisted $[Mn^{III}_4O_5]$ tetragon that is capped by four Mn^{III} ions alternating above and below the tetragon with oxo-bridges. It should be mentioned that the central oxygen atom of $[Mn^{III}_4O_5]$ acts as μ_4-oxo bridge binding the $[Mn^{III}_4]$ unit in **1** and a μ_5-oxo bridge binding $[Mn^{III}_4]$ and the central Ln^{III} ion of a $[Ln^{III}_3]$ trimer in **2**. The main symmetry differences between the two cores arise from the orientation of the $[Ln^{III}_3]$ units which leads to differing orientations of the Jahn–Teller axes in the central twisted $[Mn^{III}_4O_5]$ tetragon in **1** and **2**.

The coordination environments and orientations of the two linear $[Ln^{III}_3]$ units of **1** and **2** differ significantly. The coordination sphere of each Ln^{III} ion comprises only O atoms, presenting various types of coordination environments: (i) For **1**, the central Ln^{III} of fragment B, $[Ln^{III}_3O_6]$, is 8-coordinate, whereas both end-positions are 9-coordinate. The Ln^{III} polyhedra are all face-sharing within fragment B while the end polyhedra are vertex-sharing with the second B fragment in **1**; (ii) For **2**, the Ln^{III} ions in fragment B′, $[Ln^{III}_3O_4]$, are all 8-coordinate edge-sharing polyhedra whereas fragment B″, $[Ln^{III}_3O_6]$, comprises three face-sharing 9-coordinate Ln^{III} polyhedra. In other words, two identical $[Ln^{III}_3O_6]$ trimers link together with oxo-bridges to form a $[Ln^{III}_6O_{14}]$ unit as a twisted hexagon in **1**, while differing $[Ln^{III}_3O_4]$ and $[Ln^{III}_3O_6]$ timers remain magnetically separated from one another in **2**. It is worth mentioning that the two $[Ln^{III}_3]$ units are nearly parallel (~11°) and perpendicular (~83°) to one another in **1** and **2**, respectively.

Dc magnetic susceptibility data were collected in the temperature range 1.8–300 K at 500 Oe (Fig. 2). At 300 K, the $\chi_M T$ values are 123.6 and 120.3 cm^3 K mol^{-1} for **1-Dy** and **2-Dy**, respectively, which are close to the expected value of 121.0 cm^3 K mol^{-1} for an uncoupled $[Dy^{III}_6Mn^{III}_{12}]$ core (Dy^{III}: $S = {}^5/_2$, $L = 5$, ${}^6H_{15/2}$, $g = {}^4/_3$; Mn^{III}: $S = 2$, $g = 2$).[18,25] Upon lowering the temperature, the $\chi_M T$ value of **1-Dy** remains roughly constant and then sharply increases to a maximum value of 409.5 cm^3 K mol^{-1} at 3.5 K, suggesting a high-spin ground state. The $\chi_M T$ value of **2-Dy** first slightly decreases to 107.0 cm^3 K mol^{-1} at 23 K, then increases to a maximum of 117.9 cm^3 K mol^{-1} at 5 K and then lowers again sharply to 100.88 cm^3 K mol^{-1} at 2 K, which is likely attributed to competition between ferromagnetic and antiferromagnetic coupling and/or crystal field effects of Dy^{III}.[14a,26,27]

Ac susceptibility measurements were carried out in a 5 Oe ac field oscillating at 1–1488 Hz, and with a zero dc field (Fig. 4, S3, S4†) in order to investigate the presence of SMM-like behavior.

An intriguing question is why the magnetic behaviour of **1-Dy** and **2-Dy** is so different (Fig. 2) despite common structural blocks. In order to further investigate the interactions of the spin carriers in **2**, Y^{III} without spins are the candidate ions to replace the Dy^{III} ions, so we make a try to have a look at **2-Y**. The decay of $\chi_M T$ data suggests the presence of an antiferromagnetic interaction between Mn···Mn. We can subtract the plot **2-Y** from

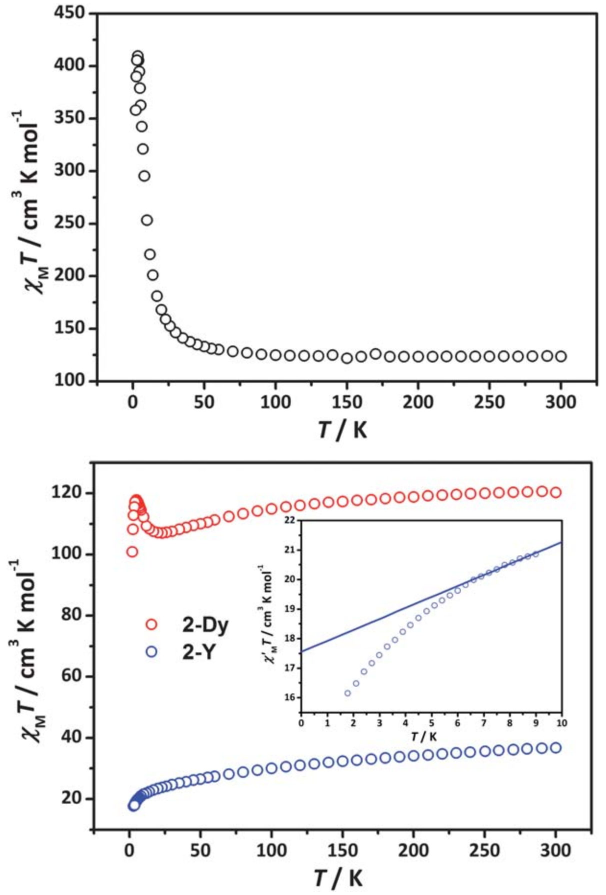

Fig. 2 Temperature dependence of the $\chi_M T$ products at 500 Oe for **1-Dy** (*up*), **2-Dy** (*bottom*, *red*) and **2-Y** (*bottom*, *blue*). Inset: The low-frequency $\chi_M' T$ data were extrapolated to 0 K for **2-Y**.

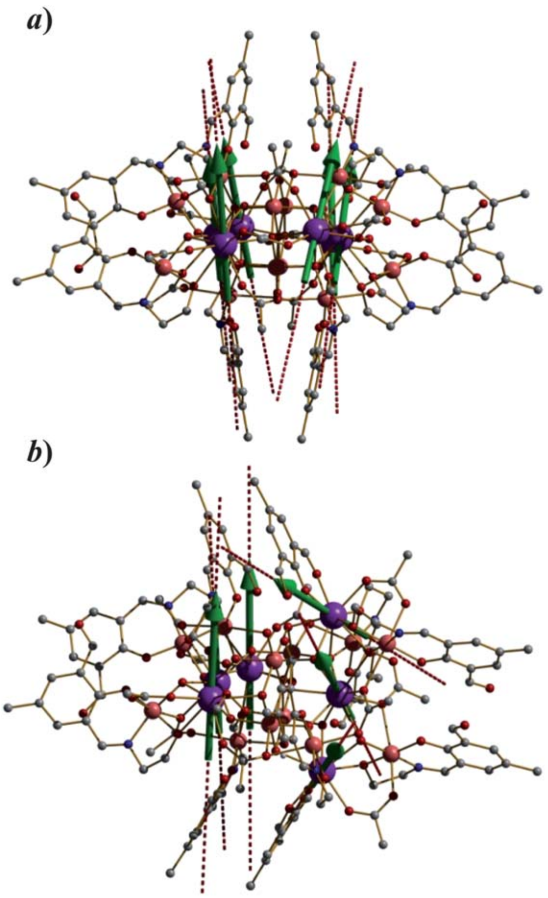

Fig. 3 Local magnetic moments in the ground state on Dy ions of a) **1-Dy**; b) **2-Dy**. Dashed lines represent the local anisotropy axes, while the arrows show the orientation of the local magnetization.

the plot **2-Dy** (Figure S6†) to investigate the interactions between Ln···Ln and Ln···Mn. The resulting $\Delta\chi_M T$ values increase on low temperature, confirming the ferromagnetic interactions between Ln···Ln and/or Ln···Mn in **2-Dy**. Going to the low-frequency (1 Hz) $\chi_M'T$ data extrapolated to 0 K for **2-Y** (Fig. 2), the values of 17.7 cm^3 K mol^{-1} corresponds to an $S = 3$ [$Mn^{III}_8O_{13}$] unit (fragment C) and four uncoupled Mn^{III} ($S = 2$) ions as fragment A and C are magnetically separated by two [Y^{III}_3] units. Indeed, the $S = 3$ for the fragment [$Mn^{III}_8O_{13}$] in **2-Y** is also apparently supported by the field-dependent magnetization measurement (Figure S5†), approaching a value of 22 μ_B at 7 T for **2-Y**, which would be true in the case of four isotropic marginal Mn^{III} ($S = 2$) and an isotropic $S = 3$ for the central [$Mn^{III}_8O_{13}$].

However, the *ab initio* calculations of the four Mn^{III} fragments (see ESI† for details) reveal a zero-field splitting of the ground $S = 2$ of *ca.* 12 cm^{-1}. This relatively strong ionic anisotropy will induce the zero-field splitting of the ground term. Despite a much lower value of the supposed ground state spin ($S = 3$) compared to the maximal possible ($S = 16$) in this unit, the zero-field splitting of both these manifolds is expected to be of similar extent, as it was also the case in Mn$_{12}$ acetate complex.[28] Given their structural similarity, it is reasonable to suppose that the amplitude of zero-field splitting of the ground spin ($S = 3$) should be comparable to the latter compound, *i.e.* it cannot be ignored. As a result, the total molar magnetization at low temperature will be much lower than in the case of an isotropic spin. In conclusion, the total spin of the central fragment [$Mn^{III}_8O_{13}$] in **2-Y** *should be larger* than 3 but still lower than 8, in order to keep an overall antiferromagnetic coupling seen in susceptibility measurements.

This conclusion is also confirmed by the molar magnetization of **2-Dy** which approaches 57 μ_B at fields of 7 T, a value higher than 52 μ_B corresponding to four isotropic Mn^{III} ions ($4 \times 4 = 16$ μ_B), six Ising Dy(III) ions ($6 \times 5 = 30$ μ_B) and an isotropic $S = 3$ (6 μ_B) of the central [$Mn^{III}_8O_{13}$] core. The difference is even larger if one takes into account the lowering of the magnetization due to zero-field splitting on marginal Mn^{III} ions and of the spin of the central [$Mn^{III}_8O_{13}$] core.

For the complex **1-Dy**, the difference between the measured magnetization (71 μ_B) and the predicted one in the case of four Mn^{III} ($4 \times 4 = 16$ μ_B), six Dy ions ($6 \times 5 = 30$ μ_B) leads to a value of 25 μ_B, which clearly can only be expected in the case of predominantly ferromagnetic coupling ($S > 8$ total spin) of the [$Mn^{III}_8O_{13}$] core. This difference is, again, larger if one takes into account the lowering of the total magnetization due to the zero-field splitting, as discussed above.

The difference in the magnetic behavior between complexes **1-Dy** and **2-Dy** is therefore due to several factors: 1) the value of the spin of the [$Mn^{III}_8O_{13}$] central core is larger in **1-Dy** compared to **2-Dy**; 2) the orientations of the main anisotropy axes on Dy ions are different due to the structural arrangements of the [Dy^{III}_3] triades (see Tables S5 and S9†); 3) the exchange coupling between the [Dy^{III}_3] triades and the spin of the central [$Mn^{III}_8O_{13}$] core is ferromagnetic in **1-Dy** and antiferromagnetic in **2-Dy**. Note that whatever the sign of the exchange interaction between [Dy^{III}_3] triades and the central core, the arrangements of the total magnetic moments within each of [Dy^{III}_3] triades is ferromagnetic in both complexes.

The *ab initio* calculated[29] main anisotropy axes of the ground Kramers doublets on Dy sites in **1-Dy** and **2-Dy** are shown in Fig. 3 (see ESI† for computational details, energies local *g* tensors of the ground Kramers doublets on Dy sites and relative angles between main anisotropy axes in **1-Dy** and **2-Dy**).

Frequency-dependent out-of-phase (χ_M'') signals in the ac susceptibility show that both complexes behave as SMMs but exhibit different slow relaxation of magnetization. For **1-Dy**, one peak is observable at 3.7 K for 1488 Hz, while at 2.0 K for **2-Dy** for 1488 Hz. A higher spin and the more colinear local anisotropy axes of **1-Dy** are likely to enhance the blocking temperature (T_B) in contrast to **2-Dy**. The ac susceptibilities, along with Cole-Cole plots showing quasi-semicircles and fitting Debye functions[30] for **1-Dy** and **2-Dy** (Figure S7, α_1 = 0.30–0.36, α_2 = 0.48–0.51†), indicate the presence of different distribution processes of slow relaxation. According to $\varphi = (\Delta T_p/T_p)/\Delta(\log f)$, the value of φ is, respectively, 0.14 for **1-Dy** and 0.23 for **2-Dy** (Figure S8†), suggesting a superparamagnetic-like behavior rather than spin glass behavior.[31] Hence, the effective energy barriers (and characteristic relaxation time) can be obtained by fitting to the Arrhenius law giving $\Delta_{eff}/k_B = 35.1(5)$ K ($\tau_0 = 1.00 \times 10^{-8}$ s) for **1-Dy** and $\Delta_{eff}/k_B = 18.2(5)$ K ($\tau_0 = 3.02 \times 10^{-8}$ s) for **2-Dy**, respectively (insets of Fig. 4).

However, no out-of-phase signals were observed under the resolution limit of the susceptometer above 1.8 K for **2-Y**

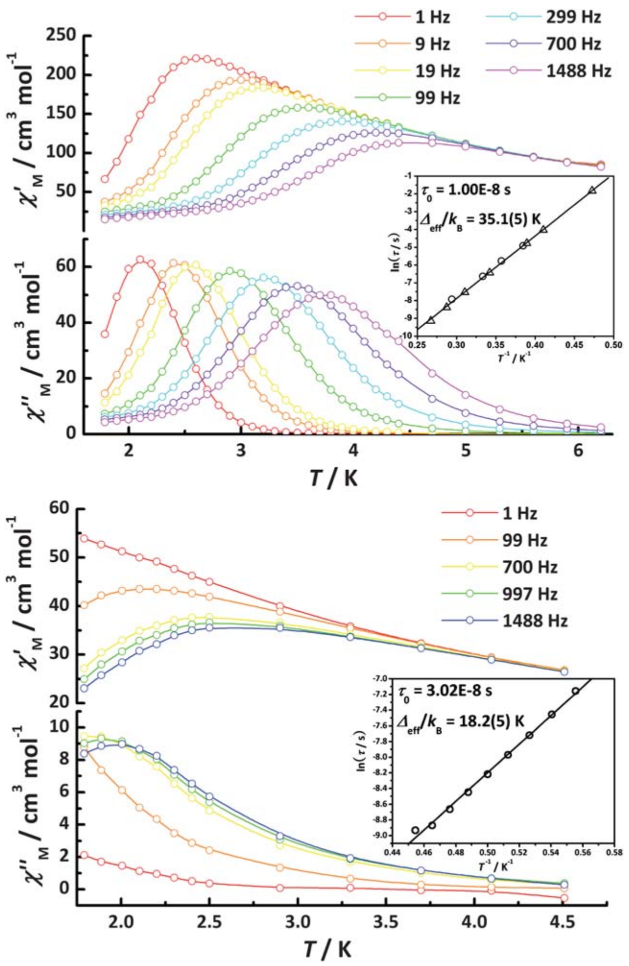

Fig. 4 Plots of ac susceptibility *vs.* temperature for **1-Dy** (*left*) and **2-Dy** (*right*) oscillating at 1–1488 Hz at $H_{ac} = 5$ G and $H_{dc} = 0$. Inset: The ln(τ) *versus* T^{-1} plots obtained from $\chi_M''(T)$ (△) and $\chi_M''(\nu)$ (○); The solid lines correspond to the Arrhenius law for **1-Dy** (*left*) and **2-Dy** (*right*).

(Figure S4†). In terms of ac susceptibility, strong frequency-dependent signals were observed for **2-Dy** while absent for **2-Y**. We inferred it mainly originate from the [Dy$^{III}_3$] units. It is clear that introducing the highly anisotropic lanthanide ions into [Ln$^{III}_6$Mn$^{III}_{12}$] do play an important role, making it towards SMM.

In summary, we have generated two giant 3*d*–4*f* clusters with symmetry related [Dy$^{III}_6$Mn$^{III}_{12}$] cores which possess different molecular symmetry, resulting in different magnetic behaviors and energy barriers. For the high-symmetry one, the existing Dy^{III} ions do not only introduce large anisotropy but also enhances the ground-state simultaneously in this system. For the low-symmetry one, we successfully replace the anisotropic Dy^{III} with diamagnetic Y^{III}, confirming the ferromagnetic interaction of Dy⋯Dy and/or Dy⋯Mn and demonstrating the anisotropic lanthanide ions make it toward an SMM.

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