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Lanthanide discs chill well and relax slowly†

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The synthesis, structure and magnetic properties of two isostructural heptametallic lanthanide discs are reported, showing single molecule magnet (SMM) behaviour with a large energy barrier for the dysprosium analogue and a large magnetocaloric effect (MCE) for the gadolinium analogue.

Transition metal clusters are being intensively studied because of their fascinating magnetic properties, including as molecular magnetic coolers^{1,2} or SMMs.³ There has been a recent increase in interest in lanthanides in these areas, in particular with dysprosium-based SMMs⁴ and gadolinium-containing mixed d–f species as magnetic coolers.^{2,5} This exploits the large spins of Ln^{3+} , and the choice of isotropic [e.g. Gd^{3+} , favouring a large MCE] or anisotropic (e.g. Dy^{3+} , favouring a large energy barrier to relaxation) magnetic behaviour. The similarity in size of Dy^{3+} and Gd^{3+} ions should make it possible to isolate isostructural species showing one or other of these properties; however, examples of this are rare.⁶ Here, we report isostructural heptametallic clusters with disc-like structures. When $\text{Ln} = \text{Gd}$ a large MCE is found, when $\text{Ln} = \text{Dy}$ the molecule is a SMM.

Solvothermal⁷ reactions of $\text{Ln}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.1 g, 0.22 mmol) with the tripodal alcohol thmeH_3 [tris(hydroxymethyl)ethane, Fig. S1†; 0.11 mmol], triphenylacetic acid (tpaH ; 0.11 mmol) and NEt_3 (0.165 mmol) in MeCN (8 mL) at 100 °C give colourless crystals of **1** or **2** ($\text{Ln} = \text{Dy}$ or Gd , respectively; ca. 50%).† Single crystal X-ray diffraction shows these to be $[\text{Ln}_7(\text{OH})_6(\text{thmeH}_2)_5(\text{thmeH})(\text{tpa})_6(\text{MeCN})_2](\text{NO}_3)_2$ (Fig. 1). The clusters have centred-hexagonal Ln_7 cores (Fig. S2†). This topology has been seen for 3d metals including Ni, Fe, Cu, Co and Mn,⁸ but not for Ln (although “empty” Ln_6 rings are known).⁹ The molecule lies on a crystallographic inversion centre; the central Ln^{3+} ion lies just out of the Ln_6 plane (and hence is disordered over two sites).

The peripheral and central Ln ions are bound by six μ_3 -OH groups, alternating above and below the Ln_7 plane. Each edge of the Ln_6 hexagon is bridged by a triphenylacetate and a $(\text{thmeH}_2)^-$ ligand. The latter are singly deprotonated, the alkoxide arm μ_2 -bridging while the protonated arms each bind terminally to

Fig. 1 Structure of $[\text{Gd}_7(\text{OH})_6(\text{thmeH}_2)_5(\text{thmeH})(\text{tpa})_6(\text{MeCN})_2]^{2+}$ (**2**). Scheme: Gd (purple), O (yellow), N (blue), C (skeletal), H not shown.

one of the Ln ions. Charge balance requires that only one ligand must lose an additional proton, but this must be disordered. Although thmeH_3 has been used extensively in 3d metal cluster chemistry,¹⁰ to the best of our knowledge this is the first example of a homometallic 4f cluster incorporating this ligand. The central Ln ion has two terminal MeCN groups, making all metal ions eight co-ordinate. The coordination geometry at the central ion approximates closely to 3-fold symmetric (Fig. S3†). The cluster is a dication, with nitrates providing the charge balance.

We start with the magnetic properties of **2** containing the spin-only Gd^{3+} ion. At room temperature $\chi_{\text{M}}T$ (χ_{M} is the molar magnetic susceptibility) is $54.3 \text{ cm}^3 \text{ K mol}^{-1}$ (Fig. 2), in agreement with the value for seven uncoupled $s = 7/2$ ions with $g = 2.0$. On cooling, $\chi_{\text{M}}T$ decreases slowly until ca. 30 K where it decreases more rapidly. We have not attempted to model the data given the 8⁷-dimensional spin system, but it is only consistent with weak antiferromagnetic coupling between the Gd^{3+} ions. The low temperature molar magnetisation (M) saturates at $49 \mu_{\text{B}}$ above ca. 6 T (Fig. S4†). Note that this does not indicate an $S = 49/2$ ground state, simply that this state becomes the ground state in these applied fields. The centred-hexagonal topology, consisting of six edge-sharing triangles is highly frustrated and this, combined with the weak antiferromagnetic nature of the coupling, will give

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Fig. 2 $\chi_M T(T)$ (■) and $\chi_M(T)$ (○) for **2** at $H = 500$ G.

Fig. 3 Calculated $-\Delta S_m(T)$ for **2** at various fields (10–70 kG).

rise to many low-lying states that are populated even at base temperature. The maximum spin state ($S = 49/2$) will then become the ground state in relatively small applied magnetic fields. This situation is promising for a large low-temperature MCE because the possible magnetic entropy change on magnetisation is enhanced by the multiple low-lying states that are thermally accessible in zero-field (large entropy) while the magnetisation can still be saturated (nil entropy) in applied field.^{1,5a}

We have calculated the magnetic entropy change $-\Delta S_m$ for various field changes and temperatures from the $M(H, T)$ data (Fig. 3). The maximum change, at 3 K and for a field change of 0–7 T, is $23 \text{ J kg}^{-1} \text{ K}^{-1}$. This compares against 26 and $31 \text{ J kg}^{-1} \text{ K}^{-1}$, the largest values reported to date, for Ni_6Gd_6 ($\Delta H = 7 \text{ T}$ at 3 K) and Cu_5Gd_4 ($\Delta H = 9 \text{ T}$ at 3 K) clusters.² This $-\Delta S_m$ value, equivalent to 10.6 R where R is the gas constant, is much larger than that expected for an $S = 49/2$ paramagnet (3.9 R), showing the massive enhancement due to the high density of low-lying states in low fields, a result of the weak coupling and spin frustration. The maximum possible value for seven Gd^{3+} ions is 14.6 R.

However, a disadvantage of the antiferromagnetic nature of the coupling is shown by comparison of the experimental low temperature $M(H)$ curves against the calculated Brillouin curves for seven uncoupled $s = 7/2$ ions (Fig. S4†). The antiferromagnetic coupling leads to slower magnetisation as a function of applied field *cf.* uncoupled ions. This would translate as a slower cooling rate. The conclusion is that a weakly ferromagnetically

Fig. 4 $\chi_M T(T)$ of **1** in 500 G applied magnetic field. Inset: $\chi_M(T)$.

coupled system would be ideal for magnetic cooling, coupling the advantages of low-lying excited states with ease of magnetisation. A recent example is Murray's Cu_5Gd_4 cluster.^{2b}

For the isostructural Dy_7 analogue **1**, $\chi_M T$ is $98.0 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature (Fig. 4), in good agreement with the calculated value of $99.2 \text{ cm}^3 \text{ K mol}^{-1}$ for seven uncoupled Dy^{III} ions ($^6\text{H}_{15/2}$ ground term, $g = 4/3$). $\chi_M T$ decreases gradually on cooling, then more rapidly below 30 K. This indicates either weak antiferromagnetic interactions and/or depopulation of the Dy^{3+} excited Stark sub-levels.¹¹ $\chi_M(T)$ displays a maximum at 2.9 K (Fig. 4, inset) which shifts to lower temperatures for applied fields $> 3 \text{ kG}$. $M(H)$ approaches saturation at *ca.* $36 \mu_B$ at low temperature (Fig. S5†). Reduced magnetisation curves do not superimpose, suggesting the presence of significant magnetic anisotropy and/or low-lying excited states.

The magnetization dynamics were investigated by alternating current (*ac*) susceptibility measurements as a function of temperature (2–25 K) and frequency ($\nu = 0.1$ –1400 Hz), in zero dc field (Fig. 5 and S6†). Both the in-phase (χ_M') and out-of-phase (χ_M'') components of the susceptibility show frequency dependence below *ca.* 28 K; maxima are observed in $\chi_M''(T)$. These observations are characteristic of SMM behaviour.

Although at lower frequencies only a single peak is observed in $\chi_M''(T)$ (e.g. at 3 K for 1 Hz; Fig. 5), multiple peaks are observed at higher frequencies (at 2.9 and 14.1 K, with a shoulder at 24 K, for $\nu = 1.2 \text{ kHz}$) indicating multiple relaxation processes. This is likely due to the presence of two types of Dy^{3+} ion, the central ion and peripheral sites, because their anisotropy axes are not expected to be collinear.^{12,13} Relaxation time constant (τ) data, evaluated from $\chi_M''(T, \nu)$, are linear with $1/T$ above 10.5 K (Fig. 5): fitting to an Arrhenius law gives a thermal energy barrier to magnetisation relaxation $U_{\text{eff}} = 140 \text{ K}$ with $\tau_0 = 7.2 \times 10^{-9} \text{ s}$. This is among the highest observed for a cluster SMM, exceeded only by two Dy_4 (U_{eff} *ca.* 170 K),¹² a Dy_6 (200 K),¹³ and the recent observation of 530 K in a Dy_5 cluster.¹⁴ Higher barriers have been reported for high symmetry monometallic Tb^{3+} complexes.¹⁵

Below 10 K, τ tends to saturate, suggesting a quantum tunneling relaxation pathway. This is supported by field-dependence studies at 1.8 K, which show a minimum in τ in zero applied field, and is also consistent with the lack of hysteresis in $M(H)$ at 1.8 K (Fig. S7†). The latter has an inflection point at 4.3 kG, presumably indicating a level crossing. The onset of quantum behaviour is also reflected in Cole-Cole

Fig. 5 Temperature dependence of: (top) χ_M' and (bottom) χ_M'' for **1**, measured in 1.55 G ac field and zero dc field. Inset: $\tau(T^{-1})$ for **1**, under zero dc field, based on data collected in frequency (■) and temperature (○) variation regimes, and best fit to the Arrhenius law of the thermally activated region (solid line).

diagrams and the fitted α parameters (Fig. S8†). Below 10 K the plots are asymmetric and α increases with decreasing temperature; between 18 and 10 K α is almost constant at 0.22. We can speculate that at the higher temperatures the slow relaxation is dominated by the single ion behaviour of the central (highly symmetric) Dy^{3+} ion, while at low temperatures the weak coupling with the peripheral ions is important.

In summary, two isostructural heptametallic lanthanide discs have been made. Magnetic investigations show a significant MCE for the Gd_7 disc and slow relaxation behaviour with a high thermal energy barrier for the Dy_7 analogue. Further analysis of the complicated Dy_7 dynamic behaviour will require single crystal magnetic studies, including of doped diamagnetic and isostructural analogues: efforts towards this are underway.

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Notes and references

† Elemental analyses (calc.: found): (**1**) Dy 29.29: 28.78, C 47.63: 47.18, H 4.33: 3.77, N 1.44: 1.29; (**2**) Gd 28.61: 27.25, C 48.08: 46.08, H 4.38: 4.26, N 1.46: 1.55. The magnetic properties of polycrystalline samples were investigated in the temperature range 1.8–300 K using a Quantum Design MPMS-XL SQUID magnetometer; loose samples tended to orient in the magnetic field and hence were fixed in eicosane. Data are corrected for

the diamagnetism of the compounds (Pascal constants) and sample holder and eicosane by measurement. Ac susceptibility measurements were performed with an ac magnetic field of 1.55 G oscillating at frequencies ranging from 1 to 1400 Hz.

Crystal data. For **1**, $\text{C}_{154}\text{H}_{164}\text{Dy}_7\text{N}_4\text{O}_{42}$, $M = 3880.39$, monoclinic, space group $P\bar{1}$, $T = 100(2)\text{K}$, $a = 16.263(4)$, $b = 16.500(4)$, $c = 17.299(4)$ Å, $\alpha = 97.2170(10)^\circ$, $\beta = 113.906(4)^\circ$, $\gamma = 115.0080(10)^\circ$, $V = 3590.4(15)$ Å³, $Z = 1$, $\rho = 1.795$ g cm⁻³, total data 29 169, unique data 12 278 ($R_{\text{int}} = 0.1473$), $\mu = 3.680$ mm⁻¹, 937 parameters, $R_1 = 0.0725$ for $I \geq 2\sigma(I)$ and $wR_2 = 0.2585$ for all data. For **2**, $\text{C}_{154}\text{H}_{164}\text{Gd}_7\text{N}_4\text{O}_{42}$, $M = 3843.64$, triclinic, space group $P\bar{1}$, $T = 100(2)\text{K}$, $a = 16.1991(8)$, $b = 16.3943(8)$, $c = 17.2829(9)$ Å, $\alpha = 97.2230(10)^\circ$, $\beta = 113.8990(10)^\circ$, $\gamma = 114.9720(10)^\circ$, $V = 3551.8(3)$ Å³, $Z = 1$, $\rho = 1.797$ g cm⁻³, total data 24 854, unique data 12 349 ($R_{\text{int}} = 0.0685$), $\mu = 3.306$ mm⁻¹, 937 parameters, $R_1 = 0.1013$ for $I \geq 2\sigma(I)$ and $wR_2 = 0.2293$ for all data. The data of **1** and **2** were recorded on a Bruker SMART CCD diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 using SHELXTL. CCDC 823957 and 823958 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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