The search for 3d–4f single-molecule magnets: synthesis, structure and magnetic properties of a $[Mn^{III}{}_2Dy^{III}{}_2]$ cluster

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Tetranuclear $[Mn^{III}{}_2Ln^{III}{}_2]$ complexes formed using tripodal ligands display frequency dependent out-of-phase ac susceptibility signals and temperature and sweep rate dependent hysteresis loops.

The synthesis and characterization of polynuclear clusters of paramagnetic metal ions have attracted intense study since the discovery that such molecules can display the phenomenon of single-molecule magnetism (SMM).[1] In these molecules there exists an energy barrier to the relaxation of the magnetization due to the combination of a large ground state spin multiplicity and a significant negative zero-field splitting of that ground state. This imparts a molecular magnetic memory effect that can be observed as temperature and sweep rate dependent hysteresis loops in single crystal *M vs. H* studies.[2] There are now several species displaying such behaviour—the majority of which are transition metal clusters containing Mn ions, since Mn clusters often display large spin ground states and large and negative magneto-anisotropies associated with the presence of Jahn–Teller distorted Mn^{III} ions. In contrast there are only three reports of 3d–4f complexes behaving as SMMs: the tetranuclear complex $[Cu^{II}LTb^{III}(hfac)_2]_2$ (where H_3L = 1-(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxy-benzylideneamino)-ethane); the dodecanuclear complex $[Mn^{IV}{}_2Mn^{III}{}_4Dy^{III}{}_6(H_2shi)_4(Hshi)_2(shi)_{10}(CH_3OH)_{10}(H_2O)_2]$ (where H_3shi = salicylhydroxamic acid); and the pentadecanuclear compound $[Mn_{11}Dy_4O_8(OH)_6(OMe)_2(O_2CPh)_{16}(NO_3)_5(H_2O)_3]$.[3–5]

The first two complexes display frequency dependent out-of-phase ac susceptibility signals at low temperature, but these in themselves are not definitive evidence of SMM behaviour. Only the $[Mn_{11}Dy_4]$ complex has been shown to display temperature and sweep rate dependent hysteresis loops in low temperature magnetization studies. These loops are unambiguous evidence of SMM behaviour.

The advantages of using lanthanide ions in the synthesis of new SMMs is that they will provide both large spin and considerable single ion anisotropy. It therefore seemed logical to extend our previous work on the synthesis of Mn^{III} SMMs using tripodal organic bridging ligands[6] to the synthesis of new heterometallic Mn^{III}–Ln^{III} clusters. Herein we describe the magnetic properties of $[Mn^{III}{}_2Ln^{III}{}_2]$ complexes that not only show frequency dependent out-of-phase ac susceptibility signals but also temperature and sweep rate dependent hysteresis loops. These loops also display the step-like features associated with quantum tunnelling of the magnetization. Combination of the trimetallic species $[Mn_3O(O_2CR)_6(py)_3]$ (R = CH_3, CMe_3, Ph) with H_3tripod (H_3tmp, H_3thme, H_4peol, Fig. 1), $Ln(NO_3)_3\cdot xH_2O$, (Ln = Gd, Dy, Tb) and NMe_4OH in MeCN produces the tetranuclear species $[NMe_4]_2[Mn^{III}{}_2Ln^{III}{}_2(tripod)_2(O_2CR)_4(NO_3)_4]$ in good yield after 2 days. In this communication we will limit our discussion to the complex $[NMe_4]_2[Mn^{III}{}_2Dy^{III}{}_2(tmp)_2(O_2CMe_3)_4(NO_3)_4]\cdot 2MeCN\cdot 0.5H_2O$, **1**·2MeCN·0.5H$_2$O.

Complex **1**†‡ (Fig. 1) crystallizes in the monoclinic space group $P2_1/c$. The central metallic core has a planar diamond-like topology with the Mn^{III} ions in the centre and the Dy^{III} ions in

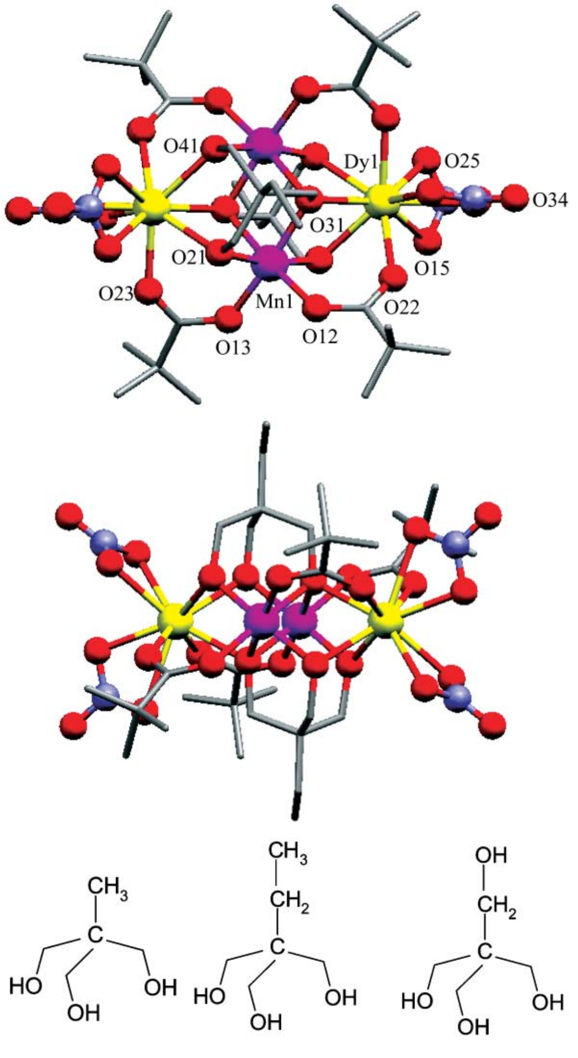

Fig. 1 The structure of the anion of complex **1** viewed from above the $[Mn_2Dy_2]$ plane (top), from the side of the $[Mn_2Dy_2]$ plane (middle) and the structures of H_3thme, H_3tmp and H_4peol, respectively (bottom).

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the periphery. They are linked together *via* two tmp^{3-} ligands which sit one above and one below this plane, each providing two μ_2-oxygen arms and one μ_3-oxygen arm—the former linking one Mn ion to one Dy ion (*e.g.* O21, O41) and the latter bridging between the two central Mn ions and the peripheral Dy ion (*e.g.* O31), forming a $[\text{Mn}^{\text{III}}{}_2\text{Dy}^{\text{III}}{}_2\text{O}_6]^{6+}$ unit. The four pivalates bridge in their usual *syn*, *syn*, μ-fashion around this core between the two different metal centres. The Mn ions are in distorted octahedral geometries with the Jahn–Teller axes co-parallel, defined by the direction O12–Mn1–O31A. The Dy ions are nine-coordinate with their geometries completed by two chelating NO_3^- ions.

In the crystal the anions pack in columns, one unit sitting directly upon its neighbour, with the unbound oxygen atoms of the coordinating NO_3^- ions in close contact with the NMe_4^+ cations (N–O···C–N, ~3.2–3.8 Å) which sit in between these columns.

Complex **1** is not the first example of a $[\text{Mn}_2\text{Ln}_2]$ cluster: the complexes $[\text{Mn}_2\text{Ln}_2\text{O}_2(\text{piv})_8(\text{pivH})_2(\text{MeOH})_2]$ (where Ln = Gd, Dy) were reported some time ago[7] and there have also been a number of reports of $[\text{Ln}^{\text{III}}{}_2\text{M}^{\text{II}}{}_2]$ complexes.[8] In $[\text{Mn}_2\text{Ln}_2\text{O}_2(\text{piv})_8(\text{pivH})_2(\text{MeOH})_2]$ the metal centres are linked together *via* a combination of oxides and carboxylates, but the metal topology is somewhat similar to that observed in **1**.

Solid state dc magnetic susceptibility measurements were collected for complex **1** in the temperature range 1.8–300 K in an applied field of 1 kG. The room temperature $\chi_M T$ value of approximately 35 cm^3 K mol^{-1} (Mn^{3+}, $S = 2$; Dy^{3+}, $^6\text{H}_{15/2}$, $S = 5/2$, $L = 5$) remains constant until around 50 K where it begins to drop sharply to a value of approximately 20 cm^3 K mol^{-1} at 1.8 K, indicative of the presence of dominant antiferromagnetic interactions between the metal centres. Ac susceptibility measurements (Fig. 2) taken in the frequency range 250–1500 Hz

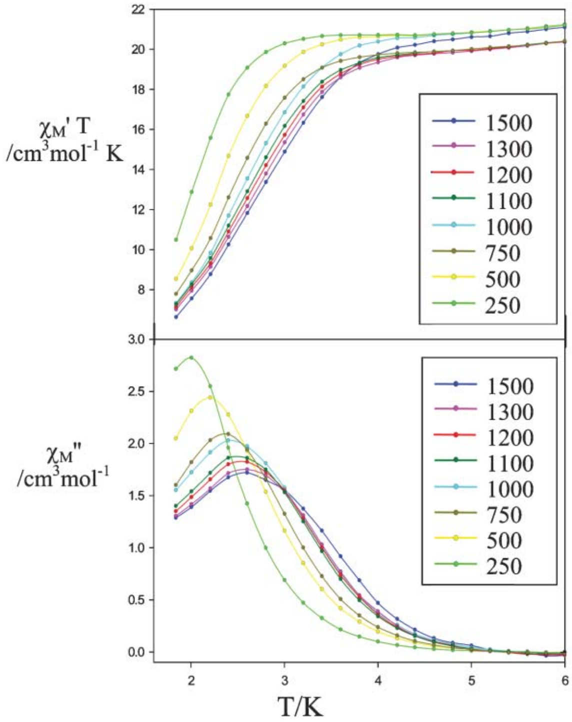

Fig. 2 Plots of the in-phase (χ_M') signal as $\chi_M'T$ and out-of-phase (χ_M'') signal in ac susceptibility studies *vs.* T in a 3.5 G field oscillating at the indicated frequencies.

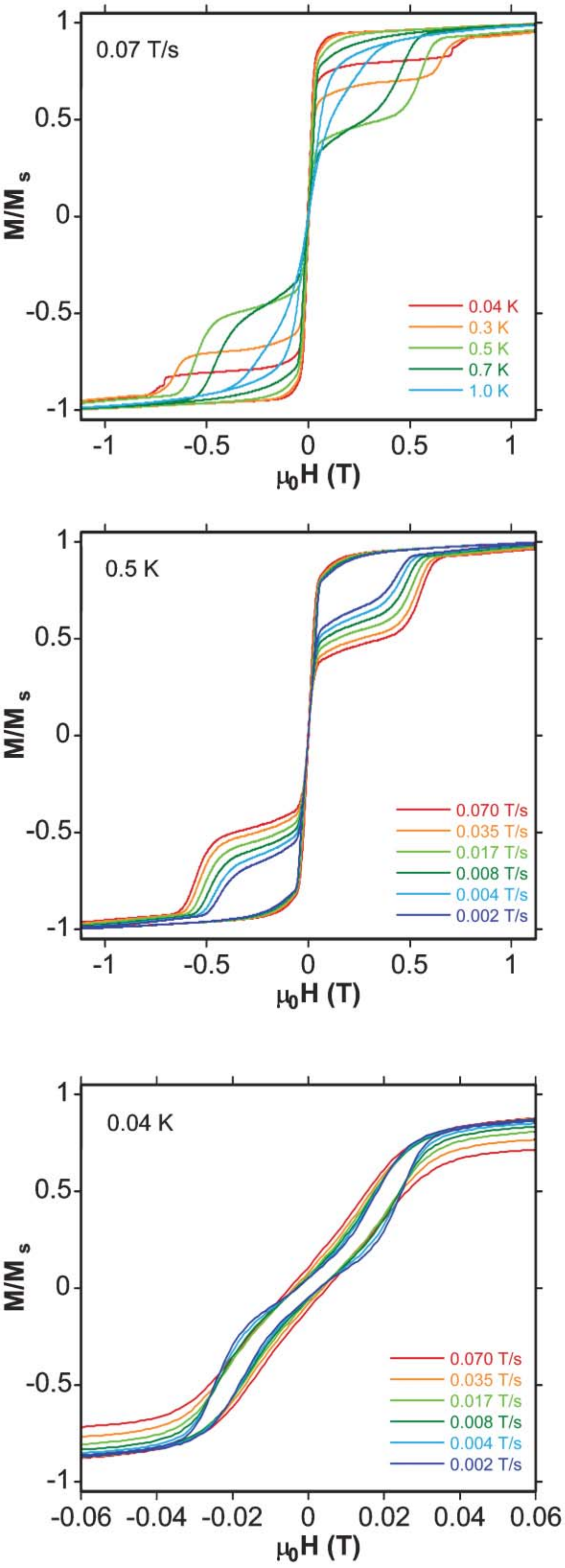

Fig. 3 Magnetization (M) of **1** (plotted as fraction of maximum value M_s) *vs.* applied field ($\mu_0 H$). The resulting loops are shown at different temperatures (top), and different field sweep rates (middle, bottom).

and at temperatures between 1.8 and 6 K display the frequency-dependent out-of-phase signals indicative of SMM behaviour. The data obtained were fit to the Arrhenius equation to give an effective energy barrier for the reorientation of the magnetization (U_{eff}) of 15 K and $\tau_0 = 3.31 \times 10^{-7}$ s. In order to investigate possible SMM behaviour, single crystal magnetization measurements were performed using an array of micro-SQUIDS at temperatures down to 40 mK.[9] Hysteresis loops collected for complex **1** at varying temperatures and sweep rates are shown in Fig. 3. The loops are somewhat unusual in that extremely fast tunnelling occurs at zero-applied field. Thus at $H = 0$ complex **1** does not show superparamagnetic-like behaviour. However, when a field is applied the tunnelling is switched off and sweep rate and temperature dependent hysteresis loops are observed. The fast tunnelling at $H = 0$ is not due to the intermolecular interactions observed in the crystal of **1**. These interactions are of the order of 20 mT—a value comparable to the dipolar interactions observed in $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]$. Therefore even if the $[Mn_2Dy_2]$ units were 'decoupled', similar loops would be observed—meaning that the observed hysteresis is due only to intramolecular slow relaxation of the magnetization. Further studies of complex **1** and its analogues (Ln = Gd, Tb) are underway and will be reported in a full paper.

In summary, complex **1** is only the second example of a 3d–4f cluster that displays temperature and sweep-rate dependent hysteresis loops. These loops also display the step-like features characteristic of QTM. The loops are unusual however in that little coercivity is observed at $H = 0$, and perhaps complex **1** is therefore best described as either a SMM with a fast tunnel transition at $H = 0$ or as a compound whose SMM behaviour is only 'switched-on' by the application of an external magnetic field. The paper also highlights the danger in assuming that the presence of frequency-dependent out-of-phase ac susceptibility signals are guarantees to the observation of hysteresis at $H = 0$. The synthesis of Mn^{III}-containing clusters is now a well established route to observing SMM behaviour, and Ln^{III} ions are excellent sources of both large spin and large anisotropy. Therefore, the combination of Mn^{III} and Ln^{III} ions in the same molecular species may promise to deliver new families of SMMs with exciting properties. However, whether the presence of Ln^{3+} ions also increases tunnelling rates to such an extent that the observed hysteresis is actually decreased or totally destroyed despite increased S and/or D is as yet unclear.

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Notes and references

† Analysis, calcd (found, %) for $1\cdot 1MeCN\cdot 0.5Et_2O$: C, 33.5 (33.5); H, 5.8 (5.3); N, 6.2 (6.1).

‡ Crystal structure data for **1**: $C_{44}H_{89}Dy_2Mn_2N_8O_{26.50}$, $M_r = 1589.11$, monoclinic, space group, $P2_1/c$, $a = 14.6304(4)$, $b = 13.3520(4)$, $c = 17.0340(5)$ Å, $\beta = 101.689(2)°$, $V = 3258.50(16)$ Å^3, $T = 150(2)$ K, $Z = 2$, $\rho_{calcd} = 1.620$ g cm^{-3}, $\mu(\lambda = 0.71073$ Å$) = 2.726$ mm^{-1}, 47521 reflections collected, 9572 independent reflections [R(int) = 0.0333], $R(F) = 0.0295$ and $wR2 = 0.0823$ using 800 reflections with $I > 2\sigma(I)$. The structure was solved and refined using the programs DIRDIF and SHELXL: P. T. Beurskens, G. Beurskens, W.P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel and J. M. M. Smits, The DIRDIF96 Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1996. G.M. Sheldrick. SHELXL-97. University of Gottingen, Germany, 1997. The structure has some disorder, full details are supplied in the cif file. CCDC 259056. See http://www.rsc.org/suppdata/cc/b5/b501508a/ for crystallographic data in CIF or other electronic format.

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