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A family of dodecanuclear Mn₁₁Ln single-molecule magnets

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A B S T R A C T

A series of four isostructural dodecanuclear complexes $[Mn^{III}_9Mn^{II}_2Ln^{III}(O)_8(OH)(piv)_{16}(NO_3)(CH_3CN)]\cdot xCH_3CN\cdot yC_7H_{16}$ (piv = pivalate; $x = \frac{1}{2}$, $y = \frac{3}{4}$, Ln = Tb (**1**); $x = 2$, $y = \frac{1}{2}$, Ln = Dy (**2**), Ho (**3**), and Y (**4**)) has been prepared for which the structural motif described as 'a lanthanide ion nested in a large manganese shell' is observed. All compounds show out-of-phase signals in their ac susceptibilities, and their single-molecule magnet behaviour was confirmed by single-crystal micro-SQUID studies of **1-3** which show hysteresis loops of molecular origin at $T < 1.0$ K. The SMM behaviour observed in compounds **1-3** is more pronounced than that for **4**, which contains the diamagnetic Y^{III} ion. This is principally the result of ferromagnetic coupling between the paramagnetic anisotropic Ln^{III} ions (Tb^{III}, Dy^{III} and Ho^{III}) and the manganese shell, which enhances the total spin ground state of the complexes.

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1. Introduction

While many structural types of single-molecule magnets, SMMs, are now known, spanning a wide range of metals, a majority of them are complexes containing the high spin Mn^{III} ion which contributes a large spin and uniaxial anisotropy [1]. That notwithstanding, an approach that is increasingly gaining ground is the incorporation of lanthanide ions into SMM systems since these can contribute up to seven unpaired electrons and many show significant single-ion anisotropy. In particular, the creation of 3d-4f systems using lanthanides to modulate the magnetic properties of transition metal single-molecule magnets has become a very active area of research in recent years [2–5].

The interactions between 4f- or 4f- and 3d-electronic systems are essentially of magnetic dipolar nature and the contribution of the exchange interaction term appears to be very small, if not negligible, compared with that of the dipolar term in coordination clusters involving 4f ions. Furthermore, the mechanisms of slow relaxation of the magnetisation can be different for 3d and 4f ions. Nevertheless, it is clear that the resulting electronic structure, and therefore the magnetic behaviour, of coordination clusters built from both 3d and 4f ions can lead to SMMs with higher barriers Δ_{eff} to reversal of magnetization, and it is therefore of interest to investigate such clusters.

Earlier efforts in synthesising 3d/4f coordination clusters mostly concentrated on Cu/Gd systems which are usually ferromagnetically coupled, leading to high spin ground states but showing negligible anisotropy [6]. More recently, the idea of combining 3d and 4f metals ions so that one or both partners contribute high single-ion anisotropy as well as significant spin has been explored. For example, $CuDy_2$ or Co^{II}_2Gd compounds were recently reported with Δ_{eff} around 47 to 28 K [2b,5]. Similarly, the combination of manganese or iron and lanthanides has resulted in barriers Δ_{eff} of up to 103 K [3n] and 33.4 K [4f], respectively.

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As part of intense efforts aiming to synthesise novel types of Mn-Ln compounds, we and several other groups have been exploring mixed-metal cluster complexes that have the appropriate properties to function as SMMs [3]. Our own contributions to this new field have included $Mn_{11}Gd_2$ [3d], Mn_5Ln_4 [3e], $Mn_{10}Ln_2$ [3f], Mn_2Ln_2 [3k], Mn_2Ln_3 [3j], $Mn_{18}Dy$ [3h] and Mn_4Ln_4 [3l]. Following on from our previous report on a $\{Mn_{11}Gd_2\}$ complex [3d] which shows SMM properties, and the synthesis of a series of complexes with lighter lanthanides isostructural to the $\{Mn_{11}Gd_2\}$ [7], we decided to apply the same synthetic procedure to the heavier lanthanides. Many reactions in various solvents were explored, but only after excluding furoic acid from the original reaction conditions and using diffusion of heptane into the reaction mixture could we isolate and characterise four isostructural dodecanuclear $[Mn^{III}_9Mn^{II}_2Ln^{III}(O)_8(OH)(piv)_{16}(NO_3)(CH_3CN)]\cdot xCH_3CN\cdot y\,C_7H_{16}$ (piv = pivalate; $x = \frac{1}{2}$, $y = \frac{3}{4}$, Ln = Tb (1); $x = 2$, $y = \frac{1}{2}$, Ln = Dy (2), Ho (3), and Y (4)) complexes. Compounds **1-4** all exhibit SMM behaviour, showing out-of-phase signals in their ac susceptibilities; **1-3** additionally show hysteresis loops in microsquid measurements made below 1 K.

2. Experimental

2.1. General

All the reactions were carried out under aerobic conditions. $[Mn^{III}_2Mn^{II}_4O_2(piv)_{10}(4\text{-Me-py})_{2.5}(PivH)_{1.5}]$ (2) was obtained as reported [3d]. Elemental analyses for C, H and N were carried out at the Institute for Inorganic Chemistry at Karlsruhe Institute of Technology.

2.2. Preparation

$[Mn_{11}Dy(O)_8(OH)(piv)_{16}(NO_3)(CH_3CN)]\cdot 2CH_3CN\cdot\frac{1}{2}C_7H_{16}$ (2·2CH_3CN·½C_7H_{16}): a stirred slurry of $[Mn_6O_2(Piv)_{10}(4\text{-Me-py})_{2.5}(PivH)_{1.5}]$ (0.20 g, 0.11 mmol) in MeCN (10 ml) was heated to 70 °C, followed by addition of $Dy(NO_3)_3\cdot 6H_2O$ (0.20 g, 0.44 mmol), resulting in a dark-brown solution after 20 min. After stirring under reflux for an additional 30 min, the solution was cooled to room temperature and divided between five small (8 ml) vials, each with 2 ml of solution. Each of these vials was placed into a larger (25 ml) vial containing 2 ml of heptane and the larger vial was sealed. After 2–3 days some white microcrystalline powder appeared on the walls and bottom of the small vials. At this point each large vial was opened every day to check for monocrystals with a microscope and then resealed. After 7–8 days the white material disappeared and brown crystals began to appear. After a further 7 days the brown crystals were collected by filtration, washed with MeCN + H_2O (1:1) to remove residual traces of the (water-soluble) white impurity, and dried in air. A similar yield of the final crystals was obtained after more than 4–5 weeks if the big vials were not opened during the crystallization period. With the procedure which is to briefly open the big vial every day, the crystallisation period can be shortened to 2 weeks. Probably, this procedure, in addition to faster evaporation of solvent, facilitates also the release of the pressure which

may speed up the crystallisation. Combined yield from all vials = 0.065 g (46.0% based on Mn). Calc. for $C_{82.1}H_{149.8}DyMn_{11}NO_{44}$ (= **2**·0.3 C_7H_{16}): C 37.61, H 5.76, N 0.53%; found: C 37.47, H 5.82, N 0.47%. IR (KBr disk, cm^{-1}): 3430 (s), 2965 (s), 2932 (s), 2908 (s), 2323 (w), 1554 (vs), 1485 (vs), 1461 (s), 1431 (vs), 1382 (s), 1360 (s), 1303 (s), 1230 (vs), 1032 (w), 939 (m), 893 (m), 800 (s), 785 (m), 665 (s), 623 (s), 587 (s), 458 (w).

$[Mn_{11}Tb(O)_8(OH)(piv)_{16}(NO_3)(CH_3CN)]\cdot\frac{1}{2}CH_3CN\cdot\frac{3}{4}C_7H_{16}$ (**1**·½CH_3CN·¾C_7H_{16}): this compound as brown crystals was obtained using the same procedure as for **2** with $Tb(NO_3)_3\cdot 6H_2O$ in place of $Dy(NO_3)_3\cdot 6H_2O$. Total yield: 0.060 g (43.0% based on Mn). Calc. for $C_{82.1}H_{149.8}TbMn_{11}NO_{44}$ (= **1**·0.3 C_7H_{16}): C 37.66, H 5.77, N 0.53%; found: C 37.48, H 5.79, N 0.47%. IR (KBr disk, cm^{-1}): 3431 (s), 2964 (s), 2932 (s), 2907 (s), 2323 (w), 1553 (vs), 1485 (vs), 1461 (s), 1431 (vs), 1381 (s), 1359 (s), 1302 (s), 1229 (vs), 1032 (w), 938 (m), 893 (m), 799 (s), 785 (m), 664 (s), 623 (s), 587 (s), 457 (w).

$[Mn_{11}Ho(O)_8(OH)(piv)_{16}(NO_3)(CH_3CN)]\cdot 2CH_3CN\cdot\frac{1}{2}\,C_7H_{16}$ (**3**·2CH_3CN·½C_7H_{16}): this compound as brown crystals was obtained using the same procedure as for **2** with Ho $(NO_3)_3\cdot 6H_2O$ in place of $Dy(NO_3)_3\cdot 6H_2O$. Yield: ~0.055 g (39.0% based on Mn). Calc. for $C_{81.4}H_{148.2}HoMn_{11}NO_{44}$ (= **3**·0.2 C_7H_{16}): C 37.40, H 5.71, N 0.53%; found: C 37.23, H 5.78, N 0.46%. IR (KBr disk, cm^{-1}): 3419 (s), 2964 (s), 2932 (s), 2907 (s), 2320 (w), 1553 (vs), 1485 (vs), 1460 (s), 1430 (vs), 1381 (s), 1359 (s), 1302 (s), 1228 (vs), 1032 (w), 938 (m), 893 (m), 799 (s), 785 (m), 667 (s), 623 (s), 587 (s), 457 (w).

$[Mn_{11}Y(O)_8(OH)(piv)_{16}(NO_3)(CH_3CN)]\cdot 2CH_3CN\cdot\frac{1}{2}\,C_7H_{16}$ (**4**·2CH_3CN·½C_7H_{16}): this compound as brown crystals was obtained using the same procedure as for **2** with $Y(NO_3)_3\cdot 6H_2O$ in place of $Dy(NO_3)_3\cdot 6H_2O$. Yield: ~0.050 g (35.7% based on Mn). Calcd for $C_{82.1}H_{149.8}YMn_{11}NO_{44}$ (= **4**·0.3 C_7H_{16}): C 38.70, H 5.92, N 0.55%; found: C 38.51, H 6.11, N 0.46%. IR (KBr disk, cm^{-1}): 3412 (s), 2965 (s), 2932 (s), 2907 (s), 2319 (w), 1551 (vs), 1486 (vs), 1460 (s), 1431 (vs), 1379 (s), 1359 (s), 1302 (s), 1229 (vs), 1033 (w), 938 (m), 892 (m), 797 (s), 782 (m), 663 (s), 620 (s), 585 (s), 458 (w).

2.3. Magnetic measurements

The magnetic susceptibility measurements were carried out on polycrystalline samples using a Quantum Design SQUID magnetometer MPMS XL over the temperature range 1.8–300 K for dc applied fields up to 7 T. Alternating current (ac) susceptibility measurements were performed with an oscillating field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. M versus H measurements were performed at 100 K to check for the presence of ferromagnetic impurities and none were found. The magnetic data were corrected for the sample holder and the diamagnetic contribution.

2.4. Crystal structure determinations

Data for compounds **1-3** were collected at 100 K on a Bruker SMART Apex CCD diffractometer using graphite-monochromated MoKα radiation. Semiempirical absorption corrections were made using *SADABS* [8a].