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Contribution of Spin and Anisotropy to Single Molecule Magnet Behavior in a Family of Bell-Shaped $Mn_{11}Ln_2$ Coordination Clusters

Valeriu Mereacre,[†] Yanhua Lan,[†] Rodolphe Clérac,[§,⊥] Ayuk M. Ako,[†,‡] Wolfgang Wernsdorfer,[‖] Gernot Buth,[⊗] Christopher E. Anson,[†] and Annie K. Powell[*,†,‡]

[†]Institut für Anorganische Chemie, Karlsruhe Institute of Technology (KIT), Engesserstrasse 15, D-76131, Karlsruhe, Germany

[‡]Institut für Nanotechnologie and [⊗]Institut für Synchrotronstrahlung, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[§]Equipe "Matériaux Moléculaires Magnétiques", Centre de Recherche Paul Pascal (CRPP), CNRS, UPR 8641, 115 avenue du Dr. Albert Schweitzer, Pessac, F-33600, France

[⊥]Université de Bordeaux, UPR 8641, Pessac, F-33600, France

[‖]Institut Néel, CNRS, 38042 Grenoble Cedex 9, France

S *Supporting Information*

ABSTRACT: The synthesis, structures, and magnetic properties of a family of isostructural "bell-shaped" heterometallic coordination clusters $[Mn^{III}_9Mn^{II}_2La^{III}_2(\mu_4\text{-}O)_7(\mu_3\text{-}O)(\mu_3\text{-}OH)_2(piv)_{10.8}(O_2CC_4H_3O)_{6.2}(NO_3)_2(OH_2)_{1.5}(MeCN)_{0.5}]\cdot 12CH_3CN\cdot 2H_2O$ (**1**) and $[Mn^{III}_9Mn^{II}_2Ln_2(\mu_4\text{-}O)_7(\mu_3\text{-}O)(\mu_3\text{-}OH)_2(piv)_{10.6}(O_2CC_4H_3O)_{6.4}(NO_3)_2(OH_2)]\cdot nCH_3CN\cdot H_2O$ ($Ln = Pr^{III}$, $n = 8$ (**2**); $Ln = Nd^{III}$, $n = 10$ (**3**); $Ln = Eu^{III}$, $n = 17$ (**4**); $Ln = Gd^{III}$, $n = 13$ (**5**); piv = pivalate) are reported. The complexes were obtained from the reaction of $[Mn^{III}_2Mn^{II}_4O_2(piv)_{10}(4\text{-Me-py})_{2.5}(pivH)_{1.5}]$ and $Ln(NO_3)_3\cdot 6H_2O$ in the presence of 2-furan-carboxylic acid (C_4H_3OCOOH) in CH_3CN. Compounds **1**−**5** are isomorphous, crystallizing in the triclinic space group $P\bar{1}$ with $Z = 2$. The Mn^{III} and Mn^{II} centers together form the shell of the bell, while the two Ln^{III} centers can be regarded as the bell's clapper. The magnetic properties of **1**−**4** reveal dominant antiferromagnetic interactions between the magnetic centers leading to small spin ground states; while those of **5** indicate similar antiferromagnetic interactions between the manganese ions but with unusually strong ferromagnetic interactions between the Gd^{III} ions leading to a large overall spin ground state of $S = 11-12$. While *ac* and *dc* magnetic measurements confirmed that $Mn_{11}Gd_2$ (**5**) is a single-molecule magnet (SMM) showing hysteresis loops at low temperatures, compounds **1**−**4** do not show any slow relaxation of the magnetization, indicating that the $S = 7$ spin of the ferromagnetic Gd_2 unit in **5** is a necessary contribution to its SMM behavior.

INTRODUCTION

Studies of the magnetic interactions involving transition-metal ions have become an intense research area since the discovery of single-molecule magnets (SMMs).[1] SMMs have been defined as molecules showing relaxation of the magnetization which is purely molecular in origin and are thus individual molecules that behave as magnets below a certain blocking temperature.[2] Such tiny magnets have potential applications in information storage or else as qubits in quantum computing.[3] The general prerequisites for SMM behavior are a combination of a nonzero (and usually ground) spin state (S) and a large uniaxial anisotropy of an Ising type. The anisotropy can result from a favorable zero-field splitting parameter or, for highly anisotropic ions such as many of the lanthanides, can arise from an overall uniaxial "easy axis" type molecular anisotropy.[4] The quest for new SMMs displaying high blocking temperatures has, until relatively recently, focused mainly on the use of paramagnetic 3d metal ions.[5] Now, however, much attention has been turned toward exploring the combination of 3d and 4f ions in complexes to enhance both spin and anisotropy.[6−10] While such a combination of 3d and 4f spin carriers within a given complex does not always yield SMMs,[11] the systematic study of such molecular systems provides valuable insights into the magnetic interactions, as well as the correlation of these with structural parameters and the conditions necessary for producing SMM behavior.[8,9]

Our own work in the area has been focused on incorporating lanthanide ions, as well as appropriate diamagnetic rare earth ions such as Y^{III}, into 3d/Ln coordination clusters to provide a systematic survey of the structural types and characteristics of the resulting coordination compounds. Not surprisingly, we found that such isostructural series were easily accessible,[8e,l,m,10d,10e,10f] although it is relatively unusual for the same molecular structural motif to be maintained across the whole lanthanide series, with the structural type often varying when moving from the lighter to heavier 4f ions in their +3 oxidation states.[8j,k] Clearly the large

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decrease in ionic radius on moving from left to right plays a deciding role in determining the structural outcome.

Recent success in synthesizing mixed transition metal and lanthanide SMMs presenting various core topologies includes Cu_xLn_y,[6] Co_xLn_y,[7] Mn_xLn_y,[8] Fe_xLn_y,[10] Ni_xLn_y,[12] and Cr_xLn_y,[13] and a few 3d-3d′-4f,[14] 3d-4d-4f[15] or 3d-5d-4f[16] systems which have been described as SMMs based on the observation of frequency-dependent out-of-phase *ac* signals and/or hysteresis loops in the magnetization.

Previously we communicated the structure and magnetic properties of a $\{Mn_{11}Gd_2\}$ complex[8d] which shows SMM behavior. It is widely accepted that a combination of both nonzero spin and uniaxial anisotropy is generally required for SMM behavior to be observed, but it is reasonable to ask whether one of these factors is more important for the SMM behavior, in this case either the high spin of Gd^{III} or the anisotropy of Mn^{III}, or are they equally important? Thus it seemed pertinent to change the most easily variable component of the system, the rare earth ion Gd^{III}, by using various other Ln^{III} to quantify the relative contributions of both partners to the system. We can also note that in comparison with changing the lanthanide in an isostructural series,[8e,l,m,10d,10e,10f,17] exchanging the anisotropic paramagnetic 3d component for an isotropic or diamagnetic cation seems much more of a synthetic challenge, and only a few such examples have been reported.[7c,10c,11d,11e,18]

Thus we report here an efficient synthetic procedure for the isolation of high-nuclearity heterometallic complexes using a preformed hexanuclear Mn complex, $[Mn^{III}_2Mn^{II}_4O_2(piv)_{10}(4\text{-}Me\text{-}py)_{2.5}(pivH)_{1.5}]$,[19] as a source of $Mn^{II/III}$ ions. This extends our original work on the $\{Mn_{11}Gd_2\}$ complex and describes the syntheses, structures, and magnetic properties of the family of isostructural clusters with a central $\{Mn_{11}Ln_2\}$ core, where Ln = La^{III}, Pr^{III}, Nd^{III}, Eu^{III}, and Gd^{III}. The magnetic studies indicate the presence of strong antiferromagnetic interactions within the Mn_{11} shell, and ferromagnetic Mn−Ln and Gd−Gd interactions.

■ EXPERIMENTAL SECTION

General Information. All reagents were obtained from commercial sources and used as received without further purification. $[Mn_6O_2(piv)_{10}(4\text{-}Me\text{-}py)_{2.5}(PivH)_{1.5}]$ and $Mn_{11}Gd_2(O)_8(OH)_2(piv)_{10.6}(C_4H_3OCOO)_{6.4}(NO_3)_2(H_2O)]\cdot13CH_3CN\cdot H_2O$ (**5**) were prepared according to the method in ref 8d. All reactions were carried out under aerobic conditions. Elemental analyses for C, H, and N were performed using an Elementar Vario EL analyzer and were carried out at the Institute of Inorganic Chemistry, Karlsruhe Institute of Technology. FTIR spectra were measured on a Perkin-Elmer Spectrum One spectrometer with samples prepared as KBr discs.

Synthesis. *$[Mn_{11}La_2(O)_8(OH)_2(piv)_{10.8}(C_4H_3OCOO)_{6.2}(NO_3)_2(H_2O)_{1.5}(CH_3CN)_{0.5}]\cdot12CH_3CN\cdot2H_2O$ (**1**).* A stirred slurry of $[Mn_6O_2(piv)_{10}(4\text{-}Me\text{-}py)_{2.5}(PivH)_{1.5}]$ (0.2 g, 0.11 mmol) in MeCN (10 mL) was heated to 70 °C, then $La(NO_3)_3\cdot6H_2O$ (0.19 g, 0.45 mmol) and furoic acid (C_4H_3OCOOH) (0.17 g, 1.52 mmol) were added in small portions over 20 min, resulting in a dark-brown solution. After stirring under reflux for a further 30 min, the solution was filtered and concentrated by slow evaporation to give dark-brown crystals after 3 days. The resulting crystals were collected by filtration, washed with MeCN, and dried in air. Yield: ∼0.06 g (19% based on Mn). Anal. Calcd for $[C_{86}H_{122.3}Mn_{11}N_{2.5}O_{57.7}La_2]\cdot3H_2O$: C 33.86, H 4.23, N 1.15%; found: C 33.90, H 4.05, N 0.91%. IR (KBr disk, cm^{-1}): 3430 (m, br), 2965 (s), 2933 (s), 1581 (vs), 1554 (vs), 1486 (vs), 1463 (s), 1431 (vs), 1381 (s), 1363 (s), 1280 (m), 1229 (vs), 1206 (s), 1142 (m), 1075 (w), 1011 (s), 936 (m), 888 (m), 784 (s), 755 (m), 663 (vs), 622 (vs), 595 (m), 495 (m), 456 (w).

*$[Mn_{11}Pr_2(O)_8(OH)_2(piv)_{10.6}(C_4H_3OCOO)_{6.4}(NO_3)_2(H_2O)]\cdot8CH_3CN\cdot H_2O$ (**2**).* This compound was obtained by the same procedure as for **1** using $Pr(NO_3)_3\cdot6H_2O$ in place of $La(NO_3)_3\cdot6H_2O$. Yield: ∼0.07 g (21% based on Mn). Anal. Calc. for $[C_{85}H_{118.6}Mn_{11}N_2O_{57.4}Pr_2]\cdot3H_2O$: C 33.73, H 4.15, N 0.93%; found: C 33.72, H 4.01, N 1.11%. IR (KBr disk, cm^{-1}): 3435 (m, br), 2965 (m), 2931 (m), 1584 (vs), 1557 (vs), 1485 (vs), 1461 (s), 1429 (vs), 1383 (s), 1375 (s), 1364 (s), 1281 (m), 1231 (s), 1205 (s), 1142 (m), 1080 (w), 1012 (s), 935 (m), 885 (m), 785 (m), 755 (m), 661 (vs), 623 (vs), 595 (m), 495 (m), 455 (w).

*$[Mn_{11}Nd_2(O)_8(OH)_2(piv)_{10.6}(C_4H_3OCOO)_{6.4}(NO_3)_2(H_2O)]\cdot ca.10CH_3CN\cdot H_2O$ (**3**).* This compound was obtained by the same procedure as for **1** using $Nd(NO_3)_3\cdot6H_2O$ in place of $La(NO_3)_3\cdot6H_2O$. Yield: ∼0.10 g (30% based on Mn). Anal. Calcd for $[C_{85}H_{118.6}Mn_{11}N_2Nd_2O_{57.4}]$: C 34.26, H 4.01, N 0.94%; found: C 34.41, H 4.39, N 0.85%. IR (KBr disk, cm^{-1}): 3434 (m, br), 2964 (s), 2932 (s), 1582 (vs), 1556 (vs), 1484 (vs), 1463 (s), 1430 (vs), 1379 (s), 1365 (s), 1281 (m), 1228 (vs), 1208 (s), 1141 (m), 1075 (w), 1010 (s), 937 (m), 887 (m), 783 (s), 756 (m), 662 (vs), 622 (vs), 594 (m), 494 (m), 454 (w).

*$[Mn_{11}Eu_2(O)_8(OH)_2(piv)_{10.6}(C_4H_3OCOO)_{6.4}(NO_3)_2(H_2O)]\cdot17CH_3CN\cdot H_2O$ (**4**).* This compound was obtained by the same procedure as for **1** using $Eu(NO_3)_3\cdot6H_2O$ in place of $La(NO_3)_3\cdot6H_2O$. Yield: ∼0.10 g (30% based on Mn). Anal. Calc. for $[C_{85}H_{118.6}Mn_{11}N_2O_{57.4}Eu_2]\cdot H_2O$: C 33.88, H 4.03, N 0.93%; found: C 33.86, H 4.05, N 0.90%. IR (KBr disk, cm^{-1}): 3439 (m, br), 2961 (s), 2930 (s), 1580 (vs), 1555 (vs), 1484 (vs), 1462 (s), 1428 (vs), 1377 (s), 1366 (s), 1283 (m), 1229 (vs), 1211 (s), 1141 (m), 1076 (w), 1011 (s), 934 (m), 884 (m), 784 (s), 756 (m), 663 (vs), 621 (vs), 593 (m), 492 (m), 457 (w).

X-ray Crystallography. Data for **1** and **3**−**5** were measured at 100(2) K on a Bruker SMART Apex diffractometer with graphite-monochromated Mo−Kα radiation from a rotating anode source. The crystal quality for compound **3** was poor, only diffracting out to a resolution of 1.00 Å, preventing a full refinement of the structure to an adequate standard; however, the unit cell shows that **3** is isomorphous to **1**, **4**, and **5**, and the complex could be seen to be isostructural. Compound **2** forms only very small crystals, necessitating a measurement on the SCD beamline of the ANKA synchrotron at KIT Campus Nord using Si-monochromated radiation of wavelength λ = 0.8000 Å. Data were measured from three crystals; in each case technical problems prevented the acquisition of a complete data set. The data presented here are 89.2% complete to $(\sin\theta)/\lambda = 0.6$ Å^{-1}, but are clearly adequate to show that **2** is isostructural to the other compounds. Thus compounds **1**−**5** are isomorphous (Table 1), crystallizing as dark brown plates.

Data were corrected for polarization and semiempirically[20] for absorption. Structure solution by direct methods and full-matrix least-squares refinement against F^2 (all data) were carried out using SHELXTL.[21] All ordered non-H atoms were assigned anisotropic thermal parameters. H atoms were assigned isotropic thermal parameters equal to $1.2U_{eq}$ or $1.5U_{eq}$ of the atom to which they are bonded. Coordinates of hydroxo H-atoms were refined with organic H-atoms placed in calculated positions.

For compound **1** the lanthanum center La(2) is disordered over two adjacent positions. La(2a) is ligated by two chelating nitrates and a terminal acetonitrile ligand, La(2b) by two nitrates and an aqua ligand. Refinement with 50:50 relative occupancies and geometrical similarity restraints for the disordered nitrates resulted in very similar anisotropic temperature factors for La(2a) and La(2b). In compounds **2**−**5**, the corresponding Ln(2) cations are smaller and only chelated by two nitrates so that this disorder is not observed.

In all compounds, many of the pivalate ligands were found to show 2-fold disorder of their *t*-butyl groups. Similarly, one furoate ligand

Table 1. Crystallographic Data and Structure Refinement for Complexes **1**−**5**

	1	**2**	**3**[a]	**4**	**5** (ref 8d)
formula	$C_{110}H_{162.3}La_2Mn_{11}N_{14.5}O_{59.2}$	$C_{101}H_{144.6}Mn_{11}N_{10}O_{58.8}Pr_2$		$C_{119}H_{171.6}Eu_2Mn_{11}N_{19}O_{58.4}$	$C_{111}H_{157.6}Gd_2Mn_{11}N_2O_{58.4}$
formula weight	3517.20	3335.83		3711.01	3555.36
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	15.7862(13)	15.9529(14)	15.9151(9)	15.8668(6)	15.8893(10)
b/Å	17.6035(15)	17.5919(15)	17.5407(10)	17.4947(6)	17.5285(11)
c/Å	27.017(2)	27.197(2)	27.2129(16)	27.0806(10)	27.2474(17)
α/deg	87.277(1)	87.064(2)	87.187(1)	86.793(1)	86.985(1)
β/deg	79.974(1)	78.281(2)	78.810(1)	78.593(1)	78.083(1)
γ/deg	75.055(1)	72.950(2)	73.412(1)	73.304(1)	72.737(1)
U/Å^3	7143.0(10)	7144.7(11)	7142.1(7)	7058.0(4)	7090.5(8)
Z	2	2	2	2	2
T/K	100(2)	150(2)	100(2)	100(2)	100(2)
$F(000)$	3573	3368		3774	3598
D_c/Mg m^{-3}	1.635	1.546		1.746	1.665
$\mu(\lambda)$/mm^{-1}	1.613	2.276		1.920	1.957
λ/Å	0.71073	0.80000		0.71073	0.71073
data measured	54084	29448		48343	33399
unique data	31058	23522		27362	28136
R_{int}	0.0228	0.0397		0.0308	0.0246
data with $I \geq 2\sigma(I)$	21155	18110		20583	18636
parameters/restraints	1382/79	1400/64		1406/71	1408/18
wR_2 (all data)	0.1408	0.1590		0.1576	0.0907
S (all data)	1.070	1.053		1.082	0.992
R_1 [$I \geq 2\sigma(I)$]	0.0490	0.0626		0.0513	0.0409
biggest diff. peak/hole/e Å^{-3}	+1.22/−0.86	+2.11/−1.08		+2.02/−2.00	+1.51/−1.21
CCDC no.	829909	820010		820011	637050

[a] The structure of **3** could not be fully refined, as a result of poor crystal quality.

shows 2-fold disorder between the two possible orientations of the furyl ring in the plane. One ligand (involving carboxylate carbon C(47)) was found to be a disordered superposition of a pivalate and a furoate. In the final refinements of **2**, **4**, and **5** the pivalate and furoate occupancies were set at 0.4 and 0.6, respectively, while for **1** the pivalate contribution to the disorder was more minor and the respective occupancies were 0.2 and 0.8. In **2**−**5**, the aqua ligand O(51) coordinated to Mn(10) is ordered. However in **1** it is disordered against the furoate ligand bridging Mn(9) and Mn(11), such that while C(26b) forms a carboxylate group with O(26) and O(27), with O(51) as the aqua ligand, C(26a) forms a carboxylate group with O(26) and O(51), with O(27) now representing the aqua ligand. Geometrical similarity restraints were applied to partial-occupancy pivalate *t*-butyl groups as appropriate, while disordered furan rings were refined as regular pentagons.

In all structures, one MeCN in the lattice was well-behaved and could be refined anisotropically, and a lattice water could also be refined. However, many other disordered MeCN molecules could be identified from Fourier difference maps but could not be refined satisfactorily. These were omitted, and their electron density corrected using the SQUEEZE option in PLATON;[22] electron density corresponding to 11 (**1**), 7 (**2**), 16 (**4**), and 12 (**5**) lattice MeCN molecules was found.

Crystallographic data (excluding structure factors) for the structures of **1**, **2**, and **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 829909−829911. The corresponding data for **5** were previously deposited as CCDC 637050. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.: http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

Magnetic Measurements. The magnetic susceptibility measurements were obtained between 1.8 and 400 K on a Quantum Design SQUID magnetometer MPMS-XL for direct current (*dc*) applied fields ranging from −7 to 7 T. Measurements were performed on polycrystalline samples of 8.36, 7.20, 31.8, 20.4, and 12.43 mg for **1** [$Mn_{11}La_2$], **2** [$Mn_{11}Pr_2$], **3** [$Mn_{11}Nd_2$], **4** [$Mn_{11}Eu_2$], and **5** [$Mn_{11}Gd_2$], respectively. The lattice MeCN solvent molecules in these compounds are lost rather easily, and on longer storage in air almost all are lost, as judged from the CHN microanalytical data. Samples of the complexes were therefore filtered from their respective mother liquors and transferred immediately to the SQUID to minimize such solvent loss. Alternating current (*ac*) susceptibility measurements were performed with an oscillating *ac* field of 3 Oe with frequencies ranging from 1 to 1500 Hz. *M* vs *H* measurements were performed at 100 K to check for the presence of ferromagnetic impurities; no evidence for these was found. The magnetic data were corrected for the sample holder and the diamagnetic contribution.

RESULTS AND DISCUSSION

Synthesis. Previously, we communicated the synthesis, crystal structure, and magnetic properties of the 3d-4f coordination cluster [$Mn^{III}{}_9Mn^{II}{}_2Gd^{III}{}_2(O)_8(OH)_2(Piv)_{10.6}(C_4H_3OCO-O)_{6.4}(NO_3)_2H_2O$]·$13CH_3CN\cdot H_2O$ **5**, where Hpiv is pivalic acid and $C_4H_3OCO_2H$ is furoic acid.[8d] This [$Mn_{11}Gd_2$] complex

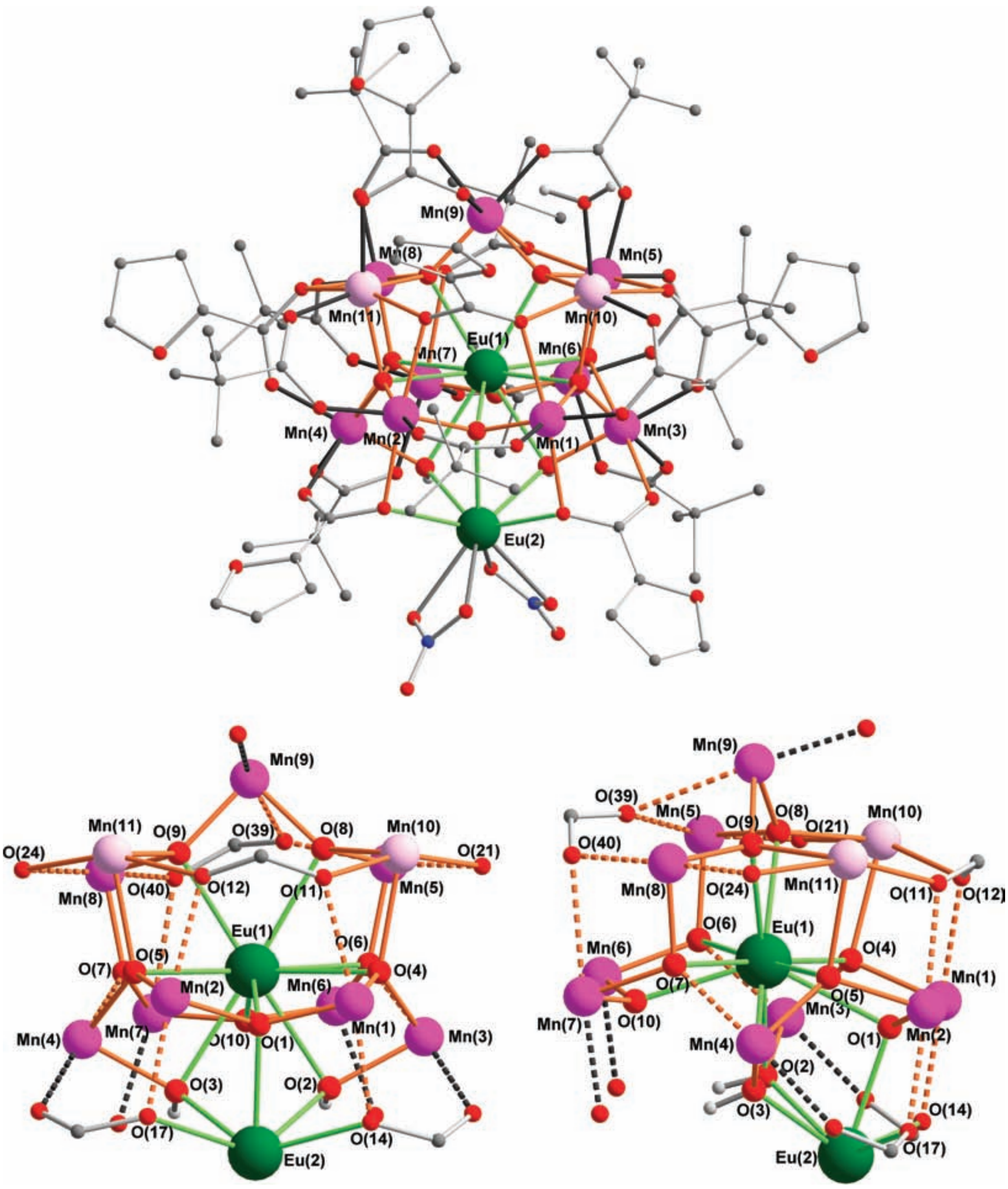

Figure 1. Molecular structure of **4** (disorder and organic H-atoms omitted for clarity) with two views of the cluster core. Bonds defining the Mn^{III} Jahn–Teller axes shown as dotted lines; Eu green, Mn^{III} purple, Mn^{II} pink, O red, N blue, C gray.

has a large spin ground state and showed hysteresis loops in the magnetization at low temperature as evidence of SMM behavior. This result prompted us to extend this work to analogous $Mn^{III}_9Mn^{II}_2Ln^{III}_2$ systems, to shed more light on the magnetic behavior of **5**.

The structure of the starting material $[Mn^{III}_2Mn^{II}_4O_2(piv)_{10}(4\text{-Me-py})_{2.5}(pivH)_{1.5}]$ has a similar structural fragment to the first reported hexanuclear mixed valence manganese complex $[Mn_6O_2(Piv)_{10}(PivH)_4]$[23] which was prepared by the reaction of $MnCO_3$ with pivalic acid in toluene. It was found that by refluxing a dioxane solution of $Mn(NO_3)_2$ and pivalic acid a similar compound[24] can be obtained. In the case of our Mn_6 starting material the 2.5 monodentate pivalic acid molecules coordinated to the four outer Mn(II) ions in the original structure are substituted by 2.5 molecules of 4-Me-py.

Other groups have used a tetrahydrofuran (THF) derivative $[Mn_6O_2(Piv)_{10}(THF)_4]$ as starting material for obtaining, for example, $[Mn_9K_2(O)_7(piv)_{15}(PivH)_2]$[25] and a series $[Mn_6O_2(Piv)_{10}(Lig)_4]$ complexes with nitroxides.[26] The first reaction between $[Mn_6O_2(Piv)_{10}(THF)_4]$ and salts of lanthanides was reported by Winpenny's group[27] where the reaction was done in a mixture of CH_2Cl_2/CH_3OH and the final product has a tetranuclear $[Mn_2Ln_2O_2]$ core with a distorted butterfly configuration. The Mn_6 starting material used in the present paper also has a similar structure to other $[Mn_6O_2(O_2CR)_{10}(Lig)_4]$ complexes, where HO_2CR is benzoic acid or its derivatives and Lig is a neutral ligand such as CH_3CN, Py, Et–OH, DMF, and so forth.[28]

It should be noted, that all above-mentioned Mn_6 complexes have an edge-sharing bi-tetrahedral $[Mn^{II}_4Mn^{III}_2(\mu_4\text{-}O)_2]^{10+}$ core with common $Mn^{II}_4Mn^{III}_2$ oxidation levels. In these complexes, the two Mn^{III} atoms occupy the central edge-sharing positions, and the four Mn^{II} atoms occupy the end sites. The magnetic properties of all

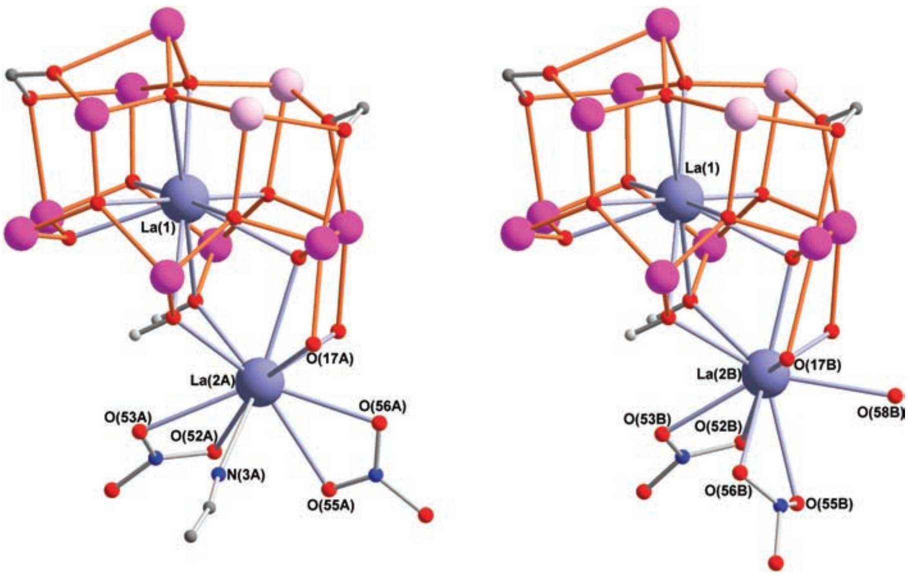

Figure 2. Core of compound **1** showing the ligand and metal disorder on La(2).

these complexes are dominated by antiferromagnetic exchange interactions leading to a diamagnetic ground state. Recently, a series of Mn_6 compounds with similar structural fragments, but with the core now comprising $2Mn^{II}$ and $4Mn^{III}$ atoms to give a $[Mn^{II}_2Mn^{III}_4(\mu_4\text{-}O)_2]^{12+}$ edge-sharing bitetrahedral core, were obtained.[29] Magnetic susceptibility measurements on these compounds, in contrast to the complexes with the common $[Mn^{II}_4Mn^{III}_2]$ core, reveal the occurrence of competing exchange interactions resulting in an $S = 5$ ground spin state.

The reaction of $[Mn_6O_2(Piv)_{10}(4\text{-Me-py})_{2.5}(PivH)_{1.5}]$ with $Ln(NO_3)_3\cdot 6H_2O$ in a 1:4 molar ratio in MeCN in the presence of furoic acid gave a dark brown solution from which, after filtration and slow evaporation, dark brown crystals of $[Mn_{11}Ln_2(O)_8(OH)_2(Piv)_{17-x}(C_4H_3OCOO)_x(NO_3)_2H_2O]\cdot nCH_3CN\cdot H_2O$ could be isolated in a yield of about 25%. The yields could be optimized to 40% if the solutions were not disturbed and allowed to stand for one week or more. It should be mentioned at this point that all attempts to synthesize the Tb^{III} or Dy^{III} (that usually display high magnetic anisotropy) analogues, as well those of the heavier lanthanides, under either the same or the modified reaction conditions resulted in different materials, which will be published elsewhere. However, although the synthesis of analogues with lanthanides heavier than gadolinium failed to produce the desired materials, analogues for most of the lighter lanthanide ions situated to the left of gadolinium could be isolated. As we have previously shown,[8e] it is of considerable assistance for the analysis of the magnetic behavior of families of isostructural 3d-4f aggregates to produce an analogue containing a diamagnetic rare earth ion to judge the contribution of the 3d ions, and here we were able to obtain the La^{III} analogue.

Description of Crystal Structures. The $Mn_{11}Ln_2$ aggregates **1**−**5** crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$. We have previously communicated the structure of compound **5**;[8d] the structure of the $Mn_{11}Eu_2$ analogue **4** will be briefly described here (Figure 1). The oxidation states of the Mn centers were determined by bond-valence sum (BVS) calculations,[30] with Mn(1)−Mn(9) assigned as Mn^{III}, and Mn(10) and Mn(11) as Mn^{II}. The assignments of O(10) as $(\mu_3\text{-}O)^{2-}$ and of O(2) and O(3) as $(\mu_3\text{-}OH)^{-}$ were also confirmed by BVS calculations, although in any case the H-atoms on O(2) and O(3) could be located and refined.

The core of the complex **4** can be described as bell-shaped. The Mn^{III} and Mn^{II} centers form the shell of the bell, with Mn(9) at the apex, Mn(5), Mn(8), Mn(10), and Mn(11) at the shoulder of the bell, and the remaining six Mn^{III} centers forming the rim of the bell. The 11 Mn centers are linked via the 8 oxido ligands, and also by two (μ_4,η^2,η^2)-carboxylate bridges, in which each oxygen bridges two metal sites. The Mn−O bonds to bridging oxygens are shown as orange, and the bridging Eu−O bonds as pale green, in Figure 1. The two Eu centers can be thought of as forming the clapper of the bell, and since the Eu··Eu vector is inclined with respect to the axis of the bell, this gives the impression that the bell is ringing. Eu(1) is 10-coordinate, and is connected to each of the 11 Mn atoms through the 6 $(\mu_4\text{-}O)$, 1 $(\mu_3\text{-}O)$, and 2 $(\mu_3\text{-}OH)$ bridges. Its coordination polyhedron may be best described as a bicapped square-antiprism. The second Eu is nine-coordinate and hangs below the rim of the bell. It is connected to the other Eu and to four Mn^{III} ions in the rim of the bell through one $(\mu_4\text{-}O)$, O(1), and the two $(\mu_3\text{-}OH)$ bridges, and two oxygen atoms from two $(\mu_3\text{-carboxylate})$ bridges. The Eu−O bonds to bridging oxygens are highlighted in pale green in Figure 1. The coordination sphere of Eu(2) is completed by two chelating nitrate ions. The $Mn_{11}Pr_2$ and $Mn_{11}Nd_2$ compounds, **2** and **3**, are isostructural to **4** and **5**.

The Mn centers all have octahedral coordination geometries, except for Mn(6) which is square-pyramidal, with the Mn^{III} centers Mn(1)−Mn(9) all showing the expected Jahn−Teller distortions; the elongated Mn^{III}−O bonds are shown dotted in Figure 1. The Mn^{III} Jahn−Teller axes have an irregular arrangement within the aggregate core. Of the 17 carboxylate ligands (10 pivalate, 6 furoate, and 1 that is a disordered superposition of the two), the unusual (μ_4,η^2,η^2) bridging mode is seen for one furoate and one pivalate ligand. In addition to these μ_4-bridging carboxylates, four of the furoates adopt a (μ_3,η^2,η^1) triply bridging mode, while the sixth furoate and all the remaining pivalates form simple *syn,syn*-bridges between two metal centers. Overall, five of the six furoates bridge between either three or four

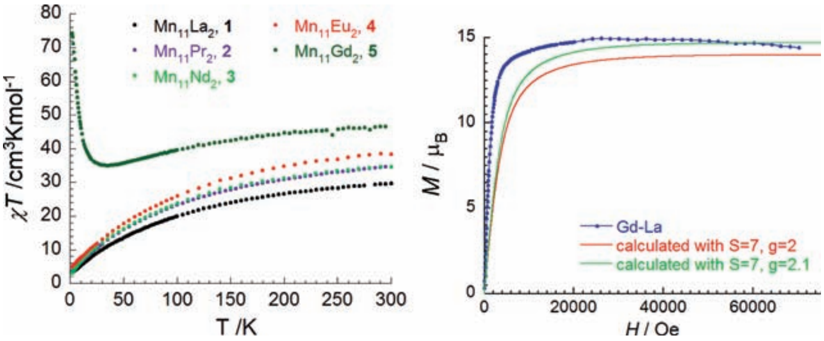

Figure 3. (Left): χT vs T plots for complexes **1**−**5** ($Mn_{11}La_2$, $Mn_{11}Pr_2$, $Mn_{11}Nd_2$, $Mn_{11}Eu_2$, and $Mn_{11}Gd_2$, respectively) in 1000 Oe applied *dc* field. (Right): Field dependence of residual contribution of [Gd_2] to the magnetization at 1.8 K (see text for information); the two solid lines (green and red) correspond to the calculated curves with the indicated Brillouin functions.

metal centers, whereas all but one of the pivalates adopt a simple μ_2-bridging mode.

In the structure of **1**, the significantly larger ionic radius of La^{III} is reflected in a higher coordination number for La(2), which is now also 10-coordinate, with an additional terminal ligand compared to **2**−**5**. In approximately half the molecules in the crystal, this extra neutral ligand is an acetonitrile; in the other molecules it is water molecule. This ligand disorder then resulted in a slight but resolvable disorder for La(2); when La(2a) and La(2b) were each set at 50% occupancy, their anisotropic thermal parameters could be refined independently and gave very similar values, and the disorder was therefore fixed at 50:50 in the refinement. The resulting disordered superposition is shown in Figure 2.

Magnetic Properties of 1−**5.** The temperature dependence of the magnetic susceptibility for compounds **1**−**5** under a 1000 Oe applied field are plotted in Figure 3, left. The χT versus T plots of $Mn_{11}La_2$ (**1**), $Mn_{11}Pr_2$ (**2**), $Mn_{11}Nd_2$ (**3**), and $Mn_{11}Eu_2$ (**4**) show a similar profile, where the χT value decreases continuously from room temperature to 1.8 K upon lowering the temperature. For the analogue containing diamagnetic La^{III}, **1**, this behavior indicates the presence of dominating antiferromagnetic (AF) interactions between the nine Mn^{III} and two Mn^{II} centers. The room temperature χT value of 29.7 cm^3 K mol^{-1} in **1** is lower than that expected for noninteracting Mn^{III} and Mn^{II} ions (35.75 cm^3 K mol^{-1}) suggesting that these antiferromagnetic interactions are rather strong. This is further supported by the magnetization curves at low temperatures (Supporting Information, Figure S1a), where the magnetization of **1** at 1.8 K and 70 kOe approaches only 8.1 μ_B which is significantly lower than the value (46 μ_B) for all spins aligned in the same direction; the antiferromagnetic interactions are here too strong to be overcome by the available applied *dc* field. The room temperature χT values of **2**, **3**, and **4** are 34.6, 34.7, and 38.4 cm^3 K mol^{-1}, respectively. Compared to the experimental χT value of **1** (29.7 cm^3 K mol^{-1}), the higher values of the susceptibility product for **2** and **3** are close to the additional contribution of the Curie constant for two Pr^{III}, or two Nd^{III}, respectively, while that for **4** can be ascribed to the thermal population of low-lying excited states of the Eu^{III} ions.[31] Therefore, we can conclude that in compounds **2**, **3**, and **4**, the interactions between $Mn^{II/III}$ and Ln^{III} (Pr^{III} and Nd^{III}) are very weak, and that the antiferromagnetic interactions within the [Mn_{11}] shell are probably very similar to those observed in the $Mn_{11}La_2$ analogue **1**. In these systems, the Mn-Ln^{III} magnetic interactions are difficult to evaluate in both sign and magnitude because of the complicated intrinsic magnetic properties of the Pr^{III} and Nd^{III} metal ions (spin−orbit coupling and low symmetry of the crystal field) and the weak nature of these interactions compared to the strongly antiferromagnetic Mn−Mn interactions. The continuous decrease of the χT values down to 1.8 K suggests that the ground states are not well-defined in these compounds. This observation is also consistent with the field dependence of magnetization measurements, in which the continuous rise of the magnetization up to 70 kOe is indicative of the presence of populated excited levels (Supporting Information, Figure S1a−d).

In the case of compound **5**, a different thermal evolution of χT was observed below 30 K (Figure 3, left).[8d] The *dc* magnetic susceptibility of **5** reveals a room temperature χT value per complex of 46.9 cm^3 K mol^{-1}, which is lower than the expected value for nine Mn^{III} (S = 2), two Mn^{II} (S = 5/2), and two Gd^{III} (S = 7/2) noninteracting ions (51.5 cm^3 K mol^{-1}). On lowering the temperature, the χT at first decreases continuously, reaching 35.2 cm^3 K mol^{-1} at 37 K, but then increases sharply to a maximum value at 1.81 K of 74.5 cm^3 K mol^{-1}. The χT product starts to saturate at 1.8 K suggesting that below this temperature a well-defined high-spin ground state with S = 11−12 is almost exclusively thermally populated. The increase of the χT product below 37 K suggests a noncompensated spin arrangement within the spin carriers. The main contribution to the spin structure at low temperature probably arises from the Gd_2 unit, which appears to have a ferromagnetic Gd−Gd interaction. This hypothesis is supported by the sharp increase of magnetization at fields of 5000 Oe below (Supporting Information, Figure S1e). Such ferromagnetic couplings between Gd^{III} ions are not commonly observed, but a few examples are known.[32] The Gd−Gd separations in those reported examples are in the range 4.18−4.93 Å, with the angles of the corresponding oxido bridges in the range 112−140°. In compound **5**, the Gd−Gd separation is only 3.728 Å and the three Gd−O−Gd angles are only 96.44(10), 97.24(10), and 98.77(11)°. This, together with a comparison of the structural parameters, allows us to conclude that the Gd−Gd unit in **5** is ferromagnetically coupled and its coupling strength is likely to be larger than those observed in the reported examples,[32] as a consequence of the close to orthogonal (∼97°) magnetic orbitals between the interacting Gd^{III} ions. To investigate the magnetic interaction between the Mn_{11} shell and the Gd^{III} ions, the magnetization of **1** containing diamagnetic La^{III} and thus no contribution from 4f electrons, can be subtracted from that of **5**. This gives an indication of the contribution of the [Gd_2] unit to the magnetization. However, a Brillouin function of $S = 7$ with $g = 2.0$ or 2.1, corresponding to a ferromagnetically coupled $[Gd_2]$ moiety (Figure 3, right), does not reproduce the experimental magnetization curve below 10 kOe with the experimental data lying higher than the calculated curves. Although the anisotropy is significant, the spin ground state is not the only one thermally populated and therefore the ferromagnetic interactions between the Mn_{11} shell and the Gd^{III} ions dominate the magnetic behavior at low temperature.

A more quantitative analysis of the magnetic properties of the present compounds is however not possible as a result of (i) the large number of magnetic pathways for exchange between spin carriers, even in the La^{III} case, (ii) the presence of Pr^{III}, Nd^{III} with a small unquenched orbital contribution that cannot be easily modeled, (iii) the presence of Gd^{III} ions resulting in a very high number of spins in **5**, (iv) the progressive thermal population of paramagnetic Eu^{III} excited states in **4** with increasing temperature, and (v) the magnetic interactions between the $Mn^{II/III}$ and Ln^{III} metal ions appear weak in **2**−**4**, such that excited states may be populated even at 1.8 K in these compounds.

The *ac* susceptibility of these compounds in zero *dc* field was measured to probe the slow relaxation of magnetization. For compounds **1**−**4**, the *ac* susceptibilities show a complete absence of any out-of-phase component, confirming that these complexes do not behave as SMMs above 1.8 K. However, as we previously reported, the *ac* susceptibility measurements for **5** over the frequency range 1−1500 Hz and in the temperature range 1.8−3 K display frequency-dependent out-of-phase signals suggesting that the complex exhibits slow relaxation of its magnetization and thus potential SMM behavior.[8d] This was further investigated using single crystal magnetization measurements performed on an array of micro-SQUIDs at temperatures down to 40 mK.[8d,33] Hysteresis loops collected for complex **5** at varying temperatures and sweep rates show a superparamagnet-like increasing coercivity with decreasing temperature confirming **5** to be a SMM (Supporting Information, Figures S2 and S3). No steps due to quantum tunneling of magnetization (QTM) were observed; *dc* magnetization decay data was collected in the 0.04−1.0 K range. At each temperature, the magnetization was saturated with a *dc* field, the temperature lowered to a chosen value, the field switched off, and the decay monitored with time. The data were scaled in a single master curve to construct the Arrhenius plot (Supporting Information, Figure S4), and the fit of the thermally activated region above ~0.5 K gave $\tau_0 = 2 \times 10^{-12}$ s and an effective barrier $\Delta_{\mathrm{eff}} = 18.4$ K. Below ~0.16 K, the relaxation time becomes essentially temperature-independent, consistent with a purely quantum regime where QTM is only via the lowest energy $\pm m_s$ levels.

The Jahn−Teller axes of six of the nine Mn^{III} centers (Figure 1) subtend reasonably small angles with the vertical axis of the "bell". The axes of the other three Mn^{III} ions (Mn(5), Mn(8), and Mn(9)) are approximately perpendicular to the vertical axis, resulting in an incomplete cancellation of the single-ion anisotropies. It is thus likely that the Jahn−Teller distortions of the Mn^{III} centers make the major contribution to the molecular anisotropy (D_m), with the essentially isotropic Mn^{II} and Gd^{III} centers contributing mainly to the spin (S). In the La^{III} compound **1**, strong antiferromagnetic interactions within the Mn_{11} unit lead to a rather small spin ground state (S) of less than 4. From the M vs H plot of $Mn_{11}La_2$ compound we also see a lack of saturation of magnetization indicating the Mn_{11} shell (bell) is the underlying cause of the molecular anisotropy. While this could also be true for the $Mn_{11}Gd_2$ compound, where it is generally expected that the anisotropy from the $4f^7$ Gd^{3+} will be small, this reasoning ignores the contributions which single ion excited states can provide for seemingly isotropic ions such as Gd^{III}. As an example, the contributions to magnetic anisotropy made by high spin Fe^{III} is well-documented, but nevertlhess often ignored, and the suggestion that the Gd^{III} is able to provide anisotropic contributions cannot be completely excluded.

Nvertheless, we can expect the molecular anisotropy originates mostly from the Mn_{11} shell and is probably similar in all the compounds. Therefore, the reason for SMM behavior being observed in the Gd^{III} compound but not in the other analogues (La^{III}, Pr^{III}, Nd^{III}, Eu^{III}) is likely to be the much higher molecular spin ground state ($S = 11-12$) observed for **5**. This results from the ferromagnetic coupling of the two Gd^{III} ions to each other and of this unit to the Mn_{11} bell. The combination of this with the Mn_{11}-based anisotropy results in a sufficiently high energy barrier to reversal of magnetization for SMM behavior to be observed. We can also note that in the case of our previously reported polynuclear $Mn_{10}Pr_2$ and $Mn_{10}Nd_2$ complexes, with similar nuclearity to **1**−**5**, we observed weak but obvious *ac* signals, and this is probably the result of the much higher spin ground states ($S = 17/2$)[9f] for these compared with those in **2** and **3**.

■ CONCLUSIONS

We have synthesized and characterized analogues of our previously reported[8d] $Mn_{11}Gd_2$ aggregate **5** using lanthanides (La, Pr, Nd, Eu) from the left half of the lanthanide series. Strong antiferromagnetic interactions are present between the manganese ions leading to a small spin ground state for the Mn_{11} shell unit. However, in the Gd^{III} compound **5** the effect of ferromagnetic interactions is observed below 37 K, probably as a result of two ferromagnetically coupled Gd^{III} ions being in turn ferromagnetically coupled to the surrounding Mn_{11} shell, giving a spin ground state of $S = 11-12$. Only the $Mn_{11}Gd_2$ compound **5** shows evidence of magnetic slow relaxation above 1.8 K, and this appears to be the consequence of the much higher spin ground state compared with those of **1**−**4**, combined with a relatively small overall molecular anisotropy. The frequency-dependent out-of-phase *ac* susceptibility data for **5** are the result of slow relaxation of the magnetization characteristic of SMMs, which is confirmed by the observation of hysteresis loops at low temperatures. This work has demonstrated that an in-depth study of analogues of our previously reported $Mn_{11}Gd_2$ aggregate can contribute to the understanding of its magnetic properties. Finally, the presence of two different types of carboxylate ligands in the structure opens the possibility to introduce different S-containing derivatives in place of furoic acid, to give similar clusters that could be deposited on gold surfaces. This is the target of future work.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Further details are given in Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: annie.powell@kit.edu. Fax: +49 721 608 48142. Phone: +49 721 608 42135.

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