Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 8067–8072 **8067**
DOI: 10.1021/ic1011605

Series of Isostructural Planar Lanthanide Complexes $[Ln^{III}_4(\mu_3\text{-}OH)_2(mdeaH)_2(piv)_8]$ with Single Molecule Magnet Behavior for the Dy_4 Analogue

Ghulam Abbas,[†] **Yanhua Lan,**[†] **George E. Kostakis,**[‡] **Wolfgang Wernsdorfer,**[§] **Christopher E. Anson,**[†] and **Annie K. Powell***[,†,‡]

[†]*Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesser Strasse 15, D-76131, Karlsruhe, Germany,* [‡]*Institute of Nanotechnology, Karlsruhe Institute of Technology, Postfach 3640, D-76021, Karlsruhe, Germany, and* [§]*Institut Néel, CNRS & University J. Fourier, BP 166, 38042, Grenoble, Cedex 9, France*

Received June 9, 2010

A series of five isostructural tetranuclear lanthanide complexes of formula $[Ln_4(\mu_3\text{-}OH)_2(mdeaH)_2(piv)_8]$, ($mdeaH_2$ = *N*-methyldiethanolamine; piv = pivalate; Ln = Tb (**1**), Dy (**2**), Ho (**3**), Er (**4**), and Tm (**5**)) have been synthesized and characterized. These clusters have a planar "butterfly" Ln_4 core. Magnetically, the Ln^{III} ions are weakly coupled in all cases; the Dy_4 compound **2** shows Single Molecule Magnet (SMM) behavior.

Introduction

It is now well established that paramagnetic metal ion coordination clusters can display the phenomenon of single-molecule magnetism (SMM).[1] Whereas attention was initially focused on coordination clusters containing 3d metal ions, especially the high spin Mn^{III} ion,[2] significant attention is now being paid to incorporating 4f ions into SMMs in either mixed 3d/4f or pure 4f clusters.[3] The nature of the 4f orbitals and the fact that 4f electrons are well shielded from external fields by the overlying $5s^2$ and $5p^6$ shells means that the ligand field approach and relatively strong quenching of the orbital component contribution to the magnetism seen for most 3d configurations no longer apply when 4f electrons are present. Thus, although the couplings between 3d and 4f and between 4f metal ions are expected to be significantly weaker than those seen for 3d coordination clusters, the contribution of the orbital component to the magnetic anisotropy of the coordination cluster can significantly enhance the barrier height to spin inversion in 3d/4f compounds,[4] or in pure 4f compounds lead to unusual situations such as non-collinear Ising spins and SMM behavior arising from excited states.[5] The synthesis of polynuclear lanthanide clusters is achieved by controlling the hydrolysis of the metal ion[6] aqueous solution or else in the presence of water molecules (e.g., from the metal salt) in a mixture of organic solvents through the presence of organic ligands. In this way, 4f metal clusters with nuclearities ranging from Ln_2,[7] Ln_3,[5] Ln_4,[8] Ln_5,[9] Ln_6,[10] Ln_7,[11] Ln_8,[12] Ln_9,[13] Ln_{10},[14]

---

*To whom correspondence should be addressed. E-mail: annie.powell@kit.edu. Fax: +49 721 608 8142. Phone: +49 721 608 2135.

(1) Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804.

(2) (a) Milios, C. J.; Vinslava, A.; Moggach, S.; Parsons, S.; Wernsdorfer, W.; Christou, G.; Perlepes, S. P.; Brechin, E. K. *J. Am. Chem. Soc.* **2007**, *129*, 2754. (b) Kostakis, G. E.; Ako, A. M.; Powell, A. K. *Chem. Soc. Rev.* **2010**, *39*, 2238.

(3) Sessoli, R.; Powell, A. K. *Coord. Chem. Rev.* **2009**, *253*, 2328.

(4) Mereacre, V.; Ako, A. M.; Clérac, R.; Wernsdorfer, W.; Hewitt, I. J.; Anson, C. E.; Powell, A. K. *Chem.—Eur. J.* **2008**, *14*, 3577.

(5) (a) Tang, J.; Hewitt, I. J.; Madhu, T. N.; Chastanet, G.; Wernsdorfer, W.; Anson, C. E.; Powell, A. K. *Angew. Chem., Int. Ed.* **2006**, *45*, 1729. (b) Luzon, J.; Bernot, K.; Hewitt, I. J.; Anson, C. E.; Powell, A. K.; Sessoli, R. *Phy. Rev. Lett.* **2008**, *100*, 247205. (c) Hewitt, I. J.; Lan, Y.; Anson, C. E.; Luzon, J.; Sessoli, R.; Powell, A. K. *Chem. Commun.* **2009**, 6765.

(6) Zheng, Z. *Chem. Commun.* **2001**, 2521.

(7) (a) Lin, P.-H.; Burchell, T. J.; Clérac, R.; Murugesu, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 8848. (b) Bao, S.-S.; Ma, L.-F.; Wang, Y.; Fang, L.; Zhu, C.-J.; Li, Y.-Z.; Zheng, L.-M. *Chem.—Eur. J.* **2007**, *13*, 2333. (c) Messimeri, A.; Papadimitriou, C.; Raptopoulou, C. P.; Escuer, A.; Perlepes, S. P.; Boudalis, A. K. *Inorg. Chem. Commun.* **2007**, *10*, 800. (d) Thiakou, K. A.; Bekiari, V.; Raptopoulou, C. P.; Psycharis, V.; Lianos, P.; Perlepes, S. P. *Polyhedron* **2006**, *25*, 2869. (e) Saalfrank, R. W.; Nakajima, T.; Mooren, N.; Scheurer, A.; Maid, H.; Hampel, F.; Trieflinger, C.; Daub, J. *Eur. J. Inorg. Chem.* **2005**, 1149. (f) Xu, G.-F.; Wang, Q.-L.; Gamez, P.; Ma, Y.; Clérac, R.; Tang, J.; Yan, S.-P.; Cheng, P.; Liao, D.-Z. *Chem. Commun.* **2010**, *46*, 1506.

(8) (a) Ma, B.-Q.; Zhang, D.-S.; Gao, S.; Jin, T.-Z.; Yan, C.-H.; Xu, G.-X. *Angew. Chem., Int. Ed.* **2000**, *39*, 3644. (b) Bi, Y.; Wang, X.-T.; Liao, W.; Wang, X.; Deng, R.; Zhang, H.; Gao, S. *Inorg. Chem.* **2009**, *48*, 11743. (c) Lin, P.-H.; Burchell, T. J.; Ungur, L.; Chibotaru, L. F.; Wernsdorfer, W.; Murugesu, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 9489. (d) Gao, Y.; Xu, G.-F.; Zhao, L.; Tang, J.; Liu, Z. *Inorg. Chem.* **2009**, *48*, 11495. (e) Zheng, Y.-Z.; Lan, Y.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2008**, *47*, 10813.

(9) (a) Poncelet, O.; Sartain, W. J.; Hubert-Pfalzgraf, L. G.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 263. (b) Roesky, P. W.; Canseco-Melchor, G.; Zulys, A. *Chem. Commun.* **2004**, 738. (c) Gamer, M. T.; Lan, Y.; Roesky, P. W.; Powell, A. K.; Clérac, R. *Inorg. Chem.* **2008**, *47*, 6581.

(10) (a) Zhang, D.-S.; Ma, B.-Q.; Jin, T.-Z.; Gao, S.; Yan, C.-H.; Mak, T. C. W. *New J. Chem.* **2000**, *24*, 61. (b) Wang, R.; Carducci, M. D.; Zheng, Z. *Inorg. Chem.* **2000**, *39*, 1836. (c) Mahe, N.; Guillou, O.; Daiguebonne, C.; Gérault, Y.; Caneschi, A.; Sangregorio, C.; Chane-Ching, J. Y.; Car, P. E.; Roisnel, T. *Inorg. Chem.* **2005**, *44*, 7743. (d) Hussain, B.; Savard, D.; Burchell, T. J.; Wernsdorfer, W.; Murugesu, M. *Chem. Commun.* **2009**, 1100. (e) Calvez, G.; Daiguebonne, C.; Guillou, O.; Le Dret, F. *Eur. J. Inorg. Chem.* **2009**, 3172.

Ln_{12},[15] Ln_{13},[16] Ln_{14},[17] Ln_{15},[15,18] Ln_{26},[19] through to Ln_{60},[20] have been reported. To understand how the magnetic anisotropy of 4f ions directs the SMM properties of multinuclear compounds of these, we have found that it is helpful to focus on lower nuclearity clusters such as a Dy_3,[5] Dy_4,[8e] and Dy_5.[9c]

Using *N*-methyldiethanolamine ($mdeaH_2$), a ligand which has been widely employed in the synthesis of 3d and 3d/4f coordination clusters,[21,22] we reported the synthesis of an isostructural series of dinuclear lanthanide complexes formulated as $[Ln_2(mdeaH_2)_2(piv)_6]$ where Ln = La, Ce, Pr, Nd, Sm, and Gd, piv = pivalate.[21] The magnetic studies of those compounds showed that the *syn,syn*-carboxylate bridges mediate vanishingly small magnetic interactions between these lighter Ln^{III} cations. It is well-known that the decrease of the ionic radius and preferred coordination number on going across the lanthanide series (the lanthanide contraction) affects the shape and the nuclearity of the final product. The same synthetic procedure, when applied to the magnetically interesting heavier lanthanides, results in the formation of five isostructural tetranuclear complexes of general molecular formula $[Ln_4(\mu_3\text{-}OH)_2(mdeaH)_2(piv)_8]$ where Ln = Tb (**1**), Dy (**2**), Ho (**3**), Er (**4**), and Tm (**5**), the syntheses, characterization, and magnetic properties of which we report here.

Experimental Section

General Information. All chemicals and solvents used for synthesis were obtained from commercial sources and were used as received, without further purification. All reactions were carried out at aerobic conditions. The elemental analysis (C, H, N) were carried out at the Institute of Inorganic Chemistry, Karlsruhe Institute of Technology (TH) using an Elementar Vario EL analyzer. Fourier transform IR spectra were measured on a Perkin-Elmer Spectrum one spectrometer with samples prepared as KBr discs.

Synthesis of $[Dy_4(\mu_3\text{-}OH)_2(mdeaH)_2(piv)_8]$ (2). The same procedure was employed to prepare all complexes and hence only the compound **2** is described here in detail. Furthermore, although reactions with the corresponding Yb^{III} and Lu^{III} salts were performed, it was not possible to obtain pure products. Since neither of these analogues would be magnetically interesting, we did not pursue this further.

A solution of *N*-methyldiethanolamine (0.089 g, 0.75 mmol) in MeCN (15 mL) was added dropwise over 20 min to stirred solution of $Dy(NO_3)_3 \cdot 6H_2O$ (0.114 g, 0.25 mmol) and pivalic acid (0.101 g, 1.00 mmol) in MeCN (15 mL). The resulting mixture was stirred at room temperature (RT) for 2 h more, filtered and allowed to stand undisturbed in a sealed vial. Colorless needles of **2** suitable for X-ray crystallography were obtained after 3 days.The crystals of **2** were maintained in mother liquor for X-ray crystallography or collected by filtration, washed with MeCN and dried in vacuum; Yield: ~ 45%. Anal. Calcd (found) for $C_{48}H_{96}N_2O_{20}Dy_4$: C, 34.50 (34.20); H, 5.79 (5.45); N, 1.68 (1.82)%. IR (KBr): ν (cm^{-1}) = 3423 (w), 2960 (s), 2927 (w), 2867 (w), 1566 (vs), 1514 (m), 1485 (s), 1423 (s), 1376 (m), 1361 (m), 1320 (w), 1327 (m), 1228 (s), 1151 (w), 1137 (w), 1086 (w), 1077 (w), 1046 (w), 971 (w), 938 (w), 897 (m), 808 (m), 792 (m), 776 (w), 608 (m), 559 (w), 468 (w). Compound **1**: Yield: ~ 45%. Anal. Calcd (found) for $C_{50}H_{98}N_2O_{22}Tb_4$: C, 35.00 (35.00); H, 5.76 (5.81); N, 1.63 (1.64)%. IR (KBr): ν (cm^{-1}) = 3414 (w), 2959 (s), 2926 (w), 2867 (w), 2812 (w), 1566 (vs), 1513 (w), 1485 (s), 1459 (m), 1423 (s), 1375 (m), 1360 (m), 1321 (w), 1228 (s), 1137 (w), 1085 (s), 1046 (w), 1030 (w), 995 (w), 971 (w), 937 (w), 896 (s), 808 (m), 792 (m), 774 (w), 658 (w), 607 (m), 561 (w), 464 (w). Compound **3**: Yield: ~ 45%. Anal. Calcd (found) for $C_{50}H_{98}N_2O_{22}Ho_4$: C, 34.51 (34.13); H, 5.68 (5.20); N, 1.61 (1.55)%. IR (KBr): ν (cm^{-1}) = 3434 (m), 2960 (s), 2926 (w), 2866 (w), 1567 (vs), 1544 (w), 1485 (s), 1459 (m), 1426 (s), 1376 (m), 1360 (m), 1319 (w), 1229 (s), 1137 (w), 1088 (s), 1046 (w), 971 (w), 937 (w), 898 (s), 809 (m), 792 (m), 658 (w), 608 (m), 562 (w), 468 (w). Compound **4**: Yield: ~ 35%. Anal. Calcd (found) for $C_{50}H_{98}N_2O_{22}Er_4$: C, 35.00 (35.00); H, 5.76 (5.81); N, 1.63 (1.64)%. IR (KBr): ν (cm^{-1}) = 3427 (m), 2960 (s), 2923 (w), 2865 (w), 1568 (vs), 1516 (m), 1485 (s), 1460 (w), 1422 (s), 1376 (m), 1360 (m), 1318 (w), 1229 (s), 1137 (w), 1089 (s), 1046 (w), 971 (w), 937 (w), 898 (s), 809 (m), 792 (m), 608 (m), 562 (w), 470 (w). Compound **5**: Yield: ~ 45%. Anal. Calcd (found) for $C_{50}H_{98}N_2O_{22}Tm_4$: C, 34.20 (34.25); H, 5.63 (5.63); N, 1.60 (1.63)%. IR (KBr): ν (cm^{-1}) = 3412 (m), 2960 (s), 2926 (w), 2866 (w), 1570 (vs), 1546 (w), 1518 (w), 1485 (s), 1459 (m), 1432 (s), 1376 (m), 1360 (m), 1318 (w), 1229 (s), 1137 (w), 1089 (s), 1064 (w), 1046 (w), 971 (w), 938 (w), 899 (s), 810 (m), 792 (m), 683 (w), 608 (m), 563 (w), 472 (w).

Magnetic Measurements. The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for direct current (dc) applied fields ranging from −7 to 7 T. Measurements were performed on a polycrystalline sample of 8.8, 8.0, 7.9, 11.6, and 8.1 mg for compound **1**, **2**, **3**, **4**, and **5**, respectively. Alternating current (ac) susceptibility measurements for compounds **1**, **3**, **4**, and **5** have been checked with an oscillating ac field of 3 Oe and ac frequencies at 1000 Hz. For compound **2**, ac susceptibility data have been measured with an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. *M* versus *H* measurements have been performed at 100 K to check for the presence of ferromagnetic impurities that have been found absent. The magnetic data were corrected for the sample holder and diamagnetic contribution.

X-ray Data Collection and Structure Determination. Data were collected at 150 K on a Stoe IPDS II area detector diffractometer (**1**) or at 100 K on a Bruker SMART Apex CCD diffractometer (**2**−**5**) using graphite-monochromated Mo Kα radiation. Semiempirical absorption corrections were

---

(11) Zheng, X.-J.; Jin, L.-P.; Gao, S. *Inorg. Chem.* **2004**, *43*, 1600.

(12) Kajiwara, T.; Wu, H.; Ito, T.; Iki, N.; Miyano, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1832.

(13) (a) Hubert-Pfalzgraf, L. G.; Miele−Pajot, N.; Papiernik, R.; Vaissermann, J. *J. Chem. Soc., Dalton Trans.* **1999**, 4127. (b) Xu, G.; Wang, Z.-M.; He, Z.; Lü, Z.; Liao, C.-S.; Yan, C.-H. *Inorg. Chem.* **2002**, *41*, 6802. (c) Manseki, K.; Yanagida, S. *Chem. Commun.* **2007**, 1242. (d) Xu, G.-F.; Gamez, P.; Teat, S. J.; Tang, J. *Dalton Trans.* **2010**, *39*, 4353.

(14) (a) Westin, L. G.; Kritikos, M.; Caneschi, A. *Chem Commun.* **2003**, 1012. (b) Kornienko, A.; Emge, T. J.; Kumar, G. A.; Riman, R. E.; Brennan, J. G. *J. Am. Chem. Soc.* **2005**, *127*, 3501. (c) Yang, X.; Jones, R. A.; Wiester, M. J. *Dalton Trans.* **2004**, 1787. (d) Ke, H.; Xu, G.-F.; Zhao, L.; Tang, J.; Zhang, X.-Y.; Zhang, H.-J. *Chem.—Eur. J.* **2009**, *15*, 10335. (e) Ke, H.; Zhao, L.; Xu, G.-F.; Guo, Y.-N.; Tang, J.; Zhang, X.-Y.; Zhang, H.-J. *Dalton Trans.* **2009**, 10609.

(15) (a) Wang, R.; Selby, H. D.; Liu, H.; Carducci, M. D.; Jin, T.; Zheng, Z.; Anthis, J. W.; Staples, R. J. *Inorg. Chem.* **2002**, *41*, 278. (b) Andrews, P. C.; Beck, T.; Forsyth, C. M.; Fraser, B. H.; Junk, P. C.; Massi, M.; Roesky, P. W. *Dalton Trans.* **2007**, 5651.

(16) Chesman, A. S. R.; Turner, D. R.; Moubaraki, B.; Murray, K. S.; Deacon, G. B.; Batten, S. R. *Chem.—Eur. J.* **2009**, *15*, 5203.

(17) (a) Bürgstein, M. R.; Gamer, M. T.; Roesky, P. W. *J. Am. Chem. Soc.* **2004**, *126*, 5213. (b) Bürgstein, M. R.; Roesky, P. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 549. (c) Wang, R.; Song, D.; Wang, S. *Chem Commun.* **2002**, 368.

(18) Wang, R.; Zheng, Z.; Jin, T.; Staples, R. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1813.

(19) Gu, X.; Xue, D. *Inorg. Chem.* **2007**, *46*, 3212.

(20) Kong, X.-J.; Wu, Y.; Long, L.-S.; Zheng, L.-S.; Zheng, Z. *J. Am. Chem. Soc.* **2009**, *131*, 6918.

(21) Abbas, G.; Lan, Y.; Kostakis, G.; Anson, C. E.; Powell, A. K. *Inorg. Chim. Acta* **2008**, *361*, 3494.

(22) (a) Mishra, S.; Daniele, S.; Petit, S.; Jeanneau, E.; Rolland, M. *Dalton Trans.* **2009**, 2569. (b) Biswas, B.; Weyhermüller, T.; Bill, E.; Chaudhuri, P. *Inorg. Chem.* **2009**, *48*, 1524.

made using SADABS[23a] or XPREP in SHELXTL.[23b] The structures were solved using direct methods, followed by full-matrix least-squares refinement against F^2 (all data) using SHELXTL.[23b] Anisotropic refinement was used for all ordered non-H atoms; organic H atoms were placed in calculated positions, while coordinates of hydroxo H atoms were refined. Some *t*-butyl groups were rotationally disordered and were refined with two sets of partial methyl carbon atoms; suitable restraints were applied to the geometries and to the thermal parameters of the partial atoms. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 779341−779345. 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/cgi-bin/catreq.cgi, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

Results and Discussion

Synthesis. All the compounds were synthesized using refluxing conditions from the reaction of *N*-methyldiethanolamine, $Ln(NO_3)_3 \cdot 6H_2O$, and pivalic acid in molar ratio of 3:1:4 in MeCN (15 mL). In this case *N*-methyldiethanolamine acts not only as a ligand but also as the hydrolyzing base (note no other base is present). Changes to the molar ratio by decreasing the amount of *N*-methyldiethanolamine and increasing the amount of pivalic acid result in non-crystalline materials. Furthermore the usage of a polar solvent such as MeOH instead of MeCN, or a mixture of MeOH/MeCN, also lead to different products.

Description of the Structures. X-ray crystallographic analysis of all five compounds showed that they crystallize isomorphously in the triclinic space group $P\bar{1}$ with $Z = 1$. The molecular structure of the Ln = Dy analogue **2** is discussed here in detail and is shown in Figure 1. Selected bond lengths and angles for the five compounds are given in Table 2. Compound **2** has a crystallographically centrosymmetric, and therefore strictly planar, $Dy^{III}{}_4$ tetranuclear core. This motif is often referred to as a butterfly motif in terms of the positions of the metal centers with Dy(1) and Dy(1′) defining the hinge (or body) and Dy(2) and Dy(2′) the wing-tips. Although butterflies do not tend to lie completely flat, the descriptor recognizes the fact that the intermetallic distances are grouped, and it is thus to be expected that the magnitudes of pairwise couplings will also be different. The $Dy_3(\mu_3\text{-OH})$ bridge is slightly unsymmetrical, with Dy(1)−O(1) and Dy(2)−O(1), 2.373(4) and 2.334(4) Å, respectively, being rather shorter than Dy(1′)−O(1), 2.447(4) Å. Similarly the Dy−O−Dy angles are all rather different, at 101.72(16), 106.50(16) and 113.90(17)°. This results in a scalene Dy_3 triangle, with Dy(1)···Dy(1′), Dy(1)···Dy(2), and Dy(1′)···Dy(2) equal to 4.0407(6), 3.6509(4), and 3.8319(4) Å, respectively. The two $(\mu_3\text{-OH})^-$ ions are displaced above and below the Dy_4 plane by 0.872(4) Å (Table 1). Tetranuclear lanthanide coordination clusters with such coplanar core structures are so far not very common with only two other examples in the literature.[8c,e]

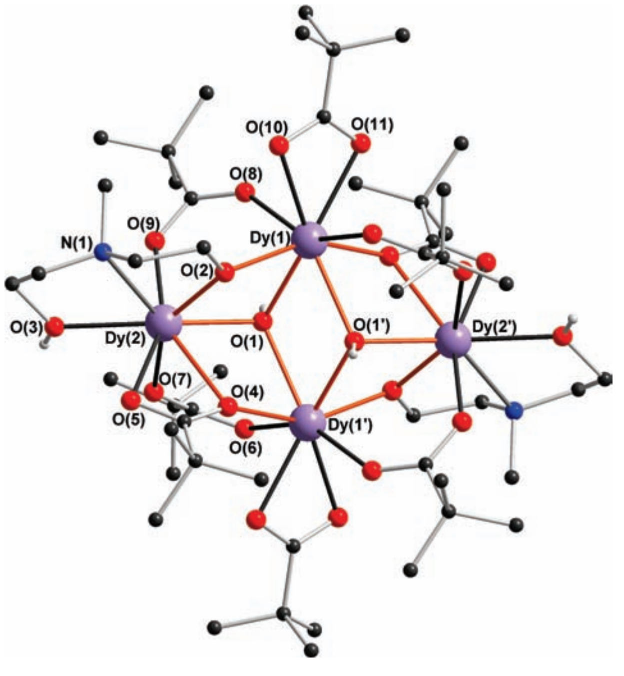

Figure 1. Molecular structure of **2**. Color code: Dy purple; O red; N blue; C gray. All C−H hydrogen atoms and minor components of disorder omitted for clarity.

Dy(2) is chelated by a singly deprotonated $(mdeaH)^-$ ligand. The deprotonated oxygen O(2) forms a bridge to Dy(1), with Dy(1)−O(2) 2.284(4) Å, Dy(2)−O(2) 2.258(4) Å, and Dy(1)−O(2)−Dy(2) 106.97(17)°, while the protonated ethanol arm is only unidentate. The remaining two edges of the core are bridged by $(\mu\text{-}\eta^1\text{:}\eta^2)$ chelating-bridging pivalates with O(4) bridging between Dy(2) and Dy(1′). Dy(1′)−O(4) is 2.370(4) Å, and Dy(2)−O(4) significantly longer at 2.543(4) Å, and the angle Dy(1′)−O(4)−Dy(2) is 102.43(16)°. Four further (μ-*syn,syn*) pivalates each bridge an outer edge of the Dy_4 core, and the coordination sphere of Dy(1) is completed by a chelating pivalate. The coordination numbers of the Dy^{III} ions are eight, DyO_8 for Dy(1) and DyO_7N for Dy(2). A detailed analysis of the coordination environments[24] reveals that Dy(1) has a geometry somewhat between dodecahedral (DOD) and bicapped trigonal-prismatic (BCTP) (φ angles 2.39° and 11.99°, dihedral angles 26.11°, 38.84°, 41.46°, 43.08°), while Dy(2) has a distorted dodecahedral (DOD) coordination environment (φ angles 0.23° and 3.03°, dihedral angles 13.66°, 32.39°, 32.42°, 44.52°). The complexes are linked via hydrogen bonds between O(3)−H(3) and O(5) of the molecule at {2−*x*, 1−*y*, 1−*z*}, forming linear chains in the crystal, with O(3)···O(5′) distances in the range 2.749−2.807 Å. The shortest intermolecular Dy···Dy distance is 5.998 Å and is between adjacent molecules in such a chain. All other intermolecular Dy···Dy distances are over 8 Å.

Magnetic Properties. Variable-temperature dc magnetic susceptibility data for compounds **1**−**5** were collected in the temperature range 1.8−300 K under an applied field of 1000 Oe (Figure 2). The dc magnetic data of **1**−**5** are summarized in Table 3. The observed χT products at RT are in good agreement with the expected values for four non-interacting Ln^{III} ions. The temperature dependence of the magnetic susceptibilities for all

---

[23] (a) Sheldrick, G. M. *SADABS* (*the Siemens Area Detector Absorption Correction*); University of Göttingen: Göttingen, Germany, 1996. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

[24] Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

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

	1	**2**	**3**	**4**	**5**
formula	$C_{50}H_{98}N_2O_{22}Tb_4$	$C_{50}H_{98}Dy_4N_2O_{22}$	$C_{50}H_{98}Ho_4N_2O_{22}$	$C_{50}H_{98}Er_4N_2O_{22}$	$C_{50}H_{98}N_2O_{22}Tm_4$
M_r	1715.01	1734.38	1739.03	1748.34	1755.02
cryst size [mm]	0.09 × 0.06 × 0.03	0.19 × 0.16 × 0.13	0.15 × 0.12 × 0.06	0.22 × 0.18 × 0.13	0.21 × 0.18 × 0.14
color	colorless block	colorless block	colorless block	colorless block	colorless block
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T [K]	150(2)	100(2)	100(2)	100(2)	100(2)
a [Å]	11.690(2)	11.6333(6)	11.5997(9)	11.5786(6)	11.5849(13)
b [Å]	12.590(3)	12.5247(7)	12.4766(10)	12.4649(7)	12.4410(14)
c [Å]	12.785(4)	12.7437(7)	12.7131(10)	12.7065(7)	12.6697(15)
α [deg]	109.679(19)	109.759(1)	109.529(1)	109.510(1)	108.982(2)
β [deg]	98.642(19)	98.639(1)	98.669(1)	98.647(1)	98.675(2)
γ [deg]	102.994(17)	102.900(1)	102.859(1)	102.853(1)	102.897(2)
V [Å^3]	1673.2(7)	1651.0(3)	1639.0(2)	1634.14(15)	1633.20(3)
Z	1	1	1	1	1
ρ_{calcd} [g cm^{-3}]	1.702	1.739	1.7613	1.7765	1.7843
μ(Mo Kα) [mm^{-1}]	4.243	4.542	4.84	5.152	5.449
F(000)	848	852	856	860	864
reflns collected	9504	13701	11391	11442	11085
unique reflns	5913	7209	6537	7106	6917
R_{int}	0.0890	0.0275	0.0339	0.0282	0.0347
reflns obsd [$I > 2\sigma(I)$]	3005	5848	4724	5660	5097
parameters/restraints	349/87	349/92	361/90	379/92	358/3
GOF on F^2	0.959	1.055	1.014	1.037	1.009
R1 [$I > 2\sigma(I)$]	0.0693	0.0426	0.0483	0.0434	0.0409
wR2 (all data)	0.1488	0.1022	0.1129	0.1046	0.0996
largest diff. peak/hole [e Å^{-3}]	+0.97/−1.95	+2.71/−0.82	+1.60/−0.95	+2.51/−0.86	+2.15/−0.94
CCDC number	779341	779342	779343	779344	779345

Table 2. Structural Parameters (Å, deg) for Ln−O−Ln Bridges, Ln Coordination Geometry, and Ln_4 Butterfly Core for Compounds **1**−**5**

	1 (Ln = Tb)	**2** (Ln = Dy)	**3** (Ln = Ho)	**4** (Ln = Er)	**5** (Ln = Tm)
Ln(1)−O(1)	2.386(11)	2.373(4)	2.366(5)	2.347(4)	2.348(5)
Ln(1′)−O(1)	2.460(11)	2.447(4)	2.430(5)	2.427(4)	2.419(5)
Ln(2)−O(1)	2.354(11)	2.334(4)	2.323(5)	2.300(4)	2.296(4)
Ln(1)−O(2)	2.291(11	2.284(4)	2.270(5)	2.250(4)	2.237(5)
Ln(2)−O(2)	2.261(11)	2.258(4)	2.257(5)	2.245(4)	2.243(5)
Ln(1′)−O(4)	2.364(10)	2.370(4)	2.350(5)	2.341(4)	2.341(4)
Ln(2)−O(4)	2.544(11)	2.543(4)	2.530(6)	2.510(5)	2.515(5)
Ln(1)−O(1)−Ln(1′)	114.2(4)	113.90(17)	114.1(2)	113.94(17)	113.8(2)
Ln(1)−O(1)−Ln(2)	101.6(4)	101.72(16)	101.4(2)	101.96(17)	101.69(18)
Ln(1′)−O(1)−Ln(2)	106.6(4)	106.50(16)	106.8(2)	106.89(17)	107.30(19)
Ln(1)−O(2)−Ln(2)	107.7(5)	106.97(17)	106.6(2)	106.87(18)	106.99(19)
Ln(1′)−O(4)−Ln(2)	103.7(4)	102.43(16)	102.80(19)	102.99(17)	102.86(18)
Ln(1)−Ln(1′)	4.069(2)	4.0407(6)	4.0233(8)	4.0029(6)	3.9938(7)
Ln(1)−Ln(2)	3.6744(14)	3.6509(4)	3.6284(6)	3.6107(4)	3.6009(6)
Ln(1′)−Ln(2)	3.8614(14)	3.8319(4)	3.8155(6)	3.7976(4)	3.7980(5)
displ. of O(1) out of Ln_3 Δ	0.873(11)	0.872(4)	0.865(5)	0.853(5)	0.852(5)
O(3)···O(5′)	2.749(15)	2.780(7)	2.786(8)	2.797(7)	2.807(7)
Ln (1) geometry	DOD−BCTP	DOD−BCTP	DOD−BCTP	DOD−BCTP	DOD−BCTP
φ angles (deg)	1.59, 11.79	2.39, 11.99	2.57, 12.16	2.77, 12.50	2.36, 12.38
dihedral angles (deg)	26.59, 39.23, 40.62, 42.69	26.11, 38.84, 41.46, 43.08	25.48, 38.84, 42.01, 42.62	25.12, 37.91, 41.55, 42.76	25.30, 38.19, 41.14, 42.28
Ln (2) geometry	DOD	DOD	DOD	DOD	DOD
φ angles (deg)	1.06, 2.99	0.23, 3.03	0.42, 3.23	0.46, 3.19	0.44, 4.00
dihedral angles (deg)	14.04, 31.77, 32.33, 44.17	13.66, 32.39, 2.42, 44.52	13.85, 32.42, 32.65, 44.42	13.56, 32.30, 32.51, 44.50	11.70, 32.67, 33.07, 44.87

compounds show similar thermal evolution in the full temperature range. For **1** (Tb_4), **2** (Dy_4), and **5** (Tm_4), the χT product at 1000 Oe is essentially temperature independent over the range 300−60 K, followed by a rapid decrease on lowering the temperature from 60 to 1.8 K. For **3** (Ho_4) and **4** (Er_4) the χT product begins a very slow decrease at higher temperatures, with the rate of decrease becoming steadily larger below 100 K. The Stark sublevels of the anisotropic Ln^{III} (Tb, Dy, Ho, Er, and Tm) ions are thermally depopulated when the temperature is lowered resulting in a decrease of the χT product.[25] It is thus likely that this thermal behavior is associated with the thermal depopulation of the Ln^{III} excited states and that Ln··Ln interactions are insignificant by comparison.

The field dependence of the magnetization of compounds **1**−**5** at low temperatures shows that the magnetization increases smoothly with increasing applied dc field without saturation even at 7 T (Supporting Information, Figure S1). The magnitude of magnetization is also

---

[25] (a) Kahn, M. L.; Ballou, R.; Porcher, P.; Kahn, O.; Sutter, J.-P. *Chem.—Eur. J.* **2002**, *8*, 525. (b) Kahn, M. L.; Sutter, J.-P.; Golhen, S.; Guionneau, P.; Ouahab, L.; Kahn, O.; Chasseau, D. *J. Am. Chem. Soc.* **2000**, *122*, 3413.

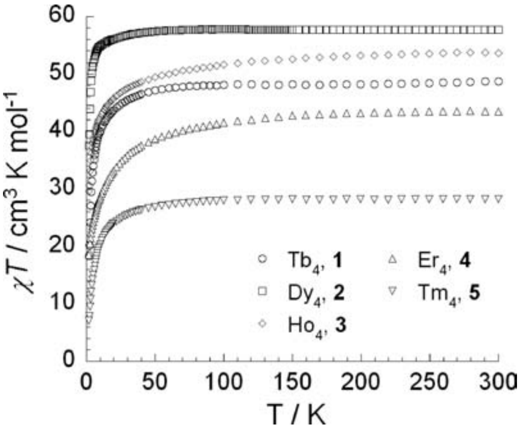

Figure 2. Temperature dependence of the χT products for compounds **1**−**5** at 1000 Oe (with χ being the molar susceptibility defined as M/H).

Table 3. Summary of the dc Magnetic Data for Compounds **1**−**5**

	1 (Tb)	**2** (Dy)	**3** (Ho)	**4** (Er)	**5** (Tm)
ground state term of Ln^{III} ion	$^7F_6$	$^6H_{15/2}$	$^5I_8$	$^4I_{15/2}$	$^3H_6$
S	3	5/2	2	3/2	1
L	3	5	6	6	5
g	3/2	4/3	5/4	6/5	7/6
C (cm^3 K mol^{-1}) for each Ln ion[26]	11.82	14.17	14.07	11.5	7.15
χT (cm^3 K mol^{-1}) expected value for 4 non-interacting Ln$_4$ at RT	47.28	56.68	56.28	46.0	28.6
χT (cm^3 K mol^{-1}) experimental value for Ln$_4$ at RT	48.4	57.7	53.7	43.4	28.2
χT (cm^3 K mol^{-1}) experimental value for Ln$_4$ at 1.8 K	18.2	37.6	29.6	18.6	7.1
magnetization (μ_B) observed at 7 T and 1.8 K	22.4	25.6	24.6	21.7	17.9

given in Table 3. This behavior indicates the presence of magnetic anisotropy and/or the lack of a well-defined ground state suggesting the presence of low-lying excited states that might be populated when a field is applied. Furthermore, the plots of the M versus H/T at low temperatures for compounds **1**−**5** (Supporting Information, Figure S1) show that the curves are not superposed, as expected for an isotropic system, giving a further indication of the presence of magnetic anisotropy and also the low-lying excited states already suggested. Furthermore, the M versus H data for **2** at 1.8 K reveal the existence of a hysteresis effect with a very small coercive field (about 12 Oe) (Supporting Information, Figure S2).

The presence of magnetic anisotropy was probed further by examining the magnetization relaxation under zero dc field for all compounds **1**−**5**. We found that only compound **2** exhibits slow relaxation of its magnetization under these conditions. Figure 3 shows that the frequency dependence of both in-phase and out-of-phase components can be observed in zero dc field below 12 K indicating slow relaxation of the magnetization. The ratio of the intensity of the out-of-phase and in-phase signal is about 2:3, which indicates that this behavior is intrinsically molecular. In addition, frequency sweeping ac susceptibilities (Figure 3) were measured at different temperatures, and the shape and frequency dependence both indicate that this compound is a SMM. Fitting the frequency sweeping ac data to an Arrhenius law gives an energy gap (Δ) of 6.2 K and a pre-exponential factor (τ_0) of 2.4×10^{-5} s (Supporting Information, Figure S6, left). These parameters are in the region of those we recently reported for a similarly planar Dy$_4$ compound.[8e] A generalized Debye model was used in an attempt to fit the Cole−Cole diagram of **2** (Supporting Information, Figure S3), but no good fit to the data in the temperature range 1.8−2.6 K could be obtained, indicating that more than one relaxation process operates in this compound. Multiple relaxation processes have been also observed for other Dy^{III} complexes.[5c]

To study the relaxation behavior further and check for quantum tunneling effects above 1.8 K, the frequency dependence of the ac susceptibility at 1.8 K was also measured with application of small dc fields up to 1500 Oe (Supporting Information, Figure S4). In SMMs with a relaxation partially influenced by quantum effects, the application of a small dc field removes the ground state degeneracy and thus the possibility of quantum tunneling, inducing a slowing down of the magnetization relaxation.[27] In zero field, the characteristic frequency was 240 Hz at 1.8 K. By increasing the field, this frequency decreased to 75 Hz around 800 Oe indicating that this applied dc field indeed slows down the relaxation time by reducing or suppressing quantum tunneling of the magnetization. Therefore ac susceptibility measurements as a function of temperature were carried out again under a dc field of 800 Oe. (Supporting Information, Figure S5) Fitting the data to an Arrhenius law, the characteristic SMM energy gap, Δ, was now estimated to be 6.9 K and the pre-exponential factor, τ_0, 4.8×10^{-5} s (Supporting Information, Figure S6, right). This is only a slight increase of the energy barrier and indicates that the quantum tunneling effect in this compound is not very pronounced.

The study of slow relaxation process of **2** was carried out by magnetization measurements on single-crystals using an array of micro-SQUID magnetometers[28] between 0.04 and 7 K (Figure 4 and Supporting Information, Figure S7). The measurements were performed with the applied field parallel to an easy axis of the magnetization. The opening of hysteresis loops was observed at 1.1 K. The coercivity fields of the hysteresis loops increase with decreasing temperature and increasing field sweep rates, which is consistent with the phenomenon of superparamagnetic behavior, further supporting the suggestion that complex **2** behaves as SMM with hysteresis effects clearly seen below 0.5 K at 0.002 T/s. The loops display step-like features below 0.3 K, indicating that the resonant quantum tunneling occurs below this temperature. Furthermore, the loops are relatively wide with a field up to 0.3 T and become narrow on increasing the field. This observation confirms that **2** has a SMM behavior with a very slow zero-field relaxation. This is also in line with the very slow relaxation time 2.4×10^{-5} s we obtained from the ac

---

[26] Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369.

[27] (a) Koizumi, S.; Nihei, M.; Shiga, T.; Nakano, M.; Nojiri, H.; Bircher, R.; Waldmann, O.; Ochsenbein, S. T.; Güdel, H. U.; Fernandez-Alonso, F.; Oshio, H. *Chem.—Eur. J.* **2007**, *13*, 8445. (b) Lecren, L.; Wernsdorfer, W.; Li, Y.; Roubeau, O.; Miyasaka, H.; Clérac, R. *J. Am. Chem. Soc.* **2005**, *127*, 11311. (c) Mishra, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *J. Am. Chem. Soc.* **2004**, *126*, 15648. (d) Moragues-Canovas, M.; Riviere, E.; Ricard, L.; Paulsen, C.; Wernsdorfer, W.; Rajaraman, G.; Brechin, E. K.; Mallah, T. *Adv. Mater.* **2004**, *16*, 1101.

[28] Wernsdorfer, W. *Adv. Chem. Phys.* **2001**, *118*, 99.

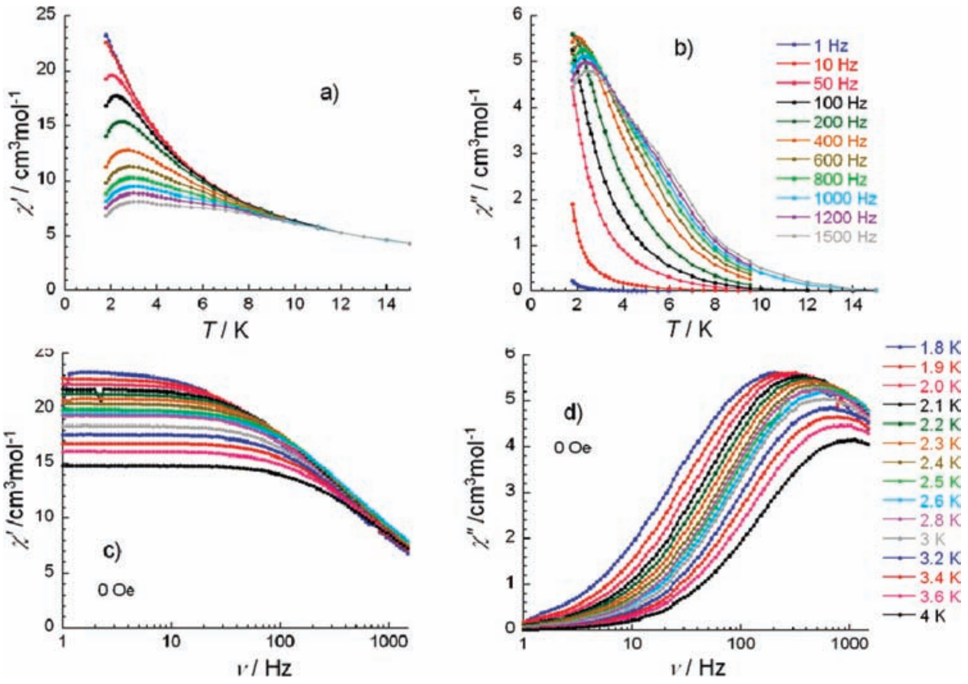

Figure 3. Temperature dependence of the in-phase (a) and out-of-phase (b) components of the ac magnetic susceptibility, for **2** under zero dc field. Frequency dependence of the in-phase (c) and the out-of-phase (d) components of the ac susceptibility at different temperature for compound **2** under zero dc field.

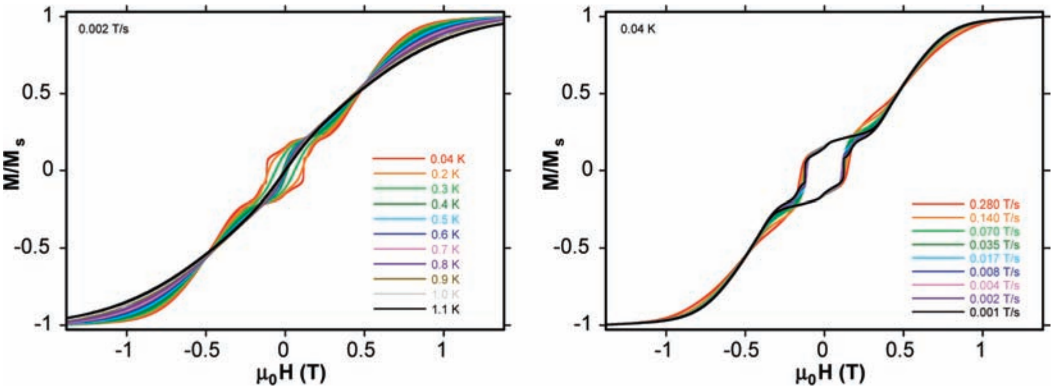

Figure 4. Normalized magnetization (*M* being normalized at the saturated magnetization M_S) versus applied field (μ_oH) of **2**. The loops are shown at different temperatures (left) and at different field sweep rates (right).

measurements under zero dc field. However, it was not possible to obtain a reliable value for the energy barrier from the magnetization versus time decay data. The origin of the irregular shape of the hysteresis loops is under further investigation.

Conclusion

Following on from our report[21] on a series of dinuclear lanthanide complexes resulting from reactions with the lighter lanthanide ions, we have successfully synthesized and characterized a new family of isostructural tetranuclear Ln^{III} clusters with the incorporation of heavier lanthanides using the same reaction system. These clusters present a planar butterfly core. In all five compounds the Ln^{III} ions are either very weakly coupled or effectively uncoupled, while compound **2** shows single molecule magnet behavior.

Acknowledgment. This work was supported by the DFG (SPP 1137 and the Center for Functional Nanostructures) and MAGMANet (NMP3-CT-2005-515767).

Supporting Information Available: Additional information in the form of Figures S1−S7 and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.