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Slow Magnetic Relaxation in Novel Dy_4 and Dy_8 Compounds

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Two novel dysprosium(III) clusters have been prepared and structurally characterized. One has a tetranuclear core with a rare zigzag arrangement, and the other is an unprecedented octanuclear cluster with six triangular Dy_3 units sharing vertices. Both dysprosium(III) clusters possess frequency-dependent on alternating-current magnetic susceptibilities, indicating possible single-molecule magnet behavior.

In the past 2 decades, single-molecule magnets (SMMs)[1] have attracted increasing attention of both physicists and chemists owing to their potential applications for use in high-density magnetic memories, quantum computing devices, and molecular spintronics.[2−4] For transition-metal complexes, the SMM behavior is due to these compounds displaying a large-spin ground state (S_T) and a sufficiently large magnetic anisotropy due to a negative axial zero-field splitting (D).[5−8] This leads to an energy barrier (Δ) to the reversal of the magnetization vector $|D|S_T^2$ for integer spin and $|D|(S_T^2 - {}^1/_4)$ for half-integer spin. Many different directions are being pursued in the study of SMMs.[9−11] One of them focuses on how to obtain molecules with the large-spin ground state (S_T) so that the energy barrier is increased.[12] Exceptional efforts have led to a significant increase in the spin ground state, with a record value as high as $S = {}^{83}/_2$.[13] However, it has proven to be remarkably difficult to optimize both parameters,[14] and a recent reappraisal of this suggests that the relationship is linearly dependent on the spin S_T,[15] in turn directing research toward increasing the anisotropy in new systems; thus, maximizing D represents a new challenge.

As is well-known, lanthanide ions have a large anisotropy arising from the strong spin−orbit coupling. Fewer pure lanthanide-based SMMs have been reported so far, and most of them contain dysprosium(III) ions, such as di-,[16] tri-,[17] tetra-,[18] penta-,[19] hexa-,[20] and decanuclear[21] and wheel dysprosium compounds.[22] Among them, a tetranuclear dysprosium(III) cluster with a defect-dicubane geometry has the highest anisotropic barrier for the reported SMMs at 170 K.[18d] This indicates that the lanthanide-based cluster compounds have been some of the most highly promising systems for the development of higher-barrier SMMs. For polymetallic lanthanide SMMs, single-ion anisotropy, which is sensitive to the strength and symmetry of the local crystal

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(1) (a) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268–297. (b) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141–143. (c) Gatteschi, D.; Sessoli, R.; Villain, J. *Molecular Nanomagnets*; Oxford University Press: Oxford, U.K., 2006. (d) 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*, 1804–1806. (e) Murugesu, M.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 892–896.

(2) (a) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *410*, 789–793. (b) Hill, S.; Edwards, R. S.; Aliaga-Alcalde, N.; Christou, G. *Science* **2003**, *302*, 1015–1018.

(3) Meier, F.; Levy, J.; Loss, D. *Phys. Rev. Lett.* **2003**, *90*, 047901.

(4) Bogani, L.; Wernsdorfer, W. *Nat. Mater.* **2008**, *7*, 179–186.

(5) Christou, G.; Gatteschi, D.; Hendrickson, D. N.; Sessoli, R. *MRS Bull.* **2000**, *25*, 66–71.

(6) Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. *Nature* **1996**, *383*, 145–147.

(7) Sokol, J. J.; Hee, A. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 7656–7657.

(8) Maheswaran, S.; Chastanet, G.; Teat, S. J.; Mallah, T.; Sessoli, R.; Wernsdorfer, W.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 5044–5048.

(9) Ruiz-Molina, D.; Mas-Torrent, M.; Gómez, J.; Balana, A. I.; Domingo, N.; Tejada, J.; Martinez, M. T.; Rovira, C.; Veciana, J. *Adv. Mater.* **2003**, *15*, 42–45.

(10) Cornia, A.; Fabretti, A. C.; Pacchioni, M.; Zobbi, L.; Bonacchi, D.; Caneschi, A.; Gatteschi, D.; Biagi, R.; Del Pennino, U.; De Renzi, V.; Gurevich, L.; Van der Zant, H. S. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 1645–1648.

(11) Clemente-León, M.; Soyer, H.; Coronado, E.; Mingotaud, C.; Gómez-García, C. J.; Delhaès, P. *Angew. Chem., Int. Ed.* **1998**, *37*, 2842–2845.

(12) Yang, E.-C.; Wernsdorfer, W.; Zakharov, L. N.; Karaki, Y.; Yamaguchi, A.; Isidro, R. M.; Lu, G.-D.; Wilson, S. A.; Rheingold, A. L.; Ishimoto, H.; Hendrickson, D. N. *Inorg. Chem.* **2006**, *45*, 529–546.

(13) Ako, A. M.; Hewitt, I. J.; Mereacre, V.; Clérac., R.; Wernsdorfer, W.; Anson, C. E.; Powell, A. K. *Angew. Chem., Int. Ed.* **2006**, *45*, 4926–4929.

(14) Sessoli, R. *Inorg. Chim. Acta* **2008**, *361*, 3356–3364.

(15) (a) Waldmann, O. *Inorg. Chem.* **2007**, *46*, 10035–10037. (b) Ruiz, E.; Cirera, J.; Cano, J.; Alvarez, S.; Loose, C.; Kortus, J. *Chem. Commun.* **2008**, 52–54.

(16) (a) Lin, P.-H.; Burchell, T. J.; Clérac, R.; Murugesu, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 8848–8851. (b) Xu, G.-F.; Wang, Q.-L.; Gamez, P.; Ma, Y.; Clérac, R.; Tang, J.-K.; Yan, S.-P.; Cheng, P.; Liao, D.-Z. *Chem. Commun.* **2010**, *46*, 1506–1508. (c) Layfield, R. A.; McDouall, J. J. W.; Sulway, S. A.; Tuna, F.; Collison, D.; Winpenny, R. E. P. *Chem.—Eur. J.* **2010**, *16*, 4442–4446.

(17) (a) Tang, J.-K.; Hewitt, I.; Madhu, N. T.; Chastanet, G.; Wernsdorfer, W.; Anson, C. A.; Benelli, C.; Sessoli, R.; Powell, A. K. *Angew. Chem., Int. Ed.* **2006**, *45*, 1729–1733. (b) Hewitt, I. J.; Lan, Y.; Anson, C. E.; Luzon, J.; Sessoli, R.; Powell, A. K. *Chem. Commun.* **2009**, 6765–6767.

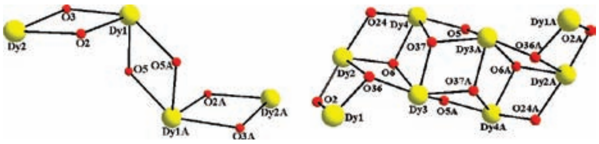
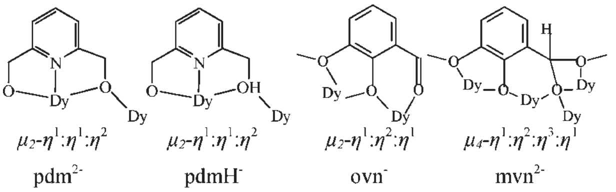


Figure 1. Cores in compounds **1** (left) and **2** (right). Color codes: yellow, Dy; red, O. Other atoms were omitted for clarity.

field, is probably the most important factor and magnetic exchange is a secondary consideration that moderates the magnetic relaxation of the single ions.[16c] How to increase single-ion anisotropy and promote magnetic coupling remain an exciting challenge in polymetallic lanthanide systems. Thus, it is necessary to design novel structures to enlarge the available database in order to improve our knowledge of the structure−property relationship of lanthanide-based SMMs. As is known, the *o*-vanillin aldehyde ligand is especially useful in forming polynuclear lanthanide complexes. Pyridine-2,6-dimethanol is extensively employed for manganese cluster chemistry. This ligand should form homometallic lanthanide clusters, with the hard O-donor alkoxy arms being able to bind and form bridges to the oxophilic lanthanide ions. The ancillary carboxylate ligands can be used as bridging ligands or to meet the coordination spheres of metal ions. We decided to investigate using the mixed-ligand strategy. Herein we report the successful isolation of two novel pure dysprosium compounds with unprecedented structural motifs, namely, $[Dy_4(pdmH)_2(pdm)_4(PhCO_2)_2(PhCO_2H)_4]\cdot CH_3OH\cdot H_2O$ (**1**) and $[Dy_8(\mu_3\text{-}OH)_4(ovn)_2(mvn)_2(p\text{-}NO_2bz)_{14}(CH_3OH)_2]\cdot 3.09CH_3CN\cdot 6CH_3OH\cdot H_2O$ (**2**), where $pdmH_2$ is pyridine-2,6-dimethanol, ovnH is *o*-vanillin, $mvnH_2$ is the methyl hemiacetal derivative of *o*-vanillin, and p-NO_2bz is *p*-nitrobenzoate.

Single-crystal X-ray analysis revealed that compound **1** has a tetranuclear core (Figure 1). The four Dy^{III} atoms arrange in a zigzag fashion and are all eight-coordinated with a distorted square-antiprismatic geometry, where Dy1 (Dy1A) sites are surrounded by an O atom from a $pdmH^-$ ligand and two N atoms and five O atoms from three pdm^{2-} ligands while Dy2 (Dy2A) ions are surrounded by an O atom from a pdm^{2-} ligand, a N atom and two O atoms from a $pdmH^-$ ligand, and two O atoms from a $PhCO_2^-$ ion together with two O atoms from two $PhCO_2H$ molecules. All of the $pdmH^-$ and pdm^{2-} groups in compound **1** adopt a μ_2-η^1:η^1:η^2 mode (Scheme 1). Dy1 and Dy2 are bridged by two μ_2-$O_{alkoxide}$ atoms from $pdmH^-$ and pdm^{2-} groups, forming a binuclear unit, which are further connected by two μ_2-$O_{alkoxide}$ atoms from two pdm^{2-} groups, obtaining the central tetranuclear core. The Dy−O bond lengths are in the range of 2.270(16)−2.517(7) Å, and Dy−N are in the range of 2.480(10)−2.514(8) Å, which are comparable to those of the reported dysprosium(III) complexes.[18d] The intracluster Dy---Dy separations are 3.7222(10) and 3.7289(10) Å, respectively. The zigzag tetranuclear core in **1** is an unprecedented structural type in pure lanthanide clusters. Compound **2** consists of a centrosymmetric octanuclear dysprosium(III) cluster that contains three types of ligands, *p*-nitrobenzoate (p-NO_2bz), *o*-vanillin (ovnH), and the methyl hemiacetal derivative of *o*-vanillin ($mvnH_2$).[23] It is known that unstable hemiacetals are widely recognized as intermediates in many organic reactions;[24] however, to our best knowledge, only one lanthanide compound with a methyl hemiacetal ligand was reported.[23] In **2**, eight Dy^{III} ions are held together by four μ_3-OH^- ligands and two O atoms of the hemiacetal ligands to form a $[Dy_8(\mu_3\text{-}OH)_4(\mu_3\text{-}OR)_2]$ core (Figure 1), which is composed of six triangular Dy_3 units sharing vertices with Dy---Dy separations of 3.8412(5) Å for Dy1---Dy2, 3.8317(6) Å for Dy2---Dy3, and 3.7341(6) Å for Dy3---Dy4. The OH^- or alkoxide groups lie in the centers of the triangles. These μ_3-OH^--capped triangular units are similar to those of previously reported trinuclear lanthanide(III) compounds.[17a,23,25] Peripheral ligation is provided by 2 ovn ligands, 14 *p*-nitrobenzoate molecules, and 2 methanol molecules. The ovn^- ligand links two Dy atoms in a μ_2-η^1:η^2:η^1 mode, while the mvn^{2-} ligand bridges four Dy atoms in a μ_4-η^1:η^2:η^3:η^1 fashion (Scheme 1). Another feature of **2** is the coexistence of three different coordination modes of carboxyl groups of *p*-nitrobenzoate, namely, μ_2-η^1:η^1, η^1:η^1, and μ_2-η^2. It should be noted that the methyl hemiacetal ligand chelates Dy ions, which may play a crucial role in forming the large cluster. Both chelating and bridging capacities of *o*-vanillin and the hemiacetal ligand together with the hydroxo and versatile carboxyl groups consolidate this Dy_8 cluster.

Scheme 1. Binding Modes of pdm^{2-} and $pdmH^-$ in Compound **1** and ovn^- and mvn^{2-} in Compound **2**



Magnetic susceptibility data for the two compounds were measured in the temperature range 2−300 K under a field of 2 kG. The resulting plots of $\chi_M T$ vs T for **1** and **2** are depicted in Figure 2. For **1**, the $\chi_M T$ value at room temperature is slightly smaller than that of 56.68 cm^3 mol^{-1} K calculated for four noninteracting Dy^{III} ions ($S = {}^5/_2$, $L = 5$, ${}^6H_{15/2}$, and $g = {}^4/_3$). $\chi_M T$ decreases smoothly from a value of 55.67 cm^3 mol^{-1} K at 300 K to 49.09 cm^3 mol^{-1} K at 24.0 K, and then the value falls sharply to 18.13 cm^3 mol^{-1} K at 2.0 K,

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(18) (a) Isele, K.; Gigon, F.; Williams, A. F.; Bernardinelli, G.; Franz, P.; Decurtins, S. *Dalton Trans.* **2007**, 332–341. (b) Galloway, K. W.; Whyte, A. M.; Wernsdorfer, W.; Sanchez-Benitez, J.; Kamenev, K. V.; Parkin, A.; Peacock, R. D.; Murrie, M. *Inorg. Chem.* **2008**, *47*, 7438–7442. (c) Zheng, Y.-Z.; Lan, Y.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2008**, *47*, 10813–10815. (d) Lin, P.-H.; Burchell, T. J.; Ungur, L.; Chibotaru, L. F.; Wernsdorfer, W.; Murugesu, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 9489–9492. (e) Gao, Y.-J.; Xu, G.-F.; Zhao, L.; Tang, J.-K.; Liu, Z. L. *Inorg. Chem.* **2009**, *48*, 11495–11497. (f) Guo, Y. N.; Xu, G.-F.; Gamez, P.; Zhao, L.; Lin, S.-Y.; Deng, R.-P.; Tang, J.-K.; Zhang, H.-J. *J. Am. Chem. Soc.* **2010**, *132*, 8538–8539. (g) Ke, H.-S.; Xu, G.-F.; Guo, Y.-N.; Gamez, P.; Beavers, C. M.; Teat, S. J.; Tang, J. *Chem. Commun.* **2010**, *46*, 6057–6059.

(19) Gamer, M. T.; Lan, Y.; Roesky, P. W.; Powell, A. K.; Clérac, R. *Inorg. Chem.* **2008**, *47*, 6581–6583.

(20) Hussain, B.; Savard, D.; Burchell, T. J.; Wernsdorfer, W.; Murugesu, M. *Chem. Commun.* **2009**, 1100–1102.

(21) Ke, H.; Xu, G.-F.; Zhao, L.; Tang, J.-K.; Zhang, X.-Y.; Zhang, H.-J. *Chem.—Eur. J.* **2009**, *15*, 10335–10338.

(22) Langley, S. K.; Moubaraki, B.; Forsyth, C. M.; Gass, I. A.; Murray, K. S. *Dalton Trans.* **2010**, *39*, 1075–1078.

(23) Yang, X.-P.; Jones, R. A.; Wiester, M. J. *Dalton Trans.* **2004**, 1787–1788.

(24) (a) Crampton, M. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 185. (b) Tam, S.-W.; Jimenez, L.; Diederich, F. *J. Am. Chem. Soc.* **1992**, *114*, 1503–1505.

(25) Costes, J.-P.; Dahan, F.; Nicodeme, F. *Inorg. Chem.* **2001**, *40*, 5285–5287.

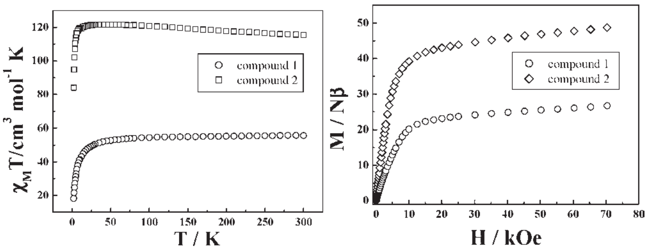

Figure 2. (left) Temperature dependence of $\chi_M T$ values for **1** and **2**. (right) Isothermal (2 K) field dependence of magnetization for **1** and **2**.

which probably ascribes to a combination of the exchange interaction between the Dy^{III} ions and the progressive depopulation of excited Stark sublevels.[18e] For **2**, at room temperature, the $\chi_M T$ value of 115.3 cm^3 K mol^{-1} is slightly higher than the expected value of 113.36 cm^3 mol^{-1} K for eight noninteracting Dy^{III} ions. Upon cooling, the $\chi_M T$ product gradually increases to reach a maximum of 121.6 cm^3 mol^{-1} K at about 45 K and then decreases to 83.9 cm^3 mol^{-1} K at 2.0 K. The increase of $\chi_M T$ suggests the presence of an intramolecular ferromagnetic interaction between the Dy^{III} ions. The decrease of $\chi_M T$ at low temperature is likely due to a combination of intermolecular magnetic coupling, large magnetic anisotropy, and depopulation of excited Stark sublevels.

The field dependences of magnetization (*M*) for **1** and **2** have been determined at 2 K in the range of 0−70 kOe (Figure 2). For **2**, as expected for ferromagnetically coupled spins, the *M* value displays a rapid increase at low magnetic fields, whereas the *M* value gradually increases for **1**. At high fields, *M* increases to reach 26.7 and 48.7 Nβ at 70 kOe for **1** and **2**, respectively, but does not reach the expected saturation values of 40 and 80 Nβ, respectively (10 Nβ for each Dy^{III} ion for $J = {}^{15}/_2$ and $g = {}^4/_3$), indicating the presence of magnetic anisotropy and/or low-lying excited states in the system, which correspond to the reported results.[26] In addition, the *M* vs *H* plots for **1** and **2** do not show hysteresis above 2.0 K (Figures S5 and S6 in the Supporting Information).

To examine the spin dynamics, the temperature dependencies of the alternating-current (ac) magnetic susceptibility for **1** and **2** were collected at zero direct-current (dc) field with an ac field of 3.5 Oe with oscillating frequencies, given in Figure 3 as plots of χ'' vs *T*, respectively. Strikingly, frequency-dependent out-of-phase signals are observed for both compounds, indicating the onset of slow magnetization, which might be the signature of a SMM behavior. The absence of frequency-dependent peaks in out-of-phase susceptibility signals for the two compounds is likely because of the fast quantum tunneling of the magnetization that is too fast to observe at the operating limits of our SQUID. As is well-known, the tunneling mechanism can be suppressed by applying a static magnetic field. In order to find out whether tunneling affects the magnetization dynamics, the ac susceptibilities are measured in 3 kOe external field (Figure S9 and S10 in the Supporting Information) for two compounds to remove the degeneracy of the levels on opposite sides of the anisotropy barrier.

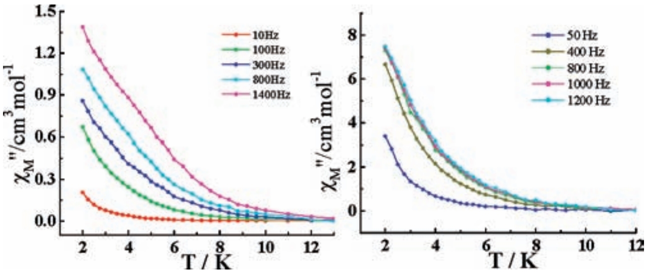

Figure 3. Temperature dependence of the out-of-phase (χ'') ac susceptibility components at different frequencies for **1** (left) and **2** (right) with zero dc field and an oscillation of 3.5 G.

Clearly, this is not the case above 2.0 K. The height of the signal is reduced, but the similar frequency dependence is observed. Thus, quantum tunneling in zero field is negligible for the two compounds. This is generally observed in the absence of fast zero-field ground-state quantum tunneling.[27] As is seen, different slow relaxation behaviors are observed in the two compounds. The SMM properties of lanthanide-containing polynuclear compounds are dominated by single-ion anisotropy and are extremely sensitive to distortions of the coordination geometry of rare-earth ions.[28] Thus, the different magnetic relaxation behaviors in **1** and **2** are probably the result of different structures, which are likely to affect the nature or directions of the easy axes through the ligand fields, as well as magnetic coupling among the lanthanide ions.

In summary, we have reported two pure polynuclear dysprosium(III) clusters. Compound **1** possesses a tetranuclear core with an unprecedented zigzag array in pure lanthanide clusters, while compound **2** is composed of six triangular Dy$_3$ units sharing a Dy---Dy edge between every two neighboring triangles. The frequency dependence of the ac signals suggests that the two compounds may be SMMs and quantum tunneling in zero field is negligible for both compounds. Further work is underway to use the polydentate ancillary ligands to obtain new dysprosium clusters with SMM behavior.

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Supporting Information Available: Crystallographic data in CIF format, experimental details, and additional structure diagrams and magnetic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) (a) Zheng, Y.-Z.; Lan, Y.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2008**, *47*, 10813–10815. (b) Kanegawa, S.; Maeyama, M.; Nakano, M.; Koga, N. *J. Am. Chem. Soc.* **2008**, *130*, 3079–3094. (c) Bernot, K.; Luzon, J.; Bogani, L.; Etienne, M.; Sangregorio, C.; Shanmugam, M.; Caneschi, A.; Sessoli, R.; Gatteschi, D. *J. Am. Chem. Soc.* **2009**, *131*, 5573–5579. (d) Lin, P. H.; Burchell, T. J.; Clérac, R.; Murugesu, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 8848–8851.

(27) Mereacre, V.; Akhtar, M. N.; Lan, Y.; Ako, A. M.; Clérac, R.; Anson, C. E.; Powell, A. K. *Dalton Trans.* **2010**, *39*, 4918–4927.

(28) Gonidec, M.; Luis, F.; Vílchez, A.; Esquena, J.; Amabilino, D. B.; Veciana, J. *Angew. Chem., Int.Ed.* **2010**, *49*, 1623–1626.