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A Dy$_6$ Cluster Displays Slow Magnetic Relaxation with an Edge-to-Edge Arrangement of Two Dy$_3$ Triangles

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A new dysprosium(III) cluster, namely [Dy$_6^{III}$(**L**)$_4$(μ_3-OH)$_4$(CH$_3$OH)$_2$(NO$_3$)$_2$]·6CH$_3$CN (**1**), has been synthesized from the Schiff base ligand 1,3-bis(salicylideneamino)-2-propanol and dysprosium nitrate. A single-crystal X-ray diffraction study reveals that the core of **1** consists of an edge-to-edge arrangement of two Dy$_3$ triangles. Both static (dc) and dynamic (ac) magnetic properties of **1** have been studied. The results show that slow magnetic relaxation is operating in compound **1**.

Introduction

The design, synthesis, and investigation of single-molecule magnets (SMMs)[1] continue to receive a great deal of attention owing to their potential applications in high-density information storage at the molecular level[2] and as qubits in quantum computation.[3] SMMs are molecular species that are characterized by the slow relaxation of magnetization originating from the combination of a high-spin ground state and easy-axis magnetic anisotropy.[1a] It is well established that the incorporation of heavy lanthanide ions, such as Tb^{III}[4] and Dy^{III}[5] ions possessing significant inherent magnetic anisotropy arising from the large, unquenched orbital angular momentum, is one of the most promising strategies to design new SMMs.[6] Especially, research interest in SMMs based on pure lanthanide systems has grown dramatically after the observation of slow magnetic relaxation in the case of mononuclear complexes.[7] However, only a few pure lanthanide[8] SMMs have been reported relative to those of transition-metal[9] clusters because of synthetic challenges and the difficulty in improving magnetic interactions through the overlap of the bridging ligand orbitals with the "contracted" 4f orbitals of the lanthanide ions. In addition, several polynuclear lanthanide compounds[10] with a nuclearity number of up to thirty[11] have been shown to exhibit slow magnetic relaxation.

Powell and co-workers have prepared two "dysprosium triangles" that show unusual slow magnetic relaxation arising from an almost non-magnetic ground state, which gives an interesting system with unprecedented magnetic properties.[8d,12] More recently, the linkage and opening up of high anisotropic dysprosium triangles has become a hot topic in order to create new SMMs and to possibly enhance the slow magnetic relaxation. In efforts to create new polynuclear lanthanide clusters exhibiting slow magnetic relaxation, we have obtained an unprecedented hexanuclear dysprosium cluster (Dy$_6$, Dy$_6$-**1**) using 1,3-bis(salicylideneamino)-2-propanol (H$_3$L) as ligand, which has proven to be a versatile chelating and bridging group that has yielded a number of 3d metal clusters.[13] More interestingly, from a structural point of view, Dy$_6$-**1** shows an "edge-to-edge" arrangement of two Dy$_3$ triangles, which is quite different from previously reported Dy$_6$ cases (Dy$_6$-**2**[8f] and Dy$_6$-**3**[10b]), in which the vertices of two almost parallel triangles are linked through bridging alkoxide oxygen atoms of two ligands. Meanwhile, Dy$_6$-**1** exhibits slow magnetic relaxation with a frequency-dependent, out-of-phase signal. Herein, we describe the synthesis, crystal structure, and magnetic properties of the hexanuclear dysprosium complex with a novel "edge-to-edge" arrangement of two Dy$_3$ triangles.

Results and Discussion

The reaction of dysprosium nitrate with H$_3$L in the mixture of methanol and acetonitrile, in the presence of triethylamine, produces the Dy$_6$ cluster with the formula [Dy$_6^{III}$(L)$_4$(μ_3-OH)$_4$(CH$_3$OH)$_2$(NO$_3$)$_2$]·6CH$_3$CN (**1**), whose molecular structure is depicted in Figure 1. The [Dy$_6$(μ_2-O)$_6$(μ_3-OH)$_4$(μ_3-O)$_2$]$^{6+}$ core consists of two [Dy$_3$(μ_3-O)(μ_3-OH)] triangular units in an "edge-to-edge" arrangement linked by two μ_3-OH$^-$ ions and two deprotonated alcohol oxygen atoms from two η_1:η_1:η_3:η_3:μ_4-L^{3-} ligands. The other four Dy$_2$ edges (Dy2A–Dy3 and Dy1–Dy3) are each bridged by one deprotonated phenol oxygen atom from two

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η_1:η_1:η_3:η_3:μ_4-L^{3-} ligands. The Dy2 and Dy2A ions are located in the center of the core, in which all six dysprosium ions effectively lie on the same plane. The four ligands are fully deprotonated and located directly above and below the [Dy_6] plane. For dysprosium triangle Dy1Dy2ADy3, one μ_3-OH^- ion (O12A) and one μ_3-O (O2) atom are capped above and below the plane of the triangle, with Dy···Dy distances of 3.5321(5), 3.5460(5), and 3.5825(6) Å. Two sides of the triangle are bridged by two deprotonated phenol oxygen atoms, while the remaining side is linked by one μ_3-OH^- ion (O11).The equivalent atom (O11A) together with two alcohol oxygen atoms link the two dysprosium triangular units, which results in an"edge-to-edge" arrangement of the dysprosium triangles. It should be mentioned that the topology in **1** is quite different from previously reported Dy_6 cases, in which the vertices of two almost-parallel triangles are linked through bridging alkoxide oxygen atoms of two ligands, which leads to a "head-to-head" arrangement of the dysprosium triangles (Scheme 1). Each Dy ion is eight coordinate. The ligation is completed by four ligands, four μ_3-OH^- ions, two methanol molecules, and two nitrate anions. The values of the dysprosium–oxygen and dysprosium–nitrogen bond lengths cover the range 2.197(6)–2.507(6) and 2.488(7)–2.520(7) Å, respectively. The Dy–O–Dy angles are in the range 94.34(18)–113.1(2)°. The coordination spheres of the dysprosium ions are illustrated in Figure S1. In a word, it is noteworthy that such a structural motif is relatively rare in lanthanide chemistry.[14]

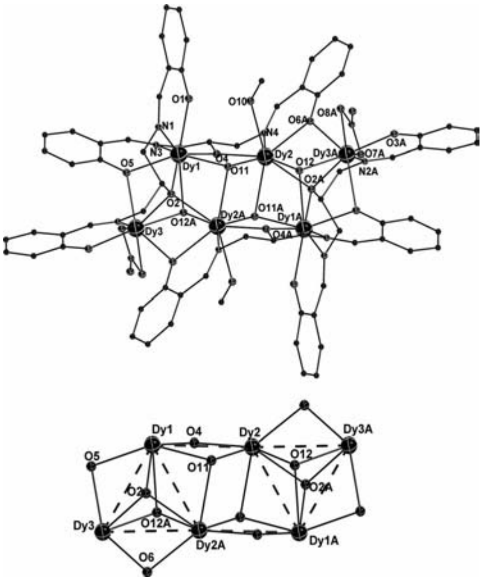
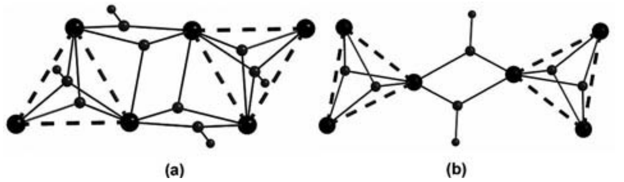


Figure 1. Structure of **1** (top) and its core (bottom) highlighting the dysprosium triangle subunits (dashed lines).

Additionally, in **1**, the oxygen atom (O1) from the η_1:η_3:η_3:μ_3-L^{3-} ligand form intramolecular hydrogen bonds to the oxygen atom (O10) from the coordinated methanol molecule. On the other hand, two oxygen atoms (O11 and O12) from two μ_3-OH^- ions form hydrogen bonds to the uncoordinated acetonitrile lattice solvent molecule, and there are no direct intermolecular hydrogen bonds (see Figure S2).



Scheme 1. The cores of three Dy_6 complexes based on two different Dy_3 triangle arrangements.

The plot of $\chi_M T$ vs. T (in which χ_M is the molar magnetic susceptibility) is shown in Figure 2. At 300 K, the $\chi_M T$ value of 83.6 $cm^3 K mol^{-1}$ is close to the expected value of 85.0 $cm^3 K mol^{-1}$ for six uncoupled Dy^{III} ions ($S = 5/2$, $L = 5$, $J = 15/2$, $^6H_{15/2}$, $g = 4/3$). The value of $\chi_M T$ gradually decreases until 75 K and then further decreases to 56.6 $cm^3 K mol^{-1}$ at 2 K, which may conceivably be ascribed to a combination of the progressive depopulation of the excited Stark sublevels and the exchange interaction between the Dy^{III} ions.

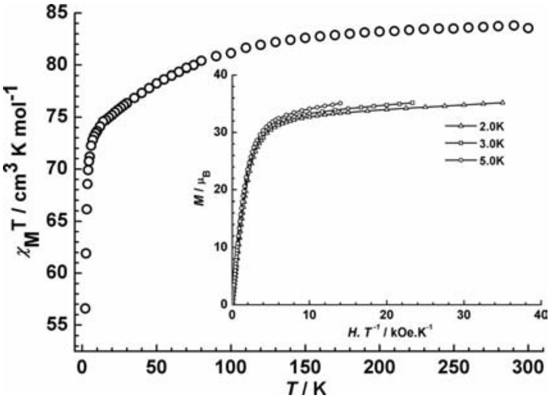


Figure 2. Temperature dependence of the $\chi_M T$ product at 1000 Oe for **1**. Inset: M vs. H/T plots for **1** below 5 K.

The non-superimposition of the M vs. H/T data on a single master curve suggests the presence of a significant magnetic anisotropy and/or low-lying excited states. The magnetization eventually reaches the value of 35.2 μ_B for **1** at 2 K and 70 kOe without clear saturation. This value is much lower than the expected saturation value of 60 μ_B for six free, non-interacting Dy^{III} ions, most likely because of the crystal-field effect at the Dy^{III} ion, which eliminates the 16-fold degeneracy of the $^6H_{15/2}$ ground state. Indeed, the maximum value for the magnetization is consistent with the expected value ($6 \times 5.2\ \mu_B$) for six uncorrelated Dy^{III} ions with a value of 5.2 μ_B per Dy^{III} ion, assuming the presence of considerable ligand-field effects.[8d]

The dynamics of magnetization are given in Figure 3 as plots of χ' vs. T and χ'' vs. T. Compound **1** shows frequency-dependent in-phase (χ') and out-of-phase (χ'') signals, which indicate the presence of slow magnetic relaxation at low temperature. However, there is an absence of frequency-dependent peaks in the out-of-phase susceptibility signals for **1** because of fast quantum tunneling of the magnetization, which is too fast to observe at the limits of our equipment – we thus cannot determine the energy barrier and corresponding relaxation time. Alternatively, ac susceptibility measurements as a function of frequency at different temperatures were carried out with the results shown in Figure 4. The relaxation time at different temperatures was extracted by fitting the curves χ'' vs. frequency. The plotting of the relaxation time vs. the reciprocal temperature generated the Arrhenius plot, which furnishes Δ = 3.2 K and $\tau_0 = 2.8 \times 10^{-5}$ s.

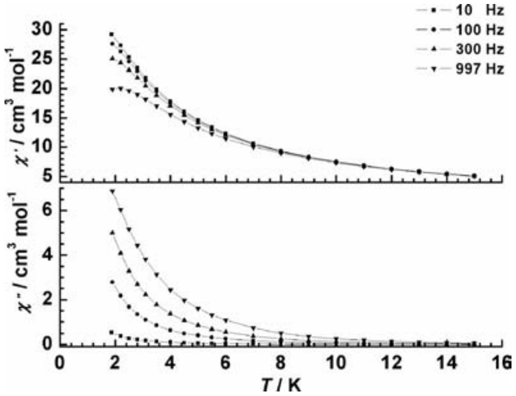


Figure 3. Temperature dependence of in-phase (top) and out-of-phase (bottom) ac susceptibility components at different frequencies and zero applied dc field for **1**.

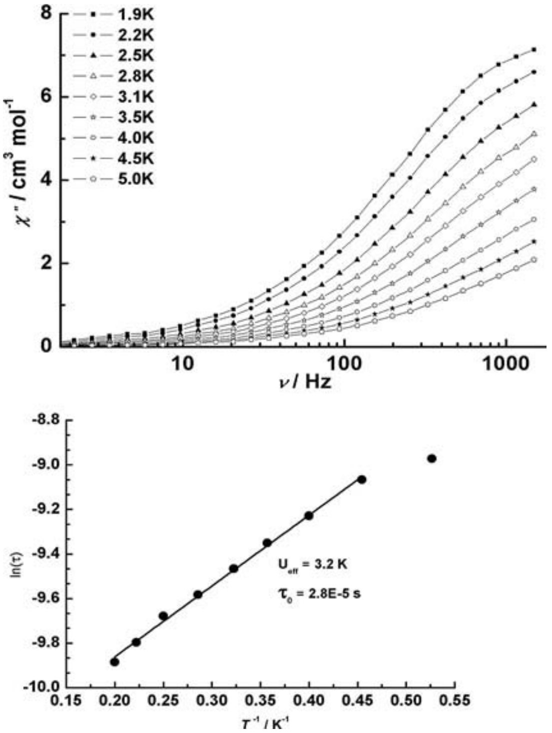


Figure 4. Frequency dependence of out-of-phase ac susceptibility of **1** (top) and the resulting Arrhenius plot from the ac susceptibility of **1** under zero-dc field (bottom).

Conclusions

We have shown the formation of an unprecedented Dy_6 cluster with two edge-to-edge Dy_3 triangles by incorporating the pentadentate Schiff base ligand H_3L in two different binding modes and its slow magnetic relaxation behavior. The interesting magnetic behavior in dysprosium compounds can presumably be attributed to the magnetic anisotropy of the molecules, which depends not only on the individual anisotropies of the metal ions but also on the relative orientation of the local axes. This new edge-to-edge arrangement of two triangles provides a unique opportunity to probe the relaxation dynamics of polynuclear lanthanide systems; thus, this may enrich the structure correlation to magnetic properties of the Dy_3 triangle family. However, further in-depth studies are required to determine the relaxation dynamics of such systems.

Experimental Section

Synthesis of 1: A methanol solution of triethylamine (0.8 mL, 0.4 mmol) was added to the ligand H_3L (0.2 mmol, 63 mg) dissolved in methanol (4 mL). The reaction mixture was stirred for 1 h. Solid dysprosium nitrate hexahydrate (0.2 mmol, 95 mg) was then added, and the resulting yellow solution was stirred for 1 h. Acetonitrile (10 mL) was subsequently added. The reaction mixture was left unperturbed to allow the slow evaporation of the solvent. Yellow single crystals, suitable for X-ray diffraction analysis, were obtained after one week. Yield: 40 mg, (45%, based on the metal). $C_{82}H_{90}Dy_6N_{16}O_{24}$ (2658.71): calcd. C 37.04, H 3.41, N 8.43; found C 36.92, H 3.48, N 8.33. IR (KBr): $\tilde{\nu}$ = 3428 (w), 3022 (w), 2891 (w), 2842 (w), 1632 (s), 1599 (m), 1551 (m), 1475 (s), 1448 (s), 1398 (m), 1289 (s), 1246 (w), 1197 (m), 1150 (m), 1127 (w), 1061 (w), 1044 (m), 1031 (m), 1004 (w), 973 (w), 899 (w), 886 (w), 857 (w), 818 (w), 795 (w), 758 (s), 742 (m), 709 (w), 648 (w), 634 (m), 594 (m), 562 (w), 511 (w), 477 (w) cm^{-1}.

CCDC-816968 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental section, physical measurements, X-ray crystal structure determination, and additional structural data and diagrams.

Acknowledgments

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[1] a) G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, *25*, 66–71; b) D. Gatteschi, R. Sessoli, *Angew. Chem.* **2003**, *115*, 278–309; *Angew. Chem. Int. Ed.* **2003**, *42*, 268–297.
[2] W. Wernsdorfer, R. Sessoli, *Science* **1999**, *284*, 133–135.
[3] M. N. Leuenberger, D. Loss, *Nature* **2001**, *410*, 789–793.
[4] a) J. P. Costes, S. Shova, W. Wernsdorfer, *Dalton Trans.* **2008**, *37*, 1843–1849; b) T. Shiga, T. Onuki, T. Matsumoto, H. Nojiri, G. N. Newton, N. Hoshino, H. Oshio, *Chem. Commun.* **2009**, 3568–3570.
[5] a) C. Aronica, G. Pilet, G. Chastanet, W. Wernsdorfer, J. F. Jacquot, D. Luneau, *Angew. Chem.* **2006**, *118*, 4775–4778; *Angew. Chem. Int. Ed.* **2006**, *45*, 4659–4662; b) M. Gonidec, F. Luis, A. Vilchez, J. Esquena, D. B. Amabilino, J. Veciana, *Angew. Chem.* **2010**, *122*, 1667–1670; *Angew. Chem. Int. Ed.* **2010**,

49, 1623–1626; c) J. Rinck, G. Novitchi, W. Van den Heuvel, L. Ungur, Y. H. Lan, W. Wernsdorfer, C. E. Anson, L. F. Chibotaru, A. K. Powell, *Angew. Chem.* **2010**, *122*, 7746–7750; *Angew. Chem. Int. Ed.* **2010**, *49*, 7583–7587.

[6] R. Sessoli, A. K. Powell, *Coord. Chem. Rev.* **2009**, *253*, 2328–2341.

[7] a) M. A. Aldamen, J. M. Clemente-Juan, E. Coronado, C. Marti-Gastaldo, A. Gaita-Arino, *J. Am. Chem. Soc.* **2008**, *130*, 8874–8875; b) N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.* **2003**, *125*, 8694–8695.

[8] a) S. D. Jiang, B. W. Wang, G. Su, Z. M. Wang, S. Gao, *Angew. Chem.* **2010**, *122*, 7610–7613; *Angew. Chem. Int. Ed.* **2010**, *49*, 7448–7451; b) X. L. Wang, L. C. Li, D. Z. Liao, *Inorg. Chem.* **2010**, *49*, 4735–4737; c) Y. Ma, G. F. Xu, X. Yang, L. C. Li, J. K. Tang, S. P. Yan, P. Cheng, D. Z. Liao, *Chem. Commun.* **2010**, *46*, 8264–8266; d) J. K. Tang, I. Hewitt, N. T. Madhu, G. Chastanet, W. Wernsdorfer, C. E. Anson, C. Benelli, R. Sessoli, A. K. Powell, *Angew. Chem.* **2006**, *118*, 1761–1765; *Angew. Chem. Int. Ed.* **2006**, *45*, 1729–1733; e) Y. N. Guo, G. F. Xu, P. Gamez, L. Zhao, S. Y. Lin, R. P. Deng, J. K. Tang, H. J. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 8538–8539; f) B. Hussain, D. Savard, T. J. Burchell, W. Wernsdorfer, M. Murugesu, *Chem. Commun.* **2009**, 1100–1102.

[9] a) G. Aromi, E. K. Brechin, *Struct. Bonding (Berlin)* **2006**, *122*, 1–67; b) T. Glaser, *Chem. Commun.* **2011**, 116–130.

[10] a) M. T. Gamer, Y. Lan, P. W. Roesky, A. K. Powell, R. Clerac, *Inorg. Chem.* **2008**, *47*, 6581–6583; b) I. J. Hewitt, J. Tang, N. T. Madhu, C. E. Anson, Y. Lan, J. Luzon, M. Etienne, R. Sessoli, A. K. Powell, *Angew. Chem.* **2010**, *122*, 6496–6500; *Angew. Chem. Int. Ed.* **2010**, *49*, 6352–6356; c) S. K. Langley, B. Moubaraki, C. M. Forsyth, I. A. Gass, K. S. Murray, *Dalton Trans.* **2010**, *39*, 1705–1708; d) J. B. Peng, Y. P. Ren, X. J. Kong, L. S. Long, R. B. Huang, L. S. Zheng, *CrystEngComm* **2011**, *13*, 2084–2090; e) P. P. Yang, X. F. Gao, H. B. Song, S. Zhang, X. L. Mei, L. C. Li, D. Z. Liao, *Inorg. Chem.* **2011**, *50*, 720–722.

[11] X. J. Gu, R. Clerac, A. Houri, D. F. Xue, *Inorg. Chim. Acta* **2008**, *361*, 3873–3876.

[12] L. F. Chibotaru, L. Ungur, A. Soncini, *Angew. Chem.* **2008**, *120*, 4194–4197; *Angew. Chem. Int. Ed.* **2008**, *47*, 4126–4129.

[13] a) A. Mukherjee, R. Raghunathan, M. K. Saha, M. Nethaji, S. Ramasesha, A. R. Chakravarty, *Chem. Eur. J.* **2005**, *11*, 3087–3096; b) K. Dhara, P. Roy, J. Ratha, M. Manassero, P. Banerjee, *Polyhedron* **2007**, *26*, 4509–4517; c) J. W. Lu, C. Y. Chen, M. C. Kao, C. M. Cheng, H. H. Wei, *J. Mol. Struct.* **2009**, *936*, 228–233.

[14] a) K. J. Heroux, S. J. Shah, J. R. O'Brien, M. Nakano, A. G. DiPasquale, D. N. Hendrickson, *Inorg. Chim. Acta* **2010**, *364*, 46–54; b) K. Mason, I. A. Gass, S. Parsons, A. Collins, F. J. White, A. M. Z. Slawin, E. K. Brechin, P. A. Tasker, *Dalton Trans.* **2010**, *39*, 2727–2734; c) C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.* **2007**, *129*, 2754–2755; d) V. Tudor, A. Madalan, V. Lupu, F. Lloret, M. Julve, M. Andruh, *Inorg. Chim. Acta* **2010**, *363*, 823–826.

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