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Two-Step Relaxation in a Linear Tetranuclear Dysprosium(III) Aggregate Showing Single-Molecule Magnet Behavior

Yun-Nan Guo,[†,‡] Gong-Feng Xu,[†] Patrick Gamez,[§] Lang Zhao,[†] Shuang-Yan Lin,[†] Ruiping Deng,[†] Jinkui Tang,*[,†] and Hong-Jie Zhang*[,†]

State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China, Graduate School of the Chinese Academy of Sciences, Beijing 100039, P. R. China, and Leiden Institute of Chemistry, Leiden University, 2300 RA Leiden, The Netherlands

Received April 10, 2010; E-mail: tang@ciac.jl.cn; hongjie@ciac.jl.cn

Single-molecule magnets (SMMs) exhibiting slow relaxation of the magnetization have attracted increasing interest because of the prospect of storing and processing magnetic information at a molecular level.[1] For such molecules, the relaxation depends on the energy barrier, which is significantly affected by the strength of the spin−orbit coupling.[2] 4f-based polynuclear compounds are highly promising systems for the development of higher-barrier SMMs because of their significant magnetic anisotropy arising from the strong spin−orbit coupling in low-symmetry crystal fields.[3] Indeed, a single anisotropic magnetic lanthanide ion in an axial crystal-field environment may provide a sufficient condition for the establishment of a thermal barrier for reversing the magnetization and for observing quantum tunneling effects.[4] A number of pure lanthanide-based SMMs have been described in the literature. Most of them contain Dy^{III} ions within different network topologies[5] derived from a dimeric,[5d,l] triangular,[5b] defect-dicubane,[5d,e] or square-pyramidal core[5c] or a wheel.[5a,i] Among them, a tetranuclear Dy$^{III}_4$ coordination compound with a defect-dicubane geometry was reported to exhibit an anisotropic barrier of 170 K.[5h]

On the other hand, the crystal-field analysis in low-symmetry environments is not fully reliable because of the large number of parameters that must be included in the treatment,[6] thereby hampering the development of a rational and efficient strategy for increasing the anisotropy barrier in lanthanide-based systems. Hence, there is a continuing need for the creation of novel structures to enlarge the available database and thus improve the current knowledge of the structure−property relationship in lanthanide-containing SMMs. In the present study, a hexadentate, rigid N,O-donor ligand, 2-hydroxy-3-methoxybenzoic acid [(2-hydroxy-3-methoxyphenyl)methylene] hydrazide (H_3L) was used to generate a linear tetranuclear Dy^{III} aggregate exhibiting SMM behavior with a high anisotropic barrier of 173 K. Strikingly, magnetization dynamics studies revealed that two separate relaxation processes, which can be nicely described by the sum of two modified Debye functions, occur for this compound.

The reaction of $DyCl_3 \cdot 6H_2O$ with H_3L in 1:4 methanol/acetonitrile in the presence of triethylamine produces pale-yellow crystals of $[Dy_4(L)_4(MeOH)_6] \cdot 2MeOH$ (**1**), whose molecular structure determined by single-crystal X-ray diffraction is depicted in Figure 1. The centrosymmetric complex has a nearly linear Dy_4 core characterized by Dy−Dy−Dy angles of 149.99(1)°. Dy1 and Dy2 are bridged by three oxygen atoms (O3, O6, O9) from three ligands. The central Dy ions of the Dy_4 core are connected by two μ-O units. The coordination spheres of the dysprosium ions are completed by methanol ligands, generating eight-coordinate Dy1/Dy1A centers with a distorted bicapped trigonal-prismatic geometry and nine-coordinate Dy2/Dy2A ions with a nearly perfect monocapped square-antiprismatic environment (Figure S1 in the Supporting Information). Strong inter- and intramolecular hydrogen-bonding interactions produce a two-dimensional supramolecular plane with a zigzag arrangement of the molecules (Figure S2). The shortest intermolecular Dy···Dy distance is 8.37 Å.

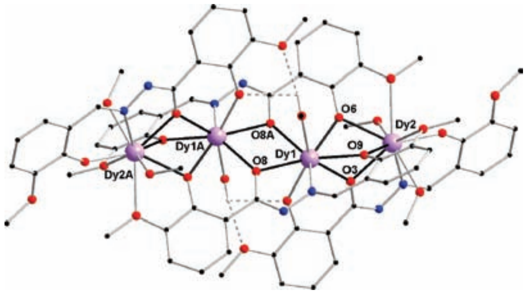

Figure 1. Tetranuclear unit of **1** with the central core highlighted by thicker black bonds. Color scheme: pink, Dy; red, O; blue, N.

Direct-current (dc) magnetic susceptibility studies of **1** were carried out in an applied magnetic field of 1 kOe over the temperature range 300−2 K. The plot of $\chi_M T$ versus T, where χ_M is the molar magnetic susceptibility, is shown in Figure S3. The observed $\chi_M T$ value of 54.9 cm^3 K mol^{-1} at 300 K is slightly lower than the value of 56.7 cm^3 K mol^{-1} expected for four uncoupled Dy^{III} ions ($^6H_{15/2}$, $S = {}^5/_2$, $L = 5$, $J = {}^{15}/_2$, $g = {}^4/_3$). The value of $\chi_M T$ gradually decreases until ∼30 K, where it drops abruptly to a minimum of 31.3 cm^3 K mol^{-1} at 2 K, indicating a progressive depopulation of excited Stark sublevels.[5g] Magnetization data are shown in the inset of Figure S3 and in Figure S4. The nonsuperposition of the M versus H/T data on a single master curve suggests the presence of significant magnetic anisotropy and/or low-lying excited states.

Alternating current (ac) susceptibility measurements were carried out for **1** under a zero-dc field to investigate the dynamics of the magnetization. The occurrence of two distinct peaks for the out-of-phase ac signals (χ'') is evident at higher frequencies (Figure S5), indicating the possible occurrence of a multiple relaxation process.[5f,h] For instance, the χ'' versus frequency plot at 7 K (Figure 2) clearly evidences two peaks, which are centered at 1.2 and 1200 Hz, respectively. These two χ'' maxima may stem from the spin noncollinearity of two types of dysprosium ions in the weakly coupled molecular system **1**.[5h] It is noteworthy that the peaks in the frequency-dependent ac susceptibility are quite distorted, exhibiting a unique double-ridge structure (Figure 2 and Figures

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[†] Changchun Institute of Applied Chemistry.
[‡] Graduate School of the Chinese Academy of Sciences.
[§] Leiden University.

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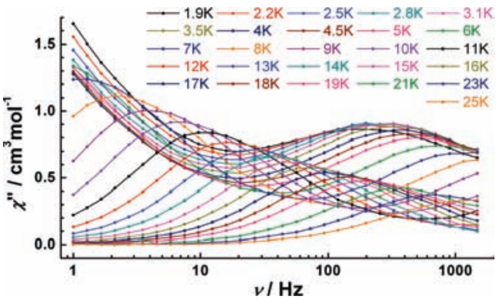

Figure 2. Out-of-phase ac-susceptibility χ'' vs frequency ν on a logarithmic scale for **1** over the temperature range 1.9−25 K.

S6 and S7) as opposed to the shoulder structure in the Dy_3 system.[5b] These frequency-dependent signals are indicative of SMM behavior.

To better understand the nature of the two types of dynamics, the relaxation time of **1** was extracted from the two ridges of the frequency-dependent data between 1.9 and 25 K by fitting the χ'' versus frequency curves, illustrating two relaxation phases corresponding to the high-frequency peaks (fast relaxation phase, FR) and the low-frequency peaks (slow relaxation phase, SR). Arrhenius analysis gave effective energy barriers (Δ) of 19.7 and 173 K and pre-exponential factors (τ_0) of 7.8×10^{-6} and 1.2×10^{-7} s for the FR and SR, respectively (Figure S8). It is noteworthy that $\log(\tau_1)$ (FR) is proportional to $1/T$ for $T > 6$ K and becomes weakly dependent on T (more specifically, $1/\tau_1 \propto T$; see Figure S9) at lower temperatures. This behavior characterizes a crossover from a thermally activated Orbach mechanism that is predominant at high temperature to a direct or phonon-induced tunneling process that takes over at $T < 6$ K.[4d] For the SR, however, the data between 7 and 18 K show good conformity with $1/\tau_2 \propto T^5$, which indicates that the relaxation is dominated by a Raman process.[7]

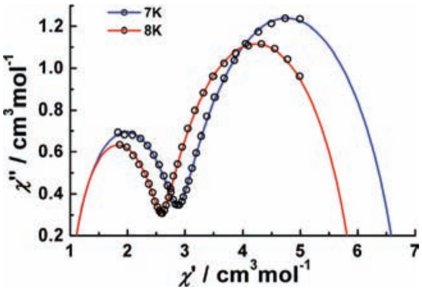

Figure 3. Dynamical susceptibility $\chi(\omega)$ at 7 and 8 K for **1**, displayed as a Cole−Cole diagram. Solid lines indicate fits to eq 1.

As the temperature increases, the Cole−Cole plots go through an evolution from FR to SR at the frequency range of the test (Figure S10). Two separate relaxation processes are clearly observed at 7 and 8 K (Figure 3) that can be nicely described by the sum of two modified Debye functions:[8]

$$\chi_{ac}(\omega) = \frac{\chi_2 - \chi_1}{1 + (i\omega\tau_2)^{(1-\alpha_2)}} + \frac{\chi_1 - \chi_0}{1 + (i\omega\tau_1)^{(1-\alpha_1)}} + \chi_0 \quad (1)$$

The small parameters α_1 and α_2 in eq 1 account for slight deviations from pure Debye processes (see Figures S11−S13 and Table S1). On the basis of the above analysis, the left semicircles in Figure 3 are assigned to faster relaxation dynamics, representative of an Orbach process; on the contrary, the right semicircles suggest a dominant Raman process for the slower relaxation dynamics.

Since the single-ion anisotropy of 4f ions is probably the most important factor, while the exchange is a secondary consideration that moderates the magnetic relaxation of 4f-based SMMs,[4,5j,k] the nature of these slower and faster relaxation processes are most likely associated with distinct anisotropic centers (Figure S1).[5h] This behavior is essentially different from the crossover between two different activated regimes observed in single-chain magnets, which is attributable to finite-size effects,[9] and from that noted in a mononuclear system.[4b] It is well-known that the relaxation rates reflect the local molecular symmetry and are extremely sensitive to tiny distortions of the coordination geometry;[4d] however, further in-depth studies as well as ab initio calculations are required to corroborate this hypothesis, since the presence of two crystallographically independent Dy^{III} sites may not be the sole origin of the two relaxation processes.

In conclusion, a new alkoxido-bridged linear tetranuclear Dy^{III} aggregate showing SMM behavior with a remarkably large energy barrier has been assembled using a rigid ligand. The two maxima observed in the out-of-phase ac signals are indicative of the operation of more than one relaxation process in this compound, which are likely to be affected by the nature or directions of the easy axes through the ligand fields.

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Supporting Information Available: Detailed experimental procedures, structural and magnetic data, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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