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Unusual magnetic relaxation in a single-molecule magnet with toroidal magnetic moments

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We report the synthesis and characterization of a single-molecule magnet composed of triangular clusters of dysprosium ions. The structural study shows that the symmetry changes from one polar point group (*mm*2) at room temperature to another polar point group (*m*) at low temperature. Magnetic studies and theory calculations illustrate that the vortex distribution of magnetic dipoles in the triangular dysprosium clusters forms a toroidal magnetic moment. Interestingly, the analysis of AC magnetic susceptibility reveals the coexistence of three distinct magnetic relaxation processes, corresponding to the Raman, Orbach, and QTM relaxation pathways, respectively. The sum of three modified Debye functions is successfully used to describe the multiple relaxation behavior.

Keywords: single-molecule magnet, magnetic relaxation, toroidal moment

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1. Introduction

Single-molecule magnets (SMMs) are a special class of organic magnets in which nanomagnetic units are isolated by organic ligands.[1–3] SMMs are characterized by slow magnetic relaxation below a magnetic blocking temperature and resonant quantum tunneling of magnetization at low temperatures, which make them promising candidates for applications in high-density spintronic devices[4,5] and quantum computing.[6,7] In recent years, SMMs with a vortex distribution of magnetic dipoles have received special attention, known as single-molecule toroids (SMTs).[8–14] In addition to the traditional polarization and magnetization, the toroidal magnetic moment is also regarded as an electromagnetic moment.[15] In SMTs, the triangular Dy_3 complex is an archetype system. The first example of triangular Dy_3 complex with ring magnetic moment shows an abnormal nonmagnetic ground state.[8] Theory studies suggest that the origin of this nonmagnetic ground state in Dy_3 is the circular arrangement of magnetic moments of three dysprosium ions.[16] After that, a series of Dy_3 compounds have been reported successively.[13,17–20] These SMMs with toroidal magnetic moment provide a playground to better understand the quantum mechanism of complex interactions in the SMT structures, and lay the foundation for the design and synthesis of high-performance SMMs.

In this work, we have synthesized a new type of SMT composed of Dy_3 clusters, $[Dy_3(HL)(H_2L)(NO_3)_4]\cdot(CH_3)_2CHOH$ (H_4L = N,N,N′,N′-tetrakis(2-hydroxyethyl)–ethylene–diamine), named as Dy_3. The structural study shows that the symmetry changes from one polar point group (*mm*2) with 2_1-screw axes (*c*-axes) and glide planes at 298 K to another polar point group (*m*) with glide planes at 30 K. Magnetic measurements and theoretical analyses reveal that distinct magnetic relaxation processes dominate at different temperatures. Especially, the coexistence of three relaxation processes is observed between 5 K and 11 K, which may arise from the three near-degenerate exchange excited Kramers doublets.

2. Experiments

The Dy_3 SMM in this study was synthesized by a solvothermal method. A mixture of 0.5 mmol $Dy(NO_3)_3\cdot 6H_2O$, 1.0 mmol ligand (H_4L) and 0.4 mmol LiOH dissolved in 20 ml isopropanol solution. Then the solution was moved to a clean sample bottle after 2 hours stirring. Colorless crystals with a yield of 46% (based on Dy) were obtained after the solution was reacted at 100 °C for 3 days.

Single-crystal x-ray diffraction was measured on an Agilent Super-Nova diffractometer at 298 K and a Bruker D8 Venture diffractometer at 30 K equipped with graphite monochromatic Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by the full matrix least-squares method on F^2 with anisotropic thermal parameters for all nonhydrogen atoms using the SHELXL program. The obtained structures were deposited in the Cambridge Crystallographic Data Centre (CCDC-2088723 @298 K, CCDC-2088724 @30 K). Magnetic measurements of the powder sam-

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ples were performed by using a quantum design superconducting quantum interference device (MPMS-3).

3. Results and discussion

3.1. Crystal structures

The Dy_3-SMM crystallizes in the polar space group $Pna2_1$ at 298 K but transforms into another polar space group Pc at 30 K with decreasing temperature (Fig. 1). At 298 K, each asymmetric unit contains three Dy^{3+} ions (named Dy1, Dy2, and Dy3) and one isopropanol molecule. Dy1 is coordinated by eight oxygen atoms from two nitrates and two ligands, while Dy2 and Dy3 are coordinated by two nitrogen atoms and seven oxygen atoms provided by one nitrate and two ligands. One free isopropanol molecule is in Dy_3. It contains 2_1-screw axes (c-axes) and glide planes which are parallel to the (010) and (100) planes (Fig. 1(a)).

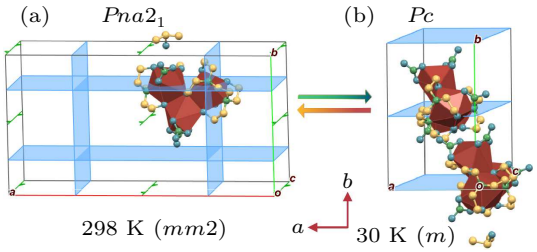


Fig. 1. (a) Symmetry elements of Dy_3 at 298 K. It belongs to the $mm2$ polar point group with 2_1-screw axes (c-axes) and glide planes parallel to the (010) and (100). (b) Symmetry elements of Dy_3 at 30 K. The polar point group changes to m and the 2_1-screw axes disappeared. It contains the glide planes parallel to the (010). The green axes and the blue planes are 2_1-screw axes and glide planes, respectively.

At 30 K, the space group changes to Pc, another polar space group. The main difference between the two structures of $Pna2_1$ and Pc lies in the ordering of solvent isopropanol molecules and the Z value. Moreover, the 2_1-screw axes disappear and the glide plane is parallel to the (010) plane (Fig. 1(b)). As a result, there are two types of triangular molecular structure in the polar Pc space group, expressed as A and B.

To accurately analyse the local coordination symmetry of each Dy^{3+} center, continuous shape measure (CSM)[21] calculations are performed on the DyO_8 and DyN_2O_7 sites. At 298 K, the ideal model reveals that Dy^{3+} ions are situated in a slightly distorted D_{4d} and C_{4v} coordination environment merely with different deviation values. Hence, the Dy_3 is a potential SMM. At 30 K, the calculated results are different from the above results due to the symmetry changes from $Pna2_1$ to Pc. All the nine-coordinated Dy^{3+} ions (Dy2A, Dy2B, Dy3A, Dy3B) are situated within a C_{4v} coordination environment, while the eight-coordinated Dy^{3+} ions are separately in a slightly distorted D_{4d} (Dy1A) and D_{2d} (Dy1B) geometries.

3.2. Magnetism

Complete-active-space self-consistent field (CASSCF) calculations on individual Dy^{3+} fragments for Dy_3 based on the determined geometries at 30 K had been carried out with MOLCAS 8.4 program package.[22] Each individual Dy^{3+} fragment was calculated by keeping the experimentally determined structure of the corresponding compound while replacing the neighboring Dy^{3+} ion with diamagnetic Lu^{3+}. To obtain the exchange interactions in the Dy_3 complex, we took two steps. Firstly, we calculated individual Dy^{3+} fragments using CASSCF/RASSI-SO to obtain the corresponding magnetic properties. Then, the exchange interaction between the magnetic centers was considered within the Lines model,[23] while the account of the dipole–dipole magnetic coupling was treated exactly. The Lines model is effective and has been widely used in the research field of SMMs.[24,25]

The calculations suggest that the Dy^{3+}–Dy^{3+} interaction within the Lines model in the Dy_3 cluster is antiferromagnetic. The main magnetic axes on Dy^{3+} ions are indicated in Fig. 2. The included angles between the main magnetic axes of Dy^{3+} ions for the complex are all larger than 97° so that the local magnetization vectors of Dy^{3+} ions can be approximately regarded as a triangle. Subsequently, a toroidal moment is formed based on the Dy_3 magnetic triangles.

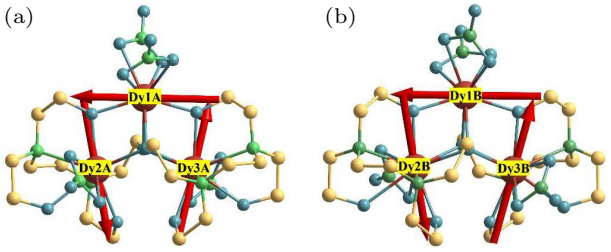


Fig. 2. The toroidal magnetic moment is formed in the Dy_3 clusters ((a) and (b)) at low temperatures. The arrows represent the calculated orientations of the local main magnetic axes on Dy^{3+} ions of the complex. The hydrogen atoms and the isopropanol molecules are omitted for clarity.

The temperature and frequency dependence of AC magnetic susceptibility of the Dy_3 SMM is shown in Fig. 3. Both the in-phase (χ') and out-of-phase (χ'') components of AC magnetic susceptibility show frequency-dependent peaks, which is a characteristic of the SMMs. At low temperatures (2 K–19 K), the frequency dependence of AC magnetic susceptibility shows wide multiple peaks, indicating that there are multiple relaxation processes in the Dy_3-SMM. Especially, three independent relaxation processes can be distinguished from the frequency dependent behavior of $\chi''(\nu)$.

As shown in Fig. 4, the $\chi''(\nu)$ could be well described by a modified Debye function with three relaxation processes (named the faster, medium and slower processes). In the low-temperature region (2 K–4 K), two peaks appear, corresponding to the faster and medium relaxation processes, respectively

(Fig. 4(a)). The faster process is almost temperature independent and is ascribed to quantum tunneling of magnetization (QTM). In contrast, the medium relaxation process shifts to a higher frequency as temperature increases. In the temperature range between 5 K and 11 K, three peaks can be simultaneously observed, indicating the coexistence of three relaxation processes (Fig. 4(b)). Both the slower and medium processes shift to a higher frequency with increasing temperature. Between 12 K and 19 K, the faster relaxation process due to QTM disappears, while the medium and slower relaxation processes persist (Fig. 4(c)). The clear shift of the medium and slower processes with temperature suggests that they originated from thermally activated relaxation processes.

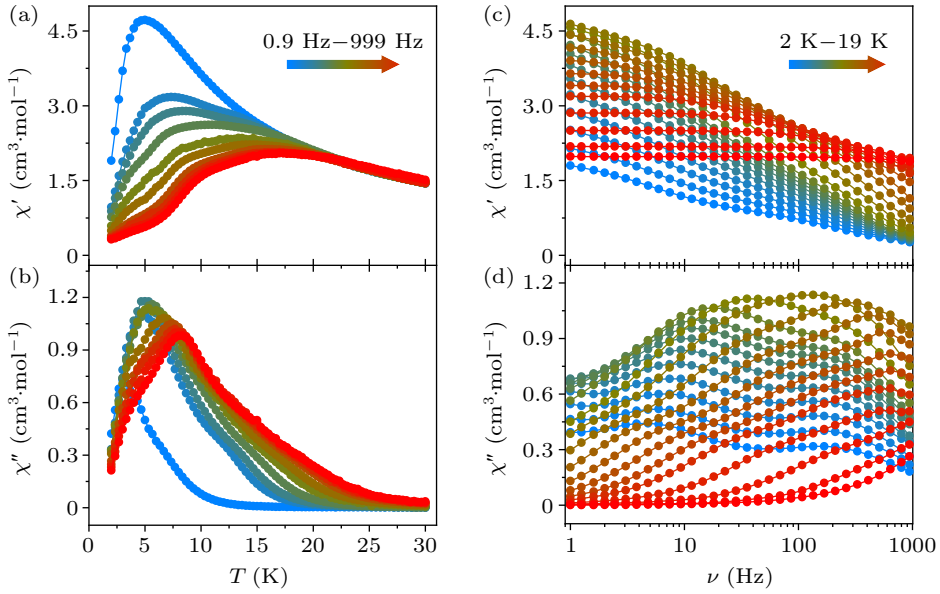


Fig. 3. (a) and (b) Temperature dependence of AC magnetic susceptibility of Dy_3. The frequency dependent peak is a characteristic of magnetic blocking of SMMs. (c) and (d) Frequency dependence of AC magnetic susceptibility in the temperature range of 2 K–19 K.

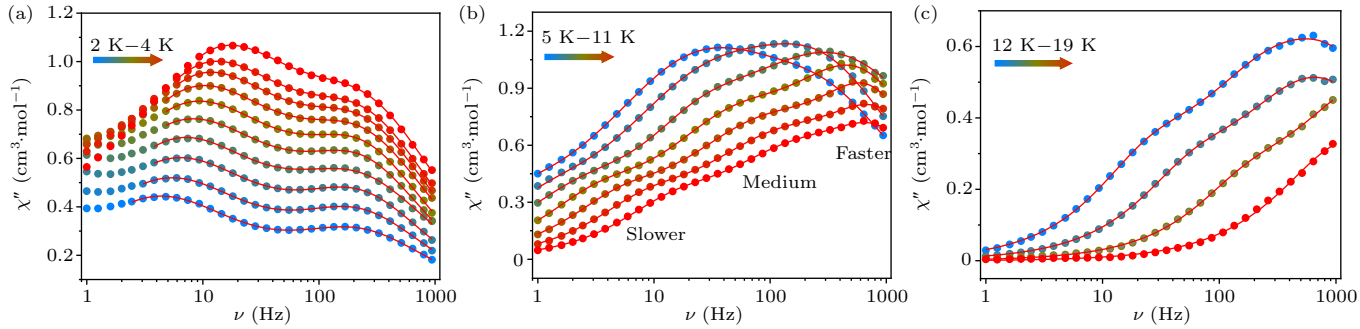


Fig. 4. The frequency-dependence of out-of-phase (χ'') component of AC magnetic susceptibility in the temperatures ranging from 2 K to 19 K. The solid lines are the best fitting results of the modified sum of three Debye functions.

The experimental data of $\chi''(\nu)$ between 5 K and 11 K can be well simulated and depicted as the Cole–Cole plots,[26] which provide a more indicative view of the evolution and coexistence of multiple relaxation processes, as shown in Fig. 5. The relaxation time of each process is extracted by the sum of three modified Debye functions[27]

$$\chi_{\rm ac}(\omega) = \chi'(\omega) - {\rm i}\chi''(\omega),$$
$$\chi_{\rm ac}(\omega) = \chi_{\rm S} + \sum_k \frac{\Delta\chi_k}{1+({\rm i}\omega\tau)^{(1-a_k)}},$$
$$\chi_{\rm S} = \sum_k \chi_{{\rm S},k}, \quad \Delta\chi_k = \chi_{{\rm T},k} - \chi_{{\rm S},k},$$

where $\chi_{\rm S} = \chi_{\rm S1} + \chi_{\rm S2} + \chi_{\rm S3}$ is the sum of the adiabatic susceptibility of three relaxing species; $\Delta\chi_k$ is the difference between the adiabatic susceptibility ($\chi_{{\rm S},k}$) and the isothermal susceptibility ($\chi_{{\rm T},k}$) of each magnetic phase; α is the parameter to quantify the width of the relaxation time (τ) distribution. The small α values ($\alpha < 0.35$) indicate that each relaxation process has a relative contribution to the whole relaxation time. In other temperature ranges, the data are well described with the sum of two modified Debye functions ($\chi_{\rm S} = \chi_{\rm S1} + \chi_{\rm S2}$).

The correlation between the relaxation time (τ) and temperature (T) can be obtained from the $\ln(\tau)$ versus $\ln(T)$ plot to give the n values of the three relaxation processes (n represents the parameter of the relationship between T and τ, in the equation $\tau = T^{-n}$). According to the fitting results, the Raman process and Orbach relaxation path due to spin-phonon coupling[28] mainly dominate the medium and slower

processes whereas the faster process is determined by QTM (Fig. 5(b)).

The presence of multiple relaxation channels in SMMs is not unusual, but they usually dominate in different temperature regimes. The coexistence of three distinct relaxation processes at the same temperature has never been observed. It implies the inhomogeneity of magnetic relaxation units in the system. This could be related to the inequality of three Dy^{3+} ions in the triangular Dy_3 clusters or the slight difference between Dy_3 molecules.

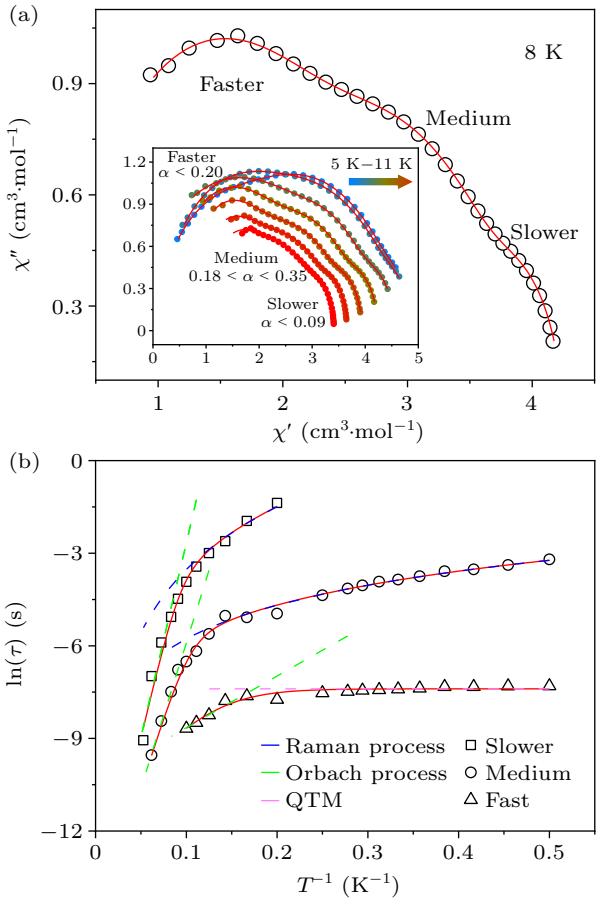


Fig. 5. (a) The Cole–Cole plot at 8 K. The inset shows the Cole–Cole plots in the temperature range of 5 K–11 K. (b) The correlation between relaxation time (τ) and temperature (T). The solid lines are the best fitting results.

4. Conclusion

A Dy_3 SMM has been synthesized and investigated. The local magnetization vectors of Dy^{3+} ions are approximately regarded as a triangle with a toroidal magnetic moment. This Dy_3 single-molecule toroid exhibits unusual magnetic relaxation behavior. Three distinct relaxation processes, corresponding to Raman, Orbach and QTM relaxation paths, can coexist in the same temperature range. The sum of three modified Debye functions is successfully used to describe the multiple magnetic relaxation process. Our study suggests that single-molecule toroids may have more complex and intriguing properties than conventional SMMs.

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