Single-Ion Magnets

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A Mononuclear Dysprosium Complex Featuring Single-Molecule-Magnet Behavior**

Shang-Da Jiang, Bing-Wu Wang, Gang Su, Zhe-Ming Wang, and Song Gao**

Single-molecule magnets (SMMs)[1] have received much attention owing to their quantum tunneling and slow relaxation.[2] These behaviors can be observed when the molecule has large ground spin state with a uniaxial magnetic anisotropy, namely negative zero-field splitting (ZFS) parameter D. Besides a large ground state, to increase the SMMs' energy barrier and blocking temperature, it is of fundamental importance to control the magnetic anisotropy.[3] It is also of great complexity to understand the conditions that determine the anisotropy or zero-field splitting properties for a cluster.[4] As a result, SMMs containing only one spin carrier are of great interest because of the simplification in the analysis of local anisotropy and ZFS. Recently, some molecules with isolated 3d[5] or 4f[6] metal ions were observed to show a direct-current (dc) field-induced slow magnetic relaxation. Studies show that this kind of dc-field-dependent relaxation phenomenon is thermally activated, and the quench of fast quantum tunneling by the dc field could give rise to the slow relaxation. However, as commented by Benelli and Gatteschi,[7] it is an unexpected and puzzling behavior, and the underlying mechanism is still unclear. Ishikawa et al. reported that the phthalocyanine (Pc) double-decker anion complexes $[Pc_2Ln]^-$ with a single Tb^{III} or Dy^{III} ion show slow relaxation without a dc field.[8] A single Er^{III} ion in the polyoxometallate system $[ErW_{10}O_{36}]^{9-}$ showed similar relaxation behavior in zero static magnetic field.[9] The first single-actinide complex $[U(Ph_2BPz_2)_3]$ (containing the U^{III} ion; Ph_2BPz_2 = diphenylbis(pyrazolylborate)) reported by Rinehart and Long shows a similar slow relaxation.[10] Owing to the single-ion features, these complexes could be called "single-ion magnets". In these complexes, ligand fields with a high-order single axis C_n ($n > 2$; $n = 4$ for Ref. [8,9] and $n = 3$ for Ref. [10]) split the $(2J+1)$ degenerate ground states into new sublevels, which produces a uniaxial anisotropy, thus giving rise to a higher energy barrier for relaxation.[8b] The Dy^{III} ion, which possesses a Kramers ground state of $^6H_{15/2}$, is an appealing paramagnetic source for the construction of SMMs in a suitable ligand-field symmetry and strength. Moreover, among reported SMMs, some of them are clusters containing Dy^{III}: Dy_2,[11] Dy_3,[12] Dy_4,[13] Dy_5,[14] Dy^{III}-containing chain,[15] and tens of Dy^{III}-containing 3d–4f clusters.[16]

All three reported types of single-ion magnets[8] are found with a high-order single axis defining the local symmetry. Pursuing this clue, we synthesized a series of mononuclear Ln^{III} compounds with a local symmetry close to D_{4d}. Crystal analysis shows that the isomorphous complexes consist of a neutral mononuclear $[Ln(acac)_3(H_2O)_2]$ complex (Ln = Dy, Ho, Er, acac = acetylacetonate) together with an uncoordinated water molecule and an uncoordinated ethanol molecule (Figure 1 a). In the Dy^{III} complex, Dy^{3+} is coordinated by eight oxygen atoms with Dy–O bonds of 2.311–2.434 Å, six of which come from the acetylacetonate ligand and two from coordinated water molecules. The eight oxygen atoms form an approximately square-antiprismatic coordination polyhedron, and the local symmetry of Dy^{III} is nearly D_{4d} (Figure 1 b). Actually, a similar lanthanide acac complex was firstly reported in 1968,[17] but the uncoordinated water and

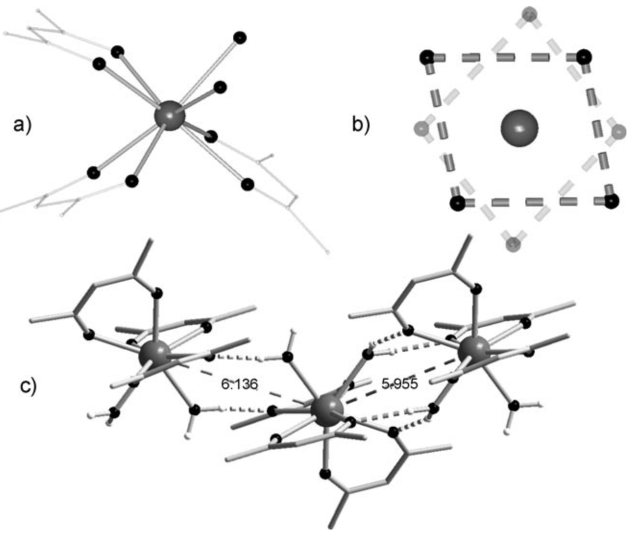

Figure 1. a) The molecular structure of $[Dy(acac)_3(H_2O)_2]$ (hydrogen atoms are omitted). b) The D_{4d} coordination mode of the complex. c) The hydrogen bonds between the molecules. C gray, H light gray, O black, Dy dark gray.

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[*] S.-D. Jiang, Prof. Dr. B.-W. Wang, Prof. Dr. Z.-M. Wang, Prof. Dr. S. Gao
Beijing National Laboratory of Molecular Science
State Key Laboratory of Rare Earth Materials Chemistry and Applications
College of Chemistry and Molecular Engineering, Peking University
Beijing 100871 (China)
Fax: (+86) 10-6275-1708
E-mail: wangbw@pku.edu.cn
gaosong@pku.edu.cn
Homepage: http://www.chem.pku.edu.cn/mmm/

Prof. Dr. G. Su
College of Physical Sciences
Graduate University of Chinese Academy of Sciences
P. O. Box 4588, Beijing 100049 (China)

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ethanol did not crystallize in the cell. The neutral $[Dy(acac)_3(H_2O)_2]$ molecules are connected by hydrogen bonds that are formed by the hydrogen atoms of coordinated water molecules and the oxygen atoms of acetylacetonate along the *c* axis, which results in Dy⋯Dy distances of 5.956 and 6.136 Å (Figure 1c).

The temperature dependence of the magnetic susceptibility $\chi_M T$ for the three complexes is shown in Figure S1 in the Supporting Information. The values of $\chi_M T$ are 14.18, 14.08, and 11.48 emu mol^{-1} K at 300 K for the Dy, Ho, and Er complexes, respectively, in good agreement with the theoretical values. On cooling, $\chi_M T$ for the three complexes decreases gradually and more rapidly below 50 K, which is mostly due to crystal-field effects (i.e. thermal depopulation of the Ln^{III} Stark sublevels) and possible antiferromagnetic dipole–dipole interaction between the molecules. The magnetizations of the three complexes from zero dc field to 50 kOe at 2 K are shown in the inset of Figure S1, and the corresponding maximum values reached are 5.52, 5.41, and 5.19 Nβ. The lack of saturation of magnetization at 50 kOe can likely be attributed to crystal-field effects and the low-lying excited states, while the non-superposition of the temperature-dependence under different fields (Figure S2 in the Supporting Information) implies the presence of significant magnetic anisotropy.[11–14]

Figure 2 shows the alternating-current (ac) susceptibility at various frequencies and temperatures in the absence of a dc field. Both in-phase (χ') and out-of-phase (χ'') susceptibilities show a frequency dependence, while the peaks can only be found at frequencies higher than 31.6 Hz. On cooling, the increase of χ' and χ'' is observed below 5 K, which could be attributed to quantum tunneling effects at zero dc field. This kind of observation is consistent with some previous studies on SMMs;[8,9b,11,15] the tunneling mechanism was investigated in a dense spin system.[18] For the relaxation from quantum tunneling, the values of χ' and χ'' are proportional to the population of ground states, because quantum tunneling happens between the degenerated ground states. The increase of the population of ground states on cooling can give rise to the increase in χ' and χ'' versus T plots in the quantum tunneling regime. The relaxation time from both χ'' versus T and Argand diagrams at temperatures from 2 to 11 K can be deduced. Arrhenius law fitting of the relaxation time above 8 K shows an energy barrier as high as 66.1 K (45.9 cm^{-1}) and a relaxation time constant of 8.0×10^{-7} s (Figure 3). The frequency-dependent ac susceptibility of magnetic-site-diluted samples reveals the single-ion origin of such slow relaxation behavior. It should be noted that for the diluted samples the peaks of χ'' versus T can be observed at frequencies as low as 1 Hz (Figures S4 and S5 in the Supporting Information), which indicates that the quantum tunneling is not as obvious as that in a pure sample. The energy barriers are determined to be 64.3 K (44.7 cm^{-1}) and 67.3 K (46.8 cm^{-1}) for 1:20 and 1:50 dilution, respectively (Figure 3).

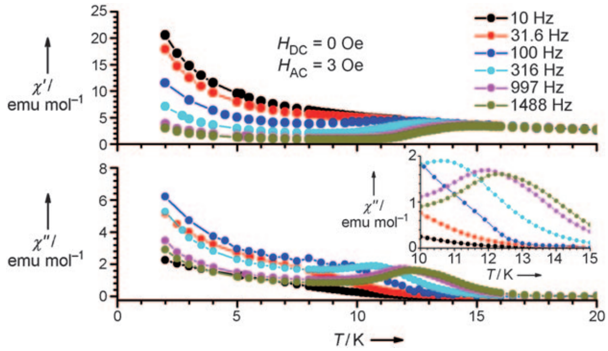

Figure 2. The temperature dependence of ac susceptibility at frequencies from 10 to 1488 Hz for the undiluted Dy^{3+} complex.

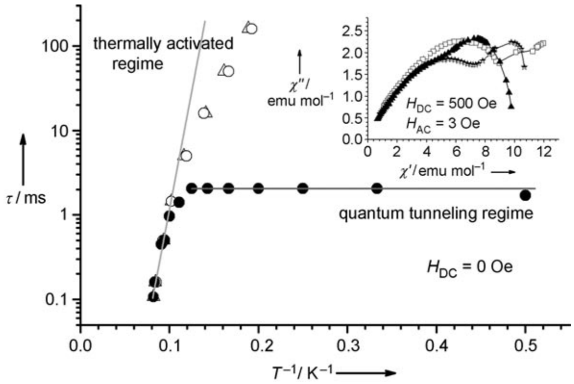

Figure 3. The relaxation time (τ) of the Dy^{3+} complex at different concentrations in $[Y(acac)_3(H_2O)_2]$ in the temperature range 2–12 K. The undiluted sample shows a crossover around 8 K at zero dc field, and the thermally activated regime of the samples can be approximately fitted to Arrhenius law. ● undiluted sample, ○ 1:20 dilution, △ 1:50 dilution. Inset: The Argand diagram of the undiluted Dy^{3+} complex at 500 Oe from 3 to 5 K. □ 3 K, ★ 4 K, ▲ 5 K.

Magnetization hysteresis is another important characteristic of magnetic bistability of SMMs in addition to the frequency dependence of χ_{ac}. When the dc magnetization is measured at 2 K within ±5 kOe, no obvious hysteresis loop is detected (Figure S5 in the Supporting Information). However, when the temperature goes down to 0.5 K with a ^{3}He system, a butterfly-shaped hysteresis loop emerges (Figure S6 in the Supporting Information). For the diluted complexes, the hysteresis loop can be observed at both 2 and 0.5 K (Figures S7–S9 in the Supporting Information). As can be seen in Figure 4, the loop of the 1:20 diluted complex at 0.5 K is much larger and wider than that of the pure complex. The zero-field cooled (ZFC) and field cooled (FC) susceptibilities at 20 and 800 Oe for the diluted sample are consistent with the butterfly-shaped loop (Figure S10 in the Supporting Information). The butterfly-shaped hysteresis loop does not show a remanence and a coercive field. This lack is owing to the sweep rate (150 Oe min^{-1}) of the loop, which is slow compared with the fast zero-field relaxation between the two ground states. Although the dilution has depressed the tunneling to some extent, the non-strict D_{4d} local symmetry may introduce a transverse component of the anisotropy, which may give rise to the mixture of the degenerated states, and thus the quantum tunneling is possible.

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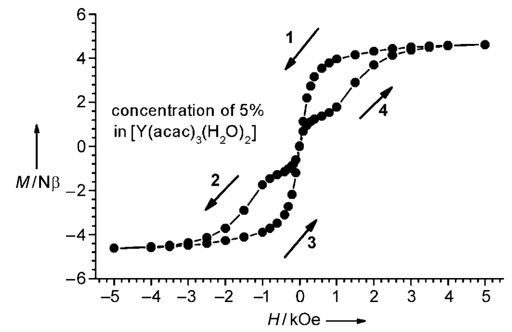

Figure 4. Hysteresis loop for the Dy^{3+} complex diluted 1:20 with the Y^{3+} complex at 0.5 K.

As indicated in Figure 3, the relaxation time above 8 K (the crossover temperature, T_{cross}) is temperature-dependent, suggesting that the corresponding magnetic relaxation process is thermally activated. However, as the temperature goes down below T_{cross}, the relaxation time keeps a constant value of 2.1×10^{-3} s. Obviously, the temperature independence of the relaxation time below T_{cross} cannot be explained by the spin–spin relaxation mechanism proposed in DyVO$_4$ and DyPO$_4$,[19] since 2 ms is too long a time for the spin–spin relaxation, which is at the nanosecond level. The temperature-independent relaxation below T_{cross} might be realized through quantum tunneling between the two degenerate Kramers ground states. This kind of quantum relaxation behavior is found only in a few SMM clusters at very low temperature,[20] and there is a unique example of such relaxations in a dense spin system as well.[18] Furthermore, the slow quantum relaxation was also observed at low temperature in single-ion magnets [Pc$_2$Tb]$^-$, [Pc$_2$Dy]$^-$,[8b] and [ErW$_{10}$O$_{36}$]$^{9-}$.[9b] On cooling below T_{cross}, the relaxation appears to have a crossover from a thermally activated process to a quantum tunneling process. The Argand diagram measured in the dc field gives solid support for this analysis (inset of Figure 3). In a dc field of 500 Oe, the Argand diagram shows a gradual transition from one peak to two peaks on cooling, thus indicating the coexistence of thermally activated and quantum tunneling relaxation.

Quantum tunneling cannot happen when the Kramers ground states are orthogonal to each other unless a perturbation Hamiltonian that allows the mixing of the two states is introduced.[2b] In the present situation, the dipole–dipole interaction, as well as the non-strict D_{4d} local symmetry of the structure, may be taken as such a perturbation. By dilution, as the dipole–dipole interaction is weakened, the quantum tunneling is suppressed. The degeneracy of the Kramers states can be lifted by applying a dc field, preventing mixing of the ground states. We have found that, for the undiluted Dy complex, by applying a static field of 500 Oe, the ac susceptibility at different temperatures is similar to the behavior of the diluted sample in zero dc field (Figure S11 in the Supporting Information). This observation is in good agreement with the above analysis that the quantum tunneling is suppressed by applying a dc field. By combining both dilution and a dc field, we can successfully block the quantum tunneling in the low-temperature range, and no rising can be observed upon cooling below 5 K (Figure S12 in the Supporting Information).

The magnetic properties of isomorphous complexes containing Ho and Er ions were also studied, but neither of them is found to exhibit such a slow relaxation behavior as the Dy$^{\mathrm{III}}$ compounds. To investigate the difference between Dy$^{\mathrm{III}}$ and other lanthanide complexes, the fine electronic structures of heavy rare-earth elements from Dy to Er were explored by ligand-field theory using the package code CONDON developed by Lueken and co-workers.[21] The model Hamiltonian for the present single lanthanide ion compound could be expressed as in Equation (1).

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_0 + \hat{\mathbf{H}}_{\mathrm{ee}} + \hat{\mathbf{H}}_{\mathrm{SO}} + \hat{\mathbf{H}}_{\mathrm{LF}} + \hat{\mathbf{H}}_{\mathrm{MF}} \tag{1}$$

$\hat{\mathbf{H}}_0$, $\hat{\mathbf{H}}_{\mathrm{ee}}$, $\hat{\mathbf{H}}_{\mathrm{SO}}$, $\hat{\mathbf{H}}_{\mathrm{LF}}$, and $\hat{\mathbf{H}}_{\mathrm{MF}}$ account for the Hamiltonians of zero level energy, interelectronic repulsion, spin–orbit effect, ligand-field effect, and Zeeman effect, respectively. By fitting the dc magnetic susceptibility data at 1000 Oe from 50 to 300 K (Figure S13 in the Supporting Information), the fine structures and low-energy spectra of [Ln(acac)$_3$(H$_2$O)$_2$] (Ln = Dy, Ho, Er) were obtained, as listed in Table 1.

Table 1: The fine electronic structures and low-energy spectra of [Ln(acac)$_3$(H$_2$O)$_2$] (Ln = Dy, Ho, Er).

Ln^{3+} in [Ln(acac)$_3$(H$_2$O)$_2$]	Dy^{3+}	Ho^{3+}	Er^{3+}
Ground state (M_J)	±13/2	±4	±1/2
First excited state (M_J)	±11/2	±8	±13/2
Energy separation [cm^{-1}]	27.8	5.6	11.6
Type of ground state	Ising	non-Ising	non-Ising

In these complexes, Dy$^{\mathrm{III}}$ is the only ion with the quantum number $|M_J|$ of the ground state (13/2) larger than that of the first excited state (11/2), which suggests that the Dy$^{\mathrm{III}}$ complex has Ising ground states and that the ZFS parameter D is negative, corresponding to uniaxial anisotropy. The absent slow magnetic relaxation behavior of Ho$^{\mathrm{III}}$ and Er$^{\mathrm{III}}$ compounds can be mainly attributed to their non-Ising ground states, although they have the same geometrical structures. It should be noted that [Pc$_2$Tb]$^-$ and [Pc$_2$Dy]$^-$ possess Ising ground states as well. The D_{4d} local symmetry for lanthanide ions introduces Ising ground states in both [Pc$_2$Ln]$^-$ systems and ours; however, for different ligands, the energy sublevels can be various owing to the distinct ligand-field strength and distortion observed in the Ln^{3+} site. Accordingly, the ligand-field effect plays a very important role in the slow relaxation behavior in the absence of a dc field, just as the spin–orbit coupling does.

In our measurements, the linear relationship of $\ln(1/\tau)$ with $1/T$ indicates that the Orbach process is dominant in the temperature range of 8 to 12 K at zero dc field. According to the Orbach process, the potential energy barrier should be the gap between the ground state and first excited state. The energy barrier of 45.9 cm^{-1} fitted by the Arrhenius law is consistent with the result from the ligand-field theory (27.8 cm^{-1}) in the range of quantum calculation accuracy.

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In conclusion, we have synthesized a single-ion magnet containing a Dy^{III} ion with approximate D_{4d} local symmetry. The complex exhibits a crossover at $T_{cross} = 8$ K between thermally activated relaxation ($T > T_{cross}$) and quantum tunneling relaxation ($T < T_{cross}$). By dilution or application of a magnetic field, the quantum tunneling is suppressed. Meanwhile, the thermally activated relaxation happens in a wider temperature range and the hysteresis loop becomes more obvious. We propose that the Ising ground states can give rise to the slow magnetic relaxation, while the various energy sublevels for Ln^{III} can be affected by spin–orbit coupling and ligand field. The dynamic magnetic behavior is a combined result of these properties.

Experimental Section

$[Dy(acac)_3(H_2O)_2]\cdot H_2O\cdot C_2H_5OH$: A mixture of acetylactone (0.40 g) and KOH (0.20 g) was heated at reflux in ethanol (20.0 mL). A white precipitate was generated as soon as $Dy(NO_3)_3\cdot 6H_2O$ (0.45 g) was added. After water (5.0 mL) was injected, a transparent, light yellow solution was obtained. The solution was cooled at 4 °C overnight, then it was filtrated and left to stand at room temperature with slow evaporation for several days; colorless crystals were obtained. Elemental analysis calcd (%) for $C_{17}H_{33}DyO_{10}$: C 36.47, H 5.94; found: C 36.42, H 5.99. The isomorphous complexes with Ho^{3+} and Er^{3+} are also synthesized in the same way. The magnetic-site dilution was performed by adding $Dy(NO_3)_3\cdot 6H_2O$ and $Y(NO_3)_3\cdot 6H_2O$ together in the synthesis process. CCDC 770557, 770558, and 770559 contain 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. The data were collected on a Nonius KappaCCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using the Sortav program. Magnetic measurements were performed on a Quantum Design MPMS XL-5 SQUID magnetometer on polycrystalline samples. Data were corrected for the diamagnetism of the samples using Pascal constants and of the sample holder by measurement. The hysteresis loops at 0.5 K were measured on the *i*Helium Measurement Console in coordination with MPMS MultiVu, and the samples were fixed by eicosane to avoid movement during the measurement.

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