Inorganic Chemistry
Communication

Inorg. Chem. **2009**, *48*, 11495–11497 **11495**
DOI: 10.1021/ic901806g

Observation of Slow Magnetic Relaxation in Discrete Dysprosium Cubane

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Received September 11, 2009

A discrete dysprosium cubane has been prepared and structurally characterized. Slow relaxation of magnetization in this complex is observed, which may stimulate further investigations into the dynamics of magnetization in lanthanide clusters with different topologies.

The study of single molecule magnets (SMMs) for which slow relaxation and quantum tunneling of the magnetization is purely of molecular origin has long been of great interest. The observation of slow magnetic relaxation in these molecules is recognized as an important breakthrough in the field of molecular magnetism with the promise of a revolution in data storage and processing.[1,2] A large number of complexes displaying this property have been reported since the discovery in the early 1990s of the first SMM, Mn_{12} acetate.[1] Most of the SMMs synthesized so far are polynuclear transition-metal complexes.[3] Slow magnetic relaxation has only been found in a few molecules either incorporating[4] or made exclusively from 4f ions[5] because of the synthetic challenges and the difficulty in promoting magnetic interactions via the overlap of bridging ligand orbitals with the "contracted" 4f orbitals of the lanthanide ions. Lanthanide ions are incorporated into these complexes to take advantage of the potentially large number of unpaired f electrons available and their potential to introduce anisotropy to a molecule as a result of the nature of the f-electron shell. This magnetic anisotropy is the major component in observing slow relaxation of magnetization. The mononuclear lanthanide complexes exhibiting SMM behavior have significantly large axial magnetic anisotropy, which is given to the complexes by essentially a different mechanism than those of the well-established 3d-based SMMs.[5b]

The observation of slow magnetic relaxation in lanthanide mononuclear complexes has stimulated much further work involving the synthesis of polynuclear complexes and assemblies based on 4f ions.[5b] Very recently, novel high-nuclearity lanthanide complexes with discrete structures, Er_{26} and two analogue dysprosium assemblies Dy_{30} and Dy_{26}, have been prepared by a surface modification strategy under hydrothermal conditions.[6] Interestingly, alternating current (ac)

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susceptibility measurements reveal that slow relaxation of magnetization is found in Dy_{30} constructed from Dy_{26} and Dy_4 cluster units, while Dy_{26} itself does not exhibit any out-of-phase ac signal considering that both are built from Dy_{26} aggregates.[6b] Noting that many of those large yet molecular species built from Ln_4O_4 cubane-like cores display aesthetically pleasing structures and interesting properties,[7-9] herein we report the successful isolation of a discrete dysprosium cubane-like complex, $[Dy_4(\mu_3\text{-}OH)_4(\text{isonicotinate})_6(\text{py})(CH_3OH)_7](ClO_4)_2\cdot\text{py}\cdot 4CH_3OH$ (**1**; py = pyridine), which displays slow relaxation of magnetization. To the best of our knowledge, this is the first example of a discrete dysprosium cubane exhibiting slow magnetic relaxation behavior.

The reaction of dysprosium(III) perchlorate with isonicotinic acid in methanol and pyridine (2:1, v/v) in the presence of a Schiff base produces the Dy_4 cubane of formula $[Dy_4(\mu_3\text{-}OH)_4(\text{isonicotinate})_6(\text{py})(CH_3OH)_7](ClO_4)_2\cdot\text{py}\cdot 4CH_3OH$ (**1**). Attempts to grow single crystals of this complex in the absence of the Schiff base were unsuccessful, indicating that this Schiff base might promote the formation of this complex. The structure of complex **1** determined by single-crystal X-ray diffraction consists of tetranuclear $[Dy_4(\mu_3\text{-}OH)_4(\text{isonicotinate})_6(\text{py})(CH_3OH)_7]^{2+}$ cations, perchlorate anions, and pyridine and methanol molecules. A perspective view of the tetranuclear cations is depicted in Figure 1. Four dysprosium atoms and four bridging μ_3-OH groups form a distorted cubane-like $[Dy_4(\mu_3\text{-}OH)_4]^{8+}$ core, which is structurally similar to the tetranuclear units in the above-mentioned Dy_{30} complex.[6] The cluster core is encapsulated by six isonicotinate ligands through bridging carboxylate groups, and the metal coordination sphere is completed by methanol and pyridine ligands. The terminal pyridine ligand instead of a bridging isonicotinate ligand may prevent the formation of extended structures and result in the isolation of a discrete Dy_4 cubane.[6,9a] Each dysprosium ion is eight-coordinated. The cubic array of alternating dysprosium and oxygen atoms gives intracluster metal−metal separations in the range of 3.720 and 3.857 Å. The shortest intercubane distance between dysprosium ions is 9.732 Å. It is noteworthy that coordination by a pyridine rather than by two methanol molecules disrupts the T_d (tetrahedral) symmetry of the cubane core, leading to idealized C_3 symmetry and to the appearance of magnetic anisotropy (see Figure S1 in the Supporting Information). The magnetization relaxation of the complex is consequently influenced by this molecular anisotropy (see below).

This discrete cubane-like Dy_4 complex presents us a unique opportunity to study the magnetic properties and to probe the dynamics of magnetization in this system.

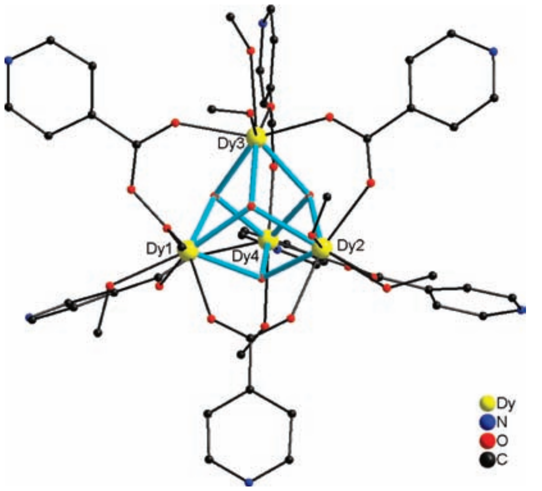

Figure 1. View of the $[Dy_4(\mu_3\text{−}OH)_4(\text{isonicotinate})_6(\text{py})(CH_3OH)_7]^{2+}$ cationic part in complex **1** highlighting the cubic core in sky-blue lines.

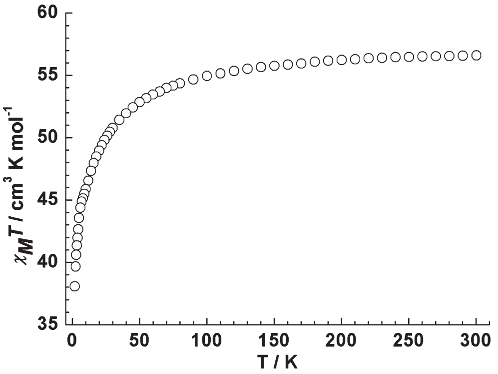

Figure 2. Temperature dependence of the $\chi_M T$ product at 1000 Oe.

Direct-current (dc) magnetic susceptibility studies of **1** have been carried out in an applied magnetic field of 1000 Oe in the temperature range 300−2 K. The plot of $\chi_M T$ vs T, where χ_M is the molar magnetic susceptibility, is shown in Figure 2. The observed $\chi_M T$ value at 300 K of 56.6 cm^3 K mol^{-1} corresponds exactly to the expected value of 56.7 cm^3 K mol^{-1} for four uncoupled Dy^{III} ions ($S = {}^5/_2$, $L = 5$, $^6H_{15/2}$, $g = {}^4/_3$). $\chi_M T$ gradually decreases until 50 K and then further decreases to reach a minimum of 38.1 cm^3 K mol^{-1} at 2 K, which probably ascribes to a combination of the exchange interaction between the Dy^{III} ions and the progressive depopulation of excited Stark sublevels.

The M vs H/T (Figure 3) data at different temperatures show nonsuperposition plots and a rapid increase of magnetization at low field, which eventually reaches the value of 23.7 μ_B at 2 K and 7 T without any sign of saturation. This value is lower than the expected saturation value of 40 μ_B (10 μ_B for each Dy^{III} ion). This difference is most likely due to anisotropy and the crystal-field effect at the Dy^{III} ion that eliminates the 16-fold degeneracy of the $^6H_{15/2}$ ground state. Indeed, the maximum of magnetization is consistent with the expected value (4 × 5.23 μ_B) for four uncorrelated Dy^{III} ions with a value of 5.23 μ_B per Dy^{III} ion assuming the presence of considerable ligand-field effects.[5a]

The dynamics of magnetization were investigated from the ac susceptibility measurements, with the results in zero static field and a 3.0 G ac field oscillating at the indicated frequencies (1−1400 Hz) given in Figure 4 as plots of χ' vs T and χ'' vs T. Strikingly, the frequency-dependent increase of the in-phase signal and the concomitant appearance of the

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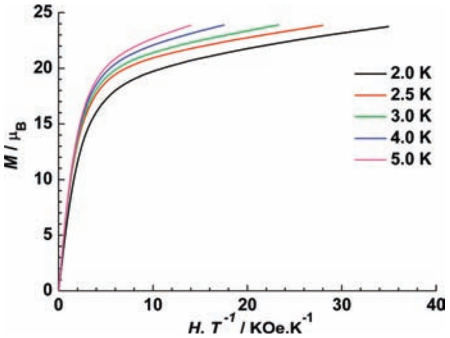

Figure 3. M vs H/T plots at different temperatures below 5 K.

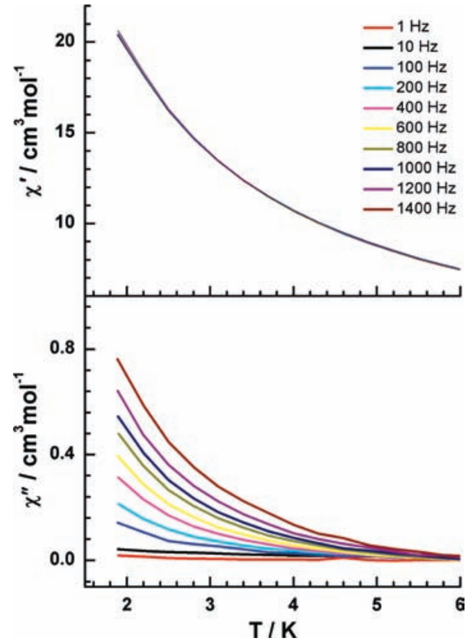

Figure 4. Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibility of the complex under zero dc field.

out-of-phase signal were observed below 6 K, indicating the onset of slow magnetization relaxation. To probe further the dynamics of this system, ac susceptibility measurements as a function of the frequency at different temperatures were carried out. The relaxation time at different temperatures was extracted by fitting the χ'' vs frequency curves[5c] (Figure S2 in the Supporting Information). Plotting the relaxation time versus the reciprocal temperature afforded the Arrhenius plot in Figure S3 in the Supporting Information. Above 3.1 K, the relaxation follows a thermally activated mechanism with an energy gap of 40.2 K and a preexponential factor, τ_0, of about 1.1×10^{-11} s. Because of the fact that slow relaxation of magnetization is experimentally observed only over a short range of temperature[5e] and no maximum of χ'' is observed in the temperature window technically available, the estimation of these characteristic parameters might not be very accurate, but τ_0 is consistent with the expected numbers ($\tau_0 = 10^{-6}-10^{-11}$ s) for a SMM. At lower temperature, a gradual crossover to a temperature-independent regime is observed. Preliminary field-dependent ac measurements may suggest that the dc magnetic field cannot effectively suppress the possible zero-field quantum relaxation above 1.9 K (see Figure S4 in the Supporting Information).

In summary, a discrete dysprosium cubane has been prepared and structurally and magnetically characterized. ac susceptibility measurements reveal a frequency-dependent out-of-phase signal, indicative of slow relaxation of magnetization. Our preliminary investigation could shed light on the origin of slow relaxation of magnetization found in Dy_{30} constructed from Dy_{26} and Dy_4 cluster units,[6b] and more detailed studies are currently carried out to probe further the dynamics of magnetization in lanthanide clusters with different topologies.

Acknowledgment. We thank Changchun Institute of Applied Chemistry (start-up) and National Natural Science Foundation of China (Grants 20921002, 20871113, and 20761004) for their financial support. Dr. Patrick Gamez is gratefully acknowledged for fruitful discussions.

Supporting Information Available: Detailed experimental procedures and structural and magnetic data for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates for CCDC 742708 have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.