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Pentanuclear Dysprosium Hydroxy Cluster Showing Single-Molecule-Magnet Behavior

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A pentanuclear dysprosium hydroxy cluster of composition $[Dy_5(\mu_4\text{-}OH)(\mu_3\text{-}OH)_4(\mu\text{-}\eta^2\text{-}Ph_2acac)_4(\eta^2\text{-}Ph_2acac)_6]$ (**1**; Ph_2acac = dibenzoylmethanide) was prepared starting from $[DyCl_3 \cdot 6H_2O]$ and dibenzoylmethane. Both static (dc) and dynamic (ac) magnetic properties of **1** have been studied. Below 3 K, the appearance of slow relaxation of the magnetization typical for single-molecule magnets is seen, even if no hysteresis effects on the *M* vs *H* data are observed above 1.8 K.

Inorganic clusters continue to attract considerable attention because they represent the bridge linking molecular and solid-state chemistry and also because they act as useful tools for understanding size-dependent physical properties such as magnetism, optics, and electronics.[1] In d-block transition-metal chemistry, huge clusters, in particular, of molybdenum,[2] manganese,[3] copper,[4] silver,[5] and gold[6] have been isolated, but the analogous chemistry of the lanthanides is virtually undeveloped.[7,8] In recent years, some research groups have started to develop the synthesis of large lanthanide clusters. The main focus in this research is to increase the size of the clusters. In this context, we reported a number of lanthanide oxo/hydroxo clusters.[9] Now, we have started to investigate the magnetic properties of one such cluster. Although the study of paramagnetic metal-ion aggregates has been of increasing interest in attempts to assemble single-molecule magnets (SMMs), little work has been reported on purely lanthanide-based systems. In this context, some of us very recently synthesized hydroxo-bridged dysprosium triangles showing SMM behavior of thermally excited spin states,[10] noting that dysprosium(III) shows manifold magnetic behavior and was the first known example of the so-called "spin ice" effect.[11] With these considerations in mind, we aimed to synthesize a pentanuclear oxo/hydroxo dysprosium cluster given that a pentanuclear arrangement of the lanthanide core is a common structural motif for lanthanide oxo/hydroxo clusters.[12,13] In this contribution, we report the synthesis and structural

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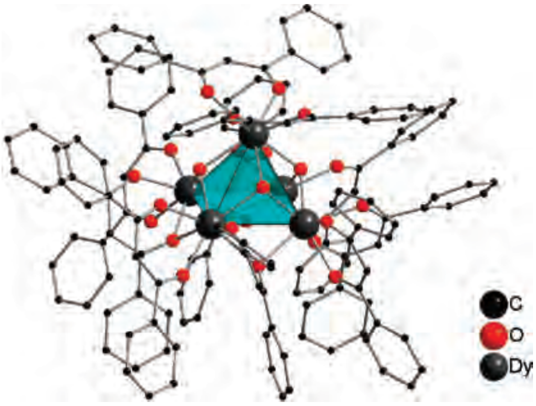
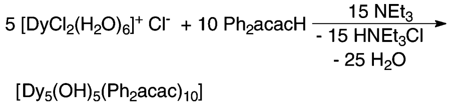


Figure 1. Solid-state structure of **1**, omitting hydrogen atoms.

Scheme 1


$$5\,[DyCl_2(H_2O)_6]^+\,Cl^- + 10\,Ph_2acacH \xrightarrow[\substack{-\,15\,HNEt_3Cl\\ -\,25\,H_2O}]{15\,NEt_3} [Dy_5(OH)_5(Ph_2acac)_{10}]$$

1

characterization of the pentanuclear dysprosium compound $[Dy_5(\mu_4\text{-}OH)(\mu_3\text{-}OH)_4(\mu\text{-}\eta^2\text{-}Ph_2acac)_4(\eta^2\text{-}Ph_2acac)_6]$ (**1**; Ph_2acac = dibenzoylmethanide; Figure 1) as well as its magnetic properties.

For the synthesis of **1**, we followed a route that is comparable to a procedure described earlier.[13] The reaction of 1 equiv of $[DyCl_3{\cdot}6H_2O]$ with 2 equiv of dibenzoylmethane in the presence of triethylamine yields **1** as yellow crystals (Scheme 1). Compound **1** crystallizes in the tetragonal space group $P4/n$, and the dysprosium atoms adopt the expected square-based pyramidal arrangement, isostructural with $[Y_5(\mu_4\text{-}OH)(\mu_3\text{-}OH)_4(\mu\text{-}\eta^2\text{-}Ph_2acac)_4(\eta^2\text{-}Ph_2acac)_6]$.[13c] Each triangular face of the square pyramid is capped by one μ_3-O moiety similar to $[Y_9O_2(OH)_8(aacac)_{16}]^-$ (aacac = allylacetoacetate),[14] $[Ln_9O_2(OH)_8(BA)_{16}]^-$ (BA = benzoylacetone and Ln = Sm, Eu, Gd, Dy, Er),[13b] and $[Ln_{14}(OH)_{18}(o\text{-}O_2NC_6H_4O)_{24}]$ (Ln = Er, Yb).[9] In the square-based face, four dysprosium atoms are linked by one μ_4-O atom (from OH). A total of 10 peripheral ligands surround the Dy_5 cluster core. The ligand shows two different coordination modes. Six ligands are terminally chelating and four are bridging chelating, bonding to two metal ions that belong to the base of the polyhedron. The apical dysprosium, which lies on a 4-fold symmetry axis, is bonded to two disordered chelate ligands.

Both static (dc) and dynamic (ac) magnetic properties of **1** have been studied on a polycrystalline sample maintained in toluene during the measurements to avoid a decomposition of the crystals. At room temperature, the temperature dependence of dc susceptibility at 1000 Oe is 63 $cm^3\ K\ mol^{-1}$. Upon a decrease in the temperature, the χT product very slowly decreases until 50 K and then further decreases to reach a minimum value of 31.0 $cm^3\ K\ mol^{-1}$ at 1.81 K. A fit of the experimental data to a Curie−Weiss law above 1.8 K leads to the following Curie and Weiss constants: 63.2 $cm^3\ K\ mol^{-1}$ and −1.5 K, respectively. As is often observed in Dy^{III}-based compounds,[10,15] the Curie constant is slightly low in comparison to the expected value (70.85 $cm^3\ K\ mol^{-1}$) for five Dy^{III} metal ions ($S = {}^5/_2$, $L = 5$, ${}^6H_{15/2}$ $g = {}^4/_3$; $C = 14.17\ cm^3\ K\ mol^{-1}$). The negative Weiss ($\theta$) constant suggests the presence of some antiferromagnetic interactions between spin carriers (likely intracomplex interactions) even if some other effects like the thermal depopulation of the Dy^{III} excited states (Stark sublevels of the ${}^6H_{15/2}$ state) or magnetic anisotropy might also be partially included in θ. The lack of a clear saturation on the M vs H data further confirms the effects arising from low-lying excited states and/or anisotropy. It is also interesting to note (Figure 2) a significant difference between the M vs H data above and below 3 K that is concomitant with the appearance of slow relaxation of the magnetization (vide infra). Nevertheless, it is worth noting that no hysteresis on the M vs H data has been observed above 1.8 K.

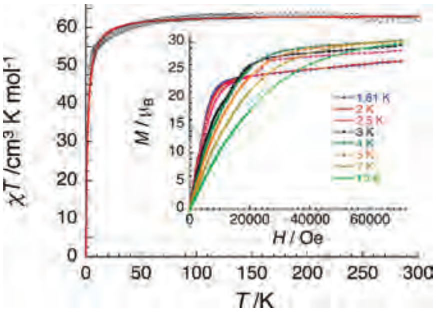


Figure 2. Temperature dependence of magnetic susceptibility at 1000 Oe and field dependence of the magnetization at low temperatures (inset) for **1**.

The temperature-dependent ac susceptibilities of this compound were measured under zero dc field (Figure 3). Clearly, at low temperatures below 8 K (for a frequency of around 1500 Hz), slow relaxation of the magnetization is observed based on the appearance of an out-of-phase signal. The frequency dependence of the ac susceptibility was also measured in order to complete the investigation and to establish the temperature dependence of the characteristic relaxation time. The relaxation time deduced from the whole set of data between 1.8 and 3.6 K nicely follows an activated behavior, as shown in Figure 4, with an energy gap of 33 K and a preexponential factor, τ_0, of about 4.5×10^{-9} s. Because of the fact that the slow relaxation of the magnetization is experimentally observed only over a short range of temperature and frequency, the estimation of these characteristic parameters might not be very accurate, but they have magnitudes similar to those of other SMM systems.[10,15] ac data have also been recorded under a small dc field in order to suppress possible fast zero-field quantum relaxation (Figure S2 in the Supporting Information). Under these field

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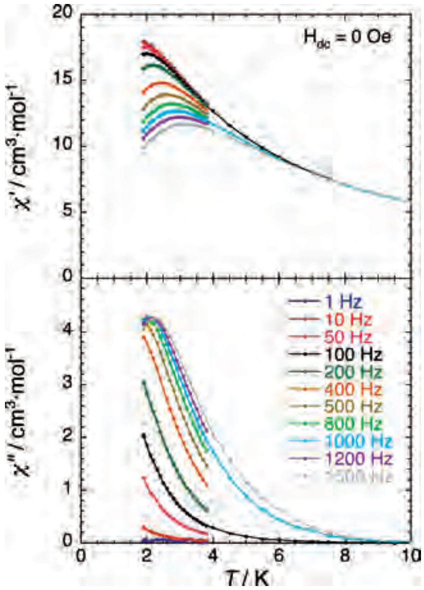

Figure 3. Temperature dependence of the in-phase (top) and out-of-phase (bottom) components of the ac magnetic susceptibility, for **1** under zero dc field.

conditions, the relaxation mode is slightly moved to higher frequency (i.e., the slow relaxation becomes faster), suggesting the absence of any quantum relaxation above 1.8 K.

In summary, the reaction of 1 equiv of [$DyCl_3 \cdot 6H_2O$] with 2 equiv of dibenzoylmethane in the presence of triethylamine yields the pentanuclear dysprosium hydroxy cluster of composition [$Dy_5(\mu_4\text{-}OH)(\mu_3\text{-}OH)_4(\mu\text{-}\eta^2\text{-}Ph_2acac)_4(\eta^2\text{-}Ph_2acac)_6$] ($Ph_2acac$ = dibenzoylmethanide). Both static and dynamic magnetic properties of **1** have been studied, and the appearance of slow relaxation of the magnetization below 3 K is typical for SMMs.

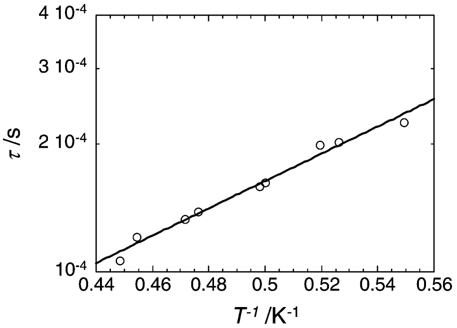

Figure 4. τ vs $1/T$ plot for **1** obtained from both temperature- and frequency-dependent ac susceptibility measurements under zero dc field.

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Supporting Information Available: Magnetic and structural data including the X-ray crystallographic file in CIF format for the structure determinations of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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