Metal-Organic Frameworks

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Single Pyramid Magnets: Dy_5 Pyramids with Slow Magnetic Relaxation to 40 K**

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There has recently been a huge renaissance in the study of the magnetism of 4f-coordination complexes.[1] There have been remarkable results, such as slow relaxation of magnetization in the "single-ion magnets" $(Bu_4N)[Tb(Pc)_2]$ (H_2Pc = phthalocyanine), for which the thermal energy barrier for relaxation is 330 K.[2] Equally remarkable has been the slow relaxation brought about by the toroidal arrangement of local magnetization vectors in a $\{Dy_3\}$ triangle ("spin chirality").[3] In parallel, studies of polymetallic dysprosium cages have shown slow relaxation in a variety of cages with energy barriers as high as 200 K,[4a] and showing magnetic hysteresis to 8 K.[4b]

Much of the fascinating physics of $(Bu_4N)[Tb(Pc)_2]$[2] and other single-ion magnets, such as $Na_9[Er(W_5O_{18})_2]$,[5] is associated with their fourfold symmetry. Equally, the toroidal magnetism of the $\{Dy_3\}$ cage is associated with the triangular array of 4f-ions.[3] Therefore, we targeted a molecule that had fourfold symmetry and metal triangles. The obvious polyhedron is a square-based pyramid. Oxo-centered $\{Ln_5\}$ pyramids of general formula $[Ln_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu_2\text{-}OR)_4(OR)_5]$ are known for around half of the lanthanoids ($R = i$Pr, Ln = Nd,[6,7] Eu,[8] Gd,[6] Er,[6,9] Yb;[10] $R = t$Bu, Ln = La,[11] Nd[11,12]) but not with dysprosium.

The *iso*-propoxide-bridged dysprosium square-based pyramid $[Dy_5O(OiPr)_{13}]$ (**1**) is made by the reaction of freshly generated KO*i*Pr with $DyCl_3$ in *i*PrOH/toluene with a stoichiometric amount of H_2O (see the Experimental Section). Crystals of **1** form in two different crystal systems: one is isostructural with the previously reported[9] $\{Er_5\}$ cage whereas the second has a new unit cell.[13] Both polymorphs have essentially identical magnetic behavior. There is no evidence, either visual or by X-ray diffraction,[14] that samples ever contain a mixture of polymorphs, that is, we have studied pure samples of each. Polymorphs have been previously reported for lanthanide alkoxides.[6,9]

In the new structure the square-based pyramid is disordered, with four of the Dy sites common to both disorder forms. The final Dy site is 50:50 disordered over two positions, however it is clear that the square-based pyramid is slightly elongated (Figure 1), with the average distance between the apical dysprosium and the basal dysprosia 3.43 Å, while the average distance between the adjacent dysprosia within the basal plane is 3.37 Å in one of the two models and 3.40 Å in the second. The structure has no crystallographic symmetry.

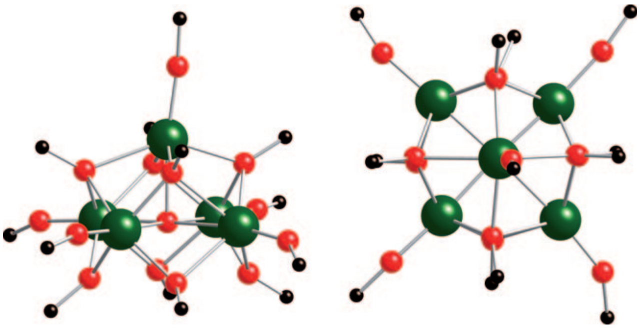

Figure 1. Structure of $[Dy_5O(OiPr)_{13}]$, viewed: left) perpendicular and right) parallel to the pseudo-fourfold axis (*i*Pr groups trimmed for clarity).

All Dy sites are six-coordinate. The geometry at each site is based on octahedral, but with the Dy shifted towards the terminal alkoxide and away from the central μ_5-oxide—thus each Dy site has local, but non-crystallographic, C_{4v} symmetry. The distances of the central oxide to the Dy sites fall in the range 2.25–2.60 Å. The thirteen alkoxides fall into three groups: there is a terminal alkoxide on each metal site; a second group of four alkoxides bridges on each of the four triangular faces; the third group forms a μ_2-bridge along one of the edges of the square basal plane. The disorder in the structure limits what can usefully be said about metric parameters, however the Dy–O distances to terminal alkoxides are much shorter than the other Dy–O distances; the former distances fall in the range 1.95–2.15 Å, while the latter distances fall in the range 2.27 to 2.66 Å.

The room-temperature $\chi_M T$ value of **1** is 70.5 $cm^3 K mol^{-1}$ (χ_M is the molar magnetic susceptibility) in good agreement with that expected for five uncoupled Dy^{III} ions (70.8 $cm^3 K mol^{-1}$ calculated for $^6H_{15/2}$, $S = 5/2$, $L = 5$, $J = 15/2$, $g = 4/3$). $\chi_M T$ decreases gradually on cooling, and then more rapidly below 30 K (see Figure S1 in the Supporting Information). This behavior is because of the depopulation of the Dy^{III} excited Stark sublevels possibly with weak antiferromagnetic coupling.[1] The molar magnetization (M) at 1.8 K approaches saturation at around 27 μ_B, and there is a

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very narrow hysteresis observed at this temperature (see Figure S2 in the Supporting Information). Reduced magnetization data do not lie on a single master-curve, suggesting the presence of significant magnetic anisotropy in **1** (see the inset in Figure S1 in the Supporting Information).

Alternating current (ac) magnetic susceptibility measurements on polycrystalline samples of **1** as a function of temperature (Figure 2) and frequency (see Figure S3 in the Supporting Information) were carried out to investigate the dynamics of the magnetization. The $\chi_M' T$ product (measured in zero applied static field) decreases rapidly at a temperature dictated by the ac frequency, reaching around 46 K for $\nu = 1.4$ kHz. This is accompanied by a peak in both the in-phase (χ_M') and out-of-phase (χ_M'') susceptibility. The maximum in χ_M'' is observed at temperatures as high as 41 K (for $\nu = 1.4$ kHz) and at frequencies as small as 0.5 Hz (at $T = 3$ K). All these features are indicative of slow relaxation of the molecular magnetization, and hence of single-molecule magnet (SMM) behavior, with a very high thermal energy barrier to relaxation. This allows us to monitor the relaxation process over a rather large temperature range (3–56 K) under zero static field.

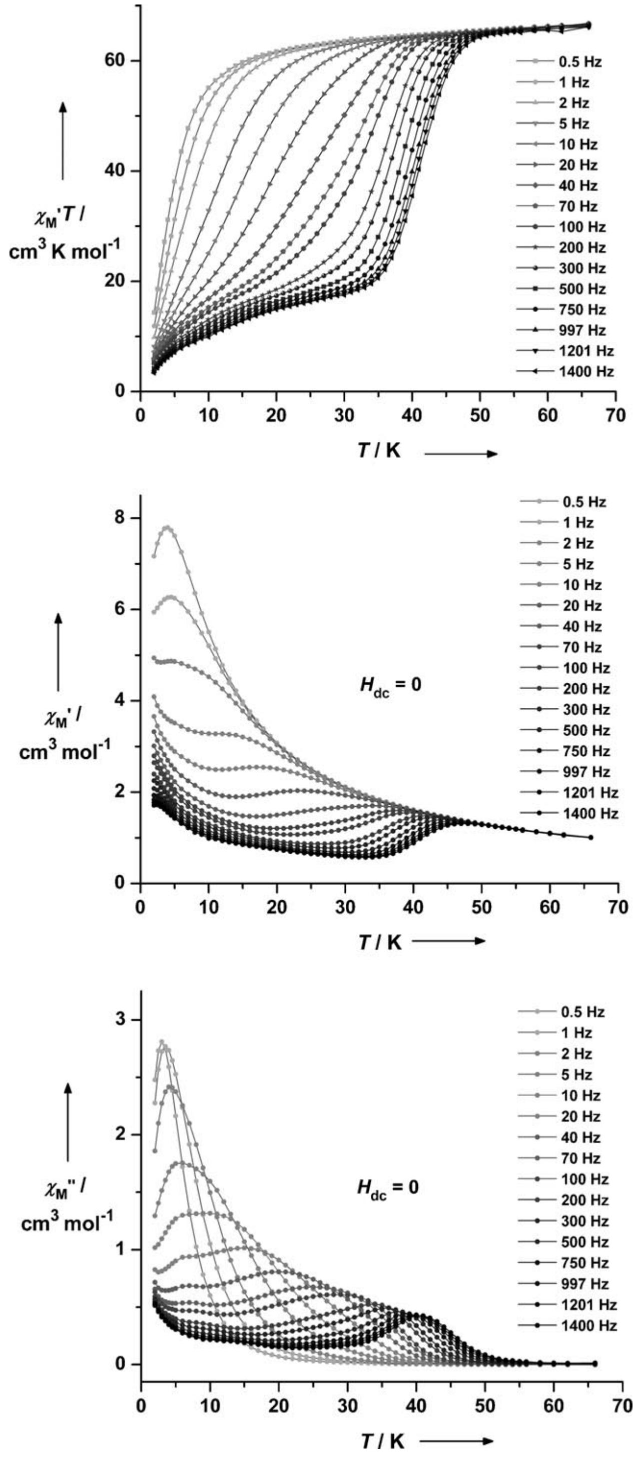

Figure 2. Temperature dependence of top) $\chi_M' T$, middle) χ_M', and bottom) χ_M'' for **1** under zero static field and 1.55 G alternating current field oscillating at the indicated frequencies.

The relaxation time (τ) can be determined from both $\chi_M''(T)$ and from Argand (χ_M'' vs. χ_M') diagrams. For the latter, semicircular plots are obtained for fixed temperatures below 42 K (Figure 3), which can be fit to a generalized Debye model with the α parameter in the range 0.16–0.23, indicating a small distribution of relaxation times. A plot of $\ln(\tau)$ versus T^{-1} (Figure 4) is linear above 35 K, hence can be fit to the Arrhenius law $\tau = \tau_0 \exp(\Delta E / k_B T)$, giving the thermal energy barrier for the relaxation of magnetization $\Delta E = 528 \pm 11$ K with a pre-exponentional factor of $\tau_0 = 4.7 \times 10^{-10}$ s. At lower temperatures $\ln(\tau)$ increases much more slowly with decreasing T, indicative of the onset of a quantum tunneling regime. The existence of a quantum tunneling regime explains why, despite the very high thermal barrier, the hysteresis observed is narrow (see Figure S2 in the Supporting Information).

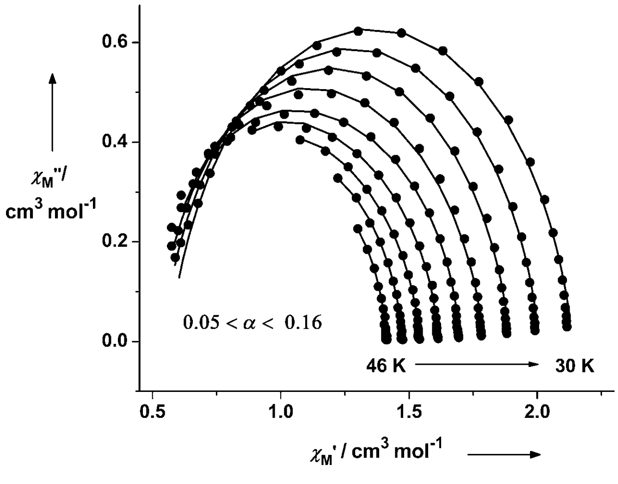

Figure 3. Cole–Cole plots[15] for **1** for temperatures between 30 and 46 K, with best fits (solid lines; ● experimental values).

Below 12 K there are minor features that may suggest the presence of a second relaxation process. For example, a second, low-temperature maximum is observed in $\chi_M''(T)$ for lower frequencies (Figure 2). Best fitting to the Arrhenius law gives $\Delta E_2 = 46.6 \pm 0.7$ K and $\tau_{0(2)} = 3.8 \times 10^{-6}$ s. These values should be regarded with caution because this relaxation process appears in the quantum tunneling region of the first relaxation process.

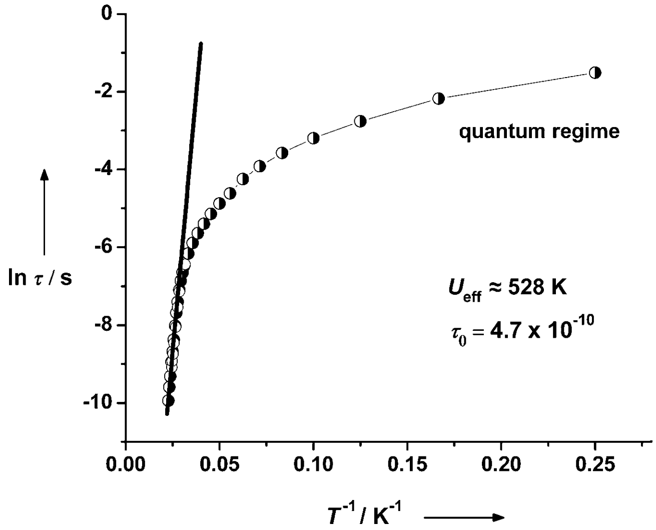

Figure 4. Magnetization relaxation time (τ) versus T^{-1} for **1** under zero static field, from data collected in frequency (●) and temperature (○) variation regimes, and best fit to the Arrhenius law of the thermally activated regime (solid line).

In conclusion, the $\{Dy_5\}$ square-based pyramid is an SMM with a thermal energy barrier to magnetization relaxation of around 530 K. This is by far the largest barrier yet observed for any d- or f-block cluster, exceeding the 86 and 200 K reported for a $\{Mn^{III}_6\}$[16] and a $\{Dy_6\}$ clusters,[4a] respectively. The only molecular species that exceed this value are Ishikawa's family of $[Tb(Pc)_2]^{n-}$ single-ion magnets which with chemical and redox modification have reached energy barriers of 790 K.[17] We have also prepared the Er and Gd analogues of **1**, but their magnetic properties are less interesting in this context.

Understanding these results will require detailed study of a wider range of compounds, however we can offer a hypothesis at this stage. We believe the properties are largely associated with single ions, weakly perturbed by exchange interactions.[4a,18] There is a previous $\{Dy_5\}$ square-based pyramid in the literature, $[Dy_5(OH)_5(dbm)_{10}]$ (dbm = dibenzoylmethanide),[19] but with a thermal energy barrier of only 33 K. There the individual Dy sites are eight-coordinate, with at most two-fold symmetry, and there is no μ_5-oxide present. In **1**, we have six-coordinate Dy sites with a distorted octahedral geometry, with a clear unique anisotropy axis defined by the μ_5-oxide. Therefore, here the crystal field about the 4f-centers are much closer to fourfold symmetry than has been found in any previous polymetallic 4f-cage. In this case, as in the $[Tb(Pc)_2]^{n-}$ complexes[2] the fourfold symmetry seems to be very important. If we could crystallize a form of this $\{Dy_5\}$ pyramid with genuine crystallographic fourfold symmetry we believe this could also reduce the quantum tunneling of the magnetization. Control of crystallization in this class of compounds is difficult, but a project we are now pursuing.

Experimental Section

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of dry nitrogen. Toluene was dried using an Innovative Technologies solvent purification system, *n*-hexane was dried by heating to reflux over CaH_2, and anhydrous HO*i*Pr was purchased from Sigma–Aldrich; all solvents were stored over 3 Å molecular sieves and deoxygenated prior to use. Anhydrous $DyCl_3$ was purchased from Strem Chemicals Inc.

Synthesis of $[Dy_5O(OiPr)_{13}]$: Potassium metal (0.5 g, 12.8 mmol) was dissolved in HO*i*Pr/toluene (20 cm^3) of 1:1 (v/v) ratio before addition of 1.0 mmol cm^{-3} H_2O in the same solvent mixture (0.85 cm^3, 0.85 mmol H_2O). $DyCl_3$ (1.15 g, 4.3 mmol) was added after one hour. After stirring for at least 48 h, the reaction mixture was filtered through dry celite and the volatile solvents removed in vacuo. The solid was dissolved in *n*-hexane and stored at −20°C to give crystalline **1** (40%). Elemental analysis calcd (%) for $C_{39}H_{91}Dy_5O_{14}$: C 29.34, H 5.74, Dy 50.89; found: C 29.47, H 5.82, Dy 50.62. Unit cell of polymorph one: orthorhombic *Pbca*, $a = 21.6087(7)$, $b = 20.9893(10)$, and $c = 25.2104(12)$ Å which is equivalent to $[Er_5O(OiPr)_{13}]$.[9]

Magnetic properties of polycrystalline samples were investigated in the temperature range 1.8–300 K, using a Quantum Design MPMS XL7 SQUID magnetometer. Data were corrected for the diamagnetism of the compounds (Pascal constants) and the sample holder. Ac susceptibility measurements were performed with an ac field of 1.55 G oscillating at frequencies ranging from 1 to 1400 Hz.

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[13] Crystal data. For **1**, $C_{39}H_{91}Dy_5O_{14}$, $M = 1596.62$, monoclinic, space group $C2$, $T = 100(2)$ K, $a = 19.5597(6)$, $b = 16.4537(6)$, $c = 16.6240(5)$ Å, $\beta = 92.385(3)°$, $V = 5345.5(3)$ Å^3, $Z = 4$, $\rho = 1.984$ g cm^{-3}, total data 17428, unique data 8294 ($R_{\text{int}} = 0.0361$), $\mu = 6.956$ mm^{-1}, 644 parameters, 941 restraints, $R_1 = 0.0672$ for $I \geq 2\sigma(I)$ and $wR_2 = 0.2091$ for all data. The data were recorded on a Oxford Xcalibur CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 using SHELXTL. CCDC 817819 contains 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.

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