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Dysprosium Triangles Showing Single-Molecule Magnet Behavior of Thermally Excited Spin States***Jinkui Tang, Ian Hewitt, N. T. Madhu, Guillaume Chastanet, Wolfgang Wernsdorfer, Christopher E. Anson, Cristiano Benelli, Roberta Sessoli, and Annie K. Powell***Dedicated to Professor Dante Gatteschi on the occasion of his 60th birthday*

The study of paramagnetic metal-ion aggregates has been of increasing interest since the observation that such molecules can exhibit magnetic memory effects.^[1–3] Termed single-molecule magnets or SMMs, the important factors leading to such properties derive from the combination of a large ground-state spin and a large magnetic anisotropy of the Ising (easy-axis) type. Studies have largely been based on transition-metal compounds since they typically exhibit both of the aforementioned features. The incorporation of lanthanides into these complexes has been investigated to take advantage of the potentially large number of unpaired f-electrons available.^[4–7] However, very little work has been done to date on purely lanthanide-based systems.^[8,9] The origin of SMM behavior in lanthanide-containing compounds is more complicated than that of d-block transition-metal ions since there is likely to be a significant orbital component. In the lanthanide-containing phthalocyanine complexes reported in the literature the ligand environment induces a large splitting of the ground *J* manifold, whereas in SMMs large-spin ground states arising from magnetic interactions between the metal centers of the cluster can enhance the weaker single-ion

[*] Dr. J. Tang, Dr. I. Hewitt, Dr. N. T. Madhu, Dr. C. E. Anson, Prof. A. K. Powell

Institut für Anorganische Chemie
Universität Karlsruhe
Engesserstrasse Geb. 30.45, 76128 Karlsruhe (Germany)
Fax: (+49) 721-608-8142
E-mail: powell@chemie.uni-karlsruhe.de

Dr. G. Chastanet, Prof. C. Benelli, Prof. R. Sessoli
Department of Chemistry
University of Florence
Via della Lastruccia 3, 50019 Sesto Fiorentino (Italy)

Dr. W. Wernsdorfer
Laboratoire Louis Néel—CNRS
BP 166, 25 Avenue des Martyrs, 38042 Grenoble Cedex 9 (France)

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anisotropies. Given that such aggregates are almost exclusively oxo-bridged systems, and noting that dysprosium(III) shows manifold magnetic behavior and was the first known example of the so called “spin ice” effect,^[10] we decided to explore the possibility of obtaining oxo-bridged Dy^{III} aggregates.

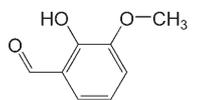
Herein we report the synthesis, structures, and preliminary magnetic studies of two similar triangular dysprosium compounds, [Dy₃(μ₃-OH)₂L₃Cl₂(H₂O)₄] [Dy₃(μ₃-OH)₂L₃Cl(H₂O)₅]Cl₅·19H₂O (**1**) and [Dy₃(μ₃-OH)₂L₃Cl(H₂O)₅]Cl₃·4H₂O·2MeOH·0.7MeCN (**2**) (where HL = *o*-vanillin, Scheme 1), which display a complex and unprecedented magnetic behavior.

The crystal structure of **1** consists of triangles of dysprosium centers capped by two μ₃-hydroxo centers (Figure 1 a). This motif has previously been reported for the gadolinium analogue.^[11] Along each side of the triangle, a deprotonated *o*-vanillin ligand bridges

by its phenoxo group. Aldehyde and methoxy groups also coordinate to the dysprosium center. Two water molecules coordinate to Dy(1) and Dy(2) above and below the plane of the triangle, but for Dy(3) these sites are occupied by a chloride ion above the plane and below a chloride or a water molecule with a 50:50 disorder. Each of the dysprosium centers is eight-coordinate and displays a distorted geometry. The irregular coordination can be described as being based on a pentagonal bipyramid but where one site in the pentagonal plane is vacant; instead there are the two μ₃-hydroxo sites above and below it. The pentagon is defined for Dy(1) thus: methoxy of a ligand O(5), phenolate from the same ligand O(3), which also bridges to Dy(2), O(9) from the phenolate of a neighboring ligand bridging to Dy(3), O(10) from the aldehyde of this bridging ligand, O(1) and O(2) from the bridging μ₃-hydroxo groups above and below the fifth site. The coordination sphere is completed by two water ligands above and below this plane, or, in the case of Dy(3), a chloride ligand and either a chloride or water ligand. Attempts were made to refine the structure in acentric space groups taking into account the possibility of twinning, however, no evidence for an ordered structure involving the chloride and water ligands was found. We conclude that these two ligands are essentially disordered, or at best display only short-range order.

Pairs of such triangular units are linked by a chloride counterion Cl(3) which is hydrogen bonded to two water ligands (Cl(3)–O(H₂O) 3.06 Å) and a capping hydroxide (Cl(3)–O(OH) 3.21 Å) from each unit. The resulting pairs of triangles are linked into a chain (Figure 1 b) through hydrogen bonds between the disordered chloride/water ligands on the Dy(3) (Cl(2)–O(H₂O) 3.12 Å). These show the shortest intertriangle Dy···Dy distances at 7.48 Å. There are π–π effects between these chains. Each of the triangular pairs along the chain is interleaved by a phenyl ring from a unit in the neighboring chain, giving a side-on phenyl carbon C(12)–Cl(3) distance of 3.84 Å. This phenyl is also placed between two other phenyl groups on a neighboring chain at about 3.7 Å. Through these interactions and because of the hydrogen bonding along the chains, they converge through the π-effects and then diverge to create a criss-cross pattern with channels running in the [110] direction with side entrances in the [001] direction (see Supporting Information).

Compound **2** crystallizes to give solely the mono-chloride form of the dysprosium triangles observed in compound **1**. For each triangular unit there are hydrogen bonds to the two chloride counterions, Cl(2) and Cl(3), through the five water ligands and the capping hydroxide. Furthermore, the molecules are linked into chains (Figure 1 c) through this hydrogen bonding between the chloride counterions and water ligands with the shortest interactions, Cl(2)···O(12) (3.07 Å) and Cl(3)···O(16) (3.02 Å), and with the closest intertriangle distance of 6.80 Å. In contrast to **1** there are no direct hydrogen bonds between donor atoms coordinated to Dy^{III} ions of different trimers present in **2**. We also note that the arrangement of chlorides as either ligands or counterions differs in both **1** and **2** from that of the nitrates in the gadolinium analogue.^[11] There are also π–π effects in the packing arrangement, but in this case because the linking of



Scheme 1. *o*-Vanillin (2-hydroxy-3-methoxybenzaldehyde).

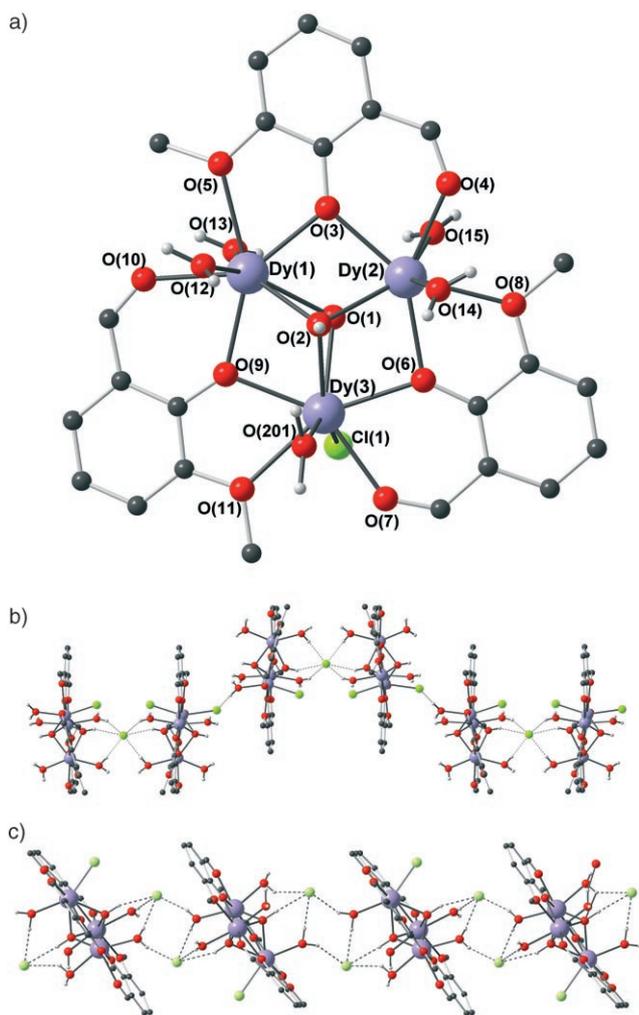


Figure 1. a) Structure of the triangular units in **1** and **2** with numbering scheme. In **1** there is 50:50 disorder of Cl and H₂O at O(201) as described in the text. Intratriangle Dy···Dy distances: **1** 3.50–3.53 Å; **2** 3.51–3.54 Å. The hydrogen bonding is highlighted between trinuclear units in **1** (b) and **2** (c). Color scheme: blue Dy^{III}, red O, green Cl, dark gray C, white H.^[18]

the molecules into chains is simpler only the interleaving is important. Each triangle has π - π interactions to five nearest neighbors, although none of the interactions are as strong as those in the structure of **1**.

The static magnetic moment of polycrystalline samples of both **1** and **2** were measured using a SQUID magnetometer in the temperature range 1.8 to 300 K at 0.1 T (Figure 2). The

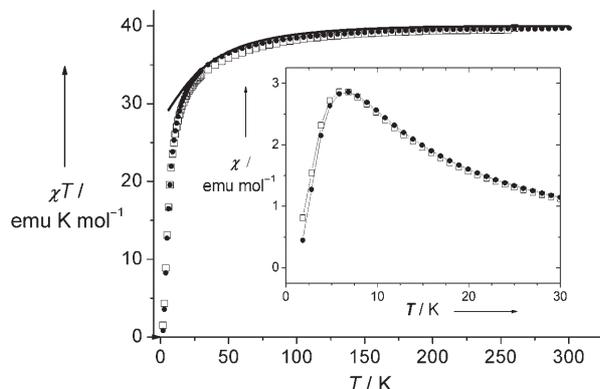


Figure 2. Temperature dependence of the χT product (per trimeric unit) for **1** (\square) and **2** (\bullet). The solid line represents the calculated value for three uncorrelated Dy^{III} ions (see text). Inset: low-temperature susceptibility χ .

microcrystals of both compounds tend to orientate in the magnetic field and were fixed by either pressing into a pellet or freezing with nujol. The two compounds show an identical behavior with the margin of error produced by a small residual orientation. The room-temperature χT value of $40.5 \text{ emu K mol}^{-1}$ is in good agreement with that expected for three uncoupled Dy^{III} ions ($J=15/2$, $g=4/3$)^[12] and decreases almost to zero at low temperature. The susceptibility (inset of Figure 2) goes through a maximum around 6.5 K. Crystal-field effects are expected to reduce the susceptibility, and indeed down to 30 K the observed behavior can be modeled by taking into account the splitting of the $J=15/2$ of non-interacting Dy^{III} ions, as shown in Figure 2. In order to reduce the number of parameters an idealized C_{2v} symmetry has been assumed, introducing even terms up to the sixth order in Stevens' operators.^[13] The detailed analysis of the crystal field is not the aim of this Communication and would require single-crystal data on this system as well as on the dysprosium-doped diamagnetic analogue to define unambiguously a set of parameters. It is, however, interesting to note that, even by allowing the nine crystal-field parameters to vary freely, the pronounced decrease of χT below 30 K cannot be reproduced, and therefore the presence of some significant intratrimer antiferromagnetic interactions can be postulated as, indeed, observed in the gadolinium analogue.^[11] The vanishing susceptibility at low T is, however, totally unexpected for a system comprising an odd number of centers with half-integer J value. The magnetization versus field data of a polycrystalline sample confirms the presence of antiferromagnetic interactions as the slope is less steep at low field and increases around $H=0.95 \text{ T}$ for both compounds (Figure 3). Above this field the magnetization increases

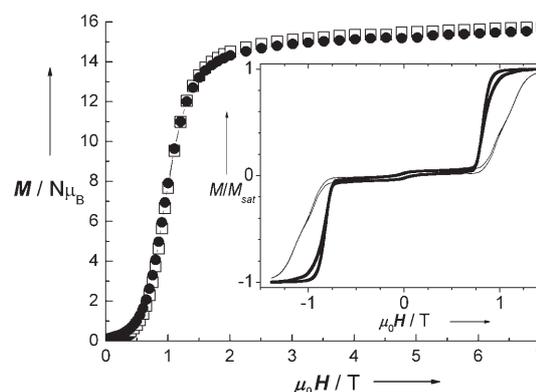


Figure 3. Molar magnetization M versus applied field $\mu_0 H$ measured at $T=1.8 \text{ K}$ on a polycrystalline sample of **1** (\square) and **2** (\bullet). Inset: micro-SQUID measurements at 0.1 K and 28 mT s^{-1} on a single crystal of **2** applying the magnetic field in the plane (light) and perpendicular to the plane (bold) of the Dy^{III} ions.

slowly reaching at 7 T the value of $15.6 \mu_B$. This value is consistent with that calculated for three uncorrelated Dy^{III} magnetic moments ($3 \times 5.23 \mu_B$), assuming the crystal-field parameters are the same as those used to reproduce the χT versus T curve of Figure 2. This implies the presence of considerable ligand-field effects. The application of a field stronger than 2 T apparently overcomes all antiferromagnetic interactions.

Single crystals of both **1** and **2** were studied further using the microSQUID technique,^[14] and again were found to produce an identical and rather surprising behavior (inset of Figure 3). The curves show a step behavior, in agreement with the higher temperature data, but the position of the step, H_c , depends on the orientation of the magnetic field with respect to the plane of the dysprosium triangle. However, the absolute value of the magnetization is not accessible with this technique and each curve has been rescaled to the value measured at the largest field. The initial susceptibility is not exactly zero even at 0.1 K, and a first saturation to a value of $0.05 M_{\text{sat}}$ is observed, as well as a small hysteresis both below and above H_c .

To investigate the dynamics of the magnetization further, ac-susceptibility studies were undertaken for **1** and **2**. For both compounds the temperature dependence of the complex susceptibility behavior shows a strong frequency dependence below 20 K. On decreasing the frequency the χ' versus T curve approaches the static one and shows a maximum around 6.5 K. The out-of-phase component, χ'' , when plotted against T , shows maxima, the positions of which are frequency-dependent as typically observed for SMMs. However, the peaks are quite distorted with a shoulder structure (see Figure 4 and Supporting Information). In order to extract the temperature dependence of the relaxation time in the presence of complex behavior like non-monotonic equilibrium susceptibility, we have plotted the χ'' data against the logarithm of the frequency (Figure 4), because the average relaxation time can be easily extracted from the frequency at which a maximum in χ'' occurs, being $\tau = 1/(2\pi\nu)$.^[15]

Plotting the relaxation time versus the inverse temperature reveals that the behavior is only linear at very high

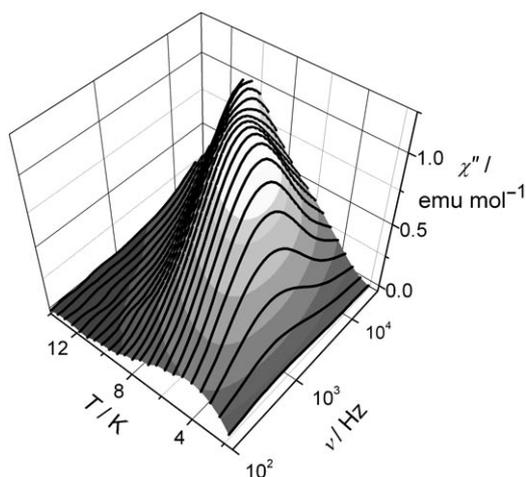


Figure 4. Out-of-phase ac-susceptibility χ'' versus frequency ν in logarithmic scale for a polycrystalline sample of **2** in the temperature range 1.5–14 K.

temperature with $\tau = 2.2 \times 10^{-8} \exp(61.7 T^{-1})$, while at low temperature the relaxation time saturates (Figure 5).

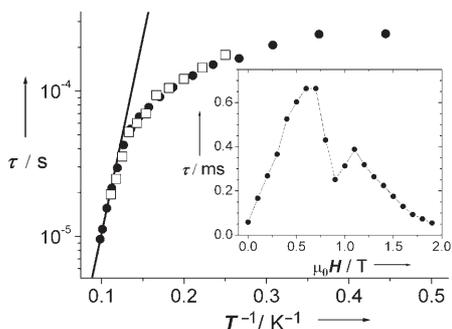


Figure 5. Relaxation time τ of the magnetization for **1** (\square) and **2** (\bullet) versus inverse temperature. The solid line is a fit of the Arrhenius law to the high temperature data of **2**. Inset: the field dependence of the relaxation time for **2** at $T = 7.15$ K.

In order to explore the dynamic behavior even further the frequency dependence of χ'' for **2** has been investigated as a function of the applied field at $T = 7.15$ K, the point at which τ starts to saturate (see Supporting Information). The field dependence of τ , shown in the inset of Figure 5, is strongly reminiscent of resonant quantum tunneling as it shows a minimum in zero field.^[16] A second minimum is observed around 0.9 T, the field at which a step in the magnetization curve is observed.

Both the static and dynamic magnetic properties of these trimeric Dy^{III} species are unprecedented. The observation of a non-magnetic state for a system carrying an odd number of unpaired electrons could be explained by the presence of intercluster interactions. Whereas the presence in **1** and **2** of a hydrogen-bonded network could give rise to antiferromagnetic interactions, these interactions should be very weak. On the contrary, both the temperature of the maximum in χ and the critical field in the M versus H curve are compatible with an interaction in the order of the Kelvin, that is, of the same

order of magnitude of the intratriangle interaction observed in the gadolinium analogue, and of that found in Dy(OH)₃.^[11,17] Moreover, **1** and **2** have a virtually identical magnetic behavior even in the presence of very different hydrogen-bonding networks. In particular, a significantly weaker intercluster interaction is expected for **2** as no direct hydrogen bonds between donor atoms are observed. Thus, the vanishing susceptibility at low T seems to be a feature of the triangular arrangement of the spins and is possibly related to the anisotropic nature of the intratrimer exchange interaction. The anisotropy axes of each Dy^{III} ion are not expected to be collinear and this further complicates the analysis. The step in the magnetization observed at H_c could be explained by field-induced level crossing between the first excited magnetic state and the almost non-magnetic ground state. More detailed studies, such as ESR spectroscopy of a diamagnetic analogue doped with dysprosium, could provide information on the local anisotropy and allow a rationalization of the observed behavior.

Beyond the unprecedented static properties, the compounds show the unusual coexistence of slow relaxation of the magnetization and an almost diamagnetic ground state. The slow dynamics observed in the ac susceptibility between 2 and 20 K could be associated with the excited state, and interestingly show strong deviation from the Arrhenius law as this state depopulates. The sharp decrease of τ at zero field and at H_c suggests that an additional relaxation pathway short-cutting the energy barrier is active as predicted at level crossings when resonant quantum tunneling is observed.

The two dysprosium triangles we have investigated here show a vanishing susceptibility at low temperature, which is unprecedented in systems comprising an odd number of unpaired electrons. In spite of the almost non-magnetic ground state, features typical of SMM behavior are observed for the thermally populated excited state, suggesting that a resonant under-barrier relaxation process is also active. This observation is strongly relevant to molecular nanomagnetism because the presence of a large spin ground state appears not to be a necessary condition to observe slow relaxation of the magnetization.

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- [18] CCDC 284870 (1) and CCDC 284871 (2) 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.