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A Discrete Dysprosium Trigonal Prism Showing Single-Molecule Magnet Behaviour

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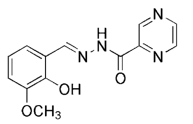
The synthesis of new single-molecule magnets (SMMs) based on appealing topologies and fascinating magnetic behaviours remains an exciting challenge. In recent years, many synthetic chemists and physicists have employed several lanthanide (Ln) ions (Tb^{III}, Dy^{III}, Ho^{III} and Er^{III}) and bridging ligands to synthesise novel SMMs[1] and have studied in detail their unique magnetic properties at the molecular level (e.g., SMM behaviour,[2] such as slow relaxation and quantum tunnelling of the magnetisation[3]). Ln ions are incorporated into these systems because they not only contribute high spins but also introduce anisotropy to the molecule as a result of the nature of the f-electron shell. Among the Ln family, the Dy^{III} ions seem to have indisputable virtue in this respect, as we and others have recently demonstrated.[4] A number of pure Dy^{III}-containing compounds exhibiting various topologies based on a linear,[5] triangular,[4a] planar,[6] cubane,[7] pyramid,[8] wheel,[9] or a disc,[10] have been described in the literature. It is worth noting that the interesting magnetic behaviour, which has been increasingly identified in dysprosium compounds can be attributed to the magnetic anisotropy of the molecules. This anisotropy depends not only on the individual anisotropies of the metal ions but also on the relative orientation of the local axes. In this respect, the design of a new dysprosium cluster with a new topology might provide unique opportunity to probe the relaxation dynamics of polynuclear complexes, thus enriching the structure correlation to magnetic properties of dysprosium family. In addition, selection of a suitable bridging ligand is crucial for assembling a new lanthanide cluster with interesting magnetic properties, due to the difficulty in promoting magnetic interactions between the lanthanide ions through overlap of bridging ligand orbitals with the "contracted" 4 f orbitals of the Ln ions.[4 g] With these issues in mind, we designed a new multidentate ligand, namely, (*E*)-*N′*-(2-hyborxy-3-methoxybenzylidene)pyrazine-2-carbohydrazide (H_2L) (see Scheme 1) and isolated a dysprosium trigonal prism that behaves as SMM. To our knowledge, a dysprosium SMM with trigonal prism geometry has not been reported.



Scheme 1. Structural formulae for (*E*)-*N′*-(2-hyborxy-3-methoxybenzylidene)pyrazine-2-carbohydrazide, H_2L.

The selection of hydrazone ligand, formed by reaction between the *o*-vanillin aldehyde and pyrazine-2-carbohydrazide, is especially useful to construct polynuclear dysprosium complexes because of the following considerations: 1) This type of N, O-donor linear ligand has a strong coordination ability for lanthanide ions with suitable relative positions. 2) Similar ligands have successfully synthesised several structurally and magnetically interesting dysprosium SMMs.[1b,4c,h] Herein, we report the structure and magnetic properties of a unique dysprosium trigonal prism SMM assembled from this new ligand, H_2L.

The reaction of $Dy(OAc)_3{\cdot}6H_2O$ with H_2L (1:1 ratio) in $MeOH/EtOH/CH_2Cl_2$ (1:1:2 ratio), in the presence of triethylamine (6 equiv), produces yellow crystals of $[Dy_6(OAc)_3(\mu_3\text{-}CO_3)_2(L)_5(HL)(MeOH)_2]{\cdot}4H_2O{\cdot}5MeOH{\cdot}EtOH$ (**1**). The molecular structure was determined by single-crystal X-ray diffraction and is depicted in Figure 1 (top) and the crystal data are summarised in the Supporting Information (Table S1). Compound **1** crystallises in the monoclinic space group $P2_1/c$ and can be described as having a unique trigonal prism architecture. Each triangular face of the trigonal prism is an approximate equilateral triangle based on the Dy···Dy interatomic distances ranging from 4.8009(8) to 4.9105(8) Å and angles from 59.114(11)° to 61.151(11)°; moreover, a CO_3^{2-} is encapsulated in the Dy^{III}_3 plane and ligated by its oxygen atoms at the midpoints of the sides of the triangle formed by the Dy^{III} ions (see the Supporting Information, Scheme S1 a); in doing so the C···C distance of two central CO_3^{2-} ligands is 4.4085(8) Å and the perpendicular distance between the two triangular faces is 3.8245(8) Å. It is interesting to note that the carbonate adopts a less

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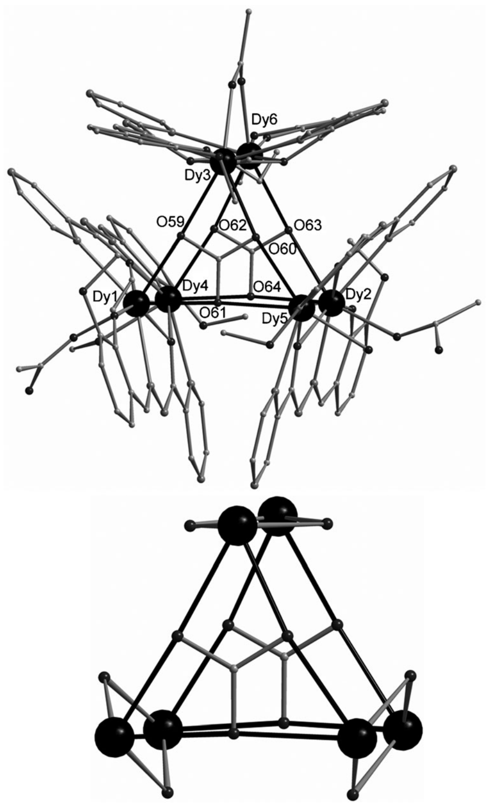

Figure 1. Top: the molecular structure of **1**, showing one of the two isomers. Solvents, counter ions and hydrogen atoms are omitted for clarity. Bottom: the Dy_6 core.

common hexadentate μ_3-fashion to bridge three metal centres.[11] The parallelisms of the two triangular faces are linked through bridging carboxy oxygen atoms of six hydrazone ligands, stacked on the top of each triangular face, resulting in the hexanuclear trigonal prism (see Figure 1, bottom). All of the Dy^{III} ions are eight-coordinate, displaying distorted dodecahedral geometry. Only one coordination and bridging mode (η^1:η^1:η^2:η^1:μ_2-fashion) can be observed for the unique polydentate Schiff-base ligand (see the Supporting Information, Scheme S1 b). Two different coordination modes of acetate groups (syn η^1-fashion and syn–syn μ_2-η^1:η^1-fashion) coexist in the crystal structure (see the Supporting Information, Scheme S1 c). Two methanol molecules occupy the remaining coordination sites of the Dy_2 and Dy_4 metal centres. Additionally, the structure consists of two isomers in the unit cell and four non-coordinated water molecules, five methanol molecules and one ethanol molecule of crystallisation are located in the crystal lattice, as depicted in the Supporting Information (Figures S1 and S2). Strong intermolecular hydrogen-bonding interactions produce a one-dimensional supramolecular chain of the molecules (see the Supporting Information, Figure S3). The shortest intermolecular Dy···Dy distance is 8.8153(8) Å.

The assignment of bridging carbonate was made based on careful consideration of the diffraction data, which indicated the presence of a trigonal fragment, and charge balance requiring a dianion in these sites. In particular, IR stretching bands characteristic of the coordinated carbonate are observed at $\tilde{\nu} = 1558$ and $1333\ cm^{-1}$ (see Figure S4 in the Supporting Information).[12] Nitrate was not present in the reaction at any stage, therefore it appears that atmospheric CO_2 has been incorporated into the structure, thus templating further aggregation and growth of the cluster.[13]

Direct-current (dc) magnetic susceptibility studies of **1** have been carried out in an applied magnetic field of 1 kOe in the temperature range 300–2 K. The plot of $\chi_M T$ versus T, in which χ_M is the molar magnetic susceptibility, is shown in Figure 2. At 300 K, the $\chi_M T$ value of $85.78\ cm^3 K mol^{-1}$ is very close to the expected value of $85.02\ cm^3 K mol^{-1}$ if the six Dy^{III} ions ($S = 5/2$, $L = 5$, $^6H_{15/2}$, $g = 4/3$) were non-interacting. The $\chi_M T$ product gradually decreases with the temperature to reach a minimum of $66.93\ cm^3 K mol^{-1}$ at about 2 K, which is mainly ascribed to the progressive depopulation of excited Stark sublevels.[14] The shoulder observed around 20 K might suggest a competition between ligand field effect and possible weak ferromagnetic interactions between the Dy^{III} ions.

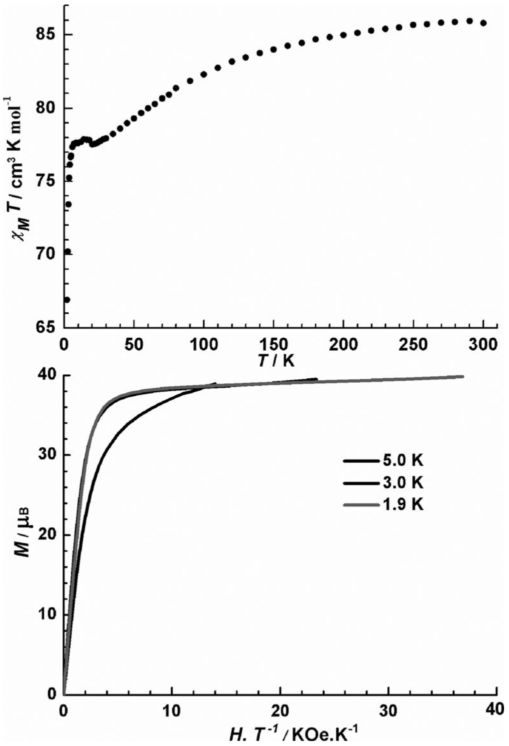

Figure 2. Top: temperature dependence of the $\chi_M T$ product at 1 kOe. Bottom: M versus H/T plots at different temperatures below 5 K.

The M versus H/T (Figure 2, bottom) data at different temperatures show non-superposition plots and a rapid increase of the magnetisation at low magnetic fields, which eventually reaches the value of $40.58\ \mu_B$ at 1.9 K and 7 T without any sign of saturation. This value is lower than the expected saturation value of $60\ \mu_B$ (for six noninteracting Dy^{III} ions). This difference is most likely due to significant anisotropy and the crystal-field effect at the Dy^{III} ion that eliminates the 16-fold degeneracy of the $^6H_{15/2}$ ground state.[4a,15] The non-superposition of the M versus H/T data on a single master curve and the high-field non-saturation suggests the presence of a significant magnetic anisotropy and/or low lying excited states in compound **1**.

To investigate the dynamics of the magnetisation, the temperature and frequency dependences of the ac-susceptibility were undertaken under zero-dc field (Figure 3 and S5 (see the Supporting Information)) for **1**. They both reveal the presence of slow relaxation of the magnetisation typical of a SMM behaviour. It is noteworthy that the temperature dependence of in-phase and out-of-phase ac susceptibilities do not go to zero after the maxima for low frequencies (see the Supporting Information, Figure S5), as for most 3d SMMs, might be indicative of a fast relaxation process that becomes dominant in the lower temperature region.[2d,16] The temperature dependence of the ac-susceptibility measurement on the gadolinium analogue (see the Supporting Information and Figure S6 for details) under zero-dc field does not exhibit any out-of-phase ac signals (Figure S7), corroborating further that the magnetic relaxation phenomena basically originates from an intrinsic molecular properties of the compound, rather than intermolecular interactions and long-range magnetic order. The relaxation time was extracted from the frequency-dependent data between 1.9 and 26 K and the Arrhenius plot obtained from these data is given in Figure S8 (see the Supporting Information). Below 3 K, a temperature-independent relaxation regime is observed with a characteristic time of 0.07461 s. This behaviour is expected for a SMM when the quantum tunnelling of the magnetisation becomes dominant (i.e., faster than the thermal-activated relaxation).[1b,17] Above 3 K, the relaxation becomes thermal-activated (Arrhenius-like behaviour). An estimation of the anisotropic barrier around 56 K can be obtained through fitting τ values above 8 K utilising an Arrhenius law, and the pre-exponential factor (τ_0) is 6.6×10^{-6} s for **1**.

Although such ac signals were observed above 1.9 K, no hysteresis was detected in the M versus H data obtained using a traditional SQUID magnetometer (see the Supporting Information, Figure S9). Therefore, to probe further the relaxation dynamics of **1**, hysteresis measurements were performed on a SQUID-VSM in the temperature range 1.8–5 K with a higher sweep rate (70 mTs^{-1}). Below 5 K, hysteresis loops were clearly observed, which were strongly temperature dependent down to 1.8 K (Figure 4). The coercivities of the hysteresis loops increase with decreasing temperature, as expected for an SMM. This behaviour confirms further the SMM nature of **1**.[4f]

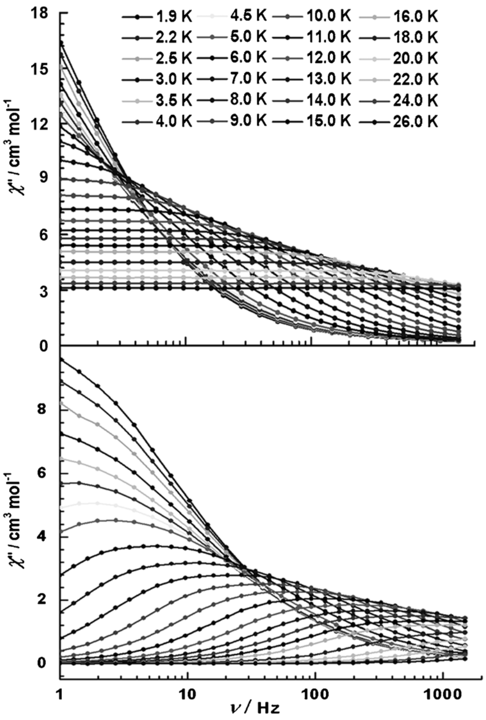

Figure 3. Frequency dependence of the in-phase (top) and out-of-phase ac susceptibility (bottom) of **1** below 26.0 K, under zero-dc field.

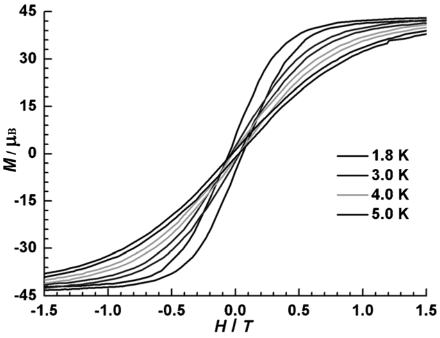

Figure 4. Hysteresis loops for **1** (powder sample) at different temperatures and a constant field sweep rate of 0.07 Ts^{-1}.

In conclusion, a novel hexanuclear Dy^{III} SMM with a particular trigonal prismatic topology has been synthesised from a new H_2L ligand. It should be noted that the rare μ_3-fashion CO_3^{2-} ligands derived from the capture of atmospheric CO_2 play a crucial role for assembling the peculiar triangles of the trigonal prism. This Dy_6 complex behaves as a SMM with an anisotropic barrier of 56 K, and a quantum regime of relaxation below 3 K. In addition, hysteresis loops can be observed below 5 K. We believe this unique trigonal prismatic SMM will not only enrich the polynuclear dysprosium SMMs family but also stimulate further research into the relaxation dynamics of SMMs with different topologies based on versatile multidentate ligands.

Experimental Section

Synthesis of the complex 1: A solution of $Dy(OAc)_3\cdot6H_2O$ (53.3 mg, 0.15 mmol) and the H_2L (40.5 mg, 0.15 mmol) in $CH_3OH/CH_3CH_2OH/$

CH_2Cl_2 (15 mL, 1:1:2 v/v) was stirred with triethylamine (0.6 mmol) for 8 h. The resultant yellow solution was left unperturbed to allow the slow evaporation of the solvent. Yellow single crystals, suitable for X-ray diffraction analysis, were formed after one week. Yield: 16 mg (43 %, based on metal salt). IR (KBr): $\tilde{\nu} = 3051$(w), 2930(w), 1605(vs), 1558(s), 1475(vs), 1446(vs), 1416(m), 1373(w), 1333(vs), 1240(s), 1152(m), 1107(w), 1036(s), 971(w), 870(w), 742(s), 645(w), 589(w), 430(m) cm^{-1}; elemental analysis calcd (%) for $C_{183}H_{190}Dy_{12}N_{48}O_{74}$: C, 34.20, H, 2.49, N, 12.20: found C, 34.13, H, 2.37, N, 12.05.

Magnetic measurements were performed in the temperature range 2–300 K using Quantum Design MPMS-XL SQUID and 1.9–5.0 K using SQUID-VSM magnetometers, respectively. The diamagnetic corrections for the compounds were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

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Keywords: dysprosium trigonal prism · hydrazones · magnetic properties · Schiff bases · slow magnetic relaxation

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