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Influence of the N-Bridging Ligand on Magnetic Relaxation in an Organometallic Dysprosium Single-Molecule Magnet

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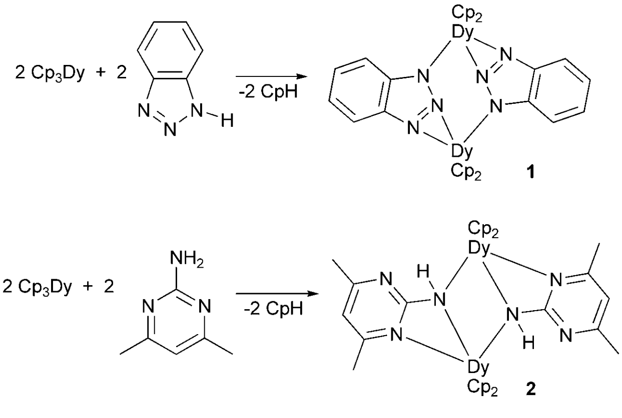
In memory of Dr J. Philip Day—a great friend and colleague

The large magnetic anisotropy within lanthanide (Ln) ions has made complexes of the 4f ions attractive candidates for making new single-molecule magnets (SMMs).[1,2] Perhaps the most interesting results have been reported by the Ishikawa group for the phthalocyanine (Pc) double-decker complexes $[Pc_2Ln]^-$,[1] which in the cases of Ln = terbium(III) and dysprosium(III) display very large energy barriers for the relaxation of magnetisation. Coronado and co-workers have reported similar slow relaxation for a single erbium(III) centre coordinated to a polyoxometallate ligand.[3] In addition to these monometallic complexes, polymetallic lanthanide clusters can also exhibit SMM properties, such as phenoxide-bridged dysprosium dimers in which there is ferromagnetic exchange between the Dy^{III} ions,[4] and a tetranuclear dysprosium(III) cage compound with the largest observed relaxation barrier in an SMM.[5] Other polymetallic dysprosium(III) complexes are interesting for their very unusual physics; for example, a dysprosium triangle with a diamagnetic ground state despite having an odd-number of unpaired electrons has been reported, which is probably the first example of a toroidal spin state.[6]

The slow relaxation in monometallic phthalocyanine complexes of Tb^{III} and polyoxometallate complexes of Er^{III} show that the strength of the crystal field at the Ln^{III} ion is important in controlling relaxation.[1,3] It is also odd that the energy barriers in polymetallic lanthanide SMMs are larger than the exchange interactions, suggesting that single-ion anisotropy, due to the strength and symmetry of the local crystal field, is probably the most important factor, and that exchange is a secondary consideration that moderates the magnetic relaxation of the single ions. These thoughts led us to examine organometallic lanthanide complexes to look for new SMMs: ligands such as cyclopentadienyl ($Cp = \eta^5$-C_5H_5) produce a much stronger crystal field than N- or O-donor ligands. Herein we report two organometallic dimers of dysprosium: $[\{Cp_2Dy(\mu\text{-bta})\}_2]$ (**1**) (btaH = 1*H*-1,2,3-benzotriazole) and $[\{Cp_2Dy[\mu\text{-}N(H)pmMe_2]\}_2]$ (**2**) (NH_2pmMe_2 = 2-amino-4,6-dimethylpyrimidine). Compound **1** was prepared by employing an N–H deprotonation reaction between $[Cp_3Dy]$[7] and benzotriazole, according to Scheme 1.

The benzotriazolide-bridged dimer **1** was crystallised by slow cooling of a saturated thf solution to result in the formation of colourless blocks suitable for X-ray crystallography. Compound **2** was prepared according to a literature procedure.[8] The molecular structure of **1** (Figure 1) consists of a non-centrosymmetric dimer in which two dysprosium



Scheme 1. Synthesis of the didysprosium compounds **1** and **2**.

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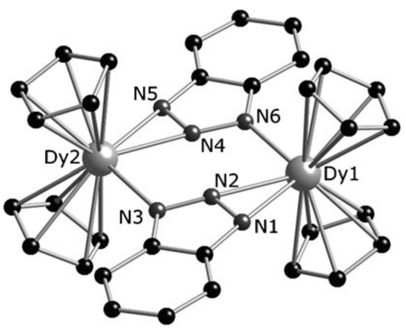

Figure 1. Molecular structure of **1**. Selected bond lengths [Å]: Dy1−N1 2.534(15), Dy1−N2 2.368(14), Dy1−N6 2.448(14), Dy2−N3 2.448(15), Dy2−N4 2.360(14), Dy2−N5 2.545(14). Carbon atoms are black spheres; hydrogen atoms not shown.

atoms are bridged by two [bta]$^-$ ligands, with each dysprosium atom also being complexed by two terminal η^5-Cp ligands. The three Dy−N bond lengths per dysprosium in **1** can be classified as short, medium and long, averaging 2.364, 2.448 and 2.540 Å, respectively, resulting in a Dy···Dy separation of 4.901 Å. The Dy−C distances in **1** are in the range 2.625(17)–2.681(18) Å for Dy1 and 2.63(2)–2.680(18) Å for Dy2, which are typical of dysprosium cyclopentadienides. The Dy sites in **1** are nine-coordinate. Although the structural motif $[\{Cp_2Ln(\mu\text{-}E_n)\}_2]$ (E_n = heteroatom group) is common in organolanthanide chemistry,[8,9] compound **1** is the first example to contain [bta]$^-$ as the bridging ligand. Compound **2** is an amido-bridged dimer containing nine-coordinate Dy^{III} centres with a Dy···Dy separation of 3.789 Å; the structure has been discussed in detail elsewhere.[8]

Magnetic studies were performed on polycrystalline samples of compounds **1** and **2**. Both dimers show very similar behaviour in both magnetisation against field and susceptibility against temperature measurements. At room temperature, the $\chi_M T$ values of 27.2 and 28.1 cm^3 K mol^{-1} for **1** and **2**, respectively (Figure 2), are in good agreement with the expected value of 28.34 cm^3 K mol^{-1} for two non-interacting dysprosium(III) ions ($S=5/2$, $L=5$, $J=15/2$, $g=4/3$, $^6H_{15/2}$).

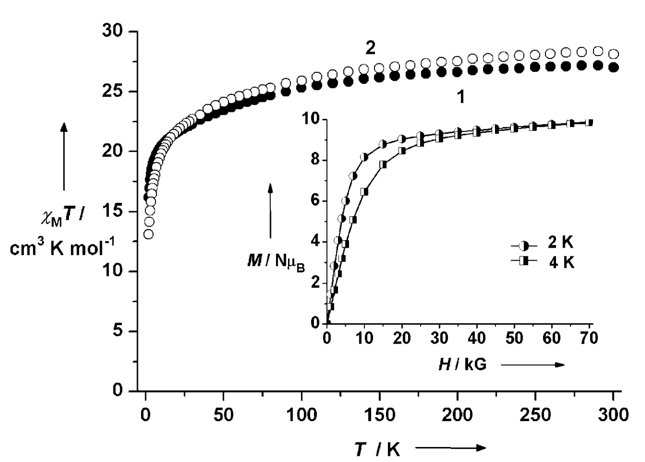

Figure 2. Temperature dependence of $\chi_M T$ of **1** and **2** for the field strength $H=1000$ G. Inset: Plot of magnetisation (M) of **1** versus field at 2 and 4 K.

Upon cooling, $\chi_M T$ decreases gradually and then more rapidly below 30 K to reach 16.2 (for **1**) and 13.1 cm^3 K mol^{-1} (for **2**) at 2 K (1 kG field). The decline in $\chi_M T$ with T is mostly due to crystal field effects (i.e. thermal depopulation of the Dy^{III} Stark sub-levels). The magnetisation versus field curves, measured below 4 K, are the same shape for **1** and **2**, and do not reach saturation up to a field of 70 kG. The maximum value reached at 2 K and 70 kG is 9.88 Nμ_B for **1** (inset of Figure 2) and 9.99 Nμ_B for **2**. Our data can be compared with the expected magnetisation value of 10.46 N$_B$ (2 × 5.23 N$_B$) for two uncorrelated Dy^{III} ions in an environment affected by crystal field effects, as has been developed using Stevens operators in low symmetry and then elaborated further.[10] This treatment has been applied successfully to a variety of different Dy^{III} ion environments.[11] The lack of saturation of the M versus H data and similarly non-superposition on a single master-curve of the M versus H/T data suggest the presence of significant magnetic anisotropy in **1** and **2**.

Low-temperature ac magnetic susceptibility measurements on **1** (Figure 3, and Figures S1 and S2 in the Supporting Information) reveal features associated with SMMs,[12] while compound **2** only shows a weak increase in χ_M'' below 4 K (see Figure S3 in the Supporting Information), but no maxima were observed down to 1.8 K. For compound **1**, however, both the in-phase (χ_M') and out-of-phase (χ_M'') components of the ac susceptibility recorded with zero-dc field show strong frequency dependence below about 12 K, and maxima are observed in χ_M'' (Figure 3 a). At fixed temperatures between 1.8 and 7 K and zero applied magnetic field, we obtained semicircular Cole–Cole diagrams (χ_M'' *versus* χ_M'; see Figure S4 in the Supporting Information), which could be fitted by a generalised Debye model with the α parameters in the range 0.02–0.1, which indicates a narrow distribution of relaxation times.[13] Plotting the magnetisation relaxation times (τ) obtained from the ac data as ln τ versus $1/T$ (Figure 3 b) one can observe that the relaxation time tends to saturate at approximately 4.5 K ($\tau=7.0\times10^{-4}$ s), when the dynamics of the magnetisation become temperature independent and enter a pure quantum tunnelling regime. Above 4.5 K, the relaxation process becomes thermally activated and the data above 6.3 K obey the Arrhenius law $\tau=\tau_0\, exp(\Delta E/k_BT)$ with $\Delta E=46.5\pm2.4$ K and $\tau_0=4.5\times10^{-7}$ s, where ΔE is the energy barrier for the relaxation of the magnetisation and τ_0 is the pre-exponential factor. The energy barrier in **1** is one of the largest observed in a polymetallic lanthanide compound, albeit lower than that observed in [Pc$_2$Tb]$^-$,[1] and in the polynuclear dysprosium complexes reported by Murugesu and co-workers.[4,5] Interestingly, the presence of a fast tunnelling relaxation channel in **1**, marked by the divergence in χ_M'' below the blocking temperature (Figure 3 a),[3b] allows the direct study of the crossover between thermally activated relaxation and direct tunnelling by employing only one experimental technique, namely: linear ac susceptibility measurements. Such

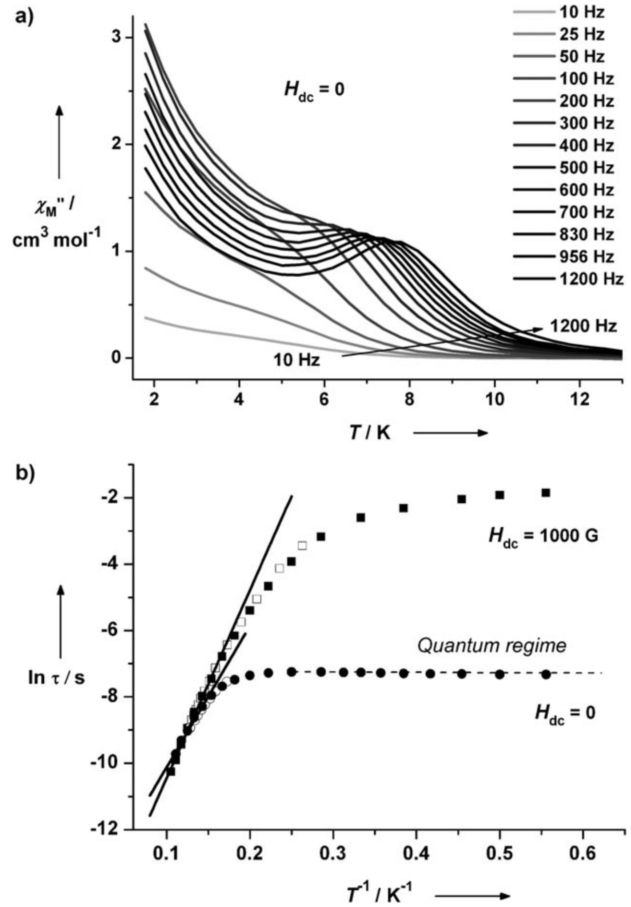

Figure 3. a) Temperature dependence under zero-dc field of the out-of-phase magnetic susceptibility (χ_M'') of **1**, in an ac field of 1.55 G oscillating at frequencies between 1 and 1200 Hz. b) Magnetisation relaxation time (τ) versus T^{-1} plot for **1** under zero-dc field (circles) and under a dc field of 1000 G (squares), based on data collected in frequency (shaded symbols) and temperature (open symbols) variation regimes. The solid lines represent the best fits to the Arrhenius law of the thermally activated region with the parameters given in the text.

behaviour is specific for lanthanide-based SMMs. It implies that the superparamagnetic blocking (e.g. $\tau > 1$) in **1** is only achieved for high frequencies, because of the fast zero-field quantum tunnelling relaxation. To minimise this effect, we performed ac susceptibility studies under an applied dc field of 1000 G (see Figure S2 in the Supporting Information). As expected for a SMM with a large energy barrier, the relaxation time remains almost unchanged in the thermally activated regime, but increases significantly in the quantum regime (Figure 3b), allowing the observation of the thermally activated regime at lower temperatures. Fitting the data to the Arrhenius law yielded a slightly larger energy barrier ΔE of 56.6 ± 0.9 K and τ_0 of 1.0×10^{-7} s. This large energy barrier to magnetisation reversal in **1** is an exciting result. An almost greater surprise was that the related dimer **2** shows very similar behaviour to **1** in *static* fields, but produces no significant response in the ac susceptibility measurements (see Figure S3 in the Supporting Information). On comparing **1** and **2**, the most obvious difference is the exchange pathway present in the two molecules; in **2** the bridge is a single amido nitrogen, but in **1** the pathway is more complicated.

To elucidate the electronic structures of **1** and **2** we carried out density functional calculations[14] at the crystallographically determined geometries. The electronic states calculated were for the Dy^{III} $4f^9$ ions, each with spin, $s = 5/2$. Taking the spins on the two Dy centres to be parallel gives a total spin of $S = 5$ and a multiplicity of 11. To describe appropriately the Dy atoms we employed the large core (54 electron) CRENBL[15] relativistic effective core potential. The accompanying valence basis set, from reference [15], was fully uncontracted to the primitive set (6s 6p 6d 6f). All other atoms were described with the all-electron 6-31G(d,p) basis,[16] and the B3LYP[17] exchange-correlation functional was used. The calculations were carried out using the *tight* convergence criterion and *ultrafine* grid. The results give us a working explanation for the differing behaviour. Firstly, calculating the spin density in each case gives very similar results (see Figure S5 in the Supporting Information); the spin density is located entirely in the f orbitals of the two dysprosium ions in each case. There is no sign of an exchange path involving spin density at the bridging N atoms for either structure. This is completely consistent with the measurements in static magnetic field.

Looking closely at the electronic distribution, we find (using the atom-numbering scheme of Figure 1) that in **1** there are significant bonding interactions between N1 and N6 with Dy1, and N3 and N5 with Dy2, and only a very small interaction of N2 and N4 with their respective Dy centres. This is despite the N2–Dy1 and N4–Dy2 contacts being the shortest N–Dy contacts in the structures. We have quantified these interactions using Mayer bond orders[18] (Figure 4) calculated with our in-house code. For comparison we have included two of the Dy–C(Cp) bond orders. For example, summing the bond orders of Dy1 to all the carbon atoms of the Cp ring above gives a total bond order of 0.98. Hence the Dy1–N1 and Dy1–N6 bond orders (and the equivalent interactions on Dy2) indicate significant bonding. By contrast, the short Dy1–N2 and Dy2–N4 distances show very small bond orders, indicating no appreciable covalent bonding between these centres.

Using Mulliken population analysis we find charges on Dy1/Dy2 of $+1.12/+1.14$ and on the N atoms: $N1 = -0.39$; $N2 = -0.25$; $N3 = -0.47$; $N4 = -0.24$; $N5 = -0.40$; $N6 = -0.48$. These parameters again suggest that the Dy–N interactions are significantly less in the case of the central N atoms. This behaviour probably stems from the nature of the π orbitals of the $[bta]^-$ ligand. Simple π symmetry arguments quickly tell us that the HOMO of each $[bta]^-$ ligand has a node on the central nitrogen atom, hence in terms of simple frontier orbital interactions we should not expect to see a bond between these centres. Furthermore, if we consider a plane perpendicular to the bta planes and passing through the N2 and N4 atoms, thus bisecting the molecule, we find that all ten high-spin singly occupied orbitals in **1** are distributed such that there is no orbital communication

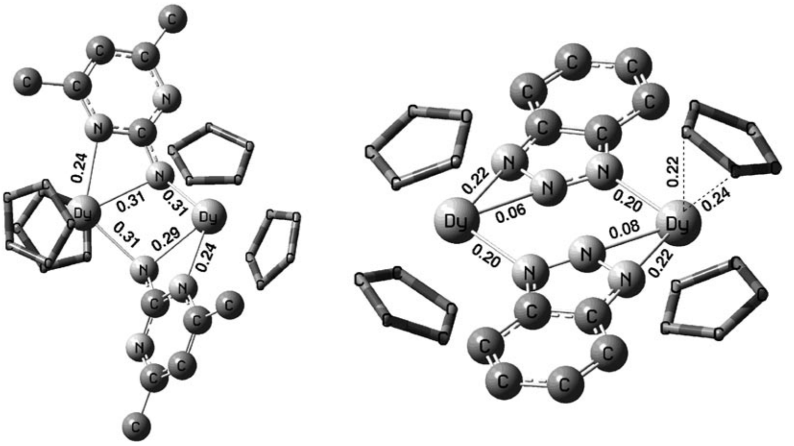

Figure 4. Mayer bond orders for **1** (left) and **2** (right). The Cp ligands are shown as capped sticks and all H atoms have been omitted.

between the two halves of the molecule across this plane. This indicates there is no pathway for communication between the Dy centres via the $[bta]^-$ ligand. In **2**, by contrast, the lowest energy high-spin singly occupied orbital shows a significant bonding interaction involving Dy d orbitals with p orbitals on the bridging amide nitrogen (Figure 5). The two Dy atoms in **2** are symmetrically bonded to the two central amido nitrogen atoms with essentially equivalent bond orders of about 0.3. These bond orders are larger than any of the Dy–N bond orders in **1**. This interaction provides a path for communication between the Dy^{III} ions in **2** which is not present in **1** (we have confirmed this by searching deep within the orbital manifold of **1**). Looking at the Mulliken analysis for **2**, we find charges on the two Dy atoms of $+0.92/+0.89$ and on the two central amido nitrogens of $-0.85/-0.84$, while the N atoms of the six-membered ring nearest to the Dy carry charges of $-0.55/-0.54$ and the distant N atoms have charges of $-0.40/-0.39$. This also suggests a much stronger ionic interaction between the Dy and the two central amido nitrogens than that found in **2**.

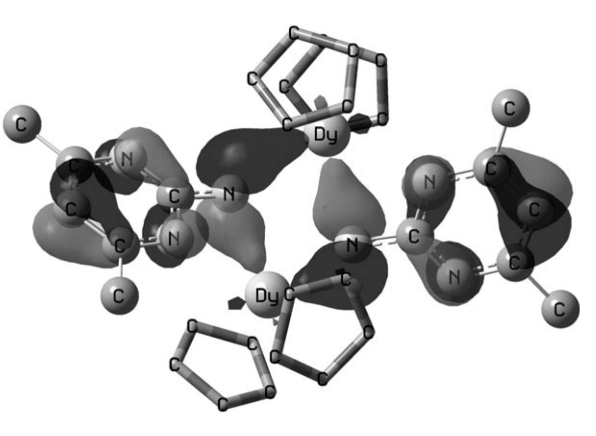

Figure 5. Lowest energy high-spin orbital of **2** (shown as isosurface of 0.035 au). The Cp ligands have been shown as capped sticks and all H atoms have been omitted (large grey spheres = Dy; darker grey = N; light grey = C).

We conclude there is an interaction between Dy^{III} ions in **2** but not in **1**. The interaction in **2** is too weak to have a significant influence on the static magnetic behaviour, and so is not detectable in either the susceptibility or magnetisation measurements. However, the interaction in **2** appears to be sufficient to provide a relaxation mechanism for the magnetisation, hence **2** is not an SMM. In **1**, the dysprosium ions are essentially isolated electronically from each other, and the observed slow relaxation is due to single ion factors. This contrasts with the dimetallic dysprosium SMM reported by Murugesu et al.[4] where the *static* magnetic measurements show a ferromagnetic exchange between the Dy^{III} ions, and a larger energy barrier for relaxation of magnetisation is found from the *dynamic* studies. Our results, combined with the previous work of others,[3,4] suggest that lanthanide-only SMMs with high energy barriers could be created if control could be exerted over the magnetic exchange interaction.

Experimental Section

1: A solution of $[Cp_3Dy]$ (0.18 g, 0.50 mmol) in THF (10 mL) was added to a solution of btaH (0.060 g, 0.50 mmol) in THF (10 mL) at $-78\,^{\circ}C$. The mixture was stirred at $-78\,^{\circ}C$ (30 mins) and then slowly warmed to room temperature. After the mixture was stirred at room temperature for 16 h, a white precipitate formed. Following addition of more THF (10 mL), the reaction mixture was briefly heated to reflux to give a colourless solution, and then slowly cooled to room temperature. Storage overnight resulted in the formation of colourless crystals of **1** (0.10 g, 24 %). Elemental analysis calcd (%) for $C_{32}H_{28}Dy_2N_6$: C 46.77, H 3.44, N 10.23; found: C 46.66, H 3.46, N 10.24. Crystal data for **1**: $C_{32}H_{28}Dy_2N_6$, $M_r = 821.38$, colourless blocks, crystal dimensions $0.2 \times 0.2 \times 0.14\ mm^3$, orthorhombic, $P2_12_12_1$, $a = 7.8821(8)$, $b = 16.5857(18)$, $c = 21.506(2)$ Å, $V = 2811.5(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.941\ Mg\,m^{-3}$, $\mu = 5.307\ mm^{-1}$, $\lambda(Mo_{K\alpha}) = 0.7103$ Å, $T = 100(2)$ K, completeness to $2\theta_{max}$ (27.5°) = 93.8 %, 7077 reflections, 5533 unique reflections ($R_{int} = 0.0583$), $R1 = 0.0682$, $wR2 = 0.149$ using 5533 reflections with $I > 2\sigma(I)$, absolute structure parameter = 0.08(5). Crystals of **1** were mounted on thin glass fibres using perfluoropolyether oil and frozen in a flow of cold nitrogen gas from an Oxford Cryostream instrument. Data were collected using an Oxford Diffraction XCaliber 2 X-ray diffractometer. CCDC-750397 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. Magnetic measurements were performed on a Quantum Design MPMS XL SQUID magnetometer on polycrystalline samples. Data were corrected for the diamagnetism of the samples using Pascal constants, and the sample holder by measurement. Frequency-dependent ac-susceptibility measurements used a QD MPMS AC option.

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Keywords: density functional calculations • dysprosium • lanthanides • magnetic properties • organometallics • single-molecule magnetism

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