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A hydride-ligated dysprosium single-molecule magnet†

Cite this: *Chem. Commun.*, 2013, **49**, 901

Received 6th November 2012,
Accepted 7th December 2012

DOI: 10.1039/c2cc38036f

www.rsc.org/chemcomm

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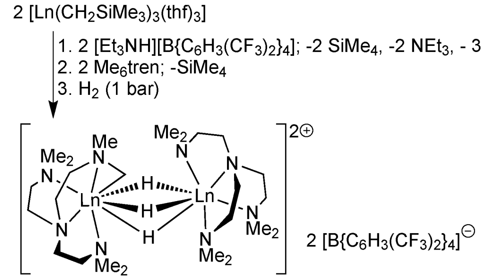
An experimental and *ab initio* computational study of an unsymmetrical, hydride-bridged di-dysprosium single-molecule magnet is reported.

Lanthanide coordination compounds have accounted for some of the most important developments in studies of single-molecule magnets (SMMs), a family of molecules that exhibit magnetic memory effects.[1] The temperatures at which Ln-SMMs function far exceed the limits previously set by transition metal SMMs,[2] and the benchmark SMM blocking temperature was recently re-defined by $[Tb_2\{N(SiMe_3)_2\}_4(thf)_2(\mu\text{-}N_2)]^-$, where magnetic hysteresis up to 14 K was measured.[3] Indeed, energy barriers to reversal of the magnetization (the anisotropy barrier, U_{eff}) in Ln-SMMs often exceed 100 cm^{-1},[4] which has created renewed confidence that such materials may eventually be developed for device applications.[5]

Single-ion effects, such as the symmetry and electrostatic potential of the crystal field, strongly influence the relaxation of the magnetization in SMMs,[1e] and exploring ligands that are new to Ln-SMMs could push the field in new directions.[6] The hydride ligand – which has never been applied in SMM studies – offers an interesting opportunity because its strong ligand-field effects, and potential to promote strong exchange, could influence the relaxation in Ln-SMMs in completely different ways to oxygen-donor ligands, which are ubiquitous in SMM studies.[1] We now report the hydride-bridged compounds $[Ln(Me_5trenCH_2)(\mu\text{-}H)_3Ln(Me_6tren)][B\{C_6H_3(CF_3)_2\}_4]_2$, where Ln = Gd(III) is $[\mathbf{1}][X]_2$, Ln = Dy(III) is $[\mathbf{2}][X]_2$, and Me_6tren = tris{2-(dimethylamino)ethylamine. Compound $[\mathbf{2}][X]_2$ is the first hydride-ligated SMM.



Scheme 1 Synthesis of $[\mathbf{1}][X]_2$ (Ln = Gd) and $[\mathbf{2}][X]_2$ (Ln = Dy).

Adding $[Et_3NH][B\{C_6H_3(CF_3)_2\}_4]$ to $[Ln(CH_2SiMe_3)_3(thf)_3]$ in ether at −40 °C, followed by Me_6tren and then by dihydrogen produced $[\mathbf{1}][X]_2\cdot 2Et_2O$ and $[\mathbf{2}][X]_2\cdot 2Et_2O$ (Scheme 1). Both $[\mathbf{1}][X]_2\cdot 2Et_2O$ (Fig. S1, ESI†) and $[\mathbf{2}][X]_2\cdot 2Et_2O$ (Fig. 1) crystallize in the space group $P\bar{1}$, with the Ln centres being related by crystallographic inversion symmetry. Disorder within the ligands was resolved with split positions for the carbons. Taking the disorder into account, the eight-coordinate Ln(III) ion is complexed by three μ-hydrides, four nitrogens and a carbon atom of a C–H-activated $[Me_5trenCH_2]^-$ ligand. The seven-coordinate Ln(III) ion is complexed by the four nitrogens of the Me_6tren ligand in addition to the μ-hydrides. Key parameters are presented in Tables S1 and S2 (ESI†). The coordination geometries of the Ln centres in $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ are similar: the seven-coordinate environment of Ln(1A) can be roughly described as mono-capped octahedral, whereas the eight-coordinate Ln(1) occupies a very low symmetry site.

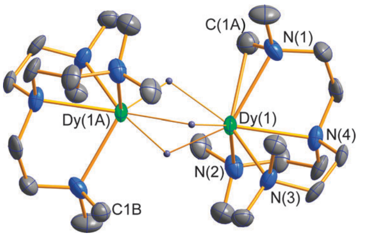


Fig. 1 Structure of $[\mathbf{2}]^{2+}$ (50% thermal ellipsoids). Only one split position of disordered atoms shown. Hydrogen atoms omitted, except μ-hydrides.

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† Electronic supplementary information (ESI) available: Synthetic, analytical, crystallographic details. Magnetism graphs, computational details. CCDC 901745 and 901746. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc38036f

The considerable interest in molecular rare earth hydrides stems from their applications in synthesis and catalysis, and from their potential to activate dihydrogen.[7,8] Solid-state rare-earth hydrides are valued for their magnetic, optical and semiconductor properties.[9] However, [**2**][X]$_2$ provides the first opportunity to investigate the SMM properties of a rare-earth hydride. Mindful of the crucial role of crystal field symmetry in SMMs, [**2**]$^{2+}$ also enables an investigation of how two different, low-symmetry environments within the same hydride species can impact upon dynamic magnetic behaviour.

Compounds [**1**][X]$_2$ and [**2**][X]$_2$ were investigated by SQUID magnetometry in the temperature range 1.8–300 K. At 300 K in a field of H_{dc} = 1000 G, the $\chi_M T$ product for [**1**][X]$_2$ (χ_M is the molar magnetic susceptibility) is 15.2 cm^3 K mol^{-1} (Fig. S2, ESI†), which is consistent with the value of 15.76 cm^3 K mol^{-1} predicted for two non-interacting Gd(III) ions ($^8S_{7/2}$, $g = 2$). On cooling, $\chi_M T$ decreases gradually down to 50 K, and then rapidly to reach 1.22 cm^3 K mol^{-1} at 1.8 K, which indicates antiferromagnetic exchange. In agreement with this, the magnetisation (M) *versus* field (H) isotherms are well below the calculated Brillouin function of two uncoupled $S = 7/2$ ions (Fig. S3, ESI†). The maximum M value at 2 K and 70 kG is 9.3 μ_B, which is much smaller than the calculated value of 15.0 μ_B for two uncoupled Gd(III) centres with $g = 2$. The magnetism of [**1**][X]$_2$ was modelled with the Hamiltonian $H = -JS_{Gd1}S_{Gd2}$, where J is the exchange coupling constant and S_{Gd1} and S_{Gd2} represent the spins on the Gd(III) ions. A good fit of the $\chi_M T(T)$ data was obtained with $g = 1.995$ (expected for Gd^{3+}) and $J = -1.22$ cm^{-1}, thus indicating weak antiferromagnetic coupling. Studies of hydride-mediated exchange are hitherto unknown in lanthanide chemistry, however the value of J determined for [**1**][X]$_2$ is similar to those measured in other exchange-coupled gadolinium compounds.[3b]

The $\chi_M T$ data for [**2**][X]$_2$ (Fig. S2, ESI†) reveal a value of 28.17 cm^3 K mol^{-1} at 300 K, in good agreement with the theoretical value of 28.34 cm^3 K mol^{-1} for two uncoupled Dy(III) ions ($^6H_{15/2}$, $g = 4/3$), suggesting that all the m_J sub-levels within the electronic ground term of Dy(III) are populated at 300 K. At lower temperatures, $\chi_M T$ decreases gradually to 24.7 cm^3 K mol^{-1} at 25 K, and then more rapidly below 25 K, to reach a value of 16.57 cm^3 K mol^{-1} at 2 K. The decrease of $\chi_M T$ on cooling can be assigned to depopulation of excited m_J sub-levels and weak antiferromagnetic exchange. The $M(H)$ data of **2**, acquired at several temperatures between 1.8 and 10 K (Fig. S4, ESI†), reveal a rapid increase of the magnetisation at small fields, followed by a more gradual increase at high fields, without reaching saturation. Isothermal $M(H/T)$ curves do not superimpose, confirming the presence of significant magnetic anisotropy and/or low-lying excited states. The value of M at 1.8 K and 70 kG is 10.71 μ_B, (5.35 μ_B per Dy), as typically observed in other Dy$_2$ SMMs.[6]

The dynamic magnetism of [2]X$_2$ was investigated using alternating current (ac) magnetic susceptibility measurements as a function of temperature and of frequency. In zero dc field, an ac field of H_{ac} = 1.55 G and ac frequencies (ν) oscillating at 1–1200 Hz, the in-phase (χ'_M) (Fig. S5 and S6, ESI†) and the out-of-phase (χ''_M) (Fig. 2 and 3) components of the magnetic susceptibility are temperature and frequency dependent below 22 K. The maximum in $\chi''_M(\nu)$ gradually shifts to lower frequencies as the temperature is lowered from 13 K to 1.85 K, indicating that [**2**]$^{2+}$ is an SMM. The temperature dependence of χ''_M in [**2**][X]$_2$ shows unsymmetrical maxima at several frequencies up to 1200 Hz in zero applied field (Fig. 3). Deconvolution of the overlapping maxima (Fig. S8, ESI†) enabled two Lorenzian curves to be fitted, and two relaxation processes to be identified. At fixed temperatures in the range 1.85–12 K, semi-circular Cole–Cole plots of χ'_M *vs.* χ''_M were obtained, and were fitted to a generalized Debye model with α = 0.27–0.33 (Fig. S9, ESI†). The relatively high values of the α parameters imply that more than one relaxation process is occurring, which is consistent with the unsymmetrical $\chi''_M(T)$ curves, and the presence of two distinct Dy sites in [**2**]$^{2+}$.

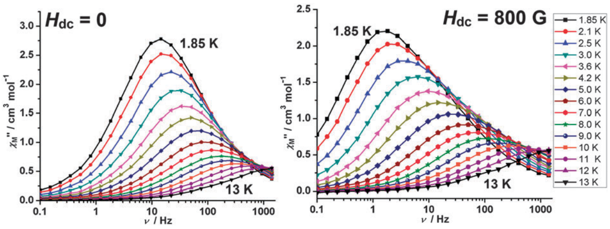

Fig. 2 $\chi''_M(\nu)$ isotherms in [**2**]X$_2$ with H_{ac} = 1.55 G.

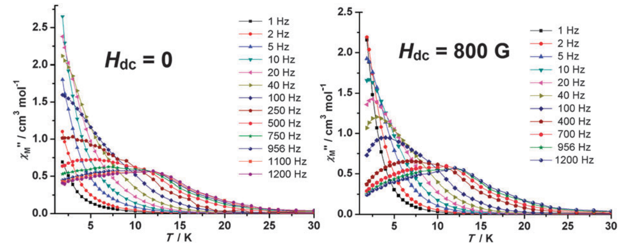

Fig. 3 $\chi''_M(T)$ in [**2**]X$_2$ with H_{ac} = 1.55 G applied at various frequencies.

The relaxation of the magnetization in SMMs can be characterized by a relaxation time, τ.[1b] Plots of ln τ *versus* $1/T$ for [**2**]$^{2+}$ in zero dc field using $\chi''_M(T)$ and $\chi''_M(\nu)$ data are linear above 11 K (Fig. S10, ESI†), suggesting that the magnetization relaxes *via* an Orbach process involving the ground and first-excited m_J levels. The Arrhenius relationship $\tau = \tau_0 \exp(U_{eff}/k_BT)$ allowed the anisotropy barrier for the slower relaxation process to be estimated as U_{eff} = 65 cm^{-1}, with $\tau_0 = 1.04 \times 10^{-7}$ s. Below 11 K, a gradual crossover to a temperature-independent regime is observed, suggesting relaxation *via* quantum tunnelling of the magnetization (QTM). From the $\chi''_M(\nu)$ data, the second relaxation process was estimated to have U_{eff} = 15 cm^{-1}.

Application of a static field to [2]X$_2$ reduces the QTM rate. Field-dependence studies at 4 K showed a rapid increase in τ upon increasing the field from zero to 800 G, and χ''_{max} shifts to lower frequencies. Above 800 G, τ decreases rapidly, passing through a minimum at 2.5 kG (Fig. S11, ESI†). This indicates an additional relaxation pathway that shortcuts the energy barrier, as predicted at level crossings when resonant QTM occurs. Application of the optimum field of 800 G to [**2**][X]$_2$ thus shifts the maxima in $\chi''_M(\nu)$ to lower frequencies (Fig. 2), and additional maxima at lower frequencies were observed in $\chi''_M(T)$ (Fig. 3). At 800 G, the Arrhenius analysis produced U_{eff} = 85 cm^{-1} and $\tau_0 = 5.7 \times 10^{-9}$ s (Fig. S10, ESI†).

To gain more insight into the two relaxation processes in [**2**]$^{2+}$, *ab initio* calculations were carried out using MOLCAS 7.6.[10]

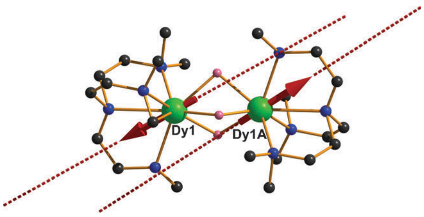

Fig. 4 Orientation of the magnetic moments in the ground Kramers' doublet of $[\mathbf{2}]^{2+}$ (dashed lines). The arrows show the antiferromagnetic coupling. Pink atoms = hydrides, blue = N, grey = C.

The calculations revealed that the ground Kramers' doublet for each of the two Dy(III) centres is well separated from the first excited state, but that the energy separation is 231 cm^{-1} in the eight-coordinate Dy(1) and 94 cm^{-1} for the seven-coordinate Dy(1A) (Table 2 and Table S4–S8, ESI†). The calculated g values of the ground Kramers' doublets for Dy(1) are $g_x = 0.0187$, $g_y = 0.0298$ and $g_z = 19.7236$; those for Dy(1A) are $g_x = 0.0615$, $g_y = 0.1374$ and $g_z = 19.2638$. Thus, the transverse g-values are approximately four times smaller for Dy(1) than for Dy(1A), and the different symmetry of the Dy coordination environments influences the energies and axiality of the Kramers' doublets.[11] SMMs in which the Ln centres are weakly exchange coupled relative to the measurement temperature, as in $[\mathbf{2}]^{2+}$ (see below), are likely to have their slowly relaxing magnetization associated with individual lanthanide ions. Thus, despite the high axiality for both dysprosiums, the eight-coordinate Dy(1) will be characterized by a stronger suppression of QTM, which can explain the observation of only one blocking centre in the ac susceptibility measurements. In polymetallic Ln-SMMs that feature more than one relaxation process, assigning each processes to a specific lanthanide is not straightforward using only bulk susceptibility measurements,[12] so here the calculations are crucial.

The U_{eff} value of 65 cm^{-1} in $[\mathbf{2}]^{2+}$ in zero field is markedly less than the calculated energies of both first excited Kramers' doublets. The discrepancies can be explained by considering the possible relaxation mechanisms, *i.e.* an Orbach process *via* the first excited Kramers' doublet, or directly from the ground state *via* QTM and/or a Raman process. The deviation from linearity of the Arrhenius plot for $[\mathbf{2}]^{2+}$ in zero field (Fig. S10, ESI†) shows that the QTM regime is entered below about $T = 11$ K, hence the poor match between the experimental U_{eff} value and the energies of the first excited Kramers' doublets. However, in the optimum dc field of 800 G the QTM is effectively suppressed, and the close match of the theoretical (94 cm^{-1}) and experimental (85 cm^{-1}) energy barriers in Dy(1A) suggests that relaxation probably occurs *via* the first excited Kramers' doublet.

The magnetic moments of the dysprosiums in the ground Kramers' doublets of $[\mathbf{2}]^{2+}$ intersect at an angle of 4.85° (Fig. 4). The small values of g_x and g_y for Dy(1) and Dy(1A) suggest that an Ising-type exchange interaction occurs in $[\mathbf{2}]^{2+}$. The total magnetic interaction (J_{tot}) is a sum of the magnetic dipole–dipole contribution (J_{dip}) and the exchange part (J_{exch}). The magnetic interaction between the ground Kramers' doublets on the two dysprosiums is described by $\hat{H} = -(J_{\mathrm{dip}} + J_{\mathrm{exch}})\hat{\tilde{s}}_{1,z}\hat{\tilde{s}}_{2,z}$, where $\tilde{s}_{i,z} = 1/2$ is the projection of the pseudospin corresponding to the lowest Kramers doublet on Dy$_i$ on the main anisotropy axis, z. Using the calculated g tensors for the ground Kramers' doublets, J_{dip} was calculated exactly as $+5.16$ cm^{-1} (Table S11, ESI†). A fit of the experimental data allowed $J_{\mathrm{exch}} = -7.62$ cm^{-1} to be calculated (Fig. S13–S18, Table S11, ESI†). Whereas the dipolar interaction is ferromagnetic, the exchange interaction is antiferromagnetic and stronger than the dipolar contribution, hence the total interaction in $[\mathbf{2}]^{2+}$ is antiferromagnetic with $J_{\mathrm{tot}} = -2.46$ cm^{-1}, which is consistent with the exchange coupling in $[\mathbf{1}]^{2+}$.

In summary, the hydride-bridged species $[\mathrm{Ln(Me_5trenCH_2)(\mu\text{-}H)_3Ln(Me_6tren)}]^{2+}$, (Ln = Gd, Dy) contain seven-coordinate and eight-coordinate Ln(III) centres. Two relaxation processes in the SMM $[\mathbf{2}]^{2+}$ were identified from ac susceptibility studies, with anisotropy barriers of $U_{\mathrm{eff}} = 65$ cm^{-1} and 15 cm^{-1}, respectively. *Ab initio* calculation of the g-values for Dy(1) and Dy(1A) in $[\mathbf{2}]^{2+}$ allowed the process with $U_{\mathrm{eff}} = 65$ cm^{-1} to be assigned to the eight-coordinate Dy(1), while fast QTM within seven-coordinate Dy(1A) prevents detection of a blocking process.

We acknowledge the support of the EPSRC (RAL, FT), The Humboldt Foundation (AV, RAL), the DFG (JO), the FWO-Vlaanderen (LU), and the KU-Leuven (LU, LFC).

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