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Chemical tuning of the magnetic relaxation  
in dysprosium(III) mononuclear complexes†Luke J. Batchelor,<sup>a</sup> Irene Cimatti,<sup>a</sup> Régis Guillot,<sup>a</sup> Floriana Tuna,<sup>b</sup>  
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**A dysprosium(III) complex, exhibiting slow relaxation of magnetization, was prepared. Crystallographic studies showed a perturbation of local symmetry upon deprotonation of the ligand, with concomitant faster relaxation of magnetization. This was attributed to a large shift in the direction of the main magnetic axis, as indicated by *ab initio* calculations.**

Interest in the magnetic relaxation and quantum fluctuations of ionic lanthanides doped in oxides began over 30 years ago.<sup>1,2</sup> The discovery in 2003 of slow relaxation of the magnetization in molecules containing a single lanthanide ion has rejuvenated interest in the study of magnetism of rare earth elements.<sup>3</sup> Molecules are attractive because it is possible to manipulate them with precision and tune and tailor them to meet specific functions. In the past decade, a vast array of mono- and polynuclear lanthanide containing complexes, which have rich and varied magnetic behaviors, have been synthesized.<sup>4–11</sup> Recently, a spin valve fabricated from single wall carbon nanotubes decorated with terbium(III) phthalocyanine (Pc) single molecule magnets (SMMs) was reported to operate at low temperature.<sup>12</sup> Before we can make SMMs active components in devices for quantum data storage applications for example, it is imperative to comprehend the mechanisms that govern slow relaxation and in turn design molecules with predictable behavior. Many groups have taken successful steps towards this goal.<sup>9,10,13</sup> Furthermore, efforts have started to focus on rationalizing the nature of slow relaxation of the mag-

netization in lanthanide complexes, by employing experiments and theory in unison.<sup>14–16</sup> Small modifications in the ligand field have been known to significantly influence the magnetic properties of the resulting compounds.<sup>17–19</sup> In a study by Ishikawa and co-workers, the SMM properties of the terbium(III)Pc molecule were switched on and off by deprotonation of the ligand.<sup>20</sup> They attribute this behavior to the loss of  $D_{4d}$  symmetry upon deprotonation. However, they did not analyze the orientation and changes to the main anisotropy tensor, which is crucial in the synthesis of tailored lanthanide SMMs.

Herein, we present a chemical tuning of the magnetic relaxation of mononuclear complexes obtained from the reaction of dysprosium(III) and the organic ligand H<sub>2</sub>DABPH (DABPH = 2,6-diacetylpyridinebis(benzoic acid hydrazone)).<sup>21</sup> Deprotonation of the ligand perturbed the local symmetry and afforded two complexes with different rates of relaxation of the magnetization. The origins of these differences were studied by micro-SQUID magnetometry, which indicated axial anisotropy and by *ab initio* calculations, which determined a shift in the direction of the main magnetic axis.

The dysprosium(III) compounds [Dy(H<sub>2</sub>DABPH)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>·2.5H<sub>2</sub>O (**1**) and [Dy(H<sub>2</sub>DABPH)(HDABPH)](NO<sub>3</sub>)<sub>2</sub>·EtOH·4H<sub>2</sub>O (**2**) were prepared by reaction of two equivalents of H<sub>2</sub>DABPH with Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O in EtOH and in EtOH–H<sub>2</sub>O, respectively. The relative stability of the complexes in solution was observed by electrospray mass spectra, which indicated little evidence of ligand degradation, loss or polymerization (Fig. S1, ESI†). The major species observed was the [Dy(HDABPH)<sub>2</sub>]<sup>+</sup> cation, which is unsurprising under harsh electrospray conditions. However, the amino protons are quite acidic and were not observed at all in our previous work with transition metals.<sup>22</sup>

Analysis of the X-ray crystal structures of **1** and **2** revealed that both complexes crystallized in the triclinic  $P\bar{1}$  space group (Fig. 1 and Table S1, ESI†). Structurally, **2** is very similar to **1**, the major differences arising from the deprotonation of the amino nitrogen (N1) of one of the ligands. The two species are indistinguishable by infrared and mass spectrometry. The deprotonated amido nitrogen was located crystallographically,

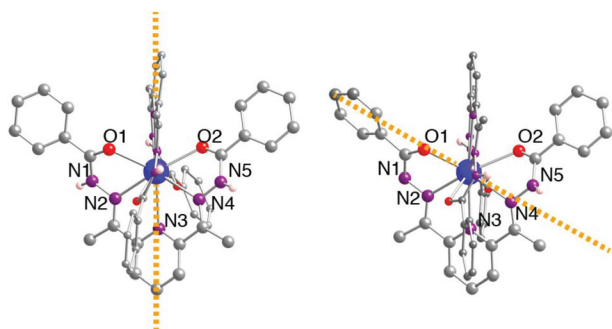
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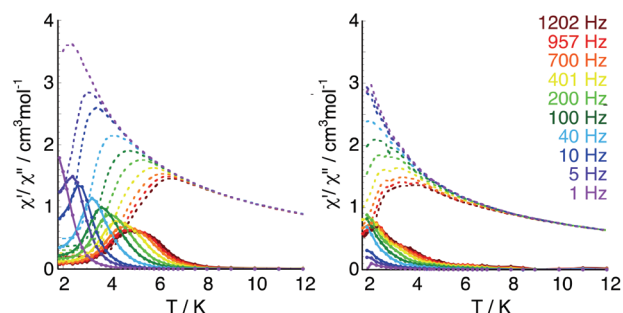


**Fig. 1** Left: Crystal structure of **1**. Right: Crystal structure of **2**. Blur, purple, red, grey and white spheres represent Dy, N, O, C and H, respectively; non-amino hydrogen atoms and counter ions are removed for clarity. The yellow lines represent the orientation of the main magnetic axis.

with the assignment supported by elemental analysis of the crystals. Two interlocked pentachelating ligands make up the coordination sphere of the dysprosium(III) (neutral H<sub>2</sub>DABPH for **1** and one neutral H<sub>2</sub>DABPH and one anionic HDABPH for **2**). Each ligand coordinates *via* the pyridyl nitrogen, both hydrazone nitrogen and both carbonyl oxygen atoms resulting in a ten coordinate distorted bicapped square antiprismatic geometry, capped by the pyridyl nitrogen atoms (N3 and N8). Charge balance is provided by the three (**1**) or two (**2**) nitrate ions.

All Dy–ligand bond lengths are comparable between **1** and **2** (Table S2, ESI†). The only exception being the length of the Dy–N(hydrazone) (N2) and Dy–O(carbonyl) (O1) bonds adjacent to the amido nitrogen (N1), which, at 2.506 and 2.318 Å respectively, are the shortest of their kind in either species. The C–O bond lengths are all in good agreement with their assignment as carbonyls (1.242–1.250 Å) rather than alkoxides. The average value of the “skew angles” in the bicapped square anti-prism is approximately 27° for **1** and 29° for **2** (45° for a D<sub>4</sub> symmetry).<sup>23</sup> There is an axial compression (average edge length of 3.106 Å *vs.* interplane separation of 2.331 Å).

In order to probe into the magnetic properties and differences of **1** and **2**, magnetic susceptibility measurements were carried out under direct current (dc) applied field (Fig. S3 and S4†). The room temperature  $\chi T$  values of 14.17 (**1**) and 13.92 (**2**) cm<sup>3</sup> K mol<sup>-1</sup> for the complexes are in good agreement with the expected value of 14.18 cm<sup>3</sup> K mol<sup>-1</sup> for Dy(III) ( $S = 5/2$ ,  $L = 5$ ,  $J = 15/2$ ,  $g = 4/3$ ,  $^6\text{H}_{15/2}$ ). For both **1** and **2**  $\chi T$  gradually decreases with decreasing temperature to 100 K, below which it decreases more rapidly, which is likely due to thermal depopulation of the  $M_J$  sublevels of the  $J = 15/2$  ground state. The collapse in  $\chi T$  begins at higher temperatures for **1**, suggesting a more anisotropic ground state. Magnetization *vs.* field data for **1** and **2** were collected at 2, 4 and 6 K, and reach values of 4.98 and 5.50  $\mu_B$  respectively at 5.5 T and 2 K without saturating. The lack of saturation and the non-superposition of the  $M$  *vs.*  $H/T$  data onto single master curves suggest the presence of considerable magnetic anisotropy (Fig. S5 and S6,



**Fig. 2** Temperature dependence of  $\chi'$  (dotted lines) and  $\chi''$  (solid lines) of **1** (left) and **2** (right) under 1000 Oe applied dc field, in an ac field of 1.55 G oscillating at frequencies from 1 to 1200 Hz.

ESI†). Again, the lower value of magnetization for **1** at 5.5 T and 2 K implies greater anisotropy in the ground state.

Low temperature ac magnetic measurements were performed on **1** and **2**, initially in zero applied field but the signals were very noisy and maxima were not observed. Applying a dc magnetic field during dynamic susceptibility studies suppresses tunneling effects and leads to a slow relaxation at higher temperature.<sup>2</sup> A dc magnetic field of 1000 Oe was applied and both **1** and **2** displayed features associated with SMM behavior (Fig. 2 and S2, ESI†). Both the in phase ( $\chi'$ ) and out of phase ( $\chi''$ ) components of magnetic susceptibility show strong frequency dependence and maxima are observed. The maximum in  $\chi'$  for **1** was observed at temperatures up to 5.1 K (at 1200 Hz) and frequencies down to 1 Hz (at 1.9 K). For **2**, the maximum of the out of phase signal measured up to 2.3 K (at 1200 Hz) indicating faster magnetic relaxation (Fig. 2). For both complexes, at temperatures above 4 K, the relaxation follows a thermally activated mechanism. Therefore, it is possible to plot  $\ln \tau$  *vs.*  $1/T$  and fit to the Arrhenius law ( $\tau = \tau_0 \exp(-\Delta E/k_B T)$ ) giving an effective relaxation barrier of  $\Delta E = 32.4$  and  $<19$  K for **1** and **2**, respectively. These values are in good agreement with other mononuclear Dy(III)-complexes reported in the literature.<sup>24,25</sup> Below this temperature a gradual cross-over to a temperature independent regime is observed, suggesting a quantum tunneling relaxation pathway.

We carried out micro-SQUID studies on an oriented single crystal of **1** and **2**.<sup>26</sup> Using the transverse field method we found an easy axis of magnetization.<sup>27</sup> The applied magnetic field was cycled at different sweep rates (0.002 T s<sup>-1</sup> to 0.280 T s<sup>-1</sup>) between different fields (–0.5 and 0.5 T) and at different temperatures (0.03 and 5.0 K).

Hysteresis loops were observed for both complexes (Fig. 3). For **1** it is possible to see two-step hysteresis loops composed of a broad one at around 0.15 T and another very close to zero (Fig. 3 and S7, ESI†). The presence of the hysteresis loops indicates that below 1.3 K the magnetization is blocked. The occurrence of steps is the result of rapid relaxation of the magnetization where level crossing is avoided and quantum tunneling of the magnetization may occur. As the temperature decreases below 0.5 K, the number of molecules undergoing thermal relaxation decreases, with concomitant increase in

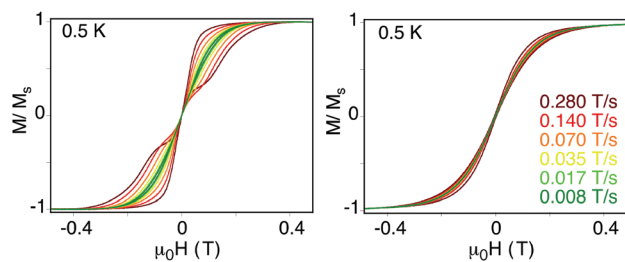


Fig. 3 Hysteresis loops for **1** (left) and **2** (right) taken at 0.5 K and at variable scan rates.

those involved in quantum tunneling. This causes the narrowing of the hysteresis loop and steeper steps. Micro-SQUID studies indicate that **2** also has an easy axis of magnetization (Fig. 3 and S6, ESI†) and undergoes much faster relaxation, in agreement with the ac measurements and the *ab initio* calculations.

The presence in **2** of two bonds shorter than the average bond lengths introduces a larger distortion, compared to **1**, which is responsible of the faster relaxation of the magnetization. The two compounds possess similar crystal structures and the shortest distances between the Dy(III) differs by only 0.8 Å *i.e.* 10.7 and 9.9 Å for **1** and **2**, respectively. Thus, dipolar interactions cannot be responsible for the difference in the relaxation behavior. In addition, we have recently shown that dilution had almost no effect on the magnetic behaviour of complexes with Dy–Dy with similar distances.<sup>19</sup> A possible slight temperature dependence of the structures is expected to have weaker effect than the electronic and the structural changes due to deprotonation. Tuning the magnetic anisotropy by deprotonation is interesting to investigate the effect of a change in the local structure on the relaxation of the magnetization. In order to gain better understanding of the parameters that govern slow relaxation, static magnetic behavior of **1** and **2** was simulated by *ab initio* calculations of the CASSCF/RASSI/SINGLE\_ANISO type carried out with the MOLCAS 7.6 and 7.8 programs.<sup>28,29</sup> Theoretical and experimental magnetic data were in good agreement (see ESI†). The obtained energy gaps for the first eight Kramers doublets and the value of the parallel and perpendicular components of the *g* tensor of the ground Kramers doublet are listed in Table 1. The difference in the SMM behavior of **1** and **2** can be understood in light of these data. The perpendicular components of the *g* tensor ( $g_x$  and  $g_y$ ) are much larger in **2** than in **1** in their ground doublet states. This directly translates to a larger tunneling gap in **2** than in **1**. Therefore, as observed in the magnetic measurements, complex **2** will relax faster than **1**. Furthermore, the orientation of the main magnetic axis ( $g_z$ ) shifts between **1** and **2**. As shown in Fig. 1, in **1** the main magnetic tensor is linked to the idealized four-fold symmetry axis and is oriented along the coordination bond Dy–N(pyridyl). Protonation of the ligand, causes a rotation of the magnetic tensor of 60° towards the Dy–O(carbonyl). This strong effect of deprotonation on the direction of anisotropy axis and on magnetization blocking in **1** and **2** ultimately comes from a high

Table 1 Energies of the Kramers doublets and the main component of the *g* factors of the ground state for complexes **1** and **2**

Doublet/ $\Delta E$ (cm <sup>-1</sup> )	<b>1</b>	<b>2</b>
1	0.000	0.000
2	44.586	44.075
3	83.810	125.206
4	100.261	177.649
5	158.605	217.537
6	185.944	237.683
7	268.356	316.033
8	412.986	423.099
$g_x$	0.1738	0.2480
$g_y$	0.3356	0.6494
$g_z$	17.1879	18.7799

sensitivity of the crystal field on Dy sites. Indeed, as shown in Tables S8 and S14,† the *ab initio* calculated crystal field parameters significantly differ for the two compounds.

In conclusion, tuning the magnetic anisotropy by deprotonation is a way to investigate the effect of a change in the local structure on the relaxation of the magnetization. It is, unfortunately, not of practical use as a stimulus for switching between two states, like for example pressure.<sup>30</sup> The use of an electrical field is very appealing if a change of the coordination sphere of the dysprosium(III) ion can be induced. Complex **2** is a good candidate to do so because of the presence of an electrical dipole due to the negative charge localized on one of the ligands. By a minor pH adjustment, we have also isolated another complex with one di-deprotonated ligand that should possess a larger electrical dipole and be more sensitive to an electrical field. The investigation of the relaxation behavior of the new complex is underway.

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