Terminal solvent effects on the anisotropy barriers of Dy$_2$ systems†

Y. Jiang, G. Brunet, R. J. Holmberg, F. Habib, I. Korobkov and M. Murugesu*

A family of three dinuclear dysprosium complexes have been successfully synthesized and studied in terms of their magnetic properties. Complexes 1 and 2 share the formula [Dy$_2$(ovph)$_2$Cl$_2$(solvent)$_2$], where \(\text{H}_2\text{ovph} = \text{pyridine-2-carboxylic acid} \ [2\text{-hydroxy-3-methoxyphenyl}]\text{methylene} \text{hydrazide}, \) and solvent = DMF (1), i-PrOH (2), while complex 3, [Dy$_2$(ovph)$_2$Cl$_2$(H$_2$O)$_2$(EtOH)], exhibits differences in terms of the identity and number of coordinated solvent molecules. Thus, we investigate the impact of terminally bonded solvent molecules on the slow relaxation dynamics of {Dy$_2$} SMMs, a parameter which can sometimes be overlooked in the quest to attain higher energy barriers. Notably, the exchange of DMF for i-PrOH, both of which coordinate through a single oxygen atom, results in a near 2-fold increase in \(U_{\text{eff}}\) from 58 to 98 K, for 1 and 2, respectively.

Introduction

The emergence of lanthanide Single-Molecule Magnets (SMMs) in the past decade has attracted significant interest in the field of molecular nanomagnets. The enthusiasm behind the specific use of lanthanide ions in the design of novel SMMs is primarily due to their significant inherent magnetic anisotropy, which invariably governs much of the overall slow magnetic relaxation dynamics.\(^3\) Although there are a few reports of complexes containing early lanthanide metal ions exhibiting SMM behaviour,\(^2\) the research field is primarily dominated by late lanthanide ions as they possess large spin-orbit coupling constants, and thus, unparalleled single-ion anisotropies.\(^1\) Currently, the best performing SMMs are isolated with late lanthanide metals such as Tb\(^{III}\), Dy\(^{III}\), and Er\(^{III}\) ions.\(^3\) In the pursuit of providing a better understanding of the origin of slow relaxation, an approach based on minute changes to the structure and/or electronic properties of lanthanide-based SMMs had led to significant advances in the design of higher performance SMMs.\(^5\) Notably, the addition of electron-withdrawing substituents on terminal ligands has been shown to dramatically improve energy barriers, by stabilizing the ground Kramers doublet.\(^6\) Analogously, the enhancement of single-ion anisotropies, through precise control over crystal field symmetry, has also yielded Ln-SMMs with large anisotropy barriers.\(^7\)

The basis of the strategy presented herein, relies on the use of multidentate Schiff base ligands, which are well-known to compartmentalize Ln\(^{III}\) ions through nitrogen and oxygen-based coordination pockets.\(^8\) In addition to their facile synthesis, Schiff bases also offer the advantage of being easily tunable, where the chemical features of the ligand can be tuned without directly affecting the coordination pockets responsible for metal ligation. The capacity of multidentate Schiff base ligands, such as salen\(^2\)− and valden\(^2\)−, to generate high blocking temperatures and high energy barriers to spin reversal, has been highlighted in a number of previous studies.\(^6a,9\) In the present case, the use of the pyridine-2-carboxylic acid \([2\text{-hydroxy-3-methoxyphenyl}]\text{methylene} \text{hydrazide} (\text{H}_2\text{ovph}) \) ligand favours the formation of \{Dy$_2$\} systems,\(^10\) while also permitting the targeted modification of terminally bound secondary ligands. Thus, we can evaluate the impact of terminal solvents on the slow relaxation dynamics of \{Dy$_2$\} complexes. By maintaining a structurally comparable core, and substituting the identity of terminally coordinated solvent molecules, we can directly probe the changes in the magnetic behaviour. The impact of a seemingly trivial variation in solvent molecule is particularly relevant in lanthanide SMMs as the metal ions are highly oxophilic, and commonly coordinate to one or more solvent molecules. Bao, Zheng and co-workers have elegantly demonstrated that the magnetic dynamics of dinuclear complexes can be manipulated by controlling the number of solvent molecules coordinated to the Ln\(^{III}\) ion.\(^11\) Similarly, Sessoli and others have outlined the importance of apical water molecules in the magnetic anisotropy of lanthanide/DOTA complexes.\(^12\) Herein, we seek to...
reinforce the notion that secondary ligands, in the form of terminally-bound solvents, can drastically impact the energy barriers of SMMs. We describe two unique centrosymmetric dinuclear Dy\textsuperscript{III} SMMs, which differ only in terms of terminal solvent molecule, as well as an additional asymmetric \{Dy\textsubscript{2}\} system, which incorporates more solvent molecules into a previously reported high performance SMM.\textsuperscript{10a} All complexes display ferromagnetic interactions and SMM behaviour at zero applied dc field.

Experimental

Materials and methods

All chemicals were of reagent grade, purchased from TCI, Alfa Aesar, or Strem Chemicals, and used without any further purification.

Synthesis of Schiff base pyridine-2-carboxylic acid [(2-hydroxy-3-methoxyphenyl)methylene] hydrazide (H\textsubscript{2}ovph). The ligand H\textsubscript{2}ovph was synthesized in accordance with previously published procedures.\textsuperscript{13} 2-Pyridinecarboxylic acid hydrazide (1.37 g, 10 mmol) and o-vanillin (1.52 g, 10 mmol) were mixed in 20 mL of methanol and stirred for one hour at room temperature. The resulting white powder was collected by suction filtration and washed with cold methanol. Yield = 92%.

Infrared spectrometry. IR spectra were collected on all samples in the solid state on a Varian 640 FT-IR spectrometer in the range of 4000–400 cm\textsuperscript{-1}. Alternating current (ac) susceptibility measurements were conducted under an oscillating ac field of 3 Oe and at frequencies ranging from 0.1 to 1500 Hz. The magnetization data was acquired at 525 K–−300 K for direct current (dc)-applied fields ranging from −7 to 7 T. Magnetic analyses were performed on polycrystalline samples of 9.3, 5.0 and 7.0 mg for 1–3, respectively. All samples were wrapped in a polyethylene membrane.

NMR analyses were conducted on a Bruker Avance 400 MHz spectrometer equipped with an automatic sample holder and a 5 mm auto tuning broadband probe with Z gradient.
Elemental analysis. Elemental analysis was performed at the G. G. Hatch Stable Isotope Laboratory at the University of Ottawa.

Results and discussion

Structural analysis

The analysis of the solid-state structure, determined by single crystal X-ray measurements, revealed that 1 crystallizes in the monoclinic $P2_1/n$ space group (Table S1†). The centrosymmetric dinuclear complex is comprised of two seven-coordinate Dy$^{III}$ ions bridged by alkoxido groups (O3, O3a) of the ovph$^{2-}$ ligands with a Dy1–O3–Dy1a angle of 113.60(9)° and a Dy⋯Dy distance equal to 3.8937(3) Å (Fig. 1). The central core, consisting of Dy$_2$O$_2$Cl, appears to be nearly rhombic with two Dy–O3 distances being 2.316(2) and 2.337(2) Å. Each asymmetric unit also contains one Cl$^{-}$ ion and one DMF solvent molecule coordinated to the Dy$^{III}$ ion leading to an overall $N_2O_4Cl$ coordination environment with a Dy1–Cl1 distance of 2.613(1) Å and a Dy1–O4 distance of 2.288(4) Å (Table S2†). The heptacoordinated Dy$^{III}$ center exhibits a distorted pentagonal bipyramidal coordination environment with a nearly linear O4–Dy1–Cl1 angle equal to 176.2(1)°. The shortest intermolecular Dy⋯Dy distance is 7.5646(3) Å.

Complex 2 has a relatively similar structure to complex 1 (Fig. 1). The main difference arises from a change in the solvent system, where coordinated DMF molecules have been replaced by 2-propanol (i-PrOH) molecules. Thus, complex 2 also crystallizes in the monoclinic $P2_1/n$ space group (Table S1†). The bridging alkoxido groups (O3, O3a) give a Dy1–O3–Dy1a angle of 112.4(1)° with a Dy⋯Dy distance of 3.8538(1) Å, which are both in close proximity to the values observed in complex 1 (Table S2†). The coordination sphere of each Dy center consists of two N atoms (N1, N3) and three O atoms (O1, O3, O3a) that are provided by the ligands, as well as one O atom from the i-PrOH solvent molecule (O4), and one Cl$^{-}$ ion to complete the coordination environment. Therefore, the direct coordination geometry of the Dy metal centers in 1 and 2 are identical. By maintaining a structurally comparable core, we allow precise structure–property relationships to be established, and thus, rationalize the impact of small changes in the electronics of a system on the overall magnetic behavior. It is important to note however, that the O4–Dy1–Cl1 angle in complex 2 is considerably smaller, with a value of 163.5(1)°, when compared to the corresponding angle in complex 1 of 176.2(3)°. Such changes may alter the orientation of the anisotropy axes, and impact the generation of slow magnetic relaxation.

While the packing arrangement of complexes 1 and 2 appear to be similar, the slightly smaller size of the i-PrOH molecules, which participate in hydrogen bonds with chloride anions from an adjacent non-parallel layer, result in a slightly denser packing arrangement, with the closest distance between two parallel layers being 16.94 Å (Fig. S1†). The corresponding value for 1, which contains coordinated DMF molecules, is 17.51 Å (Fig. S1†). Nevertheless, similar intermolecular Dy⋯Dy distances were observed in 1 and 2, with the smallest separation being 7.5646(3) and 7.7415(3) Å, respectively.

The single crystal X-ray crystallography studies reveal that complex 3 crystallizes in monoclinic $P2_1/n$ space group (Table S1†). The main structural features resemble a previously described compound, however significant changes are observed in the coordination environment of the Dy$^{III}$ ion ligated to solvent molecules (eight- vs. nine-coordinate). Such significant changes in the coordination environment are expected to alter the magnetic behavior of the described complex. More precisely, complex 3 consists of two ovph$^{2-}$ ligands that follow the same antiparallel architecture as complexes 1 and 2, however there is the notable loss of centrosymmetry (Fig. 2). The alkoxido oxygen atoms, O3 and O6, are bridging the two Dy$^{III}$ metal centres with an average Dy–O–Dy angle of 113.5° (Table S3†). The doubly deprotonated ligand format can be confirmed by the change in the bond distances of C9–O3 (C23–O6) and C9–N2 (C23–N5). The seven-coordinate Dy1 centre exhibits a slightly distorted pentagonal bipyramidal geometry, with two chloride ions occupying the axial positions. The Cl1–Dy1–Cl2 angle of 169.3(1)° is intermediate to complexes 1 and 2. The nine-coordinate Dy2 centre is most closely related to a distorted spherical capped square antiprism ($C_{4v}$), as determined using the SHAPE software, however it is important to note that the muffin ($C_{4}$) and spherical tricapped...
trigonal prism ($D_{3h}$) geometries are also similar in value (Table S4†). Close analysis of the crystal structure reveals that Dy2 coordinates to four oxygen atoms belonging to solvent molecules, namely one EtOH and three H2O molecules, as well as two nitrogen and three oxygen atoms belonging to the oph2−ligand. The previously reported complex, which closely resembles 3, only contains three coordinated solvent molecules (MeOH), instead of four, and thus adopts a significantly different coordination geometry (eight- vs. nine-coordinate). Moreover, in the case of 3, there are intramolecular hydrogen bonds between C1–O9 and Cl2–O10, with bond distances equal to 3.12 and 3.17 Å, respectively, while the latter interaction may influence the position of the EtOH molecule. Furthermore, a number of intermolecular hydrogen bonds result in a tight packing arrangement with the closest intermolecular Dy⋯Dy distance being 6.256(1) Å. The close contacts between O1⋯O7 and O2⋯O9 were found to significantly bend the oph2−ligand.

**Magnetic properties**

The direct current (dc) magnetic properties of complexes 1–3 were investigated using an applied field of 1000 Oe in the 1.8–300 K temperature range (Fig. 3). In all complexes, the $\chi T$ product remains relatively constant with decreasing temperatures. The room temperature $\chi T$ values for complexes 1–3 are 26.60, 25.60 and 26.20 cm$^3$ K mol$^{-1}$, respectively, which are lower but within reach of the theoretical value for two non-interacting Dy$^{III}$ ions ($^{5}H_{15/2}$, $S = 5/2$, $\chi T = 28.34$ cm$^3$ K mol$^{-1}$) below 50 K, we observe a rapid increase of the $\chi T$ product, reaching a maximum value of 42.37 cm$^3$ K mol$^{-1}$ at 1.8 K for complex 1. Similarly, complexes 2 and 3 reach values of 40.54 and 26.79 cm$^3$ K mol$^{-1}$ at 1.8 K, respectively, testifying to the presence of intramolecular ferromagnetic interactions, as observed in other [Dy2]3+ systems.†

The field dependence of the magnetization below 7 K was plotted for complexes 1–3; non-saturation of the magnetization indicates the presence of significant magnetic anisotropy and/or low-lying excited states in all systems (Fig. S2–S4†). This can be further confirmed by the lack of superposition and high field variation on a single master curve of each $M$ vs. $H/T$ plots. The values of the magnetization at 1.8 K and 7 T are 9.80, 9.29 and 8.49 µB for complexes 1–3 respectively. Within the more comparable systems in 1 and 2, a highly similar behaviour was observed, which indicates the presence of weak intramolecular magnetic interactions in both samples.

In order to investigate the potential slow magnetization relaxation, alternating current (ac) measurements were performed. It was found that all three complexes exhibited temperature and frequency dependent ac susceptibility signals under zero applied dc fields (Fig. 4), indicative of SMM behaviour. The in-phase ($\chi’$) and out-of-phase ($\chi”$) susceptibilities were measured in the temperature range of 1.8–17 K and 1.8–20 K for complexes 1 and 2, respectively. The shifting of the peaks to lower frequencies with decreasing temperatures is indicative of slow relaxation of the magnetization.

The anisotropy barrier can be obtained from the high temperature regions of the relaxation where it is thermally activated.
Fitting with the Arrhenius equation ($\tau = \tau_0 \exp(U_{eff}/kT)$) yields $U_{eff} = 58$ K ($\tau_0 = 3.51 \times 10^{-6}$ s) for 1, and $U_{eff} = 98$ K ($\tau_0 = 6.69 \times 10^{-7}$ s) for 2 (Fig. 5). It is worth mentioning that $\ln(\tau)$ becomes nearly temperature independent at lower temperatures for both complexes, where a quantum tunneling relaxation pathway becomes dominant. The Cole–Cole plots (Fig. S5 and S6†) show a relatively symmetrical shape and have been fitted using a generalized Debye model, with $\alpha$ parameters below 0.1 for complexes 1 and 2 above 5 K. This low degree of deviation from the pure Debye model confirms that a single relaxation mechanism is mainly involved in the relaxation process. For 2, an increase in the $\alpha$ parameter, up to 0.22 (1.8 K), is observed below 4 K, which may be due to potential Dy–Dy interactions at very low temperatures.

Ac susceptibility measurements were performed in the temperature range of 1.8–20 K under zero applied dc fields for complex 3. The out-of-phase ($\chi''$) component of the ac susceptibility (Fig. 6) clearly exhibits temperature- and frequency-dependent behaviour, which indicates the presence of slow magnetization relaxation. In the high-temperature regime, the relaxation process follows an Arrhenius law with an effective energy barrier $U_{eff} = 110$ K ($\tau_0 = 1.36 \times 10^{-7}$ s) [Fig. 7]. An evaluation of the distribution of the relaxation times from analysis of the Cole–Cole plot for complex 3 yielded a relatively large $\alpha$ parameter (ca. 0.20; Fig. 7), which suggests a potential multi-pathway relaxation mechanism. This could be related to the structure of the compound, which comprises two different DyIII centres. When the system enters the quantum regime (below 5 K), an increase in the $\alpha$ parameter, up to 0.31 (1.8 K), is observed. When comparing the energy barrier of 3 to that of the previously reported compound,10x we discover that the change in coordination environment of the Dy3 ion results in a lower $U_{eff}$, from 198 and 150 K, for each relaxation phase, to 110 K. We propose that this change in the local environment of the Dy3 ion, diminishes the axiality of the DyIII ions and thus affects the efficient blockage of magnetization in the lowest exchange states.

**Magneto-structural correlations**

In centrosymmetric complexes 1 and 2, both Dy centres display distorted pentagonal bipyramidal geometry (Fig. 8). It is well-documented that the effective energy barrier is influenced by
several different parameters, including metal centre geometry, magnetic coupling and orientation of the magnetic anisotropic axes. The successful isolation of two isostructural complexes provides a unique opportunity to study the impact of small structural changes on the magnetic properties. In deriving magnetostructural correlations, it is essential to provide a quantifiable structural comparison of the coordination spheres between the two complexes. To that end, the shape-measure approach was utilized, which is calculated by comparing the dihedral angles along the edges of the polyhedron of Dy1 (Fig. 8) and compared to a reference compound using the following equation:

$$SM = \min \left[ \sqrt{\frac{1}{m} \sum_{i=1}^{m} (\delta_i - \theta_i)^2} \right]$$  \hspace{1cm} (1)

where $SM$ = shape measure, $\delta_i$ = observed dihedral angle along $m$ edges of the coordination polyhedron (angle between the normals of adjacent faces) and $\theta_i$ = corresponding dihedral angle for the reference polyhedron. Complex 2 was selected as the reference compound yielding a deviation of 4.55° between 1 and 2 (Table 1). The principal structural difference between 1 and 2 corresponds to the exchange of DMF molecules (1) with $i$-PrOH molecules (2), both of which are bound in a monodentate fashion (Fig. 9). This change causes a significant variation in the O4–Dy1–Cl1 angles, as mentioned previously. It is presumed that this is the main reason for the large difference in energy barriers between 1 and 2, since the structural parameters of the rest of the polyhedron remain highly comparable.

We have shown in previous work that the addition of electronegative atoms on terminal ligands can significantly increase the energy barriers of {Dy$_2$}-based systems. In the present case, a simple change in terminal solvent from DMF to $i$-PrOH resulted in a near 2-fold increase of the energy barrier. By examination of the backbone of each solvent molecule, we discover that DMF contains a more electron-withdrawing moiety, while $i$-PrOH, which contains an alkyl group, is expected to be more electron-donating (Fig. 10). On that basis alone, and relying on our previous work, we would expect the DMF containing compound (1) to exhibit the higher energy barrier. However, we observe that the opposite is true, and that the more electron-donating solvent results in a larger $U_{\text{eff}}$. This behaviour can be rationalized by the fact that DMF contains an additional carbon, which drastically diminishes the electron-withdrawing effects. Furthermore, the slight change in the O4–Dy1–Cl1 angle likely alters the orientation of the anisotropy axes, thus also affecting the slow relaxation properties. In order to further confirm this hypothesis, a series of Ln$^{III}$ systems are currently underway.

---

**Table 1** Dihedral angles along the edges of the coordination polyhedra (°) of dysprosium complexes 1 and 2

<table>
<thead>
<tr>
<th>Edge</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1–N1</td>
<td>75.617</td>
<td>80.029</td>
</tr>
<tr>
<td>O1–N3</td>
<td>70.081</td>
<td>77.818</td>
</tr>
<tr>
<td>O1–O4</td>
<td>54.279</td>
<td>51.376</td>
</tr>
<tr>
<td>O1–Cl1</td>
<td>58.919</td>
<td>54.832</td>
</tr>
<tr>
<td>O3a–O3</td>
<td>75.281</td>
<td>64.567</td>
</tr>
<tr>
<td>O3a–O4</td>
<td>43.285</td>
<td>48.766</td>
</tr>
<tr>
<td>O3a–Cl1</td>
<td>52.577</td>
<td>54.823</td>
</tr>
<tr>
<td>O3a–N1</td>
<td>79.35</td>
<td>72.837</td>
</tr>
<tr>
<td>N1–O4</td>
<td>57.684</td>
<td>57.993</td>
</tr>
<tr>
<td>N1–Cl1</td>
<td>59.276</td>
<td>60.373</td>
</tr>
<tr>
<td>N3–O3</td>
<td>78.065</td>
<td>74.86</td>
</tr>
<tr>
<td>N3–Cl1</td>
<td>69.149</td>
<td>68.093</td>
</tr>
<tr>
<td>N3–O4</td>
<td>61.174</td>
<td>60.298</td>
</tr>
<tr>
<td>O3–Cl1</td>
<td>49.378</td>
<td>50.272</td>
</tr>
<tr>
<td>SM</td>
<td>4.553</td>
<td>0</td>
</tr>
</tbody>
</table>

---

**Fig. 8** Structure of 1 highlighting the distorted pentagonal bipyramidal coordination polyhedron of Dy1 in orange used in the Shape-Measure Approach calculations. The structures of 1 and 2 follow the same labelling scheme.

**Fig. 9** Overlay of the molecular structures of 1 (orange) and 2 (blue), displaying the minimal structural changes induced by replacing DMF with $i$-PrOH.

**Fig. 10** Comparison of the electron-donating and -withdrawing effects of the terminally-bound solvent molecules in 1 and 2.
Conclusions

In conclusion, a detailed magnetic study of three \{Dy\}_2 structures was performed. The synthesis of the described complexes was carried out in order to elucidate the effects of terminal solvent molecules on the SMM behaviour of dinuclear lanthanide complexes. This was achieved by maintaining the overall structure of the Dy\_2 complexes, while exchanging the identity of the solvent molecule. Thus, we reveal that solvent molecules can indeed have a significant impact on the slow relaxation properties, and, while seemingly trivial, should not be overlooked in the optimization of SMMs. The replacement of DMF by i-ProH resulted in a near 2-fold increase in \(U_{\text{eff}}\), while the incorporation of additional solvent molecules, in a different Dy\_2 system, resulted in a slightly lower energy barrier. Our results exemplify a relatively simple, yet effective method of tuning the energy barriers, and hence provide an alternative strategy to attaining increasingly higher energy barriers.

Acknowledgements

We wish to thank the University of Ottawa, NSERC and CFI for their financial support.

Notes and references


