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Unprecedented magnetic relaxation *via* the fourth excited state in low-coordinate lanthanide single-ion magnets: a theoretical perspective†

Saurabh Kumar Singh, Tulika Gupta, Maheswaran Shanmugam* and Gopalan Rajaraman*

Four low-coordinate SIMs have been studied to probe their relaxation dynamics using *ab initio* calculations. Our calculations reveal that both the symmetry and the equatorial ligand field play a key role in controlling the barrier heights in three-coordinate [Ln^{III}(NSiMe₃)₃] complexes (Ln = Dy/Er). This study reveals an unprecedented blockade of magnetization up to three excited states for the Er(III) complex.

Mononuclear single-ion magnets (SIMs) have received significant interest in the field of molecular magnetism, as many of them show a high blocking temperature for magnetization reversal^{1–3} and have potential applications in high-density storage devices, spintronics and quantum computing.^{4–7} The majority of the SIMs reported to date are lanthanide based compounds, however, SIMs based on d-block and 5f-elements are also known.^{8–13} 4f-element based SIMs hold the record for the highest blocking temperature for magnetization reversal (U_{eff}) and thus are the popular choice for experimental chemists.^{9,14–16} In several instances the relaxation of magnetization in polynuclear lanthanide clusters is found to be single-ion in origin. An illustrative example is the discovery of the {Dy₅} cluster which has a barrier height of more than 800 K, while the origin of the magnetic relaxation is found to be

single-ion in nature.¹⁷ This revitalizes the field of lanthanide based SIMs, as the barrier height can be controlled by the ligand field interaction.^{16,18}

Despite several lanthanide complexes possessing a very large barrier height, only a few molecules exhibit hysteretic behaviour at low temperatures due to rapid magnetization relaxation. This underlines the need to understand the mechanism of magnetic relaxation in these complexes to gain ground for future research directions. Large barrier heights in lanthanide based SIMs are attainable either by fine-tuning the ligand field around the lanthanide ions or by inducing stronger metal–ligand interactions.^{21,22} An illustrative example for stronger metal–ligand interaction is the {Dy₄K₂} cluster, where the coincidence of magnetic anisotropy leads to suppression of the relaxation of magnetization reversal *via* the first excited KD, yielding large U_{eff} values.¹⁷ The presence of a large rotational symmetry axis in the [Er(COT)₂][–] complex³ leads to the second-highest blocking temperature for magnetization reversal of 10 K. Although high symmetry is desirable, lanthanide complexes often possess large coordination numbers (C.N.) and therefore maintaining the site symmetry is a challenging task. In this regard, low-coordinate lanthanide complexes are attractive, as the symmetry around the lanthanide ions are to a certain extent controllable and hence can yield larger U_{eff} values.

Recently, Tang and co-workers reported low-coordinate Er(III) and Dy(III) complexes to probe the role of the ligand field in the design of SMMs.²³ The first set comprises tri-coordinate [Ln^{III}(N(SiMe₃)₂)₃] (where Ln = Er (**1a**), Dy (**1b**)) complexes where Ln(III) is located slightly above the trigonal plane of the donor atoms (out-of-plane-shift τ is 0.53 Å). These complexes possess a C_{3v} local symmetry around the Ln(III) ion. The second set comprises [Ln^{III}(NHPhPr₂)₃(THF)₂] (where Ln = Er (**2a**), Dy (**2b**)) complexes possessing trigonal bipyramidal geometry with two tetrahydrofuran ligands coordinated in the axial positions.²⁴ Complex **1a** is the first example where zero-field SMM behaviour ($U_{\text{eff}} = 85 \text{ cm}^{-1}$) was noted for an equatorially coordinated Er(III) complex. On the other hand, complex **1b** lacks SMM behaviour. In the other set, complex **2b** is a zero-field SMM with an U_{eff} of 23 cm^{-1} ,

Department of Chemistry, Indian Institute of Technology Bombay, Mumbai, 400076, India. E-mail: rajaraman@chem.iitb.ac.in, eswar@chem.iitb.ac.in; Fax: +91-022-2576-7156; Tel: +91-022-2576-7183

† Electronic supplementary information (ESI) available: CASSCF + RASSI computed spin free states, spin orbit states, energies of the low-lying Kramer's doublet, magnetic susceptibility along with *g*-tensor orientations for all four complexes, DFT computed spin densities and details of developed magneto-structural correlations. The mechanism of magnetic relaxation has been probed *via* both experiment and theory, and the following dominant processes are noticed in these complexes: (i) the Raman/Orbach¹⁹ process; (ii) thermally assisted QTM between the excited state Kramer's doublets (KDs); and (iii) ground state QTM due to lack of axiality in the ground state KD.^{17,20} The presence of a non-collinear structure of the magnetic moment in low symmetry complexes activates multiple processes of magnetic relaxation. The competing nature of all these processes of magnetic relaxation drastically reduces the effective energy barrier and apparently liquidates the Single Molecule Magnet (SMM) behaviour. See DOI: 10.1039/c4cc05522e

while complex **2a** lacks zero-field SMM behaviour. A butterfly-shaped magnetic hysteresis loop has been reported for both **1a** and **2b**, confirming the SMM behaviour. Although these four complexes illustrate the importance of coordination geometry around the lanthanide ions, the reasons behind the presence/absence of SMM behaviour and the mechanisms of magnetic relaxation have not been clearly resolved. Here, we aim to achieve this by probing the magnetic anisotropy and the magnetic relaxation pathways associated with these complexes using *ab initio* CASSCF + RASSI/SINGLE_ANISO calculations on the X-ray structures^{24–28} using MOLCAS 7.8 code (see ESI† for computational details).

The atomic ground states for Er(III) and Dy(III) are $^4I_{15/2}$ and $^6H_{15/2}$, respectively, each possessing eight ground state KDs for which the *g*-tensors are estimated (see ESI†, Tables S5–S8). The computed orientations of the *g*-tensors for the ground state KDs in all four complexes are shown in Fig. 1 (see ESI†, Fig. S1 for the orientation of the *g*-tensors of other excited KDs). The computed energy spectrum of eight KDs spanned up to 539 cm⁻¹ and 1337 cm⁻¹ for complexes **1a** and **1b**, respectively. The computed *g*-tensor for complex **1a** is found to be purely axial in nature ($g_{xx} = 0.0000$, $g_{yy} = 0.0005$ and $g_{zz} = 17.8770$) and stabilizes $m_j = \pm 15/2$ as the ground state (Table 1). On the other hand, in the case of complex **1b** the opposite trend has been noted, with stabilization of $m_j = \pm 1/2$ as the ground state. This state naturally possesses high transverse *g*-components ($g_{xx} = 10.9845$, $g_{yy} = 10.3215$ and $g_{zz} = 1.3844$). The stabilization of

$m_j = 1/2$ as the ground state has also been noted previously in the [Dy(COT)₂]⁻ sandwich complex.²⁹ The principal magnetization axis of the ground state KD is oriented along the C₃ axis for both complexes **1a** and **1b**. This is in agreement with the expected orientation based on the electrostatic potential.^{18,30} The presence of C₃ symmetry around the metal ion leads to collinearity of the principal magnetization axes up to the third excited KDs (*ca.* <2 degree deviation; see ESI†, Tables S5 and S6), and this sets the theoretical barrier height to 331 cm⁻¹ for **1a** (*vide infra*).

In the case of complexes **2a** and **2b**, the computed energy spectrum of eight KDs spanned up to 372 cm⁻¹ and 790 cm⁻¹, respectively. The computed *g*-tensors for both these complexes followed the general pattern observed for low-symmetry complexes (see ESI†, Tables S7 and S8).^{31,32} The computed *g*-tensor for the ground state KD of complex **2a** shows axiality ($g_{xx} = 0.0383$, $g_{yy} = 0.6381$ and $g_{zz} = 16.1980$) but lacks pure Ising nature. The first excited KD possesses high transverse anisotropy ($g_{xx} = 3.56$, $g_{yy} = 5.49$ and $g_{zz} = 9.97$) and lies 76 cm⁻¹ from the ground state. The corresponding principal magnetization axis is tilted by 55.39 degrees from the ground state KD for complex **2a**. On the other hand, the computed *g*-tensor for the ground state KD of complex **2b** reflects a higher degree of axiality ($g_{xx} = 0.0074$, $g_{yy} = 0.0128$ and $g_{zz} = 19.6742$) compared to complex **2a**. The first excited state is 199 cm⁻¹ higher in energy than the ground state KD, with an 18.67 degrees tilt with respect to the ground state KD. The presence of two oxygen donor ligands in the axial positions provides the desired ligand field for the oblate Dy(III) ion and thus leads to a larger barrier height compared to its Er(III) analogue. The computed magnetic susceptibility data are in good agreement with the experiments for all four complexes (see Fig. S3 in ESI†).

To gain insight into the mechanism of magnetic relaxation, here we have computed the mean absolute values of the transversal magnetic moments between the connecting pairs of opposite magnetization for all four complexes (see Fig. 2).³³ The best SIM among the four studied complexes is **1a** with an U_{eff} of 85 cm⁻¹. For complex **1a**, the transversal magnetic moments between the ground state KDs are negligible (*ca.* 10⁻⁴ μ_B), which suggests that QTM is quenched in the ground state. Due to the presence of symmetry, the major relaxation is found to proceed *via* the 4th excited KD, *i.e.* following the [-1 → -2 → -3 → -4 → -5] → [+5 → +4 → +3 → +2 → +1] path (see Fig. 2a). However, the transversal magnetic moments between the excited KDs are moderate in **1a** (*ca.* 10⁻¹ μ_B), suggesting that partial TA-QTM is operative through all the four excited KDs. Besides, the off-diagonal terms of the transversal magnetic moments (*ca.* 10⁻¹ μ_B) between the ground state and excited state of opposite magnetization related to the Orbach process are also moderate and open up further relaxation paths in **1a**. Although the theoretical estimate of the barrier is 331 cm⁻¹, these multiple relaxation paths (TA-QTM and the Orbach process), which are weakly operational, reduce the U_{eff} value. However, our calculations predict a perceivable magnetization blockade up to three excited states and relaxation *via* the fourth excited KDs. This phenomenon is unprecedented among lanthanide based magnets. This suggests that

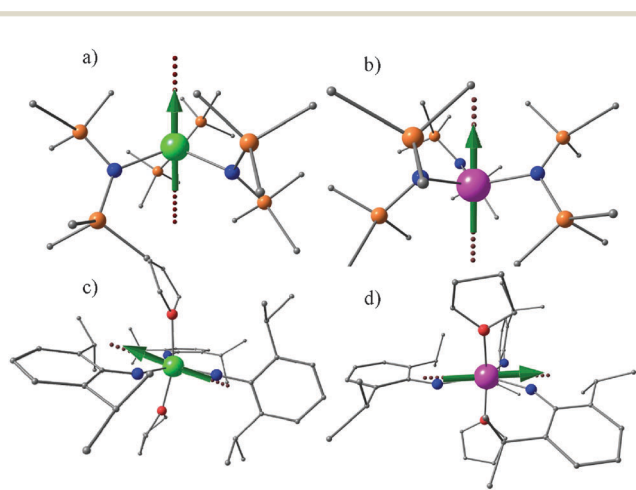


Fig. 1 *Ab initio* computed orientation of the principal magnetization axis of the ground state KDs for complexes (a) **1a**, (b) **1b**, (c) **2a** and (d) **2b** plotted on top of the X-ray structure. Color code: green (Er), pink (Dy), blue (N), red (O), orange (Si) and grey (C). The hydrogens are omitted for clarity.

Table 1 *Ab initio* computed principal values of the ground state *g*-tensors for all four complexes

Complexes	1a	1b	2a	2b
g_{xx}	0.0000	10.9845	0.0383	0.0075
g_{yy}	0.0005	10.3215	0.6381	0.0128
g_{zz}	17.8770	1.3844	16.1980	19.6742

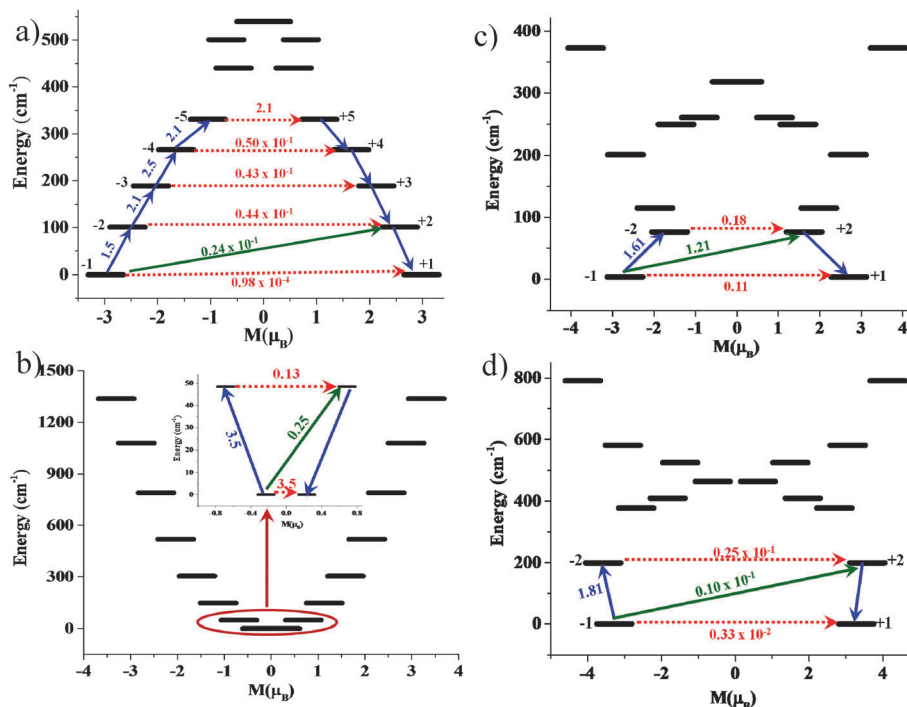


Fig. 2 The *ab initio* computed magnetization blocking barrier for all four complexes: (a) **1a**, (b) **1b**, (c) **2a** and (d) **2b**. The thick black line indicates the Kramer's doublets (KDs) as a function of magnetic moment. The green lines show the possible pathway of the Orbach process. The blue lines show the most probable relaxation pathways for magnetization reversal. The dotted red lines represent the presence of QTM/TA-QTM between the connecting pairs. The numbers provided on each arrow are the mean absolute values for the corresponding matrix elements of the transition magnetic moment.

complex **1a** possesses a large U_{eff} value, and dilution experiments with diamagnetic analogues could raise the barrier beyond the observed experimental U_{eff} values (note that beyond the single-ion relaxation mechanism discussed, intermolecular interactions also lead to a significant relaxation; this is expected to be significant especially when the intermolecular Er(III) ··· Er(III) distances are as short as 7.34 Å as found in complex **1a**). Due to these effects, one-to-one comparison of U_{eff} values between theory and experiment is not straightforward.

For complex **1b**, on the other hand, the $m_j = \pm 1/2$ is stabilized as the ground state, followed by other higher m_j excited states, resulting in a barrierless potential well. This difference in behaviour between **1a** and **1b** is visible in the DFT-computed spin density plots (see ESI,† Fig. S2). The computed transversal magnetic moments shown in Fig. 2b (subset) clearly suggest that ground state QTM is the major relaxation pathway for this complex, and this wipes out the SMM behaviour.

In the case of complexes **2a** and **2b**, the relaxation of magnetization occurs through the first excited state *via* Orbach/TA-QTM processes due to the non-collinear magnetic moments. The computed transversal magnetic moments between the ground state KDs clearly suggest the presence of significant QTM (0.11 μ_B) in the case of complex **2a**, while QTM is weak (*ca.* 10⁻² μ_B) in the case of complex **2b**. For these reasons, **2b** is a zero-field SMM, while **2a** is a field-induced SMM. Quite interestingly, the axial coordination of THF ligands dramatically changes the energies of

the KDs and thus the magnetic properties (see Fig. 2c and d). The presence of axial ligands stabilizes $m_j = \pm 15/2$ as the ground state for both species, however, the collinearity of the magnetization axes is lost, resulting in relaxation *via* the first excited KDs in both cases. Besides, the wavefunction of the ground state KD of **2b** is almost pure $m_j = \pm 15/2$ state with negligible contributions from other m_j projections, while the wavefunction of **2a** has significant contributions from other m_j projections, leading to a smaller gap between the ground state and first excited state KD for **2a** compared to **2b**.

This demonstrates that the ligand field around the metal ions needs to be carefully tailored towards SMM behaviour, with the observation that an equatorial ligand field favours Er(III) ions while an axial ligand field favours Dy(III) ions. The change is particularly dramatic for the Dy(III) ion, where the ground state and the magnetic properties switch completely as we move from **1b** to **2b**. However, such changes are marginal as we move from **1a** to **2a**, and the difference in magnetic properties observed is essentially due to lower mixing of the m_j levels brought about by the axial ligands.

To gain further insight, we also computed the crystal field parameters for all four complexes, which provides a better picture of the QTM process.^{27,28} The computed axial B_0^2 terms are quite high for **1a** and **1b** compared to their non-axial terms (see ESI,† Table S9). In the case of complexes **1a** and **1b**, the

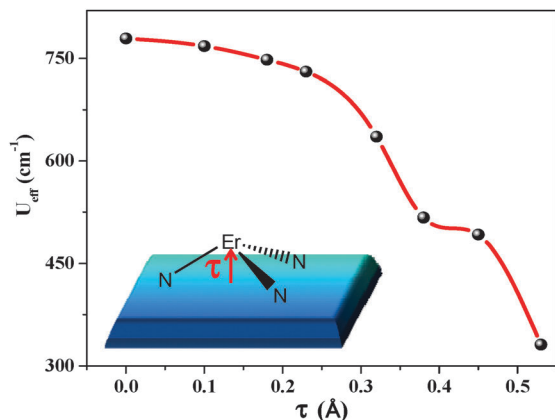


Fig. 3 Magneto-structural correlation performed to observe the effect of the out-of-plane-shift (τ parameter) on the computed U_{eff} value.

B_0^{-2} and B_0^{-4} parameters are found to have opposite signs, which supports the observed change in the energy level pattern.²¹ On the other hand, the same sign is observed for the axial terms for both **2a** and **2b**, leading to a similar energy pattern. A large QTM in the case of **2a** is expected due to the large non-axial B_2^{-2} term, while axial terms are dominant in complex **2b**.

To seek larger U_{eff} values for complex **1b**, we have developed a magneto-structural correlation for the out-of-plane-shift parameter (τ parameter), where the Er(III) ion is moved into the plane of the ligands gradually (see Fig. 3, ESI,† Fig. S4 and Table S10). Significant increases in the U_{eff} values are observed with a maximum U_{eff} value being achieved for the planar structure (*i.e.*, when $\tau = 0$ Å).

Besides, for the planar structure, all the principal magnetization axes of all the KDs are collinear, leading to relaxation *via* the 7th excited state. This leads to a very large barrier height (> 750 cm⁻¹) for the planar structure. This highlights the importance of coordination number and the symmetry in enhancing the barrier heights in lanthanide based SMMs.

To this end, using *ab initio* calculations, we have probed the mechanism of magnetic relaxation in four low-coordinate lanthanide complexes, and our study reveals an unprecedented magnetization blockade for a three-coordinate Er(III) complex up to the third excited state. The developed magneto-structural correlation reveals that even minuscule changes can drastically increase the U_{eff} values – a strategy that can be adapted by experimentalists to fine-tune the barrier height. Combined experimental and theoretical work is currently in progress in our laboratory.

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