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Design Criteria for High-Temperature Single-Molecule Magnets

Nicholas F. Chilton*

School of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom

Supporting Information

ABSTRACT: Design criteria to obtain slow magnetic relaxation are theoretically investigated for two-coordinate complexes of Dy^{III}. It is shown that large energy barriers to magnetic relaxation, U_{eff}, can be achieved in the absence of near-linearity and generally that any two-coordinate complex of Dy^{III} is an attractive synthetic target that may possess $U_{eff} > 1000$ cm^{-1}. These large U_{eff} values are immediately diminished if axial ligation is disrupted by solvent coordination.

From spin valves[1] and transistors[2,3] to qubits[4,5] and data storage bits,[6] the proposed applications for single-molecule magnets (SMMs) are as diverse as they are ground-breaking. Much of the most interesting SMM physics reported recently involves highly air-sensitive lanthanide complexes,[7−11] including the N_2^{3-}-bridged Dy^{III} and Tb^{III} dimers by Rinehart et al.,[12,13] the lanthanide(III) alkoxides by Blagg et al.,[14] and the symmetrical $[Er(COT)_2]^-$ species of Meihaus and Long.[15] In contrast to the original 3d SMMs,[6,16] 4f SMMs take advantage of the strongly spin−orbit coupled orbital angular momentum and its interaction with the ligand field to yield massive magnetic anisotropy. When the ligand field provides a uniaxial potential and stabilizes the largest angular momentum projections of the ground spin−orbit multiplet, there is an effective energy barrier to magnetic reorientation, U_{eff}, resulting in magnetic bistability and SMM behavior. The U_{eff} barrier is therefore directly related to the ligand-field splitting, where magnetic relaxation is usually assumed to occur by an Orbach process via the excited ligand-field states,[6,17] although when the U_{eff} barrier is small, other relaxation processes become competitive[18] because of a higher degree of mixing between the magnetic states. If uniaxiality cannot be maintained or the presence of perturbations such as transverse magnetic fields is nonnegligable, mixing of opposing angular momentum projections can occur and quantum tunneling of magnetization (QTM) results in poor SMM properties. Therefore, fine control over both the symmetry and nature of the ligand field is crucial in order to mitigate such perturbations and obtain improved SMMs. Rinehart and Long[19] proposed using the intrinsic anisotropic electron density distributions of the lanthanide ions[20] in an extremely tangible electrostatic[21] manner to design complexes that stabilize these large angular momentum states. The application of this strategy suggests that an axial ligand field is required for ions whose largest angular momentum states have oblate spheroid distributions, such as Tb^{III} and Dy^{III}, while an equatorial field is required for those ions with prolate spheroid states, such as Er^{III} and Yb^{III}.

The blossoming of lanthanide SMMs[22] was spurred by Ishikawa et al., who, with $[Tb(Pc)_2]^-$ (where Pc is phthalocyaninate),[23] presented the first SMM using just a single lanthanide ion. The “sandwich” geometry stabilizes the $m_J = \pm 6$ states of the $^7F_6$ ground-state spin−orbit multiplet of Tb^{III}, and the pseudo-D_{4d} symmetry results in small off-axial ligand-field terms, therefore disfavoring QTM.[24,25] However, $[Dy(Pc)_2]^-$ is a poor SMM despite the uniaxial ligand field because it has an $m_J = \pm {}^{13}/_2$ ground state and not the maximal $m_J = \pm {}^{15}/_2$ of the $^6H_{15/2}$ multiplet. This seemingly contradictory situation is due to the complex relationship between the proximity of the Pc ligands and the effective ligand-field potential, which determines the ordering of the magnetic states. It was also recently shown that “sandwich” complexes employing the cyclooctatetrene anion actually generate equatorial ligand fields that stabilize the prolate electron density of Er^{III}, rendering the Dy^{III} analogues poor SMMs.[15,26−30] Notwithstanding the progress made with such “sandwich” complexes, there is a much simpler geometry that can provide an axial ligand-field potential: a linear two-coordinate complex. In this case, predictable ordering of the m_J states results as a simple function of the 4f electron density along the coordination axis.

The recent report of a near-linear (N−Ln−N angle θ = 175.5°), pseudo-two-coordinate Sm^{II} complex presents exactly this geometry, and the proposed Dy^{III} analogue ($[Dy\{N(Si^iPr_3)_2\}_2]^+$, hereafter **1Dy**) was predicted to show a barrier to magnetization reversal of $U_{eff} \approx 1800$ cm^{-1} and is so large that **1Dy** should display magnetic hysteresis above the temperature of liquid N_2.[31] Indeed, such a strong axial potential reduces the propensity for ground-state QTM as the transverse anisotropies become negligible. The synthesis of a two-coordinate Dy^{III} complex is challenging enough, let alone the requirement for near-linearity, and therefore it seems worthwhile to examine how rigorous the requirement for an E−Dy−E bond angle near 180° really is. Herein the electronic and magnetic characteristics of some model two-coordinate Dy^{III} complexes of the general formula $[Dy\{ER_x\}_2]$ are investigated by ab initio calculations, primarily as a function of the bending angle, θ, to yield a set of structural design guidelines and to assist in the identification of target complexes.

In order to make comparisons to the previously proposed Dy^{III} complex **1Dy** in a computationally tractable manner, a simplified version of the $^-N(Si^iPr_3)_2$ ligand in the form of $L_1 = {}^-N(SiH_3)_2$ was employed. The simplification of the ligand allows the effect of structural deformations to be examined, and the exact alkyl substituents do not qualitatively change the results. The bending angle θ was varied along with the torsion angle ϕ in the ranges

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$90° \leq \theta \leq 180°$ and $0° \leq \phi \leq 90°$ for a fixed Dy−N bond length of r = 2.5 Å (Figure 1a, inset). The average magnetic relaxation barrier for each value of θ, averaged over all torsion angles, was calculated with the complete active space self-consistent-field (CASSCF) ab initio method according to the procedure given in the Supporting Information (SI). Figure 1a shows that there does not seem to be a threshold value of θ where U_{eff} decreases suddenly and that a strong axial field can be maintained in the absence of linearity, along with a constant main magnetic axis (x axis in Figure 1a, inset). Furthermore, despite the low symmetry in these bent complexes, the strong axial field seems to prevent the mixing of m_J states with opposing projections until the highest energy states, thus not favoring QTM (Figure 1b). This surprising result indicates that it is not a requirement for an E−Dy−E angle to approach θ = 180° in order to obtain a large U_{eff} barrier, but rather just a two-coordinate Dy^{III} complex is needed.

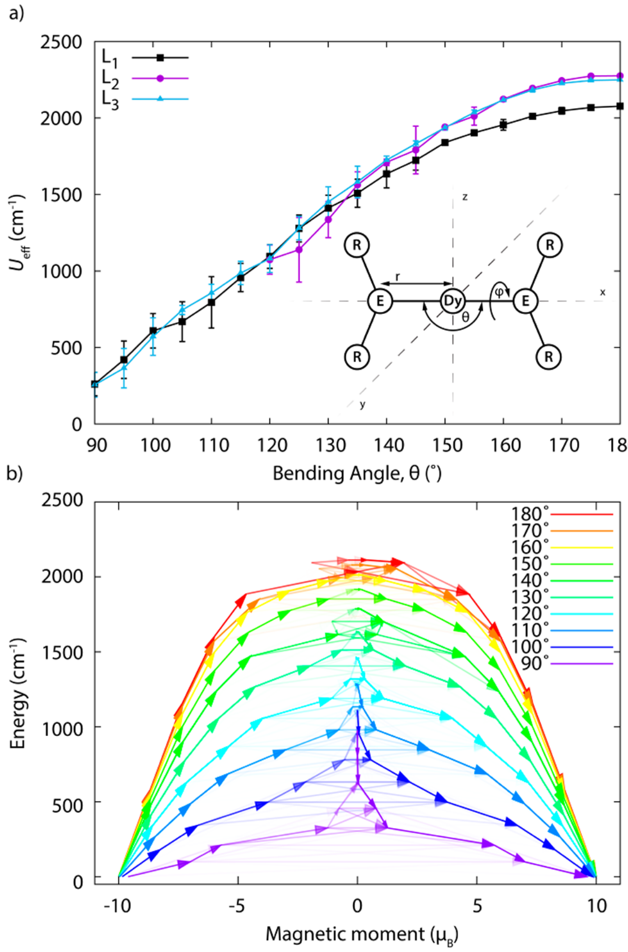

Figure 1. (a) Relaxation barrier U_{eff} for model complexes as a function of the bending angle θ, averaged for all torsion angles ϕ. Error bars are 1 standard deviation from the mean of the torsion angles ϕ. Inset: Structure of the model complexes. (b) Zero-field magnetic transition probabilities for a complex of L_1 $[Dy\{N(SiH_3)_2\}_2]^+$ with ϕ = 90°. The x axis shows the magnetic moment of each state (start and end of each arrow) along the main magnetic axis of the molecule. Relaxation commences from the $|-{}^{15}/_2\rangle$ state and only includes pathways that reverse the magnetization. The transparency of each arrow is proportional to the normalized transition probability.

To confirm that this trend is generally applicable, structural investigations on model complexes with the simplified ligands L_2 = $^-C(SiH_3)_3$ and L_3 = $^-CH(SiH_3)_2$ (Figure 1a; note that structures for L_2 with θ < 120° were not included because of unrealistic clashing of hydrogen atoms) were performed. Indeed, these ligands show a similar robustness toward the lowering of θ as L_1 does, indicating that this angle generally needs not be a major consideration in the isolation of such two-coordinate dysprosium analogues. Interestingly, all three ligands show an almost linear dependence in U_{eff} with respect to the bending angle within $90° \leq \theta \leq 150°$, with a gradient of approximately 28 cm^{-1} per degree. The dependence of U_{eff} on the Dy−E distance within $2.0 \text{ Å} \leq r \leq 3.0 \text{ Å}$ with fixed θ = 180° and ϕ = 90° was also studied. Unsurprisingly, a reduction of the bond length leads to a substantial increase in U_{eff} (Figure S1 in the SI) because of the stronger crystal-field splitting of the ground multiplet. Indeed, minima in the total energies of the S = $^5/_2$ CASSCF wave functions are observed for each complex (Figures S2 and S3 in the SI), indicating that these cationic complexes are stable. However, these equilibrium bond lengths and angles should not be expected when the complete ligands are employed because of crystal-packing forces and steric effects.

To test these conclusions, ab initio calculations were performed on model $[Dy\{C(SiMe_3)_3\}_2]^+$ cations based on two previously reported structures, $[Yb\{C(SiMe_3)_3\}_2]$ (**2**)[32] and $[Sm\{C(SiMe_3)_3\}_2]$ (**3**),[33] which have C−Ln−C bending angles of θ = 137.0° and 143.4°, respectively, in a methodology identical with that employed for **1Dy**[31] (Tables S1−S6 in the SI). The results indicate that, despite the more acute C−Dy−C angles and symmetry-lowering agostic interactions, the main magnetic axis is still found to be parallel to the E−E vector and that efficient relaxation would occur via the fifth or sixth excited state (Figures 2 and S4 in the SI). The calculated barriers for **2Dy** and **3Dy** are U_{eff} = 1247 and 1484 cm^{-1}, respectively, compared to U_{eff} = 1837 cm^{-1} for **1Dy**. This is consistent with Figure 1a, where the deviation of θ from 180° does not completely quench the barrier to magnetization reversal, and therefore $[Dy\{C(SiR_3)_3\}_2]^+$ complexes should be considered highly desirable synthetic targets along with $[Dy\{N(SiR_3)_2\}_2]^+$ complexes.

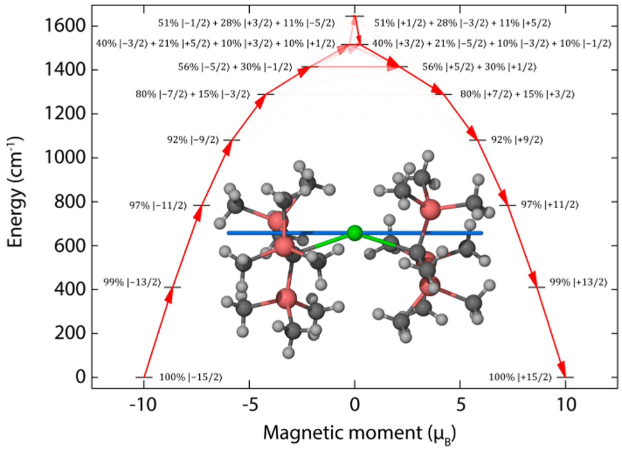

Figure 2. Zero-field magnetic transition probabilities within the ground-state multiplet for **3Dy**. The x axis shows the magnetic moment of each state along the main magnetic axis of the molecule. Relaxation commences from the $|-{}^{15}/_2\rangle$ state and only includes pathways that reverse the magnetization. The transparency of each arrow is proportional to the normalized transition probability. Inset: main magnetic axis of the ground-state Kramers doublet for **3Dy** (blue rod), Color code: Dy, green; Si, pink; C, gray; H, white.

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The proposed synthetic routes to such two-coordinate Dy^{III} species may involve intermediates with bound solvent molecules that ultimately may or may not be displaced. Therefore, the impact on the Ueff barrier by additional coordination of tetrahydrofuran (THF) molecule(s) for a number of coordination numbers and geometries has been examined in a qualitative manner (Figure 3). These results show that large decreases in the U_{eff} barrier of 50−70% could be expected upon coordination of solvent molecules like THF, and therefore such complexes should ideally be synthesized in the absence of a coordinating solvent. However, there does not seem to be any relationship between U_{eff} and the number of coordinated solvent molecules.

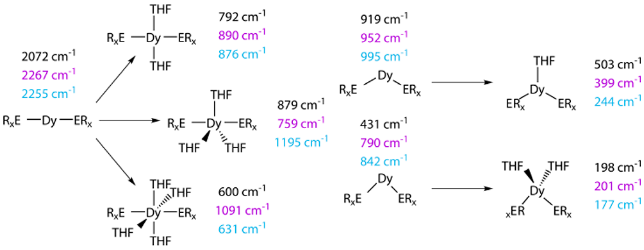

Figure 3. U_{eff} values for solvated complexes of L_1 (black), L_2 (purple), and L_3 (blue). The E−Dy−E angles are $\theta = 180°$ (left), 120° (right, top), and 109.5° (right, bottom), and all complexes have $\phi = 0°$.

In summary, the design criteria for two-coordinate dysprosium complexes with favorable SMM properties have been theoretically examined with ab initio calculations, and the task for synthetic chemists pursuing lanthanide-based SMMs is clear; any Dy^{III} complex with only two anionic donor atoms is desirable, where the presence of weak agostic-type interactions should have negligible effects. However, the coordination of solvent molecules such as THF has catastrophic consequences on the U_{eff} values. If such pseudo-two-coordinate Dy^{III} complexes can be isolated, they should be accompanied by a phenomenal increase to the current record magnetic relaxation barrier, which should result in much higher blocking temperatures, leading the way to technologically relevant high-temperature lanthanide SMMs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Computational details, electronic and magnetic properties of **2Dy** and **3Dy**, and structural trends for model complexes of L_1, L_2, and L_3. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nicholas.chilton@manchester.ac.uk.

Notes

The authors declare no competing financial interest.

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