Hard versus Soft: Zero-Field dinuclear Dy(III) oxygen bridged SMM and theoretical predictions of the sulfur and selenium analogues

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Complete List of Authors:	Vignesh, Kuduva; Texas A&M University, Chemistry Alexandropoulos, Dimitris; Texas A&M University College Station Dolinar, Brian; Texas A&M University College Station, Dunbar, Kim; Texas A and M University, Chemistry

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Kuduva R. Vignesh, Dimitris I. Alexandropoulos, Brian S. Dolinar, and Kim R. Dunbar*

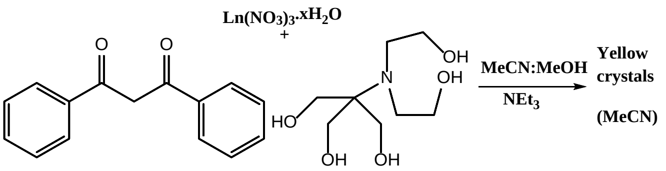
Two dinuclear lanthanide complexes (Gd and Dy) were prepared and characterized by X-ray, magnetic and computational methods. The Dy analogue shows SMM behavior with an energy barrier of 98.4 K in the absence of an applied *dc* field. Theoretical calculations were performed on model complexes which support the hypothesis that the energy barrier will increase if the soft-donor atoms S and Se are used in lieu of an O donor.

Single Molecule Magnets (SMMs)[1] are prominent members of coordination chemistry field, owing to their promising potential applications in information storage devices,[2] Q-bits[3] and in spintronic devices [3a,4] SMMs are mononuclear or transition, rare earth or mixed d/f metal complexes which exhibit slow relaxation of the magnetization, and act as nano-magnets below a certain blocking temperature. The electronic structure of the metal ions, magnetic anisotropy and magnetic exchange interactions constitute the fundamental ingredients for the existence of a barrier and quantum tunnelling, which lead to bistability and relaxation in SMMs.[5] Since the discovery of slow relaxation of magnetization in single-ion lanthanide complexes,[6] tremendous progress in the synthesis and study of lanthanide based SMMs.[7] The inherent magnetic anisotropy and the number of unpaired f-electrons are responsible for the high energy barrier for the reversal of magnetization in Ln SMMs.[8] Importantly, Dy^{III} is the most promising candidate,[8d] which includes Dy^{III} organometallic molecules exhibiting a blocking temperature of 60 K and 80 K having been reported.[7b, 7d,9] Research has also focused on the 4f-ion based polynuclear clusters[8a-c] and their combination with transition metals {3d-4f} or radicals {2p-4f}.[10] The observed SMM characteristics of these complexes can be ascribed to the single ion anisotropy of Dy^{III} ions, but a primary challenge in such clusters is the very weak exchange interaction leading to the existence of low-lying excited states, the population of which leads fast quantum tunnelling of the magnetization (QTM).[8a, 11] Although there have been considerable efforts to elucidate the mechanisms operative for mononuclear 4f SMMs, much less attention has been devoted in understanding the relaxation mechanisms in polynuclear 4f SMMs. The primary hurdle is to assess the consequence of the Ln···Ln exchange interaction on the SMM property where the individual single-ion anisotropies are assumed to be the dominant phenomenon. The choice of the bridging group is important to overcome the core nature of the 4f orbitals and subsequently induce significant exchange interaction between the paramagnetic centres. Moreover, the ligand field as well as the coordination geometry exerts a strong influence on the local anisotropy of the lanthanide ion. To put it in simple terms, the SMM behaviour is governed by the interplay between the ligand field effect, the geometry, and the strength of the magnetic exchange interaction between the lanthanide ions. Notably, a study on a $[Dy_2(ovph)_2Cl_2(MeOH)_3]$(where H_2ovph = pyridine-2-carboxylic acid [(2-hydroxy-3-methoxyphenyl)methylene] hydrazide) dinuclear complex by Powell et al.[12] have shown that the Ising type exchange interaction between the Dy^{III} ions suppresses the QTM at zero field and shows the importance of the exchange interaction in developing next generation SMMs. Also, the work of Murray et al.[13] on $\{Co^{III}{}_2Dy_2\}$ butterfly complexes and their *ab initio* calculations suggest that the exchange interaction between Dy^{III} ions can be improved to suppress the QTM by utilising diamagnetic 3d ions adjacent to the Dy^{III} centres.

With the aforementioned issues as a backdrop, herein we report the synthesis, structures, magnetic and theoretical studies of two new homodinuclear lanthanide (III) complexes, $[HNEt_3]_x[Ln^{III}{}_2(LH_4)_2(dbm)_2](NO_3)_y$ (Ln = Gd, x = 1, y = 3 for (**1**), and Ln = Dy, x = 0, y = 2 for (**2**), where LH_4^- = singly deprotonated 2,2-bis(hydroxymethyl)-2,2',2''-nitrilotriethanol, dbm = 1,3-diphenyl-1,3-propanedionate) (Scheme 1). The principal aim is to fully understand the electronic structure, quantify the magnetic anisotropy, investigate the magnetic exchange between the lanthanide centres and, finally, to

‡ *Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012, United States.*

Electronic Supplementary Information (ESI) available: Synthetic, Crystallographic, Computational, and Magnetic details. See DOI: 10.1039/x0xx00000x. CCDC 1880175-1880176 predict how to improve the relevant parameters that contribute to an increase in the magnetisation reversal barrier by replacing the O-donor bridging atoms with the softer donor atoms S and Se.



Scheme 1. Synthetic route employed for the synthesis of **1** and **2**.

Reactions of $Ln(NO_3)_3 \cdot xH_2O$ (Ln = Gd^{III} and Dy^{III}), dbmH and LH_5 in a 1 : 2 : 1 molar ratio with triethylamine (Et_3N) solution in MeCN produce pale yellow crystals of $[HNEt_3][Ln^{III}_2(LH_4)_2(dbm)_2](NO_3)_3$ (**1**) and $[Dy_2(LH_4)_2(dbm)_2](NO_3)_2$ (**2**). The chemical and structural identities of the compounds were confirmed by single-crystal X-ray crystallography (Table S1), elemental analyses (C, H, N), and IR spectral data (SI).

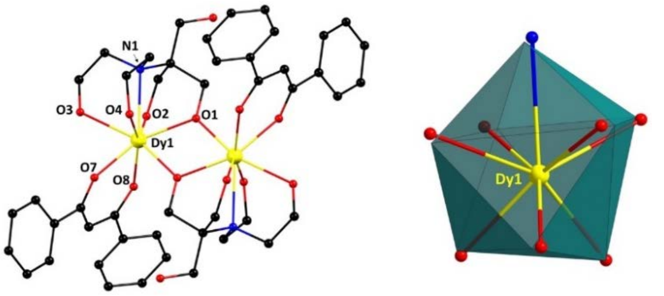


Figure 1. (left) Structure of the cation of **2** and (right) triangular dodecahedral geometry of Dy1 in the structure of **2**. H atoms were omitted for the sake of clarity. Colour scheme: Dy, yellow; N, blue; O, red; C, black.

Due to the structural similarities of complexes **1** and **2**, only complex **2** will be described as a representative example. Complex **2** crystalizes in the triclinic space group $P\bar{1}$ and its asymmetric unit consists of one half of the $[Dy_2(LH_4)_2(dbm)_2]^{2+}$ cation and a nitrate anion, with the remainder related through a crystallographic centre of inversion. A labelled representation of the cation of **2** is presented in Fig. 1. and consists of two Dy atoms doubly bridged by deprotonated alkoxido arms of two η^1:η^1:η^1:η^1:η^2:μ LH_4^- moieties and act as tetradentate N/O-chelates and O-bridging ligands. The resulting $\{Dy_2(\mu\text{-}OR)_2\}^{4+}$ core is nearly planar with the Dy1…Dy1′ axis (3.743(2) Å) with a Dy1-O1-Dy1′ angle of 110.67(2)°. The Dy-O/N bond distances are slightly shorter than the corresponding Gd-O/N ones due to the lanthanide contraction. The eight-coordinate Dy ions are completed by the O atoms of two chelating dbm$^-$ ligands. The coordination geometry of the Dy ions can be better described as triangular dodecahedral, based on SHAPE[14] calculations (Table S2).

The unit cell of **2** also contains two NO_3^- ions which are involved in strong intermolecular hydrogen bonding with the protonated (R-OH) arms of the LH_4^- ligands (this includes the O atoms of the LH_4^- ligand, O2, O4, and O5, as the donors, and the nitrate O atoms, O8, and O9, as the acceptors) (SI). In addition, there are some weak hydrogen bonding contacts between the protonated (R-OH) arms of the LH_4^- ligands and the lattice MeCN molecules (Fig. S1). The closest intermolecular Dy···Dy contact is 8.070(2) Å. Complex **1** crystallizes in the monoclinic $P2_1/c$ space group, where the $[Gd_2(LH_4)_2(dbm)_2]^{2+}$ cation is stabilised by one $HNEt^+$ and three NO_3^- ions.

The magnetic properties of the two compounds were investigated by direct current (dc) magnetic susceptibility measurements. The $\chi_M T$ vs. T plots for **1** and **2** (Fig. 2) reveal room temperature values of 15.15 cm^3 K mol^{-1} and 28.35 cm^3 K mol^{-1} which are in good agreement with the expected values of 15.75 cm^3 K mol^{-1} and 28.34 cm^3 K mol^{-1} for two non-interacting Gd^{III} ($^8S_{7/2}$, S = 7/2, L = 0, g = 2) and Dy^{III} ($^6H_{15/2}$, S = 5/2, L = 5, g = 4/3) ions, respectively. The $\chi_M T$ vs. T plots are similar at temperatures between 300–15 K; the $\chi_M T$ values decrease as the temperature is lowered due to depopulation of the Starks sub-levels as a result of single ion crystal-field effects. These results are further supported by the magnitude of the magnetization and the saturation values (Fig. S2).

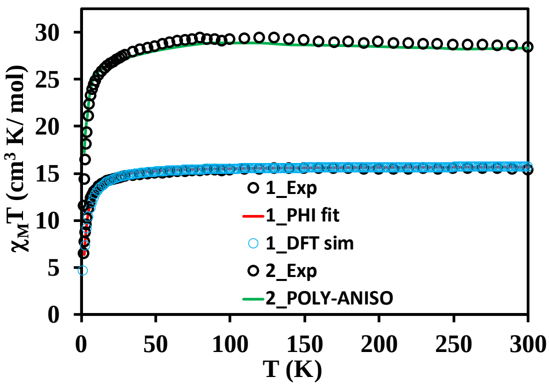


Figure 2. Variable-temperature dc magnetic susceptibility data for **1** and **2**, under an applied field of 0.1 T.

The magnetic exchange interaction between the Gd^{III} ions in **1** were extracted by fitting the susceptibility data (Fig. 2) using PHI program[15] which led to a weak antiferromagnetic interaction of -0.1 cm^{-1}. DFT calculations (See computational details in SI) were carried out to compute the magnetic interactions between the Gd^{III} ions, the results of which predict a value of -0.14 cm^{-1}, in good agreement with the fitted value.

In order to probe the SMM properties of **2**, frequency dependent out-of-phase magnetic susceptibility and Cole-Cole measurements for **2** were performed using a 2 Oe oscillating ac field at frequencies from 0.1–1000 Hz between 1.8 and 14 K, under a zero static dc field. Evidence of SMM behaviour is observed for **2** (Dy) with χ_M″ versus frequency plots displaying out-of-phase susceptibility maxima (Fig. 3, top). Cole–Cole plots of χ_M' versus χ_M'' data exhibit semi-circular profiles which indicate a single relaxation process for **2** (Fig. 3, bottom inset). Plots of ln(τ) versus 1/T are linear (Fig. 3, bottom) between 10.5–14 K, indicating that a thermally activated Orbach process is operative. The data were fit (Table S3) considering all the possible relaxation processes using the equation, $1/\tau = 1/\tau_{QTM} + CT^n + \tau_o^{-1}\exp(U_{eff}/k_BT)$, where $1/\tau_{QTM}$ corresponds to the relaxation process via quantum tunnelling pathway, the CT^n term corresponds to the relaxation via Raman process, and the last term accounts for the Orbach relaxation pathway.[13] The values obtained from the best fit are n = 3.5(2), C = 0.11(4) s^{-1} $K^{-3.5}$, U_{eff} = 98.4(8) K and τ_o = 3.7(1) × 10^{-5} s (R = 0.997) for **2**. The n value is lower than the expected and this can be attributed to the presence of both optical and acoustic Raman processes involving magnetic relaxation.[16] A QTM relaxation time, τ_{QTM}, of 0.06 s is estimated and a convincing pre-exponential factor (10^{-5} s) allows confidence in the extracted values for an SMM.[8d]

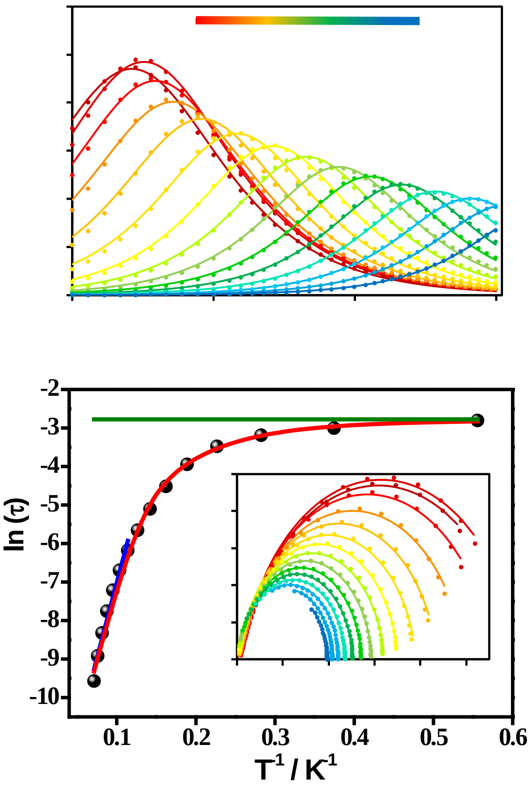


Figure 3. (top) Frequency dependence of χ_M'' for **2** in a zero applied dc field, with an ac magnetic field of 2 Oe. (bottom) Magnetization relaxation time (τ), plotted as ln τ vs. T^{-1} for **2**. The solid blue line corresponds to fitting of the Orbach relaxation process, and the solid red line represents the fitting to multiple relaxation processes. The horizontal green line represents the QTM relaxation time. (inset) Cole–Cole plots between 1.8 and 14 K. The colour lines are fitted data extracted from CC-FIT program.[17]

To understand the single ion relaxation process, we performed CASSCF+RASSI-SO calculations to compute the anisotropy of both Dy^{III} ions in **2** (See Computational details in SI). In both Dy^{III} ions, m_J = ±15/2 states were found to be stabilized as the ground state. Moreover, the g_z values were almost purely axial in nature with negligible transverse (g_x = 0.0044, g_y = 0.0072, and g_z = 19.696 for Dy ions) components (Table S4). Thus, the mixing of the m_J = ±15/2 states with other m_J states was significantly reduced due to the increased energy gap between the ground and the first excited Kramers doublet (KD). The energy gaps were found to be 158.0 cm^{-1} for both Dy ions (Table S5), indicating that they are symmetrically equivalent. Since the first excited KD is significantly higher in energy, this suggests a possibility for the magnetization blockade at the single ion level.

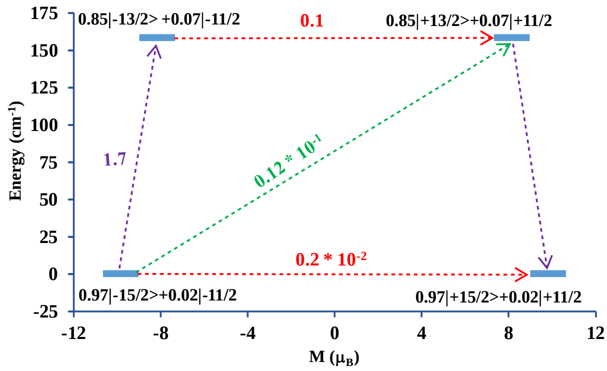


Figure 4. The *ab initio* computed magnetization blocking barrier for Dy1 site in **2**. The thick blue line indicates the KDs as a function of the computed magnetic moment. The green/purple dotted arrows show the possible pathway through the Orbach/Raman relaxation. The red dotted arrows represent the presence of QTM and TA-QTM between the connecting pairs. The numbers provided at each arrow are the mean absolute value for the corresponding matrix element of the transition magnetic moment.

To determine the relaxation processes associated with the single ion anisotropy of Dy^{III} ions, the relaxation mechanisms were developed and are shown in Fig. 4. In both Dy ions in **2**, the ground state QTM probability is small (0.2 x 10^{-2} μ_B) due to the dominance of axial crystal field parameters (Table S6) and the first excited state TA-QTM (Temperature Assisted QTM) probability is significantly large.[13] This suggests that the magnetic relaxation occurs via the first excited state with an energy barrier of 158 cm^{-1} (227.3 K). The anisotropy barrier of **2** was then computed considering the exchange coupled states of both Dy^{III} ions using the POLY_ANISO program.[18] The magnetic susceptibility data were used to extract the $Dy^{III}\cdots Dy^{III}$ exchange coupling, yielding a value of -0.01 cm^{-1} (see Figure 2). Although weak antiferromagnetic exchange introduces several low-lying states, the relaxation occurs via second excited states, due to the tunnelling of the magnetization (Table S7 and Fig. S4). The coupled state anisotropy barrier, U_{cal} = 158.2 cm^{-1} (227.6 K) is relatively large as compared to the experimentally determined barrier of 98.4 K.

It is well known that structural parameters can profoundly affect the magnetic behaviour of a particular complex, especially through the bridging atoms. These considerations include structural modifications of donor atoms such as S and Se lieu of O atom. This strategy has been successfully achieved to increase the magnetic coupling constants and the zero-field splitting parameter (*D*) in transition metal complexes,[19] but this strategy has not been widely utilised in lanthanide coordination complexes although some organometallic compounds exhibit improved SMM properties.[20] In this vein, we postulated that it would be interesting to model two complexes by replacing the bridging O-atoms with S and Se atoms in **2**. The model complexes **2-S** and **2-Se** were optimised using DFT calculations (Figure S3) and the optimised structures were used to study the magnetic behaviour using ab initio calculations.

The single-ion calculations performed for **2-S** and **2-Se** on both Dy^{III} ions suggest that the local g-tensors in the ground KD are purely axial in nature, with very small transverse components (g_x = 0.0027, g_y = 0.0037, and g_z = 19.7358 for Dy1 of **2-S** and g_x = 0.0017, g_y = 0.0020, and g_z = 19.7847 for Dy1 of **2-Se**). The presence of soft-donor atoms yields even smaller transverse terms compared to those for **2**. A small TA-QTM in the first excited state (0.6×10^{-1} μ_B for Dy1 of **2-S** and 0.4×10^{-1} μ_B for Dy1 of **2-Se**) allows the magnetization to relax via the second excited state and the energy barriers were found to be 192.7 cm^{-1} (Dy1) and 201.9 cm^{-1} (Dy2) in **2-S**, 315.3 cm^{-1} (Dy1) and 353.3 cm^{-1} (Dy2) in **2-Se** (Table S5). These values are larger than that observed for complex **2**, owing to a stronger electrostatic interaction afforded by the soft-donor atoms. A qualitative mechanism for the magnetic relaxation for the Dy1 sites in **2-S** and **2-Se** obtained from the *ab initio* calculations is shown in Fig. 5. The coupled states barriers were extracted with a $Dy^{III}\cdots Dy^{III}$ exchange of -0.05 and -0.07 cm^{-1} for **2-S** and **2-Se**, respectively using POLY_ANISO. The improved magnetic couplings predict a smaller tunnelling probability in the ground state (1.5×10^{-7} cm^{-1} for **2-S** and 3.7×10^{-8} cm^{-1} for **2-Se**). Furthermore, it was found that the tunnelling probability is very small until the 9th and 10th excited states and the magnetic relaxation proceeds to the 10th and 11th excited states (Table S8 and S9) for **2-S** and **2-Se**, respectively. It evidences that the $Dy^{III}\cdots Dy^{III}$ exchange suppresses the tunnelling for both complexes, in comparison to the single ion, leading to a barrier height of 239.8 and 419.8 cm^{-1} for **2-S** and **2-Se**, respectively. These U_{cal} are larger than that computed for complex **2** (158.2 cm^{-1}), which suggest the conclusion that there is an advantage in using soft-donors in place of hard-donor atoms.

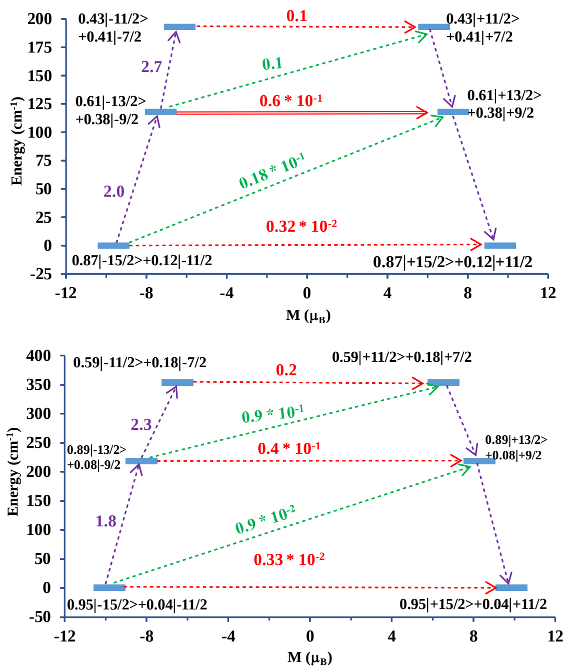


Figure 5. The *ab initio* computed magnetization blocking barrier for the Dy1 sites in (left) **2-S**, (right) **2-Se**.

Structural, magnetic and *ab initio* CASSCF studies were used to quantify the observed magnetic behaviour of two lanthanide dinuclear complexes. The effect of soft-donor atoms was probed using theory in order to ascertain the effect of magnetic anisotropy combined with magnetic coupling of the individual Dy ions in the dinuclear SMMs. These combined experimental and computational analyses serve as a benchmark for the theoretical model, which can be used for the design and optimization of lanthanide-based SMMs. Work is in progress to synthesize polynuclear 4f complexes with soft-donor atoms.

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Conflicts of interest

There are no conflicts to declare.

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