Single-Molecule Magnets Hot Paper

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Magnetic Anisotropy in Divalent Lanthanide Compounds

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Abstract: *Complexes of trivalent lanthanides (Ln) are known to possess strong magnetic anisotropy, which enables them to be efficient single-molecule magnets. High-level ab initio calculations are reported for [LnO] (where Ln is terbium (Tb), dysprosium (Dy), or holmium (Ho)), which show that divalent lanthanides can exhibit equally strong magnetic anisotropy and magnetization blocking barriers. In particular, detailed calculations predict a multilevel magnetization blocking barrier exceeding 3000 K for a [DyO] complex deposited on a hexagonal boron nitride (h-BN) surface, bringing the expected performance of single-molecule magnets to a qualitatively new level compared to the current state-of-the art complexes.*

Complexes with strong magnetic anisotropy, often displaying single-molecule magnet (SMM) behavior,[1] have attracted interest in connection with various applications, such as molecular spintronics[2] and quantum computation.[3] Recently, the emphasis has moved toward lanthanide complexes that have already demonstrated several exciting properties.[4,5] As established by prior literature,[1,6] the ability of paramagnetic molecules to display a SMM behavior (magnetic hysteresis, out-of-phase magnetic susceptibility χ'', and so on) is strongly influenced by the height of the magnetization blocking barrier and the degree of magnetic axiality of the low-lying doublet states. In comparison, the degree of magnetic axiality in low-lying multiplets is fully determined by the axiality of the crystal field (CF). The latter was found to be perfectly axial in diatomic complexes such as lanthanide monoxides,[7] for which all doublets arising from the crystal-field (CF) splitting of the ground atomic *J*-multiplet of the lanthanide ion are characterized by a definite projection of the total angular momentum.

All lanthanide SMMs investigated to date involved Ln^{III} ions.[4,5] On the other hand, complexes with divalent lanthanide ions, although not as ubiquitous as the former, also exist in various coordination geometries.[8] Recently, the divalent state was discovered across the entire lanthanide series in compounds with the core $[Cp'_3Ln]^-$ where $Cp' = C_5H_4SiMe_3$.[9] The magnetic measurements have shown that some of these complexes exhibit larger magnetic moments than the corresponding trivalent lanthanides; however, none of them was found to be a SMM.[5l] It is of interest, therefore, to establish whether divalent lanthanide complexes can in principle display magnetization blocking and how strong this characteristic can be in comparison to trivalent lanthanides.

The multiplet spectrum of $[DyO]^+$ has been investigated in the past.[7,10] Such compounds represent a limit for strongest SMMs because their blocking barriers involve all states arising from the atomic *J*-multiplet of the corresponding Ln^{III} ion;[7] that is, all eight low-lying Kramers doublets in the case of Dy^{III}. All performant single-Ln SMMs only approach this ideal limit to some extent. Thus, on individual Dy^{III} sites in Dy_5 and K_2Dy_4 alkoxide cage complexes,[11] as well as in the NCN-pincer ligand dysprosium single-ion complex,[12] the relaxation proceeds via the second excited KD, in the pentagonal bipyramidal Dy^{III}-containing complex [Dy(bbpen)X].[13] This occurs via the third excited KD and, in a hypothetical near-linear bis(amide) Dy^{III} complex,[8d] via the fourth excited KD.[5z,14] Based on this evidence, it is natural to assume that neutral [LnO] monoxides will represent a limit for SMM performance of Ln^{II} complexes.

To assess the strength of magnetic anisotropy in divalent lanthanide complexes, and their potential for blocking of magnetization, herein we focus on the ab initio investigation of [TbO], [DyO], and [HoO]. Notably, these lanthanide monoxides are produced routinely and have been thoroughly investigated in a series of laser spectroscopy studies since the 1980s.[15]

We investigated the multiplet structure of diatomic lanthanide oxides by multiconfiguration ab initio methods (Supporting Information). Compared to conventional lanthanide complexes characterized by a high coordination number ($6 \div 12$), in diatomic lanthanide compounds the metal–ligand covalency is more pronounced because of a much shorter M–L bond, leading to a much larger CF splitting of the ground atomic multiplet of the Ln ion. To take this effect properly into account, after the standard complete active space self-consistent field (CASSCF) step the multi-configurational second order perturbation theory (CASPT2) calculations were performed. To establish precisely the type of the orbital accommodating the additional electron in the Ln^{II} ion, the active space involving 4f orbitals was augmented with 6s, 6p, or 5d Ln orbitals, requiring a treatment at the level of restricted active space self-consistent field (RASSCF) combined with the corresponding multiconfigurational second order perturbation theory (RASPT2, Supporting Information).

The calculated low-lying terms of divalent lanthanide monoxides, done with the RASSCF/RASPT2 module of MOLCAS, are shown in Figure S1 (Supporting Information). Surprisingly, the dominant electronic configurations

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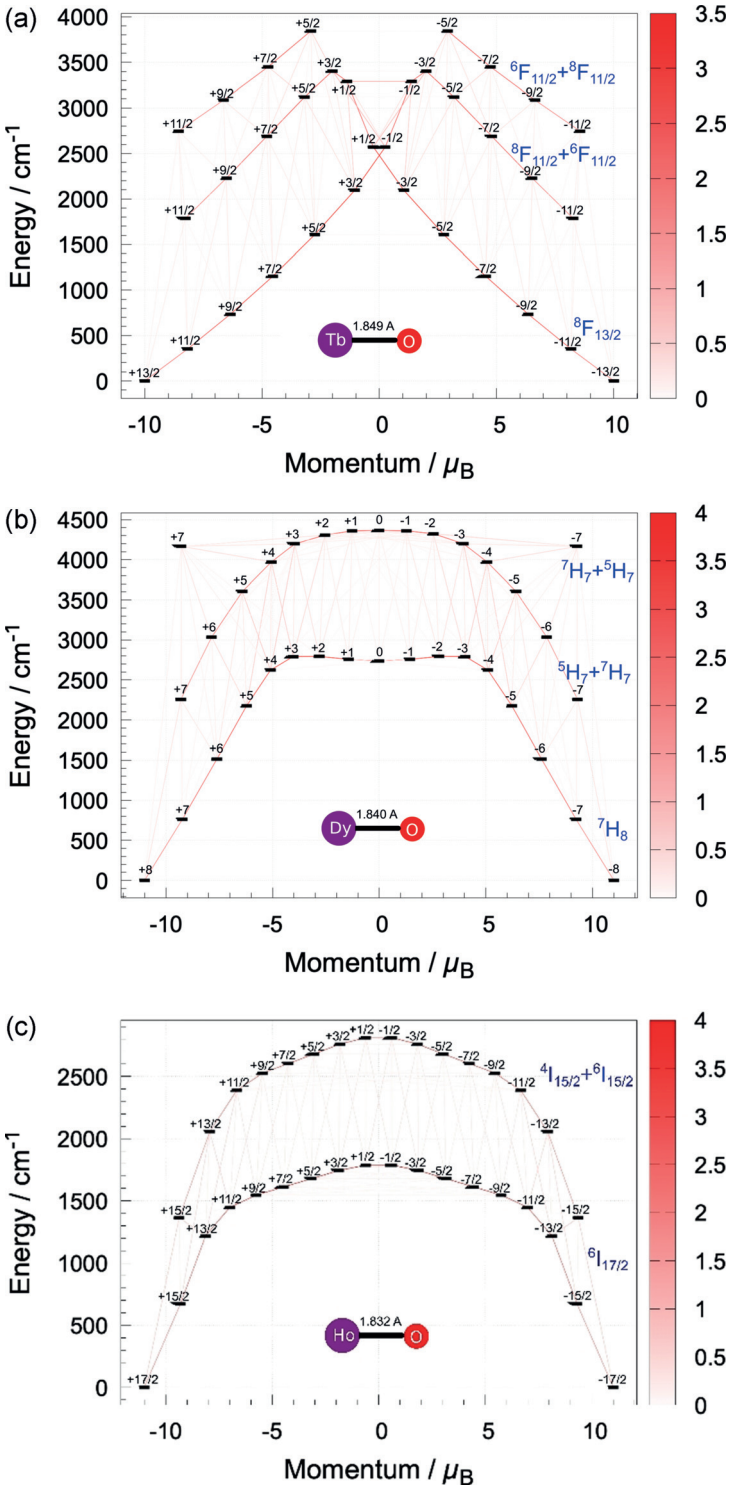

Figure 1. Multiplet spectrum and the magnetization blocking barrier of a) [TbO], b) [DyO], and c) [HoO]. Each doublet state $\pm mJ$ arising from a given atomic multiplet ^{2S+1}L is placed according to its saturation magnetic moment (horizontal axis). The intensity of the pink lines indicates the amplitude of the average transition magnetic dipole moment in μ_B between the connected states (the legend on the right-hand side), the square of which roughly scales with the rate of spin-phonon transition between them.[7,16] The low-lying red lines outline the magnetization blocking barrier.

contributing to these terms in [LnO] (Ln = Tb, Dy, and Ho) are $4f^N6s^1$. The density functional theory (DFT) calculations also show that, for Ln^{III}, the additional electron occupies the 6s orbital rather than the 5d orbital. The weight of this configuration is above 98% in the low-lying terms.

The effects of spin-orbit coupling in [LnO] were considered within restricted active space state interaction (RASSI) calculations. The calculated low-lying multiplets are collected in Tables S1–S3 (Supporting Information) and are shown in Figure 1. The perfect axial symmetry of [LnO] conserves the projection mJ of the total angular momentum on the molecular symmetry axis. As a result, the molecular multiplets are Kramers doublets (mJ, $-mJ$) in [TbO] and [HoO], and Ising doublets (mJ, $-mJ$; or singlets for $mJ = 0$) in [DyO]. As for monoxides of trivalent lanthanides,[7] the CF of oxygen is very strong, resulting in a splitting of atomic terms (Figure S1) and atomic J-multiplets (Figure 1) of several thousand wavenumbers. As presented in the last column of Tables S1–S3, the calculated energies of the multiplets compare quite well with available spectroscopic data,[15] thus providing confidence to the results presented here. We also performed the calculations of the multiplet structure of $[DyO]^+$ at the same level of theory (Figure S2),[10] showing a very similar splitting of the low-lying multiplets compared to the [DyO] compound (Figure 1b). Conforming to the established rule,[6b] the CF splitting decreases in the row Tb, Dy, and Ho—in analogy to trivalent lanthanide complexes. The detailed analysis of multiplets in the [LnO] compounds and their comparison with the $[DyO]^+$ compound is given in the Supporting Information.

To assess the magnetization blocking capability of the investigated complexes, we applied a method that permits estimation of the relative strength of spin-phonon relaxation rates.[6,7,16] Figure 1 shows that, in full analogy with $[DyO]^+$ (Figure S2), the barrier of magnetization blocking outlines the relaxation path connecting all doublet states arising from the ground atomic multiplet. This is so even in the case when the group of levels belonging to the ground atomic multiplet overlaps with the states from the excited atomic multiplet, as in [TbO] and [DyO] (Figure 1; Tables S1–S3). Ultimately, this is a consequence of the infinite-order anisotropy axis resulting in a net mJ character of all doublet states.[6b,7] We can conclude from Figure 1 that the height of the barriers of investigated divalent complexes is comparable to the trivalent lanthanide monoxides (Figure S2).

In contrast, the investigated [LnO] are characterized by a ground state $|mJ|$ larger by 1/2 than in $[LnO]^+$. As a result, the blocking barrier acquires one more state in [LnO]. Thus, in $[DyO]^+$ the ground doublet is $mJ = \pm 15/2$ and the blocking barrier consists of eight KDs (Figure S2), whereas in $[DyO]^0$ the ground doublet is $mJ = \pm 8$ and the blocking barrier consists of eight Ising doublets and one singlet (Figure 1b). Accordingly, the magnetic moment in the ground doublet state increases in [LnO] by 1 μ_B compared to $[LnO]^+$.

If the additional electron added on top of the Ln^{III} were to reside in the 5d rather than 6s orbital, this increase of magnetic moment would be smaller because of an opposite orientation of unquenched orbital momentum with respect to the spin of this electron, which is required by the (positive) spin-orbit coupling in the 5d shell. This conclusion is general for arbitrary complexes of divalent lanthanides.[9,51]

To get further insight into the origin of high blocking barriers in [LnO], Figure 2 shows the effective CF splitting of the active orbitals bearing the magnetic electrons in the respective compounds (Supporting Information). We can see that, in all compounds, the ground and the first excited orbitals ($mL = \pm 3$ and ± 2, respectively) are separated by a characteristic large gap to the high-lying orbitals $mL = \pm 1$ and 0. The origin of this energy gap clearly emerges from the shape of the active orbitals shown in Figure S3. This Figure indicates that the first two pairs of orbitals do not hybridize to the oxygen orbitals on the symmetry reasons (see also Tables S5–S8), implying the lack of the covalent destabilization in contrast to the latter orbitals ($\pm 1, 0$). We may conclude that the high blocking barriers in Figure 1 arise because of a strong covalent contribution to the CF splitting of active orbitals.

Subsequently, we studied the deposition of the neutral DyO on the hexagonal boron nitride (h-BN) surface. This substrate was recently used for the investigation of magnetization blocking of adsorbed Co ions.[17] The geometry optimization was carried out with DFT for a fragment of h-BN layer with saturated dangled bonds and deposited DyO unit. Figure 3a shows the optimized structure of the DyO@h-BN. Predicted bonding energy of the deposited molecule to the h-BN surface is 2.3 eV (53.5 kcal mol^{-1}). The DyO unit lies on the surface along the B–N bond, the corresponding atoms being shifted slightly out of the h-BN plane. Table S4 and Figure 3b display the calculated multiplets and the magnetization blocking barrier for this compound.

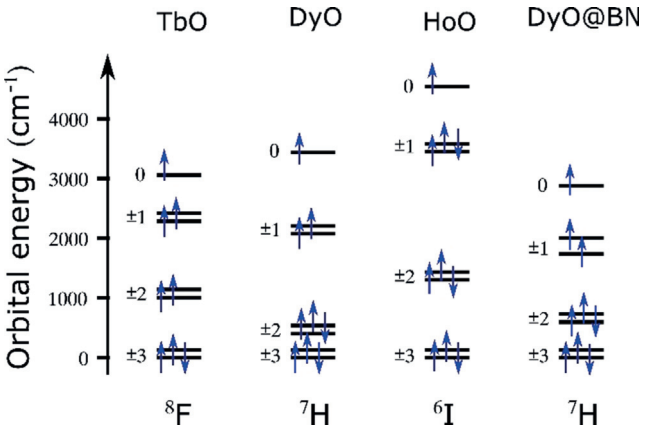

Figure 2. CF splitting of the active orbitals bearing the magnetic electrons in the [LnO] complexes, including the deposited neutral [DyO] on the h-BN surface (Figure 3). Not shown is the higher lying 6s orbital of the Ln^{II} nucleus bearing one unpaired electron. The shape of the orbitals for $[TbO]^+$ are shown in Figure S3. The indicated electronic population corresponds to the ground multiplet, $mJ = 13/2$ for [TbO], $mJ = 8$ for [DyO], and $mJ = 17/2$ for [HoO].

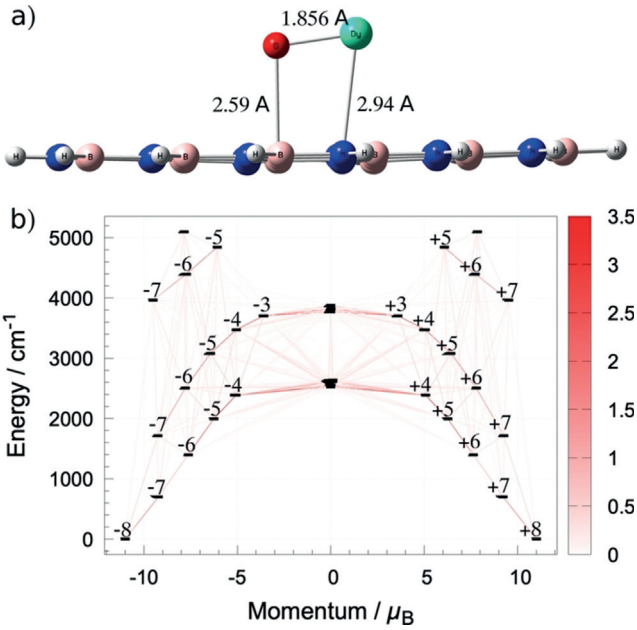

Figure 3. a) DFT-predicted structure of the deposited DyO on the h-BN surface. b) Calculated magnetization blocking barrier for the predicted structure.

The height of the obtained magnetization blocking barrier still exceeds 2000 cm^{-1}, matching those for isolated diatomic lanthanide complexes in Figure 1, and in spite of the substantial non-axial contribution to the CF of Dy^{II} ion that is provided by the substrate as a consequence of the "horizontal" alignment on the DyO unit. We want to emphasize that the present calculations are more accurate compared to the previous treatment of $[DyO]^+$ deposited on a MgO surface,[6] where the geometry optimization was not complete and the CASPT2 step was not done. In this respect, the result in Figure 3b is really remarkable because it indicates, using realistic calculations, the possibility to achieve very high magnetization blocking barriers that exceed twice the barriers of the best reported SMMs,[5z,14] for a structurally robust [DyO] unit exhibiting substantial adsorption energy to the surface.

This finding seems to be important for two reasons. As a series of recent studies show,[5z,14] the Cp–Dy–Cp-based SMMs have reached the limit for a blocking barrier height of approximately 1200 cm^{-1}, and without apparent means of being overcome because of a fundamental difficulty in synthesizing low-coordination lanthanide magnetic complexes. Hence, turning to [LnO] compounds represents a viable alternative, allowing for further enhancement of the SMM efficiency. This is evidenced by a very large axial CF intrinsically present in such units because of a strong covalent contribution arising at short Ln–O separations. On the other hand, the conceptual application of SMMs as memory units is related to their deposition on surfaces. Here the [LnO] units have the advantage of being robust both structurally and magnetically as a consequence of a prevailing intrinsic axial CF over possible low-symmetric contributions from the surface, which will preserve their blocking properties after

their deposition on different substrates.[18] Ab initio investigation and the electronic structures of other [LnX] magnetic units deposited on various surfaces will be reported in subsequent publications.

In summary, we have investigated the magnetization blocking barriers in divalent lanthanide monoxides of Tb, Dy, and Ho with state of the art ab initio methods. We have found that the Ln^{II} compounds possess a potential for magnetization blocking as high as the Ln^{III} compounds. Besides being indicative for arbitrary lanthanide complexes, these results also suggest that units of [LnO] can be used as highly anisotropic blocks in future complexes and magnetic materials. As a confirmation, the [DyO] unit preserved its anisotropic properties to a significant extent when adsorbed on the h-BN surface, in spite of the preferred "horizontal" alignment. The obtained multilevel magnetization blocking barrier exceeding 3000 K brings the expected performance of SMMs to a qualitatively new level compared to the current state-of-the art complexes, thus making feasible their application as memory units.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: ab initio calculations · divalent charge · lanthanides · magnetization blocking barrier

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[10] In previous work, the multiplet spectrum of $[DyO]^+$ was calculated within CASSCF approximation, which is a suitable

approximation for the ordinary lanthanide complexes but underestimates the metal–ligand covalency in diatomic compounds because of their much shorter M–L distances. For the sake of comparision with compounds investigated here, the multiplet spectrum of $[DyO]^+$ has been recalculated within a higher (CASPT2) approximation (Figure S2). Qualitatively, a similar shape of magnetization blocking barriers is obtained by both approximations; however, the present calculation produces a barrier that is higher by ca. 1000 cm^{-1}. For further information, see Ref. [7].

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