Slow Magnetic Relaxation in Lanthanoid Crown Ether Complexes: Interplay of Raman and Anomalous Phonon Bottleneck Processes


Abstract: The combination of lanthanoid nitrates with 18-crown-6 (18-c-6) and tetrahalocatecholate (X,CatX = Cl, Br) ligands has afforded two compound series [Ln(18-c-6)(X,Cat)(NO3)2]·MeCN (X = Cl, 1-Ln; X = Br, 2-Ln; Ln = La, Ce, Nd, Gd, Tb, Dy). The 18-c-6 ligands occupy equatorial positions of a distorted sphenocorona geometry, while the charged ligands occupy the axial positions. The analogues of both series with Ln = Ce, Nd, Tb and Dy exhibit out-of-phase ac magnetic susceptibility signals in the presence of an applied field, indicative of slow magnetization relaxation. When diluted into a diamagnetic La host to reduce dipolar interactions, the Dy analogue exhibits slow relaxation up to 20 K in the absence of an applied dc field. Concerted magnetic measurements, EPR spectroscopy and ab initio calculations have allowed elucidation of the mechanisms responsible for slow magnetic relaxation. A consistent approach has been applied to quantitatively model the relaxation data for different lanthanoid analogues, suggesting that the spin dynamics are governed by Raman processes at higher temperatures, transitioning to a dominant phonon bottleneck process as the temperature is decreased, with an observed transitioning to a dominant phonon bottleneck process as the temperature.

Introduction

Since their discovery more than 25 years ago, single-molecule magnets (SMMs), i.e. compounds which show slow relaxation of the magnetization at low temperature, have offered much promise for applications that can make use of slow magnetic relaxation and/or magnetization quantum tunnelling (QTM). Proposed potential applications of such nanoscale molecular materials include high density data storage, quantum computing or quantum magnetometry.

Lanthanoid (LnIII) ions, due to their structural simplicity and ease of functionalization, have set a new record with an energy barrier of 1277 cm⁻¹ (1837 K) and magnetization hysteresis up to 60 K. Although practical applications for SMMs now seems closer than ever, at least at liquid nitrogen temperatures, efforts to understand the underlying mechanisms of magnetization relaxation remain of paramount importance for the development of high performance SMMs.

The last few years have seen reconsideration of the role that different pathways can play in determining the relaxation of the magnetization. In zero field, relaxation of Ln-SMMs is often through a thermally-activated mechanism. In both cases, the energy splitting of the Kramers doublet (K D) or via a higher energy KD dominated by QTM between the quasi-degenerate levels of the lanthanoid(III) ion corresponding to the highest T² dependence (T is temperature). The anomalous thermal dependence of the phonon bottleneck relaxation is consistent with anharmonic effects in the lattice dynamics, which was predicted by Van Vleck more than 70 years ago.

This electrostatic approach relies on the assumption that relaxation in lanthanoid(III) complexes occurs predominantly through an Orbach process, generally involving the first energy level above the ground level. In the past couple of years, the design strategy outlined above has proved extremely effective for achieving high performance Dy-SMMs. A new rationally designed complex has successively broken the records of highest energy barrier to magnetization reversal and/or hysteresis temperature. Most recently, the compound [(Cp3)2Dy][B(C6F5)4] (Cp3 = 1,2,4-tri(tert-butyl)cyclopentadienide) has set a new record with an energy barrier of 1277 cm⁻¹ (1837 K) and magnetization hysteresis up to 60 K. Although practical applications for SMMs now seems closer than ever, at least at liquid nitrogen temperatures, efforts to understand the underlying mechanisms of magnetization relaxation remain of paramount importance for the development of high performance SMMs.

Highly favorable conditions for SMM behavior include an isolated doubly degenerate ground microstate, with easy axis anisotropy, i.e. dominated by a large m component. Compared to d-block metals, many lanthanoid(III) ions possess a large magnetic moment and a significant orbital angular momentum that gives rise to the magnetic anisotropy. Moreover, the energy splitting of 4fions affords J multiplets arising from the spin-orbit coupling, that are further split by the crystal field (CF) into m, microstates.

It is well established that the local lanthanoid(III) coordination geometry and symmetry are crucial considerations for the design of complexes with these features. The choice of a suitable ligand environment thus depends on the oblate or prolate nature of the quadrupole moment of the f-electron cloud of the lanthanoid(III) ion corresponding to the highest m value. For instance, to minimize the repulsion between ligand electrons and the f-electron cloud of oblate ions like trivalent Ce, Pr, Tb, Dy, a high density of ligand electrons along the local lanthanoid(III) symmetry axis can maximize the magnetic anisotropy of the complex.

Supporting information for this article is given via a link at the end of the document.

[a] Dr. E. Rousset, Dr. M. Piccardo, Dr. R. W. Gable, Dr. A. Soncini, Assoc. Prof. C. Boskovic
School of Chemistry
University of Melbourne
Victoria 3010, Australia
E-mail: c.boskovic@unimelb.edu.au

[b] Dr. M. E. Boulon, Prof. L. Sorace
UnI/R INSTM and Department of Chemistry “U. Schiff”
University of Florence
50019 Sesto Fiorentino (FI), Italy

Fuller details and information for this article are given via a link at the end of the document.
KDs. The magnetization can then relax via three temperature-dependent pathways: (i) direct relaxation within the lowest KD, (ii) Orbach relaxation, involving higher energy KDs, and (iii) Raman relaxation, involving a virtual intermediate state. As the Orbach process involves higher energy microstates, it is usually characterized via an effective energy barrier ($U_{\text{Orb}}$), as well as the infinite-temperature relaxation time ($\tau_0$). In the past, the dynamics of numerous Ln-SMMs have been described primarily in terms of an Orbach mechanism; however, the effective energy barrier to magnetization reversal, $U_{\text{Orb}}$, determined by fitting measured relaxation times to an Arrhenius expression, is frequently less, and in some cases much less, than the relevant energy gap determined by spectroscopy and/or calculations.[11] It is now recognized that the dynamic behavior of many Ln-SMMs is more complex and the resulting temperature dependence of the relaxation rate is a combination of the different dependencies of the above mentioned processes.[9a, b]

Moreover, lattice-related processes can also be highly influential, including phonon bottleneck effects at low temperatures. A phonon bottleneck is due to inefficient exchange between the spins and the thermal bath mediated by low-frequency phonons, with the resulting slowing down of the relaxation process.[12] This is an environmental effect that depends both on the crystallite size and on the concentration of paramagnetic ions, and is particularly relevant when the relaxation occurs through the direct process, which involves low energy resonant phonons. However, these processes have generally been neglected in the quantitative modeling of the relaxation of Ln-SMMs.

Elucidating the roles of the multiple processes involved in the relaxation of the magnetization will ultimately allow optimization of SMM performance. Achieving the requisite understanding of SMM relaxation necessarily relies on a multipronged approach that combines magnetic, spectroscopic and theoretical analysis of SMMs and compounds that exhibit slow magnetic relaxation.

According to the electrostatic approach outlined above,[6,7] a suitable electronic structure to engender SMM behavior might be anticipated for an oblate lanthanoid(III) ion with a neutral O6-donor suitable electronic structure to engender SMM behavior might be Nd(III) and Dy(III) included in crown ethers, along with analogues with larger crown-ether ligands and their derivatives.[18b, 20] Dynamic relaxation of Ln-SMMs.

Results and Discussion

Synthesis

The reaction of lanthanoid(III) nitrate salts with 18-crown-6 and deprotonated tetrahalocatechol (X2Cat$^2-$ where $X = \text{Cl, Br}$) affords neutral mononuclear complexes of general formula $[\text{Ln}(18\text{-c-6})(X_4\text{Cat})(\text{NO}_3)]$.[13] $\text{ClO}_4^-$, $\text{CF}_3\text{COO}^-$, or SCN$^-$[17] as well as with smaller or larger crown-ether ligands and their derivatives.[16a, 18] Dynamic magnetic studies were conducted on Ln/crown-ether systems where the crown-ether acts as a capping ligand,[23] however, it is only recently that Kajiwara[22] and Zheng[22d] reported SMM behavior for complexes of the earlier lanthanoids (Ce$^{3+}$, Pr$^{3+}$ and Nd$^{3+}$) and Dy$^{3+}$ included in crown ethers, along with analogues with aza-functionalized crown ether ligands.

The aim of the present work was to explore more complicated co-ligands with the proven 18-crown-6 and thus modulate the lanthanoid coordination environment by incorporating a dianionic $\alpha$-catecholate ligand in an axial position. We report herein the resulting families of $[\text{Ln}(18\text{-c-6})(X_2\text{Cat})(\text{NO}_3)]\cdot\text{MeCN}$ compounds, where $X = \text{Cl}$ gives the tetrachlorocatecholate 1-Ln series (with Ln = La (1-La), Ce (1-Ce), Nd (1-Nd), Gd (1-Gd), Tb (1-Tb) and Dy (1-Dy)) or $X = \text{Br}$ for the tetrabromocatecholate series 2-Ln (with Ln = La (2-La), Ce (2-Ce), Nd (2-Nd), Gd (2-Gd), Tb (2-Tb) and Dy (2-Dy)). While most Ln-SMMs are based on Dy and Tb, calculations performed on model cerium(III) complexes indicate the possibility of achieving high energy barrier Ce-SMMs in the presence of high symmetry and a suitable ligand environment.[23] This is important as cerium is one of the most abundant lanthanoid metals, although examples of slowly relaxing Ce(III)-compounds are relatively scarce.[24] With this in mind, we investigated the range of lanthanoid metals and indeed observed slow magnetization relaxation for various lanthanoid complexes in the series. For these species, we have demonstrated the dominance of Raman rather than Orbach relaxation. Furthermore, upon reducing dipolar effects by dilution of the Dy analogue, we have identified an unusual phonon bottleneck effect at low temperature, which, to the best of our knowledge, has been included for the first time in a quantitative model of the magnetic relaxation.

Scheme 1. Synthetic pathway to the formation of $[\text{Ln}(18\text{-c-6})(X_2\text{Cat})(\text{NO}_3)]$
All tetrachlorocatecholate compounds are colorless, while the tetrabromocatecholate compounds are yellow. The compounds are obtained as the trivalent lanthanoid complexes, although the dark color of the mother liquor from the cerium reactions suggests oxidation to a cerium(IV) species in solution, as reported previously for Ce complexes with dioxolene ligands. Attempts to crystallize the cerium(IV) byproduct affords dark purple oils instead. The formation of this byproduct is likely responsible for the lower yield of around 40% obtained for the Ce analogues, as well as the necessity for increased reflux time in this case. To the best of our knowledge, compounds 1-Ce and 2-Ce are the first structurally-characterized Ce-dioxolene complexes with cerium(III) rather than cerium(IV). The rapid crystallization of the neutral complex and incorporation of electron-withdrawing substituents on the dioxolene ligands appears to inhibit in situ oxidation of either metal or ligand in the isolated complex. The other lanthanoid analogues are obtained with yields in the range 60-95%. The yield decreases from left to right across the period, due to the weaker interaction between the smaller lanthanoid(III) ions and the 18-crown-6 ligand. In fact, for the later lanthanoids Ho, Er and Yb, the synthesis yields only the previously reported cocrystallized of 18-crown-6 and [Ln(NO3)3(H2O)3].

One molecule of acetonitrile cocrystallizes with the lanthanoid complexes for all 1-Ln and 2-Ln compounds. Microanalyses and thermogravimetric analyses (Figures S1 and S2) of bulk samples indicate the solvation is maintained. The purity of the bulk compounds was also confirmed by X-ray powder diffraction (Figures S3 and S4). The compounds 1-Ln and 2-Ln are insoluble in all common solvents, preventing any solution characterization.

Investigation of the magnetic properties required dilution of the Tb and Dy complexes into diamagnetic hosts (see later). Typically, isomorphous yttrium compounds are employed; however, the size-constraining effect of the 18-crown-6 prevents the formation of yttrium analogues of the present compounds, restricting our choice to La as a host. The percentage of dilution obtained by ICP-OES (Table S1) is consistent with magnetometry data (Figure S5) and confirmation that the dilution occurs within each crystal comes from EPR studies.

Structure description

Compounds 1-Ln (Ln = La, Ce, Nd, Gd, Tb and Dy) crystallize as an isomorphous series in the triclinic space group P-1 (Table S2). Due to the lower solubility of the tetrabromocatecholate analogues, the 2-Ln series crystallizes more rapidly, which affords higher yields but poorer diffracting single crystals. A tendency to form twinned crystals is also apparent. Although a well-diffracting single crystal of a 2-Ln compound has proved elusive, it was possible to perform single crystal X-ray diffraction data (Figure S3). To reduce the size of the crystals mounted, and potentially avoid twinning, we attempted to obtain a better 2-Ln dataset using synchrotron radiation for 2-Ce (Table S3). Although overcoming the radiation damage was successfully achieved by collecting at a lower energy, the quality of the structure solution was no better than that for 2-La. Compounds 2-La and 2-Ce are isomorphous and the lanthanoid complex is approximately isostructural to the tetrachlorocatecholate analogues of 1-Ln. These poor-quality structures allowed the identification of the atom connectivity of the 2-Ln series as per 1-Ln and the generation of calculated powder diffraction patterns (Figure S4). Powder diffraction data for the remaining analogues of 2-Ln indicate that they are isomorphous with 2-Ce.

![Figure 1. Ball and stick structural representation of the lanthanoid(III) complexes in 1-Ln (top) and 2-La (bottom) and the sphenocorona coordination polyhedron around the lanthanoid centers (center); hydrogen atoms have been omitted for clarity. Color code: Ln (pink), O (red), N (Blue), C (black), Cl (green), Br (orange).](https://example.com/figure1)

The lanthanoid centers in 1-Ln are 10-coordinate for all complexes. Continuous shape measurements performed with the Shape 2.1 software suggest that the coordination geometry is best described as a sphenocorona (Figure 1 and Table S4), with approximate C2, point symmetry, which is among the rarest for 10-coordinated lanthanoid species. The Shape distortion parameters for 1-Ln are in the range 2.104–3.015, where the further the value is from zero, the greater the distortion from ideal geometry. The six O atoms from the crown-ether occupy the nominal (bent) equatorial plane and the four O atoms from the catecholate and nitrate ligands occupy the axial sites. Due to the difference in steric hindrance of the two apical ligands, the crown ether shows a distortion toward the nitrate anion and the eclipsed disposition of the axial ligands is characterized by a dihedral angle of 77.68(5)° between the two respective planes of inclusion. The lanthanoid contraction is evident in the variation of the Ln-O distances throughout the series, which decrease from 2.361(3)-2.698(3) Å for 1-La to 2.234(4)-2.657(3) Å for 1-Dy (Table S5). The trivalent oxidation state of the cerium center was confirmed by Bond Valence Sum (BVS) analysis (Table S6).
For all compounds, the acetonitrile molecule of crystallization is situated in a solvent accessible void, where it can adopt different orientations, two of which have been modeled for all compounds. Around this void, the crystal structures exhibit disorder, localized mainly on two adjacent methylene groups of the 18-crown-6 as well as the nitrate anion. Examination of the crystal packing of 1-Ln (Figure S6 to S8) sees the lanthanoid complexes oriented in a head to tail arrangement along the c axis (Figure S8), with no particular supramolecular interactions evident. The shortest intermolecular distance between lanthanoid centers is ~7.9 Å (Table S5). Although the term isostructural is used throughout this work, it must be noted that the Shape parameters calculated for the complexes of the larger, early lanthanoids 1-La and 1-Ce, are very close for the tetradecahedral and sphenocorona coordination geometries (Table S4). However, the infrared spectra (Figure S9 and S10) are essentially superimposable for all analogues within each 1-Ln or 2-Ln family, providing further evidence for the isostructural nature of the metal complexes.

Static Magnetic Properties

The static magnetic susceptibility data of both 1-Ln and 2-Ln families were measured as a function of temperature with an applied field of 0.1 T (2-40 K) and 1 T (40-300 K). The thermal dependence of the $\chi_M T$ products, where $\chi_M$ is defined as the molar magnetic susceptibility, are presented in Figure 2 for compounds 1-Ce, 1-Nd, 1-Tb and 1-Dy, ESI Figure S11 for the tetrabromocatecholate equivalents 2-Ce, 2-Nd, 2-Tb and 2-Dy and Figure S12 for the two gadolinium analogues 1-Gd and 2-Gd. The $\chi_M T$ profiles for each of the pairs of 1-Ln and 2-Ln analogues are in very close agreement in all cases (Figure S13), indicating similar CF effects arising from the tetrachloro- and tetrabromocatecholate ligands. The room temperature values of

**Figure 2** Static magnetic susceptibility data (black dots) and ab initio calculated profiles (red lines) for 1-Ce, 1-Nd, 1-Tb and 1-Dy. Inset: magnetization data at the indicated temperatures (black data points) and ab initio calculated profiles (red lines).
the \( \chi T \) products are 0.69/0.72, 1.49/1.50, 7.89/7.88, 11.51/11.30 and 13.50/13.48 cm\(^3\) K mol\(^{-1}\) for 1-Ce/2-Ce, 1-Nd/2-Nd, 1-Gd/2-Gd, 1-Tb/2-Tb and 1-Dy/2-Dy, respectively, consistent with the expected free-ion values of 0.80, 1.64, 7.87, 11.82 and 14.17 cm\(^3\) K mol\(^{-1}\) for Ce\(^{III}\), Nd\(^{III}\), Gd\(^{III}\), Tb\(^{III}\) and Dy\(^{III}\) ions. The \( \chi T \) products for 1-Gd and 2-Gd are essentially constant across the temperature range (Figure S12), as expected for spin-only Gd\(^{III}\) states. The \( \chi T \) products of all other compounds decrease as the temperature decreases, either due to the thermal depopulation of the energy levels split by the CF or the presence of a relevant temperature dependent paramagnetism (TIP) contribution (resulting \( \chi T \) will decrease with \( T \)), while the Curie contribution from the lowest energy level remains constant (assuming it is reasonably well-isolated).

Isothermal field-dependent magnetization data were collected at 1.9, 2.5 and 4.5 K with applied fields up to 50 kOe (insets, Figures 2 and ESI Figure S11 and S12). At 1.9 K in the maximum field of 5 T, the magnetization curves of the complexes of the early lanthanoids, Ce and Nd, do not saturate, in contrast to the curves for the later lanthanoids analogues Gd, Tb and Dy. Qualitatively, the lack of saturation for the early lanthanoids is consistent with a relatively large TIP contribution, while saturation for Tb and Dy derivatives is indicative of well isolated ground states.

**Ab Initio Studies**

As compounds 1-Ln and 2-Ln exhibit very similar magnetic behavior, **ab initio** calculations were performed on the 1-Ln family only, both to reduce the computational cost of the calculations, and because better quality structural data are available for the 1-Ln family. The acetonitrile molecule of solvation was omitted from the calculations (Tables S7-S11). The energy levels and wavefunction compositions calculated for 1-Ln are available in the ESI (Tables S12-S21), together with the \( g \) tensors calculated for the lowest energy levels (ESI Table S22).

The calculated thermal dependence of the \( \chi T \) products and magnetization curves are overall in good agreement with the experimental data (Figure 2), especially for the strongly oblate ground states of 1-Ce, 1-Tb and 1-Dy, while some larger deviations between theory and experiment are observed for the weakly oblate ground state of 1-Nd, for which the subtleties of the CF energy spectrum can be more difficult to describe. Problems with the electronic structure of Nd\(^{III}\) (and in general ions with less than half-filled 4f shells) might arise from a higher sensitivity to covalent effects, especially dynamical correlation with ligand electrons, which is absent from these calculations. Dynamical correlation is known also to be crucial to better describe excited spin-orbit multiplets, which in less than half-filled 4f ions, are lower in energy and hence more amenable to mixing via the crystal field potential. This is a problem that should affect Ce\(^{III}\) to a lesser extent, given its single 4f electron. The computational results show in fact that the CF splitting of the (2J+1)-fold degeneracy of the ground multiplets in 1-Ce, 1-Nd, 1-Tb and 1-Dy, always stabilizes a (quasi)degenerate (pseudo)doublet ground state dominated by maximal angular momentum projection (\( m_J = \pm J \)), and a well-separated first excited (pseudo)doublet with \( (m_J = \pm (J-1)) \) (Figure 3 and Table 1). In 1-Gd, as expected, mixed spin-orbit and CF effects remove the pure spin degeneracy of \( S = \frac{5}{2} \) only in second order, resulting in much smaller energy splittings, which are described by the **ab initio** calculations only when excited CF-split Russell-Saunders terms with non-zero orbital angular momentum \( L \) are allowed to mix with the ground term via spin-orbit coupling (see computational experimental section). The ground KDS of 1-Ce (\( m_J = \pm \frac{5}{2} \)), 1-Gd (\( m_J = \pm \frac{7}{2} \)), and 1-Dy (\( m_J = \pm \frac{15}{2} \)) are calculated to be close to pure \( m_J = \pm J \) states (Figure 3 and Tables S17-21). The respective effective \( g^{eff} \) values calculated within the pseudo-spin \( S = \frac{5}{2} \) formalism, present relatively small transverse components (\( g_x^{eff} \) and \( g_y^{eff} \) smaller than 0.5 for 1-Ce, smaller than 0.020 for 1-Gd and 1-Dy), and \( g_z^{eff} \) axial components (3.843, 13.943, and 19.795 for the three ions) close to the values expected for a pure \( m_J = \pm J \) K D (4.286, 14 and 20). The magnetic anisotropy easy-axis orientation is calculated to be almost coincident with the Cl\(_4\)Cat-Ln-NO\(_3\) axis (Figure 4).

Since Tb\(^{III}\) is not a Kramers ion, the lowest doublet of 1-Tb forms a ground pseudo-KD featuring a tunneling gap of \( \Delta E = 0.09 \) cm\(^{-1}\), with \( g_x^{eff} = 0 \) components and a \( g_y^{eff} \) component equal to 17.874 (cf. \( g_y^{eff} = 18 \) for a pure \( m_J = \pm 6 \) ground doublet). The orientation is again coincident with the Cl\(_4\)Cat-Tb-NO\(_3\) axis, consistent with the oblate character of the Tb\(^{III}\) ion and the ligand charge distribution. The \( m_J \) decomposition of the corresponding wave functions accordingly shows the ground pseudo-doublet to be dominated by a superposition of the \( m_J = \pm 6 \) Ising states.

On the other hand, the ground state of 1-Nd, while dominated by the maximal angular momentum component \( m_J = \pm \frac{5}{2} \), features sizeable contributions from a mixture of different \( m_J \) states, where the largest contributions come from \( m_J = \pm \frac{7}{2} \) and \( m_J = \pm \frac{15}{2} \) components (Figure 3). This mixing leads to a low axial anisotropy, with a \( g_x^{eff} \) tensor for the 1-Nd ground KD characterized by relatively large transverse components \( g_y^{eff} = 0.876 \), \( g_z^{eff} = \).
2.124, and a relatively low axial component \( g_{z}^{\text{eff}} = 4.103 \) with respect to \( g_{z}^{\text{eff}} = 6.545 \) for a pure \( m_J = \pm 9/2 \) level. Not surprisingly, the orientation of the main magnetic \( z \) axis significantly diverges from the ClC4Cat-Nd-NO3 axis found for the other four compounds, by an angle of about 28 degrees (Figure S15).

Overall, the (quasi)-degenerate \( m_J = J \) (pseudo) doublet, and first excited \( m_J = J-1 \) (pseudo) doublet, as determined by \textit{ab initio} calculations, are consistent with the \( \chi_{MT} \) (Figure 2 and S11) decrease with the temperature due to TIP contribution. The \( \chi_{MT} \) values obtained at the lowest measured temperatures of 2 K are all non-zero, corresponding to an almost pure Curie contribution with a small TIP correction.

<table>
<thead>
<tr>
<th>Compound</th>
<th>KD</th>
<th>Energy / cm(^{-1})</th>
<th>( g_x^{\text{eff}} )</th>
<th>( g_y^{\text{eff}} )</th>
<th>( g_z^{\text{eff}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Ce</td>
<td>1</td>
<td>0.0</td>
<td>0.262</td>
<td>0.402</td>
<td>3.843</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(&lt;0.5)[^a]</td>
<td>(0.81 \pm 0.01)[^a]</td>
<td>(3.590 \pm 0.005)[^a]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>443.0</td>
<td>1.035</td>
<td>1.415</td>
<td>2.159</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>891.7</td>
<td>0.726</td>
<td>1.015</td>
<td>3.485</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2369.4</td>
<td>1.446</td>
<td>2.492</td>
<td>4.593</td>
</tr>
<tr>
<td>1-Nd</td>
<td>1</td>
<td>0.0</td>
<td>0.876</td>
<td>2.124</td>
<td>4.103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.727 \pm 0.005)[^a]</td>
<td>(2.01 \pm 0.01)[^a]</td>
<td>(3.850 \pm 0.002)[^a]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>94.0</td>
<td>0.352</td>
<td>0.631</td>
<td>4.887</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>224.2</td>
<td>0.442</td>
<td>1.284</td>
<td>5.005</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>408.0</td>
<td>0.312</td>
<td>1.917</td>
<td>3.893</td>
</tr>
<tr>
<td>1-Gd</td>
<td>1</td>
<td>0.0</td>
<td>0.010</td>
<td>0.012</td>
<td>3.943</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.589</td>
<td>0.596</td>
<td>0.681</td>
<td>9.786</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.966</td>
<td>5.333</td>
<td>5.250</td>
<td>4.824</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.258</td>
<td>0.996</td>
<td>2.042</td>
<td>12.730</td>
</tr>
<tr>
<td>1-Tb</td>
<td>1</td>
<td>0.0 / 0.1</td>
<td>0.000</td>
<td>0.000</td>
<td>17.874</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(&lt;17.7\pm0.2)[^a]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>169.5/170.6</td>
<td>0.000</td>
<td>0.000</td>
<td>14.663</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>334.7/349.9</td>
<td>0.000</td>
<td>0.000</td>
<td>11.218</td>
</tr>
<tr>
<td>1-Dy</td>
<td>1</td>
<td>0.0</td>
<td>0.012</td>
<td>0.017</td>
<td>19.795</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>251.1</td>
<td>0.276</td>
<td>0.420</td>
<td>16.805</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>380.8</td>
<td>1.291</td>
<td>1.526</td>
<td>13.525</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>497.5</td>
<td>3.784</td>
<td>5.864</td>
<td>9.431</td>
</tr>
</tbody>
</table>

\[^a\] From EPR Spectroscopy.

EPR Spectroscopy

Electron Paramagnetic Resonance (EPR) spectroscopy is a powerful technique to obtain information about the magnetic anisotropy of the ground doublet (or pseudo-doublet for non-Kramers ions) of lanthanoid complexes.\[^{9d, 11b, 32}\] The response of the ground doublet to the applied field can be modeled using an effective Zeeman Hamiltonian, for which the determined anisotropic \( g \)-values contain encoded information about the composition of the ground wave function. In the present work, we used EPR, both for an independent determination of the low temperature magnetic anisotropy of the complexes, and to provide additional independent experimental data to assess the accuracy of the \textit{ab initio} results. In all cases measured (Figure 5 and S16) analogues of both 1-Ln and 2-Ln exhibited very similar spectra, consistent with the very similar electronic structures of the two systems. Except when otherwise stated, simulations were performed on the 1-Ln series to provide a more direct comparison with calculations.
Compounds 1-Ce and 2-Ce. The experimental EPR spectra of the cerium analogues measured at low temperature (10 K) show a clear parallel-type transition at low field and a much broader one at higher field (Figure 5, top left). Given the absence of Ce isotopes with non-zero nuclear spin, a simulation of the spectrum was then performed on the basis of the $S^{\text{eff}} = \frac{1}{2}$ effective spin Hamiltonian:

$$\hat{H}_{\text{eff}} = \mu_B \mathbf{B} \cdot \mathbf{S}^{\text{eff}}$$

(1)

The simulation parameters that provided the best agreement with the experimental spectrum were $g_x^{\text{eff}} < 0.5$ (not visible), $g_y^{\text{eff}} = 0.81 \pm 0.01$ and $g_z^{\text{eff}} = 3.590 \pm 0.005$. When compared with the results of \textit{ab initio} calculations (i.e. 0.262, 0.402, and 3.843), it is evident that the dominant easy axis nature of the complex is confirmed. However, the measured axiality of the ground doublet, estimated as the difference between $g_z^{\text{eff}}$ and the average of $g_x^{\text{eff}}$ and $g_y^{\text{eff}}$, is smaller than calculated. At the same time the experimental rhombicity is more than three times higher than calculated.

Compounds 1-Nd and 2-Nd. The experimental EPR spectra of 1-Nd and 2-Nd show the clear features of a completely rhombic system (Figure 5, top right). A set of peaks is observed below 200 mT which can be attributed to parallel transitions of different Nd isotopes. The main peak at 175 mT is due to the even isotopes of Nd ($I = 0$, natural abundance 79.5%) while the satellite ones arise as a consequence of hyperfine coupling with $^{143}$Nd and $^{145}$Nd nuclear spins (both with $I = 7/2$). The hyperfine structure is only partially visible in the second feature centered at about 330 mT, while it is completely lost for the high field feature. According to this interpretation, the simulation of the spectrum was performed taking into account the natural abundance of the three isotopes on the basis of the effective Hamiltonian:
\[ \hat{H}_{\text{eff}} = \mu_B \mathbf{B} \cdot \mathbf{g}^{\text{eff}} \cdot \mathbf{S}^{\text{eff}} + \hbar \mathbf{1} \cdot \mathbf{A}^{\text{eff}} \cdot \mathbf{S}^{\text{eff}} \]  

(2)

where \( \mathbf{A}^{\text{eff}} \) is the effective anisotropic hyperfine coupling tensor between the nuclear spin \( I \) and the effective \( \mathbf{S}^{\text{eff}} = \frac{1}{2} \mathbf{I} \) of the ground doublet. A good reproduction of the experimental data was obtained with \( g_z^{\text{eff}} = 0.728 \pm 0.005 \), \( g_x^{\text{eff}} = 2.01 \pm 0.01 \), \( g_x^{\text{eff}} = 3.850 \pm 0.002 \) and \( A_x^{\text{eff}} = 500 \pm 200 \text{ MHz} \), \( A_y^{\text{eff}} = 700 \pm 200 \text{ MHz} \) and \( A_z^{\text{eff}} = 1250 \pm 10 \text{ MHz} \) for both \(^{145}\text{Nd}\) and \(^{147}\text{Nd}\) isotopes. The relatively large uncertainty over the \( x \) and \( y \) components of the effective hyperfine coupling reflects the broadness of the corresponding transitions. The effective \( g \) values of the ground doublet obtained by spectral simulation are in good agreement with (if slightly smaller than) those estimated from \textit{ab initio} calculations (i.e. \( g_z^{\text{eff}} = 0.876 \), \( g_x^{\text{eff}} = 2.124 \), and \( g_y^{\text{eff}} = 4.103 \)), so that the mixed-\( m_I \) character of the ground state wave function, as in the case of \( \text{Ce}^{3+} \), is supported by these experimental observations.

**Compounds 1-Gd and 2-Gd.** Gadolinium(III), as an \( ^{8}\text{S}_{7/2} \) ion with no first order angular momentum due to its half-filled \( 4f \) shell, is well known to show very different EPR behavior to that of the other \( \text{Ln}^{3+} \) ions. Indeed, its spectra are often visible even at room temperature, and are much richer than those of the anisotropic lanthanoid(III) ions, due to zero-field splitting of the \( S = 7/2 \) which arises as a second-order perturbation of the electronic structure and is thus quite small (\(< 0.3 \text{ cm}^{-1} \)). The EPR spectra of 1-Gd and 2-Gd are no exception: the X-band spectra are characterized by a large number of transitions extending from zero-field to 1 T and beyond. Given the complexity of the X-band spectrum (Figure S16), a high frequency \( W \)-band EPR spectrum was recorded at 15 K on 2-Gd (Figure 5, bottom left) with the aim of simplifying the analysis by going toward the high-field.\(^{[33]}\)

This \( W \)-band spectrum is characterized by a clear series of almost equispaced (\( \Delta B = 300 \text{ mT} \)) transitions and by a strong, isotropic transition around \( g_{\text{iso}} = 2.00 \) (\( B = 3300 \text{ mT} \)). Furthermore, a series of weak forbidden transitions is observed close to \( g_{\text{iso}} = 4.00 \) (\( B = 1650 \text{ mT} \)). This behavior is typical for a largely rhombic system with a zero-field splitting parameter estimated by the line separation as \( 2D \sim (\Delta B/g_{\text{iso}}) \sim 0.28 \text{ cm}^{-1} \). Following these considerations, the experimental data were reproduced on the basis of the following spin Hamiltonian:

\[ \hat{H}_{\text{cd}} = \mu_B g_{\text{iso}} \mathbf{B} \cdot \mathbf{S} + D \mathbf{S}_z^2 + E \left( \mathbf{S}_z^2 - \mathbf{S}_x^2 \right) + B_x \mathbf{S}_x^0 + B_z \mathbf{S}_z^0 \]  

(3)

where \( D \) and \( E \) are the second order axial and transverse zero-field splitting parameters, respectively, and \( B_x^0, B_z^0 \) is the axial fourth order anisotropy expressed in terms of Stevens operators.\(^{[34]}\) The best simulation was obtained with the parameters \( g_{\text{iso}} = 1.995 \pm 0.002 \), \( D = -0.150 \pm 0.005 \text{ cm}^{-1} \), \( E = 0.045 \pm 0.005 \text{ cm}^{-1} \) and \( B_x^0 = -22 \pm 2 \text{ cm}^{-1} \).

From the \textit{ab initio} wave function for 1-Gd, the estimated zero-field splitting parameters are \( D = -0.10 \text{ cm}^{-1} \) and \( E = 0.01 \text{ cm}^{-1} \), which are in quite good agreement with those determined from EPR results, with absolute differences between experimental and calculated values smaller than \( 10^{-1} \text{ cm}^{-1} \). However, also in this case, \textit{ab initio} calculations partially underestimate the degree of rhombicity, since \( \lambda = E/D = 0.13 \) and 0.3 for calculated and experimental values, respectively.

**Compounds 1-Tb and 2-Tb.** The X-band EPR spectra of both 1-Tb and 2-Tb, measured at 10 K, show a broad absorption extending over 200 mT (Figure 5, bottom right). To reduce the dipolar interactions between neighboring molecules, which we supposed to be at the origin of the broad linewidth, we measured the spectrum of a dilute 2-Tb@La for which the level of doping was estimated by dc magnetic measurements and ICP-OES as 7.93 (Tb:La) (Table S1 and Figure S5). For this sample four almost equispaced resonances, centered at a field corresponding to an effective \( g_z^{\text{eff}} = 4.5 \) and with line-line separation of ca. 25 mT is observed. This type of spectrum has been previously reported for Tb(III) inorganic systems\(^{[35]}\) and can be related to the coupling of a ground pseudo-doublet of essentially \( m_J = \pm 6 \) nature with the \( J = 3/2 \) nuclear spin of \(^{159}\text{Nd} \) (nat. ab. = 100 %) (Figure S17). The observation of a spectrum centered at such high effective \( g \) values \( g_z^{\text{eff}} \) is a signature of the fact that the system is indeed not perfectly axial, since in the latter case the transition probability would be zero and no spectrum would be observed. The formation of a ground pseudo-doublet, hyperfine split in 2-Tb@La, is further confirmed by the fact that by measuring in parallel polarization, \( i.e. \) with the microwave magnetic field \( (B_{\text{mw}}) \) parallel to the static \( (B_0) \), one, a more intense spectrum is detected (Figure 5, bottom right). This indicates that the levels among which resonance occurs are not completely orthogonal and thus a gap between them is expected, since in this setup the selection rule is \( \Delta m_J = 0 \). Such spectra were interpreted in literature\(^{[26]}\) on the basis of an effective pseudo-doublet Hamiltonian taking into account the zero-field gap induced by transverse anisotropy:

\[ \hat{H} = \mu_B g_x^{\text{eff}} \mathbf{S}_x \cdot \mathbf{B}_z + \delta \mathbf{S}_x + h A_x^{\text{eff}} \mathbf{S}_x^{\text{eff}} \]  

(4)

where \( \delta \) expresses the zero-field induced gap by the transverse anisotropy terms, which are also responsible for the lowering of \( g_z^{\text{eff}} \) from the value of 18 expected for a pure \( m_J = \pm 6 \) state. Thus, from a qualitative point of view, the observed EPR spectra for 2-Tb@La confirms the findings from \textit{ab initio} calculations for 2-Tb: a ground pseudo-doublet characterized by a large \( g_z^{\text{eff}} \) (ca. 17.5) and a small, but crucial, non-zero transverse component.

To more accurately test the agreement of \textit{ab initio} calculations with the experimental results, we simulated the EPR spectra\(^{[36]}\) assuming the following Hamiltonian:

\[ \hat{H}_{\text{TB}} = \mu_B \mathbf{J} \cdot \mathbf{B} + \hbar J_I \cdot \mathbf{I} + \sum_{k,l=2,3} \alpha_{kl} B_k^2 \mathbf{I}_z^2 \]  

(5)

where \( J = 6 \), \( g_I = 3/2 \), \( I = 3/2 \) and \( \mathbf{S}_x^0, \mathbf{S}_y^0 \) are Stevens’ operators expressed in terms of the global angular momentum \( J \). We neglected the quadrupolar interaction for the sake of simplicity. To reduce the number of parameters, we only considered \( B_x^2 \) and \( B_y^2 \) and fixed \( B_z^2 = 5 \text{ cm}^{-1} \). In agreement with \textit{ab initio} calculations, this set of parameters provides an \( m_J = \pm 6 \) ground state with a separation of 165 cm\(^{-1} \) from the first excited state, and a zero field gap in the absence of hyperfine interactions of ca. 0.1 cm\(^{-1} \) (ESI Figure S17). In this framework, the only adjustable parameter is \( A_x \), the hyperfine coupling constant: nice spectral simulations (Figure 5, bottom right) were achieved using a single set of parameters for spectra measured in the two microwave
polarizations, by assuming $A_2 = 470$ MHz, in line with expected values.\cite{34} It is worth stressing that the quality of the simulation is not much affected as long as the ground pseudo-doublet is predominantly $m_I = \pm 6$ with a first excited pseudo-doublet lying at an energy higher than 40 cm$^{-1}$, but it is strongly dependent on the magnitude of the zero-field gap, which needs to be lower than 0.2 cm$^{-1}$. As a whole, the analysis of the spectra of the Tb derivatives provides quantitative confirmation of the results of ab initio calculations.

### Dynamic Magnetic Properties

Dynamic magnetic susceptibility studies were performed on the Ce$^{III}$, Nd$^{III}$, Tb$^{III}$ and Dy$^{III}$ analogues of both tetrachloro- and tetrabromocatecholate families to explore possible SMM behavior (Figure 6 and ESI Figures S18 to S27). The ab initio calculated CF splitting and $g$ tensors for 1-Ce and 1-Dy suggested that the Ce$^{III}$ and Dy$^{III}$ analogues might be particularly promising in this regard. However, in the absence of an applied dc field, no out-of-phase signal was observed for any of the compounds, possibly due to QTM promoted by dipolar interactions. The optimum dc field to suppress such relaxation pathways was determined for each compound at a temperature of 2 or 5 K by varying the field from 0 to 2000 Oe. All eight compounds 1-Ce, 2-Ce, 1-Nd, 2-Nd, 1-Tb, 2-Tb, 1-Dy, 2-Dy exhibit a non-zero imaginary susceptibility $\chi''$ under an optimum dc field ($B_{OC}$). Alternating current susceptibilities as a function of frequency were measured at different temperatures for each compound in the presence of the optimum dc field. When possible, the frequency-dependent $\chi''$ were fit to the Debye equation to obtain the characteristic relaxation time ($\tau$) and lifetime distribution ($\sigma$) at each temperature (Table S23). The temperature dependence of the resulting relaxation times was rationalized on the basis of multiple relaxation processes given in the equation:\cite{22}

$$\chi'' = \sigma^{-1} \exp\left(-\frac{U_{Ober}}{k_B T}\right) + C \tau'' + AT + \tau_{QTM}^{-1}$$

where $\sigma$ is the pre-exponential factor and $U_{Ober}$ the effective energy barrier of an Orbach process, $C$ and $n$ are the Raman constants. $A$ is the direct relaxation parameter (which is suppressed in zero applied field) and $\tau_{QTM}$ is the QTM relaxation time, which was assumed to be zero in the presence of the applied dc field (Table 2).

### Compounds 1-Ce and 2-Ce.

Alternating current susceptibility data for 1-Ce and 2-Ce are essentially independent of the intensity of the applied dc field (Figure S18) when it is non-zero. This suggests low efficiency of direct relaxation processes (which are linearly dependent on field) and a rapid quench of the QTM. The temperature (2 to 4.3 K) and frequency (0.1 to 1000 Hz) dependence of the ac susceptibility were measured under fields of 1500 and 800 Oe for 1-Ce and 2-Ce, respectively (Figure 6 and Figure S19). For 1-Ce, the Arrhenius plot (Figure S20) is non-linear across all temperatures, excluding purely Orbach relaxation. With this in mind, the fit of the temperature dependence was achieved by fixing the QTM and Orbach terms to zero and including only direct and Raman-type relaxation (Figure S21). Parameter $C$ was evaluated at 1.22 ± 0.03 s$^{-1}$ K$^{-1}$ with $n$ fixed at 5 (when left to vary, the fit gave a value very close to 5), and $A$ determined as 31.9 ± 1.5 s$^{-1}$ K$^{-1}$. The large energy gap between the lowest energy KDs from ab initio calculations is not evident from the experimental relaxation data. Including an Orbach pathway by fixing $U_{Ober}$ at 637 K, which corresponds to the 443 cm$^{-1}$ energy splitting obtained from ab initio calculations, does not affect the quality of the fit: indeed, this would provide a relaxation much slower than actually measured in the experimental temperature range. In fact, for both 1-Ce and 2-Ce, a combination of Raman and direct relaxation processes are sufficient to account for the measured relaxation and the second KD does not play a major role in the reversal of the magnetization.

### Compounds 1-Nd and 2-Nd.

Alternating current susceptibility data for 1-Nd and 2-Nd ($T = 2-3.4$ K, $\nu = 0.1-1000$ Hz) also display a frequency-dependence of $\chi''$ in external applied field: although an out-of-phase signal appears at low field, the optimum response is observed at 1200 Oe (Figure S22). In contrast to the Ce system, a continuous increase in the amplitude of the out-of-phase signal is observed, but keeping the peak frequency at around 130 Hz. The $\chi''$ peak maxima occur at higher frequencies than for the Ce analogues (Figure 6 and Figure S23), indicating faster relaxation. For this reason, a satisfactory fit to the Debye model could not be obtained for either 1-Nd or 2-Nd at temperatures higher than 2 K, due to the limitations of our experimental setup ($\nu < 10$ KHz). The faster relaxation observed for the Nd derivatives compared to Ce is consistent with the small energy separations (Figure 3 and Table 1) as well as with the greater rhombicity of the Nd ground state, as determined by both ab initio calculations and EPR spectroscopy. This result is further confirmed by the average matrix elements of the magnetic moments calculated on the ab initio wave functions (Figure S28), which indicate a significantly larger transition probability for 1-Nd (0.50) than for 1-Ce (0.11) for QTM within the ground KD states.
Compounds 1-Dy and 2-Dy. The ac susceptibility data for 1-Dy and 2-Dy ($T = 2-15$ K, $\nu = 0.1-1000$ Hz) were acquired both as a function of applied dc field at 2 K and as a function of temperature with an optimum field of 1500 Oe and found to be similar for the two analogues (Figure 6 and Figure S26 and S27). The zero-field data suggest for both derivatives the existence of a relatively fast ($\nu > 1000$ Hz) process, active at low temperature. On application of the field, this process is clearly quenched, indicating that the magnetic relaxation at zero field occurs via QTM, while a slower one is activated. Such behavior is now quite commonly reported for highly axial Dy SMMs. The frequency-dependence of the out-of-phase susceptibility as a function of temperature measured at the optimum field is characteristic of SMM slow relaxation up to 15 K. Here the maximum of the out-of-phase susceptibility peaks range between 0.1 Hz for $T = 2$ K to 1000 Hz for $T = 15$ K, indicating significantly slower relaxation than those observed for the Ce and Nd analogues. This trend is in agreement with the $ab$ initio results for the ground state QTM probabilities (Figure S28). The fit to the Debye model for each analogue gives a range of $\alpha$ coefficients from 0.028/0.045 (high $T$) to 0.348/0.234 (low $T$) for 1-Dy and 2-Dy, respectively (Table S23), indicating a narrow distribution of relaxation times at high temperature but a wider one at low temperature. Any attempts to reproduce the temperature dependence of $\tau$ for both derivatives using Eq. (6) failed. Notably, the plots of $\tau^{-1}$ vs $T$ on a log-log scale (Figure S29) provides clear evidence for the existence of two different linear regimes with different slopes. We tentatively attribute this behavior to the onset of a phonon bottleneck effect at low temperature, a phenomenon due to the lack of efficient energy exchange between the spins and the thermal bath.\[38\] In the presence of this effect, ac susceptibility actually measures the spin-bath relaxation time. This can be described\[39\] as the sum of the spin-lattice relaxation time $\tau_{SL}$ (which is the quantity actually measured in absence of phonon bottleneck effect) and the lattice-bath one $\tau_{LB}$, weighted for the ratio of the heat capacities of spin ($C_S$) and lattice systems ($C_L$):\[368\]

$$\tau = \tau_{SL} + (C_S/C_L) \tau_{LB}$$  \(7\)
If we assume that $\tau_{SL}$ and $\tau_{LB}$ both follow a power temperature dependence, respectively parameterized by $C$ and $n$, and $B$ and $m$, then the measured temperature dependence of $\tau$ can be modeled as:

$$\tau = C^{-1}T^{-n} + BT^{-m}$$  \hspace{1cm} (8)

This is exactly the behavior that is observed for 2-Dy, with two different linear regimes in the log-log plot (Figure S29). It should however be remarked that different sets of parameters reproduce equally well the experimental data, with $n$ ranging from 1 to 4, and $m$ ranging from 5 to 7.

**Compounds 1-Tb and 2-Tb.** As the only investigated non-Kramers ion of the series, the terbium(III) analogues exhibit a very complicated dependence of the out-of-phase susceptibility on the temperature and the ac frequency after applying a dc field. A broad distribution of relaxation time is evident for 1-Tb, possibly obscuring the existence of distinct relaxation processes, while two overlapping processes are evident or 2-Tb (Figure 6 and Figure S25). It was thus impossible to obtain reasonable fits of the ac data using the Debye model, and further data analysis was then not pursued for the undiluted samples.

**Magnetically dilute samples**

As mentioned above in the crystallographic section, the shortest intermolecular separation between lanthanoid centres is around 7.9 Å, thus with intermolecular dipolar interactions potentially influencing the dynamic magnetic behavior presented above. The lack of out-of-phase susceptibility in the absence of an applied field for any of the compounds, the complicated ac profiles of the terbium analogues and the relatively high values of the $\alpha$ parameters obtained for 1-Dy and 2-Dy at low temperature, prompted us to study samples diluted into diamagnetic hosts to minimize the effects of any dipolar interactions. Further, Eq. (7) indicates that, if a phonon bottleneck effect is active in the pure sample, a reduction of the magnetic ion concentration, which results in a change of $C_I/C_S$, should decrease the observed relaxation time. Two samples of the tetrabromocatecholate compounds 2-Dy@La (10%) and 2-Tb@La (7 %) were then chosen to probe the influence of intermolecular dipolar interactions in such systems, with the degree of doping determined by static magnetic measurements as well as ICP-OES (Table S1 and Figure S5).

The dynamic magnetic behavior was studied for 2-Dy@La and 2-Tb@La at zero applied field and an experimentally determined optimal dc field (Figures 7 and Figure S30-S34). The doping has a significant effect for the Dy compound, with 2-Dy@La exhibiting slow relaxation ($\nu = 10-10000 \text{ Hz}$) up to 20 K in zero-field (Figure 7). Here two regimes are apparent: from 1.9 to 4.5 K, the $\chi''$ peak maxima do not show a temperature-dependence, suggesting relaxation is occurring dominantly via QTM; this confirms literature reports that, despite being reduced compared to the pure sample, intermolecular interactions promoting quantum tunnelling are not completely suppressed at this doping level.\(^{[40]}\) Above 4.5 K, the $\chi''$ peak maxima shift towards higher frequency, indicating the dominant contribution of other, thermally activated, relaxation mechanisms. In contrast, when measurements are performed under an applied external dc field of 4000 Oe, temperature dependence is observed even at the lowest temperature, indicating that QTM is suppressed in the whole temperature range.

![Figure 7.](image-url) Frequency dependence at different temperatures of the out-of-phase susceptibility $\chi''$ data for 2-Dy@La under an applied dc field of 0 Oe (top), or 4000 Oe (bottom). Experimental data are in dots and the lines are the fits to the generalized Debye model.

**Compound 2-Dy@La.** The ac data for 2-Dy@La at 0 and 4000 Oe dc fields (Figures 7 and S34) were fit as described above using the generalized Debye model to obtain a range of $\alpha$ coefficients from 0.091/0.054 (high $T$) to 0.497/0.142 (low $T$) at 0/4000 Oe (Table S23). It can be readily seen that, contrary to what is usually observed, the relaxation rate observed in the doped sample at low temperature is faster than that in the pure sample, lending support to the hypothesis of a phonon bottleneck-controlled relaxation in the non-dilute sample. On the basis of this analysis, the temperature dependent relaxation data were fit using Eq. (6) including only a single Raman term for the in-field
data, and Raman and QTM for the data collected in zero applied field (Figure S35). This consistently provided the following set of best fit parameters: $\tau_{\text{QTM}} = 685 s^{-1}$, and $C = 1.14 \pm 0.08 s^{-1} K^{-n}$, $n = 3.5 \pm 0.2$ for zero-field measurements, and $C = 0.31 \pm 0.28 s^{-1} K^n$ and $n = 3.75 \pm 0.27$ for the in-field data (Table 2). It is worth stressing that inclusion of an Orbach term does not improve the fit at all, which is unsurprising given that, as discussed above for the Ce analogues, the investigated temperature range is much lower than that where Arrhenius-like behavior is expected on the basis of the calculated anisotropy barrier.

**Compound 2-Tb@La.** The doped 2-Tb@La sample does not show any out-of-phase signal in the absence of an external dc field. However, on application of a field, the relaxation behavior is much simpler than that observed for the pure sample, with a single, temperature dependent process for which reliable $\tau$ values could be extracted from the Debye fit up to 10 K (Table S23). The relaxation process was found to be slowest for an optimal dc field of 1600 Oe at 2 K (Figure S30). No evidence of temperature-independent QTM relaxation is observed in this case (Figures S31). In this case again, the presence of an anisotropy barrier, as obtained by ab initio calculations, could not be determined from the ac data. Indeed, the relaxation in this temperature range is dominated by a combination of Raman and direct process with $A = 343 \pm 13 s^{-1} K^{-1}$, $C = 6.57 \pm 1.20 s^{-1} K^n$ and an unrestrained $n$ value of 3.82 \pm 0.09 (Figure S32).

**Unified Relaxation Model**

*Ab initio* calculations, benchmarked by both EPR spectroscopy and dc magnetic susceptibility data, indicate the presence of large axiality and a sizable energy gap for the lowest energy KDS for the Ce, Dy and Tb derivatives of 1-Ln and 2-Ln. These compounds might then be anticipated to exhibit slow magnetic relaxation associated with an Orbach process. A substantial change in dynamic magnetic behavior upon dilution of the Dy and Tb complexes into a diamagnetic host indicates a considerable influence of dipolar intermolecular interactions on the magnetic relaxation. However, despite decreasing the intermolecular interactions by dilution, for none of the samples can the observed slow magnetic relaxation be attributed to an Orbach process. The analysis of the dynamic behavior of the series consistently indicates that, in the relaxation rate range that can be investigated by ac susceptibility, the spin dynamics are dominated by Raman-like processes. Interestingly the value of the Raman exponents obtained for the dilute Tb and Dy derivatives are very similar (3.75 vs 3.86), and lower than predicted by Orbach classic paper on relaxation.[41] This is often observed in molecular complexes and might be attributed to a non-negligible role of the optical phonons in determining the relaxation.[40] At the same time, the importance of the direct process in the Tb derivative is consistent with its non-Kramers nature, which results in a larger gap of the ground pseudo-doublet compared to the Dy system. In this respect we note that, despite the presence of a magnetic anisotropy barrier that could not be directly evidenced by ac susceptibility, the only derivative to show slow relaxation in zero field is the dilute DyII system: this can be related to the strong axiality of its ground KD (compared to the much lower axiality of the Ce and Nd derivatives), the small transition probabilities of the magnetic moment between the two states of the ground KD (Figure S28), and the low natural abundance of isotopes with a non-zero nuclear spin, resulting in inefficient QTM.

On the basis of these observations, we attempted next to develop a comprehensive model based on Eqs. (6-8), to simulate in a unified manner the temperature dependence of the relaxation times for all the undiluted samples (in which we postulate a phonon bottleneck mechanism to be active), in particular 2-Dy, 1-Ce, and 2-Ce. Unfortunately, experimental limitations prohibited the collection of sufficient data to consider the Nd and Tb species. Data for dilute 2-Dy@La are also included in our simulations, to show the high-temperature convergence of the models applied to data for the diluted and undiluted samples, and reveal the role of QTM.

The *ab initio* results can in fact partially guide the development of model Eq. (9). For instance, in the 2-30 K range of temperatures explored, we can exclude from the start any relevance of the Orbach relaxation mechanism for both Dy and Ce complexes, since the *ab initio* energy gaps to the first excited KD calculated for both 1-Ce and 1-Dy greatly exceed these temperatures. Furthermore, as we will see below, our *ab initio* results are also useful (i) to set approximate QTM rates in the models considered here, thus reducing the number of free parameters, and (ii) to make an approximate argument as to why the phonon bottleneck regime can be expected to arise in 1-Ce and 2-Ce at lower temperatures than observed for 2-Dy.

Assuming parameterization of the lattice bath relaxation time $\tau_{\text{LB}}$ as per Eqs. (7 and 8) (i.e. $(C_{\text{m}}/C_{\text{L}}) \tau_{\text{LB}} = B/T^{m}$), and that for the spin-lattice relaxation time $\tau_{\text{SL}}$ as per Eq. (6) but excluding the Orbach process as per our *ab initio* results (i.e. $\tau_{\text{SL}} \approx AT^{n} + CT^{n} + \tau_{\text{QTM}}^{-1}$), we can write a general model for all the diluted (and by extension, for the diluted) samples as:

$$\tau^{-1} = \left( \frac{\theta}{\tau_{\text{m}} + \frac{C^{-1}}{\tau_{\text{m}} + A C^{-1} T + A C^{-1} \tau_{\text{QTM}}}^{-1} } \right)^{-1}$$

where $n, m, A, B, C,$ and $\tau_{\text{QTM}}$ are all fitting parameters, which in principle, can be optimized to different values for the four different compounds considered here. We will try however to limit as much as possible the variation of these parameters from one system to another to discuss the data within a more unified framework.

We start by using Eq. (9) to fit the data for 2-Dy in an applied 1500 Oe DC field, as this is the only case where we clearly observe two different linear regimes in a log-log plot of $\tau^{-1}$ vs $T$ (Figure S29), associated with the appearance of a phonon bottleneck regime at low T. Thanks to these two readily identifiable linear regimes for 2-Dy, the exponents $n$ and $m$ in Eq. (9), associated with the Raman and phonon bottleneck relaxation mechanisms, respectively, can be fixed as a *priori* for the case of 2-Dy, by noting that Eq. (8), written as $(1/\tau) = T^n (C^{1-n} T^{m-n} + B)$, tends at low temperatures (more exactly, when $T^{m-n} \ll B/C^n$) to the phonon bottleneck regime $T^n/B$, in which log($\tau^{-1}$) is observed to be linear in log($T$), while it tends at high temperatures (more exactly, when $T^{m-n} \gg B/C^n$) to the Raman regime $T^n/C^n$, also linear in log($T$). Fitting the high and low temperature data
separately is thus expedient to fix m and n, which leads to m = 6 (when left to vary, the fit gave a value very close to 6) and n = 3.4 ± 0.1. We also rely on our ab initio calculations of a magnetic tunneling matrix element (m_o) between the easy axis Zeeman eigenstates of the ground KD doublet, amounting to |m_o| = 4.7 x 10^-3 μB (see Figure S28 for 1-Dy). The maximal tunneling rate can be estimated as τ_{0→M} = 2|m_o|^2/ℏ where B_r are fluctuating dipolar fields. These can be calculated on the basis of ab initio results and molecular structure as being of the order of B_r ~ 10 mT in undiluted samples. A rough estimate can in fact be carried out as follows. Considering that the crystal symmetry allows all magnetic axes to be parallel to each other, let the unit vector u_i (u_i) lie along the direction parallel (perpendicular) to the easy axes of all Dy ions. Assuming that tunneling events are induced by transversal dipolar fields B_i, a magnetic dipole m ~ 10 μB u_i at position r = r u_i, so that (m · u_i) = 0, induces at the origin a transversal field of the order B_i = (λ/μ_B^2) |u_i · u_j| |m · u_i|, where λ = (μ_B^2/4π a_0^3) = 6.257 T is the magnetic field strength induced by a dipole of 1 μB at distance of 1 bohr (1 a_0 ~ 0.529 Å) from the probe dipole, and r is the dimensionless distance measured in a_0. From the direction of the molecular easy axis obtained from the ab initio calculations, and the details of the experimental crystal structure, we obtain for nearest neighbour Dy ions at r = 14.8 a_0 (7.85 Å), that |u_i · u_j| = 0.787, |u_i · u_i| = 0.616, hence B_i ~ 9.3 mT, which we approximate as B_i ~ 10 mT.

In a diluted crystal the source of stray fields is provided by nuclear dipoles. The nearest neighbour proton lies at 6.61 a_0 (3.5 Å), and possess a magnetic moment that is 2.8 μB (1.5 x 10^3 μB), from which we can roughly estimate the field induced at the Dy site as 10^-3λ/μ_B^2 ~ 2.2 x 10^2 mT, thus approximate B_i ~ 10^2 mT in diluted samples (hyperfine fields), 1000 times smaller than in undiluted samples. The actual incoherent tunneling rate, modulated by spin-photon coupling broadening Γ("\text{DC}") and by the application of an external dc field, B_{DC} (for simplicity assumed to be aligned with easy axis), can then be approximately evaluated, as:[43]

\[ τ_{0→M} = \frac{Γ^2}{4π^2 (2\hbar M_J B_{DC} μ_B)} \]  

(10)

where from our ab initio calculations we know that in 1-Dy we have g_i M_J B_{DC} ~ 10 μB in the ground KD (i.e. Μ_{iJ} ~ 15/2). For 2-Dy in an external field B_{DC} = 1500 Oe and a dipolar field strength of B_i = 100 Oe, and assuming Γ ~ 10^2 s^-1 we get τ_{0→M} ~ 10^-4 s^-1, so that tunneling can be safely ignored in fitting the experimental data via Eq. (9) with B_{DC} = 1500 Oe.

Thus, we can proceed to optimize only three parameters in Eq. (9) for the 2-Dy data by fixing n = 3.4, m = 6 and τ_{0→M} = 0, which yields an optimal fit (Figure 8) for B = 202.4 ± 28.9 s^-1 K^-n, C = 0.68 s^-1 K^-C (C = 1.48 ± 0.07 s K^-n) and A = 94.9 ± 28.4 s^-1 K^-a (Table 3). Using these fitted parameters, we can also compute an approximate critical temperature T_C = (B/Γ("\text{DC}"))^{1/(m+1)} ~ 7 K, marking a transition, upon cooling, between the Raman regime linear in log(T) with slope n = 3.4, to the phonon-bottleneck regime, also linear in log(T), with the steeper slope m = 6. A more thorough estimation including the effect of the direct and quantum tunneling mechanisms can be obtained numerically by determining the temperature that makes the two terms in brackets on the left-hand side of Eq. (9) equal to each other, leading to the polynomial equation:

\[ T^6 - (B/Γ("\text{DC}"))T^n - BAT - Bτ_{0→M}^{-1} = 0 \]  

(11)

Solving Eq. (11) after substitution of the fitted parameters for 2-Dy yields T_C ~ 8.4 K, in good agreement with the more approximate estimate (7 K). The estimated critical temperature T_C ~ 8.4 K is consistent with the measurements (Figures 8 and S29), where the transition between the two linear regimes can be clearly identified in the range 5-10 K.

To fit the data for the diluted sample 2-Dy@La in zero field (Figure 8) we fix all parameters in Eq. (9) to those optimized for 2-Dy, except for (i) switching off the phonon bottleneck effect by setting B = 0, (ii) evaluating the incoherent tunneling rate with the same ab initio tunneling matrix element |m_o| = 4.7 x 10^-3 μB, but this time using B_{DC} = 0, and due to dilution reducing the fluctuating fields by 1000 times, to hyperfine fluctuating fields B_{DC} = 0.1 Oe, (iii) setting the direct process to zero (A = 0) accounting for the time reversal even character of the unsplit component of a KD, and, especially, for the absence of phonons at zero energy, and (iv) letting vary the Raman parameters C and n, as it is known that Raman relaxation exhibits some magnetic field dependence.[41] With these assumptions, we can calculate the tunneling rate via Eq. (10), yielding τ_{0→M} = 683.7 s^-1 and fix this parameter in Eq. (9), while only optimizing the Raman parameters C and n, a procedure that leads to an excellent fit of the experimental data.
as presented in Figure 8, with $C = 2.56 \text{s}^{-1} \text{K}^{-n}$ ($C^{-1} = 0.39 \pm 0.02 \text{s} \text{K}^{m}$), and $n = 3.12 \pm 0.02$. Overall, the parameters of the Raman mechanism in zero field are not dissimilar from those obtained for the undiluted sample 2-Dy in an applied dc field, while the dominant feature at low temperature is now sizeable temperature-independent QTM.

<table>
<thead>
<tr>
<th>$B_{dc}$ / Oe</th>
<th>1-Ce</th>
<th>2-Ce</th>
<th>2-Dy</th>
<th>2-Dy@La</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500 Oe</td>
<td>800</td>
<td>1500</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$B / \text{s}^{-1} \text{K}^{-n}$</td>
<td>0.35 ± 0.04</td>
<td>0.099 ± 0.02</td>
<td>202.4 ± 0.02</td>
<td>0.39 ± 0.02</td>
</tr>
<tr>
<td>$m$</td>
<td>6 (from 2-Dy)</td>
<td>6 (from 2-Dy)</td>
<td>6 (fixed)</td>
<td>6 (from 2-Dy)</td>
</tr>
<tr>
<td>$C^{-1} / \text{s} \text{K}^{n}$</td>
<td>0 ± 0.06</td>
<td>0.62 ± 0.06</td>
<td>1.48 ± 0.07</td>
<td>0.39 ± 0.02</td>
</tr>
<tr>
<td>$n$</td>
<td>5.16 ± 0.10</td>
<td>5.16 ± 0.10</td>
<td>3.4 ± 0.07</td>
<td>3.12 ± 0.02</td>
</tr>
<tr>
<td>$A / \text{s}^{-1} \text{K}^{-1}$</td>
<td>64.87 ± 8.62</td>
<td>18.45 ± 8.62</td>
<td>95.0 ± 28.4</td>
<td>0</td>
</tr>
<tr>
<td>$\tau_{\text{QTM}}^{-1} \text{s}^{-1} \text{K}^{-1}$</td>
<td>24</td>
<td>85</td>
<td>0</td>
<td>683.7</td>
</tr>
</tbody>
</table>

Finally, to fit the data for 1-Ce and 2-Ce, since we have no reason to believe that the temperature dependence of the phonon-bottleneck is going to differ from that of 2-Dy, we find all parameters in Eq. (9) to the experimental data points (Figure 8), fixing $m$ as 6 as found from the 2-Dy data, and evaluating the QTM rate via Eq. (10) on the basis of the ab initio data, which still leaves $A$, $B$, $C$ and $n$ as four fitting parameters. The calculation of the QTM rates for 1-Ce in $B_{dc} = 1500$ Oe, and 2-Ce in $B_{dc} = 800$ Oe, on the basis of the 2.14 $\text{A}^2$ / Ce ground magnetic moment, and the sizeable ab initio dipolar tunnelling matrix element $|m|_C = 0.5 \mu_B$, yields $\tau_{\text{QTM}}^{-1} = 24\text{s}^{-1}$ (1-Ce) and $\tau_{\text{QTM}}^{-1} = 85\text{s}^{-1}$ (2-Ce). These are clearly significant QTM rates despite the applied dc field, and are thus used in Eq. (9) to reduce the number of free parameters. Under these assumptions, our best fit for 1-Ce is displayed in Figure 8, yielding the best parameters $n = 5.16 \pm 0.10$, $B = 0.35 \pm 0.04 \text{s} \text{K}^{-1}$, $C^{-1} = 1.04 \pm 0.10 \text{s} \text{K}^{-1}$, and $A = 64.87 \pm 8.62 \text{s}^{-1} \text{K}^{-1}$ (Table 3). The best fit for 2-Ce (Figure 8) was obtained by fitting the sole Raman relaxation parameter $C^{-1}$, while assuming that all other parameters only vary as a consequence of the smaller dc field employed for the 2-Ce experiments. Thus, assuming a quadratic dependence of the direct mechanism on the applied field,[24] we fix $A_{2-Ce} = A_{1-Ce} \times (800/1500)^2 = 18.45 \text{s}^{-1} \text{K}^{-1}$. Furthermore, assuming that the magnetic field dependence of the phonon-bottleneck is mainly due to the variation of the spin specific heat (see Eq. (12) below), we get $B_{2-Ce} = B_{1-Ce}$ [$\sqrt{(C_{\text{C}}/C_{\text{Ln}})_{B_{dc}=800}/(C_{\text{C}}/C_{\text{Ln}})_{B_{dc}=1500}} = 0.999 \text{s} \text{K}^{-1}$. Further fixing $m = 6$ and $n = 5.16$ as in 1-Ce, we could fit the single Raman relaxation parameter $C^{-1} = 0.64 \pm 0.06 \text{s} \text{K}^{-1}$.

While different parameters ranges can most probably be found yielding good fits of the 1-Ce and 2-Ce data, our choice seems to suggest that while a phonon bottleneck is active also for 1-Ce and 2-Ce, the rate of this process is significantly faster than for 2-Dy, and thus shows up at lower temperatures for which it was not possible to measure clear out-of-phase maxima in the ac experiment. The critical temperature predicted by our model is in this case can be obtained by solving Eq (11) with the parameters optimized for 1-Ce and 2-Ce, which yields $T_C \approx 2.01 \text{K}$ (1-Ce) and $1.32 \text{K}$ (2-Ce), as highlighted by the extrapolation to lower temperature of our fitting model in Figure 8. This difference for the three compounds might arise from a difference in the crystallite size in the powders used to carry out the experiments, which is difficult to control.[33] Alternatively, this can be rationalized in terms of the different magnetic moments of Dy and Ce, and the consequence on the ratio between the specific heats $C_{\text{Dy}}/C_{\text{Ce}}$ of the spin system and the lattice (insensitive to variations of the magnetic concentration), hence on the ratio between the associated heat capacities $C_{\text{Dy}}/C_{\text{Ce}}$ appearing in Eq. (7) (proportional to $C_{\text{Dy}}/C_{\text{Ce}}$, but now sensitive to the magnetic concentration). In simple models,[34] this ratio $C_{\text{Dy}}/C_{\text{Ce}}$ varies as:

$$C_{\text{Ce}} \sim \tanh^2 \left( \frac{2g_B \mu_B B_{dc}}{2kT} \right)$$

so that for $B_{dc} = 1500$ Oe and temperature in the range 2-10 K, the increase in magnetic moment from Ce (2.14 $\mu_B$) to Dy (10 $\mu_B$) in these systems yields an increase in $C_{\text{Dy}}/C_{\text{Ce}}$ of about 20 times, which at least partially explains the higher $T_C$ below which the phonon bottleneck regime is observed in 2-Dy ($T_C \approx 8.4$ K) versus the $T_C$ we expect to observe for 1-Ce (2.01 K) and 2-Ce (1.32 K), which is below our experimentally accessible range.

**Concluding Remarks**

The combination of neutral 18-crown-6 and charged tetrahalocatecholate ligands with the nitrate salts of lanthanoid ions affords two series of neutral compounds of formula $[\text{Ln}(18-c-6)\text{X}_4\text{Cat})(\text{NO}_3)_2] \cdot \text{MeCN}$. This series includes the first cerium-dioxene complexes with paramagnetic cerium(III), rather than cerium(IV). The Ce, Nd, Tb and Dy analogues all exhibit slow relaxation of the magnetization under an applied dc field and the Ce and Nd analogues represent new members of the small family of slow relaxing lanthanoid systems based on early lanthanoid metals. All analogues exhibit complex relaxation behavior. Using a comprehensive approach including ab initio calculations, EPR spectroscopy and magnetic dilution studies, we have succeeded in rationalizing the behavior of the Ce and Dy analogues. This includes revealing the importance of intermolecular dipolar interactions in the relaxation, the removal of which through magnetic dilution of the Dy analogues, affords slow relaxation of the magnetization in the absence of an external dc field. Despite
following the classic "axial symmetry approach" in the design of a Dy SMM, and observing relaxation up to 20 K, our systems relax through a combination of Raman and direct relaxation pathways. The dominance of Raman rather than Orbach relaxation may originate from the lack of rigidity of the equatorial 18-crown-6 ligand, highlighting another structural parameter that must be controlled in the design of high-performance SMMs.

Magnetic dilution studies have allowed us to identify a phonon bottleneck effect at low temperature, which to the best of our knowledge, has been included for the first time to model a transition of the magnetic relaxation from a high temperature Raman regime to a low temperature phonon bottleneck regime, in which the relaxation time displays an unusual $T^{-4}$ dependence. Such an unusual temperature dependence for the phonon bottleneck relaxation time, instead of the more common $T^{-2}$ dependence that arises from the specific heat of the spin system, was predicted by Van Vleck in 1941. The $T^{-4}$ dependence is a signature of anharmonic terms in the elastic potential, causing interactions between resonant low frequency phonons and higher frequency phonons (i.e. introducing phonon finite lifetime effects), which results in multiplication of the specific heat $C_v$ (with $T^{-2}$ dependence) by the inverse thermal conductivity between low and high frequency phonons, which varies as $T$ (see Eq. (21) in Ref [44]). This results in an overall $T^{-6}$ dependence of the lattice-bath contribution to the observed relaxation time. Whether the Van Vleck anharmonic theory of phonon bottleneck can be invoked here to explain the observed relaxation time. Whether the findings appear to provide further indication that going beyond the harmonic approximation to describe the lattice dynamics could prove crucial for developing predictive microscopic models of slow spin relaxation also in Ln-SMMs.

The combined treatment of the Ce and Dy analogues has allowed the consistent identification of Raman and QTM relaxation processes in addition to the phonon bottleneck. The multi-technique experimental investigation of different lanthanoid analogues, combined with the incorporation of multiple relaxation processes in the theoretical modeling, represents a powerful approach for understanding the limitations of candidate SMMs and unveiling the effects of the lattice environment. Ultimately, we anticipate that the application to other systems of the comprehensive approach developed herein is essential for the development of high temperature SMMs that can be employed in devices or materials.

Experimental Section

Synthesis. Tetrabromocatechol was synthesized as previously reported. All other chemicals were purchased from commercial suppliers and used without further purification.

General Preparation of [Ln(18-c-6)(X(Cat)(NO$_3$))MeCN] (X = Cl (1-Ln), Br (2-Ln)). A solution comprised of stoichiometric amounts of 18-crown-6 (37 mg, 0.14 mmol) and [Ln(NO$_3$)$_3$]$\cdot$4H$_2$O (Ln = La, Ce, Nd, Gd, Tb, Dy) in acetonitrile (4 mL) was refluxed for 10 (La, Nd), 30 (Ce, Gd, Tb) or 60 minutes (Dy). The resulting solution was allowed to cool to room temperature. One molar equivalent of the corresponding tetrabromocatechol (X(Cat)H$_2$) was deprotonated with two equivalents of Et$_3$N in acetonitrile (4 mL) and added dropwise to the lanthanoid reaction mixture without stirring. Needle shaped crystals form after a few minutes. The mixture was left to stand for an hour to allow complete crystallization of the product. The crystals were collected by filtration, washed with cold acetonitrile and diethyl ether, and dried under air.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Color</th>
<th>Yield (%)</th>
<th>Anal. Calcd</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>[La(18-c-6)(Cl(Cat)(NO$_3$))MeCN]</td>
<td>C$<em>{18}$H$</em>{28}$CuCl$_2$N$_2$: C, 31.94; H, 3.62; N, 3.72.</td>
<td>yellow needles</td>
<td>90-95%</td>
<td>C, 24.64; H, 2.69; N, 1.86.</td>
<td></td>
</tr>
<tr>
<td>[Ce(18-c-6)(Cl(Cat)(NO$_3$))MeCN]</td>
<td>C$<em>{20}$H$</em>{27}$CuCl$_2$N$_2$: C, 31.71; H, 3.59; N, 3.70.</td>
<td>yellow needles</td>
<td>60-70%</td>
<td>C, 31.20; H, 3.45; N, 3.52.</td>
<td></td>
</tr>
<tr>
<td>[Gd(18-c-6)(Cl(Cat)(NO$_3$))MeCN]</td>
<td>C$<em>{20}$H$</em>{27}$CuCl$_2$N$_2$: C, 31.81; H, 3.59; N, 3.64.</td>
<td>yellow needles</td>
<td>75-80%</td>
<td>C, 31.90; H, 3.59; N, 3.83.</td>
<td></td>
</tr>
<tr>
<td>[Tb(18-c-6)(Br(Cat)(NO$_3$))MeCN]</td>
<td>C$<em>{20}$H$</em>{27}$CuBr$_2$: C, 31.11; H, 3.52; N, 3.63.</td>
<td>yellow needles</td>
<td>60-70%</td>
<td>C, 31.20; H, 3.45; N, 3.50.</td>
<td></td>
</tr>
<tr>
<td>[Nd(18-c-6)(Br(Cat)(NO$_3$))MeCN]</td>
<td>C$<em>{20}$H$</em>{27}$CuBr$_2$: C, 31.18; H, 3.53; N, 3.64.</td>
<td>yellow needles</td>
<td>85-90%</td>
<td>C, 31.28; H, 3.55; N, 3.49.</td>
<td></td>
</tr>
<tr>
<td>[Dy(18-c-6)(Br(Cat)(NO$_3$))MeCN]</td>
<td>C$<em>{20}$H$</em>{27}$CuBr$_2$: C, 31.11; H, 3.52; N, 3.63.</td>
<td>yellow needles</td>
<td>60-70%</td>
<td>C, 31.20; H, 3.45; N, 3.50.</td>
<td></td>
</tr>
<tr>
<td>[Tb(18-c-6)(Br(Cat)(NO$_3$))MeCN]</td>
<td>C$<em>{20}$H$</em>{27}$CuBr$_2$: C, 31.11; H, 3.52; N, 3.63.</td>
<td>yellow needles</td>
<td>60-65%</td>
<td>C, 31.27; H, 3.47; N, 3.52.</td>
<td></td>
</tr>
<tr>
<td>[Ce(18-c-6)(Br(Cat)(NO$_3$))MeCN]</td>
<td>C$<em>{20}$H$</em>{27}$CuBr$_2$: C, 31.20; H, 3.45; N, 3.50.</td>
<td>yellow needles</td>
<td>60-70%</td>
<td>C, 31.28; H, 3.55; N, 3.49.</td>
<td></td>
</tr>
<tr>
<td>[Nd(18-c-6)(Br(Cat)(NO$_3$))MeCN]</td>
<td>C$<em>{20}$H$</em>{27}$CuBr$_2$: C, 31.20; H, 3.45; N, 3.50.</td>
<td>yellow needles</td>
<td>85-90%</td>
<td>C, 31.28; H, 3.55; N, 3.49.</td>
<td></td>
</tr>
<tr>
<td>[Gd(18-c-6)(Br(Cat)(NO$_3$))MeCN]</td>
<td>C$<em>{20}$H$</em>{27}$CuBr$_2$: C, 31.20; H, 3.45; N, 3.50.</td>
<td>yellow needles</td>
<td>60-70%</td>
<td>C, 31.28; H, 3.55; N, 3.49.</td>
<td></td>
</tr>
<tr>
<td>[Ce(18-c-6)(Br(Cat)(NO$_3$))MeCN]</td>
<td>C$<em>{20}$H$</em>{27}$CuBr$_2$: C, 31.20; H, 3.45; N, 3.50.</td>
<td>yellow needles</td>
<td>60-70%</td>
<td>C, 31.28; H, 3.55; N, 3.49.</td>
<td></td>
</tr>
</tbody>
</table>
Electron Paramagnetic Resonance. X-band (ν = 9.41 GHz) spectroscopic studies on microcrystalline powder samples were carried out at low temperatures using a Bruker E500 spectrometer equipped with an ESR900 (Oxford Instruments) continuous-flow He cryostat and a SHQ resonator. The crystalline powder of each sample was ground in order to avoid preferential orientation and then placed in 4 mm diameter quartz tubes. X-band EPR spectrum of Tb@La was also acquired in parallel polarization (i.e. with microwave field parallel to the static one), using a ER 4116DM Dual Mode Resonator.

The W-band (ν = 94 GHz) EPR spectrum of 2-Gd was recorded on a Bruker E600 continuous-wave spectrometer with cylindrical cavity equipped with a split-coil superconducting magnet that generates a horizontal magnetic field (Oxford Instruments). Temperature was controlled with a continuous-flow cryostat (Oxford CF935), operating from room temperature down to 4.2 K. Ground powder was dispersed in wax to avoid preferential orientation of the microcrystals due to magnetic torque, and inserted in 0.8 mm diameter quartz tube to perform the measurement.

Spectral simulations were performed using EasySpin[52] 5.2.11 running under Matlab R2017b

Inductively Coupled Plasma – Optical Emission Spectroscopy. ICP-OES was performed on a 1000 W Varian 720-ES equipped with a baffled cyclonic spray chamber. Samples were digested in concentrated nitric acid and diluted with water down to ca 5% HNO₃ prior to analysis. Auxiliary gas (Ar) flow rate, carrier gas (Ar) flow rate and plasma gas (Ar) flow rate were set at 1.5, 1.0 and 15 L min⁻¹ respectively, and the wavelengths Dy 267.716 nm; Tb 324.754 nm and La 220.353 nm were monitored. Solution uptake rate was 1.0 mL min⁻¹ and the integration time was 5 s with five replicate measurements performed at each wavelength. Polyboost was switched on to provide an additional 30% Ar flow rate which increases the sensitivity of spectral lines especially of low UV wavelengths.

Computational details. Wave function based calculations were carried out on the X-ray crystal structures of the Ln complexes to analyze their magnetic properties (i.e. main magnetic axes, magnetic susceptibility, and magnetization) and the g tensors of the spin-orbital multiplets. The State-Averaged Complete Active Space Self-Consistent Field method (SA-CASSCF),[52] where the usual notation SA-CAS(r,m)SCF is used to indicate that r electrons are distributed in all the possible ways in m active orbitals, has been coupled with the Restricted Active Space State Interaction with Spin-Orbit (RASSI-SO) method,[53] as implemented in the MOLCAS quantum chemistry package (version 8.2).[54] In this approach, the relativistic effects are treated in two steps. First, scalar relativistic terms are included both via the use of basis sets optimized for relativistic calculations (ANO-RCC),[55] and more explicitly in the one-electron part of the electrostatic Hamiltonian used to optimize the SA-CASSCF wave functions within each relevant spin-manifold, within the second order Douglas-Kroll-Hess (DKH2) approximation.[56] Next, an effective one-electron spin-orbit coupling Hamiltonian, where average bielectronic contributions are accounted for within the Atomic Mean Field Interaction (AMFI) approximation,[57] is diagonalized in the basis of all optimized SA-CASSCF spin states, which is the essence of the RASSI-SO method. The magnetic properties and m-decomposition of the resulting wave functions are then obtained using the SINGLE-ANISO routine.[58]

Cholesky decomposition of the two-electron integrals was employed to speed-up the calculations, with 8 = 10⁻⁸ decomposition threshold.[59] All atoms were described by the ANO-RCC basis set,[53] with the contraction [8s7p5d3g2f1h] for the Ln atoms, [4s3p2d] for O, [5s4p2d] for Cl, [3s2p] for N and C, [2s] for H.

[Sources and references provided in the original text]
Through RASSI-SO, all the spin-adapted configurations were mixed for 1Ce (7 doublets from SA-CAS(1,7)/SCF), and 1Nd (35 quartets and 112 doublets from SA-CAS(3,7)/SCF), while the SA-CAS(7,7)/SCF octuplet (1) and sextets (48) were mixed with the low lying 119 of 392 quadruplets for 1Gd, all SA-CAS(8,7)/SCF septets (7) and quintets (140) with the low lying 96 out of 586 triplets and 96 out of 490 singlets for 1Tb, and all SA-CAS(9,7)/SCF sextets (21) with the low lying 96 out of 224 quadruplets and 63 out of 490 doublets for 1-Dy, due to computational limitations.

Other measurements. Attenuated Total Reflectance infrared (ATR-IR) spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Band intensity is described as strong (s), medium (m) or weak (w). Elemental analyses were performed at Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo thermal analyzer using a ramp rate of 5 °C min⁻¹ up to a maximum temperature of 400 °C.

Acknowledgements

The authors thank Dr. Augustine Doronila and the TrACEES Platform of the University of Melbourne for their help with the ICP-OES analysis, Dr Nick Chilton for helpful discussions and Mr Robin Sanchez Arlt for preliminary synthetic work. Part of this research was undertaken on the MX1 beamline at the Australian Synchrotron (ANSTO), Victoria, Australia; the authors thank the beamline scientists for their valuable support and fruitful discussions. C.B. and A.S. acknowledge support from the Australian Research Council, Discovery Project Grant ID: DP1700034. This research was supported by use of the Nectar Research Cloud (https://nectar.org.au), a collaborative Australian research platform supported by the National Collaborative Research Infrastructure Strategy (NCRIS). L.S. and M.-E. B. acknowledge financial support from Italian MIUR through Project No. PRIN 2015-HYFSRT.

Keywords: single-molecule magnets • phonon bottleneck • Raman relaxation • EPR spectroscopy • ab initio calculations

References

Lanthanoid Crown Ether SMMs: Magnetic and EPR measurements, coupled with ab initio calculations, have revealed magnetization relaxation governed by Raman processes at higher temperatures, transitioning to a dominant phonon bottleneck process as the temperature decreases.

Elodie Rousset, Matteo Piccardo, Marie-Emmanuelle Boulon, Robert W. Gable, Alessandro Sorcini, Lorenzo Sorace, and Colette Boskovic

Page No. – Page No.
Slow Magnetic Relaxation in Lanthanoid Crown Ether Complexes: Interplay of Raman and Anomalous Phonon Bottleneck Processes