Impact of Spin-Phonon Coupling on Magnetic Relaxation of a Co(II) Single-Molecule Magnet

Sakshi Nain, Manish Kumar, and Md. Ehesan Ali

Abstract

Single-molecule magnets (SMMs) based on transition metals have appeared as enticing targets exploiting the magnetic anisotropy in 3d elements. Among transition metals, Co based SMMs are very prominent as they often exhibit a high spin-reversal barrier ($U_{\text{eff}}$), owing to large unquenched orbital angular momentum. Employing the wave function-based multireference CASSCF/NEVPT2 calculations, herein we substantiate the zero-field splitting parameters of four mononuclear Co complexes and one of them has been realized as a prospective SMM. The mechanism of magnetic relaxation has been studied to underpin the molecular origin of the slow relaxation of magnetization. The combination of suppressed quantum tunneling of magnetization (QTM) at the ground state and the high negative $D$ value usually manifests SMM behavior at zero-applied magnetic field. However, mere fulfillment of these conditions ensure little about their SMM behavior, as spin-vibrational coupling often plays the role of spoilsport by lowering the spin-relaxation channels. A detailed study accounting all the 46 vibrational modes below first-excited state, for the prospective Co(II) complex, reveals one of the vibrational modes, providing lower spin-relaxation pathway. This results an SMM with $U_{\text{eff}}$ value of 239.30 cm$^{-1}$, decreased by $\sim$81 cm$^{-1}$ from the value without spin-vibrational coupling.
Introduction

Single-molecule magnets (SMMs) have spurred major research interest in the field of molecular magnetism due to their magnetic bi-stability.\(^1\)\(^2\) These are envisaged as potential contenders for information storage devices,\(^3\) quantum computing\(^4\)\(^5\) and multifunctional molecular spintronics applications.\(^6\)\(^7\) Since the last decade, magnetic bi-stability in such free ions, originating from unpaired electrons, has been a subject of immense interest. SMMs exhibit slow relaxation of magnetization and magnetic hysteresis below a critical temperature, defined as the blocking temperature \(T_B\).\(^8\) In contrast to classical bulk magnets, these can store information at the molecular level. Nonetheless, the fast spin memory loss hinders their way towards practical applications. Forgoing efforts are towards looking for the systems with large unquenched orbital angular momentum and hence, the higher barrier height of magnetization reversal \((U_{\text{eff}})\). The intriguing features of SMMs are decided by their total spin \(S\) and orbital angular momentum \(L\). The total spin for ground state \((S)\) is fixed for an individual complex, so to ameliorate the magnetic properties, one has to look for another variable, the orbital angular momentum \((L)\). Unquenched \(L\) underpins the magnetic anisotropy, which is the appealing key parameter of SMMs.\(^9\) Since their discovery, intense research efforts have been made towards deciphering the origin of magnetic anisotropy and ways to enhance it.\(^10\)\(^-\)\(^13\) On account of this, lanthanide-based SMMs have appeared as clear front-runners, as in the case of \(f\)-series elements, the first-order spin-orbit coupling (SOC) is sufficient for high barrier energies.\(^14\)\(^-\)\(^16\) The highest axial magnetic anisotropy has been proclaimed in dysprosium and related Dy(III) SMMs.\(^17\)\(^-\)\(^20\) Subsequently, a large coercive magnetic field of 14 T has recently been reported by Gould et al. at temperatures as high as 60 K for a dilanthanide complex of Dy.\(^21\) On the other hand, transition metals generally possess weak spin-orbit coupling and their barrier heights are governed by second-order SOC. So, to invoke dominant SOC in such systems, a strong “axial” crystal field of ligands\(^22\) and high symmetry of geometry are needed.\(^23\) However, these are not the quintessential or
requisite conditions for such systems. Alternatively, the notable weak crystal field could also be proved beneficial to generate potentially large magnetic anisotropy, by originating unquenched orbital angular momentum through non-Aufbau electronic configuration and enforcing stronger second-order SOC by mixing of low lying excited states. Such weak ligand field is usually produced by low coordination number and low oxidation state. In addition to this, large ZFS has also been observed to be acquired by lowering the symmetry and hence enabling the mixing of the wavefunction for few Co(II) based SMMs. Besides, a low symmetrical complex of Dy has also been observed with significant axial magnetic anisotropy by Lucaccini et al. Out of transition metals, numerous polynuclear complexes have been witnessed as SMMs, though several remarkable examples of mononuclear SMMs have also been revealed in the past few years. For instance, the studies of spin state structures for SAMs of Mn$_6$ SMMs, grafted on the substrate, have been well explained using periodic density functional (DF) studies by Totti et al. The leading 3$d$ transition element based single-molecule magnets include Fe, Co and Ni atoms with distinctly tunable properties. In particular, Co(II) with $d^7$ electronic configuration has the advantage of Kramers ground spin state due to its non-integer spin. As a result, plethora of high-coordinated Co complexes have been synthesized and characterized along with some mononuclear Co complexes with substantial magnetic anisotropies. A large barrier of 152 cm$^{-1}$ for Orbach relaxation has been reported by Novikov et al. for a mononuclear Co complex. The highest reported $U_{eff}$ among 3$d$-series based SMMs (450 cm$^{-1}$) also belongs to a two-coordinated Co complex named Co(C(SiMe$_2$ONaph)$_3$)$_2$, which reflects the supremacy of interelectronic repulsion over crystal field to govern the energetics of the system, and consequently, generating non-Aufbau electronic configuration.

Besides, the chemical stability and commanding magneto-structural correlations are the added benefits of mononuclear transition metal complexes, motivating one to explore their single molecule magnetic behavior. The magnetic anisotropy of such complexes is strongly dependent on the symmetry as well as the surrounding environment around the central
Figure 1: Optimized geometries of the mononuclear Co complexes. \([\text{Cp}'\text{Co(hmds)}] (1); \; \text{Cp}^*\text{Co(IPr)} \; (2); \; [\text{Co(CO)}(\text{hmds})_2]^{-1} \; (3); \; [\text{Co(Br)}(\text{hmds})_2]^{-1} \; (4). \) \((\text{Cp}' = \eta^5-1,2,4\text{-tri-tert-butylcyclopentadienyl}); \; (\text{hmds} = -\text{N(SiMe}_3)_2); \; (\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazole-2-ylidene}). \) Colour code: purple, Co; blue, N; green, Si; red, O; brown, Br; gray, C. Hydrogens have been omitted for clarity.

metal.\(^{41}\) Hence, it becomes crucial to look into the electronic structure of the system in order to have a comprehensive understanding of the origin of slow relaxation of magnetization.\(^{42-44}\) Into the bargain, Gereka and co-workers have explained the impact of the distortion of the coordination sphere on the slow relaxation for \(\text{Co}^{\text{II}}\text{N}_6\) trigonal prismatic cationic complexes.\(^{45}\) Hitherto there are many reports available in the published literature regarding poly-coordinated Co(II) complexes, yet theoretical work focused on an in-depth study on low-coordinated Co(II) complexes is limited. Besides, the low-coordinate metal complexes are more efficacious towards SMMs due to their controllable symmetry around the metal ions, which eventually leads to larger barrier heights for magnetization reversal. In view of this, applying state-of-the-art \textit{ab initio} calculations, we have investigated the magnetic anisotropy of four mononuclear high-spin (HS) cobalt complexes namely \([\text{Cp}'\text{Co(hmds)}] (1) \; (\text{Cp}' = \eta^5-1,2,4\text{-tri-tert-butylcyclopenta-dienyl}) \; (\text{hmds} = -\text{N(SiMe}_3)_2), \; \text{Cp}^*\text{Co(IPr)} \; (2)\)
(IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene), [Co(CO)(h-mds)]$^{-1}$ (3) and [Co(Br)(hmds)]$^{-1}$ (4) (see Figure 1). All of the examined complexes are observed to possess non-Aufbau ground state electronic configuration. In this regard of violation of the Aufbau rule, Bunting et al. have reported the dominance of interelectronic repulsion over ligand field destabilization energy due to weak crystal field for a Co(II) complex, permitting non-Aufbau electron filling.\(^{24}\) Furthermore, magnetic anisotropy could also be tweaked due to contrast between Aufbau and Hund’s rule by anticipating the change of orientation of magnetic anisotropy.\(^{20}\) Out of the four chosen systems, complex 1 and 2 are Co(II) and Co(I) neutral systems while 3 and 4 are Co(I) and Co(II) anionic systems respectively. The former two complexes 1 and 2 are featured as quasi-linear systems, having two-coordinated Co at the centre. However, the later two complexes 3 and 4 demonstrate trigonal planar geometries with two axial ligands of hmds. In addition, complex 1 and 3 have been synthesized experimentally and characterized with large negative $D$ values using a standard-spin Hamiltonian fit approach.\(^{46,47}\) This fit is considered to be insensitive to the sign of $D$ parameter.\(^{48}\) So even though, their outcomes unambiguously specify the high magnitude of the $D$ value, yet its sign has not been verified precisely. We have attempted to provide the possible analysis and confirmation of the sign as well as the magnitude of $D$ value using the sophisticated $ab\ initio$ methods, which have been extensively used to address the electronic structure and predict spin-Hamiltonian parameters of magnetic systems. Further, complex 2 and 4 have been identified by Andjaba et al. and Weller et al. respectively.\(^{49,50}\) We have explicitly examined the spin-Hamiltonian parameters (ZFS parameters and $g$-values) for these four complexes. To ascertain the various relaxation pathways, including quantum tunneling of magnetization (QTM) in the ground state,\(^{51}\) blocking barrier to magnetic relaxation have also been studied in detail. The computed $D$ values of complex 1 and 3 by multireference methods have been found to be in good agreement with the experimentally reported values. Moreover, in order to accomplish and design SMMs operating at higher temperatures, the spin relaxation phenomena via vibronic couplings needs to be deciphered explicitly.\(^{52–55}\)
Therefore, we have attempted to determine the bottleneck effects of spin-vibrational coupling, prominently engendering the spin relaxation for complex 1 with strong axial magnetic anisotropy.

**Computational Details**

All the calculations have been performed using ORCA 5.0 suite. The geometries of all the four complexes have been optimized employing density functional theory (DFT) using hybrid B3LYP exchange-correlation functional (Figure 1). A valence triple-zeta basis set with polarization functions, def2-TZVP, together with an automatically generated auxiliary basis set using AUTOAUX command is used for all the geometry optimizations and single point ab initio calculations. SCF energies are converged up to $10^{-8}$ Eh with tightSCF convergence criteria. Grimme’s DFT dispersion correction with Becke-Johnson damping (DFT-D3BJ) has been employed during geometry optimizations. All the single-point and wave function-based calculations have been performed on the geometries optimized using DFT (Table S1 in SI). The multi-configurational Complete Active Space Self Consistent Field (CASSCF) method has been used to compute the axial and rhombic ZFS parameters ($D$ and $E$ respectively). State-averaged (SA-CASSCF) approach accounts for the static correlations while the dynamical correlations are included using $N$-electron valence state perturbation theory (NEVPT2). A more recent method of multi-state extension to the reference wavefunction, quasi-degenerate $N$-electron valence-state perturbation theory (QD-NEVPT2), has also been carried out to get reliable results without the influence of any intruder states, which may arise due to the proximity of energies. A complete active space of CAS(7,5) incorporating seven electrons in five $d$-orbitals of Co atom has been used for complex 1 and 4. For complex 2 and 3, minimal active space of CAS(8,5) has been employed for CASSCF calculations, having $d^8$ electronic configuration. It is noteworthy to mention that the complex 3 and 4 are anionic Co(I) and Co(II) systems with $d^8$ and
The $g$-value anisotropy for the two coordinated linear Co(II) complex 1, presenting the unique one-legged piano stool geometry, has been shown up by Peters et al. using three different methods namely standard spin-Hamiltonian approach, X-band EPR measurements and variable temperature (VT) and variable field (VH) magnetization measurements. Similarly, an axial anisotropy has been proclaimed for the trigonal planar Co(I) complex 3, using experimental $\chi_M T$ vs. T data modeled by a Hamiltonian fit procedure. The multiconfigurational CASSCF/NEVPT2 approach, that accounts for both the dynamical as well as static electronic correlations, has been employed to determine the sign and magnitude of
D parameter. The estimated magnitudes of D values using experimental methods are well reproduced by the adopted computational methodology for both complex 1 and 3. Moreover, the studies of magnetization relaxation dynamics have been carried out to elucidate the relaxation mechanism and various pathways responsible for spin relaxation in all the respective complexes. Apart from ZFS parameters and magnetization barrier relaxation analysis, further the impact of vibronic couplings on magnetic anisotropy has also been investigated to identify the detrimental modes involved in vibrational-induced relaxation for complex 1 with large negative D value.

Electronic Structures and Spin-states

All the molecular geometries have been fully optimized in the two possible different spin states (HS and LS) along with numerical frequency calculations employing density functional theory at B3LYP/def2-TZVP level. The absence of any imaginary frequency verified the corresponding energy minima at possible spin-states. Between the two possible spin-states for complex 1 and 4 i.e., high-spin (HS) S = 3/2 and low-spin (LS) S = 1/2, quartet state (S = 3/2) is found to be more stabilized as ground spin-state. Complex 1 is observed to have HS quartet as the ground spin-state with an adiabatic energy difference of 32.60 kJ/mol with respect to the LS doublet state. On the other hand, for complex 4, the high-spin state is more stabilized with an adiabatic energy difference of 83.28 kJ/mol as compared to the doublet state. Besides, complex 2 and 3 yield triplet (S = 1) as ground state with adiabatic energy difference of 83.62 and 73.01 kJ/mol, respectively than the LS singlet state (S = 0). The sizeable magnitudes of the adiabatic energy difference between the DFT computed HS and LS states, rule out the possibility of spin-crossover phenomena in the respective complexes. For complex 3, the HS ground state is also observed by Schneider et al. from solid state magnetic measurements and quantum chemical studies. The well isolated ground spin-states of the rest three complexes also corroborate with the experimentally reported ground spin-states.
Table 1: Computed spin-state energies (Eh) for DFT optimized geometries and $< S^2 >$ values of all the studied complexes for individual spin-states together with spin-only moment values on Co atom for ground spin-state geometry computed at B3LYP/def2-TZVP level.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Energies (Eh)</th>
<th>Spin-only moment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E(HS)</td>
<td>E(LS)</td>
</tr>
<tr>
<td>1</td>
<td>-2921.14490</td>
<td>-2921.13248</td>
</tr>
<tr>
<td>2</td>
<td>-2932.63159</td>
<td>-2932.59974</td>
</tr>
<tr>
<td>3</td>
<td>-3242.69138</td>
<td>-3242.66357</td>
</tr>
<tr>
<td>4</td>
<td>-5703.47518</td>
<td>-5703.44346</td>
</tr>
</tbody>
</table>

The energies of DFT optimized geometries for all the complexes in two possible spin states (HS and LS) are tabulated in Table 1. Following the structural optimization, single point calculations have been performed on the ground-spin state optimized geometry (Table S1 in SI). Complex 1 and 2 are observed to have quasi-linear geometry while distorted trigonal planar motif is exhibited by complex 3 and 4. For complex 1, the stabilization of Co(II) atom is attributed to nitrogen to metal $\pi$-donation, noted by almost linear Cp$'$/Co-N angle (171.64° for X-ray geometry).

Besides, careful inspection of the Loewdin population analysis of DFT optimized geometry reveals the composition of $\alpha-$HOMO-3 orbital as admixture of 13% Co $d$-orbital and 24% N $p$-orbital. Similarly, in the case of complex 2, Andjaba and others have observed ligand to metal back donation for its bent geometry optimized in triplet state with Cp*-Co-C$_{IPr}$ angle of 159°. Although, for this complex, Co metal acquires a +1 oxidation state with a total electron count of 16 electrons and is reported as an unsaturated system with only small reactivity. However, for anionic complex 3, CO being $\pi$ acceptor ligand initiates back bonding from Co’s $d$-orbital, as inspected by Schneider et al. It has also been inferred that the HS ground state is maintained by the low-coordinated system and weak ligand-field of silylamides. Likewise, complex 4 is another anionic system with a Co atom
Table 2: Reported magnetic moments ($\mu_B$) and spin-Hamiltonian parameters using different experimental methods. The $D$ values have been represented in cm$^{-1}$.

| Complex | Magnetic moment | $D$   | $|E/D|$ | $g_x$ | $g_y$ | $g_z$ |
|---------|-----------------|-------|--------|-------|-------|-------|
| 1       | 5.13$^a$        | -101.7$^b$ | 0.33   | 1.37  | 1.85  | 3.58  |
|         |                 | -100$^c$ | 0.33   | 1.58  | 2.05  | 3.67  |
| 2       | 2.6$^d$         | -99.7$^d$ | 0.29   | 1.42  | 1.95  | 3.58  |
| 3       | 3.32$^f$        | -53$^g$ | $^i$    | $^j$    | $^i$    | $^i$    |
| 4       | 4.39$^h$        | $^i$    | $^j$    | $^i$    | $^i$    | $^i$    |

$^a$This value was obtained using solid-state magnetic susceptibility measurements at ambient temperature by Peters et al.$^{46}$

$^b$It was estimated using standard spin-Hamiltonian approach.$^{46}$

$^c$This value was reported employing X-band EPR measurements.$^{46}$

$^d$It was obtained by performing variable temperature (VT) and variable field (VH) magnetization measurements.$^{46}$

$^e$The value was estimated utilizing solution magnetic susceptibility studies (Evans method).$^{49}$

$^f$It was reported using solid state magnetic measurements.$^{47}$

$^g$It was obtained by modeling experimental $\chi_M T$ vs. $T$ data using a Hamiltonian fit procedure.$^{47}$

$^h$It was reported using the Evans method.$^{50}$

This data is not available for the respective complex.

surrounded by two silylamide and one bromide ligand, presenting almost perfect trigonal planar geometry. In regards to complex 3 and 4, CO and Br both are monodentate ligands, though CO ligand is neutral as well as strong $\pi$ acceptor as compared to Br. The negatively charged Br$^-$ and two hmds ligands result in $d^7$ Co anionic complex 4, with +2 oxidation state and hence a Kramer system. The comparison of structural parameters between X-ray crystal geometries and optimized geometries for all the examined complexes is provided in Table S6-S9 in SI. By magnetic susceptibility measurements, an effective magnetic moment of $\mu_{eff} = 5.13 \mu_B$ is observed for complex 1 which is far more than the spin-only ($\mu_{S,O.}$) value of 2.52 $\mu_B$ on Co atom of optimized geometry.$^{46,68}$ This clearly indicates the pivotal role of orbital angular momentum contribution to the magnetic susceptibility for Co$^{II}$ complexes.$^{46,68}$ Likewise, experimentally measured effective magnetic moment for complex 3 is 3.32 $\mu_B$ which is again higher than computed $\mu_{S,O.}$ of 2.01 $\mu_B$ on Co metal. The magnetic
data thus far available in the literature, obtained using different experimental methods, is presented in Table 2. The spin-only value of $2.59\ \mu_B$ is calculated for the Co atom of complex 4 while the effective magnetic moment of $4.39\ \mu_B$ is reported by Weller and others using the experimental method. The computed spin-only moments from DFT on the central Co atom of ground-spin state geometry for the respective complexes are compiled in Table 1. Later on, single-point multi-configurational \textit{ab initio} calculations have been performed on the top of ground spin-state geometry. CASSCF calculations also validate HS as the ground spin-state for all the studied complexes.

**ZFS Parameters**

The geometries optimized using DFT are carried forward for wave function-based calculations to obtain the spin-Hamiltonian parameters. Additionally, CASSCF calculations are also conducted on the experimentally reported X-ray crystal geometries (Table S4 in SI). However, only minor differences have been observed between the computed $D$ values using optimized and the X-ray crystal structure geometries (0.2 - 20 cm$^{-1}$). So, all the results reported here in the main text are using geometries optimized by DFT. Complex 1 is established with $D$ value of $-135.03\ \text{cm}^{-1}$ with small $|E/D|$ of 0.0080 employing an active space of CAS(7,5) comprising seven electrons in five $d$-orbitals. For complex 1 and 3, it is observed that the multireference methods are slightly overestimating the $D$ values as compared to experimentally reported $D$ values. However, it is of little surprise as this kind of discrepancy has already been observed in foregoing studies also.$^{30,69,70}$ The inconsistency in magnitude of $D$ value could be attributed to the environmental effects, limitation of the basis set and the active space employed in the multireference calculations. Magnetic parameters of $D$ and $|E/D|$ for all the examined complexes have been computed using SA-NEVPT2 and QD-NEVPT2 approaches (Table 3). The corresponding $g$-tensor, to predict the preferred direction of magnetization, along with $M_S$ composition of ground state are collected in Table 5. The estimated $g$-values for complex 1 and 3 indicate axial anisotropy with $g_x \approx g_y \approx 0 << g_z$, however complex 3
lacks the pure “easy-axis” nature.\textsuperscript{71} This confirms the presence of \( g \)-value anisotropy, earlier observed by experimental techniques for both the complexes.\textsuperscript{46,47}

**Table 3:** Computed \( D \) values (cm\(^{-1}\)) and \(|E/D|\) quotients employing different multireference methods for all the studied Co complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>CAS(^a)</th>
<th>Nroots(^b)</th>
<th>SA-CASSCF</th>
<th>SA-NEVPT2</th>
<th>QD-NEVPT2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( D )</td>
<td>(</td>
<td>E/D</td>
</tr>
<tr>
<td>1(^c)</td>
<td>(7,5)</td>
<td>7,28</td>
<td>-136.83</td>
<td>0.0114</td>
<td>-135.03</td>
</tr>
<tr>
<td>2</td>
<td>(8,5)</td>
<td>7,5</td>
<td>71.27</td>
<td>0.3129</td>
<td>55.95</td>
</tr>
<tr>
<td>3(^d)</td>
<td>(8,5)</td>
<td>7,5</td>
<td>-211.24</td>
<td>0.0096</td>
<td>-61.87</td>
</tr>
<tr>
<td>4</td>
<td>(7,5)</td>
<td>7,28</td>
<td>-86.26</td>
<td>0.3010</td>
<td>78.89</td>
</tr>
</tbody>
</table>

\(^a\)CAS refers to the Complete Active Space employed for the wave function-based multireference calculations.

\(^b\)Nroots indicate the number of roots included in the CASSCF/NEVPT2 calculations with respective to individual multiplicity.

\(^c\)With standard spin-Hamiltonian approach, -101.7 cm\(^{-1}\) of \( D \) and 0.33 \(|E/D|\) has been reported by Peters et al. Besides, \( D \) and \(|E/D|\) parameters, rationalized using two different methods of VTVH and X-band EPR measurements, are -99.7 cm\(^{-1}\), 0.29 and -100 cm\(^{-1}\), 0.33 respectively.

\(^d\)\( D \) value of -53 cm\(^{-1}\) is shown up by Schneider et al. with experimental \( \chi_M T \) vs. \( T \) data modeled using a Hamiltonian fit procedure.

In addition, the following \( d \)-orbital splitting analysis satisfactorily predicts the uni-axial magnetic anisotropy exhibited by complex 1 and 3. In regards to complex 1, the \( d \)-orbital splitting pattern elucidated by CASSCF+NEVPT2 calculations conveys that \( d_{xy} \) and \( d_{x^2-y^2} \) orbitals are the most stabilized and near degenerate. Assuming the \( C_\infty v \) point group for the quasi-linear optimized geometry, ground state configuration from \( ^4F \) ground state is \( \delta^3\pi^3\sigma^1 \) from the occupation of \( d_{xy}^2 d_{x^2-y^2}^1 d_{y^2}^1 d_{xz}^1 \) displaying non-Aufbau configuration. The ground state term of \( ^4\Phi \) arises due to degenerate \( \delta \) orbitals (Figure 2). The weak ligand field has splitted the \( ^4F \) originated states up to 5352 cm\(^{-1}\). Further incorporating spin-orbit coupling, the \( ^4F \) ground state splitting leads to four Kramers doublets (Figure 3). It is presumably to avert inter-electronic repulsion, due to orbital near-degeneracy between \( d_{xy} \) and \( d_{x^2-y^2} \) orbitals with small energy difference of 143.5 cm\(^{-1}\) (Figure 2). Hence, the maximal orbital angular momentum further ensuing large magnetic anisotropy can be realized for this
The first electronic transition arising from ground to first excited state occurs between same $|m_l|$ states i.e. from $d_{yz}$ to $d_{xz}$ with configuration of $d_{xy}^2 d_{x^2-y^2}^{1} d_{z^2}^{1} d_{yz}^1 d_{xz}^2$. Moreover among the other examined cases, the energy gap of ground and first excited state is least for this complex (320 cm$^{-1}$), indicating small energy required for this electronic excitation (Table 4). This spin-conserved transition accompanies a substantial negative contribution of $\sim 95\%$ to the net $D$ value. Apart from it, the second excited state arises from the transition of more than one electron, contributing equally to $D$ and $E$ values but with opposite signs (Table 4). Further electronic transitions were considered trivial due to minor contributions to the overall $D$ value. Besides, its ground state composition is primarily having the Kramers doublet with maximum spin projection $M_S = \pm 3/2$ (Table 5). As a consequence, the half sandwiched Co$^{II}$ complex 1 emerges as a possible SMM with pronounced Ising-type magnetic anisotropy.

For coordinately unsaturated complex 2, $D$ value of 55.95 cm$^{-1}$ with $|E/D|$ of 0.2378 is computed using CASSCF(8,5) +NEVPT2 calculations. The non-negligible magnitude of the $|E/D|$ quotient denotes the transverse nature of ZFS and the positive value of $D$ implicates the easy-plane kind of magnetic anisotropy present in this complex. Also, its ground state composition consists of almost pure $M_S = 0$ state with $\sim 85\%$ probability, due to its non-Kramers nature and positive $D$ value. Employing the $C_\infty$ point group notation for it, the ground state configuration from the free-ion state of $^3D$ is $d_{xy}^2 d_{x^2-y^2}^{1} d_{z^2}^{1} d_{yz}^1 d_{xz}^2$. The $^3\Delta$ term is acquired by Co(I) ion displaying non-Aufbau $\delta^3\sigma^1\pi^4$ configuration. The $D$ value is positive due to its first excited state, with configuration $d_{xy}^2 d_{x^2-y^2}^{1} d_{z^2}^{1} d_{yz}^1 d_{xz}^2$, resulting from different $|m_l|$ transition i.e. $d_{yz} \rightarrow d_{z^2}$, predominantly contributing to the $D_{XX}$ and $D_{YY}$ terms. The second and third excited states are found to be significantly mixed with the ground state having different spin-conserved electronic transitions $d_{xz}/d_{z^2} \rightarrow d_{yz}/d_{x^2-y^2}$ and thus contributing to final positive $D$ value. Complex 3 is found to have an axial ZFS parameter $D$ of -57.86 cm$^{-1}$ with estimated $|E/D|$ of 0.0403. Our computational methodology produces very similar results to the experimentally observed $D$ value of -53 cm$^{-1}$. The
ground state composition for this complex comprises of $M_S = 1$ state with $\sim 85\%$ probability. The AILFT analysis depicts that $d_{xz}$ orbital is more stabilized due to partial mixing with $p_z$ orbital. The ground state occupation from free-ion state of $^3F$ emerges from non-Aufbau filling of electrons. Co(I) ion attains $^3\Phi$ term by $\pi^3\sigma^2\delta^3$ electronic configuration. The ground state electronic configuration for this complex is $d^1_{xz}d^2_{yz}d^2_{z^2}d^2_{x^2-y^2}d^1_{xy}$ and the first excited state is attained by spin-allowed transition of electron from $d_{x^2-y^2}$ to $d_{xy}$ with configuration of $d^1_{xz}d^2_{yz}d^2_{z^2}d^1_{xy}$. This transition primarily contributes to the $D_{XX}$ component and consequently provides sufficient negative $D$ value. An upcoming second excited state is obtained by electron transfer from $d_{yz}$ to $d_{x^2-y^2}$ leading to a small positive contribution to the $D$ value (Table 4). The AILFT orbital eigfunctions computed from NEVPT2 are tabulated in Table S3 for all of the four complexes.

**Table 4:** Computed lowest spin-free and spin-orbit energy states (cm$^{-1}$) with their individual contribution to $D$ (cm$^{-1}$) and $E$ (cm$^{-1}$) values using SA-CASSCF+NEVPT2 method.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Excited state</th>
<th>Spin-free states</th>
<th>Spin-orbit states</th>
<th>contrib. $D$</th>
<th>contrib. $E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>320.0</td>
<td>0.00</td>
<td>-154.20</td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5235.2</td>
<td>270.1</td>
<td>6.45</td>
<td>-6.65</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2576.9</td>
<td>42.6</td>
<td>29.84</td>
<td>31.82</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3279.2</td>
<td>69.3</td>
<td>12.93</td>
<td>-10.50</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2022.8</td>
<td>5.0</td>
<td>-98.73</td>
<td>-0.00</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9966.9</td>
<td>64.4</td>
<td>5.47</td>
<td>-4.29</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1048.1</td>
<td>0.00</td>
<td>63.41</td>
<td>63.41</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1606.2</td>
<td>177.0</td>
<td>41.96</td>
<td>-41.96</td>
</tr>
</tbody>
</table>

Complex 4 is an exceptional case having triaxial anisotropy rather than easy-plane and easy-axis anisotropy with $g_x < g_y < g_z$ (Table 5) and $E/D \approx 1/3$ (Table 3). For this system, there is an anomaly regarding the sign of $D$ parameter as CASSCF computed it as -86.26 cm$^{-1}$, while NEVPT2 computed value is 78.62 cm$^{-1}$. Quite interestingly, the ground state composition is $M_S = \pm 3/2$ largely mixed with the $M_S = \pm 1/2$ state (Table 5). The significant contribution from another $M_S$ projection to the ground state wavefunction results in a smaller energy gap of 194.91 cm$^{-1}$ between the ground state and first excited state KDs (Figure 3). We would like to mention here that the sizable magnitude of transverse ZFS
Figure 2: CAS\((n,5)\)+NEVPT2 computed AILFT \(d\)-orbital splitting pattern and energy ordering for all the studied complexes using five orbitals active space, where \(n\) corresponds to the number of electrons in the active space. The \(z\)-axis is selected as the highest-order symmetry axis for all the four complexes, while Co at the center acts as the origin of the coordinate system. The reference frame for complex 1 and 2 has been chosen such that the \(z\)-axis is pointing approximately perpendicular to the plane of Cp ring, while, for complex 3 and 4, it is along Co-CO and Co-Br bonds, respectively.

Moreover, its free-ion term \(4\)D corresponds to non-Aufbau electronic occupation \(\sigma^2\delta^3\pi^2\) in the ground state. Subsequently inclusion of spin-orbit coupling leads to the splitting of \(4\Delta\) ground state into four Kramers doublets (Figure 2). Its electronic configuration for the ground state is \(d_{xy}^4d_{yz}^1d_{x^2-y^2}^2d_{z^2}^1d_{xz}^1\). For the first electronic excitation parameter along with mixed \(M_S\) levels in ground state accompanies ground state QTM in this complex (Figure 3).\(^{74}\)
Table 5: CAS($n$,5)+NEVPT2 computed principal $g$ tensor components of the ground state Kramers doublet along with $M_S$ composition for all the examined Co complexes, where $n$ corresponds to the number of electrons in the active space.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>$M_S$ composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^a$</td>
<td>0.0482</td>
<td>0.0503</td>
<td>9.8647</td>
<td>0.62</td>
</tr>
<tr>
<td>2</td>
<td>2.0656</td>
<td>2.4302</td>
<td>2.6725</td>
<td>0.85</td>
</tr>
<tr>
<td>3$^b$</td>
<td>2.0307</td>
<td>2.1182</td>
<td>2.7394</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>1.4955</td>
<td>2.9421</td>
<td>8.3808</td>
<td>0.44</td>
</tr>
</tbody>
</table>

$^a$Reported $g$-values for this complex using standard spin-Hamiltonian approach are $g_x = 1.37$, $g_y = 1.85$ and $g_z = 3.58$.

$^b$By experimental $\chi_M T$ vs. $T$ data, reported $g_x$, $g_y$, $g_z$ are 2.11, 2.11 and 2.75 respectively.

with configuration $d_{xy}^2d_{yz}^1d_{x^2-y^2}^1d_{z^2}^2d_{xz}^1$, the trade-off between $d_{x^2-y^2}$ and $d_{xy}$ orbital engenders negative $D$ value in CASSCF. However, the same orbital ordering is carried forward in NEVPT2 calculation so the same first electronic transition has been observed in the NEVPT2 approach but with a positive sign of $D$. Moreover, the first electronic excitation provides exactly equal contribution to the $D$ and $E$ parameters (Table 4). Out of curiosity, we included the extended double $d$-shell in the active space CAS(7,10) and found a consistent positive sign of $D$ both in CASSCF and NEVPT2 calculations (Table S5 in SI). To come to an end, it has been deduced that the dynamical correlations play major role in determining the accurate sign of $D$. Additionally, the extended double $d$-shell in active space may also be advantageous to have consistent sign of $D$, employing CASSCF and NEVPT2 methods. This kind of ambiguity has been reported by Singh et al.$^{70}$ earlier and by Gereka et al.$^{45}$ only recently suggesting the requirement of specific theoretical calculations or the experimental techniques like HFEPRT to determine the magnetic anisotropy for this kind of complex reliably. The lowest spin-free energies for all the complexes together with the corresponding contribution to $D$ and $E$ values are enlisted in Table 4.
Magnetic Relaxation Mechanism

Out of the four investigated cases, only complex 1 and 4 have half-integer total spin $S = \frac{3}{2}$, hence are Kramers systems. In an effort to have intricate details of magnetic relaxation phenomena, we have plotted the \textit{ab-initio} blocking barrier for optimized geometries of complex 1 and 4 computed from SINGLE_ANISO$^{75}$ approach as implemented in Orca 5.0 (Figure 3). There are various magnetic relaxation pathways that need to be addressed to have an insight into the genesis of the relaxation of magnetization. These include the Orbach process, quantum tunneling of magnetization (QTM), Raman relaxation, and thermally assisted quantum tunneling of magnetization (TA-QTM). Among them, QTM occurs within the ground KDs, which is usually operative at low temperatures. The direct process of TA-QTM occurs within excited KDs involving one phonon. The relaxation through $U_{\text{eff}}$ barrier by spontaneous emission of phonons is termed as Orbach process, which generally appears at high temperature. Orbach process is characterized as the spin-lattice relaxation occurring through a real intermediate state. On the contrary, Raman process is a two phonon process arising through a virtual excited state and hence can not be justified. To begin with complex 1 with substantial $D$ value, it possesses axially anisotropic ground KD (Figure 3). For this complex, the transition-magnetic-moment matrix element between the ground state KD is negligibly small (i.e., $3 \times 10^{-4}$). This means the tunneling relaxation at ground state, which shortcuts the energy barrier, is not active here. Furthermore, the cancellation principle of van Vleck suggests the imperceptible probability of ground state QTM in Kramers ions.$^{76,77}$ The axial coordination environment also suppresses the QTM effect by preserving lower $M_S$ level as ground state.$^{78}$ Correspondingly, it implies that this complex does not relax without overcoming the possible energy barrier for magnetization reversal. Orbach process involving the ground and first excited KDs is slow with the off-diagonal matrix element of 0.001, albeit moderate between the first and second excited state (0.39). The energy difference between ground and first excited KDs, assumed as $U_{\text{eff}}$, is $320.29 \text{ cm}^{-1}$ (460.82 K).$^{78}$ Nonetheless, re-
laxation through TA-QTM within first and second excited state is prominently in effect with moderate magnitudes (0.77, 1.13, 1.08). The ground KD, corresponding to 100% ±7/2 > wavefunction, is nearly perfect axial with \( g_x = 0.001, g_y = 0.001, g_z = 9.895 \). Similarly, the axially has been maintained in the first excited KD composed of 96% ±5/2 > wavefunction (\( g_x = 2.39, g_y = 2.39 \) and \( g_z = 5.21 \)), while the second excited KD is observed to have transversal \( g \)-tensor values (\( g_x = 2.41, g_y = 2.36 \) and \( g_z = 1.21 \)), demonstrating significant spin-relaxation through the second excited state with transition magnetic moment of 0.77 \( \mu_B \) (Figure 3). It is also supported by the wavefunction of KD4 (87% ±3/2 >) having partial contribution from the respective \( M_S \) state.\(^{27,79}\) The low coordination number coming together with low oxidation state engender weak ligand field\(^{25}\) and it could be responsible for the mixing of \( M_S \) states in higher KDs. Besides, this Co(II) system owing to Kramers ground state, is presumed not to relax largely via direct and under-the-barrier QTM process, in the vicinity of zero external magnetic field.\(^{45}\) Consequently, it is deduced to have slow magnetic relaxation, likely in absence of any field, and is anticipated to demonstrate magnetic hysteresis.

![Figure 3](image-url)

**Figure 3:** *Ab-initio* derived magnetization blockade barrier for complex 1 and 4. The thick black lines represent the Kramers doublets (KD) as a function of their magnetic moment along the magnetic axis. The dotted red line signifies diagonal quantum tunneling of magnetization (QTM). The dotted green line denotes the most probable relaxation pathway. The number at each arrow corresponds to mean absolute value of the corresponding matrix element of the transition magnetic moment.
In case of complex 4 with positive $D$ value, the first excited state is $194.91 \text{ cm}^{-1}$ ($280.43 \text{ K}$) higher in energy than the ground state KD and possesses $g$ values of $g_x = 2.3498$, $g_y = 2.4410$ and $g_z = 5.2933$. The QTM process within ground KD is found to be triggered by the substantial magnitude of transverse anisotropy ($|E/D| = 0.29$). Moreover, $M_S = \pm 3/2$ level is observed to be more stabilized than $M_S = \pm 5/2$ level. The magnetic relaxation is observed to emerge from the interplay of significant QTM (0.76), partial Orbach process (0.61), and TA-QTM through the first excited state (1.27). Although, faster relaxation of the magnetization shows absence of the SMM behavior here and the sign of $D$ parameter is also counterproductive towards designing the potent zero-field SMMs. Still, this complex may exhibit slow magnetic relaxation in the presence of an applied dc field, indicating field-induced SMM behavior with large positive $D$ and $E$ parameters as previously observed for poly-coordinated Co complexes. To ascertain this behavior extensively, further investigations such as dc and ac susceptibility measurements, high-field EPR measurements need to be done.

In case of non-Kramers systems i.e. complex 2 and 3, qualitative energy profile diagram derived from CASSCF+NEVPT2 method is depicted in the Supporting Information (Figure S3). Complex 2 with positive $D$ value owns $M_S = 0$ ground state. However, complex 3 pretends to have large axial magnetic anisotropy with negative $D$ of $-57.86 \text{ cm}^{-1}$, it is found to relax appreciably via QTM mechanism in the ground state, which impedes its probable avenues of behaving as an SMM under zero applied field. Taking into account the computed high $D$ value and analysis of magnetization blocking barrier, complex 1 is expected to behave as prospective SMM. However, the magnetic anisotropy could also be diminished due to spin relaxation induced via spin-vibrational couplings. Therefore, to investigate the bottleneck effects of spin-vibrational couplings and ensure the SMM behavior of complex 1, we have explored this complex for spin-vibrational studies.
Magnetization Relaxation via Spin-vibrational Coupling for complex 1

The energy barrier $U_{\text{eff}}$ decides the value of $T_B$ for a specific system however that temperature is achievable or not will be determined by the under-barrier relaxation via spin-vibrational coupling. A plethora of stimulating reports appeared recently, interpreting the impact of lattice vibrations coupled with electronic spins on the magnetization relaxation.\textsuperscript{15,87–89} Here, we have probed complex 1, with strong axial magnetic anisotropy, for spin-vibrational dynamics to predict the corresponding relaxation mechanism. The vibrational modes energetically closer to the barrier height are expected to couple with the spin and provide the relaxation pathway.\textsuperscript{90} Therefore, in this work, we have considered all the vibrational modes lying up to the energy of the first excited KD, i.e. lower than the $U_{\text{eff}}$ value of 320.29 cm\textsuperscript{-1}, 46 vibrational modes ($\nu_1$ to $\nu_{46}$) to compute the effect of spin-vibrational coupling on the relaxation pathway. The computed normal modes of optimized geometries are displaced by 0.2 Å up to ± 0.8 Å. To identify the vibrational modes with strong spin-vibrational coupling, we have adopted two different approaches. In the first approach, we have computed the spin-vibrational coupling constants, as proposed by Escalera-Moreno et al., using the following equation describing spin-vibrational term for individual vibrational mode $k$.\textsuperscript{91}

$$C_k = \frac{\hbar}{4\pi} \left( \frac{\delta^2 g_z}{\delta Q_k^2} \right) \frac{1}{m_k \nu_k}$$ (1)

It comprises of the second derivative of $g_z$ component with respect to the structural distortion coordinate $Q_k$, related to the corresponding vibrational mode $k$. The product of reduced mass and frequency for the $k^{th}$ vibrational mode is denoted by $m_k \nu_k$. The coupling strength of a given mode is indicated by the coupling constant $C_k$. Figure 4a illustrates the estimated coupling constants $C_k$ of first 46 normal modes. These depict $\nu_{12}$, $\nu_{15}$ and $\nu_{16}$ (115.95, 140.13 and 143.40 cm\textsuperscript{-1}) exhibit positive coupling while $\nu_{26}$, $\nu_{28}$ and $\nu_{29}$ (198.58,
210.88 and 214.16 cm\(^{-1}\)) show strong negative coupling.

**Figure 4:** a) Computed values of spin-vibrational coupling constant \(C_k\), corresponding to individual vibrational mode \(k\) at CASSCF level, for complex 1. b) Variation of \(D\) value with respect to the distortion parameter \(Q_k\), for few specific modes of complex 1.

Besides, \(\nu_{29}\) has shown a decrease in \(g_z\) value up to 0.2, which is the highest deviation observed in \(g_z\) among all the examined modes. Thus, the magnetic parameters are strongly dependent on the vibration for \(\nu_{29}\) (Table S10 in SI. It is pointed out that this is a bending harmonic mode involving wagging motion of the methyl of tert-butyl group present on the Cp ring and so is observed to be the most detrimental benefactor to the vibrational induced relaxation. The modes with high spin-vibrational coupling constants (\(\nu_{12}, \nu_{15}, \nu_{16}, \nu_{26}, \nu_{28}, \nu_{29}\)) also involve more shift in the first coordination sphere, probably due to molecular rotations and delocalized intramolecular distortions (see animated GIF files in SI).\(^{54}\) Nevertheless, Briganti et al. have revealed the crucial role of molecular vibrations beyond the ion’s first coordination sphere in governing spin-vibrational coupling through an electrostatic polarization effect for a Dy SMM.\(^{92}\) Except for the six modes, the impact of spin-vibrational coupling on magnetic anisotropy is just nominal (Figure 4). Accordingly for rest of the inspected modes, the corresponding \(g_z\) values have not been diminished extensively, as reflected by small deviation in the magnitude of second derivatives \((g_z'')\) of \(g_z\) (Table S10 in SI). The derivatives of \(g\)-tensor have been employed suitably for an isotropic system of \(S = 1/2\) organometallic molecule to compute the spin-vibrational coupling while the first derivatives
of the zero-field splitting tensor have been employed to determine spin-vibrational coupling of SMMs.\textsuperscript{93–96} Apart from it, for a system with $S > 1/2$, the zero-field splitting is assumed to have larger energy and hence the zero-field splitting parameters become dominant spin Hamiltonian terms. Therefore, in the second approach, we have computed the derivative of $D$ and $E$, based on the Hamiltonian expressed as\textsuperscript{34}

$$H_{s-vib} = \left(\frac{\delta E}{\delta Q_k}\right)_0 Q_k \left(\hat{S}_x^2 - \hat{S}_y^2\right) + \left(\frac{\delta D}{\delta Q_k}\right)_0 Q_k \left(\hat{S}_z^2 - \frac{S(S+1)}{3}\right)$$ \hspace{1cm} (2)

In this approach, the variation of the largest spin Hamiltonian parameter $D$ with respect to the structural distortion coordinate $Q_k$ has been plotted for few selected modes in Figure 4b. Simultaneously, the numerical values of first derivatives of $D$ and $E$ with respect to $Q_k$ are tabulated in Table S10 in SI. For mode 29, a maximum decrease of $D$ is observed in Figure 4a. Likewise, the $E$ parameter shows largest enhancement for $\nu_{29}$ (Figure S11 in SI), which means both the plots ($D$ vs $Q_k$ and $E$ vs $Q_k$) indicate maximum deviation for this mode. The $U_{eff}$ value is also decreased up to 239.30 cm\textsuperscript{−1} for $\nu_{29}$ using geometry distorted by 0.8 Å, which is the minimum magnitude observed among all the investigated modes. It is quite evident that the modes showing exceptionally high values of $C_k$ using $g_z$ term, as obtained in equation (1), provide a fair indication of extent of the spin-vibrational coupling and correspondingly large change of $D$ value are observed in those modes. This reflects that the results with both the approaches are parallel to each other. Hence, it is deduced that the vibronic couplings are effective to reduce magnetic anisotropy for this complex prominently with mode 29. Moreover, it is observed that not all the low energy modes with large spin-vibrational coupling constants are accountable for relaxing the spin-reversal barrier, yet only a few specific ones, out of them, are detrimental towards it. From all the studies performed in this work, despite of having under-barrier relaxation, complex 1 is accomplished as an potential zero-field SMM with high axial ZFS parameter.
Conclusion

In conclusion, employing ab initio calculations, the present study unravels the origin and nature of magnetic anisotropy in the mononuclear Co complexes having non-Aufbau configuration. The correlated computational methodology of CASSCF/NEVPT2, estimates the spin-Hamiltonian parameters, matching well with the previously reported experimental data for complex 1 and 3. The complex 2 and 4 are found to have easy-plane and tri-axial anisotropy respectively, with large positive $D$ value. The peculiar case of complex 4 highlights the pivotal role of dynamical correlations and extended $d$-shell to evaluate the consistent sign of $D$ using multiconfigurational methods. The magnetization barrier relaxation studies reveal notable relaxation via multiple pathways except for complex 1. Accordingly, complex 1 is ascertained to display SMM behavior in absence of any external applied field, with large axial magnetic anisotropy and suppressed QTM process in ground state, pertaining to diminished rhombicity. Further the extensive analysis of vibronic effects reveals a single mode, below the first excited state, instigating the spin relaxation conspicuously. Due to large spin-vibrational coupling in the 29th mode, the $U_{eff}$ is found to be reduced by $\sim$81 cm$^{-1}$ from the value without spin-vibrational coupling. With the identified spin-vibrational coupling operative in this mode, still this complex could behave as SMM with $U_{eff}$ value of 239.30 cm$^{-1}$. We note that for this bending mode, the vibration is originating from the methyl groups and there is a probability to cease this motion by substituting the hydrogen atoms of these methyl groups. We have the foresight to explore it further with the aim to ameliorate the properties of SMMs.
Acknowledgement

The financial support from Department of Science and Technology through DST-SERB Core Research Grant No. CRG/2019/003237 is greatly acknowledged.

Supporting Information Available: Vertical energies, structural parameters of optimized geometry, vibrational frequencies, computed IR plots, extended active space results, energy profile diagrams.
Animated images of vibrational modes (ZIP).

References


(22) Gupta, S. K.; Rajeshkumar, T.; Rajaraman, G.; Murugavel, R. Is a strong axial crystal-field the only essential condition for a large magnetic anisotropy barrier? The case of non-Kramers Ho (III) versus Tb (III). Dalton Trans. 2018, 47, 357–366.


(64) Park, J. W. Analytical gradient theory for quasidegenerate N-electron valence state 


(66) Heß, B. A.; Marian, C. M.; Wahlgren, U.; Gropen, O. A mean-field spin-orbit method 

(67) Singh, S. K.; Eng, J.; Atanasov, M.; Neese, F. Covalency and chemical bonding in 
transition metal complexes: An ab initio based ligand field perspective. *Coord. Chem. 

(68) Enachi, A.; Baabe, D.; Zaretzke, M.-K.; Schwyen, P.; Freytag, M.; Raeder, J.; Walter, M. D. 

Liu, J.; Bendeif, E.-E.; Pillet, S.; Hill, S., et al. Giant ising-type magnetic anisotropy 
**2013**, *135*, 3017–3026.

(70) Singh, S. K.; Rajaraman, G. Deciphering the origin of giant magnetic anisotropy and 
*7*, 1–8.


Walsh, J. P.; Murray, K. S.; Rajaraman, G.; Shanmugam, M. A synthetic strategy


(80) Gómez-Coca, S.; Urtizberea, A.; Cremades, E.; Alonso, P. J.; Camón, A.; Ruiz, E.;


