Multi-Technique Experimental Benchmarking of the Local Magnetic Anisotropy of a Cobalt(II) Single-Ion Magnet

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ABSTRACT: A comprehensive understanding of the ligand field and its influence on the degeneracy and population of d-orbitals in a specific coordination environment are crucial for the rational design and enhancement of magnetic anisotropy of single-ion magnets (SIMs). Herein, we report the synthesis and comprehensive magnetic characterization of a highly anisotropic Co\(^{II}\) SIM, [L\(_2\)Co\(\)TBA\(_2\)]\(_2\) (L is an N\(_N'\)-chelating oxalinilido ligand), that is stable under ambient conditions. Dynamic magnetization measurements show that this SIM exhibits a large energy barrier to spin reversal U\(_{\text{eff}}\) > 300 K and magnetic blocking up to 3.5 K, and the property is retained in a frozen solution. Low-temperature single-crystal synchrotron X-ray diffraction used to determine the experimental electron density gave access to Co d-orbital populations and a derived U\(_{\text{eff}}\) 261 cm\(^{-1}\), when the coupling between the d\(_x^2\) - y\(^2\) and d\(_{xy}\) orbitals is taken into account, in very good agreement with ab initio calculations and superconducting quantum interference device results. Powder and single-crystal polarized neutron diffraction (PNPD, PND) have been used to quantify the magnetic anisotropy via the atomic susceptibility tensor, revealing that the easy axis of magnetization is pointing along the N–Co–N' bisectors of the N\(_N'\)-chelating ligands (3.4° offset), close to the molecular axis, in good agreement with complete active space self-consistent field/N-electron valence perturbation theory to second order ab initio calculations. This study provides benchmarking for two methods, PNPD and single-crystal PND, on the same 3d SIM, and key benchmarking for current theoretical methods to determine local magnetic anisotropy parameters.

KEYWORDS: cobalt single-ion magnet, magnetic anisotropy, single-crystal polarized neutron diffraction, experimental electron density, polarized neutron powder diffraction, magnetic blocking, single-crystal synchrotron X-ray diffraction

INTRODUCTION

The rapid growth of the digital ecosystem in recent decades has made the need for powerful processors and high-density data storage systems more apparent, and single-molecule magnets (SMMs) are considered as having great potential in this regard.\(^1\)--\(^6\) The last three decades have seen tremendous progress in this field, both on the synthetic side as well as in the development of computational methods and new advanced spectroscopic techniques that provide a direct correlation between experimental findings and theoretical models.\(^7\)--\(^15\) In recent years, some excellent high-performance 3d- and 4f-ion-based SMMs have been reported that possess a very high effective energy barrier for magnetization reversal (U\(_{\text{eff}}\)) and blocking temperature (T\(_{\text{B}}\)).\(^16\)--\(^25\) In the case of SMMs based on 3d metal ions, magnetic bistability originates from an energy barrier (U\(_{\text{eff}}\)) that in turn results from the zero-field splitting (ZFS) of the ground spin multiplet. Current synthetic strategies thus target systems that minimize quenching of the angular momentum L, usually via ligand field design that preserves degeneracy of the (d\(_x^2\) - y\(^2\), d\(_{xy}\)) and/or (d\(_{xz}\), d\(_{yz}\)) orbital pairs. Even in the case of largely quenched orbital angular momentum, however, sizable ZFS may result from spin–orbit coupling (SOC). Here, the axial ZFS parameter (D) and the total ground spin-state (S) define the energy barrier for a 3d SMM with U\(_{\text{eff}}\) = |D|S\(^2\) or U\(_{\text{eff}}\) = |D|(S\(^2\) – 0.25) for integer and non-integer spin systems, respectively.

Among the 3d transition metals, Co\(^{II}\) ions are particularly exploited for the development of single-ion magnets (SIMs).\(^26\)--\(^28\) The main emphasis is to increase the effect of SOC to enhance ZFS by designing systems with a defined geometry and coordination environment to achieve quasi-degenerate sets of orbitals.\(^26\) Prominent examples are two-
coordinate nearly linear d<sub>4</sub> complexes such as [Fe<sup>II</sup>(C\((\text{SiMe}_3)_2\))<sub>2</sub>]<sup>−</sup> and [(SPr)Co<sup>IV</sup>Ndmp] which feature a large orbital angular momentum contribution or the linear dialkyl complex Co<sup>II</sup>(C\((\text{SiMe}_3)\text{ONaph})<sub>2</sub>)<sup>−</sup> exhibiting a limiting magnetic anisotropy for a Co<sup>III</sup> ion with a non-Aufbau ground state \( L = 3.16<sup>−</sup>18 \). However, the highly reactive nature and low stability of these complexes render them impractical for, e.g., anchoring on surfaces and for any device fabrication process. On the other hand, some four, six, and eight coordinate Co<sup>II</sup> complexes have been shown to serve as rugged and air-stable SIMs with moderate and high energy barriers;<sup>16,29–33</sup> however, only a few of these Co<sup>II</sup> SIMs have been reported to exhibit slow relaxation dynamics in the absence of an applied magnetic field (see Table S5), the first reported one being the highly air-sensitive complex (Ph<sub>3</sub>P)<sub>2</sub>[Co(SPH<sub>3</sub>)]<sup>2</sup>.<sup>42</sup>

While beneficial design guidelines for conceiving SIMs with higher operating temperatures have emerged, further progress is still hampered by the difficulty of experimentally accessing the molecular magnetic susceptibility tensor, and by a limited understanding of the effects of local molecular and lattice vibrations and hyperfine coupling effects, etc., on the dynamics of the relaxation mechanism.<sup>34,35</sup> Common theoretical methods still have their limitations as they mostly exclude various intermolecular interactions and packing effects in the crystalline state to avoid overparameterization, whereas experimental parameters obtained from superconducting quantum interference device (SQUID) magnetometry include the entirety of effects operative in the solid state. To obtain more precise local magnetic anisotropy parameters, sophisticated techniques such as low-temperature high-field high-frequency electron paramagnetic resonance (EPR), X-band EPR, variable field far-infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) paramagnetic shift, and torque magnetometry have been used.<sup>9,11,13</sup> These techniques not only enable direct estimation of the magnitude and sign of \( D \) but simultaneously allow for cross-verification of the theoretical models used.

In addition to the above-mentioned spectroscopic techniques, low-temperature single-crystal synchrotron X-ray diffraction has been employed to model an atom-centered experimental electron density (EED).<sup>7</sup> EED studies have been recently applied in the field of molecular magnetism to obtain the experimental \( d \)-orbital population in SMMs.<sup>6,45</sup> The \( d \)-orbital populations not only give an idea about the ligand field splitting but also a direct estimation of the ZFS. The strengths of the EED approach have also recently been exploited to quantify the oblateness of the 4f-valence EED in a Dy<sup>III</sup> SIM, and thus the magnetic easy axis as well as an estimate of the \( M \)-composition of the electronic ground state.<sup>8</sup> In addition to EED studies, polarized neutron diffraction (PND) provides local atomic magnetic susceptibility tensors and the direction of the easy-axis or easy-plane with respect to the local coordination environment. This has been utilized in a few cases to study the correlation of magnetic anisotropy with the local coordination structure.<sup>12,66–50</sup> The major drawback of this method is the requirement of \(+1\) mm\(^2\) single crystals suitable for diffraction. However, it has recently been shown by some of us that the atomic susceptibility tensor can also be obtained reliably from powder PND measurements,<sup>46,51,52</sup> substantially advancing this method as it is now pertinent to nearly all materials. These experimentally observable parameters also give confidence and reliability to the results obtained from theoretical calculations that are crucial for making significant progress toward the realization of high-performance SMMs. In particular, the magnetic easy axes derived from interpreting low-temperature high-resolution synchrotron X-ray diffraction in two Dy<sup>III</sup> SIMs were found to deviate by only 13.1 and 8.7° compared to those obtained by ab initio calculations.<sup>6</sup>

In this report, we introduce an air-stable dianionic Co<sup>II</sup> complex derived from an \( N,N' \)-chelating bis(4-chlorophenyl)-oxanilido ligand (H<sub>2</sub>L)<sup>33</sup> [L<sub>2</sub>Co](TBA)<sub>2</sub> (1), which exhibits a very high energy barrier for magnetization reversal under zero magnetic field and displays magnetic blocking up to 3.5 K. This new complex has been magnetically characterized both in solid state and frozen solution by direct current (dc) and alternating current (ac) magnetometry. A bouquet of advanced experimental and computational techniques including low-temperature single-crystal synchrotron X-ray diffraction with multipole refinement of the electron density (ED), powder PND, single-crystal PND, and ab initio calculations have then been applied to interrogate the signatures and the origin of the large magnetic anisotropy of I. This study demonstrates that polarized neutron powder diffraction can be very useful to benchmark the local magnetic anisotropy of a Co<sup>II</sup> SIM, opening a way to bypass the requirement of large single crystals.

### RESULTS AND DISCUSSION

**Synthesis, Characterization, and Molecular Structure**

The Co<sup>II</sup> complex [L<sub>2</sub>Co](TBA)<sub>2</sub> (1) and its Zn<sup>II</sup> analogue [L<sub>2</sub>Zn](TBA)<sub>2</sub> (2) were synthesized by the reaction of anhydrous CoCl<sub>2</sub> or ZnCl<sub>2</sub> respectively, with the dipotassium salt of the ligand (H<sub>2</sub>L) under inert dinitrogen atmosphere and subsequent cation exchange with tetrabutylammonium bromide (TBABr; Scheme S1). Large block-shaped crystals were grown by slow diffusion of diethyl ether into MeCN solutions of the products. Complexes 1 and 2 were found to be stable under ambient aerobic conditions in the solid state for months without any significant decomposition.

After initial structure elucidation by standard single-crystal X-ray diffraction (see the SI for details), low-temperature high-resolution single-crystal X-ray synchrotron diffraction data of complex 1 were recorded at 25 K. I crystallizes in the triclinic space group PI with the Co<sup>III</sup> ion in a distorted tetrahedral \( [N_4] \) coordination environment with two dianionic ligands close to an orthogonal arrangement (Figure 1). The charge of the \([L_2Co]^{2−}\) dianion is balanced by two TBA cations. The Co–N bond lengths lie in the narrow range 1.9766(4)–1.9969(9) Å. The N(1)–Co–N(2) and N(3)–Co–N(4) bite angles of the chelating oxanilido ligands [83.88(2) and 83.63(2)°] are considerably smaller than the other four N–Co–N angles [120.23(2)–129.50(2)°], thus giving rise to an approximate \( D_{4h} \) symmetry or elongated tetrahedron (\( r_e = 0.756\), Table S9).<sup>54</sup> The dihedral angle between the chelating \( N = Co–N \) planes is 87.88°, close to an orthogonal situation (Figure 1). The nearest metal ions in the lattice are separated by 11.82 Å. The isomorphous Zn<sup>II</sup> complex (2) displays similar structural features as complex 1 (see the SI for details). Selected bond lengths and angles of complexes 1 and 2 are listed in Table S10.

The Vis–NIR spectrum of solid 1 reveals apparent absorption bands at 529 and 566 nm as well as a broad absorption extending from 800 to 1600 nm, centered around 1120 nm (Figure S8). In an environment of ideal \( T_d \) symmetry,
Co\textsuperscript{II} ions with a\textsuperscript{3}A ground state feature three spin-allowed transitions to the \( ^4T_{2u}, ^4T_{1u}(\text{F}) \), and \( ^4T_{1u}(\text{P}) \) excited states. However, as evident from the crystal structure (Figure 1 inset and Table S9), the \( \{N_2\} \) coordination sphere of the Co\textsuperscript{II} ion in I is tetragonally elongated away from \( T_d \) toward \( D_{2h} \) symmetry, giving rise to multiple transitions that lead to broad absorption bands.\textsuperscript{32} The Vis–NIR spectrum of I in MeCN (Figure S9) shows similar bands at 530 and 568 as well as the broad feature centered around 1130 nm, indicating that the molecular structure is retained in solution. Rather low extinction coefficients (\( \epsilon < 800 \text{ M}^{-1} \text{cm}^{-1} \)) corroborate that the absorption bands in the visible and NIR region originate from \( d-\delta \) transitions.

**Magnetic Properties of 1**

The static magnetic properties of complex I have been studied using a polycrystalline powdered sample covered with low-viscosity inert oil to prevent any torquing in the magnetic field. At 200 K, the \( \chi_MT \) value of 3.16 cm\(^3\) K mol\(^{-1}\) is higher than the spin-only value of one isolated Co\textsuperscript{II} ion (S = 3/2, \( g = 2.0 \), \( \chi_MT = 1.875 \text{ cm}^3 \text{ K mol}^{-1} \)), evidencing significant orbital contributions to the magnetic moment (Figure 2). The \( \chi_MT \) value decreases slowly upon lowering the temperature before decreasing more sharply below 6 K to finally reach a value of 2.32 cm\(^3\) K mol\(^{-1}\) at 2 K, the latter decrease indicates the presence of substantial magnetic anisotropy. The magnetization of I at 2.0 K rises steeply with magnetic fields up to 1.5 T before showing a more gradual further increase until 7 T, finally reaching 2.31 \( \mu_B \), without complete saturation (Figure S15). This value is well below the expected \( M_{sat} \) value of 3.0 \( \mu_B \) for an isolated isotropic \( S = 3/2 \) system.

To gain further insight, the magnetic susceptibility and variable-temperature variable-field magnetization data (Figure S14) were simultaneously simulated with the program julX_\textsuperscript{2}a\textsuperscript{55} using the spin Hamiltonian in eq 1

\[
\hat{H} = D\left[S_z^2 - \frac{1}{3}(S + 1)\right] + E(S_x^2 - S_y^2) + \mu_B\vec{B}\vec{g}\vec{S} 
\]

where the first term represents magnetic relaxation through QTM, the second and third terms correspond to relaxation via magnetic relaxation through QTM, \( \chi_M' \) component was observed from 4.5 to 20.0 K in the absence of any external dc field (Figure 3a). Cole–Cole plots of the ac susceptibilities show two merging semi-circular curves, indicating the existence of two distinct relaxation processes with one dominating at a lower temperature (Figure 3b). The \( \chi_M' \) versus \( \chi_M'' \) curves were fitted with a generalized Debye function, and the relaxation rates (\( \tau^{-1} \)) for the fast and slow relaxation processes (FRP and SRP) were extracted (Table S1). Insight into the mechanism of magnetic relaxation was obtained by fitting the relaxation rates (\( \tau^{-1} \)) using the following function,

\[
\tau^{-1} = \tau_{QTM}^{-1} + AH^4T + CT^4 + \tau_0^{-1}\exp\left(-U_{diss}/k_BT\right) 
\]

Figure 1. Molecular structure of the anion of 1 at 25 K (90% probability ellipsoids); hydrogen atoms, disordered parts, and cations have been omitted for clarity. The inset shows the nearly orthogonal arrangement of the Co-NCCN metallocycles.

Figure 2. Temperature dependence of \( \chi_MT \) for 1 measured under an applied dc field of 0.5 T. The black solid line is the best fit to the spin Hamiltonian in eq 1. Inset: Zero field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility measurements showing clear blocking at ca. 3.5 K for 1. The solid lines are only a guide to the eye.
direct and Raman processes, and the last term accounts for relaxation through the Orbach mechanism. The fast relaxation process exhibits temperature-independent relaxation rates at lower temperatures indicating the presence of QTM (Figure S18). Fitting the relaxation rates of the FRP over the entire temperature range with a combination of Raman and QTM processes yields $n = 4.73 \pm 0.18$ and $C = 1.36 \pm 0.07 \times 10^{-2} \text{s}^{-1} K^{-n}$ and $\tau_{QTM} = 2.04 \pm 0.24 \times 10^{-3} \text{s}$ (Figure S18d).

Multiple attempts were made to fit the relaxation rates of the SRP using a combination of different relaxation processes, but a complete fit could not be obtained at lower temperatures. It is interesting to note that the relaxation rates obtained under zero dc field for a frozen dimethylformamide (DMF) solution of complex 1 could be satisfactorily fitted with a combination of Orbach and Raman relaxation pathways (vide infra, Figure 3d). A reasonable fit was obtained by treating the relaxation rates of the SRP with a combination of Orbach and Raman processes with $U_{eff} = 325 \text{ K}$ (fixed to $|2D|$), $\tau_0 = 1.46 \pm 0.13 \times 10^{-11} \text{s}$, $n = 4.54 \pm 0.04$, and $C = 4.92 \pm 0.59 \times 10^{-3} \text{s}^{-1} K^{-n}$. The inclusion of a QTM process did not influence the quality of the fit. The best-fit parameters obtained are comparable with those reported in the literature for Co$^{II}$ SIMs. Complex 1 displays a bite angle and dihedral angle close to those of highly anisotropic four-coordinate Co$^{II}$ SIMs reported in the literature (see Table S5). The application of an optimum dc field of 2000 Oe quenches the FRP, and only one relaxation process is evident from the Cole−Cole plots (Figure S19). The relaxation rates obtained under a dc field of 2000 Oe are comparable to the relaxation rates obtained (SRP) under a zero-dc field (Figure S30 and Table S2). As in the previous case, the relaxation rates could be fitted assuming a combination of Orbach and Raman mechanisms, yielding $U_{eff} = 325 \text{ K}$ (fixed to $|2D|$) with $\tau_0 = 3.62 \pm 0.08 \times 10^{-11} \text{s}$, $n = 4.98 \pm 0.05$, and $C = 1.47 \pm 0.21 \times 10^{-3} \text{s}^{-1} K^{-n}$ (Figure S19d).

To establish the intrinsic relaxation dynamics of 1 in the absence of intermolecular dipolar interactions, we prepared magnetically diluted samples containing ca. 5% (1′) or 2% (1″) of Co$^{II}$ complex 1 in the isomorphous diamagnetic matrix of Zn$^{II}$ complex 2. In contrast to the zero-field ac susceptibility measurements for the crystalline sample of pure 1, interestingly only a single relaxation process was observed for magnetically diluted 1′ throughout the whole temperature range (Figure S20, Table S3), similar to the ac susceptibility signature found for 1 upon application of a 2000 Oe dc field. Best-fit parameters are $U_{eff} = 325 \text{ K}$ (fixed to $|2D|$), $\tau_0 = 1.37 \pm 0.07 \times 10^{-10} \text{s}$, $n = 4.75 \pm 0.04$, and $C = 2.61 \pm 0.29 \times 10^{-3} \text{s}^{-1} K^{-n}$ (Figure S20d). Overall, the relaxation rates (SRP) extracted for

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**Figure 3.** (a) Out-of-phase ($\chi''$) component of the frequency-dependent ac susceptibility measured in an oscillating ac field of 3.0 Oe and zero applied dc field for 1. (b) Cole−Cole plots for 1 under zero dc field revealing two relaxation processes. (c) Cole−Cole plots for the frozen DMF solution of 1 under zero dc field revealing a single relaxation process. (d) Plot of the relaxation rate $\tau^{-1}$ (logarithmic scale) versus $T$ for the SRP (green circles) and for the frozen DMF solution of 1 under zero applied dc field. The solid blue line corresponds to the best fit including Orbach and Raman mechanisms.
pure 1 and magnetically diluted 1’ are comparable over the entire temperature range (Figure S30 and Table S3). Temperature-dependent hysteresis measurements for 1’ (Figures S24 and S25) show slightly larger hysteresis loops with a minimal increase in coercivity compared to pure 1. In addition, ZFC and FC magnetic susceptibility measurements reveal no major change in the blocking temperature ($T_B$) of 3.5 K (Figure S26), confirming the molecular origin of the SIM behavior.

Magnetic properties in solution have been reported only for a few SMMs, though it is a prerequisite for many potential SMM applications that they preserve their slow relaxation signatures as isolated molecules outside a crystal lattice. The lack of lattice solvent molecules facilitates a comparison of the magnetic properties of 1 in the solid state/powder and in solution. The high solubility of complex 1 prompted us to investigate a frozen 100 mM DMF solution of 1 (Figure S29), which indeed exhibits relaxation dynamics and hysteretic behavior very similar to the pristine solid sample of 1, though only a single relaxation is observed (Figure 3c). This corroborates that the relaxation dynamics observed for the solid material reflect an intrinsic property of the complex. The relaxation rates are comparable to those observed in the solid state (Figure S30 and Table S4) and could be fitted by a combination of Orbach and Raman relaxation mechanisms over the entire temperature range (Figure 3d); the best-fit parameters are $U_{eff} = 325$ K (fixed to I2DI) with $T_B = 7.38 \pm 0.27 \times 10^{-10}$ s, $n = 4.13 \pm 0.03$, and $C = 1.93 \pm 0.20 \times 10^{2}$ s$^{-1}$ K$^{-n}$.

**Experimental Electron Density**

We have recently shown how the ED, and more specifically the $d$-orbital populations derived from it, can be exploited to extract the energy barrier for magnetic relaxation and facilitate a comparison with the values obtained using magnetization measurements. Therefore, the low-temperature high-resolution single-crystal X-ray synchrotron diffraction data of complex 1 in the ground electronic state have been used to refine a multipole model (MM) of the EED. A detailed account of the data collection and model refinement is given in the SI. We note that one of the cations is strongly disordered, even at this low temperature (25 K). However, the largest residual density features around the cations (~1.3 eÅ$^{-3}$) are much higher than those found near the [L$_2$Co]$^{2-}$ dianion (~0.6 eÅ$^{-3}$), which gives confidence in the extracted $d$-orbital populations for the central Co ion.

It is well-known that for a metal ion in an elongated tetrahedral coordination sphere with the unique axis along the elongation axis, the $d$-orbital energies are ordered as follows: $d_3^z < d_{x^2-y^2} < d_{xy} < d_{yz} < d_{xz}$. From the MM, $d$-orbital populations for I were extracted as shown in Table 1. This table highlights two conspicuous points. First, when the total population in the $d$-orbitals is taken into account, all orbitals show significant deviation from integer populations. For $d_{x^2-y^2}$ and $d_{xy}$, this clearly indicates strong mixing of the ground ($d_{x^2}$) and excited state ($d_{z^2}$) via SOC, while the deviations for the other three orbitals are the results of ligand-to-metal charge transfer. The second point is the asymmetry in the $d_{xy}$ and $d_{xz}$ orbital populations, which are expected to be nearly degenerate. Table 1 also provides the $d$-orbital populations resulting from a theoretical MM (theoretical electron density, TED; for details, see the SI). The overall distribution is similar but does not replicate the variations in obtained from the theoretical calculation. We exploit the nearly single Slater-determinant nature of the two lowest-lying and energetically isolated states, (1) and (2), prior to SOC. This paves the way to directly quantify the effect of SOC from the contribution, or weight, of (2) in the ground state, KD1. In addition, clearly given the discernible $d$-orbital distribution of (1) and (2), this weight is easily retrieved from the experimental $d$-orbital populations. We note that the experimental temperature of 25 K ensures that we have probed the ED of KD1 exclusively, with no contamination from KD2. The final step, converting the $d$-orbital distribution to an energy barrier involves an existing linear correlation between the energy barrier and weight of (2), see Scheme 1.

### Table 1. $d$-Orbital Populations on Co$^{II}$ in 1 from Various Methods

<table>
<thead>
<tr>
<th>$d$-orbital</th>
<th>MM-idealized</th>
<th>MM-experimental</th>
<th>ab initio (KD1)</th>
<th>ab initio (KD2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{xy}$</td>
<td>1.05 (13.6%)</td>
<td>1.14 (15.4%)</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>$d_{xz}$</td>
<td>1.38 (17.9%)</td>
<td>1.14 (15.4%)</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>$d_{yz}$</td>
<td>1.47 (19.1%)</td>
<td>1.33 (17.9%)</td>
<td>1.282</td>
<td>1.089</td>
</tr>
<tr>
<td>$d_{x^2-y^2}$</td>
<td>1.97 (25.5%)</td>
<td>1.75 (23.6%)</td>
<td>1.715</td>
<td>1.903</td>
</tr>
<tr>
<td>$d_{z^2}$</td>
<td>1.84 (23.8%)</td>
<td>2.06 (27.7%)</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>total</td>
<td>7.71</td>
<td>7.43</td>
<td>6.997</td>
<td>6.992</td>
</tr>
</tbody>
</table>

*For ab initio, the $d$-orbital populations have been obtained by directly taking the weights of (1) and (2) as the face value of $d_{xy}$ and $d_{x^2-y^2}$. This has been done both for KD1 and KD2. For MM, this is the conversion from refined multipole parameters on Co$^{II}$. See text for more details.*

**Scheme 1. Scheme Showing the Two Lowest-Lying CASSCF States and the Kramers Doubles Appearing Due to Spin–Orbit Coupling**

![Scheme 1](https://doi.org/10.1021/jacsau.2c00575)

"Dashed lines show which CASSCF states contribute to the Kramers doubles (KD2). The dashed line between (2) and KD1 is colored as a guide for the eye due to the linear relation between this weight and the energy barrier, $\Delta_{K}$."

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While the MM gives access to the d-orbital populations through the refined multipole parameters, both from the theoretical (TED) and the EED, the theoretical calculations lead directly to the weight of (2) in the ground state KD1, which is 0.282 (see the SI for more details). The d-orbital population from the ab initio calculation, the TED, and EED are summarized in Table 1.

We note that the weight of 0.282 of (2) in KD1 found for the theoretical calculation leads to an energy barrier of $\Delta E = 236.3 \text{ cm}^{-1}$, in perfect accordance with the calculated D value of $-118.1 \text{ cm}^{-1}$ (vide supra). This confirms the accuracy of the linear relationship between $\Delta E$ and the weight of (2). The significant coupling between $d_x^2 - y^2$ and $d_{xy}$ orbitals is clearly reflected in the populations, both from the ab initio calculation (1.715 and 1.282, respectively) and experimentally (1.967 and 1.472, respectively). The $d_z^2$ orbital is significantly depopulated in the EED relative to the expected 2.0 electrons, while the $d_{yz}$, on the other hand, deviates from the expected population of 1e$^-$ with a higher value. All these deviations are signs of the mixing of states.

We use two different approaches for calculating the value of the energy barrier, $\Delta K$, from the experimental d-orbital population. In the first approach (A), the population in the $d_x^2 - y^2$ orbital (1.967) is used to represent the weight (0.967) of the ground state, (1), followed by a remaining contribution (0.033) which is the weight of the first excited state. This leads to the following wave function for the ground state: $\text{GS}(A) : 0.967|1, \pm 3/2 \rangle + 0.033|2, \pm 3/2 \rangle$. With this composition, $\Delta K$ is calculated to be only 30.8 cm$^{-1}$. In the second approach (B), we posit that the populations of $d_x^2 - y^2$ and $d_{xy}$ represent the weights of the ground and first excited states, respectively. This leads to the wave function $0.967|1, \pm 3/2 \rangle + 0.472|2, \pm 3/2 \rangle$, which after normalization gives $\text{GS}(B) : 0.672|1, \pm 3/2 \rangle + 0.328|2, \pm 3/2 \rangle$. This composition gives a $\Delta K$ value of 261 cm$^{-1}$. In the first approach (A), where the wave function is based solely on the population of the $d_x^2 - y^2$ orbital, the contribution to the first excited state is very low, which underestimates the energy barrier, $\Delta K$. The reason is the large total d-electron count, making this approach less reliable. In the second approach (B), where populations of both the $d_x^2 - y^2$ and $d_{xy}$ orbitals are taken into account, the effect of the total d-electron count is removed and leads to a more realistic value compared to magnetic measurements and theoretical calculations. This shows that the coupling of the two orbitals is important to consider when the energy barrier is estimated from the EED.

**Polarized Neutron Diffraction**

While the EED approach can estimate the energy barrier with good precision, it assumes the existence of a magnetic anisotropy axis as the d-orbitals are defined according to a coordinate system in which the z axis is along the elongation direction and the $x,y$ axes point in-between ligands. Indeed, information on these axes is not directly accessible via the EED. In contrast, the local magnetic anisotropy in paramagnetic compounds can be quantified using PND via the site susceptibility model. The method has been successfully used to determine the atomic susceptibility tensors in several SMMs. Recently, the applicability of the method was extended to powder samples (polarized neutron powder diffraction, PNPD), alleviating the demanding need for large single-crystals and time-consuming measurements at multiple crystal orientations. However, this remarkable progress has so far only been exploited on a single occasion to study the atomic susceptibility tensor, without independent verification from the single-crystal method. Importantly, the present work thus includes benchmarking the two methods, PNPD and single crystal PND, on the same compound. PNPD data of 1 were collected at the D20 diffractometer of ILL using neutrons of a 2.41 Å wavelength at 2 K and an applied field of 1 T. Single-crystal PND data of 1 were collected at the HB-3A/DEMAND diffractometer of Oak Ridge National Laboratory (ORNL), high flux isotope reactor (HFIR) using neutrons of a 1.5424 Å wavelength at 4 K and an applied field of 0.48 T. Susceptibility tensors were refined using the Python-package Cryspy (0.5.9)/Cryspy_Editor (1.6.0). The synchrotron X-ray structure discussed earlier was used to simulate the nuclear structure factors. Describing the tensor required the refinement of six independent susceptibility parameters due to the site symmetry of the Co$^{II}$ ion (for details see the SI). In Figure 4, the refined susceptibility tensor for the Co site in 1 is visualized as an ellipsoid overlaid on the molecular structure, in a manner similar to depicting atomic displacement parameters.

For the PNPD model, the $2\theta$ range 7.6–32.1° was used. Background, shape parameters, asymmetry parameters, scale factor, and beam offset were refined using the sum and difference patterns. These parameters were then fixed, and the susceptibility parameters were modeled using only the difference pattern. The obtained susceptibility tensor leads to a prolate surface and thus a clearly discernible easy axis anisotropy of 1. The eigenvector corresponding to the most
magnetically susceptible direction nearly bisects the bridging C–C bond of the amides of the oxanilido ligand, thus lying close to the molecular axis (3.8° offset to the N1–N2 midpoint). The eigenvalues of the susceptibility tensor [3.35(17), −0.12(15), 0.56(18) μµB T−1] indicate a strong axial magnetic anisotropy of I. These results agree with the magnetization data and ab initio calculations, which also suggest easy-axis anisotropy. We find a close agreement (7.3° deviation) between the easy-axis directions from CASSCF calculations and PNPD, Figure 5. As the PNPD measurements were performed in the linear region of the magnetization curve, the powder-averaged magnetization can be estimated using the expression 1/3(χx + χy + χz)H, resulting in a value of 1.3(1) μµB. This value is somewhat lower than the expected value of ~1.65 μµB at 2 K and 1 T obtained from the bulk magnetization curve shown in Figure S15. It should be noted that the crystal structure coordinates used in the refining of the PND data were based on an X-ray synchrotron diffraction experiment, which may explain the discrepancy of the estimated powder averaged magnetization using local anisotropy parameters with the expected value. Indeed, it is well known that neutrons are more sensitive to the hydrogen position than X-rays. Thus, since the polarized signal is proportional to the product of nuclear and magnetic structure factors, uncertainty in the estimation of the former can cause a systematic error in the calculation of the atomic susceptibility tensor.

A refinement model using only single-crystal PND data was not possible, as we could only extract flipping ratios from one magnetic field direction for the single-crystal PND experiment. This was because the crystal broke during the multiple heating and cooling cycles. However, it has been possible to refine a joint PND/PNPD model using the 38 extracted flipping ratios together with the PNPD data. From this, a similar susceptibility ellipsoid was found, Figure 4 (bottom), as well as a similar gₓ direction, Figure 5 (10.1° offset to PNPD easy axis). The found discrepancies between easy axis directions from ab initio calculations and PND/PNPD measurements are of similar magnitudes to those found by other studies.12,51

CONCLUSIONS

In summary, we have employed a set of sophisticated techniques, including static and dynamic magnetometry, EED based on high-quality, low-temperature synchrotron diffraction data, powder and single-crystal PND, and ab initio electronic structure analysis to decipher the origin and quantify the large magnetic anisotropy of a new Co II based SIM. This Co II SIM with two chelating diamido ligands and strongly distorted local tetrahedral geometry around Co II features a large energy separation of over 300 K between the ground and excited-state KDs and shows magnetic hysteresis up to 3.5 K. The slow relaxation dynamics are preserved upon magnetic dilution and in frozen solution, indicating that it is an intrinsic molecular property of I. From the EED, we were able to extract d orbital populations for the Co II ion, which show a clear coupling between the dₓz – y² and dxy orbitals. Calculations of the energy barrier between the two lowest Kramers’ doublets were performed based on results from the EED. When this coupling is taken into account, the resulting energy barrier is 261 cm⁻¹, which correlates well with both magnetic measurements and theoretical calculations. Results from PNPD and PND allow experimental determination of the magnetic susceptibility tensor, showing clear easy axis anisotropy for I; the direction of the easy axis being in good agreement with the ab initio results. The present fundamental study demonstrates the unique strengths of combining a complete magnetic characterization with advanced diffraction methods, in particular single-crystal synchrotron X-ray diffraction and PNPD, in the assessment of SMMs.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Materials

All solvents employed in the syntheses were dried and distilled before use according to standard procedures. Syntheses of the complexes were carried out under a dry and inert nitrogen atmosphere. Unless otherwise stated, all chemicals were purchased from commercial sources and used as received. The proligand H₄L₁, N,N’-bis(4-chlorophenyl)oxanilide, was synthesized following a previously reported procedure.3 Complexes 1 and 2 were found to be stable under ambient atmospheric conditions.

Instruments for Spectroscopic and Analytical Characterization

¹H NMR and ¹³C NMR spectra were recorded on Bruker Avance 400 spectrometers at room temperature. Chemical shifts are reported in parts per million (ppm) relative to residual proton and carbon signals of the solvent. IR spectra were recorded on a Cary 630 FTIR spectrometer equipped with Dial Path Technology and analyzed by FTIR MicroLab software. Vis–NIR (visible–near-IR) spectra of solutions and solid material were recorded with a Varian Cary 5000 spectrophotometer. ESI mass spectra were collected using a Bruker HCT ultra spectrometer. Elemental analyses were performed by the analytical laboratory of the Institute of Inorganic Chemistry at the University of Göttingen using an Elementar Vario EL III instrument.

Synthesis Protocols

[L₂Co(TBA)₃] (1). H₂L₁ (309 mg, 1.0 mmol) was dissolved in dry THF (20.0 mL) and KH (80.0 mg, 2.0 mmol) was added, leading to the evolution of dihydrogen. The solution was stirred overnight and solid anhydrous CoCl₂ (65 mg, 0.5 mmol) was then added. The reaction mixture was stirred at room temperature for 24 h. Tetrabutylammonium bromide (354 mg, 1.1 mmol) was added and stirring continued for a further 24 h. The red solution was allowed to settle and then filtered. The volume of the filtrate was reduced under vacuum to around 4.0 mL. Diffusion of diethyl ether into the solution

Figure 5. Visualization of the magnetic easy axis of I from CASSCF calculations (blue), PNPD (red), and joint PND/PNPD refinement (green). Counterions and hydrogen atoms are omitted for clarity.
led to the formation of reddish pink blocked-shaped crystals (Figure S1) within a few days. Yield: (475 mg, 82% based on Co). Elemental analysis calculated for CoC₆H₄Cl₂CoN₅O₅C₂ 62.23; H 7.66; N 7.26. Found C 61.99; H 7.72; N 7.28. FTIR (cm⁻¹) 2961 (w), 2934 (w), 2874 (w), 1646 (w), 1604 (s), 1582 (s), 1561 (m), 1480 (s), 1458 (m), 1403 (w), 1373 (m), 1302 (s), 1291 (s), 1265 (s), 1211 (w), 1164 (w), 1101 (w), 1087 (m), 1031 (w), 987 (w), 940 (w), 919 (m), 881 (w), 857 (w), 831 (m), 738 (w), 706 (w), 677 (w), 589 (w), 522 (w), 502 (m), 471 (m). ESI-MS (negative ion mode, CH₃CN): m/z 915.1 [M-TBA]⁻, 536.3 [M-T2BA]⁻.

Preparation of the Magnetically Diluted Samples

[L₂Zn](TBA)₂ (1). L₂HCl (309 mg, 1.0 mmol) was dissolved in dry THF (20.0 mL) and KH (80.0 mg, 2.0 mmol) was added, leading to the formation of dihydrogen. The reaction mixture was stirred overnight and solid anhydrous ZnCl₂ (68 mg, 0.5 mmol) was then added. The solution was stirred at room temperature for 24 h. Tetrabutylammonium bromide (354 mg, 1.1 mmol) was added and reduced under vacuum to around 4.0 mL. Diffusion of diethyl ether stirring continued for 24 h. The colorless solution was allowed to settle and then filtered. The volume of the reaction mixture was reduced under vacuum to around 4.0 mL. Diffusion of diethyl ether into the solution led to the formation of colorless block-shaped crystals within a few days. Yield: (490 mg, 84% based on Zn).

Magnetic Measurements

Magnetic measurements were carried out using a Quantum-Design MPMS3 SQUID magnetometer equipped with a 7 T magnet. dc magnetic susceptibility measurements were performed under an applied dc field of 0.5 T with powder polycrystalline samples in the range from 200.0 to 2.0 K. The powdered samples were packed in a polycarbonate or gelatine capsule and covered with low-viscosity perfluoropolyether-based inert oil Fomblin Y45 in a non-magnetic sample holder. Each raw data for the measured magnetic moment was corrected for the diamagnetic contribution of the capsules (including the inert oil) according to $M_{mag} = \chi_H m_H$, with an experimentally obtained gram susceptibility of the capsules including the inert oil. The diamagnetic contribution of the compounds was corrected using Pascal’s constants. Magnetic measurements of frozen solutions were carried out by dissolving the sample in DMF in an NMR tube and sealing the tube under a vacuum to exclude dioxygen. Experimental data were modeled using a fitting procedure to the spin Hamiltonian:

$$\hat{H} = D \sum_i \left( S_i^2 - \frac{1}{3} (S + 1) \right) + E \left( S_i^+ S_j^- + S_i^- S_j^+ \right) + \mu_B \mathbf{g} \mathbf{S}$$

Full-matrix diagonalization of the spin Hamiltonian for ZFS and Zeeman splitting was performed with the julX_2s program. ⁵ ³ ⁵ ac susceptibility measurements were carried out in an oscillating ac field of 3.0 Oe and frequencies ranging from 0.1 to 1000 Hz.
Further spectroscopic and analytical data, crystallographic information, magnetic characterization, and details of theoretical calculations (PDF) ORCA output file from theoretical calculation (TXT)

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