Supporting Information for:

# Slow Magnetic Relaxation in a Pseudotetrahedral Cobalt(II) Complex with Easy-Plane Anisotropy

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## **Table of Contents**

Experimental Details	S4
Additional HF-EPR Interpretation Details	<b>S</b> 7
Table S1: Crystallographic data for 1.	
Figure S1: Variable temperature dc magnetic susceptibility of 1 in	
crystalline and solution phases.	S10
Figure S2: Frequency dependence of the high-frequency EPR peak positions	
of a powder sample of <b>1</b> .	<b>S</b> 11
Figure S3: Temperature dependence of the 333.33 GHz spectrum of a single	
crystal of 1.	S12
Figure S4: Simulations of the parallel and perpendicular Zeeman diagrams	
of <b>1</b> for $D > 0$ and $D < 0$ .	S13
Figure S5: Magnetization data collected on frozen solution of 1.	S14
Figure S6: Magnetization data collected on powder sample of 1.	
<b>Figure S7</b> : Frequency dependence of $\chi_M$ " as a function of dc applied field	
for crystalline 1.	S16
<b>Figure S8</b> : Frequency dependence of $\chi_M$ as a function of dc applied field	
for a frozen butyronitrile solution of <b>1</b> .	S17
Figure S9: Cole-Cole plots used for the determination of the field dependence	
of the magnetic relaxation time, $\tau$ , for crystalline <b>1</b> .	S18
<b>Figure S10</b> : Field dependence of $\tau$ for crystalline 1.	
Figure S11: Cole-Cole plots used for the elucidation of the temperature	

dependence of $\tau$ for crystalline 1.	S20
Figure S12: Graphical representation of the proposed relaxation mechanism.	S21
Figure S13: Solution and Solid-State UV-Vis spectra for 1.	S22
References	S23

#### **Full Experimental Details**

Synthetic Materials and Methods. Unless otherwise noted, all manipulations were carried out at room temperature under an atmosphere of dinitrogen in a Vacuum Atmospheres glovebox or using Schlenk techniques. Acetonitrile (MeCN), diethylether (Et<sub>2</sub>O), and tetrahydrofuran (THF) were deoxygenated by sparging with dinitrogen and dried via a Vacuum atmospheres solvent purification system. CoCl<sub>2</sub> and Na(CF<sub>3</sub>SO<sub>3</sub>) were purchased from Strem. Diatomaceous earth (Celite 545) was purchased from Fisher Scientific and dried by heating under vacuum. All other reagents were used as received. Literature procedures were used to prepare 3G.<sup>1</sup> NMR spectra were recorded on Bruker DRX-500 spectrometer with Oxford Instruments 11.7 T magnet. Chemical shifts are reported in ppm and referenced to residual protiated solvent. Fullwidth at half maxima ( $\Delta v_{1/2}$ ) are reported in Hz. IR spectra were recorded with a Bruker ALPHA FT-IR spectrometer fitted with a diamond ATR module. Elemental analyses were performed at the Microanalytical Facility at the University of California, Berkeley.

Synthesis of [(3G)CoCl](CF<sub>3</sub>SO<sub>3</sub>) (1). To a solution of 3G (560 mg, 1.36 mmol) in acetonitrile (3 mL) was added an acetonitrile solution (5 mL) of anhydrous CoCl<sub>2</sub> (176 mg, 1.36 mmol). The blue solution was stirred for 2 min, and then a solution of Na(CF<sub>3</sub>SO<sub>3</sub>) (235 mg, 1.37 mmol) was added to the mixture. A suspension formed and the mixture was stirred for several hours. The resulting slurry was filtered through a bed of diatomaceous earth and the blue filtrate was concentrated to dryness under dynamic vacuum. The oily residue was dissolved in THF (5 mL) and the product was crystallized from this solution by vapor diffusion of Et<sub>2</sub>O into the solution. The crystalline blue product was collected and dried under vacuum (650 mg, 0.99 mmol, 73% yield). Anal. Calcd. for C<sub>21</sub>H<sub>45</sub>N<sub>9</sub>CoClO<sub>3</sub>F<sub>3</sub>S: C, 38.50; H, 6.92; N, 19.24 %. Found: C, 38.69; H, 7.14; N, 18.84 %. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz, 20 °C): 58.7 ( $\Delta v_{1/2} = 650$  Hz, NMe,

9H), 19.0 ( $\Delta v_{1/2} = 130$  Hz, NMe<sub>2</sub>, 18H), 16.9 ( $\Delta v_{1/2} = 440$  Hz, NMe, 9H), -15.2 ( $\Delta v_{1/2} = 40$  Hz, CMe, 3H) ppm.\* FT-IR (ATR): 2896 (m), 1615 (m), 1532 (s), 1425 (m), 1397 (s), 1262 (CF<sub>3</sub>SO<sub>3</sub>, s), 1146 (CF<sub>3</sub>SO<sub>3</sub>, s), 1067 (CF<sub>3</sub>SO<sub>3</sub>, m), 1027 (CF<sub>3</sub>SO<sub>3</sub>, s), 921 (m), 780 (m), 635 (CF<sub>3</sub>SO<sub>3</sub>, s), 517 (CF<sub>3</sub>SO<sub>3</sub>, m) cm<sup>-1</sup>.



\*Hindered rotation around the C=N bond makes the *trans* (*a* and *b*) and *cis* (*c*) NMe<sub>2</sub> substituents inequivalent, and hindered rotation about one of the two C-NMe<sub>2</sub> bonds (presumably the *trans*, due to steric crowding around the metal) makes the two methyls on one of the nitrogens (*a* and *b*) inequivalent. The set of methylene resonances (*e*) is unobserved in the <sup>1</sup>H NMR, likely due to being paramagnetically broadened into the baseline (or outside the range – 500 to 500 ppm).

**HF-EPR Measurements.** Single-crystal high-frequency EPR measurements were performed in a spectrometer that enabled in-situ rotation of the sample about a fixed axis; details can be found elsewhere.<sup>2</sup> The magnetic field was generated by a 36 T resistive magnet at the National High Magnetic Field Laboratory at FSU, Tallahassee. Variable frequency (300-450 GHz) and temperature measurements were conducted with the field aligned close to the molecular *z*-axis. Powder EPR measurements were carried out in a transmission type spectrometer based on a 17 T superconducting magnet at various frequencies in the range of 50-160 GHz.<sup>3</sup> The sample was finely ground and restrained with KBr in a Teflon container.

Magnetic Measurements. Magnetic data were collected using a Quantum Design MPMS-XL SQUID magnetometer. Measurements for 1 were obtained on finely ground microcrystalline powders (referred to as "solid samples" in the main manuscript) restrained in a frozen eicosane matrix within a polycarbonate capsule or as a butyronitrile solution sealed (under vacuum) in a quartz tube. All sample preparations were performed under an inert atmosphere and very quickly loaded into the SQUID to minimize any contact with air. Dc susceptibility measurements were collected in the temperature range 2-300 K under a dc field of 1000 Oe. Dc magnetization measurements were obtained in the temperature range 1.8-5 K under dc fields of 1, 2, 3, 4, 5, 6, and 7 T. Variable temperature, variable field magnetization data were fit with the program ANISOFIT 2.0.<sup>4</sup> In general, several different values of *E* could be obtained from fitting attempts and had little to no effect on the goodness-of-fit, depending only on the input values for E. As such, only the maximum values of E are reported for fits to magnetization data. Ac susceptibility measurements were obtained in the temperature range 1.8 to 3.0 K under a 4 Oe ac field oscillating at frequencies of 1-1488 Hz, under an applied dc field of 1500 Oe. Dc magnetic susceptibility data were corrected for diamagnetic contributions from the sample holder and eicosane (or butyronitrile), as well as for the core diamagnetism of each sample (estimated using Pascal's constants). No differences in ac and dc susceptibility data were observed for crystals either dried *in vacuo* or moved immediately from the mother liquor to the sample holder with little time to dry.

**X-ray Structure Determination.** Data collection was performed on a single crystal coated with Paratone-N oil and mounted on Kaptan loops. During mounting, the crystals did not show

any signs of desolvation, and the crystal was frozen under a stream of N<sub>2</sub> during measurements. Data were collected using a Bruker QUAZAR diffractometer equipped with a Bruker MICROSTAR X-ray source, APEX-II detector, and using Mo Ka ( $\lambda = 0.71073$  Å) radiation. Raw data were integrated and corrected for Lorentz and polarization effects using Bruker APEX2 v. 2009.1.<sup>5</sup> Absorption corrections were applied using SADABS.<sup>6</sup> Space group assignments were determined by examination of systematic absences, *E*-statistics, and successive refinement of the structures. The crystal structure was solved by direct methods with the aid of successive difference Fourier maps in SHELXL.<sup>7</sup> The crystal did not show significant decay during data collection. Thermal parameters were refined anisotropically for all non-hydrogen atoms in the main body and the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> counterion. Hydrogen atoms were placed in ideal positions and refined using a riding model for all structures.

**Electronic Absorption Spectroscopy.** Solutions were prepared with butyronitrile that had been degassed by successive freeze pump thaw cycles and stored over activated sieves prior to use. Both solution and solid-state spectra were obtained on samples sealed under an inert atmosphere. Solution UV-vis-NIR absorption and diffuse reflectance spectra were collected over the range of 5000-30,000 cm<sup>-1</sup> using a CARY5000 spectrophotometer interfaced to Varian WinUV software.

#### **Additional EPR Interpretive Details**

As can be seen in Fig. S4, panels (a) and (b) reproduce all of the features of the experiments remarkably well (see also Fig. 2 in the main article). Although panels (c) and (d) were obviously generated using parameters optimized for the easy-plane (D > 0) case, they clearly illustrate the incompatibility of the easy-axis scenario. Indeed, it is impossible to find a set of physically realistic parameters that comes close to the experimental observations. For

example, to reproduce the powder results would require both a significant reduction in the magnitude of D and an unphysical E (> |D|/3) parameter. Furthermore, although it is possible to produce a spectrum consisting of three ground state resonances for the D < 0, B//x case, it again involves unphysical parameters that are also completely at odds with the magnetic measurements. Finally, we remark on the fact that the parameters obtained for the easy-plane case are rather well constrained by the combined multi-frequency powder and single-crystal EPR measurements. The powder measurements constrain the g tensor and E to some extent (though there is interdependence of these terms), but are highly insensitive to D. On the other hand, the single-crystal measurements separately constrain D and E very well: D primarily determines the field location (~14 T) of the avoided crossing between the  $m_S = +\frac{1}{2}$  and  $-\frac{3}{2}$  states, while E determines the magnitude of the gap at the avoided crossing. Meanwhile, neither of these features is particularly sensitive to the field misalignment. Consequently, the location of the maximum at  $\sim 14$  T in the main panel of Fig. 2 constrains D, while the curvature at this maximum determines E; it is the minimum at  $\sim 22$  T that necessitates the 15° of field misalignment. Combining these results with the powder measurements then provides a stronger constraint on the g tensor. Overall, the obtained parameter set is quite reasonable for pseudo-tetrahedrally coordinated Co<sup>II</sup>. Finally, we note also that the frequency dependence of the line widths and line shapes is in good accord with the simulations. In the vicinity of the avoided crossing at  $\sim 14$  T and  $\sim 22$  T, the dependence of the resonance frequencies on the applied field becomes very weak and non-linear. Thus, the curved positions on the blue simulation in Fig. 2 produce broad resonance, in contrast to the linear regions at high and low fields.

Empirical formula	$C_{21}H_{45}ClCoF_3N_9O_3S$
Formula weight	655.11
<i>Т</i> , К	100(2)
λ, Å	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> , Å	8.5546(3)
<i>b</i> , Å	13.9935(5)
<i>c</i> , Å	13.9935(5)
<i>α</i> , °	82.2440(10)
β, °	87.1460(10)
γ, °	72.3580(10)
<i>V</i> , Å <sup>3</sup>	1529.76(9)
Ζ	2
$ ho_{\rm calculated}$ , g/cm <sup>3</sup>	1.422
$\mu$ , mm <sup>-1</sup>	0.774
$F_{000}$	690
Crystal dimensions	$0.32 \ge 0.19 \ge 0.10 \text{ mm}^3$
$\theta$ range	2.50 to 28.90 °
Index ranges	$-10 \leq h \leq 11$
	$-17 \le k \le 18$
	$-17 \le l \le 18$
Reflections collected	30253
Independent reflections	6563 [ $R_{\rm int} = 0.0287$ ]
Completeness to $\theta = 28.90$	99.50%
Data / restraints / parameters	6563 / 0 / 354
Goodness-of-fit on $F^2$	1.026
Final <i>R</i> indices $[I > 2\sigma(I)]^b$	$R_1 = 0.0310, wR_2 = 0.0816$
R indices (all data)	$R_1 = 0.0345, wR_2 = 0.0840$
Largest diff. peak and hole	0.470 and -0.378 eÅ <sup>3</sup>

*Table S1.* Crystallographic Data<sup>*a*</sup> for [(3G)CoCl](CF<sub>3</sub>SO<sub>3</sub>) (1).

<sup>*a*</sup>Obtained with Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation monochromated by QUAZAR multilayer mirrors. <sup>*b*</sup> $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ,  $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$ .



**Figure S1.** Variable temperature dc susceptibility data of microcrystalline (dark blue circles) and butyronitrile solution (light blue triangles) samples of **1**. Inset: Magnification of data collected at  $T \le 40$  K. The increase in  $\chi_M T$  above 250 K is reproducible and could be due to a structural phase transition as has been observed in the past.<sup>8</sup> Apparent differences in the low temperature  $\chi_M T$  data could be due to the disruption of a very small long-range exchange interaction by the solution.



**Figure S2.** Frequency dependence of the high-frequency EPR peak positions deduced from studies of a powder sample of 1 at 5 K. Representative spectra recorded in first-derivate mode are displayed in the inset (see ref. 2 for details of the measurement technique). Three branches of resonance are observed, corresponding to the three components of the Landé *g*-tensor (field parallel to *x*, *y* and *z*). The solid lines are simulations of these three branches employing the optimum parameters given in the main text. The presence of a lone high-field component ( $g_{z,eff} = 2.14$ ), well separated from two low-field components ( $g_{y,eff} = 3.81$  and  $g_{x,eff} = 5.28$ ), is indicative of easy-plane type anisotropy; this is explained in more detail by means of the Zeeman diagrams in Fig. S4. It is also noteworthy that the parallel (*z*) component is weaker than expected, suggesting a possible reorientation of the microcrystallites in the powder under the application of the magnetic field. Such an effect would tend to weaken the parallel (*z*) component in the case of an easy-plane (D > 0) anisotropy. Finally, the splitting between the two low-field components ( $g_{y,eff}$  and  $g_{x,eff}$ ) is due to the non-negligible rhombic *E* term.



**Figure S3.** Temperature dependence of the 333.9 GHz spectra displayed in Fig. 2. These measurements demonstrate that all three resonances strengthen and persist to the lowest temperature ( $k_BT \ll$  inter-Kramers separation). Consequently, all three excitations must occur within the ground state doublet.



**Figure S4.** Simulations of the field parallel (B//z) and perpendicular  $(B\perp z)$  Zeeman diagrams of 1 for the two cases D > 0 [(a) and (b)] and D < 0 [(c) and (d)]. The employed Hamiltonian and the magnitudes of the parameters used in these simulations are given in the main text; (a) corresponds exactly to the lower inset to Fig. 2 in the main article, with the different curves representing successive 5° misalignments of the applied field away from the parallel (z) orientation (black curve). The green vertical arrows correspond to allowed excitations of ~200 GHz from the ground state, thus denoting the locations of components of the low-temperature powder spectrum, i.e., one parallel component (B//z) and two perpendicular components (B//x and B//y) which are split as a consequence of the rhombic *E* term. The vertical magenta arrows in (a) correspond to allowed excitations of ~330 GHz from the ground state, illustrating the three low-temperature resonances observed in Fig. S3.



**Figure S5.** Variable temperature, variable field magnetization data collected on a solution sample of 1. Solid blue lines indicate the best fit to the data via ANISOFIT:  $D = +11.5 \text{ cm}^{-1}$ ,  $|E| \le 1.9 \text{ cm}^{-1}$ ,  $g_{iso} = 2.15$ . The similarity of the *D* values between the solid and solution measurements is the best indication that a structural distortion in solution is not taking place, as small coordination environment changes have been observed to induce large changes to *D* in the pseudotetrahedral Co molecule  $[Co(SPh)_4]^{2-.9}$ 



**Figure S6.** Magnetization data collected on microcrystalline 1 at various dc fields. Black lines correspond to best fits obtained with ANISOFIT 2.0, yielding D = +11.3 cm<sup>-1</sup>,  $|E| \le 0.8$  cm<sup>-1</sup>, and g = 2.32.



**Figure S7.** Frequency dependence of  $\chi_M$ " for a polycrystalline sample of 1 at 2 K under various applied dc field strengths. Data are shown only to the plateau in  $\tau$  for clarity (see Fig. S10). Lines are guides for the eye.



**Figure S8.** Frequency dependence of  $\chi_M$ " under various applied dc field strengths for a butyronitrile solution of 1 at 2 K. Solid lines are guides for the eye. Lack of defined maxima precluded accurate determination of the field dependence of  $\tau$  for 1 in solution.



**Figure S9.** Cole-Cole plot for determining field dependence of the magnetic relaxation time of **1**. Black lines indicate fits via a generalized Debye model, as described in the main text.



**Figure S10.** Field dependence of the magnetic relaxation time,  $\tau$ , of a microcrystalline sample of 1 at 2 K.



**Figure S11.** Cole-Cole plot used to determine the temperature dependence of the magnetic relaxation time,  $\tau$ . Black lines represent best fits to a generalized Debye model, as discussed in the main body of the communication.



**Figure S12.** Zeeman energy diagram for an  $S = {}^{3}/{}_{2}$  spin center with g, D, and E as determined by EPR. All energies correspond to H = 1500 Oe. Red arrows and energy indicate slow direct relaxation pathway. Purple arrows and labels indicate excitations utilized for Orbach relaxation pathways. Blue arrows indicate relaxations involved in the magnetic relaxation processes. Splitting of the  $m_{s}$  levels by the applied magnetic field is exaggerated for ease of depiction.



**Figure S13.** Solution UV-Vis (red) and solid-state diffuse reflectance (blue) data obtained on **1**. Diffuse reflectance data are reported in terms of F(R), the Kubelka-Munk transform of the % reflectance, for easier comparison to the solution data. The similarity spectral data of the solution and solid states eliminates a large structural distortion away from the crystal structure geometry as the source of the enhancement of the relaxation rate, as discussed in the main body of the report.

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