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Slow magnetic relaxation in a pseudotetrahedral cobalt(11) complex with easy-plane anisotropy[†]

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A pseudotetrahedral cobalt(II) complex with a positive axial zero-field splitting parameter of $D = 12.7 \text{ cm}^{-1}$, as determined by high-field EPR spectroscopy, is shown to exhibit slow magnetic relaxation under an applied dc field.

Molecules that possess an axially bistable magnetic moment, referred to as single-molecule magnets, display slow magnetic relaxation upon removal of a magnetizing field, and have been suggested for applications in high-density information storage and quantum computing.¹ The recent demonstration of such behavior in low-coordinate, high-spin iron(II) complexes² has prompted a new research effort geared toward developing mononuclear transition metal complexes as single-molecule magnets, since these species can exhibit significantly greater anisotropies than their multinuclear counterparts. Early observations of single-molecule magnet behavior in mononuclear complexes were restricted to the lanthanides,³ where the spin-orbit coupling is great enough to compensate for any quenching effect from the ligand field. In contrast, for first-row transition metal complexes, the ligand field is usually much stronger than the spin-orbit coupling, such that first-order orbital angular momentum is largely quenched.⁴ Here, however, a low coordination number can ensure a relatively weak ligand field, thereby maximizing the spin and spin-orbit coupling. Furthermore, variation of the ligand donor characteristics can then provide a means of tuning the magnetic anisotropy. Indeed, a variety of complexes of iron(II) with coordination numbers of four,⁵ three,⁶ and two⁷ have been shown to possess a large axial zero-field splitting parameter, D, or even unquenched first-order orbital angular momentum.

For easy-axis (D < 0) integer-spin systems, resonant zerofield quantum tunnelling relaxation processes can be mediated by (i) dipolar interactions, (ii) hyperfine interactions, or (iii) transverse anisotropy (E).⁸ In some instances, application of a small, static magnetic field can shut down such relaxation processes by removing the resonance through the Zeeman effect, thereby enabling the observation of slow magnetic relaxation via thermally activated mechanisms.^{2,9} For example, field-induced slow relaxation has been observed for trigonal pyramidal iron(II) complexes, wherein the tunnelling between the $M_S = \pm 2$ levels was attributed to transverse anisotropy and/ or dipolar interactions.^{2a,b} According to Kramers' theorem.¹⁰ however, transverse anisotropy would not facilitate tunneling through mixing of the ground $\pm M_S$ levels for a non-integer spin system with D < 0. We are therefore investigating low-coordinate $S = \frac{3}{2}$ cobalt(II) complexes with potentially large D values in an effort to find mononuclear transition metal complexes that display slow magnetic relaxation with no applied field.11 In the course of this research, we unexpectedly discovered slow relaxation for a pseudotetrahedral cobalt(II) complex with D > 0 under a dc field.

Spin-lattice relaxation in easy-plane (D > 0) half-integer systems can occur directly between the ground $M_S = \pm \frac{1}{2}$ levels in the absence of transverse, hyperfine, and dipolar interactions, since the spin-phonon transition is allowed. Thus, even under an applied magnetic field, fast relaxation is expected. However, if the coupling between the spin system and the phonons is weak, or if there are very few phonons of the appropriate frequency, then the $M_S = +\frac{1}{2}$ to $M_S = -\frac{1}{2}$ relaxation could be slow. Here, we report the first well-documented example of a mononuclear complex for which a phonon bottleneck appears to slow this direct relaxation process sufficiently to enable Orbach relaxation through the higher energy $M_S = \pm \frac{3}{2}$ levels.

The compound $[(3G)CoCl](CF_3SO_3)$ (1; 3G = 1, 1, 1-tris-[2*N*-(1,1,3,3-tetramethylguanidino)methyl]ethane)¹² was synthesized by addition of Na(CF₃SO₃) to an acetonitrile solution of CoCl₂ and 3G. Diffusion of diethyl ether vapor into a THF solution of the isolated product subsequently afforded blue block-shaped crystals of **1** in 73% yield. X-ray analysis revealed pseudotetrahedral coordination for the [(3G)CoCl]⁺ complex, with three N donor atoms from the 3G ligand and an axial chloride ligand (see Fig. 1). The complex deviates somewhat from local C_{3v} symmetry at the Co^{II} center, owing mainly to the chloride ligand being slightly displaced from the

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Fig. 1 Left: Crystal structure of the pseudotetrahedral complex $[(3G)CoCl]^+$, as observed in 1. Purple, green, blue, and gray spheres represent Co, Cl, N, and C atoms, respectively; H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Co–N 1.993(1), 2.014(2), 2.024(1), Co–Cl 2.262(1), N–Co–N 96.14(6), 94.92(6), 94.27(6), N–Co–Cl 115.93(4), 120.50(4), 128.03(4). Right: Idealized d-orbital splitting diagram and electronic configuration for the complex, assuming C_{3v} symmetry.

principal axis. With a shortest $Co \cdots Co$ separation of 8.593(1) Å, no close intermolecular exchange pathways are apparent in the structure.

Dc magnetic susceptibility data were collected between 2 and 300 K for both crystalline powder and solution samples of **1** (see Fig. S1). At room temperature, $\chi_M T = 2.62$ and 2.52 cm³ K mol⁻¹ for the crystalline and solution samples, corresponding to an $S = \frac{3}{2}$ spin center with g = 2.36 and 2.15, respectively. For both samples, $\chi_M T$ begins to drop below 70 K, reaching respective values of 1.69 and 1.79 cm³ K mol⁻¹ at 2 K. In the absence of any close Co…Co contacts, this downturn is likely attributable to magnetic anisotropy.

High-field, high-frequency EPR measurements were carried out on both powder and single crystal samples of 1 to obtain a definitive determination of the zero-field splitting parameters (see Fig. 2). The low-temperature powder data are typical for a system described by the zero-field Hamiltonian $H = DS_z^2 + E(S_x^2 - S_y^2)$. Here, three components are observed, corresponding to transitions within the lowest $M_S = \pm \frac{1}{2}$ Kramers doublet, with the parallel component (effective Landé constant $g_{z,\text{eff}} = 5.28$ and $g_{y,\text{eff}} = 3.81$), which are split due to a finite rhombic term (see Fig. S2).

The top panel of Fig. 2 shows the variable-frequency spectra collected at 4.2 K for a single crystal of 1 oriented such that the field was close to the parallel (z) direction, while the bottom panel plots the resulting peak positions as blue circles. Most notable is the fact that three resonances are observed in the frequency range between 315 and 355 GHz (see also Fig. S3). This observation can only be explained if D > 0 and the applied field is close to the parallel orientation; only a single resonance would be observed under all other physically relevant scenarios (see Fig. S4). The solid blue curve shows the best simulation of the data, as obtained for $D = +12.7 \text{ cm}^{-1}$, E =1.2 cm⁻¹, $g_z = 2.17$ and a field misalignment of 15°. Note that, even though the simulation included four parameters, the values obtained are robust, as explained in the ESI. Moreover, the same parameterization (with $g_x = g_y = 2.30$) accounts perfectly for the powder data (see lower left portion of Fig. 2), and the D value is in reasonable agreement with the +11.4(1) cm⁻¹ obtained by fitting magnetization data (see Fig. S5 and S6).

Under zero applied dc field, no out-of-phase ac susceptibility (χ_M'') signal was observed for either the solid-state or solution



Fig. 2 Top: Variable-frequency EPR spectra collected on a single crystal of **1** aligned 15° away from the *z*-axis at 4.2 K. The fine structure seen for some of the peaks is due either to weak disorder in the sample¹³ or an experimental artifact associated with the over-moded waveguide. Bottom: Peak positions as a function of frequency (*f*) from spectra collected on a powder sample of **1** at 5 K (*f* < 200 GHz) and a single crystal at 4.2 K (*f* > 300 GHz) aligned 15° away from the parallel (*z*) direction. Solid lines are simulations of the frequency dependence of the peak positions employing the parameters given in the main text. Upper inset: Powder EPR spectrum recorded at 5 K and f = 151 GHz, showing *x*, *y*, and *z* transitions. Lower inset: Zeeman diagrams for various field misalignments; *M*_S levels are labelled and the arrow indicates the intra-Kramers doublet transition.

sample at 2.0 K. Upon application of a 100 Oe dc field, however, a non-zero signal appeared for both phases (see Fig. S7 and S8). For the crystalline sample, the peak maximum moves to lower frequencies until reaching a minimum of 65 Hz at 1500 Oe, staying relatively invariant to 4000 Oe. In contrast, the solution sample shows a high frequency shoulder that never develops into a full peak under applied dc fields of up to 1000 Oe. Cole-Cole plots were constructed from the molar in- and out-of-phase ac susceptibility data of the solid-state sample and fit to a generalized Debye model to obtain values of the magnetic relaxation time for a given applied dc field (see Fig. S9). With increasing field strength, the relaxation time increases to a maximum of 0.28 ms at 1500 Oe and then remains approximately constant up 4000 Oe (see Fig. S10).

Variable-temperature ac frequency scans were performed on crystalline 1 to explore the thermal dependence of the magnetic relaxation time. As shown in Fig. 3, under a 1500 Oe dc field, a peak maximum is apparent from 1.8 to 2.6 K. Extraction of the magnetic relaxation times *via* fits to the Debye model were performed (see Fig. S11) and the subsequent data used to prepare the Arrhenius plot, depicted as the inset in Fig. 3. A fit to the linear portion of the data affords an effective relaxation barrier of $U_{\rm eff} = 24 {\rm cm}^{-1}$ and $\tau_0 = 1.9 \times 10^{-10} {\rm s}$.



Fig. 3 Variable-temperature ac magnetic susceptibility data obtained for **1** in a 1500 Oe dc field. Solid lines are guides for the eye. Inset: Arrhenius plot of τ data (1 σ error bars). The solid black line represents a fit to the linear region, giving $U_{\text{eff}} = 24 \text{ cm}^{-1}$ and $\tau_0 = 2 \times 10^{-10} \text{ s}$.

Under an applied field of 1500 Oe, any hyperfine and dipolar mediated relaxation processes are suppressed. In concert, the ground $M_S = \pm \frac{1}{2}$ levels are split by 0.12 cm⁻¹ and direct relaxation between them is slow, possibly due to a lack of accessible phonon modes or inefficient spin-phonon coupling. In addition, the transverse anisotropy mixes the $M_S = \pm \frac{1}{2}$ and $M_S = \pm \frac{3}{2}$ levels of opposite sign. The spin system thus follows a more efficient Orbach relaxation pathway through the excited $M_S = \pm \frac{3}{2}$ levels, leading to the observed barrier of 24 cm⁻¹, which is in close agreement with the $\pm \frac{1}{2}$ and $\pm \frac{3}{2}$ level separations calculated with the D values obtained from EPR and magnetization data (25 and 23 cm⁻¹, respectively). A graphical representation of the proposed relaxation mechanism is given in Fig. S12. A similar mechanism has been invoked recently for several polynuclear transition metal clusters, where relaxation has been proposed to occur through excited exchange coupled states.¹⁴

The faster relaxation rate of **1** in frozen solution can likely be attributed to a more efficient coupling between the spins and the phonon modes of the frozen glass compared to the crystal lattice. A substantial minimization of *D via* a distortion of the cobalt(II) coordination environment away from the crystal structure geometry is unlikely in view of the strong correlation of the spectral and magnetic data (see Fig. S2, S5, S6, and S13). The solution measurement also reveals that the phonon bottleneck is not due to poor contact with the thermal bath, as sometimes occurs for crystalline samples.¹⁵ The value of τ_0 is in line with this idea, as it is much smaller than usual for a relaxation process involving a phonon bottleneck.

The foregoing results demonstrate conclusively that typical single-molecule magnet behavior can be observed under an applied field for a mononuclear complex that has a positive axial zero-field splitting.¹⁶ The direct relaxation between the $M_S = \pm \frac{1}{2}$ levels of the $S = \frac{3}{2} [(3G)CoCl]^+$ complex in **1** is very slow, forcing the spin system to reach equilbrium through the higher-lying $M_S = \pm \frac{3}{2}$ levels *via* an Orbach mechanism. In such a situation, the thermal relaxation barrier, which corresponds to the energy difference between these levels, is identical to what would be expected if D were negative and of the same magnitude. In addition, the value of τ_0 obtained from the relaxation time data is within the usual range for single-molecule magnets with negative D. Thus, while higher-spin systems with negative D may potentially have a larger overall barrier, it is nonetheless of interest to look for slow relaxation in other complexes with large positive D values.

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