

Slow Magnetic Relaxation at Zero Field in the Tetrahedral Complex $[\text{Co}(\text{SPh})_4]^{2-}$

Joseph M. Zadrozny and Jeffrey R. Long*

Department of Chemistry, University of California, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: The Ph_4P^+ salt of the tetrahedral complex $[\text{Co}(\text{SPh})_4]^{2-}$, possessing an $S = 3/2$ ground state with an axial zero-field splitting of $D = -70 \text{ cm}^{-1}$, displays single-molecule magnet behavior in the absence of an applied magnetic field. At very low temperatures, ac magnetic susceptibility data show the magnetic relaxation time, τ , to be temperature-independent, while above 2.5 K thermally activated Arrhenius behavior is apparent with $U_{\text{eff}} = 21(1) \text{ cm}^{-1}$ and $\tau_0 = 1.0(3) \times 10^{-7} \text{ s}$. Under an applied field of 1 kOe, τ more closely approximates Arrhenius behavior over the entire temperature range. Upon dilution of the complex within a matrix of the isomorphous compound $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{SPh})_4]$, ac susceptibility data reveal the molecular nature of the slow magnetic relaxation and indicate that the quantum tunneling pathway observed at low temperatures is likely mediated by intermolecular dipolar interactions.

Molecules possessing an easy-axis anisotropy can display slow relaxation of the magnetic moment upon removal of a polarizing field. If the time scale of the relaxation exceeds that of computation, such single-molecule magnets could potentially find applications in high-density information storage or quantum computing.¹ The first molecule shown to exhibit magnetic bistability, $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4$, has a magnetic relaxation time of 2 months at 2 K.² Since this discovery, chemists have sought new, synthetically tunable systems wherein the relaxation barrier might be systematically increased. In 2003, slow magnetic relaxation was observed in lanthanide complexes,³ while more recently this behavior has also been reported for simple mononuclear complexes of actinides⁴ and first-row transition metals.⁵ Significantly, the ability to enhance the relaxation barrier by manipulating the ligand field has now been demonstrated for a series of trigonal pyramidal iron(II) complexes with $S = 2$ ground states.^{5b} To date, however, all such mononuclear transition metal-based single-molecule magnets require application of a dc field to disrupt fast quantum tunneling relaxation processes.

Quantum tunneling of the magnetization stems from the mixing of $\pm M_S$ levels via hyperfine interactions, dipolar interactions, or transverse zero-field splitting (E).⁶ The latter two possibilities can potentially be avoided by ensuring a large separation between molecules and by utilizing a non-integer spin system, for which Kramers's theorem predicts that mixing of the ground $\pm M_S$ levels by E is forbidden.⁷ Herein, we show

that the $S = 3/2$ complex $[\text{Co}(\text{SPh})_4]^{2-}$ can indeed display slow magnetic relaxation in the absence of an applied magnetic field.

The compound $(\text{Ph}_4\text{P})_2[\text{Co}(\text{SPh})_4]$ (**1**)⁸ was identified as a likely candidate for exhibiting slow magnetic relaxation in zero field, owing to its well-established ground-state properties. In contrast to other mononuclear cobalt(II) systems probed for single-molecule magnet behavior, where the sign of D is either undetermined^{5c} or positive,⁹ extensive single-crystal EPR spectroscopy and magnetic susceptibility experiments,¹⁰ as well as computations,¹¹ have shown **1** to possess a large, negative D value of -70 cm^{-1} and a relatively low rhombicity ($E/D < 0.09$). The large magnetic anisotropy of this system can be understood qualitatively by considering the electronic configuration and splitting of the d-orbitals, as shown in Figure 1. Calculations employing the angular overlap model indicate

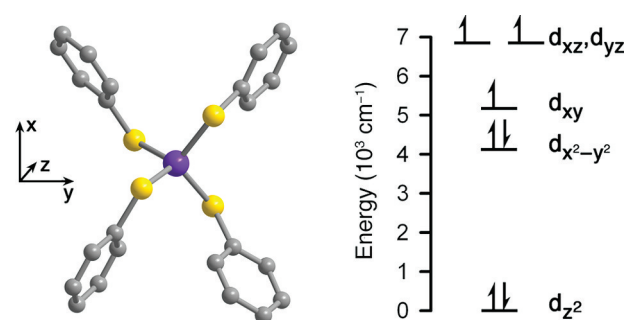


Figure 1. Left: Structure of the tetrahedral $[\text{Co}(\text{SPh})_4]^{2-}$ complex in **1**,^{8b} as viewed approximately along the z -axis. Purple, yellow, and gray spheres represent Co, S, and C atoms, respectively; H atoms are omitted for clarity. The molecule is somewhat elongated along z , so as to give approximate D_{2d} symmetry at the Co^{II} center. Selected interatomic distances (\AA) and angles ($^\circ$): Co–S 2.316(4)–2.342(4), S–Co–S 95.6(2), 97.0(2), 113.5(2), 114.8(2), 116.1(2), 121.3(2); mean Co–S–C 110(2).^{8b} Right: Electronic configuration and d-orbital energy level splitting for the molecule, with energies derived using the angular overlap model.^{10b}

the close energetic proximity of the filled $3d_{x^2-y^2}$ orbital and the singly occupied $3d_{xy}$ orbital.^{10b} This near degeneracy results in a low-lying electronic excited state that can couple to the ground electronic state through spin–orbit coupling to afford a large zero-field splitting.

Dc magnetic susceptibility data collected for **1** reveal the hallmarks of a significant magnetic anisotropy (see Figures S1

Received: October 24, 2011

Published: December 5, 2011

and S2 in the Supporting Information). At 300 K, $\chi_M T = 3.11$ cm³K/mol, consistent with an $S = 3/2$ complex with $g = 2.57$. This value of $\chi_M T$ remains relatively constant down to 80 K, where it begins to decrease, reaching 2.46 cm³K/mol at 2 K. Variable-temperature magnetization data were collected between 2 and 5 K at selected applied fields to extract a D value for comparison with the results obtained previously from EPR spectra. Employing ANISOFIT 2.0,¹² the best fit to the data afforded $D = -74$ cm⁻¹ and $|E| \leq 0.01$ cm⁻¹. While the D value is comparable to that observed by EPR spectroscopy, the E value, albeit here only crudely determined, is lower by at least 2 orders of magnitude.

As depicted in Figure 2, ac magnetic susceptibility data collected in the absence of an applied dc field display a

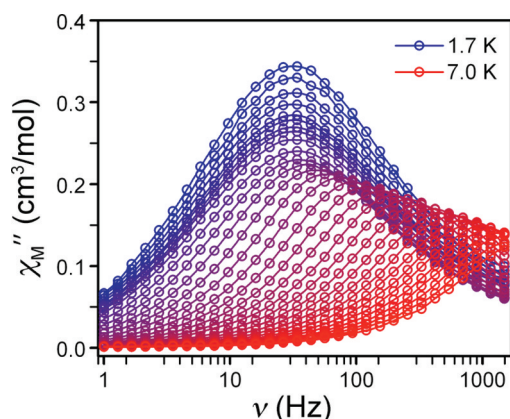


Figure 2. Frequency dependence of the molar out-of-phase ac susceptibility (χ_M'') of **1** collected at temperature intervals of 0.1 K between 1.7 and 2.4 K and intervals of 0.2 K between 2.4 and 7.0 K with no applied dc field. Solid lines are guides for the eye.

temperature-dependent peak in the out-of-phase ac susceptibility (χ_M''), indicating a slowly relaxing magnetic moment. From 1.8 to 2.5 K, the peak appears at 28 Hz and decreases in height with increasing temperature. At temperatures above 2.5 K, the peak begins to shift to higher frequencies, until at 7 K it reaches the frequency limit of the instrument. Thus, compound **1** represents the first example of a mononuclear transition metal complex that behaves as a single-molecule magnet without requiring an applied field to suppress quantum relaxation processes.

Application of a small dc field at 2 K does, however, dramatically alter the profile of the χ_M'' frequency scan, as shown in Figure 3. Here, the peak observed at 28 Hz under zero field rapidly diminishes while a much lower-frequency peak simultaneously intensifies. This change continues until 1 kOe, at which point the high-frequency peak has completely disappeared. The low-frequency peak is strongly temperature-dependent over the entire temperature region probed (see Figure S3), and above 5 K it begins to overlay with the peak obtained in zero field. Overall, this nearly isosbestic behavior nicely illustrates the change in the relaxation mechanism from quantum tunneling to thermal activation, as discussed below.

To elucidate the role of intermolecular interactions in the magnetic relaxation of **1**, a magnetically dilute sample was prepared by cocrystallization with the isostructural compound $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{SPh})_4]^{8a,b}$ to yield $(\text{Ph}_4\text{P})_2[\text{Co}_{0.09}\text{Zn}_{0.91}(\text{SPh})_4]$ (**2**). The relaxation dynamics of this diluted phase at zero field are slow and display strong temperature dependence from

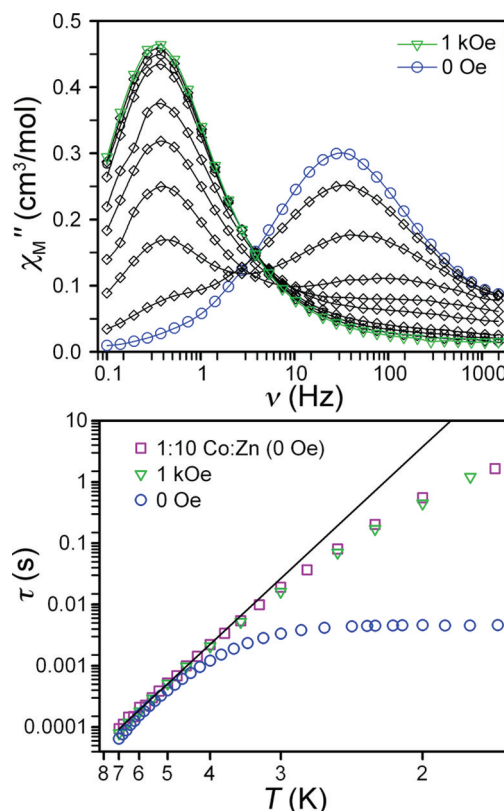


Figure 3. Top: Molar out-of-phase ac susceptibility (χ_M'') collected on pure **1** at 2 K under applied dc fields from 0 to 1 kOe in 100 Oe increments. Solid lines are guides for the eye. Bottom: Arrhenius plots of relaxation times of **1** as a pure substance under 0 and 1 kOe, and diluted in a matrix of $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{SPh})_4]$ under 0 Oe. The black line corresponds to a linear fit to the highest-temperature data of the diluted sample, as described in the main text.

1.7 to 7.0 K (see Figure S4). Importantly, the peaks approximately overlay those of pure **1** under an applied field. Application of a static dc field to **2** also slows the magnetization dynamics (see Figure S5), but in a much less dramatic fashion. Here, a single low-frequency peak shifts slightly from 1.8 Hz at 0 Oe to 0.2 Hz at 800 Oe instead of generating a second peak at a much different frequency.

The temperature dependence of the magnetic relaxation time, τ , provides valuable information about the magnetic relaxation processes that occur in **1** and **2**. Cole–Cole plots (see Figures S6–S9) were generated from the ac magnetic susceptibility data, and a generalized Debye model¹³ was used to extract relaxation times. The results were employed in constructing the Arrhenius plots shown at the bottom of Figure 3. For compound **1**, τ is temperature-independent between 1.8 and 2.5 K, a common observation for relaxation processes that are associated with quantum tunneling of the magnetization. In contrast, above 2.5 K, τ becomes temperature-dependent, eventually approximating the Arrhenius behavior associated with a thermally activated regime. In contrast, upon application of a dc field of 1 kOe, τ shows a strong temperature dependence at all temperatures. The relaxation times for **2** almost perfectly overlay those obtained for **1** under a 1 kOe dc field and do not display the dramatic field dependence associated with **1**. Here, τ shifts from 0.55 s at 0 Oe to only 1.01 s at 600 Oe (see Figure S5). Linear fits to the relaxation times observed between 5 and 7 K for **1** under 0 and 1 kOe, as

well as for **2**, yield the following average values for the spin reversal barrier and attempt time for the tetrahedral $[\text{Co}(\text{SPh})_4]^{2-}$ complex in this structure: $U_{\text{eff}} = 21(1) \text{ cm}^{-1}$ and $\tau_0 = 1.0(3) \times 10^{-7} \text{ s}$. We note that the latter value is within the range typically observed for single-molecule magnets. The observation of slow magnetic relaxation for the diluted compound **2** confirms that the slow magnetic relaxation is intrinsic to the individual $[\text{Co}(\text{SPh})_4]^{2-}$ molecules and is not associated with phonon bottleneck effects or polymolecular relaxation processes.¹⁴

In light of the large negative D values obtained from magnetization and EPR data, which predict a relaxation barrier of at least 140 cm^{-1} , the relatively small value of U_{eff} is somewhat surprising. The temperature-independent region of the Arrhenius plot for **1** in zero applied dc field indicates that quantum relaxation processes are operational, and these could be hindering the observation of the full barrier. The dilution experiments, however, show that the barrier height is unchanged after mitigating the intermolecular interactions. The source of the small U_{eff} must therefore be a different mediator for quantum tunneling or something else entirely. Inspection of the bistable ground-state wave functions of an $S = 3/2$ system with a negative D and non-zero E reveals that the $|M_S = \pm 3/2\rangle$ wave functions contain a small but non-negligible contribution from the $M_S = \pm 1/2$ levels.¹⁵ Although E does not directly mix the $M_S = \pm 3/2$ levels, the mixing of the ground and excited levels could perhaps be at the root of the observation of a U_{eff} value much less than $2D$.

The foregoing results constitute the first instance of slow magnetic relaxation for a mononuclear transition metal complex without the requirement of a static applied dc field, as directly probed via ac magnetic susceptibility measurements. Importantly, dilution of the $[\text{Co}(\text{SPh})_4]^{2-}$ complex within an isostructural diamagnetic matrix was shown to eliminate quantum tunneling relaxation processes, indicating that they occur via intermolecular dipolar interactions. Future efforts will focus on effects of varying the geometry and ligand field of this complex on the single-molecule magnet behavior through changes in the counteranion and thiolate ligands, as well as the exploration of other low-coordinate complexes with non-integer spin and a large axial anisotropy.

■ ASSOCIATED CONTENT

■ Supporting Information

Full experimental details; variable-temperature, variable-field magnetic susceptibility and magnetization data; variable-frequency ac susceptibility data; Cole–Cole plots; powder X-ray diffraction patterns; and pictures of pure and diluted samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

jrlong@berkeley.edu

■ ACKNOWLEDGMENTS

This research was supported by NSF grant CHE-1111900. We thank Tyco Electronics for fellowship support of J.M.Z., and Dr. T. D. Harris and Dr. D. E. Freedman for helpful discussions.

■ REFERENCES

- (1) (a) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *410*, 789. (b) Gatteschi, D.; Sessoli, R.; Villain, J. *Molecular Nanomagnets*; Oxford University Press: Oxford, 2006.
- (2) (a) Sessoli, R.; Hui, L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, J.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804. (b) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141.
- (3) (a) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.-Y.; Kaizu, S. *J. Am. Chem. Soc.* **2003**, *125*, 8694. (b) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, S. *J. Phys. Chem. B* **2004**, *108*, 11265. (c) Aldamen, M. A.; Clemente-Juan, J. M.; Coronado, E.; Martí-Gastaldo, C.; Gaita-Ariño, A. *J. Am. Chem. Soc.* **2008**, *130*, 8874. (d) Aldamen, M. A.; Cardona-Serra, S.; Clemente-Juan, J. M.; Coronado, E.; Gaita-Ariño, A.; Martí-Gastaldo, C.; Luis, F.; Montero, O. *Inorg. Chem.* **2009**, *48*, 3467.
- (4) (a) Rinehart, J. D.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 12558. (b) Rinehart, J. D.; Meihaus, K. R.; Long, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 7572. (c) Magnani, N.; Apostolidis, C.; Morgenstern, A.; Colineau, E.; Griveau, J.-C.; Bolvin, H.; Walter, O.; Caciuffo, R. *Angew. Chem., Int. Ed.* **2011**, *50*, 1696. (d) Antunes, M. A.; Pereira, L. C. J.; Santos, I. C.; Mazzanti, M.; Marçalo, J.; Almeida, M. *Inorg. Chem.* **2011**, *50*, 9915.
- (5) (a) Freedman, D. E.; Harman, W. H.; Harris, T. D.; Long, G. J.; Chang, C. J.; Long, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 1224. (b) Harman, W. H.; Harris, T. D.; Freedman, D. E.; Fong, H.; Chang, A.; Rinehart, J. D.; Ozarowski, A.; Sougrati, M. T.; Grandjean, F.; Long, G. J.; Long, J. R.; Chang, C. J. *J. Am. Chem. Soc.* **2010**, *132*, 18115. (c) Weismann, D.; Sun, Y.; Lan, Y.; Wolmershäuser, G.; Powell, A. K.; Sitzmann, H. *Chem.—Eur. J.* **2011**, *17*, 4700. (d) Lin, P.-H.; Smythe, N. C.; Gorelsky, S. I.; Maguire, S.; Henson, N. J.; Korobkov, I.; Scott, B. L.; Gordon, J. C.; Baker, R. T.; Murugesu, M. *J. Am. Chem. Soc.* **2011**, *133*, 15806. (e) Jurca, T.; Farghal, A.; Lin, P.-H.; Korobkov, I.; Murugesu, M.; Richeson, D. S. *J. Am. Chem. Soc.* **2011**, *133*, 15814.
- (6) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268.
- (7) Kramers, H. A. *Proc. R. Acad. Sci. Amsterdam* **1930**, *33*, 959.
- (8) (a) Holah, D. G.; Coucouvanis, D. *J. Am. Chem. Soc.* **1975**, *97*, 6917. (b) Swenson, D.; Baenziger, N. C.; Coucouvanis, D. *J. Am. Chem. Soc.* **1978**, *100*, 1932. (c) Dance, I. G. *J. Am. Chem. Soc.* **1979**, *101*, 6264.
- (9) Zadrozny, J. M.; Liu, J.; Piro, N. A.; Chang, C. J.; Hill, S.; Long, J. R. *Chem. Commun.* **2011**, DOI: 10.1039/C2CC16430B.
- (10) (a) Fukui, K.; Ohya-Nishiguchi, H.; Hirota, N. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1205. (b) Fukui, K.; Kojima, N.; Ohya-Nishiguchi, H.; Hirota, N. *Inorg. Chem.* **1992**, *31*, 1338. (c) Fukui, K.; Masuda, H.; Ohya-Nishiguchi, H.; Kamada, H. *Inorg. Chim. Acta* **1995**, *238*, 73.
- (11) Maganas, D.; Sottini, S.; Kyritsis, P.; Groene, E. J. J.; Neese, F. *Inorg. Chem.* **2011**, *50*, 8741.
- (12) Shores, M. P.; Sokol, J. J.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 2279.
- (13) (a) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1941**, *9*, 341. (b) Böttcher, C. J. F. *Theory of Electric Polarisation*; Elsevier: New York, 1952. (c) Aubin, S. M. J.; Sun, Z. M.; Pardi, L.; Krzystek, J.; Folting, K.; Brunel, L. C.; Rheingold, A. L.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1999**, *38*, 5329.
- (14) (a) Schenker, R.; Leuenberger, M. N.; Chaboussant, G.; Loss, D.; Güdel, H. U. *Phys. Rev. B* **2005**, *72*, 184403. (b) Lopez, N.; Prosvirin, A. V.; Zhao, H.; Wernsdorfer, W.; Dunbar, K. R. *Chem.—Eur. J.* **2009**, *15*, 11390. (c) Meihaus, K. R.; Rinehart, J. D.; Long, J. R. *Inorg. Chem.* **2011**, *50*, 8484.
- (15) Atherton, N. M. *Principles of Electron Spin Resonance*; Ellis Horwood Ltd.: Chichester, 1993.