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Tristability in a Light-Actuated Single-Molecule Magnet

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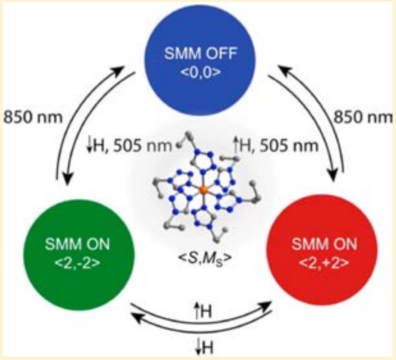
Supporting Information

ABSTRACT: Molecules exhibiting bistability have been proposed as elementary binary units (bits) for information storage, potentially enabling fast and efficient computing. In particular, transition metal complexes can display magnetic bistability via either spin-crossover or single-molecule magnet behavior. We now show that the octahedral iron(II) complexes in the molecular salt [Fe(1-propyltetrazole)$_6$](BF$_4$)$_2$, when placed in its high-symmetry form, can combine both types of behavior. Light irradiation under an applied magnetic field enables fully reversible switching between an $S = 0$ state and an $S = 2$ state with either up ($M_S = +2$) or down ($M_S = -2$) polarities. The resulting tristability suggests the possibility of using molecules for ternary information storage in direct analogy to current binary systems that employ magnetic switching and the magneto-optical Kerr effect as write and read mechanisms.



INTRODUCTION

Silicon-based electronics may ultimately be replaced by circuits and devices composed of molecular-scale components capable of switching between distinct states at high speeds with minimal energy input.[1−4] As a result, researchers are actively seeking molecules exhibiting bistable physical states that can be interchanged via external stimuli, such as temperature, light, electric or magnetic fields, or pressure. Here, molecules capable of interconverting between two stable magnetic polarization directions, known as single-molecule magnets, are of particular interest, owing to the prominent use of magnetic field-based switching in information storage over the past half-century. The introduction of additional physical states that can be accessed in such molecules via other stimuli stands as a challenge that could enable access to increased information density and, for the interesting case of light-based switching, potentially even result in molecular manifestations of magneto-optical effects observed in solids. Herein, we provide an initial demonstration of how spin-crossover behavior in a transition metal complex can give rise to a photoswitchable single-molecule magnet exhibiting tristability.

Spin-crossover complexes of 3d^4 to 3d^7 metal ions have been a focus of research for nearly 80 years,[5−7] due in part to their potential applications as molecular memory media, switches, displays, and sensors.[8] Of these, by far the majority are pseudo-octahedral 3d^6 iron(II) complexes possessing coordination geometries dominated by N-donor ligands that place the ligand field splitting energy near the spin pairing energy.[9] For molecules of this type, the low-spin $t_{2g}{}^6e_g{}^0$ electron configuration with $S = 0$ is the ground state at low temperature, but at higher temperatures the high-spin $t_{2g}{}^4e_g{}^2$ electron configuration with $S = 2$ becomes significantly thermally populated, owing to differences in the entropy contributions to the Gibbs free energy associated with the spin degrees of freedom. Importantly, in some instances it is possible to switch between the two states using light irradiation, a phenomenon known as light-induced excited spin state trapping or the LIESST effect.[10−12] Thus, certain spin-crossover complexes can offer optically switchable bistability.

Another type of magnetic bistability is found in single-molecule magnets, molecules for which the magnetic dipole associated with a high spin ground state prefers to align along a unique axis.[13−15] Here, an axial magnetic anisotropy creates an energy barrier for converting between up ($M_S = +S$) and down ($M_S = -S$) orientations of the spin, as described by the zero-field splitting Hamiltonian $H = DS_z{}^2 + E(S_x{}^2 - S_y{}^2)$ with usually D large and negative, and E small. As a result, at low temperatures, these molecules exhibit slow relaxation of their magnetization and magnetic hysteresis associated with switch-

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ing between the two states via application of a magnetic field. While most single-molecule magnets are polynuclear complexes, it was recently discovered that high-spin iron(II) complexes with an appropriate axial ligand field could also behave in this fashion.[16−20] These results motivated us to search for photoactive spin-crossover complexes that might additionally behave as single-molecule magnets when switched into their high-spin configuration. Among the possibilities, the compound $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ (ptz = 1-propyltetrazole), representing the first system ever shown to exhibit the LIESST effect in the solid state,[10,11,21−27] caught our attention, owing to its remarkable photosensitivity and the axial symmetry of its photoinduced high-spin state. Indeed, this molecular salt now provides the first example of a light-actuated single-molecule magnet based on a spin-crossover phenomenon.

Over the course of the past 20 years, a series of crystallographic studies were carried out on $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$, revealing the details of the structures of the octahedral complex $[\mathrm{Fe(ptz)_6}]^{2+}$ in its various physical states (Figure 1).[22−27]

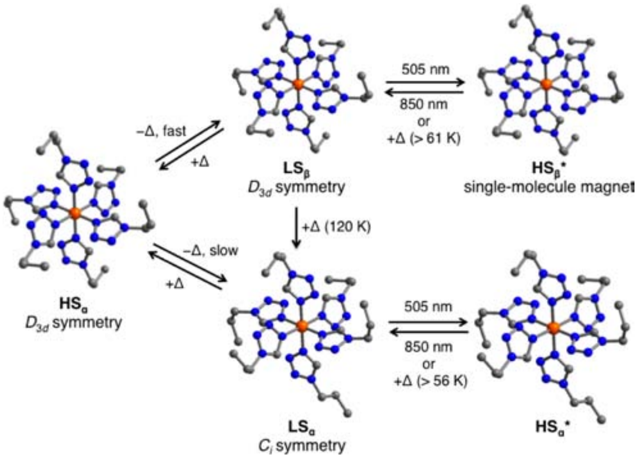

Figure 1. Interconversions between five different states of the octahedral iron(II) complexes in $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$. Orange, gray, and blue spheres represent Fe, C, and N atoms, respectively; H atoms are omitted for clarity. The conversions between the various high-spin (HS) and low-spin (LS) forms of the complex can be affected through application of heat (Δ) or in some cases by irradiation with light of 505- or 850-nm wavelength. With the exception of $\mathbf{HS}_{\alpha}^{*}$, all of the structures have been well-characterized crystallographically.[11−13,22−27] In these crystal structures, the Fe−N distances are 1.97(1), 2.01(1), and 2.03(1) Å for $\mathbf{LS}_{\alpha}$; 1.99(2) Å for $\mathbf{LS}_{\beta}$; 2.20(2) Å for $\mathbf{HS}_{\alpha}$; and 2.18(2) Å at 10 K for $\mathbf{HS}_{\beta}^{*}$, reflecting the differences in spin configuration and local symmetry at the iron(II) center.

Above its spin-transition temperature of ∼130 K, this compound crystallizes in a high symmetry $R\bar{3}$ structure (here denoted $\mathbf{HS}_{\alpha}$), wherein the high-spin iron(II) centers experience a D_{3d} local symmetry.[22] Upon cooling gradually to below 130 K, the symmetry of the structure (designated $\mathbf{LS}_{\alpha}$) is reduced to $P\bar{1}$ as a result of the ligands relaxing about the iron(II) centers to give C_i local symmetry upon conversion to a low spin configuration.[26] Intriguingly, however, it was found that by rapidly cooling below the spin-transition temperature, a form of the compound (designated $\mathbf{LS}_{\beta}$) could be obtained in which the $R\bar{3}$ symmetry of the parent structure is preserved, resulting in low-spin iron(II) centers that maintain an axial D_{3d} local symmetry.[21,23,25] By photoexciting the $\mathbf{LS}_{\alpha}$ and $\mathbf{LS}_{\beta}$ phases, the compound is selectively converted into long-lived metastable high-spin phases (designated $\mathbf{HS}_{\alpha}^{*}$ and $\mathbf{HS}_{\beta}^{*}$, respectively). Further structural studies performed under irradiation indicate $\mathbf{HS}_{\beta}^{*}$ to retain $R\bar{3}$ symmetry[24,25,27] and suggest that $\mathbf{HS}_{\alpha}^{*}$ has a similar low symmetry structure as $\mathbf{LS}_{\alpha}$.[26] In particular, the clear axial symmetry of $\mathbf{HS}_{\beta}^{*}$ provides the tantalizing prospect of enabling the large magnetic anisotropy required for a single-molecule magnet to develop.

■ RESULTS AND DISCUSSION

The synthesis and characterization of $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ proceeded as expected (details are provided in the Supporting Information), and its magnetic properties were investigated, with particular attention to the low temperature magnetization dynamics for the photoinduced $\mathbf{HS}_{\alpha}^{*}$ and $\mathbf{HS}_{\beta}^{*}$ phases. Static magnetic susceptibility data collected for a powder sample of the compound yielded $\chi_{\mathrm{M}}T$ = 3.9 cm^3·K/mol at 300 K (Supplementary Figure S1), corresponding to an S = 2 spin state with a g factor of 2.3. Upon lowering the temperature at a rate of 0.4 K/min, an abrupt decrease in $\chi_{\mathrm{M}}T$ product is observed between 140 and 110 K, indicative of a magnetic and structural phase transition between the $\mathbf{HS}_{\alpha}$ (S = 2) and $\mathbf{LS}_{\alpha}$ (S = 0) phases. These data are in good agreement with previously reported results.[11,26] The sample was then cooled to 10 K and irradiated with 505-nm LED light (P = 10 mW/cm^2) for 9 h, whereupon the $\chi_{\mathrm{M}}T$ value increased abruptly before reaching a plateau at ∼3.6 cm^3·K/mol (Supplementary Figure S2). Under such treatment, $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ is fully converted from $\mathbf{LS}_{\alpha}$ to the $\mathbf{HS}_{\alpha}^{*}$ phase.[11,26] After irradiation, ac magnetic susceptibility data as a function of frequency were measured in the dark at 1.9 K to check for slow magnetization dynamics, including in the presence of dc fields of up to 3000 Oe. The results showed no significant out-of phase signal, consistent with an absence of single-molecule magnet behavior for the low-symmetry form of the high-spin iron(II) complex (Supplementary Figure S3).

To investigate the magnetic properties of $\mathbf{HS}_{\beta}^{*}$, a sample of $[\mathrm{Fe(ptz)_6}](\mathrm{BF_4})_2$ was cooled rapidly at ∼100 K/min from 300 to 10 K and irradiated with 505-nm LED light (P = 10 mW/cm^2) to initiate photoconversion. After 7 h, the $\chi_{\mathrm{M}}T$ value reached a plateau at 4.4 cm^3·K/mol (Supplementary Figures S4 and S5). Maintaining a temperature of 10 K, the metastable $\mathbf{HS}_{\beta}^{*}$ phase obtained in this way showed no significant decay over time after switching off the light. To check for possible slow dynamics, ac magnetic susceptibility measurements were carried out from 10 K down to 1.8 K. Under zero applied dc field, no significant out-of-phase susceptibility signal was observed (Supplementary Figure S6); however, upon application of a small dc field, a frequency-dependent signal indicative of a slowly relaxing single-molecule magnet became apparent. This behavior is typical for mononuclear iron(II) single-molecule magnets, in which fast ground state quantum tunneling of the magnetization short-cuts the thermal relaxation barrier under zero magnetic field but is minimized upon application of a dc field to break the energy degeneracy of the $\pm M_S$ states.[16−20]

Ac magnetic susceptibility data collected at applied fields as high as 7000 Oe enabled quantification of the effective spin reversal barrier associated with the single-molecule magnet behavior of $\mathbf{HS}_{\beta}^{*}$ (Supplementary Figure S7). Figure 2 shows the frequency and temperature dependence of the data obtained under an optimum dc field of 2000 Oe (i.e., that minimizes the quantum relaxation pathway of relaxation; Supplementary Figure S8). On the basis of the frequency dependence of these data, the temperature dependence of the relaxation time τ was determined experimentally. This was

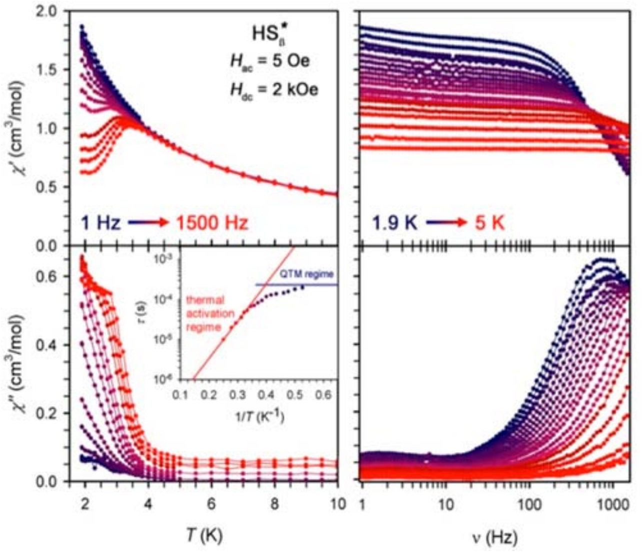

Figure 2. Temperature (left) and frequency (right) dependence of the in-phase (χ', top) and out-of-phase (χ'', bottom) components of the ac magnetic susceptibility data for **HS$_\beta$*** at oscillating frequencies between 1 and 1500 Hz and temperatures between 1.9 and 5 K. Measurements were performed with a 5-Oe ac field and a 2000-Oe dc field. The solid lines are guides for the eye. Inset: Arrhenius plot showing the dependence of the magnetization relaxation time τ upon inverse temperature, as obtained from the χ'' versus ν data. The solid red line corresponds to a linear fit to the data above 3 K, where relaxation can occur via a thermally activated process. At lower temperatures, relaxation becomes dominated by quantum tunneling of the magnetization (QTM).

accomplished by utilizing the maxima of the $\chi''(\nu)$ curves at a given temperature, for which $\tau = (2\pi\nu_{max})^{-1}$, and for portions of the data where a maximum could not be observed, by applying a classical scaling method[28] (Supplementary Figure S9). For a single-molecule magnet, τ follows a thermally activated relaxation process, resulting in an exponential increase with decreasing temperature. Accordingly, the corresponding plot of ln(τ) versus 1/T should feature a linear region with the slope giving the relaxation energy barrier. Indeed, the Arrhenius plot shown in Figure 2 features a linear region above 3 K, indicative of a thermally activated relaxation time, and a fit to the data affords a relaxation barrier of U_{eff} = 15 cm^{-1} (22 K) and $\tau_0 = 4.2 \times 10^{-8}$ s. The value of τ_0 provides a quantitative measure of the attempt time of relaxation, and the value obtained here is comparable to those found for other single-molecule magnets.[13−20] Below 3 K, the relaxation time becomes progressively less temperature-dependent, as expected in the vicinity of a quantum relaxation regime, with a relaxation time of 2.4×10^{-4} s. Consistent with the measured relaxation times, no magnetic hysteresis was observed at temperatures down to 1.9 K employing the field sweep rates of 100−300 Oe/min attainable with a conventional SQUID magnetometer.

An important characteristic of the **HS$_\beta$*** phase is the presence of D_{3d} symmetry at the iron(II) sites,[24,25,27] which provides a substantial axial magnetic anisotropy D and limits the development of transverse anisotropy E. As a result, the rate of quantum tunneling is reduced significantly. Nevertheless, as shown in Figure 2, the system maintains some probability of quantum tunneling below 3 K, suggesting the possibility of an undetected local structural distortion to lower the symmetry at the iron(II) centers at low temperatures. Indeed, the much lower symmetry likely present in **HS$_\alpha$*** appears to suppress the single-molecule magnet behavior entirely.

As a direct probe of the magnetic anisotropy, high-field high-frequency EPR spectra were collected at 10 K for the photoinduced **HS$_\alpha$*** and **HS$_\beta$*** forms of [Fe(ptz)$_6$](BF$_4$)$_2$. The spectra for the latter, higher-symmetry phase display the forbidden ΔM_S = 4 transition expected for a high-spin iron(II) metal center (Supplementary Figure S10), but well-resolved peaks corresponding to allowed transitions were not observed even at magnetic fields of up to 14 T and frequencies of up to 600 GHz. The absence of observable allowed transitions in the spectra is indicative of a remarkably large axial zero-field splitting parameter, while the presence of the ΔM_S = 4 transition at very low temperatures indicates that the sign of D is negative. The only visible transition, from M_S = −2 to M_S = +2, can be simulated with many pairs of D and E parameters over a wide energy range, but the magnitude of |D| is constrained to be less than ∼15 cm^{-1}. Close to this limiting value, the set of parameters D = −14.8 cm^{-1} (−21.3 K), E = −0.95 cm^{-1} (−1.4 K), and g_z = 2.3 is found to be consistent with both the frequency dependencies (Supplementary Figure S11) and the X-band EPR spectrum (Supplementary Figure S12). These anisotropy parameters are in agreement with the observation of single-molecule magnet behavior for **HS$_\beta$*** and indicate a total spin reversal barrier of $U = S^2|D|$ = 50 cm^{-1} (72 K). The observation of a somewhat reduced effective relaxation barrier of 15 cm^{-1} through ac magnetic susceptibility experiments is typical for mononuclear single-molecule magnets and can generally be attributed to the presence of vibronic coupling.[29] EPR spectra obtained for **HS$_\alpha$*** show the forbidden ΔM_S = 4 resonance moving to lower field, suggesting a reduction in symmetry at the iron(II) centers and a significant transverse anisotropy (Supplementary Figure S12). These observations are consistent with the absence of single-molecule magnet behavior for the phase. It should be noted that this work represents the first high-field EPR study performed on a photoinduced phase of a spin-crossover system.

The ability to utilize light in reversibly switching "on" and "off" the single-molecule magnet properties of [Fe(ptz)$_6$](BF$_4$)$_2$ was also investigated. Since the compound is known to show a reverse LIESST effect (i.e., a conversion back to the low-spin ground state) when the high-spin photoexcited state is irradiated with the longer wavelength light,[12] these experiments involved excitation to form **HS$_\beta$*** and deexcitation back to **LS$_\beta$** via irradiation using LED light with wavelengths of 505 and 850 nm, respectively. Figure 3 plots $\chi_M T$ as a function of time, demonstrating reversible excitation−deexcitation cycles during successive irradiations at 10 K. After a first complete conversion of **LS$_\beta$** to **HS$_\beta$*** using 505-nm light, $\chi_M T$ decreases under irradiation with 850-nm light, reaching a value of 0.8 cm^3·K/mol after 8 h. This value indicates a nearly complete deexcitation, with only 17% of the iron(II) centers remaining in the high-spin configuration. To verify the reproducibility of the switching properties, 10 excitation−deexcitation cycles were performed, yielding a sequence of essentially identical $\chi_M T$ versus time traces. Ac magnetic susceptibility data were collected before the cycling, after the first excitation at 505 nm, after the first deexcitation at 850 nm, and after the last excitation at 505 nm. Remarkably, these data confirm the ability of the system to recover precisely the single-molecule magnet behavior of **HS$_\beta$*** (Figure 2) upon reexcitation and to negate that behavior upon subsequent deexcitation (Supplementary Figure S13). Thus, the octahedral iron(II) complexes in

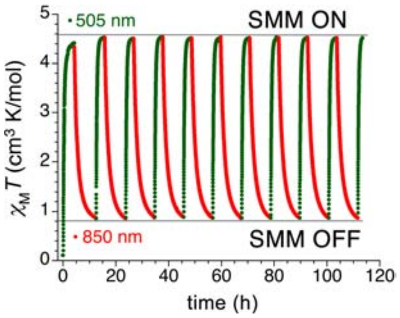

Figure 3. Excitation−deexcitation cycling between the **LS**$_{\beta}$ and **HS**$_{\beta}$* forms of $[Fe(ptz)_6](BF_4)_2$ at 10 K, as probed by dc magnetic susceptibility measurements performed under a 5000-Oe field. Irradiation with a 505-nm LED light source operating at 25 mW/cm^2 converts **LS**$_{\beta}$ to **HS**$_{\beta}$* over the course of 3 h, thereby switching on single-molecule magnet (SMM) behavior (as confirmed by ac magnetic susceptibility measurements). Subsequent irradiation with 850-nm LED light source operating at 40 mW/cm^2 converts **HS**$_{\beta}$* back to **LS**$_{\beta}$ over the course of 8 h, thereby switching off single-molecule magnet behavior. The gray lines are guides to the eye that help show the reproducibility of the cycling.

$[Fe(ptz)_6](BF_4)_2$ are seen to exhibit tristability, with the application of light and a magnetic field at low temperature enabling switching between three long-lived states: | 0 >, | +2 >, and | −2 >.

CONCLUSIONS AND OUTLOOK

The foregoing results represent the first example of a light-actuated single-molecule magnet based upon a spin-crossover phenomenon. The tristability offered by this system intimates the possibility of one day using molecules for ternary information storage.[30] Indeed, the manipulation of the information states for the molecules could potentially be carried out in direct analogy to current binary storage systems that employ magnetic switching and the magneto-optical Kerr effect (MOKE) as write and read mechanisms (see Supplementary Figure S14). Here, starting with the molecules in the "0" low-spin state, one could write a "1" or a "2" by application of short-wavelength light in combination with a magnetic field to convert it to a high-spin state with the moment polarized either up or down along the easy axis. Information could then be read through application of the magneto-optical Kerr effect, wherein the moment of the molecule shifts the phase of polarized light either not at all for a "0" or in a positive or negative sense for a "1" or a "2". Information could be erased by irradiation with long-wavelength light to return the molecules to their low-spin form. Among other challenges, implementation of such a computing scheme would require significant further developments in the confinement of light at a molecular level[31] and the synthesis of new molecules of the type established here with larger relaxation barriers and longer polarization lifetimes.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and figures giving additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Mannini, M.; Pineider, F.; Sainctavit, P.; Danieli, C.; Otero, E.; Sciancalepore, C.; Talarico, A. M.; Arrio, M.-A.; Cornia, A.; Gatteschi, D.; Sessoli, R. *Nat. Mater.* **2009**, *8*, 194−197.

(2) Mannini, M.; Pineider, F.; Danieli, C.; Totti, F.; Sorace, L.; Sainctavit, P.; Arrio, M.-A.; Otero, E.; Joly, L.; Cezar, J. C.; Cornia, A.; Sessoli, R. *Nature* **2010**, *468*, 417−421.

(3) Vincent, R.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W.; Balestro, F. *Nature* **2012**, *488*, 357−359.

(4) Coskun, A.; Spruell, J. M.; Barin, G.; Dichtel, W. R.; Flood, A. H.; Botros, Y. Y.; Stoddart, J. F. *Chem. Soc. Rev.* **2012**, *41*, 4827−4859.

(5) Cambi, L.; Szego, L. *Chem. Ber. Dtsch. Ges.* **1931**, *64*, 2591−2598.

(6) Franke, P. L.; Haasnoot, J. G.; Zuur, A. P. *Inorg. Chim. Acta* **1982**, *59*, 5−9.

(7) Bousseksou, A.; Molnar, G.; Salmon, L.; Nicolazzi, W. *Chem. Soc. Rev.* **2011**, *40*, 3313−3335.

(8) Kahn, O.; Martinez, C. J. *Science* **1998**, *279*, 44−48.

(9) Halcrow, M. A. *Polyhedron* **2007**, *26*, 3523−3576.

(10) Decurtins, S.; Gütlich, P.; Kohler, C. P.; Spiering, H.; Hauser, A. *Chem. Phys. Lett.* **1984**, *105*, 1−4.

(11) Decurtins, S.; Gütlich, P.; Hasselbach, K. M.; Hauser, A.; Spiering, H. *Inorg. Chem.* **1985**, *24*, 2174−2178.

(12) Hauser, A. *Chem. Phys. Lett.* **1986**, *124*, 543−548.

(13) Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804−1816.

(14) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141−143.

(15) Sessoli, R.; Villain, J.; Gatteschi, D. *Molecular Nanomagnets*; Oxford University Press: Oxford, 2006.

(16) Freedman, D. E.; Harman, W. H.; Harris, T. D.; Long, G. J.; Chang, C. J.; Long, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 1224−1225.

(17) Harman, W. H.; Harris, T. D.; Freeman, 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*, 18115−18126.

(18) 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*, 15806−15809.

(19) Weismann, D.; Sun, Y.; Lan, Y.; Wolmershauser, G.; Powell, A. K.; Sitzmann, H. *Chem.—Eur. J.* **2011**, *17*, 4700−4704.

(20) Zadrozny, J. M.; Atanasov, M.; Bryan, A. M.; Lin, C.-Y.; Rekken, B. D.; Power, P. P.; Neese, F.; Long, J. R. *Chem. Sci.* **2012**, *4*, 125−138.

(21) Ozarowski, A.; McGarvey, B. R. *Inorg. Chem.* **1989**, *28*, 2262−2266.

(22) Wiehl, L. *Acta Crystallogr.* **1993**, *B49*, 289−303.

(23) Moritomo, Y.; Kato, K.; Nakamoto, A.; Kojima, N.; Nishibori, E.; Takata, M.; Sakata, M. *J. Phys. Soc. Jpn.* **2002**, *71*, 1015−1018.

(24) Jeftic, J.; Gillon, B.; Goujon, A.; Nau, Q.; Gukasov, A.; Codjovi, E.; Varret, F. *Polyhedron* **2003**, *22*, 2155−2160.

(25) Kusz, J.; Gütlich, P.; Spiering, H. *Top. Curr. Chem.* **2004**, *234*, 129−153.

(26) Kusz, J.; Zubko, M.; Neder, R. B.; Gütlich, P. *Acta Crystallogr.* **2012**, *B68*, 40−56.

(27) Kusz, J.; Spiering, H.; Gütlich, P. *J. Appl. Crystallogr.* **2004**, *37*, 589−595.

(28) Labarta, A.; Iglesias, O.; Balcells, L.; Badia, F. *Phys. Rev. B* **1993**, *48*, 10240−10246.

(29) Atanasov, M.; Zadrozny, J. M.; Long, J. R.; Neese, F. *Chem. Sci.* **2013**, *4*, 139−156.

(30) (a) Sakamoto, R.; Murata, M.; Kume, S.; Sampei, H.; Sugimoto, M.; Nishihara, H. *Chem. Commun.* **2005**, 1215−1217. (b) Schaniel, D.; Woike, Th.; Schefer, J.; Petricek, V.; Kranmer, K. W.; Gudel, H. U. *Phys, Rev. B* **2006**, *73*, 174108. (c) Ould Moussa, N. O.; Trzop, E.; Mouri, S.; Zein, S.; Molnar, G.; Gaspar, A. B.; Collet, E.; Buron-Le Cointe, M.; Real, J. A.; Borshch, S.; Tanaka, K.; Cailleau, H.; Bousseksou, A. *Phys. Rev. B* **2007**, *75*, 054101. (d) Mossin, S.; Tran, B. L.; Adhikari, D.; Pink, M.; Heinemann, F. W.; Sutter, J.; Szilagyi, R. K.; Meyer, K.; Mindiola, D. J. *J. Am. Chem. Soc.* **2012**, *134*, 13651−13661. (e) Nihei, M.; Okamoto, Y.; Sekine, Y.; Hoshino, N.; Shiga, T.; Liu, I. P.-C.; Oshio, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 6361−6364.

(31) Bao, W.; Melli, M.; Caselli, N.; Riboli, F.; Wiersma, D. S.; Staffaroni, M.; Choo, H.; Ogletree, D. F.; Aloni, S.; Bokor, J.; Cabrini, S.; Intonti, F.; Salmeron, M. B.; Yablonovitch, E.; Schuck, P. J.; Weber-Bargioni, A. *Science* **2012**, *338*, 1317−1321.