Field-Induced Slow Magnetic Relaxation in Cobalt(II) Compounds with Pentagonal Bipyramid Geometry

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Supporting Information

ABSTRACT: Field-induced slow magnetic relaxation was observed for air-stable mononuclear cobalt(II) compounds with pentagonal bipyramid geometry. These are the first examples of such behavior observed in the seven-coordinated mononuclear 3d metal compounds.

Single-molecule magnets (SMMs) continue to fascinate scientific communities thanks to their unique intrinsic magnetic properties and their possible applications in spintronic devices and quantum computing. For the majority of SMMs containing 3d metal centers, the energy barrier $U$ is proportional to the square of the ground state spin value $S$. However, it was found to be extremely difficult to increase the barrier of SMMs despite the obvious success of synthesizing the metal clusters with very large $S$ values. It is now a consensus that the high magnetic anisotropy is the most important to achieve better SMMs, although it is also the most difficult to design and control.

In this regard, the preparation of SMMs with a single metal center (single-ion magnet, SIM) has attracted intense interest. The most fascinating aspect of SIMs lies in the possible prediction and design of their magnetic anisotropy, and thus the SIM properties, based on the basic principles of the ligand field theory. In parallel with the fruitful SIMs based on lanthanides and actinides, considerable efforts have also been devoted to the research of SIMs with 3d metal centers (3d-SIMs) since the first discovery of the FeII SIM in 2010. For all the reported 3d-SIMs, which are still quite limited, one common feature is the low coordination number of the metal centers, which affords a relatively weak ligand field to reduce the 3d orbital splitting energy, and to enhance the magnetic anisotropy. With the coordination number ranging from 2 to 6, the most interesting 3d-SIMs contain the following metal centers: two-coordinated FeI and NiI ions, two-, three-, four-, and six-coordinated FeII ions; five-coordinated FeIII ion; three-, four-, five-, and six-coordinated CoII ions; and six-coordinated MnIII ion.

Meanwhile, the seven-coordinated metal centers with pentagonal bipyramid geometry (point group $D_{5h}$) exhibit very large anisotropy, as established by both experimental and theoretical studies. Supported by the magnetization measurements and ab initio calculations, the zero-field splitting (ZFS) parameter $D$ value of the pentagonal bipyramidal CoII center was found to be positive, which reflects the easy-plane magnetic anisotropy and seems to be unfavorable for a SIM at first glance. However, it has now been shown that slow magnetic relaxation is possible in the compounds of positive $D$ values, as observed recently in several CoII and FeI/II compounds. For all of them, an external dc field was required to observe the slow magnetic relaxation. Interestingly, observation of the field-induced slow magnetic relaxation in a pentagonal bipyramidal CoII compound $[\text{Co}^{II}(\text{H}_2\text{dapb})(\text{H}_2\text{O})(\text{NO}_3)](\text{NO}_3)$ (1) ($\text{H}_2\text{dapb} = 2,6$-diacetylpyridine bis(benzoyl hydrazine), Figure 1) was actually suggested in the theoretical work by Ruiz et al., but no ac measurements have been reported for 1.

Very recently, Ruiz and Luis et al. proposed that the field-induced slow magnetic relaxation in the Kramers ions is a general consequence of the time-reversal symmetry that hinders the direct spin–phonon process. Inspired by these studies, we reported here the dynamic magnetization study of compounds 1–3 $[\text{Co}^{II}(\text{H}_2\text{O})_2]{\text{L}}_{\text{NS}}\text{Cl}$, 4$\text{H}_2\text{O}$ (2) and $[\text{Co}^{II}(\text{dapb})(\text{im})_2]{\text{L}}_{\text{NS}}\text{H}_2\text{O}$ (3), $\text{L}_{\text{NS}} = 2,13$-dimethyl-3,6,9,12-tetraaza-$1(2,6)$-pyridina-cyclotridecaphane-2,12-diene, $\text{im} = \text{imidazole}$, Figure 1). Despite the different coordination environments of the CoII centers, field-induced slow magnetic relaxation was observed in all of them. This constitutes the very first observation of field-induced slow relaxation in compounds with pentagonal bipyramid geometry.

Air-stable compounds 1–3 can be synthesized conveniently (see details in the Supporting Information). The structure and dc magnetic property of 1 have been remeasured and are consistent with the reported results. A single-crystal X-ray diffraction study reveals that compound 2 crystallizes in the monoclinic space group $P2_1/n$ and compound 3 in orthorhombic space group $C222_1$ (Table S1). Their molecule structures are plotted in Figure 1. As shown, the CoII centers are in a pentagonal bipyramidal environment with seven coordinated atoms, five of which are from equatorial ligands ($\text{N}_5$ for 2 and $\text{N}_2\text{O}_5$ for 1 and

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To probe the magnetic relaxation dynamics of all three compounds, temperature- and frequency-dependent ac susceptibilities were measured in the temperature range of 1.8–10 K. Under a zero dc field, no out-of-phase ac susceptibility ($\chi'$) signal was observed for them (Figures S4, S7, S12). However, upon application of a 1000 Oe dc field, all compounds display temperature- and frequency-dependent ac signals typically observed for field-induced 3d-SIM species (Figure 3, Figures S5–S6, S8–S9, S13–S14). In the temperature-dependent ac plots, the highest peaks of the $\chi'$ at a frequency of 950 Hz are at 6.4, 5.8, and 6.2 K for 1–3, respectively. Furthermore, the Cole–Cole plots below 7 K (Figure 4a, Figures S10, S15) were generated from the frequency-dependent ac susceptibility data. A generalized Debye model was used to extract the values and distribution of the relaxation time ($\tau$). The obtained $\alpha$ values are 0.02–0.21, 0.01–0.26, and 0.03–0.14 for 1–3, respectively. These values suggest the narrow distribution of the relaxation time. To estimate the effective energy barrier ($U_{\text{eff}}$), Arrhenius plots [$\ln(\tau) \times T^{-1}$] were constructed and plotted in Figure 4b. A linear fit to the high temperature data according to $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$ affords $U_{\text{eff}} = 56.3$ cm$^{-1}$ (81.2 K), 20.7 cm$^{-1}$ (29.8 K), and 62.3 cm$^{-1}$ (89.6 K) with $\tau_0 = 6.0 \times 10^{-10}$ s, 1.2 $\times 10^{-8}$ s, and 8.7 $\times 10^{-11}$ s for 1–3, respectively.

For a magnetic system with a positive $D$ value, the mechanisms responsible for the slow magnetic relaxation are still a matter of debate. One of them arises from a transverse anisotropy barrier located in the easy plane, and the energy barrier is governed by a considerable $E$ value. For our compounds, this mechanism does not seem applicable as the $E$ values obtained experimentally (and as reported in other similar compounds with pentagonal bipyramid geometry) are very close to zero. The other mechanism was ascribed to a field-induced phonon bottleneck effect of the direct relaxation of the ground $M_0 = \pm 1/2$ levels. As a matter of fact, suggested by the very recent work of Ruiz and Luis, direct phonon-induced processes are strongly suppressed.

Figure 3. Variable-temperature (a) and variable-frequency (b) out-of-phase ac magnetic susceptibility data for 1 in a 1000 Oe dc field.

Figure 4. (a) Cole–Cole plots of 1 under 1000 Oe dc field and (b) Arrhenius plot of $\ln(\tau) \times T^{-1}$ for 1. Solid line represents a fit to the high temperature region. Inset: Power law analysis in the form $\ln(\tau)$ vs $\ln(T)$.
in a Kramers system with a considerable anisotropy irrespective of the sign of D. Thus, magnetic relaxation has to proceed either by the Orbach relaxation pathway through the excited $M_1 = 3/2$ levels\textsuperscript{10,11} or by the optical acoustic Raman process involving a virtual state.\textsuperscript{10h} For compound 2, as the obtained energy barrier (20.7 cm$^{-1}$) is much lower than the energy gap between the $M_0 = 1/2$ and $M_0 = 3/2$ doublets, the Orbach pathway is not very likely. The relaxation times for 2 in the temperature range of 4–6 K can be fitted to a T$^{-3}$ law with n = 4.9 (Figure S11), which is close to the value of 4.5 for the Co–Y SIM reported by Colacio et al.,\textsuperscript{10h} suggesting a dominant optical acoustic Raman process for the spin relaxation. However, for 1 and 3, the obtained energy barriers are close to the 2D values. At the same time, the power law treatment of the data for 1 and 3 in the temperature range of 5–7 K gave n = 8.7 (for 1, Figure 4b) and 11.2 (for 3, Figure S16), which is close to the expected n = 9 for Raman relaxation in Kramers ions.\textsuperscript{10h} These results suggest that the Orbach and Raman processes seem possible for 1 and 3.

In conclusion, our results demonstrate that slow magnetic relaxation can be observed under an applied dc field in the high-spin hepta-coordinate mononuclear Co$^{III}$ compounds with pentagonal bipyramidal symmetry. This field-induced slow relaxation seems to be a quite common phenomenon for a Kramers compound with an easy-plane magnetic anisotropy. Studies on the dynamic magnetic properties of other metal centers, such as Fe$^{II}$, Cr$^{III}$, and Mn$^{III}$, in the similar pentagonal bipyramidal geometry are underway.

**ASSOCIATED CONTENT**

X-ray crystallographic files (CIFs), experimental details, crystallographic data, and additional structural and magnetic figures. 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**


