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Cobalt(II) Coordination Polymer Exhibiting Single-Ion-Magnet-Type Field-Induced Slow Relaxation Behavior

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Supporting Information

ABSTRACT: A one-dimensional cobalt(II) coordination polymer, $[Co(btm)_2(SCN)_2{\cdot}H_2O]_n$ [btm = bis(1*H*-1,2,4-triazol-1-yl)methane], was synthesized and magnetically characterized. The isolated slightly distorted octahedral Co^{II} ion displays field-induced slow relaxation with a big positive axial and a negative rhombic magnetic anisotropy ($D = 93.9$ cm^{-1} and $E = -10.5$ cm^{-1}), and the anisotropy energy barrier is 45.4 K.

Single-molecule magnets (SMMs) possess a bistable magnetic moment and can display slow magnetic relaxation upon removal of a magnetizing field.[1] They provide wonderful models for understanding the quantum phenomenon in the mesoscopic world and have potential applications in information storage, quantum computing, and spintronics.[2] Recently, single-ion magnets (SIMs) as a type of mononuclear SMM have attracted considerable attention. The mononuclear characteristic of SIMs provides the advantage of tuning zero-field splitting (ZFS) through regulation of the coordination number and ligand field. Since the first lanthanide-ion-based SIM $Tb^{III}Pc_2$ reported in 2003,[3] several SIMs containing single lanthanide and actinide ions have been reported.[4] More recently, the exploration of new SIMs has been extended to transition-metal ions. Wide research demonstrated that some mononuclear cobalt(II),[5] iron(I,II,III),[6] nickel(I),[7] manganese(III),[8] and rhenium(IV)[9] complexes could display field-induced slow magnetic relaxation or slow magnetic relaxation with no applied field. For many compounds containing a Kramers ion, field-induced magnetic relaxation is a general phenomenon. Different from traditional SMMs in which the axial parameter of ZFS *D* value is negative, a few mononuclear 3d complexes display field-induced slow relaxation behavior with a positive *D* value.[5c,d,h,k,n,v,7] Interestingly, we found a one-dimensional cobalt(II) coordination polymer that exhibited SIM-type field-induced slow relaxation behavior with positive axial anisotropy. Herein, we reported the magnetic study of this cobalt(II) coordination polymer (**1**) and its nickel(II) analogue (**2**).

Air-stable coordination polymer compound **1** with the formula $[Co(btm)_2(SCN)_2{\cdot}H_2O]_n$ [btm = bis(1*H*-1,2,4-triazol-1-yl)methane] was obtained as pink needlelike crystals by the hydrothermal method (see the Experimental Section in the Supporting Information, SI). Single-crystal sX-ray tructure analysis revealed that **1** crystallizes in the space group *Cmcm*. In the crystal, there is only one independent Co^{II} ion. Four nitrogen atoms from two btm ligands comprise the basal plane with a Co−N distance of 2.144(3) Å (Co1−N1). Two thiocyanate ions are coordinated in the axial site with a Co−N distance of 2.094(4) Å (Co1−N4; see Figure 1). The local symmetry of the Co^{II} ion is D_{2h}. The continuous-shape measurement gives the deviation value of ideal O_h symmetry as 0.068,[10] indicating that the local symmetry of the Co^{II} ion is close to an ideal octahedron with just a little compression in the axial direction. Two btm ligands connect adjacent Co^{II} ions to form a one-dimensional chainlike coordination polymer along the *c*-axis direction. The shortest neighboring cobalt(II) distances in and between chains are 8.748(2) and 7.883(1) Å, respectively. So the Co^{II} ion is in an isolated magnetic environment. The isostructural nickel(II) compound (**2**) was also synthesized and characterized by using a similar method (see section SI2 in the SI).

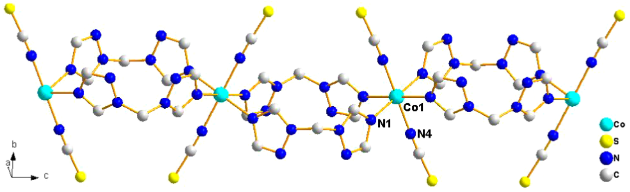

Figure 1. Molecular structure of compound **1**.

Magnetic measurements were performed on polycrystalline samples using Quantum-Design MPMS and PPMS magnetometers. For **1**, it was found that the temperature dependence of its molar magnetic susceptibility is characteristic of noninteracting mononuclear cobalt(II) complexes. The corresponding $\chi_M T$ versus *T* plot is provided in Figure 2a. The $\chi_M T$ value at 300 K is 3.23 cm^3 K mol^{-1}, which is in the range of a single noninteracting d^7 Co^{II} ion with considerable contribution from

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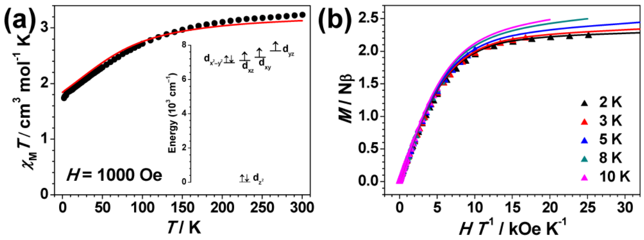

Figure 2. (a) $\chi_M T$ versus T plots on a 1 kOe applied dc field at 2–300 K for **1**. The red solid line represents the calculated magnetic susceptibilities by the CASPT2/RASSI/SINGLE-ANISO method.[12] Inset: Calculated energy splitting of d orbits for the Co^{II} ion in **1**. (b) Experimental and theoretical M versus H/T plots at different temperatures.

the orbital angular momentum. As the temperature is lowered, the $\chi_M T$ value decreases slowly at the high-temperature regime and decreases rapidly when the temperature is below 100 K mainly because of the magnetic anisotropy of the Co^{II} ion. A spin Hamiltonian of eq 1 was utilized to describe the magnetic anisotropy qualitatively by using the *MOLCAS 7.8* program,[11] and some simplification of the structure was performed (see section SI6 in the SI):

$$H = D[\hat{S}_z^{\,2} - S(S+1)/3] + E(\hat{S}_x^{\,2} - \hat{S}_y^{\,2}) + \mu_B g \hat{S} \hat{B} \quad (1)$$

where μ_B is the Bohr magneton and D, E, S, and B represent the axial and rhombic ZFS parameters, spin operator, and magnetic field vector, respectively. The calculation gives $D = 93.9$ cm^{-1}, $E = -10.5$ cm^{-1}, $g_x = 2.733$, $g_y = 2.525$, and $g_z = 1.855$.

The field-dependent magnetizations were performed in up to a 5 T direct-current (dc) field at 2, 3, 5, 8, and 10 K (see Figure 2b). The fitting to the M versus H/T plots using the *PHI* program[13] affords $D = 56.6$ cm^{-1}, $|E| = 3.70$ cm^{-1}, and $g = 2.49$, while the fitting to the experimental $\chi_M T$ versus T plots gives $D = 91.0$ cm^{-1}, $|E| = 3.85$ cm^{-1}, and $g = 2.58$ (see Figure S6 in the SI). The fitting D and E values have some differences, and they are all smaller than those of the calculated results.

The temperature dependence of the molar magnetic susceptibility of **2** is also characteristic of mononuclear complexes (see Figure S7 in the SI). The calculation gives $D = 2.8$ cm^{-1}, $E = -0.85$ cm^{-1}, $g_x = 2.245$, $g_y = 2.237$, and $g_z = 2.255$, respectively. It implies that the magnetic anisotropy of the Ni^{II} ion is much smaller than that of the Co^{II} ion.

The alternating-current (ac) susceptibility of **1** in the absence of a dc field was first measured, and it is found to display fast magnetic relaxation. When a 1500 Oe dc field was applied, however, both in-phase (χ') and out-of-phase (χ'') susceptibilities show significant frequency dependence within a broad temperature range (see Figure 3). The χ'' peaks from $\nu = 158$ to 10000 Hz appear in the temperature range of 3.7–8.0 K and upturn strongly at the low-temperature and low-frequency regime because of quantum tunneling magnetization (QTM). The anisotropy energy barrier of **1** under a 1500 Oe fitting by the Arrhenius law $[\tau = \tau_0 \exp(U_{eff}/k_B T)]$ gives $U_{eff} = 45.4$ K (31.6 cm^{-1}) and a preexponential factor of $\tau_0 = 5.6 \times 10^{-8}$ s (see Figure S13 in the SI). A field dependence study at 2 K indicates that this relaxation process is suppressed when a higher field is applied. A new relaxation process, however, appeared at low frequency when QTM is suppressed (see Figure S14 in the SI). The temperature dependence of the ac susceptibility under 5000 Oe shows that the intensities of the peaks at low frequencies are decreased (see Figure S15 in the SI). It verifies that this relaxation process is suppressed under a higher applied field. In order to elucidate the role of intermolecular interactions between adjacent Co^{II} ions in the magnetic relaxation of **1**, a magnetically dilute sample **3** (the Co^{2+}/Zn^{2+} ratio is 0.23:0.77) was prepared. The relaxation dynamics of **1** and the diluted compound **3** under 1500 Oe are almost the same (see Figure S17 in the SI), indicating that intermolecular interaction is weak or the extent of magnetic dilution is not great enough.[14] The nickel(II) analogue **2**, however, does not show frequency dependence under either zero or applied field (see Figures S18 and S19 in the SI).

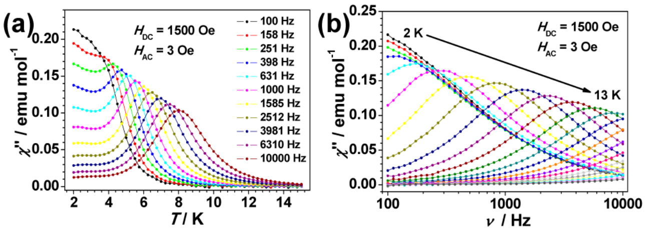

Figure 3. Temperature (a) and frequency (b) dependences of the out-of-phase (χ'') ac susceptibilities of **1**.

To inspect the distribution of the relaxation time, the Cole–Cole plots were fitted by the generalized Debye model (see Figure S20 and Table S5 in the SI). The resulting α values vary in the range of 0.001–0.232 (α is the deviation from the pure Debye model). The small α values in the higher-temperature regime suggest only one single slow relaxation process. In the low-temperature regime, the α values become larger because of the remaining QTM. This implies that multiple relaxation processes are present in the low-temperature regime.

Recently, there have been two types of mechanisms for explaining the slow magnetic relaxation from a 3d metal system with a positive D value. The first one was proposed by Pardo et al.[5c] They proposed that this type of slow relaxation comes from a transverse anisotropy barrier within the easy (xy) plane, and the energy barrier is governed by a considerable E value. The other one was based on a field-induced phonon bottleneck effect proposed by Luis et al.[5o] For a Kramers ion system with considerable anisotropy irrespective of the sign of D, if the direct relaxation processes of the ground $M_s = \pm^1/_2$ levels are strongly suppressed, the magnetic relaxation has to proceed via the Orbach relaxation pathway by the excited $M_s = \pm^3/_2$ levels[5d] or the optical acoustic Raman process involving a virtual state.[5g,o,t] For our compound **1**, the N–Co–N angles in the plane take two different values (86.7° and 93.3°), so that the system is not purely axial but partially rhombic. Distortion of the coordination sphere causes anisotropy in the easy plane and produces a big E value. The energy of the transverse barrier for rotation in the xy plane provides an energy barrier of $E_a = 2|E| = 21.0$ cm^{-1}, which is smaller than the experimental result of 31.6 cm^{-1}. It indeed shows that the transverse anisotropy energy makes a contribution to the slow relaxation behavior of **1**. Because compound **1** possesses a big positive D value, according to the second explanation, the field-induced phonon bottleneck effect may occur. The relaxation times for **1** in 3–8 K were fitted by the Power law (see Figure S21 in the SI), giving $n = 5.6$. This value is a little bigger than that of Co–Y SIM ($n = 4.5$) by Colacio et al.[5g] and the pentagonal-bipyramid Co SIM ($n = 4.9$) by Wang et al.[5t] It suggests that the optical acoustic Raman process may also have considerable contribution to the relaxation behavior of **1**.

In conclusion, we reported the observation of SIM-type field-induced slow relaxation from one-dimensional cobalt(II)

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coordination polymer **1**. Ab initio calculation shows the presence of transverse anisotropy with a big positive D value and a negative E value for the six-coordinate octahedral Co^{II} ion in **1**. The anisotropy energy barrier is 45.4 K. Our work demonstrated that a coordination polymer constructed by a SIM unit could also display significant slow relaxation behavior. It will provide a new route to the design and synthesis of a stable molecular magnetic material based on a mononuclear complex unit and toward the construction of multifunctional coordination polymer materials. In the next step, we will try to replace the thiocyanate ions with other ligands to tune the anisotropy of the Co^{II} ion in these types of compounds. Further research is underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files of **1**−**3**, experimental procedures, structure and magnetic characterization, and theoretical calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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