Slow Magnetic Relaxation in One-Dimensional Azido-Bridged CoII Complexes

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ABSTRACT: Crystal structures and magnetic properties of three one-dimensional (1D) azido-bridged cobalt(II) chains with different amide ligands (L), [Co2(N3)4(DMF)3] (1), [Co2(N3)4(DEF)3] (2), and [Co2(N3)4(DIPF)3] (3) (DMF = N,N-dimethylformamide, DEF = N,N-diethylformamide, and DIPF = N,N-diiisopropylformamide), are reported to investigate the influence of L on their structures and magnetic properties. Single-crystal X-ray crystallographic analysis revealed that, although 1–3 all consist of cobalt chains bridged by end-on (EO) azides, the coordination geometry of the CoII ions and the repeating units of the 1D structures are quite different. As the size of L increases, the ratio of L to CoII decreases from 6:4 in 1 to 5:4 and 4:4 in 2 and 3, respectively. In 1, two [CoN3O1] and two [CoN5O2] distorted octahedra form the [[CoN5O2][CoN5O1][CoN5O1]] tetrarner (denoted as Co4A unit similar to that in 1) and two [CoN5O1] trigonal bipyramids because of the larger steric effect of the DIPF ligand, while, for compound 2 of the medium-sized amide, it has the transition structure between those of 1 and 3. The chain is composed of two different repeating units, one in which one of the CoII centers is in the [CoN5] trigonal bipyramid of the 1D systems and lead to the spin glass behavior.16 In this regard, the amide derivatives, which usually exhibit analogical magnetic properties. Direct-current magnetic measurements demonstrated that all compounds show intrachain ferromagnetic coupling through the EO azides and interchain anti-ferromagnetic interactions. Alternating-current data revealed the slow magnetic relaxation in the anti-ferromagnetic ordered phases. While compound 1 exhibits spin glass behavior, compounds 2 and 3 behave as the single-chain magnets. This difference might come from the interference of the anti-ferromagnetic ordering on the magnetic dynamic of the chain.

INTRODUCTION

Slow magnetic relaxation is characteristic for spin glasses, superparamagnets, and molecular nanomagnets including single-molecular magnets (SMMs) and single-chain magnets (SCMs).1 Since the discovery of the very first examples of SCMs in 2002,7 rational design and synthesis of these very interesting one-dimensional (1D) magnetic materials have attracted considerable interest in virtue of their potential applications in information storage and quantum computing.3 Various synthetic strategies have been developed,4 leading to a large number of SCMs based on transition-metal ions,5 rare-earth ions,6 or heterometallic 3d/4d environments and/or tuning the interchain magnetic interactions (J).13 While strong interchain interactions may stabilize the long-range magnetic ordering,14 weak interchain interactions favor the SCMs.8 Besides, an appropriate ratio of J/J’ can induce the coexistence and even mutual transformation of long-range ordering and SCM behavior.8a,13 It has also been reported that suitable J’ interactions could cause the randomness and frustration in the 1D systems and lead to the spin glass behavior.15 In this regard, the amide derivatives, which usually serve as terminal ligands, provide an effective way to tune the magnetic properties of the 1D compounds due to their different steric and electronic properties.17 As an illustrative example, a
series of cyano-bridged compounds $L_xFeReCl_4(CN)_2$ (where $L$ is amide ligands) reported by Long et al. are all SCMs with tunable magnetic properties. By varying the amide ligands, the strength of ferromagnetic interactions between ReIV and FeII ions and the energy barriers of the SCMs can be effectively modified.

Given the aforementioned findings, we devoted to construct azido-bridged 1D CoII magnetic materials using amides (Scheme 1) as the terminal ligands. Herein, we report the syntheses, structures, and magnetic properties of a series of amide ligands: $[Co_4(N_3)_8(DEF)_5]$ (1), $[Co_4(N_3)_8(DEF)_5]$ (2), and $[Co_4(N_3)_8(DIPF)_2]$ (3) $\text{DMF} = \text{N,N-dimethylformamide}$, $\text{DEF} = \text{N,N-diethylformamide}$, and $\text{DIPF} = \text{N,N-disopropylformamide}$. Structurally, we noticed that the repeating units of the 1D structures of these complexes have interesting dependence on the size of the amide. For complexes 1 and 3, the repeating units are two different Co4 clusters, namely, CoA and CoB units (CoA = $[[\text{CoN_3O}]_2[\text{CoN_3O}_2]]_2$; CoB = $[[\text{CoN_3}]_2[\text{CoN_3O}_2_2][\text{CoN_3}]]$), while for compound 2 of the medium-sized amide, the 1D structure is composed of CoA and CoB units. Magnetic studies revealed that all these compounds exhibit AFM ordering as well as slow magnetic relaxation in the ordered phases. While compound 1 exhibits spin glass behavior, compounds 2 and 3 behave as the SCM-like behavior.

![Scheme 1. Amide Ligands (L) Used to Prepare Compounds 1–3](image)

### Table 1. Crystallographic Data and Structure Refinement Parameters for Compounds 1–3

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<tr>
<th>compound</th>
<th>1</th>
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<th>3</th>
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<tr>
<td>formula</td>
<td>$C_9H_{21}Co_2N_{15}O_3$</td>
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<td>296</td>
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<td>triclinic</td>
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<td>$P$</td>
<td>$P$</td>
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<td>1112</td>
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<td>$b$ [Å]</td>
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<td>14.449(5)</td>
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<td>$c$ [Å]</td>
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<td>$\gamma$ [deg]</td>
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<td>0.0517, 0.1120</td>
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### EXPERIMENTAL SECTION

**Physical Measurements.** Infrared spectral samples were prepared as KBr pellets, and the spectra were obtained over the range of 4000–400 cm$^{-1}$ on a Bruker Tensor 27 FT-IR spectrometer. Elemental analyses for C, H, and N were performed on an Elementar Vario EL III elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer with a Cu Ka X-ray source (Operated at 40 kV and 40 mA). Magnetic measurements were performed on a Quantum Design SQUID VSM magnetometer on the ground single crystals of 1 to 3. Direct-current (dc) measurements were conducted from 300 to 2 K under an external magnetic field of 1000 Oe. The field-dependent magnetizations were measured at 2 K with dc field up to 7 T. Experimental susceptibilities were corrected for diamagnetism of the sample holders and that of the compounds ($x_{	ext{dia}} = -0.4 \times 10^{-6}$) $\text{mol}^{-1}$). For all compounds 1–3, $[Co_4(N_3)_8(L)_5]$ ($L = \text{DMF}$, $n = 3$, (1); $L = \text{DEF}$, $n = 2.5$, (2); $L = \text{DIPF}$, $n = 2$, (3)) was used as the magnetic unit for consistency in the magnetic analysis.

**Materials and Preparation of Compounds 1–3.** The starting materials, including CoCl$_2$·6H$_2$O, NaN$_3$, DMF, DEF, and DIPF were used as purchased without further purification. Deoxygenated solvents were prepared by bubbling them with nitrogen for 1 h or distilling under nitrogen. All the synthesis procedures and all product handling were performed in a nitrogen atmosphere to avoid the possible oxidation of CoII ion.

**Caution! Although our samples never exploded during handling, azido metal complexes are potentially explosive. Only a small amount of material should be prepared, and it should be handled with great care.**

$[Co_4(N_3)_8(\text{DMF})_3]$ (1). A 2 mL DMF solution containing CoCl$_2$·6H$_2$O (59.5 mg, 0.25 mmol) was mixed with a 2 mL DMF solution of NaN$_3$ (32.5 mg, 0.5 mmol). The resulting solution was then filtered and added to a test tube. Diethyl ether vapor was then allowed to diffuse into the test tube. Purple needle single crystals suitable for single-crystal X-ray experiment formed in the tube in one week.

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$[Co_4(N_3)_8(\text{DEF})_2]$ (2). A procedure similar to that of 1 was followed to prepare compound 2 using DEF instead of DMF. Blue needle crystals formed in the tube in one week. Yield: 10 mg, 15% based on...
Crystallographic analysis revealed that compounds 1–3 all consist of parallel 1D chains, where the Co\(^{II}\) centers are bridged by EO azides. Their phase purities were confirmed by the PXRD spectra (Figure S1). Compound 1 crystallizes in a monoclinic space group \(P2_1/c\) with an asymmetric unit containing two unique Co\(^{II}\) ions, three DMF molecules, and four azido ligands (Figure 1). The Co1 center is hexa-coordinated by two \(\mu_{1,1,1}-N^2_3\), two \(\mu_{1,1}-N^3_1\), and two DMF molecules with Co1–N/O bond lengths from 2.089 to 2.186 Å. While for Co2 ion, its coordination geometry is completed by four N atoms from \(\mu_{1,1,1}-N^2_3\), one N atom from \(\mu_{1,1,1}-N^3_1\), and one O atom from DMF. The Co2–N/O distances range from 2.103 to 2.331 Å. The Co1 and Co2 centers reside in the slightly distorted octahedral coordination environment \([\text{CoN}_4\text{O}_2]\) (Co1, pink) and \([\text{CoN}_5\text{O}_1]\) (Co2, sky-blue, Figure 1), respectively, with continuous shape measures (CShM values)\(^{22}\) related to the ideal octahedron calculated to be 1.021 and 1.783. Linked by one \(\mu_{1,1,1}-N^2_3\) and one \(\mu_{1,1,1}-N^3_1\) between Co1 and Co2 centers and two \(\mu_{1,1,1}-N^3_1\) between two Co1 centers related by the inversion center, four octahedra (two Co1 and two Co2 ions) are connected to each other by sharing the edges (namely, N4–N4A, N4–N7, N4–N13A, N4A–N7A, and N4A–N13) to form a centrosymmetric \([\text{CoN}_4\text{O}_2][\text{CoN}_2\text{O}_2][\text{CoN}_2\text{O}_2]\) tetramer unit (denoted as Co4A) with a defective dicubane core (Figure 1). These Co4A clusters are then linked to each other by sharing the N10–N10A edge between two Co2 centers to form the 1D chains running along the \(a\) axis (Figure 2a). All the individual chains are separated by the terminal DMF molecules with the shortest interchain Co3–Co3 distance being 9.965 Å (Figure 2b). No significant supramolecular interactions such as the hydrogen bonding between chains are evident.

Compound 3 crystallizes in the triclinic \(P\bar{1}\) space group. Its asymmetric unit consists of two unique Co\(^{II}\) ions, two DIPF ligands, and four azido ligands (Figure 3). Similar to 1, Co1 ion adopts the distorted \([\text{CoN}_4\text{O}_2]\) octahedral geometry (red) completed by two \(\mu_{1,1,1}-N^2_3\), two \(\mu_{1,1}-N^3_1\), and two DIPF molecules with Co–N/O bond lengths from 2.080 to 2.230 Å. Different from 1, the coordination geometry of Co2 ion is made of four N atoms from four \(\mu_{1,1,1}-N^2_3\) and one N atom from one \(\mu_{1,1,1}-N^3_1\), with the Co2–N distances ranging from 1.969 to
2.342 Å. Thus, the coordination geometry of Co2 is a \([\text{CoN}_5]\) trigonal bipyramid (green). The CShM values of Co1 and Co2 were calculated to be 1.093 for \([\text{CoN}_6\text{O}_2]\) related to octahedron and 1.370 for \([\text{CoN}_5]\) related to trigonal bipyramid, respectively. As in compound 1, two Co1 octahedra and two Co2 trigonal bipyramids are connected to each other by sharing the edges to form a centrosymmetric \([\text{CoN}_5\text{O}_2]\) tetramer unit (denoted as CoB) with also a defective dicubane core. These CoB clusters are further linked to each other by sharing the N12−N12A edge to generate a chain parallel to the \(a\) axis (Figure 4a). The chains are also separated from each other by the terminal DIPF molecules, with the shortest interchain CoII−CoII distance being 9.766 Å (Figure 4b). Also, there are no significant supramolecular interactions between the chains.

For compound 2, it also crystallizes into a triclinic \(P\overline{1}\) space group. Although it also consists of 1D EO azido-bridged CoII chains, its chain structure is of significant difference as those in 1 and 3. The asymmetric unit of 2 contains four unique CoII ions (Co1 to Co4), five DEF molecules, and eight azido ligands (Figure 5). For the coordination geometry of the CoII ions, Co1, Co2, and Co3 ions are hexa-coordinated and adopt the distorted octahedral geometry, while Co4 ion is penta-coordinated and adopts a trigonal bipyramidal geometry. The CShM values are calculated to be 0.775 (Co1, \([\text{CoN}_6\text{O}_2]\) octahedron), 0.965 (Co2, \([\text{CoN}_6\text{O}_2]\) octahedron), 0.873 (Co3, \([\text{CoN}_5\text{O}_2]\) octahedron), and 1.800 (Co4, \([\text{CoN}_5]\) trigonal bipyramid), respectively. Interestingly, the 1D structure of 2 consists of both the CoA tetranuclear unit (Figure 5a) similar to that in 1 and CoB tetranuclear unit (Figure 5b) similar to that in 3. These two kinds of tetramers (CoA and CoB) are linked to each other by sharing the N15−N18 edges of the polyhedra of Co2 and Co4 to form the 1D chains along the diagonal of the \(bc\) plane (Figure 6a). These 1D chains are separated from each other by the DEF molecules. The shortest interchain CoII−CoII distance is 9.120 Å (Figure 6b).

### Magnetic Properties

Variable-temperature dc magnetic susceptibility data for 1–3 were measured on ground single crystals between 2 and 300 K at 1 kOe (Figure 7 and Figure S2). The \(\chi_MT\) versus \(T\) plots are all similar. At 300 K, the measured \(\chi_MT\) values are 8.44, 8.40, and 7.18 cm³ mol⁻¹ K for 1–3, respectively, falling in the usual range for two high-spin CoII ions with unquenched orbital momentum. When cooled,
the $\chi_M T$ value increases gradually at high temperatures and then increases more abruptly below 50 K to a maximum of 123.85 cm$^3$ mol$^{-1}$ K at 8 K for 1, 118.77 cm$^3$ mol$^{-1}$ K at 8 K for 2, and 148.83 cm$^3$ mol$^{-1}$ K at 12 K for 3. After the maximum, $\chi_M T$ drops sharply to a minimum at 1.8 K. The sharp peak of the $\chi_M T$ indicates the long-range magnetic ordering and the sharp decrease is likely because of AFM interchain interactions or field saturation effect at low temperature. The Curie–Weiss fit of the susceptibility data above 100 K gave the Curie constants $C = 7.56, 7.48, 6.51$ cm$^3$ mol$^{-1}$ K and Weiss constants $\theta = 32.39, 33.77, 42.02$ K for compounds 1–3, respectively. The positive $\theta$ values clearly indicate the FM couplings between the Co$^{II}$ ions transmitted by the $\mu_{1,1}$-$\text{N}_3$ or $\mu_{1,1,1}$-$\text{N}_3$ ions.

However, because of the complexity of the structures of 1–3, quantitative analyses on the magnetic data for the exchange magnetic interactions and magnetic anisotropies are inherently difficult. A lot of different parameters must be considered to model their magnetic data. For instance, for compounds 1 and 3, there are three nearest exchange interactions between the Co$^{II}$ centers (namely, $J$(Co1–Co2), $J$(Co1–Co1A), and $J$(Co2–Co2A)), two different sources of magnetic anisotropies (different $g$ factors and/or zero-field splitting parameters for Co1 and Co2), and at least one interchain dipole–dipole exchange interaction ($zf$, using a mean-field theory approximation, which is apparently also a rough estimation, since the distances between the chains are different along different directions). The situation is even worse for compound 2, as it contains four different Co$^{II}$ centers and five different Co–Co exchange interactions.

The field-dependent magnetization $M(H)$ curves of 1 to 3 from 0 to 70 kOe were also measured at 2 K (Figure 8). For all the compounds, the magnetization rises rapidly at low fields and then increases slowly to the maximum values at 70 kOe. Clearly, the magnetization is not saturated at 70 kOe, which could be due to the large magnetic anisotropy of the octahedral or trigonal bipyramidal Co$^{II}$ systems. Interestingly, small hysteresis loops can be observed at 2 K for all three compounds with the remnant magnetization $M_R = 1.0, 2.4$, and 2.2 $\mu_B$, and a coercive field of $H_C = 170, 600$, and 1300 Oe, for 1–3, respectively (with a field sweep rate of 300 Oe/s). Observation of the loops indicates the very slow dynamics of the magnetization in compounds 1–3, which might originate from the classic long-range magnetic ordering, spin glass or the SCM behavior. Furthermore, the hysteresis loops for compound 3 at different temperatures and different field sweep rates were also measured to investigate the slow magnetic relaxation. As shown in Figure S3, these loops show obvious temperature and field sweep rate dependence. With decreasing temperature and increasing field sweep rate, the coercive field increases significantly. The hysteresis loop can be observed up to 3.0 K at a rate of 300 Oe/s.

The zero-field-cooled (ZFC) and field-cooled (FC, $H_{dc} = 10$ Oe) magnetizations were also measured. As depicted in Figure 9 and Figure S4, all these compounds behave in a similar manner. Taking compound 1 as an example, the ZFC and FC curves coincide with each other at high temperatures and show a very sharp peak at 7.7 K. Below 7.2 K, these two curves diverge from each other: while the FC curve remains almost constant, the ZFC curve drops sharply upon cooling. Similarly, a peak at 7.0/10.4 K and a divergence point at 6.4/6.0 K were observed for compounds 2 and 3. All these features indicate the occurrence of AFM magnetic ordering at higher temperature. The magnetic irreversibility at lower temperatures might originate from either spontaneous magnetization or slow magnetic relaxation, such as that found for glassy magnets or SCMs, considering the chain structures of compounds 1–3.

To probe their slow magnetic relaxation, variable-temperature ac susceptibility measurements were performed for compounds 1–3 at multiple frequencies under zero dc field. As shown in Figure 10, in all cases, the AFM ordering is confirmed by the frequency-independent peaks in the $\chi'$ curves, and the ordering temperatures are consistent with those observed in ZFC/FC curves. Interestingly, at lower temperatures, both the in-phase ($\chi''$) and the out-of-phase ($\chi''$) signals show frequency dependence, indicating the slow magnetic relaxation. The shift of the peak temperatures ($T_p$) in the $\chi''$ plots measured by the Mydosh parameter $\phi = (\Delta T_p/T_p)/ (\Delta \log f)$ are estimated to be 0.06, 0.14, and 0.11 for 1–3, respectively. On the one hand, the relatively small $\phi$ value of 1 (<0.1) indicates that compound 1 exhibits the spin glass behavior, rather than that of a typical super-paramagnet. For compounds 2 and 3, on the other hand, $\phi$ falls in the normal range ($0.1 < \phi < 0.3$) expected for super-paramagnetic behavior, indicating the SCM behavior of 2 and 3. From the $\chi'$ data, relaxation time ($\tau$) can be extracted for each peak through the expression $\tau = 1/(2\pi\nu)$, where $\nu$ is the frequency of the ac field. Fitting of the relaxation time according to the Arrhenius equation $\tau(T) = \tau_0 \exp(\Delta E/k_B T)$ gives the energy barriers of $\Delta E/k_B = 201.93, 60.17, 71.54$ K and pre-exponential factors of $\tau_0 = 1.71 \times 10^{-18}, 1.95 \times 10^{-9}, 7.10 \times 10^{-12}$ s for compounds 1–3, respectively (Figure 11).
We noticed that both the $\phi$ value and the pre-exponential factor $\tau_0$ for compound 1 are out of the normal range for a SCM, indicating its spin glass behavior. Therefore, the conventional critical scaling law of the spin dynamics,\textsuperscript{24} $r = \tau_0\left[(T_p - T_f)/T_f\right]^{-z}\nu$, was used to evaluate the dynamic property of magnetization of 1, where $r$ is the relaxation time, $T_f$ is the freezing temperature, $T_p$ is the spin glass temperature, and $z\nu$ is the critical exponent, respectively. According to this equation, three parameters $\tau_0 = 4.5 \times 10^{-10}$ s, $T_f = 4.4$ K, and $z\nu = 11.55$ were estimated for compound 1 (Figure S5). The value of $z\nu$ is in the range of various spin glass behaviors from 4 to 12, which further confirms the canonical spin glass behavior for compound 1.

The Cole–Cole plots (Figures S6a and S7a) for compounds 2 and 3 were also measured to investigate the relaxation dynamics. A generalized Debye model was used to extract the values and distribution of the relaxation time ($\tau$).\textsuperscript{24} The obtained $\alpha$ values are 0.23–0.31 and 0.34–0.43 for 2 and 3 (Tables S4 and S5), respectively, indicating a relatively broad distribution of the relaxation time. A least-squares fit based on the Arrhenius relationship $r(T) = \tau_0\exp(\Delta_f/k_B T)$ gives parameters $\Delta_f/k_B = 69.89$ and $62.66$ K and $\tau_0 = 1.14 \times 10^{-9}$ and $5.04 \times 10^{-9}$ s for compounds 2 and 3, respectively (Figures S6b and S7b). These parameters are slightly different from those obtained from the temperature-dependent ac susceptibility data. The frequency dependence fit could be more reliable, because the whole curve is used for fitting instead of peak maximum only.

In an anisotropic Heisenberg or Ising-like 1D system, it is well-known that the $\chi_{M}\tau$ value is proportional to the correlation length ($\xi$) and that it increases exponentially with decreasing temperature, following the equation $\chi_{M}\tau = C_{\text{eff}}\exp(\Delta_f/k_B T)$.\textsuperscript{25,26} The $C_{\text{eff}}$ is the effective Curie constant, and $\Delta_f$ is the correlation energy, which gives an estimation of the intrachain exchange energy needed to create a domain wall within the chain. The resulting $\ln(\chi_{M}\tau)$ versus $1/T$ plots of 1–3 increase linearly in the temperature ranges of 12–110, 20–100, and 16–90 K, and linear fitting of the data gives $C_{\text{eff}} = 8.33, 8.41$, and 6.75 cm$^3$ mol$^{-1}$ K$^{-1}$ and $\Delta_f/k_B = 27.85$, 27.98, and 51.06 K, respectively (Figure S8).

The value of $\Delta_f/k_B$ for compound 3 increases linearly in the temperature ranges of 12–110, 20–100, and 16–90 K, and linear fitting of the data gives $C_{\text{eff}} = 8.33, 8.41$, and 6.75 cm$^3$ mol$^{-1}$ K$^{-1}$ and $\Delta_f/k_B = 27.85$, 27.98, and 51.06 K, respectively (Figure S8).

In the ideal Ising chain system, the Glauber dynamics predicts that $\Delta_f = \Delta_f$ for “infinite” chains and $\Delta_f = 2\Delta_f$ for “finite” chains.\textsuperscript{25} Comparing the $\Delta_f$ and $\tau_f$ values for compounds 2 and 3, we found that these $\Delta_f$ values are significantly smaller than the $\Delta_f$ values estimated from ac measurements, and the difference between $\Delta_f$ and $\tau_f$ in these two compounds can be associated with the anisotropy energy barrier ($\Delta_A$) induced by the relaxation of the single Co$^{II}$ ion. As the magnetic relaxation of 2 and 3 occurs in the low-temperature “finite-size” regime, the energy barrier should be given as $\Delta_f = \Delta_f + \Delta_A$.\textsuperscript{25} According to this relationship, the magnetic anisotropy energy $\Delta_A/k_B$ for the Co$^{II}$ centers can be estimated as 41.91 and 11.60 K for compounds 2 and 3, respectively.

## DISCUSSION

In this work, a straightforward and effective strategy in which the amide solvent molecules (L) are directly utilized as the terminal ligands was employed to construct the azido-bridged 1D Co$^{II}$ chains. This synthesis method is distinctive from the traditional ones, where the extra molecules are required to act as the blocking ligands, such as zwitterionic carboxylate ligands,\textsuperscript{27} and 2,2′-bipyridine as well as their derivatives.\textsuperscript{27} From this strategy, a series of Co–N$_3$ 1D chains was successfully synthesized. Moreover, the coordination environment for the Co$^{II}$ ions and the repeating units for the 1D structures of these compounds have interesting dependence on the size of L. As shown in Figure 12, across compounds 1–3,
half of the CoII ions (Co1 in compounds 1 and 3, Co1 and Co3 in compound 2) reside in the similar coordination environment [CoN5O1] with four azides and two amides, while the coordination geometry of the other half of the CoII ions (Co2 in compounds 1 and 3, Co2 and Co4 in compound 2) are quite different. For compound 1, the coordination geometry of Co2 is completed by five N3 and one DMF ligand to form the [CoN5O1] octahedron. In 2, where the DMF ligand is replaced by the larger DEF ligand, half of the Co2 ions (with a new label of Co4) change to penta-coordinated and adopt the [CoN5] trigonal bipyramid. Furthermore, with the largest DIPF ligand, all the Co2 ions in compound 3 are penta-coordinated in a [CoN5] trigonal bipyramid. These results indicate that the number of the coordinated L decreases with the increasing size of L. For compounds 1–3, the ratios of L to CoII centers are 6:5, 5:4 and 4:4, respectively. Because of the different coordination polyhedra of CoII centers, the 1D structures of compounds 1–3 are constructed from distinct repeating units. For compounds 1 and 3, the repeating units are CoA ([CoN2O2][CoN3O1]2[CoN2O1]) and CoB ([CoN4]-[CoN5][CoN2][CoN3]), respectively, while for compound 2, the 1D structure is completed by alternating CoA (blue square in Figure 12) and CoB (red square in Figure 12) units. These results indicate that by using amides of different steric effect, more novel CoII-azide compounds are expected, which can shed some light on the complicated and fascinating magnetostructure relationships.

Because of their similar structures, 1–3 exhibit analogical magnetic properties. For all these compounds, the EO N3− bridges transmit FM couplings between the adjacent CoII ions and lead to the ferromagnetic chains, which are AFM coupled further to give the long-range AFM ordering at higher temperatures. The AFM ordering is attributed to the dipole–dipole magnetic couplings between the chains. For compounds 1 to 3, all individual chains are separated by the terminal amide molecules with the shortest interchain distance being ~10 Å. Although no significant supramolecular interactions between chains are evident, dipole–dipole interactions can always function between the chains. Usually, this dipole–dipole magnetic interaction is anti-ferromagnetic, and this should be the reason for the AFM ordering. In fact, this result is consistent well with the earlier reports of the SCM-based anti-ferromagnets.8b,28

At low temperature, all compounds show slow magnetic relaxation in the AFM ordered phases. However, their magnetic dynamics slightly differs from each other: only compound 1 shows spin glass behavior, while 2 and 3 behave as the SCMs. Frankly speaking, we are not sure about the reason for these differences. However, we think that it might be because of the interference of the AFM ordering. As we can see from the χ′ plots (Figure 10), the temperature for the observation of the slow magnetic relaxation (where frequency dependence starts in the χ′ plots) of 1 is very close to its peak temperature (Tc of the AFM ordering), while for compounds 2 and 3, these temperatures are far from the peak temperatures. As reported by Coulon et al.,6b the AFM ordering influences the magnetic relaxation dramatically for the SCM-based anti-ferromagnets. The relaxation time is expected to increase in the region close to the AFM-paramagnetic boundary. Meanwhile, deeper inside the AFM phase, as that for compounds 2 and 3, the dynamics are essentially due to the SCM part of the compounds. As for the reason why only compound 1 shows the slow magnetic relaxation in the temperature region close to the Tc value, we cannot come to any conclusion.

Finally, for compounds 2 and 3 exhibiting both SCM behavior in the AFM ordered state, no general trend of the effective energy barriers can be formulated. As reported in the earlier reports, the effective energy barrier of an SCM can be attributed to two components, namely, the energy barrier for the magnetic anisotropy of the individual metal ions and the correlation energy originates from the intrachain magnetic coupling.6a,29 However, because of their complicated chain structures and existence of two or four different CoII centers, we do not think it is possible to extract any meaningful parameters for the exchange interactions, magnetic anisotropies, and interchain interactions. This statement is also true for the different energy barriers.

## CONCLUSIONS

In summary, we have reported here the syntheses, structures, and magnetic properties of three 1D azido-bridged cobalt chains with different amide terminals. All compounds consist of parallel 1D chains, where the CoII sites are linked through EO N3− bridges. Because of the different steric effect of the amides, the coordination geometry of the CoII ions and the repeating units of the 1D structures in compounds 1 to 3 are quite different from each other. Most interestingly, we noticed that
for the medium-sized amide, the resulting structure is also the transition structure of the other two structures. However, the interchain distances and the interchain CoIII−CoII distances have no clear correlation with the size of the amides. Because of their similar 1D structures, compounds 1−3 exhibit analogous magnetic behaviors. Magnetic studies indicated that all these compounds exhibit intrachain FM couplings and interchain AFM interactions, as well as the slow magnetic relaxation in the AFM ordered phases. However, their magnetic dynamics slightly differs from each other: compound 1 shows spin glass behavior, while compounds 2 and 3 behave as the SCMs. To further explore the complex dynamics and the magnetostructure correlation, the construction of other Co−N3 1D systems with different amide terminals is currently underway.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00736.

Structure information in detail, powder XRD spectra, and the additional magnetic data (PDF)

Accession Codes

CCDC 1535669−1535671 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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