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An Azide-Bridged Homospin Single-Chain Magnet:  $[\text{Co}(\text{2,2'}$ -bithiazoline) $(\text{N}_3)_2]_n$ Tian-Fu Liu,<sup>†</sup> Dan Fu,<sup>†</sup> Song Gao,<sup>\*,†</sup> Yuan-Zhu Zhang,<sup>†</sup> Hao-Ling Sun,<sup>†</sup> Gang Su,<sup>‡</sup> and Yong-Jiang Liu<sup>§</sup>

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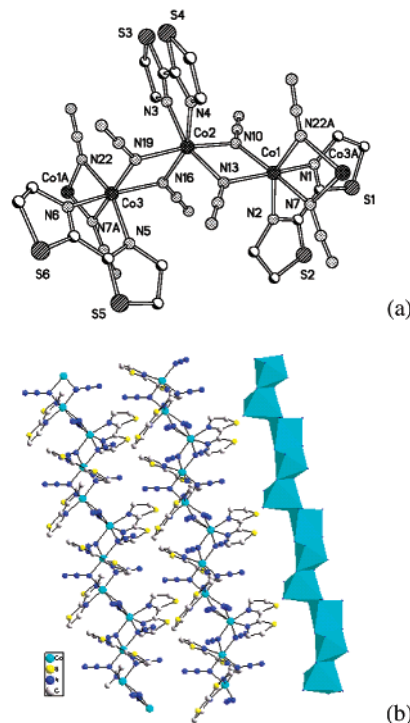
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Single-chain magnets (SCMs) are of high interest because of their unusual physical properties, and they open the possibility of potential use of one-dimensional (1D) magnetic molecular nanowires for information storage. A few samples are reported, and each of them contains heterospin in the chain.<sup>1</sup> As a versatile bridge ligand, an azide ion can bind metal ions in a number of coordination modes, giving rise to a wide variety of molecular architectures from clusters to 3D compounds.<sup>2</sup> Here we report a novel 1D helical chain complex,  $\text{Co}(\text{bt})(\text{N}_3)_2$  **1** (bt = 2,2'-bithiazoline), bridged by end-on (EO) azides, which shows intrachain ferromagnetic coupling, slow relaxation of the magnetization, and hysteresis effects. It is the first example of a homospin SCM.

The reaction of  $\text{NaN}_3$  with  $\text{Co}(\text{NO}_3)_2$  and bt in 1:1:1 molar ratio in methanol solution yielded deep-red small needle-like crystals of complex **1**. Complex **1** crystallizes in the monoclinic system with space group  $P2(1)/n$ .<sup>3</sup>

A perspective view of a trinuclear fragment of the chain is presented in Figure 1a. The structure consists of homometallic cobalt chains linked by double EO azido bridges. Each Co(II) ion has a slightly distorted octahedron geometry, while Co(1), Co(2), and Co(3) are located in three different octahedron environments. Two nitrogen atoms from bt occupy the in-plane positions, and the other four nitrogen atoms from EO azides occupy the other two in-plane positions and two apical positions. The distances of Co(II)–N are slightly different: 2.107(6) and 2.350(9) Å for Co(1)–N, 2.110(5) and 2.171(5) Å for Co(2)–N, and 2.125(6) and 2.246(9) Å for Co(3)–N, respectively, which are comparable with 2.118(2)–2.189(2) Å in other Co–N<sub>3</sub> systems.<sup>4</sup> The bond angles of Co–N–Co are in the range between 102.9(2)° and 116.0(4)°, and the intrachain metal–metal separations through EO azide are Co(1)–Co(2), 3.334(1) Å; Co(2)–Co(3), 3.344(1) Å; and Co(3)–Co(1a), 3.636(2) Å (*a*, 1 + *x*, *y*, *z*). The two quinquicycles of bt are not coplanar, and the dihedral angle is from 9.8° to 12.2°. The unique feature of the chains along the crystallographic axis *a* is developed as helices (Figure 1b). The neighboring chains are in opposite directions. The shortest distance of Co(II) ions among the chains is 8.541(1) Å, and no hydrogen bond or  $\pi$ – $\pi$  stacking can be found. The shortest S...S and S...N separations between chains are 3.859(2), and 3.430(5) Å, larger than the sum of van der Waals radii (see Figure S1, Supporting Information, for details).

Magnetic measurements were performed on a sample of **1** containing a collection of very small needle-like single crystals with random orientation. The measured  $\chi_{\text{M}}T$  value at room temperature is ca. 3.51 cm<sup>3</sup> mol<sup>−1</sup> K, higher than the spin-only value of 1.88 cm<sup>3</sup> mol<sup>−1</sup> K for  $S = 3/2$ , owing to a significant orbital contribution of high-spin Co(II) in an octahedral surrounding, which increases



**Figure 1.** (a) Molecular structure of complex **1**. (b) Helical chains along the *a* axis and the octahedrons of Co(II) ions.

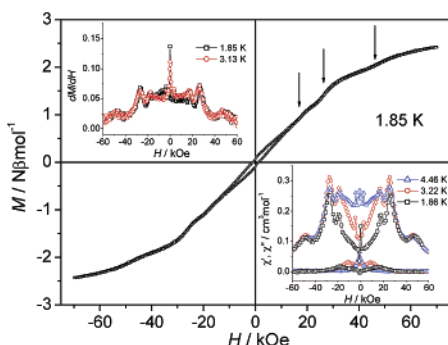
smoothly upon cooling to ca. 35 K and reaches a maximum value of 6.27 cm<sup>3</sup> mol<sup>−1</sup> K, and then decreases sharply to 0.84 cm<sup>3</sup> mol<sup>−1</sup> K at 2 K (Figure S2, Supporting Information). The magnetic susceptibility in the range 100–300 K obeys the Curie–Weiss law ( $\chi_{\text{M}} = C/(T - \theta)$ ), with  $C = 3.095(8)$  cm<sup>3</sup> mol<sup>−1</sup> K and  $\theta = +35.9$  (2) K. The  $C$  value corresponds to  $g = 2.57$ . The positive Weiss constant indicates a ferromagnetic coupling between Co(II) ions bridged by EO azide ligands. The same set of data above 100 K can be fitted well by a Fisher 1D chain ( $S = 3/2$ ) model ( $H = -JS_zS_j$ , intrachain coupling  $J$ ), giving  $J = 12.4(1)$  cm<sup>−1</sup> = 17.8 K,  $g = 2.542(3)$ , and  $R = 2.7 \times 10^{-5}$  ( $R = \sum[(\chi_{\text{M}}T)_{\text{obs}} - (\chi_{\text{M}}T)_{\text{calcd}}]^2 / \sum[(\chi_{\text{M}}T)_{\text{obs}}]^2$ ). Using the mean-field expression for the Curie–Weiss temperature,  $\theta = zJS(S + 1)/3k_{\text{B}}$  (keeping the same  $H = -JS_zS_j$ ), the magnetic interaction  $J/k_{\text{B}}$  along the chain can be estimated to be ca. 14.4 K when  $S = 3/2$  and average  $z = 2$  for such an isolated chain.<sup>5</sup> The  $J$  values (17.8 and 14.4 K) are in good agreement with the value of 20.7(3) K observed in an EO N<sub>3</sub>-bridged dimer,  $\text{Co}_2(\text{DMphen})_2(\text{N}_3)_4$  (**2**).<sup>6</sup>

As shown in Figure 2, a hysteresis loop is observed clearly at 1.85 K when the field is less than 20 kOe, but gives a coercive field of ca. 1.0 kOe and a very small remnant magnetization of ca.

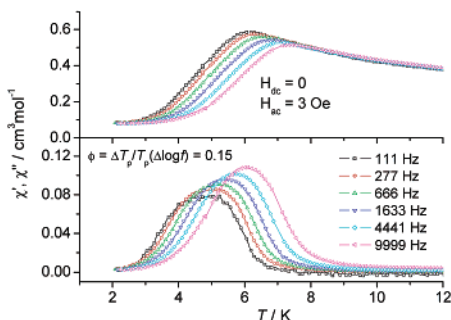
<sup>†</sup> Peking University.

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<sup>§</sup> Nanjing University.



**Figure 2.** Field dependence of magnetization measured at 1.85 K. (Inset) Upper left, field dependence of  $dM/dH$ ; lower right, field dependence of ac susceptibility.



**Figure 3.** Temperature dependence of the real (top) and imaginary (bottom) components of the ac susceptibility in zero applied static field with an oscillating field of 3 Oe at a frequency of 111–9999 Hz. The lines are guides.

$0.08 \text{ N}\beta \text{ mol}^{-1}$ . With the increase of field, several steps are observable at ca. 17, 26, and 46 kOe, which are clearly characterized by the peaks in the field dependence of  $dM/dH$  and  $\chi'$ ,  $\chi''$  (inset of Figure 2), even to ca. 4.6 K. These reversible steps in the hysteresis loop could be attributed to the different anisotropy axes of Co(II) spins in the helical chain.<sup>1a</sup> Field-cooled magnetization (FCM) and zero-field-cooled magnetization (ZFCM) measurements (Figure S3, Supporting Information) under a field of 10 Oe, with a temperature step of 0.3 K and a rate of 4.8 min/point, show the irreversibility below ca. 5 K, which is defined as the blocking temperature.

The blocking of the magnetization below 5 K is not due to a phase transition to a 3D order or a spin glass, which is confirmed by ac magnetic susceptibility measurements performed in the range of 111–9999 Hz. The strong frequency dependence of the real and imaginary parts of linear ac susceptibility  $\chi'$ ,  $\chi''$  is shown in Figure 3. The shift of peak temperature ( $T_p$ ) of  $\chi''$  is measured by a parameter  $\phi = (\Delta T_p/T_p)/\Delta(\log f) = 0.15$ , which is 2 orders larger than that for a canonical spin glass, closer to a normal value for a superparamagnet. Moreover, although this dependence on frequency can be fitted by the conventional critical scaling law of the spin dynamics, as described by  $\tau = \tau_0((T_p - T)/T_p)^{-z\nu}$ , where  $\tau = 1/(2\pi f)$ , giving  $\tau_0 = 10^{-4} \text{ s}$ ,  $z\nu = 3.6$ , and  $T_i = 2.8 \text{ K}$  ( $T_i$  is the critical temperature for a spin glass phase), the obtained  $z\nu$  value is out of the range (from 4 to 12) for various spin glasses (Figure S4a, Supporting Information). Meanwhile the Arrhenius law,  $\tau = \tau_0 \exp(-\Delta E/k_B T)$ , does hold for **1**, and the best fit gives a more physical set of parameter values:  $\tau_0 = 3.4 \times 10^{-12} \text{ s}$ ,  $\Delta E/k_B = 94(2) \text{ K}$  (Figure S4b, Supporting Information).<sup>7</sup> The gap is

comparable with the expected value  $\Delta_{\text{Glauber}}/k_B = 2J_{\text{eff}}' = 2S_T^2 J = 2 \times (3/2)^2 \times 17.8 = 80 \text{ K}$ , based on Glauber's theory.<sup>1b,8</sup> At fixed temperatures 4.01 and 4.63 K around the cusp of out-of-phase  $\chi''$ , a semicircle Cole–Cole diagram was obtained ( $\chi''$  vs  $\chi'$  in Figure S5, Supporting Information), which can be fitted by a generalized Debye model, with the  $\alpha$  parameter being 0.65–0.70, indicating a large distribution of relaxation time, consistent with the wide shape of the ac susceptibility as a function of the temperature. In a word, the frequency dependence of the linear ac susceptibility suggests a superparamagnetic-like behavior. The magnetic relaxation behavior is reminiscent of that observed in single-molecule magnets, as well as in molecular magnetic nanowires, where the energy barrier originates from the magnetic anisotropy.<sup>1,9</sup> On the other hand, both the second and third harmonics shown in Figure S6 (Supporting Information) are negligibly small, essentially at a noise level. The absence of an even harmonic response of  $\chi'$  and  $\chi''$  excludes any spontaneous moment,<sup>10</sup> further supporting the low dimensionality of **1**.

In summary, a well-isolated azide-bridged 1D homospin cobalt compound is synthesized. The magnetic measurements justify that it does show a single-chain-magnet behavior.

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**Supporting Information Available:** Synthesis, IR, and more magnetic data (PDF); crystal data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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