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Uncommon Ferromagnetic Interactions in a Homometallic Co(II) Chain Bridged by a Single End-to-End Azide

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A new one-dimensional heterochiral coordination polymer $[Co(bmdt)(N_3)_2]$·MeCN (**1**·MeCN) with well-isolated chains was prepared via a self-assembly process. Magnetic data show that intrachain ferromagnetic couplings via the single end-to-end azide group are observed, which is an extraordinary case among the azide-bridged Co(II) systems.

Recently, low-dimensional magnetic materials have attracted extensive attention because of the emergence of intriguing anisotropic systems such as single-molecule magnets (SMMs) and single-chain magnets (SCMs).[1] To realize these systems, it is of ultimate importance to select appropriate bridging units and anisotropic paramagnetic centers. As one of the recognized linkers, the azide ligand is frequently employed in virtue of its magnetic predictability and coordinating power. The magnetic nature of azide can be generally predefined depending on its coordination mode; the end-on mode provides ferromagnetic coupling, and the end-to-end (EE) mode gives antiferromagnetic alignment. Moreover, it has diverse binding ability, acting as if holding one to six metal ions simultaneously,[2] and, often together with ancillary ligands, forms discrete molecules,[2] one-dimensional (1D) chains,[3] two-dimensional (2D) sheets,[4] and three-dimensional networks.[5] On the other hand, it is well-known that Co(II) is one of the useful anisotropic sources. However, examples of azide-bridged Co(II) complexes are still limited until now,[6−8] and the magnetic characters of the reported Co(II) assemblies obeyed the aforementioned general rule except for the 1D Co(II) chain system in which ferromagnetic interactions are working via EE azide.[7] Some isolated systems displayed slow magnetic relaxation and hysteretic behavior below a blocking temperature typical of SMMs and SCMs.[8] Therefore, it would be valuable to seek magnetically well-segregated 1D systems with the aim of gaining insight into the genuine magnetic characteristics in a specific coordination mode of azide and attaining isolated anisotropic materials for potential SCMs.

Herein we present the synthesis, structures, and magnetic properties of a new 1D Co(II) compound $[Co(bmdt)(N_3)_2]$·MeCN (**1**·MeCN) [bmdt = *N*,*N*′-bis(4-methoxybenzyl)-diethylenetriamine] with well-isolated heterochiral chains. Magnetic data reveal ferromagnetic interactions between Co(II) centers within a chain mediated by single EE azides, which is very unusual because the EE mode mostly promotes antiferromagnetic coupling.[2−8]

A stoichiometric reaction of Co(II)/bmdt/NaN_3 in mixed solvent gave pink-brown crystals of **1** in 46% yield.[9] We attempted to prepare analogues of **1** using similar capping

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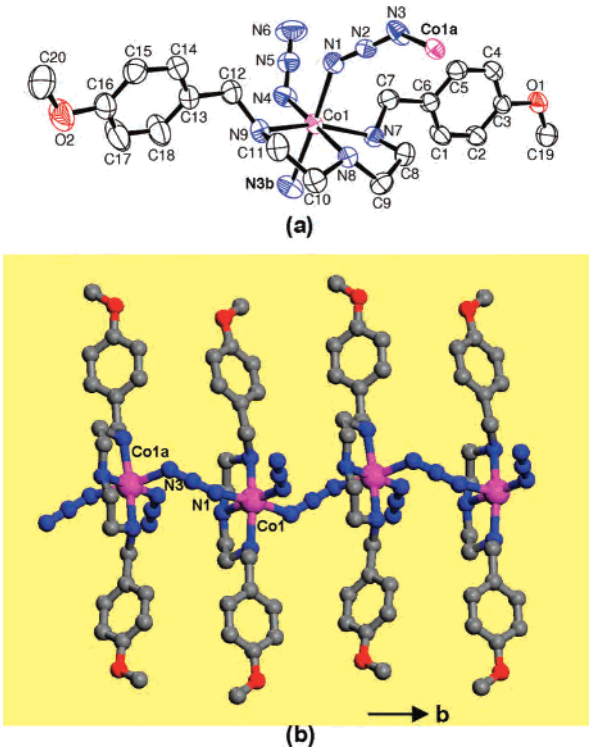

Figure 1. Molecular view of **1** showing (a) 50% ellipsoid probability and the atom-labeling scheme and (b) the homometallic chain structure running along the *b* axis. Symmetry code: a = 1.5 − *x*, 0.5 + *y*, 1.5 − *z*; b = 1.5 − *x*, −0.5 + *y*, 1.5 − *z*.

ligands such as bbdt and bedt but have isolated only traces of oxidized monomers of $[Co(L)(N_3)_3]$ [L = bbdt (**2**), bedt (**3**)] (Figures S1 and S2 in the Supporting Information).[9] For **1**, there are no Cl−O stretching vibrations in the IR spectrum, indicating that the reaction is complete. The characteristic peaks of azide are observed at 2073vs, 2046vs, and 2036vs (sh) cm^{-1}.

Compound **1** crystallizes in the monoclinic system with space group $P2_1/n$ as analyzed by X-ray crystallography.[10] Figure 1 shows the representative molecular structures of **1** with the atom-labeling scheme. The Co center is in a distorted octahedral geometry consisting of three N atoms from bmdt and three other N atoms from bridging and terminal azides with an average Co−N of 2.16(8) Å. The bond lengths associated with bridging azide groups are 2.1711(15) Å for Co1−N1 and 2.2550(15) Å for Co1−N3b (b = 1.5 − *x*, −0.5 + *y*, 1.5 − *z*). The magnetically related bond angles are 135.48(13)° for Co1−N1−N2 and 126.17(12)° for Co1a−N3−N2, which are in the normal range of azide-bridged metal complexes.[2−8] Interestingly, the azide bridge links two neighboring Co centers in a cis mode with respect to the bridging azide ligand, which is quite rare because most of azide-bridged systems are trans-positioned.[2−8] This conspicuous mode generates a large torsion angle of 69.91(16)° for Co1−N1···N3b−Co1b, which is significantly greater than that of the Ni analogue (49.2°)[11] and comparable to those

(10) Crystal data for **1**: $C_{22}H_{32}CoN_{10}O_2$, M_r = 527.51, monoclinic, space group $P2_1/n$, *a* = 10.1320(6) Å, *b* = 11.0295(7) Å, *c* = 23.3101(13) Å, β = 95.294(3)°, *V* = 2593.8(3) Å^3, *Z* = 4, ρ_{calcd} = 1.351 g cm^{-3}, μ = 0.701 mm^{-1}, *T* = 293 K, 24 253 reflections collected, 6381 unique (R_{int} = 0.0261), R1 = 0.0347, wR2 = 0.0815 [$I > 2\sigma(I)$].

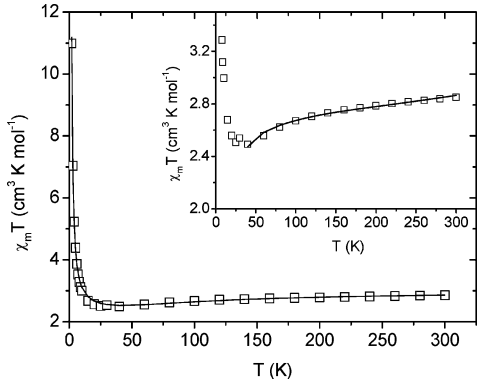

Figure 2. Plot of $\chi_m T$ vs *T* of **1**. The solid lines show the best fits of experimental data with appropriate magnetic models (see text).

of methylpyrazole-capped 1D azide-linked systems.[7] Two nearest CoN_4 basal planes are slanted with a dihedral angle of 77.56(3)°, even larger than those of the relevant 1D chains.[7] The intrachain Co−Co distance is 5.5951(5) Å.

Chains in **1** are well-isolated because of the presence of the bulky ligand bmdt (Figure S3 in the Supporting Information). The $\pi-\pi$ contacts with distances spanning from 3.889 to 3.914 Å are present between the benzene rings of the bmdt ligands residing in adjacent chains, and Co(II) ions in the parallel chains are separated by 13.828(1) Å. However, the shortest interchain Co−Co distance is found between different chains to be 10.132(1) Å. It is worth noting that each chain exhibits helicity with a long pitch of 11.030(1) Å; P- and M-helical chains in **1** are running along the *b* axis and stacked in a heterochiral fashion, eventually leading to a racemate (Figure S4 in the Supporting Information). This racemic feature is commonly observed in systems produced by archiral components.[12]

Figure 2 shows the temperature dependence of molar magnetic susceptibility in the temperature range of 2−300 K at 1000 G. The $\chi_m T$ value at 300 K of 2.85 cm^3 K mol^{-1} undergoes a steady decay upon cooling to 40 K. This magnetic behavior is associated with spin−orbit coupling for Co(II) ions with a $^4T_{1g}$ ground state in an octahedral field. The Curie−Weiss fit at $T > 60$ K affords C = 2.94 cm^3 K mol^{-1} and $\theta = -10.0$ K. The Curie constant is in the usual range of octahedral high-spin Co(II) ions (2.8−3.4 cm^3 K mol^{-1}).[13] To analyze the spin−orbit effect, the expression for an isolated hexacoordinated Co(II) ion along with a molecular field approximation (zJ') was employed in the temperature range of 40−300 K (inset of Figure 2).[14] A best result gives parameters of λ (spin−orbit coupling constant) = −72 cm^{-1}, consistent with Co(II) complexes,[15] *A* (crystal-

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field parameter: 1.5 for the weak-field limit and 1.0 for the strong-field limit) = 1.0, and $zJ' = 1.1$ cm^{-1}. On the basis of $k = \lambda/\lambda'$, where k is a reduction factor of spin−orbit coupling owing to covalency and λ' is the spin−orbit coupling parameter for a free ion ($\lambda' = -170$ cm^{-1}), k is 0.42. The positive zJ' value implies that the ferromagnetic contribution within a chain is evident.

To estimate both magnetic exchange interactions and the spin−orbit coupling effect in the temperature range of 2−300 K, we used the simple phenomenological equation given by

$$\chi_m T = A \exp(-E_1/k_B T) + B \exp(-E_2/k_B T)$$

where $A + B$ is equal to the Curie constant and E_1 and E_2 are ascribed to the spin−orbit coupling and the magnetic interaction, respectively.[13] The fitted parameters are $A + B = 3.04$ cm^3 K mol^{-1}, close to the Curie constant, $E_1 = 65.4$ cm^{-1}, and $E_2 = -2.22$ cm^{-1}. E_1 is consistent with those reported for 1D and 2D Co(II) systems.[13] The negative activation energy (E_2) demonstrates that ferromagnetic interactions are operative within a chain in relation with the Ising chain model $\chi_m T \propto \exp(+\beta J/k_B T)$.

To extract the magnetic exchange contribution only (Figure S5 in the Supporting Information), we subtracted the spin−orbit coupling effect from the experimental data by referring to $(\chi_m T)^F = (\chi_m T)^{exp} - A \exp(-E_1/k_B T)$. We used an infinite chain model based on the spin Hamiltonian $H = -J\sum_i S_i S_{i+1}$ to fit the resulting data.[16] A best fit gives $g = 2.15$ and $J = 1.09$ cm^{-1}. Thus, the intrachain ferromagnetic interactions are established via the single EE azide linkage. Taking into account that antiferromagnetic coupling is normally predicted in the EE mode, this observed ferromagnetic nature is quite unusual. To the best of our knowledge, only one other ferromagnetic example among the Co(II) systems with EE bridging patterns was reported to date.[7] From the structural parameters, the bond angles (135.48° and 126.17°) of Co−N−N(azide) fall in the antiferromagnetic range.[2−8] Accordingly, the large torsion angle of 69.91(16)° in **1** should be responsible for the observed ferromagnetic coupling as found in 1D EE azide-bridged Co(II), Ni(II), and Cu(II) complexes in which the torsion angles correspond to 71.6°, 75.6°, and 91.6°, respectively.[7,17]

The zero-field-cooled and field-cooled magnetizations are superimposed at low temperatures (Figure S6 in the Supporting Information), implying that there is no long-range magnetic order. This is also ascertained by applying noncritical scaling theory in the form of d log(T)/d log$(\chi_m T)^F$ vs T, where no intercept at the T axis exists (Figure S7 in the Supporting Information).[18] The alternating current magnetic susceptibility data designate that any transition in the in-phase component (χ_m') is invisible and the out-of-phase part (χ_m'') is virtually zero in the measured temperature region

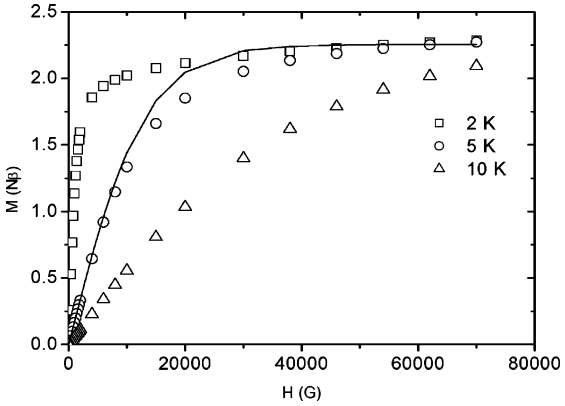

Figure 3. Plot of M vs H at indicated temperatures of **1**. The solid line represents the theoretical curve derived from the Brillouin equation at 2 K with an effective spin $S' = 1/2$ for Co(II) in an octahedral environment.

(Figure S8 in the Supporting Information). These features suggest that each chain in **1** is magnetically well-isolated in spite of the presence of the $\pi-\pi$ stackings, which is the required ingredient for SCMs.[19]

To further probe the underlying magnetic nature in **1**, the field dependence of the magnetization at 0−7 T and several temperatures was explored (Figure 3). At low temperature below 30 K, Co(II) is treated as an effective spin $S' = 1/2$. The magnetization data at 2 K grow very fast at low field and are saturated at 2.28 $N\beta$ in 7 T, which agrees with the expected values for Co(II) (2−3 $N\beta$).[12] When compared with the Brillouin curve at 2 K derived from $S' = 1/2$ and $g = 4.5$, where the g values of high-spin Co(II) in an octahedral geometry are typically greater than 4,[20] the data points lie above the calculated ones, pointing out that intrachain ferromagnetic couplings are firmly operating.

In summary, we have prepared a 1D homometallic complex **1**·MeCN with well-separated heterochiral chains. The ferromagnetic nature through the single EE azide is observed under the large torsion angle, which is a very rare example among the azide-bridged Co(II) systems. Fine-tuning of relevant constituents in magnetically isolated chain systems like **1** might provide a way to achieve SCMs.

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Supporting Information Available: X-ray crystallographic files in CIF format and additional synthetic, structural, and magnetic data for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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