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Synthesis, Structure, and Magnetism of Three Azido-Bridged Co^{2+} Compounds with a Flexible Coligand 1,2-(Tetrazole-1-yl)ethane

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By utilizing suitable coligand endi (1,2-(tetrazole-1-yl)ethane)) with variable conformations, we synthesized three new azido-bridged Co^{2+} compounds with molecular formulas $Co(endi)(N_3)_2$ (**1**, **3**) and $Co(endi)_2(N_3)_2$ (**2**) by tuning the stoichiometric ratio of ligand/metal and the concentration of the solution. All of the compounds have been characterized structurally and magnetically. In all three structures, the azide ions use the end-to-end mode to link the Co^{2+} centers to the 1D chain (**1**) and 2D (4,4) layers (**2** and **3**). The endi coligands adopt a trans conformation in compound **1** and a gauche conformation in compounds **2** and **3**. Linked by bridging endi, the 1D chains in compound **1** and 2D layers in compound **3** are extended, resulting in the final 2D layer for compound **1** and the 3D network for compound **3**, whereas in compound **2**, the endi acts as only a terminal ligand to separate the 2D layers. Compound **1** consists of dual end-to-end azido-bridged 1D Co^{2+} chains that are linked by trans endi into a 2D layer and are further extended to a 3D framework through H bonds. Compound **2** is a 2D (4,4) layer that is connected by end-to-end azido ions. The gauche endi ligands act as terminal ligands to separate the neighboring layers thoroughly. Compound **3** has a (4,4) 2D layer that is similar to that of compound **2**, and these layers are further extended to a 3D network through gauche endi. The magnetic investigation shows that compound **3** is antiferromagnetically coupled and compound **2** is a weak ferromagnet with a critical temperature of 22 K, which is quite high compared with that of the previously reported 2D azido-bridged Co^{2+} compounds.

Introduction

In the past three decades, plenty of attempts have been made to produce molecular magnetic materials by the use of azide as the short bridge because of its various coordination fashions and effective ability to transmit superexchange coupling between transition-metal ions. By introducing cobridging ligands, we have obtained a huge number of complexes with various structures of different dimensionalities and remarkable magnetic properties.[1−10] High-dimensional molecular magnetic systems have always been a classic realm for scientists to seek higher critical temperature (T_C) ferromagnets[11−15] and to finally enhance the bulk magnetic property of the materials.[16] Many azido-bridged

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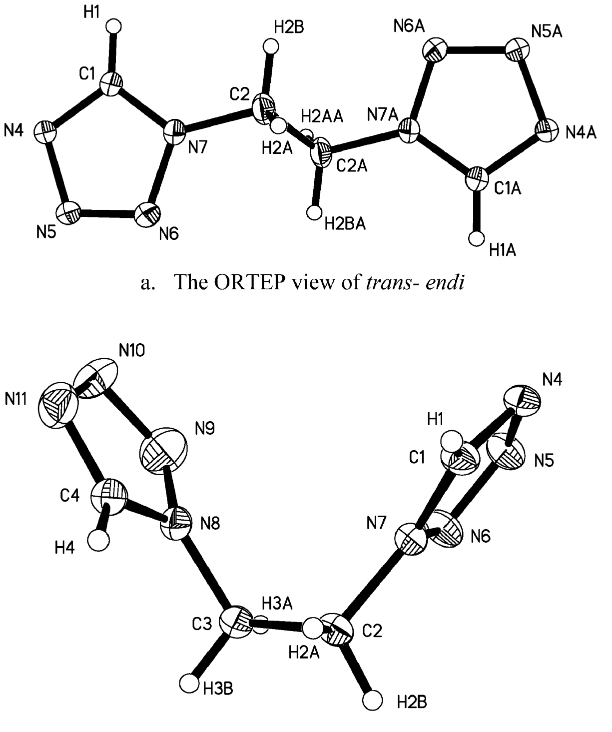
metal complexes with higher dimensionalities consist of metal−azido stuctures with several fixed topologies. The neighboring 2D layers are linked by the coligand into a higher dimension or are stacked through the van der Waals force.

The azide ions of the end-to-end (EE) mode are useful short bridges that connect paramagnetic centers into a higher dimensionality and transmit efficient magnetic interactions between them.[17] The coupling between paramagnetic ions through the EE mode of the azido bridge is always antiferromagnetic. Without centrosymmetry between neighboring metal ions, spin canting could emerge in suitable crystal systems and result in weak ferromagnetic behavior below the critical temperature.[18−21] The magnetic behaviors and the critical temperatures of these weak ferromagnetic compounds are different from those of the structural parameters, the magnitudes of the anisotropy properties of metal ions, and the intra/interlayer couplings.[22,23] As an element with obvious anisotropy, a cobalt ion could be a good spin center to form weak ferromagnets via an EE-azido bridge. Furthermore, it provides the possibility to build molecular magnets with a higher critical temperature. The known azido-bridged cobalt compounds in a high dimension with estimated magnetic properties are rare.

The 3D antiferromagnet $Co(pm)(N_3)_2$ (pm is pyrimide) with the 2D square $[Co(N_3)_2]_6$ layer and the long-range ordering that was below 41 K was reported by Ishida and Nogami.[24] Three 3D networks of Co^{2+} with the similar formula $Co(bpg)(N_3)_2$ (bpg = *meso*-α,*β*-bi(4-pyridyl) glycol) were obtained by Gao et al. They were EE-azido-bridged 2D structures of square, honeycomb, and Kagomé topologies. All of the structures were weak ferromagnets.[25] By the use of acpy (acpy = 4-acetylpyridine) as a half fragment of bpg, the weak ferromagnetic compound $Co(acpy)_2(N_3)_2$ with a 2D square structure similar to that of $[Co(N_3)_2]_n$ was first reported by Vicente et al.,[22] wheras its magnetic properties were intensively investigated by Wang by the use of powders and well-oriented single crystals.[26] Another kind of azido-bridged Co^{2+} layer with weak ferromagnetic property was reported by Wang. In this case, the honeycomb layer was from the bridging of azido and N_2H_4.[27] It is easy to figure out that the structure and magnetic property have a lot to do with a coligand.

For the reason discussed above, we adopt azide as a short bridge and endi as a coligand (endi = 1,2-(tetrazole-1-yl)-ethane) that contains two tetrazole rings to coordinate with the metal centers and the flexible group $-CH_2-CH_2-$. The two possible conformations of azide are shown in Scheme 1. The structure could be tuned by means of different conformations of the coligand and various coordination modes of azide ions. To obtain and distinguish many possible compounds with the same components, the tuning of the concentration and stoichiometric dose of each component is required. Three compounds of $[Co(N_3)_2]_n$ with the same coligand are obtained and characterized structurally and magnetically. Compounds **1** and **3** are antiferromagnetically coupled, whereas compound **2** is a weak ferromagnet with T_C = 22 K, which is much higher than known weak ferromagnets with similar structures.

Scheme 1



a. The ORTEP view of *trans- endi*

b. The ORTEP view of *gauche- endi*

Experimental Section

Materials and Apparatus. All starting materials were commercially available analytical grade and were used without further purification. Elemental analyses were carried out on an Elementary Vario EL analyzer. Crystallographic data of compounds **1**, **2**, and **3** were collected at 293 K on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).[28,29] Empirical absorption corrections were applied by the use of the Sortav program.[29−31] The structures were solved by the direct method and were refined by the full-matrix least-squares method on F^2 with anisotropy thermal parameters for all non-hydrogen

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Table 1. Crystallographic Data and Structure Refinement Results for Compounds **1**·Co, **2**·Co, and **3**·Co

compound	**1**·Co	**2**·Co	**3**·Co
formula	$C_4H_6CoN_{14}$	$C_8H_{12}CoN_{22}$	$C_4H_6CoN_{14}$
fw	309.16	475.33	309.16
cryst syst	triclinic	monoclinic	triclinic
space group, Z	$P\bar{1}$, 1	$P2_1/c$, 2	$P\bar{1}$, 2
a (Å)	5.3024(3)	15.1781(2)	6.5645(2)
b (Å)	6.1218(4)	6.2444(2)	9.0680(3)
c (Å)	8.6207(5)	9.8825(5)	9.6467(4)
α (deg)	71.807(4)	90	75.6290(14)
β (deg)	87.818(4)	101.1850(1)	88.1640(14)
γ (deg)	81.955(2)	90	70.200(2)
V (Å^3)	263.22(3)	918.85(6)	522.53(3)
ρ_{calcd} (g·cm^{-3})	1.950	1.718	1.965
μ (mm^{-1})	1.647	0.988	1.659
R_1 ($I > 2\sigma(I)$)^a	0.0324	0.0434	0.0460
wR$_2$ (all data)^b	0.0632	0.1198	0.0979
GOF	0.981	1.063	0.952

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

atoms by the use of the SHELX-97 program.[32,33] Hydrogen atoms were added geometrically and were refined by the use of the riding model. Crystallography data and refinement results are listed in Table 1.

Magnetic data of compounds were obtained on a Quantum Design MPMS-XL5 SQUID system. The experimental susceptibility data were corrected for diamagnetism (Pascal's parameters)[34] and background by an experimental measurement on a sample holder.

Caution! *Although not encountered in our experiment, azido salts and complexes of metal ions are potentially explosive. Only a small amount of materials should be prepared and handled with care.*

Synthesis. The endi ligands were prepared by the literature method.[35]

Preparation of Co(endi)(N_3)$_2$ (1). An aqueous solution (12 mL) of $Co(CH_3COO)_2$ (0.5 mmol) and NaN_3 (1.0 mmol) was mixed with a DMF solution (6 mL) of endi (0.5 mmol). After 30 min of stirring, the resulting carmine solution was filtered and kept undisturbed at room temperature. Dark-red prism crystals were obtained after 2 weeks in 70% yield. Anal. Calcd for C_4 $H_6N_{14}Co$: C, 15.54; N, 63.43; H, 1.95. Found: C, 15.45; N, 63.35; H, 2.00.

Preparation of Co(endi)$_2$(N_3)$_2$ (2). An aqueous solution (6 mL) of $Co(CH_3COO)_2$ (0.5 mmol) and NaN_3 (1.0 mmol) was mixed with a DMF solution (3 mL) of endi (1.0 mmol). After 30 min of stirring, the resulting pink solution was filtered and left at room temperature. Pink thin rectangular plate crystals were harvested the next day in 70% yield. Anal. Calcd for $C_8H_{12}N_{22}Co$: C, 20.24; N, 64.83; H, 2.54. Found: C, 20.33; N, 65.30; H, 2.37.

Preparation of Co(endi)(N_3)$_2$ (3). An aqueous solution (6 mL) of $Co(CH_3COO)_2$ (0.5 mmol) and NaN_3 (1.0 mmol) was mixed with a DMF solution (3 mL) of endi (0.5 mmol). After 10 min of stirring, the resulting rosy solution was filtered and left at room temperature. Pink prism crystals were obtained the next day in 40% yield. Anal. Calcd for $C_4H_6N_{14}Co$: C, 15.54; N, 63.43; H, 1.95. Found: C, 15.54; N, 63.03; H, 2.17.

Results and Discussion

The three compounds with different structure were obtained by reactions of endi with sodium azide and cobalt acetate under a different ratio or a different concentration of the starting materials. Using the preparation of compound **1** as reference, we obtained compound **2** by using a double amount of the endi ligand but half-volumes of the solvents. We obtained compound **3** in the same molar ratio as that of starting chemicals used for compound **1**, but the concentration of the starting materials was doubled. It is rational that the use of a doubled amount of the endi ligand led to one more endi ligand per formula in compound **2**. The ORTEP views of the three compounds are shown in the Supporting Information. Compounds **1** and **3** are polymorphs. Compound **1** has a 2D layerlike structure with the endi ligand in the trans conformation, whereas compound **3** is a 3D coordination framework with endi in the gauche conformation. (See the later discussion on structures.) It is well known that the trans conformation is more stable than the gauche conformation;[36−38] therefore, compound **3** should be the dynamic product with a higher solubility, whereas compound **1** should be the thermodynamic stable form with a lower solubility. This is also supported by the experimental observation that compound **3** appeared in a solution of high concentration in a short crystallization time whereas compound **1** appeared in a solution of low concentration in a long crystallization time. The coordination versatility of azide ions together with the flexibility of the endi ligand have made it possible to tune the dimensionality of compounds rationally through chemical reactions and to further master the magnetic properties.

Structures. Co(endi)(N_3)$_2$.(1). Compound **1** is in the triclinic space group $P\bar{1}$. The structure consists of 2D coordination layers (Figure 1). In the layer, the unique octahedral Co^{2+} ion at the inversion center is equatorially coordinated by four nitrogen atoms from four azide ions in EE mode, and the double-EE-azido bridges connect Co^{2+} ions into a $[Co(N_3)_2]_n$ chain running along the a direction. This kind of metal−azido chain has been observed in other metals, such as Cu and Fe.[37,39,40] The axial positions of the Co^{2+} ion are occupied by tetrazole nitrogen atoms of endi, and the endi ligands link the $[Co(N_3)_2]_n$ chains into a layer that is parallel to the (01$\bar{1}$) plane (Figure 1a). The geometries around the Co^{2+} ion are Co−N$_{azido}$ = 2.142−2.145 Å and Co−N$_{endi}$ = 2.135 Å, the cis N−Co−N angles are 88.10−91.13°, and the trans N−Co−N angles are ideally 180°. Within the $[Co(N_3)_2]_n$ chain, the Co···Co separation is 5.302 Å, the bridging Co−N−N angles are 124.21−137.14°, and the torsion angles of Co−N−N−Co are 35.68°. The endi

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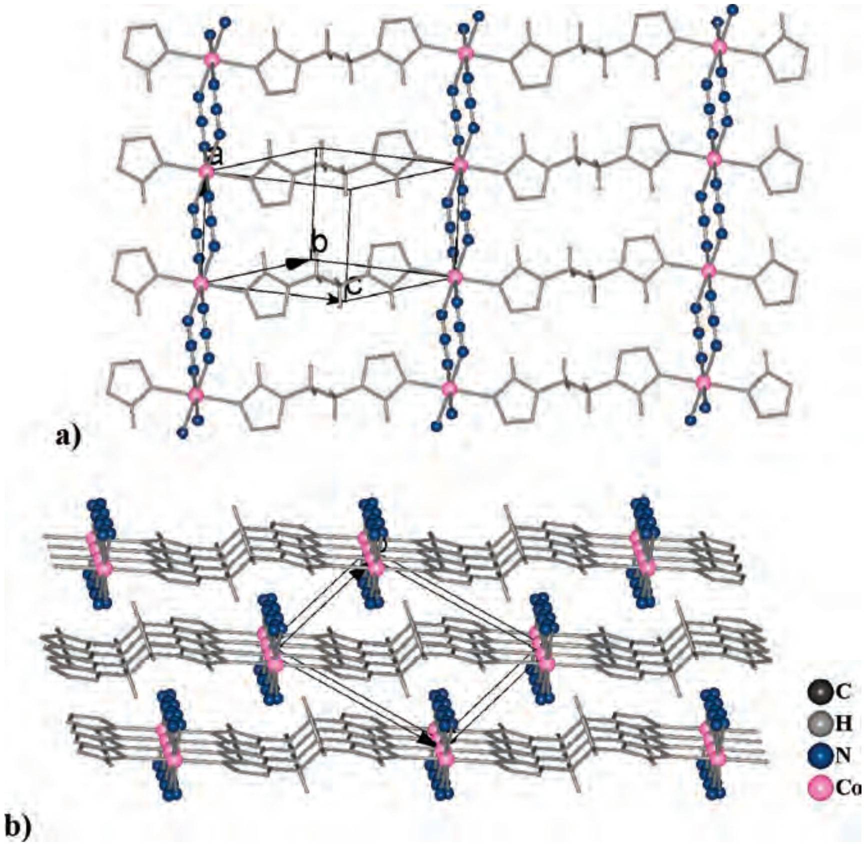

Figure 1. Crystal structure of compound **1**. (a) The 2D layer made of $[Co(N_3)_2]_n$ chains linked by trans endi ligands and (b) the 3D packing view down the *a* axis.

ligand is completely extended and is in the trans conformation. The adjacent endi ligands form many C−H···N hydrogen bonds with C···N distances of 3.23−3.63 Å and C−H···N angles of 152−155°. The layers are stacking along the [011] direction, and interlayer C−H···N hydrogen-bonding (C···N distances of 3.38−3.43 Å and C−H···N angles of 131−134°) between endi and azide further enforces the packing. The interlayer Co···Co separation, 6.12 Å, is only half of the interchain Co···Co distance of 12.03 Å within the layer.

$Co(endi)_2(N_3)_2$ (2). Compound **2** crystallized in the monoclinic space group $P2_1/c$. The structure of compound **2** is also a 2D layer (Figure 2), but the involution of an extra endi ligand per formula resulted in a different layer structure than that of compound **1**. The layer of compound **2** is a (4,4) Co−azide network along the *bc* plane, where the Co^{2+} nodes are connected by EE-azido linkages (Figure 2a). This kind of sheet was observed in many metal−azide compounds,[16,41−43] but examples for Co^{2+} continue to be limited, as mentioned above. The crystallographically independent Co^{2+} ion at the inversion center possesses octahedral geometry by six nitrogen atoms, four of which are equatorial from EE-azide ions within the Co−azide network, and two of which are apical from endi ligands above and below the Co−azide network (Figure 2a). The slightly distorted CoN_6 octahedron has Co−N distances of 2.105−2.160 Å, cis N−Co−N angles of 88.66−91.77°, and trans N−Co−N angles of 180°. The bridging Co−N−N angles are 120.16−146.11°, and the unique torsion angle of Co−N−N−Co is 124.11°. The intralayer Co···Co distance spanned by EE azide is 5.845 Å. It is noted that the adjacent CoN_6 octahedra within the layer are titled to each other with angles of 59° between the $N_{endi}−Co−N_{endi}$ axes and 61° between the $CoN_{4_{azido}}$ planes. It is easy to figure out that there is no central symmetry between adjacent Co^{2+} ions which results in spin-canting magnetism in this material (discussed later) because of the Dzyaloshinski−Moriya mechanism. Instead, the ditopic endi in a gauche conformation (N−C−C−N torsion angle of 61.2°) now acts as the terminal ligand and is arranged on both sides of the Co−azide sheet, resulting in a very thick layer of ca. 15 Å. Again, the C−H···N hydrogen bonds between neighboring endi ligands and between endi and azide ions are observed. Hydrogen bonding geometries include C···N distances of 3.37−3.55 Å and C−H···N angles of 139−163°. The thick layers are repeated along the *a* direction, and the shortest Co···Co distance between adjacent layers is 15.2 Å.

$Co(endi)_2(N_3)_2$ (3). Compound **3** is polymorphous with compound **1** and is in the triclinic space group $P\bar{1}$ with a unit cell that is slightly smaller than the double of the unit cell of compound **1** (Table 1). The structure is a 3D NaCl-type coordination network that is made of Co−EE−azido (4,4) sheets connected by ditopic endi ligands between the

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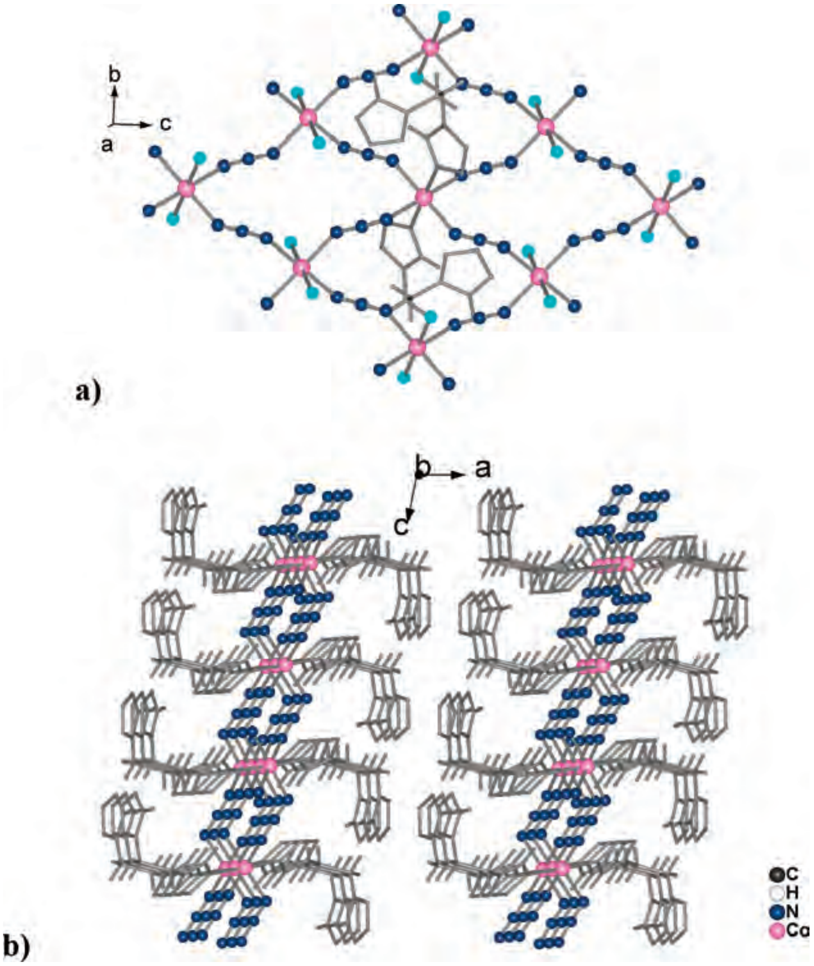

Figure 2. Structure of compound **2**. (a) The (4,4) layer. For clarity, only the two gauche endi ligands are shown with N atoms in light blue at the apical position of the central Co^{2+} ion; they are above and below the Co−EE−azido (4,4) layer. (b) The stacking of the layers viewed along the *b* direction. The color scheme is the same as that of Figure 1.

sheets (Figure 3). There are two unique Co^{2+} ions. One is at the inversion center of (000) (Co1) and the other is at (1/2, 0, 1/2) (Co(2)). Both ions are octahedral with four equatorial EE-azido ions and two axial endi ligands, and they have Co−N distances of 2.096−2.144 Å, cis N−Co−N angles of 86.73−92.28°, and trans N−Co−N angles of 180°. The bridging Co−N−N angles are 123.58−145.16°, and the unique torsion angles of Co−N−N−Co are 180−107.97 and 75.19°. The two unique intralayer Co···Co distances spanned by EE azido are 5.747 and 5.921 Å. These molecular geometries are similar to those observed in compound **2** and other compounds.[16,41−43] However, there is a significant difference in compound **3**: the titling of the adjacent CoN_6 octahedra, which is 75° between the N_{endi}−Co−N_{endi} axes, is 82° between the CoN_{4azido} planes. These angles are significantly larger compared with the angle in compound **2**. Again, the two unique endi ligands adopt a gauche conformation with N−C−C−N torsion angles of 61.2°, and they bridge Co−EE−azido (4,4) sheets along the *b* axis into the 3D framework of NaCl type. The C−H···N hydrogen bonds observed between neighboring endi possess C···N distances of 3.34−3.46 Å and C−H···N angles of 131−144°, which might stabilize the gauche conformation and the 3D framework. The shortest intersheet Co···Co distance is 8.68 Å.

Magnetic Properties. Compound 1. The detailed magnetic behavior of compound **1** is measured in an applied field of 1 kOe in the range of 2−300 K and is plotted in Figure 4. The magnetic susceptibility exhibits a broad maximum of χ_M around 100 K, and a small increase below 22 K occurs because of the trace paramagnetic impurity. The room-temperature value of $\chi_M T$ is 2.38 $cm^3 \cdot mol^{-1} \cdot K$, which is higher than the spin-only value of $S = {}^3/_2$. The curve of $\chi_M T$ gradually decreases upon cooling until 2 K, which is consistent with the predicted antiferromagnetic coupling. The magnetic data at the high temperature region obey the Curie−Weiss law ($\chi_M = C/(T - \theta)$), with $C = 4.1$ $cm^3 \cdot mol^{-1} \cdot K$ and $\theta = -212$ K. The Curie constant is much larger than the expected spin-only value, which indicates the orbital contribution of Co^{2+} ions, whereas the large negative value of θ indicates the strong antiferromagnetic coupling between Co^{2+} ions and the strong spin−orbital coupling through the ^4T_g state of the octahedral Co^{2+} center. The coupling constant *J* is obtained by fitting the data with Fisher's classic model for a chain of $S = 3/2$[44] (spin Hamiltonian $H = -JS_iS_j$)

$$\chi_M = 6Ng^2\beta^2/3kT[(1-u)/(1+u)] \tag{1}$$

where $u = kT/12J - \coth(kT/12J)$, J is the coupling constant, and N, g, β, and so on have the usual meanings. The best fit

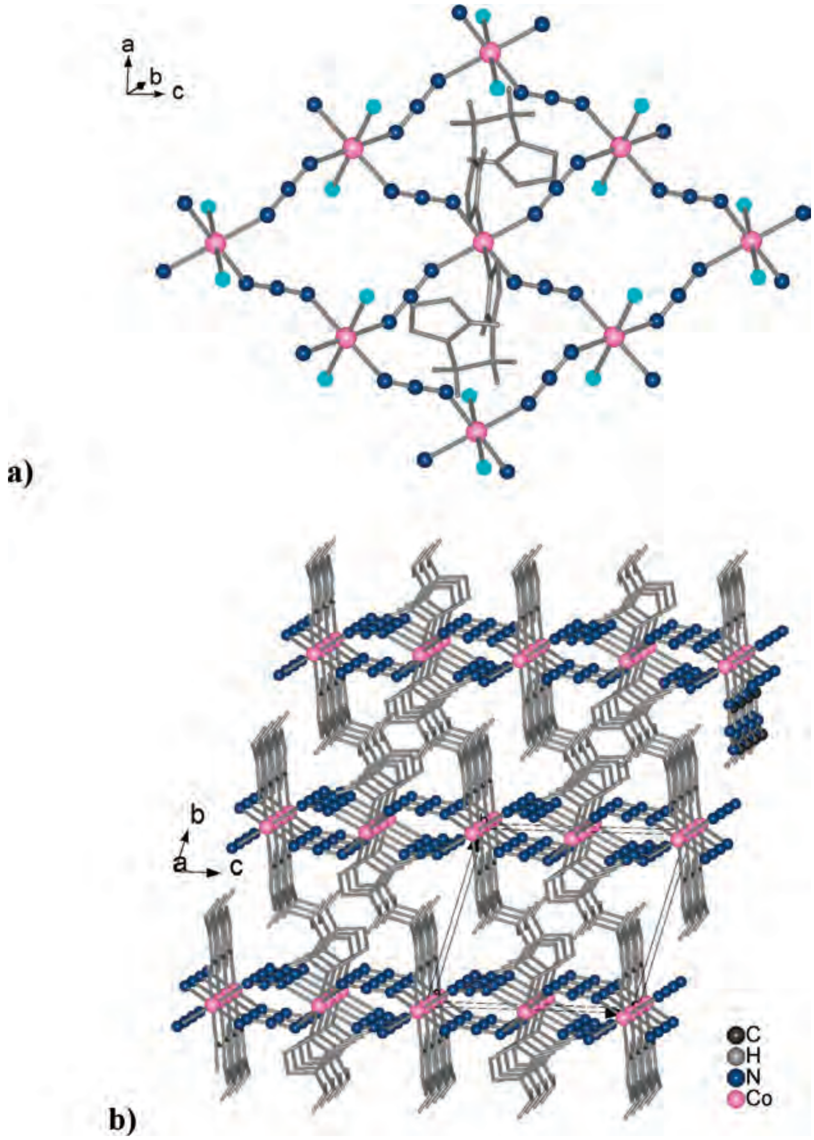

Figure 3. Crystal structure of compound **3**. (a) The coordinate environment of Co^{2+} ions and (b) the perspective view of the 3D network of compound **3**.

to the χ_M data above 80 K gives $g = 2.88$ and $J = -20.3$ cm^{-1}, with a reliability factor $R = 8.5 \times 10^{-5}$ ($R = [\Sigma((\chi_M T)_{calcd} - (\chi_M T)_{obsd})^2/\Sigma((\chi_M T)_{obsd})^2]$).

The field-dependent magnetization is measured at 2 K, as shown in Figure S4 in the Supporting Information. The magnetization increases linearly along the field. The magnetization at 50 kOe reaches only 0.064 Nβ, which is significantly lower than the expected saturated value of 3 Nβ per Co^{2+} unit with high spin.

According to the crystal structure, the magnetic properties should be attributed to the antiferromagnetic coupling transmitted by dual EE-azido bridges between Co^{2+} ions. The antiferromagnetic interactions spread along the 1D Co$-N_3$ chain. No long-range order is observed above 2 K.

Compound 2. As shown in Figure 5, the measurement of the thermal variation of the magnetic susceptibility has been carried out in the range of 2$-$300 K in an applied field of 1 kOe. The room-temperature value of $\chi_M T$ is 2.65 cm$^3\cdot$mol$^{-1}\cdot$K, and it gradually decreases to 1.47 cm$^3\cdot$mol$^{-1}\cdot$K at 32 K. Upon further cooling, $\chi_M T$ increases and reaches a maximum of 22.5 cm$^3\cdot$mol$^{-1}\cdot$K at 20 K and then decreases. The Curie$-$Weiss fit of the data above 50 K gives $C = 3.04$ cm$^3\cdot$mol$^{-1}\cdot$K and $\theta = -48.2$ K. The values of C and $\chi_M T$ at room temperature are larger than the spin-only value for Co^{2+} because of the orbital contribution. The large negative value of the Weiss constant reveals the

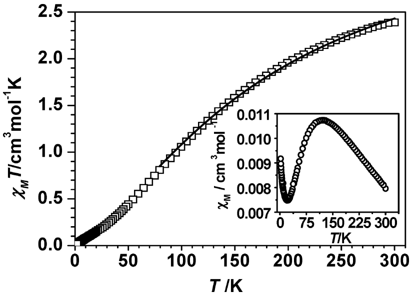

Figure 4. Plots of $\chi_M T$ vs T and χ_M vs T for compound **1** in an applied field of 1 kOe. Solid lines show the best fit.

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(44) Fisher, M. E. *Am. J. Phys.* **1964**, *32*, 343.

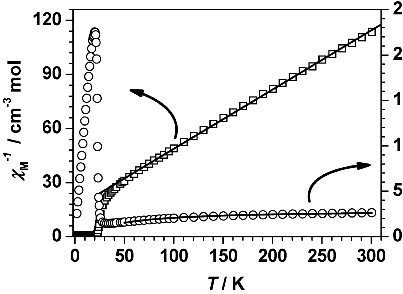

Figure 5. Plots of $\chi_M T$ vs T and χ_M^{-1} vs T for compound **2** in an applied field of 1 kOe. Solid lines show the best fit.

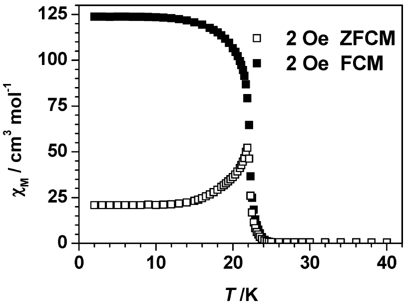

Figure 6. FC and ZFC magnetization vs T plots of compound **2** in an applied field of 2 Oe.

antiferromagnetic interactions between Co^{2+} ions and the spin−orbital coupling. The entire $\chi_M T$ curve at the low-temperature range looks like ferromagnetic behavior. With the absence of the ferromagnetic coupling, the behavior of the spontaneous magnetization of compound **2** should be attributed to the noncompensation of canted spins between neighboring paramagnetic centers. The structure of compound **2** could be simulated as a homogeneous system with only one J superexchange-coupling constant over all nearest-neighboring spins. The temperature-dependent susceptibility data in the range of 50−300 K are fitted with the high-temperature expansion series of Lines[45] for a $S = 3/2$ antiferromagnetic quadratic layer with $H = -\sum_{i,j} J S_i S_j$

$$\chi T = \frac{Ng^2\beta^2 T}{J}\left(3x + \sum_{n=1}^{6}\frac{C_n}{x^{n-1}}\right)^{-1} \qquad (2)$$

where $x = k_B T/(|J|S(S+1))$, $C_1 = 4$, $C_2 = 1.6$, $C_3 = 0.304$, $C_4 = 0.249$, $C_5 = 0.132$, and $C_6 = 0.013$. The symbols N, g, and β have the usual meanings. The best fit is given by $J = -5.13(5)$ cm^{-1}, $g = 2.49$, and $R = 2.12 \times 10^{-4}$ ($R = [\sum((\chi_M T)_{calcd} - (\chi_M T)_{obsd})^2/\sum((\chi_M T)_{obsd})^2]$). The result of the best fit reveals an antiferromagnetic superexchange between Co^{2+} ions transmitted by azide ions.

To investigate the intrinsic properties of compound **2**, zero-field-cooled and field-cooled magnetization (ZFCM/FCM) curves have been measured at 20 Oe and are plotted in Figure 6. The ZFCM curve increases as the temperature rises from 2 K, reaches the maximum at 21.9 K, and then decreases rapidly, which reveals the antiferromagnetic intrinsic state. As the sample cools, the FCM curve increases rapidly and diverges with the FCM curve around 22 K, which indicates the existence of spontaneous ferromagnetic ordering.

As plotted in Figure S5 in the Supporting Information, zero-field ac susceptibility is measured in an ac applied field of 3 Oe with frequencies of 10, 100, and 1000 Hz; there is no dc applied field. The in-phase χ_M' displays peaks at 22.1 K in all frequencies. The corresponding feature appears in the out-phase χ_M'' too, which is evidence of the ferromagnetic order of compound **2**. The critical temperature is much higher than those that have been reported for compounds with similar structure, as listed in Table 2.

To understand the nature of compound **2** further, the isorthermal magnetization and hysteresis loops below the critical temperature are measured at 2 K (Figure 7). The molar magnetization curve exhibits a quick increase for the spontaneous magnetization below 10 kOe and then a linear increase until 50 kOe with the effective moment of 0.49 Nβ, which is far from the expected saturate value per unit Co^{2+} ion with $S = {}^3/_2$ owing to the existence of a strong antiferromagnetic interaction. A distinct loop is observed with a remanence of 0.22 Nβ and a coercive field of approximately 3.2 kOe. We calculated the canting angle to be 4.2° by using $\sin^{-1}(M_R/M_S)$, with M_S representing the saturated magnetization and M_R representing the remanence. As observed from the above measurements, the spin canting feature may be attributed to single ion anisotropy and the spin canting.

Compound 3. For compound **3**, the temperature variation of the molar magnetic susceptibility χ_M per unit Co has been measured for a collection of single crystals in the region of 2−300 K, as plotted in Figure 8. The χ_M increases rapidly as the temperature decreases below 50 K and reaches a maximum at 9 K, which indicates a 3D order. The subsequent decrease in χ_M along with the continuous cooling appears at 3.5 K. The magnetic data of χ_M obeys the Curie−Weiss law at the high-temperature region. The best-fit results give $C = 3.62$ cm^3·mol^{-1}·K and $\theta = -48.5$ K. The large negative value of θ indicates the antiferromagnetic coupling between neighboring Co^{2+} ions, whereas the large C value can be attributed to spin−orbital coupling. The expansion series of Lines[45] gives a best fit to the high-temperature magnetic-susceptibility data of compound **3** with $S = 3/2$ by the use of eq 2, as mentioned above. The best fit is given by $J = -3.50$ cm^{-1}, $g = 2.6$, and $R = 8.6 \times 10^{-4}$ ($R = [\sum((\chi_M T)_{calcd} - (\chi_M T)_{obsd})^2/\sum((\chi_M T)_{obsd})^2]$).

Detailed ZFCM measurements and FCM at 2 Oe are exhibited in Figure 9. The ZFCM curve almost totally overlaps with the FCM curve. Both present an apex at 8.8 K, a decrease with continuous cooling, and a slight increase below 4 K.

The structural and magnetic properties of compounds **2** and **3** are comparable to those of known compounds with similar $[Co(N_3)_2]_n$ 2D layered structures, as summarized in Table 2. As in compound **2**, the referred compound $Co(N_3)_2$(acpy) has a 4,4 $[Co(N_3)_2]_n$ 2D structure, coligands that are coordinated in trans arrangement, and results-neutral infinite layers; it is stacked by the van der Waals force. The compound $Co(N_3)_2$(bpg) is constructed with a similar 4,4 $[Co(N_3)_2]_n$ 2D layer that is connected to 3D networks by the bridging ligand bpg, which is similar to compound **3**. It

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(45) Lines, M. E. *J. Phys. Chem. Solids* **1970**, *31*, 101.

Table 2. Summary of Structure Parameters and Magnetic Properties of Compounds with Similar Structures

		cryst syst	$Co-N_{4_{azido}}$ (Å)	$Co-N_{ligand}$ (Å)	intralayer Co−Co (Å)	interlayer Co−Co (Å)	bridging angle of azide Co−N−N (deg)	torsion angle of azide Co1−N−N−Co2 (deg)	torsion angle of N_L−Co1−Co2−N_L (deg)[a]	interplanar angle (deg)[b]	canting angle (deg)	magnetic behavior	J (cm^{-1})	T_N/K	ref
$Co(N_3)_2(bpg)$		monoclinic	2.113, 2.142	2.185	5.932	13.6	121.1, 149.9	130.9	50.0	55.5	5.2	weak F	−3.6	10.6	25
$Co(N_3)_2(acpy)$	R. Vicente	monoclinic	2.109, 2.131	2.159	5.792	11.59	146.6, 126.6	89.3		83.8		weak F		25	21
	X.−Y. Wang	monoclinic	2.125, 2.133	2.172	5.848	11.73	128.2, 149.1	84.9	62.3	83.2	15	weak F	−2.64	11.2	26
2·Co		monoclinic	2.161, 2.099	2.136	5.845	15.18	120.1, 146.1	124.1	58.9	61.1	4.2	weak F	−5.13	22.1	this work
3·Co		triclinic	2.140, 2.118, 2.136, 2.095	2.144, 2.125	5.746	8.68	123.6, 136.7, 140.1, 145.1	107.9, 75.2	75.0	81.7		AF	−3.5	7.8	this work

[a] The torsion angle of N(Ligand)−Co1−Co2−N(Ligand). [b] The angle formed by two $CoN_{4_{azido}}$ planes that are constructed with Co^{2+} ions and four surrounded N atoms from azide.

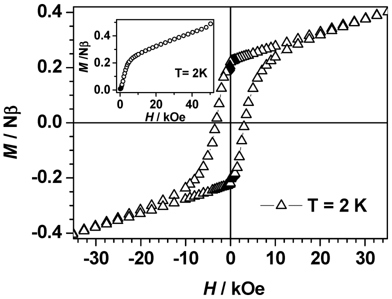

Figure 7. Plots of M vs H for compound **2** at 2 K. The insert shows the hysteresis loop measured at 2 K.

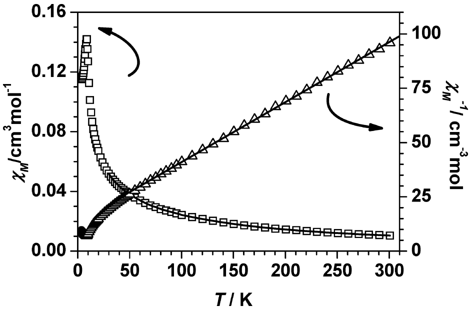

Figure 8. Plots of $\chi_M T$ vs T and χ_M^{-1} vs T for compound **3** in an applied field of 2 kOe. Solid lines show the best fit.

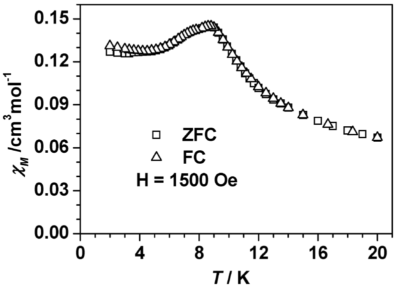

Figure 9. FC and ZFC magnetization of compound **3** versus T plots at 1500 Oe.

is easy to figure out that the symmetry and crystal coordination environment as well as the structure of the 2D azido-bridged layer and the intralayer distance of Co^{2+} ions of these four compounds are comparable. As a short bridge, azide ions link neighboring cobalt ions in EE mode and effectively transmit antiferromagnetic coupling. The values of the intralayer distances of Co^{2+} ions are close to each other. It has been conventional to consider the interplanar angles between neighboring CoN_4 planes to be the origin of spin canting, although no quantifiying relationships are discovered between structural parameters and magnetic behavior. The analogous structural features of these 2D layers result in the same mechanism of canted spins as those of Co^{2+} ions, which exist in $Co(N_3)_2(acpy)_2$, $Co(N_3)_2(bpg)$, and compound **2** but are absent in compound **3** with its unique triclinic crystal system. The canting angles of the three compounds are obtained by calculating the remanence from hysteresis loop. This results in canting-angle values of 5.2 and 15° for $Co(N_3)_2(bpg)$ and $Co(N_3)_2(acpy)_2$, respectivley.[26] In this work, the canting angle is 4.2° for compound **2**. Their spin-canting behaviors are supported by the Dzyaloshinski−Moriya mechanism.[18−21] The interlayer distances vary among the compounds as a result of the different length of coligands and the dimensionalities. The longest interlayer distance belongs to compound **2**. In addition to the difference between these bridging and torsion angles of azide, coordination is determined by the different *J* values. Without hydrogen bonds and $\pi-\pi$ interactions between neighboring layers, the obviously higher critical temperature of compound **2** could be induced by the larger *J* value between neighboring Co^{2+} ions and the existence of dipole−dipole interactions between the next-nearest neighboring Co^{2+} ions in adjacent layers.

Conclusions

Three azido-bridged Co^{2+} compounds are obtained through the tuning of experimental conditions. The suitable coligand endi with variable conformations is crucial to the aim-to-tune novel structures with dimensionality that obviously gain magnetic properties, which can also be concluded in the known compound.[25,46] The difference in magnetic properties among compounds **1**−**3** may be a result of the varied crystal systems. For compounds **1**−**3**, antiferromagnetic couplings are transmitted by an EE-azido bridge. Spin canting is observed in only compound **2**, which possesses a spontaneous magnetization below $T_C = 22$ K. The critical temperature value is not strictly proportional to dimensionality, even in the same system. In compound **2**, the larger *J* value of -5.13 cm^{-1} and the dipolar interactions between adjacent layers could be carefully considered.

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Supporting Information Available: X-ray crystallographic files and crystal structures for compounds **1**−**3**, plots of *M* versus *H* for compound **1**, and temperature dependence of the in-phase and out-of-phase components of the ac susceptibility of compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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