# Design and Synthesis of Stable Cobalt-Based Weak Ferromagnetic Framework with Large Spin Canting Angle

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S *Supporting Information*

ABSTRACT: It still remains a great challenge to design and construct framework-structured weak ferromagnets with large canting angle which is an effective approach for high performance magnets. According to the strategy of antisymmetric interaction causing spin canting, we report the design of four cobalt compounds, which were tested by X-ray single crystal diffraction, TGA, PXRD, and magnetic measurement. Single-crystal structure analysis reveals that compound **1** has a 2D structure, complex **2** has a 3,4-connected 3D framework, and complex **3** exhibits a 3D net structure with rare 3,5-connected 2-nodal β-SnF_2 topology and the solvent MeOH trapped in the 3D channels as guests. The magnetic property of **3** is spin canting just as designed, with T_N about 4.0 K and large canting angle of 14.8°. Highly stable compound **3** sustains its framework in air for more than 12 months, in which the guest MeOH molecules can be replaced by water to form complex **4**.
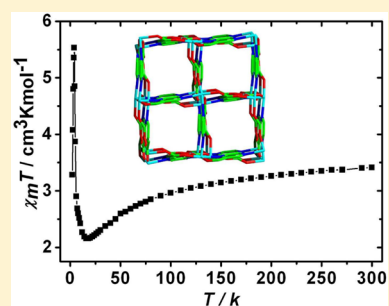
1. INTRODUCTION

In recent years, molecule-based magnetic materials, with great potential applications for high-density information storage, quantum computing, and magnetic refrigeration, are the focus for physical and chemical researchers.[1,2] In this field, framework-structured weak ferromagnets are a new research hot point, in which the framework structure is effective for long-range ordering of spins.[3] The desired spontaneous magnetization will be gained as long as the canting angle (γ) is large enough. Up to the present, the canting angle in the framework structure system usually is small; accordingly, the relevant weak ferromagnets caused by spin canting do not have large spontaneous magnetization.[4] Generally speaking, the phenomenon of spin canting is caused by two mechanisms, one by the existence of single-ion magnetic anisotropy and the other by antisymmetric interaction.[5] The antisymmetric interaction is not convenient to control, while single-ion magnetic anisotropy is easy to realize by using anisotropic metal ions such as Mn^{III}, Co^{II}, and so on.[6,7] From the structural point of view, the lack of inversion center is necessary for spin canting in local symmetry between the two coupling paramagnetic centers.[4c] Thus, if a ligand shows predicable asymmetric coordination modes, the phenomenon of spin canting may occur. Some bridging ligands, including dicyanamide, azido, and carboxylate, are potential candidates for constructing spin canting complexes.[8] It is worth mentioning that bridging ligands with asymmetric coordination models are a good choice to obtain spin canting. A representative example has been reported by Bu and his co-

workers with the use of 3,4-dicyano-1,2,5-thiadiazolea ligand.[9] Enormous magnetic 3D frameworks with weak ferromagnetism have been explored, but the canting angle larger than 5° is very rare,[4c,10] with only one sample reported with angles exceeding 10°.[4a] Construction of framework-structured weak ferromagnet with large canting angle still remains a great challenge.

Herein, on the basis of current research for a desired framework-structured weak ferromagnet, the Co^{II} ion with single-ion magnetic anisotropy[11] and pyrazine-2-carboxylate (Pzc) as bridging ligand were selected. By varying the coligand accommodated in the mother framework that is constructed by Co^{II} and Pzc, we report here a case of magnetic modulation. Our results suggest that the obtained cobalt complex $\{[Co(Pzc)(HCOO)]\cdot MeOH\}_n$ (**3**) with spin-canting behavior presents a rare β-SnF_2 net and exhibits weak ferromagnetism with T_N about 4.0 K and a big canting angle of 14.8°. Our further experiments suggest that complex **3** can transform to complex **4**, when the guest MeOH molecules are replaced by water molecules by means of single-crystal-to-single-crystal transformation.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. The chemical reagents used in these experiments are analytical grade and used without further purification. The X-ray powder diffraction (PXRD) of a sample was done by Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and

Table 1. Crystal Data and Structure Refinement Results for 1−4

	1	2	3	4
chemical formula	$C_6H_7ClCoN_2O_3$	$C_{20}H_{16}Cl_2Co_3N_8O_{10}$	$C_7H_8CoN_2O_5$	$C_6H_8CoN_2O_6$
fw	249.52	776.10	259.08	263.07
space group	$P2_1/n$	$P4/ncc$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	7.4930(15)	11.3528(16)	8.9978(18)	8.9199(18)
b (Å)	10.348(2)	11.3528(16)	9.4638(19)	9.4566(19)
c (Å)	11.220(2)	23.145(5)	10.433(2)	10.414(2)
α/deg	90.00	90.00	90.00	90.00
β/deg	94.62(3)	90.00	90.00	90.00
γ/deg	90.00	90.00	90.00	90.00
V/Å^3	867.1(3)	2983.1(11)	888.4(3)	878.4(3)
Z	4	4	4	4
D (g cm^{-3})	1.911	1.728	1.937	1.989
μ (mm^{-1})	2.260	1.892	1.935	1.966
F (000)	500.0	1548	524	532
R_{int}	0.029	0.099	0.090	0.120
GOF	1.135	1.343	1.253	1.396
T/K	293(2)	293(2)	293(2)	293(2)
R1[a]	0.0270	0.0841	0.0746	0.0885
wR2[b]	0.0635	0.1783	0.1902	0.2164

[a]$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

a graphite monochromator. Thermal stability studies were taken using a NETSCHZ STA 449C thermoanalyzer under N_2 (30−1000 °C range) at a heating rate of 10 K/min. The magnetic measurement was carried out on a Quantum Design MPMS-XL SQUID magnetometer by using crushed crystals of the sample. The magnetic field was 7 T. The diamagnetic susceptibility corrections were calculated from Pascal's constants; an experimental correction for the sample holder was applied.

2.2. Syntheses. *[Co(Pzc)Cl(MeOH)]ₙ (1).* A mixture of pyrazine-2-carboxylate acid (0.4 mmol), CoCl₂·6H₂O (2 mmol), and methanol (15 mL) was sealed in a Teflon-lined bomb, heated to 140 °C for 3 days, and then cooled to room temperature. Block-shaped purple crystals of **1** were collected and washed sequentially by methanol.

{[Co₃(Pzc)₄Cl₂]·2H₂O}ₙ (2). A mixture of pyrazine-2-carboxylate acid (0.8 mmol), CoCl₂·6H₂O (2 mmol), and methanol (15 mL) was sealed in a Teflon-lined bomb and heated under autogenous pressure to 140 °C. After maintaining for 3 days, and then cooled to room temperature, the complex **2** was collected and washed by methanol.

{[Co(Pzc)(HCOO)]·MeOH}ₙ (3). A mixture of pyrazine-2-carboxylate acid (0.5 mmol), Co(HCO₂)₂·4H₂O (1.5 mmol), and methanol (15 mL) was sealed in a Teflon-lined bomb and heated under autogenous pressure to 140 °C for 3 days. It was then cooled to room temperature, and the complex **3** was collected, washed with methanol, and dried.

{[Co(Pzc)(HCOO)]·2H₂O}ₙ (4). With the complex **3** in air for a few months, the methanol molecules in the framework were replaced by water molecules, and the complex {[Co(Pzc)(HCOO)]·MeOH}ₙ (**3**) undergoes a single-crystal-to-single-crystal structural transition to the complex {[Co(Pzc)(HCOO)]·2H₂O}ₙ (**4**).

2.3. Single-Crystal X-ray Diffraction. Diffraction data collection for complexes **1−4** were performed at 293(2) K on a Rigaku SCX-mini diffractometer with Mo Kα radiation ($\lambda = 0.710\ 73$ Å) by ω scan mode. Rigaku CrystalClear[12] program was applied to integrate the diffraction profiles. The structures were solved by the direct method and refined by full-matrix least-squares methods on F^2, with all non-hydrogen atoms refined with anisotropic thermal parameters (semi-empirical absorption corrections were applied using SADABS program).[13] All of the metal atoms were located from the E-maps. The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. All calculations were solved by using the SHELXTL crystallographic software. Crystallographic crystal data and refinement parameters are summarized in Table 1. Selected bond lengths are listed in Table S1 of the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Synthesis, Structure, and Description of Complexes 1−3. During the experiments, three complexes were obtained step by step. The complex [Co(Pzc)Cl(MeOH)]ₙ (**1**) containing one coordinated methanol molecule was synthesized by mixing pyrazine-2-carboxylate acid and CoCl₂·6H₂O in methanol solvent (complex **1** is unstable). With an adjustment to the molar ratio of the reactants, 3D formwork {[Co₃(Pzc)₄Cl₂]·2H₂O}ₙ (**2**) supported by guest water molecules was produced (complex **2** is unstable in humid air). The ratio of the reactants is very important for getting different crystals of **1** and **2**, despite those being synthesized under similar conditions. Also, pure phase complex **2** (checked by PXRD, Supporting Information Figure S1) could be obtained with ligand−metal ratio of 2:5. The complex {[Co(Pzc)(HCOO)]·MeOH}ₙ (**3**) was gained by mixing the pyrazine-2-carboxylate acid and Co(HCO₂)₂·4H₂O in the methanol solvent (complex **3** is stable). In this work, we aimed to get the magnetic materials; however, we found complex **1** was unstable and out of the testing requirement of other measurement. We speculate that the instability of complex **1** is caused by the methanol molecule participating in the coordination, and the instability of **2** is due to the coordination of the chloride anions which are easy to decoordinate in humid condition. Aimed at solving these problems, we change the reactants and introduced the bridging molecules (formate anions) which can make the molecule framework stable. Finally, the stable complex **3** was gained, and structural analysis shows that formate anions participate in the coordination and bridge the metal ions forming a 3D net with rare 3,5-connected 2-nodal β-SnF₂ topology.[14] Thermal stability studies indicate complex **3** has high thermal stability and decomposes above 300 °C (Supporting Information Figure S2a). Its phase purity was confirmed by PXRD (Supporting Information Figure S2b), and the magnetic measurement reveals that complex **3** exhibits weak ferromagnetic with T_N about 4.0 K and big canting angle of 14.8°.

[Co(Pzc)Cl(MeOH)]ₙ (1). Complex **1** crystallizes in monoclinic space group $P2_1/n$ with an asymmetric unit consisting of one crystallographically independent Co^{II} center, one deproto-
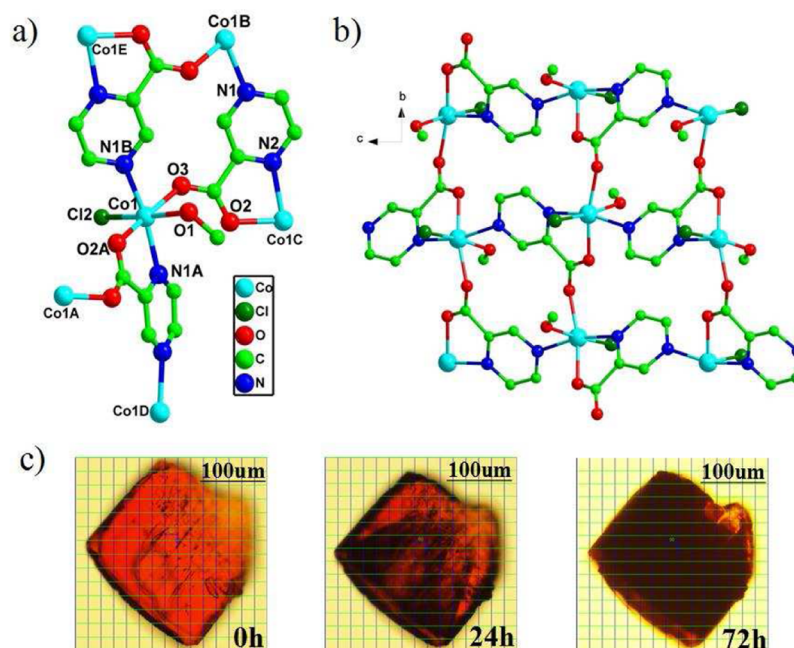
Figure 1. (a) Coordination modes of Co^{II} ions and linkage of the Pzc anions in **1**. Symmetry mode: A, $1.5 - x, -0.5 + y, 1.5 - z$; B, $2 - x, 1 - y, 1 - z$; C, $1.5 - x, 0.5 + y, 1.5 - z$; D, $-0.5 + x, 0.5 - y, 0.5 + z$; E, $0.5 + x, 0.5 - y, -0.5 + z$. (b) The two-dimensional layer structure of complex **1**. (c) Complex **1** collapses quickly when putting the crystals in the air at room temperature; it will lose crystallinity completely in about 72 h.
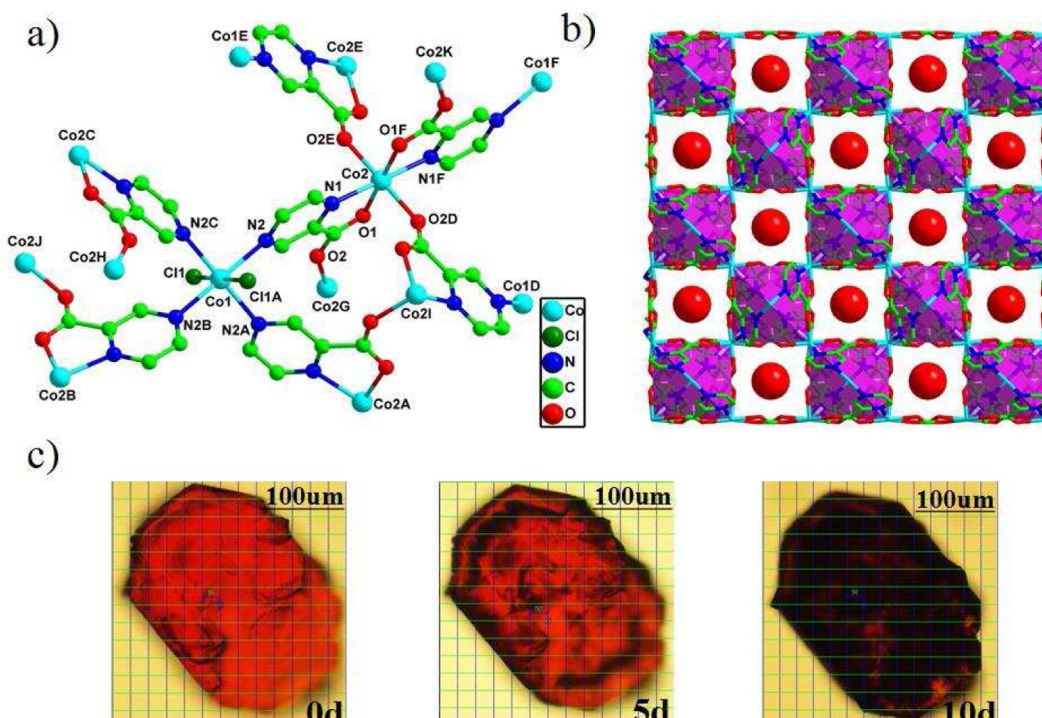

Figure 2. (a) Coordination modes of Co^{II} ions and linkage of the Pzc in **2**. Symmetry mode: A, $0.5 - x, 1.5 - y, z$; B, $-0.5 + y, 0.5 + x, 0.5 - z$; C, $1 - y, 1 - x, 0.5 - z$; D, $-0.5 + y, 1 - x, -z$; E, $0.5 - y, 1 + x, z$; F, $-x, 2 - y, -z$; G, $-1 + y, 0.5 - x, z$; H, $0.5 + x, 2 - y, 0.5 - z$; I, $1.5 - y, 1 + x, z$; J, $-x, -0.5 + y, 0.5 - z$; K, $-1 + y, 1.5 - x, z$. (b) The 3D structure of **2** with water molecules filled in the channels of the cages. (c) The picture of complex **2** in the air at room temperature at different time.

nated ligand Pzc anion, one chlorine anion, and one coordinated methanol molecule. The Co^{II} ion is coordinated by one inorganic chloride atom, one methanol oxygen atom, two oxygen atoms, and two nitrogen atoms from three Pzc anions forming a distorted octahedral geometry with normal bond lengths (Supporting Information Table S1). Each Pzc anion adopts a μ_3 coordination mode to bridge three Co^{II} ions, while the chlorine atom and the methanol molecule both take the axis positions to coordinate to the Co^{II} ion [bond lengths: Co1–Cl2 = 2.3759 (10) Å, Co1–O1 = 2.1627 (18) Å] (Figure 1a). In this way, every Co^{II} is connecting to three Pzc anions,
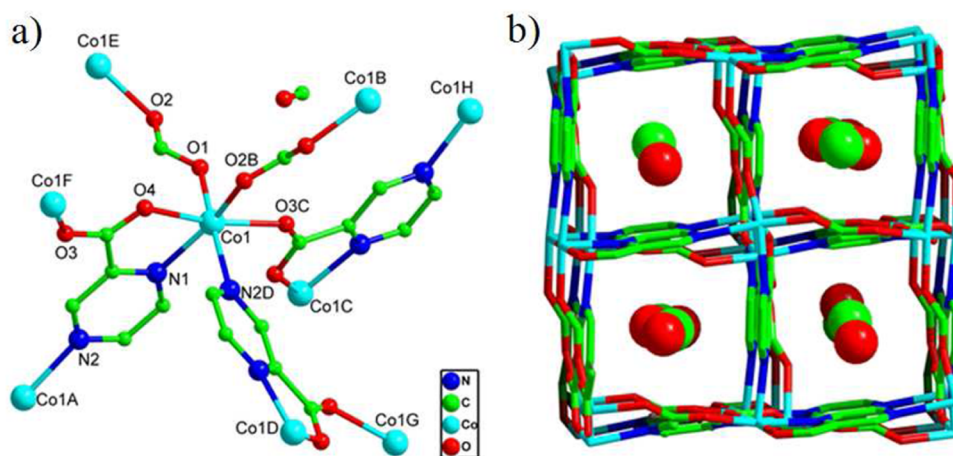
Figure 3. (a) Coordination modes of Co^{II} ions and linkage of the Pzc in **3**. Symmetry mode: A, $-x$, $-0.5 + y$, $0.5 - z$; B, $1 - x$, $0.5 + y$, $0.5 - z$; C, $0.5 - x$, $2 - y$, $0.5 + z$; D, $-x$, $0.5 + y$, $0.5 - z$; E, $1 - x$, $-0.5 + y$, z; F, $0.5 - x$, $2 - y$, $-0.5 + z$; G, $-0.5 + x$, $2.5 - y$, $1 - z$; H, $0.5 + x$, $2.5 - y$, $1 - z$. (b) Along c direction, the methanol molecule filled channels.

and every Pzc anion is linking three metal ions, to form a 2D layer structure (Figure 1b).

{[Co$_3$(Pzc)$_4$Cl$_2$]·2H$_2$O}$_n$ **(2)**. Complex **2** crystallizes in the tetragonal space group $P4/ncc$, and the asymmetric unit of **2** contains one and a half crystallographic Co^{II} ions, two Pzc anions, one chlorine anion, and two solvated water molecules. Co1 is coordinated by two chloride anions and four nitrogen atoms from four Pzc anions. Co2 is coordinated by four Pzc anions, in which two Pzc anions take chelating mode. The Pzc anion adopts a μ_3 coordination mode to bridge Co1, Co2, and Co2G ions. The Pzc anion chelates to Co2 ion via 1-position N1 atom and a carboxylate O1 atom, and coordinates to Co1 and Co2G in a monodentate fashion via the 4-position N2 atom and the other carboxylate O2 atom of the *syn−anti* carboxylate, respectively (Figure 2a). It is worth noticing that an elongated octahedral cage was formed by four Co2 ions, two Co1 ions, and four Pzc anions (Supporting Information Figure S3a), and linked by Co1 ions generating a 1D chain (Supporting Information Figure S3b). The 1D chains share Co2 ions forming a 3D net structure with water molecules filled in the channels of the cages (Figure 2b). Also, the whole framework could be viewed as 3,4-connected topology net (Supporting Information Figure S3c).

{[Co(Pzc)(HCOO)]·MeOH}$_n$ **(3)**. Complex **3** has a 3D structure with the space group of $P2_12_12_1$. In the crystallographic asymmetric unit, there exists one crystallographically independent Co^{II} ion, one Pzc anion, one formate anion, and one solvated methanol molecule (Figure 3a). Each Co^{II} lies in a general position with a distorted octahedral geometry constructed by two nitrogen atoms, two oxygen atoms of three Pzc anions, and two oxygen atoms of two formate anions. The Pzc taking μ_3 mode coordinates to two Co^{II} ions in monodentate model by one carboxylate oxygen and 4-position nitrogen, and to the third Co^{II} ion in a chelating fashion via the other carboxylate oxygen and 1-position nitrogen (Figure 3b). The Pzc cobalt network exhibits a (10, 3)-a[14] net (Supporting Information Figure S4a), which is different from the (10,3)-d net in {[Ni(Pzc)Cl(H$_2$O)]·MeOH}$_n$.[15] In b direction, the formate anions take *anti−anti* bridging mode linking two Co^{II} ions, which strengthens the net (Supporting Information Figures S4b and S5). From the point of view of topology, in the 3D structure, the Pzc linked three Co^{II} ions could be viewed

as 3-connected nodes, while the Co^{II} ion was defined as 5-connected nodes due to Co^{II} ions bridged by the formate anions which are not linked by the Pzc directly. Thus, the whole network exhibits a rare 3, 5-connected 2-nodal β-SnF$_2$ topology with Schläfli symbol $\{5^2 \cdot 6\}\{5^3 \cdot 6^3 \cdot 7^3 \cdot 8\}$ (Supporting Information Figure S4b).[14]

Herein, we need to further summarize the process of obtaining stable framework. As is shown in Figure 4, the design
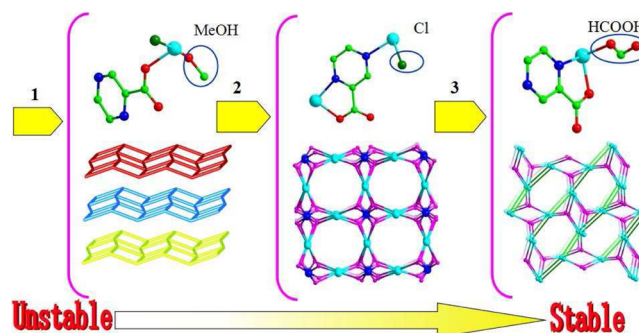

Figure 4. Stability of framework structures is different when different solvent molecules participate in the coordination. In complex **1**, methanol molecules participate in the coordination, and the 2D framework structure is unstable. In complex **2**, chlorine anion participates in the coordination instead of methanol molecules, and the 3D framework structure is still unstable. In complex **3** the formate anions participate in the coordination, and the 3D framework structure of **3** is stable.

and synthesis of the stable framework is realized step-by-step. In **1**, as terminal groups, the methanol molecules coordinate to Co^{II} centers; thus, further extension of the 2D network is impossible. When exposed to the air, complex **1** collapses quickly at room temperature, and loses its crystalline state in about 72 h (Figure 1c). Such instability may be caused by the terminal coordination groups of methanol molecules. In the further exploration of the stable structures, compound **2** was obtained. In **2**, by adjusting the molar ratio of initial reactants, the terminal methanol molecules in **1** are driven off from the structure, and the Cl atoms are introduced to coordinate to Co^{II} centers. Subsequently, compound **2** extends itself into 3D 3,4-connected framework supported by guest water molecules.

It is found that compound **2** exhibits higher stability as compared with **1**. It loses its crystalline state gradually in 10 days. As is shown in Figure 2c, the stability of this structure has been improved greatly. With further exploration, with the hope of introducing bridging ligands to further strengthen the whole structure, $Co(HCO_2)_2 \cdot 4H_2O$ was used instead of $CoCl_2 \cdot 6H_2O$. As expected, the formate anions in **3** participate in the construction of the whole 3D framework. Stable an experiment shows that complex **3** is stable and could remain crystalline for more than 12 months. From the structural design and stability of complexes **1−3**, we can see that the auxiliary ligand-directed strategy is an effective method for gaining stable magnetic frameworks. Moreover, due to the host−guest structural characteristics of the frameworks, it is possible to design and construct other multifunctional magnetic materials by changing the guest molecules.

3.2. Magnetic Properties. Variable-temperature susceptibilities on pure powder samples of **2** were collected under an external field of 1 kOe. χ_m versus T and $\chi_m T$ versus T plots were shown in Supporting Information Figure S6 and Figure 5.
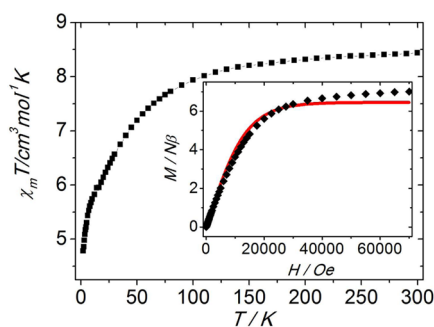

Figure 5. $\chi_m T$ vs T plots of **2**. Inset: field dependent magnetization at 2.0 K of **2**, and the red line is the curve of the Brillouin function.

The $\chi_m T$ product at 300 K is 8.44 cm^3 K mol^{-1} and is a typical value of the three high spin Co^{II} ions with strong spin−orbit coupling in octahedral geometry.[16] Also, the $\chi_m T$ curve decreases smoothly with cooling and gives a value of 4.78 cm^3 K mol^{-1} at 2 K. The susceptibilities above 30 K following the Curie−Weiss law (Supporting Information Figure S7) defined the constant of $\Theta = -10.31$ K. The field-dependent magnetizations follow the Brillouin function ($S = ^1/_2$, $g = 4.3$) and reach saturation at 7 T. In the structure, the *syn−anti* carboxylate bridged Co2 ions give a 4,4 net, and then the Co2 ions of the 4,4 nets were linked with the Co1 ions by pyrazine ring to construct a 3D framework of complex **2**. It is worth noticing that a Weiss constant −10.31 K of **2** is larger than the value −20 K of one isolated high-spin Co^{II} ion with the contribution of spin−orbit coupling,[11,17] so the ferromagnetic coupling contributions should be expected in **2**. A ferrimagnetic state would be present if the magnetic interactions conducted by the carboxylate groups are ferromagnetic and those by the pyrazine ring are antiferromagnetic. That is inconsistent with the tendency of $\chi_m T$ and field dependent magnetization at 2 K. Thus, the magnetic interactions should be antiferromagnetically conducted by *syn,syn* carboxylate,[18] and ferromagnetic by pyrazine ring.[19]

Variable-temperature susceptibilities of complex **3** were investigated on powder samples in temperature range of 2−300 K under an applied field of 2 kOe. As shown in Supporting Information Figure S8 and Figure 6, the χ_m versus T plots have
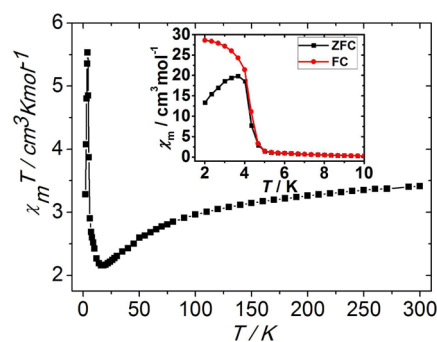

Figure 6. $\chi_m T$ vs T plots of **3**. Inset: the ZFC and FC magnetization measurements at 2−10 K with applied field 20 Oe.

a increase below 20 K, and the $\chi_m T$ plots have a value of 3.40 cm^3 K mol^{-1} at 300 K, which is a typical value of one Co^{II} ion located in an octahedral environment.[16] Above 40 K the susceptibility data could be fitted by the Curie−Weiss law and give a Weiss constant $\Theta = -21.20$ K (Supporting Information Figure S9). The initial decrease of $\chi_m T$ product on cooling and the negative value of Weiss constant should be due to the antiferromagnetic interactions and single ion effect of the octahedral Co^{II} ions.[11,17,20,21] Each Co^{II} ion in **3** was connected to eight neighbors through two *anti−anti* formate anions and three Pzc ligands. Antiferromagnetic interactions should be conducted by the *syn−syn* carboxylate and formate anions in *anti−anti* fashion. Weak ferro- or antiferromagnetic magnetic interactions were transferred through the pyrazine rings for long exchange distances. The trend of the $\chi_m T$ plots with a minimum is typical behavior of weak ferromagnets.[22] The presence of spontaneous magnetization is suggested by the sharp peak at 4 K. Also, the long-range order was further confirmed by the zero-field cooled (ZFC) and field cooled (FC) magnetization collected at 20 Oe (Figure 6 inset). The ZFC and FC magnetization curves diverge below 4.0 K, confirmed the presence of spontaneous magnetization. In order to further comprehend the characteristic at low temperature, ac susceptibilities were measured in different ac frequencies (10−1000 Hz) with oscillating field of 3.5 Oe. Both the in- and out-of-phase signals are strong (Supporting Information Figure S10). The in-phase signals χ_m' show peaks at 4.2 K, and the peaks of χ_m'' are unsymmetrical and have little frequency dependence. That may be attributed to the moving of the domain walls[23] and/or the orbital liquid behavior,[24] which has also been found in recently reported canting systems.[10d,25]

The canted antiferromagnetic order was also confirmed by the magnetization $M(H)$ at low temperature 2 K (inset of Figure 7). At very low field, the magnetization increases quickly to 0.6 $N\beta$, and then increases linearly to 1.44 $N\beta$ at 50 kOe. The value of 1.44 $N\beta$ is much less than the value of 2.15 $N\beta$ for a Co^{II} ion at 2 K ($S = ^1/_2$, $g = 4.3$), which confirms the antiferromagnetic interaction between the metal ions in **3**. The intercept of the linear part of the magnetization curve in high field gives a value of 0.57 $N\beta$. That value could be taken as the compensating magnetization (M_r) arising from the canted antiferromagnetic spins. Thus, a canting angle of 14.8° can be estimated roughly, on the basis of the equation $\theta = \tan^{-1}(M_r/M_s)$.[26]

As is discussed above, complex **3** is a 3D host−guest stable framework. To achieve the functional design of magnetic materials, the framework requires tunable host−guest characteristics. In our following experiments, we further confirmed that
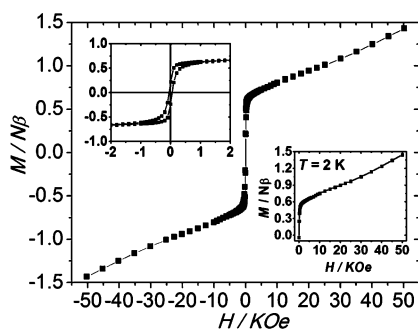
Figure 7. Hysteresis loop of **3** at 2 K. Inset left: Detailed hysteresis loop of **3** at low field range. Inset right: Field dependent magnetization of **3** at 2.0 K.

the solvent methanol molecules in complex **3** could be replaced by water molecules, and then complex **4** was gained. The coordination condition of Co^{II} ions and linkage modes of the Pzc in **4** are shown in Figure 8. The 3D framework structure of **4** is similar to that of **3** but with free water molecules filled in the channels. It is worth pointing out that such crystal-to-crystal transformation opens the way to synthesize a large family of multifunctional magnetic materials. Here we should further
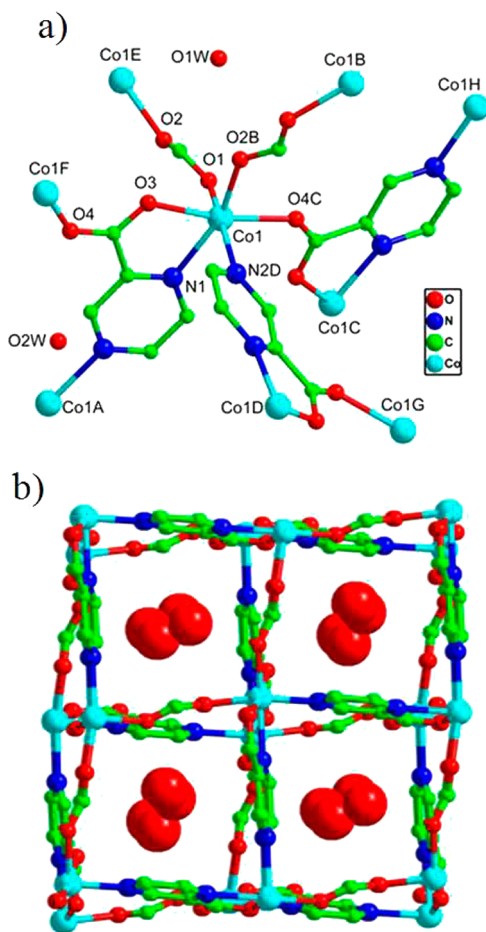
point out that according to the diverse extendable ligands (such as pyridine-carboxylate, 4-carboxyphenoxyacetic acid, pyrimidine-carboxylate, imidazole-carboxylate, etc.)[9,11] and anisotropic metal ions (Co^{II}, Fe^{II}, Ni^{II}, etc.),[4c,6,7] it could be expected that such a spin canting strategy would expand the functional design of magnetic materials, and relevant work has been undertaken.

4. CONCLUSIONS

A formate anion auxiliary-coordination strategy for designing and fabricating stable magnetic framework has been developed by using pyrazine-2-carboxylate and Co^{II} ions. Complex **3** has a 3D net structure with rare 3,5-connected 2-nodal β-SnF$_2$ topology, and the solvent MeOH molecules are filled in the 3D channel as guests. The magnetic properties of **3** include spin canting just as designed with T_N about 4.0 K and a large canting angle of 14.8°. Moreover, the guest MeOH molecules in **3** can be replaced by water molecules to form new crystal materials **4**. This work may further provide reference in the field of designing magnetic materials and guidance in related fields.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Selected bond lengths, TGA, PXRD, additional structural figures, Curie−Weiss plot, χ_m vs T plot, and ac magnetic susceptibility plots. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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Figure 8. (a) Coordination modes of Co^{II} ions and linkage of the Pzc in **4**. Symmetry mode: A, −x, −0.5 + y, 0.5 − z; B, 1 − x, −0.5 + y, 0.5 − z; C, 0.5 − x, −y, −0.5 + z; D, −x, −0.5 + y, 0.5 − z; E, 1 − x, 0.5 + y, 0.5 − z; F, 0.5 − x, −y, 0.5 + z; G, −0.5 + x, −0.5 − y, −z; H, 0.5 + x, −0.5 − y, −z. (b) The 3D framework of complex **4** with the water molecules dotted in the tunnel.

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