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A Three-Dimensional Complex with a One-Dimensional Cobalt-Hydroxyl Chain Based on Planar Nonanuclear Clusters Showing Spin-Canted Antiferromagnetism

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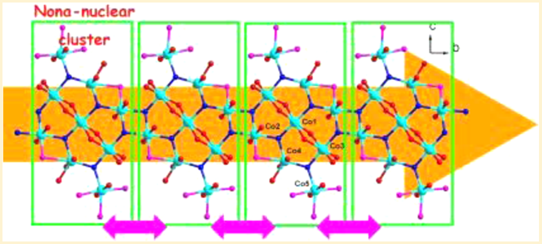
Supporting Information

ABSTRACT: A new three-dimensional magnetic network, $[Co_9(OH)_6(C_{42}H_{24}O_{18}P_3N_3)_2(H_2O)_8]$ (**1**), has been successfully prepared by utilizing the flexible hexacarboxylate ligand derived from cyclotriphosphazene, which had been characterized by single-crystal X-ray diffraction and magnetic measurement. This compound consists of one-dimensional (1D) cobalt-hydroxyl chains based on planar nonanuclear clusters, which are located in the *b*−*c* plane to form the nearly two-dimensional cobalt layer. Magnetic measurements reveal that **1** shows spin-canted antiferromagnetism with spin-glass behavior. These results suggest that reasonable design and choice of large carboxylate ligand based on a specific scaffold could be effective for the construction of magnetic materials based on a novel 1D magnetic chain.



INTRODUCTION

Magnetic coordination polymers (MCPs) or frameworks have attracted a great deal of attention in recent years because of their intriguing magnetic behaviors and their fascinating topological structure.[1] MCPs with visualized crystal structure are very beneficial for understanding magnetostructural relationships and could provide a powerful platform for further development of magnetic materials based on academic and industrial interests.[2] Despite the considerable success that has been achieved in this field, one of the main challenges in this field is the design of molecule-based metal complexes exhibiting spontaneous magnetization.[3] Magnetic CPs, especially those displaying long-range ordering, are viewed as one of the significant candidates of multifunctional molecular materials. To achieve long-range ordered magnetic materials, one of the first requirement is the consideration of distance between the nearest-neighbor moment carriers.[4] Commonly, utilizing the paramagnetic transition metal ions with a large spin state and appropriate bridging ligands via the self-assembly approach is seen as a general strategy for constructing MCP exhibiting interesting magnetic behavior.[5] The bridging ligands, such as carboxylate, cyano, oxalate/oxamate, and azide, always play a critical role, because of their ability to transmit efficient magnetic coupling,[6] but in recent years, there has been growing interest in hydroxyl-based systems, especially in cobalt-hydroxyl systems because the paramagnetic center Co^{2+} ion usually has large single-ion magnetic anisotropy and could lead to interesting magnetic character.[7] The μ_3-hydroxide often ligates three cobalt atoms to form triangular subunits that exhibit favorable M−O−M magnetic exchanges because of the presence of short M−M distances and favorable angles for strong magnetic exchange interactions.[8] Furthermore, thus, triangular subunits could share the vertexes or edges to form the oligo-nuclear clusters, infinite one-dimensional (1D) chains, two-dimensional (2D) layers, or three-dimensional (3D) framework with fantastic magnetic properties, in which the 1D cobalt-hydroxyl chain is of interest from structural and magnetic points of view.[7−9] However, the reported 1D chains usually present the repeated the triangular subunits that consisted of cobalt ions and μ_3-hydroxyl groups. Therefore, one of the most attractive targets is exploring the novel 1D cobalt-hydroxyl chain with interesting magnetic properties, which represents a great challenge theoretically and experimentally.

On the other hand, the 1D cobalt-hydroxyl chain, also seen as rod-shaped secondary building units (SBUs), could be further extended into 3D frameworks by employing ligating ligands, which is very essential for the construction of bulk functional materials.[9,10] In this aspect, carboxylates have been widely used as bridging ligands to construct molecular magnetic materials, because of their wide range of coordination modes

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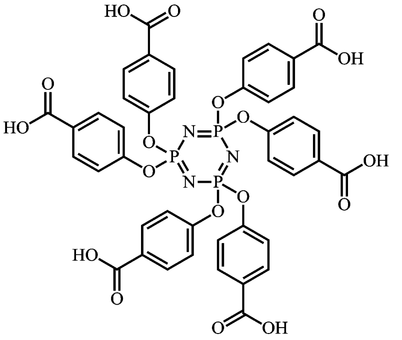
that provide superexchange pathways for magnetic coupling among paramagnetic metal centers.[3a,11] Recently, our group has utilized the flexible hexacarboxylate ligands, hexakis(4-carboxylato-phenoxy)cyclotriphosphazene (H_6L1) (Scheme 1), derived from famous inorganic scaffold cyclotriphosphazene, to construct luminescent CPs with nonparamagnetic metal ions.[12] Thus, the flexible ligand truly exhibits multiple connection modes and variable conformations because of the six twisted carboxylate arms around the central heterocyclic ring. However, MCPs constructed by the hexacarboxylate ligand are rarely reported. With the considerations mentioned above in mind, we intend to explore novel MCPs based on the unprecedented 1D cobalt-hydroxyl chain by utilizing the flexible hexacarboxylate ligand because of its advantages in assembling a framework. Herein, we reported a novel three-dimensional MCP, $[Co_9(OH)_6(C_{42}H_{24}O_{18}P_3N_3)_2(H_2O)_8]$ (**1**), showing a 1D chain based on planar nonanuclear cobalt clusters. Interestingly, these 1D chains are arrayed in the b−c plane to form the nearly 2D layer, which exhibits spin canting antiferromagnetic coupling with spin-glass behavior.

Scheme 1. Hexacarboxylate Ligand H_6L1



RESULTS AND DISCUSSION

Synthesis of 1. Red crystalline samples of **1** were obtained from the hydrothermal reaction in basic water solvent containing the $Co(NO_3)_2·6H_2O$ (30 mg) and H_6L1 (16 mg) at 140 °C for ~5 days. X-ray diffraction for a crystalline sample of **1** was finally conducted at 293 K after repeated attempts, showing the 1D cobalt-hydroxyl chain based on the novel nonanuclear cobalt clusters. Crystal data and selected bond lengths of **1** are listed in Tables S1 and S2 of the Supporting Information. In the infrared (IR) spectra of compounds **1**, the broad peaks near ~3400 cm^{-1} indicate the presence of water molecules. The IR spectra also show characteristic absorption bands mainly attributed to the asymmetric (ν_{as}, ~1600 cm^{-1}) and symmetric (ν_s, ~1385 cm^{-1}) stretching vibrations of the carboxylate groups. No band in the region of 1690−1730 cm^{-1} indicates complete deprotonation of the carboxylate groups[13] and is consistent with the result of the X-ray diffraction analysis.

Crystal Structure of 1. Compound **1** crystallizes in monoclinic space group $P2_1/c$, and the asymmetric unit contains four complete cobalt ions (Co2−Co5) and one-half occupied cobalt ion (Co1), one complete hexacarboxylate ligand, three independent hydroxyl ions, and four coordinated aqua molecules (Figure 1). All of the cobalt ions adopt hexacoordinated mode and are surrounded by six oxygen atoms, and the coordination spheres could be seen as slightly distorted octahedra except for Co4. The axial and equatorial coordination sites of Co1, sitting on an inversion center, are separately occupied by two symmetric μ_3-hydroxyl groups (O20) and four inversely related μ_3-η^2:η bridging carboxyls of different hexacarboxylate ligands. The axial coordination sites of Co2 are separately occupied by two carboxyls of different hexacarboxylate ligands in μ_3-η^2:η and *syn-syn*-μ_2 bridging modes, while the equatorial ones are occupied by three μ_3-hydroxyl groups (O19, O19, and O20) and one μ_2 bridging aqua molecule. The axial coordination sites of Co3 are separately occupied by two μ_3-hydroxyl groups (O19 and O21), while the equatorial ones are occupied by four carboxyls of two hexacarboxylate ligands (O2 and O7 from one ligand and O4 and O10 from another) in μ_3-η^2:η and *syn-syn*-μ_2 bridging modes. The coordination spheres of Co4 could be seen as a highly distorted square pyramid conformation, in which the equatorial sites are occupied by one μ_2 bridging aqua molecule (O1W), one chelating carboxylate group, and one μ_3-hydroxyl (O21) and η-oxygen atom (O8) of the μ_3-η^2:η carboxylate group, and the remaining axial site is occupied by μ_3-hydroxyl (O20). The axial coordination sites of Co5 are separately occupied by two carboxyls of two hexacarboxylate ligands in monodentate η and *syn-syn*-μ_2 bridging modes, while the equatorial ones are occupied by one μ_3-hydroxyl group (O21) and three coordinated aqua molecules. Each Co1 atom is further interconnected to four other cobalt ions (symmetrically related Co2 and Co4 ions) via two μ_3-hydroxyls (O20) and two Co3 ions by double η^2-oxygen atoms (O7 and O10) of the μ_3-η^2:η carboxylate group. Each μ_3-hydroxyl (O20) ligates Co1, Co2, and Co4 ions to form the typical triangular subunit, in which Co2 and Co4 ions are further connected by a μ_2-bridging aqua molecule. Differently, in the isosceles triangular subunit formed by two symmetric Co2 ions and one Co3 ion via the μ_3-hydroxyl (O19), Co2 and Co3 ions are further connected by the μ_3-η^2:η carboxylate group, and symmetric Co2 ions are linked via two μ_3-hydroxyls (O19). In addition, μ_3-hydroxyl (O21) ligates Co3−Co5 ions to form another triangular subunit, in which Co3 and Co5 ions are further interconnected by the μ_3-η^2:η carboxylate group. In this way, an unprecedented planar nonanuclear cobalt cluster is formed related to the inversion center, and the Co⋯Co distance ranged from 3.308 to 3.610 Å, shown in Figure S1 of the Supporting Information. All of the Co−O distances range from 2.015(8) to 2.146(10) Å, excepted for a Co4−O1w bond length of 2.740(10) Å, corresponding to the normal Co^{II}−O values.[14] Furthermore, the adjacent nonanuclear clusters are interlinked to form the infinite 1D cobalt-hydroxyl chain along the b-axial

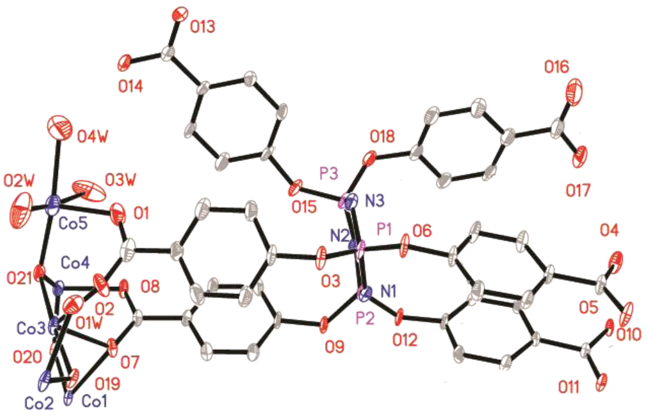


Figure 1. Perspective view of the asymmetric unit of **1** at the 30% probability level (hydrogen atoms were omitted for the sake of clarity).

direction by sharing the edge of isosceles triangular subunits based on two μ_3-hydroxyls (O19), shown in Figure 2.

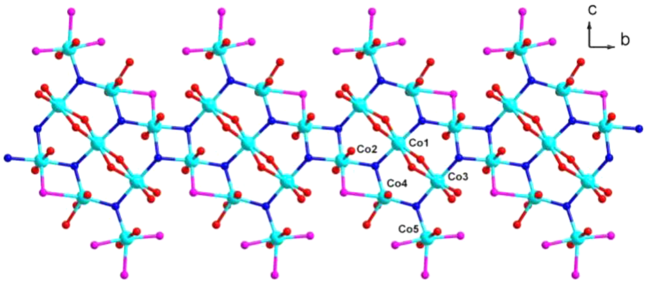


Figure 2. Perspective view of the 1D cobalt-hydroxyl chain along the *b*-axis in **1** with hydrogen and carbon atoms omitted for the sake of clarity.

In the crystal structure of **1**, to adapt to the conformation of the 1D chain structure, the flexible hexacarboxylate ligand adopts a nearly linear configuration and tries to directly connect 10 cobalt ions by its carboxyls in four modes (Scheme S2 of the Supporting Information), shown in Figure S1 of the Supporting Information. The central P_3N_3 rings in the hexacarboxylate ligands are nearly planar, while the P−N distances and N−P−N and P−N−P angles are very similar to those of previously reported P_3N_3 derivatives.[12] Three of the six 4-carboxylato-phenoxy substituents on three phosphorus centers that are on one side of the central ring bind to one 1D chain, while the other three are located on the other side and link two parallel 1D chains, shown in Figure 3, with the range of distorted $C_{\mathrm{carboxyl}}{-}O_{\mathrm{substituted}}{-}P_{\mathrm{central}}$ angles from 119.8° to 136.5°. In this way, the 1D cobalt-hydroxyl chains are interrupted by the coordinated aqua molecules on Co5 ions with a Co5···Co5 distance of 5.733 Å and arranged in the *b*−*c* plane to form the nearly 2D layer structure. The hexacarboxylate ligands act as the pillared struts to connect adjacent 2D cobalt-hydroxyl layers to form the whole 3D structure.

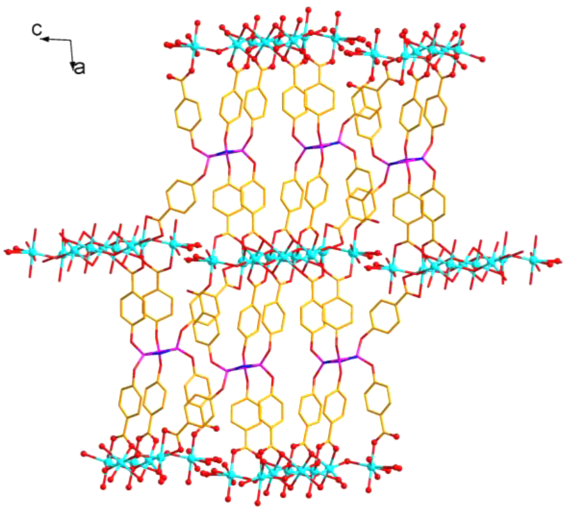


Figure 3. Perspective view of the 3D structure of **1** (hydrogen atoms were omitted for the sake of clarity), showing the 2D layer consisted of 1D cobalt-hydroxyl chains.

Magnetic Properties of 1. The variable-temperature magnetic susceptibilities of **1** were measured on crystalline samples under 1 kOe in the range of 2−300 K and are shown as $\chi_M T$ and χ_M versus T plots in Figure 4.

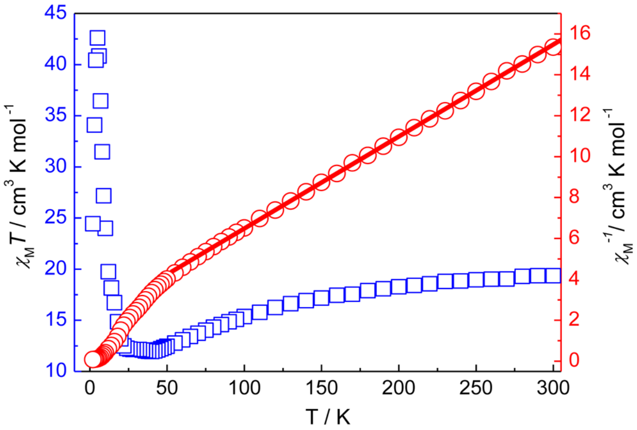


Figure 4. $\chi_M T$ and χ_M vs T plots of **1** in the temperature range of 2−300 K under 1 kOe.

The $\chi_M T$ value of **1** at 300 K is ∼19.35 emu K mol^{-1}, slightly larger than the experimental value of the spin-only value (16.875 emu K mol^{-1} from g = 2.00) expected for nine magnetically isolated Co$^{\mathrm{II}}$ ions. As the temperature is lowered, the $\chi_M T$ value decreases continuously to 11.91 emu K mol^{-1} at 40 K. The data above 50 K follow the Curie−Weiss law with C = 22.2 emu K mol^{-1} and θ = −44.2 K. These characteristics clearly suggest overall antiferromagnetic interactions between Co$^{\mathrm{II}}$ ions in the cobalt-hydroxyl chain of compound **1** above 50 K. Then the $\chi_M T$ value increases rapidly to a maximal value of 42.61 emu K mol^{-1} at ∼5 K, suggesting the onset of weak ferromagnetic behavior. The upturn of the $\chi_M T$ value below 43 K suggests an uncompensated magnetic moment of the system possibly arising from spin canting of the antiferromagnetically coupled Co(II) ions.[14] With a further decrease in the temperature to <5 K, the $\chi_M T$ value drops rapidly to 24.43 emu K mol^{-1} at 2 K because of the saturation effect.

To elucidate the actual coupling nature, more detailed measurements for **1** were performed. It is noticeable that the magnetic susceptibility shows a strong field dependence below 25 K. Via the application of different magnetic fields, the magnetic susceptibility increases with a decreasing magnetic field because of small spontaneous magnetization of canted antiferromagnetism, shown in Figure 5. Moreover, to character-

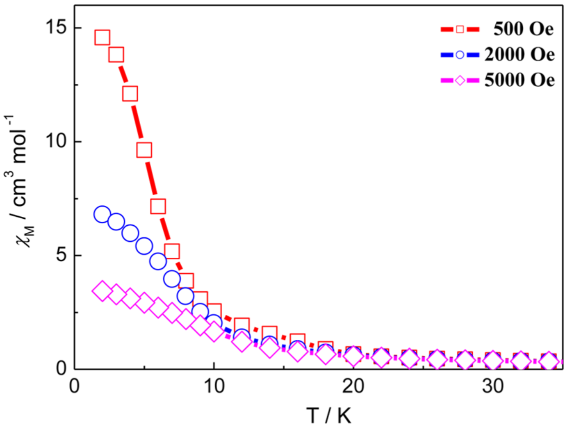


Figure 5. Field-dependent magnetic susceptibilities of **1** below 40 K.

ize the low-temperature behaviors, the field-cooled (FC) and zero-field-cooled (ZFC) magnetizations were measured at 200 Oe upon warming from 2 to 30 K (Figure 6). The ZFC and FC plots completely diverge below 16 K, suggesting the onset of a long-range ordering, spin-glass, or superparamagnetic state. The temperature dependencies of ac magnetic susceptibility under H_{dc} = 0 Oe and H_{ac} = 3 Oe had also been measured with frequencies of 1 and 1000 Hz from 2 to 10 K to further investigate the underlying magnetic nature. As depicted in Figure 7, a slight frequency-dependent behavior is observed in the ac susceptibility. The frequency shift parameter can be estimated by the equation $\Phi = \Delta T_p/[T_p\Delta(\log \omega)]$, where ΔT_p is the shift of peak in χ', T_p is the peak temperature, and ω is the applied frequency. The value of Φ is determined to be 0.067, which falls within the usual range (10^{-2}–10^{-3}) of a spin-glass behavior.[15] The magnetization dynamics occur because not only the chains of **1** are structurally well-isolated. From the χ'' signals, the relaxation times (τ) were determined using the equation $\tau = 1/(2\pi\nu)$. The resulting relaxation times obey the Arrhenius law [$\tau = \tau_0 \exp(\Delta_\tau/kBT)$] (see Figure 8) ($k_B$ is the Boltzmann constant and τ_0 a pre-exponential factor). From the data, the relaxation barrier (Δ_τ/k_B) was determined to be 83.7 K (58.1 cm^{-1}), with a τ_0 of 2.17 × 10^{-14} s. All these features suggest that **1** shows the coexistence of spin-canted antiferromagnetism and spin glass.

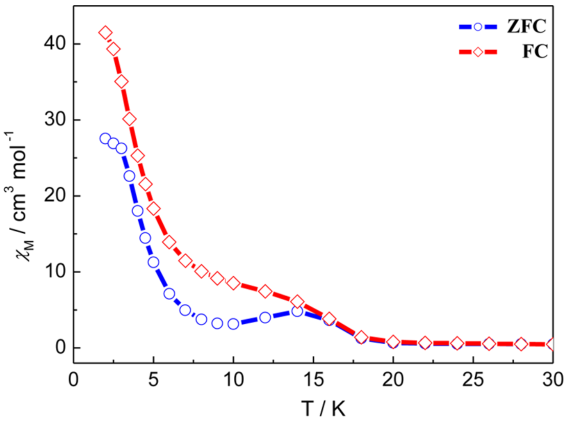


Figure 6. ZFC and FC magnetization at 200 Oe warming from 2 K.

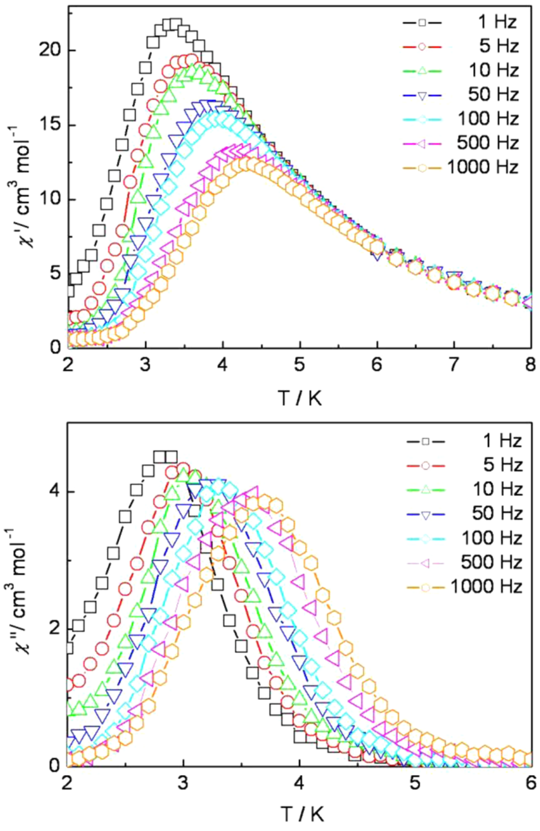


Figure 7. In-phase (up) and out-of-phase (below) ac susceptibility for **1** in a zero dc and 3 Oe ac applied field.

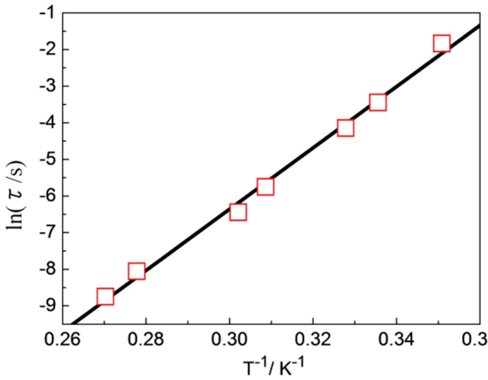


Figure 8. Arrhenius plot of the relaxation time τ vs reciprocal temperature for **1**. The solid line represents the least-squares fitting of the experimental data.

The nearly linear increase in field-dependent magnetization for **1** at 2 K also indicates the antiferromagnetic interactions. The magnetization at 70 kOe is 6.78 $N\beta$, much lower than the expected saturation value. A hysteresis loop is observed clearly at 2.0 K, giving a coercive field of $H_c \approx$ 0.26 kOe and a remnant magnetization of M_r = 0.26 $N\beta$ (Figure 9, inset, and Figure S5 of the Supporting Information). The canting angle can then be estimated to be ~0.76° based on the equation[14,16] α =

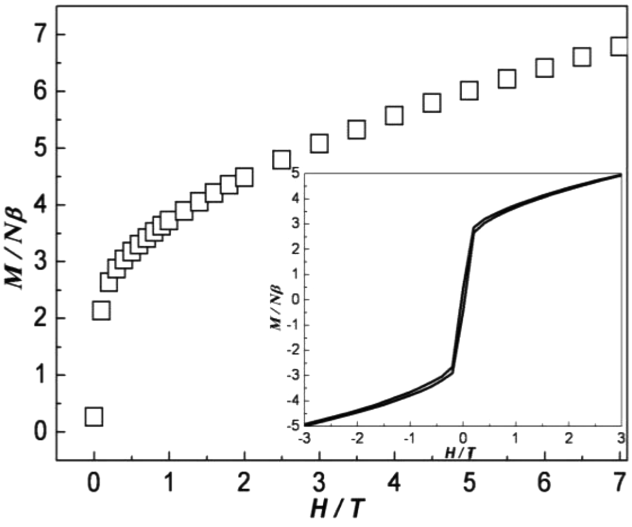


Figure 9. Field dependence of the magnetization for **1**. The inset shows the hysteresis loop for **1** at 2 K.

$\tan^{-1}(M_r/M_s)$ (M_s = 19.48 $N\beta$, S' = $^1/_2$, and g' = 4.33 for octahedral Co^{II} at 2 K).

The exchange interaction between individual Co^{II} ions of **1** is difficult to accurately estimate because of the effects of spin−orbit coupling. However, the rough interaction trend and magnetostructural relationship could be given by the examination of the bond lengths and angles between the Co^{II} centers from the detailed crystal structure of **1**. The different 1D chains arranged in the *b*−*c* plane are disconnected by coordinated aqua molecules. Therefore, magnetically, **1** could be considered as a weakly interacting infinite 1D chain. The cobalt ions in the 1D chain are interconnected by triply bridging hydroxide and bridging carboxylate groups. Traditionally, the *syn-syn* bridging carboxyl and a Co−O−Co angle of >100° afford antiferromagnetic interaction between paramagnetic ions, and the Co−O−Co angle that ranged from 94.5° to 100° is expected to transfer weakly ferromagnetic interactions.[17] If antiferromagnetic coupling transferred by carboxyls is excluded, in the planar nonanuclear cluster, the Co−OH−Co group should give rise to antiferromagnetic interaction because of the range from 111.82° to 119.79°. However, a Co2−O19−Co2 angle of 95.8° should favor ferromagnetic interactions. In this way, the magnetic structures of **1** can be described as that 1D chain that formed by antiferromagnetically coupled Co_9 units linked by the triply bridging OH ligands (O19), and the coupling between adjacent Co_9 units along the chain is weakly ferromagnetic. In addition, with respect to the magnetic measurements described above, **1** displays spin-canted antiferromagnetic behavior, which may originate from the single-ion anisotropy of Co(II).[15] Because the presence of an inversion center between cobalt ions in **1** with space group $P2_1/c$ forbids the occurrence of antisymmetric exchange interaction, the possible reason for the structural phase transition had been excluded according to the low-temperature heat capacity measurement (Figure S4 of the Supporting Information).

CONCLUSION

In summary, a new 3D magnetic network, $[Co_9(OH)_6(C_{42}H_{24}O_{18}P_3N_3)_2(H_2O)_8]$, has been successfully prepared by utilizing the flexible hexacarboxylate ligand derived from cyclotriphosphazene. This compound consists of 1D cobalt-hydroxyl chains based on planar nonanuclear clusters, which is the first found in the field of MCP. Furthermore, these 1D chains are located in the *b*−*c* plane to form the nearly 2D cobalt layer. Magnetic measurements revealed that **1** shows spin-canted antiferromagnetism with spin-glass behavior. These results suggest that reasonable design and choice of large carboxylate ligand based on a specific scaffold could be effective for the construction of magnetic materials based on a novel 1D magnetic chain. The flexible ligand used in this context presents four types of coordination modes and a high coordination number, thus forming the high-nuclearity magnetic chain. Future work will be needed to investigate the possibilities of novel 1D magnetic SUB stabilized by thus hexacarboxylate ligands derived from cyclotriphosphazene.

EXPERIMENTAL SECTION

Materials and General Methods. The hexacarboxylate ligand was synthesized according to the previous literature.[12] All starting materials were obtained commercially and used without further purification. Elemental analyses for C, H, and N were performed on a PerkinElmer 240Q elemental analyzer. The IR spectra were recorded in range of 400−4000 cm^{-1} on a Nicolet 5DX spectrometer (KBr pellets). Magnetic susceptibility measurements were taken in the temperature range of 2−300 K with a magnetic field of 1000 Oe on a Quantum Design MPMS XL-7 magnetometer.

Synthesis of $[Co_9(OH)_6(C_{42}H_{24}O_{18}P_3N_3)_2(H_2O)_8]$ (1). A mixture of H_6L1 (0.05 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (0.3 mmol), and NaOH (0.3 mmol) was dissolved in 24 mL of H_2O and 1.5 mL of DMF. The mixture was stirred at room temperature for 30 min, equally divided into three 25 mL Teflon-lined stainless steel vessels, and heated at 140 °C for 5 days, and red crystals were obtained from the filtrate. The yield of the reaction was ~30% based on the hexacarboxylate ligand. Anal. Calcd for $C_{84}H_{70}Co_9P_6N_6O_{50}$: H, 2.63%; C, 37.65%; N, 3.14%. Found: H, 3.11%; C, 38.04%; N, 2.93%. IR (KBr): 3462, 1603, 1548, 1401, 1277, 1205, 1170, 788 cm^{-1}.

X-ray Structural Determination. X-ray diffraction data of **1** (0.1 mm × 0.05 mm × 0.05 mm) were collected on an Oxford Gemini S Ultra diffractometer using Mo Kα (λ = 0.71073 Å) radiation at room temperature. The structures of the complex were determined by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure based on F^2 values.[18] The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. Because the O19 is the hydroxyl atom, no hydrogen bonds needed to be formed, which gave the alert B. CCDC-996960 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed crystal data, XRD, structural figures, low-temperature heat capacities, and an X-ray crystallographic file in cif format for **1**. 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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