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Synthesis, Structure, and Magnetic Properties of Three 1D Chain Complexes Based on High-Spin Metal–Cyanide Clusters: [$Mn^{III}_6M^{III}$] (M = Cr, Fe, Co)

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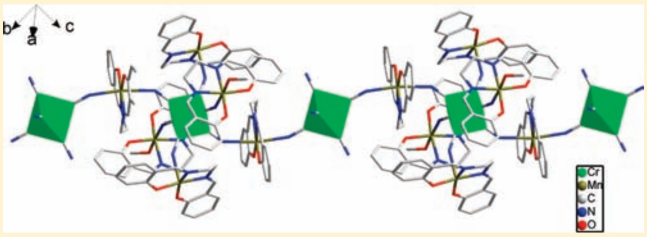
S *Supporting Information*



ABSTRACT: On the basis of high-spin metal–cyanide clusters of $Mn^{III}_6M^{III}$ (M = Cr, Fe, Co), three one-dimensional (1D) chain complexes, $[Mn(salen)]_6[Cr(CN)_6]_2 \cdot 6CH_3OH \cdot H_2O$ (**1**), $[Mn(5\text{-}CH_3)salen)]_6[Fe(CN)_6]_2 \cdot 2CH_3CN \cdot 10H_2O$ (**2**), and $[Mn(5\text{-}CH_3)salen)]_6[Co(CN)_6]_2 \cdot 2CH_3CN \cdot 10H_2O$ (**3**) [salen = *N*,*N*′-ethylenebis(salicylideneiminato) dianion], have been synthesized and characterized structurally as well as magnetically. Complexes **2** and **3** are isomorphic but slightly different from complex **1**. All three complexes contain a 1D chain structure which is comprised of alternating high-spin metal–cyanide clusters of $[Mn_6M]^{3+}$ and a bridging group $[M(CN)_6]^{3-}$ in the trans mode. Furthermore, the three complexes all exhibit extended 3D supramolecular networks originating from short intermolecular contacts. Magnetic investigation indicates that the coupling mechanisms are intrachain antiferromagnetic interactions for **1** and ferromagnetic interactions for **2**, respectively. Complex **3** is a magnetic dilute system due to the diamagnetic nature of Co^{III}. Further magnetic investigations show that complexes **1** and **2** are dominated by the 3D antiferromagnetic ordering with $T_N = 7.2$ K for **1** and 9.5 K for **2**. It is worth noting that the weak frequency-dependent phenomenon of AC susceptibilities was observed in the low-temperature region in both **1** and **2**, suggesting the presence of slow magnetic relaxations.

INTRODUCTION

In the past decade, low-dimensional magnetic materials such as single-molecule magnets (SMMs) and single-chain magnets (SCMs) have attracted extensive attention owing to their well-known potential applications in high-density information storage, quantum computation, and other relative molecular devices.[1] In order to obtain new low-dimensional magnets with a higher block temperature and to clarify the magneto-structural correlation, a great number of SMMs[2] and SCMs[3] with novel structure and interesting magnetic properties have been synthesized, characterized, and theoretically investigated. It has been widely approved that the magnetic behavior of SMMs and SCMs is closely related to a high-spin ground state (S) and a high uniaxial anisotropy (D) $H = -2J\Sigma_{-\infty}^{+\infty}\vec{S}_i\vec{S}_{i+1}+D\Sigma_{-\infty}^{+\infty}\vec{S}_{iz}^2$.[4] Therefore, more attention has been paid to synthesize high-spin clusters containing paramagnetic metal centers with large magnetic anisotropy, such as Mn^{III},[5] Co^{II},[6] and low-spin Fe^{III}.[7] Particularly, the one-dimensional connection of SMMs usually produces the corresponding SCMs, which are called SMM-based SCMs.[8] However, the attractive designing idea of SMM-based SCMs is difficult to be actualized, and several typical SMM-based SCMs have been reported to date.[9] An alternative method is to fall back on uniaxial anisotropic complexes even if they are not SMMs.[8] Complexes self-assembled by Mn^{III}–(Schiff bases) are always of great interest because of the high-spin state and the strong uniaxial anisotropy. Thus far many relevant magnetic complexes including some SMMs and SCMs have been reported.[10] Among those high-spin complexes, $[Mn_6M]^{3+}[M(CN)_6]^{3-}$ (M = Cr, Fe)[11] attracted our attention most because the high-spin heptanuclear $[Mn_6M]^{3+}$ cations not only possess six solvent substitution labile sites but also are charge balanced by free $[M(CN)_6]^{3-}$ anions. On the basis of the above-mentioned facts, if the reaction conditions were modified, the clusters $[Mn_6M]^{3+}$ might be connected into a 1D, 2D, or 3D structure by counteranions such as $[M(CN)_6]^{3-}$ or some other bridging groups, as shown in Scheme 1a. Although the $[Mn_6M]^{3+}$ cluster does not behave as SMM,[12] it is promising to obtain new SMMs, SCMs, or bulk magnets based on this assembling strategy.[8] In fact, we obtained three 1D chain complexes by using $[M(CN)_6]^{3-}$ to connect $[Mn_6M]^{3+}$ clusters. Herein, we report the synthesis, crystal structures, and magnetic properties of the three complexes, $[Mn(salen)]_6[Cr(CN)_6]_2 \cdot 6CH_3OH \cdot H_2O$ (**1**), $[Mn(5\text{-}CH_3)salen)]_6[Fe(CN)_6]_2 \cdot 2CH_3CN \cdot 10H_2O$ (**2**), and $[Mn(5\text{-}CH_3)salen)]_6$ $[Co(CN)_6]_2 \cdot 2CH_3CN \cdot 10H_2O$ (**3**) [salen = *N*,*N*′-ethylenebis (salicylideneiminato) dianion]. Scheme 1b is the corresponding Schiff base ligands used in this work. Magnetic investigation shows the dominant 3D antiferromagnetic ordering with $T_N = 7.2$ K for **1** and 9.5 K for **2**.

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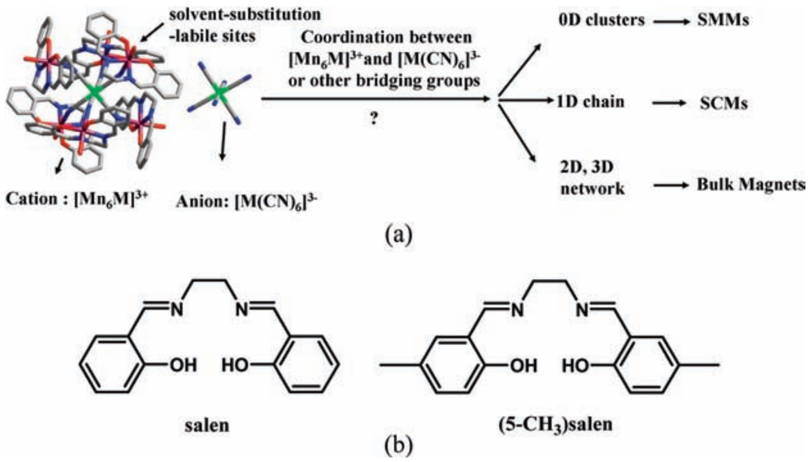
Scheme 1. (a) Strategy of Constructing Molecular Magnets Based on High-Spin Clusters $[Mn_6M]^{3+}[M(CN)_6]^{3-}$ and (b) Corresponding Schiff Base Ligands Used in This Work



Meanwhile, their slow magnetic relaxations at very low temperature were detected.

EXPERIMENTAL SECTION

General Procedures and Materials. All experimental operations were carried out under an air atmosphere in the dark. All chemicals and solvents were reagent grade and used as purchased without any further purification. $[Mn(salen)\cdot H_2O]ClO_4\cdot H_2O$ and $[Mn(5\text{-}CH_3)\text{-}salen\cdot H_2O]ClO_4\cdot H_2O$ were prepared according to the modified literature procedure;[13] $K_3Cr(CN)_6$ and LiTCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) were also synthesized as described elsewhere.[14,15] $K_3[Fe(CN)_6]$ and $K_3[Co(CN)_6]$ were commercially available.

***Caution*!** KCN is toxic and hazardous, while perchlorate salts of metal complexes are potentially explosive. Thus, handing them carefully with small quantities is highly suggested for safety considerations.

Synthesis of Complex 1. A solution of 10.7 mg (0.033 mmol) of $K_3Cr(CN)_6$ in 2.5 mL of water was added into a solution of 45.6 mg (0.1 mmol) of $[Mn(salen)\cdot H_2O]ClO_4\cdot H_2O$ in 7.5 mL of acetonitrile with constant stirring, and 6.9 mg (0.033 mmol) of LiTCNQ was then added. About 10 min later, the brown mixture obtained was filtered and the filtrate was kept undisturbed in the dark to avoid decomposition of the cyanide-containing building blocks. One week later, the brown-black block crystals suitable for X-ray diffraction were formed and carefully collected by filtration, washed with 1:1 (v/v) acetonitrile—water, and dried at room temperature. Yield: 18.0 mg, 42.1%. Anal. Calcd for $C_{114}H_{110}Cr_2Mn_6N_{24}O_{19}$: C, 53.61; H, 4.34; N, 13.16. Found: C, 53.91; H, 4.61; N,13.07. Main IR bands (cm^{-1}): 3438(s), 2129 (w, $\upsilon_{C\equiv N}$), 2122 (m, $\upsilon_{C\equiv N}$), 1624(s, $\upsilon_{O=N}$), 1601(m), 1547(m), 1443(m), 1388(m), 1334(m), 1284(s), 1210(m), 1148(m), 1128(w), 1088(w), 907(m), 802(w), 764 (m), 632(m), 595(w).

Synthesis of Complex 2. The synthesis method of complex **2** is similar to that of **1** but no LiTCNQ was added. To a solution of 48.4 mg (0.1 mmol) of $[Mn(5\text{-}CH_3)salen\cdot H_2O]ClO_4\cdot H_2O$ in 7.5 mL of acetonitrile, a solution of 10.9 mg (0.033 mmol) of $K_3Fe(CN)_6$ in 2.5 mL of water was then added. The mixture was treated using the same procedure as **1**. One week later, the brown-black block crystals suitable for X-ray diffraction were obtained. Yield: 22.1 mg, 48.6%. Anal. Calcd for $C_{124}H_{134}Fe_2Mn_6N_{26}O_{22}$: C, 53.54; H, 4.85; N, 13.09. Found: C, 53.11; H, 4.92; N, 12.86. Main IR bands (cm^{-1}): 3435(s), 2126 (m, $\upsilon_{C\equiv N}$), 2114(m, $\upsilon_{C\equiv N}$), 1626(s, $\upsilon_{C=N}$), 1600(m), 1546(m), 1447(m), 1389(m), 1336(m), 1284(s), 1209(m), 1148(m), 1129(w), 1086(w), 905(m), 801(w), 765 (m), 631(m), 594(w), 463(m).

Synthesis of Complex 3. Substituting $K_3[Fe(CN)_6]$ for $K_3[Co(CN)_6]$ in the synthesis procedure of complex **2** resulted in formation of complex **3**. Brown-black block crystals suitable for X-ray diffraction were obtained by slow evaporation of the filtrate. Yield: 18.3 mg, 41.0%. Anal. Calcd for $C_{124}H_{134}Co_2Mn_6N_{26}O_{22}$: C, 53.41; H, 4.84; N, 13.06. Found: C, 53.05; H, 4.96; N, 13.08. Main IR bands (cm^{-1}): 3436(s), 2127 (m, $\upsilon_{C\equiv N}$), 2116(m, $\upsilon_{C\equiv N}$), 1627(s, $\upsilon_{C=N}$), 1603(m), 1547(m), 1446(m), 1388(m), 1334(m), 1285(s), 1208(m), 1149(m), 1130(w), 1087(w), 906(m), 803(w), 766 (m), 632(m), 595(w), 463(m).

Physical Measurements. Infrared spectra (400—4000 cm^{-1}) were recorded as KBr disks with a VECTOR 22 spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Perkin-Elmer 240C elemental analyzer. All magnetic measurements on microcrystalline sample were conducted on a Quantum Design MPMP-XL7 superconducting quantum interference device (SQUID) magnetometer. Measurements of the DC magnetic susceptibility were carried out from 1.8 to 300 K and from 0 to 70 kOe, and the AC magnetic data were collected at various frequencies ranging from 1 to 1488 Hz with an AC field amplitude of 3 G and zero, 2 kOe DC magnetic field. Corrections of measured susceptibilities were carried out considering both the sample holder as the background and the diamagnetism of the constituent atoms according to Pascal's tables.[16]

X-ray Structure Determination. Single crystals with suitable dimensions for X-ray diffraction analyses were mounted on a glass rod; the crystal data was collected with a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293K. The method used to solve the structure was direct method, and the structure was further expanded using Fourier difference techniques with the SHELXTL-97 program package.[17] Absorption corrections were carried out using the SADABS program supplied by Bruker.[18] Anisotropic refinement was applied for all non-hydrogen atoms, while the hydrogen atoms were added geometrically and refined isotropically with fixed U values using a riding model. Details of the crystallographic data collection, structural determination, and refinement are summarized in Table 1. Crystallographic data for the structures of complexes **1**, **2**, and **3** reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as CCDC 798088, 798089, and 798090, respectively.

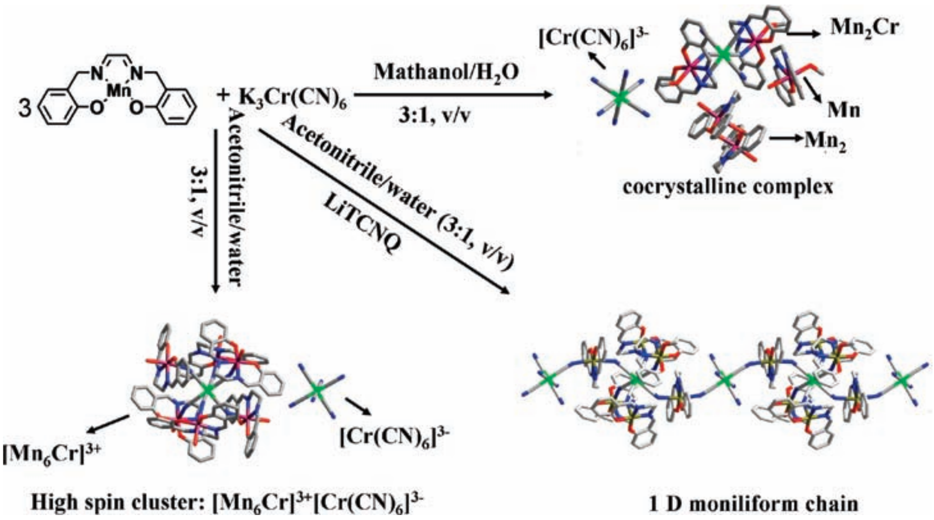
RESULTS AND DISCUSSION

Synthesis and Characterization. As for the reaction of *trans*-$[Mn^{III}(\text{Schiff bases})]^+$ and $[M(CN)_6]^{3-}$, the polarity of

Table 1. Details of the Crystallographic Data Collection, Structural Determination, and Refinement for Complexes 1−3 at 293 K

	1	2	3
formula	$C_{114}H_{110}Cr_2Mn_6N_{24}O_{19}$	$C_{124}H_{134}Fe_2Mn_6N_{26}O_{22}$	$C_{124}H_{134}Co_2Mn_6N_{26}O_{22}$
fw	2553.90	2781.92	2788.08
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	14.188(7)	13.561(8)	13.561(8)
b/Å	15.174(8)	15.201(6)	15.201(6)
c/Å	16.069(7)	17.647(8)	17.647(8)
α/deg	76.896(10)	70.277(2)	70.277(2)
β/deg	79.473(10)	76.339(2)	76.339(2)
γ/deg	66.342(9)	86.548(2)	86.548(2)
V/Å^3	3070(3)	3327.2(6)	3327.2(6)
Z	1	1	1
ρ_{calcd}/g cm^{-3}	1.381	1.388	1.391
F(000)	1312	1438	1440
θ/deg	1.89−26.00	2.00−25.00	2.00−25.00
index ranges	$-17 \le h \le 14$	$-15 \le h \le 16$	$-16 \le h \le 15$
	$-18 \le k \le 14$	$-18 \le k \le 15$	$-18 \le k \le 12$
	$-17 \le l \le 19$	$-20 \le l \le 11$	$-20 \le l \le 17$
reflns collected	11 715	11 499	11 482
independent reflns	8135	8294	6996
R(int)	0.0235	0.0237	0.0288
data/restraints/parameters	8135/0/750	8294/0/805	6996/0/792
GOF on F^2	1.026	1.007	0.948
$R_1[I > 2\sigma(I)]$	0.0563	0.0588	0.0612
wR_2 (all data)	0.1146	0.1634	0.1790

Scheme 2. Outlines of the Subtle Relationship between the Reaction Conditions and the Self-Assembling Structural Styles of Mn^{III}(Schiff-bases) and $K_3Cr(CN)_6$



solvents plays a very important role in determining the self-assembling process of these complexes. Indeed, as shown in Scheme 2, reaction of $[Mn(salen)\cdot H_2O]\cdot ClO_4\cdot H_2O$ and $K_3[Cr(CN)_6]$ in 3:1 in methanol/water (3:1,v/v) produces a cocrystalline complex with trinuclear $[Mn_2Cr]$, dimeric $[Mn_2]$, and mononuclear [Mn] moieties.[19] By changing the solvent from methanol to acetonitrile, the heptanuclear clusters $[Mn_6Cr]^{3+}[Cr(CN)_6]^{3-}$ were obtained[11] in which six coordinating water molecules are arranged around the spherical $[Mn_6Cr]^{3+}$ cluster at the solvent substitution labile sites. The dehydration reaction was used in order to substitute $[Cr(CN)_6]^{3-}$ anions for water molecules, but the target complex was not obtained.[20] When LiTCNQ was added as the possible bridging ligand, the isolated $[Cr(CN)_6]^{3-}$ anions unexpectedly connect the heptanuclear

Table 2. Selected Bond Lengths [Å] and Angles [deg]

1		2		3	
Mn1−O2	1.878(2)	Mn1−O2	1.874(3)	Mn1−O1	1.877(4)
Mn1−O1	1.879(3)	Mn1−O1	1.881(3)	Mn1−O2	1.885(3)
Mn1−N7	1.967(3)	Mn1−N8	1.981(4)	Mn1−N7	1.991(4)
Mn1−N8	1.985(3)	Mn1−N7	1.985(3)	Mn1−N8	1.992(5)
Mn1−N4	2.267(3)	Mn1−N4	2.236(4)	Mn1−N4	2.227(5)
Mn1−N1	2.376(3)	Mn1−N1	2.382(3)	Mn1−N1	2.401(4)
Mn2−O3	1.873(2)	Mn2−O4	1.861(3)	Mn2−O4	1.851(4)
Mn2−O4	1.882(2)	Mn2−O3	1.867(3)	Mn2−O3	1.879(3)
Mn2−N9	1.980(3)	Mn2−N10	1.962(4)	Mn2−N10	1.970(5)
Mn2−N10	2.001(3)	Mn2−N9	1.972(4)	Mn2−N9	1.993(5)
Mn2−N2	2.274(3)	Mn2−O7	2.271(3)	Mn2−O7	2.262(4)
Mn2−O7	2.282(3)	Mn2−N2	2.302(3)	Mn2−N2	2.326(4)
Mn3−O6	1.850(3)	Mn3−O6	1.861(3)	Mn3−O6	1.871(3)
Mn3−O5	1.853(3)	Mn3−O5	1.882(3)	Mn3−O5	1.893(3)
Mn3−N11	1.952(3)	Mn3−N12	1.969(3)	Mn3−N12	1.983(4)
Mn3−N12	1.956(3)	Mn3−N11	1.979(3)	Mn3−N11	1.991(4)
Mn3−N3	2.216(3)	Mn3−N3	2.190(3)	Mn3−N3	2.189(4)
C1−Cr1	2.067(3)	C1−Fe1	1.936(4)	C1−Co1	1.888(5)
C2−Cr1	2.066(3)	C2−Fe1	1.937(4)	C2−Co1	1.887(5)
C3−Cr1	2.032(4)	C3−Fe1	1.940(4)	C3−Co1	1.912(6)
C4−Cr2	2.076(4)	C4−Fe2	1.929(5)	C4−Co2	1.900(6)
C5−Cr2	2.034(4)	C5−Fe2	1.933(7)	C5−Co2	1.873(9)
C6−Cr2	2.070(4)	C6−Fe2	1.939(6)	C6−Co2	1.885(7)
N1−C1−Cr1	177.3(3)	N1−C1−Fe1	176.1(3)	N1−C1−Co1	176.0(4)
N2−C2−Cr1	179.5(3)	N2−C2−Fe1	179.1(4)	N2−C2−Co1	179.5(5)
N3−C3−Cr1	174.3(3)	N3−C3−Fe1	176.9(3)	N3−C3−Co1	177.6(4)
N4−C4−Cr2	176.8(3)	N4−C4−Fe2	177.6(5)	N4−C4−Co2	178.4(6)
N5−C5−Cr2	177.2(4)	N5−C5−Fe2	179.1(7)	N5−C5−Co2	176.9(9)
N6−C6−Cr2	178.5(4)	N6−C6−Fe2	178.8(6)	N6−C6−Co2	178.3(7)
C1−N1−Mn1	143.8(2)	C1−N1−Mn1	145.2(3)	C1−N1−Mn1	146.2(4)
C2−N2−Mn2	155.6(3)	C2−N2−Mn2	148.8(3)	C2−N2−Mn2	151.4(4)
C3−N3−Mn3	148.5(3)	C3−N3−Mn3	146.4(3)	C3−N3−Mn3	146.5(4)
C4−N4−Mn1	154.1(3)	C4−N4−Mn1	153.6(4)	C4−N4−Mn1	153.3(5)

clusters $[Mn_6Cr]^{3+}$, forming the 1D chain structure of complex **1**. No $TCNQ^-$ was found, but the role of LiTCNQ in the synthesis process is not clear for the formation of complex **1**. In a latest report, Yang, et al. synthesized almost the same complex as complex **1** in different solvent and method, which indicates the structure style of complex **1** is available in a different synthesis procedure.[10r] When $[Mn(salen)\cdot H_2O]ClO_4\cdot H_2O$ and $K_3[Cr(CN)_6]$ were changed into $[Mn(5\text{-}CH_3)salen\cdot H_2O]\cdot ClO_4\cdot H_2O$ and $K_3[Fe(CN)_6]$ or $K_3[Co(CN)_6]$, complexes **2** and **3** with structural features similar to complex **1** were obtained. Interestingly, in the synthesis reaction of complexes **2** and **3**, only a chain-like structure but no cluster was obtained. All of these data indicate that Mn^{III}−(Schiff bases) is very sensitive to the subtle variations in both reaction conditions and reaction precursors. IR spectroscopy characterization of the three complexes was carried out (Figure S1 in the Supporting Information). All three complexes displayed two peaks at 2122, 2129 cm^{-1} for **1**, 2114, 2126 cm^{-1} for **2**, and 2116, 2127 cm^{-1} for **3**, manifesting the presence of two or more nonequivalent CN^- such as bridging and terminal modes in these complexes, which also agrees with the X-ray single-crystal structure. The IR spectrum also indicates that the +3 oxidation state of iron is maintained in complex **2**.[12] The absorption between 1620 and 1630 cm^{-1} and 1400−1600 cm^{-1} is the stretching vibration of the N=C group and the benzene ring in salen-type ligands. The similarity of the IR spectroscopy of these complexes indicates they have a very similar structure.

Crystal Structures of Complexes 1−3. Important structural parameters such as key bond distances and angles are listed in Table 2. The X-ray structures of complexes **1**, **2**, and **3** are shown in Figure 1 and Figure S2, Supporting Information. The interchain short contacts and $\pi-\pi$ stacking for the three complexes are depicted in Figure S3, Supporting Information. Complexes **2** and **3** are isomorphic, so only complexes **1** and **2** are described. As shown in Figure 1, complex **1** and **2** possess a similar structure motif though their Schiff base ligands are different. Their common structural feature is that the counteranions $[M(CN)_6]^{3-}$ bridge between heptanuclear clusters $[Mn_6M]^{3+}$ in the trans mode, leading to a 1D chain. As for the $[Mn_6M]^{3+}$ moiety, central $[M(CN)_6]^{3-}$ is coordinated by six $[Mn^{III}(\text{Schiff bases})]^+$ through the bridging ligand CN, forming a slightly distorted octahedron configuration. The M−C−N linkages are almost linear, and the

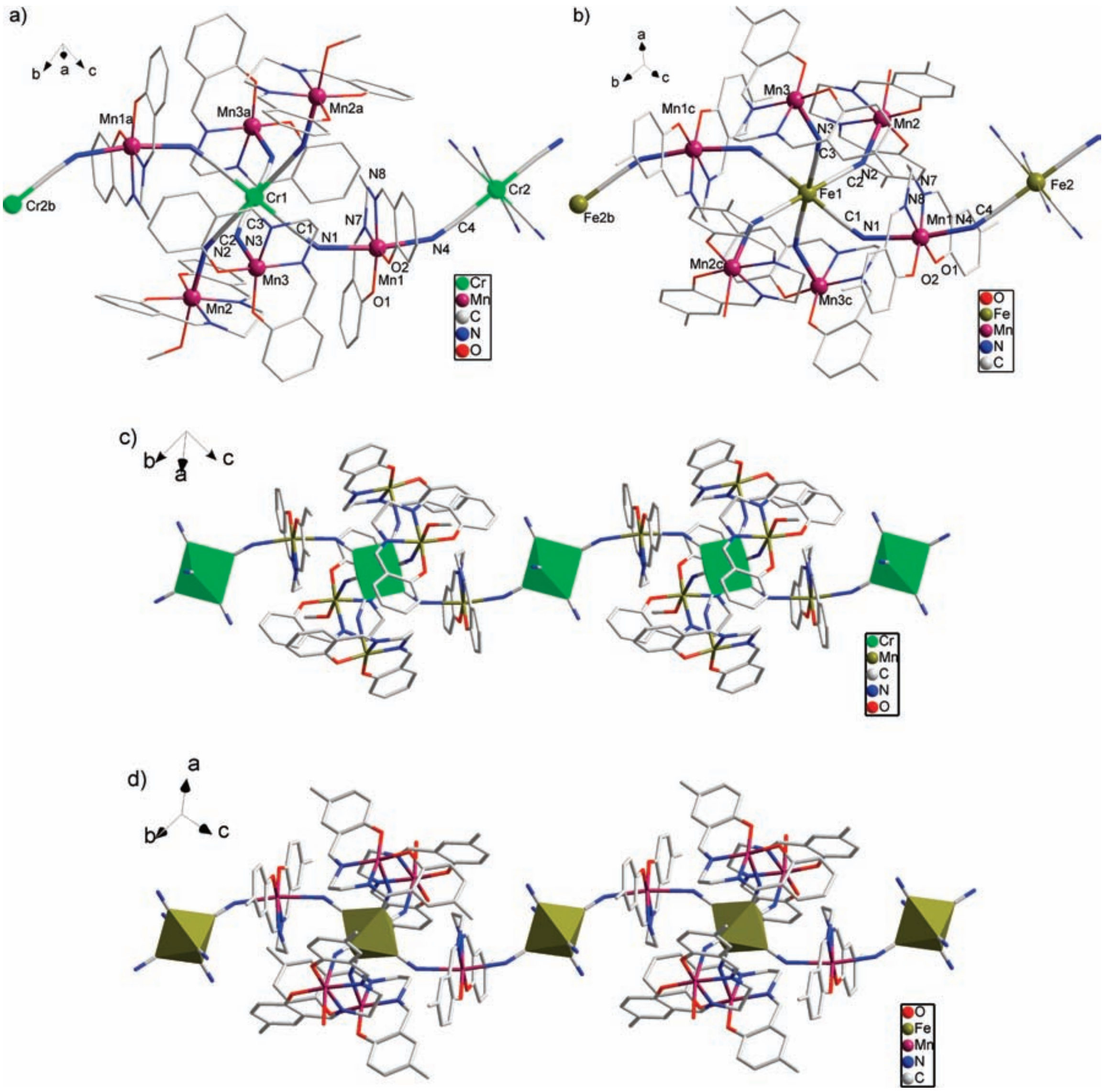


Figure 1. Molecular views with selected atom-labeling scheme for **1** (a) and **2** (b) (symmetry codes a $-x$, $1 - y$, $1 - z$; b x, $1 + y$, $-1 + z$; c $1 - x$, $1 - y$, $-z$). (b) 1D chain structure for **1** (c) and **2** (d).

average bond angles are 177.0(3)° for **1** and 177.4(3)° for **2**. In contrast to M−C−N, the Mn^{III}−N−C linkages exhibit significant bending with angles ranging from 143.8(2)° to 155.6(3)° for **1** and from 145.2(3)° to 148.8(3)° for **2**. All Mn^{III} ions are located in the elongated octahedral environments due to the Jahn−Teller effect with the axial Mn^{III}−O/N (O/N from solvents or CN bridges) distance of 2.216(3)−2.376(3) Å for **1** and 2.190(3)−2.382(3) Å for **2**, longer than the equatorial Mn^{III}−O/N [O/N from Schiff bases] distances of 1.850(3)−2.001(3) Å for **1** and 1.861(3)−1.985(3) Å for **2**, respectively. The whole $[Mn_6M]^{3+}$ moiety is centrosymmetric and does not exhibit an obvious difference from the discrete heptanuclear $[Mn_6M]^{3+}$ cations found in $[Mn_6M]^{3+}[M(CN)_6]^{3-}$,[11] which has a similar octahedral geometric configuration to other heptanuclear clusters.[21] A solvent substitution labile site in each Mn^{III} of the $[Mn_6M]^{3+}$ clusters remains, so that the free $[M(CN)_6]^{3-}$ ion can further coordinate to $[Mn_6M]^{3+}$ in the trans mode, constructing the 1D chain, which is reminiscent of the 3D connection of $[Mn^{III}{}_6Fe^{II}]^{3+}$ by a diamagnetic $[Nb_6Cl_{12}(CN)_6]^{4-}$ building block.[22] Thus, the intercluster $[M(CN)_6]^{3-}$ unit provides two trans CNs coordinating to Mn^{III}, and the left four ones are all terminal. The intercluster Mn^{III}−N distances and Mn^{III}−N−C angles are 2.267(3) Å, 154.1(3)° for **1** and 2.236(4) Å, 153.6(4)° for **2**, respectively, which is comparable to the corresponding intracluster values.

In the packing diagrams of the three complexes (Figure S3, Supporting Information), interchain short contacts and $\pi-\pi$ stacking are observed. The chains first stack parallel to each other along the *a* axis via the weak interchain Mn···O contacts where the O donor is in the phenoxido group and then through $\pi-\pi$ stacking in the *bc* plane to form a 3D supramolecular structure. The Mn···O distance of the weak contact is 3.503(3) and 2.777(4) Å for **1** and **2**, respectively. The centroid distance between the phenoxide rings for the interchain $\pi-\pi$ stacking is 4.215(3) and 3.823(6) Å for **1** and **2**, respectively. These weak contacts indicate that the chains are more isolated in **1** than **2**, which may be ascribed to the steric effect. The shortest intrachain distance between M^{III} and Mn^{III} is 5.166(5)−5.345(4) Å for **1** and 5.026(4)−5.182(5) Å for **2**, while the shortest interchain

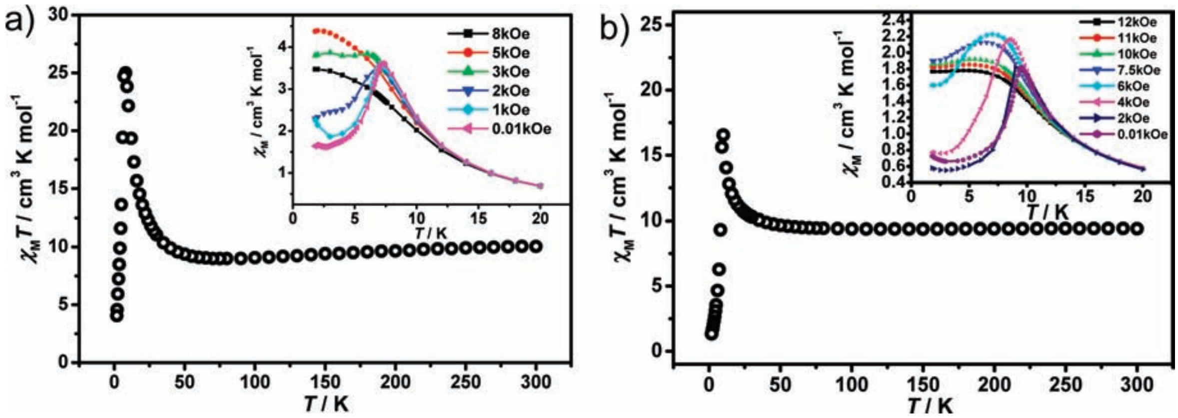


Figure 2. Temperature dependence of magnetic susceptibilities data for complexes **1** (a) and **2** (b) collected in the range of 1.8−300 K under the applied magnetic field of 2 kOe. (Inset) Corresponding field-cooled magnetization for complexes **1** and **2** in different applied fields.

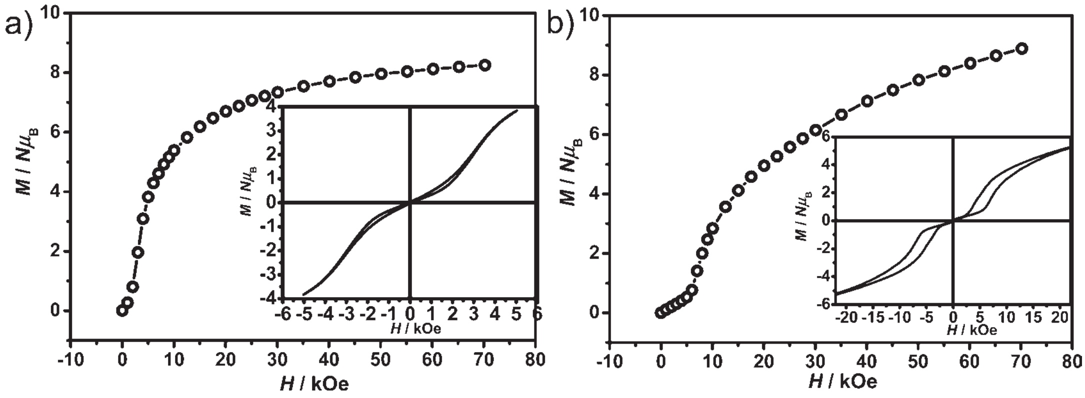


Figure 3. Magnetization vs magnetic field curve at 1.8 K for complexes **1** (a) and **2** (b); the solid line is a guide. (Inset) Magnetic hysteresis loop for complexes **1** and **2**, respectively.

metal−metal distance (Mn···Mn) is 4.005(6) Å for **1** and 3.550(3) Å for **2**. In a word, the three complexes do not show the obvious structural differences except the larger interchain distance found in **1** compared with **2** and **3**. However, it is worth noting that the intermolecular distance could be a major influencing factor of the magnetic properties in these complexes.[23]

Magnetic Properties of Complexes 1 and 2. The temperature dependence of magnetic data for complexes **1** and **2** was collected in the range of 1.8−300 K under an applied magnetic field of 2 kOe as plotted in Figure 2. The $\chi_M T$ value per Mn_3Cr for **1** at 300 K is 10.0 cm^3 K mol^{-1}, which is slightly smaller than the spin-only values (10.88 cm^3 K mol^{-1}) calculated from noncoupled three high-spin Mn^{III} ($S_{Mn} = 2$) and one Cr^{III} ($S_{Cr} = 3/2$) ions assuming $g = 2$. The slightly smaller room-temperature $\chi_M T$ values than the theoretical ones for **1** are ascribed to the overestimated g value for Mn^{III}.[24] As the temperature is lowered, the $\chi_M T$ value of complex **1** decreases smoothly and reaches a minimum of 9.0 cm^3 K mol^{-1} at about 90 K. Below 90 K the $\chi_M T$ value increases rapidly to the maximum of 25.0 cm^3 K mol^{-1} at about 8 K and then is followed by a sudden decrease to 4.1 cm^3 K mol^{-1} at 1.8 K. All these phenomena show the ferrimagnetic-type arrangement of complex **1**, indicating that the dominant intrachain antiferromagnetic interaction, takes place between Mn^{III} and Cr^{III} mediated by cyanide bridges due to the fact that the antiferromagnetically coupled t_{2g} orbitals between Cr^{III} and Mn^{III} ions contributes more than the orthogonal orbitals t_{2g} of Cr^{III} and e_g of Mn^{III} ions through the Mn^{III}−N−C−Cr^{III} pathway.[25] From 90 to 8 K the increase of the $\chi_M T$ value is simply resulting from the noncompensation of the spins along the chain. The sudden decrease below 8 K is mainly ascribed to the antiferromagnetic interaction between chains. The $\chi_M T$ value for complex **2** at room temperature is 9.4 cm^3 K mol^{-1}, which is close to the theoretical values (9.37 cm^3 K mol^{-1}) based on three high-spin Mn^{III} ($S_{Mn} = 2$) and one low-spin Fe^{III} ($S_{Fe} = 1/2$) ions assuming $g = 2$. The $\chi_M T$ value increases slowly with decreasing temperature until it reaches the maximum of 16.6 cm^3 K mol^{-1} at 10 K and then dramatically drops to 1.3 cm^3 K mol^{-1} at 1.8 K. The increase tendency of the $\chi_M T$ value for complex **2** above 10 K suggests the presence of overall intrachain ferromagnetic coupling. The magnetic couplings type of Mn−NC−Fe depends strongly on the geometry, which has been thoroughly discussed in the literature.[10s,26] The behavior below 10 K is similar to that of complex **1**. The magnetic data of both **1** and **2** between 90 and 300 K obeys the Curie−Weiss law [$\chi_M = C/(T - \theta)$] very well, affording $C = 10.4$ cm^3 K mol^{-1}, $\theta = -15.2$ K for **1** and $C = 9.4$ cm^3 K mol^{-1}, $\theta = 0.7$ K for **2**. The negative and positive Weiss constants are in agreement with the intrachain antiferromagnetic and ferromagnetic nature for **1** and **2**, respectively.

The field-dependent magnetization measured up to 70 KOe at 1.8 K is shown in Figure 3. Both the curves of **1** and **2** have a

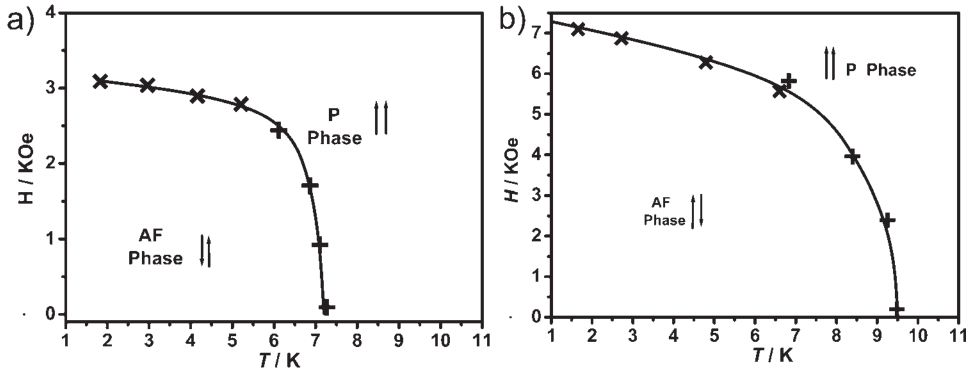


Figure 4. Magnetic phase (T, H) diagrams for **1** (a) and **2** (b). (+) Location of the maximum of susceptibility from χ_M vs T data. (×) Location of the maximum of susceptibility from dM/dH vs H data; the solid line is a guide.

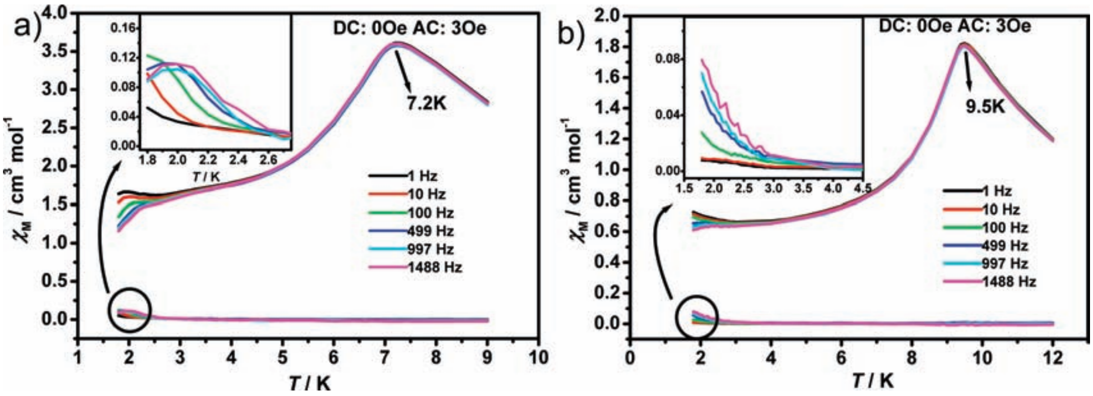


Figure 5. Real (χ_M') and imaginary (χ_M'') parts of AC magnetic susceptibility for **1** (a) and **2** (b) under 0 DC and 3 Oe AC magnetic field.

sigmoid shape, and the critical field (H_c) in 1.8 K is 3 kOe for **1** and 7 kOe for **2** (Figure S4, Supporting Information), which are typical features of the metamagnetic behavior[27] with significant interchain interactions. The value of H_c allows estimation of a value for the interchain interactions of -0.3 cm^{-1} for **1** and -0.7 cm^{-1} for **2**, respectively. The magnetization first increases linearly with increasing external field and then increases rapidly until reaching its highest values at about 8.25 $N\mu_B$ for **1** and 8.89 $N\mu_B$ for **2** at 70 kOe, respectively, which do not fulfill the saturation values of 9 $N\mu_B$ for **1** (calculated from $M_S = g(3S_{Mn}-S_M)$ with $g = 2$) and 13 $N\mu_B$ for **2** ($M_S = g(3S_{Mn} + S_M)$). The steep increasing tendency of magnetization still maintained at 70 kOe for **2** indicates that the magnetization is far-forth unsaturated, probably due to the magnetic anisotropy. The linear parts of both **1** and **2** in low fields correspond to the antiferromagnet phase. The sharp increase of magnetization observed at high fields implies that complexes **1** and **2** are both metamagnets (inset of Figure 3).

Further evidence of a metamagnet is derived from the susceptibility under differently applied fields in the range of 1.8–20 K deduced by field-cooling magnetization (FCM) as shown in the inset of Figure 2. As for complex **1** in low fields, the susceptibility curves show peaks at about 7 K, corresponding to the antiferromagnetic phase transition temperature (T_N). Above 3 kOe the peaks become less prominent and invisible, confirming the presence of metamagnetic transitions induced by the external fields. Complex **2** shows similar properties with complex **1**, whereas T_N and the H_C are slightly higher, which can be attributed to the stronger antiferromagnetic intermolecular interactions arising from the shorter interchain distances in **2**.

Combining M vs H and M vs T data (Figure S5, Supporting Information) of **1** and **2**, the magnetic phase (T, H) diagrams were plotted as shown in Figure 4. H_C is about 3 and 7 kOe for **1** and **2** at 1.8 K, respectively. As the temperature increases, H_C decreases and finally disappears at about 7.2 K for **1** and 9.5 K for **2**. The solid $H_C(T)$ line of **1** and **2**, on analysis of $M-H$ curves, signifies a typical transition from AF to P corresponding to metamagnetic materials. Thus, both complexes **1** and **2** exhibit an antiferromagnetic ground state at low temperature and low fields.

The chain-like structural characteristic urges us to verify the SCM property of complexes **1** and **2**, so the alternating current (AC) magnetic properties were measured for investigating the dynamics of spins. As shown in Figure 5, AC magnetic susceptibility for **1** at zero direct current (DC) and 3 Oe AC magnetic field show a frequency-independent maximum in χ_M' accompanied by χ_M'' without signal at about 7.2 K. The discussion on variable-temperature and -field magnetic properties described above suggests that the occurrence of antiferromagnetic ordering below this temperature is caused by the interchain antiferromagnetic interaction. In the low-temperature region (1.8–3.0K), the temperature dependence (Figure 5) and frequency dependence (Figure S6, Supporting Information) of the AC susceptibilities reflect the frequency-dependent effect, which proves the presence of the slowly relaxed magnetized phase. Complex **2** shows similar AC magnetic properties to complex **1**, but the peak temperature (T_p) is lower than that of **1** at the same frequency.

To see if complexes **1** and **2** are one dimensional by nature above the transition temperature, a study on the correlation length (ξ) of the systems has thus been carried out. The curves of $\ln(\chi_M'T)$ vs T^{-1} (Figure S7, Supporting Information) above T_N of both **1** and **2** are linear, supporting the one-dimensional nature (anisotropic Heisenberg or Ising-like 1D behavior).[28a,b] The fitting based on the expression of $\chi'T = C_{\text{eff}}\exp(\Delta_\xi/kT)$ gives parameters of $\Delta_\xi = 4.99$ K, $C_{\text{eff}} = 10.54$ cm^3 K mol^{-1} for **1** and $\Delta_\xi = 2.00$ K, $C_{\text{eff}} = 12.8$ cm^3 K mol^{-1} for **2**. However, comparison of obtained Δ_ξ with intrachain couplings for both complexes cannot be evaluated quantitatively due to the lack of J data. Further measurement of AC magnetic susceptibility under DC field was carried out (Figure S8, Supporting Information). The result shows that the signals are weakened and become harder to distinguish. The applied DC field often enhances the activation energy and shifts the maxima peaks of AC signals to higher temperature; however, at the same time it also can weaken[2m,29] or enhance[28] the signals, whose mechanism has not been clarified yet. Because suppression of the field affecting spin reversal and the small spin value in the antiferromagnetic phase of complexes **1** and **2**, the undistinguished AC signals at very low temperature make it rather difficult to conduct further investigation on the dynamics of the relaxation process. Nevertheless, the structural feature and the magnetic behavior suggest that complexes **1** and **2** behave as antiferromagnets with a special relaxation process induced by the presence of chains similar to the reported complex reported by Miyasaka et al.[28a,b] It is worth noting complexes **1** and **2** show a relaxation of magnetization as compared with their parent discrete clusters of $[\text{Mn}_6\text{M}]^{3+}[\text{M(CN)}_6]^{3-}$,[12] suggesting the magnetic anisotropy is enhanced when the structure changes from 0D clusters to 1D chains.

Magnetic Properties of Complex 3. Influenced by the diamagnetic Co$^{\text{III}}$ ion, complex **3** is proved to be a magnetically dilute system; thus, the temperature-dependent magnetic susceptibilities were also measured. Complex **3** can provide a proper contrast model in studying the magnetism of this type of structural style. Data are collected in the range of 1.8−300 K under an applied magnetic field of 2 kOe (Figure S9, Supporting Information). The χ_MT value per Mn$_3$Co at 300 K is 8.7 cm^3 K mol^{-1} ($S_{\text{Mn}} = 2$ and $S_{\text{Co}} = 0$). As the temperature is lowered, the value remains nearly constant until 25 K and then drops rapidly to 7.2 cm^3 K mol^{-1} at 1.8 K. The Curie−Weiss law [$\chi_M = C/(T - \theta)$] fitting at 20−300 K for **3** gives $C = 8.8$ cm^3 K mol^{-1} and $\theta = -0.2$ K. The negative Weiss constants reveal the very weak antiferromagnetic interactions.

CONCLUSIONS

In this work, three heterobimetallic cyano-bridged complexes **1**−**3**, constructed by linking heptanuclear clusters [Mn$_6$M] (M = Cr, Fe, and Co for **1**, **2**, and **3**) with corresponding counteranions $[\text{M(CN)}_6]^{3-}$ into a 1D chain, have been synthesized and magnetically characterized. It is found that perturbation of the reaction conditions can largely change the structural features of the products. Magnetic studies reveal that complexes **1** and **2** behave as metamagnets in low fields with antiferromagnetic ordering below 7.2 and 9.5 K, respectively. The slow relaxation of magnetization was observed in the low-temperature region, suggesting 3D magnetic ordering in complexes **1** and **2** with a special relaxation process induced by the presence of chains in the materials having intrinsically SCM properties.[28a,b] This work provides further reference of constructing SCMs by employing the 0D cluster as a building block.

ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data for complexes **1**−**3** in CIF format, IR spectroscopy of all complexes, and structure diagrams of complex **3**, diagram of short intermolecular contact, and related magnetic diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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